The answer for the review comments for BG-2018-284.

In the following the authors will address review comments one by one. the review comment will be marked as R1 or R2, for reviewer1 and 2, respectively. Authors' response will be marked as A.

General Comments:

R1:   1. The Introduction needs to be better written. I was confused by the logical construction of the main points being made too many times. For example, the statement "changes in the remineralization rate of DOM might rather be linked to lack of bioavailable OM supply into the OMZ than to low-O2 conditions" was not preceded by any mention that DOM consumption rates vary in the water column. Instead, we were told that "Recent studies in the upwelling area and the corresponding OMZ off Chile… found bacterial activity of similar range to the oxygenated waters." This finding does not tell us about DOM.

A: We thank the R1 for his/her comments.

The sentence (page 2 line 20): "Thus, the rapid microbial decomposition of labile organic matter in the euphotic zone is commonly followed by slower decomposition of less bioavailable semi-labile DOM and very slow decomposition of extensively reworked refractory DOM deeper the water column (e.g. Hansell, 2013)." Was added to the revised version of the manuscript.

The paragraph (page 2, line 25-34) was rephrased into: "Microbial decomposition of organic matter has previously been suggested to be limited under anoxia (Harvey et al., 1995; Nguyen and Harvey, 1997). Following this suggestion, one may assume that, if labile DOM is supported to the OMZ, it would not be reworked as rapidly as in oxygenated waters. Recent studies in the upwelling area and the corresponding OMZ off Chile found, however, that even under anoxia the ability of microbes to decompose labile DOM (Leucine-incorporation rate) did not differ from the oxygenated waters (Sempéré et al., 2008, Pantoja et al., 2009). These studies suggest that slower remineralization of DOM in OMZ might rather be caused by lack of bioavailable organic matter supply into the OMZ than by low-O_2 conditions. Herewith, measured concentrations of bioavailable components of DOM over the water column in the ETSP are yet controversary. For instance, Pantoja et al. (2009) reported relatively high concentrations of free and combined AA in the OMZ off Chile. Sempere et al. (2008) reported low concentrations of neutral CHO in the corresponding upwelling area, compared to the open Pacific Ocean."

R1: Another example of confusing text: "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." I do not know what that means.

A: The sentence has been removed.

R1: I am not a fan of averaging all of the measurements (as in Figure 4) and then evaluating the profiles of the mean concentrations for vertical fluxes. Clearly, the waters very near the coast are upwelling while those further offshore are highly stratified. In O2 (Fig 4a), for example, we see surface concentrations ranging from near zero at the coast to >200 uM offshore; the mean of O2 is neither useful nor insightful. I suggest evaluating the stratified region for diapyncal fluxes. Inclusion of the waters that are actually upwelling will bias the answer to the question posed. The authors agree with the when they state that "This spatial averaging is likely responsible for a lower near-surface diapycnal O2 flux compared to other eastern boundary upwelling systems", so why do the averaging?

A: We thank the R1 for the comment. We would like to draw the reviewer's attention to the chapter 2.3, and that the diapycnal fluxes were calculated using a solutes profile and the microstructure profiles collected directly afterwards or before this individual profile. Averaging was then done for the fluxes to get one mean flux profile and further calculating of the diapycnal solute supply. The Figure 4, where the mean distribution is shown, is used only for easier visualization of the solute's gradients and only for the sake of discussion.

Following the reviewer's suggestion, we have added the separated presentation of average solute's profiles on the onshore (<40 km) and offshore (>40 km) to the Figure 4. We have added a discussion of the onshore and offshore diapycnal oxygen fluxes and supply (page 8, line 14):

"Onshore (<40 km) and offshore (>40 km) O_2 fluxes did not differ statistically. This likely was due to the fact that while vertical oxygen gradients were enhanced in the offshore region (Fig.4), the turbulence and, thus, eddy diffusivities were elevated in the onshore region."

and on page 8 line 17:

"Again, onshore (<40 km) and offshore (>40km) the diapycnal O_2 supply was not statistically different."

