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Interactive comment on "Sediment release of dissolved organic matter to the oxygen minimum zone off Peru" *by* Alexandra N. Loginova et al.

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Replies to comments on the manuscript by Loginova et al. (BGD, 2020) In the following Reviewer's comments are marked as "R2" and the authors' responses are marked as "A".

R2: This manuscript reports assessments of benthic dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) fluxes and pore water profiles from six sites on a transect of stations off central Peru. The chemical characteristics of DOM pools are also explored using absorbance and fluorescence spectral analyses. The work follows a series of other papers (e.g., Dale et al 2015 and 2016; Sommer et al 2016) reporting on benthic studies completed on research cruises to the Peruvian continental margin

in 2017. A: That is correct, and it also provides first measurements of dissolved organic matter in the pore waters and in benthic chambers in the area.

R2: Generally, the manuscript was poorly prepared for external review. The English wording of sentences is often awkward, and many sentences contain extraneous words or are missing key prepositions. Some of these problem sentences are listed below. A: The sentences listed below will be corrected according to the reviewer's suggestions in the reviewed manuscript. The reviewed version of manuscript will be checked by a native speaker.

R2: The paper presentation is also lacking depth and rigor. A more focused introduction and a much more informative description of the study area under section 2.1 are needed to set the stage for this work. The study area description should summarize the already published and spatially variable sediment carbon accumulation rates and benthic remineralization rates (e.g. DIC and nitrate fluxes) that are critical to the later discussion. This information could be incorporated into a more informative Figure 1. A: The Introduction will be restructured in the reviewed version of the manuscript into following:

"The eastern tropical South Pacific (ETSP) is one of the most productive areas of the world ocean (Pennington et al., 2006). High productivity, followed by intense organic matter remineralisation (e.g. Loginova et al., 2019; Maßmig et al., 2020) in combination with sluggish ventilation (Stramma et al., 2005; Keeling et al., 2010) leads to a formation of pronounced oxygen minimum zone (OMZ) (e.g. Stramma et al., 2008). Remineralisation of organic matter under anoxia induces nitrogen (N)-loss by denitrification, anammox and dissimilatory nitrate reduction to ammonium (DNRA) in the water column and sediments off the coast of Peru (Kalvelage et al., 2013; Arévalo-Martínez et al., 2015; Dale et al., 2016; Sommer et al., 2016; Glock et al., 2019). Although organic matter remineralisation is classically assumed to be limited by the absence of oxygen (Demaison and Moore, 1980), recent studies report similar abilities of marine microbes to degrade organic matter in oxygenated surface waters and within OMZs

(Pantoja et al., 2009; Maßmig et al., 2019, 2020), suggesting that other factors, such as the quality of organic matter may regulate microbial activity within OMZs (Pantoja et al., 2009; Le Moigne et al., 2017). Similar to the water column studies, extensive fieldwork campaigns conducted on sediments off Peru also suggested intensive particulate organic matter (POM) remineralisation under full anoxia (Dale et al., 2015). While POM degradation in sediments is mostly associated with its full remineralisation to dissolved inorganic carbon (DIC) and inorganic nutrients, the mechanism of POM remineralisation implies important intermediate stages of dissolved organic matter (DOM) production, reworking and mineralisation processes (Smith et al., 1992; Komada et al., 2013). Thus, around 10 % of remineralised particulate organic carbon (POC) may accumulate as dissolved organic carbon (DOC) in the pore waters (Alperin et al., 1999). In turn, DOM efflux may represent an important escape mechanism for carbon from sediments (e.g. Ludwig et al., 1996; Burdige et al., 1999) and a source of organic matter to the water column (e.g. Burdige et al., 2016). Despite the acknowledged importance of sediment DOM for organic matter cycling, the measurements of benthic DOM fluxes remain scarce, and the reactivity of the porewater DOM is not well constrained. The release of dissolved substances from anoxic sediments is regulated mainly by diffusion through the sediment-water interface (e.g. Lavery et al., 2001, and references therein). Diffusion driven DOM fluxes (hereafter named “diffusive fluxes”) and net DOM fluxes (hereafter termed “net fluxes”) are commonly evaluated from porewater gradients using Fick’s First Law and by enclosing and incubating a small area of the sediment surface over time, respectively. Diffusive DOM fluxes have been found to be consistent with net DOM flux in non-bioturbated anoxic sediments (Burdige et al., 1992). In some sediments, however, the diffusive flux may overestimate the net flux (Burdige et al., 1992; Lavery et al., 2001). This may be attributed to bioturbation, “unfavourable” redox conditions (Lavery et al., 2001), irreversible adsorption onto particles, and biological DOM consumption at the sediment-water interface or in the bottom waters (Burdige et al., 1992). The determination of in situ net DOM fluxes using benthic incubation chambers are independent of such uncertainties. This approach is based on the assumption

that solutes, released into the benthic chamber, behave conservatively during the time course of the incubation, and, show linear trends over time.

