

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 N₂O 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 O₂ concentrations typically above 40 μmol kg⁻¹, whereas the large and
15 persistent OMZ in the ETSP located off Peru and Chile has O₂ concentrations below the
16 detection limit based on conventional methods (~2 μmol kg⁻¹, 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 O₂ below the highly productive surface waters and
20 contribute to the development and maintenance of OMZ waters (Walsh, 1981, Quinones et al.,
21 2010). The intensity of the OMZ may be determined by a positive feedback, with increased
22 primary production leading to enhanced organic matter export back to underlying O₂-depleted
23 waters (Dale et al. 2015). As a consequence of enhanced organic matter export, respiration
24 processes may increase. Anoxia on the other hand would promote O₂ sensitive N loss
25 processes, creating a nitrogen (N) deficit in upwelled waters. This would then stimulate N₂
26 fixation at the sea surface and enhance again primary production. In how far a feedback
27 between primary production, organic matter remineralization and the N cycle is a valid model
28 in OMZ waters and what role sulphidic conditions play in there is critical to understand.

29 Modeling results (Bopp et al., 2013; Cocco et al., 2013), predict that O₂ levels will decrease
30 significantly over the next decades in response to climate change and eutrophication. Hence,
31 the future ocean may experience major shifts in nutrient cycling triggered by the possible
32 expansion and intensification of tropical OMZs (Codispoti, 2010). Currently, the estimated
33 volume of OMZs with O₂ concentrations <20 μmol kg⁻¹ is about 1% of the global ocean
34 volume (Lam and Kuypers, 2011). Approximately 0.05% of the global ocean volume has O₂

1 levels below $5 \mu\text{mol kg}^{-1}$. The effects of O_2 -sensitive nutrient cycling processes occurring in
2 these relatively small regions (Codispoti, 2010) are conveyed to the rest of the ocean (see e.g.
3 Deutsch et al. 2007). Hence comparatively "small" volumes of OMZs can significantly impact
4 nutrient budgets, biological productivity and the overall potential for CO_2 fixation in the
5 ocean. An important factor is further that deoxygenation of OMZs has been proposed to
6 increase the production of the greenhouse gas nitrous oxide (N_2O) (Codispoti, 2010).
7 Therefore, understanding the present biogeochemistry of those systems and exploring the
8 potential to respond to climate change is critical.

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

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17 2 Primary production in the ETSP and ETNA

18 In eastern boundary upwelling systems, phytoplankton blooms are stimulated by nutrient
19 supply from upwelled waters and provide the basis for vibrant ecological systems. Both, the
20 ETNA and the ETSP, are major sites of primary production (Longhurst, 1995); with the
21 ETNA exceeding primary production of the ETSP by a factor of ~ 2 depending on the applied
22 method (see Table 1 for an overview of major primary production-related parameters). This
23 difference may be explained, e.g. by the stoichiometry of the macronutrients N and phosphate
24 (P), with the deficit of N based on a Redfieldian equilibrium of $\text{N:P} = 16:1$ being significantly
25 stronger in the ETSP compared to the ETNA (Deutsch et al., 2007). This difference may be
26 due to intensified N loss mirrored by a strongly positive $d^{15}\text{N}$ -nitrate signal (Ryabenko et al.,
27 2012) in the more O_2 depleted water column and sediments of the ETSP. On the other hand,
28 enhanced P release from the sediments at decreasing O_2 (Ingall and Jahnke, 1994), or a
29 difference between N and P remineralization from organic material (Jilbert et al., 2011) may
30 impact decreased N:P ratios. A stronger N deficit in the water column may influence primary
31 production in different ways: It may either stimulate N_2 fixation in order to replenish the N
32 deficit, or it may stimulate non-Redfield primary production. A way to detangle these
33 potential responses is thus to understand the community composition.

1 Franz et al. (2012a) reported in situ observations along an east-west transect in the ETSP at
2 10°S stretching from the upwelling region above the narrow continental shelf to the well-
3 stratified oceanic section of the eastern boundary regime. The study showed that new
4 production in the coastal upwelling was driven by large-sized phytoplankton (e.g. diatoms)
5 with generally low N:P ratios (<16:1), thus speaking for non-Redfield surface water primary
6 production. A deep chlorophyll *a* maximum consisting of nano- (*Synechococcus*, flagellates)
7 and microphytoplankton occurred within a pronounced thermocline in subsurface waters
8 above the shelf break. Here, intermediate particulate N:P ratios were close to Redfield
9 proportions. High PON:POP (>20:1) ratios were observed in a stratified open ocean section,
10 coinciding with a high abundance of the pico-cyanobacterium *Prochlorococcus*. Excess P was
11 present along the entire transect but did not appear to stimulate growth of N₂ fixing
12 cyanobacteria, as pigment fingerprinting and phylogenetic studies did not indicate the
13 presence of diazotrophic cyanobacteria at most of our sampling stations (Franz et al., 2012a;
14 Löscher et al., 2014). These findings are mostly in accordance with other studies from this
15 area (Bonnet et al., 2013; Fernandez et al., 2011; Turk-Kubo et al., 2014). The excess P
16 generated within the OMZ seemed to be rather consumed by non-Redfield processes, i.e.
17 primary production by large phytoplankton found in shelf surface waters, instead of
18 stimulating surface N₂ fixation. A possible explanation can be deduced from the optimality-
19 based model of N₂ fixation by Pahlow et al. (2013). The model is based on the assumption that
20 natural selection should tend to produce organisms optimally adapted to their environment.
21 The competitive advantage of diazotrophs is most pronounced under conditions of low
22 dissolved inorganic N and increased dissolved inorganic P (DIN, DIP) availability (Houlton et
23 al., 2008). The ability to compete for DIP is therefore less important at high DIP. Thus, high P
24 concentrations above the ETSP OMZ might actually reduce the selective advantage of
25 diazotrophs compared to non-Redfield primary producers. This could partially explain why
26 cyanobacterial N₂ fixers were apparently not stimulated by excess phosphate in surface waters
27 of the abovementioned transect.

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29 2.1 The impact of changing N:P ratios as a result of ocean deoxygenation: a 30 mesocosm approach

31 A series of on board mesocosm experiments and bioassay incubations were performed in
32 order to identify nutrient limitations in both areas and to specifically address the impact of
33 stoichiometry on primary production. Despite the fundamental differences between the

1 ETNA and ETSP with regard to the N deficit, the results of short-term mesocosm experiments
2 implied N limitation of surface plankton communities in both areas (Franz et al., 2012a; Franz
3 et al., 2012b). Further, the partitioning and elemental composition of dissolved and particulate
4 organic matter was investigated. Maximum accumulation of POC and PON was observed
5 under high N supply, indicating that primary production was controlled by N availability. Part
6 of the excess P was consumed by non-Redfield production, predominantly by diatoms, as also
7 observed from direct monitoring as described above. While particulate N:P of the
8 accumulated biomass generally exceeded the supply ratio (Franz et al., 2012b), excess P of
9 the dissolved nutrient pool was channeled into release of dissolved organic phosphorus (DOP)
10 by phytoplankton. These results demonstrated that excess P upwelled into the surface ocean
11 overlying O₂-deficient waters represents a net source for DOP and motivated further
12 dedicated mesocosm experiments in the ETNA to elucidate the fate of DOP. While the direct
13 monitoring and the results of mesocosm studies were strongly speaking for a shift to non-
14 Redfield primary production due to changes in N:P, a general stimulating effect of DOP on N₂
15 fixation has been observed (Meyer et al., 2015). This is in line with a recent modeling study
16 based on large-scale surface data sets of global DON and Atlantic ocean DOP. Here, the
17 model suggests an important role of DOP for stimulating growth of N₂ fixing organisms
18 (Somes and Oschlies, 2015). This model indicates that the marine N- budget is sensitive to
19 DOP, provided that access to the relatively labile DOP pool expands the ecological niche for
20 diazotrophs. Taken together, changes in N:P may lead to a combination of both, non-Redfield
21 primary production and enhanced N₂ fixation via DOP.