However, we refrained from presenting numbers of diapycnal fluxes and supply of O_2, DOC, DON, DCCHO and DHAA for the onshore and offshore regions separately. This is because the 95% confidence intervals for the regionally separated fluxes become very unfavourable. The elevated uncertainty originates from the elevated temporal variability of turbulence in the ocean. Diapycnal fluxes of solutes in the ocean are driven by turbulent

mixing events that are short-lived, patchy and occur sporadically. With time, elevated mixing events are distributed near-logarithmically and very strong events, having 10000 (10^4) times more energy than weak events and enhancing turbulent mixing by the same order of magnitude, occur very infrequent. Yet, it is the strength and the frequency of occurrence of these elevated mixing events that determines the magnitude of the diapycnal flux of DOM or of oxygen. The variability of the turbulence is reflected in the elevated spread of the upper and lower 95% confidence limits presented in the Table 2. Thus, in order to estimate a representative diapycnal flux of O_2 and DOM we had to combine all data available from the study area to determine a single diapycnal solute flux and supply profile. This study uses 263 turbulence profiles collected in the study area along with respective oxygen and DOM profiles. Each turbulence profile collected during the cruise required about 20 min of the ship time. Thus, the used data set represents more than 3.5 days of continuous turbulence measurements. Any separation of the dataset would strongly degrade statistical confidence of the calculated fluxes and supply.

Certainly, we expect regional differences within the study area. However, a different measurement program would need to be designed focusing solely on those differences. In our contribution, we intend to provide the first estimates of average diapycnal fluxes of O_2, DOC, DON, DCCHO and DHAA in the Peruvian upwelling region aiming at advancing the understanding of the prominent biogeochemical processes.

R: I'm unclear on why the authors offered in this paper two disconnected questions: i) how important is the diapycnal flux of DOM and ii) does the low O2 in the OMZ cause changes in the DOM composition?

A: As the cycling of DOM in the ETSP was little studied prior to our cruise, our research questions were based on the limited information that we had and the general understanding of the DOM cycling and the OMZ.

The ETSP is characterized by high primary production (which could potentially lead to high concentrations of DOM) in surface waters over a permanent OMZ in the subsurface layer. Those characteristics motivate our first research question about whether bioavailable DOM may be supplied to the upper OMZ via turbulent mixing.

Consequently, the first question then led to the investigation of related scientific issues, such as: How strong the O_2 supply (which is supposed to ventilate upper oxycline of the OMZ) is actually reduced due to utilization of the DOM/or how important is DOM for sustaining of the OMZ? How would DOM cycling be altered in the upper OMZ? Will the reworking of DOM slow down? How it will affect the composition of DOM?

We formulated those question prior to our work and to access those questions we combined two approaches: physical flux measurements and analyses of DOM composition. We estimated the diapycnal supplies of solutes, compared the supply of DOM to supply of O_2 and also compared the composition of DOM from OMZ influenced water column to the composition of DOM from well oxygenated waters. In the Introduction section we discuss possible effects of anoxia on DOM cycling to provide context to our scientific questions.

Herewith, our very different approaches agreed well, and the results of our study suggested that DOM is extensively reworked already above the upper oxycline by aerobic respiration; thus, DOM may be supplied to the OMZ is in already highly reworked stage. However, the remineralization of DOM above the upper oxycline may substantially attenuate O_2 supply that ventilates OMZ.

R1: Specific Comments:

Page/Line

R1:   3/20: the "L" is missing in the units for P.

A: "μmo" was replaced with "μmol"

R1:   3/22: "where" rather than "here"

A: "here" was replaced with "where"

R1:   5/1: remove "," after "significant". In general, the authors should look at every comma used and determined whether or not it is used correctly; there were too many poorly placed commas in the text. Do not use them where a pause is not intended.

A: The comma was removed. We also removed not needed commas throughout the text.

R1:   7/11: I appreciate the author's doubting the very high DOC values they report. DOC concentrations of 100-120 uM are not typically observed unless a river is nearby. Franz et al 2012 was cited as a paper similarly reporting high DOC off Peru, but that work was done in a mesocosm; I do not see where the authors reported high DOC in a natural setting. And the DOC data coming out of the Romankevich lab in the 80's, another paper cited for high values off Peru, are also highly suspect. I wouldn't cite that paper since the data are not reliable. I hope these high values were not included in calculating the diapycnal fluxes of DOC; the high values should be excluded.

A: We thank the R1 for this comment. However, the R1 refers to Franz et al 2012b – paper in the "Biogeosciences" Journal. For the DOC, we cited Franz et. al. 2012a in the Journal "Deep Sea Research Part I". This paper contains field DOC data. The DOC concentrations reported by Franz et al 2012a vary from ~50 to 300 µmol/L. Therefore, our data are within the reported range.