It was suggested previously that porewater DOM consists of recalcitrant low molecular weight (LMW) compounds (Burdige and Gardner, 1998; Burdige and Komada, 2015). Therefore, the sediment outflux of DOM was hypothesised to serve as an important source of recalcitrant DOM to the water column (e.g. Burdige and Komada, 2015; Burdige et al., 2016). On the other hand, elevated concentrations of dissolved organic nitrogen (DON) suggest the presence of labile proteinaceous organic matter in the porewaters (e.g. Faganeli and Herndl, 1991). Furthermore, measurements and modelling of isotopic carbon composition in the anoxic and suboxic sediments off California, suggest that about 50 % of DOM within upper sediments represents isotopically young and labile DOM components, that may be released to the water column, where they are actively utilised by heterotrophs (Bauer et al., 1995; Komada et al., 2013; Burdige et al., 2016). Similarly to DOM in the water column, porewater DOM consists of a complex mixture of organic components, only a little fraction of which may be characterised by chemical analyses (e.g. Burdige and Komada, 2015). Therefore, examining the elemental composition or DOM optical properties may be useful for accessing quality and reactivity of porewater DOM. The elemental ratio DOC/DON that is commonly used for inferring organic matter bioavailability in the water column, in sediment pore waters, displays controversial patterns. Some of the studies suggest that low DOC/DON ratios of 2 to 5 found in sediments with reduced O2 levels, may indicate an accumulation of bioavailable DOM under low O2 conditions (Faganeli and Herndl, 1991; Alkhatib et al., 2013). Other studies, however, found DOC/DON ratios, which were lower under oxic conditions compared to those of anoxic sediments (Burdige and Gardner, 1998). Optical properties were also shown to provide important insights in DOM cycling not only in the water column (e.g. Coble, 1996; Zsolnay et al., 1999; Jørgensen et al., 2011; Catalá et al., 2016; Loginova et al., 2016) but also in porewaters of marine and freshwater sediments (e.g. Chen et al., 2016). The fraction of DOM that exhibits optical activity owing to the presence of chromophoric groups âĂŤ a combination of conjugated double

bonds and heteroatoms âĂŤ in its molecular structure is referred to as chromophoric DOM (CDOM) and fluorescent DOM (FDOM). CDOM refers to DOM that absorbs light over a broad spectrum from UV to visible wavelengths. A typical CDOM absorbance spectrum is shaped as an exponential curve (Del Vecchio and Blough, 2004). The spectrum inclination (S) and absorption coefficients are used to learn on bulk DOM properties. For instance, steepness of the S is suggestive of relative differences in DOM molecular weight. Thus, a decrease of CDOM absorption in the visible spectra, compared to UV wavelength implies a decrease in DOM molecular weight (e.g. Helms et al., 2008). This is due to the ability of high molecular weight (HMW)DOM to absorb light at longer wavelengths, compared to LMWDOM. The part of CDOM that may fluoresce due to its aromatic nature is referred to as FDOM and is used to infer DOM quality (Coble, 1996; Zsolnay et al., 1999; Jørgensen et al., 2011; Catalá et al., 2016; Loginova et al., 2016). Thus, 3D fluorescence spectroscopy, followed by parallel factor analysis (PARAFAC), has been recognised as a useful tool for distinguishing between different organic matter pools (Murphy et al., 2013). Fluorophores that are excited and emit at UV wavelengths are often referred to as amino acid-like DOM. Components that are excited at UV, but emit at visible wavelengths, are mainly referred to as humic-like or fulvic-like DOM (e.g. Coble, 1996; Murphy et al., 2014, and references therein). Thus, based on optical measurements, similar suggestions as in studies based on isotopic and elemental DOM composition could be drawn. For instance, CDOM distributions in sediment cores from the Chukchi Sea suggested that anoxic sediments may serve as a production site of humic-like substances and a potential source of pre-altered DOM into the water column (Chen et al., 2016). In turn, FDOM measurements made during incubations of sediment cores (Yang et al., 2014), indicated that DOM released into the overlying water might also be further altered by microbial communities, serving as a source of bioavailable organic matter. In the ETSP off Peru, fine spatial resolution FDOM measurements suggested DOM release from anoxic sediments into the water column (Loginova et al., 2016). High FDOM fluorescence associated with the benthic release of DOM reached the euphotic zone, likely influencing organic carbon turnover

of the whole water column. Hence, sediment release of DOM could potentially serve as an important carbon and N source (e.g. Moran and Zepp, 1997) and reduce penetration depth of light in the water column (e.g. Belzile et al., 2002) for pelagic microbial communities, affecting biogeochemical processes of the water column. However, the release of porewater DOM and its reactivity had not been well studied yet in the area. In this study, we combine measurements of diffusive and in situ net fluxes of DOC and DON, and interpret those fluxes in relation to DOM optical properties measured in the sediments in the Peruvian OMZ. Our objectives are to provide a deeper understanding of DOM cycling in Peruvian sediments."

