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Following the N_2O consumption in the oxygen minimum zone of the eastern South Pacific

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Abstract. Oxygen minimum zones (OMZs), such as those found in the eastern South Pacific (ESP), are the most important N_2O sources in the global ocean relative to their volume. N_2O production is related to low O_2 concentrations and high primary productivity. However, when O_2 is sufficiently low, canonical denitrification takes place and N_2O consumption can be expected. N_2O distribution in the ESP was analyzed over a wide latitudinal and longitudinal range (from 5° to 30° S and from 71–76° to ∼84° W) based on ∼890 N_2O measurements. Intense N_2O consumption, driving undersaturations as low as 40 %, was always associated with secondary NO_2^- accumulation (SNM), a good indicator of suboxic/anoxic O_2 levels. First, we explore relationships between ΔN_2O and O_2 based on existing data of denitrifying bacteria cultures and field observations. Given the uncertainties in the O_2 measurements, a second relationship between ΔN_2O and NO_2^- (> 0.75 µM) was established for suboxic waters (O_2 < 8 µM). We reproduced the apparent N_2O production (ΔN_2O) along the OMZ in ESP with high reliability ($r^2 = 0.73$ $p = 0.01$). Our results will contribute to the quantification of the N_2O that is recycled in O_2 deficient waters, and improve the prediction of N_2O behavior under future scenarios of OMZ expansion and intensification.

1 Introduction

Nitrous oxide (N_2O), a strong greenhouse gas and contributor to stratospheric ozone depletion, is produced in the oceans by archaeal and bacterial nitrification (Santoro et al., 2011) under a wide range of oxygen concentrations, including hypoxic and suboxic levels (Goreau et al., 1980; Frame and Casciotti, 2010). It is also generated by partial denitrification (dissimilative nitrate reduction to N_2O) in O_2 deficient environments (Codispoti and Christensen, 1985). Both the above mentioned processes contribute around 30 % of the global atmospheric N_2O sources (IPCC, 2007). However, when O_2 is near zero or anoxia is found, N_2O is consumed by canonical denitrification, producing N_2. Denitrification is an anaerobic respiration process which uses NO_3^- as an electron acceptor instead of O_2 and consists of several steps ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$), each one mediated by different enzymes (i.e. NO_3^-, NO_2^-, NO and N_2O reductases), which show different sensitivities to O_2 levels (Bonin et al., 1989; Naqvi et al., 2000). For instance, in *Pseudomonas nautica* cultures, NO_3^- begins to be consumed at O_2 < 125 µM, whereas N_2O is consumed at O_2 <∼ 7.8 µM (Bonin et al., 1989). NO_2^- is accumulated in the first stages of denitrification (Samuelsson, 1985; Bonin et al., 1987; Kester et al., 1997), while N_2O production stops at high NO_2^- concentrations (Bonin et al., 1987). The reasons by which NO_2^- accumulates and N_2O disappears are not well known, but when NO_2^- decreases, N_2O production is reestablished and its accumulation takes place.

Oxygen minimum zones (OMZs) have marked vertical oxygen gradients from their upper and lower boundaries (oxyclines) towards the core. This kind of O_2 distribution triggers intense nitrogen species cycling, particularly for N_2O. In these zones, N_2O levels can drop up to 20 times in less than 50 m depth (Farías et al., 2009). Thus, it is common to observe a zone of high N_2O production and accumulation

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located at the oxyclines, but below those there is intense N_2O consumption and depletion at the OMZ's core. Within the core, O_2 concentration has been reported to be lower than 0.5 µM (Codispoti and Christensen, 1985; Naqvi and Noronha, 1991; Farías et al., 2009), and even as low as nanomolar concentrations (Thamdrup et al., 2012).

Consumption in the OMZ's core is offset by high N_2O production at the oxycline. Many of these areas are associated with eastern boundary upwelling ecosystems, which are major sources of oceanic atmospheric N_2O (Naqvi et al., 2010). This is the case of the OMZ in the eastern South Pacific (ESP) where intense N_2O exchange with the atmosphere has been reported (Farías et al., 2009). The ESP's OMZ is characterized by O_2 concentrations as low as 2 nM at its core (Revsbech et al., 2009), being one of the most intense and shallow in the world ocean (upper boundary as shallow as 50 m; Morales et al., 1999). Recent results suggest that the accumulation of more than 0.5 mmol kg^{-1} nitrite is a robust indicator of oxygen depletion (at least in nanomolar range, Thamdrup et al., 2012). This layer is subject to intense denitrification with N_2O consumption exceeding its production (Codispoti et al., 1986). It leads to important fixed nitrogen (N) losses with climate implications. Despite this, the N cycle of the ESP's OMZ has not been the subject of systematic and intensive research. During the 70s and 80s, many studies were conducted in the ESP's OMZ to assess the role of denitrification in N loss along the secondary nitrite maximum (Carlucci and Schubert, 1969; Cline and Richards, 1972; Codispoti and Christensen, 1985). In recent years, the focus has been put on the anammox process as the main cause of nitrogen loss in OMZs (Thamdrup et al., 2006; Lam et al., 2009). The latter has led to the dichotomy regarding the main process responsible for global N loss, i.e. denitrification vs. anammox (Kuypers et al., 2005; Ward et al., 2009), but the origin and cycling of N_2O in these areas has been ignored. In particular, no explanation has been provided for the high N_2O consumption, which occurs only by denitrification under very low O_2 conditions (Castro-González and Farías, 2004; Farías et al., 2007). This was recently shown by isotopes signal profiles from NO_2^- and NO_3^-, which are consistent with denitrification (Ryabenko et al., 2012).

