

1 **Water column biogeochemistry of oxygen minimum zones in the eastern**  
2 **tropical North Atlantic and eastern tropical South Pacific oceans**

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1 **Abstract**

2 Recent modeling results suggest that oceanic oxygen levels will decrease significantly over  
3 the next decades to centuries in response to climate change and altered ocean circulation.  
4 Hence the future ocean may experience major shifts in nutrient cycling triggered by the  
5 expansion and intensification of tropical oxygen minimum zones (OMZs), which are  
6 connected to the most productive upwelling systems in the ocean. There are numerous  
7 feedbacks among oxygen concentrations, nutrient cycling and biological productivity;  
8 however, existing knowledge is insufficient to understand physical, chemical and biological  
9 interactions in order to adequately assess past and potential future changes.

10 In the following, one decade of research performed in the framework of the collaborative  
11 research center SFB 754 focusing on Climate- Biogeochemistry interactions in tropical OMZs  
12 is summarized. The influence of low environmental oxygen conditions on biogeochemical  
13 cycles organic matter formation and remineralization, greenhouse gas production and the  
14 ecology in OMZ regions of the eastern tropical South Pacific compared to the weaker OMZ of  
15 the eastern tropical North Atlantic were investigated. The impact of sulfidic events on water  
16 column biogeochemistry, as well as their specific microbial community capable of highly  
17 efficient carbon fixation, nitrogen turnover and N<sub>2</sub>O production is discussed. Based on our  
18 findings, a coupling of primary production and organic matter export via the nitrogen cycle is  
19 proposed, which may, however, be impacted by several additional factors, e.g. micronutrients,  
20 particles acting as microniches, vertical and horizontal transport of organic material and the  
21 role of zooplankton and viruses therein.

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# 1 Introduction

2 Eastern boundary upwelling systems are ocean areas where cold and nutrient-rich waters are  
3 upwelled to the sea surface, where they fuel high biomass production (Carr, 2002; Chavez and  
4 Messie, 2009). While covering only 0.2% of the ocean, those upwelling areas account for  
5 about 50-58% of global fish catch (Pauly and Christensen, 1995). Two eastern boundary  
6 upwelling systems were subject to this study: the upwelling off Mauritania, located in the  
7 eastern tropical North Atlantic (ETNA) and the upwelling system off Peru located in the  
8 eastern tropical South Pacific (ETSP). While both systems are characterized by intense  
9 primary production, their biogeochemical properties differ strongly (Karstensen et al., 2008),  
10 which partially results from a combination of different water mass ages and characteristics  
11 (Körtzinger et al., 2004), topography and atmospheric impacts (e.g. Duce et al., 2008). A  
12 major difference between the ETNA and the ETSP is the intensity of the oxygen minimum  
13 zone (OMZ) associated with those upwelling regions (Capone and Hutchins, 2013): The  
14 ETNA OMZ has O<sub>2</sub> concentrations typically above 40 μmol kg<sup>-1</sup>, whereas the large and  
15 persistent OMZ in the ETSP located off Peru and Chile has O<sub>2</sub> concentrations below the  
16 detection limit based on conventional methods (~2 μmol kg<sup>-1</sup>, Figure 1) with sometimes even  
17 sulfidic conditions on the shallower shelf (Schunck et al., 2013).

18 Besides the age of the water mass and other physical constraints, biological remineralization  
19 and respiration processes consume O<sub>2</sub> below the highly productive surface waters and  
20 contribute therefore to the development and maintenance of OMZ waters (Walsh, 1981,  
21 Quinones et al., 2010). The intensity of the OMZ may therefore be determined by a positive  
22 feedback, with increased primary production leading to enhanced organic matter export back  
23 to underlying O<sub>2</sub>-depleted waters (Dale et al. 2015). As a consequence of enhanced organic  
24 matter export, respiration processes may increase. Stronger anoxia on the other hand would  
25 promote O<sub>2</sub> sensitive N loss processes, therefore creating an nitrogen (N) deficit in upwelled  
26 waters. This would then stimulate N<sub>2</sub> fixation at the sea surface and enhance again primary  
27 production. In how far a feedback between primary production, organic matter  
28 remineralization and the N cycle is a valid model in OMZ waters and what role sulphidic  
29 conditions play in there is critical to understand.

30 Modeling results (Bopp et al., 2013; Cocco et al., 2013), predict that O<sub>2</sub> levels will decrease  
31 significantly over the next decades in response to climate change and eutrophication. Hence,  
32 the future ocean may experience major shifts in nutrient cycling triggered by the possible  
33 expansion and intensification of tropical OMZs (Codispoti, 2010). Currently, the estimated  
34 volume of OMZs with O<sub>2</sub> concentrations <20 μmol kg<sup>-1</sup> is about 1% of the global ocean

1 volume (Lam and Kuypers, 2011). Approximately 0.05% of the global ocean volume has O<sub>2</sub>  
2 levels below 5 μmol kg<sup>-1</sup>. The effects of O<sub>2</sub>-sensitive nutrient cycling processes occurring in  
3 these relatively small regions (Codispoti, 2010) are conveyed to the rest of the ocean (see e.g.  
4 Deutsch et al. 2007). Hence comparatively "small" volumes of OMZs can significantly impact  
5 nutrient budgets, biological productivity and the overall potential for CO<sub>2</sub> fixation of the  
6 ocean. An important factor is further that deoxygenation of OMZs has been proposed to  
7 increase the production of the greenhouse gas nitrous oxide (N<sub>2</sub>O) (Codispoti, 2010).  
8 Therefore, understanding the present biogeochemistry of those systems and exploring the  
9 potential to respond to climate change is critical.

10 The following review of the major biogeochemical processes in OMZ waters is based on  
11 studies of the Collaborative Research Centre 754 (SFB754) "Climate-Biogeochemistry  
12 Interactions in the Tropical Ocean" ([www.sfb754.de](http://www.sfb754.de)). The comparison between the ETNA  
13 and ETSP upwelling systems, their OMZs and differences in remineralization processes and  
14 associated marine sources and sinks of important nutrient elements are discussed in order to  
15 understand potential controls on the intensity of those OMZs, as well as their future  
16 development.

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## 18 2 Primary production in the ETSP and ETNA

19 In eastern boundary upwelling systems, phytoplankton blooms are stimulated by nutrient  
20 supply from upwelled waters and provide the basis for vibrant ecological systems. Both, the  
21 ETNA and the ETSP, are major sites of primary production (Longhurst, 1995); with the  
22 ETNA exceeding primary production of the ETSP by a factor of ~2 depending on the applied  
23 method (see Table 1 for an overview of major primary production-related parameters). This  
24 difference may be explained, e.g. by the stoichiometry of the macronutrients N and phosphate  
25 (P), with the deficit of N based on a Redfieldian equilibrium of N:P = 16:1 being significantly  
26 stronger in the ETSP compared to the ETNA (Deutsch et al., 2007). This difference may be  
27 due to intensified N loss mirrored by a strongly positive *d*<sup>15</sup>N-nitrate signal (Ryabenko et al.,  
28 2012) in the more O<sub>2</sub> depleted water column and sediments of the ETSP. On the other hand,  
29 enhanced P release from the sediments at decreasing O<sub>2</sub> (Ingall and Jahnke, 1994), or a  
30 difference between N and P remineralization from organic material (Jilbert et al., 2011) may  
31 impact decreased N:P ratios. A stronger N deficit in the water column may influence primary  
32 production in different ways: It may either stimulate N<sub>2</sub> fixation in order to replenish the N

1 deficit, or it may stimulate non-Redfield primary production. A major aspect to detangle these  
2 potential responses is therefore to understand the community composition.

3 Franz et al. (2012a) reported in situ observations along an east-west transect in the ETSP at  
4 10°S stretching from the upwelling region above the narrow continental shelf to the well-  
5 stratified oceanic section of the eastern boundary regime. The study showed that new  
6 production in the coastal upwelling was driven by large-sized phytoplankton (e.g. diatoms)  
7 with generally low N:P ratios (<16:1), thus speaking for non-Redfield surface water primary  
8 production. A deep chlorophyll *a* maximum consisting of nano- (*Synechococcus*, flagellates)  
9 and microphytoplankton occurred within a pronounced thermocline in subsurface waters  
10 above the shelf break. Here, intermediate particulate N:P ratios were close to Redfield  
11 proportions. High PON:POP (>20:1) ratios were observed in a stratified open ocean section,  
12 coinciding with a high abundance of the pico-cyanobacterium *Prochlorococcus*. Excess P was  
13 present along the entire transect but did not appear to stimulate growth of N<sub>2</sub> fixing  
14 cyanobacteria, as pigment fingerprinting and phylogenetic studies did not indicate the  
15 presence of diazotrophic cyanobacteria at most of our sampling stations (Franz et al., 2012a;  
16 Löscher et al., 2014). These findings are mostly in accordance with other studies from this  
17 area (Bonnet et al., 2013; Fernandez et al., 2011; Turk-Kubo et al., 2014). Therefore, the  
18 excess P generated within the OMZ seemed to be rather consumed by non-Redfield processes,  
19 i.e. primary production by large phytoplankton found in shelf surface waters, instead of  
20 stimulating surface N<sub>2</sub> fixation. A possible explanation can be deduced from the optimality-  
21 based model of N<sub>2</sub> fixation by Pahlow et al. (2013). The model is based on the assumption that  
22 natural selection should tend to produce organisms optimally adapted to their environment.  
23 The competitive advantage of diazotrophs is most pronounced under conditions of low  
24 dissolved inorganic N and increased dissolved inorganic P (DIN, DIP) availability (Houlton et  
25 al., 2008). The ability to compete for DIP is therefore less important at high DIP. Thus, high P  
26 concentrations above the ETSP OMZ might actually reduce the selective advantage of  
27 diazotrophs compared to non-Redfield primary producers. This could partially explain why  
28 cyanobacterial N<sub>2</sub> fixers were apparently not stimulated by excess phosphate in surface waters  
29 of the abovementioned transect.

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31 2.1 The impact of changing N:P ratios as a result of ocean deoxygenation: a  
32 mesocosm approach

1 A series of on board mesocosm experiments and bioassay incubations were performed in  
2 order to identify nutrient limitations in both areas and to specifically address the impact of  
3 stoichiometry on primary production. Despite the fundamental differences between the  
4 ETNA and ETSP with regard to the N deficit, the results of short-term mesocosm experiments  
5 implied N limitation of surface plankton communities in both areas (Franz et al., 2012a; Franz  
6 et al., 2012b). Further, the partitioning and elemental composition of dissolved and particulate  
7 organic matter was investigated. Maximum accumulation of POC and PON was observed  
8 under high N supply, indicating that primary production was controlled by N availability. Part  
9 of the excess P was consumed by non-Redfield production, predominantly by diatoms, as also  
10 observed from direct monitoring as described above. While particulate N:P of the  
11 accumulated biomass generally exceeded the supply ratio (Franz et al., 2012b), excess P of  
12 the dissolved nutrient pool was channeled into release of dissolved organic phosphorus (DOP)  
13 by phytoplankton. These results demonstrated that excess P upwelled into the surface ocean  
14 overlying O<sub>2</sub>-deficient waters represents a net source for DOP and motivated further  
15 dedicated mesocosm experiments in the ETNA to elucidate the fate of DOP. While the direct  
16 monitoring and the results of mesocosm studies were strongly speaking for a shift to non-  
17 Redfield primary production due to changes in N:P, a general stimulating effect of DOP on N<sub>2</sub>  
18 fixation has been observed (Meyer et al., 2015). This is in line with a recent modeling study  
19 based on large-scale surface data sets of global DON and Atlantic ocean DOP. Here, the  
20 model suggests an important role of DOP for stimulating growth of N<sub>2</sub> fixing organisms  
21 (Somes and Oschlies, 2015). This model indicates that the marine N- budget is sensitive to  
22 DOP, provided that access to the relatively labile DOP pool expands the ecological niche for  
23 diazotrophs. Taken together, changes in N:P may lead to a combination of both, non-Redfield  
24 primary production and enhanced N<sub>2</sub> fixation via DOP.