More information on previously published sediment type and fluxes will be added to the text of the revised manuscript on Page 4 line 25: "Sediments at the sampling stations are fine-grained diatomaceous dark-olive anoxic muds (Gutiérrez et al., 2009; Mosch et al., 2012) with porosity ranging between 0.8 and >0.9 (Table 1). Polychaetes and oligochaetes were found in the sampling area (Dale et al., 2015; Sommer et al., 2016). However, the sediment showed little evidence of strong mixing by bioturbation (Bohlen et al., 2011; Dale et al., 2015). In turn, the sediments are densely colonized by mats of large filamentous sulfur bacteria of the genera Tiloploca and Beggiatoa (Gutiérrez et al., 2009; Mosch et al., 2012). Dale et al. (2015) reported that mats of these sulphide oxidizing bacteria cover up to 100 % of the sediment surface at shallowest stations extending their trichomes 2 cm into the water column to access bottom water NO3-. They could be observed from the sediment surface down to 20 cm sediment depth. At offshore stations, bacterial mats of several dm in diameter were covering up to 40 % of the sediment surface. Their occurrence was related to high carbon rain rates, which ranged from 10 mmol m-2 d-1 on the continental slope to 80 mmol m-2 d-1 on the shallowest shelf station (Fig. S1). Furthermore, the region was characterized by substantial organic matter utilization as indicated from high DIC fluxes and pore water NH4+ concentrations (Dale et al., 2015). Thus, despite the highest sediment accumulation rates and POC content of the sediments, the highest organic matter respiration, as follows from large sediment DIC (Dale et al., 2015) and NH4+ (Sommer et

al., 2016) fluxes at middle shelf stations, led to the smallest percentage of carbon burial efficiency (∼17%), compared to the outer shelf and the continental slope (24-74 %). Furthermore, Sommer et al. (2016) and Dale et al. (2016) suggested spatial variability of biological N cycling pathways in the area. Thus, outer shelf stations displayed the highest sediment uptake rate of NO3- and NO2- followed by high N2 outflux (Fig. S1). At shallower stations, NO3- and NO2- were entirely exhausted and excessively high fluxes of NH4+ were observed. Those spatial variabilities in N fluxes were suggested to be a result of dominating mechanisms of denitrification and anammox on the outer shelf and continental slope, and DNRA in the middle shelf. A further detailed description of the sediment and bottom waters at 12oS may be found in Dale et al. (2015, 2016) and Sommer et al. (2016)."

Instead of Figure 1 the discussed information from section 2.1 will be added to the Supplement as figure S1.

R2: Meanwhile, Figure 2 is not needed and only repeats information given in the text about routine sampling and flux calculation methods. A: Figure 2 will be moved to Supplement

R2: With respect to the analytical work there are other concerns. There is no reporting of analytical blanks, precision or accuracy. A: The following information will be added to the revised version of the manuscript:

to page5 lines 8-11:

"This method has a detection limit of ∼0.001 absorption units (that may be referred to ∼0.5 m-1) and a precision <5%, estimated as maximal standard deviation of CDOM absorbance spectra from 275 to 400 nm divided by the mean value of three repeated measurements.",

to page 5 lines 23-24:

"The precision of this method does not exceed 3% if estimated as a standard deviation

of Raman peaks at 275 nm of each measurement day, divided by the mean value.",

to page 5 line32 – Page6 line16:

"DOC samples were analysed by the high-temperature catalytic oxidation (TOC - VCSH, Shimadzu) with a detection limit of 1 μmol L-1 as described in detail by Engel and Galgani (2016). Calibration of the instrument was performed every second week using six standard solutions of 0, 500, 1000, 1500, 2500 and 5000 μg C L-1, which were prepared using a potassium hydrogen phthalate standard (Merck 109017). Before each set of measurements, a baseline of the instrument was set using ultrapure water. The deep-sea standard (Dennis Hansell, RSMAS, University of Miami) with known DOC concentration was measured after setting the baseline to verify accuracy by the instrument. Typically, the precision of the method did not exceed 4 %. Furthermore, two control samples with known concentrations of DOC were prepared for each day of measurement using a potassium hydrogen phthalate standard (Merck 109017). The DOC concentrations of those control samples were typically within the range of samples' concentrations and were measured at the time of sample analyses to control baseline flow during measurements. The DOC concentration was determined in each sample out of five to eight replicate injections. A TNM-1 N detector of Shimadzu analyser was used to determine total dissolved nitrogen (TDN) in parallel to DOC with a detection limit of 2 μmol L-1 (Dickson et al., 2007). Calibration was performed simultaneously with the calibration of carbon detector using standard solutions of 0, 100, 250, 500 and 800 μg N L-1, which was prepared using potassium nitrate Suprapur (Merck 105065). The deep-sea standard (Dennis Hansell, RSMAS, University of Miami) with the known concentration of TDN was measured daily to verify the accuracy of the instrument. The precision of the method did not exceed 2 % estimated as the standard deviation of 5–8 injections divided by the mean value. Concentrations of DON were calculated as a difference of TDN and the sum of concentrations of inorganic N components."