The importance of the OMZ in nitrogen loss and N_2O production, makes it necessary a better understanding of current and future N_2O behavior in the region under predicted scenarios of expansion (involved volume) and intensification (decreasing O_2 levels) of OMZs (Stramma et al., 2008). In this regard, it is also important to understand the sensitivity of the N_2O cycle to O_2 levels.

Models of N_2O in the OMZ are based on the premise that N_2O is produced by nitrification and denitrification according to O_2 concentrations observed in the ocean (Nevison et al., 1995; Suntharalingam et al., 2000; Freing et al., 2009). These models are supported by both experiments of N_2O production by nitrification (Goreau et al., 1980) and estimations of in-situ N_2O production by denitrification resulting in increasing N_2O production as O_2 decreases (Kester et al., 1997). But the models do not include consumption by denitrification at low O_2 concentrations (< 8 µM) (Nevison et al., 2003). For this reason, the results of these model outputs are poorly fitted in areas such as OMZ's cores of the Arabian Sea and eastern tropical North Pacific.

Here we analyzed the behavior of N_2O in the OMZ of the ESP, examining the factors that drive its consumption. Then we assessed an approach for determining N_2O distribution when O_2 concentrations fall below 8 µM, observed most of the time in the coastal band of the ESP. We examined two correlations: one dependent on O_2 concentrations measured with high sensitivity methods (STOX) and the other dependent on NO_2^- concentrations. Finally, we combine our results with previously reported equations for N_2O production in the OMZ, when O_2 concentrations are higher than 8 µM.

2 Methods

2.1 Hydrographic, biogeochemical and N_2O variables

Data from 10 cruises carried out between 5° S and 30° S and from the coast to 81° W, were analyzed, including CTD, O_2, NO_3^-, NO_2^-, PO_4^{-3} and N_2O concentration data collected between 2000 and 2010 (Table 1; Fig. 1a). Oxygen concentrations were obtained by two methods: standard Winkler analysis (analytical error 1.26 %) and a STOX sensor (more information in Revsbech et al., 2009), as indicated in Table 1. The STOX sensor has a detection limit of 10 nmol kg^{-1}.

N_2O concentrations were obtained by discrete sampling of seawater from different depths using 20 ml-vials that were poisoned with $HgCl_2$ (50 µl of 50 % saturated $HgCl_2$). The determination of N_2O concentrations was done using the headspace technique (McAullife, 1971) with a gas chromatograph (Varian 3380) equipped with a Poropack-Q column and an electron capture detector (ECD). The calibration curve was made with 5 points (He, 0.1 ppm, air, 0.5 ppm and 1 ppm) and the detector lineally responded to this concentration range. The analytical error for the N_2O analysis was 3 % and a total of 890 measurements were analyzed. Filtered water was collected for nutrient analyses in clean plastic flasks (30 ml) and was analyzed on board (for the case of NO_2^- and PO_4^{-3}) or frozen until analysis in the laboratory in the case of NO_3^-. Nutrient concentrations were obtained by manual or automatized colorimetric methods depending on the cruise. Their respective analytical errors are reported by (Farías et al., 2009; Thamdrup et al., 2012).

2.2 Data Analysis

Apparent oxygen utilization (AOU) (Murray and Riley, 1969) was estimated by subtracting in-situ O_2 concentrations from the oxygen saturation value (as a function of temperature, salinity and depth), while apparent N_2O production

