Dear editor,

Thank you for the thorough review and editing of our manuscript. We addressed the open questions and issues according to your suggestions. Besides the formal modifications (language, grammar, numbering of chapters), some headings were shortened, the reference list was formatted and missing references were added.
Below, a version with highlighted changes is given.

Best regards,
Carolin Löscher

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

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Abstract

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

In the following, one decade of research performed in the framework of the collaborative research center SFB 754 focusing on Climate- Biogeochemistry interactions in tropical OMZs is summarized. The influence of low environmental oxygen conditions on biogeochemical cycles organic matter formation and remineralization, greenhouse gas production and the ecology in OMZ regions of the eastern tropical South Pacific compared to the weaker OMZ of the eastern tropical North Atlantic were investigated. The impact of sulfidic events on water column biogeochemistry, as well as their specific microbial community capable of highly efficient carbon fixation, nitrogen turnover and N_2O production is discussed. Based on our findings, a coupling of primary production and organic matter export via the nitrogen cycle is proposed, which may, however, be impacted by several additional factors, e.g. micronutrients, particles acting as microniches, vertical and horizontal transport of organic material and the role of zooplankton and viruses therein.

1 Introduction

Eastern boundary upwelling systems are ocean areas where cold and nutrient-rich waters are upwelled to the sea surface, where they fuel high biomass production (Carr, 2002; Chavez and Messie, 2009). While covering only 0.2% of the ocean, those upwelling areas account for about 50-58% of global fish catch (Pauly and Christensen, 1995). Two eastern boundary upwelling systems were subject to this study: the upwelling off Mauritania, located in the eastern tropical North Atlantic (ETNA) and the upwelling system off Peru located in the eastern tropical South Pacific (ETSP). While both systems are characterized by intense primary production, their biogeochemical properties differ strongly (Karstensen et al., 2008), which partially results from a combination of different water mass ages and characteristics (Körtzinger et al., 2004), topography and atmospheric impacts (e.g. Duce et al., 2008). A major difference between the ETNA and the ETSP is the intensity of the oxygen minimum zone (OMZ) associated with those upwelling regions (Capone and Hutchins, 2013): The ETNA OMZ has O_2 concentrations typically above 40 µmol kg^{-1}, whereas the large and persistent OMZ in the ETSP located off Peru and Chile has O_2 concentrations below the detection limit based on conventional methods (~2 µmol kg^{-1}, Figure 1) with sometimes even sulfidic conditions on the shallower shelf (Schunck et al., 2013).

Besides the age of the water mass and other physical constraints, biological remineralization and respiration processes consume O_2 below the highly productive surface waters and contribute therefore to the development and maintenance of OMZ waters (Walsh, 1981, Quinones et al., 2010). The intensity of the OMZ may therefore be determined by a positive feedback, with increased primary production leading to enhanced organic matter export back to underlying O_2-depleted waters (Dale et al.2015). As a consequence of enhanced organic matter export, respiration processes may increase. Stronger anoxia on the other hand would promote O_2 sensitive N loss processes, therefore creating an nitrogen (N) deficit in upwelled waters. This would then stimulate N_2 fixation at the sea surface and enhance again primary production. In how far a feedback between primary production, organic matter remineralization and the N cycle is a valid model in OMZ waters and what role sulphidic conditions play in there is critical to understand.

Modeling results (Bopp et al., 2013; Cocco et al., 2013), predict that O_2 levels will decrease significantly over the next decades in response to climate change and eutrophication. Hence, the future ocean may experience major shifts in nutrient cycling triggered by the possible expansion and intensification of tropical OMZs (Codispoti, 2010). Currently, the estimated volume of OMZs with O_2 concentrations <20 µmol kg^{-1} is about 1% of the global ocean volume (Lam and Kuypers, 2011). Approximately 0.05% of the global ocean volume has O_2 levels below 5 µmol kg^{-1}. The effects of O_2-sensitive nutrient cycling processes occurring in these relatively small regions (Codispoti, 2010) are conveyed to the rest of the ocean (see e.g. Deutsch et al. 2007). Hence comparatively "small" volumes of OMZs can significantly impact nutrient budgets, biological productivity and the overall potential for CO_2 fixation of the ocean. An important factor is further that deoxygenation of OMZs has been proposed to increase the production of the greenhouse gas nitrous oxide (N_2O) (Codispoti, 2010). Therefore, understanding the present biogeochemistry of those systems and exploring the potential to respond to climate change is critical.

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

2 Primary production in the ETSP and ETNA

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

Franz et al. (2012a) reported in situ observations along an east-west transect in the ETSP at 10°S stretching from the upwelling region above the narrow continental shelf to the well-stratified oceanic section of the eastern boundary regime. The study showed that new production in the coastal upwelling was driven by large-sized phytoplankton (e.g. diatoms) with generally low N:P ratios (<16:1), thus speaking for non-Redfield surface water primary production. A deep chlorophyll *a* maximum consisting of nano- (*Synechococcus*, flagellates) and microphytoplankton occurred within a pronounced thermocline in subsurface waters above the shelf break. Here, intermediate particulate N:P ratios were close to Redfield proportions. High PON:POP (>20:1) ratios were observed in a stratified open ocean section, coinciding with a high abundance of the pico-cyanobacterium *Prochlorococcus*. Excess P was present along the entire transect but did not appear to stimulate growth of N_2 fixing cyanobacteria, as pigment fingerprinting and phylogenetic studies did not indicate the presence of diazotrophic cyanobacteria at most of our sampling stations (Franz et al., 2012a; Löscher et al., 2014). These findings are mostly in accordance with other studies from this area (Bonnet et al., 2013; Fernandez et al., 2011; Turk-Kubo et al., 2014). Therefore, the excess P generated within the OMZ seemed to be rather consumed by non-Redfield processes, i.e. primary production by large phytoplankton found in shelf surface waters, instead of stimulating surface N_2 fixation. A possible explanation can be deducted from the optimality-based model of N_2 fixation by Pahlow et al. (2013). The model is based on the assumption that natural selection should tend to produce organisms optimally adapted to their environment. The competitive advantage of diazotrophs is most pronounced under conditions of low dissolved inorganic N and increased dissolved inorganic P (DIN, DIP) availability (Houlton et al., 2008). The ability to compete for DIP is therefore less important at high DIP. Thus, high P concentrations above the ETSP OMZ might actually reduce the selective advantage of diazotrophs compared to non-Redfield primary producers. This could partially explain why cyanobacterial N_2 fixers were apparently not stimulated by excess phosphate in surface waters of the abovementioned transect.

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

A series of on board mesocosm experiments and bioassay incubations were performed in order to identify nutrient limitations in both areas and to specifically address the impact of stoichiometry on primary production. Despite the fundamental differences between the ETNA and ETSP with regard to the N deficit, the results of short-term mesocosm experiments implied N limitation of surface plankton communities in both areas (Franz et al., 2012a; Franz et al., 2012b). Further, the partitioning and elemental composition of dissolved and particulate organic matter was investigated. Maximum accumulation of POC and PON was observed under high N supply, indicating that primary production was controlled by N availability. Part of the excess P was consumed by non-Redfield production, predominantly by diatoms, as also observed from direct monitoring as described above. While particulate N:P of the accumulated biomass generally exceeded the supply ratio (Franz et al., 2012b), excess P of the dissolved nutrient pool was channeled into release of dissolved organic phosphorus (DOP) by phytoplankton. These results demonstrated that excess P upwelled into the surface ocean overlying O_2-deficient waters represents a net source for DOP and motivated further dedicated mesocosm experiments in the ETNA to elucidate the fate of DOP. While the direct monitoring and the results of mesocosm studies were strongly speaking for a shift to non-Redfield primary production due to changes in N:P, a general stimulating effect of DOP on N_2 fixation has been observed (Meyer et al., 2015). This is in line with a recent modeling study based on large-scale surface data sets of global DON and Atlantic ocean DOP. Here, the model suggests an important role of DOP for stimulating growth of N_2 fixing organisms (Somes and Oschlies, 2015). This model indicates that the marine N- budget is sensitive to DOP, provided that access to the relatively labile DOP pool expands the ecological niche for diazotrophs. Taken together, changes in N:P may lead to a combination of both, non-Redfield primary production and enhanced N_2 fixation via DOP.

Besides a direct effects of N:P ratios, primary production and N_2 fixation, due to the comparably high Fe requirements of the diazotrophs (Gruber, 1997) is largely influenced by trace metal availability (Mills et al., 2004). Comparing the ETNA and ETSP regions, an obvious difference with regard to potentially limiting nutrients is related to the iron (Fe) source: In the ETNA, Saharan dust input contributes 71-87% of dissolved Fe to the water (Conway, 2014). Several studies highlighted the importance of atmospheric Fe supply to the ETNA (Voss et al., 2002; Mills et al., 2004) as a major factor of primary production. A comparable atmospheric Fe source is however missing in the ETSP (Baker et al., 2016). Previous studies (Scholz et al., 2014) identified the ETSP Fe supply as benthic, however, the question on how much Fe is transported from the sediments to the sea surface is so far not fully clarified.

Results of bioassay incubations and correlation studies demonstrated that primary production and N_2 fixation in this region respond significantly to Fe additions (Dekaezemacker et al., 2013). N_2 fixation could further be directly limited by inorganic nutrient availability, or indirectly through the stimulation of primary production and the subsequent excretion of dissolved organic matter and/or the formation of micro-environments favorable for heterotrophic N_2 fixation (Dekaezemacker et al., 2013).

2.2 What is the role of N_2 fixation for primary production in the ETNA and ETSP?

Several studies (Voss et al., 2002; Mills et al., 2004; Langlois et al, 2005 & 2007) demonstrated the important role of N_2 fixation for surface primary production in ETNA waters. Voss et al. (2002) estimated an average N_2 fixation of 24-140 µmol m^{-2} d^{-1} translating into a contribution of 0.1-0.7% to primary production assuming Redfield stoichiometry on the basis of the rates given in Table 1. This is below the global average of 5.3% (Duce et al., 2008), potentially due to the relatively high deposition of reactive N via Saharan dust input. For the ETSP, N_2 fixation was higher compared to the ETNA with rates of 25-657 µmol m^{-2} d^{-1} (Dekaezamacker et al., 2013; Löscher et al., 2014); while C fixation was rather lower (Table 1). Here, theoretically, N_2 fixation contributes 0.2-7.1% C fixation (Table 1). However, while N loss does not play a role in the ETNA water column (see, e.g., Bange et al. (2010)) with the exception of O_2 depleted mesoscale eddies (Löscher et al., 2015), high N loss removes between one and three orders of magnitude more N (Kalvelage et al., 2013; Table 1) than is made available by N_2 fixation. This would decrease the contribution of N_2 fixation to C fixation to zero. When comparing N_2 fixation to N loss, it must be considered that first N loss has only been detected on and close to the shelf, while N_2 fixation rates were detectable throughout the OMZ water column (Fig. 2). Second, while N_2 fixation is measured via direct N_2 incorporation and herefore mirroring *in situ* rates, N loss is likely being overestimated as measured following addition of the substrates, which may artificially stimulate the respective process (up to 2-3 orders of magnitude, as discussed in Kalvelage et al., 2013) . An entirely correct budget of N_2 fixation vs. N loss based on rate measurements is therefore difficult to obtain.

In both areas, N_2 fixation may however be considered important for the productivity of the respective system. Still, given the previously described observations of non-Redfield primary production, the contribution to C fixation remains to be fully established.

From the comparison of the N_2 fixation in the ETNA and ETSP, the question raises why there is such a strong difference between those systems. A possible explanation may be found in the character of the diazotrophic communities: While the classical view of oceanic N_2 fixation mainly attributed to phototrophic cyanobacteria, such as *Trichodesmium* or *Crocosphaera,* (Capone et al., 1997; Zehr and Turner, 2001) may be mostly true for the ETNA (e.g. Langlois et al., 2005, 2007; Großkopf et al., 2012), a different community of diazotrophs is present in the ETSP.

A growing number of different *nifH* sequences (the key functional gene of N_2 fixation, encoding the α subunit of nitrogenase) detected within the Peruvian OMZ (Bonnet et al., 2013; Dekaezemacker et al., 2013; Fernandez et al., 2011; Löscher et al., 2014; Turk-Kubo et al., 2014), did not belong to common oxygenic phototrophs, but to some unknown diazotrophic microorganisms that might be specifically adapted to O_2 deficient conditions.

These diazotrophs, as well as the extension of their habitat to deeper waters might be one reason for the possible underestimation of N gain compared to N loss in the ocean (Codispoti, 2007). In combination with a novel method for N_2 fixation rate measurements (Mohr et al., 2010) (Großkopf et al., 2012) revealed up to 6-fold higher N_2 fixation rates when considering N_2 fixation below the euphotic zone. When extrapolated to all ocean basins this resulted in a N_2 fixation rate of 177 ±8 Tg N yr^{-1}, which-depending on the assumed budget may balance 50-100% of oceanic N loss (Codispoti, 2007;Gruber and Sarmiento, 1997).

2.3 In how far is N_2 fixation in the ETSP OMZ coupled to N loss?

Model studies (Deutsch et al., 2007) assume that a N-deficit resulting from N loss or enhanced P release (Ingall and Jahnke, 1994) provides a niche for diazotrophs. A coupling of N loss in OMZs and N_2 fixation in overlying surface waters might therefore restore the N:P ratio towards Redfield proportions.

In the ETSP OMZ, N is indeed continuously removed by the anaerobic oxidation of ammonium (anammox) (Francis et al., 2007; Kuypers et al., 2005; Kuypers et al., 2003; Thamdrup and Dalsgaard, 2002), which has been shown to be the dominating N loss process in this region (Kalvelage et al., 2013, Lam et al., 2009), as well as in other OMZ waters (off Namibia (Kuypers et al., 2005), Peru (Hamersley et al., 2007) and Chile (Thamdrup et al., 2006)). Moreover, N is (i) lost by denitrification (the 4-step reduction of NO_3^- to N_2 (Devol, 2008)), e.g. in the Arabian Sea OMZ (Ward et al., 2009), where denitrification has been identified the dominant N loss process. However, off Peru, denitrification was only detectable in connection to sulfidic events (Kalvelage et al, 2013, Schunck et al., 2013).

