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Dissolved Organic Matter in the Upwelling System off Peru: Imprints of Bacterial Activity and Water Mass Characteristics

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Abstract Microbial degradation of dissolved organic matter (DOM) contributes to the formation and preservation of oxygen minimum zones (OMZs) in the ocean, but information on the spatial distribution and molecular composition of DOM in OMZ regions is scarce. We quantified molecular components of DOM that is, dissolved amino acids (DAA) and dissolved combined carbohydrates (DCCHO), in the upwelling region off Peru. We found the highest concentrations of DCCHO in fully oxygenated surface waters steeply declining at shallow depth. The highest DAA concentrations were observed close to the surface also, but attenuation of DAA concentration over depth was less pronounced. Compositional changes of DCCHO were strongest within more oxygenated waters. Compositional changes of DAA were also evident under suboxic conditions (<5 μmol O_2 kg^{-1}) and indicated bacterial peptide degradation. Moreover, specific free amino acids (alanine and threonine) were enhanced within suboxic waters, pointing to a potential production of dissolved organic nitrogen under suboxic conditions. Our results therewith suggest that deoxygenation supports a spatial decoupling of DCCHO and DAA production and degradation dynamics and give new insights to carbon and nitrogen cycling in the OMZ off Peru.

Plain Language Summary The molecular composition of dissolved organic matter (DOM) in seawater mainly depends on production and consumption processes by plankton organisms. The biological consumption of DOM reduces the amount of oxygen in seawater, but little is known about the composition of DOM in so-called oxygen minimum zones (OMZs). We studied the distribution of DOM, specifically of dissolved sugars and amino acids in the OMZ off Peru. We observed that the reworking and degradation of sugars and amino acids differed between more and less oxygenated waters. We also found indications for the production of specific amino acids within the OMZ. Our study therewith suggests, that oxygen concentrations affect dissolved amino acid and sugar dynamics and may help to better understand carbon and nitrogen cycling within OMZs.

Key Points:

- Decoupling of dissolved combined carbohydrates and dissolved amino acids dynamics, in the oxygen minimum zone off Peru
- Free amino acids indicate production of dissolved organic nitrogen within suboxic waters

Supporting Information:

Supporting Information may be found in the online version of this article.

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1. Introduction

The availability of oxygen determines energy flows and elemental cycling within marine ecosystems (e.g., Diaz & Rosenberg, 2008; Ward, 2013). Globally the oceanic oxygen content decreased by 2% over the past 50 years (Schmidtko et al., 2017). For the future, models mainly agree on a further declining trend of oceanic oxygen concentrations, depending on the investigated region and the climate change scenarios (summarized in Levin, 2018). One of the world's largest oxygen minimum zones (OMZs) can be found in the Peruvian upwelling system, located in the Eastern South Pacific Ocean and spreading until the Eastern Equatorial Pacific Ocean. Here, the oxygen content in the depth layer between 300 to 700 m has decreased by 0.13 (±0.32) μmol O_2 kg^1 $year^{-1}$ since 1960 (Stramma et al., 2008). Off Peru, waters between 100 and 500 m depth are permanently hypoxic (<60 μmol O_2 L^{-1}), suboxic (<5 μmol O_2 L^{-1}), or even anoxic, as ventilation is too weak to replace the amount of oxygen required for the degradation of organic matter (Czeschel et al., 2011; Graco et al., 2017; Kämpf & Chapman, 2016; Llanillo et al., 2013; Silva et al., 2009). The Peruvian OMZ is associated with different water masses, affecting oxygen concentrations and probably also the distribution of dissolved organic matter (DOM) in the OMZ. Nutrient-rich and oxygen-depleted Equatorial Subsurface Water (ESSW) (Kämpf & Chapman, 2016; Thamdrup et al., 2012) and, further offshore, Eastern South Pacific Intermediate Water (ESPIW) form the suboxic OMZ core (Lüdke et al., 2020). Below, the mixing of ESSW with Antarctic Intermediate Water (AAIW) forms the lower oxycline. Above the suboxic OMZ core, the mixing of ESSW with subtropical water (STW) forms the upper oxycline (Llanillo

et al., 2013; Silva et al., 2009). The distribution of the different water masses along the Peruvian coast varies with longitude, latitude, season and the intensities of the El Niño–Southern Oscillation. Upwelling of nutrient-rich, oxygen-depleted waters and therewith shallowing of the oxycline and enhanced nutrient supply in the euphotic zone are stronger in austral winter and during La Niña events than in austral summer and El Niño events (Graco et al., 2017; Helly & Levin, 2004; Kämpf & Chapman, 2016; Llanillo et al., 2013; Silva et al., 2009). Still, phytoplankton growth in surface waters is enhanced during austral summer due to a shallowing of the mixed layer (Echevin et al., 2008).

One important factor controlling the oxygen concentration in subsurface waters of the OMZ is bacterial aerobic degradation of DOM (Loginova et al., 2019; Maßmig et al., 2020). Marine DOM (~662 Pg carbon) represents by far the largest pool of organic matter in the ocean (Hansell et al., 2009). The main sources of marine DOM are phytoplankton release (Biddanda & Benner, 1997; Mague et al., 1980), cell lysis, for example after viral attack, sloppy feeding by zooplankton, solubilization of particulate organic matter (POM), and allochthonous inputs (Burdige & Komada, 2015; Carlson & Hansell, 2015; Raymond & Spencer, 2015). The major sink of DOM is the uptake by microorganisms for subsequent biomass production or respiration (Azam et al., 1983; Carlson & Hansell, 2015). Low molecular weight DOM <0.6 kDa can directly be taken up by bacteria; for the uptake larger molecules, bacteria release extracellular enzymes that hydrolyze the substrate into smaller components (Hoppe, 1983; Weiss et al., 1991). Microbial alteration of DOM, in turn, reduces the lability of DOM (Jiao et al., 2010).

The lability of DOM may therefore serve as an indicator for microbial processing and is typically decreasing from the productive surface to largely heterotrophic deep waters. DOM lability is indicated by its molecular composition and weight (e.g., Amon & Benner, 1996; Amon et al., 2001). Labile DOM makes only a minor fraction of the marine dissolved organic carbon (DOC; <1%) because of rapid turn-over (hours-days) by bacteria (Hansell et al., 2009). Semi-labile DOM, with turn-overtimes of months to years, contributes ~1% to the total marine DOC inventory and is of high importance for the biological mineralization below the euphotic zone (Carlson & Hansell, 2015; Hansell et al., 2012). Amino acids and carbohydrates are chemically characterizable components of DOM (Repeta, 2015) and largely represent the labile and semi-labile organic matter (Amon et al., 2001; Ogawa & Taoue, 2003; Repeta, 2015). Carbohydrates, with a few exceptions, can solely serve as carbon sources. In contrast, amino acids provide carbon and nitrogen simultaneously. They belong to the more labile forms of dissolved organic nitrogen (DON) and can represent >12% of the DON. Next to ammonia, DON can be substantial for bacterial growth. For instance, free amino acids (FAA) were shown to cover ~50% of the bacterial nitrogen-demand (Keil & Kirchman, 1991; Sipler & Bronk, 2015). FAA and sugars are assumed to be among the most labile components and are preferentially degraded. Dissolved combined carbohydrates (DCCHO) and dissolved hydrolyzable amino acids (DHAA) have been classified as semi-labile DOM (e.g., Amon et al., 2001; Davis et al., 2009; Fuhrman, 1987). However, differences in bioavailability have been recognized also within the DHAA and DCCHO pools (e.g., Dauwe & Middelburg, 1998; Engel et al., 2012; Yamashita & Tanoue, 2003). For instance, a high glycine (Gly) content points toward lower lability, a high-leucine (Leu) content toward higher lability of DHAA and organic matter in general (Amon et al., 2001; Dauwe & Middelburg, 1998; Kaiser & Benner, 2009). Moreover, studies in the Pacific and Atlantic oceans showed a relative increase of glucose (Glc) concentration at depth, suggesting that a high Glc content indicates less bioavailable DCCHO and organic matter in general (Engel et al., 2012; Kaiser & Benner, 2009). The degradation index (DI), an indicator for organic matter lability, has often been assessed from the proportional change of amino acids (Dauwe et al., 1999; Kaiser & Benner, 2009; Yamashita & Tanoue, 2003). Biochemicals within the DOM pool also allow for the attribution of specific sources and sinks. For instance, certain amino acids and hexosamines can be attributed to bacterial origin (Kawasaki & Benner, 2006). The release of glucosamine (Glc_N) and specific D-amino acids has been associated with viral lysis of bacterial cells, the production of nonprotein amino acids, for example *γ*-aminobutyric acid (GABA), with bacterial decarboxylation of proteinaceous amino acids (discussed in Lee & Cronin, 1982; Middelboe & Jørgensen, 2006; Schroeder, 1975).

How the interplay between oxygen concentration and the concentration and composition of organic matter control bacterial degradation activity, in particular in OMZs, is largely unknown. It has been suggested that bacterial degradation of organic matter is reduced under suboxic and anoxic conditions (Devol & Hartnett, 2001; Keil et al., 2016), as aerobic respiration is replaced by anaerobic processes such as denitrification

or chemolithoautotrophic anaerobic ammonium oxidation (anammox) (e.g., Lam & Kuypers, 2011). Furthermore, bacteria may preferentially degrade nitrogen-rich organic matter within suboxic waters to support denitrification (Van Mooy et al., 2002) or anammox by the released ammonia (Sipler & Bronk, 2015; Ward, 2013). Experimental approaches indeed showed a reduced degradation of organic matter under anoxic or suboxic conditions (Harvey et al., 1995; Le Moigne et al., 2017; Nguyen & Harvey, 1997) and a prioritized degradation of proteins over carbohydrates (Harvey et al., 1995) pointing to a strong influence of oxygen availability on organic matter concentration and composition. Other studies, however, did not corroborate a reduced microbial degradation of organic matter in suboxic compared to oxic waters and suggested organic matter lability as one reason for differences in degradation rates (Lee, 1992; Maßmig et al., 2020; Pantoja et al., 2009).

To better understand, the potential control of organic matter availability on bacterial activity in OMZs, we investigated the distribution and composition of labile and semi-labile DOM that is, FAA, dissolved amino acids (DAA), and DCCHO, at different in situ oxygen concentrations, in the OMZ off Peru. Since oxygen-dependent and anoxic processes might be fueled by or contribute to specific DOM compounds in OMZs, we expected to find distinct patterns of DOM composition depending on water column depth, or on oxygen concentration. Based on previously reported heterotrophic bacterial production within the core of the OMZ off Peru (Maßmig et al., 2020), we furthermore expected to find traces of DOM degradation within suboxic waters.

2. Materials and Methods

2.1. Study Site and CTD Measurements

Sampling took place during the research cruises M136 and M138 to the upwelling regions off Peru on the R/V METEOR in April and June 2017, respectively (Figure 1). Between 5 and 11 discrete samples were taken from a rosette coupled with Niskin bottles of 10 L each. Water was sampled between 1 and 2,200 m depth at 38 stations in total. Temperature, oxygen, and pressure were measured using a Sea-Bird SBE 9-plus CTD system (Sea-Bird Electronics, Inc.) and chlorophyll a (chl *a*) concentrations were detected using a WETStar sensor (WET Labs) (see Maßmig et al., 2020 for details).