25 Besides a direct effects of N:P ratios, primary production and N<sub>2</sub> fixation, due to the  
26 comparably high Fe requirements of the diazotrophs (Gruber, 1997) is largely influenced by  
27 trace metal availability (Mills et al., 2004). Comparing the ETNA and ETSP regions, an  
28 obvious difference with regard to potentially limiting nutrients is related to the iron (Fe)  
29 source: In the ETNA, Saharan dust input contributes 71-87% of dissolved Fe to the water  
30 (Conway, 2014). Several studies highlighted the importance of atmospheric Fe supply to the  
31 ETNA (Voss et al., 2002; Mills et al., 2004) as a major factor of primary production. A  
32 comparable atmospheric Fe source is however missing in the ETSP (Baker et al., 2016).  
33 Previous studies (Scholz et al., 2014) identified the ETSP Fe supply as benthic, however, the

1 question on how much Fe is transported from the sediments to the sea surface is so far not  
2 fully clarified.

3 Results of bioassay incubations and correlation studies demonstrated that primary production  
4 and N<sub>2</sub> fixation in this region respond significantly to Fe additions (Dekaezemaker et al.,  
5 2013). N<sub>2</sub> fixation could further be directly limited by inorganic nutrient availability, or  
6 indirectly through the stimulation of primary production and the subsequent excretion of  
7 dissolved organic matter and/or the formation of micro-environments favorable for  
8 heterotrophic N<sub>2</sub> fixation (Dekaezemaker et al., 2013).

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## 10 2.2 What is the role of N<sub>2</sub> fixation for primary production in the ETNA and ETSP?

11 Several studies (Voss et al., 2002; Mills et al., 2004; Langlois et al., 2005 & 2007)  
12 demonstrated the important role of N<sub>2</sub> fixation for surface primary production in ETNA  
13 waters. Voss et al. (2002) estimated an average N<sub>2</sub> fixation of 24-140 μmol m<sup>-2</sup> d<sup>-1</sup> translating  
14 into a contribution of 0.1-0.7% to primary production assuming Redfield stoichiometry on the  
15 basis of the rates given in Table 1. This is below the global average of 5.3% (Duce et al.,  
16 2008), potentially due to the relatively high deposition of reactive N via Saharan dust input.

17 For the ETSP, N<sub>2</sub> fixation was higher compared to the ETNA with rates of 25-657 μmol m<sup>-2</sup>  
18 d<sup>-1</sup> (Dekaezemaker et al., 2013; Löscher et al., 2014); while C fixation was rather lower  
19 (Table 1). Here, theoretically, N<sub>2</sub> fixation contributes 0.2-7.1% C fixation (Table 1). However,  
20 while N loss does not play a role in the ETNA water column (see, e.g., Bange et al. (2010))  
21 with the exception of O<sub>2</sub> depleted mesoscale eddies (Löscher et al., 2015), high N loss  
22 removes between one and three orders of magnitude more N (Kalvelage et al., 2013; Table 1)  
23 than is made available by N<sub>2</sub> fixation. This would decrease the contribution of N<sub>2</sub> fixation to  
24 C fixation to zero. When comparing N<sub>2</sub> fixation to N loss, it must be considered that first N  
25 loss has only been detected on and close to the shelf, while N<sub>2</sub> fixation rates were detectable  
26 throughout the OMZ water column (Fig. 2). Second, while N<sub>2</sub> fixation is measured via direct  
27 N<sub>2</sub> incorporation and therefore mirroring *in situ* rates, N loss is likely being overestimated as  
28 measured following addition of the substrates, which may artificially stimulate the respective  
29 process (up to 2-3 orders of magnitude, as discussed in Kalvelage et al., 2013). An entirely  
30 correct budget of N<sub>2</sub> fixation vs. N loss based on rate measurements is therefore difficult to  
31 obtain.

1 In both areas, N<sub>2</sub> fixation may however be considered important for the productivity of the  
2 respective system. Still, given the previously described observations of non-Redfield primary  
3 production, the contribution to C fixation remains to be fully established.

4 From the comparison of the N<sub>2</sub> fixation in the ETNA and ETSP, the question raises why there  
5 is such a strong difference between those systems. A possible explanation may be found in the  
6 character of the diazotrophic communities: While the classical view of oceanic N<sub>2</sub> fixation  
7 mainly attributed to phototrophic cyanobacteria, such as *Trichodesmium* or *Crocospaera*,  
8 (Capone et al., 1997; Zehr and Turner, 2001) may be mostly true for the ETNA (e.g. Langlois  
9 et al., 2005, 2007; Großkopf et al., 2012), a different community of diazotrophs is present in  
10 the ETSP.

11 A growing number of different *nifH* sequences (the key functional gene of N<sub>2</sub> fixation,  
12 encoding the  $\alpha$  subunit of nitrogenase) detected within the Peruvian OMZ (Bonnet et al.,  
13 2013; Dekaezemacker et al., 2013; Fernandez et al., 2011; Löscher et al., 2014; Turk-Kubo et  
14 al., 2014), did not belong to common oxygenic phototrophs, but to some unknown  
15 diazotrophic microorganisms that might be specifically adapted to O<sub>2</sub> deficient conditions.

16 These diazotrophs, as well as the extension of their habitat to deeper waters might be one  
17 reason for the possible underestimation of N gain compared to N loss in the ocean (Codispoti,  
18 2007). In combination with a novel method for N<sub>2</sub> fixation rate measurements (Mohr et al.,  
19 2010) (Großkopf et al., 2012) revealed up to 6-fold higher N<sub>2</sub> fixation rates when considering  
20 N<sub>2</sub> fixation below the euphotic zone. When extrapolated to all ocean basins this resulted in a  
21 N<sub>2</sub> fixation rate of  $177 \pm 8 \text{ Tg N yr}^{-1}$ , which—depending on the assumed budget may balance  
22 50-100% of oceanic N loss (Codispoti, 2007; Gruber and Sarmiento, 1997).

23

### 24 2.3 In how far is N<sub>2</sub> fixation in the ETSP OMZ coupled to N loss?

25 Model studies (Deutsch et al., 2007) assume that a N-deficit resulting from N loss or  
26 enhanced P release (Ingall and Jahnke, 1994) provides a niche for diazotrophs. A coupling of  
27 N loss in OMZs and N<sub>2</sub> fixation in overlying surface waters might therefore restore the N:P  
28 ratio towards Redfield proportions.

29 In the ETSP OMZ, N is indeed continuously removed by the anaerobic oxidation of  
30 ammonium (anammox) (Francis et al., 2007; Kuypers et al., 2005; Kuypers et al., 2003;  
31 Thamdrup and Dalsgaard, 2002), which has been shown to be the dominating N loss process  
32 in this region (Kalvelage et al., 2013, Lam et al., 2009), as well as in other OMZ waters (off  
33 Namibia (Kuypers et al., 2005), Peru (Hamersley et al., 2007) and Chile (Thamdrup et al.,  
34 2006)). Moreover, N is (i) lost by denitrification (the 4-step reduction of NO<sub>3</sub><sup>-</sup> to N<sub>2</sub> (Devol,



1 2008)), e.g. in the Arabian Sea OMZ (Ward et al., 2009), where denitrification has been  
2 identified the dominant N loss process. However, off Peru, denitrification was only detectable  
3 in connection to sulfidic events (Kalvelage et al., 2013, Schunck et al., 2013).

4 The prevalence of novel *nifH* genes and active N<sub>2</sub> fixation, derived from samples collected  
5 directly in the OMZ waters off Peru, where anammox bacteria were abundant and active  
6 (Kalvelage et al., 2013; Löscher et al., 2014), supports the view of a positive feedback  
7 between N loss and N gain communities (Figure 3). Evidence for co-occurrence of  
8 denitrification and N<sub>2</sub> fixation has previously been documented only for an anoxic lake (Halm  
9 et al., 2009), and for cyanobacterial aggregates in the Baltic Sea (Klawonn et al., 2015).  
10 Recent investigations from Baltic Sea sediments on N<sub>2</sub> fixation and diazotrophic abundance in  
11 sediments show, however, that a very close spatial link between N loss and N<sub>2</sub> fixation might  
12 exist (Bertics et al., 2013). Still, too little is currently known about the interactions among the  
13 stoichiometry of inorganic nutrient supply, primary production, N<sub>2</sub> fixation, and  
14 remineralization under anoxic conditions, to allow a definite characterization of the conditions  
15 leading to fixed-nitrogen exhaustion in the OMZs.

16 This coupling which seems to exist in OMZ waters may in fact have far reaching  
17 consequences: While N loss may provide a niche for N<sub>2</sub> fixation, model studies, suggest that  
18 denitrification of N<sub>2</sub> fixation-derived organic matter may lead to a net N loss that further  
19 stimulates N<sub>2</sub> fixation, because 120 moles of nitrate per mole of phosphorus are used to  
20 remineralize Redfield organic matter via denitrification (Landolfi et al., 2013). In contrast, N<sub>2</sub>  
21 fixation fixes only 16 moles N (per mole P). Because of those stoichiometric constraints, any  
22 addition of fixed N to the surface ocean only exacerbates the problem (Canfield, 2006) unless  
23 the corresponding primary production is prevented from being remineralized in the underlying  
24 OMZ (Landolfi et al., 2013). Lipschultz et al. (1990) indeed stated that N loss in the ETSP  
25 OMZ is high enough to respire all produced organic material. Only by spatial or temporal  
26 decoupling of N<sub>2</sub> Fe limitation or dissolved organic matter cycling, the N inventory may  
27 stabilize, otherwise the OMZ would become completely void of fixed inorganic N. Whether  
28 these stoichiometric constraints are valid for anammox as dominant N loss process instead of  
29 denitrification is however not clear.

30 Concerning the stoichiometric aspects of ultimate N loss from OMZ waters, a to date largely  
31 disregarded aspect should be taken into consideration: As shown for the Gotland basin (Jilbert  
32 et al., 2011) enhanced preferential P release from organic matter remineralization was  
33 quantitatively important for creating a N deficit. This preferential P release was present in the

1 water column and was further increased under O<sub>2</sub> depleted, reduced conditions. Although the  
2 quantitative contribution to the N deficit in the ETSP is not entirely clear, yet, it may act as a  
3 factor decoupling the ‘vicious’ cycle between N<sub>2</sub> fixation and N loss (Landolfi et al., 2013), as  
4 shifting the abovementioned stoichiometric constraints.

#### 5 2.4 Factors determining N loss

6 The net rate of N loss in OMZs is determined by the balance of remineralization of sinking  
7 particulate organic carbon (POC) and O<sub>2</sub> supply to the OMZ. Interestingly, recent studies  
8 attributed the dominance of either anammox or denitrification in a certain environment to  
9 organic matter composition and availability (Babbin et al., 2014). While the supply of O<sub>2</sub> is  
10 mostly determined by physical transport, the rate of N loss depends on the activity of the  
11 bacteria responsible for denitrification and anammox as well as the POC export and sinking  
12 velocity.