22 Besides direct effects of N:P ratios, primary production and N₂ fixation, due to the
23 comparably high Fe requirements of the diazotrophs (Gruber, 1997) is largely influenced by
24 trace metal availability (Mills et al., 2004). Comparing the ETNA and ETSP regions, an
25 obvious difference with regard to potentially limiting nutrients is related to the iron (Fe)
26 source: In the ETNA, Saharan dust input contributes 71-87% of dissolved Fe to the water
27 (Conway, 2014). Several studies highlighted the importance of atmospheric Fe supply to the
28 ETNA (Voss et al., 2002; Mills et al., 2004) as a major factor of primary production. A
29 comparable atmospheric Fe source is however missing in the ETSP (Baker et al., 2016).
30 Previous studies (Scholz et al., 2014) identified the ETSP Fe supply as benthic, however, the
31 question on how much Fe is transported from the sediments to the sea surface is so far not
32 fully clarified.

1 Results of bioassay incubations and correlation studies demonstrated that primary production
2 and N₂ fixation in this region respond significantly to Fe additions (Dekaezemaker et al.,
3 2013). N₂ fixation could be directly limited by inorganic nutrient availability, or indirectly
4 through the stimulation of primary production and the subsequent excretion of dissolved
5 organic matter and/or the formation of micro-environments favorable for heterotrophic N₂
6 fixation (Dekaezemaker et al., 2013).

7

8 2.2 What is the role of N₂ fixation for primary production in the ETNA and ETSP?

9 Several studies (Voss et al., 2002; Mills et al., 2004; Langlois et al., 2005 & 2007)
10 demonstrated the important role of N₂ fixation for surface primary production in ETNA
11 waters. Voss et al. (2002) estimated an average N₂ fixation of 24-140 μmol m⁻² d⁻¹ translating
12 into a contribution of 0.1-0.7% to primary production assuming Redfield stoichiometry on the
13 basis of the rates given in Table 1. This is below the global average of 5.3% (Duce et al.,
14 2008), potentially due to the relatively high deposition of reactive N via Saharan dust input.
15 For the ETSP, N₂ fixation was higher compared to the ETNA with rates of 25-657 μmol m⁻²
16 d⁻¹ (Dekaezemaker et al., 2013; Löscher et al., 2014); while C fixation was rather lower
17 (Table 1). Here, theoretically, N₂ fixation contributes 0.2-7.1% C fixation (Table 1). However,
18 while N loss does not play a role in the ETNA water column (see, e.g., Bange et al. (2010))
19 with the exception of O₂ depleted mesoscale eddies (Löscher et al., 2015), high N loss
20 removes between one and three orders of magnitude more N (Kalvelage et al., 2013; Table 1)
21 than is made available by N₂ fixation. This would decrease the contribution of N₂ fixation to
22 C fixation to zero. When comparing N₂ fixation to N loss, it must be considered that first N
23 loss has only been detected on and close to the shelf, while N₂ fixation rates were detectable
24 throughout the OMZ water column (Fig. 2). Second, while N₂ fixation is measured via direct
25 N₂ incorporation and therefore mirroring *in situ* rates, N loss is likely being overestimated as
26 measured following addition of the substrates, which may artificially stimulate the respective
27 process (up to 2-3 orders of magnitude, as discussed in Kalvelage et al., 2013). As a result, an
28 entirely correct budget of N₂ fixation vs. N loss based on rate measurements is difficult to
29 obtain.
30 In both areas, N₂ fixation may however be considered important for the productivity of the
31 respective system. Still, given the previously described observations of non-Redfield primary
32 production, the contribution to C fixation remains to be fully established.

1 From the comparison of the N₂ fixation in the ETNA and ETSP, the question raises why there
2 is such a strong difference between those systems. A possible explanation may be found in the
3 character of the diazotrophic communities: While the classical view of oceanic N₂ fixation
4 mainly attributed to phototrophic cyanobacteria, such as *Trichodesmium* or *Crocospaera*,
5 (Capone et al., 1997; Zehr and Turner, 2001) may be mostly true for the ETNA (e.g. Langlois
6 et al., 2005, 2007; Großkopf et al., 2012), a different community of diazotrophs is present in
7 the ETSP.

8 A growing number of different *nifH* sequences (the key functional gene of N₂ fixation,
9 encoding the α subunit of nitrogenase) detected within the Peruvian OMZ (Bonnet et al.,
10 2013; Dekaezemacker et al., 2013; Fernandez et al., 2011; Löscher et al., 2014; Turk-Kubo et
11 al., 2014), did not belong to common oxygenic phototrophs, but to some unknown
12 diazotrophic microorganisms that might be specifically adapted to O₂ deficient conditions.

13 These diazotrophs, as well as the extension of their habitat to deeper waters might be one
14 reason for the possible underestimation of N gain compared to N loss in the ocean (Codispoti,
15 2007). In combination with a novel method for N₂ fixation rate measurements (Mohr et al.,
16 2010) (Großkopf et al., 2012) revealed up to 6-fold higher N₂ fixation rates when considering
17 N₂ fixation below the euphotic zone. When extrapolated to all ocean basins this resulted in a
18 N₂ fixation rate of $177 \pm 8 \text{ Tg N yr}^{-1}$, which depending on the assumed budget may balance
19 50-100% of oceanic N loss (Codispoti, 2007; Gruber and Sarmiento, 1997).

20

21 2.3 In how far is N₂ fixation in the ETSP OMZ coupled to N loss?

22 Model studies (Deutsch et al., 2007) assume that a N-deficit resulting from N loss or
23 enhanced P release (Ingall and Jahnke, 1994) provides a niche for diazotrophs. A coupling of
24 N loss in OMZs and N₂ fixation in overlying surface waters might restore the N:P ratio
25 towards Redfield proportions.