2.2. Dissolved Organic Carbon and Nitrogen

DOC and total dissolved nitrogen (TDN) were sampled at every station. Samples were analyzed from the same 20 ml subsample that was filtered through a syringe filter (0.45 μm glass microfiber GD/X membrane, Whatman ™, pre-rinsed with 50 ml sample) into a combusted glass ampoule (8 h, 500°C). Ultrapure hydrochloric acid (20 μl of 30%) was added before sealing and storing the ampules at 4°C in the dark, for 3 months. Samples were analyzed as described in Engel and Galgani (2016) applying a high-temperature catalytic oxidation method modified from Sugimura and Suzuki (1988) on a TOC−VCSH with a TNM-1 detector (Shimadzu). The detection limit was 1 and 2 μmol L^{-1} and the relative standard deviation between repeated measurements was <1.1% and <3.6% for DOC and TDN, respectively.

DON was calculated as the difference between TDN and dissolved inorganic nitrogen (DIN), including nitrate, nitrite and ammonia. Nitrate and nitrite were measured with a QuAAtro auto-analyzer (Seal Analytical), with nitrate being reduced to nitrite before analysis (method from SEAL Analytical–Q-068-05). Precision was calculated for all nutrient measurements from triplicate samples and resulted in a precision of 0.11 μmol L^{-1} for nitrate and 0.01 μmol L^{-1} for nitrite. The detection limit was 0.01 μmol L^{-1} for nitrite and 0.03 μmol L^{-1} for nitrate. Ammonia was measured after (Holmes et al., 1999) with a precision of 0.02 μmol L^{-1} and a detection limit of ~0.03 μmol L^{-1}.

Semi-labile DOM was defined by the sum of DAA and DCCHO. Semi-labile DOC was calculated by the sum of carbon contained in DCCHO and DAA and compared to the total concentration of DOC. Similarly, the proportion of semi-labile DON was calculated using the nitrogen content of DAA and DCCHO that is, amino sugars.

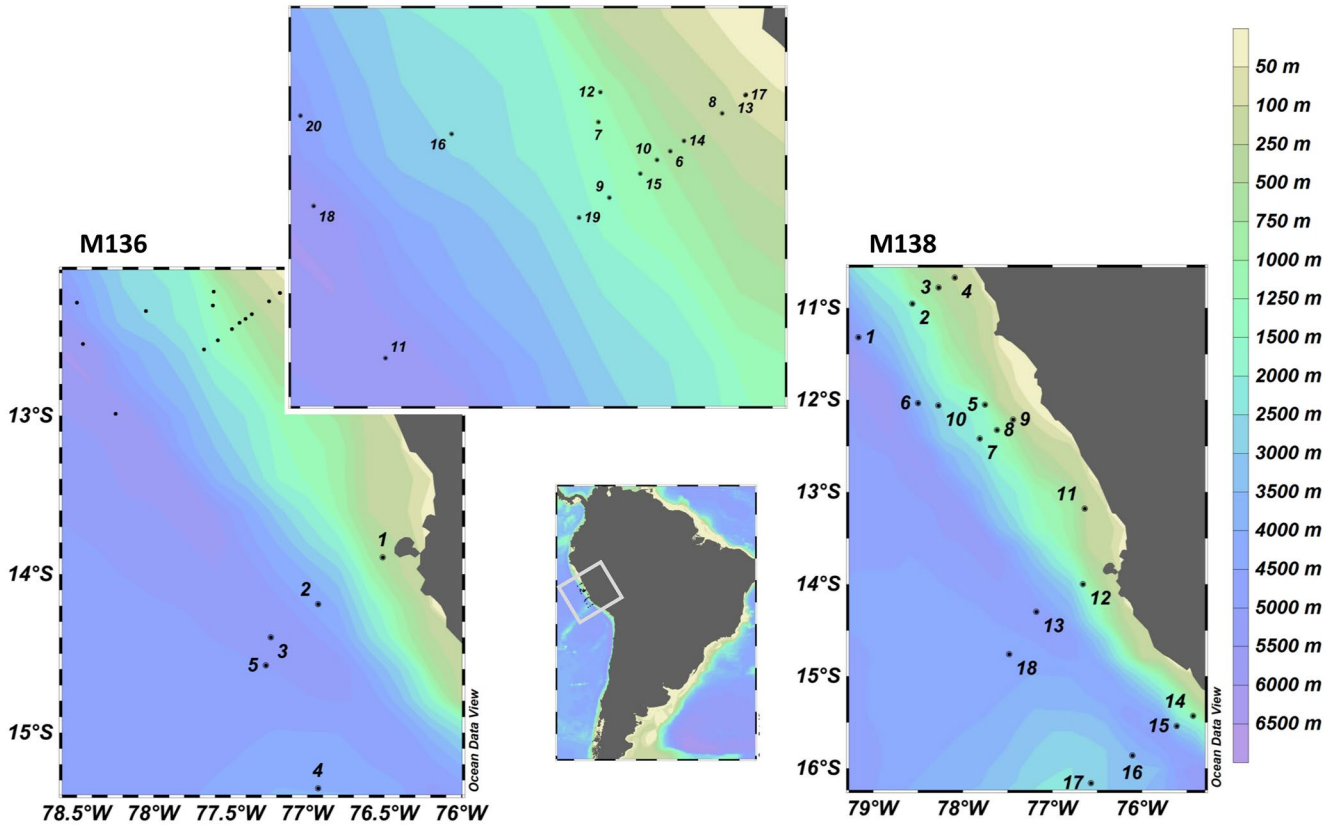


Figure 1. The Peruvian upwelling system (overview map) with sampled stations during the cruises M136 (left) and M138 (right) in April and June 2017, respectively.

2.3. Dissolved Amino Acids and the Derived Degradation Index

Concentrations of DAA were determined for all stations of M136 and stations 1–5 and 10–18 of M138. FAA comprise a small fraction of DAA and were measured at the same stations except for stations 12 and 13 during the M138 cruise. For DAA and FAA 4 ml sample were filtered through 0.45 μm syringe filters (GHP membrane, Acrodisc®, Pall Corporation; pre-rinsed with 10 ml sample), into combusted (8 h, 500°C) glass vials and stored at −20°C in the dark for 3 months. DAA samples were analyzed with a high-performance liquid chromatography system after samples were derivatized with ortho-phthaldialdehyde, following the protocols of Lindroth and Mopper (1979) and Dittmar et al. (2009) modified after Engel and Galgani (2016). FAA were analyzed from the same samples without prior hydrolyzation. The following amino acids were analyzed with a detection limit of ~1.4 nmol L^{-1} and a precision of 2%: alanine (Ala), arginine (Arg), glycine (Gly), leucine (Leu), phenylalanine (Phe), serine (Ser), threonine (Thr), tyrosine (Tyr), valine (Val), aspartic acid and asparagine (co-eluted; AsX), glutamine and glutamic acid (co-eluted; GlX), γ-aminobutyric acid (GABA) and isoleucine (Iso). GABA was analyzed only from DAA. The decrease of DAA concentration over depth was described with a power-law function calculated in *R* version 3.4.2. (R Core Team, 2017) with a nonlinear least-squares model. For the illustration of the goodness-of-fit R^2 was calculated in *R* (R^2 = 1-residual sum of squares/total sum of squares). The DI, as an indicator for the diagenetic state of organic matter, was calculated from DAA molecular composition following Dauwe et al. (1999) and applying a principal component analysis (PCA) with the function prcomp in *R* version 3.4.2. (R Core Team, 2017).

2.4. Dissolved Combined Carbohydrates

DCCHO was sampled at every station. Sampling and storage of DCCHO samples were identical to DAA sampling, except for a higher sampling volume of 16 ml. Before analysis, DCCHO samples had to be desalted by membrane dialysis (1 kDa molecular weight cutoff, Spectra Por) after Engel and Händel (2011). This

method yields recoveries of >90% for high molecular weight (HMW) carbohydrates. Neutral, amino and acidic sugars were analyzed following Engel and Händel (2011) with high-performance anion exchange chromatography (HPAEC) (DIONEX ICS3000DC). The following single sugars were analyzed with a detection limit of ~1 nmol L^{-1} and a precision of 5%: fucose (Fuc), rhamnose (Rha), arabinose (Ara), galactose (Gal), glucose (Glc), mannose and xylose (co-eluted; ManXyl), glucosamine (Glc_N), galactosamine (Gal_N), muramic acid (Mur_A), gluconic acid (Glu_A), galacturonic acid (Gal_URA) and glucuronic acid (Gluc_URA). To describe the change in DCCHO composition the first principle component (PC1) was determined. We therefore performed a PCA including the molar percentages of neutral sugars (Fuc, Rha, Ara, Gal, Glc, and ManXyl) using the precomp function in *R* version 3.4.2. (R Core Team, 2017). The variability of DCCHO concentrations was then fit into a power-law function (see Section 2.3 for details).

2.5. Extracellular Enzyme Rates

As indicators for bacterial turnover of DOM potential hydrolytic rates of the extracellular enzymes leucine aminopeptidase (LAPase) and β-glucosidase (GLUCase) that were analyzed during the same cruises by Maßmig et al. (2020), were included within this study. Extracellular enzyme rates are available for five stations of M136 (14–17, 19) and six stations of M138 (12, 13, 15–18). The hydrolytic turnover [% d^{-1}] was determined by incubating a 200 µl sample with fluorescent substrate analogs (L-leucine-7-amido-4-methylcoumarin, 4-methylumbelliferyl-β-D-glucopyranoside) in final concentrations of 10^3 µmol m^{-3} after Hoppe (1983) and Piontek et al. (2014). The degradation rates of DCCHO and DAA [µmol C m^{-3} d^{-1}] were based on the hydrolytic turnover of GLUCase and LAPase [% d^{-1}] and the carbon and nitrogen concentrations defined by DAA and DCCHO following Piontek et al. (2014). For details about measurements, incubation conditions and subsequent calculations see Maßmig et al. (2020).

2.6. Data Analysis

Figures were created with *R* version 3.4.2 using the package ggplot2 (R Core Team, 2017; Wickham, 2009) or with Ocean Data View 4.74 (Schlitzer, 2016). Statistical significances were tested with a Wilcoxon test (*W*) or *t*-test (*t*) in *R* version 3.4.2 (R Core Team, 2017), and data were summarized using the *R* package FSA (Ogle, 2017). Averages were calculated as the arithmetic mean and given with standard deviation.

For statistical tests, samples were grouped into different oxygen regimes inspired by important thresholds of oxygen concentrations for biological processes (Gruber, 2011): "suboxic OMZ core" (≤5 µmol O_2 kg^{-1}), oxycline (>5 to <60 µmol O_2 kg^{-1}) and oxic (>60 µmol O_2 kg^{-1}). The oxycline was separated into "upper oxycline" and "lower oxycline" defined as hypoxic regimes above or below the suboxic OMZ core or as "oxyclines" summarizing the upper and lower oxycline.

