

Author Comment 1 (AC1) for Anonymous Review Comment 1 (RC1) on “Diapycnal dissolved organic matter supply into the Peruvian oxycline”.

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 lines: 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 lines: 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) 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 line: 19

The line:

“suggesting that the labile DOM is already utilized”

will be changed to:

“suggesting that the labile DOM is extensively consumed”

Abstract lines: 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 oxycline in the ETSP”

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 transport 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. The following sentences will be added to discussion (Page 9, line 21-25): “The observed distributions of O₂ and of DOC and DON components are the result of sinks and sources in the water column, mainly due to microbial processes and isopycnal and diapycnal supply (i.e. flux divergences) controlled by physical processes. A quantification of each of those individual processes is essential for understanding of important mechanisms, controlling O₂ and OM cycling off Peru and, therefore, the formation and maintenance of the Peruvian 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.”

The following will be added to the discussion (Page 12, line 25-28): “Herewith, the diapycnal supply of DHAA and DCCO could explain up to 38% of $\overline{\nabla\Phi}_{O_2}$. This suggest, that despite the diapycnal fluxes of labile and semi-labile fractions of DOM may not reach deep into the core of the OMZ, DOM based microbial respiration above the OMZ may substantially attenuate the diapycnal O₂ flux that ventilates the upper oxycline. In other words, DOM may alter the shape of the upper oxycline, and, therefore, contribute to the formation and maintenance of the OMZ.”

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).

The following will be added to the discussion (Page 10-11; lines 25-4): “Like for O₂, transport of DOM through the water column is achieved by advective and diffusive transport processes. Therefore, along with turbulent mixing, other transport terms will also take their part in shaping the DOM distribution off Peru. <...> Additionally, meso- (Thomsen et al., 2016a) and submesoscale (Thomsen et al., 2016b) dynamics have been observed in the studied area. They were shown to modify nutrient and O₂ distributions by stirring the water across continental slope and likely influence the DOM distribution off Peru too. However, no quantitative information on DOM fluxes, associated with upwelling, meso- or submesoscale dynamics off Peru are available to date. Seasonal and interannual variations in physical dynamics may as well affect DOM distribution off Peru, e.g. deepening of the mixed layer during Austral winter (Echevin et al., 2008) or intense downwelling/upwelling during El Niño/La Niña events (e.g. Graco et al., 2017) may result in the diapycnal DOM supply to a different depth than during typical Austral summer season.”

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 (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 interface 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 will improve the description for the diapycnal supply calculation in the revised manuscript.

Page 6, lines 2-7

“Here, we define the diapycnal supply (in $\text{mol m}^{-3} \text{s}^{-1}$) of a solute as its vertical flux divergence, i.e. the

change of the diapycnal flux with depth:

$$-\overline{\nabla\Phi_s} = -\frac{\partial}{\partial z}\overline{\Phi_s}, \quad (3)''$$

will be edited to:

“The mean diapycnal supply ($-\overline{\nabla\Phi_s}$, $\mu\text{mol kg}^{-1} \text{ day}^{-1}$) of a solute was determined at 28 m depth intervals as an attenuation of the diapycnal solute flux profile over depth, according to the Eq. 3:

$$-\overline{\nabla\Phi_s} = -\frac{1}{\rho} \frac{\partial}{\partial z} \overline{\Phi_s}, \quad (3)$$

where ρ – is the *in-situ* density of the seawater (kg m^{-3}), z - is depth (m) and $\overline{\Phi_s}$ ($\text{mmol m}^{-2} \text{ day}^{-1}$) – is the estimated mean diapycnal flux profile of a solute. The mean diapycnal solute supply was interpreted to balance the amount of a solute that is lost per unit of time over a specific depth interval of the water column due to the microbial utilization 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 $\mu\text{mol/L}$ 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 μM 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 70 $\mu\text{mol/L}$ to 130 $\mu\text{mol/L}$ for the sea surface microlayer. Franz et al. (2012) (Deep Sea Res. I) reported DOC concentrations ranging from 50 to 300 $\mu\text{mol/L}$ for the upper 200m. Romankevich and Ljutsarev (1990) (Mar. Chem.) reported DOC concentrations ranging from ~40 $\mu\text{mol L}$ to ~130 $\mu\text{mol L}$ 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.

However, we may not fully exclude possible contamination, therefore the following will be added to Results (Page7, lines 21-25): “DOC concentrations of $>100 \mu\text{mol L}^{-1}$ had been reported previously for the water column off Peru (Romankevich and Ljutsarev, 1990; Franz et al., 2012a). However, since concentrations $>100 \mu\text{mol L}^{-1}$ were observed only sporadically, we cannot exclude a possible contamination of these samples.”

We would like to thank R. Benner for his time and valuable comments to this manuscript.

In the following, we will address the comments one by one.

RC2: The authors present compelling physical and biogeochemical data indicating microbial utilization of DOM plays an important role in shaping the upper oxycline in the Peruvian upwelling system. Diapycnal fluxes of O₂ and DOM from productive surface waters are estimated, and analyses of DOM concentrations and compositions indicate the microbial utilization of bioavailable components (e.g. amino acids and carbohydrates) occurs mostly in the upper 50 m of the water column.

In addition to the mol% compositional data presented for carbohydrates and amino acids, the DOC-normalized yields of neutral sugars and amino acids can provide insights about the bioavailability of DOC. These data should be presented in a table (e.g. Table 1) or figure (e.g. Fig. 4).

AC2: We thank R. Benner for highlighting the interdisciplinarity of our study, which combines complex physical and biogeochemical datasets. Following his suggestion, we will add the information of DCCCHO and DHAA yields (in %DOC) to Table 1:

Table 1: Relative composition (mol%) of dissolved hydrolysable amino acids (DHAA) and dissolved combined carbohydrates (DCCCHO) in the water column, “n.d.” - not detectable. The DCCCHO are divided into three classes, nS – neutral sugars, S-N – amino-sugars, and S-H – acidic sugars. The number of samples at each depth interval, used for calculation of the average value, is given as “n”. The mean values for DHAA and DCCCHO composition below the mixed layer (10 to 122 m) are reported for similar depth intervals (14 m) as diapycnal DOM and O₂ fluxes. The mean values for DHAA and DCCCHO within the mixed layer are reported for ~5 m depth intervals.

Depth (m)	n	DHAA			mol% DHAA											
		($\mu\text{mol L}^{-1}$)	(%DOC)	(%DON)	Gly	Thr	Ala	Asp	Glu	Ser	Arg	Leu	Val	Ileu	Phe	Tyr
1-5	30	0.6±0.3	2±1	15±10	22±4	9±1	11±1	17±1	15±3	11±2	2.3±0.3	4±1	3.0±0.4	2.5±0.6	2.4±0.4	1.8±0.4
5-10	25	0.5±0.3	2.3±0.9	15±9	23±4	9±2	11±1	17±1	15±4	10±1	2.2±0.4	4±1	2.9±0.6	2.1±0.5	2.1±0.4	1.7±0.3
10-24	48	0.4±0.2	1.8±0.8	16±14	25±4	9±2	11±1	17±1	13±2	9±1	2.1±0.6	3±1	2.8±0.7	2.2±0.7	2.1±0.6	1.9±0.5
24-38	28	0.24±0.07	1.2±0.3	12±14	28±3	10±1	12±1	17±1	11±2	9±1	1.9±0.4	3±1	2.4±0.6	1.9±0.6	1.8±0.4	2.0±0.7
38-52	34	0.20±0.05	1.0±0.4	9±7	29±6	10±2	12±2	16±2	11±2	9±1	1.8±0.6	3±2	2.3±0.8	1.7±0.5	1.8±0.4	1.7±0.4
52-66	35	0.17±0.03	0.9±0.3	13±19	31±3	10±2	12±1	16±1	10±2	8±1	1.7±0.4	2±1	2.4±0.5	1.6±0.7	1.7±0.3	1.7±0.5
66-80	27	0.16±0.05	0.9±0.3	9±8	32±4	10±1	12±1	15±2	10±2	8±1	1.7±0.5	2±1	2.5±0.6	1.7±0.8	1.7±0.4	1.8±0.5
80-94	22	0.15±0.08	0.9±0.4	8±7	34±3	10±2	12±2	15±1	10±2	9±1	1.6±0.4	2±1	2.2±0.7	1.3±0.7	1.6±0.4	1.6±0.4
94-108	14	0.13±0.03	0.7±0.2	9±8	34±3	10±2	13±2	15±2	9±2	8±2	1.6±0.5	2±1	2.3±0.7	2±1	1.7±0.4	1.7±0.9
108-122	13	0.13±0.03	0.8±0.2	6±4	32±3	10±2	12±1	16±2	10±2	8±1	1.7±0.3	3±1	2.3±0.8	2±1	1.9±0.4	1.7±0.5
122-200	18	0.12±0.03	0.7±0.3	8±6	35±3	10±1	12±2	15±2	9±1	8±2	1.5±0.7	2±1	2.5±0.6	1.7±0.7	1.5±0.4	1.5±0.5
Depth (m)	n	DCCCHO ($\mu\text{mol L}^{-1}$)			mol%DOC			mol% nS					mol% S-H			
		nS	S-N	S-H	nS	S-N	S-H	Glc	ManXyl	Gal	Rhm	Fuc	Ara	Glu-URA	Gal-URA	Glc-H
1-5	30	1.5±0.8	0.10±0.03	0.10±0.08	9±4	0.6±0.2	0.6±0.3	30±13	32±6	17±6	11±8	8±2	2±1	48±21	51±21	0.4±2
5-10	25	1.1±0.6	0.08±0.03	0.07±0.05	8±4	0.5±0.1	0.5±0.3	33±11	33±5	16±6	8±6	8±2	2±1	43±26	55±24	2±10
10-24	47	0.7±0.3	0.06±0.02	0.04±0.03	5±2	0.4±0.1	0.3±0.2	36±13	37±8	12±5	5±4	7±2	2±1	32±25	67±25	1±7
24-38	28	0.4±0.1	0.04±0.01	0.02±0.02	4±1	0.3±0.1	0.2±0.1	43±11	38±7	9±4	2±2	6±2	0.4±1.0	20±20	80±20	n.d.
38-52	35	0.4±0.2	0.03±0.01	0.02±0.01	4±2	0.3±0.1	0.1±0.1	42±10	41±9	9±3	2±2	5±2	0.3±0.8	28±30	72±30	n.d.
52-66	34	0.5±0.2	0.03±0.01	0.02±0.02	4±2	0.2±0.1	0.2±0.2	45±9	41±9	7±4	2±2	5±2	0.2±0.6	21±27	77±28	2±11
66-80	27	0.4±0.2	0.02±0.01	0.01±0.01	4±2	0.2±0.1	0.1±0.1	47±13	44±12	5±3	1±1	3±2	0.3±0.7	19±28	81±28	n.d.
80-94	22	0.4±0.2	0.02±0.01	0.01±0.01	4±2	0.2±0.1	0.1±0.1	47±11	45±10	4±3	0.1±0.6	2±2	0.7±1.3	32±33	68±33	n.d.
94-108	15	0.3±0.1	0.02±0.01	0.01±0.01	3±1	0.2±0.1	0.1±0.1	53±11	40±10	4±3	0.1±0.5	2±2	0.2±0.9	28±29	72±29	n.d.
108-122	13	0.4±0.1	0.02±0.01	0.02±0.02	4±2	0.2±0.1	0.2±0.2	51±16	43±14	3±3	0.2±0.7	2±2	0.3±1.0	44±46	56±46	n.d.
122-200	18	0.4±0.2	0.02±0.01	0.01±0.02	4±1	0.2±0.1	0.1±0.2	52±10	44±9	2±2	n.d.	1±2	0.7±2.3	22±30	78±30	n.d.