The prevalence of novel *nifH* genes and active N_2 fixation, derived from samples collected directly in the OMZ waters off Peru, where anammox bacteria were abundant and active (Kalvelage et al., 2013; Löscher et al., 2014), supports the view of a positive feedback between N loss and N gain communities (Figure 3). Evidence for co-occurrence of denitrification and N_2 fixation has previously been documented only for an anoxic lake (Halm et al., 2009), and for cyanobacterial aggregates in the Baltic Sea (Klawonn et al., 2015). Recent investigations from Baltic Sea sediments on N_2 fixation and diazotrophic abundance in sediments show, however, that a very close spatial link between N loss and N_2 fixation might exist (Bertics et al., 2013). Still, too little is currently known about the interactions among the stoichiometry of inorganic nutrient supply, primary production, N_2 fixation, and remineralization under anoxic conditions, to allow a definite characterization of the conditions leading to fixed-nitrogen exhaustion in the OMZs.

This coupling which seems to exist in OMZ waters may in fact have far reaching consequences: While N loss may provide a niche for N_2 fixation, model studies, suggest that denitrification of N_2 fixation-derived organic matter may lead to a net N loss that further stimulates N_2 fixation, because 120 moles of nitrate per mole of phosphorus are used to remineralize Redfield organic matter via denitrification (Landolfi et al., 2013). In contrast, N_2 fixation fixes only 16 moles N (per mole P). Because of those stoichiometric constraints, any addition of fixed N to the surface ocean only exacerbates the problem (Canfield, 2006) unless the corresponding primary production is prevented from being remineralized in the underlying OMZ (Landolfi et al., 2013). Lipschultz et al. (1990) indeed stated that N loss in the ETSP OMZ is high enough to respire all produced organic material. Only by spatial or temporal decoupling of N_2 Fe limitation or dissolved organic matter cycling, the N inventory may stabilize, otherwise the OMZ would become completely void of fixed inorganic N. Whether these stoichiometric constraints are valid for anammox as dominant N loss process instead of denitrification is however not clear.

Concerning the stoichiometric aspects of ultimate N loss from OMZ waters, a to date largely disregarded aspect should be taken into consideration: As shown for the Gotland basin (Jilbert et al., 2011) enhanced preferential P release from organic matter remineralization was quantitatively important for creating a N deficit. This preferential P release was present in the water column and was further increased under O_2 depleted, reduced conditions. Although the quantitative contribution to the N deficit in the ETSP is not entirely clear, yet, it may act as a factor decoupling the ‘vicious’ cycle between N_2 fixation and N loss (Landolfi et al., 2013), as shifting the abovementioned stoichiometric constraints.

2.4 Factors determining N loss

The net rate of N loss in OMZs is determined by the balance of remineralization of sinking particulate organic carbon (POC) and O_2 supply to the OMZ. Interestingly, recent studies attributed the dominance of either anammox or denitrification in a certain environment to organic matter composition and availability (Babbin et al., 2014). While the supply of O_2 is mostly determined by physical transport, the rate of N loss depends on the activity of the bacteria responsible for denitrification and anammox as well as the POC export and sinking velocity.

The intensity of this feedback may be overestimated in current biogeochemical models, owing to spurious nutrient trapping (Dietze and Loeptien, 2013). The extent of the coupling between primary production at the surface and denitrification in the OMZ, and hence the strength of the positive feedback, is a strong function of the elemental (C:N:P) stoichiometry of the exported primary production. Phytoplankton C:N:P stoichiometry in turn is influenced by the stoichiometry of inorganic nutrients (Franz et al., 2012a; Franz et al., 2012b). Recently developed process models of primary production and N_2 fixation (Pahlow et al., 2013; Pahlow and Oschlies, 2013) specifically address the response of phytoplankton elemental stoichiometry to ambient nutrient concentrations and light.

It is generally assumed that both zooplankton and heterotrophic bacteria vary much less in their elemental stoichiometry than phytoplankton (e.g., Touratier et al. (2001)). In both cases, the heterotrophs appear to respond to variable nitrogen content in their food by regulating their gross growth efficiency for carbon (Anderson and Williams, 1998; Kiørboe, 1989). In OMZ regions, this implies that strong nutrient limitation in the surface ocean, which is associated with high C:N ratios in primary producers (e.g., data used in Pahlow et al. (2013)), should intensify denitrification in the OMZ relative to the export flux from the surface. Higher surface nutrient concentrations would then be expected to reduce C:N ratios in the export flux and hence have a somewhat mitigating effect. Since denitrification and anammox in the OMZ cause lower nitrate concentrations in upwelled waters, the variable stoichiometry of phytoplankton could add to the positive feedback between denitrification and N_2 fixation by increasing C:N ratios in response to decreasing surface nitrate concentrations.

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

3 Organic matter export and remineralization in the ETSP OMZ

3.1 Sinking of particles

Knowledge about particle fluxes in areas of tropical OMZs is scarce and predominantly derived from deep moored traps (Honjo et al., 2008) or models (Dale et al., 2015, Table 1). Only few studies have addressed upper ocean export fluxes and mesopelagic flux attenuation in tropical OMZs (Martin et al. (1987), Devol and Hartnett (2001) and VanMooy et al. (2002) for the Eastern Tropical Pacific by means of surface tethered sediment traps, Buesseler et al. (1998) for the Arabian Sea by means of ^{234}Th, and Iversen et al. (2010) at the northern edge of the ETNA OMZ by means of particle camera profiling). In the eastern tropical north Pacific (ETNP; Martin et al. (1987); Van Mooy et al. (2002); Devol and Hartnett (2001)), as well as in the ETSP (Martin et al. 1987; Dale et al., 2015) mesopelagic POC fluxes were less attenuated with depth (Martin curve exponent ‘b’ of 0.32-0.81) compared with the widely used “open ocean composite” of b=0.86 (Martin et al., 1987). Those studies indicate that a greater proportion of the sinking OM escapes degradation while sinking through the eastern tropical Pacific OMZ. On the other hand, it has been shown that microbial degradation of organic N and proteins under suboxia is not strongly affected (Pantoja et al., 2009; Pantoja et al., 2004; Van Mooy et al., 2002). In addition, organic matter degradation seems not to be significantly affected by decreased O_2 (Dale et al., 2015).

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

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

3.2 The impact of zooplankton for organic matter export and remineralization

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

Zooplankton and nekton organisms are essential components of the biological pump as they egest packaged organic matter as rapidly sinking fecal pellets. Many zooplankton and nekton species also feed in surface waters during the night and migrate to midwater depth at daybreak to avoid predation (Lampert, 1989), and to conserve energy (McLaren, 1963). This behavior is known as diel vertical migration (DVM) and also contributes to the activity of the biological pump as it enhances the export of organic matter from the photic zone by continued respiration, excretion and egestion in mid-water layers (Burd et al., 2010; Hannides et al., 2009; Robinson et al., 2010; Steinberg et al., 2000). In addition to changes in temperature with depth, DVM organisms experience low O_2 concentrations during the daytime in OMZ regions (Brewer and Peltzer, 2009; Paulmier et al., 2011), and O_2 concentrations below a certain threshold level can restrict DVM of most zooplankton and nekton (e.g. Hauss et al Biogeosciences Discussions). On a regional scale, the upper boundary of the oxycline is the single most critical factor structuring the habitat of most zooplankton organisms in the Peruvian upwelling system (Escribano et al., 2009). Nevertheless, some specifically adapted species are able to downregulate their metabolic activity at low oxygen levels and can remain at OMZ depth (non-migrators) or actively migrate into suboxic or anoxic OMZs (Seibel 2011, Kiko et al. 2015 a, b).

Abundance and biomass of metazoans living permanently at extremely low oxygen concentrations is rather low (Auel and Verheye, 2007; Escribano et al., 2009; Fernández-Álamo and Färber-Lorda, 2006; Saltzmann and Wishner, 1997; Wishner et al., 1998) although animals have evolved physiological (such as metabolic suppression) and/or morphological adaptations (such as increased gill surface area) allowing them to cope temporarily or permanently with O_2 depleted conditions (e.g. copepods, e.g. *Eucalanus inermis*, (Flint et al., 1991), euphausiids, e.g. *Euphausia mucronata* (Antezana, 2009), decapods (Pearcy et al., 1977), cephalopods, e.g. *Dosidicus gigas* (Rosa and Seibel, 2010), and teleosts (Friedman et al., 2012; Luo et al., 2000)). According to Seibel (2011), adaptations to low oxygen levels are needed below approximately 40 µmol O_2 kg^{-1}. Strong physiological adaptations seem thus necessary to thrive in the ETSP OMZ, but not in the ETNA OMZ where O_2 concentrations are normally greater than 40 µmol kg^{-1} (Teuber et al., 2013).

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

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

A recent model study quantifying the effect of viruses on ecosystem function in the ocean demonstrated that viruses affect biological productivity and remineralization (Weitz et al., 2015). In line with field studies (Breitbart, 2012), this model showed enhanced organic matter cycling, e.g. by cell lysis. Viruses lyse ~10-40% of the present prokaryotes every day (Suttle, 2005), which may- besides generally supplying nutrients to the surrounding waters- impact stoichiometry on smaller scales. Specifically, (cyano)phages in the ETSP have been shown to release micronutrients such as Fe into surrounding waters at an estimated flux of 10 pmol L^{-1} d^{-1} (Poorvin et al., 2004). Likewise, virus-induced bacterial lysis was calculated to contribute ~1-6 Gt N a^{-1} to bacterial primary production, which would significantly support phytoplankton production (Shelford et al., 2012). The transfer of nutrients from living organisms into the dissolved phase is called the 'viral shunt' (Breitbart, 2012). Besides the ‘viral shunt’, the model showed a reduced transfer of organic material to higher trophic levels, which was interpreted to stabilize primary production. Quantitatively, net primary production was found increased by ~11% in the presence of viruses. This strongly speaks for a viral impact on the efficiency of the biological pump (Azam, 1998). On the other side, viruses were shown to influence particle formation and disaggregation through discharging adhesive cell components (Peduzzi and Weinbauer, 1993) and cell lysis (Weinbauer et al., 2011), respectively.

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

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

3.4 Physical fluxes of DOM

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

(2011) found that mesoscale eddy activity in upwelling regimes results in a net reduction of biological productivity. Additionally, sub-mesoscale upwelling filaments can enhance the off-shelf flux of labile DOM (Alvarez-Salgado et al., 2001). Vertical velocities are higher at sub-mesoscale density fronts (Klein and Lapeyre, 2009; Levy et al., 2012; Thomas et al., 2008), which are prominent features in eastern boundary upwelling systems (Durski and Allen, 2005). These vertical velocities often extend to below the mixed layer (Klein et al., 2008), where they can drive sizeable vertical fluxes of solutes. Mahadevan (2014) proposes the subduction of organic matter-rich surface water into the subsurface layers within submesoscale cold filaments as a new export mechanism, which differs strongly from export via particle sinking. In filaments the organic matter is subducted together with large amounts of O_2, which then can directly be used for decomposition of organic matter. Vertical mixing of DOM from the euphotic into to the upper mesopelagic zone is another important transport mechanism in (sub)tropical waters (Hansell, 2002). The Bermuda Atlantic Time-Series Study provides a well-documented example of this process (Carlson et al., 1994). The efficiency of the downward DOM transport depends on the concentration gradient of DOM between the surface layer and the OMZ, and on the activity of the microbial population along this gradient. Produced by high primary production in upwelling regions, DOM can accumulate in the euphotic zone with maximum concentrations of 100-300 µmol C L^{-1} off Peru (Franz et al., 2012a; Romankevich and Ljutsarev, 1990). Due to the vicinity of the DOM-rich surface layer above and the O_2-depleted waters below the shallow and sharp oxycline of the Peruvian OMZ, physical vertical transport may bring large amounts of labile organic matter to the OMZ, where it may be utilized by heterotrophic communities (Hoppe et al., 2000; Hoppe and Ullrich, 1999; Pantoja et al., 2009). DOM supply via (sub-) mesoscale vertical transport processes and diapycnal mixing may therefore contribute importantly to sustaining microbial activity in the Peruvian OMZ and may thus largely impact biogeochemical cycles.

4 Sulfidic events in the ETSP

Oceanic sulfidic events are cases of extreme anoxia following periods of enhanced primary production and organic matter export. They are understood to mostly originate from sulfide production in sediments (Figure 5) and have been documented sporadically since the 19th century for the ETSP OMZ (Burtt, 1852; Dugdale et al., 1977). To date sulfidic events have been reported from the eastern tropical South Pacific, the Arabian Sea and the Benguela upwelling system by only a handful of studies and hence our current understanding of their regulation, initiation and termination is still limited. Possible analogs for oceanic events are permanently sulfidic areas in enclosed basins of the Baltic Sea (Brettar et al., 2006; Brettar and Rheinheimer, 1991; Glaubitz et al., 2009), the Black Sea (Glaubitz et al., 2010; Jørgensen et al., 1991; Sorokin et al., 1995), the Cariaco basin off Venezuela (Hayes et al., 2006; Taylor et al., 2001; Zhang and Millero, 1993) and Saanich Inlet in Canada (Tebo and Emerson, 1986; Walsh et al., 2009). Here, sulfide accumulates to milli-molar concentrations under O_2 and nitrate-free conditions and is released by a diffusive flux into the overlying pelagic water column where it reaches low micro-molar concentrations (Lavik et al., 2009; Schunck et al., 2013). These events are then terminated or detoxified in the pelagic water column by a community of sulfide-oxidizing bacteria. This occurs when sulfide and nitrate are both present thus stimulating sulfide-oxidizing nitrate-reducing bacteria (soNRB). soNRB re-oxidize sulfide back to sulfate or elemental sulfur while reducing nitrate to either N_2 via autotrophic denitrification or NH_4^+ via dissimilatory nitrate reduction to ammonium (Lam and Kuypers, 2011). If nitrate is limiting, sulfur is the more likely end product of sulfide oxidation, which occurs in the following reaction stoichiometry for the denitrification pathway, $2NO^-_3 + 5HS^- + 7H^+ \rightarrow N_2 + 5S^0 + 6H_2O$. A steady state is reached when the diffusive fluxes (mmol m^{-2} d^{-1}) of nitrate and sulfide are in a 1:2.5 ratio. If the sulfide flux exceeds the nitrate flux by more than a factor of 2.5, then sulfide will diffuse into the oxic layer (Lam and Kuypers, 2011). Importantly, the activity of soNRB help to detoxify sulfide to sulfur, preventing it from reaching overlying productive surface waters, hence most sulfidic events likely go unnoticed (Lavik et al., 2009). However, with the increase in eutrophication and the expansion of OMZs in both the Atlantic and Pacific (Stramma et al., 2008), sulfidic events are expected to become more frequent., as already demonstrated for a time series station in the Baltic Sea (Lennartz et al., 2014).