26 In the ETSP OMZ, N is indeed continuously removed by the anaerobic oxidation of
27 ammonium (anammox) (Francis et al., 2007; Kuypers et al., 2005; Kuypers et al., 2003;
28 Thamdrup and Dalsgaard, 2002), which has been shown to be the dominating N loss process
29 in this region (Kalvelage et al., 2013, Lam et al., 2009), as well as in other OMZ waters (off
30 Namibia (Kuypers et al., 2005), Peru (Hamersley et al., 2007) and Chile (Thamdrup et al.,
31 2006)). Moreover, N is (i) lost by denitrification (the 4-step reduction of NO₃⁻ to N₂ (Devol,
32 2008)), e.g. in the Arabian Sea OMZ (Ward et al., 2009), where denitrification has been
33 identified the dominant N loss process. However, off Peru, denitrification was only detectable
34 in connection to sulfidic events (Kalvelage et al., 2013, Schunck et al., 2013).

1 The prevalence of novel *nifH* genes and active N₂ fixation, derived from samples collected
2 directly in the OMZ waters off Peru, where anammox bacteria were abundant and active
3 (Kalvelage et al., 2013; Löscher et al., 2014), supports the view of a positive feedback
4 between N loss and N gain communities (Figure 3). Evidence for co-occurrence of
5 denitrification and N₂ fixation has previously been documented only for an anoxic lake (Halm
6 et al., 2009), and for cyanobacterial aggregates in the Baltic Sea (Klawonn et al., 2015).
7 Recent investigations from Baltic Sea sediments on N₂ fixation and diazotrophic abundance in
8 sediments show, however, that a very close spatial link between N loss and N₂ fixation might
9 exist (Bertics et al., 2013). Still, too little is currently known about the interactions among the
10 stoichiometry of inorganic nutrient supply, primary production, N₂ fixation, and
11 remineralization under anoxic conditions, to allow a definite characterization of the conditions
12 leading to fixed-nitrogen exhaustion in the OMZs.

13 This coupling which seems to exist in OMZ waters may in fact have far reaching
14 consequences: While N loss may provide a niche for N₂ fixation, model studies, suggest that
15 denitrification of N₂ fixation-derived organic matter may lead to a net N loss that further
16 stimulates N₂ fixation, because 120 moles of nitrate per mole of phosphorus are used to
17 remineralize Redfield organic matter via denitrification (Landolfi et al., 2013). In contrast, N₂
18 fixation fixes only 16 moles N (per mole P). Because of those stoichiometric constraints, any
19 addition of fixed N to the surface ocean only exacerbates the problem (Canfield, 2006) unless
20 the corresponding primary production is prevented from being remineralized in the underlying
21 OMZ (Landolfi et al., 2013). Lipschultz et al. (1990) indeed stated that N loss in the ETSP
22 OMZ is high enough to respire all produced organic material. Only by spatial or temporal
23 decoupling of N₂ Fe limitation or dissolved organic matter cycling, the N inventory may
24 stabilize, otherwise the OMZ would become completely void of fixed inorganic N. Whether
25 these stoichiometric constraints are valid for anammox as dominant N loss process instead of
26 denitrification is however not clear.

27 Concerning the stoichiometric aspects of ultimate N loss from OMZ waters, a to date largely
28 disregarded aspect should be taken into consideration: As shown for the Gotland basin (Jilbert
29 et al., 2011) enhanced preferential P release from organic matter remineralization was
30 quantitatively important for creating a N deficit. This preferential P release was present in the
31 water column and was further increased under O₂ depleted, reduced conditions. Although the
32 quantitative contribution to the N deficit in the ETSP is not entirely clear, yet, it may act as a

1 factor decoupling the ‘vicious’ cycle between N₂ fixation and N loss (Landolfi et al., 2013), as
2 shifting the abovementioned stoichiometric constraints.

3 2.4 Factors determining N loss

4 The net rate of N loss in OMZs is determined by the balance of remineralization of sinking
5 particulate organic carbon (POC) and O₂ supply to the OMZ. Interestingly, recent studies
6 attributed the dominance of either anammox or denitrification in a certain environment to
7 organic matter composition and availability (Babbin et al., 2014). While the supply of O₂ is
8 mostly determined by physical transport, the rate of N loss depends on the activity of the
9 bacteria responsible for denitrification and anammox as well as the POC export and sinking
10 velocity.

11 The intensity of this feedback may be overestimated in current biogeochemical models, owing
12 to spurious nutrient trapping (Dietze and Loeptien, 2013). The extent of the coupling between
13 primary production at the surface and denitrification in the OMZ, and hence the strength of
14 the positive feedback, is a strong function of the elemental (C:N:P) stoichiometry of the
15 exported primary production. Phytoplankton C:N:P stoichiometry in turn is influenced by the
16 stoichiometry of inorganic nutrients (Franz et al., 2012a; Franz et al., 2012b). Recently
17 developed process models of primary production and N₂ fixation (Pahlow et al., 2013; Pahlow
18 and Oschlies, 2013) specifically address the response of phytoplankton elemental
19 stoichiometry to ambient nutrient concentrations and light.

20 It is generally assumed that both zooplankton and heterotrophic bacteria vary much less in
21 their elemental stoichiometry than phytoplankton (e.g., Touratier et al. (2001)). In both cases,
22 the heterotrophs appear to respond to variable nitrogen content in their food by regulating
23 their gross growth efficiency for carbon (Anderson and Williams, 1998; Kiørboe, 1989). In
24 OMZ regions, this implies that strong nutrient limitation in the surface ocean, which is
25 associated with high C:N ratios in primary producers (e.g., data used in Pahlow et al. (2013)),
26 should intensify denitrification in the OMZ relative to the export flux from the surface. Higher
27 surface nutrient concentrations would then be expected to reduce C:N ratios in the export flux
28 and hence have a somewhat mitigating effect. Since denitrification and anammox in the OMZ
29 cause lower nitrate concentrations in upwelled waters, the variable stoichiometry of
30 phytoplankton could add to the positive feedback between denitrification and N₂ fixation by
31 increasing C:N ratios in response to decreasing surface nitrate concentrations.

32 Combined ¹⁵N-incubation experiments and functional gene expression analyses indicate that
33 anammox in the Peruvian OMZ benefits from other N-cycling processes for reactive

1 substrates (Kalvelage et al., 2011). Excretion of ammonium and other reduced N-compounds
2 by diel vertical migrators was also proposed (Bianchi et al., 2014), but recent experiments
3 indicate that ammonium excretion of diel vertical migrators is strongly reduced at anoxia
4 (Kiko et al. 2015 a, Kiko et al. 2015 b). Additionally, anammox activity has been described to
5 depend on export of organic matter (Kalvelage et al., 2013), potentially resulting from the
6 availability of ammonium recycled from particulate organic N (Ganesh et al., 2015). In the
7 absence of significant denitrification, these results indicate that anammox relies on NH_4^+
8 oxidation and NO_3^- reduction as NO_2^- source. Further, NH_4^+ may be derived from
9 remineralization of organic matter via NO_3^- reduction with a possibly important role of
10 microaerobic respiration (Kalvelage et al., 2015). The overlap between aerobic and anaerobic
11 N-cycling processes in particular in the coastal shelf waters and the upper part of the OMZ is
12 supportive of microaerobic activity in the OMZ. As DNRA was insignificant in the water
13 column during our studies in the ETSP, sedimentary fluxes could be an important ammonium
14 source, particularly for the inner shelf sediments (Bohlen et al., 2011; Kalvelage et al., 2013).
15 However, it has been suggested that sulfate reduction is more widespread in OMZ waters than
16 previously believed and could be responsible for substantial NH_4^+ production (Canfield et al.,
17 2010) and sulfate reducers have been detected in the Peruvian OMZ (Schunck et al., 2013).
18 Direct evidence for the actual link between sulfate reduction and NH_4^+ production is,
19 however, still missing.