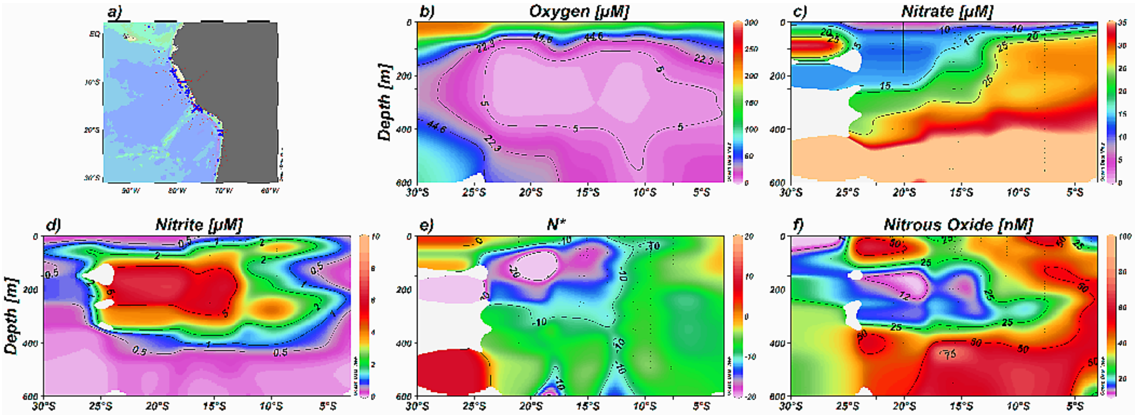

Fig. 1. **(a)** Study area. Blue points indicate the stations included in meridional vertical distributions of **(b)** oxygen [µM]; **(c)** nitrate [µM]; **(d)** nitrite [µM]; **(e)** N* according to Deutsch et al. (2001); and **(f)** nitrous oxide [nM].

Table 1. Number of N_2O profiles and locations of cruises included in the analysis.

Cruise	Date	N° of profiles	Latitudinal range of sampling
MINOX	Mar 2000	4	20.8° S–21.2° S
Iquique 2000	Sep 2000	2	21.1° S
Iquique 2001	May 2001	7	21.1° S
Iquique 2002	Apr 2002	1	21.1° S
Dinamo	Mar 2004	1	20.1° S
Prodeploy	Jul 2004	1	20.3° S
Knorr	Nov 2005	26	3.6° S–17.7° S
Galathea	Feb 2007	16	5.3° S–29.3° S
MOOMZ II	Aug 2009	7	20.1° S
MOOMZ III	Jan 2010	5	20.1° S

(ΔN_2O) (Yoshinari, 1976) was computed by subtracting the N_2O saturation concentration (Weiss and Price, 1980) as a function of depth and temperature from the in-situ N_2O concentration. In order to obtain the N_2O equilibrium concentrations at every depth, the age of the water mass and then the atmospheric N_2O concentration during the year of the water mass formation was estimated by using CFC-11 and CFC-12 concentrations from the P19 and P21 transects of WOCE, according to Fine (2011). The water samples collected in this study were assumed to be the same age as the calculated water mass age from WOCE. As WOCE transects were located only in one part of our study region, in order to estimate the age of water masses south of 17° S, we assumed a water mass velocity of $10\,cm\,s^{-1}$ (Pizarro et al., 2002). With the ages of the water mass, we obtained the atmospheric N_2O concentrations from historical data (Holland et al., 2005). The mixing between water masses was not considered in the present study. Negative/positive AOU values indicated production/consumption of O_2, while the reverse is true for ΔN_2O.

3 Results and Discussions

3.1 Observing the ESP's OMZ (0–30° S)

The meridional distributions of O_2, NO_3^-, NO_2^- and N_2O are shown in Fig. 1. Oxygen deficient waters are clearly observed off Peru and northern Chile, delimiting an OMZ that has become one of the shallowest and most intense in the world ocean (Paulmier and Ruiz-Pino, 2009). Vertically, the depth of the upper boundary of the OMZ, considered here as O_2 concentrations of ~45 µM, fluctuated between 22 and 80 m. This location depends on the distance from the coast. Below the upper boundary, O_2 concentrations decreased abruptly until they reached ~zero, creating an anoxic environment. In fact, our data show a nucleus of O_2 concentrations under 5 µM that occupy most of the OMZ (58 % of the data from the OMZ). The lower boundary of the OMZ was observed between 450 and 730 m depth. As the OMZ spreads southward with the Peru–Chile undercurrent (Strub et al., 1998), associated with Equatorial Subsurface Water (ESSW), its structure changes, with maximum thickness between 5° and 17° S. At southern latitudes (26° S), the ventilation of the OMZ via the intrusion of minimum salinity waters results in increasing O_2 concentrations to above 45 µM.

Thus, the OMZ core is an isolated environment surrounded by two sharp oxyclines and also haloclines, where most processes take place under very low O_2 conditions (microaerofilic or even anaerobic processes), with several consequences for the N cycle. Nitrate reduction and denitrification is thermodynamically favorable, driving along with anammox, to an intense N loss and N-species recycling (Codispoti and Richards, 1976; Farías et al., 2009; Lam et al., 2009; Ward et al., 2009). Both processes can produce N_2, but only denitrification consumes NO_3^-, leading to strong NO_2^-, and sometimes N_2O accumulation (Fig. 1c and d). On the other hand, meridional and vertical N_2O profiles reveal the sensitivity of the N_2O cycle to O_2 levels, and reflect the intensity and

