We would like to thank the reviewers for their useful suggestions to improve our manuscript. We carefully revised our manuscript according to the reviewers' remarks. We included a description of the hydrographic settings and a TS-diagram in the revised manuscript, as suggested by reviewer 1, and re-structured some paragraphs of the manuscript to emphasize the main findings of the manuscript. Please find a detailed reply to the reviews and the revised manuscript with all changes highlighted below.

Review 1

R1: "Firstly, the title of the work is confusing. The authors should distinguish the difference between distribution in coastal and open waters."

We changed the title to: "Extreme N_2O accumulation in the coastal oxygen minimum zone off Peru."

R1: "I also expect to see an oceanographic analysis of how the authors distinguish between coastal and oceanic region. Since this region is subjected to coastal upwelling the areas should be separated, taking into account, for example, of Rossby ratio."

We agree with the reviewer that objective criterion is needed to distinguish between coastal and open ocean stations. As suggested by the reviewer, we used the first baroclinic rossby radius as defined by Chelton et al. (1998) to determine open ocean and shelf stations. Stations with a distance to the shelf break (2000 m isobath) shorter than the rossby radius were classified as "coastal" whereas samples with a larger distance were classified as "offshore". This classification was used to create Figure 5 and 6 (the newly added TS diagrams), and the stations shown in Figure 4 were colorcoded according to this classification.

Chelton, D. B., DeSzoeke, R. A., Schlax, M. G., El Naggar, K., and Siwertz, N.: Geographical variability of the first baroclinic Rossby radius of deformation, Journal of Physical Oceanography, 28, 433-460, 10.1175/1520-0485(1998)028<0433:gvotfb>2.0.co;2, 1998.

R1: "I feel that in order to interpret the observed results, the study lacks an analysis of distribution and mixing of water masses. For ejemple the presense of the emblematic equatorial subsurface water (ESSW) is omitted. Also, the study region is characterized by different zones (the occurrence of shelf and coastal upwelling), and by an intricate regional oceanography that is influenced by equatorial dynamics."

We included a brief description of the hydrographic setting of the ETSP in the introduction section (lines 101-112) and an additional figure showing the TS-diagrams of the offshore and onshore stations. These are discussed in detail in the results and discussion section to further assess the oceanographic influence on the N_2O distribution in our study area (lines 220-229 and 249-262).

R1: "The paper does not touch on any of these regional oceanographic aspects, nor aspects regarding the temporal variability of ENSO (El Niño, or coastal trapped wave of intraseasonal frequency), even though the sampling strategy considered different years. Despite the several years of analysis carried out for this study, part of the variability could be caused by temporal scales or by mesoscale phenomena previously described for the same study area. This can be clearly observed when the authors present the latitudinal distribution along 86 _W (Fig. 2), temporary differences, for example, are observed (between cruise M77-4 and M90) that result in different spatial structures (for example see the peak of nitrite and maximum observed in nitrous oxide)."

We disagree with the reviewer that the differences observed in the M77-4 and M90 sections shown in Figure 2 can be interpreted as an indication for strong temporal differences between these cruises. At the oxygen concentrations present in the OMZ, the nitrous oxide and nitrite distributions are highly sensitive to marginal changes in the oxygen concentrations. The differences could be furthermore be the result of the rather coarse depth resolution of our sampling which leaves the opportunity that sharp maxima in N_2O *or nitrite were undersampled. On the contrary, the similarities in the oxygen distributions along 86°W and the very similar* $\Delta N_2O/AOU$ *relationships observed during M77-4 and M90 indicate rather similar conditions between the measurement campaigns in 2008/2009 and 2012/2013. This is supported by Southern Oscillation Indices that did not indicate El Niño conditions for both sampling periods. We nevertheless agree with the authors that the discussion of the influence of ENSO on the hydrographic settings in the ETSP is a useful addition to our manuscript. We therefore included a paragraph on the influence of ENSO on the variability and the conditions prevalent during the measurements in the introduction and methods sections (lines 115-120 & 126-129).*

R1: "Furthermore I am concerned with the explanation about the distribution and that it is "ventilation or re-ventilation" of the water; this is both discussed and concluded as a key issue. In truth, under the context in which it is referred to, I find that this term is not clear or is not correctly used. First the authors should clarify precisely what they mean by the term "ventilation", as it is not very obvious to myself, nor I believe to other Oceanographers; for example, coastal upwelling is properly not a ventilation process, on the contrary has the reverse effect as vertical advection dominates. […] I think that there are many diapycnal mixing processes, as well as vertical and lateral advection, that is likely to cause the observed heterogeneity."

In the context of our manuscript we used the terms "ventilation" and "re-ventilation" for processes that irreversibly increased the oxygen concentrations in a certain water parcel, i. e. (diapycnal or isopycnal) mixing or the direct exchange of the waters with the atmosphere. To avoid confusion we exchanged the term "ventilation" by the more precise term "(re)-oxygenation.

R1: "A further point to consider is that the biogeochemical processes which cause accumulation and consumption of N_2O are not suitably addressed, and they even fail to consider the relationship between AOU and nitrite and nitrate (only AOU vs. N_2O, Figure 5)."

We disagree with the reviewer that we did not sufficiently address the biogeochemical processes that influence N_2O *production and consumption.*

We used N' $(([NO_3^-]+[NO_2^-])-16[PO_4^-])$ *to colorcode the scatterplots in Figure 5. The argumentation that extreme* N_2O *accumulation was found in samples that were also depleted in inorganic N is an integral part of our argumentation, and we thoroughly discussed the processes that could lead to both, N depletion and* N_2O *accumulation. We also discussed the relationship between* N_2O *and nitrite distribution and argued that nitrite accumulation coincided with* N_2O *depletion, but no relationship between* N_2O *and nitrite accumulation was observed.*

We do not think that showing the relationship between AOU and nitrate and nitrite would significantly improve our understanding of the processes that lead to N_2O *accumulation in this area.*

R1: "On analysing Figure 5, the coast and the open ocean are not very different, except for the fact that is seems there is even greater dispersal in the coastal zone."

The greater dispersal of delta N_2O values in the coastal data is indeed the main finding of our manuscript. An increase of delta N_2O with AOU similar to our offshore observations has been observed in different oceanic areas and has frequently been used to parameterize N_2O concentrations from oxygen in oceanic modeling (see e.g. Nevison et al. (2003), Zamora et al (2012)). One of the main findings of our manuscripts is that this approach does not account for the extreme N_2O accumulation over the Peruvian shelf which would lead to a significant underestimation of the N_2O emissions from this area.

Nevison, C., Butler, J. H., and Elkins, J. W.: Global distribution of N2O and the Delta N2O-AOU yield in the subsurface ocean, Global Biogeochemical Cycles, 17, 1119 10.1029/2003gb002068, 2003.

Zamora, L. M., Oschlies, A., Bange, H. W., Huebert, K. B., Craig, J. D., Kock, A., and Loscher, C. R.: Nitrous oxide dynamics in low oxygen regions of the Pacific: insights from the MEMENTO database, Biogeosciences, 9, 5007-5022, 10.5194/bg-9-5007-2012, 2012.

R1: “So, when the authors conclude that the coastal upwelling off the Peruvian shelf causes conditions that lead to the extreme accumulation of N_2O, what would these conditions be? Are the authors referring to benthic processes?

Assuming that the reviewer refers to the last sentence of the abstract, we specified the conditions leading to extreme N_2O accumulation there. We think that the main factors that influence the N_2O concentrations are higher rates of N cycle processes due to the strong remineralization on the shelf in conjunction with strong mixing processes that lead to frequent transitions from anoxic to oxic conditions. Benthic processes may have only an indirect influence on the N_2O production (please see our response to reviewer 2 for a detailed discussion of this point).

Review 2

R2: “I feel that overall, the structural organization of ideas in the introduction and methods are clear, but the results and discussion are not as clear or well organized, and this makes it somewhat difficult to follow. This is likely due to the complexity of the data and the many approaches used during interpretation. However, some of the sentences refer to multiple ideas, and could probably be broken up into two or more sentences.”

We revised the manuscript according to the reviewer’s suggestions to improve the structure of the Results and Discussions.

R2: “Furthermore, some of the ideas put forward in the results/discussion section were not presented in the introduction, and I felt that some of the material in the discussion would be better situated in the introduction (e.g. evidence for increased N_2O production following reventilation, and the link between sulfur cycling and N_2O cycling).”

We agree with the reviewer that a potential link between sulfur cycling and N_2O production and the occurrence of peak N_2O production over the shelf should be mentioned in the Introduction. We therefore shifted parts of the Results and Discussion to the Introduction section (lines 59-67).