For better comparison with open ocean data from Kaiser and Benner (2009), we will divide our DCCHO data onto neutral sugars (nS), aminosugars(S-N) and acidic sugars (S-H) and report them in $\mu\text{mol L}^{-1}$ and in mol%DOC. The single sugar contribution to nS, S-N and S-H, will be given, as mol%nS, mol%S-N and mol%S-H, respectively. For DHAA both, mol%DOC and mol%DON will be added.

GABA (mol%DHAA) will be removed from the table and will be described in the text of the reviewed manuscript as “The concentrations of GABA, which is commonly used as a signature of microbial activity (Davis et al., 2009), was very low in all samples and represented generally <1% of DHAA” (page8/line 11).

RC2: It appears carbohydrate and amino acid yields (%DOC) decline rapidly in the upper 50 m of the water column, indicating the preferential utilization of these bioavailable DOM components. The yields and bioavailability of DOC at 100 m can be compared to those at HOT and BATS to provide a more definitive #indicator of the relative bioavailability and diagenetic state of DOM at these sites.

AC: The following will be added to discussion (page12, lines 1-13):

“As DHAA and DCCHO are preferentially utilized during microbial decomposition of OM (Skoog and Benner, 1997; Lee et al., 2000; Amon et al., 2001), their carbon yield (%DOC) and composition may serve as indicators of diagenetic history of DOM (e.g. Kaiser and Benner, 2009; Davis et al., 2009). Thus, the relatively high carbon yield of DHAA and DCCHO (Table 1), found near the surface during our study, suggests that DOM in surface waters off Peru is more bioavailable, compared to the open ocean (Davis and Benner, 2007; Kaiser and Benner, 2009). It is, however, rapidly altered at shallow depth. Applying the classification of Davis and Benner (2007), that implies that carbon yields of DHAA above 1.6 %DOC and 1.09 %DOC are corresponding to labile and semi-labile DOM, respectively, to our data suggests that the labile and semi-labile DOM off Peru was restricted upper 50 m of the water column.”

RC2: Observations of the low bioavailability and highly altered chemical composition of DOM at relatively shallow depths (<120 m) is likely due to upwelling of aged and altered DOM as well as active microbial utilization in surface waters (e.g. Steinfeldt et al. 2015). It appears upwelling compresses the vertical profiles of DOM concentration and composition. The manuscript would benefit from a discussion of the role of upwelling in shaping the observed biogeochemical distributions.

AC2: We thank R. Benner for this suggestion. The upwelling flux is likely one of the important processes governing the distribution of solutes (including DOM) in the ETSP off Peru, particularly near the coast (bottom depth less than 500m).

In the revised manuscript, we will extend the discussion on upwelling (Page 10, lines 25-33):

“Like for O₂, transport of DOM through the water column is achieved by advective and diffusive transport processes. Therefore, along with turbulent mixing, other transport terms will also take their part in shaping the DOM distribution off Peru. For instance, vertical advection (i.e. upwelling) transports deep water, which is characterized by highly altered DOM and low DOC concentrations, into the upper ocean near the continental margins. The upwelling may counteract the turbulent downward flux of DOC and, therefore, contribute to a “compression” or sharpening of the vertical DOM concentration and composition profiles. This is unique to upwelling systems and different to the open ocean regions where low DOC concentration gradients and smaller changes in the DOM composition were observed at similar depth (Kaiser and Benner, 2009). “

(Page 12, lines 15-23):

“Therewith, our data suggest that DOM in the shallow OMZ off Peru was characterized by stronger alteration compared to open ocean samples (Kaiser and Benner, 2009) at even much greater depths (up to 4000m). This may be due to both, an upwelling of altered DOM from the deep and a rapid and very extensive heterotrophic DOM utilization in the ETSP. The upwelling may “compress” labile and semi-labile DOM towards the surface, while the rapid microbial utilization of DOM shall prevent labile and semi-labile DOM export into the OMZ, and also would imply a pronounced heterotrophic respiration”

RC2: Specific comment:

The reported concentrations of the amino sugar, GalN, are very low in comparison to values in the north Pacific (HOT). The resulting GlcN:GalN ratios are extremely high (40-70). It appears there is a problem with the GalN measurements.

AC2: We are thankful to Dr. R. Benner for spotting this mistake. GalN during this study was almost always below detection limit of 10nM. Table1, however included an average of these data. We will remove GalN from the table and explicitly state that the values were below detection (Page 8, line 2):

“S-N were represented solely by GlcN, as GalN was below DL in most samples.”

GlcN, could be detected in most samples, this is in accordance with GlcN:GalN ratios, typically ≥ 1 .

Diapycnal dissolved organic matter supply into the upper Peruvian oxycline

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Abstract. The Eastern Tropical South Pacific (ETSP) hosts the Peruvian upwelling system, which represents one of the most productive areas in the world ocean. High primary production followed by rapid heterotrophic utilization of organic matter supports the formation of one of the most intense oxygen minimum zones (OMZ) in the world ocean, where dissolved oxygen (O₂) concentrations reach well below 1 μmol kg⁻¹. The high productivity leads to an accumulation of dissolved organic matter (DOM) in the surface layers that may serve as a substrate for heterotrophic respiration. However, the importance of DOM utilization for O₂ respiration ~~within~~ the Peruvian ~~OMZ~~ upwelling system in general and for shaping the upper oxycline in particular remains unclear so far. ~~Here, we evaluate the~~ 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) for the ETSP off Peru. Diapycnal flux and the supply estimates were obtained by combining measured vertical diffusivities and solute concentration gradients. They were analysed together with the molecular composition of DOM in the ETSP off Peru DCCHO and DHAA to learn, whether infer the transport of labile DOM is reaching into the core of the upper OMZ and how important the potential role of DOM utilization might be for O₂ the attenuation of the diapycnal O₂ flux that ventilates the OMZ. The observed diapycnal O₂ flux (50 mmol O₂ m⁻² day⁻¹ at max) was limited to the upper 80 m of the water column, the ~~flux attenuation~~ O₂ supply of ~1 μmol L⁻¹ day⁻¹, was comparable to previously published O₂ consumption rates for the North and South Pacific OMZs. The diapycnal DOM flux (31 mmol C m⁻² day⁻¹ at max) was limited to ~30 m water depth, suggesting that the labile DOM is ~~already utilized~~ extensively consumed within the upper part of the shallow oxycline off Peru. The analyses of DCCHO and DHAA composition support this finding, suggesting that DOM undergoes comprehensive remineralization already within the upper part of the oxycline, as the DOM within the core of the OMZ was found to be largely altered. Estimated by a simple equation for carbon combustion, aerobic respiration of DCCHO and DHAA, supplied by diapycnal mixing (0.46 μmol L⁻¹ day⁻¹ at max), could account for up to 38% of the diapycnal O₂ supply in the upper oxycline, which suggests that DOM utilization ~~may play~~ plays a significant role for ~~shaping~~ shaping of the upper ~~Peruvian~~ oxycline in the ETSP.

1 Introduction

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Dissolved oxygen (O₂) plays a key role for biological production and cycling of elements in marine ecosystems as well as for the spatial distribution of marine organisms (Ekau et al., 2010; Gilly et al., 2013). The majority of catabolic processes in organisms are conducted by oxidation with O₂ (e.g. Bender and Heggie 1984). ~~Due to the presence of a pronounced oxygen minimum zone (OMZ) (Karstensen et al., 2008), the~~ The eastern tropical South Pacific (ETSP) ~~is~~embodies one of the largest regions, ~~where the role of oxygen minimum zones (OMZ) in the world ocean (Karstensen et al., 2008; Paulmier and Ruiz-Pino, 2009). The core of the Peruvian OMZ is considered fully anoxic (e.g. Ulloa et al. 2012), as~~ O₂ concentrations ~~discriminates. There, O₂ concentrations lower than~~ below the detection limit (DL) of ~0.01 μmol kg⁻¹ ~~are frequently~~were observed between ~~5020~~ 20 and 400 m ~~depths~~depth by high precision STOX sensor measurements (Revsbech et al., 2009; Kalvelage et al., 2013; Thomsen et al., 2016a). Those low O₂ concentrations are due to a sluggish ventilation by ocean currents, carrying low-O₂ waters to the ETSP and ~~high~~microbial ~~respiration attributed to~~utilization ~~and to respiration~~ of organic matter (OM) originating from the upper water column (e.g. Czeschel et al., 2011; Brandt et al., 2015; Kalvelage et al., 2015). Elevated primary production in the Peruvian upwelling region above the OMZ (Pennington et al., 2006) leads to an accumulation of both particulate (POM) (Franz et al., 2012a) and dissolved (DOM) organic matter (Romankevich and Ljutsarev 1990; Franz et al., 2012a; Letscher et al., 2013; Loginova et al., 2016) in the euphotic zone at the continental margin. POM was recognized to be an important source of carbon (C) for microbial OM mineralization (e.g. Dale et al., 2015), utilization of O₂ (Kalvelage et al., 2015), and ~~anoxia related~~anaerobic processes, ~~such as denitrification~~ (Kalvelage et al., 2013) ~~in the area. Also, the remineralization of DOM was suggested to contribute significantly to C and O₂ cycling (i.e. Aristegui et al., 2002; Carlson et al., 2011).~~ However, the cycling of DOM in the Peruvian upwelling system has been little studied.

DOM, originating in the euphotic zone, as a result of extracellular release by phytoplankton, cell lysis, particle degradation and sloppy zooplankton feeding (Benner, 2002), is commonly enriched in labile and semi-labile DOM, which are mainly composed of carbohydrates (CHO) and amino acids (AA) (e.g. Ogawa and Tanoue, 2003). Those are preferentially utilized during microbial decomposition of OM, as they serve as energy sources and “building blocks” for microbes to respire and grow (Skoog and Benner, 1997; Lee et al., 2000; Amon et al., 2001). The contribution of CHO and AA to OM, may be used as a measure of OM bioavailability (Davis et al., 2007; 2009; Kaiser and Benner, 2009).

Low-O₂ conditions have been suggested to slow down microbial decomposition rates of OM (Harvey et al., 1995; Nguyen and Harvey, 1997). Hence, it could be expected that CHO and AA entering the OMZ would not undergo significant changes. Recent studies in the upwelling area and the corresponding OMZ off Chile, however, found bacterial activity (Leucine-incorporation) of similar range to the oxygenated waters (Sempere et al., 2008, Pantoja et al., 2009). These results suggest that the changes in the remineralization rates of DOM might rather be linked to lack of bioavailable OM supply into the OMZ than to low-O₂ conditions. Herewith, Pantoja et al. (2009) reported relatively high concentrations of free and combined AA in the OMZ off Chile. Sempere et al. (2008) reported lower concentrations of neutral CHO in the corresponding upwelling area, compared to the open Pacific Ocean.

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~~Assessing~~Assessing the possible effects of low-O₂ conditions on the composition of DOM implies that the DOM is transported into the OMZ from the oxygenated waters. Contrary to POM, DOM does not obtain its own ~~gravity-flow~~buoyancy and its transport is exclusively due to advective and diffusive physical transport processes (e.g. Löscher et al. 2016). In upwelling regimes, turbulent mixing processes are often enhanced ~~near~~at the ~~shelf~~continental margin resulting in high diapycnal fluxes of various solutes (e.g. Schafstall et al., 2010; Kock et al., 2012; Brandt et al., 2015; Steinfeldt et al., 2015). On the other hand, the downward fluxes of DOM, or other solutes, may be reduced or even predominated by upwelling fluxes due to Ekman divergence in the coastal upwelling region (e.g. Steinfeldt et al., 2015).