13 The intensity of this feedback may be overestimated in current biogeochemical models, owing  
14 to spurious nutrient trapping (Dietze and Loeptien, 2013). The extent of the coupling between  
15 primary production at the surface and denitrification in the OMZ, and hence the strength of  
16 the positive feedback, is a strong function of the elemental (C:N:P) stoichiometry of the  
17 exported primary production. Phytoplankton C:N:P stoichiometry in turn is influenced by the  
18 stoichiometry of inorganic nutrients (Franz et al., 2012a; Franz et al., 2012b). Recently  
19 developed process models of primary production and N<sub>2</sub> fixation (Pahlow et al., 2013; Pahlow  
20 and Oschlies, 2013) specifically address the response of phytoplankton elemental  
21 stoichiometry to ambient nutrient concentrations and light.

22 It is generally assumed that both zooplankton and heterotrophic bacteria vary much less in  
23 their elemental stoichiometry than phytoplankton (e.g., Touratier et al. (2001)). In both cases,  
24 the heterotrophs appear to respond to variable nitrogen content in their food by regulating  
25 their gross growth efficiency for carbon (Anderson and Williams, 1998; Kiørboe, 1989). In  
26 OMZ regions, this implies that strong nutrient limitation in the surface ocean, which is  
27 associated with high C:N ratios in primary producers (e.g., data used in Pahlow et al. (2013)),  
28 should intensify denitrification in the OMZ relative to the export flux from the surface. Higher  
29 surface nutrient concentrations would then be expected to reduce C:N ratios in the export flux  
30 and hence have a somewhat mitigating effect. Since denitrification and anammox in the OMZ  
31 cause lower nitrate concentrations in upwelled waters, the variable stoichiometry of  
32 phytoplankton could add to the positive feedback between denitrification and N<sub>2</sub> fixation by  
33 increasing C:N ratios in response to decreasing surface nitrate concentrations.

1 Combined  $^{15}\text{N}$ -incubation experiments and functional gene expression analyses indicate that  
2 anammox in the Peruvian OMZ benefits from other N-cycling processes for reactive  
3 substrates (Kalvelage et al., 2011). Excretion of ammonium and other reduced N-compounds  
4 by diel vertical migrators was also proposed (Bianchi et al., 2014), but recent experiments  
5 indicate that ammonium excretion of diel vertical migrators is strongly reduced at anoxia  
6 (Kiko et al. 2015 a, Kiko et al. 2015 b). Additionally, anammox activity has been described to  
7 depend on export of organic matter (Kalvelage et al., 2013), potentially resulting from the  
8 availability of ammonium recycled from particulate organic N (Ganesh et al., 2015). In the  
9 absence of significant denitrification, these results indicate that anammox relies on  $\text{NH}_4^+$   
10 oxidation and  $\text{NO}_3^-$  reduction as  $\text{NO}_2^-$  source. Further,  $\text{NH}_4^+$  may be derived from  
11 remineralization of organic matter via  $\text{NO}_3^-$  reduction with a possibly important role of  
12 microaerobic respiration (Kalvelage et al., 2015). The overlap between aerobic and anaerobic  
13 N-cycling processes in particular in the coastal shelf waters and the upper part of the OMZ is  
14 supportive of microaerobic activity in the OMZ. As DNRA was insignificant in the water  
15 column during our studies in the ETSP, sedimentary fluxes could be an important ammonium  
16 source, particularly for the inner shelf sediments (Bohlen et al., 2011; Kalvelage et al., 2013).  
17 However, it has been suggested that sulfate reduction is more widespread in OMZ waters than  
18 previously believed and could be responsible for substantial  $\text{NH}_4^+$  production (Canfield et al.,  
19 2010) and sulfate reducers have been detected in the Peruvian OMZ (Schunck et al., 2013).  
20 Direct evidence for the actual link between sulfate reduction and  $\text{NH}_4^+$  production is,  
21 however, still missing.

22

### 23 3 Organic matter export and remineralization in the ETSP OMZ

#### 24 3.1 Sinking of particles

25 Knowledge about particle fluxes in areas of tropical OMZs is scarce and predominantly  
26 derived from deep moored traps (Honjo et al., 2008) or models (Dale et al., 2015, Table 1).  
27 Only few studies have addressed upper ocean export fluxes and mesopelagic flux attenuation  
28 in tropical OMZs (Martin et al. (1987), Devol and Hartnett (2001) and VanMooy et al. (2002)  
29 for the Eastern Tropical Pacific by means of surface tethered sediment traps, Buesseler et al.  
30 (1998) for the Arabian Sea by means of  $^{234}\text{Th}$ , and Iversen et al. (2010) at the northern edge of  
31 the ETNA OMZ by means of particle camera profiling). In the eastern tropical north Pacific  
32 (ETNP; Martin et al. (1987); Van Mooy et al. (2002); Devol and Hartnett (2001)), as well as  
33 in the ETSP (Martin et al. 1987; Dale et al., 2015) mesopelagic POC fluxes were less

1 attenuated with depth (Martin curve exponent 'b' of 0.32-0.81) compared with the widely  
2 used "open ocean composite" of  $b=0.86$  (Martin et al., 1987). Those studies indicate that a  
3 greater proportion of the sinking OM escapes degradation while sinking through the eastern  
4 tropical Pacific OMZ. On the other hand, it has been shown that microbial degradation of  
5 organic N and proteins under suboxia is not strongly affected (Pantoja et al., 2009; Pantoja et  
6 al., 2004; Van Mooy et al., 2002). In addition, organic matter degradation seems not to be  
7 significantly affected by decreased  $O_2$  (Dale et al., 2015).

8 Still, little is known about the microbial controls on the decomposition of organic matter  
9 under lower  $O_2$  concentrations. Microorganisms are generally considered responsible for most  
10 of the remineralization in the ocean. This view is probably justified with respect to carbon,  
11 given the high rates of microbial respiration (del Giorgio and Cole, 1998). Owing to the  
12 relatively low N and phosphorous (P) content of dissolved organic matter, however, bacteria  
13 may be less important for the remineralization of N and P and in fact often compete with  
14 phytoplankton for inorganic nutrients in the surface ocean (Anderson and Williams, 1998;  
15 Pahlow and Vézina, 2003). Remineralization of N and P may thus be largely due to  
16 zooplankton activity (Caron et al., 1988; Garber, 1984; Pahlow et al., 2008).

17 Classically, the most abundant organisms detected in OMZs belong to the Proteobacteria,  
18 Bacteroidetes, Thaumarchaeota of the marine group A, Actinobacteria and Planctomycetes  
19 (Schunck et al., 2013; Wright et al., 2012). Several candidate clusters have previously been  
20 identified among which are the SAR11, SAR324 and SUP05 clusters (Schunck et al., 2013;  
21 Wright et al., 2012). Most investigations of the microbial phylogenetic and functional  
22 diversity resort to observing and correlating changes in oxygen concentrations to changes in  
23 the microbial phylogenetic diversity. Indeed, several studies, including our own datasets  
24 corroborate this idea: A combined statistical analysis of our metagenomic data of the ETSP  
25 OMZ (Kalvelage et al., 2015) and datasets from the Chilean OMZ (Canfield et al., 2010;  
26 Stewart et al., 2011) has resulted in a partitioning of the OMZ in 5 different habitats, namely  
27 surface, subsurface (defined as below the mixed layer and above waters with  $O_2 > 20\mu\text{mol kg}^{-1}$ )  
28  $^1$ ), oxyclines, OMZ core ( $O_2 < 5 \mu\text{mol kg}^{-1}$ ) and sulfidic waters (Figure 4). High-resolution  
29 sampling in the eastern tropical North Pacific OMZ has shown that the microbial richness is  
30 highest at the base of the euphotic zone and the upper oxycline (Beman and Carolan, 2013),  
31 often along with high organic flux, low  $O_2$  concentrations and dynamic cycling of C, N, and  
32 sulfur (S). This may be interpreted in a way that the upper oxycline is of higher importance  
33 for remineralization than the OMZ.

34

### 1 3.2 The impact of zooplankton for organic matter export and remineralization

2 An important consideration for explaining the lowered flux attenuation in the OMZ could be  
3 deducted from the diminished abundance of metazoans in the core of the OMZ. If particles  
4 are not repackaged, fed upon, or destroyed, they might sink at greater speeds through the  
5 OMZ, which would result in decreased degradation.

6 Zooplankton and nekton organisms are essential components of the biological pump as they  
7 egest packaged organic matter as rapidly sinking fecal pellets. Many zooplankton and nekton  
8 species also feed in surface waters during the night and migrate to midwater depth at daybreak  
9 to avoid predation (Lampert, 1989), and to conserve energy (McLaren, 1963). This behavior  
10 is known as diel vertical migration (DVM) and also contributes to the activity of the  
11 biological pump as it enhances the export of organic matter from the photic zone by continued  
12 respiration, excretion and egestion in mid-water layers (Burd et al., 2010; Hannides et al.,  
13 2009; Robinson et al., 2010; Steinberg et al., 2000). In addition to changes in temperature  
14 with depth, DVM organisms experience low O<sub>2</sub> concentrations during the daytime in OMZ  
15 regions (Brewer and Peltzer, 2009; Paulmier et al., 2011), and O<sub>2</sub> concentrations below a  
16 certain threshold level can restrict DVM of most zooplankton and nekton (e.g. Hauss et al  
17 Biogeosciences Discussions). On a regional scale, the upper boundary of the oxycline is the  
18 single most critical factor structuring the habitat of most zooplankton organisms in the  
19 Peruvian upwelling system (Escribano et al., 2009). Nevertheless, some specifically adapted  
20 species are able to downregulate their metabolic activity at low oxygen levels and can remain  
21 at OMZ depth (non-migrators) or actively migrate into suboxic or anoxic OMZs (Seibel 2011,  
22 Kiko et al. 2015 a, b).

23 Abundance and biomass of metazoans living permanently at extremely low oxygen  
24 concentrations is rather low (Auel and Verheye, 2007; Escribano et al., 2009; Fernández-  
25 Álamo and Färber-Lorda, 2006; Saltzmann and Wishner, 1997; Wishner et al., 1998) although  
26 animals have evolved physiological (such as metabolic suppression) and/or morphological  
27 adaptations (such as increased gill surface area) allowing them to cope temporarily or  
28 permanently with O<sub>2</sub> depleted conditions (e.g. copepods, e.g. *Eucalanus inermis*, (Flint et al.,  
29 1991), euphausiids, e.g. *Euphausia mucronata* (Antezana, 2009), decapods (Pearcy et al.,  
30 1977), cephalopods, e.g. *Dosidicus gigas* (Rosa and Seibel, 2010), and teleosts (Friedman et  
31 al., 2012; Luo et al., 2000)). According to Seibel (2011), adaptations to low oxygen levels are  
32 needed below approximately 40 μmol O<sub>2</sub> kg<sup>-1</sup>. Strong physiological adaptations seem thus  
33 necessary to thrive in the ETSP OMZ, but not in the ETNA OMZ where O<sub>2</sub> concentrations are  
34 normally greater than 40 μmol kg<sup>-1</sup> (Teuber et al., 2013).