20

21 3 Organic matter export and remineralization in the ETSP OMZ

22 3.1 Sinking of particles

23 Knowledge about particle fluxes in areas of tropical OMZs is scarce and predominantly
24 derived from deep moored traps (Honjo et al., 2008) or models (Dale et al., 2015, Table 1).
25 Only few studies have addressed upper ocean export fluxes and mesopelagic flux attenuation
26 in tropical OMZs (Martin et al. (1987), Devol and Hartnett (2001) and VanMooy et al. (2002)
27 for the Eastern Tropical Pacific by means of surface tethered sediment traps, Buesseler et al.
28 (1998) for the Arabian Sea by means of ^{234}Th , and Iversen et al. (2010) at the northern edge of
29 the ETNA OMZ by means of particle camera profiling). In the eastern tropical north Pacific
30 (ETNP), Martin et al. (1987); Van Mooy et al. (2002); Devol and Hartnett (2001)), as well as
31 in the ETSP (Martin et al. 1987; Dale et al., 2015) mesopelagic POC fluxes were less
32 attenuated with depth (Martin curve exponent 'b' of 0.32-0.81) compared with the widely
33 used "open ocean composite" of $b=0.86$ (Martin et al., 1987). Those studies indicate that a

1 greater proportion of the sinking OM escapes degradation while sinking through the eastern
2 tropical Pacific OMZ. On the other hand, it has been shown that microbial degradation of
3 organic N and proteins under suboxia ($< 20 \mu\text{M O}_2$) is not strongly affected (Pantoja et al.,
4 2009; Pantoja et al., 2004; Van Mooy et al., 2002). In addition, organic matter degradation
5 seems not to be significantly affected by decreased O_2 (Dale et al., 2015).

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

15 Classically, the most abundant organisms detected in OMZs belong to the Proteobacteria,
16 Bacteroidetes, Thaumarchaeota of the marine group A, Actinobacteria and Planctomycetes
17 (Schunck et al., 2013; Wright et al., 2012). Several candidate clusters have previously been
18 identified among which are the SAR11, SAR324 and SUP05 clusters (Schunck et al., 2013;
19 Wright et al., 2012). Most investigations of the microbial phylogenetic and functional
20 diversity resort to observing and correlating changes in oxygen concentrations to changes in
21 the microbial phylogenetic diversity. Indeed, several studies, including our own datasets
22 (NCBI accession number: SRP064135) corroborate this idea: A combined statistical analysis
23 of our metagenomic data of the ETSP OMZ (Kalvelage et al., 2015) and datasets from the
24 Chilean OMZ (Canfield et al., 2010; Stewart et al., 2011) has resulted in a partitioning of the
25 OMZ into 5 different habitats, namely surface, subsurface (defined as below the mixed layer
26 and above waters with $\text{O}_2 > 20 \mu\text{mol kg}^{-1}$), oxyclines, OMZ core ($\text{O}_2 < 5 \mu\text{mol kg}^{-1}$) and
27 sulfidic waters (Figure 4). High-resolution sampling in the eastern tropical North Pacific
28 OMZ has shown that the microbial richness is highest at the base of the euphotic zone and the
29 upper oxycline (Beman and Carolan, 2013), often along with high organic flux, low O_2
30 concentrations and dynamic cycling of C, N, and sulfur (S). This may be interpreted in a way
31 that the upper oxycline is of higher importance for remineralization than the OMZ.

32

33 3.2 The impact of zooplankton on organic matter export and remineralization

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

5 Zooplankton and nekton organisms are essential components of the biological pump as they
6 egest packaged organic matter as rapidly sinking fecal pellets. Many zooplankton and nekton
7 species also feed in surface waters during the night and migrate to midwater depth at daybreak
8 to avoid predation (Lampert, 1989), and to conserve energy (McLaren, 1963). This behavior
9 is known as diel vertical migration (DVM) and also contributes to the activity of the
10 biological pump as it enhances the export of organic matter from the photic zone by continued
11 respiration, excretion and egestion in mid-water layers (Burd et al., 2010; Hannides et al.,
12 2009; Robinson et al., 2010; Steinberg et al., 2000). In addition to changes in temperature
13 with depth, DVM organisms experience low O₂ concentrations during the daytime in OMZ
14 regions (Brewer and Peltzer, 2009; Paulmier et al., 2011), and O₂ concentrations below a
15 certain threshold level can restrict DVM of most zooplankton and nekton (e.g. Hauss et al
16 Biogeosciences Discussions). On a regional scale, the upper boundary of the oxycline is the
17 single most critical factor structuring the habitat of most zooplankton organisms in the
18 Peruvian upwelling system (Escribano et al., 2009). Nevertheless, some specifically adapted
19 species are able to downregulate their metabolic activity at low oxygen levels and can remain
20 at OMZ depth (non-migrators) or actively migrate into suboxic or anoxic OMZs (Seibel 2011,
21 Kiko et al. 2015 a, b).

22 Abundance and biomass of metazoans living permanently at extremely low oxygen
23 concentrations <0.6ml L⁻¹ is rather low (Auel and Verheye, 2007; Escribano et al., 2009;
24 Fernández-Álamo and Färber-Lorda, 2006; Saltzmann and Wishner, 1997; Wishner et al.,
25 1998) although animals have evolved physiological (such as metabolic suppression) and/or
26 morphological adaptations (such as increased gill surface area) allowing them to cope
27 temporarily or permanently with O₂ depleted conditions (e.g. copepods, e.g. *Eucalanus*
28 *inermis*, (Flint et al., 1991), euphausiids, e.g. *Euphausia mucronata* (Antezana, 2009),
29 decapods (Percy et al., 1977), cephalopods, e.g. *Dosidicus gigas* (Rosa and Seibel, 2010),
30 and teleosts (Friedman et al., 2012; Luo et al., 2000)). According to Seibel (2011), adaptations
31 to low oxygen levels are needed below approximately 40 μmol O₂ kg⁻¹. Strong physiological
32 adaptations seem thus necessary to thrive in the ETSP OMZ, but not in the ETNA OMZ
33 where O₂ concentrations are normally greater than 40 μmol kg⁻¹ (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⁻² d⁻¹ 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 in 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⁻¹
27 d⁻¹ (Poorvin et al., 2004). Likewise, virus-induced bacterial lysis was calculated to contribute
28 ~1-6 Gt N a⁻¹ 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 O₂, 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⁻¹ 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 O₂-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 extreme cases of 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 19th
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 O₂ 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 N₂ via autotrophic
12 denitrification or NH₄⁺ 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 km² and contained approximately 2.2×10^4 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 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 CO_2
14 assimilation exceed rates possible by chemolithoautotrophic processes alone. Thus, while
15 chemolithoautotrophic CO_2 -fixation is considered a significant process, the specific activity
16 and main contributors of 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. Simultaneous reduction of different electron
20 acceptors (like NO_3^- , SO_4^{2-} and CO_2) can occur in defined niches where particle aggregates
21 have formed and are sinking through the water column (Wright et al., 2012). These
22 aggregates, more commonly known as marine snow, contain micro-scale redoxclines under
23 anoxic conditions (Aldredge and Cohen, 1987; Karl and Tilbrook, 1994; Woebken et al.,
24 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 (CO₂), nitrous oxide (N₂O),
7 methane (CH₄) and dimethyl sulfide (DMS) occurs (see, e.g., Liss and Johnson (2014)).
8 While the pathways of CO₂ and DMS are dominated by phytoplankton in the oxic euphotic
9 zone, N₂O and CH₄ 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 CO₂, N₂O
12 and CH₄ — 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 (N₂O) in OMZ