3. Results

3.1. Study Site at the Time of Sampling

The research cruises M136 and M138 took place in the upwelling system off Peru in April and June 2017, thus during early austral winter (Figure 1). Average Chl *a* concentration within the upper 10 m was 1.1 µg L^{-1} higher in April (M136) compared to June (M138). Maximum Chl *a* concentration was 11.5 µg L^{-1}. Below ~40 m Chl *a* concentration fell below the detection limit (Figure S1a). Similar to Chl *a* concentration, water temperature within the upper 10 m (16.9–23.9°C) was on average only slightly higher (+2.2°C) during M136 compared to M138 (Figure S1b). Between the mixed layer depth (~10–40 m) and ~100 m depth, the temperature decreased steeply from ~19°C to 15°C and continued to decrease down to ~6°C at ~850 m depth. Below ~850 m, the temperature was constant (Figure S1b). Oxygen concentration steeply decreased with depth. Between 5 and 92 m, oxygen concentrations fell below 60 µmol O_2 kg^{-1}, indicating the beginning of the upper oxycline (Figure 2a). Suboxic waters (<5 µmol O_2 kg^{-1}) were first detectable from depths of 14 to 207 m. From 497 to 634 m, oxygen concentrations rose again above 5 µmol L^{-1}, indicating the beginning of the lower oxycline. Salinity ranged between 34.5 and 35.5 and decreased strongly below the mixed layer depth and ~100 m. Between ~100 to ~500 m the decrease in salinity was less pronounced and below 500 m salinity was around 34.5 before it started to increase again to 34.6 below 1,000 m (Figure 2b).

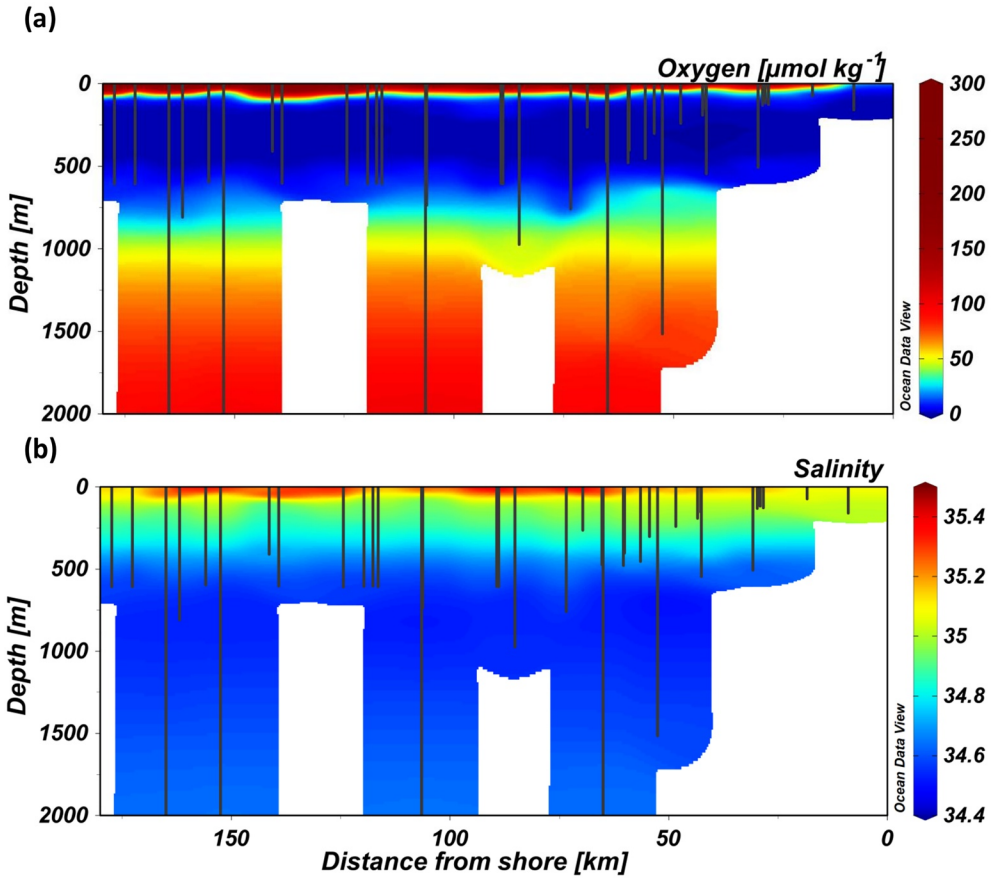


Figure 2. Oxygen concentrations (a) and salinity (b) over depth for all sampled stations during the cruises M136 and M138 sorted by distance from shore.

Overall, the mean DOC concentration was 61 ± 20 µmol L^{-1} and ranged between 37 and 208 µmol L^{-1} (Table 1, Figure 3a). Carbon contained in DAA accounted for 0.5% to 2.4% of DOC, the carbon content of DCCHO contributed 1.0%–7.7% to DOC concentration (Figures S2a and S2b). No significant difference in the proportion of semi-labile DOC was observed between cruises. DOC, and even more pronounced, semi-labile DOC concentrations decreased with depth (Figure S2). Thus, semi-labile DOC decreased significantly between the oxic surface and the upper oxycline ($n_{surface}$ = 79, $n_{upper\_oxiclne}$ = 66, W = 3,875, $p < 0.01$) and was significantly higher in the upper oxycline compared to suboxic waters ($n_{upper\_oxycline}$ = 66, $n_{suboxic}$ = 128, W = 3,289, $p < 0.05$). The average DON concentration, calculated from the difference between TDN (29 ± 10 µmol L^{-1}) and DIN (26 ± 10 µmol L^{-1}) was 4.5 ± 2.9 µmol L^{-1} (Tables 1 and S1). Semi-labile DON, that is, DON defined by DAA and DCCHO comprised a huge range from 1% to 87% DON, possibly representing uncertainties in the determination and calculation method. Average semi-labile DON decreased over depth from 13 ± 12% in the surface waters to 8 ± 8% in the suboxic waters and 5 ± 4% in the lower oxycline (Table S1).

3.2. Amino Acid Concentration and Composition at Different Oxygen Regimes

DAA concentration was on average 0.2 ± 0.1 µmol L^{-1} and similar between cruises. The average carbon and nitrogen content of DAA was 0.7 ± 0.3 µmol C L^{-1} and 0.3 ± 0.1 µmol N L^{-1}, respectively. DAA decreased over depth at all stations, with the strongest decrease between the oxic surface and the upper oxycline (Figures 3b and 4 and Table 1). The decrease of DAA concentration over depth followed a power-law function (DAA [nmol L^{-1}] = 430 x Depth [m] $^{-0.20}$, r^2 = 0.60, residual standard error = 46), and appeared at shallower depth than for total hydrolyzable amino acids in the open Pacific (Kaiser & Benner, 2009) (Figure 4). The coefficient of the power-law function describes the apparent attenuation of DAA over depth. For DAA,

Table 1
Concentrations of Organic Carbon and Nitrogen

	DOC			DON		
	[μmol L^{-1}]					
Oxygen regime	*n*	Avg.	SD	*n*	Avg.	SD
Oxic surface 1.3–81 m	101	80	28	87	5	4
Upper oxycline 4.3–199 m	77	59	12	69	4	2
Suboxic OMZ 15–601 m	164	53	5	120	4	3
Lower oxycline 497–799 m	21	46	3	18	6	3
Oxic deep water 1499–1999 m	3	40	3	3	7	4
	DCCHO-C			DCCHO-N		
	[μmol L^{-1}]					
Oxygen regime	*n*	Avg.	SD	*n*	Avg.	SD
Oxic surface 1.3–81 m	98	2.80	1.01	98	0.05	0.02
Upper oxycline 4.3–199 m	78	1.63	0.53	78	0.02	0.01
Suboxic OMZ 15–601 m	158	1.34	0.46	158	0.02	0.01
Lower oxycline 497–799 m	21	1.02	0.24	21	<0.01	<0.01
Oxic deep water 1499–1999 m	3	0.78	0.09	3	<0.01	<0.01
	DAA-C			DAA-N		
	[μmol L^{-1}]					
Oxygen regime	*n*	Avg.	SD	*n*	Avg.	SD
Oxic surface 1.3–81 m	82	0.97	0.29	82	0.39	0.10
Upper oxycline 4.3–199 m	68	0.61	0.22	68	0.25	0.08
Suboxic OMZ 15–601 m	133	0.51	0.15	133	0.21	0.06
Lower oxycline 497–799 m	20	0.42	0.10	20	0.19	0.05
Oxic deep water 1499–1999 m	3	0.25	0.06	3	0.12	0.04

Note. Concentrations of dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and the concentrations of carbon (C) and nitrogen (N) defined by dissolved combined carbohydrates (DCCHO) and dissolved amino acids (DAA) at different oxygen regimes for all sampled stations during M136 and M138. Given are the average (Avg.), the standard deviation (SD) and the number of samples (*n*). See Figures S2a and 2b for DOC defined by DAA-C and DCCHO-C.

the attenuation coefficient varied between stations and ranged between −0.34 and −0.06. The decrease of DAA stretched over greater depth at stations with deeper oxyclines compared to stations with shallower oxyclines (Figures 4 and S5). The mol percentages of single amino acids differed over depth with the strongest changes of DAA composition occurring between the oxic surface and the upper oxycline, and between the suboxic waters and lower oxycline (Figure 5a). Gly was a dominant amino acid (23–74 mol%) and the only one that proportionally increased clearly over depth (Figure 5a). The contribution of Gly to DAA was similar between the upper oxycline and the suboxic waters (40.6 ± 10.5 mol%), but significantly higher at the lower oxycline (65.3 ± 5.5 mol%) ($n_{lower\_oxycline} = 20$, $n_{suboxic} = 133$, $W = 2{,}557$, $p < 0.01$) (Figures 5a and 6a). A proportional decline between the suboxic OMZ core and the lower oxycline was common to all other single amino acids (Figure 5a). For instance, the contribution of Leu to DAA was similar between the upper oxycline and the suboxic waters (~1.6 mol%), but decreased significantly at the lower oxycline (0.6 ± 0.6 mol%) compared to the suboxic waters (1.6 ± 0.8 mol%) ($n_{lower\_oxycline} = 20$, $n_{suboxic} = 133$, $W = 405$, $p < 0.01$) (Figures 5a and 6b). Likewise, GABA was similar in the upper oxycline and the suboxic waters (~0.6 mol%) (Figure 5a). The concentration of GABA slightly decreased over depth until they appeared to increase in the more oxygenated deeper water (below the lower oxycline), although the sample size at the oxygenated deep water was very limited ($n = 3$) (Figure S3a).