1 Estimates of zooplankton and nekton mediated carbon fluxes in OMZ regions are rare. For the  
2 northern Chilean upwelling in the ETSP, Escribano (2009) found that migrations of only two  
3 key species (*Eucalanus inermis* and *Euphausia mucronata*) contribute approximately 7.2 g C  
4 m<sup>-2</sup> d<sup>-1</sup> to the OMZ through respiration, mortality, and production of fecal pellets within the  
5 OMZ. However, these estimates are probably too high, as the reduction of respiration at low  
6 oxygen levels (Kiko et al. 2015, Kiko et al. 2015b) was not accounted for in the calculations.  
7 As stated above, a particular role of DVMs for the N cycle could result from the secretion of  
8 ammonium: Ammonium is an important nutrient in the anammox reaction which represents  
9 nearly 30-50% of N-loss activity in the OMZ (Codispoti et al., 2001; Emery et al., 1955;  
10 Gruber, 2004). Bianchi et al. (2014) suggested that DVMs could supply as much as 30% of  
11 the ammonium for the anammox reaction, assuming no reduction of the rate ammonium  
12 excretion under OMZ conditions. This assumption is unlikely to hold, however, as  
13 ammonium excretion is e.g. reduced four-fold in the squat lobster *Pleuroncodes monodon*  
14 (Kiko et al., 2015a; Kiko et al., 2015b) and six-fold in the euphausiid *Euphausia mucronata*  
15 (Kiko et al., 2015a; Kiko et al., 2015b) upon exposure to anoxia at OMZ temperatures. Thus,  
16 the significance of excretion by zooplankton as a source of ammonium for the anammox  
17 reaction remains to be established.

18

### 19 3.3 The impact of viruses on primary production and organic matter feedbacks

20 A recent model study quantifying the effect of viruses on ecosystem function in the ocean  
21 demonstrated that viruses affect biological productivity and remineralization (Weitz et al.,  
22 2015). In line with field studies (Breitbart, 2012), this model showed enhanced organic matter  
23 cycling, e.g. by cell lysis. Viruses lyse ~10-40% of the present prokaryotes every day (Suttle,  
24 2005), which may- besides generally supplying nutrients to the surrounding waters- impact  
25 stoichiometry on smaller scales. Specifically, (cyano)phages in the ETSP have been shown to  
26 release micronutrients such as Fe into surrounding waters at an estimated flux of 10 pmol L<sup>-1</sup>  
27 d<sup>-1</sup> (Poorvin et al., 2004). Likewise, virus-induced bacterial lysis was calculated to contribute  
28 ~1-6 Gt N a<sup>-1</sup> to bacterial primary production, which would significantly support  
29 phytoplankton production (Shelford et al., 2012). The transfer of nutrients from living  
30 organisms into the dissolved phase is called the 'viral shunt' (Breitbart, 2012). Besides the  
31 'viral shunt', the model showed a reduced transfer of organic material to higher trophic levels,  
32 which was interpreted to stabilize primary production. Quantitatively, net primary production  
33 was found increased by ~11% in the presence of viruses. This strongly speaks for a viral  
34 impact on the efficiency of the biological pump (Azam, 1998). On the other side, viruses were

1 shown to influence particle formation and disaggregation through discharging adhesive cell  
2 components (Peduzzi and Weinbauer, 1993) and cell lysis (Weinbauer et al., 2011),  
3 respectively.

4 In OMZ waters, highly specific viral communities have been discovered which show  
5 unusually low diversity and a low viral-to-microbial ratio (VMR) (Cassmann et al., 2012).  
6 Specific viruses appear to be only present in OMZ waters as exemplarily shown by genomic  
7 studies of uncultivated SUP05 bacteria isolated from the ETSP OMZ (Roux et al., 2014).  
8 Interestingly, various genes involved in the cycling of nitrogen and sulfur have also been  
9 found in viromes of ETSP waters (see Tables S3 and S4 in Cassman et al. (2012), Roux et al.,  
10 2014)).

11 Recent studies analyzing samples from the weaker ETNA OMZ indicated that one of the most  
12 abundant archaeal nitrifiers in the ETNA OMZ (Thaumarchaeota, “*Cand. Nitrosopelagicus*  
13 *brevis*”) contains several viral genes in its genome arguing that this archaeon is infected by an  
14 OMZ-specific hitherto uncharacterized virus (Neulinger and Schmitz, unpublished results),  
15 thus confirming earlier studies from the global ocean dataset (Santoro et al., 2015).  
16 Considering that *Cand. Nitrosopelagicus brevis* is most likely the most important producer of  
17 the greenhouse gas nitrous oxide in the ETNA and ETSP OMZs (Löscher et al., 2012), these  
18 findings add a potential role for greenhouse gas production to the current picture of viruses in  
19 the ocean.

20

### 21 3.4 Physical fluxes of DOM

22 Besides particle fluxes and organic matter export via DVM, DOM transport is due exclusively  
23 to physical horizontal and vertical transport processes, induced by mesoscale (horizontal  
24 scales of 10 – 100 km) and sub-mesoscale (100 m – 10 km) motion and vertical fluxes due to  
25 diapycnal mixing. As an example of lateral eddy transport, elevated DOM concentrations  
26 have been detected (+11  $\mu\text{mol C L}^{-1}$ ) in the Canada Basin within an eddy originating from the  
27 shelf region (Mathis et al., 2007). Lasternas et al. (2013) suggested a mechanism for DOM  
28 accumulation within anticyclonic eddies, where nutrient downwelling causes a progressive  
29 oligotrophication, enhanced cell mortality and lysis, which results in additional DOM release.  
30 Numerical model simulations of the Peruvian upwelling regime show that mesoscale  
31 dynamics increase the downward and offshore export of nutrients and biomass out of the  
32 coastal surface ocean (Lathuiliere et al., 2010). For the understanding of remineralization  
33 processes and feedbacks in upwelling systems, a quantification of the material that is lost to  
34 the open ocean is critical as it may directly impact the system’s productivity. Gruber et al.

1 (2011) found that mesoscale eddy activity in upwelling regimes results in a net reduction of  
2 biological productivity. Additionally, sub-mesoscale upwelling filaments can enhance the off-  
3 shelf flux of labile DOM (Alvarez-Salgado et al., 2001). Vertical velocities are higher at sub-  
4 mesoscale density fronts (Klein and Lapeyre, 2009; Levy et al., 2012; Thomas et al., 2008),  
5 which are prominent features in eastern boundary upwelling systems (Durski and Allen,  
6 2005). These vertical velocities often extend to below the mixed layer (Klein et al., 2008),  
7 where they can drive sizeable vertical fluxes of solutes. Mahadevan (2014) proposes the  
8 subduction of organic matter-rich surface water into the subsurface layers within  
9 submesoscale cold filaments as a new export mechanism, which differs strongly from export  
10 via particle sinking. In filaments the organic matter is subducted together with large amounts  
11 of O<sub>2</sub>, which then can directly be used for decomposition of organic matter. Vertical mixing  
12 of DOM from the euphotic into to the upper mesopelagic zone is another important transport  
13 mechanism in (sub)tropical waters (Hansell, 2002). The Bermuda Atlantic Time-Series Study  
14 provides a well-documented example of this process (Carlson et al., 1994). The efficiency of  
15 the downward DOM transport depends on the concentration gradient of DOM between the  
16 surface layer and the OMZ, and on the activity of the microbial population along this gradient.  
17 Produced by high primary production in upwelling regions, DOM can accumulate in the  
18 euphotic zone with maximum concentrations of 100-300 μmol C L<sup>-1</sup> off Peru (Franz et al.,  
19 2012a; Romankevich and Ljutsarev, 1990). Due to the vicinity of the DOM-rich surface layer  
20 above and the O<sub>2</sub>-depleted waters below the shallow and sharp oxycline of the Peruvian  
21 OMZ, physical vertical transport may bring large amounts of labile organic matter to the  
22 OMZ, where it may be utilized by heterotrophic communities (Hoppe et al., 2000; Hoppe and  
23 Ullrich, 1999; Pantoja et al., 2009). DOM supply via (sub-) mesoscale vertical transport  
24 processes and diapycnal mixing may therefore contribute importantly to sustaining microbial  
25 activity in the Peruvian OMZ and may thus largely impact biogeochemical cycles.

26

#### 27 4 Sulfidic events in the ETSP

28 Oceanic sulfidic events are cases of extreme anoxia following periods of enhanced primary  
29 production and organic matter export. They are understood to mostly originate from sulfide  
30 production in sediments (Figure 5) and have been documented sporadically since the 19<sup>th</sup>  
31 century for the ETSP OMZ (Burt, 1852; Dugdale et al., 1977). To date sulfidic events have  
32 been reported from the eastern tropical South Pacific, the Arabian Sea and the Benguela  
33 upwelling system by only a handful of studies and hence our current understanding of their  
34 regulation, initiation and termination is still limited. Possible analogs for oceanic events are



1 permanently sulfidic areas in enclosed basins of the Baltic Sea (Brettar et al., 2006; Brettar  
2 and Rheinheimer, 1991; Glaubitz et al., 2009), the Black Sea (Glaubitz et al., 2010; Jørgensen  
3 et al., 1991; Sorokin et al., 1995), the Cariaco basin off Venezuela (Hayes et al., 2006; Taylor  
4 et al., 2001; Zhang and Millero, 1993) and Saanich Inlet in Canada (Tebo and Emerson, 1986;  
5 Walsh et al., 2009). Here, sulfide accumulates to milli-molar concentrations under O<sub>2</sub> and  
6 nitrate-free conditions and is released by a diffusive flux into the overlying pelagic water  
7 column where it reaches low micro-molar concentrations (Lavik et al., 2009; Schunck et al.,  
8 2013). These events are then terminated or detoxified in the pelagic water column by a  
9 community of sulfide-oxidizing bacteria. This occurs when sulfide and nitrate are both present  
10 thus stimulating sulfide-oxidizing nitrate-reducing bacteria (soNRB). soNRB re-oxidize  
11 sulfide back to sulfate or elemental sulfur while reducing nitrate to either N<sub>2</sub> via autotrophic  
12 denitrification or NH<sub>4</sub><sup>+</sup> via dissimilatory nitrate reduction to ammonium (Lam and Kuypers,  
13 2011). If nitrate is limiting, sulfur is the more likely end product of sulfide oxidation, which  
14 occurs in the following reaction stoichiometry for the denitrification pathway,  $2\text{NO}_3^- + 5\text{HS}^- +$   
15  $7\text{H}^+ \rightarrow \text{N}_2 + 5\text{S}^0 + 6\text{H}_2\text{O}$ . A steady state is reached when the diffusive fluxes ( $\text{mmol m}^{-2} \text{d}^{-1}$ )  
16 of nitrate and sulfide are in a 1:2.5 ratio. If the sulfide flux exceeds the nitrate flux by more  
17 than a factor of 2.5, then sulfide will diffuse into the oxic layer (Lam and Kuypers, 2011).  
18 Importantly, the activity of soNRB help to detoxify sulfide to sulfur, preventing it from  
19 reaching overlying productive surface waters, hence most sulfidic events likely go unnoticed  
20 (Lavik et al., 2009). However, with the increase in eutrophication and the expansion of OMZs  
21 in both the Atlantic and Pacific (Stramma et al., 2008), sulfidic events are expected to become  
22 more frequent., as already demonstrated for a time series station in the Baltic Sea (Lennartz et  
23 al., 2014).