R1: 7/20: "DCCHO represented from 1 to 25% of DOC". I am confused about which DCCHO data to look at when considering that statement. In Table 1 I see the DCCHO in the depth range of 1-5 m sums to 1.7 umol/L (nS+S-N+S-H), while in Fig. 4d the DCCHO mean is closer to 10 umol/L. Which DCCHO data should I be looking at; the two sources (table vs figure) seem to disagree with one another.

A: We thank the R1 for the comment. Please, note that the data presented in the figure 4 is expressed in µmol C/L for DCCHO and DHAA and in µmol N/ L for DHAA, while the values in the Table 1 are expressed in µmol monomer /L of DCCHO and DHAA.

R1: Table 2: why are the numbers in bold type? I do not see the need for that. And why in the lower section is the upper most depth range "BML-38", which reaches into the middle of the depth range just below it (24-52). Should it be "BML-24", as in the upper section of the table?

A: We thank the R1 for the comment. The bold type was changed to the plain text.

We would like to draw the attention of the R1 that the diapycnal supply was obtained by calculating the difference between two flux values (and dividing by the depth distance and the density) as described in the chapter 2.3. Therefore, each supply value is based on the two flux estimates, resulting in the larger, shifted and overlapping depth ranges.

R1: 8/21: remove ',' after "to understand"

A: The comma has been removed

Report #2

R2:   This study provides novel and interesting observations of dissolved oxygen and DOM dynamics in the upper water column of the highly productive Peru upwelling system. The microbial utilization of DOM and dissolved oxygen plays an important role in shaping the upper oxycline and maintaining the oxygen minimum zone. The carbohydrate and amino acid components of DOM were preferentially utilized in the upper water column, indicating rapid utilization of labile and semi-labile components of DOM. The composition of DOM in the oxygen minimum zone indicated extensive alteration and the removal of most bioavailable components.

R2:   I think the authors should consider particles as potentially important sources of DOM in the upper water column. Particulate matter is abundant in this system and the microbial utilization of POM is a major sink for dissolved oxygen in the upper water column. Microbial degradation of POM also releases DOM and is a potentially important source of labile and semi-labile components of DOM (Smith et al. 1992). Therefore, the diapycnal flux approach in this study likely underestimates the role of microbial respiration of DOM in shaping the upper oxycline.

A: We thank R. Benner for the comment.
       We added following paragraph to the Discussion (page 10 Lines 23-29):
       "DOM might also be transported to depth within particles. Thus, the "uncoupled" dissolution of large sinking aggregates as a result of bacterial enzymatic activity (Smith et al., 1992) or abiotically (Sempéré et al., 2000) may serve as an additional DOM source and, therefore, affect the distribution of DOM in the water column. The sporadic dissolution of particles may bias the diapycnal DOM flux estimates at individual stations. Therefore, the bias may be reduced by calculating the mean diapycnal flux over a large number of depth profiles. The continuous DOM release from POM over the water column (e.g. Lefèvre et al., 1996), in turn, may lead to an overestimation of diapycnal DOM fluxes and DOM based microbial respiration. However, no direct measurements of the DOM fraction resulting from particle dissolution exist so far in the studied area."

Specific comments:

R2:   The authors use many abbreviations, some of which are not common. This makes reading the article tedious in some areas, and I recommend eliminating uncommon abbreviations (e.g. n-S, S-H, S-N, DURA, etc.).

A: The abbreviations nS, S-H, S-N and DURA have been removed from the revised version of the text, the abbreviations for the individual analysed acidic, uronic and amino sugars were replaced according to the abbreviation list given in FEBS Journal Volume 74, pp 1-6, 1977

(doi:10.1111/j.1432-1033.1977.tb11359.x.). Acronyms nS, SN and SA for neutral sugars, amino sugars and acidic sugars, respectively, however had to be kept in the Table1 for the sake of space. Those acronyms are introduced in the Table's legend.

R2:   Pg 5, line 7: The amino acids asparagine and glutamine are deaminated during acid hydrolysis, and they contribute to the measured concentrations of aspartic acid and glutamic acid, respectively.

A: We added the following sentence to the Page 5 Line 14:

"The amino acids asparagine and glutamine likely contributed to the measured Asp and Glu concentrations, respectively, due to deamination during hydrolysis."