R2: I note the authors used cellulose acetate membrane syringe filters rather than

combusted GF/F, so there could have been blank issues. A: We thank the Reviewer 2 for noticing that. Indeed, we did not add the details behind choosing a filter type. As collected samples were expected to be highly concentrated. Due to relatively long storage of our unfixed CDOM and FDOM samples prior to analyses, we thought of the easy way for removing most of the bacteria. Therefore, using the pore size of 0.2 μm rather than 0.7 μm (as GFF may give) was preferred. Prior to the research cruise, we did several checks for different filters of that pore size, which are commonly used during pore water work, including PES, nylon, CA and RC. All the filters gave one or another background level, therefore, we tested which volume of ultrapure water was the optimal for cleaning. CA and RC filters gave the minimum values for DOC and for DON after rinsing with 60 ml of ultrapure water. CA was chosen over RC due to lower binding affinity to macromolecules and proteins, as we did not want to influence recovery of organic components during filtration.

Following will be added to the page 4 lines 25-30 to the revised version of the manuscript: "All samples were passed through pre-washed (60 mL of ultrapure water) cellulose acetate (CA) membrane syringe filters (0.2 μm) and first five mL of the filtrate were discarded to waste before filling the sample into storage vials. Several types of filters (PES, nylon, CA and regenerated cellulose (RC)) were examined for background DOC and total dissolved nitrogen (TDN) signal before the cruise. CA and RC filters gave minimal background concentrations for both parameters after rinsing with 60 ml of ultrapure water (Fig.S4). CA filters were chosen over RC due to their lower binding affinity to macromolecules and proteins." Figure S4 will be also added to the Supplement.

R2: The authors themselves raise the possibility that the DON results may be in error due to incomplete or unmatched estimates of total inorganic nitrogen species that must be subtracted from total dissolved nitrogen (TDN). Rather than speculate about this as they do near the bottom of page 9, have they any samples remaining to test for elevated NO3- stemming from either ammonia oxidation or bacterial sources? Any

measurements of N2O? A: Unfortunately, we do not have spare samples left. We will omit the speculative discussion from the chapter 4.1 of the revised manuscript: "For instance, NO3 that is present at high concentrations in intracellular vacuoles of Marthioploca (Dale et al., 2016) could be leaked to the pore water during sediment handling and centrifugation. An ammonium oxidizing bacteria were shown previously to be able profiting from nitrous oxide, produced by denitrification (e.g. Kartal et al., 2013). Thus, the production of NH+4, as a result of DNRA occurring at the inner shelf stations in combination to nitrous oxide production via denitrification occurring at outer shelf, may produce a convenient niche for anammox bacteria at the rim of the inner shelf at 12oS. The intermediate product of anammox, hydrazine (e.g. Kartal et al., 2013), may, in turn, accumulate in the inner space of anammox bacteria, and be released in the pore water samples as a consequence of the cell rapture induced by centrifugation. However, the concentrations of those intermediate products are likely very small and may not explain elevated TDN values."

R2: Were the samples completely processed under N2 to prevent oxidation artifacts? A: That is correct, the sediment cores were processed under N2 atmosphere up to the point of filtering the centrifuged samples and then adding acid to the DOC samples. The sealing with fire was not possible inside the glove bag. CDOM and FDOM samples were filled under air, however, we would not expect immediate changes in optical properties. Furthermore, CDOM and FDOM samples are stored in tightly sealed vials although not under anoxic atmosphere, as this makes the transport to home laboratory very challenging. We will add following to the chapter 2.2: "Retrieved sediments were immediately transferred to the onboard cool room (10-15 C$^{\circ}$) and processed under anoxic conditions within few hours using an argon-filled glove bag."

R2: Can they report both TDN and inorganic N determinations (at least as supplemental material) so a reader can evaluate these together? A: Unfortunately, we were restricted by the data legacy and could not report on DIN from benthic chambers and pore waters, but could only use the data for our calculations of DON. The data on DIN

from the benthic chambers will be published soon in a different manuscript by MSc David Clements and co-authors. However, MSc Clements has agreed to provide us the data for DIN for publishing from one of the stations. Therefore, data for DIN components from one benthic chamber at station 3 will be added to a Supplement as a Figure S6. Due to reviewers' suggestions, measurements of ammonia may now be published for all six stations and will be added to a Supplement as a depth profile plot (Figure S5).