24 The first quantitative measurements and detailed profiles of a sulfidic event in the Peruvian  
25 upwelling came from Schunck et al. (2013). During RV Meteor cruise M77/3 in January 2009  
26 sulfidic waters covered >5500 km<sup>2</sup> and contained approximately  $2.2 \times 10^4$  tons of sulfide,  
27 making it one of the largest plumes recorded. A total of 9 stations were taken along the  
28 coastal transect from Lima to Pisco which showed a ~80 m thick sulfide-rich layer extending  
29 at times just below the oxycline. At this interface oxygen ( $< 1 \mu\text{mol kg}^{-1}$ ), nitrate ( $< 1 \mu\text{mol kg}^{-1}$ )  
30 and nitrite ( $2 \mu\text{mol kg}^{-1}$ ) profiles overlapped with detectable sulfide concentrations. Stable  
31 isotope rate measurements and targeted gene assays using quantitative PCR indicated that  
32 various oxidants could have been used by the microbial community to oxidize sulfide at the  
33 time of sampling. The most abundant sulfide oxidizers identified from the 16S rRNA  
34 diversity belonged to the phylum proteobacteria within the subphylum gamma-, including the

1 SUP05/ARCTIC96BD-19-clade, *Candidatus Ruthia magnifica*, and *Candidatus*  
2 *Vesicomysocius okutanii*, but also epsilon- such as *Sulfurovum* spp. Metagenomics  
3 confirmed that all were capable of sulfide or sulfur oxidation, either with nitrate and oxygen  
4 (facultative soNRB) or exclusively with oxygen. Indeed, both subphyla appear to be  
5 ubiquitous in other seasonally oxic/anoxic waters and OMZs, (Canfield et al., 2010; Lavik et  
6 al., 2009; Stevens and Ulloa, 2008; Stewart et al., 2011; Stewart et al., 2012; Swan et al.,  
7 2011; Walsh et al., 2009). Both gamma- and epsilon- proteobacteria members are known  
8 chemolithoautotrophs, which assimilate carbon dioxide as the carbon source without the use  
9 of sunlight. Subsurface C- assimilation rates were between 0.9 to 1.4  $\mu\text{mol C L}^{-1} \text{d}^{-1}$  during  
10 this sulfidic event. In this study, “dark” primary production had contributed up to 25% of the  
11 total  $\text{CO}_2$  fixation in the Peruvian upwelling region at the time of sampling, which is  
12 comparable to values observed in the Baltic and Black Seas (Schunck et al. (2013) and  
13 references therein). Paradoxically, some of these studies showed that measured rates of  $\text{CO}_2$   
14 assimilation exceed rates possible by chemolithoautotrophic processes alone. Thus, while  
15 chemolithoautotrophic  $\text{CO}_2$ -fixation is considered a significant process, the specific activity  
16 and main contributors of  $\text{CO}_2$ -fixation during sulfidic events (down to the genus-level) still  
17 remain unknown.

18 Different from our current knowledge of OMZ sulfur cycling is whether the production of  
19 sulfide can originate as well from pelagic waters itself. Simultaneous reduction of different  
20 electron acceptors (like  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_2$ ) can occur in defined niches where particle  
21 aggregates have formed and are sinking through the water column (Wright et al., 2012).  
22 These aggregates, more commonly known as marine snow, contain micro-scale redoxclines  
23 under anoxic conditions (Alldredge and Cohen, 1987; Karl and Tilbrook, 1994; Woebken et  
24 al., 2007). Moreover, aggregate communities appear to be distinct from bulk water collected  
25 samples (Fuchsman et al., 2011). These communities were suggested to have active  
26 manganese reduction, sulfate reduction and sulfide oxidation at the interior of the aggregates.  
27 How much sulfide is generated in the water column during a sulfidic event is not well  
28 resolved. Nevertheless, *in situ* incubation experiments done in the Chilean upwelling have  
29 shown the capacity for sulfate reduction in the offshore OMZ occurring under  
30 thermodynamically unfavorable nitrate-rich conditions. In separate incubations measured  
31 rates of potential sulfide oxidation were larger than rates of sulfate reduction indicating that  
32 any produced sulfide is immediately re-oxidized (Canfield et al., 2010). The authors  
33 intriguingly suggested an active but cryptic sulfur cycle linked to nitrogen cycling in the  
34 pelagic OMZ. From a biogeochemical perspective large-scale sulfate-reduction coupled to

1 organic matter remineralization releasing inorganic nitrogen could represent a significant  
2 supply of ammonium for anammox bacteria.

3

#### 4 5 Trace gas production in OMZ waters

5 The upper 1000 m of the ocean (incl. the euphotic zone) are the key regions where the  
6 production of climate-relevant trace gases such as carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O),  
7 methane (CH<sub>4</sub>) and dimethyl sulfide (DMS) occurs (see, e.g., Liss and Johnson (2014)).  
8 While the pathways of CO<sub>2</sub> and DMS are dominated by phytoplankton in the oxic euphotic  
9 zone, N<sub>2</sub>O and CH<sub>4</sub> pathways are dominated by microbial processes at midwater depth (i.e. in  
10 the OMZ). This is especially important since some OMZs are connected to coastal upwelling  
11 regions where OMZ waters — enriched in both nutrients and trace gases such as CO<sub>2</sub>, N<sub>2</sub>O  
12 and CH<sub>4</sub> — are brought to the surface fuelling phytoplankton blooms and releasing trace gases  
13 to the atmosphere (see, e.g., Capone and Hutchins (2013)). Thus, although they are usually  
14 not in direct contact with the atmosphere, OMZs play an important role for oceanic emissions  
15 of climate-relevant trace gases (see e.g. Arévalo-Martinez et al. (2015)).

16

#### 17 5.1 Nitrous oxide (N<sub>2</sub>O) in OMZ

18 A comprehensive overview of both nitrous oxide (N<sub>2</sub>O) distributions and pathways in OMZ  
19 has been published in (Naqvi et al., 2010). Therefore, we concentrate here on recent findings  
20 from the ETNA and ETSP.

21 N<sub>2</sub>O production in the ocean is dominated by microbial nitrification and denitrification  
22 processes. It is formed as a by-product during nitrification and as an intermediate during  
23 denitrification. The paradigm that N<sub>2</sub>O is exclusively produced by bacteria has been  
24 challenged by the discovery of nitrifying (i.e. NH<sub>4</sub><sup>+</sup> oxidising) archaea (e.g., *Cand.*  
25 *Nitrosopelagicus brevis*, see above) dominating N<sub>2</sub>O production in the ETSP and ETNA  
26 (Löscher et al., 2012), which is supported by results of a culture study (Löscher et al., 2012)  
27 and a marine microbial enrichment experiment (Santoro et al., 2011). The production of N<sub>2</sub>O  
28 by archaea (and bacteria) depends on dissolved O<sub>2</sub> and increases with decreasing O<sub>2</sub>  
29 concentrations (Frame and Casciotti, 2010; Löscher et al., 2012). Denitrifying bacteria do not  
30 produce N<sub>2</sub>O in the presence of O<sub>2</sub> (> 10 μmol kg<sup>-1</sup>); however, when O<sub>2</sub> concentrations are  
31 approaching 0 μmol kg<sup>-1</sup>, N<sub>2</sub>O is consumed during denitrification. There is no N<sub>2</sub>O production  
32 under anoxic conditions. The significance of N<sub>2</sub>O production during anammox (Kartal et al.,  
33 2007) and DNRA (Giblin et al., 2013) in OMZs (see Section 5) remains to be proven.

1 The detailed investigation of  $\Delta\text{N}_2\text{O}/\text{AOU}$  (= excess  $\text{N}_2\text{O}$ /apparent oxygen utilization) and  
2  $\Delta\text{N}_2\text{O}/\Delta^{15}\text{NO}_3^-$  relationships from the ETNA and ETSP revealed two facts (Ryabenko et al.,  
3 2012): (i) The lower  $\text{O}_2$  concentrations found in the core of the OMZ of the ETSP ( $< 5 \mu\text{mol}$   
4  $\text{kg}^{-1}$ ) favour  $\text{N}_2\text{O}$  consumption by denitrification which is not observed in the ETNA because  
5 of its comparably high  $\text{O}_2$  concentrations and (ii) the maximum observed  $\text{N}_2\text{O}$  concentrations  
6 were higher in the ETSP than in the ETNA. This is in line with the results of two model  
7 studies of  $\text{N}_2\text{O}$  in the ETSP by Zamora et al. (2012) and Cornejo and Farias (2012), which  
8 suggested that the switching point between  $\text{N}_2\text{O}$  production and  $\text{N}_2\text{O}$  consumption occurs at  
9 higher  $\text{O}_2$  concentration ( $\sim 8\text{-}10 \mu\text{mol kg}^{-1}$ ) than previously thought.

10 In contrast to the open ocean, OMZs in coastal (i.e. shelf) regions show a higher spatial and  
11 temporal variability: Seasonally occurring suboxic or even anoxic/sulfidic OMZs have been  
12 observed in coastal regions worldwide (see e.g. Diaz and Rosenberg (2008)). One of the most  
13 prominent areas where widespread sulfidic conditions have been recently observed is the shelf  
14 off Peru (Schunck et al., 2013) (Section 5). Figure 6 shows the distribution of  $\text{N}_2\text{O}$ , water  
15 temperature, nutrients and  $\text{H}_2\text{S}$  during the sulfidic event described by Schunck et al. (2013) on  
16 the shelf off Peru during December 2008/January 2009. Here, extreme  $\text{N}_2\text{O}$  concentrations are  
17 found at the boundary to the  $\text{H}_2\text{S}$  containing bottom waters. No  $\text{N}_2\text{O}$  is found in the core  
18 sulfidic layer. This suggests again that there is a narrow range of low  $\text{O}_2$  concentrations which  
19 is associated with exceptionally high  $\text{N}_2\text{O}$  production. As soon as the  $\text{O}_2$  concentrations are  
20 close to zero (anoxic/sulfidic conditions)  $\text{N}_2\text{O}$  production turns into  $\text{N}_2\text{O}$  consumption.  
21 Similar  $\text{N}_2\text{O}$  distributions during anoxic/sulfidic events were found off the west coast of India,  
22 in the Gotland Deep (central Baltic Sea) and in Saanich Inlet (Brettar and Rheinheimer, 1991;  
23 Cohen, 1978; Naqvi et al., 2000). Brettar and Rheinheimer (1991) suggested a close coupling  
24 between  $\text{H}_2\text{S}$  oxidation and  $\text{NO}_3^-$  reduction in a narrow layer where  $\text{NO}_3^-$  and  $\text{H}_2\text{S}$  coexist.  
25 This is in line with recent findings from the anoxic event off Peru by Schunck et al. (2013)  
26 and similar to the suggestion of a cryptic sulfur cycle where sulfate reduction is coupled to  
27 rapid  $\text{H}_2\text{S}$  oxidation by  $\text{NO}_3^-$  proposed for the OMZ off Chile by Canfield et al. (2010).