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

SUP05/ARCTIC96BD-19–clade, *Candidatus Ruthia magnifica*, and *Candidatus Vesicomyosocius okutanii*, but also epsilon- such as *Sulfurovum* spp. Metagenomics confirmed that all were capable of sulfide or sulfur oxidation, either with nitrate and oxygen (facultative soNRB) or exclusively with oxygen. Indeed, both subphyla appear to be ubiquitous in other seasonally oxic/anoxic waters and OMZs, (Canfield et al., 2010; Lavik et al., 2009; Stevens and Ulloa, 2008; Stewart et al., 2011; Stewart et al., 2012; Swan et al., 2011; Walsh et al., 2009). Both gamma- and epsilon- proteobacteria members are known chemolithoautotrophs, which assimilate carbon dioxide as the carbon source without the use of sunlight. Subsurface C- assimilation rates were between 0.9 to 1.4 µmol C L^{-1} d^{-1} during this sulfidic event. In this study, "dark" primary production had contributed up to 25% of the total CO_2 fixation in the Peruvian upwelling region at the time of sampling, which is comparable to values observed in the Baltic and Black Seas (Schunck et al. (2013) and references therein). Paradoxically, some of these studies showed that measured rates of CO_2 assimilation exceed rates possible by chemolithoautotrophic processes alone. Thus, while chemolithoautotrophic CO_2-fixation is considered a significant process, the specific activity and main contributors of CO_2-fixation during sulfidic events (down to the genus-level) still remain unknown.

Different from our current knowledge of OMZ sulfur cycling is whether the production of sulfide can originate as well from pelagic waters itself. Simultaneous reduction of different electron acceptors (like NO_3^-, SO_4^{2-} and CO_2) can occur in defined niches where particle aggregates have formed and are sinking through the water column (Wright et al., 2012). These aggregates, more commonly known as marine snow, contain micro-scale redoxclines under anoxic conditions (Alldredge and Cohen, 1987; Karl and Tilbrook, 1994; Woebken et al., 2007). Moreover, aggregate communities appear to be distinct from bulk water collected samples (Fuchsman et al., 2011). These communities were suggested to have active manganese reduction, sulfate reduction and sulfide oxidation at the interior of the aggregates. How much sulfide is generated in the water column during a sulfidic event is not well resolved. Nevertheless, *in situ* incubation experiments done in the Chilean upwelling have shown the capacity for sulfate reduction in the offshore OMZ occurring under thermodynamically unfavorable nitrate-rich conditions. In separate incubations measured rates of potential sulfide oxidation were larger than rates of sulfate reduction indicating that any produced sulfide is immediately re-oxidized (Canfield et al., 2010). The authors intriguingly suggested an active but cryptic sulfur cycle linked to nitrogen cycling in the pelagic OMZ. From a biogeochemical perspective large-scale sulfate-reduction coupled to organic matter remineralization releasing inorganic nitrogen could represent a significant supply of ammonium for anammox bacteria.

5 Trace gas production in OMZ waters

The upper 1000 m of the ocean (incl. the euphotic zone) are the key regions where the production of climate-relevant trace gases such as carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4) and dimethyl sulfide (DMS) occurs (see, e.g., Liss and Johnson (2014)). While the pathways of CO_2 and DMS are dominated by phytoplankton in the oxic euphotic zone, N_2O and CH_4 pathways are dominated by microbial processes at midwater depth (i.e. in the OMZ). This is especially important since some OMZs are connected to coastal upwelling regions where OMZ waters — enriched in both nutrients and trace gases such as CO_2, N_2O and CH_4 — are brought to the surface fuelling phytoplankton blooms and releasing trace gases to the atmosphere (see, e.g., Capone and Hutchins (2013)). Thus, although they are usually not in direct contact with the atmosphere, OMZs play an important role for oceanic emissions of climate-relevant trace gases (see e.g. Arévalo-Martinez et al. (2015)).

5.1 Nitrous oxide (N_2O) in OMZ

A comprehensive overview of both nitrous oxide (N_2O) distributions and pathways in OMZ has been published in (Naqvi et al., 2010). Therefore, we concentrate here on recent findings from the ETNA and ETSP.

N_2O production in the ocean is dominated by microbial nitrification and denitrification processes. It is formed as a by-product during nitrification and as an intermediate during denitrification. The paradigm that N_2O is exclusively produced by bacteria has been challenged by the discovery of nitrifying (i.e. NH_4^+ oxidising) archaea (e.g., *Cand. Nitrosopelagicus brevis*,see above) dominating N_2O production in the ETSP and ETNA (Löscher et al., 2012), which is supported by results of a culture study (Löscher et al., 2012) and a marine microbial enrichment experiment (Santoro et al., 2011). The production of N_2O by archaea (and bacteria) depends on dissolved O_2 and increases with decreasing O_2 concentrations (Frame and Casciotti, 2010; Löscher et al., 2012). Denitrifying bacteria do not produce N_2O in the presence of O_2 (> 10 µmol kg^{-1}); however, when O_2 concentrations are approaching 0 µmol kg^{-1}, N_2O is consumed during denitrification. There is no N_2O production under anoxic conditions. The significance of N_2O production during anammox (Kartal et al., 2007) and DNRA (Giblin et al., 2013) in OMZs (see Section 5) remains to be proven.

The detailed investigation of ΔN_2O/AOU (= excess N_2O/apparent oxygen utilization) and ΔN_2O/ $\Delta^{15}NO_3^-$ relationships from the ETNA and ETSP revealed two facts (Ryabenko et al., 2012): (i) The lower O_2 concentrations found in the core of the OMZ of the ETSP (< 5 µmol kg^{-1}) favour N_2O consumption by denitrification which is not observed in the ETNA because of its comparably high O_2 concentrations and (ii) the maximum observed N_2O concentrations were higher in the ETSP than in the ETNA. This is in line with the results of two model studies of N_2O in the ETSP by Zamora et al. (2012) and Cornejo and Farias (2012), which suggested that the switching point between N_2O production and N_2O consumption occurs at higher O_2 concentration (~ 8-10 µmol kg^{-1}) than previously thought.

In contrast to the open ocean, OMZs in coastal (i.e. shelf) regions show a higher spatial and temporal variability: Seasonally occurring suboxic or even anoxic/sulfidic OMZs have been observed in coastal regions worldwide (see e.g. Diaz and Rosenberg (2008)). One of the most prominent areas where widespread sulfidic conditions have been recently observed is the shelf off Peru (Schunck et al., 2013) (Section 5). Figure 6 shows the distribution of N_2O, water temperature, nutrients and H_2S during the sulfidic event described by Schunck et al. (2013) on the shelf off Peru during December 2008/January 2009. Here, extreme N_2O concentrations are found at the boundary to the H_2S containing bottom waters. No N_2O is found in the core sulfidic layer. This suggests again that there is a narrow range of low O_2 concentrations which is associated with exceptionally high N_2O production. As soon as the O_2 concentrations are close to zero (anoxic/sulfidic conditions) N_2O production turns into N_2O consumption. Similar N_2O distributions during anoxic/sulfidic events were found off the west coast of India, in the Gotland Deep (central Baltic Sea) and in Saanich Inlet (Brettar and Rheinheimer, 1991; Cohen, 1978; Naqvi et al., 2000). Brettar and Rheinheimer (1991) suggested a close coupling between H_2S oxidation and NO_3^- reduction in a narrow layer where NO_3^- and H_2S coexist. This is in line with recent findings from the anoxic event off Peru by Schunck et al. (2013) and similar to the suggestion of a cryptic sulfur cycle where sulfate reduction is coupled to rapid H_2S oxidation by NO_3^- proposed for the OMZ off Chile by Canfield et al. (2010).

5.2 The role of OMZs in trace gas emissions

In OMZs with O_2 concentrations below 20 µmol kg^{-1}, N_2O production does not take place in the core of the OMZ. Instead, N_2O production is found at the oxycline. Exceptionally high N_2O concentrations have so far only been found in temporarily occurring anoxic/sulfidic regions off Peru/Chile and West India (Farías et al., 2015; Naqvi et al., 2010). Stagnant sulfidic systems such as in the Baltic and Black Seas as well as the Cariaco Basin, have shown only slightly enhanced N_2O concentrations at the oxic/anoxic interfaces (Bange et al., 2010, and references therein). This implies that significant pulses of N_2O emissions to the atmosphere occur only when a shallow coastal system rapidly shifts from oxic to anoxic/sulfidic conditions and vice versa (Bange et al., 2010). This can be explained by a lag of N_2O reduction by denitrifiers, when they switch from oxygen to nitrogen respiration (Codispoti, 2010) or N_2O production during the reestablishment of nitrification after O_2 ventilation (Schweiger et al., 2007).

CH_4 production is also tightly connected to OMZs (see overview in Naqvi et al., 2010). Similar to N_2O, upwelling areas are considerable hotspots for CH_4 emissions, albeit organic material-enriched shallow coastal zones such as estuaries and mangroves or shallow sediments with geological CH_4 sources show higher emissions (Bakker et al., 2014).

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

5.3 Trace gas production in OMZ and environmental changes

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

OMZs. In general, we might expect enhanced production of N_2O, CH_4 and DMS in OMZs because of the on-going loss of O_2.

Deoxygenation in open ocean and coastal environments may lead, on the one hand, to enhanced N_2O production when approaching the N_2O production/consumption switching point (see above), but on the other hand, when O_2 concentrations fall below the switching point this may lead to a consumption of N_2O (Zamora et al., 2012). Moreover, we do not know whether the frequency of coastal anoxic events will continue to increase and how this may affect the coastal net N_2O production/consumption. A recent modelling study on the influence of anthropogenic nitrogen aerosol deposition on N_2O production revealed that the effect is small on a global scale but that the OMZ of the Arabian Sea is especially sensitive to atmospheric nitrogen deposition resulting in an enhanced N_2O production (Suntharalingam et al., 2012).

6 Conclusions

While there is a growing amount of data on primary production and the pelagic N cycle in and associated to OMZ waters, quantitative estimates of microbial production and respiration, particularly at ultra-low O_2 levels, are still not fully explored. This translates into an uncertainty concerning the origin of the N deficit. While it had been clearly demonstrated that N loss processes respond sensitively to minimal changes in O_2 (Dalsgaard et al., 2014), a potential uncertainty may result from additional processes, such as preferential P release directly in the water column may be important to create the N deficit in the water column. In this context, the character and size were shown important (DeVries et al., 2014), therefore linking P release from particles to the character of N loss (Babbin et al., 2014). The character of the N loss/ N deficit term is, however, highly important, as it determines the extent of N depletion of the entire OMZ due to the above explained stoichiometric discrepancy between N loss and N_2 fixation. Interestingly, a strong impact of decadal climate variations on respiration rates, primary production and the intensity of N loss has been described for the South Pacific (Deutsch et al., 2011). This may directly link to the character of N loss derived from our and other measurements and has to be taken into consideration for future studies.

A coupling via the proposed primary production chain may indeed act in OMZs associated to upwelling systems (an overview of major processes in the ETNA and ETSP is depicted in Fig. 7). The important term of organic matter export, either horizontally or vertically needs more dedicated investigations: To date, a quantification of DOM supply via (sub-) mesoscale vertical transport processes out of the OMZ area and diapycnal mixing sustaining microbial activity in the Peruvian OMZ is missing. Further, for POM supply to the OMZ, DVM seems to play a key role, despite some quantitative uncertainties. Although some organisms performing DVM have certain strategies to cope with anoxic conditions, mostly by down-regulating the aerobic metabolism, there are limits for zooplankton and nekton. Thus, a reduction of OM export by DVM may result with a further expansion and deoxygenation of OMZs. Deutsch et al (2014) describe in this context that a decrease of the habitat caused by global warming and ocean deoxygenation increases competition among species and may even result in a loss of metabolic functionality by 20%.

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

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

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

A critical consequence of ocean deoxygenation is visible from the comparison of the ETSP and ETNA regions: Massive supersaturation of N_2O, connected to sulfidic plumes, has been detected repeatedly, in the ETSP. OMZs are important sites of enhanced production of climate relevant trace gases such as N_2O, CH_4, and DMS. N_2O production is significantly enhanced at oxic/anoxic boundaries of OMZs and we suggest that it mainly results from habitat compression, where in extreme cases (such as sulfidic events, sharpening gradients) nitrification and denitrification can occur simultaneously. Maximum N_2O concentrations and subsequent emissions to the atmosphere have been observed in dynamic coastal systems that rapidly shift from oxic to anoxic conditions and vice versa. Although OMZs are usually not in direct contact with the atmosphere, their vicinity to coastal upwelling systems plays an important role for oceanic emissions of climate-relevant trace gases such as N_2O, CH_4, and DMS with potential feedbacks on global warming, which then may again impact on ocean deoxygenation. Our studies from the ETSP (Arevalo-Martinez, 2015, 2016, Kock et al., 2016) confirm intense production of N_2O in the coastal upwelling. This is in line with an increase of N2O production from OMZ areas as concluded from forced climate models. However, the same model describes a global decrease of N_2O formation by 4-12%, mostly linked to the western basins of the Pacific and Atlantic oceans (Martinez-Rey et al., 2015).

Marine ecosystems and biogeochemical cycles are increasingly impacted by a growing number of stress factors, some of which act locally, such as eutrophication and pollution, others globally. Global stressors are associated with anthropogenic carbon dioxide (CO_2) emissions and affect the ocean either directly through CO_2-induced acidification or indirectly through climate change-induced ocean warming and deoxygenation (Ciais et al., 2013). How these stressors will impact marine ecosystems and biogeochemistry, individually or in combination, is still largely unknown.