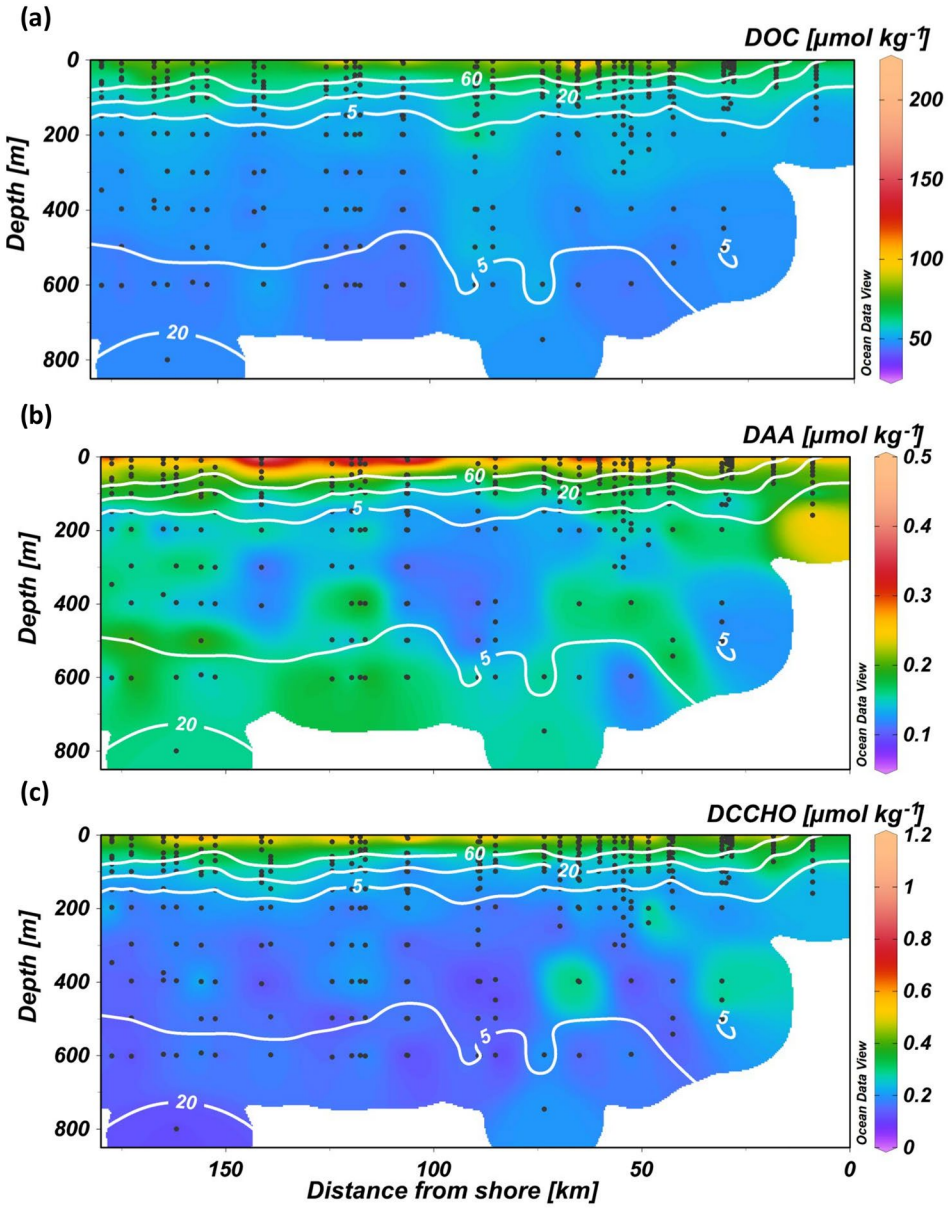


Figure 3. Concentrations of dissolved organic carbon (DOC) (a) dissolved amino acids (DAA) (b) and dissolved combined carbohydrates (DCCHO) (c) over depth for all sampled stations during the cruises M136 and M138 sorted by distance from shore.

FAA concentrations varied within the lower nanomolar range, but were similar between the cruises M136 (10 ± 9 nmol L^{-1}) and M138 (9 ± 8 nmol L^{-1}). The carbon and nitrogen content of FAA were on average 32 ± 29 nmol C L^{-1} and 12 ± 12 nmol N L^{-1}, respectively (Figures 7a and S3b). The contribution of Ala to FAA was significantly higher in suboxic waters (11 ± 14 mol%) compared to the oxyclines (8 ± 16 mol%) ($n_{suboxic}$ = 108, $n_{oxyclines}$ = 83, W = 5,509, $p < 0.005$; Figure 7b). Additionally, Ala concentration was significantly higher in suboxic waters (1.0 ± 1.1 nmol L^{-1}) compared to the oxyclines (0.7 ± 1.1 nmol L^{-1}) ($n_{suboxic}$ = 111, $n_{oxyclines}$ = 85, W = 5,600, $p < 0.05$; Figure S3b). The same was true for Thr, although concentrations of Thr were often below the detection limit (Figures 7b and S3b). The average contribution of FAA to DAA was 4 ± 4%, with an accumulation of FAA within the suboxic waters at some stations (Figure 7c). Below the suboxic OMZ core, the contribution of FAA to DAA decreased clearly. Hence, the contribution of FAA to

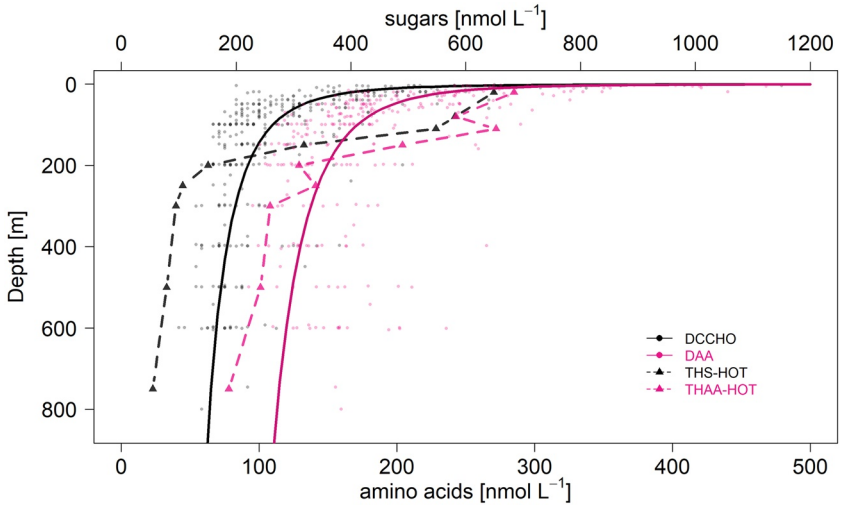


Figure 4. Concentrations of dissolved amino acids (DAA, red dots) and dissolved combined carbohydrates (DCCHO, black dots) over depth for all sampled stations during M136 and M138. The decrease of concentrations over depth can be described with a power-law function for DAA (red line, DAA [nmol L^{-1}] = 430 *x* Depth [m]$^{-0.20}$) and DCCHO (black line, DCCHO [nmol L^{-1}] = 873 *x* Depth [m]$^{-0.26}$). For comparison, concentrations of total amino acids (THAA, red triangles) and total hydrolyzable sugars (THS, black triangles) determined at the time series station "HOT" near Hawaii by Kaiser and Benner (2009) are included.

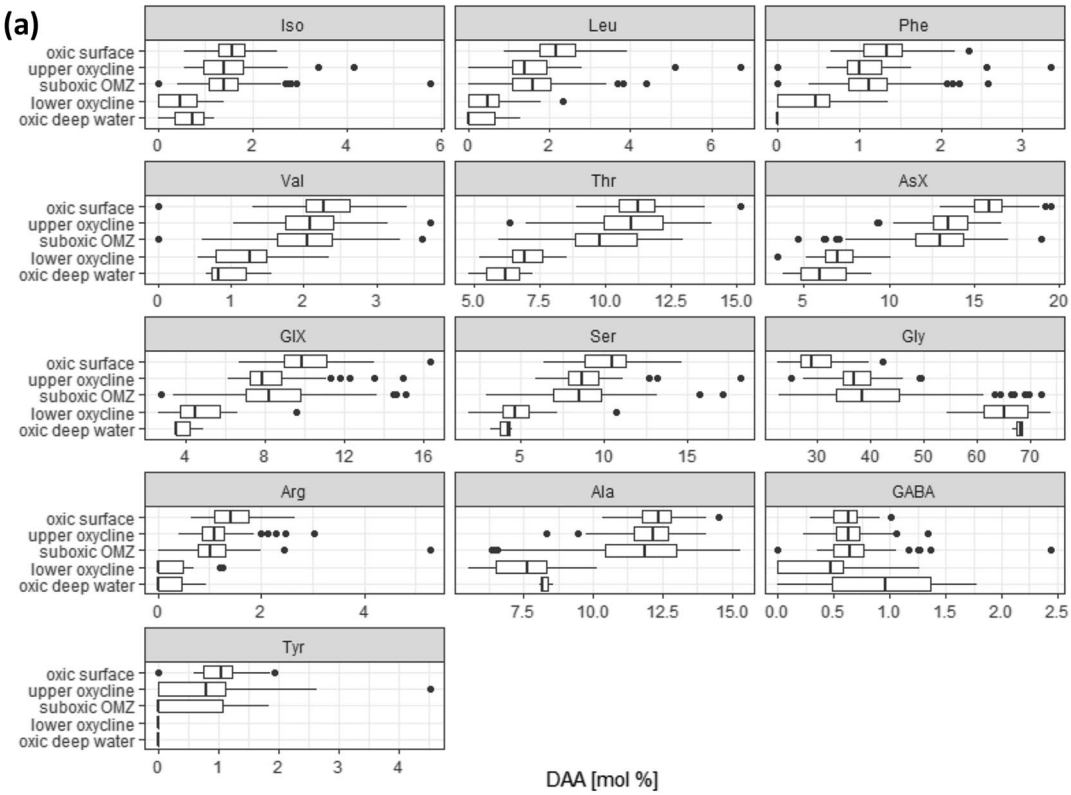
DAA was significantly higher within the suboxic waters (5 ± 4%) compared to the lower oxycline (3 ± 3%) ($n_{\text{lower\_oxycline}} = 17$, $n_{\text{suboxic}} = 107$, $W = 610$, $p < 0.05$).