28

## 29 5.2 The role of OMZs in trace gas emissions

30 In OMZs with  $\text{O}_2$  concentrations below  $20 \mu\text{mol kg}^{-1}$ ,  $\text{N}_2\text{O}$  production does not take place in  
31 the core of the OMZ. Instead,  $\text{N}_2\text{O}$  production is found at the oxycline. Exceptionally high  
32  $\text{N}_2\text{O}$  concentrations have so far only been found in temporarily occurring anoxic/sulfidic  
33 regions off Peru/Chile and West India (Farías et al., 2015; Naqvi et al., 2010). Stagnant

1 sulfidic systems such as in the Baltic and Black Seas as well as the Cariaco Basin, have  
2 shown only slightly enhanced N<sub>2</sub>O concentrations at the oxic/anoxic interfaces (Bange et al.,  
3 2010, and references therein). This implies that significant pulses of N<sub>2</sub>O emissions to the  
4 atmosphere occur only when a shallow coastal system rapidly shifts from oxic to  
5 anoxic/sulfidic conditions and vice versa (Bange et al., 2010). This can be explained by a lag  
6 of N<sub>2</sub>O reduction by denitrifiers, when they switch from oxygen to nitrogen respiration  
7 (Codispoti, 2010) or N<sub>2</sub>O production during the reestablishment of nitrification after O<sub>2</sub>  
8 ventilation (Schweiger et al., 2007).

9 CH<sub>4</sub> production is also tightly connected to OMZs (see overview in Naqvi et al., 2010).  
10 Similar to N<sub>2</sub>O, upwelling areas are considerable hotspots for CH<sub>4</sub> emissions, albeit organic  
11 material-enriched shallow coastal zones such as estuaries and mangroves or shallow  
12 sediments with geological CH<sub>4</sub> sources show higher emissions (Bakker et al., 2014).

13 Since DMS is produced by phytoplankton in the euphotic zone, an accumulation of DMS in  
14 OMZs appears unlikely. However, measurements at the Candolim Time-Series Station  
15 (CaTS) on the shelf off Goa (India) revealed an unprecedented 40-fold increase in DMS  
16 concentrations in the sulfidic layers during an anoxic event (Shenoy et al., 2012). These high  
17 concentrations could not be explained by any known pathways and may imply an unknown —  
18 most likely microbial — DMS production pathway under anoxic conditions either in the water  
19 column or in the underlying sediments (Shenoy et al., 2012). Only recently it has been shown  
20 that phytoplankton communities exposed to anoxic conditions increase their DMS production  
21 significantly (Omori et al., 2015). This implies a potential accumulation of DMS at  
22 oxic/anoxic boundaries of coastal OMZs which, in turn, might result in high DMS emissions  
23 from shallow coastal zones during anoxic/sulfidic events.

### 24 5.3 Trace gas production in OMZ and environmental changes

25 Trace gas production in OMZs is expected to be influenced primarily by deoxygenation  
26 (Naqvi et al., 2010; Stramma et al., 2012). It is also well-known that eutrophication, warming  
27 and supply of limiting nutrients (e.g. iron) will increase subsurface respiration of organic  
28 material, which leads to deoxygenation in open ocean and coastal OMZs (Bijma et al., 2013;  
29 Gruber, 2011). Acidification of the upper ocean may result in a decrease of calcium carbonate  
30 (produced by calcifying organisms), which can act as ballast material for sinking organic  
31 matter. Less ballast means a reduction in the sinking speed of organic particles, which could  
32 increase the residence time of organic material and cause higher respiration rates (Riebesell et  
33 al., 2009). Therefore, on-going environmental changes such as deoxygenation, eutrophication,  
34 warming and acidification have both direct and indirect effects on trace gas production in

1 OMZs. In general, we might expect enhanced production of N<sub>2</sub>O, CH<sub>4</sub> and DMS in OMZs  
2 because of the on-going loss of O<sub>2</sub>.

3 Deoxygenation in open ocean and coastal environments may lead, on the one hand, to  
4 enhanced N<sub>2</sub>O production when approaching the N<sub>2</sub>O production/consumption switching  
5 point (see above), but on the other hand, when O<sub>2</sub> concentrations fall below the switching  
6 point this may lead to a consumption of N<sub>2</sub>O (Zamora et al., 2012). Moreover, we do not  
7 know whether the frequency of coastal anoxic events will continue to increase and how this  
8 may affect the coastal net N<sub>2</sub>O production/consumption. A recent modelling study on the  
9 influence of anthropogenic nitrogen aerosol deposition on N<sub>2</sub>O production revealed that the  
10 effect is small on a global scale but that the OMZ of the Arabian Sea is especially sensitive to  
11 atmospheric nitrogen deposition resulting in an enhanced N<sub>2</sub>O production (Suntharalingam et  
12 al., 2012).

13

## 14 6 Conclusions

15 While there is a growing amount of data on primary production and the pelagic N cycle in and  
16 associated to OMZ waters, quantitative estimates of microbial production and respiration,  
17 particularly at ultra-low O<sub>2</sub> levels, are still not fully explored. This translates into an  
18 uncertainty concerning the origin of the N deficit. While it had been clearly demonstrated that  
19 N loss processes respond sensitively to minimal changes in O<sub>2</sub> (Dalsgaard et al., 2014), a  
20 potential uncertainty may result from additional processes, such as preferential P release  
21 directly in the water column may be important to create the N deficit in the water column. In  
22 this context, the character and size were shown important (DeVries et al., 2014), therefore  
23 linking P release from particles to the character of N loss (Babbin et al., 2014). The character  
24 of the N loss/ N deficit term is, however, highly important, as it determines the extent of N  
25 depletion of the entire OMZ due to the above explained stoichiometric discrepancy between N  
26 loss and N<sub>2</sub> fixation. Interestingly, a strong impact of decadal climate variations on respiration  
27 rates, primary production and the intensity of N loss has been described for the South Pacific  
28 (Deutsch et al., 2011). This may directly link to the character of N loss derived from our and  
29 other measurements and has to be taken into consideration for future studies.

30 A coupling via the proposed primary production chain may indeed act in OMZs associated to  
31 upwelling systems (an overview of major processes in the ETNA and ETSP is depicted in Fig.  
32 7). The important term of organic matter export, either horizontally or vertically needs more  
33 dedicated investigations: To date, a quantification of DOM supply via (sub-) mesoscale

1 vertical transport processes out of the OMZ area and diapycnal mixing sustaining microbial  
2 activity in the Peruvian OMZ is missing. Further, for POM supply to the OMZ, DVM seems  
3 to play a key role, despite some quantitative uncertainties. Although some organisms  
4 performing DVM have certain strategies to cope with anoxic conditions, mostly by down-  
5 regulating the aerobic metabolism, there are limits for zooplankton and nekton. Thus, a  
6 reduction of OM export by DVM may result with a further expansion and deoxygenation of  
7 OMZs. Deutsch et al (2014) describe in this context that a decrease of the habitat caused by  
8 global warming and ocean deoxygenation increases competition among species and may even  
9 result in a loss of metabolic functionality by 20%.

10 A quantification of DOM and POM import and export rates to and from the ETNA is  
11 currently not available, an extensive discussion of POC dynamics from the ETSP OMZs is  
12 provided in this issue (Dale et al., 2015).

13 Information on the character of microbial processes responsible for POM degradation within  
14 the OMZ is however missing. Here, first studies (e.g. Ganesh et al., 2014, 2015) indicate a  
15 key role of particulate organic matter acting as microniches for microbes and thus host for  
16 certain processes such as microaerobic respiration in OMZ waters. By containing strong redox  
17 gradients in relatively narrow vicinity, and by providing nutrients and trace metals, particles  
18 might strongly influence biogeochemical cycles. It is well-known that in the core of OMZs  
19 adjacent to coastal upwelling regions, such as those found off Peru, Mauritania and the  
20 Arabian Sea, a pronounced POM/particle-enriched turbid layer (a so-called intermediate  
21 nepheloid layer) exists (see, e.g., Stramma et al. (2013); Naqvi et al. (1993); Fischer et al.  
22 (2009)).

23 With regard to sulfidic events, which make the lower limit of anoxia, the positive feedback  
24 coupling could be thought to stabilize itself: While a direct toxic effect of H<sub>2</sub>S on primary  
25 production is mostly mitigated by the respective detoxifying community, decoupling of the  
26 supply of benthic nutrients to the sea surface might decrease primary production. This may be  
27 of particular importance in areas, such as the ETSP where the benthic supply of e.g. trace  
28 metals is dominant. Resulting decreased respiration in the OMZ could be thought to  
29 subsequently lead to regeneration to non-sulphidic, less pronounced anoxia, which may  
30 stabilize the OMZ to a certain extent. Whether this hypothesis is valid has, however, to be  
31 resolved.

32 A critical consequence of ocean deoxygenation is visible from the comparison of the ETSP  
33 and ETNA regions: Massive supersaturation of N<sub>2</sub>O, connected to sulfidic plumes, has been

1 detected repeatedly, in the ETSP. OMZs are important sites of enhanced production of climate  
2 relevant trace gases such as N<sub>2</sub>O, CH<sub>4</sub>, and DMS. N<sub>2</sub>O production is significantly enhanced at  
3 oxic/anoxic boundaries of OMZs and we suggest that it mainly results from habitat  
4 compression, where in extreme cases (such as sulfidic events, sharpening gradients)  
5 nitrification and denitrification can occur simultaneously. Maximum N<sub>2</sub>O concentrations and  
6 subsequent emissions to the atmosphere have been observed in dynamic coastal systems that  
7 rapidly shift from oxic to anoxic conditions and vice versa. Although OMZs are usually not in  
8 direct contact with the atmosphere, their vicinity to coastal upwelling systems plays an  
9 important role for oceanic emissions of climate-relevant trace gases such as N<sub>2</sub>O, CH<sub>4</sub>, and  
10 DMS with potential feedbacks on global warming, which then may again impact on ocean  
11 deoxygenation. Our studies from the ETSP (Arevalo-Martinez, 2015, 2016, Kock et al., 2016)  
12 confirm intense production of N<sub>2</sub>O in the coastal upwelling. This is in line with an increase of  
13 N<sub>2</sub>O production from OMZ areas as concluded from forced climate models. However, the  
14 same model describes a global decrease of N<sub>2</sub>O formation by 4-12%, mostly linked to the  
15 western basins of the Pacific and Atlantic oceans (Martinez-Rey et al., 2015).

16 Marine ecosystems and biogeochemical cycles are increasingly impacted by a growing  
17 number of stress factors, some of which act locally, such as eutrophication and pollution,  
18 others globally. Global stressors are associated with anthropogenic carbon dioxide (CO<sub>2</sub>)  
19 emissions and affect the ocean either directly through CO<sub>2</sub>-induced acidification or indirectly  
20 through climate change-induced ocean warming and deoxygenation (Ciais et al., 2013). How  
21 these stressors will impact marine ecosystems and biogeochemistry, individually or in  
22 combination, is still largely unknown.

23 Ocean warming, acidification and deoxygenation occur globally and simultaneously,  
24 although with distinct regional differences. Through increased stratification and decreased  
25 nutrient supply to the surface layer, ocean warming is expected to decrease the biological  
26 production in the already stratified low to mid latitudes.

27 While research on ocean warming is relatively advanced, far less is known about the impacts  
28 of ocean acidification and deoxygenation on marine organisms and ecosystems. Because the  
29 three stressors have mostly been studied in isolation, knowledge on the combined effects of  
30 two or more of them is scarce. In principle, additive, synergistic (more than additive) and  
31 antagonistic (less than additive, i.e. compensatory) interactions of effects are possible, but *a*  
32 *priori* it is impossible to judge what the combined effects will be. One example for a  
33 synergistic effect is that of ocean acidification narrowing the thermal tolerance window of  
34 some organisms, amplifying the impact of warming (Pörtner and Farrell, 2008). However,



1 we consider interactions among stressors in marine communities largely understudied.