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

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

7 Outlook

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

Future studies in the framework of the SFB 754 will therefore combine measurements of particle flux, zooplankton abundance, microbial activities and O_2 concentrations in order to answer the following key questions:

I. What is the effect of low oxygen conditions (below 20 µmol kg^{-1}) on organic matter degradation? And what is the partitioning between DOM and POM in OMZ waters?

II. How do the rates of nutrient cycling and loss in OMZs relate to particles and associated microniches?

III. What are the rates of oxygen supply and consumption in the upper OMZ? And what is regulating respiration rates?

IV. Do small-scale processes (e.g. viral lysis) affect fluxes on larger scales? And how can models represent these important processes?

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References

Alldredge, A. L. and Cohen, Y.: Can microscale chemical patches persist in the sea? Microelectrode study of marine snow, fecal pellets., Science, 235, 689-691, 1987.

Alvarez-Salgado, X. A., Doval, M. D., Borges, A. V., Joint, I., Frankignoulle, M., Woodward, E. M. S., and Figueiras, F. G.: Off-shelf fluxes of labile materials by an upwelling filament in the NW Iberian Upwelling System, Progress in Oceanography, 51, 321-337, 2001.

Anderson, T. R. and Williams, P. J.: Modelling the seasonal cycle of dissolved organic carbon at Station E$_1$ in the English Channel, Estuarine, Coastal and Shelf Science, 46, 93-109, 1998.

Antezana, T.: Species-specific patterns of diel migration into the Oxygen Minimum Zone by euphausiids in the Humboldt Current Ecosystem, Progress in Oceanography, 83, 228-236, 2009.

Arévalo-Martínez, D. L., Kock, A., Löscher, C. R., Schmitz, R. A., and Bange, H. W.: Evidence of massive nitrous oxide emissions from the tropical South Pacific Ocean, Nature Geosci., 8, 530-533, 2015.

Arévalo-Martínez, D. L., Kock, A., Löscher, C. R., Schmitz, R. A., Stramma, L., and Bange, H. W.: Influence of mesoscale eddies on the distribution of nitrous oxide in the eastern tropical South Pacific, Biogeosciences, 13, 1105-1118, doi:10.5194/bg-13-1105-2016, 2016.

Auel, H. and Verheye, H. M.: Hypoxia tolerance in the copepod Calanoides carinatus and the effect of an intermediate oxygen minimum layer on copepod vertical distribution in the northern Benguela Current upwelling system and the Angola-Benguela, Front. J. Exp. Mar. Biology and Ecology, 352, 234-243, 2007.

Azam, F.: Microbial control of oceanic carbon flux: the plot thickens, Science, 280, 694-696, 1998.

Babbin, A.R., Keil, R.G., Devol, A.H. and Ward, B.B.**:** Organic Matter Stoichiometry, Flux, and Oxygen Control Nitrogen Loss in the Ocean. Science, 344:406-408, doi: 10.1126/science.1248364, 2014.

Baker, A. R., Thomas, M., Bange, H. W., and Plasencia Sánchez, E.: Soluble trace metals in aerosols over the tropical south-east Pacific offshore of Peru, Biogeosciences, 13, 817-825, 2016.

Bakker, D. C. E., Bange, H. W., Gruber, N., Johannessen, T., Upstill-Goddard, R. C., Borges, A. V., Delille, B., Löscher, C. R., Naqvi, S. W. A., Omar, A. M., and Santana-Casiano, J. M.: Air-sea interactions of natural long-lived greenhouse gases (CO_2, N_2O, CH_4) in a changing climate. In: Ocean-Atmosphere Interactions of Gases and Particles, Liss, P. S. and Johnson, M. T. (Eds.), Springer Verlag, Heidelberg, 2014.

Bange, H. W., Freing, A., Kock, A., and Löscher, C. R.: Marine Pathways to Nitrous Oxide. In: Nitrous oxide and Climate Change, Smith, K. A. (Ed.), Earthscan, London, Washington, 2010.

Behrenfeld, MJ, PG Falkowski: Photosynthetic rates derived from satellite-based chlorophyll concentration,Limnology and Oceanography,1997a, Volume 42: 1-20

Beman, J. M. and Carolan, M. T.: Deoxygenation alters bacterial diversity and community composition in the oceans largest oxygen minimum zone, Nat Commun, 4, doi: 10.1038/ncomms3705, 2013.

Bertics, V. J., Löscher, C. R., Salonen, I., Dale, A. W., Gier, J., Schmitz, R. A., and Treude, T.: Occurrence of benthic microbial nitrogen fixation coupled to sulfate reduction in the seasonally hypoxic Eckernförde Bay, Baltic Sea, Biogeosciences, 10, 1243-1258, 2013.

Bianchi, D., Babbin, A. R., and Galbraith, E. D.: Enhancement of anammox by the excretion of diel vertical migrators, Proceedings of the National Academy of Sciences of the United States of America, 111, 15653-15658, 2014.

Bijma, J., Portner, H.-O., Yesson, C., and Rogers, A. D.: Climate change and the oceans--what does the future hold?, Marine pollution bulletin, 74, 495-505, 2013.

Bohlen, L., Dale, A. W., Sommer, S., Mosch, T., Hensen, C., Noffke, A., Scholz, F., and Wallmann, K.: Benthic Nitrogen Cycling Traversing the Peruvian Oxygen Minimum Zone, Geochimica et Cosmochimica Acta, 75, 6094-6111, 2011.

Bonnet, S., Dekaezemacker, J., Turk-Kubo, K. A., Moutin, T., Hamersley, R. M., Grosso, O., Zehr, J. P., and Capone, D. G.: Aphotic N2 Fixation in the Eastern Tropical South Pacific Ocean, PlosOne, 8, doi:10.1371/journal.pone.0081265, 2013.

Bopp, L., Resplandy, L., Orr, J. C., Doney, S. C., Dunne, J. P., Gehlen, M., Halloran, P., Heinze, C., Ilyina, T., Séférian, R., Tjiputra, J., and Vichi, M.: Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models, Biogeosciences, 10, 6225-6245, 2013.

Breitbart, M.: Marine viruses: Truth or dare, Annual Review of Marine Science, 4, 425-448, 2012.

Brettar, I. and Rheinheimer, G.: Denitrification in the Central Baltic - Evidence for H2s-Oxidation as Motor of Denitrification at the Oxic-Anoxic Interface, Marine Ecology Progress Series, 77, 157-169, 1991.

Brettar, I., Labrenz, M., Flavier, S., Botel, J., Kuosa, H., Christen, R., and Hofle, M. G.: Identification of a *Thiomicrospira denitrificans*-Like Epsilonproteobacterium as a Catalyst for Autotrophic Denitrification in the Central Baltic Sea, Appl Environ Microbiol, 72, 1364-1372, 2006.

Brewer, P. G. and Peltzer, E. T.: Limits to Marine Life, Science, 324, 347-348, 2009.

Buesseler, K. O., Ball, L., Andrews, J., Benitez-Nelson, C., Belastock, R., Chai, F., and Chao, Y.: Upper ocean Export of Particulate Organic Carbon in the Arabian Sea derived from Thorium-234., Deep-Sea Research Part II, 45, 2461-2487, 1998.

Burd, A. B., Hansell, D. A., Steinberg, D. K., Anderson, T. R., Aristegui, J., Baltar, F., Beaupre, S. R., Buesseler, K. O., DeHairs, F., Jackson, G. A., Kadko, D. C., Koppelmann, R., Lampitt, R. S., Nagata, T., Reinthaler, T., Robinson, C., Robison, B. H., Tamburini, C., and Tanaka, T.: Assessing the apparent imbalance between geochemical and biochemical indicators of meso- and bathypelagic biological activity: What the @$#! is wrong with present calculations of carbon budgets?, Deep-Sea Research Part Ii-Topical Studies in Oceanography, 57, 1557-1571, 2010.

Burtt, J.: On fish destroyed by sulphuretted hydrogen in the Bay of Callao, Am J Sci, 2, 433-434, 1852.

Canfield, D. E.: Models of oxic respiration, denitrification and sulfate reduction in zones of coastal upwelling, Geochimica et Cosmochimica Acta, 70, 5753-5765, 2006.

Canfield, D. E., Stewart, F. J., Thamdrup, B., De Brabandere, L., Dalsgaard, T., Delong, E. F., Revsbech, N. P., and Ulloa, O.: A Cryptic Sulfur Cycle in Oxygen-Minimum-Zone Waters off the Chilean Coast, Science, 330, 1375-1378, 2010.

Capone, D. G., Zehr, J. P., Paerl, H. W., Bergman, B., and Carpenter, E. J.: Trichodesmium, a globally significant marine cyanobacterium, Science, 276, 1221-1229, 1997.

Capone, D. G. and Hutchins, D. A.: Microbial biogeochemistry of coastal upwelling regimes in a changing ocean, Nature Geoscience, 6, 711-717, 2013.

Carlson, C. A., Ducklow, H. W., and Michaels, A. F.: Annual flux of dissolved organic carbon from the euphotic zone in the Northwestern Sargasso Sea, Nature, 371, 405-408, 1994.

Caron, D. A., Goldman, J. C., and Dennett, M. R.: Experimental demonstration of the roles of bacteria and bacterivorous protozoa in plankton nutrient cycles, Hydrobiologia, 159, 27-40, 1988.

Carr, M. E., Strub, P. T., Thomas, A., and Blanco, J. L.: Evolution of 1996-1999 La Niña and El Niño Conditions Off the Western Coast of South America: A Remote Sensing Perspective. Journal of Geophysical Research, 107, (C12)3236, doi:10.1029/2001JC001183, 2002.

Cassman, N., Prieto-Davó, A., Walsh, K., Silva, G. G., Angly, F., Akhter, S., Barott, K., Busch, J., McDole, T., Haggerty, J. M., Willner, D., Alarcón, G., Ulloa, O., DeLong, E. F., Dutilh, B. E., Rohwer, F., Dinsdale, E. A.: Oxygen minimum zones harbour novel viral communities with low diversity. Environmental Microbiology, 14:3043–3065. doi: 10.1111/j.1462-2920.2012.02891.x, 2012.

Chavez, F. P., Messíe, M.: A comparison of eastern boundary upwelling ecosystems. Prog. Oceanogr.83:80–96, 2009.

Ciais, P., C. Sabine, G. Bala, L. Bopp, V. Brovkin, J. Canadell, A. Chhabra, R. DeFries, J. Galloway, M. Heimann, C. Jones, C. Le Quéré, R.B. Myneni, S. Piao, and Thornton, P.: Carbon and Other Biogeochemical Cycles. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Stocker, T. F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, and Midgley, P. M. (Eds.), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.

Cocco, V., Joos, F., Steinacher, M., Frölicher, T. L., Bopp, L., Dunne, J., Gehlen, M., Heinze, C., Orr, J., Oschlies, A., Schneider, B., Segschneider, J., and Tjiputra, J.: Oxygen and indicators of stress for marine life in multi-model global warming projections, Biogeosciences, 10, 1849-1868, 2013.

Codispoti, L. A.: Interesting Times for Marine N_2O, Science, 327, 1339-1340, 2010.

Codispoti, L. A., Brandes, J. A., Christensen, J. P., Devol, A. H., Naqvi, S. W. A., Paerl, H. W., and Yoshinari, T.: The oceanic fixed nitrogen and nitrous oxide budgets: Moving targets as we enter the anthropocene?, Scientia Marina, 65, 85-105, 2001.

Codispoti, L. A.: An oceanic fixed nitrogen sink exceeding 400 Tg Na(-1) vs the concept of homeostasis in the fixed-nitrogen inventory, Biogeosciences, 4, 233-253, 2007.

Cohen, Y.: Consumption of dissolved nitrous oxide in an anoxic basin, Saanich Inlet, British Columbia, Nature, 272, 235-237, 1978.

Conway, T. M. and John, S. G.: Quantification of dissolved iron sources to the North Atlantic Ocean, Nature, 511, 212-215, 2014.

Cornejo, M. and Farias, L.: Following the N2O consumption in the oxygen minimum zone of the eastern South Pacific, Biogeosciences, 9, 3205-3212, 2012.

Dalsgaard, T., Stewart, F. J., Thamdrup, B., De Brabandere, L., Revsbech, N. P., Ulloa, OsvO., Canfield, D. E., DeLong, E. F.: Oxygen at nanomolar levels reversibly suppresses process rates and gene expression in anammox and denitrification in the oxygen minimum zone off Northern Chile. mBio (Online), Vol. 5, No. 6, e01966-14, p. 1-14, 2014.

Dale, A. W., Sommer, S., Lomnitz, U., Montes, I., Treude, T., Liebetrau, V., Gier, J., Hensen, C., Dengler, M., Stolpovsky, K., Bryant, L. D., and Wallmann, K.: Organic carbon production, mineralisation and preservation on the Peruvian margin, Biogeosciences, 12, 1537-1559, 2015.

Dekaezemacker, J., Bonnet, S., Grosso, O., Moutin, T., Bressac, M., and Capone, D. G.: Evidence of active dinitrogen fixation in surface waters of the eastern tropical South Pacific during El Nino and La Nina events and evaluation of its potential nutrient controls, Glob. Biogeochem. Cycle, 27, 768-779, 2013.

del Giorgio, P. A. and Cole, J. J.: Bacterial growth efficiency in natural aquatic systems, Annual Review of Ecology and Systematics, 29, 503-541, 1998.

Deutsch, C., Sarmiento, J. L., Sigman, D. M., Gruber, N., and Dunne, J. P.: Spatial coupling of nitrogen inputs and losses in the ocean, Nature, 445, 163-167, 2007.

Deutsch, C., Brix, H., Ito, T., Frenzel, H., and Thompson, L.: Climate forcing of ocean hypoxia, Science, 333, 336-339, 2011.

Deutsch, C., Berelson, W., Thunell, R., Weber, T., Tems, C., McManus, J., Crusius, J., Ito, T., Baumgartner, T., Ferreira, V., Mey, J., van Geen, A.: Centennial changes in North Pacific anoxia linked to tropical trade winds. Science, 345(6197), 665-668, 2014.

DeVries, T., Liang, J. H., Deutsch, C.: A mechanistic particle flux model applied to the oceanic phosphorus cycle. Biogeosciences, 11(19), 5381-5398, 2011.