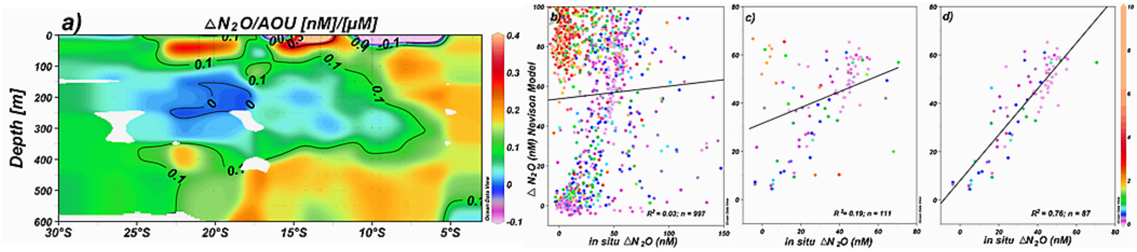

Fig. 2. **(a)** Meridional distribution of ΔN_2O / AOU ratio along the ESP. **(b–d)** In-situ ΔN_2O [nM] versus ΔN_2O modeled by the Nevison et al equation: **(b)** including the entire eastern South Pacific; **(c)** including only measurements from water with oxygen levels above 8 µM; and **(d)** ΔN_2O from waters with oxygen levels above 8 µM and nitrite below 0.75 µM. The color indicates the nitrite concentration of each datum [µM].

extent of denitrification (Fig. 1e). The N_2O vertical structure is characterized by two maxima located at both boundaries (up to 275 nM, note that the scale of the plot only extends up to 100 nM N_2O), and a strong minimum at its core, with N_2O undersaturation as low as 40 %. The N_2O minimum is located between 11 and 21° S and is centered at $\sim 26.4\sigma_t$. This is typically related to the NO_2^- maximum, called secondary nitrite maxima (SNM), where Codispoti et al. (1986) reported values of up to 23 µM. The SNM is observed not only in the ESP but also in the OMZ of the Arabian Sea (Patra et al., 1999; Nicholls et al., 2007). The SNM is a clear signal of active dissimilative nitrate reduction and denitrification, followed by the observed NO_3^- minimum and NO_3^- deficit (2–20 µM; Fig. 1e). Since N_2O reduction to N_2 by denitrification is the only known process able to consume N_2O, undersaturations indicate that this process is effectively acting within the region, as established by using an isotope's signal (Ryabenko et al., 2012), and contrary to recent reports that show denitrification to be unimportant in the OMZ of the ESP (Lam et al., 2009; Ward et al., 2009). Nevertheless, the question of why NO_2^- accumulation and N_2O consumption occur in the OMZ core remains unresolved. The high NO_3^- reduction by dissassimilative processes (Lam et al., 2009), and lower reduction rates for NO_2^- than N_2O measured in the area (Farías et al., 2009) could be influencing the NO_2^- maximum and N_2O minimum.

3.2 Existing N_2O models for the OMZ

Due to the climatic and ecological importance of N_2O, and given its extreme sensitivity to threshold O_2 concentrations, there has been interest in modeling N_2O in the ocean for several decades (Butler et al., 1989; Nevison et al., 1995, 2003). The first attempt was based on the empirical relationships between N_2O and temperature, and among AOU and NO_3^-. The correlation between AOU and NO_3^- suggested that nitrification is the main process producing N_2O (Elkins et al., 1978), given the ubiquitous presence of O_2 in the ocean (Yoshinari, 1976). Recently, a depth relationship and experimental results have been incorporated to improve models so that they reliably predict N_2O concentrations and atmospheric exchange (Butler et al., 1989; Suntharalingam et al., 2000; Nevison et al., 2003; Freing et al., 2009). However, N_2O consumption by denitrification in the OMZ has not been included in these models, leaving part of the N_2O cycle unresolved (Nevison et al., 2003).

We applied the Nevison's model (henceforth referred to as NM) to our data in order to predict N_2O distribution in the OMZ (Fig. 2) as follows:

$$\Delta N_2O = R_{N:O_2}[(a_1 \ln([O_2]_{sat}/[O_2]) + a_2 AOU)]\exp(Z/Z_{scale}) \quad (1)$$

where $a_1 = 0.26 \pm 0.06$ [mol N_2O mol^{-1} N] [µmol O_2 l^{-1}]$^{-1}$; $a_2 = -0.0004 \pm 0.0001$ [mol N_2O mol^{-1}N]; Z is the depth in meters; and Z_{scale} = 3000 m. The vertical distribution of the ΔN_2O / AOU ratio along the coast of the ESP (Fig. 2a), which is an estimation of N_2O production based on O_2 consumption, is similar to those previously reported for the area (Nevison et al., 2003). High ratios are found at the OMZ boundaries (oxyclines) because hypoxic conditions favor N_2O production (up to 0.9 nM µM^{-1}), while lower and even negative ratios in the OMZ core are mainly due to high N_2O consumption (meaning negative ΔN_2O, from -0.07 nM µM^{-1}).