R2: “One of the most striking ideas is that the data suggest N_2O cycling may be coupled to sulfur cycling, though I am surprised that this is not included in the abstract, and would like to see some figures that specifically show the relationship between O_2, H_2S and N_2O. Is it surprising that N_2O reduction only takes place in the presence of H_2S, given the tendency of conventional O_2 measurement techniques to overestimate O_2 at low concentrations?”

We did not include any figures showing the relationship between N_2O and H_2S, because from our data, a direct link between H_2S occurrence and peak N_2O production cannot be established. Although N_2O accumulation has indeed been observed in proximity to H_2S plumes in some cases, other stations showed extremely high N_2O concentrations without any indication of H_2S.

We nevertheless included the discussion of this item as we cannot exclude that sulfur cycling influences N_2O production, either. The observed differences in N_2O and H_2S distributions could be due to the different time scales of H_2S accumulation and consumption mechanisms on the one hand, which can be very rapid; and N_2O production or consumption mechanisms on the other hand, which can lead to persistent accumulation of N_2O under oxic conditions. Moreover, there is evidence that intense sulfur cycling may take place without the accumulation of H_2S (see lines 305-314 in our manuscript).

R2: “Another important finding is the inadequacy of a linear N_2O/AOU ratio to describe N_2O distributions in shelf waters, and this too could be further emphasized. I was under the impression that the N_2O/AOU relationship is highly variable, even in the open ocean, and that it is therefore not advisable to estimate N_2O concentrations from AOU alone. Nevertheless, the authors’ conclusion that the N_2O/AOU relationship is even less reliable in shelf regions underscores this, and I feel this should be emphasized in the abstract and body of the article.”

We agree with the reviewer that the inadequacity of the ΔN_2O/AOU relationship to represent the N_2O distribution at the Peruvian coast is one of the main findings in our manuscript. We hope that this conclusion is emphasized by the restructuring of the manuscript.

R2:” The authors highlighted the relatively high variability over the shelf, and suggested that advection of N_2O from other locations, localized upwelling or re-ventilation may be responsible for some of the deviations from the expected N_2O/AOU relationship, but did not include sedimentary processes, riverine/estuarine inputs, or topography as possible explanations. Could these also play a role?”

We found no indication that riverine or sedimentary inputs have a strong direct impact on the N_2O distribution.

Due to the extremely arid climate in the adjacent Atacama desert riverine inputs are only marginal. Most of the sediments on the shelf and the overlying waters are anoxic and depleted in N_2O. A sedimentary source for N_2O into the water column off Peru is thus unlikely. An indirect influence of the sediments through the supply of substrates that stimulate N_2O production (e.g. NH_4^+, H_2S) cannot be excluded, though.

The interaction of the hydrographic settings with topography may indeed influence the N_2O distribution. However, we could not find a systematic link between the topography along the Peruvian coast and the N_2O distribution, and we assume that topography has a rather indirect influence on the N_2O distribution, too.

R2: “I am curious about a few details of the analysis, some only for my own interest, but perhaps others should be included. What volume of gas was injected? Was there a second syringe to accept overflow? What was the final pressure in the vials? Were the vials weighed to confirm the volume of liquid in the vial during equilibration?“

The gas sample volume was 10 mL (see line 145).
Samples were equipped with a second syringe to collect the overflowing water until the subsample for GC injection was taken. The headspace pressure was therefore equal to the ambient pressure during the measurements. We added this information to the methods section (lines 146-147).

The volume of the sample vials was determined prior to analysis by weighing 10 random sample vials of the same type filled with distilled water and calculating the volume from the density of the samples. The volume of the individual samples was not determined by weighing due to the large number of samples measured and the difficulties of using a balance onboard a ship. We added the standard deviation of the sample volume to the text to account for the uncertainty in the sample volume (line 137).

R2: “Can you list the concentrations of the gas mixtures, and how many were calibrated against the NOAA cylinders?”

The standard gas mixtures used during M77-3& 4 and M90-93 had concentrations of 318.2 ppb (Std 4), 982.2 ppb (Std 5) and 99.9 ppb (Std 3). Std 4 and 5 were calibrated against NOAA standards, while Std 3 was internally calibrated.

R2: “Were any measurements excluded from the analysis due to large difference between replicates? If so, what threshold was used to determine this?”

Measurements with a relative standard deviation above 15% were excluded from the analysis. This applied to less than 1% of all measurements.

R2: “How did you determine that the maximum overestimate would be 17%? What are your assumptions (e.g. minimum initial concentration during the year when you expect the water last contacted the surface) Can you list the range of errors that this 17% overestimate could produce for your samples? Or give a general idea of how small the effect is?”

A ~17% overestimate of $[N_2O]_{eq}$ *would result from the difference between the 2013 atmospheric mixing ratio of 323 ppb and the preindustrial* N_2O *mixing ratio we assumed to be 275 ppb.*

The resulting error in $[N_2O]_{eq}$ *would be largest for cold waters (e.g. resulting in an overestimation of ~1.2 nM for waters at 2°C). To precisely estimate the effect of this error, the water mass age would be required for all samples. Generally, the oldest waters are also associated with high AOU and delta* N_2O *(except for samples showing signals of* N_2O *consumption, but the determination of the delta* N_2O */ AOU correlation is not applicable for these samples anyway), the error in* $[N_2O]_{eq}$ *would thus marginally change the slope of the delta* N_2O*/AOU regression.*

R2: “Is the ‘pump-CTD’ water collected from the ships flow-through system?”

The pump-CTD is a separate instrument that allows water sampling by directly pumping the water from different sampling depth onboard. It can be used for water profiling of discrete samples in high depth resolution.

R2: “Is it true that N_2O depletion coincided with high nitrate to phosphate ratios? I would have thought N_2O depletion would coincide with low N:P ratios, consistent with N loss during denitrification?”

N_2O depletion at low oxygen concentrations is indeed observed in areas with high N loss and thus low N:P ratios (see e.g. Figure 3). Our data do not indicate the opposite.

Technical corrections:

R2: “I find some of the text in some figures to be too small to read (e.g. Figures 2, 3 and 4).”

The figures were modified to improve their readability.

R2: “Page 10176 line 2 – consider replacing ‘low N’ and nitrate’, with ‘more negative N’ and low nitrate“

Changed as suggested.

R2: “Page 10178 line 1-2, consider replacing ‘when oxygen reached suboxic’, to ‘when waters reached suboxic’”

Changed as suggested.

R2: “Page 10178 Line 14: do you mean that N_2O accumulation took place during and following the ventilation of water? Please clarify.”

Increased N_2O production is likely to be triggered by transition from anoxic to oxic conditions and may be restricted to only a short time-period after re-ventilation. We added a few sentences on the oxygen conditions required for increased N_2O production to take place to clarify this context.

R2: “Page 10179 line 14: you say ‘at relatively low concentrations’, do you mean low oxygen concentrations or N_2O concentrations? Please clarify.”

In this case we meant N_2O concentrations to be low. We clarified the sentence as suggested by the reviewer.

Extreme N_2O accumulation in the coastal oxygen minimum zone off Peru

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Abstract

Depth profiles of nitrous oxide (N_2O) were measured during six cruises to the upwelling area and oxygen minimum zone (OMZ) off Peru in 2009 and 2012/2013, covering both the coastal shelf region and the adjacent open ocean. N_2O profiles displayed a strong sensitivity towards oxygen concentrations. Open ocean profiles showed a transition from a broad maximum to a double-peak structure towards the centre of the OMZ where the oxygen minimum was more pronounced. Maximum N_2O concentrations in the open ocean were about 80 nM. A linear relationship between ΔN_2O and apparent oxygen utilization (AOU) could be found for all measurements within the upper oxycline, with a slope similar to studies in other oceanic regions. N_2O profiles close to the shelf revealed a much higher variability, with N_2O concentrations in the upper oxycline reaching up to several hundred nanomoles per liter at selected stations. Due to the extremely sharp oxygen gradients at the shelf, these maxima occurred in very shallow water depths of less than 50 m. In the coastal area, a linear relationship between ΔN_2O and AOU could not be observed as extremely high ΔN_2O values were scattered over the full range of oxygen concentrations. Our results indicate that the coastal upwelling off Peru at the shelf causes conditions that lead to extreme N_2O accumulation, most likely due to the interplay of high rates of nitrogen cycling and a rapid switching of the OMZ waters from anoxic to oxic conditions as a result from coastal upwelling and subsequent strong remineralization in the water column along the Peruvian coast.