Devol, A. H.: Denitrification including anammox. In: Nitrogen in the Marine Environment, 2nd Edition, Capone, D. G., Bronk, D. A., Mulholland, M. R., and Carpenter, E. J. (Eds.), Elsevier, Amsterdam, 2008.

Devol, A. H. and Hartnett, H. E.: Role of the oxygen minimum zone in transfer of organic carbon to the deep ocean., Limnology and Oceanography., 46, 1684-1690, 2001.

Diaz, R. J. and Rosenberg, R.: Spreading dead zones and consequences for marine ecosystems, Science, 321, 926-929, 2008.

Dietze, H. and Loeptien, U.: Revisiting ``nutrient trapping'' in global coupled biogeochemical ocean circulation models, Glob. Biogeochem. Cycle, 27, 265-284, 2013.

Duce, R. A., LaRoche, J., Altieri, K., Arrigo, K. R., Baker, A. R., Capone, D. G. et al.: Impacts of atmospheric anthropogenic nitrogen on the open ocean. Science, 320: 893–897. 2008.

Dugdale, R. C., Goering, J. J., Barber, R. T., Smith, R. L., and Packard, T. T.: Denitrification and Hydrogen Sulfide in the Peru Upwelling Region during 1976, Deep-Sea Research, 24, 601-608, 1977.

Durski, S. M. and Allen, J. S.: Finite-amplitude evolution of instabilities associated with the coastal upwelling front, Journal of Physical Oceanography, 35, 1606-1628, 2005.

Emery, K. O., Orr, W. L., and Rittenberg, S. C.: Nutrient budget in the ocean. In: Essays in the Natural Sciences in Honor of Captain Alan Hanock, Univ. of S. Calif. Press, 229-310 Los Angeles, 1955.

Escribano, R., Hidalgo, P., and Krautz, C.: Zooplankton associated with the oxygen minimum zone system in the northern upwelling region of Chile during March 2000, Deep-Sea Research Part Ii-Topical Studies in Oceanography, 56, 1049-1060, 2009.

Farías, L., Besoain, V., and García-Loyola, S.: Presence of nitrous oxide hotspots in the coastal upwelling area off central Chile: an anlysis of temproral variability based on ten years of a biogeochemiocal time series, Environ. Res. Lett., 10 (4), doi:10.1088/1748-9326/10/4/044017 2015.

Fernández-Álamo, M. A. and Färber-Lorda, J.: Zooplankton and the oceanography of the eastern tropical Pacific: a review, Prog. Oceanogr., 69, 318-359, 2006.

Fernandez, C., Farias, L., and Ulloa, O.: Nitrogen Fixation in Denitrified Marine Waters, Plos One, 6, 9, 2011.

Fischer, G., Karakas, G., Blaas, M., Ratmeyer, V., Nowald, N., Schlitzer, R., Helmke, P., Davenport, R., Donner, B., Neuer, S., and Wefer, G.: Mineral ballast and particle settling rates in the coastal upwelling system off NW Africa and the South Atlantic, International Journal of Earth Sciences, 98, 281-298, 2009.

Flint, M., Drits, A., and Pasternak, A.: Characteristic features of body composition and metabolism in some interzonal copepods, Marine Biology, 111, 199-205, 1991.

Frame, C. H. and Casciotti, K. L.: Biogeochemical controls and isotopic signatures of nitrous oxide production by a marine ammonia-oxidizing bacterium, Biogeosciences, 7, 2695-2709, 2010.

Francis, C. A., Beman, J. M., and Kuypers, M. M. M.: New processes and players in the nitrogen cycle: the microbial ecology of anaerobic and archaeal ammonia oxidation, Isme Journal, 1, 19-27, 2007.

Franz, J., Krahmann, G., Lavik, G., Grasse, P., Dittmar, T., and Riebesell, U.: Dynamics and stoichiometry of nutrients and phytoplankton in waters influenced by the oxygen minimum zone in the eastern tropical Pacific, Deep-Sea Research Part I: Oceanographic Research Papers, 62, 20-31, 2012a.

Franz, J. M. S., Hauss, H., Sommer, U., Dittmar, T., and Riebesell, U.: Production, partitioning and stoichiometry of organic matter under variable nutrient supply during mesocosm experiments in the tropical Pacific and Atlantic Ocean, Biogeosciences, 9, 4629-4643, 2012b.

Friedman, J. R., Condon, N. E., and Drazen, J. C.: Gill surface area and metabolic enzyme activities of demersal fishes associated with the oxygen minimum zone off California, Limnology and Oceanography, 57, 1701, 2012.

Fuchsman, C. A., Kirkpatrick, J. B., Brazelton, W. J., Murray, J. W., and Staley, J. T.: Metabolic strategies of free-living and aggregate-associated bacterial communities inferred from biologic and chemical profiles in the Black Sea suboxic zone, FEMS Microbiol Ecol, 78, 586-603, 2011.

Ganesh, S., Bristow, L. A., Larsen, M., Sarode, N., Thamdrup, B., and Stewart, F. J.: Size-fraction partitioning of community gene transcription and nitrogen metabolism in a marine oxygen minimum zone, ISME J, doi: doi:10.1038/ismej.2015.44, 2015. 1-15, 2015.

Garber, J. H.: Laboratory Study of Nitrogen and Phosphorus Remineralization during the Decomposition of Coastal Plankton and Seston, Estuarine, Coastal and Shelf Science, 18, 685-702, 1984.

Giblin, A. E., Tobias, C. R., Song, B., Weston, N., Banta, G. T., and Rivera-Monroy, V. H.: Dissimilatory nitrate reduction to ammonium (DNRA), Oceanography, 26, 124-131, 2013.

Glaubitz, S., Labrenz, M., Jost, G., and Jürgens, K.: Diversity of active chemolithoautotrophic prokaryotes in the sulfidic zone of a Black Sea pelagic redoxcline as determined by rRNA-based stable isotope probing, FEMS Microbiol Ecol, 74, 32-41, 2010.

Glaubitz, S., Lueders, T., Abraham, W. R., Jost, G., Jürgens, K., and Labrenz, M.: ^{13}C-isotope analyses reveal that chemolithoautotrophic *Gamma-* and *Epsilonproteobacteria* feed a microbial food web in a pelagic redoxcline of the central Baltic Sea, Environ Microbiol, 11, 326-337, 2009.

Großkopf, T., Mohr, W., Baustian, T., Schunck, H., Gill, D., Kuypers, M. M. M., Lavik, G., Schmitz, R. A., Wallace, D. W. R., and LaRoche, J.: Doubling of marine dinitrogen-fixation rates based on direct measurements, Nature, 488, 361-364, 2012.

Gruber, N. and Sarmiento, J. L.: Global patterns of marine nitrogen fixation and denitrification, Glob. Biogeochem. Cycle, 11, 235-266, 1997.

Gruber, N.: The dynamics of the marine nitrogen cycle and its influence on atmospheric CO_2 variations. In: The ocean carbon cycle and climate, NATO ASI Series, Follows, M. and Oguz, T. (Eds.), Kluwer Academic, Dordrecht, 2004.

Gruber, N.: Warming up, turning sour, losing breath: ocean biogeochemistry under global change, Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences, 369, 1980-1996, 2011.

Gruber, N., Lachkar, Z., Frenzel, H., Marchesiello, P., Münnich, M., McWillisams, J., C., , Nagai, T., and Plattner, G.: Eddy-induced reduction of biological production in eastern boundary upwelling systems, Nature Geoscience 4, 787–792, 2011.

Halm, H., Musat, N., Lam, P., Langlois, R., Musat, F., Peduzzi, S., Lavik, G., Schubert, C. J., Sinha, B., LaRoche, J., and Kuypers, M. M. M.: Co-occurrence of denitrification and nitrogen fixation in a meromictic lake, Lake Cadagno (Switzerland), Environ. Microbiol., 11, 1945-1958, 2009.

Hamersley, M. R., Lavik, G., Woebken, D., Rattray, J. E., Lam, P., Hopmans, E. C., Damste, J. S. S., Kruger, S., Graco, M., Gutierrez, D., and Kuypers, M. M. M.: Anaerobic ammonium oxidation in the Peruvian oxygen minimum zone, Limnology and Oceanography, 52, 923-933, 2007.

Hannides, C. C. S., Landry, M. R., Benitez-Nelson, C. R., Styles, R. M., Montoya, J. P., and Karl, D. M.: Export stoichiometry and migrant-mediated flux of phosphorus in the North Pacific Subtropical Gyre, Deep-Sea Research Part I-Oceanographic Research Papers, 56, 73-88, 2009.

Hansell, D. A.: DOC in the global ocean cycle, In: D. A. Hansell and C. A. Carlson [eds.], Biogeochemistry of marine dissolved organic matter. Elsevier., 2002. 2002.

Hayes, M. K., Taylor, G. T., Astor, Y., and Scranton, M. I.: Vertical distributions of thiosulfate and sulfite in the Cariaco Basin, Limnol Oceanogr, 51, 280-287, 2006.

Honjo, S., Manganini, S. J., Krishfield, R. A., and Francois, R.: Particulate organic carbon fluxes to the ocean interior and factors controlling the biological pump: A synthesis of global sediment trap programs since 1983, Progress in Oceanography, 76, 217-285, 2008.

Hoppe, H.-G., Ullrich, S., von Bröckel, K., and Sellmer, C.: Bacterial C-demand (mineralization) in the aphotic depths of the Arabian Sea exceeds measured C-fluxes from the euphotic zone. , In: B. Donner, G. Wefer: Berichte aus dem Fachbereich Geowissenschaften, Universität Bremen, No 162:51., 2000. 2000.

Hoppe, H. G. and Ullrich, S.: Profiles of ectoenzymes in the Indian Ocean: phenomena of phosphatase activity in the mesopelagic zone, Aquatic Microbial Ecology, 19, 139-148, 1999.

Houlton, B. Z., Wang, Y.-P., Vitousek, P. M., and Field, C. B.: A unifying framework for dinitrogen fixation in the terrestrial biosphere, 454, doi: doi:10.1038/nature07028, 2008. 327-330, 2008.

Ingall, E. and Jahnke, R.: Evidence for enhanced phosphorus regeneration from marine sediments overlain by oxygen depleted waters., Geochimica et Cosmochimica Acta 58, 2571-2575, 1994.

Iversen, M. H., Nowald, N., Ploug, H., Jackson, G. A., and Fischer, G.: High resolution profiles of vertical particulate organic matter export off Cape Blanc, Mauritania: Degradation processes and ballasting effects, Deep-Sea Research Part I-Oceanographic Research Papers, 57, 771-784, 2010.

Jilbert, T., Slomp, C. P., Gustafsson, B. G., and Boer, W.: Beyond the Fe-P-redox connection: preferential regeneration of phosphorus from organic matter as a key control on Baltic Sea nutrient cycles, Biogeosciences, 8, 1699-1720, doi:10.5194/bg-8-1699-2011, 2011

Jørgensen, B. B., Fossing, H., Wirsen, C. O., and Jannasch, H. W.: Sulfide oxidation in the anoxic Black Sea chemocline, Deep-Sea Res, 38, S1083-S1103, 1991.

Kalvelage, T., Jensen, M. M., Contreras, S., Revsbech, N. P., Lam, P., Gunter, M., LaRoche, J., Lavik, G., and Kuypers, M. M. M.: Oxygen Sensitivity of Anammox and Coupled N-Cycle Processes in Oxygen Minimum Zones, PLoS ONE, 6, 12, 2011.

Kalvelage, T., Lavik, G., Lam, P., Contreras, S., Arteaga, L., Löscher, C. R., Oschlies, A., Paulmier, A., Stramma, L., and Kuypers, M. M. M.: Nitrogen cycling driven by organic matter export in the South Pacific oxygen minimum zone, Nature Geoscience, 6, 228-234, 2013.

Kalvelage, T., Lavik, G., Jensen, M. M., Revsbech, N. P., Löscher, C. R., Schunck, H., Desai, D. K., Hauss, H., Kiko, R., Holtappels, M., LaRoche, J., Schmitz, R. A., Graco, M. I., and Kuypers, M. M. M.: Aerobic microbial respiration in oceanic oxygen minimum zone, PlosOne, 10, 2015.

Karl, D. M. and Tilbrook, B. D.: Production and transport of methane in oceanic particulate organic matter, Nature, 368, 732 - 734, 1994.

Karstensen, J., Stramma, L., Visbeck, M.: Oxygen minimum zones in the eastern tropical Atlantic and Pacific Oceans. Progress In Oceanography 77(4):331 – 350, doi:10.1016/j.pocean.2007.05.009, 2008

Kartal, B., Kuypers, M. M. M., Lavik, G., Schalk, J., den Camp, H., Jetten, M. S. M., and Strous, M.: Anammox bacteria disguised as denitrifiers: nitrate reduction to dinitrogen gas via nitrite and ammonium, Environ. Microbiol., 9, 635-642, 2007.

Kiko, R., Hauss, H., Dengler, M., Sommer, S., and Melzner, F.: The squat lobster Pleuroncodes monodon tolerates anoxic “dead zone” conditions off Peru, Marine Biology, 162, 1-9, 2015.

Kiko, R., Hauss., H., Buchholz, F., and Melzner, F.: Ammonium excretion and oxygen respiration of tropical copepods and euphausiids exposed to oxygen minimum zone conditions, Biogeosciences, 13, 2241-2255, doi:10.5194/bg-13-2241-2016, 2016.

Kiørboe, T.: Phytoplankton growth rate and nitrogen content: implications for feeding and fecundity in a herbivorous copepod, Marine Ecology Progress Series, 55, 229-234, 1989.

Klawonn, I., Bonaglia, S., Bruchert, V., and Ploug, H.: Aerobic and anaerobic nitrogen transformation processes in N2-fixing cyanobacterial aggregates, ISME J, 9, 1456-1466, 2015.

Klein, P., Hua, B. L., Lapeyre, G., Capet, X., Le Gentil, S., and Sasaki, H.: Upper ocean turbulence from high-resolution 3D simulations, Journal of Physical Oceanography, 38, 1748-1763, 2008.

Klein, P. and Lapeyre, G.: The Oceanic Vertical Pump Induced by Mesoscale and Submesoscale Turbulence. In: Annual Review of Marine Science, Annual Review of Marine Science, 2009.