Machadevan (2014) suggested that transport of OM (via eddy fluxes) into the OMZ should be accompanied by O₂ in amount that is sufficient for full remineralization of the subducted OM. Therefore, this physical transport of OM and O₂ should stimulate heterotrophic aerobic respiration in the OMZ, which was suggested to be the main pathway of OM remineralization in the upper OMZs by Kalvelage et al. (2015). However, so far, no direct O₂ and DOM supply estimates exist for the Peruvian OMZ.

~~Using~~Here, we investigated the possible importance of diapycnal DOM supply by turbulent mixing processes for the O₂ utilization off Peru using combined physical and biogeochemical observational data; ~~that were~~ collected during the R/V METEOR “M93” (M93) research cruise to the ETSP off Peru in February-March 2013 ~~we investigate the possible importance of diapycnal DOM supply for the O₂ respiration off Peru.~~ Specifically, we directly ~~estimate~~estimated the diapycnal O₂ and DOM supply into the upper oxycline off Peru. Additionally, we ~~analyze~~analyzed diapycnal fluxes and the composition of dissolved combined ~~CHO and A~~carbohydrates (DCCHO) and dissolved hydrolysable amino acids (DHAA) to learn, whether DOM and its labile and semi-labile constituents may be supplied to the ~~core of the OMZ~~upper OMZ and the potential contribution of DOM based respiration to O₂ flux attenuation.

2 Methods

2.1 Study area

The observational data were acquired during the research cruise “M93” which took place from 7th of February to 9th of March 2013 between 12°S and 14°S and 76°W and 79°W off Peru (Fig. 1). During the measurement program, the study area was affected by moderate southeasterly winds (1-9 m/s) (Thomsen et al., 2016a). The water column was highly stratified during the cruise (Fig. 2a,b). High concentrations of inorganic nutrients (~30 μmol L⁻¹ (NO₃⁻), ~3 μmo L⁻¹ (PO₄³⁻)) just below the surface (Thomsen et al., 2016a) collocated with highest chlorophyll *a* (chl *a*) concentrations near the surface (5-80 m depth; Fig. 2c) (Loginova et al., 2016). The oxycline was located at upper 5-80 m depth, here oxygen concentrations dropped from >200 μmol kg⁻¹ to <1μmol kg⁻¹ (Fig. 2d) (Thomsen et al., 2016a). In summary, our observations were carried out during a period which corresponds to typical summer conditions off Peru.

2.2 Discrete water sampling and analyses

Seawater was sampled with a ~~GO~~-rosette (~~GO~~; General Oceanics, USA) equipped with a conductivity, temperature and depth profiler (CTD; Sea-Bird (SBE) 9-plus, Sea-Bird Electronics Inc., USA), an O₂ optode (SBE43, Sea-Bird Electronics Inc., USA), a WETStar chl *a* fluorometer (WET Labs, USA) and 24 x 10 L Niskin bottles. Additional water samples were taken with a PUMP-CTD-System (an integrated measurement device, which was developed in collaboration between Leibniz-~~Institut für Ostseeforschung~~ Institute for Baltic Research (IOW) and the Max-Planck-~~Institut für~~ Institute for Marine ~~Mikrobiologie~~Microbiology (MPI) Bremen: PUMP-CTD; Strady et al., 2008). In general, samples were collected at 3 to 8 sampling depths from 2 to 70 m at the onshore stations (~10km offshore) and from 2 to 200 m at stations offshore (~100 km offshore). DOC/DON analyses were performed for 50 GO rosette stations, and for 8 PUMP-CTD stations. ~~Dissolved combined (hydrolysable) AA (DHAA) and dissolved combined CHO (DCCHO)~~ analyses were performed only for samples from the GO rosette. CTD, O₂ and chl *a* recordings were taken at 172 profiles (Fig. 1a).

The CTD was calibrated with discrete seawater samples measured with a Guildline Autosol 8 model 8400B salinometer. The O₂ optode was calibrated by ~~a combination of~~ Winkler titration ~~above the oxycline~~ (Winkler, 1888; Hansen, 1999) ~~and~~. The STOX sensor measurements, ~~which revealed O₂ concentrations of 0.01-0.05 μmol kg⁻¹ within the OMZ~~ (Revsbech et al., 2009). ~~Salinity; Thomsen et al., 2016a) were used for O₂ optode calibration at low O₂ levels. The salinity~~ and O₂ measurements had precision of 0.002 g kg⁻¹ and ~ 1 μmol kg⁻¹, respectively. More details on the salinity and O₂ calibrations can be found in Thomsen et al. (2016a). Apparent oxygen utilization (AOU) was then calculated as a difference of measured O₂ concentrations and its equilibrium saturation using Gibbs-Sea Water Oceanographic Toolbox (McDougall and Barker, 2011) for MatLab (MathWorks, USA) for analyses of potential relationship between DOM reworking and the utilization of O₂.

The original fluorometer calibration provided by the sensor manufacturer (WET Labs, USA) was used throughout the cruise resulting in chl *a* concentrations in μg L⁻¹. More detail on the recalibration of the chl *a* fluorimeter one can find in Loginova et al. (2016).

~~Net primary production (NPP) was estimated for study area off Peru (12°S 14°S and 76°W 79°W) and the corresponding time period (February 2013) after the model of Behrenfeld and Falkowski (1997a) with Ocean Productivity toolbox (Oregon State University).~~

DOC/DON duplicate samples (20 mL) were collected into combusted glass ampoules (8 h, 450° C) after filtration with combusted GF/F filters (5 h, 450°C). Samples were acidified (80mL of 85% H₃PO₄), sealed with flame and stored at 4°C in the dark until analysis. DOC samples were analysed by the high-temperature catalytic oxidation method (TOC -VCSH, Shimadzu) modified from Sugimura and Suzuki (1988). The detection limit (DL) was ~~1 μmol~~ μmol L⁻¹. Total dissolved nitrogen (TDN) was determined simultaneously to DOC with DL of 2 μmol L⁻¹ using the TNM-1 detector of a Shimadzu analyser [Dickson et al., 2007]. DON concentrations were calculated by subtracting inorganic nitrogen concentrations from concentrations of TDN. The description of the instrument calibration and measurements may be found in Loginova et al. (2015).

Duplicate samples (~16ml) for DCCHO were collected into combusted (8hrs, 450°C) 25ml-glass vials after passing through 0.45 μm syringe filters (GHP membrane, Acrodisk, Pall Corporation) and immediately frozen at -20°C until analyses. Analyses

were conducted by high performance anion exchange chromatography (HPAEC) coupled with pulsed amperometric detection following Engel and Händel (2011). Prior to analyses samples were thawed at room temperature and desalinated by membrane dialysis (1 kDa MWCO, Spectra Por, 5 h at 1°C). Desalinated duplicate subsamples (2 mL) were hydrolyzed using 1.6mL of 1M HCl (for each) for 20 h at 100°C. The hydrolyzed samples were neutralized through acid evaporation under N₂ atmosphere and an addition of milliQ water (20mL). DCCHO monomers were determined from 17.5 mL subsamples on a Dionex ICS 3000 system. More detailed method and calibration descriptions are given in Engel and Händel (2011). The method ~~DL-precision~~ was ~~2% with a DL~~ ~10 nmol L⁻¹ ~~and precision of 2%~~. During our study, three classes of polysaccharides were measured. Those ~~are~~ were neutral sugars (nS) (fucose (Fuc), rhamnose (Rha), arabinose (Ara), galactose (Gal), glucose (Glc), mannose (Man) and xylose (Xyl)), amino sugars (S-N) (glucosamine (Glc-N) and galactosamine (Gal-N)), and ~~the~~ acidic sugars (S-H) including gluconic acid (Glu-H) and the uronic acids (DURA) galacturonic acid (Gal-URA) and glucuronic acid (Glc-URA). Man and Xyl were quantified as a mixture due to co-elution, and, therefore, reported together (ManXyl). Concentrations of DCCHO after hydrolysis are given as monomer equivalents.

Duplicate samples (~3ml) for DHAA were filtered with 0.45 µm syringe filters (GHP membrane, Acrodisk, Pall Corporation) and stored frozen (-20°C) in combusted (8hrs, 450°C) 4ml-glass vials until analyses. Samples were thawed and hydrolyzed with 6 N HCl at 100°C for 20 h prior to analysis. DHAA were determined by HPLC after ortho-phthalaldehyde derivatization (Lindroth and Mopper-, 1979; Dittmar et al., 2009) with DL of 2 nmol L⁻¹ and precision of <5%. The following amino acids were analyzed during the study: α-amino acids: aspartic acid (Asp), glutamic acid (Glu), serine (Ser), arginine (Arg), glycine (Gly), threonine (Thr), alanine (Ala), tyrosine (Tyr), valine (Val), phenylalanine (Phe), isoleucine (Ileu), leucine (Leu) and γ-amino acid: γ-aminobutyric acid (GABA). Alpha ~~amino butyric~~aminobutyric acid was used as an internal standard to account for losses during handling. Concentrations of DHAA after hydrolysis are given as monomer equivalents. More in-detail description of the method may be found in (Engel and Galgani, 2016).

2.3 Diapycnal flux calculations

To estimate the diapycnal fluxes of various solutes, CTD sensor (O₂) and bottle data (DOC, DON, DCCHO and DHAA) were combined with near-simultaneous measurements of turbulence in the water column. The turbulence measurements were performed with a microstructure profiling system (MSS) from the rear of the vessel. The loosely-tethered profiler (MSS90-D, S/N 32, Sea & Sun Technology) was optimized to sink at a rate of 0.55 m s⁻¹ and was equipped with three shear sensors and a fast-response temperature recorder, as well as an acceleration sensor, two tilt sensors and CTD, sampling with lower response time. At each CTD station, 3-6 microstructure profiles were collected. Standard processing procedures were used to determine the rate of kinetic energy dissipation of turbulence in the water column (ϵ in ~~m~~ m²s⁻³), as given in Schafstall et al. (2010). Diapycnal diffusivities (K_ρ in ~~m~~ m²s⁻¹) were determined at 14 m depth intervals, following Osbom (1980):

$$K_\rho = \Gamma \frac{\epsilon}{N^2}, \quad (1)$$

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where N is stratification (in s^{-1}) and Γ is the mixing efficiency, for a which value of 0.2 was used. The diapycnal diffusivity of the solutes (O_2 , DOC, DON, DCCHO, and DHAA) - K_S - was assumed to be equivalent to the diapycnal diffusivity of the mass K_p (e.g. Schafstall et al., 2010; Fischer et al., 2013).

The diapycnal fluxes ($\text{mmol m}^{-2} \text{day}^{-1}$) of the different solutes listed above were estimated using Eq. 2, implicitly assuming equivalency of vertical and diapycnal diffusivities ($K_S \approx K_p$).

$$\Phi_S = -K_p \nabla C_S, \quad (2)$$

where ∇C_S is the vertical gradient of the molar concentration of the solutes (mmol m^{-4}).

Here, we define the mean diapycnal supply ($\text{mmol m}^{-2} \text{day}^{-1}$) of a solute as its vertical flux divergence, i.e. the change in attenuation of the diapycnal solute flux with profile over depth, according to the Eq. 3:

$$\begin{aligned} & -\nabla \Phi_S \\ &= -\frac{\partial}{\partial z} \frac{1}{\rho} \frac{\partial \Phi_S}{\partial z}, \end{aligned} \quad (3)$$

where ρ is the *in-situ* density of the seawater (kg m^{-3}), z is depth (m) and $\overline{\Phi_S}$ ($\text{mmol m}^{-2} \text{day}^{-1}$) is the estimated mean diapycnal flux profile of a solute. The mean diapycnal solute supply was interpreted to balance the amount of a solute that is lost per unit of time over a specific depth interval of the water column due to the microbial utilization of the solute. This interpretation assumes that sources other than turbulent mixing or sinks other than microbial consumption are negligible.