Diapycnal dissolved organic matter supply into the upper Peruvian oxycline

Alexandra N. Loginova[1], Sören Thomsen[1,2], Marcus Dengler[1], Jan Lüdke[1], Anja Engel[1*]

[1]GEOMAR Helmholtz-Centre for Ocean Research Kiel, Düsternbrooker Weg 20, Kiel, 24105, Germany

[2]LOCEAN-IPSL, IRD/CNRS/Sorbonnes Universites (UPMC)/MNHN, Paris, UMR 7159, France

Correspondence to: Anja Engel (aengel@geomar.de)

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 (O_2) 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 O_2 respiration in the Peruvian upwelling system in general and for shaping the upper oxycline in particular remains unclear so far. This study reports the first estimates of diapycnal fluxes and supply of O_2, 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 O_2 flux that ventilates the OMZ. The observed diapycnal O_2 flux (50 mmol O_2 m^{-2} day^{-1} at max) was limited to the upper 80 m of the water column, the O_2 supply of ~1 µmol kg^{-1} day^{-1}, was comparable to previously published O_2 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 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 kg^{-1} day^{-1} at max), could account for up to 38% of the diapycnal O_2 supply in the upper oxycline, which suggests that DOM utilization plays a significant role for shaping of the upper oxycline in the ETSP.

1 Introduction

Dissolved oxygen (O_2) 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 O_2 (e.g. Bender and Heggie 1984). 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). The core of the Peruvian OMZ is considered to be fully anoxic (e.g. Ulloa et al. 2012), as O_2 concentrations below the detection limit (DL) of ~0.01 µmol kg^{-1} were observed between 20 and 400 m depth by high precision STOX sensor measurements (Revsbech et al., 2009; Kalvelage et al., 2013; Thomsen et al., 2016a). Those low O_2 concentrations are due to a sluggish ventilation by ocean currents, carrying low-O_2 waters to the ETSP and microbial respiration attributed to utilization 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 O_2 (Kalvelage et al.,2015), and anaerobic processes, such as nitrogen (N) loss via denitrification (Kalvelage et al., 2013; Chang et al., 2014), in the area. However, the cycling of DOM in the Peruvian upwelling system has been little studied.

DOM, ~~originating~~which originates 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~~. Those are mainly composed of carbohydrates (CHO) and amino acids (AA) (e.g. Ogawa and Tanoue, 2003). ~~Those~~CHO and AA 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~~Thus, the rapid microbial decomposition of labile organic matter in the euphotic zone is commonly followed by slower decomposition of less bioavailable semi-labile DOM and very slow decomposition of extensively reworked refractory DOM deeper the water column (e.g. Hansell, 2013). Therefore, the composition of DOM reflects its diagenetic history, and the contribution of CHO and AA to ~~OM~~DOM, may be used as a measure of ~~OM~~DOM bioavailability (Davis et al, 2007; 2009; Kaiser and Benner, 2009).

~~Low O$_2$ conditions have~~Microbial decomposition of organic matter has previously been suggested to ~~slow down microbial decomposition rates of OM~~be limited under anoxia (Harvey et al., 1995; Nguyen and Harvey, 1997). ~~Hence, it could be expected~~Following this suggestion, one may assume that ~~CHO and AA entering~~, if labile DOM is supported to the OMZ~~, it~~ would not ~~undergo significant changes.~~be reworked as rapidly as in oxygenated waters. Recent studies in the upwelling area and the corresponding OMZ off Chile found, however, ~~found bacterial activity~~that even under anoxia the ability of microbes to decompose labile DOM (Leucine-incorporation~~) of similar range to~~ rate) did not differ from the oxygenated waters (~~Sempere~~Sempéré et al., 2008, Pantoja et al., 2009). These ~~results~~studies suggest that ~~the changes in the~~slower remineralization ~~rates~~ of DOM in OMZ might rather be ~~linked to~~caused by lack of bioavailable ~~OM~~organic matter supply into the OMZ than ~~to~~by low-O_2 conditions. Herewith, measured concentrations of bioavailable components of DOM over the water column in the ETSP are yet controversary. For instance, Pantoja et al. (2009) reported relatively high concentrations of free and combined AA in the OMZ off Chile. Sempere et al. (2008) reported ~~lower~~low concentrations of neutral CHO in the corresponding upwelling area, compared to the open Pacific Ocean.

Assessing the possible effects of low O_2 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 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 at the 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 O_2 in amount that is sufficient for full remineralization of the subducted OM. Therefore, this physical transport of OM and O_2 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 O_2 and DOM supply estimates exist for the Peruvian OMZ.