However, the NM is only well fitted to our results from the ESP's OMZ at the upper and lower oxyclines, while a poor fit was obtained within the OMZ's core. There, NM predicts an extreme increase in N_2O production, while the observed data show important N_2O consumption (Fig. 2a). The same poor fit was observed by the NM's authors studying the OMZ in the Arabian Sea. The NM considers 4 µM as the critical oxygen level where N_2O production by nitrification and denitrification is enhanced at lower O_2 concentrations, but the model dismisses any N_2O consumption by denitrification. The NM output at low O_2 concentrations results in N_2O accumulation. Due to the high sensitivity of N_2O cycling to O_2 concentrations and taking into account the possible biases in O_2 standard measurements, (e.g. the detection limit of the Winkler method; CTD response; contamination during the sample collection, among others), and that about 60 % of our N_2O measurements were taken from waters with

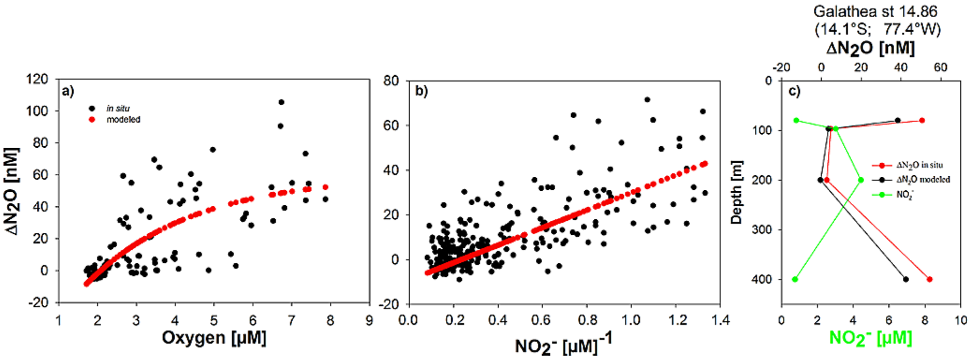

Fig. 3. (a) ΔN_2O in situ (black circles) and modeled according to Bonin experiments (red circles) varying with the oxygen; **(b)** ΔN_2O in situ (black circles) and modeled (red circles) as a function of inverse NO_2^- concentrations; **(c)** profile of ΔN_2O in situ (red points) and modeled as a function of NO_2^- (black points) and NO_2^- concentrations (green points) from Galathea expedition station 14.86.

O_2 levels under 4 µM using standard methods, the NM assumptions are not reasonable for our study area when modeling vertical and meridional N_2O distributions. Even when O_2 levels above 8 µM were taken into account, outputs were not correlated with in-situ data (r^2 N_2O modeled vs. N_2O observed = 0.19, $n = 252$; Fig. 2c).

The NM also has a depth function, which may change according to the study region. The regional dependence of the ΔN_2O / AOU ratio on depth has been demonstrated with measurements below 1000 m depth. A good fit is observed, but with different coefficients than those used in the NM. A modified NM with new coefficients still produces a poor fit between outputs and observed N_2O (data not shown).

Given that most of the poorly fitted data in the NM coincides with high NO_2^- concentrations (note the color of the points in Fig. 2b–d), where low N_2O concentrations are observed even at O_2 as high as 15.5 µM, we re-assessed the NM using NO_2^- concentrations under 0.75 µM and O_2 above 8 µM, i.e. for the region without denitrification. In this reassessment, the ΔN_2O values obtained agreed with in situ ΔN_2O ($r^2_{N_2O \text{ modeled vs. } N_2O \text{ in situ}} = 0.76$ $n = 228$; Fig. 2c).

3.3 Factors related to N_2O dynamics in the OMZ of the ESP

The relationship between O_2 concentration and N_2O yield by denitrification is poorly understood in terms of threshold O_2 levels. Some results from cultures have been reported (Firestone and Tiedje, 1979; Betlach and Tiedje, 1981; Bonin et al., 1987, 1989). For example, experiments with *P. nautica* show the evolution of every step of denitrification (i.e. NO_3^- reduction; NO_2^- reduction and N_2O reduction) as a function of O_2 levels (Bonin et al., 1989). N_2O consumption begins at 8 µM and its relationship with O_2 was modeled (Fig. 3a) to obtain the ΔN_2O in our study area as an exponential function of O_2 as follows:

$$\Delta N_2O = -123\exp(-0.35 \times [O_2]) + 70.7. \quad (2)$$

Because the wide range of O_2 is taken into account (0–8 µM) and given the high sensitivity of the N_2O cycle at the core of the OMZ to O_2 levels, Eq. (2) was tested in waters below 75 m depth and waters with O_2 concentrations lower than 8 µM, during cruises that collected high quality O_2 data (three cruises which used STOX sensors: Galathea 3 (2007), MOOMZ II (2009) and MOOMZ III (2010). The application of Eq. (2) to our results produced a good fit ($r^2 = 0.66$; Fig. 3a). However, high quality O_2 data in the ESP are scarce and the model results could produce a better fit, therefore we explored a second approximation. The development of highly sensitive STOX oxygen sensors (Revsbech et al., 2009) shows that oxygen levels were below the detection limit throughout the 200 m thick OMZ core in most profiles where STOX sensors were deployed (Thamdrup et al., 2012).