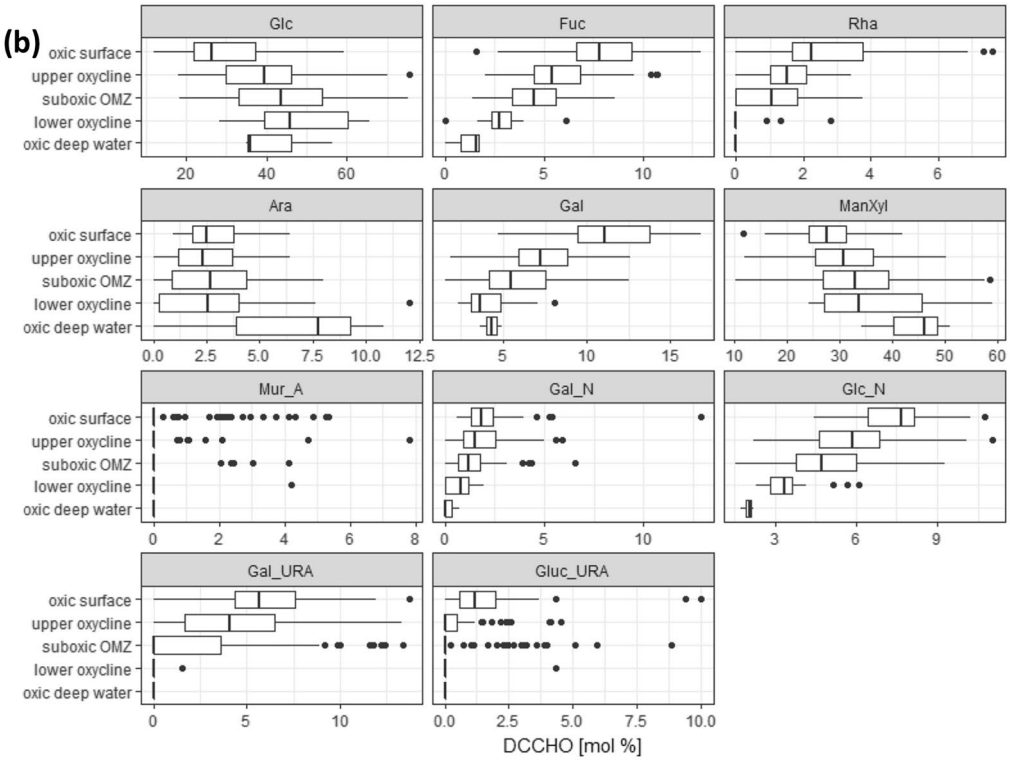
3.3. The Degradation Index as an Indicator for Changes in Organic Matter Lability Throughout the OMZ

The DI derived from amino acid composition serves as an indicator for the diagenetic state of organic matter. In our study, the DI varied over a wide range, that is, from −7.4 to 7.5, indicating the presence of more degraded and less degraded DOM, respectively. The DI values were highest at the surface and declined over depth (Figures 8a and 8b). Comparing the DI between oxygen regimes, showed significantly higher DI values at the oxygenated surface (1.9 ± 1.2) compared to the upper oxycline (0.2 ± 1.7) ($n_{\text{surface}} = 101$, $n_{\text{upper\_oxycline}} = 79$, $W = 4{,}569$, $p < 0.01$). Between the upper oxycline and the suboxic OMZ core (−0.3 ± 2.5), the DI was similar. Within suboxic waters, the DI decreased gradually over depth (DI = −0.01 × Depth [m] + 1.93, $r^2 = 0.40$). The decrease of the DI over depth (range: −0.09 to −0.01 m^{-1}) within suboxic waters could be verified at 20 stations. Within the lower oxycline, the DI continued to decrease, yielding significantly lower DI at the lower oxycline (−5.5 ± 1.3) compared to the suboxic waters ($n_{\text{suboxic}} = 133$, $n_{\text{lower\_oxycline}} = 20$, $W = 125$, $p < 0.01$).

3.4. Carbohydrate Concentration and Composition in Different Oxygen Regimes

DCCHO concentration varied between 0.1 and 1.2 μmol L^{-1} without significant differences between the cruises (Figure 3c). Overall, DCCHO concentration decreased over depth, exhibiting a power-law function (DCCHO [nmol L^{-1}] = 873 × Depth [m] $^{-0.26}$, $r^2 = 0.63$, residual standard error = 96) (Figure 4). The decrease of DCCHO concentrations over depth appeared at a shallower depth than for total hydrolyzable sugars in the open Pacific (Kaiser & Benner, 2009) (Figure 4). The apparent attenuation coefficient for DCCHO (−0.26) was 30% lower than for DAA. For statistical comparison, the attenuation coefficients for DCCHO and DAA were calculated for each sampled station. Attenuation coefficients for DCCHO varied between −0.44 and −0.01 and were significantly lower than those for DAA (−0.34 to −0.06) ($t = -4.57$, $p < 0.01$, $n_{\text{DAA}} = 34$, $n_{\text{DCCHO}} = 38$), suggesting that DCCHO declined faster over depth than DAA. According to the depth profiles of DCCHO concentration, the carbon content of DCCHO and nitrogen content of DCCHO that is, of Glc_N, Gal_N and Mur_A was highest at the surface with maximum concentrations


(a)
Iso
Leu
Phe
Val
Thr
AsX
GlX
Ser
Gly
Arg
Ala
GABA
Tyr
oxic surface
upper oxycline
suboxic OMZ
lower oxycline
oxic deep water
DAA [mol %]


(b)
Glc
Fuc
Rha
Ara
Gal
ManXyl
Mur_A
Gal_N
Glc_N
Gal_URA
Gluc_URA
oxic surface
upper oxycline
suboxic OMZ
lower oxycline
oxic deep water
DCCHO [mol %]

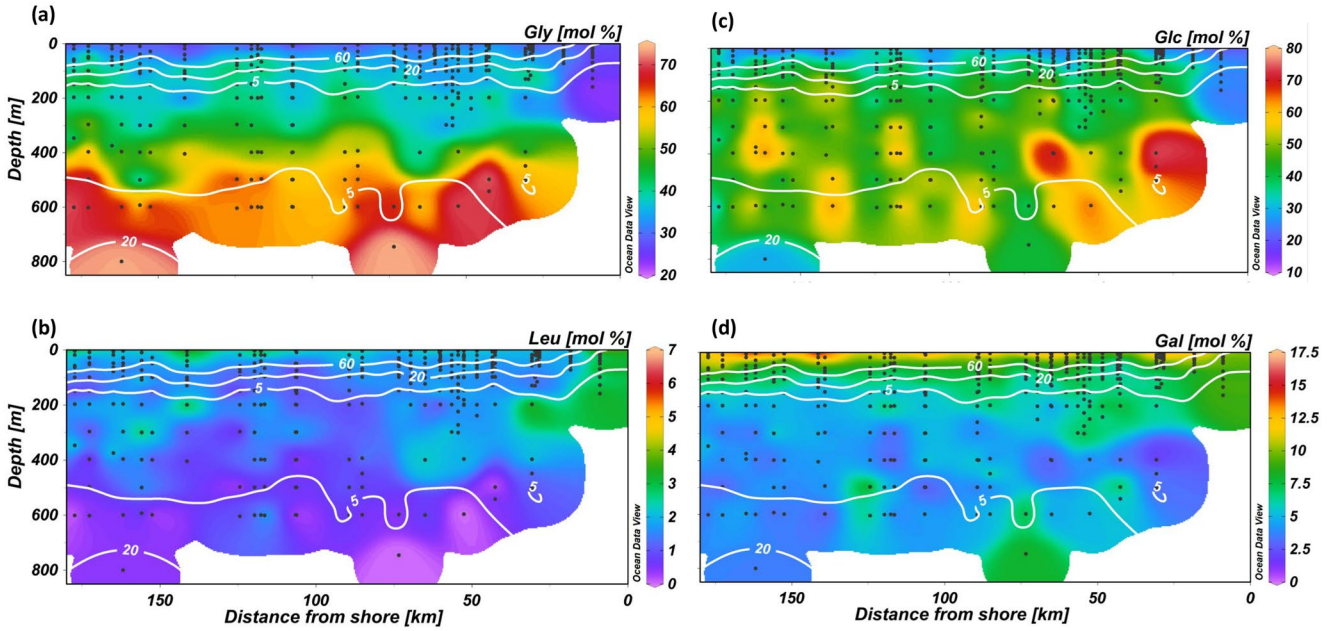


Figure 6. Percentage of the dissolved amino acids glycine (Gly) (a) and leucine (Leu) (b) and the dissolved combined carbohydrates glucose (Glc) (c) and galactose (Gal) (d) over depth for all stations sampled during the cruises M136 and M138 sorted by distance from shore. *In situ* oxygen concentrations are indicated with white contour lines.

of 6.7 μmol C L^{-1} and 0.15 μmol N L^{-1}, respectively. The carbon content of DCCHO decreased over depth reaching minimum concentrations of 0.77 μmol C L^{-1} and the nitrogen content of DCCHO was below the detection limit in deeper waters (Table 1). Like the composition of DAA, also DCCHO composition changed over depth (Figures 5b and S4). Mol percentages of Fuc, Gal, and Glc_N were decreasing and those of Glc, ManXyl, and Ara were increasing over depth (Figures 5b, 6c, and 6d). Hence, the contribution of Glc to DCCHO was significantly higher in the suboxic waters (44.1 ± 13.6 mol%) than in the upper oxycline (39.6 ± 12.7 mol%) ($n_{upper\_oxycline} = 78$, $n_{suboxic} = 158$, $W = 7{,}341$, $p < 0.05$). Gal showed the contrary trend with significantly higher mol percentages at the upper oxycline (7.3 ± 2.2 mol%) compared to the suboxic waters (5.9 ± 2.2 mol%) ($n_{upper\_oxycline} = 78$, $n_{suboxic} = 158$, $W = 3{,}856$, $p < 0.01$) (Figures 5b, 6c, and 6d). Glc_N decreased slightly with depth also, resulting in significantly higher mol percentages at the upper oxycline compared to the suboxic waters ($n_{upper\_oxycline} = 78$, $n_{suboxic} = 158$, $W = 4{,}106$, $p < 0.01$) (Figure 5b). For the other sugar fractions the change over depth was more variable (Figure 5b). In analogy to the amino acid based DI, we derived an indicator for diagenetic changes in DCCHO composition, using PCA with the composition of neutral sugars. The change in the composition of neutral sugars was described by PC1, which explained 54.2% of the variance (Figure S6). PC1 values increased with depth (Figure 8b) and ranged between −5.4 for the fresher and 3.6 for the more degraded DCCHO. The PC1 was significantly lower at the oxic surface compared to the upper oxycline ($n_{upper\_oxycline} = 78$, $n_{surface} = 98$, $W = 1{,}509$, $p < 0.01$). Additionally, the PC1 in the upper oxycline was significantly lower than in the suboxic waters ($n_{upper\_oxycline} = 78$, $n_{suboxic} = 158$, $W = 8{,}060$, $p < 0.01$) (Figure 8b).

Figure 5. Percentages of single amino acids within DAA (a) and single sugars within DCCHO (b) at different oxygen regimes for all sampled stations during M136 and M138. Presented amino acids: isoleucine (Iso), leucine (Leu) phenylalanine (Phe), valine (Val), threonine (Thr), asparagine and aspartic acid (AsX; co-eluted), glutamine and glutamic acid (GlX; co-eluted), serine (Ser), glycine (Gly), arginine (Arg), alanine (Ala), y-aminobutyric acid (GABA) and tyrosine (Tyr) in mol%. Presented sugars: glucose (Glc), fucose (Fuc), rhamnose (Rha), arabinose (Ara), galactose (Gal), mannose/xylose (ManXyl), muramic acid (Mur_A), galactosamine (Gal_N), glucosamine (Glc_N), galacturonic acid (Gal_URA) and glucuronic acid (Gluc_URA) in mol%. Measured concentrations of gluconic acid were always below the detection limit.