Here, we investigated the possible importance of diapycnal DOM supply by turbulent mixing processes for the O_2 utilization off Peru usingHere, we 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. Specifically, we directly estimated the diapycnal O_2 and DOM supply into the upper oxycline off Peru. Additionally, we analyzed diapycnal fluxes and the composition of dissolved combined carbohydrates (DCCHO) and dissolved hydrolysable amino acids (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 O_2 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} (NO_3^-), ~3 µmoµmol L^{-1} (PO_4^{3-})) 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, herewhere 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 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 O_2 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 Institute for Baltic Research (IOW) and the Max Planck Institute for Marine 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 49 CTD stations, and for 8 PUMP-CTD stations. DHAA and DCCHO analyses were performed only for samples from the GO rosette. CTD, O_2 and chl *a* recordings were taken at 172 profiles (Fig. 1a).

The CTD was calibrated with discrete seawater samples measured with a Guildline Autosal 8 model 8400B salinometer. The O_2 optode was calibrated by Winkler titration above the oxycline (Winkler, 1888; Hansen, 1999). The STOX sensor measurements, which revealed O_2 concentrations of 0.01-0.05 µmol kg^{-1} within the OMZ (Revsbech et al., 2009; Thomsen et al., 2016a)), were used for O_2 optode calibration at low O_2 levels. The salinity and O_2 measurements had precision of 0.002 g kg^{-1} and ~ 1 µmol kg^{-1}, respectively. More details on the salinity and O_2 calibrations can be found in Thomsen et al. (2016a). Apparent oxygen utilization (AOU) was then calculated as a difference of measured O_2 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 O_2.

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% H_3PO_4), 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 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 N_2 atmosphere and an addition of miliQ 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 precision was 2% with a DL ~10 nmol L^{-1}. During our study, three classes of polysaccharides were measured. Those 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~~GlcN) and galactosamine (~~Gal N~~GalN)), and acidic sugars ~~(S H)~~ including gluconic acid (~~Glu H~~GluA)) and the uronic acids ~~(DURA)~~ galacturonic acid (~~Gal URA~~GalUA) and glucuronic acid (~~Glc URA~~GlcUA). 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-phthaldialdehyde 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). The amino acids asparagine and glutamine likely contributed to the measured Asp and Glu concentrations, respectively, due to deamination during hydrolysis. Alpha 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 (O_2) 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, $m^2 s^{-3}$), as given in Schafstall et al. (2010).

Diapycnal diffusivities (K_ρ, $m^2 s^{-1}$) were determined at 14 m depth intervals, following Osborn (1980):

$$K_\rho = \Gamma \frac{\varepsilon}{N^2}, \tag{1}$$

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_ρ (e.g. Schafstall et al., 2010; Fischer et al., 2013).

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

$$\Phi_S = -K_\rho \nabla C_S, \tag{2}$$

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

The mean diapycnal supply ($-\overline{\nabla \Phi_s}$, µmol kg^{-1} 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:

$$-\overline{\nabla \Phi_s} = -\frac{1}{\rho}\frac{\partial}{\partial z}\overline{\Phi_S}, \tag{3}$$

where ρ – is the *in-situ* density of the seawater (kg m^{-3}), z - is depth (m) and $\overline{\Phi_S}$ (mmol m^{-2} 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_ρ 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 averaged in ~~density~~temperature 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 ($\overline{\nabla \Phi}_S$).

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:

$$1C + 1O_2 = 1CO_2, \tag{4}$$

was used for a rough estimation of the percentage of diapycnal O_2 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

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-O_2 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 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 O_2 and DOM

In this section the horizontal and vertical distribution of O_2 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 O_2 concentrations were observed ranging between 100 µmol kg^{-1} at the coast and 240 µmol kg^{-1} further offshore (Fig. 2d). These values dropped to less than 1 µmol kg^{-1} at <~~20m~~50m depth ~~at~~near the coast (<40 km offshore) and ~80 m depth offshore (>40 km) (Fig. 2d).

DOC concentrations ranged from more than 100 µmol L^{-1} near the surface to < 50 µmol L^{-1} below 40 m depth (Fig. 3a). Patches of isolated DOC maxima (up to 120 µmol L^{-1}) were measured at a depth range from 20 to 120 m (Fig. 3a). DOC concentrations of >100 µmol L^{-1} had been reported previously for the water column off Peru (Romankevich and Ljutsarev, 1990; Franz et al., 2012a). However, since concentrations >100 µmol L^{-1} were observed only sporadically, we cannot exclude a possible contamination of these samples. The main decrease of DOC occurred between 5 and 30 m. Thus, the main vertical DOC gradient was found at shallow depth, compared to the oxycline. This becomes even more apparent, when comparing the mean vertical profiles of O_2 and DOC (Fig. 4a,b).