## 2 7 Outlook

3 Major issues remaining unresolved, in addition to those highlighted above, concerning (1) a  
4 mechanistic understanding of organic matter degradation and nutrient cycling at low or  
5 variable oxygen concentrations in the water column and the role of DVM for organic matter  
6 supply to the OMZ, (2) the sensitivities of heterotrophic microbes and their sensitivity to low  
7 oxygen conditions, and (3) biogeochemical feedback processes in oxygen minimum zones  
8 and their impacts on local to global scales.

9 Future studies in the framework of the SFB 754 will therefore combine measurements of  
10 particle flux, zooplankton abundance, microbial activities and O<sub>2</sub> concentrations in order to  
11 answer the following key questions:

- 12 I. What is the effect of low oxygen conditions (below 20 μmol kg<sup>-1</sup>) on organic matter  
13 degradation? And what is the partitioning between DOM and POM in OMZ waters?
- 14 II. How do the rates of nutrient cycling and loss in OMZs relate to particles and  
15 associated microniches?
- 16 III. What are the rates of oxygen supply and consumption in the upper OMZ? And what  
17 is regulating respiration rates?
- 18 IV. Do small-scale processes (e.g. viral lysis) affect fluxes on larger scales? And how can  
19 models represent these important processes?

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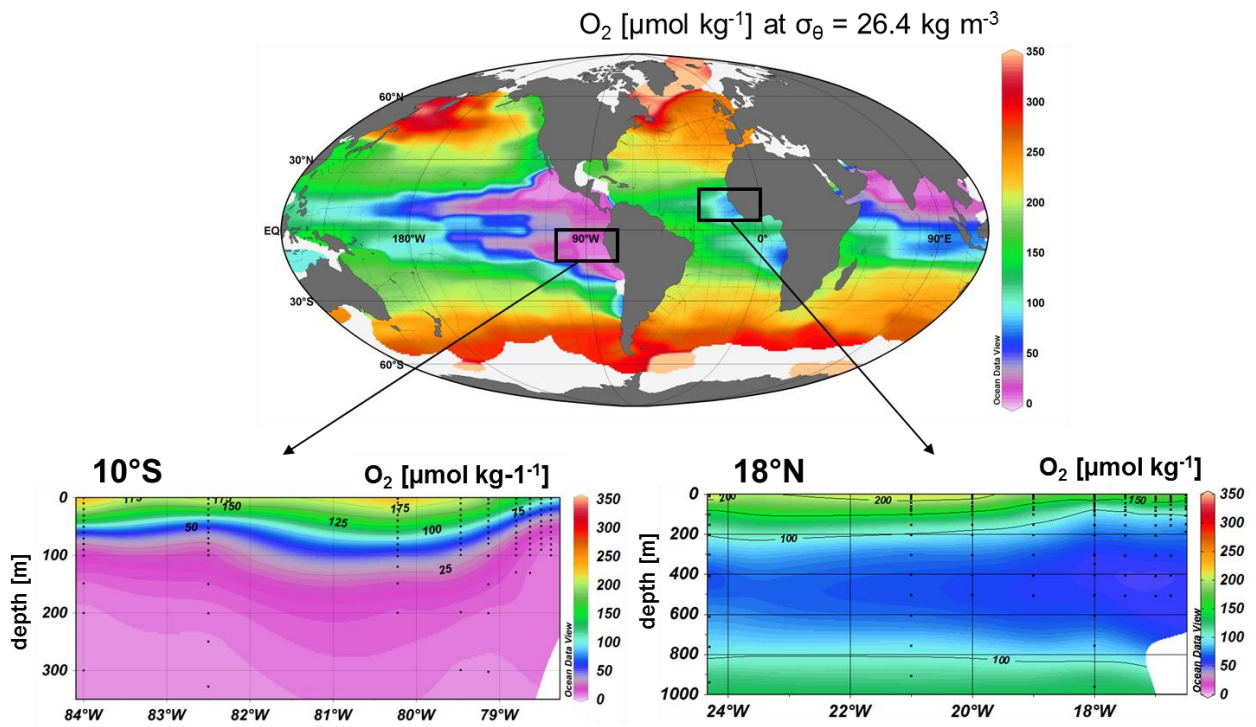
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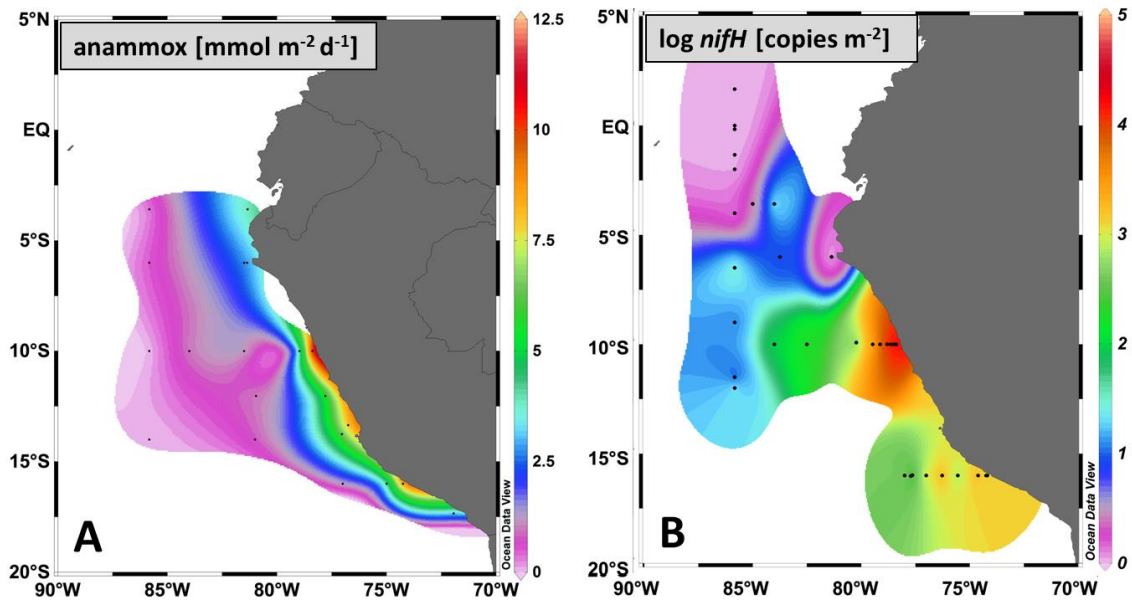
1 **Figures**



2

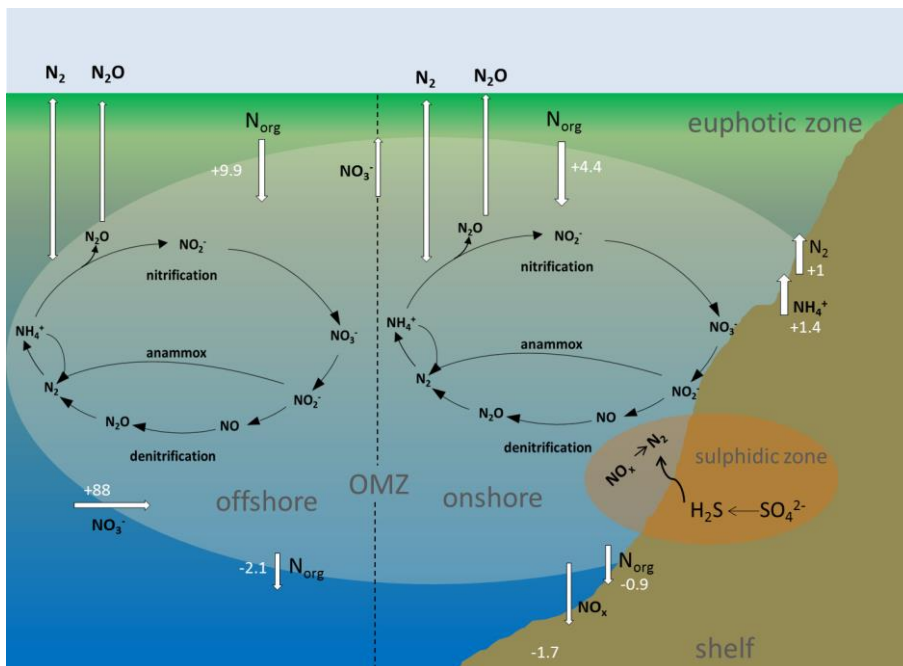
3 Figure 1. Global distribution of  $O_2$  at  $\sigma_{\theta} = 26.4 \text{ kg m}^{-3}$  ( $\sim 400 \text{ m}$  depth): The major regions of  
 4 low oxygen in the world ocean are all located in the tropical oceans, at shallow to  
 5 intermediate depths. The area off Peru represents one of the most pronounced OMZs. The  
 6 investigated areas in the eastern tropical South Pacific and the eastern tropical North Atlantic  
 7 Oceans are marked with black boxes; examples of the  $O_2$  distribution are given along two  
 8 sections from the coast to the open ocean at  $10^\circ\text{S}$  in the OMZ off Peru and at  $18^\circ\text{N}$  in the  
 9 eastern tropical North Atlantic;  $O_2$  concentrations are indicated by the color code.

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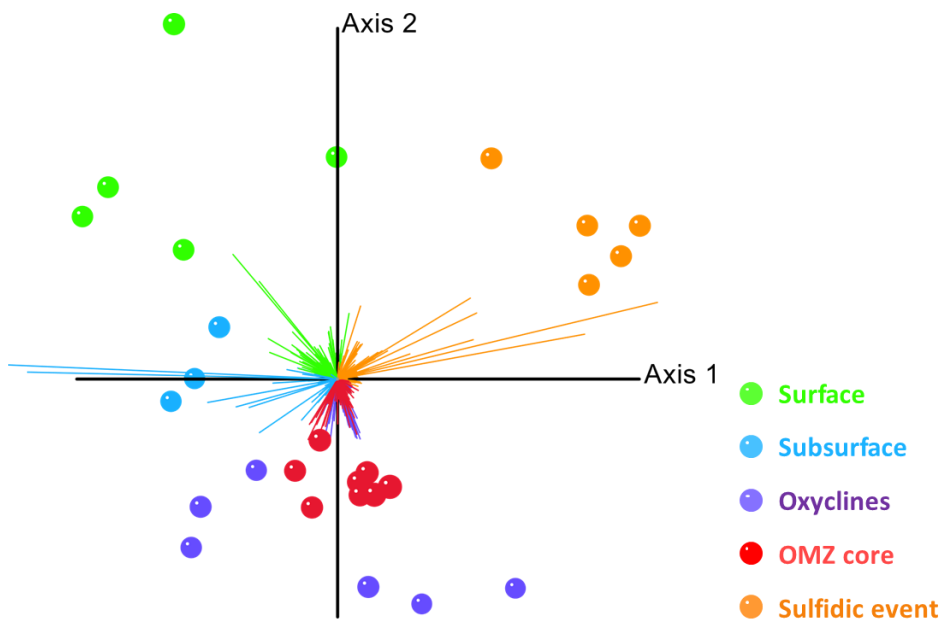
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 2 Figure 2. Co-occurrence of anammox as determined by rate measurements and the key  
 3 functional marker gene for  $\text{N}_2$  fixation, *nifH*, in the ETSP OMZ (modified from Kalvelage et  
 4 al., 2013 and Löscher et al., 2014).