For DCCHO and DHAA the diapycnal flux estimates were based on 14 combined CTD/MSS stations, while for DOC and DON fluxes 22 stations were available (Fig. 1b). The diapycnal O_2 flux was determined from 50 combined stations. All combined data sets include stations from the continental slope, as well as stations in deeper waters, where bottom depth was larger than 4000m.

For each combined CTD/MSS station a mean K_p was estimated based on a N^2 profile (CTD) and mean dissipation profile (turbulence probe) averaged over all MSS profiles conducted at the CTD station. In combination with the vertical solute gradient, a mean flux profile for each station was estimated. Only measurements below the mixed layer, which was defined by a threshold criterion of a 0.2°C temperature decrease below the maximum and a minimum depth of 10 m, were used.

Measurements from different sensors and instruments were combined and averaged in temperature-density space to reduce the impact of internal waves.

The mean diapycnal flux ($\overline{\Phi_S}$) was determined by arithmetically averaging all fluxes from individual stations in 14m depth intervals. The diapycnal solute supply was then determined from the divergence of the mean diapycnal flux ($\nabla \overline{\Phi_S}$).

The 95% confidence interval of the diapycnal flux was calculated following the procedure described by Schafstall et al. (2010).

From this error estimate the uncertainty of the supply was derived by error propagation.

A simple equation of carbon combustion:

$$1C + 1O_2 = 1CO_2, \quad (4)$$

was used for a rough estimation of the percentage of diapycnal O₂ supply, that may be consumed by heterotrophic communities, if they use all the C, supplied by the diapycnal fluxes of DOC, DCCHO and DHAA.

2.4 Statistical analyses of DOM composition

- 5 Principal component analysis (PCA) was performed using environmental factors (temperature, salinity and AOU) and relative abundances of α -DHAA and neutral DCCHO (mol%) to examine “compositional trends” (i.e. changes in composition in response to an influence of an environmental parameter) in marine DOM in the studied area. The aim of the PCA was also to explore the potential interrelation between low-O₂ and DOM composition. For this, temperature, salinity and AOU and relative abundances of labile organic matter from open Atlantic and Pacific Oceans (Kaiser and Benner, 2009) were included in the
- 10 PCA for the representation of well oxygenated water column. The covariance between principle components and an individual parameter was considered significant, when module of the coordinate of the parameter exceeded 0.5 on the “variables factor map”. The PCA was performed using “FactorMineR” package (Husson et al., 2010) for “R” (R Core Team, 2013).

3 Results

3.1 Distribution of O₂ and DOM

- 15 In this section the horizontal and vertical distribution of O₂ and the different DOM components including DOC, DON and their labile and semi-labile constituents, DCCHO and DHAA are described. The vertical gradients of the different solutes are crucial for estimating the associated diapycnal fluxes, as described in section 3.2. Near surface O₂ concentrations were observed ranging between 100 $\mu\text{mol kg}^{-1}$ at the coast and 240 $\mu\text{mol kg}^{-1}$ further offshore (Fig. 2d). These values dropped to ~~below less than~~ 1 $\mu\text{mol kg}^{-1}$ at ~~~20m depth at the coast and~~ ~80 m depth ~~offshore~~ (Fig. 2d).
- 20 DOC concentrations ranged from more than 100 $\mu\text{mol L}^{-1}$ near the surface to < 50 $\mu\text{mol L}^{-1}$ below 40 m depth (Fig. 3a). Patches of isolated DOC maxima (up to 120 $\mu\text{mol L}^{-1}$) were measured at a depth range from 20 to 120 m (Fig. 3a). ~~Beside those isolated DOC maxima, concentrations of >100 $\mu\text{mol L}^{-1}$ had been reported previously for the water column off Peru (Romankevich and Ljutsarev, 1990; Franz et al., 2012a). However, since concentrations >100 $\mu\text{mol L}^{-1}$ were observed only sporadically, we cannot exclude a possible contamination of these samples. The main decrease of DOC occurred at a depth~~
- 25 ~~range~~ between 5 and 30 m. Thus, the main vertical DOC gradient was found at ~~shallower~~ shallow depth, compared to the oxycline. This becomes ~~visible even more apparent~~, when comparing the mean vertical profiles of O₂ and DOC (Fig. 4a,b). DON concentrations were also highest (~7-8 $\mu\text{mol L}^{-1}$) near the surface (Fig. 3b) and varied from below ~~the detection limit~~ to 4-5 $\mu\text{mol L}^{-1}$ at greater depth. The main decrease of ~~the~~ DON concentrations occurred ~~in~~ within the upper 10 m of the water column (Fig. 4c). ~~The differences of the DON concentrations at greater depth were not high enough to obtain a significant~~
- 30 ~~gradient.~~

DCCHO concentrations varied from 0.2 $\mu\text{mol L}^{-1}$ to 4.2 $\mu\text{mol L}^{-1}$ (Fig. 3c), with highest concentrations near the surface. C contained in DCCHO represented from 1 to max. 25 % of DOC in the studied depth range. Amino sugars S-N were represented solely by GlcN, as GalN was below DL in most samples. S-H were mainly represented by DURA, i.e. Glu-URA and DURA and Gal-URA (Table 1), while Glc-H was detected only sporadically. Overall, S-N and S-H comprised 0.04±0.03 $\mu\text{mol L}^{-1}$ and 0.02±0.02 $\mu\text{mol L}^{-1}$, that contributed contributing 6±3 % and 3±2 % to DCCHO, respectively, leaving. Thus, the major part of DCCHO to neutral sugars, was represented by nS (Table 1). DHAA concentrations varied from 0.075 $\mu\text{mol L}^{-1}$ to 1.39 $\mu\text{mol L}^{-1}$ (Fig. 3d). Like for DCCHO, the highest DHAA concentrations were found above the oxycline, where C contained in DHAA represented up to 2±1 % DOC (max. 4 % DOC%) and nitrogen (N) contained in DHAA represented up to 82|5±14 % DON. Lowest DHAA concentrations were mainly found below 80 m depth and equivalent to ~1 %DOC and ~4-8 %DON. Similar to DOC, DCCHO and (Table 1). The major part of DHAA was represented by α -amino acids. The concentrations decreased in the upper part of the oxycline (Fig. 4a,d,e,f) of GABA, which is commonly used as a signature of microbial activity (Davis et al., 2009), was very low in all samples and represented generally <1% of DHAA. In summary, the concentrations of all the DOM compounds were highest above the oxycline, and the mean concentration gradients of the DOM compounds were restricted to a shallower depth, compared to the mean gradient of O_2 (Fig. 4).

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15 3.2 Diapycnal fluxes and supply

As outlined in the previous section ~~steep~~ vertical gradients of O_2 , DOC, DON and their constituents were observed at 30 to 80 m depth in the study area. In this section we combine these vertical gradients with turbulence measurements to estimate the associated diapycnal fluxes and supply i.e. the diapycnal flux divergences.

For O_2 , the mean diapycnal flux ($\overline{V\Phi}_{\text{O}_2}$) exhibited a maximum of 50 ~~mmol~~ O_2 ~~mmol~~ $\text{O}_2 \text{ m}^{-2} \text{ day}^{-1}$ at ~20m depth. It ~~deceased~~~~decreased~~ over ~~the~~ depth and vanished at 80m depth due to lack of vertical concentration gradients. The mean diapycnal supply O_2 ($\overline{V\Phi}_{\text{O}_2}$), ranged from 1.2 $\mu\text{mol kg}^{-1} \text{ day}^{-1}$ at 10-24 m depth to near zero at 80 m depth. (Table 2).

In contrary, mean diapycnal fluxes of DOC ($\overline{\Phi}_{\text{DOC}}$) was limited to shallower depth. Near the surface, $\overline{\Phi}_{\text{DOC}}$ was 31 ~~mmolC~~~~mmol C~~ $\text{m}^{-2} \text{ day}^{-1}$ and vanished already at ~50 m depth (Table 2). Compared to NPP, estimated to 3.9 (0.6-8.6) $\text{gC m}^{-2} \text{ day}^{-1}$ for our study area and period, the DOC flux represented from a maximum of -10(4-62) %NPP at -20 m depth to near

zero %NPP at -50 m depth. The diapycnal supply of DOC ($\overline{V\Phi}_{\text{DOC}}$) exhibited a maximum of 1.8 $\mu\text{molC}\mu\text{mol C kg}^{-1}\text{day}^{-1}$ at 10-38 m depth (1.5 times larger than $\overline{V\Phi}_{\text{O}_2}$.) (Table 2, Eq. 4). As it was mentioned in the section 3.1, we did not find a significant

vertical DON gradient, resulting in very low diapycnal DON fluxes and supply estimates (Table 2). However, significant-N fluxes were obtained from DHAA transport. Mean C and N fluxes via DCCHO and DHAA ranged from near zero below 30-40 m depth to 6 ~~mmolC~~~~mmol C~~ $\text{m}^{-2} \text{ day}^{-1}$ ($\overline{\Phi}_{\text{DCCHO(C)}}$), 0.9 ~~mmolC~~~~mmol C~~ $\text{m}^{-2} \text{ day}^{-1}$ ($\overline{\Phi}_{\text{DHAA(C)}}$) and 0.4 ~~mmolN~~~~mmol N~~ m^{-2}

day^{-1} ($\overline{\Phi}_{\text{DHAA(N)}}$) at 10-20m depth (Table 2). The diapycnal C and N supply via DCCHO and DHAA ranged from near zero to a maximum of 0.4 $\mu\text{molC}\mu\text{mol C kg}^{-1}\text{day}^{-1}$ ($\overline{V\Phi}_{\text{DCCHO(C)}}$), 0.06 $\mu\text{molC}\mu\text{mol C kg}^{-1}\text{day}^{-1}$ ($\overline{V\Phi}_{\text{DHAA(C)}}$), and 0.02 $\mu\text{molN}\mu\text{mol N kg}^{-1}\text{day}^{-1}$ ($\overline{V\Phi}_{\text{DHAA(N)}}$) at 10-38 m depth. The diapycnal C supply via DCCHO and DHAA at its maximum comprised ~38% of

$\overline{V\Phi}_{O_2}$, when estimated by Eq. (4). In summary, our diapycnal flux and supply calculation revealed that the diapycnal O_2 supply reaches deeper into the oxycline than the diapycnal DOM supply. This is especially true for DCCHO and DHAA, representing the labile and semi-labile parts of DOM.

3.3 Linking the DOM composition and the utilization of O_2

5 To understand, whether low- O_2 conditions of the OMZ may cause changes in DOM composition, we complement our quantitative estimates of the DOM and O_2 supply with the analyses of DOM quality. For this, the composition of neutral DCCHO and DHAA via PCA was compared to environmental factors, i.e. temperature, AOU and salinity, and to OM composition from the well oxygenated water column as described in Kaiser and Benner (2009). The first principle component (Dim 1) (Fig. 5, “variables factor map”) of the PCA was strongly influenced by AOU, indicating the interrelation of the DOM composition and removal of O_2 . The utilization of O_2 was accompanied by selective removal of Glu, Phe, Leu, ILeu and Ser, and Rha, Gal, and Fuc (Fig. 5, Table 1). Gly, Thr and ~~CleGlc~~ mol% were increasing along with increase in AOU (Fig. 5). In general, the composition of DOM from the surface samples from our study was similar to the composition of DOM from the samples, collected from well oxygenated open ocean sites by Kaiser and Benner (2009), as the individual scores of the samples cluster together on Dim.1 of the PCA (Fig. 5, “individuals factor map”). The samples, collected within the OMZ were much poorer in composition, even in comparison to the deepest open ocean samples (~4000m), as they grouped from the negative side of Dim. 1.