18 A comprehensive overview of both nitrous oxide (N₂O) 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 N₂O 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 N₂O is exclusively produced by bacteria has been
24 challenged by the discovery of nitrifying (i.e. NH₄⁺ oxidising) archaea (e.g., *Cand.*
25 *Nitrosopelagicus brevis*, see above) dominating N₂O 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 N₂O
28 by archaea (and bacteria) depends on dissolved O₂ and increases with decreasing O₂
29 concentrations (Frame and Casciotti, 2010; Löscher et al., 2012). Denitrifying bacteria do not
30 produce N₂O in the presence of O₂ (> 10 μmol kg⁻¹); however, when O₂ concentrations are
31 approaching 0 μmol kg⁻¹, N₂O is consumed during denitrification. There is no N₂O production
32 under anoxic conditions. The significance of N₂O 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 N_2O /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 O_2 concentrations found in the core of the OMZ of the ETSP ($< 5 \mu\text{mol}$
4 kg^{-1}) favour N_2O consumption by denitrification which is not observed in the ETNA because
5 of its comparably high O_2 concentrations and (ii) the maximum observed N_2O concentrations
6 were higher in the ETSP than in the ETNA. This is in line with the results of two model
7 studies of N_2O in the ETSP by Zamora et al. (2012) and Cornejo and Farias (2012), which
8 suggested that the switching point between N_2O production and N_2O consumption occurs at
9 higher 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 N_2O , water
15 temperature, nutrients and H_2S during the sulfidic event described by Schunck et al. (2013) on
16 the shelf off Peru during December 2008/January 2009. Here, extreme N_2O concentrations are
17 found at the boundary to the H_2S containing bottom waters. No N_2O is found in the core
18 sulfidic layer. This suggests again that there is a narrow range of low O_2 concentrations which
19 is associated with exceptionally high N_2O production. As soon as the O_2 concentrations are
20 close to zero (anoxic/sulfidic conditions) N_2O production turns into N_2O consumption.
21 Similar N_2O 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 H_2S oxidation and NO_3^- reduction in a narrow layer where NO_3^- and H_2S 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 H_2S oxidation by 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 O_2 concentrations below $20 \mu\text{mol kg}^{-1}$, N_2O production does not take place in
31 the core of the OMZ. Instead, N_2O production is found at the oxycline. Exceptionally high
32 N_2O 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 N₂O concentrations at the oxic/anoxic interfaces (Bange et al.,
3 2010, and references therein). This implies that significant pulses of N₂O 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 N₂O reduction by denitrifiers, when they switch from oxygen to nitrogen respiration
7 (Codispoti, 2010) or N₂O production during the reestablishment of nitrification after O₂
8 ventilation (Schweiger et al., 2007).

9 CH₄ production is also tightly connected to OMZs (see overview in Naqvi et al., 2010).
10 Similar to N₂O, upwelling areas are considerable hotspots for CH₄ emissions, although
11 organic material-enriched shallow coastal zones such as estuaries and mangroves or shallow
12 sediments with geological CH₄ 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). On-going environmental changes such as deoxygenation, eutrophication, warming
34 and acidification have both direct and indirect effects on trace gas production in OMZs. In

1 general, we might expect enhanced production of N₂O, CH₄ and DMS in OMZs because of
2 the on-going loss of O₂.

3 Deoxygenation in open ocean and coastal environments may lead, on the one hand, to
4 enhanced N₂O production when approaching the N₂O production/consumption switching
5 point (see above), but on the other hand, when O₂ concentrations fall below the switching
6 point this may lead to a consumption of N₂O (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 N₂O production/consumption. A recent modelling study on the
9 influence of anthropogenic nitrogen aerosol deposition on N₂O 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 N₂O 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 O₂ 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 O₂ (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 of particles were shown important (DeVries et al., 2014),
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 N₂ 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 their 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). Information on the character of microbial processes
13 responsible for POM degradation within the OMZ is however missing. First studies (e.g.
14 Ganesh et al., 2014, 2015) indicate a key role of particulate organic matter acting as
15 microniches for microbes and thus host for certain processes such as microaerobic respiration
16 in OMZ waters. By containing strong redox gradients in relatively narrow proximity, and by
17 providing nutrients and trace metals, particles might strongly influence biogeochemical
18 cycles. It is well-known that in the core of OMZs adjacent to coastal upwelling regions, such
19 as those found off Peru, Mauritania and the Arabian Sea, a pronounced POM/particle-
20 enriched turbid layer (a so-called intermediate nepheloid layer) exists (see, e.g., Stramma et
21 al. (2013); Naqvi et al. (1993); Fischer et al. (2009)).

22 With regard to sulfidic events, which represents the lower limit of anoxia, the positive
23 feedback coupling could be thought to stabilize itself: While a direct toxic effect of H₂S on
24 primary production is mostly mitigated by the respective detoxifying community, decoupling
25 of the supply of benthic nutrients to the sea surface might decrease primary production. This
26 may be of particular importance in areas, such as the ETSP where the benthic supply of e.g.
27 trace metals is dominant. Resulting decreased respiration in the OMZ could be thought to
28 subsequently lead to regeneration to non-sulphidic, less pronounced anoxia, which may
29 stabilize the OMZ to a certain extent. Whether this hypothesis is valid has, however, to be
30 resolved.

31 A critical consequence of ocean deoxygenation is visible from the comparison of the ETSP
32 and ETNA regions: Massive supersaturation of N₂O, connected to sulfidic plumes, has been
33 detected repeatedly, in the ETSP. OMZs are important sites of enhanced production of climate
34 relevant trace gases such as N₂O, CH₄, and DMS. N₂O production is significantly enhanced at

1 oxic/anoxic boundaries of OMZs and we suggest that it mainly results from habitat
2 compression, where in extreme cases (such as sulfidic events, sharpening gradients)
3 nitrification and denitrification can occur simultaneously. Maximum N₂O concentrations and
4 subsequent emissions to the atmosphere have been observed in dynamic coastal systems that
5 rapidly shift from oxic to anoxic conditions and vice versa. Although OMZs are usually not in
6 direct contact with the atmosphere, their vicinity to coastal upwelling systems plays an
7 important role for oceanic emissions of climate-relevant trace gases such as N₂O, CH₄, and
8 DMS with potential feedbacks on global warming, which then may again impact on ocean
9 deoxygenation. Our studies from the ETSP (Arevalo-Martinez, 2015, 2016, Kock et al., 2016)
10 confirm intense production of N₂O in the coastal upwelling. This is in line with an increase of
11 N₂O production from OMZ areas as concluded from forced climate models. However, the
12 same model describes a global decrease of N₂O formation by 4-12%, mostly linked to the
13 western basins of the Pacific and Atlantic oceans (Martinez-Rey et al., 2015).