1 Introduction

Nitrous oxide (N_2O) acts as a strong atmospheric greenhouse gas and contributes substantially to the stratospheric ozone depletion (IPCC, 2013;WMO, 2011). The ocean is a major source for N_2O as it is naturally produced in the water column (Ciais et al., 2013;Bange, 2008). While in large parts of the surface ocean N_2O concentrations are close to saturation, high emissions of N_2O have been observed in upwelling areas where subsurface waters enriched in N_2O are transported to the surface (e.g. Nevison et al. (2004)). The global distribution of N_2O in the ocean is closely linked to the oceanic oxygen distribution, and particularly high supersaturations are found in upwelling areas which overlay pronounced oxygen minimum zones (OMZ), e.g. in the Arabian Sea (Bange, 2004) or in the eastern South Pacific Ocean (Charpentier et al., 2010).

These OMZs are key regions for the marine nitrogen (N) cycling where active N loss via canonical denitrification and anaerobic ammonium oxidation (anammox) takes place. Recent studies furthermore indicate that they are also zones of intense nitrogen fixation (Deutsch et al., 2007;Loescher et al., 2014;Fernandez et al., 2011), and in areas where the OMZ is fuelled by high export production, high rates of other N transformation processes, such as nitrification, have been observed (Hu et al., 2015;Kalvelage et al., 2013).

Within the nitrogen cycle, N_2O evolves during nitrification and denitrification (Bange, 2008). Both processes strongly depend on the oxygen availability in the water column, with different responses to the oxygen concentration. Under oxic conditions the first step of nitrification, ammonium-oxidation to nitrite, is known to be the main production pathway for N_2O, with an increasing N_2O yield at decreasing oxygen concentrations (Goreau et al., 1980;Löscher et al., 2012;Frame and Casciotti, 2010). During bacterial ammonium-oxidation, N_2O can either be produced as a side product during the oxidation of ammonia to nitrite or through the reduction of nitrite to N_2O (nitrifier-denitrification) (Stein, 2011). Nitrifier-denitrification has been identified as an important production pathway of N_2O at low oxygen concentrations and may thus be responsible for the increased N_2O production under these conditions (Ni et al., 2014).

While the N_2O production pathways during bacterial nitrification have been studied for several decades, archaeal ammonium oxidation has only recently come into focus as a main production pathway for N_2O. The exact mechanism and the extent to which ammonium oxidation or a nitrifier-denitrification pathway are responsible for archaeal N_2O production as well as the effect of environmental controls on archaeal N_2O production are subject to ongoing research (Stieglmeier et al., 2014;Löscher et al., 2012;Santoro et al., 2011).

During denitrification, the canonical reduction of nitrate to molecular nitrogen, N_2O evolves as an intermediate product. Denitrifying genes are widespread among different groups of microorganisms, but active denitrification is restricted to suboxic to anoxic conditions (e.g. Firestone et al., (1980); Dalsgaard et al. (2014)). Denitrification is a heterotrophic process that is stimulated by the supply of organic carbon or hydrogen sulfide (Chang et al., 2014;Dalsgaard et al., 2014;Galan et al., 2014).Depending on the environmental conditions, N_2O production or consumption due to denitrification can be observed in environmental samples. There has been evidence that N_2O consumption is more sensitive to trace amounts of oxygen than N_2O production. This could lead to N_2O accumulation when oxygen is present in low concentrations (Tiedje, 1988). Exceptionally high N_2O concentrations have been measured off the West Indian Coast where anoxic waters from the Arabian Sea frequently extend over the shelf (Naqvi et al., 2000). These are the highest marine N_2O concentrations reported so far and were associated with an increased N_2O production from denitrification during transient oxygen concentrations. In a recent study it was furthermore shown that N_2O production from denitrification could be stimulated by H_2S addition (Dalsgaard et al., 2014) which could indicate a coupling between N_2O production and sulfur cycling.

Measurements of denitrification and anammox rates in different oceanic OMZs have raised the question whether denitrification or anammox is the main pathway for nitrogen loss in the water column (Hamersley et al., 2007;Ward et al., 2009;Voss and Montoya, 2009). In the ETSP, anammox has been found to play the major role in N loss, whereas denitrification was only rarely detectable (Kalvelage et al., 2013;Hamersley et al., 2007) (Thamdrup et al., 2006). As N_2O is not supposed to be involved in the anammox process (Kartal et al., 2011), anammox does not influence the N_2O distribution and only denitrification is thought to be responsible for N_2O consumption at suboxic to anoxic conditions (Bange, 2008). The widespread N_2O consumption in the OMZ core is thus an indicator for denitrification taking place in the ETSP (Farias et al., 2007). One explanation for these contradicting findings is that denitrification strongly depends on the supply of organic carbon or hydrogen sulfide (Chang et al., 2014;Dalsgaard et al., 2014;Galan et al., 2014).

As nitrification is one major process accompanying the remineralization of organic matter, a positive correlation between the excess N_2O (ΔN_2O) and the apparent oxygen utilization (AOU) is often interpreted as an indication for nitrification as the main N_2O production pathway (e.g. Walter et al. (2006), Forster et al. (2009)). An increase in the ΔN_2O/AOU ratio at low oxygen concentrations has been observed in several studies in different oceanic areas with reduced oxygen concentrations (Ryabenko et al., 2012;Upstill-Goddard et al., 1999;De Wilde and Helder, 1997), whereas a breakdown of this relationship due to N_2O consumption is observed when oxygen concentrations fall below a certain, not well defined, threshold (Zamora et al., 2012).

There is a strong indication that at low oxygen concentrations nitrification and denitrification may take place in close proximity (Kalvelage et al., 2011), and the N_2O production and consumption under these conditions are strongly influenced by the interaction of both processes. Stable isotope and consumption rate measurements of N_2O in oxygen-deficient waters indicated that N_2O accumulates within the oxycline as a result of the coupling between nitrification and denitrification whereas N_2O consumption in the OMZ core was associated with denitrification (Farias et al., 2007;Babbin et al., 2015). The exact oxygen concentration where N_2O consumption starts is not yet well determined, however (Cornejo and Farias, 2012;Zamora et al., 2012). Measurements of N_2O consumption rates in the eastern tropical North Pacific (ETNP) Ocean furthermore provided evidence for a rapid N_2O cycling within the ETNP, although depth profiles of N_2O seemed to be relatively invariant over time (Babbin et al., 2015). These quasi-stable conditions may be disturbed by rapid changes in the environmental conditions.

Although the waters off Peru harbor one of the most prominent OMZs in the world, only a few measurements of N_2O are available so far (Friederich et al., 1985;Nevison et al., 1995;Pierotti and Rasmussen, 1980), . N_2O measurements from the OMZ off Chile indicated the potential for high N_2O production and emissions due to the proximity of the OMZ to coastal upwelling taking place in this area (Charpentier et al., 2007;Castro-Gonzalez and Farias, 2004). Here we present N_2O measurements in the water column off Peru from six measurement campaigns in the ETSP. This upwelling area is one of the four major eastern boundary upwelling systems (EBUS) where alongshore trade winds induce westward transport of the surface water masses which leads to strong coastal upwelling (Chavez and Messié, 2009).The ETSP is characterized by one of the largest and most intense OMZs in the oceans, extending from the Peruvian shelf about 1000 km offshore with a maximum thickness of more than 600 m (Fuenzalida et al., 2009). It is located in the shadow zone of large ocean current systems which leads to a sluggish ventilation and long residence times of waters within the OMZ. To the North of the OMZ, equatorial current bands such as the Equatorial Undercurrent (EUC) and the Southern Subsurface Countercurrents (SSCC) supply waters to the ETSP which leads to slightly higher oxygen concentrations in the northern OMZ compared to the OMZ core (Stramma et al., 2010). The equatorial current bands also feed the poleward Peru-Chile Undercurrent (PCUC) which is the main source for waters upwelled along the coast where high primary production and high remineralization rates in the underlying waters lead to a further drawdown in oxygen concentrations (Karstensen et al., 2008). Active N loss can be observed in large parts of the OMZ which is reflected in a pronounced secondary nitrite maximum and a strong nitrogen deficit in the OMZ core (Codispoti et al., 1986). The OMZ extends over large parts of the Peruvian shelf where sulfidic conditions within the water column are frequently observed (Schunck et al., 2013). While year-round upwelling can be observed along the Peruvian coast, the region is strongly influenced by the El Niño Southern Oscillation (ENSO) leading to large interannual variability in the upwelling intensity which could lead to the interruption of the upwelling during El Niño events (Dewitte et al., 2012). While the OMZ core is largely unaffected by ENSO, a deepening of the upper oxycline and the re-oxygenation of the Peruvian shelf due to the propagation of coastal trapped waves can be observed (Gutierrez et al., 2008).

