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

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We would like to thank R. Benner for his time and valuable comments to this manuscript. In the following, we will address the comments one by one.

RC2: The authors present compelling physical and biogeochemical data indicating microbial utilization of DOM plays an important role in shaping the upper oxycline in the Peruvian upwelling system. Diapycnal fluxes of O2 and DOM from productive surface waters are estimated, and analyses of DOM concentrations and compositions indicate the microbial utilization of bioavailable components (e.g. amino acids and carbohydrates) occurs mostly in the upper 50 m of the water column. In addition to the mol% compositional data presented for carbohydrates and amino acids, the DOC-normalized yields of neutral sugars and amino acids can provide insights about the bioavailability of DOC. These data should be presented in a table (e.g. Table 1) or figure (e.g. Fig. 4).

AC2: We thank R. Benner for highlighting the interdisciplinarity of our study, which combines complex physical and biogeochemical datasets. Following his suggestion, we will add the information of DCCHO and DHAA yields (in %DOC) to Table 1 (see revised version). For better comparison with open ocean data from Kaiser and Benner (2009), we will divide our DCCHO data into neutral sugars (nS), aminosugars(S-N) and acidic sugars (S-H) and report them in μmol L-1 and in mol%DOC. The single sugar contribution to nS, S-N and S-H, will be given, as mol%nS, mol%S-N and mol%S-H, respectively. For DHAA both, mol%DOC and mol%DON will be added. GABA (mol%DHAA) will be removed from the table and will be described in the text of the reviewed manuscript as “The concentrations of GABA, which is commonly used as a signature of microbial activity (Davis et al., 2009), was very low in all samples and represented generally <1% of DHAA” (page7/line 32).

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

AC: The text on page10, line 30: “A strong reworking of the labile and semi-labile DOM could also be seen from the analyses of DHAA and DCCHO composition. For instance, 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 was also previously proposed to be reflection of low nutritional value of Gly for organisms in anoxic sediments in ETSP off Chile (Pantoja and Lee, 2003) and in sediments of the North Sea (Dauwe and Middelburg, 1998). In our study, DHAA and DCCHO below

50 m depth were mainly composed by Gly and Glc, respectively, indicating a significant stage of DOM reworking. Despite the shallow depth, DOM below 50 m depth was characterized by much stronger alteration than samples collected by Kaiser and Benner (2009) from much greater depths (up to 4000m), suggesting a rapid and extensive heterotrophic DOM utilization in ETSP." will be changed to: "A strong alteration of labile and semi-labile DOM could also be seen from the analyses of DOM composition. The relatively high carbon yield (%DOC) of DHAA and DCCHO (Table 1) 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 utilized at shallow depth. According to the classification by Davis and Benner (2007) availability of labile and semi-labile DOM in our study region was restricted to the upper 50 m of the water column. Furthermore, the compositional analyses of DHAA and DCCHO revealed that, DOM below 50 m depth was mainly composed by Gly and Glc, respectively. 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). With this, 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 suggests rapid and very extensive heterotrophic DOM utilization in the ETSP."

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

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

“DOM transport through the water column is achieved by advective and diffusive transport processes. Therefore, along with the turbulent mixing, other transport terms will also take their part in shaping DOM distribution off Peru. For instance, vertical advection (i.e. upwelling) of deeper waters, which are characterized by highly altered DOM in low concentrations likely contributes to a reduction of DOM concentrations near the surface layers. The upwelling driven vertical DOC flux thus counteracts the vertical turbulent diffusion and like remineralization contributes 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 that exhibits rather smooth DOM concentration gradients and weaker changes in the DOM composition (Kaiser and Benner, 2009). Herewith, the restriction of bioavailable DOM to shallow depths by upwelling may affect the propagation depth of diapycnal DOM flux and supply. Further research is needed to improve the understanding of this interplay. “

RC2: Specific comment: The reported concentrations of the amino sugar, GalN, are very low in comparison to values in the north Pacific (HOT). The resulting GlcN:GalN ratios are extremely high (40-70). It appears there is a problem with the GalN measurements. AC2: We are thankful to R. Benner for spotting this mistake. GalN during this study was almost always below detection limit of 10nM. Table1, however included an average of these data. We will remove GalN from the table and explicitly state that the values were below detection: “S-N were represented solely by GlcN, as GalN was below DL in most samples.” GlcN, could be detected in most samples, this is in accordance with GlcN:GalN ratios, typically $\geq$1.

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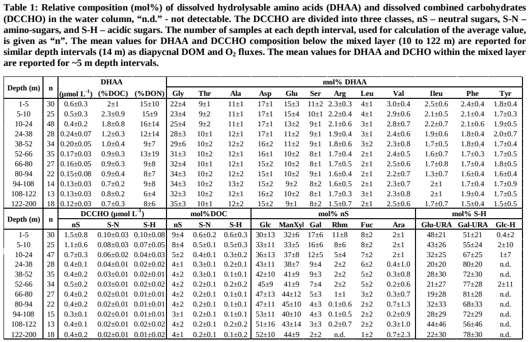