14 Marine ecosystems and biogeochemical cycles are increasingly impacted by a growing
15 number of stress factors, some of which act locally, such as eutrophication and pollution,
16 others globally. Global stressors are associated with anthropogenic carbon dioxide (CO₂)
17 emissions and affect the ocean either directly through CO₂-induced acidification or indirectly
18 through climate change-induced ocean warming and deoxygenation (Ciais et al., 2013). How
19 these stressors will impact marine ecosystems and biogeochemistry, individually or in
20 combination, is still largely unknown.

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

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

1 7 Outlook

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

8 Future studies in the framework of the SFB 754 will combine measurements of particle flux,
9 zooplankton abundance, microbial activities and O₂ concentrations in order to answer the
10 following key questions:

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

19 **Acknowledgements**

20 We thank IMARPE and INDP for close collaboration and support. We further thank the
21 authorities of Peru, Cape Verde and Mauritania for the permission to work in their territorial
22 waters. We acknowledge the support of the captains, crews of R/V Meteor and the chief
23 scientists. We thank A. Dale for discussion of the benthic perspective of the manuscript.
24 Financial support for this study was provided by the DFG Sonderforschungsbereich 754
25 (www.sfb754.de), the Max Planck Society (MPG). Additional funding was provided by the
26 European Union (Marie Curie IEF to CRL, grant #704272).

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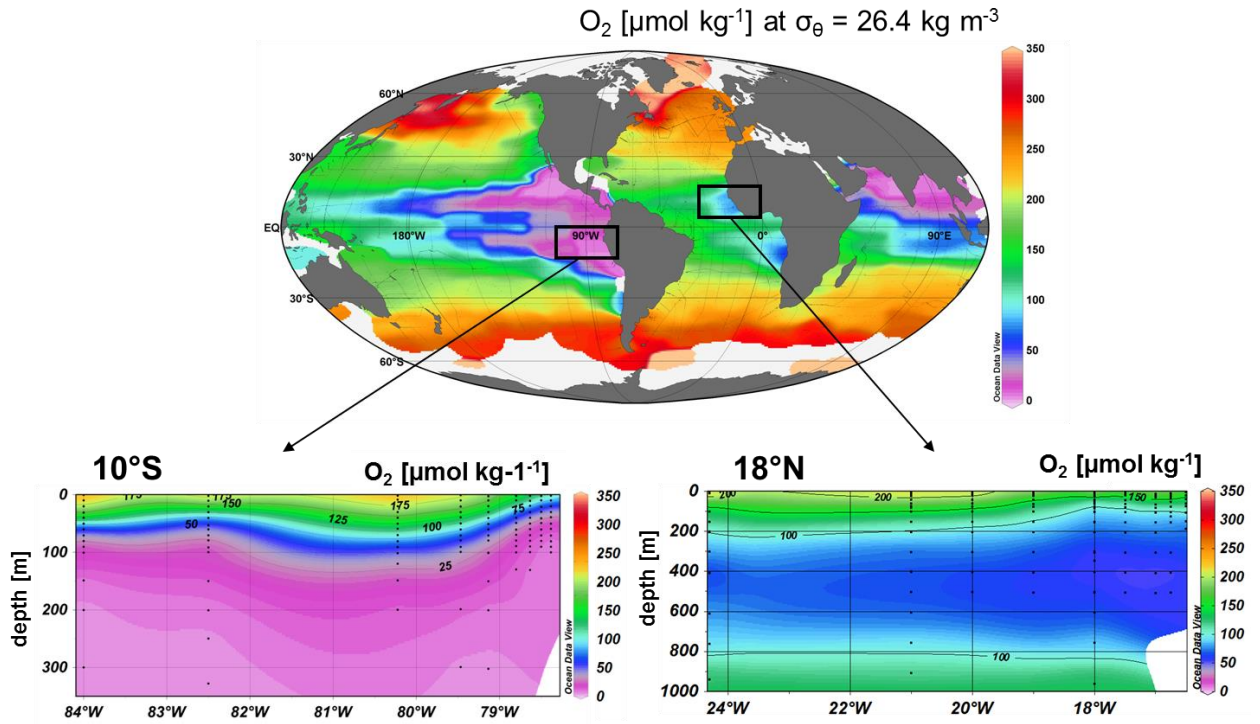
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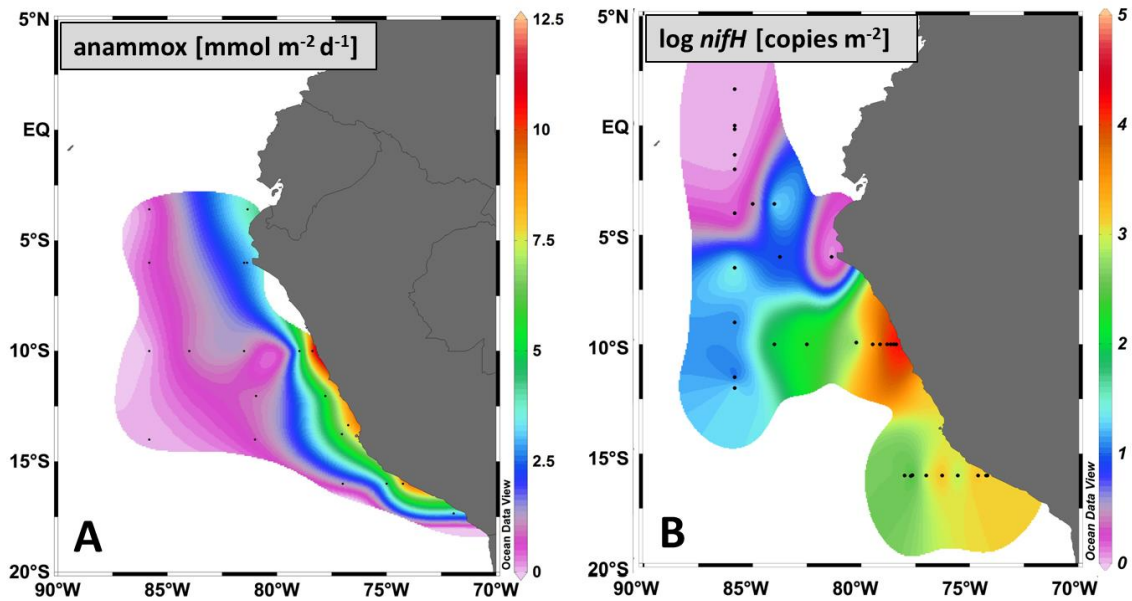
1 **Figures**