Kock, A., Arévalo-Martínez, D. L., Löscher, C. R., and Bange, H. W.: Extreme N_2O accumulation in the coastal oxygen minimum zone off Peru, Biogeosciences, 13, 827-840, doi:10.5194/bg-13-827-2016, 2016.

Körtzinger, A., Schimanski, J., Send, U. und Wallace, D. W. R.:The ocean takes a deep breath. Science, 306 (5700). doii: 10.1126/science.1102557. 2004.

Kuypers, M. M. M., Lavik, G., Woebken, D., Schmid, M., Fuchs, B. M., Amann, R., Jorgensen, B. B., and Jetten, M. S. M.: Massive nitrogen loss from the Benguela upwelling system through anaerobic ammonium oxidation, Proc. Natl. Acad. Sci. U. S. A., 102, 6478-6483, 2005.

Kuypers, M. M. M., Sliekers, A. O., Lavik, G., Schmid, M., Jorgensen, B. B., Kuenen, J. G., Damste, J. S. S., Strous, M., and Jetten, M. S. M.: Anaerobic ammonium oxidation by anammox bacteria in the Black Sea, Nature, 422, 608-611, 2003.

Lam P, Lavik G, Jensen MM, van de Vossenberg J, Schmid M, Woebken D, et al. Revising the nitrogen cycle in the Peruvian oxygen minimum zone. Proc Natl Acad Sci USA, 106:4752–4757, 2009.

Lam, P. and Kuypers, M. M. M.: Microbial nitrogen cycling processes in oxygen minimum zones., Ann Rev Mar Sci., 3, 317-345, 2011.

Lampert, W.: The adaptive significance of diel vertical migration of zooplankton, Functional Ecology, 3, 21-27, 1989.

Landolfi, A., Dietze, H., Koeve, W., and Oschlies, A.: Overlooked runaway feedback in the marine nitrogen cycle: the vicious cycle, Biogeosciences, 10, 1351-1363, 2013.

Langlois RJ, LaRoche J, Raab PA.: Diazotrophic diversity and distribution in the tropical and subtropical Atlantic ocean. Appl Environ Microbiol 71: 7910–7919, 2005.

Langlois RJ, Hummer D, LaRoche J.: Abundances and distributions of the dominant *nifH* phylotypes in the Northern Atlantic Ocean. Appl Environ Microbiol 74: 1922–1931, 2008

Lasternas, S., Piedeleu, M., Sangrà, P., Duarte, C. M., and Agustí, S.: Forcing of dissolved organic carbon release by phytoplankton by anticyclonic mesoscale eddies in the subtropical NE Atlantic Ocean, Biogeosciences, 10, 2129-2143, 2013.

Lathuiliere, C., Echevin, V., Levy, M., and Madec, G.: On the role of the mesoscale circulation on an idealized coastal upwelling ecosystem, Journal of Geophysical Research-Oceans, 115, 2010.

Lavik, G., Stuhrmann, T., Bruchert, V., Van der Plas, A., Mohrholz, V., Lam, P., Mussmann, M., Fuchs, B. M., Amann, R., Lass, U., and Kuypers, M. M. M.: Detoxification of sulphidic African shelf waters by blooming chemolithotrophs, Nature, 457, 581-584, 2009.

Lennartz, S. T., Lehmann, A., Herrford, J., Malien, F., Hansen, H.-P., Biester, H., and Bange, H. W.: Long-term trends at the Boknis Eck time series station (Baltic Sea), 1957–2013: does climate change counteract the decline in eutrophication?, Biogeosciences, 11, 6323-6339, 2014.

Levy, M., Ferrari, R., Franks, P. J. S., Martin, A. P., and Riviere, P.: Bringing physics to life at the submesoscale, Geophysical Research Letters, 39, 2012.

Lipschultz, F., Wofsy, S.C, Ward, B.B., Codispoti, L.A., Friedrich, G., Elkins, J.W.. Bacterial transformations of inorganic nitrogen in the oxygen-deficient waters of the eastern tropical South-Pacific ocean. Deep-Sea Res Part A Oceanogr Res Papers. 37:1513–1541, 1990.

Liss, P. S. and Johnson, M. T.: Ocean-Atmosphere Interactions of Gases and Particles, Springer, Heidelberg, 2014.

Löscher, C. R., Kock, A., Könneke, M., LaRoche, J., Bange, H. W., and Schmitz, R. A.: Production of oceanic nitrous oxide by ammonia-oxidizing archaea, Biogeosciences 9, 2419-2429, 2012.

Löscher, C. R., Großkopf, T., Desai, F., Gill, D., Schunck, H., Croot, P., Schlosser, C., Neulinger, S. C., Lavik, G., Kuypers, M. M. M., LaRoche, J., and Schmitz, R. A.: Facets of diazotrophy in the oxygen minimum zone off Peru, ISME J, 8, 2180-2192, 2014.

Löscher, C. R., Fischer, M. A., Neulinger, S. C., Fiedler, B., Philippi, M., Schütte, F., Singh, A., Hauss, H., Karstensen, J., Körtzinger, A., Künzel, S., and Schmitz, R. A.: Hidden biosphere in an oxygen-deficient Atlantic open-ocean eddy: future implications of ocean deoxygenation on primary production in the eastern tropical North Atlantic, Biogeosciences, 12, 7467-7482, doi:10.5194/bg-12-7467-2015, 2015.

Longhurst, A. R., Sathyendrenath, S., Platt, T., and Caverhill, C.: An est imat ion of global primary product ion in the ocean from satellite radiometer data. J. Plankton Res, 17, 1245-1271, 1995.

Luo, J., Ortner, P. B., Forcucci, D., and Cummings, S. R.: Diel vertical migration of zooplankton and mesopelagic fish in the Arabian Sea, Deep Sea Research Part II: Topical Studies in Oceanography, 47, 1451-1473, 2000.

Mahadevan: Ocean science: Eddy effects on biogeochemistry, Nature Geoscience, 506, 168-169, 2014.

Martin, J. H., Knauer, G. A., Karl, D. M., and Broenkow, W. W.: VERTEX - Carbon Cycling in the Northeast Pacific, Deep-Sea Research Part a-Oceanographic Research Papers, 34, 267-285, 1987.

Martinez-Rey, J., Bopp, L., Gehlen, M., Tagliabue, A., and Gruber, N.: Projections of oceanic N_2O emissions in the 21st century using the IPSL Earth system model, Biogeosciences, 12, 4133-4148, doi:10.5194/bg-12-4133-2015, 2015.

Mathis, J. T., Pickart, R. S., Hansell, D. A., Kadko, D., and Bates, N. R.: Eddy transport of organic carbon and nutrients from the Chukchi Shelf: Impact on the upper halocline of the western Arctic Ocean, Journal of Geophysical Research-Oceans, 112, 2007.

McLaren, I. A.: Effects of temperature on growth of zooplankton, and the adaptive value of vertical migration, Journal of the Fisheries Board of Canada, 20, 685-727, 1963.

Meyer, J., Löscher, C. R., Neulinger, S. C., Reichel, A. F., Loginova, A., Borchard, C., Schmitz, R. A., Hauss, H., Kiko, R., and Riebesell, U.: Changing nutrient stoichiometry affects phytoplankton production, DOP build up and dinitrogen fixation – a mesocosm experiment in the eastern tropical North Atlantic, Biogeosciences Discuss., 12, 9991-10029, 2015.

Mills, M. M., Ridame, C., Davey, M., La Roche, J., and Geider, R. J.: Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic, Nature, 429, 292-294, 2004.

Mohr, W., Grosskopf, T., Wallace, D. W. R., and LaRoche, J.: Methodological underestimation of oceanic nitrogen fixation rates, PLoS One, 5, e12583, 2010.

Naqvi, S. W. A., Bange, H. W., Farías, L., Monteiro, P. M. S., Scranton, M. I., and Zhang, J.: Marine hypoxia/anoxia as a source of CH_4 and N_2O, Biogeosciences, 7, 2159-2190, 2010.

Naqvi, S. W. A., Jayakumar, D. A., Narveka, P. V., Naik, H., Sarma, V. V. S. S., D'Souza, W., Joseph, S., and George, M. D.: Increased marine production of N_2O due to intensifying anoxia on the Indian continental shelf, Nature, 408, 346-349, 2000.

Naqvi, S. W. A., Kumar, M. D., Narvekar, P. V., Desousa, S. N., George, M. D., and Dsilva, C.: An Intermediate Nepheloid Layer Associated with High Microbial Metabolic Rates and Denitrification in the Northwest Indian-Ocean, Journal of Geophysical Research-Oceans, 98, 16469-16479, 1993.

Omori, Y., Tanimoto, H., Inomata, S., Wada, S., Thume, K., and Pohnert, G.: Enhancement of dimethylsulfuide production by anoxic stress in natural seawater, Geophys. Res. Lett., 42, 4047-4053, 2015.

Pahlow, M. and Vézina, A. F.: Adaptive model of DOM dynamics in the surface ocean, Journal of Marine Research, 61, 127-146, 2003.

Pahlow, M., Vézina, A. F., Casault, B., Maass, H., Malloch, L., Wright, D. G., and Lu, Y.: Adaptive model of plankton dynamics for the North Atlantic, Progress in Oceanography, 76, 151-191, 2008.

Pahlow, M., Dietze, H., and Oschlies, A.: Optimality-based model of phytoplankton growth and diazotrophy, Marine Ecology Progress Series, 489, 1-16, 2013.

Pahlow, M. and Oschlies, A.: Optimal allocation backs Droop's cell-quota model, Marine Ecology Progress Series, 473, 1-5, 2013.

Pantoja, S., Sepulveda, J. S., and Gonzalez, H. E.: Decomposition of sinking proteinaceous material during fall in the oxygen minimum zone off northern Chile, Deep-Sea Research Part I-Oceanographic Research Papers, 51, 55-70, 2004.

Pantoja, S., Rossel, P., Castro, R., Cuevas, L. A., Daneri, G., and Cordova, C.: Microbial degradation rates of small peptides and amino acids in the oxygen minimum zone of Chilean coastal waters, Deep-Sea Research Part Ii-Topical Studies in Oceanography, 56, 1019-1026, 2009.

Paulmier, A., Ruiz-Pino, D., and Garcon, V.: CO2 maximum in the oxygen minimum zone (OMZ), Biogeosciences, 8, 239-252, 2011.

Pearcy, W., Krygier, E., Mesecar, R., and Ramsey, F.: Vertical distribution and migration of oceanic micronekton off Oregon, Deep Sea Research, 24, 223-245, 1977.

Peduzzi, P., Weinbauer, M. G.: The submicron size fraction of seawater containing high numbers of virus particles as bioactive agent in unicellular plankton community successions. J Plankton Res, 15:1375-1386, 1993.

Pörtner, H. O. and Farrell, A. P.: Physiology, climate change, Science, 322, 690-692, 2008.

Poorvin, L., Rinta-Kanto, J. M., Hutchins, D. A., and Wilhelm, S. W.: Viral release of iron and its bioavailability to marine plankton, Limnology and Oceanography, 49, 1734-1741, 2004.

Quiñones, R. A., Gutierrez, M. H., Daneri, G., Aguilar, D. G., Gonzalez, H. E., Chavez, F. P.: The Humboldt Current System, in: Carbon and Nutrient Fluxes in Continental Margins: A Global Synthesis, edited by: Liu, K-. K., Atkinson, L., Quiñones, R., and Talaue-McManus, L., Springer-Verlag, Berlin, 44–64, 2010

Riebesell, U., Körtzinger, A., and Oschlies, A.: Sensitivities of marine carbon fluxes to ocean change., Proceedings of the National Academy of Sciences, 106, 20602-20609, 2009.

Robinson, C., Steinberg, D. K., Anderson, T. R., Aristegui, J., Carlson, C. A., Frost, J. R., Ghiglione, J. F., Hernandez-Leon, S., Jackson, G. A., Koppelmann, R., Queguiner, B., Ragueneau, O., Rassoulzadegan, F., Robison, B. H., Tamburini, C., Tanaka, T., Wishner, K. F., and Zhang, J.: Mesopelagic zone ecology and biogeochemistry - a synthesis, Deep-Sea Research Part Ii-Topical Studies in Oceanography, 57, 1504-1518, 2010.

Romankevich, E. A. and Ljutsarev, S. V.: Dissolved organic carbon in the Ocean, Marine Chemistry, 30, 161-178, 1990.

Rosa, R. and Seibel, B. A.: Metabolic physiology of the Humboldt squid, *Dosidicus gigas*: Implications for vertical migration in a pronounced oxygen minimum zone, Progress in Oceanography, 86, 72-80, 2010.

Roux, S., Hawley, A. K., Torres Beltran, M., Scofield, M., Schwientek, P., Stepanauskas, R., et al.: Ecology and evolution of viruses infecting uncultivated SUP05 bacteria as revealed by single-cell- and meta-genomics. eLife, *3*, e03125. http://doi.org/10.7554/eLife.03125, 2014.

Ryabenko, E., Kock, A., Bange, H. W., Altabet, M. A., and Wallace, D. W. R.: Contrasting biogeochemistry of nitrogen in the Atlantic and Pacific oxygen minimum zones, Biogeosciences, 9, 203-215, 2012.

Saltzmann, J. and Wishner, K. F.: Zooplankton ecology in the eastern tropical Pacific ozygen minimum zone above a seamout: 2. Vertical distribution of copepods, Deep Sea Research I, 44, 931-954, 1997.

Santoro, A. E., Buchwald, C., McIlvin, M. R., and Casciotti, K. L.: Isotopic Signature of N_2O Produced by Marine Ammonia-Oxidizing Archaea, Science, 333, 1282-1285, 2011.

Santoro, A.E., Dupont, C.L., Richter, R.A., et al.: Genomic and proteomic characterization of "*Candidatus* Nitrosopelagicus brevis": An ammonia-oxidizing archaeon from the open ocean. Proceedings of the National Academy of Sciences of the United States of America. 112(4):1173-1178. doi:10.1073/pnas.1416223112, 2015.

Scholz, F., McManus, J., Mix, A. C., Hensen, C., Schneider, R. R.: The impact of ocean deoxygenation on iron release from continental margin sediments. *Nature Geoscience*, doi:10.1038/NGEO2162, 2014.