The differences on the second dimension of PCA (Dim.2) were driven likely by regional differences in the DOM composition, i.e. by mol% of Ala, Arb, and Fuc, and distributions of mol% Asp, Phe, Val and Leu over depth (Fig. 5, Table 1, Kaiser and Benner, 2009).

20 4 Discussion

The observed distributions of O_2 ~~as well as the~~ and of DOC and DON components are the result of sinks and sources in the water column, mainly due to ~~biogeochemical~~ microbial processes and isopycnal and diapycnal supply (i.e. flux divergences) controlled by physical processes. A quantification of each of those individual processes is essential for understanding of important mechanisms, controlling O_2 and OM cycling off Peru and, therefore, formation and maintenance of the Peruvian OMZ.

25 Previous studies have shown that turbulent mixing processes in the eastern boundary upwelling ~~regions~~ systems (EBUS) are strongly enhanced and that the resulting diapycnal supply is often a leading term in the flux divergence balances of O_2 , 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). The diapycnal O_2 and DOM fluxes and supply determined in this study ~~represents an~~ represent average ~~value~~ values for the continental margin ranging from the shelf to about ~~100 km~~ 100 km offshore. ~~The~~ This spatial averaging is likely responsible for a lower near-surface diapycnal O_2 flux (50 mmol O_2 m⁻² day⁻¹) from our study compared to diapycnal O_2 fluxes other EBUS.

For example, Brandt et al. (2015b) determined ~~in the Mauritanian upwelling, although vertical gradients of O₂ are much reduced in the latter upwelling system. There,~~ a near-surface diapycnal O₂ flux of 73 mmolO₂ m⁻² day⁻¹ ~~was determined in the Mauritanian upwelling during the high productivity season in boreal winter (Brandt et al., 2015).~~ In their study, the diapycnal O₂ flux was able to sustain benthic ~~O₂ uptake/resp~~iration on the continental shelf ~~updown~~ to a bottom depth of 100m. ~~Rates of oxygen consumption in the upper ocean from in situ incubations in the ETSP off Peru 100 m. Herewith, the diapycnal O₂ supply, found values in our study, was of about similar magnitude as the rates of O₂ consumption (~1 μmol kg⁻¹ day⁻¹) determined by in situ incubations at 50-80 m water depth of 50-80m during the Austral summer season in the ETSP off Peru (Kalvelage et al., 2015), which are comparable to) and similar estimates for North and South Pacific OMZs from (Revsbech et al., 2009) and Tiano et al. (2014). The diapycnal O₂ supply estimated in this study is of similar magnitude and highlights~~ the important role of turbulent processes for the O₂-ventilation of the upper oxycline off Peru.

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/might play an additional loss~~ important role for the distribution of O₂ ~~to~~in the upper ocean, particularly in the region of the continental slope and the shelf. ~~In turn, the deep chl *a* maximum, formed by photosynthetic cyanobacteria, i.e. *Prochlorococcus*, that have been found in the ETSP (Lavin et al. 2010; Ulloa et al., 2012; Meyer et al., 2017) may provide an additional O₂ source at depth.~~ Furthermore, ~~seasonal variations~~ the presented diapycnal fluxes and supply of O₂ were determined from the data collected during ocean settings typical for the Austral summer season of non-El Niño/ La Niña-year. In the water column, O₂ concentrations and background settings for the production of turbulence were shown to vary substantially on seasonal and interannual time scales (e.g. Graco et al., 2017). Thus, the diapycnal ~~solute~~ fluxes ~~may occur due to, for instance, deepening the mixed layer during winter season (Echevin et al., 2008)~~ and supply of O₂ shall vary on the same timescales. Therefore, our results should be considered as the first estimates of diapycnal O₂ fluxes and supply in the ETSP off Peru during ~~austral summer. Therefore, more observations shall improve the robustness of the flux estimates~~ Austral summer season during non-El Niño/ La Niña regime.

~~DOM transport through the water column is restricted to advective and diffusive mixing processes. However, DOM is affected also~~ Like for O₂, transport of DOM through the water column is achieved by advective and diffusive transport processes. Therefore, along with turbulent mixing, other transport terms will also take their part in shaping the DOM distribution off Peru. For instance, vertical advection (i.e. upwelling) transports deep water, which is characterized by highly altered DOM and low DOC concentrations, into the upper ocean near the continental margins. The upwelling may counteract the turbulent downward flux of DOC and, therefore, contribute to a “compression” or sharpening of the vertical DOM concentration and composition profiles. This is unique to upwelling systems and different to the open ocean regions where low DOC concentration gradients and smaller changes in the DOM composition were observed at similar depth (Kaiser and Benner, 2009). Additionally, meso- (Thomsen et al., 2016a) and submesoscale (Thomsen et al., 2016b) dynamics have been observed in the studied area. They were shown to modify nutrient and O₂ distributions by stirring the water across continental slope and likely influence the DOM distribution off Peru too. However, no quantitative information on DOM fluxes, associated with

upwelling, meso- or submesoscale dynamics off Peru are available to date. Seasonal and interannual variations in physical dynamics may as well affect DOM distribution off Peru, e.g. deepening of the mixed layer during Austral winter (Echevin et al., 2008) or intense downwelling/upwelling during El Niño/La Niña events (e.g. Graco et al., 2017) may result in the diapycnal DOM supply to a different depth than during typical Austral summer season.

5 Furthermore, DOM is affected by other abiotic or biological processes in the water column. For instance, the observed very low diapycnal DON flux may suggest a DON removal in the upper water column. Low concentrations of inorganic nutrients above 20 m depth (Thomsen et al., 2016a), and an overall nitrogen limitation that was found to be characteristic for the surface communities in the ETSP off Peru (Franz et al., 2012b), might force those communities to switch to organic nitrogen sources (e.g. Bradley et al., 2010), therefore reducing DON in the upper 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). Thus, DOM composition was suggested to be affected by the photochemistry in our study area (Galgani and Engel, 2016, Loginova et al., 2016). Photochemical degradation to CO, CO₂ and other volatile compounds (Zepp et al., 1998) could lower the near surface diapycnal DOC flux, as well.

15 Herewith, ~~in our study data suggest that~~ the diapycnal DOC flux ~~was in the upper 20m of the water column off Peru is~~ in the same order of magnitude as the diapycnal O₂ flux ~~in the upper 20 m of the water column. An~~ (Table 2). The annual diapycnal DOC flux (~~4±2.7 molCmolC m⁻²yr⁻¹~~) into the upper OMZ, estimated from our results by averaging of $\bar{\Phi}_{DOC}$ ~~over above the upper 50 m water mean depth of the oxycline (from below the mixed layer to 80 m depth)~~ and integrating over a year, is in the same order of magnitude as previously reported data for the North Pacific Subtropical Gyre, where DOC export was estimated by a mass balance approach (1.6-2.7 molC m⁻² yr⁻¹; Emerson et al., 1997) and by fitting an exponential decay function over depth (0.5±0.1 molC m⁻² yr⁻¹; Kaiser and Benner 2012). ~~The diapycnal DOC flux represented a significant fraction of NPP (~10% NPP), and was comparable to the POC export, reported for~~ Furthermore, in the upper water column (from below the ETSP off Chile (~12% NPP at 30m mixed layer to 38 m water depth; Pantoja et al., 2004), and for), the ETSP off Peru (~6% NPP at 52m; Gagosian et al., 1983; 16-42% NPP near the surface; Kalvelage et al., 2013), advocating turbulent mixing of DOM to be an important C export mechanism in the upper oxycline. The diapycnal DOC supply was ~~stronger higher~~, than the diapycnal O₂ supply, suggesting that ~~DOM DOC respiration could potentially deliver more than enough organic material for O₂ to be respired in the upper water column. The exhaust all O₂. However, the~~ vanishing of DOC flux above the upper oxycline may indicate ~~suggests~~ that the bioavailable fraction of DOM is ~~consumed respired~~ well before entering the upper OMZ. This is even more apparent, when considering diapycnal DHAA and DCCHO fluxes, which ~~decay decayed~~ more rapidly compared to the diapycnal DOC flux, suggesting ~~their~~ preferential uptake of DHAA and DCCHO in the water column. The diapycnal supply of DHAA and DCCHO ~~cannot could not~~ fully explain the diapycnal supply of DOC, as those were responsible for only ~26% of $\bar{\Phi}_{DOC}$ when summed up together. This may hint to a presence of an additional bioavailable DOM component that ~~is was~~ respired in the water column, and/or to other DOM removal mechanisms in the near-surface waters. For instance, DOM may form marine microgels and hence POM (Chin et al., 1998; Engel et al., 2004, Verdugo et al., 2004) or be trapped in the pore space of already existing particles (e.g. Benner, 2002).

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A strong reworking of the labile and semi-labile DOM could also be seen from the analyses of DHAA and DCCHO composition. For instance, As DHAA and DCCHO are preferentially utilized during microbial decomposition of OM (Skoog and Benner, 1997; Lee et al., 2000; Amon et al., 2001), their carbon yield (%DOC) and composition may serve as indicators of diagenetic history of DOM (e.g. Kaiser and Benner, 2009; Davis et al., 2009). Thus, the relatively high carbon yield of DHAA and DCCHO (Table 1), found near the surface during our study, suggests that DOM in surface waters off Peru is more bioavailable, compared to the open ocean (Davis and Benner, 2007; Kaiser and Benner, 2009). It is, however, rapidly altered at shallow depth. Applying the classification of Davis and Benner (2007), that implies that carbon yields of DHAA above 1.6 %DOC and 1.09 %DOC are corresponding to labile and semi-labile DOM, respectively, to our data suggests that the labile and semi-labile DOM off Peru was restricted upper 50 m of the water column.

The compositional analyses of DHAA and DCCHO suggested preferential microbial uptake of Glu, Phe, Ser, Leu and Rha, Gal, Fuc, Ara in the near surface waters, as below 50 m depth, the composition of DHAA and DCCHO were dominated by Gly and Glc, respectively (Fig. 5, Table 1). Glc was previously suggested to be less susceptible to microbial degradation compared to preferentially removed Fuc, Gal, and Ara (Ittekkot et al., 1981; Sempere et al., 2008; Goldberg et al., 2010; Engel et al., 2012). Enrichment in Gly with depth ~~was~~ also ~~previously been~~ proposed to ~~be reflection of~~ reflect the low nutritional value of Gly ~~for organisms~~ in anoxic sediments in ETSP off Chile (Pantoja and Lee, 2003) and in sediments of the North Sea (Dauwe and Middelburg, 1998). ~~In~~ ~~There with~~, our study, DHAA and DCCHO below 50 m depth were mainly composed by Gly and Glc, respectively, indicating a significant stage of data suggest that DOM reworking. ~~Despite in~~ the shallow depth, DOM below 50 m depth OMZ off Peru was characterized by ~~much~~ stronger alteration ~~than~~ compared to open ocean samples collected by (Kaiser and Benner, 2009) ~~from~~ ~~at~~ ~~even~~ much greater depths (up to 4000m), ~~suggesting~~. This may be due to both, an upwelling of altered DOM from the deep and a rapid and very extensive heterotrophic DOM utilization in ETSP. This the ETSP. The upwelling may “compress” labile and semi-labile DOM towards the surface, while the rapid microbial utilization of DOM ~~could~~ ~~shall~~ prevent labile and semi-labile DOM export into the OMZ, and also ~~implies~~ ~~would~~ ~~imply~~ a pronounced heterotrophic respiration. ~~The latter was suggested by our PCA analyses~~, as DOM composition was highly interrelated to AOU. Herewith, the diapycnal supply of DHAA and DCCHO ~~may~~ ~~could~~ explain up to 38% of $\overline{V\Phi}_{O_2}$. This ~~suggests~~ ~~suggest~~, that despite the utilization diapycnal fluxes of labile and semi-labile fractions of DOM is an important controlling factor of ~~may~~ not reach deep into the core of the OMZ, DOM based microbial respiration above the OMZ may substantially attenuate the diapycnal O₂ flux that ventilates the upper oxycline. In other words, DOM may alter the shape of the upper oxycline of the OMZ, while the attenuation, and, therefore, contribute to the formation and maintenance of O₂ in deeper parts of the upper water column is likely to be explained by other bioavailable OM sources, such as POM, the OMZ.