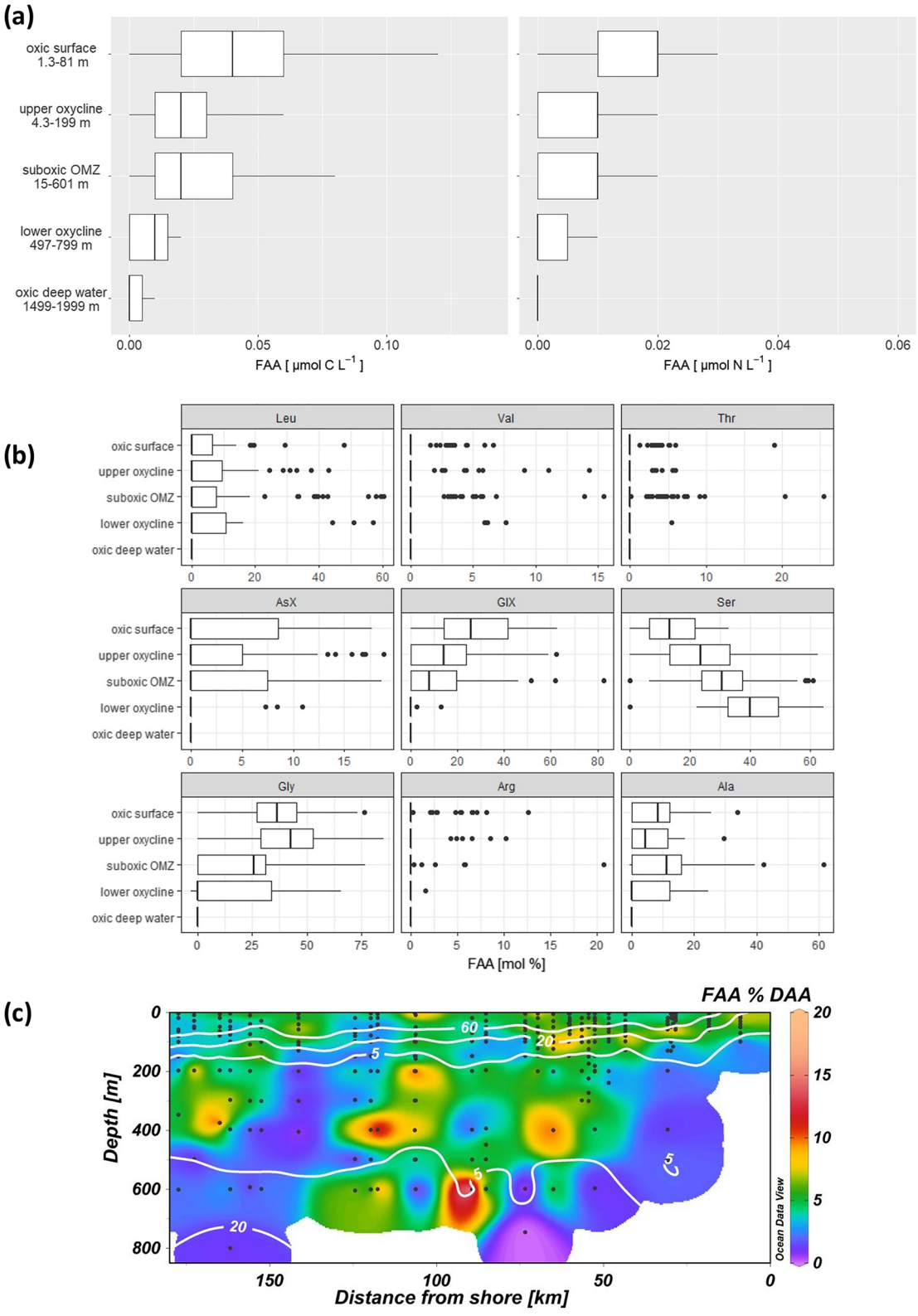


Figure 7. Carbon (C) and nitrogen (N) concentrations of free amino acids (FAA) (a) and molar percentages of FAA (b) at different oxygen regimes for all sampled stations during M136 and M138; see Figure 4 for details. Percentage of dissolved amino acids (DAA) defined by FAA over depth for all sampled stations sorted by distance from shore (c). *In situ* oxygen concentrations are indicated with white contour lines.

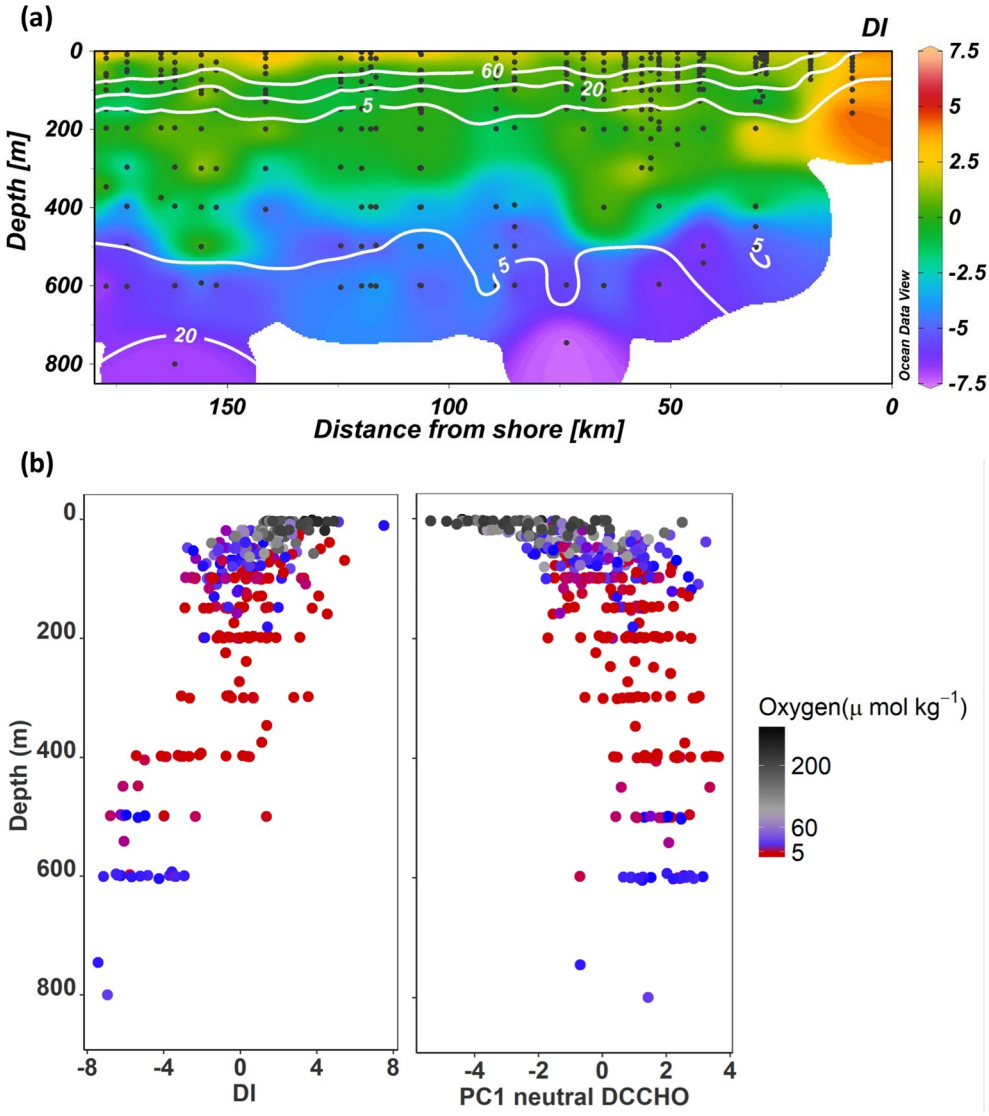


Figure 8. Degradation Index (DI) based on amino acid composition for each station separately sorted by distance from shore. *In situ* oxygen concentration is indicated with white contour lines (a). DI and first principle component (PC1) of neutral sugar composition of all sampled stations during M136 and M138 over depth; *in situ* oxygen concentrations indicated by the color coding (b).

3.5. Bacterial Hydrolysis of DOM

To further interpret patterns of DOM distribution, indicators for bacterial degradation of DOM were included in the analysis. Specifically, the hydrolysis rates of DCCHO and DAA by the extracellular enzymes GLUCase and LAPase were taken into account. These hydrolysis rates were determined during the same cruises (Maßmig et al., 2020) (Table 2). The hydrolysis rates indicated that between 0.1% and 7% d^{-1} of DAA by LAPase and between <0.1% and 0.5% d^{-1} of DCCHO by GLUCase could be hydrolyzed. The ratio between GLUCase and LAPase hydrolysis rates (GLUCase: LAPase) ranged between 0.01 and 0.3 and was significantly higher in the oxic surface and upper oxycline than in the suboxic OMZ core ($n_{\text{upper\_oxycline}} = 33$, $n_{\text{suboxic}} = 11$, $W = 19$, $p < 0.01$). Multiplying the enzymatic hydrolysis rates with the concentrations of carbon and nitrogen defined by DAA and DCCHO, Maßmig et al. (2020) estimated a degradation rate of semi-labile DOM ranging from 0.1 to 40 μmol C m^{-3} d^{-1} and from 0.3 to 17.6 μmol N m^{-3} d^{-1} (Table 2). Comparing the degradation rates, revealed a stronger degradation of DAA-C compared to DCCHO-C at all oxygen regimes. However, DAA-C degradation was especially pronounced in suboxic waters, where DAA-C

Table 2
Indicators for Bacterial Degradation of Organic Matter at Different Oxygen Regimes at Selected Stations of M136 and M138

	DCCHO hydrolytic turnover by GLUCase			DAA hydrolytic turnover by LAPase			GLUase: LAPase		
	[% d^{-1}]								
Oxygen regime	*n*	Avg.	SD	*n*	Avg.	SD	*n*	Avg.	SD
Oxic surface 1.3–81 m	23	0.12	0.10	22	1.87	1.46	18	0.09	0.05
Upper oxycline 4.3–199 m	15	0.08	0.07	15	0.60	0.42	11	0.14	0.08
Suboxic OMZ 15–601 m	38	0.05	0.07	42	1.05	0.35	33	0.04	0.04
Lower oxycline 497–799 m	3	0.03	0.02	6	0.52	0.39	3	0.04	0.02

	DCCHO-C degradation rate by GLUCase			DAA-C degradation rate by LAPase			DAA-N degradation rate by LAPase		
	μmol C m^{-3} d^{-1}						μmol N m^{-3} d^{-2}		
Oxygen regime	*n*	Avg.	SD	*n*	Avg.	SD	*n*	Avg.	SD
Oxic surface 1.3–81 m	22	3.56	3.29	20	16.28	9.14	20	7.03	3.92
Upper oxycline 4.3–199 m	15	1.26	0.98	15	3.54	2.50	15	1.63	1.15
Suboxic OMZ 15–601 m	38	0.71	1.30	40	5.52	2.07	40	2.55	0.93
Lower oxycline 497–799 m	3	0.27	0.21	6	2.05	1.31	6	1.01	0.65

Note. The degradation rates of dissolved combined carbohydrates (DCCHO) and dissolved amino acids (DAA) [μmol C m^{-3} d^{-1}] by the extracellular enzymes *β*-glucosidase (GLUCase) and leucine-aminopeptidase (LAPase) based on the hydrolytic turnover of GLUCase and LAPase [% d^{-1}] and carbon (C) and nitrogen (N) concentrations defined by DAA and DCCHO (see Table 1). Given are the average (Avg.), the standard deviation (SD) and the number of samples (*n*).

was degraded eight times faster than DCCHO-C (Table 2). In contrast, DAA-C was degraded only threefold as fast as DCCHO-C in the upper oxycline.