As was previously mentioned, an important issue in the N_2O minimum is the prominent NO_2^- accumulation. The core of the OMZ shows a strong nitrogen deficit ($-29.97 < N\cdot < -3.01$, (Deutsch et al., 2001) with no significant correlations with negative ΔN_2O ($r^2 = 0.04$; $p = 0.05$). While high NO_2^- concentrations (up to 15.6 µM) were observed in most of the OMZ, ΔN_2O was negative or net N_2O consumption occurred in the middle of the OMZ ($26.3 < \sigma_t < 26.5$) where the NO_2^- peak was detected. The sharp vertical decrease in N_2O concentration profiles may indicate N_2O consumption even though positive ΔN_2O values are present. The negative ΔN_2O were observed only in NO_2^- concentrations above 0.75 µM. On the other hand, all of the NO_2^- values higher than 0.75 µM were present under O_2 concentrations below 8 µM. Regarding ΔN_2O measurements in waters with O_2 concentrations lower than 8 µM and NO_2^- concentrations higher than 0.75 µM, the relationship between NO_2^- and ΔN_2O fitted an exponential function, with higher ΔN_2O at lower NO_2^-. In order to obtain a linear fit, ΔN_2O was plotted as a function of inverse NO_2^- (Fig. 3b). Considering this association between both these variables, the following equation was obtained:

$$\Delta N_2O = 45.871 \times [NO_2^-]^{-1} - 7.394. \quad (3)$$

It is important to note that this is a function obtained for our region and that its application to other regions must be reviewed. The ΔN_2O values obtained from Eq. (3) were reasonably fitted to the observed data inside the SNM, which covers a wide range of N_2O concentrations (1.1–70.2 nM), from undersaturation ($\Delta N_2O = -4.2$ nM) to oversaturation ($\Delta N_2O = 48.3$ nM) in the core of the OMZ, based on NO_2^- concentrations.

Equation (3), which is the better approximation for waters with O_2 below 8 µM, is combined with the NM for more oxygenated waters without NO_2^- accumulation (lower than 0.75 µM) to obtain a best fit forvertical N_2O distribution in the OMZ (Fig. 3c). A significant ($r^2 = 0.71$; $p = 0.01$) fit was obtained between the new equation and the observed data, producing a representative ΔN_2O profile. Using a combination of the two equations, the poor fit previously obtained for the OMZ core data from Nevison's work now appears to be well resolved, and a complete profile can be depicted from the $O_2$and NO_2^- concentrations.

3.4 Implications of modeling N_2O consumption in the OMZ core

As most of the ocean has higher O_2 concentrations than those required by denitrification, the assumption that the N_2O cycle is driven mostly by nitrification production and air–sea exchange is a good approximation. However, the OMZ is a complex system in relation to the N_2O cycle, where different N_2O production and consumption processes, both microaerophilic and anaerobic, are able to coexist. Taking into account our data and the WOCE data, the OMZ core between 5° and 30° S with O_2 concentrations below 8 µM occupies a volume of 8.5×10^5 km^3. N_2O is actively consumed in this volume of water. Although estimated consumption is about one order of magnitude less than N_2O production, the expansion of suboxic zones requires the inclusion of consumption in oceanic N_2O models. Our study suggests that experimental work needs to focus on determining denitrification rates and their sensitivities to oxygen and N-species. Work on precise in-situ measurement methods for O_2 and metal availability should allow the further development of global equations to better understand N_2O cycling.

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References

Betlach, M. R. and Tiedje, J. M.: Kinetic explanation for accumulation of nitrite, nitric oxide, and nitrous oxide during bacterial denitrification, Appl. Environ. Microb., 42, 1074–1084, 1981.

Bonin, P., Gilewicz, M., and Bertrand, J. C.: Denitrification by a marine bacterium Pseudomonas nautica strain 617, Ann. Inst. Pasteur Mic., 138, 371–383, 1987.

Bonin, P., Gilewicz, M., and Bertrand, J. C.: Effects of oxygen on each step of denitrification on Pseudomonas nautica, Can. J. Microbiol., 35, 1061–1064, 1989.

Butler, J. H., Elkins, J. W., Thompson, T. M., and Egan, K. B.: Tropospheric and Dissolved N2O of the West Pacific and East Indian Oceans During the El Niño Southem Oscillation Event of 1987, J. Geophys. Res., 94, 14865–14877, 1989.

Carlucci, A. F. and Schubert, H. R.: Nitrate reduction in seawater of the deep nitrite maximum off Peru, Limnol. Oceanogr., 14, 187–193, doi:10.4319/lo.1969.14.2.0187, 1969.

Castro-González, M., and Farías, L.: N_2O cycling at the core of the oxygen minimum zone off northern Chile. Marine Ecology Progress Series, 280, 1–11, doi:10.3354/meps280001, 2004.