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30 5 Conclusions

Our results suggest that DOM, i.e. DCCHO and DHAA, is significantly consumed and altered above the upper oxycline in the ETSP off Peru. Thus, despite the presence of high DOC concentrations in the euphotic zone, DOM may enter the OMZ in an

already highly reworked stage. Herewith, DOM respiration may contribute substantially (~38%) to O₂ reduction in the upper water column, potentially controlling the shape of the upper oxycline of the OMZ. The elevated diapycnal supply of DOC to the upper oxycline, which cannot be explained by microbial processes solely, hint to the presence of an additional DOM removal ~~mechanisms~~mechanism, such as microgel formation or absorption onto particles.

5 6 Data availability

The microstructure profiles are available at <https://doi.org/10.1594/PANGAEA.868400>. The O₂, temperature, salinity, chl a fluorescence and nutrients were published at <https://doi.org/10.1594/PANGAEA.860727>. The DOM data will be available at PANGAEA (www.pangaea.de, search project: sfb754) after publication.

7 Competing interests

10 The authors of this manuscript are not aware of any real or perceived financial conflicts of interests for other authors or authors that may be perceived as having a conflict of interest with respect to the results of this paper.

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5 Table 1: Relative composition (mol%) of dissolved hydrolysable amino acids (DHAA) and dissolved combined carbohydrates (DCCHO) in the water column, "n.d." - not detectable, in the water column, "n.d." - not detectable. The DCCHO are divided into three classes, nS - neutral sugars, S-N - amino-sugars, and S-H - acidic sugars. The number of samples at each depth interval, used for calculation of the average value, is given as "n". The mean values for DHAA and DCCHO composition below the mixed layer (10 to 122 m) are reported for similar depth intervals (14 m) as diapycnal DOM and O₂ fluxes. The mean values for DHAA and DCCHO within the mixed layer are reported for ~5 m depth intervals.

Depth (m)	n	DHAA			mol% DHAA											
		($\mu\text{mol L}^{-1}$)	(%DOC)	(%DON)	Gly	Thr	Ala	Asp	Glu	Ser	Arg	Leu	Val	Ileu	Phe	Tyr
1-5	30	0.6±0.3	2±1	15±10	22±4	9±1	11±1	17±1	15±3	11±2	2.3±0.3	4±1	3.0±0.4	2.5±0.6	2.4±0.4	1.8±0.4
5-10	25	0.5±0.3	2.3±0.9	15±9	23±4	9±2	11±1	17±1	15±4	10±1	2.2±0.4	4±1	2.9±0.6	2.1±0.5	2.1±0.4	1.7±0.3
10-24	48	0.4±0.2	1.8±0.8	16±14	25±4	9±2	11±1	17±1	13±2	9±1	2.1±0.6	3±1	2.8±0.7	2.2±0.7	2.1±0.6	1.9±0.5
24-38	28	0.24±0.07	1.2±0.3	12±14	28±3	10±1	12±1	17±1	11±2	9±1	1.9±0.4	3±1	2.4±0.6	1.9±0.6	1.8±0.4	2.0±0.7
38-52	34	0.20±0.05	1.0±0.4	9±7	29±6	10±2	12±2	16±2	11±2	9±1	1.8±0.6	3±2	2.3±0.8	1.7±0.5	1.8±0.4	1.7±0.4
52-66	35	0.17±0.03	0.9±0.3	13±19	31±3	10±2	12±1	16±1	10±2	8±1	1.7±0.4	2±1	2.4±0.5	1.6±0.7	1.7±0.3	1.7±0.5
66-80	27	0.16±0.05	0.9±0.3	9±8	32±4	10±1	12±1	15±2	10±2	8±1	1.7±0.5	2±1	2.5±0.6	1.7±0.8	1.7±0.4	1.8±0.5
80-94	22	0.15±0.08	0.9±0.4	8±7	34±3	10±2	12±2	15±1	10±2	9±1	1.6±0.4	2±1	2.2±0.7	1.3±0.7	1.6±0.4	1.6±0.4
94-108	14	0.13±0.03	0.7±0.2	9±8	34±3	10±2	13±2	15±2	9±2	8±2	1.6±0.5	2±1	2.3±0.7	2±1	1.7±0.4	1.7±0.9
108-122	13	0.13±0.03	0.8±0.2	6±4	32±3	10±2	12±1	16±2	10±2	8±1	1.7±0.3	3±1	2.3±0.8	2±1	1.9±0.4	1.7±0.5
122-200	18	0.12±0.03	0.7±0.3	8±6	35±3	10±1	12±2	15±2	9±1	8±2	1.5±0.7	2±1	2.5±0.6	1.7±0.7	1.5±0.4	1.5±0.5
Depth (m)	n	DCCHO ($\mu\text{mol L}^{-1}$)			mol% DOC			mol% nS					mol% S-H			
		nS	S-N	S-H	nS	S-N	S-H	Glc	ManXyl	Gal	Rhm	Fuc	Ara	Glu-URA	Gal-URA	Glc-H
1-5	30	1.5±0.8	0.10±0.03	0.10±0.08	9±4	0.6±0.2	0.6±0.3	30±13	32±6	17±6	11±8	8±2	2±1	48±21	51±21	0.4±2
5-10	25	1.1±0.6	0.08±0.03	0.07±0.05	8±4	0.5±0.1	0.5±0.3	33±11	33±5	16±6	8±6	8±2	2±1	43±26	55±24	2±10
10-24	47	0.7±0.3	0.06±0.02	0.04±0.03	5±2	0.4±0.1	0.3±0.2	36±13	37±8	12±5	5±4	7±2	2±1	32±25	67±25	1±7
24-38	28	0.4±0.1	0.04±0.01	0.02±0.02	4±1	0.3±0.1	0.2±0.1	43±11	38±7	9±4	2±2	6±2	0.4±1.0	20±20	80±20	n.d.
38-52	35	0.4±0.2	0.03±0.01	0.02±0.01	4±2	0.3±0.1	0.1±0.1	42±10	41±9	9±3	2±2	5±2	0.3±0.8	28±30	72±30	n.d.
52-66	34	0.5±0.2	0.03±0.01	0.02±0.02	4±2	0.2±0.1	0.2±0.2	45±9	41±9	7±4	2±2	5±2	0.2±0.6	21±27	77±28	2±11
66-80	27	0.4±0.2	0.02±0.01	0.01±0.01	4±2	0.2±0.1	0.1±0.1	47±13	44±12	5±3	1±1	3±2	0.3±0.7	19±28	81±28	n.d.
80-94	22	0.4±0.2	0.02±0.01	0.01±0.01	4±2	0.2±0.1	0.1±0.1	47±11	45±10	4±3	0.1±0.6	2±2	0.7±1.3	32±33	68±33	n.d.
94-108	15	0.3±0.1	0.02±0.01	0.01±0.01	3±1	0.2±0.1	0.1±0.1	53±11	40±10	4±3	0.1±0.5	2±2	0.2±0.9	28±29	72±29	n.d.
108-122	13	0.4±0.1	0.02±0.01	0.02±0.02	4±2	0.2±0.1	0.2±0.2	51±16	43±14	3±3	0.2±0.7	2±2	0.3±1.0	44±46	56±46	n.d.
122-200	18	0.4±0.2	0.02±0.01	0.01±0.02	4±1	0.2±0.1	0.1±0.2	52±10	44±9	2±2	n.d.	1±2	0.7±2.3	22±30	78±30	n.d.

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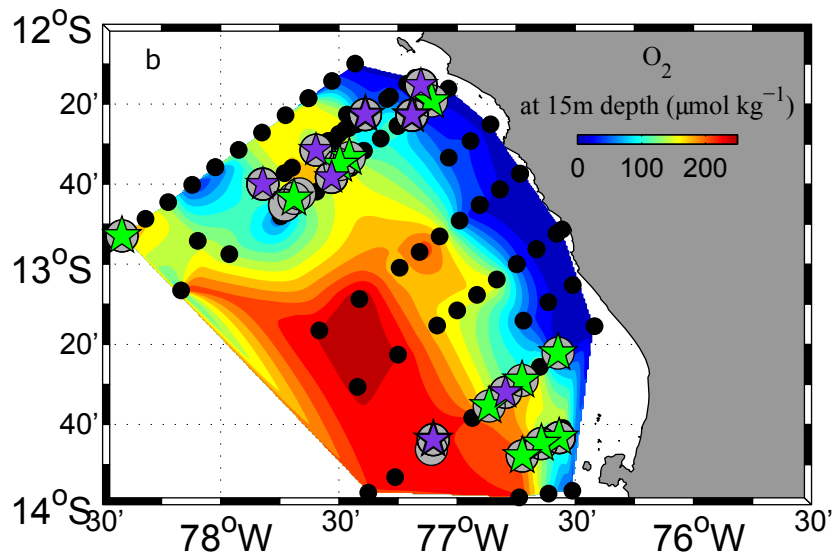
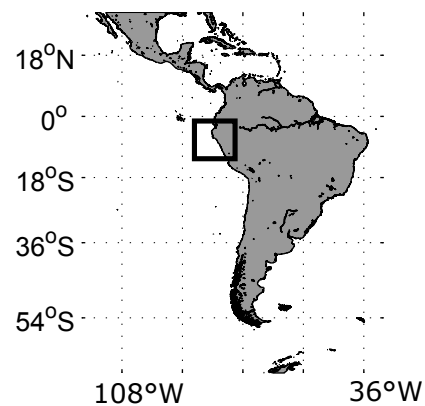
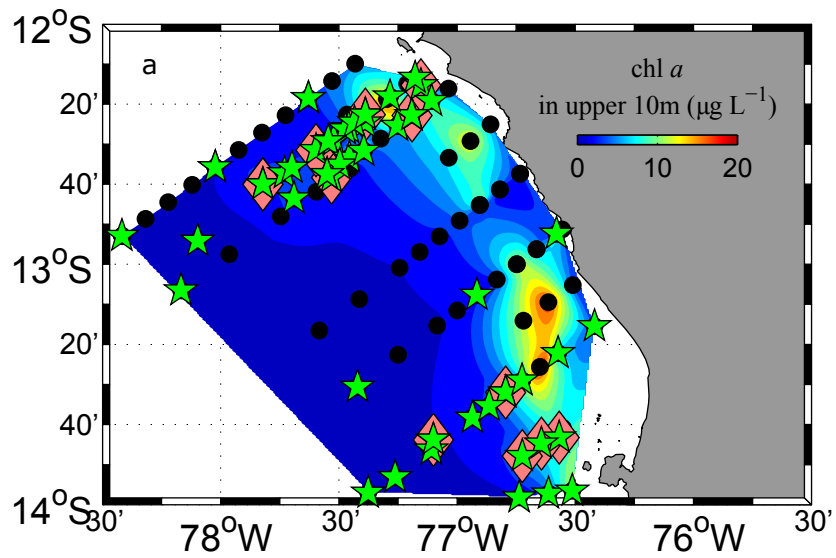
Table 2: Diapycnal fluxes and supplies (in bold) of O₂ and DOM: DOC, DON, dissolved organic carbon in DCCHO and DHAA and dissolved organic nitrogen in DHAA; averaged fluxes and supplies. Errors are presented in the brackets, 95% confidence intervals, calculated after Schafstall et al. (2010) for each parameter, are presented in brackets. BLM – “below the mixed layer” – a depth, defined below 10m of the water column, using a threshold criterion of 0.2°C temperature decrease.