4. Discussion

4.1. DOM and Seasonal Variability at the Study Site

The upwelling of oxygen-depleted, nutrient-rich waters, subsequent phytoplankton growth and DOM production off Peru is subject to strong annual and interannual variability and influenced by the El Niño–Southern Oscillation. During austral summer and especially during El Niño events, the upwelling intensity of nutrient-rich water is reduced and the upper oxycline deepens. Meanwhile, phytoplankton abundance is often enhanced during austral summer because of a reduced mixed layer depth (e.g., Echevin et al., 2008; Graco et al., 2017; Kämpf & Chapman, 2016). Since labile and semi-labile DOM compounds are mainly produced by phytoplankton, their availability for heterotrophic organisms may also vary with season (Biddanda & Benner, 1997; Mague et al., 1980). Loginova et al. (2019) investigated the amount and composition of DOM in the upwelling regime off Peru during austral summer (February 2013). Their observations might thus differ from our results that were obtained in early austral winter (April and June 2017). Neither our study nor the study by Loginova et al. (2019) took place in a strong El Niño/La Niña year. However, 1 month before our sampling campaign a strong coastal El Niño was observed (https://ggweather.com/enso/oni.htm, last access: September 7, 2019, Garreaud, 2018). Water temperatures and depth of the oxycline were similar between our study and the study during austral summer, which can probably be explained by the aftermath of the coastal El Niño. During our study, chl *a* concentrations were slightly lower than in austral summer (Loginova et al., 2019), especially those collected during the cruise in June (M138), representing the seasonal variability of phytoplankton growth (Echevin et al., 2008). In our study, average DOC and DON concentrations within the oxic surface (DOC = 80 ± 28 μmol L^{-1}; DON = 5 ± 4 μmol L^{-1}) and the upper oxycline (DOC = 59 ± 12 μmol L^{-1}, DON = 4 ± 2 μmol L^{-1}) were similar to findings of Loginova et al. (2019) within the upper 160 m (DOC ~75 μmol L^{-1}, DON ~4 μmol L^{-1}) (Table 1, Figure 3a). Furthermore, the concentrations of DAA and DCCHO give an estimate for the amount of semi-labile DOM, available for uptake by microorganisms (Amon et al., 2001; Benner, 2003; Davis et al., 2009). Concentrations of DAA and DCCHO were similar between M136 and M138, suggesting no significant difference in the amount of

semi-labile DOM between April and June. However, within the oxic surface and the upper oxycline average DAA (0.3 ± 0.1 and 0.2 ± 0.0 μmol L^{-1}) and DCCHO (0.5 ± 0.2 and 0.3 ± 0.1 μmol L^{-1}) concentrations during our study were slightly lower than concentrations of 0.4–1.7 μmol DCCHO L^{-1} and 0.1–0.6 μmol DAA L^{-1} within the upper 200 m in austral summer (Loginova et al., 2019) (Table 1, Figures 3 and 4). This suggests that more semi-labile DOM is available for bacterial degradation during austral summer than during austral winter. This difference between the two studies probably represents the seasonal progression of DOM production by phytoplankton, which is more abundant in austral summer (Echevin et al., 2008).

4.2. Hydrographical Influences on DOM Off Peru

Near the surface of our study area, the STW with high oxygen concentrations can be found (Llanillo et al., 2013; Silva et al., 2009). Below, the oxygen-poor ESSW dominates the suboxic water mass in the OMZ core (Chavez & Messié, 2009; Kämpf & Chapman, 2016). At deeper depth, the influence of the oxygen-rich AAIW enables the formation of the lower oxycline (Llanillo et al., 2013; Silva et al., 2009). The proportion of the different water masses at sampling depths can be estimated with physical parameters, knowing the initial conditions of each "pure" water mass.

Assuming that the original oxygen concentration of STW is 240.65 μmol O_2 kg^{-1} and the mixing between ESSW and STW forms the upper oxycline, we can roughly estimate an average contribution of 8% (2%–24%) STW in the upper oxycline at sampling depths (Llanillo et al., 2013). The precise influence of the different water masses on the composition of DOM in the study area is difficult to estimate since DOM has not been measured in the source waters (ESSW and STW) during the cruise. Chl *a* concentration is usually lower at the origin of STW, that is, southwestward of the study area near the rim of the subtropical gyre, compared to chl *a* concentration at the origin of ESSW, that is, near the equator (Gregg & Conkright, 2002; Llanillo et al., 2013). Hence, chl *a* concentration in source regions of the respective water masses suggest higher primary production and subsequently higher production of DOM in the source water of the ESSW, that forms the suboxic OMZ core in the study area. In contrast, semi-labile DOM accumulates in subtropical gyres, offering a source of labile DOM to the STW that is formed nearby (Hansell et al., 2009). Modeled global DOC concentration revealed lower concentration southward the equator (origin of STW) compared to the concentration in surface waters (30 m) near the equator (origin of ESSW) in the Pacific between 90°W and the Peruvian Coast (Hansell et al., 2009; Llanillo et al., 2013). This modeled distribution of DOC suggests lower concentrations of DOM and less labile DOM in the STW compared to the ESSW. Hence a decrease in DOM lability, as observed at the sampling site (e.g., Figure 8) is probably also formed by degradation of organic matter on site (see Sections 4.3 and 4.4) and not exclusively by the different water masses.

Assuming that the oxygenated water below the lower oxycline can be associated with the emerging AAIW with an original oxygen concentration of 238.2 μmol O_2 kg^{-1} (Llanillo et al., 2013), we can estimate an average input of 5% (2%–11%) AAIW into the ESSW at our sampling site. This calculation is based on the oxygen concentrations at sampling depths within the lower oxycline (Figure 2a). Mixing of different water masses should also influence the composition of DOM, in addition to the change in DOM composition by biological processes. In our study, the percentage of DAA explained by FAA significantly decreased at the lower oxycline and might indicate the mixing of different water masses (Figure 7c). Additionally, the DI remarkably decreased at the lower oxycline, since the average DI within the suboxic waters was significantly higher compared to the DI at the lower oxycline. This strong change of the DI at the lower oxycline is proposing DAA composition as a potential indicator for the intrusion of AAIW into ESSW (Figures 8a and 8b). The indicated abrupt change in lability of DOM at the lower oxycline can be explained by (a) the higher availability of oxygen enabling a faster bacterial degradation of DOM or (b) more refractory DOM in the arriving AAIW compared to the DOM in the ESSW. The first explanation seems unlikely since bacterial DOM degradation within this region was not reduced in suboxic compared to hypoxic waters (Maßmig et al., 2020) and further indications for degradation of DOM under suboxic conditions are presented within this study. Moreover, AAIW is formed in the subantarctic front in the southeast Pacific and is influenced by Antarctic Surface Water (Hartin et al., 2011; Sloyan & Rintoul, 2001). The Antarctic is a region with lower DOC surface concentrations (38–75 μmol L^{-1}) compared to the equatorial region (60–82 μmol L^{-1}) (Hansell et al., 2009; Ogawa & Taoue, 2003) were the ESSW is generated (Wyrtki, 1976). Therefore, AAIW probably transports more degraded DOM, which is reflected by a lower DI within our study.

4.3. The Potential Effect of Oxygen on DCCHO and DAA Concentrations

During this study, we observed a faster decrease of DCCHO concentration over depth relative to DAA concentration, off Peru (Table 1 and Figures 3b, 3c, and 4). Amino acids provide carbon and nitrogen simultaneously, whereas carbohydrates, with a few exceptions, can solely serve as carbon sources, suggesting that amino acids are a preferential substrate for bacteria compared to carbohydrates. In line with this theory, dissolved protein incorporation fueled heterotrophic picoplankton production in the Southern Ocean whereas Glc only gained importance in fall when the supply of protein was reduced (Simon & Rosenstock, 2007). In contrast, depth profiles (5–4,300 m) showed relatively higher losses of sugars compared to amino acids, in oxygenated waters in the Pacific and Atlantic (Kaiser & Benner, 2009), indicating that sugars are more accessible for degradation than amino acids. Moreover, a comparison between HMW-DOM in the surface (<100 m) and deep (>1,000 m) ocean revealed a stronger relative decrease in sugars and change in polysaccharide-like substances compared to amino acids and amide-like substance, based on chemical analyses and ^{13}C and ^{15}N nuclear magnetic resonance spectroscopy, respectively (Benner, 2002). Furthermore, total hydrolyzable neutral sugars were degraded at higher rates than total hydrolyzable amino acids, during experiments with algal-derived DOM, suggesting that combined neutral sugars are more bioreactive than total hydrolyzable amino acids (Amon et al., 2001). The high bioreactivity of neutral sugars in DOM might be related to its relatively higher abundance in algal-derived DOM compared to amino acids and the subsequent adaptation of bacteria (Amon et al., 2001).

In the OMZ off Peru, the decoupling of the decrease in DCCHO and DAA concentrations over depth was very pronounced, for example, there was a 30% faster attenuation of DCCHO compared to DAA (Figure 4). Moreover, the degradation of DOM in general and the decoupling appeared at a shallower depth than in fully oxygenated waters of the open Pacific that have been investigated by Kaiser and Benner (2009) (Figure 4). This may partly be related to the compression of high DOM concentration into a shallower surface layer due to the upwelling of water masses in the study area as discussed in Loginova et al. (2019). However, difference in DAA and DCCHO attenuation over depth were also observed between different oxygen regimes off Peru. For instance, the decline of DAA concentration stretched over greater depth at stations with deeper oxyclines (Figures 4 and S5). Therefore, we assume that different oxygen regimes might affect DAA and DCCHO degradation differently, resulting in more efficient uptake of DCCHO compared to DAA in oxic and hypoxic waters and a relatively enhanced uptake of DAA under suboxic conditions. Extracellular enzyme rates sampled during the same cruises by Maßmig et al. (2020) corroborate this assumption. In general, the hydrolytic turnover of DAA by LAPase exceeded the hydrolytic turnover of DCCHO by GLUCase, indicating a generally stronger enzymatic hydrolysis of DAA compared to DCCHO. However, the ratio between GLUCase and LAPase hydrolytic turnover differed between oxygen regimes and the proportion of DCCHO degradation by GLUCase was stronger within the oxic surface and the upper oxycline compared to the suboxic waters (Table 2). Van Mooy et al. (2002) found also indications for enhanced degradation of amino acid-containing POM in suboxic waters during trap deployments in the eastern tropical North Pacific. Additionally, incubation experiments revealed that bacterial metabolism favors protein degradation over the degradation of carbohydrates under anoxia (Harvey et al., 1995). Furthermore, the microbial community attached to protein-coated model particles within the anoxic waters of the Black Sea indicated active degradation of the proteinaceous material (Suominen et al., 2020). Our results are consistent with those previous studies since both DOM concentrations and enzyme rates indicate higher degradation of DCCHO at the oxygenated surface and preferred (relative to DCCHO) degradation of DAA under suboxic conditions. A preferred degradation of DON under suboxic conditions, for instance by denitrifying bacteria, may also release nitrite and ammonia, that can fuel anammox and thus the loss of nitrogen to the atmosphere (Ward, 2013).