DON concentrations were also highest (~7-8 µmol L^{-1}) near the surface (Fig. 3b) and varied from below detection to 4-5 µmol L^{-1} at greater depth. The main decrease of DON concentrations occurred within the upper 10 m of the water column (Fig. 4c).

DCCHO concentrations varied from 0.2 µmol L^{-1} to 4.2 µmol 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. ~~S N~~Amino sugars were represented solely by GlcN, as GalN was below DL in most samples. ~~S H~~Acidic sugars were mainly represented by ~~DUR~~Auronic sugars, i.e. ~~Glu URA~~GluUA and ~~Gal URA~~GalUA (Table 1), while ~~Glc H~~GlcA was

detected only sporadically. Overall, ~~S N~~amino sugars and ~~S H~~acidic sugars comprised 0.04±0.03 µmol L^{-1} and 0.02±0.02 µmol L^{-1}, contributing 6±3 % and 3±2 % to DCCHO, respectively. Thus, the major part of DCCHO was represented by ~~nS~~neutral sugars (Table 1). DHAA concentrations varied from 0.075 µmol L^{-1} to 1.39 µmol L^{-1} (Fig. 3d). Like for DCCHO, the highest DHAA concentrations were found above the oxycline, where C contained in DHAA represented 2±1 % DOC (max. 4 %) and nitrogen (N) contained in DHAA represented 15±14 % DON. Lowest DHAA concentrations were mainly found below 80 m depth and equivalent to ~1 %DOC and 6-8 %DON (Table 1). The major part of DHAA was represented by α-amino acids. 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. 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).

3.2 Diapycnal fluxes and supply

As outlined in the previous section 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 ($\overline{\nabla\Phi}_{O2}$) exhibited a maximum of 50 mmol O$_2$ m^{-2} day^{-1} at ~20m depth. It decreased over depth and vanished at 80m depth due to lack of vertical concentration gradients. Onshore (<40 km) and offshore (>40 km) O$_2$ fluxes did not differ statistically. This likely was due to the fact that while vertical oxygen gradients were enhanced in the offshore region (Fig.4a), the turbulence and, thus, eddy diffusivities were elevated in the onshore region. The mean diapycnal supply O$_2$ ($\overline{\nabla\Phi}_{O2}$), ranged from 1.2 µmol kg^{-1} day^{-1} at 10-24 m depth to near zero at 80 m depth (Table 2). Again, onshore (<40 km) and offshore (>40km) the diapycnal O$_2$ supply was not statistically different.

In contrary, mean diapycnal fluxes of DOC ($\overline{\Phi}_{DOC}$) was limited to shallower depth. Near the surface, $\overline{\Phi}_{DOC}$ was 31 mmol C m^{-2} day^{-1} and vanished already at ~50 m depth (Table 2). The diapycnal supply of DOC ($\overline{\nabla\Phi}_{DOC}$) exhibited a maximum of 1.8 µmol C kg^{-1}day^{-1} at 10-38 m depth (1.5 times larger than $\overline{\nabla\Phi}_{O2}$.) (Table 2, Eq. 4). Compared to NPP, estimated to 3.9 (0.6-8.6) gC m-2 day-1 for our study area and period, the DOC flux represented from a maximum of ~10 %NPP at ~20 m depth to near zero %NPP at ~50 m depth. As it was mentioned in the section 3.1, we did not find a vertical DON gradient, resulting in very low diapycnal DON fluxes and supply estimates (Table 2). However, 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 mmol C m^{-2} day^{-1} ($\overline{\Phi}_{DCCHO(C)}$), 0.9 mmol C m^{-2} day^{-1} ($\overline{\Phi}_{DHAA(C)}$)and 0.3 mmol N m^{-2} day^{-1} ($\overline{\Phi}_{DHAA(N)}$) 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 µmol C kg^{-1}day^{-1} ($\overline{\nabla\Phi}_{DCCHO(C)}$), 0.06 µmol C kg^{-1}day^{-1}($\overline{\nabla\Phi}_{DHAA(C)}$), and 0.02 µmol N kg^{-1}day^{-1}($\overline{\nabla\Phi}_{DHAA(N)}$) at 10-38 m depth. The diapycnal C supply via DCCHO and DHAA at its maximum comprised ~38% of $\overline{\nabla\Phi}_{O2}$, 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$_2$

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~~organic matter 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 Glc 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).

4 Discussion

The observed distributions of O$_2$ 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 O$_2$ and ~~OM~~organic matter cycling off Peru and, therefore, the formation and maintenance of the Peruvian OMZ.