2 Methods

In total, 146 depth profiles (0-~4200 m) of N_2O were measured on two cruises between December 2008 and February 2009 (M77-3 & M77-4) and four cruises between October 2012 and March 2013 (M90 - M93) to the upwelling area and the adjacent open ocean off Peru onboard the German research vessel Meteor. The Southern Oscillation Indices (http://www.ncdc.noaa.gov/teleconnections/enso/indicators/soi/) from 2008/2009 and 2012/2013 did not indicate the presence of an El Niño event during our measurement campaigns, and similar conditions between both measurement campaigns could be expected. The locations of the sampled stations are shown in Fig. 1. While the M77-4 and M90 cruises mainly covered the open ocean area, the M77-3 and M91-M93 cruises mainly took place in the Peruvian shelf area. The work was part of the German DFG collaborative research project (SFB) 754 (https://www.sfb754.de/) and the BMBF project SOPRAN (Surface Ocean PRocesses in the Antropocene, www.sopran.pangaea.de). The N_2O data set described here has been archived in MEMENTO, the MarinE MethanE and NiTrous Oxide database (https://memento.geomar.de) (Kock and Bange, 2015).

Triplicate samples were taken from 10 L Niskin bottles mounted on a rosette water sampler or a pump-CTD (M77-3) in 25 ± 0.11 mL (M77-3 & M77-4) and 20 ± 0.14 mL (M90 - M93) opaque glass vials and sealed with butyl rubber stoppers and aluminum caps, thereby avoiding the inclusion of air bubbles.

Samples were treated with 0.2 mL (M77-3 & M77-4) and 0.05 mL (M90 - M93) of a saturated mercuric chloride solution directly after the sampling to inhibit microbial N_2O production or consumption. The samples were either analyzed onboard (M77-3 & M77-4, M91, partly M90 & M93) within a few days or shipped to GEOMAR by air freight for later analysis (M92, partly M90 & M93). Samples that were shipped to Germany were additionally sealed with paraffin wax and stored upside down to avoid the formation of air bubbles in the samples due to temperature and pressure changes during transportation.

Samples were analyzed using a static equilibration method: 10 mL helium (99.9999% AirLiquide, Düsseldorf, Germany) was manually injected into each vial which was equipped with a second syringe to collect the overflowing water. Vials with added headspacewere vigorously shaken for about 20 s and allowed to equilibrate at ambient temperature for a minimum of two hours. A subsample of the equilibrated headspace was manually injected into a GC-ECD system (Hewlett-Packard 5890 Series II, Agilent Technologies, Santa Clara, CA, USA), equipped with a 6' 1/8" packed column (molsieve, 5Å, W. R. Grace & Co.-Conn., Columbia, MY). The GC was operated at 190 °C, using argon/methane (95%/5%, ECD purity, AirLiquide, Düsseldorf, Germany) as carrier gas at a flow rate of 30 mL min^{-1}.

The GC was calibrated on a daily basis with a minimum of 2 (M77-3 & M77-4) or 4 (M90 - M93) different standard gas mixtures (N_2O in synthetic air, Deuste-Steininger GmbH, Mühlhausen, Germany and Westfalen AG, Münster, Germany). Standard gases were either injected as pure gas or further diluted with helium (1:3, 1:1 or 3:1) to obtain additional standard gas concentrations. Pure standard gaseswere calibrated against NOAA primary standards at the Max Planck Institute for Biogeochemistry in Jena, Germany, if the standard gas concentrations were within the calibration range of the NOAA gases. Gases with N_2O concentrations outside the NOAA calibration range were internally calibrated using an LGR N_2O/CO analyzer (Los Gatos Research, Mountain View, CA, USA), which was proven to have a linear response and minimal drift within the calibration range (Arevalo-Martinez et al., 2013). The N_2O concentration in the samples was calculated according to Walter et al. (2006) using the solubility function of Weiss and Price (1980). The average precision of the measurements, calculated as median standard deviation from triplicate measurements, was 0.7 nM.

ΔN_2O was calculated as the difference between the in-situ concentration $[N_2O]_w$ and the equilibrium concentration $[N_2O]_{eq}$:

$$\Delta N_2O = [N_2O]_w - [N_2O]_{eq} \qquad (1)$$

We used the contemporary atmospheric mixing ratio measured at Cape Grim, Tasmania (http://agage.mit.edu/data/agage-data) for the calculation of $[N_2O]_{eq}$. This calculation underestimates the N_2O excess in subsurface waters which have been isolated from the surface for a long time as it does not account for the increase in the atmospheric mixing ratio since the beginning of the industrial revolution (Freing et al., 2009). The use of the contemporary N_2O mixing ratio of 2013 would lead to a maximum ~17% overestimate of $[N_2O]_{eq}$, thus leading to only a small error compared to the maximum N_2O concentrations measured in our study, and the use of the contemporary atmospheric mixing ratio still allows a qualitative analysis of the ΔN_2O/AOU relationship in order to investigate the formation and consumption processes of N_2O.

The potential temperature of the water parcel at a certain depth was calculated using the Gibbs Seawater Oceanographic Toolbox (McDougall and Barker, 2011).

Oxygen concentrations were measured either with a Seabird (M77-3 & M77-4: SBE-5; M90-M93: SBE 43) oxygen sensor (Sea-Bird Electronics, Bellevue, WA, USA) mounted on the CTD rosette or from 100 mL discrete samples taken from the Niskin bottles and analyzed using the Winkler titration method (Grasshoff et al., 1999). The oxygen sensor was calibrated against the Winkler measurements.

Recent studies using highly sensitive STOX (Switchable Trace amount Oxygen) sensors for oxygen measurements indicate that measurements with conventional oxygen sensors that are calibrated against Winkler measurements may be biased towards higher concentrations at near-zero oxygen conditions. Thamdrup et al. (Thamdrup et al., 2012) therefore argued that anoxic conditions are prevalent in the core of the Peruvian OMZ where oxygen concentrations of several µM have been found using the conventional Winkler-calibrated measurements. As STOX sensor measurements were not available for all measurement campaigns presented here, the minimum oxygen measurements reported here from the core of the OMZ (3-5 µM) should be considered as an overestimation.

The Apparent Oxygen Utilization (AOU) was calculated from the oxygen concentrations $[O_2]_w$ using the CSIRO SeaWater library, version 3.2 (http://www.cmar.csiro.au/datacentre/ext_docs/seawater.htm) to calculate oxygen saturation $[O_2]_{eq}$:

$$AOU = [O_2]_w - [O_2]_{eq} \qquad (2)$$

Nutrient samples from the CTD rosette were analyzed onboard following the nutrient analysis methods according to Hansen et al. (1999). Samples taken from the pump-CTD during M77-3 were stored at -20°C and shipped to Germany for later analysis. N' was calculated as a measure for the nitrogen deficit from the nitrate ($[NO_3^-]$), nitrite ($[NO_2^-]$) and phosphate ($[PO_4^{3-}]$) concentrations as follows (Altabet et al., 2012):

$$N' = ([NO_3^-] + [NO_2^-]) - 16[PO_4^{3-}] \qquad (3)$$

To distinguish between coastal and open ocean stations we calculated the distance of each station from the continental slope (2000 m isobath) and used the first baroclinic Rossby radius of deformation as described by Chelton et al. ((Chelton et al., 1998)) as threshold distance for stations that were influenced by coastal upwelling.

3 Results and Discussion

The oxygen profiles revealed an intense oxygen minimum zone throughout the studied area, with a vertical thickness of several hundreds of meters. In the open ocean, the oxygen concentrations in the core of the OMZ increased towards the north from below 3 µM south of 5 °S to ~10 µM at the equator. South of 13°S the mixed layer depth significantly increased from ~50 m to ~100 m, which is reflected in the oxygen and N_2O distributions (Fig. 2). Due to the coastal upwelling, the depth of the upper OMZ boundary significantly decreased towards the coast, with a well oxygenated mixed layer of ~50 m in the open ocean and a mixed layer depth of less than 5 m on the shelf. Oxygen was strongly undersaturated in the surface waters on the shelf as a result of upwelling of waters from the underlying OMZ. Elevated phosphate concentrations in the surface waters at the coast also reflected the upwelling on the shelf (Fig. 3).

The vertical profiles showed characteristic nutrient distributions that marked the zones of nitrogen depletion: accumulation of nitrite was observed in the core of the OMZ where oxygen concentrations fell below ~5 µM and low N’ values coincided with the nitrite maxima in the OMZ. The maximum nitrite concentration reached ~13 µM, with a more pronounced maximum at the shelf than in open ocean waters. Additionally, many profiles showed an additional, less pronounced primary nitrite maximum within the upper oxycline that is associated with nitrification (Codispoti and Christensen, 1985) (Fig. 4). At the shelf, strong signals of N loss throughout the water column are reflected in more negative N’ and low nitrate values at the coast (Fig. 3).