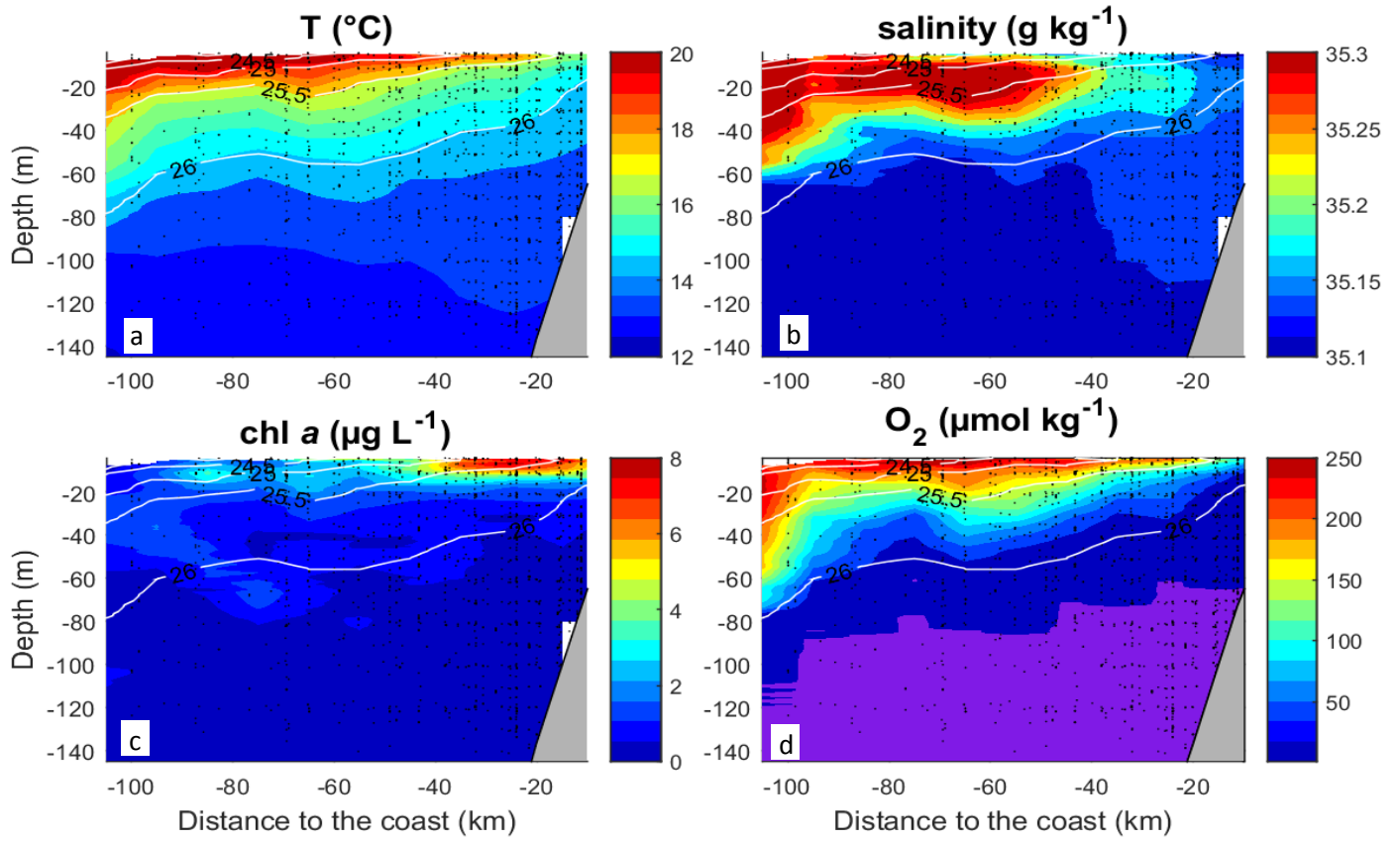
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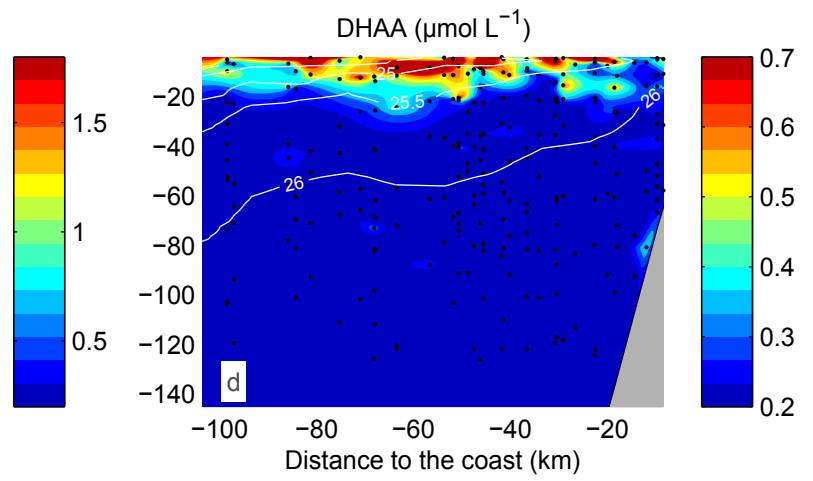
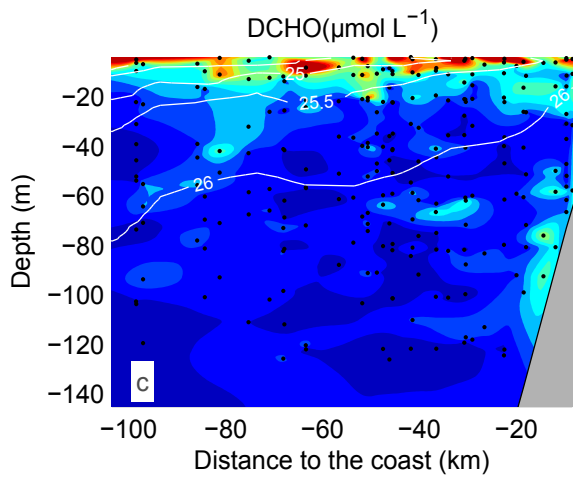
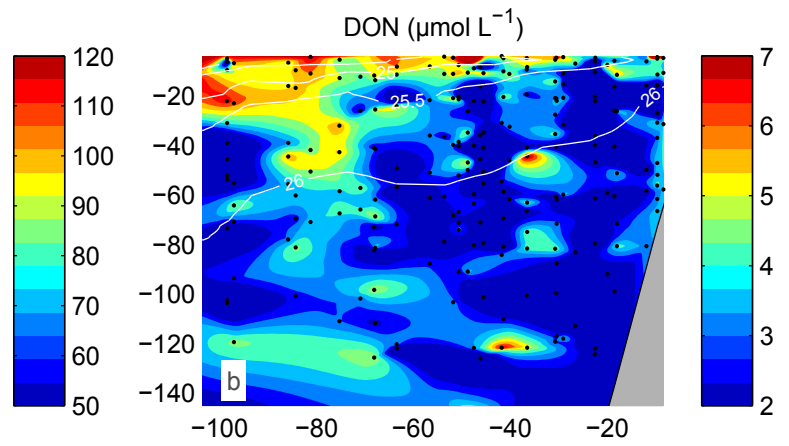
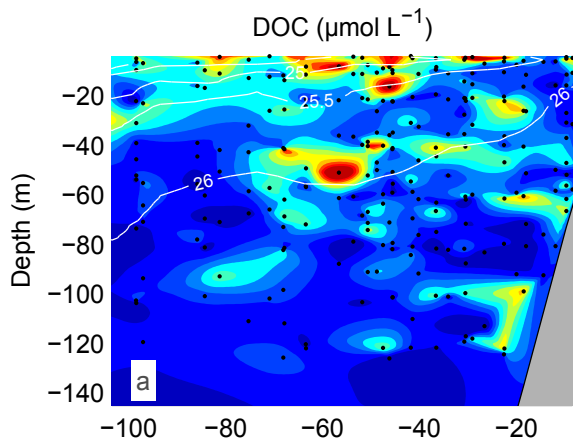
	Depth	DOC	DON	DCCHO-C	DHAA-C	DHAA-N	O ₂
Flux (mmol m ⁻² day ⁻¹)	10-24	31 (25)	-0.6 (0.4)	6 (2)	0.9 (0.4)	0.3 (0.1)	50 (14)
	24-38	5 (17)	8 (6)	0.2 (0.1)	0.07 (0.03)	0.03 (0.01)	32 (10)
	38-52	0.4 (0.5)	0.4 (0.9)	0.12 (0.07)	0.07 (0.03)	0.03 (0.02)	32 (9)
	52-66	0.2 (0.2)	0.5 (1.3)	0.01 (0.01)	0.05 (0.02)	0.02 (0.01)	17 (6)
	66-80	0.6 (0.7)	0.1 (0.3)	0.12 (0.06)	0.02 (0.01)	0.7×10⁻³ (0.4×10 ⁻³)	8 (4)
	80-94	-0.04 (0.35)	-0.1×10⁻³ (0.3×10 ⁻³)	0.14 (0.07)	0.01 (0.02)	0.4×10⁻³ (0.5×10 ⁻³)	0.12 (0.07)
	94-108	-0.2 (0.2)	0.05 (0.04)	0.09 (0.08)	0.6×10⁻³ (0.5×10 ⁻³)	0.2×10⁻³ (0.1×10 ⁻³)	0.016 (0.7×10 ⁻³)
	108-122	-0.2 (0.2)	0.01 (0.08)	-0.01 (0.01)	0.2×10⁻³ (0.3×10 ⁻³)	0.1×10⁻³ (0.2×10 ⁻³)	0.02 (0.01)
Supply (mmol m ⁻² day ⁻¹)	10-38	1.8 (2.1)	-	0.4 (0.2)	0.06 (0.03)	0.02 (0.01)	1.2 (1.2)
	24-52	0.3 (1.2)	0.6 (0.4)	0.5×10⁻³ (0.8×10 ⁻³)	0.1×10⁻³ (3.2×10 ⁻³)	0.2×10⁻⁴ (0.14×10 ⁻⁴)	0.04 (0.93)
	38-66	0.01 (0.04)	-0.01 (0.1)	0.8×10⁻² (0.5×10 ⁻²)	0.1×10⁻² (0.3×10 ⁻²)	0.1×10⁻² (0.1×10 ⁻²)	1.0 (0.8)
	52-80	-0.03 (0.05)	0.03 (0.09)	-0.8×10⁻² (0.5×10 ⁻²)	0.2×10⁻² (0.2×10 ⁻²)	0.7×10⁻³ (0.6×10 ⁻³)	0.7 (0.5)
	66-94	0.05 (0.05)	0.01 (0.02)	-0.1×10⁻² (0.7×10 ⁻²)	0.1×10⁻³ (0.2×10 ⁻³)	0.2×10⁻³ (0.5×10 ⁻³)	0.5 (0.3)
	80-108	0.01 (0.03)	-0.3×10⁻³ (0.3×10 ⁻³)	0.4×10⁻² (0.8×10 ⁻²)	0.4×10⁻³ (1.4×10 ⁻³)	0.1×10⁻³ (0.4×10 ⁻³)	0.7×10⁻² (0.5×10 ⁻²)
	94-122	0.4×10⁻³ (0.017)	0.2×10⁻³ (0.6×10 ⁻³)	0.7×10⁻² (0.6×10 ⁻²)	0.4×10⁻³ (0.3×10 ⁻³)	0.1×10⁻³ (0.1×10 ⁻³)	-0.1×10⁻² (0.1×10 ⁻²)