R2: The presentation of flux determination approaches comes across as though the authors do not trust either the diffusive gradient approach or the results from in situ chambers (see for example the last two sentences on page 3). If it was my data set, I'd have greater confidence in the chamber-based fluxes, and I would view the fluxes calculated from the concentration difference across the sediment-water interface as "potential diffusive fluxes" that could result if there is no DOM source or sink at the sediment-water interface. A: We understand the reviewer's concern. The text:" The release of dissolved substances from anoxic sediments is regulated mainly by diffusion through the sedimentâĂŤwater interface (e.g. Lavery et al., 2001, and references therein). Diffusion–driven solute fluxes (hereon "diffusive fluxes") are commonly evaluated from pore-waters gradient using Fick's First Law. Diffusive DOM fluxes have been found to be consistent with total DOM flux in non-bioturbated anoxic sediments (Burdige et al., 1992), such as those found off Peru (Dale et al., 2015; Sommer et al., 2016). In some sediments, however, the diffusive flux may overestimate the total flux (Burdige et al., 1992; Lavery et al., 2001). This may be attributed to bioturbation, "unfavourable" redox conditions (Lavery et al., 2001), irreversible adsorption onto particles, and biological DOM consumption at the sedimentâĂŤwater interface or in the bottom waters (Burdige et al., 1992). Furthermore, the assumptions or calculations of certain DOM parameters, such as molecular weight (Balch and Guéguen, 2015) and tortuosity (Ullman and Aller, 1982) may induce potential bias to the flux calculations. In situ measurements of the net solute flux using benthic incubation chambers are independent from molecular weight and tortuosity uncertainties. This approach is laborious

and based on the assumption that solutes, released into the benthic chamber, behave conservatively during the time incubation, and, show linear trends over time. Herewith, the in-situ measurements may be affected by an accidental enclosure of benthic macro-organisms, such as for instance Pleuroncodes mondon, which are abundant in the Peruvian OMZ (Kiko et al., 2015)." -on page 3, lines 20-35 will be rephrased to:

"The release of dissolved substances from anoxic sediments is regulated mainly by diffusion through the sedimentâĂŤwater interface (e.g. Lavery et al., 2001, and references therein). Diffusion–driven DOM fluxes (hereon "diffusive fluxes") and net DOM fluxes (hereon "net fluxes") are commonly evaluated from pore-water gradients using Fick's First Law and by enclosing and incubating a small area of the sediment surface over time, respectively. Diffusive DOM fluxes have been found to be consistent with net DOM flux in non-bioturbated anoxic sediments (Burdige et al., 1992). In some sediments, however, the diffusive flux may overestimate the net flux (Burdige et al., 1992; Lavery et al., 2001). This may be attributed to bioturbation, "unfavourable" redox conditions (Lavery et al., 2001), irreversible adsorption onto particles, and biological DOM consumption at the sedimentâĂŤwater interface or in the bottom waters (Burdige et al., 1992). The determination of in situ net DOM fluxes using benthic incubation chambers are independent of such uncertainties. This approach bases on the assumption that solutes, released into the benthic chamber, behave conservatively during the time incubation, and, show linear trends over time." As it goes through discussion, we suggest that diffusive fluxes are consumed at the surface sediment-bottom water interface in agreement with the reviewer's remarks.

R2: Since most sites had mats of sulfide-oxidizing bacteria at the interface, microbial utilization as presented through Figure 9 seems likely and worthy of emphasis. A: We are not very sure how to understand/ implement this comment to the revised manuscript, as our paper, and Figure 9 in particular, was supposed to reflect that a part of the DOM sediment release, that may be provided through diffusion, is utilized by microbial communities, resulting in the flux, that was obtained in benthic chambers.

R2: Differential diffusion rates and/or utilization rates of DOM pools are indicated by the FDOM components (Figure 8). These results are interesting, and they deserve more positive discussion. A: We appreciate that the Reviewer 2 gives a value to our optical data. The following will be added to the reviewed version of the manuscript at:

Page 10, line 25:

Accordingly, pore water DOM optical properties reflected the "freshest" character of organic matter at St.1 and St.2, whereby S275-295 displayed similar properties to those in the water column (Fig. 3), an enrichment in protein-like DOM fluorescence (Fig. 6) and in DON (Fig. 3). Therefore, in line to the previous findings, our data suggests that the middle shelf stations are supplied with more labile POM compared to the outer shelf stations. This labile POM, likely of proteinaceous origin (e.g. Faganeli and Herndl, 1991), is rapidly reworked, resulting in greater DOM release at the middle shelf stations. However, despite the highest sediment accumulation and POC mineralization rates at St.1 (Dale et al., 2015) and the "freshest" DOM character, the diffusive fluxes of DOC and DON here were not highest on the transect even though pore waters showed elevated DOM levels (Fig. 8). As aCDOM(325) and protein-like FDOM was previously related to the dynamics of labile DOM (Loginova et al., 2016), one may expect those fractions to be rapidly reworked by heterotrophic communities. Therefore, little dynamics of optical properties of proteinaceous character and aCDOM(325) might be a result of not only of the absence of benthic labile DOM fluxes, but also a signature of rapid microbial utilization of labile organic matter freshly released from the sediment (Komada et al., 2016). Thus, the greatest decrease in S275-295 and accumulation of humic-like substances suggest that benthic release of fresh bioavailable DOM should be rapidly and extensively reworked or consumed at the sedimentâĂŤwater column interface during the time of incubations at St.1. In turn, these results support the idea that microbial utilization is controlled by the quality of supplied organic matter (Pantoja et al., 2009; Le Moigne et al., 2017)."