Schunck, H., Lavik, G., Desai, D. K., Großkopf, T., Kalvelage, T., Löscher, C. R., Paulmier, A., Contreras, S., Siegel, H., Holtappels, M., Rosenstiel, P., Schilhabel, M. B., Graco, M., Schmitz, R. A., Kuypers, M. M. M., and LaRoche, J.: Giant Hydrogen Sulfide Plume in the Oxygen Minimum Zone off Peru Supports Chemolithoautotrophy, PLoS ONE, 2013.

Schweiger, B., Hansen, H. P., and Bange, H. W.: A time series of hydroxylamine (NH_2OH) in the southwestern Baltic Sea, Geophysical Research Letters, 34, 5, 2007.

Shelford, E. J., Middelboe, M., Møller, E. F., and Suttle, C. A.: Virus-driven nitrogen cycling enhances phytoplankton growth, Aquatic microbial ecology, 66, 41-46, 2012.

Seibel, B. A.: Critical oxygen levels and metabolic suppression in oceanic oxygen minimum zones, Journal of Experimental Biology, 214, 326-336, 2011.

Shenoy, D. M., Sujith, K. B., Gauns, M. U., Patil, S., Sarkar, A., Naik, H., Narvekar, P. V., and Naqvi, S. W. A.: Production of dimethylsulphide during the seasonal anoxia off Goa, Biogeochemistry, 110, 47-55, 2012.

Somes, C. J. and Oschlies, A. C. G. B.: On the influence of "non-Redfield" dissolved organic nutrient dynamics on the spatial distribution of N_2 fixation and the size of the marine fixed nitrogen inventory, Glob. Biogeochem. Cycle, doi: doi:10.1002/2014GB005050. , 2015. n/a-n/a, 2015.

Sorokin, Y. I., Sorokin, P. Y., Avdeev, V. A., Sorokin, D. Y., and Ilchenko, S. V.: Biomass, Production and Activity of Bacteria in the Black-Sea, with Special Reference to Chemosynthesis and the Sulfur Cycle, Hydrobiologia, 308, 61-76, 1995.

Steinberg, D. K., Carlson, C. A., Bates, N. R., Goldthwait, S. A., Madin, L. P., and Michaels, A. F.: Zooplankton vertical migration and the active transport of dissolved organic and inorganic carbon in the Sargasso Sea, Deep-Sea Research Part I-Oceanographic Research Papers, 47, 137-158, 2000.

Stevens, H. and Ulloa, O.: Bacterial diversity in the oxygen minimum zone of the eastern tropical South Pacific, Environ Microbiol, 10, 1244-1259, 2008.

Stewart, F. J., Ulloa, O., and DeLong, E. F.: Microbial metatranscriptomics in a permanent marine oxygen minimum zone, Environ Microbiol, 14, 23-40, 2011.

Stramma, L., Johnson, G. C., Sprintall, J., and Mohrholz, V.: Expanding Oxygen-Minimum Zones in the Tropical Oceans, Science, 320, 655-658, 2008.

Stramma, L., Oschlies, A., and Schmidtko, S.: Mismatch between observed and modeled trends in dissolved upper-ocean oxygen over the last 50 yr, Biogeosciences, 9, 4045-4057, 2012.

Stramma, L., Bange, H. W., Czeschel, R., Lorenzo, A., and Frank, M.: On the role of mesoscale eddies for the biological productivity and biogeochemistry in the eastern tropical Pacific Ocean off Peru. , Biogeosciences 10, 7293-7306, 2013.

Suntharalingam, P., Buitenhuis, E., Le Quere, C., Dentener, F., Nevison, C., Butler, J. H., Bange, H. W., and Forster, G.: Quantifying the impact of anthropogenic nitrogen deposition on oceanic nitrous oxide, Geophysical Research Letters, 39, 2012.

Suttle, C. A.: Viruses in the sea, Nature, 437, 356-361, 2005.

Swan, B. K., Martinez-Garcia, M., Preston, C. M., Sczyrba, A., Woyke, T., Lamy, D., Reinthaler, T., Poulton, N. J., Masland, E. D. P., Gomez, M. L., Sieracki, M. E., DeLong, E. F., Herndl, G. J., and Stepanauskas, R.: Potential for Chemolithoautotrophy Among Ubiquitous Bacteria Lineages in the Dark Ocean, Science, 333, 1296–1300, 2011.

Taylor, G. T., Iabichella, M., Ho, T. Y., Scranton, M. I., Thunell, R. C., Muller-Karger, F., and Varela, R.: Chemoautotrophy in the redox transition zone of the Cariaco Basin: A significant midwater source of organic carbon production, Limnol Oceanogr, 46, 148-163, 2001.

Tebo, B. M. and Emerson, S.: Microbial manganese(II) oxidation in the marine environment: a quantitative study, Biogeochemistry, 2, 149-161, 1986.

Teuber, L., Kiko, R., Seguin, F., and Auel, H. J.: Respiration rates of tropical Atlantic copepods in relation to the oxygen minimum zone, Exp. Mar. Biology and Ecology, 448, 28-36, 2013.

Thamdrup, B. and Dalsgaard, T.: Production of N_2 through anaerobic ammonium oxidation coupled to nitrate reduction in marine sediments, Applied and Environmental Microbiology, 68, 1312-1318, 2002.

Thamdrup, B., Dalsgaard, T., Jensen, M. M., Ulloa, O., Farias, L., and Escribano, R.: Anaerobic ammonium oxidation in the oxygen-deficient waters off northern Chile, Limnology and Oceanography, 51, 2145-2156, 2006.

Thomas, L. N., Tandon, A., and Mahadevan, A.: Submesoscale processes and dynamics., In: M. Hecht, H. Hasumi (Eds.), Ocean Modeling in an Eddying Regime. Geophysical Monograph Series, vol. 177, American Geophysical Union, Washington, DC, 17-38., 2008. 2008.

Touratier, F., Field, J. G., and Moloney, C. L.: A stoichiometric model relating growth substrate quality (C:N:P ratios) to N:P ratios in the products of heterotrophic release and excretion, Ecological Modelling, 139, 265-291, 2001.

Turk-Kubo, K. A., Karamchandani, M., Capone, D. G., and Zehr, J. P.: The paradox of marine heterotrophic nitrogen fixation: abundances of heterotrophic diazotrophs do not account for nitrogen fixation rates in the Eastern Tropical South Pacific, Environ Microbiol, 16, 3095–3114, 2014.

Van Mooy, B. A. S., Keil, R. G., and Devol, A. H.: Impact of suboxia on sinking particulate organic carbon: Enhanced carbon flux and preferential degradation of amino acids via denitrification, Geochimica Et Cosmochimica Acta, 66, 457-465, 2002.

Voss, M., Croot, P., Lochte, K., Mills, M. and Peeken, I.:Patterns of nitrogen fixation along 10°N in the tropical Atlantic. Geophysical Research Letters,. 31, L23S09, doi:10.1029/2004GL020127, 2004.

Walsh, J. J.: A carbon budget for overfishing off Peru, Nature, 290,300–304, 1981

Walsh, D. A., Zaikova, E., Howes, C. G., Song, Y. C., Wright, J. J., Tringe, S. G., Tortell, P. D., and Hallam, S. J.: Metagenome of a Versatile Chemolithoautotroph from Expanding Oceanic Dead Zones, Science, 326, 578-582, 2009.

Ward, B. B., Devol, A. H., Rich, J. J., Chang, B. X., Bulow, S. E., Naik, H., Pratihary, A., and Jayakumar, A.: Denitrification as the dominant nitrogen loss process in the Arabian Sea, Nature, 461, 78-U77, 2009.

Weinbauer M. G., Bonilla-Findji O., Chan A. M., Dolan J. R., Short S. M., Simek K., et al.:*Synechococcus* growth in the ocean may depend on the lysis of heterotrophic bacteria. J. Plankt. Res. 33 1465–1476 10.1093/plankt/fbr041, 2011.

Weitz, J. S., Stock, C. A., Wilhelm, S. W., Bourouiba, L., Coleman, M. L., Buchan, A., Follows, M. J., Fuhrman, J. A., Jover, L. F., Lennon, J. T., Middelboe, M., Sonderegger, D. L., Suttle, C. A., Taylor, B. P., Frede Thingstad, T., Wilson, W. H., and Eric Wommack, K.: A multitrophic model to quantify the effects of marine viruses on microbial food webs and ecosystem processes, ISME J, 9, 1352-1364, 2015.

Wishner, K. F., Gowing, M. M., and Gelfman, C.: Mesozooplankton biomass in the upper 1000 m in the Arabian Sea: overall seasonal and geographic patterns, and relationship to oxygen gradients, Deep Sea Research II, 45, 2405 – 2432, 1998.

Woebken, D., Teeling, H., Wecker, P., Dumitriu, A., Kostadinov, I., DeLong, E. F., Amann, R., and Glöckner, F. O.: Fosmids of novel marine planctomycetes from the Namibian and Oregon coast upwelling systems and their cross-comparison with planctomycete genomes., ISME J, 1, 419-435, 2007.

Wright, J. J., Konwar, K. M., and Hallam, S. J.: Microbial ecology of expanding oxygen minimum zones, Nature Reviews Microbiology, 10, 381-394, 2012.

Zamora, L. M., Oschlies, A., Bange, H. W., Huebert, K. B., Craig, J. D., Kock, A., and Loescher, C. R.: Nitrous oxide dynamics in low oxygen regions of the Pacific: insights from the MEMENTO database, Biogeosciences, 9, 5007-5022, 2012.

Zehr, J. P. and Turner, P. J.: Nitrogen fixation: Nitrogenase genes and gene expression. In: Methods in Microbiology, Vol 30, Methods in Microbiology, Academic Press Inc, 30, 271-286 San Diego, 2001.

Zhang, J. Z. and Millero, F. J.: The Chemistry of the Anoxic Waters in the Cariaco Trench, Deep-Sea Res Pt I, 40, 1023-1041, 1993.

Figures

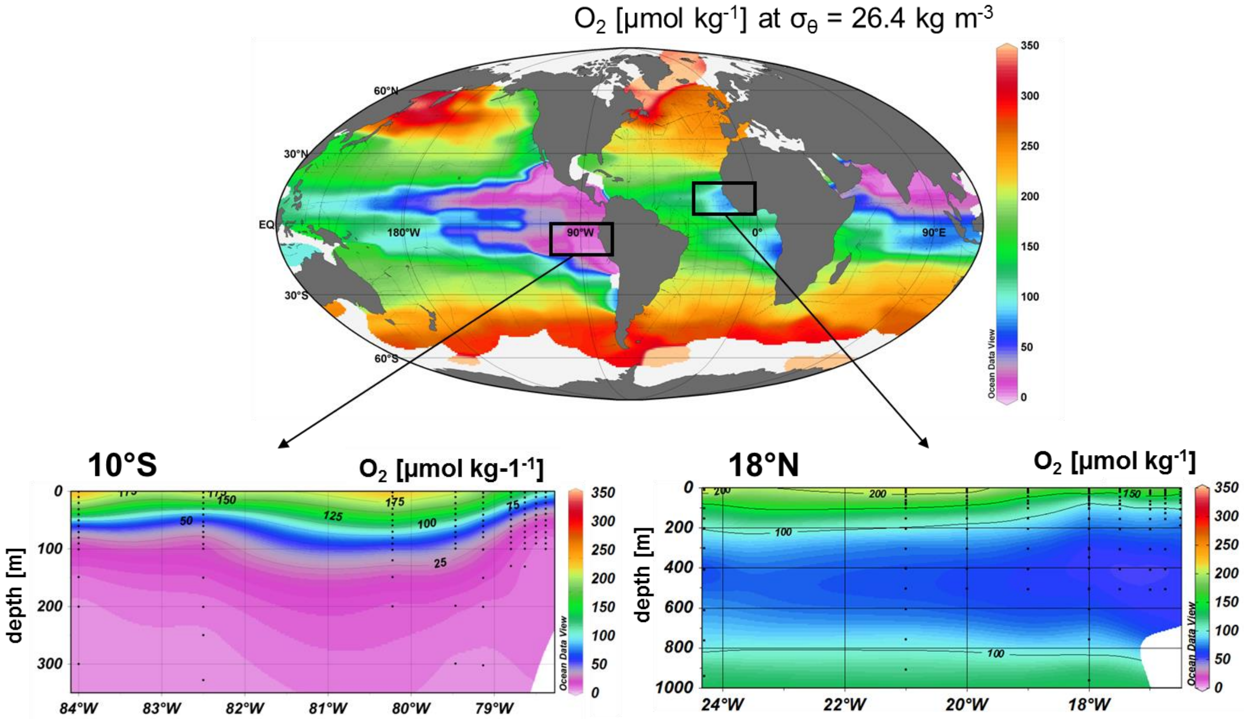

Figure 1. Global distribution of O_2 at σ_Θ= 26.4 kg m^{-3} (~ 400 m depth): The major regions of low oxygen in the world ocean are all located in the tropical oceans, at shallow to intermediate depths. The area off Peru represents one of the most pronounced OMZs. The investigated areas in the eastern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

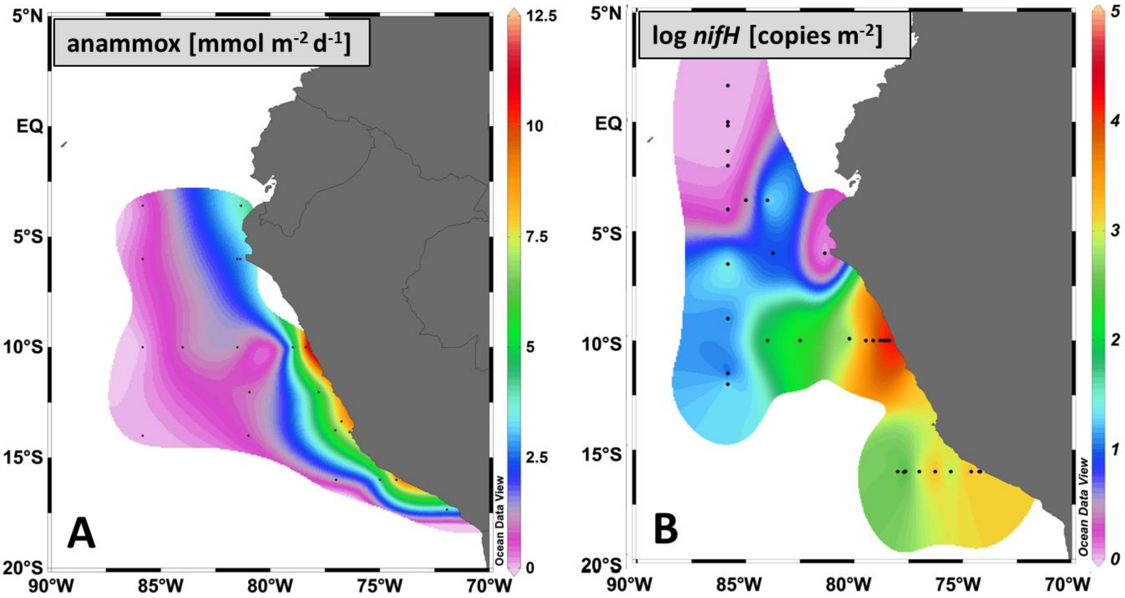

Figure 2. Co-occurrence of anammox as determined by rate measurements and the key functional marker gene for N_2 fixation, *nifH*, in the ETSP OMZ (modified from Kalvelage et al., 2013 and Löscher et al., 2014).