Cline, J. D. and Richards, F.: Oxygen Deficient Conditions and Nitrate Reduction in the Eastern Tropical North Pacific Ocean, American Society of Limnology and Oceanography, http://www.jstor.org/stable/2834, Limnology, 17, 885–900, 1972.

Codispoti, L. A. and Richards, F. A.: An analysis of the horizontal regime of denitrification in the eastern tropical North Pacific, Limnol. Oceanogr., 21, 379–388, doi:10.4319/lo.1976.21.3.0379, 1976.

Codispoti, L. A. and Christensen, J. P.: Nitrification, Denitrification and nitrous oxide cycling in the eastern tropical South Pacific Ocean, Mar. Chem., 16, 277–300, 1985.

Codispoti, L. A., Friederich, G. E., Packard, T. T., Glover, H. E., Ward, B. B., Lipschultz, F., and Lostaunau, N.: High Nitrite Levels off Northern Peru: A Signal of Instability in the Marine Denitrification Rate, Science, 233, 1200–1202, doi:10.1126/science.233.4769.1200, 1986.

Deutsch, C., Gruber, N., Key, R. M., and Sarmiento, J. L.: Denitrification and N_2 fixation in the Pacific Ocean, Global Biogeochem. Cy., 15, 483–506, 2001.

Elkins, J. W., Wofsy, S. C., Mcelroy, M. B., Kaplan, W. A., and Kolb, C. E.: Aquatic sources and sinks for nitrous oxide, Nature, 275, 602–606, 1978.

Farías, L., Paulmier, A., and Gallegos, M.: Nitrous oxide and N-nutrient cycling in the oxygen minimum zone off northern Chile, Deep-Sea Res. Pt. I, 54, 164–180, doi:10.1016/j.dsr.2006.11.003, 2007.

Farías, L., Castro-Gonzalez, Cornejo, M. M., Charpentier, J., Faúndez, J., Boontanon, N., and Yoshida, N.: Denitrification and nitrous oxide cycling within the upper oxycline of the eastern tropical South Pacific oxygen minimum zone, Limnol. Oceanogr., 54, 132–144, 2009.

Fine, R. A: Observations of CFCs and SF6 as ocean tracers, Ann. Rev. Mar. Sci., 3, 173–195, 2011.

Firestone, M. K. and Tiedje, J. M.: Temporal change in nitrous oxide and dinitrogen from denitrification following onset of anaerobiosis, Appl. Environ. Microb., 38, 673–679, 1979.

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, doi:10.5194/bg-7-2695-2010, 2010.

Freing, A., Wallace, D. W. R., Tanhua, T., Walter, S., and Bange, H. W.: North Atlantic production of nitrous oxide in the context of changing atmospheric levels, Global Biogeochem. Cy., 23, 1–13, doi:10.1029/2009GB003472, 2009.

Goreau, T. J., Kaplan, W. A., Wofsy, S. C., McElroy, M. B., Valois, F. W., and Watson, S. W.: Production of NO_2 and N_2O by Nitrifying Bacteria at Reduced Concentrations of Oxygen, Appl. Environ. Microb., 40, 526–532, 1980.

Holland, E., Lee-Taylor, J., Nevison, C., and Sulzman, J.: Global N Cycle: Fluxes and N_2O Mixing Ratios Originating from Human Activity, available at: http://www.daac.ornl.gov from Oak Ridge National, Laboratory Distributed Active Archive Center, OAK Ridge, Tennessee, USA, 2005.

IPCC: Climate Change 2007 – The Physical Science Basis: Working Group I Contribution to the Fourth Assessment Report of the IPCC, edited by: Tignor, M. and Miller, H. L., Cambridge University Press, 2007.

Kester, R. A., De Boer, W., and Laanbroek, H. J.: Production of NO and N(inf2)O by Pure Cultures of Nitrifying and Denitrifying Bacteria during Changes in Aeration, Appl. Environ. Microb., 63, 3872-7, 1997.

Kuypers, M. M. M., Lavik, G., Woebken, D., Schmid, M., Fuchs, B. M., Amann, R., Jørgensen, B. B., and Jetten, M. S. M.: Massive nitrogen loss from the Benguela upwelling system through anaerobic ammonium oxidation, P. Natl. Acad. Sci. USA, 102, 6478–6483, doi:10.1073/pnas.0502088102, 2005.

Lam, P., Lavik, G., Jensen, M. M., van de Vossenberg, J., Schmid, M., Woebken, D., Gutiérrez, D., Amann, R., Jetten, M. S. M., and Kuypers, M. M. M.: Revising the nitrogen cycle in the Peruvian oxygen minimum zone. Proceedings of the National Academy of Sciences of the United States of America, 106, 4752–4757, doi:10.1073/pnas.0812444106, 2009.

McAullife, C.: GC determination of solutes by multiple phase equilibration, Chem. Technol., 1, 46–51, 1971.