Page 11, line 14:

"In agreement to this S275-295 revealed lowest changes over time, suggesting that DOM at benthic chamber at St.2 remains "fresh" during the time of incubations. Similar to that proteinaceous Comp.3, despite its generally low variability, exhibit highest increase at St.2, suggesting relative accumulation of proteinaceous DOM in the corresponding chamber."

R2: The presentation of DOC and DON distributions and fluxes was uninspired. For some reason the authors simply compare mean $\pm$ sd of measurements, over whole profiles or incubations, across the stations. A: DOC and DON results will be rephrased in the reviewed version of the manuscript Page: 8 Line: 16 into: "Pore-water DOC generally accumulated with depth in the sediment (Fig.2). Highest concentrations of DOC were measured at the middle shelf at station 1 (St.1), ranging from 152 μmol L-1 at 0.5 cm to a maximum of 2.6 x103 μmol L-1 at 22.5 cm of sediment depth. Pore-water DOC concentrations and gradients decreased gradually towards station 4 (St.4), where DOC concentrations ranged from 122 μmol L-1 at 0.5 cm to 544 μmol L-1 at 22.5 cm of sediment depth. Further offshore, pore water DOC concentrations and gradients increased at station 5 (St.5) and station 6 (St.6), ranging from 177 μmol L-1 at 0.5 cm to 823 μmol L-1 at 22.5 cm and from 210 μmol L-1 at 1.5 cm to 702 μmol L-1 at 19.5 cm, respectively. Porewater DON was largely influenced by vicinity to the coast (Fig. S7). Highest concentrations of DON were measured at the middle shelf St.1 and St.2. The DON concentrations in pore waters at these stations were ranging from b.d.l. at 0.5 cm to a maximum of 2.6 x103 μmol L-1 at 22.5 cm and from 580 μmol L-1 at 0.5 cm to 1.1 x103 μmol L-1 at 19.5 cm of sediment depth, respectively. Similarly to DOC, the pore water DON concentrations decreased towards St.4, where they ranged from b.d.l. at surface sediment to 85 μmol L-1 at 3.5 cm sediment depth and then resumed the gradient offshore at St.5 (64âĂŤ450 μmol L-1) and St.6 (b.d.l.âĂŤ248 μmol L-1)."

R2: With all the available dissolved and solid phase biogeochemical data from these sites, they should look for relationships tied to organic matter degradation processes. For example, what do DIC or sulfate versus DOC, or ammonia versus DON property-

property plots look like? There is much more that can be done to interpret these findings. A: We very much understand the wish of the Reviewer R2 for a more extended data analysis to better constrain the link between the degradation of organic matter in the sediment and resulting DOC fluxes. However, as mentioned previously the fluxes of DIC and ammonium measured during the same cruises (M136/M137) are essential part of an ongoing PhD thesis and are not yet published. Hence, please understand that we are hesitating in providing these data in this manuscript which might endanger the originality of the PhD Thesis. We explored possible links between organic carbon degradation and DOC/DON fluxes using data from a previous cruise, but became aware that the different bottom water concentrations during these different cruises might introduce more uncertainties into the data interpretation. We consider the present manuscript as one of the first studies addressing DOC and DON fluxes measured in situ using benthic landers. A more deeply rooted synthesis paper will become possible when data from all cruises made in the SFB754 becomes available.

R2: The final speculative link to denitrification rates is completely unsupported. A: In the final paragraph of the discussion, we proposed to link estimated rates of DOC supply to that of denitrification processes. Denitrification processes are not uncommon in regions where O2 concentration is low (Lam and Kuypers, 2011). Evidences from various fieldwork suggest that at least part of the denitrification occurring at depths may be driven by the supply of OM (Liu and Kaplan 1983, Kalvelage et al., 2013). Some of these work proposed that the biological carbon pump (POC downward export) as one potential supply pathways of OM sustaining deep water denitrification (Kalvelage et al., 2013). Other suggested that DOM supply could also stimulate denitrification in anoxic waters (e.g. Chang et al., 2014, Bonaglia et al., 2016). Given the importance of denitrification and N loss for OMZ regions, it is crucial to constrain potential sources of OM potentially sustaining such rates. We show that the supply of OM from sediment release (and subsequent remineralisation) can be large. Such releases can be transported, remineralised Prokopenko et al. (2011) and potentially used by denitrifiers in the water column. It is therefore not irrelevant to provide numbers on the amount of N loss driven