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 8 Figure 3. The marine nitrogen (N) cycle with the major onshore and offshore processes in the  
 9 ETSP OMZ, modified from Kalvelage et al. (2013). Numbers indicate fluxes of N [ $\text{Tg y}^{-1}$ ].

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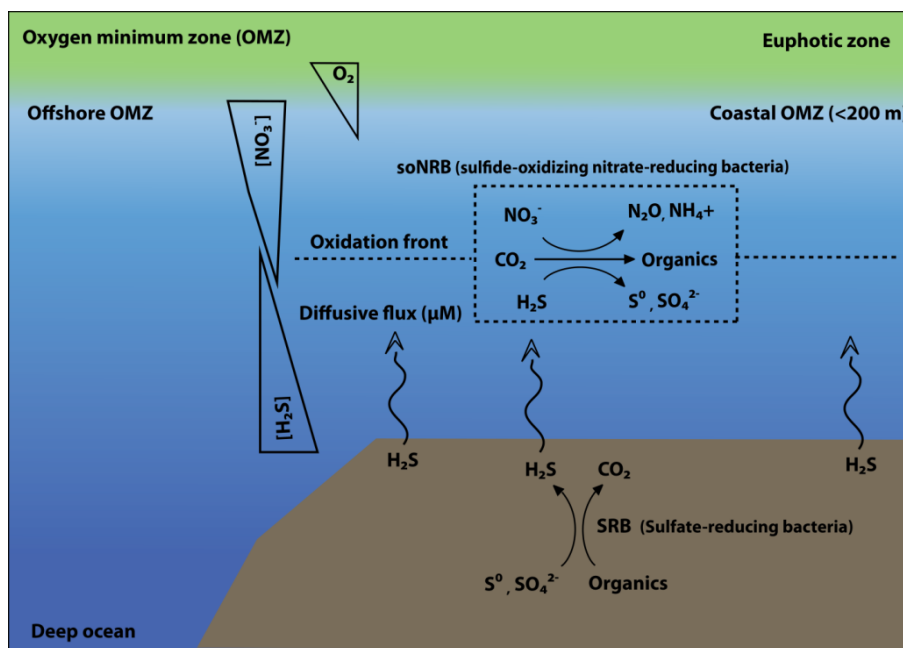


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2 Figure 4. Redundancy analysis ordination model of microbial taxa (vectors) identified from  
 3 pyrosequencing reads of multiple samples (points) in the ETSP. Spherical k-means clustering  
 4 revealed a fivefold partitioning that reflects distinct OMZ habitats (see legend). Each point is  
 5 colored according to the cluster that dominated the microbial population in the respective  
 6 sample.

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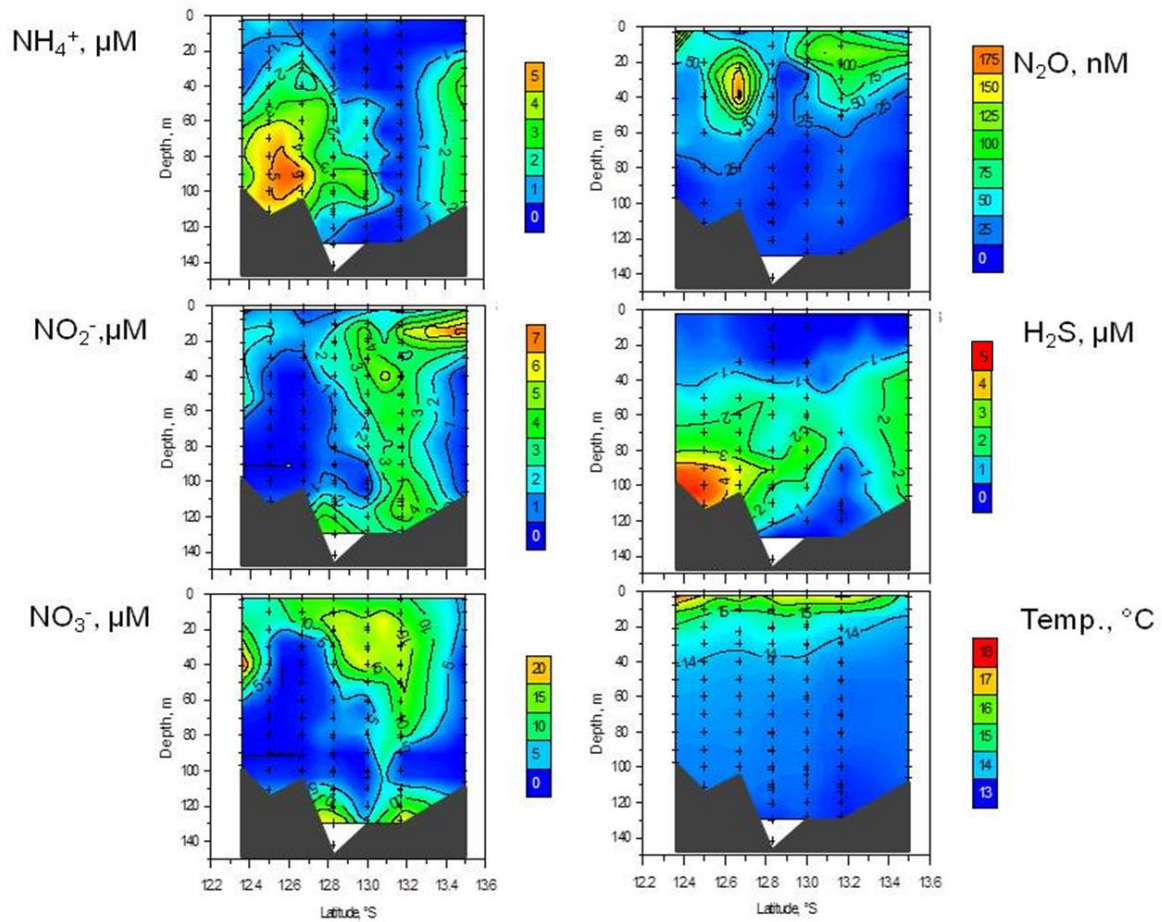
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10 Figure 5. Schematic representation of the dynamics of a sulfidic event occurring in an oxygen  
 11 minimum zone, e.g. in the ETSP. The sulfide and nitrate fluxes are shown in steady state.

- 1 Sulfate-reducing bacteria produce sulfide from the sediment while the complementary
- 2 detoxification process occurs in the water column at overlapping profiles.



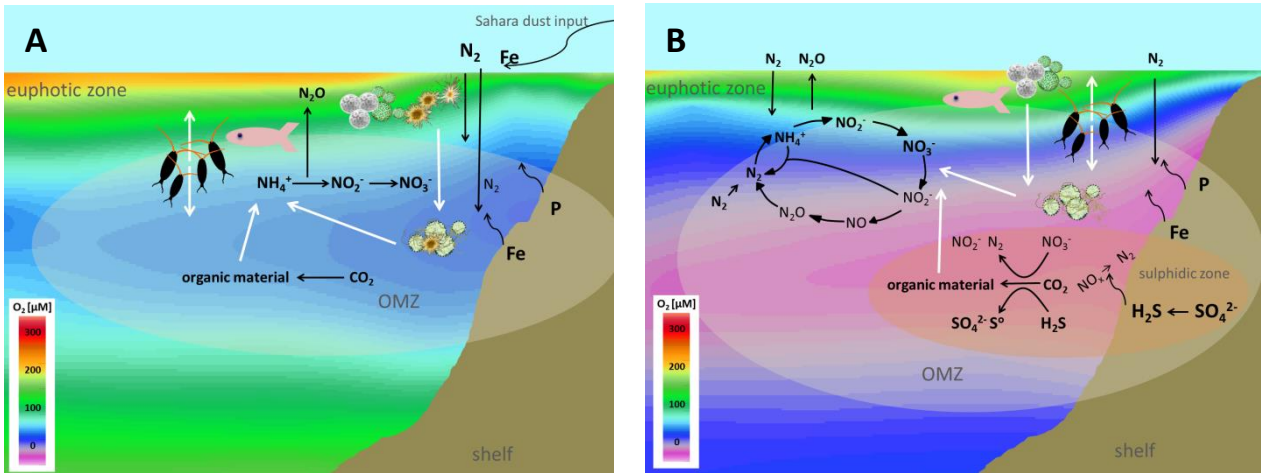
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 4 Figure 6. Distributions of  $N_2O$ ,  $NH_4^+$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $H_2S$ , and water temperature during  
 5 December 2008/January 2009 (R/V Meteor cruise M77/3) on the shelf along the coast of  
 6 Peru. Max.  $N_2O$  concentrations have been detected right above the sulfidic zone, where a  
 7 sharp oxycline is present and ammonium and nitrate are available.

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1 Figure 7. Scheme of the (A) ETNA and (B) ETSP OMZs with major processes identified. The  
 2  $O_2$  background is taken from the SOPRAN cruise P399, along  $18^\circ N$  in the ETNA and from  
 3 the SFB754 cruise M77/3, along  $10^\circ S$  in the ETSP.  
 4  
 5

1 Table 1: A comparison of the O<sub>2</sub> minimum, excess nitrogen (N\*), primary production, organic  
 2 C export, N<sub>2</sub> fixation and N loss in the ETNA and ETSP upwelling regions.

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	ETSP-shelf	ETSP- offshore	ETNA-shelf	ETNA- offshore
<b>O<sub>2</sub> min. [μmol kg<sup>-1</sup>]</b>	0 (sulfidic)	0	25	40
<b>N* [mol m<sup>-2</sup>]</b>	-1,9- (-5,98) <sup>a</sup>			
<b>Primary Production [mmol C m<sup>-2</sup> d<sup>-1</sup>]</b>	101-122 <sup>b</sup> 68,5 <sup>c</sup> 61,4 <sup>d</sup>	73-94 <sup>b</sup>	137 <sup>c</sup> 167 <sup>d</sup>	
<b>Organic C export [mmol C m<sup>-2</sup> d<sup>-1</sup>]</b>	10,6-75,3 <sup>b</sup>	2,6-11,1 <sup>b</sup>	6,4- 9,3 <sup>e</sup>	0,67-2,6 <sup>e</sup>
<b>N<sub>2</sub> fixation [μmol N m<sup>-2</sup> d<sup>-1</sup>]</b>	25-657 <sup>f</sup>		24-140 <sup>g</sup>	
<b>% contribution of N<sub>2</sub> fixation to primary production*</b>	0,2-4 <sup>b</sup> 0,2-6,4 <sup>c</sup> 0,3-7,1 <sup>d</sup>		0,2-0,7 <sup>c</sup> 0,1-0,6 <sup>d</sup>	
<b>N loss [mmol N m<sup>-2</sup> d<sup>-1</sup>]</b>				
<b>anammox</b>	1-10	0	0	
<b>denitrification</b>	up to 70 (in presence of H <sub>2</sub> S)	0	0	

4 \* Calculated based on the Redfield ratio of C:N = 106:16 using the primary production and N<sub>2</sub> fixation rates  
 5 given in this table in consistency with the % contribution given in Duce et al. (2008).

6 <sup>a</sup> Kalvelage et al., 2013, <sup>b</sup> Dale et al., 2015, <sup>c</sup> Behrenfeld and Falkowski, 1997, <sup>d</sup> Longhurst et al., 1995, <sup>e</sup> Iversen  
 7 et al., 2010, <sup>f</sup> Dekaezemacker et al., 2013 and Löscher et al., 2014, <sup>g</sup> Voss et al., 2002.

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