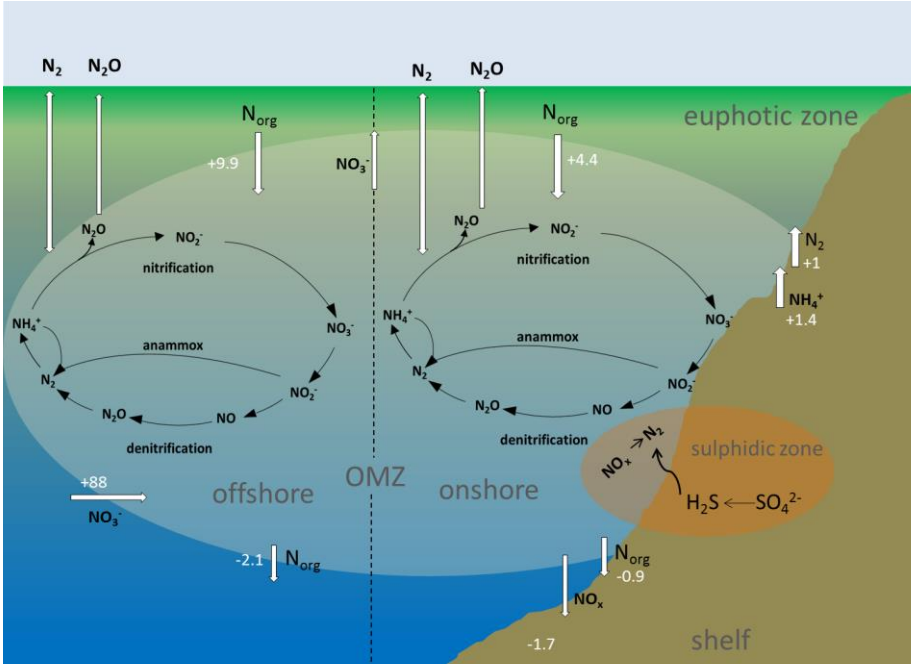

Figure 3. The marine nitrogen (N) cycle with the major onshore and offshore processes in the ETSP OMZ, modified from Kalvelage et al. (2013). Numbers indicate fluxes of N [Tg y^{-1}].

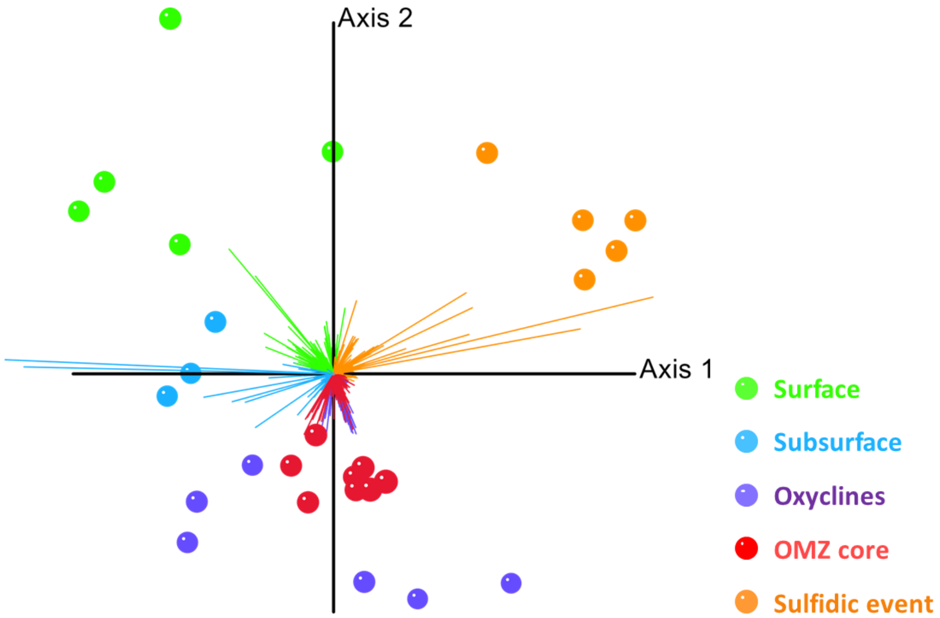

Figure 4. Redundancy analysis ordination model of microbial taxa (vectors) identified from pyrosequencing reads of multiple samples (points) in the ETSP. Spherical k-means clustering revealed a fivefold partitioning that reflects distinct OMZ habitats (see legend). Each point is colored according to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

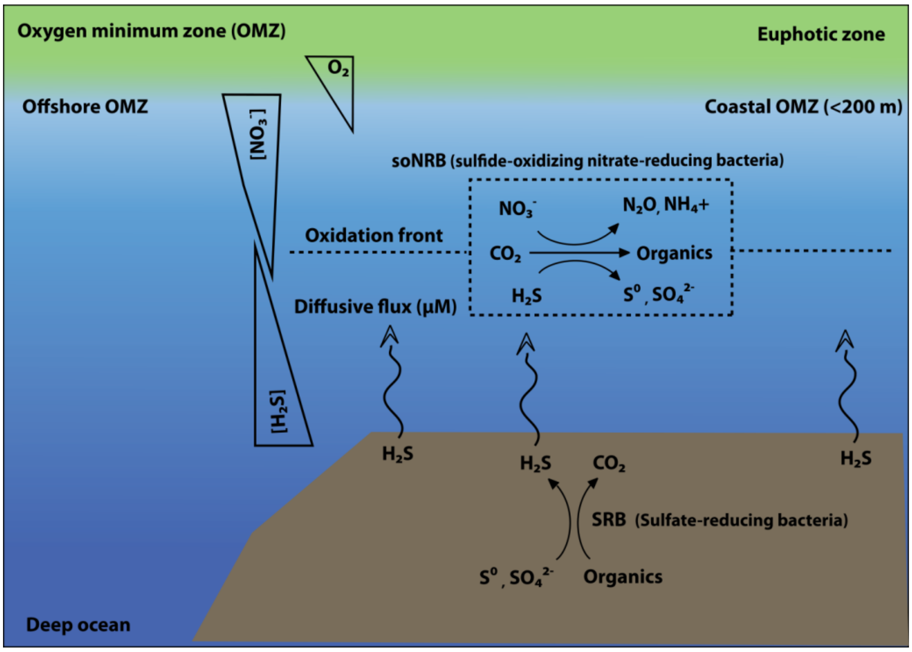

Figure 5. Schematic representation of the dynamics of a sulfidic event occurring in an oxygen minimum zone, e.g. in the ETSP. The sulfide and nitrate fluxes are shown in steady state.

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

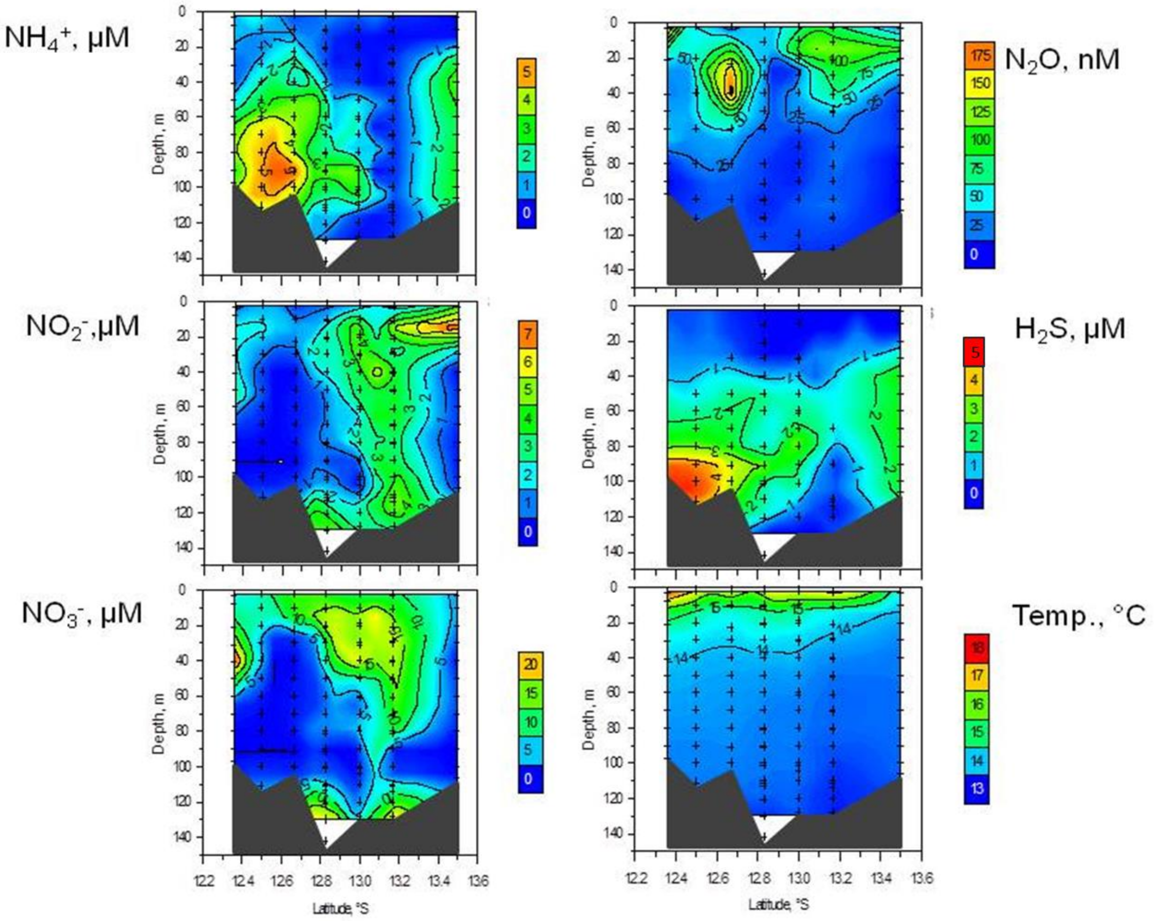

Figure 6. Distributions of N_2O, NH_4^-, NO_2^-, NO_3^-, H_2S, and water temperature during December 2008/January 2009 (R/V Meteor cruise M77/3) on the shelf along the coast of Peru. Max. N_2O concentrations have been detected right above the sulfidic zone, where a sharp oxycline is present and ammonium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

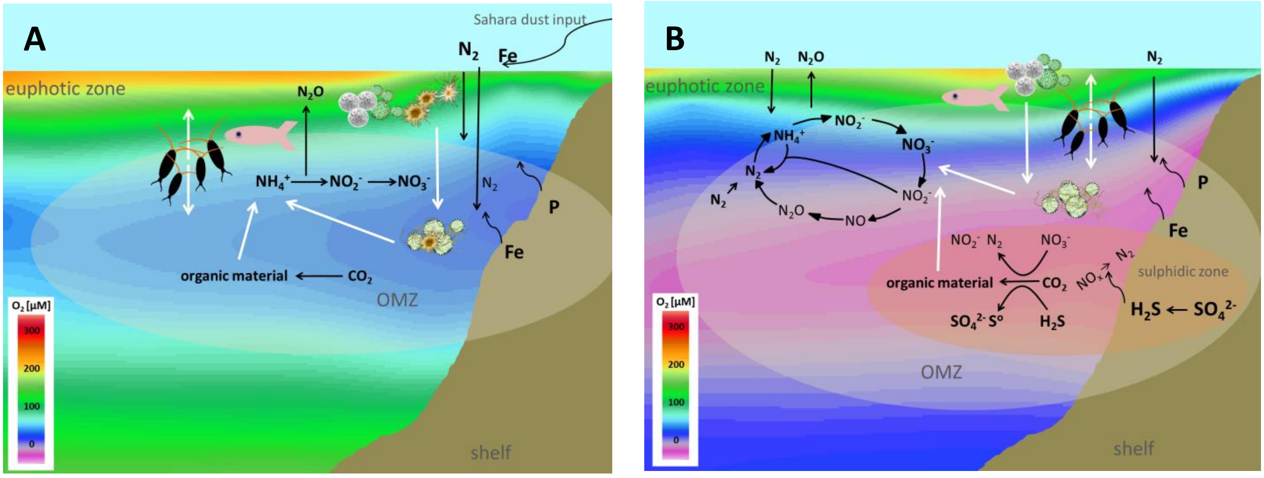

Figure 7. Scheme of the (A) ETNA and (B) ETSP OMZs with major processes identified. The O_2 background is taken from the SOPRAN cruise P399, along 18°N in the ETNA and from the SFB754 cruise M77/3, along 10°S in the ETSP.

Table 1: A comparison of the O_2 minimum, excess nitrogen (N*), primary production, organic C export, N_2 fixation and N loss in the ETNA and ETSP upwelling regions.

	ETSP-shelf	**ETSP- offshore**	**ETNA-shelf**	**ETNA- offshore**
O_2 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]
N_2 fixation [µmol N m^{-2} d^{-1}]	25-657 [f]		24-140 [g]	
% contribution of N_2 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_2S)	0	0	

* Calculated based on the Redfield ratio of C:N = 106:16 using the primary production and N_2 fixation rates given in this table in consistency with the % contribution given in Duce et al. (2008).

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