Table 1: Relative composition (mol%) of dissolved hydrolysable amino acids (DHAA) and dissolved combined carbohydrates (DCCHO) in the water column, “n.d.” - not detectable. The DCCHO are divided into three classes, nS – neutral sugars, S-N – amino-sugars, and S-H – acidic sugars. The number of samples at each depth interval, used for calculation of the average value, is given as “n”. The mean values for DHAA and DCCHO composition below the mixed layer (10 to 122 m) are reported for similar depth intervals (14 m) as diapycnal DOM and 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			mol% DHAA											
		(µmol L^{-1})	(%DOC)	(%DON)	Gly	Thr	Ala	Asp	Glu	Ser	Arg	Leu	Val	Ileu	Phe	Tyr
1-5	30	0.6±0.3	2±1	15±10	22±4	9±1	11±1	17±1	15±3	11±2	2.3±0.3	4±1	3.0±0.4	2.5±0.6	2.4±0.4	1.8±0.4
5-10	25	0.5±0.3	2.3±0.9	15±9	23±4	9±2	11±1	17±1	15±4	10±1	2.2±0.4	4±1	2.9±0.6	2.1±0.5	2.1±0.4	1.7±0.3
10-24	48	0.4±0.2	1.8±0.8	16±14	25±4	9±2	11±1	17±1	13±2	9±1	2.1±0.6	3±1	2.8±0.7	2.2±0.7	2.1±0.6	1.9±0.5
24-38	28	0.24±0.07	1.2±0.3	12±14	28±3	10±1	12±1	17±1	11±2	9±1	1.9±0.4	3±1	2.4±0.6	1.9±0.6	1.8±0.4	2.0±0.7
38-52	34	0.20±0.05	1.0±0.4	9±7	29±6	10±2	12±2	16±2	11±2	9±1	1.8±0.6	3±2	2.3±0.8	1.7±0.5	1.8±0.4	1.7±0.4
52-66	35	0.17±0.03	0.9±0.3	13±19	31±3	10±2	12±1	16±1	10±2	8±1	1.7±0.4	2±1	2.4±0.5	1.6±0.7	1.7±0.3	1.7±0.5
66-80	27	0.16±0.05	0.9±0.3	9±8	32±4	10±1	12±1	15±2	10±2	8±1	1.7±0.5	2±1	2.5±0.6	1.7±0.8	1.7±0.4	1.8±0.5
80-94	22	0.15±0.08	0.9±0.4	8±7	34±3	10±2	12±2	15±1	10±2	9±1	1.6±0.4	2±1	2.2±0.7	1.3±0.7	1.6±0.4	1.6±0.4
94-108	14	0.13±0.03	0.7±0.2	9±8	34±3	10±2	13±2	15±2	9±2	8±2	1.6±0.5	2±1	2.3±0.7	2±1	1.7±0.4	1.7±0.9
108-122	13	0.13±0.03	0.8±0.2	6±4	32±3	10±2	12±1	16±2	10±2	8±1	1.7±0.3	3±1	2.3±0.8	2±1	1.9±0.4	1.7±0.5
122-200	18	0.12±0.03	0.7±0.3	8±6	35±3	10±1	12±2	15±2	9±1	8±2	1.5±0.7	2±1	2.5±0.6	1.7±0.7	1.5±0.4	1.5±0.5

Depth (m)	n	DCCHO (µmol L^{-1})			mol%DOC			mol% nS						mol% S-H		
		nS	S-N	S-H	nS	S-N	S-H	Glc	ManXyl	Gal	Rhm	Fuc	Ara	Glu-URA	Gal-URA	Glc-H
1-5	30	1.5±0.8	0.10±0.03	0.10±0.08	9±4	0.6±0.2	0.6±0.3	30±13	32±6	17±6	11±8	8±2	2±1	48±21	51±21	0.4±2
5-10	25	1.1±0.6	0.08±0.03	0.07±0.05	8±4	0.5±0.1	0.5±0.3	33±11	33±5	16±6	8±6	8±2	2±1	43±26	55±24	2±10
10-24	47	0.7±0.3	0.06±0.02	0.04±0.03	5±2	0.4±0.1	0.3±0.2	36±13	37±8	12±5	5±4	7±2	2±1	32±25	67±25	1±7
24-38	28	0.4±0.1	0.04±0.01	0.02±0.02	4±1	0.3±0.1	0.2±0.1	43±11	38±7	9±4	2±2	6±2	0.4±1.0	20±20	80±20	n.d.
38-52	35	0.4±0.2	0.03±0.01	0.02±0.01	4±2	0.3±0.1	0.1±0.1	42±10	41±9	9±3	2±2	5±2	0.3±0.8	28±30	72±30	n.d.
52-66	34	0.5±0.2	0.03±0.01	0.02±0.02	4±2	0.2±0.1	0.2±0.2	45±9	41±9	7±4	2±2	5±2	0.2±0.6	21±27	77±28	2±11
66-80	27	0.4±0.2	0.02±0.01	0.01±0.01	4±2	0.2±0.1	0.1±0.1	47±13	44±12	5±3	1±1	3±2	0.3±0.7	19±28	81±28	n.d.
80-94	22	0.4±0.2	0.02±0.01	0.01±0.01	4±2	0.2±0.1	0.1±0.1	47±11	45±10	4±3	0.1±0.6	2±2	0.7±1.3	32±33	68±33	n.d.
94-108	15	0.3±0.1	0.02±0.01	0.01±0.01	3±1	0.2±0.1	0.1±0.1	53±11	40±10	4±3	0.1±0.5	2±2	0.2±0.9	28±29	72±29	n.d.
108-122	13	0.4±0.1	0.02±0.01	0.02±0.02	4±2	0.2±0.1	0.2±0.2	51±16	43±14	3±3	0.2±0.7	2±2	0.3±1.0	44±46	56±46	n.d.
122-200	18	0.4±0.2	0.02±0.01	0.01±0.02	4±1	0.2±0.1	0.1±0.2	52±10	44±9	2±2	n.d.	1±2	0.7±2.3	22±30	78±30	n.d.

Fig. 1.

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Discussion paper