Next to faster uptake, the stronger attenuation of DCCHO relative to DAA may also be explained by an additional source of amino acids by enhanced solubilization of amino acid-containing POM. POM makes up a large part of the organic matter supplied to the OMZ. For example, the export of POC to depths (>100 m) is ~5 times higher than that of semi-labile DOC (Hansell et al., 2009). Amino acids represent the largest fraction of characterizable biochemicals in sinking POM and are solubilized and degraded rapidly, representing 67% of POC in net-plankton at the surface and 24% of POC at 105 m depth (Kharbush et al., 2020; Wakeham et al., 1997). Hence, POM is a likely source of DAA below the surface. Since the general flux of POM is strongly decreasing below the surface and the C/N ratio is increasing with depth (e.g., Van Mooy

et al., 2002; Wakeham et al., 1997), the production of DAA by POM degradation will likely be highest in the upper water column and weakens the attenuation of DAA over depth. The preferred uptake of nitrogen-rich organic matter under suboxic conditions, however, will explain the attenuation of DAA at deeper depth.

Additionally, the release of DOM by bacteria contributes to the pool of amino acids (Kawasaki & Benner, 2006). In our study, absolute amounts and mol percentages of free Ala and Thr were enhanced within the suboxic OMZ core compared to the oxyclines, suggesting their production in suboxic waters (Figures 7b and S3b). In line with our findings are experimental studies, showing Ala production during exponential growth of bacteria (Kawasaki & Benner, 2006) and also under anaerobic conditions, that is, nitrate respiration (Cheng et al., 1989). We found a similar pattern also for Thr, suggesting that both free Ala and Thr indicate metabolic active bacteria within suboxic waters, which have been previously described for the study region (Maßmig et al., 2020). The production of organic matter by chemoautotrophic processes under suboxia was also proposed by Keil et al. (2016) as one possible explanation for seemingly reduced attenuation of organic matter export fluxes under suboxia compared to oxic conditions. A release of FAA by anaerobic bacteria corroborates earlier observations that show the accumulation of labile DOM under low-oxygen conditions (Maßmig et al., 2019).

Consequently, our study proposes a spatial decoupling of DCCHO and DAA degradation patterns in the water column off Peru. Our observations suggest that preferential hydrolyzation and heterotrophic uptake of carbohydrates at shallow more oxygenated waters, and the comparatively enhanced solubilization and degradation of peptides below the oxygenated waters stimulate the decoupling.

4.4. The Potential Effect of Oxygen on DCCHO and DAA Composition

The composition of semi-labile DOM as derived from DAA and DCCHO indicates organic matter lability (e.g., Dauwe & Middelburg, 1998; Davis et al., 2009; Engel et al., 2012; Goldberg et al., 2009). Bacterial degradation alters DOM composition and lability until only recalcitrant DOM is left behind (Jiao et al., 2010). A distinct bacterial degradation and uptake of DAA and DCCHO affected by oxygen concentrations should, therefore, be reflected in the composition of DCCHO and DAA. The DI based on amino acid composition can be used to describe the diagenetic change of DAA over depth (Dauwe et al., 1999), and the change in DCCHO composition was described by PC1, based on neutral sugar composition. In our study, the observed range of DI was within the range of previously reported values for the Pacific (Yamashita & Tanoue, 2003). Between the upper oxycline and the suboxic waters, the DI was similar (Figures 8a and 8b). In contrast, the PC1 of neutral sugar composition changed strongly between the oxic surface or the upper oxycline and the suboxic waters, supporting the assumption of a stronger degradation of DCCHO in more oxygenated waters compared to DAA.

It has been suggested, that carbon export fluxes are enhanced in suboxic and anoxic waters compared to oxic waters (e.g., Devol & Hartnett, 2001), raising, the hypothesis of reduced microbial degradation of organic matter within the OMZ. On the other hand, bacteria may rely on enhanced oxidation of organic matter to counteract the reduced amount of energy yield by anaerobic respiration (Strohm et al., 2007). In the OMZ off Peru, anammox is assumed to be the dominant pathway, and denitrification was detected occasionally (Kalvelage et al., 2013). Since anammox is a chemolithoautotrophic pathway it does not imply the oxidation of organic carbon. However, a recent study showed significant bacterial degradation of DOM and bacterial production within suboxic waters, in the upwelling system off Peru (Maßmig et al., 2020). An indicator of the bacterial degradation of DOM under suboxic conditions is a decline in DOM lability, which would be reflected in a decreasing DI within the suboxic waters (Dauwe et al., 1999). In our study, the DI continued to decrease within suboxic waters at most stations (Figures 8a and 8b), supporting the heterotrophic bacterial growth under suboxic conditions, in the suboxic OMZ core off Peru (Maßmig et al., 2020). The decrease in the DI was less in suboxic waters, compared to the surface (Figures 8a and 8b), reflecting the lower concentrations of DAA at depth and therefore little change in the degradation status of DOM, as it has also been shown in waters below 100 m within the oxygenated North Pacific (Kaiser & Benner, 2009).

Further indications of organic matter degradation can be derived from the mol fraction of specific amino acids and sugars within DAA and DCCHO, respectively. In our study, the mol fraction of Glc and Gal separated over depth, suggesting that Glc is more and Gal less resistant to degradation, being in line with

former studies on DCCHO in the Atlantic and Pacific (Engel et al., 2012; Goldberg et al., 2009; Loginova et al., 2019) (Figures 5b, 6c, and 6d). Accordingly, the composition of specific DCCHO differed between the upper oxycline and the suboxic waters. Mol% of Glc increased over depth and was higher within the suboxic waters than within the upper oxycline, whereas mol% of Gal decreased strongly below the upper oxycline. Thus, changes in DCCHO composition between oxygen regimes also suggest enhanced DCCHO degradation in more oxygenated waters (Figures 5b, 6c, 6d, and 8b).

In contrast to DCCHO, the composition of DAA was similar between the upper oxycline and the suboxic waters but changed significantly toward the lower oxycline. Molar fractions of Iso, Val, Phe, and Leu point to more labile DAA as observed previously in the Pacific (Yamashita & Tanoue, 2003) and decreased continuously over depth in our study (Figures 5a and 6b). Contribution of Gly to DAA increased with depth, especially at the lower oxycline (Figures 5a and 6a) corroborating the idea of Gly tracing more refractory organic matter, as observed also in earlier studies in the Pacific (e.g., Kaiser & Benner, 2009; Yamashita & Tanoue, 2003). In earlier studies, Ala (Yamashita & Tanoue, 2003) and GABA (Kaiser & Benner, 2009) were also identified as an indicator for less bioavailable organic matter in the Pacific and Atlantic and GABA, a nonprotein amino acid, can be produced by bacteria (Cowie & Hedges, 1994; Lee & Cronin, 1982; Schroeder, 1975). However, neither the concentrations nor the contributions of Ala and GABA to the DAA pool were increasing over the first 850 m in our study or in Loginova et al. (2019) (Figures 5a and S3a). Reasons for the absence of increasing GABA proportions or concentrations over depth might be (a) additional sources of GABA at the surface or sinks at depth that might cover the accumulation of GABA over depth, (b) a superposition of GABA by the formation of fresh amino acid-containing DOM, for example by chemoautotrophic bacteria, or (c) the limited difference in degradation state of DOM between the surface and the deeper waters, since GABA is known to be altered in a more advanced degradation process (Davis et al., 2009). The first explanation has been suggested by Kaiser and Benner (2009) after discovering higher concentrations of non-protein amino acids in waters with younger radiocarbon age. Chemoautotrophic pathways have already been suggested as organic matter sources in anoxic waters by Keil et al. (2016) and incubation experiments with Baltic Sea water showed an increase in DOM lability, indicating a release of fresh organic matter at low oxygen concentration (Maßmig et al., 2019). The results of our study strongly support the latter hypothesis, since the GABA concentrations tend to rise in the oxygenated deep waters, thus at a greater depth than the focus of our study (Figure S3a).

Our findings propose very dynamic cycling of DON in OMZs with DAA and specific DCCHO (Glc_N, Gal_N and Mur_A) being important components (Table S1). On the one hand the degradation of DAA at the surface, in the upper oxycline and under suboxic conditions is reflected in the decrease of the semi-labile fraction of DON (Table S1). On the other hand, the provision of amino acids by bacterial production and the preferred hydrolysis of nitrogen-rich POM, as also suggested by Van Mooy et al. (2002), may supply labile and semi-labile DON also under suboxic conditions. This dynamic cycling of DON may fuel denitrification and anammox and therefore a loss of nitrogen. In OMZs 30%–50% of the global marine nitrogen loss occurs since processes like denitrification and anammox lead to the formation of dinitrogen gas, for example (e.g., Lam & Kuypers, 2011). The carbon and nitrogen cycling in OMZs are closely coupled since heterotrophic anaerobic processes like denitrification also cause the production of carbon dioxide and thus counteract the storage of carbon in the ocean (e.g., Lam & Kuypers, 2011). In our study, the degradation of organic nitrogen in the suboxic OMZ core indicated by DOM composition and enzyme rates (see also 4.3), suggests ongoing heterotrophic denitrification and therewith a loss of nitrogen and carbon to the atmosphere, in the OMZ off Peru.

To summarize, the change in the composition of DCCHO and DAA between the oxygen regimes shows stronger diagenesis of DCCHO in the upper oxycline whereas DAA is more degraded within the suboxic OMZ core and near the lower oxycline. This is, again, in line with the suggested shallower degradation of DCCHO compared to DAA and also supports the hypothesis that oxygen concentration affects DAA and DCCHO degradation.

5. Conclusions

Our study revealed a strong alteration and degradation of semi-labile DOM in the OMZ off Peru. Preferential bacterial degradation of DCCHO was observed in oxygenated water. In contrast, DAA turn-over was also found and appeared to be even stimulated (relative to DCCHO) under suboxic conditions. A spatial decoupling of bacterial degradation of carbon-rich DCCHO and nitrogen-rich DAA, strengthened by different oxygen regimes might help to better understand and constrain carbon and nitrogen cycling in OMZ regions. Our study thus indicates that the storage of carbon within the ocean and the availability of reactive nitrogen species are affected by a complex interplay between DOM molecular composition, and abundant bacterial communities, which prefer different substrates in response to their aerobic or anaerobic metabolic demand. Our study thus exemplifies the significance of combined microbiological and biochemical observations to unravel element cycling in OMZs.

Conflict of Interest

The authors declare that they have no conflict of interest.

Data Availability Statement

Data are available at https://doi.pangaea.de/10.1594/PANGAEA.922796 (Maßmig and Engel, 2020).

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