by DOC sediment release may these be upper bound estimates. We simply aimed here to confront potential DOC-sediment releases derived denitrification rates to that of BCP derived rates (provided in (Kalvelage et al., 2013)). In essence, we supported our estimation by stoichiometrically converting sediment DOC release respiration rates into denitrification rates using stoichiometry previously reported by Prokopenko et al. (2011). Our estimations are within the range what is usually observed and estimated for similar regions. This further supports our approach. We state our statement by providing upper and lower range DOC-sediment releases derived denitrification rates based on the upper and lower measurement of DOC-sediment releases turnover rates (See Figure 8). Our DOC-sediment releases derived denitrification rates range now from 0.2 to 1.4 mmol $m^{-2}d^{-1}$. This in turn could explain between 5 and 45 % of denitrification rates measured in the water column in the eastern tropical South Pacific (âĹij3mmol $m^{-2}d^{-1}$; Kalvelage et al., 2013). This suggests that on occasion, sediment release of DOC may potentially serve as an important organic matter source for the water column N–loss as originally stated. We have modified the text in the revised version of the manuscript to better explain the relevance as well as the uncertainties associated to our approach (providing lower and upper bound on proportion of denitrification potentially explained by DOC sediment releases). We hope that this will satisfy the reviewer.

The text: “We suggest that the difference between the diffusive flux and netin situflux could reflect the rate of microbial DOC uti-15lization in the chamber water and/or surface sediment layer at each station. Thus, the rate of the microbial utilization at St.3–St.6 ranged from 0.2 to 1.7mmol $m^{-2}d^{-1}$(Fig. 8). These consumption rates could support a denitrification rate of 0.2–1.4mmol $m^{-2}d^{-1}$, based on reaction stoichiometry reported by Prokopenko et al. (2011). These are comparable to denitrification (0.6 ± 0.4mmol $m^{-2}d^{-1}$) and the total N2efflux (âĹij1.2mmol $m^{-2}d^{-1}$) in anoxic sediments in the eastern tropical NorthPacific off California (Prokopenko et al., 2011), to denitrification rates (0.2–2mmol $m^{-2}d^{-1}$) in the eastern tropical North At-20lantic off Mauritania (Dale et al., 2014) and to modelled denitrification rates (0.5–1.1mmol

m−2d−1) and N2fluxes (0.8–4.6mmol m−2d−1), observed along 12oS transect (Dale et al., 2016; Sommer et al., 2016). Furthermore, the estimated potentialdenitrification rates may be able to explain up toâĹij55%of denitrification rates in the water column in the eastern tropicalSouth Pacific (âĹij3mmol m−2d−1Kalvelage et al., 2013), suggesting that sediment release of DOM may potentially serve asan important organic matter source for the water column N–loss."

will be changed to: "... Therefore, DOM released to the bottom waters may be not limited only to the sedimentâĂŤwater column interface, affecting whole water column biogeochemistry. We suggest that the difference between the diffusive flux and net in situ flux could reflect the rate of microbial DOC utilization in the chamber water and/or surface sediment layer at each station. Thus, we estimate rates of microbial utilization at St.3–St.6 ranging from 0.2 to 1.7mmol m−2d−1(Fig. 8). We here propose to link these to that of denitrification processes. Evidences from fieldwork suggest that at least part of the denitrification occurring at depth may be driven by the supply of POM via the biological carbon pump (Kalvelage et al., 2013). Other suggested that DOM supply could also stimulate denitrification in oxygen deficient zones (e.g. Chang et al., 2014, Bonaglia et al., 2016). Given the importance of denitrification and N-loss rates for OMZ regions, it is crucial to evaluate various possible sources of OM potentially sustaining such rates. Conversion of the remineralisation rates of outfluxed DOM, found in our study (Fig. 8), into denitrification rates using stoichiometry previously reported by Prokopenko et al. (2011), we estimate associated denitrification rates ranging from 0.2 to 1.4 mmol m−2d−1. These are comparable to denitrification rates (0.6±0.4 mmol m−2d−1) and the total N2 efflux (âĹij1.2 mmol m−2d−1) reported in anoxic sediments in the eastern tropical North Pacific off California (Prokopenko et al., 2011), to denitrification rates (0.2–2mmol m−2d−1) in the eastern tropical North Atlantic off Mauritania (Dale et al., 2014) and to modelled denitrification rates (0.5–1.1 mmol m−2d−1) and N2 fluxes (0.8–4.6 mmol m−2d−1), observed along 12°S transect (Dale et al., 2016; Sommer et al., 2016). Our estimates could, in turn, explain between 5 and 45 % of denitrification rates measured in the water column in the eastern tropical South Pacific

(âĹij3 mmol m−2d−1; Kalvelage et al., 2013). We suggest that sediment release of DOC is not the dominant source of OM to the OMZ, but on occasions, this process may potentially serve as an important source of organic matter source for the water column N–loss."