2

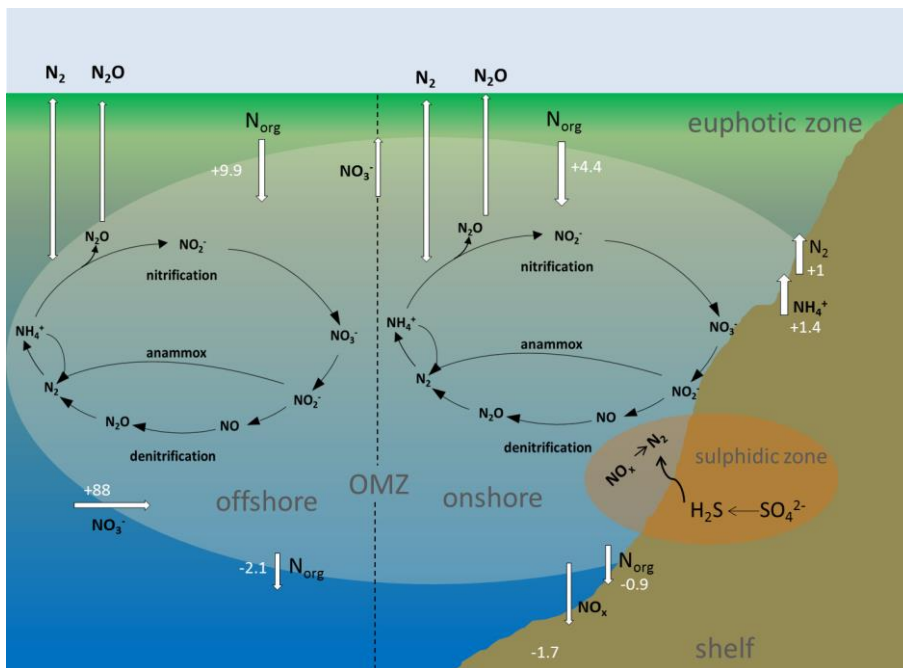
3 Figure 1. Global distribution of O_2 at $\sigma_{\theta} = 26.4 \text{ kg m}^{-3}$ ($\sim 400 \text{ m}$ depth): The major regions of
 4 low oxygen in the world ocean are all located in the tropical oceans, at shallow to
 5 intermediate depths. The area off Peru represents one of the most pronounced 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°S in the OMZ off Peru and at 18°N in the
 9 eastern tropical North Atlantic; O_2 concentrations are indicated by the color code.

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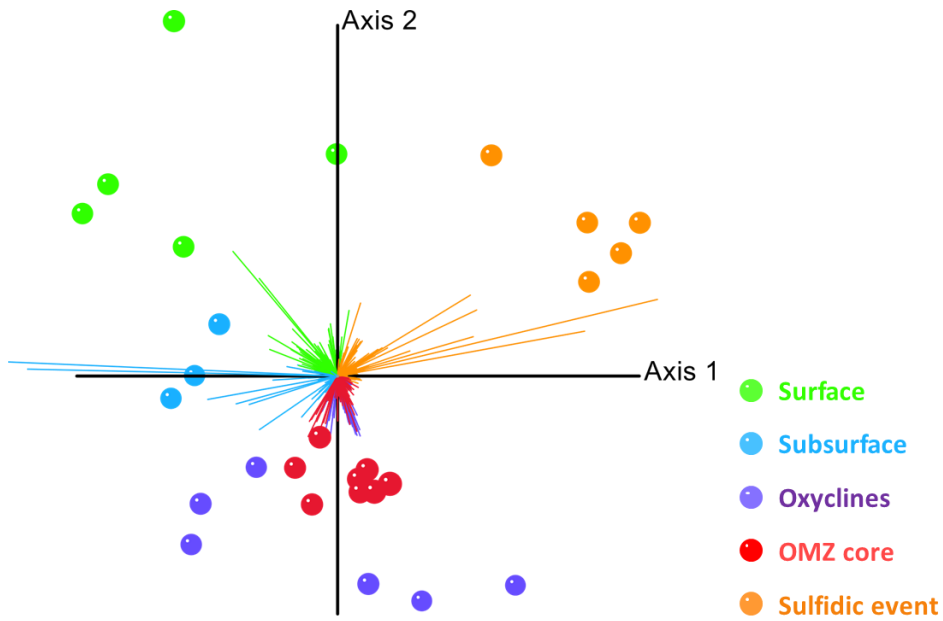
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 2 Figure 2. Co-occurrence of anammox as determined by rate measurements and the key
 3 functional marker gene for N_2 fixation, *nifH*, in the ETSP OMZ (modified from Kalvelage et
 4 al., 2013 and Löscher et al., 2014).

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 6



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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 [Tg y^{-1}].

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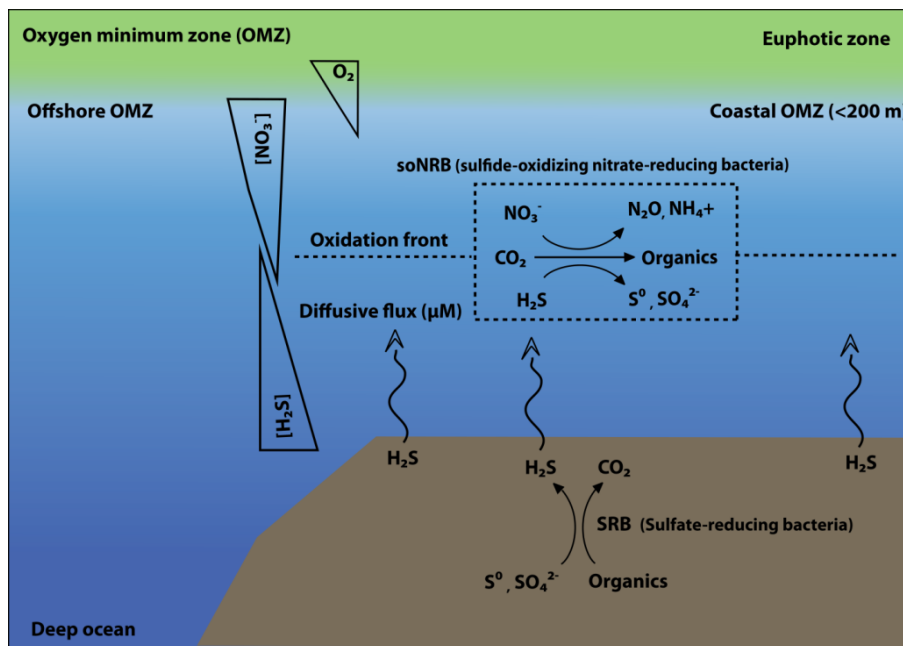


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2 Figure 4. Redundancy analysis ordination model of microbial taxa (vectors) identified from
 3 pyrosequencing reads of multiple samples (points) in the ETSP. Spherical k-means clustering
 4 revealed a fivefold partitioning that reflects distinct OMZ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