The water mass distribution in our dataset agrees well with the data presented by Pietri et al. (2014) (Fig. 5). Due to the larger area covered by our measurements our data showed a broader scattering, but we could identify the same water masses in our data: below 500 m, both the coastal and the offshore profiles carry fresh (S~34.8) and cool (T_{pot}~5°C) Antarctic Intermediate Water (AAIW) (Pietri et al., 2014), while shallower subthermocline waters are covered by the Equatorial Subsurface Water (ESSW). Waters with low salinities (~34.6) and potential temperatures between 10°C and 15°C in the offshore waters can be traced back to Eastern South Pacific Intermediate Water (ESPIW) (Schneider et al., 2003). This water mass can hardly be identified in the coastal data. Cold Coastal Water (CCW) with S ~15 and T_{pot} ~ 17°C could only be identified in the coastal data as it is directly related to the coastal upwelling, whereas the offshore surface data were associated with Subtropical Surface Water (STSW) (Pietri et al., 2013). The N_2O depth distribution showed a strong sensitivity to oxygen concentrations throughout the study area, and strong differences between coastal and offshore stations could be observed. In the offshore waters, surface N_2O concentrations were close to saturation, with a strong increase below the mixed layer (Fig. 2). Two types of depth profiles could be identified, reflecting marginal differences in the minimum oxygen concentrations observed in the OMZ: a broad N_2O maximum at the depth of the oxygen minimum was found at the northern and southern periphery of the oxygen minimum zone where the minimum oxygen concentrations did not fall below 5 µM. In contrast, N_2O depletion was found in the core of the OMZ, where oxygen concentrations below 5 µM were observed over a wide depth range. The N_2O depth profiles in the central OMZ thus revealed a double-peak structure with narrow N_2O maxima in the upper and lower oxycline (Fig. 4). This depth profile structure has been frequently observed in other oceanic areas with highly depleted oxygen concentrations (e.g.(Bange et al., 2010)). N_2O depletion coincided with nitrite accumulation in the OMZ core and high nitrate to phosphate ratios. In all offshore profiles N_2O concentrations did not exceed 80 nM.

A bilinear ΔN_2O/AOU relationship has been identified in the upper oxycline for waters with oxygen concentrations higher than 5 µM during the M77-4 cruise that took place in the offshore waters of the OMZ (Ryabenko et al., 2012). We found a very similar relationship for all offshore data with no systematic difference between the data from the M77-4 (January/February 2009) cruise and the M90 (November 2012) cruise (Figures 2, 6a). This indicates a comparable setting of the open ocean OMZ waters during both cruises. We furthermore found no difference in the ΔN_2O/AOU relationship between stations with a broad N_2O maximum and a double-peak structure. These results are similar to previously reported ΔN_2O/AOU relationships from other oceanic OMZs (Upstill-Goddard et al., 1999;Cohen and Gordon, 1978;De Wilde and Helder, 1997).The ΔN_2O distribution in the TS-diagram (Fig. 5) showed that elevated ΔN_2O values were mainly associated with

AAIW and ESSW, while surface waters were close to saturation. Compared to the offshore waters, the N_2O distribution on the shelf and in the adjacent deep waters showed a much larger variability. N_2O depletion was in fact observed at oxygen concentrations below 5 µM, too. While several N_2O profiles revealed a shape similar to the offshore profiles, an overall characteristic shape of the profiles could not be identified, however: profiles with a subsurface N_2O maximum in the oxycline were observed as well as profiles with multiple maxima or a surface N_2O maximum (Fig. 4). N_2O accumulation with concentrations which strongly exceeded the maximum offshore N_2O concentrations of 80 nM was frequently observed. Several profiles showed an extreme N_2O accumulation with concentrations up to ~850 nM (Fig. 4). The location and shape of the N_2O maxima in the different profiles was highly variable, which resulted in a very patchy distribution of N_2O in the water column over the shelf and in the adjacent waters (Fig. 3). This is also reflected in the TS-diagram of the coastal data (Fig.5), which showed that elevated ΔN_2O values were associated with CCW, but displayed a large variability within this water mass. High resolution measurements of surface N_2O during M90, M91 and M93 also revealed a very heterogeneous surface N_2O distribution with remarkably high concentrations of N_2O in vicinity of the main upwelling cells off Peru (Arevalo-Martinez et al., 2015).

In contrast to the open ocean waters, a correlation between ΔN_2O and AOU was not observed for the coastal data (Fig. 6b). The ΔN_2O/AOU ratio from the offshore waters serves as a lower limit for the coastal stations, where numerous values with much higher ΔN_2O/AOU ratios were observed. These data were highly scattered over the full range of oxygen concentrations, indicating that for the coastal stations the N_2O maxima were not associated with suboxic conditions as observed offshore. The ΔN_2O values that showed the strongest deviation from the offshore ΔN_2O/AOU ratio were associated with highly negative N’ values as a signal for a large nitrogen deficit (Fig. 6b). This indicates that these waters with extreme N_2O accumulation had been subject to extensive N loss.

Extreme accumulation of N_2O with concentrations up to 765 nM in the oceanic water column has also been found in the Arabian Sea (Naqvi et al., 2010;Naqvi et al., 2006) and at a time series station off Chile (Farías et al., 2015), where maximum concentrations of ~500 nM were found. Naqvi et al. (2000) explained the extreme N_2O accumulation over the Indian shelf with the response of denitrifying enzymes to transient oxygen depletion. N_2O thus accumulated when waters reached suboxic conditions. N_2O accumulation coincided with the accumulation of nitrite and consumption of N_2O started when these waters became sulfidic (Naqvi et al., 2010). Farías et al. (2015) measured N_2O accumulation during the transition from oxic to anoxic conditions, too, but at variable oxygen concentrations whereas N_2O depletion became dominant under suboxic conditions. In contrast to the results from the Indian Ocean, they identified enhanced remineralization due to short-term variability in coastal upwelling as the main driver for N_2O accumulation.

In our study, N_2O accumulation did not coincide with the accumulation of nitrite. N_2O was generally depleted in samples that showed marked nitrite accumulation (Fig. 4) and similar to the measurements off Chile, we found strongly elevated N_2O concentrations (>100 nM) over the full range of oxygen concentrations (Fig. 5), whereas N_2O accumulation on the Indian shelf was restricted to suboxic conditions.

The high oxygen concentrations found in the majority of our samples with extreme N_2O accumulation excludes in-situ denitrification or anammox (see e.g. Babbin et al. (2014), Dalsgaard et al. (2014)). The extraordinarily high N_2O concentrations as well as the low N' values thus have to be old signals of processes taking place under anoxic to suboxic conditions. There is no known consumption process for N_2O in oxygenated waters (Bange, 2008), and the strong signals of N loss that are produced under anoxic conditions are unlikely to be rapidly compensated by N fixation upon oxygenation. Both signals thus are likely to have remained preserved when oxygen concentrations increased due to (diapycnal or isopycnal) mixing with waters of higher oxygen concentration or due to direct contact with the atmosphere as a result of upwelling. Our observations of high N_2O concentrations in oxygenated waters furthermore indicate that this accumulation could have taken place during re-oxygenation rather than during decreasing oxygen concentrations. An increase in oxygen concentrations would lead to the preservation of the high N_2O signals in the water column whereas further decreasing oxygen concentrations would only lead to a temporal N_2O accumulation and would eventually stimulate N_2O consumption.

Enhanced production of N_2O after transition from anoxic to oxic conditions is a known process occurring in soils (e.g. Morley et al. (2008)) and may be explained by different sensitivity of denitrifying enzymes to trace concentrations of oxygen (Tiedje, 1988). In a recent incubation study, Dalsgaard et al. (2014) found no indication for an increased N_2O production by denitrification due to changes in the oxygen concentration at nanomolar levels, however. Instead, autotrophic denitrification and N_2O production have been shown to be stimulated by the addition of hydrogen sulfide (H_2S) (Galan et al., 2014;Dalsgaard et al., 2014). We did not find direct evidence for a coupling between N_2O production and the presence of H_2S in our measurements, as high N_2O accumulation was often found in proximity to H_2S plumes but was also detected when H_2S was absent in the water column. We cannot exclude that the high N_2O production we frequently observed at the shelf is stimulated by a coupling of denitrification with sulfur cycling, though: Canfield et al. (2010) found evidence for active sulfur cycling in the ETSP without H_2S accumulation, and a coupling between H_2S oxidation and denitrification has been shown before (Galan et al., 2014;Jensen et al., 2009). Indeed, active denitrification was found in proximity to H_2S plumes in the water column during M77-3 (Kalvelage et al., 2013;Schunck et al., 2013).