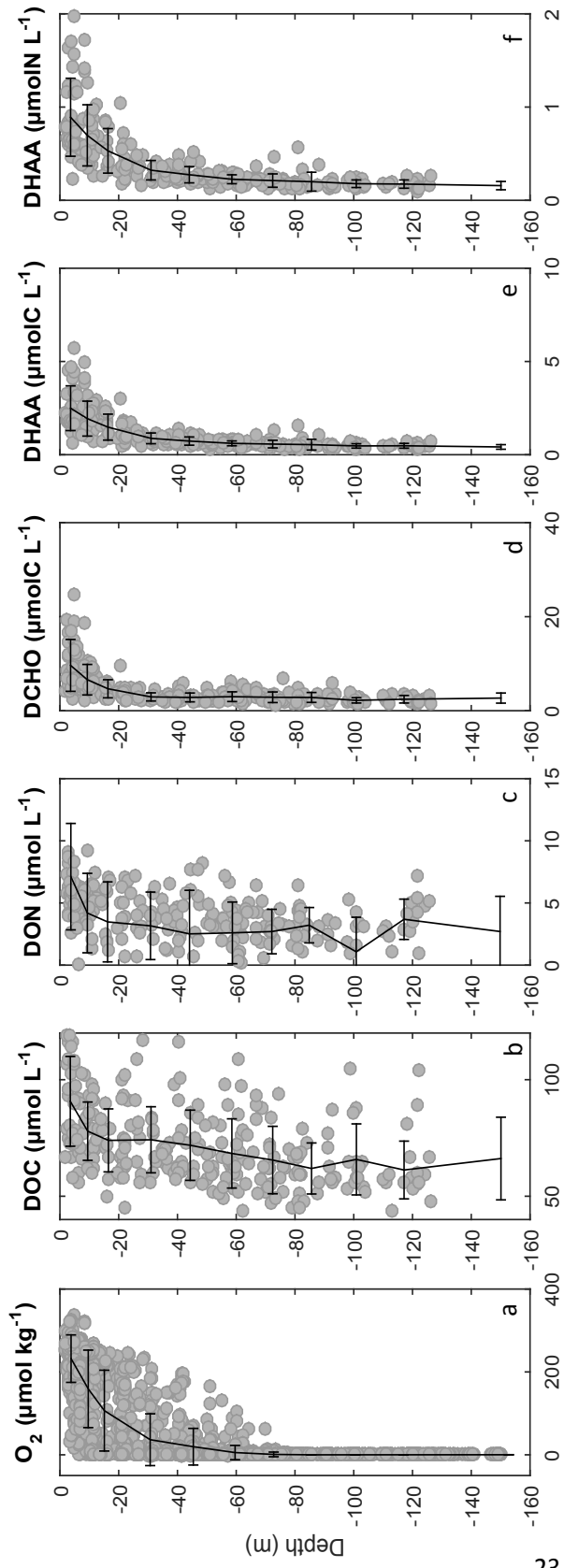
	Depth (m)	DOC	DON	DCCHO-C	DHAA-C	DHAA-N	O ₂
Flux (mmol m ⁻² day ⁻¹)	BML-24	31 (+56/-6)	-0.6 (+0.1/-1.0)	6 (+8/-0.06)	0.9 (+1.3/+0.1)	0.3 (+0.4/+0.05)	50 (+77/+17)
	24-38	5 (+24/-12)	8 (+87/-2)	0.2 (+6/-0.01)	0.07 (+0.4/+0.03)	0.03 (+0.15/+0.013)	32 (+77/+11)
	38-52	0.4 (+1.2/-0.1)	0.4 (+8/-1)	0.12 (+2/+0.04)	0.07 (+0.3/+0.04)	0.03 (+0.1/+0.01)	32 (+72/+15)
	52-66	0.2 (+0.6/-0.003)	0.5 (+14/-2)	0.01 (+16/-0.9)	0.05 (+0.2/+0.03)	0.02 (+0.1/+0.01)	17 (+89/+5)
	66-80	0.6 (+1.8/-0.03)	0.1 (+12/-2)	0.12 (+11/-0.5)	0.02 (+0.5/-0.08)	0.7×10⁻² (+0.2/-0.03)	8 (+17/+1)
	80-94	-0.5 (+0.3/-0.4)	-0.1×10⁻² (+0.01/-0.06)	0.14 (+11/-0.5)	0.01 (+0.2/-0.02)	0.4×10⁻² (+0.06/-0.01)	0.12 (+0.2/+0.03)
	94-108	-0.2 (+0.02/-0.4)	0.05 (+11/-2)	0.09 (+24/-1)	0.6×10⁻² (+0.3/-0.05)	0.2×10⁻² (+0.1/-0.02)	0.016 (+0.04/+0.01)
	108-122	-0.2 (-0.06/-0.4)	0.01 (+3/-0.5)	-0.01 (+0.3/-4)	0.2×10⁻³ (+0.01/-0.02)	0.1×10⁻³ (+0.01/-0.001)	0.02 (+0.06/+0.01)
Supply (mmol kg ⁻¹ day ⁻¹)	BML-38	1.8 (+4.0/-1.0)	-0.6 (+5/-1)	0.4 (+0.8/-0.02)	0.06 (+0.09/+0.005)	0.02 (+0.03/+0.002)	1.2 (+5/-2)
	24-52	0.3 (+1.6/-0.9)	0.6 (+6/-0.2)	0.5×10⁻² (+0.4/-0.01)	0.1×10⁻³ (+0.02/-0.003)	0.2×10⁻⁴ (+0.01/-0.001)	0.04 (+4/-2)
	38-66	0.01 (+0.07/-0.03)	-0.01 (+1/-0.2)	0.8×10⁻² (+0.2/+0.002)	0.1×10⁻² (+0.02/-0.001)	0.5×10⁻³ (+0.01/-6×10 ⁻⁴)	1.0 (+7/-0.5)
	52-80	-0.03 (+0.05/-0.08)	0.03 (+1/-0.2)	-0.8×10⁻² (+1/-0.1)	0.2×10⁻² (+0.04/-0.005)	0.7×10⁻³ (+0.01/-0.002)	0.7 (+6/-0.3)
	66-94	0.05 (+0.13/-0.006)	0.01 (+0.9/-0.1)	-0.1×10⁻² (+1/-0.1)	0.6×10⁻³ (+0.04/-0.007)	0.2×10⁻³ (+0.01/-0.003)	0.5 (+1/+0.07)
	80-108	0.8×10⁻² (+0.03/-0.02)	-0.3×10⁻² (+0.8/-0.1)	0.4×10⁻² (+2/-0.1)	0.4×10⁻³ (+0.02/-0.04)	0.1×10⁻³ (+0.007/-0.001)	0.7×10⁻² (+0.01/+0.001)
	94-122	0.4×10⁻² (+0.02/-0.01)	0.2×10⁻² (+0.8/-0.1)	0.7×10⁻² (+2/-0.3)	0.4×10⁻³ (+0.02/-0.004)	0.1×10⁻³ (+0.006/-0.001)	-0.1×10⁻² (+0.003/-0.002)

- Figure 1: Study area and station map. CTD stations, where CTD-probe and fluorimeter measurements were accomplished are marked as black dots (a,b). PUMP-CTD stations are depicted in pink diamonds (a). CTD and PUMP-CTD stations, where DOM sampling was performed are marked as green stars (a). Microstructure measurements, combined with oxygen profiles are marked as grey circles (b). Microstructure measurements, combined with dissolved organic matter (dissolved organic carbon (DOC), dissolved hydrolysable amino acids (DHAA) and dissolved combined carbohydrates (DCCHO)) measurements marked as green pentagrams (b). Extra microstructure measurements, combined with DOC measurements marked with violet pentagrams (b). Shaded colors represent chl *a* concentrations at upper 10 m depth (a) and oxygen concentrations at 15m depth (b). Spaces between data points were interpolated by using TriScatteredInterp function (MATLAB, MathWorks).
- Figure 2: Mean vertical distribution of the temperature (a), salinity (b), (c) chlorophyll *a* (chl *a*) and (d) O₂. O₂ values below 1 μmol kg⁻¹ are shaded in violet. The data from all transects and stations were averaged over intervals of 10 km on “Distance from the coast” axis and over 1 m on “Depth” axis. Isolines represent potential density, averaged over intervals of 10 km on “Distance from the coast” axis and over 1 m on “Depth” axis.
- Figure 3: Dissolved organic carbon (DOC) (a), dissolved organic nitrogen (DON) (b), dissolved combined carbohydrates (DCCHO) (c) and dissolved hydrolysable amino acids (DHAA) (d) distributions over the water column. Data from all transects and stations were plotted against distance to coast (km). Space between data points was interpolated by using TriScatteredInterp function (MATLAB, MathWorks). Isolines represent potential density, averaged over intervals of 10 km on “Distance from the coast” axis and over 1 m on “Depth” axis.
- Figure 4: Vertical distribution of O₂ (a), DOC (b), DON (c), DCCHO(C) (d), DHAA(C) (e), DHAA(C) (f). Black line and error bar represent median distribution and standard deviations of the data points (grey circles), respectively.
- Figure 5: The PCA analysis output: variables (on the left) and individuals scores of samples (from the right). The samples, collected above 50m depth are marked with acronym “s”, the ones, below 50m depth – with acronym “d”. The samples, which are used for comparison are marked with acronyms “HOT” and “BATS”, and represented well oxygenated samples, collected from open Pacific and open Atlantic Oceans, respectively (Kaiser and Benner, 2009).

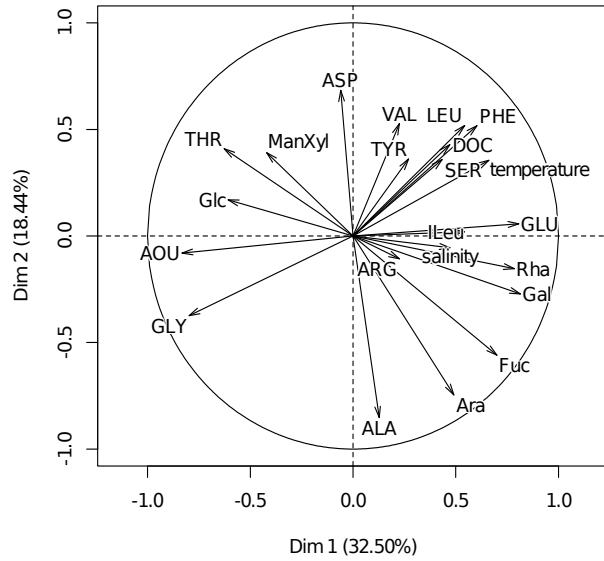








Variables factor map (PCA)



Individuals factor map (PCA)