Previous studies have shown that turbulent mixing processes in the eastern boundary upwelling 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 represent average values for the continental margin ranging from the shelf to about 100 km offshore. This spatial averaging is likely responsible for a lower near-surface diapycnal O$_2$ flux (50 mmolO$_2$ m^{-2} day^{-1}) compared to other EBUS. For example, Brandt et al. (2015b) determined a near-surface diapycnal O$_2$ flux of 73 mmolO$_2$ m^{-2} day^{-1} in the Mauritanian upwelling during the high productivity season in boreal winter. In their study, the diapycnal O$_2$ flux was able to sustain benthic respiration on the continental shelf down to a bottom depth of 100 m. Herewith, the diapycnal O$_2$ supply, found in our study, was of similar magnitude as the rates of O$_2$ consumption (~1 µmol kg^{-1} day^{-1}) determined by *in situ* incubations at 50-80 m water depth during the Austral summer season in the ETSP off Peru (Kalvelage et al., 2015) and similar estimates for North and South Pacific OMZs (Revsbech et al., 2009 and Tiano et al., 2014).

Other terms of the O_2 transport budget, such as isopycnal supply by meso- (Thomsen et al., 2016a) and submesoscale (Thomsen et al., 2016b) dynamics, or fluxes due to upwelling (e.g. Steinfeldt et al., 2015) might play an important role for the distribution of O_2 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 O_2 source at depth. Furthermore, the presented diapycnal fluxes and supply of O_2 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, O_2 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 fluxes and supply of O_2 shall vary on the same timescales. Therefore, our results should be considered as the first estimates of diapycnal O_2 fluxes and supply in the ETSP off Peru during Austral summer season during non-El Niño/ La Niña regime.

Like for O_2, the 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 O_2 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.

DOM might also be transported to depth within particles. Thus, the "uncoupled" dissolution of large sinking aggregates as a result of bacterial enzymatic activity (Smith et al., 1992) or abiotically (Sempéré et al., 2000) may serve as an additional DOM source and, therefore, affect the distribution of DOM in the water column. The sporadic dissolution of particles may bias the diapycnal DOM flux estimates at individual stations. Therefore, the bias may be reduced by calculating the mean diapycnal flux over a large number of depth profiles. The continuous DOM release from POM over the water column (e.g. Lefèvre et al., 1996), in turn, may lead to an overestimation of diapycnal DOM fluxes and DOM based microbial respiration. However, no direct measurements of the DOM fraction resulting from particle dissolution exist so far in the studied area.

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, CO_2 and other volatile compounds (Zepp et al., 1998) could lower the near surface diapycnal DOC flux, as well. Herewith, our data suggest that the diapycnal DOC flux in the upper 20m of the water column off Peru is in the same order of magnitude as the diapycnal O_2 flux (Table 2). The annual diapycnal DOC flux (2.7 mol C $m^{-2}yr^{-1}$) into the upper OMZ, estimated from our results by averaging $\overline{\Phi}_{DOC}$ above the 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).). Compared to NPP, the diapycnal DOC flux (~10% NPP) was comparable to the POC export, previously reported for the upper water column in the ETSP off Chile (~12 %NPP (30 m depth), Pantoja et al., 2004), and in the ETSP off Peru (~6 %NPP (52 m depth); 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.

Furthermore, in the upper water column (from below the mixed layer to 38 m water depth), the diapycnal DOC supply was higher, than the diapycnal O_2 supply, suggesting that DOC respiration could exhaust all O_2. However, the vanishing of DOC flux above the upper oxycline suggests that the bioavailable fraction of DOM is respired well before entering the upper OMZ. This is even more apparent, when considering diapycnal DHAA and DCCHO fluxes, which decayed more rapidly compared to the diapycnal DOC flux, suggesting preferential uptake of DHAA and DCCHO in the water column. The diapycnal supply of DHAA and DCCHO could not fully explain the diapycnal supply of DOC, as those were responsible for only ~26% of $\overline{\nabla\Phi}_{DOC}$ when summed up together. This may hint to a presence of an additional bioavailable DOM component that 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).

As DHAA and DCCHO are preferentially utilized during microbial decomposition of ~~OM~~organic matter (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 (Ittekot et al., 1981; Sempere et al., 2008; Goldberg et al., 2010; Engel et al., 2012). Enrichment in Gly with depth has also been proposed to reflect the low nutritional value of Gly in anoxic sediments off Chile (Pantoja and Lee, 2003) and in sediments of the North Sea (Dauwe and Middelburg, 1998). 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. The latter was suggested by our PCA analyses, as DOM composition was highly interrelated to AOU. Herewith, the diapycnal supply of DHAA and DCCHO could explain up to 38% of $\overline{\nabla\Phi}_{O2}$. 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 O_2 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.