7

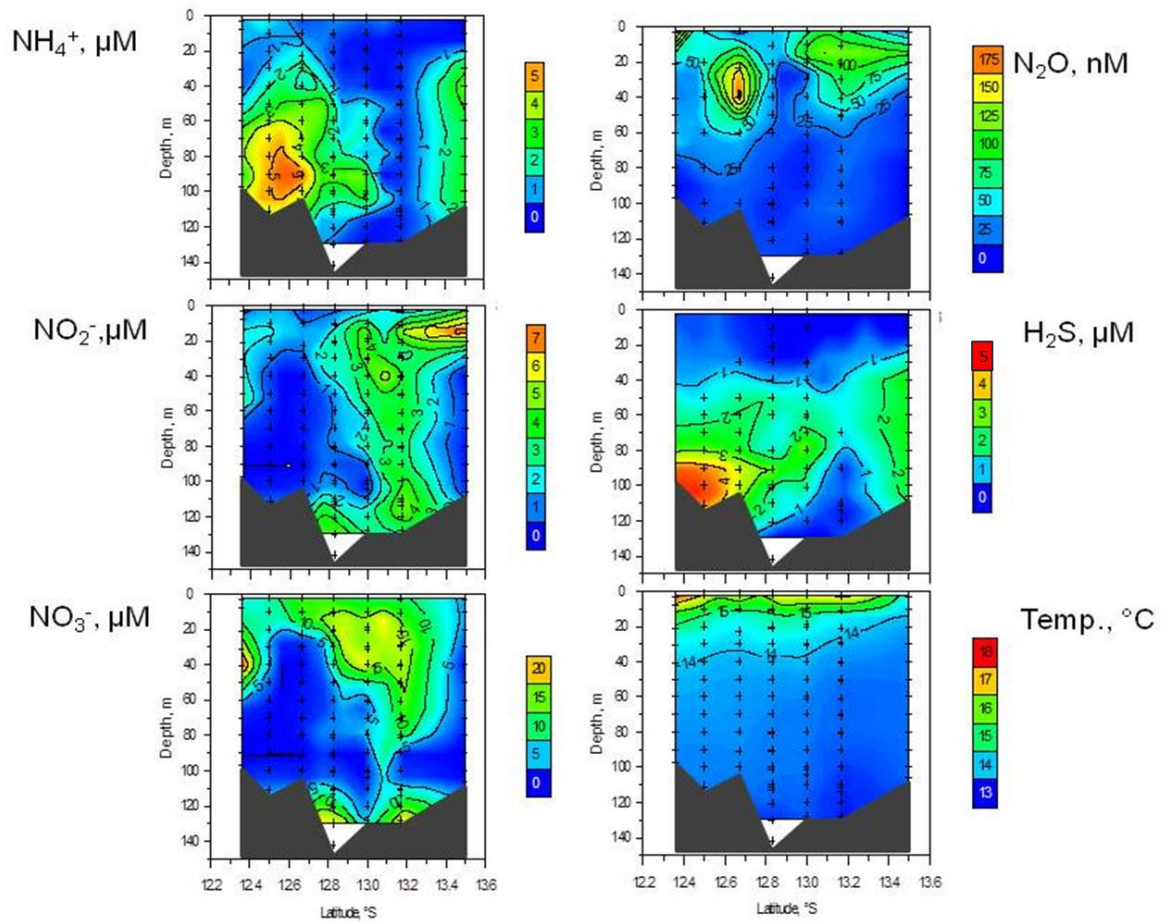
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10 Figure 5. Schematic representation of the dynamics of a sulfidic event occurring in an oxygen
 11 minimum zone, e.g. in the ETSP. The sulfide and nitrate fluxes are shown in steady state.

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



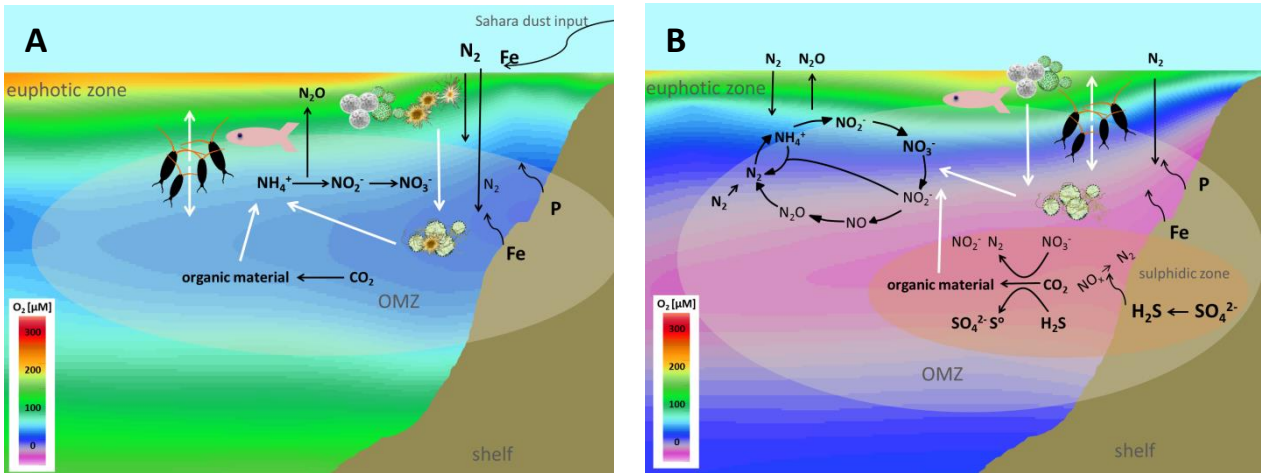
- 3
- 4 Figure 6. Distributions of N_2O , NH_4^+ , NO_2^- , NO_3^- , H_2S , and water temperature during
- 5 December 2008/January 2009 (R/V Meteor cruise M77/3) on the shelf along the coast of
- 6 Peru. Max. N_2O concentrations have been detected right above the sulfidic zone, where a
- 7 sharp oxycline 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 O₂ minimum, excess nitrogen (N*), primary production, organic
 2 C export, N₂ fixation and N loss in the ETNA and ETSP upwelling regions.
 3

	ETSP-shelf	ETSP- offshore	ETNA-shelf	ETNA- offshore
O₂ min. [μmol kg⁻¹]	0 (sulfidic)	0	25	40
N* [mol m⁻²]	-1,9- (-5,98) ^a			
Primary Production [mmol C m⁻² d⁻¹]	101-122 ^b 68,5 ^c 61,4 ^d	73-94 ^b	137 ^c 167 ^d	
Organic C export [mmol C m⁻² d⁻¹]	10,6-75,3 ^b	2,6-11,1 ^b	6,4- 9,3 ^e	0,67-2,6 ^e
N₂ fixation [μmol N m⁻² d⁻¹]	25-657 ^f		24-140 ^g	
% contribution of N₂ fixation to primary production*	0,2-4 ^b 0,2-6,4 ^c 0,3-7,1 ^d		0,2-0,7 ^c 0,1-0,6 ^d	
N loss [mmol N m⁻² d⁻¹]				
anammox	1-10	0	0	
denitrification	up to 70 (in presence of H ₂ S)	0	0	

4 * Calculated based on the Redfield ratio of C:N = 106:16 using the primary production and N₂ fixation rates
 5 given in this table in consistency with the % contribution given in Duce et al. (2008).

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