Morales, C. E., Hormazábal, S. E., and Blanco, J.: Interannual variability in the mesoscale distribution of the depth of the upper boundary of the oxygen minimum layer off northern Chile (18–24S): Implications for the pelagic system and biogeochemical cycling, J. Mar. Res., 57, 909–932, doi:10.1357/002224099321514097, 1999.

Murray, C. N. and Riley, J. P.: The solubility of gases in distilled water and sea water – II: Oxygen, Deep-Sea Res. Oceanogr. Abstr., 16, 311–320, 1969.

Naqvi, S. W. A. and Noronha, R. J.: Nitrous oxide in the Arabian Sea, Deep-Sea Res., 38, 871–890, 1991.

Naqvi, S. W., Jayakumar, D. A., Narvekar, P. V., Naik, H., Sarma, V. V., 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, doi:10.1038/35042551, 2000.

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, doi:10.5194/bg-7-2159-2010, 2010.

Nevison, C., Weiss, R., and Erickson III, D. J.: Global oceanic emissions of nitrous oxide, J. Geophys. Res., 100, 15809–15820, 1995.

Nevison, C., Butler, J. H., and Elkins, J. W.: Global distribution of N_2O and the ΔN_2O-AOU yield in the subsurface ocean, Global Biogeochem. Cy., 17, 1–18, doi:10.1029/2003GB002068, 2003.

Nicholls, J. C., Davies, C. A., and Trimmer, M.,: High-resolution profiles and nitrogen isotope tracing reveal a dominant source of nitrous oxide and multiple pathways of nitrogen gas formation in the central Arabian Sea, Water, 52, 156–168, 2007.

Patra, P. K., Lal, S., Venkataramani, S., de Sousa, S. N., Sarma, V. V. S. S. and Sardesai, S.: Seasonal and spatial variability in N_2O distribution in the Arabian Sea, Deep-Sea Res. Pt. I, 46, 529–543, doi:10.1016/S0967-0637(98)00071-5, 1999.

Paulmier A. and Ruiz-Pino D.: Oxygen minimum zones (OMZs) in the modern ocean, Prog. Oceanogr. 80, 113–128, 2009

Pizarro, O., Shaffer, G., Dewitte, B., and Ramos, M.: Dynamics of seasonal and interannual variability of the Peru-Chile Undercurrent, Geophys. Res. Lett., 29, 1581 doi:10.1029/2002GL014790, 2002.

Revsbech, N. P., Larsen, L. H., Gundersen, J., Dalsgaard, T., Ulloa, O., and Thamdrup, B.: Determination of ultra-low oxygen concentrations in oxygen minimum zones by the STOX sensor, Limnol. Oceanogr. Methods, 7, 371–381, 2009.

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, doi:10.5194/bg-9-203-2012, 2012.

Samuelsson, M. O.: Dissimilatory Nitrate Reduction to Nitrite, Nitrous Oxide and Ammonium by Pseudomonas putrefaciens, Appl. Environ. Microb., 50, 812–815, 1985.

Santoro, A. E., Buchwald, C., McIlvin, M. R., and Casciotti, K. L.: Isotopic Signature of N_2O Produced by Marine Ammonia-Oxidizing Archaea, Science, New York, NY, 333, 1282–1285, doi:10.1126/science.1208239, 2011.

Stramma, L., Johnson, G. C., Sprintall, J., and Mohrholz, V.: Expanding oxygen-minimum zones in the tropical oceans, Science, New York, NY, 320, 655–358, doi:10.1126/science.1153847, 2008.

Strub, P. T., Mesías, J. M., Montecino, V., Rutllant, J. A., and Salinas, S.: Coastal ocean circulation of western South America, in: The Sea, edited by: Robinson, A. R. and Brink, K. H., T Wiley, 273–313, 1998.

Suntharalingam, P., Sarmiento, J. L., and Toggweiler, J. R.: Global significance of nitrous-oxide production and transport from oceanic low-oxygen zones: A modeling study, Global Biogeochem. Cy., 14, 1353–1370, 2000.

Thamdrup, B., Dalsgaard, T., Jensen, M. M., Ulloa, O., Farías, L., and Escribano, R.: Anaerobic ammonium oxidation in the oxygen-deficient waters off northern Chile, Limnol. Oceanogr., 51, 2145–2156, doi:10.4319/lo.2006.51.5.2145, 2006.

Thamdrup, B., Dalsgaard, T., and Revsbech, N. P.: Widespread functional anoxia in the oxygen minimum zone of the eastern South Pacific, Deep-Sea Res. Pt. I, 65, 36–45, doi:10.1016/j.dsr.2012.03.001, 2012.

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, 78–81, doi:10.1038/nature08276, 2009.

Weiss, R. and Price, B. A.: Nitrous oxide solubility in water and seawater, Mar. Chem., 8, 347–359, doi:10.1016/0304-4203(80)90024-9, 1980.

Yoshinari, T.: Nitrous oxide in the sea, Mar. Chem., 4, 189–202, 1976.