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 O_2 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 mechanism, such as microgel formation or absorption onto particles.

6 Data availability

The microstructure profiles are available at https:/doi.org/10.1594/PANGAEA.868400. The O_2, 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

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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Table 1: Relative composition (mol%) of dissolved hydrolysable amino acids (DHAA) and dissolved combined carbohydrates (DCCHO) in the water column, "n.d." - not detectable. ~~The DCCHO are divided into three classes,~~ **Abbreviations "nS—", "SN" and "SA" stand for** neutral sugars, ~~S-N~~ amino- sugars~~,~~ and ~~S-H~~ acidic sugars, respectively. **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 O_2 fluxes. The mean values for DHAA and DCHO within the mixed layer are reported for ~5 m depth intervals.**

Depth (m)	n	DHAA (μmol L^{-1})	(%DOC)	(%DON)	Gly	Thr	Ala	Asp	Glu	Ser	Arg	Leu	Val	Ileu	Phe	Tyr
		DHAA			mol% DHAA											
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 (μmol L^{-1}) nS	S-N	S-H	mol%DOC nS	S-N	S-H	mol% nS Glc	ManXyl	Gal	Rhm	Fuc	Ara	mol% S-H 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.

Depth (m)	n	DHAA (μmol L^{-1})	(%DOC)	(%DON)	Gly	Thr	Ala	Asp	Glu	Ser	Arg	Leu	Val	Ileu	Phe	Tyr
		DHAA			mol% DHAA											
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 (μmol L^{-1}) nS	SN	SA	mol%DOC nS	SN	SA	mol% nS Glc	ManXyl	Gal	Rhm	Fuc	Ara	mol% SA GluUA	GalUA	GlcA
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.

Table 2: Diapycnal fluxes and supplies (in bold) of O$_2$ and DOM: DOC, DON, dissolved organic carbon in DCCHO and DHAA and dissolved organic nitrogen in DHAA. 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.

	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 (µmol 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)

	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 (µmol 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) O_2. O_2 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 O_2 (a), DOC (b), DON (c), DCCHO(C) (d), DHAA(C) (e), DHAA(~~C~~N) (f). Black line and error bar represent ~~median~~mean distribution and standard deviations of the data points (grey circles), respectively. The blue and red lines and shaded areas represent the mean distributions and standard deviations of parameters onshore (<40 km) and offshore (>40 km), 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).
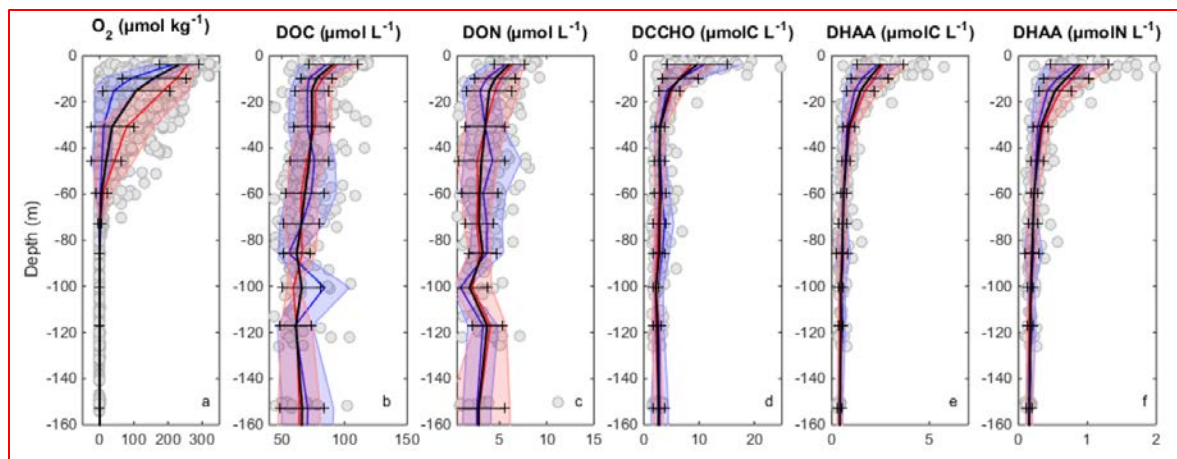
Figure 4.