In the ocean, increased N_2O production was also associated with the onset of nitrification after re-ventilation of the water column in a seasonal study in the Baltic Sea, but with relatively low resulting N_2O concentrations (Naqvi et al., 2010). Yu et al. (2010) found strongly increased N_2O production by nitrifying bacteria that was stimulated by the availability of ammonium during recovery from anoxic conditions in a chemostat culture experiment. Their results point towards an increased N_2O production via the ammonium-oxidation pathway, while N_2O production by nitrifier-denitrification seemed not to be stimulated by the shift from anoxic to oxic conditions. We frequently measured high ammonium concentrations along the Peruvian shelf, indeed (Fig. 4), which could have stimulated N_2O production from ammonium oxidation. A direct correlation between N_2O and ammonium could not be identified, however. From our concentration measurements alone we thus cannot distinguish if the observed high production of N_2O is a result of denitrification or nitrification processes. Studies of the isotopic and isotopomeric N_2O composition could reveal more detailed insights whether N_2O is produced via the ammonium oxidation or the nitrite reduction pathway during extreme accumulation.

Together with the high N_2O concentrations we found low N' values that were associated with oxygenated waters only at the shelf, whereas in the open ocean N depletion was restricted to the OMZ core (Fig. 6). This could indicate that the re-oxygenation of the oxygen-deficient waters mainly happens at the shelf, whereas waters in the open ocean OMZ are less affected by mixing processes. Strong diapycnal and isopycnal mixing on the shelf has indeed been reported from the Peruvian and Mauritanian upwelling region (Schafstall et al., 2010; Thomsen et al., JGR, submitted, 2015, (Pietri et al., 2014)).

The upwelling-induced high primary production in the surface ocean furthermore fuels rapid oxygen consumption in the underlying waters due to the export and remineralization of organic matter, thereby creating strong small-scale variability in oxygen concentrations. Kalvelage et al. (2013) showed that these high remineralization rates also induce strong N cycling in the subsurface layer. Turnover rates for different N species are therefore much faster on the shelf than in the open ocean OMZ (Hu et al., 2015),which is also reflected in the distribution of different functional gene abundances (Loescher et al., 2014). One factor that also contributes to the N_2O accumulation on the shelf could thus be generally higher rates of nitrification and/or denitrification on the shelf than in the open ocean.

4 Summary and Conclusions

We observed extreme N_2O accumulations over the Peruvian shelf and in the adjacent waters with maximum concentrations similar to the observations made by Naqvi et al. (2000) over the Indian shelf and Farías et al. (2015) off Chile, whereas N_2O concentrations in the open ocean OMZ off Peru were comparably moderate.

We found strong evidence that N_2O accumulations are preserved when oxygen concentrations increased as a result of mixing and exchange with the overlying atmosphere in the upwelling zone. Waters with high N_2O concentrations can thus be directly and frequently transported to the surface ocean. This makes this region one of the most important oceanic regions for N_2O emissions to the atmosphere (Arevalo-Martinez et al., 2015). This direct link between unusually high N_2O production and emissions over the Peruvian shelf makes it necessary to understand the biogeochemical processes involved in N_2O production and consumption to produce reliable predictions of oceanic emissions from this area. Current approaches to model the N_2O distribution rely on parameterizations based on the linear ΔN_2O/AOU relationship (Suntharalingam and Sarmiento, 2000;Nevison et al., 2003;Freing et al., 2012). These approaches could in fact reproduce the oxygen distribution in the open ocean OMZ off Peru reasonably well, but they fail to account for the extreme N_2O accumulation and its high spatial and temporal variability over the shelf area. They thus significantly underestimate the emissions from the Peruvian upwelling and potentially other upwelling areas with similar conditions, too.

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Figures:

Figure 1: Station maps of the sampled N_2O stations from cruises A) M77-3, December 2008 – January 2009 (●) and M77-4, January – February 2009 (⊙), B) M90, November 2012 (●) and M91, December 2012 (⊙), C) M92, January 2013 (●) and M93, February – March 2013 (⊙). Section annotations in A) and B) correspond to the vertical sections shown in Fig. 2 and 3.

Figure 2: Spatial distributions of oxygen (A, B), nitrite (C, D) and N_2O (E, F) along 86°W during M77-4 (2009, A, C, E) and M90 (2012, B, D, F). Small dots indicate location and depth of the discrete samples. Data gridding: ODV/DIVA.

Figure 3: Cross-shelf distribution of A) Oxygen, B) Phosphate, C) Nitrate, D) N', e) Nitrite and f) N_2O during M91 (Section F).

Figure 4: Selected depth profiles of oxygen (black dots, dotted line), sigma-theta (grey line) and N_2O (red line, open circles) (left panel) and nitrate (grey line), nitrite (black circles, dotted line), ammonium (blue diamonds, straight line) and N' (red line, small dots) (right panel) from selected open ocean and shelf stations during M90-93. Depth profiles of oxygen and sigma-theta were taken from the CTD sensors, the other parameters are taken from discrete samples. The locations of the respective stations are shown in the map. Red signals denote stations classified as "coastal" stations whereas blue signals denote "offshore" stations. Please note the changes in the scales for N_2O, sigma-theta, nitrite and ammonium.

Figure 5: Temperature-Salinity diagrams with ΔN_2O color coded for a) the offshore stations and b) the onshore stations. Different symbols denote different cruises: ☆M77-3; ◊ M77-4; ○ M92; ▷M90; ◁ M91; ✳M93.

Figure 6: ΔN_2O/AOU relationship from a) offshore stations and b) coastal stations. Samples from the upper OMZ and oxycline (sample depth < 350 m) are color coded with N'. Different symbols for different cruises are denoted the same as in Figure 5. The black line denotes the ΔN_2O/AOU relationship from the offshore

data for samples with O2>50 µM and depth < 350 m ($y=0.13x+3.73$; $r^2=0.83$). Please note the change in the scaling for ΔN_2O values of 0 - 100 nM and 100 - 1000 nM (dotted line).

Figure 1:

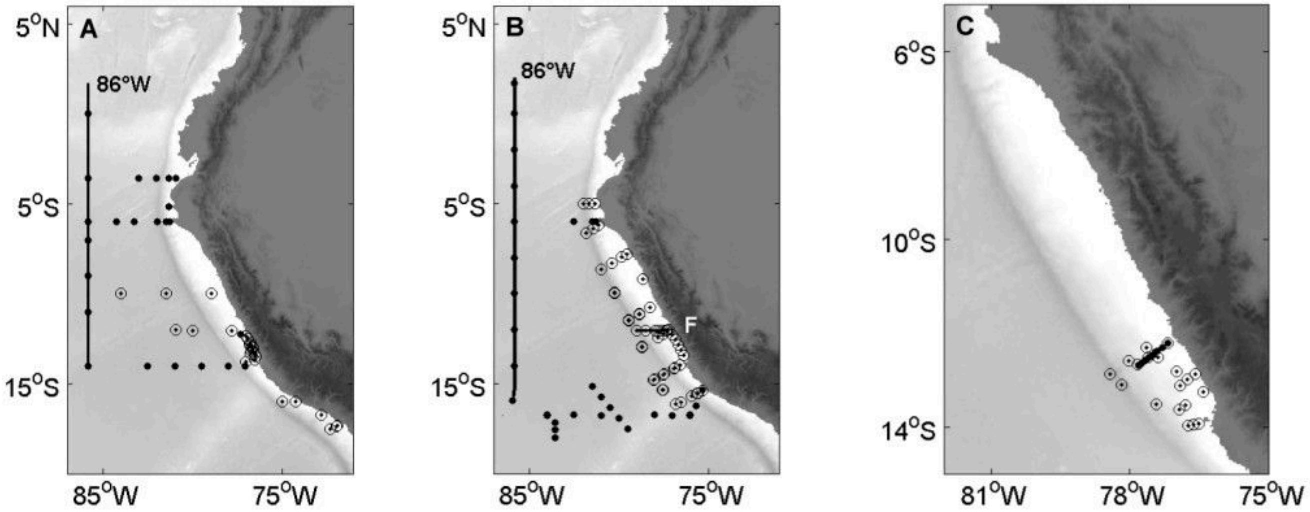


Figure 2:

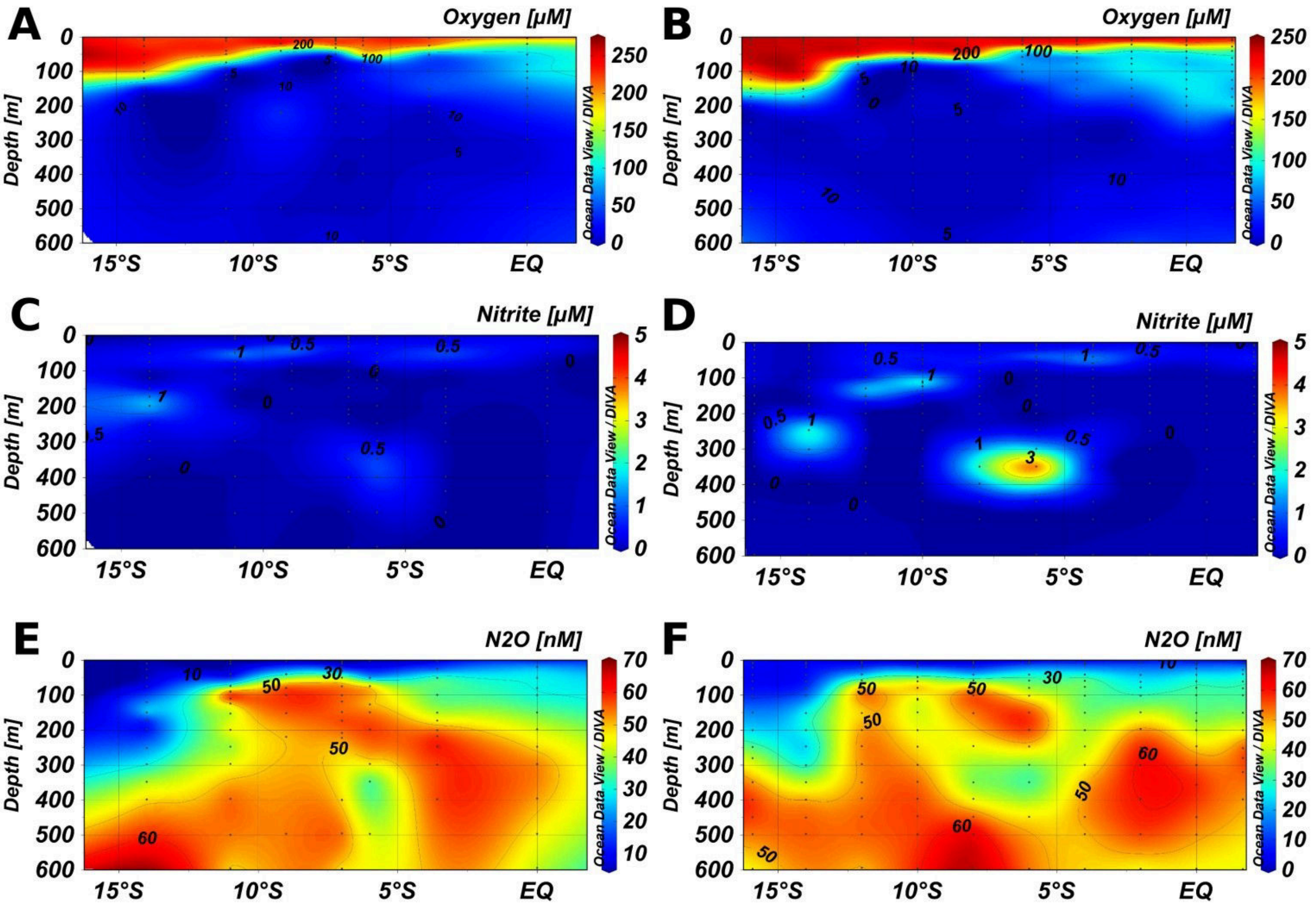

A
Oxygen [µM]
B
Oxygen [µM]
C
Nitrite [µM]
D
Nitrite [µM]
E
N2O [nM]
F
N2O [nM]
Depth [m]
0
100
200
300
400
500
600
15°S
10°S
5°S
EQ
Ocean Data View / DIVA
250
200
150
100
50
0
5
4
3
2
1
0
70
60
50
40
30
20
10
0
200
100
10
5
0.5
1
3
30
50
60

Figure 3:

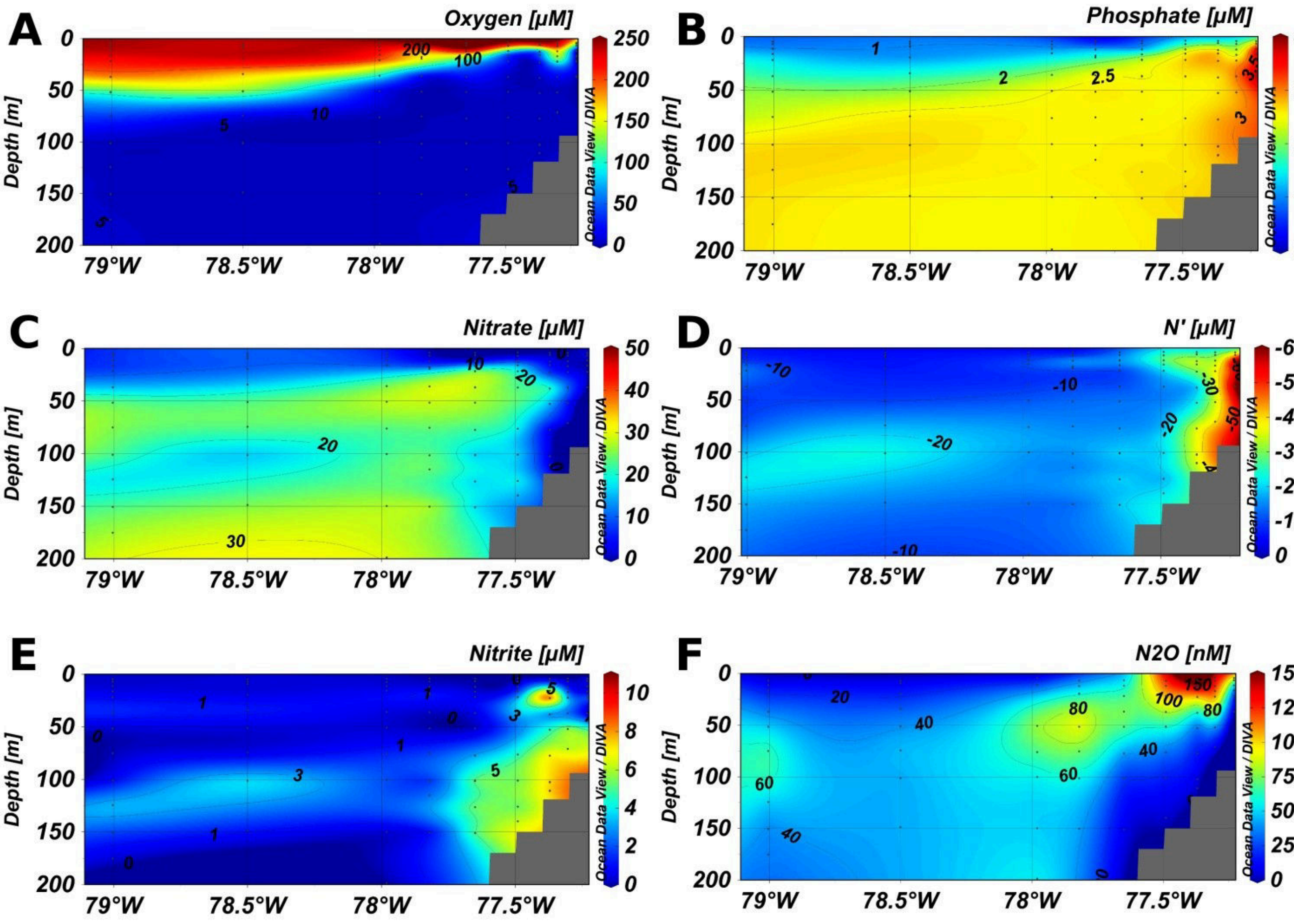

A
Oxygen [μM]
Depth [m]
0
50
100
150
200
79°W
78.5°W
78°W
77.5°W
200
100
10
5
5
5
250
200
150
100
50
0
Ocean Data View / DIVA
B
Phosphate [μM]
1
2
2.5
3.5
3
4
3
2
1
0
C
Nitrate [μM]
10
20
0
20
30
50
40
30
20
10
0
D
N' [μM]
-10
-10
-20
-30
-50
-20
-10
-60
-50
-40
-30
-20
-10
0
E
Nitrite [μM]
1
1
0
0
5
3
1
3
5
1
0
10
8
6
4
2
0
F
N2O [nM]
20
40
80
150
100
80
40
60
60
40
0
150
125
100
75
50
25
0

Figure 4:

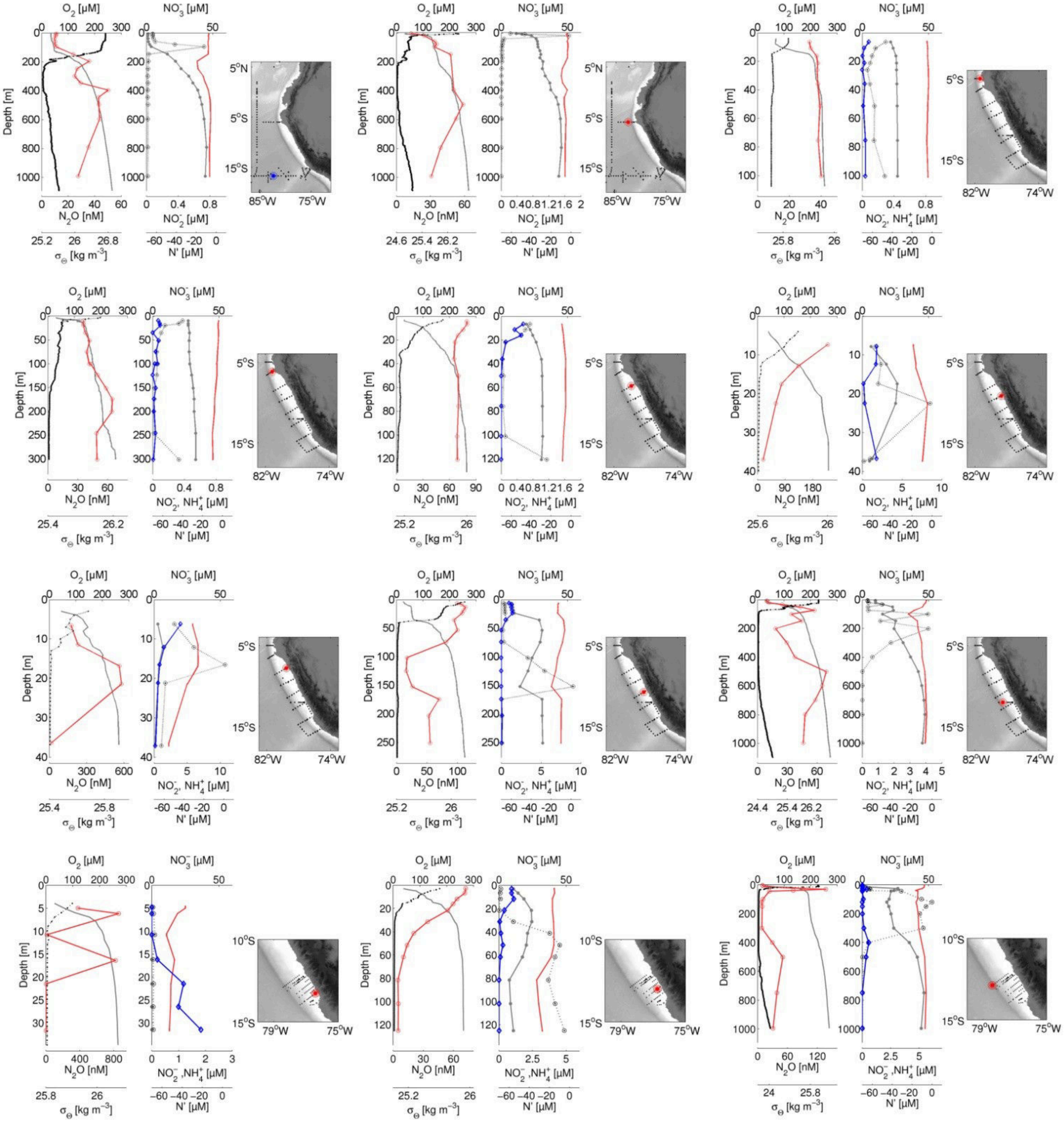

O$_2$ [µM]
NO$_3^-$ [µM]
Depth [m]
N$_2$O [nM]
NO$_2^-$ [µM]
NO$_2^-$, NH$_4^+$ [µM]
σ$_Θ$ [kg m^{-3}]
N' [µM]
5°N
5°S
10°S
15°S
85°W
75°W
82°W
74°W
79°W

Figure 5:

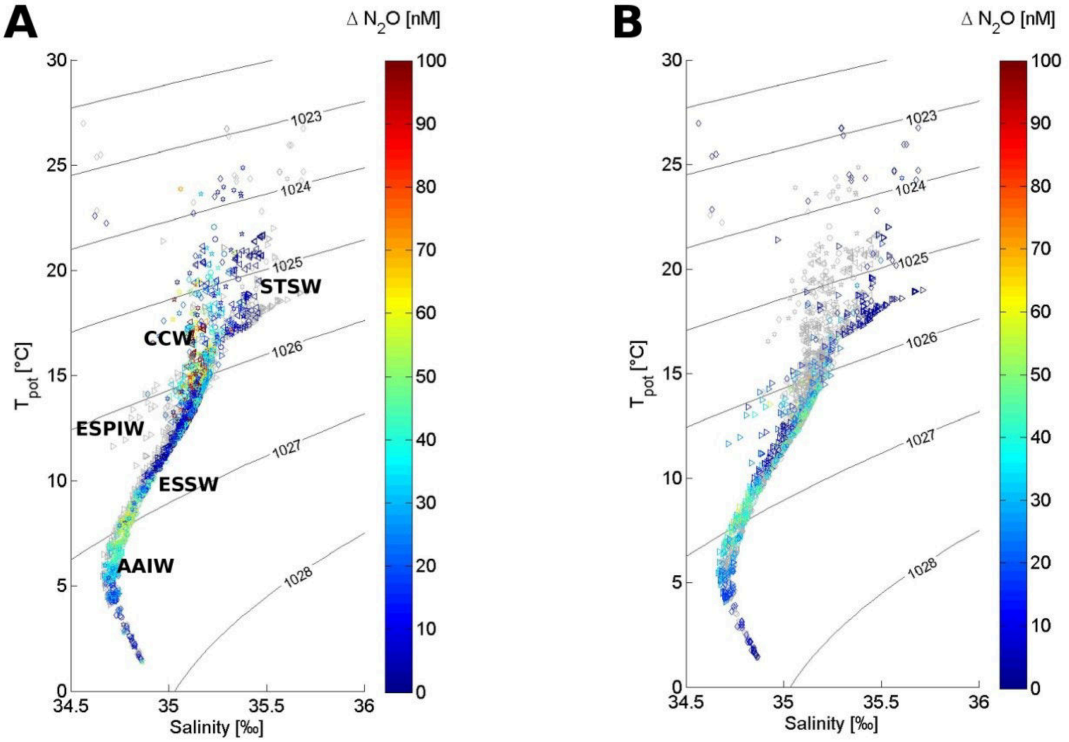
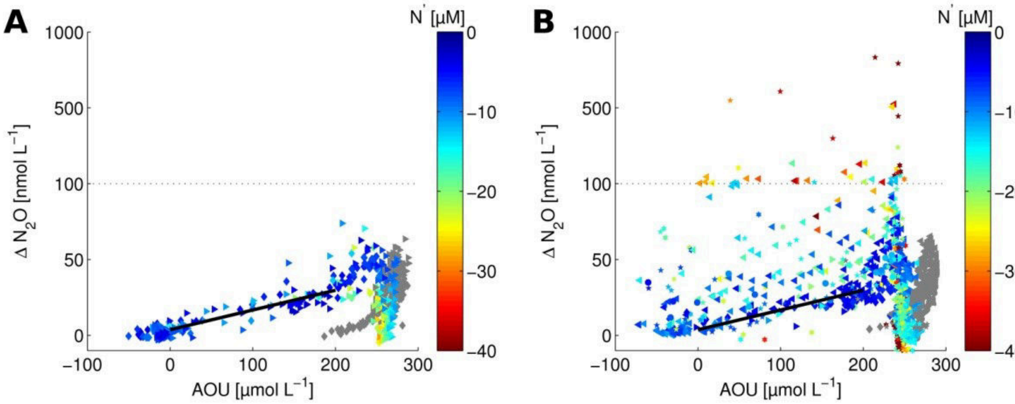

A
Δ N$_2$O [nM]
T$_{pot}$ [°C]
Salinity [‰]
1023
1024
1025
1026
1027
1028
STSW
CCW
ESPIW
ESSW
AAIW
30
25
20
15
10
5
0
34.5
35
35.5
36
100
90
80
70
60
50
40
30
20
10
0
B
Δ N$_2$O [nM]
T$_{pot}$ [°C]
Salinity [‰]

Figure 6:


A
B
Δ N_2O [nmol L^{-1}]
1000
500
100
50
0
−100
0
100
200
300
AOU [µmol L^{-1}]
N' [µM]
0
−10
−20
−30
−40