R2: Sentences with particularly awkward construction or in need of minor edits are found at: R2: Page2 lines 12-15: Awkward A: "Extensive fieldwork campaigns conducted on anoxic Peruvian sediments suggested further show that they act as "factories" for an intensive organic matter remineralization (Dale et al., 2015). Yet, the burial efficiency of particulate organic carbon (POC) varies throughout OMZ (Dale et al., 2015). For instance, burial efficiency are low at anoxic inner shelf stations despite highest carbon mineralization rates estimated from in situ dissolved inorganic carbon (DIC) fluxes (Dale et al., 2015)."

will be changed to: "Similar to the water column studies, extensive fieldwork campaigns conducted on sediments off Peru also suggested intensive particulate organic matter (POM) remineralization under full anoxia (Dale et al., 2015).

While POM degradation in sediments is mostly associated with its full remineralization to dissolved inorganic carbon (DIC) and inorganic nutrients, the mechanism of POM remineralisation implies important intermediate stages of dissolved organic matter (DOM) production, reworking and mineralization processes (Smith et al., 1992; Komada et al., 2013). Thus, around 10 % of remineralized particulate organic carbon (POC) may accumulate as dissolved organic carbon (DOC) in the pore waters (Alperin et al., 1999). In turn, DOM efflux may represent an important escape mechanism for carbon from sediments (e.g. Ludwig et al., 1996; Burdige et al., 1999) and a source of organic matter to the water column (e.g. Burdige et al., 2016). Despite the acknowledged importance of sediment DOM for organic matter cycling, the measurements of benthic DOM fluxes remain scarce and the reactivity of the pore-water DOM is not well constrained."

R2: Page2 lines 34: Awkward A: “CDOM absorbance spectra represent an exponential curve with no discernible peaks” will be changed to: “Typical CDOM absorbance spectrum is shaped as an exponential curve”

R2: Page3 lines 18: explain “insolation shield” A: “insolation shield” will be changed to “reduce penetration of hazardous or bioavailable light”

R2: Page3 lines 22: change to “from pore water gradients using” A: will be changed

R2: Page3 lines 27: Your point is unclear here. The uncertainty is in the sediment diffusion coefficient and whether DOM pools with different molecular weights are subject to different diffusion rates. A: Following will be removed from revised version: “Furthermore, the assumptions or calculations of certain DOM parameters, such as molecular weight (Balch and Guéguen, 2015) and tortuosity (Ullman and Aller, 1982) may induce potential bias to the flux calculations.”

R2: Page4 lines 13-14: unclear A: As the reviewer suggested more informative description of the study area, the brief description of the study area: “A detailed description of the sediment at 12oS is reported in Dale et al. (2015, 2016). In brief, sediments at the sampling stations are fine-grained muds with porosity ranging between 0.8 and 0.95 (Dale et al., 2015; Sommer et al., 2016)” will be omitted from the edited manuscript.

R2: Page9 lines 3-5: Awkward construction A: “The data suggests that the inner shelf stations receive of the most labile POM, likely of proteinaceous origin (e.g. Faganeli and Herndl, 1991) compared to the outer shelf stations, which is likely being rapidly reworked into DOM at the inner shelf compared to the other sites.” Will be changed to: “Our data suggests that the inner shelf stations receive of the most labile POM compared to the outer shelf stations. This labile POM, likely of proteinaceous origin (e.g. Faganeli and Herndl, 1991), is rapidly reworked, resulting in greater DOM release in the inner shelf stations.

R2: Page9 lines 35: Awkward A: “An ammonium oxidizing bacteria were shown pre-

viously to be able profiting from nitrous oxide, produced by denitrification (e.g. Kartal et al., 2013).” Will be changed to: “As ammonium oxidizing bacteria profit from nitrous oxide, produced by denitrification (e.g. Kartal et al., 2013).”

R2: Page 10 line 9. Change to “imbalance in production and consumption”. A: will be changed to “imbalance in production and consumption”

R2: Page 10 line 15. Change to “agrees well with previous observations”. A: will be changed to “agrees well with previous observations”

R2: Page 10 line 24. Omit “to” before geopolymerization. A: “to” will be deleted

R2: Page 12 line 18. Spelling “spatial”. A: will be corrected

R2: Figure 7 caption, you use “stars” not pentagons. A: “pentagons” will be changed to “pentagrams” in the plots’ descriptions.

R2: Table 1. Units for dissolved oxygen are missing “micro” μ A: μ will be added.

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