



Contrasting biogeochemistry of nitrogen in the Atlantic and Pacific Oxygen Minimum Zones

E. Ryabenko¹, A. Kock¹, H. W. Bange¹, M. A. Altabet², and D. W. R. Wallace³

¹Leibniz-Institut für Meereswissenschaften an der Universität Kiel (IFM-GEOMAR), Forschungsbereich Marine Biogeochemie, Düsternbrooker Weg 20, Kiel, Germany

²School for Marine Science and Technology (SMAST), University of Massachusetts Dartmouth, 285 Old Westport Road, North Dartmouth, MA, USA

³Halifax Marine Research Institute, Dalhousie University, 1355 Oxford Street, P.O. Box 15000, Halifax, Nova Scotia B3H 4R2, Canada

Correspondence to: E. Ryabenko (eryabenko@ifm-geomar.de)

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Abstract. We present new data for the stable isotope ratio of inorganic nitrogen species from the contrasting oxygen minimum zones (OMZs) of the Eastern Tropical North Atlantic, south of Cape Verde, and the Eastern Tropical South Pacific off Peru. Differences in minimum oxygen concentration and corresponding N-cycle processes for the two OMZs are reflected in strongly contrasting $\delta^{15}\text{N}$ distributions. Pacific surface waters are marked by strongly positive values for $\delta^{15}\text{N}$ - NO_3^- reflecting fractionation associated with subsurface N-loss and partial NO_3^- utilization. This contrasts with negative values in NO_3^- depleted surface waters of the Atlantic which are lower than can be explained by N supply via N_2 fixation. We suggest the negative values reflect inputs of nitrate, possibly transient, associated with deposition of Saharan dust. Strong signals of N-loss processes in the subsurface Pacific OMZ are evident in the isotope and N_2O data, both of which are compatible with a contribution of canonical denitrification to overall N-loss. However the apparent N isotope fractionation factor observed is relatively low ($\epsilon_d=11.4\text{‰}$) suggesting an effect of influence from denitrification in sediments. Identical positive correlation of N_2O vs. AOU for waters with oxygen concentrations ($[\text{O}_2] < 5\ \mu\text{mol l}^{-1}$) in both regions reflect a nitrification source. Sharp decrease in N_2O concentrations is observed in the Pacific OMZ due to denitrification under oxygen concentrations $\text{O}_2 < 5\ \mu\text{mol l}^{-1}$.

(Gruber, 2008). Although most chemical forms of nitrogen in the ocean are bio-available (i.e. fixed nitrogen or “fixed-N”) the most abundant form, N_2 is generally not. The sources of fixed-N include river inputs, atmospheric deposition and N_2 fixation (Duce et al., 2008; Gruber, 2008). Sinks of fixed-N, producing N_2 , include microbial denitrification and anammox processes, both requiring very low (i.e. suboxic) $[\text{O}_2]$ (Devol, 2008). Hence suboxic Oxygen Minimum Zones (OMZs) are the oceanic regions especially associated with denitrification (Cline and Richards, 1972; Codispoti et al., 2001; Ward et al., 2009) and anammox (Lam et al., 2009; Thamdrup et al., 2006; Hamersley et al., 2007; Galan et al., 2009) and play a particularly important role in the global nitrogen cycle as sites of N sinks from the ocean. They are located typically in areas of upwelling with high productivity which exhibit complex cycling of nutrients (Helly and Levin, 2004).

The relative importance of heterotrophic denitrification (a stepwise reduction process involving a number of intermediates, $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$), compared to autotrophic anammox (a chemosynthetic process, $\text{NO}_2^- + \text{NH}_4^+ \rightarrow \text{N}_2$) has been debated (Voss and Montoya, 2009; Koeve and Kähler, 2010).

Absence of ammonium in suboxic OMZs that should have accumulated from organic matter breakdown could be indicative of anammox, while the consumption of N_2O requires the denitrification process (Naqvi et al., 2010).

Although OMZs are found in all major ocean basins, their associated nitrogen cycle processes can vary dramatically due to contrasting minimum oxygen levels. In the Eastern Tropical South Pacific (ETSP), suboxic

1 Introduction

Nitrogen is a key limiting element for biological productivity and occupies a central role in ocean biogeochemistry

($[\text{O}_2] < 5 \mu\text{mol l}^{-1}$) conditions are found, whereas in Eastern Tropical North Atlantic (ETNA), more relaxed conditions exist ($[\text{O}_2] > 40 \mu\text{mol l}^{-1}$) (Karstensen et al., 2008). In addition, fixed-N inputs associated with atmospheric deposition and, possibly, N_2 -fixation, vary between the two regions (Chavez and Messie, 2009).

Cruises carried out during the collaborative research project SFB-754 (www.sfb754.de) of the German Research Foundation and the BMBF supported project SOPRAN (Surface Ocean Processes in the Anthropocene: www.sopran.pangaea.de) provided unique opportunities to sample nitrogen species in these two contrasting regions. Here we present a comparison of N_2O concentration and stable nitrogen isotope distributions, which were measured in both OMZs to highlight the similarities and differences in nitrogen cycling between the two regions.

2 Sampling and analytical methods

In the Pacific OMZ, samples were collected onboard the R/V *Meteor* (M77 Legs 3 and 4) in December 2008 and January 2009 (Fig. 1). In the Atlantic OMZ, samples were collected on the R/V *L'Atalante* (cruise leg ATA03) during February 2008 from Dakar to Cape Verde Islands and on the R/V *Meteor* (M80) in December 2009 covering the region south to Cape Verde Islands. At each station, water samples were collected using 121 Niskin bottles on a CTD rosette system equipped with temperature, pressure, conductivity and oxygen sensors. Nutrients and oxygen were determined onboard according to Grasshoff et al. (1999). Triplicate water samples were taken from the CTD/rosette casts and were analyzed for dissolved N_2O onboard using a static equilibration method. For details concerning the N_2O method, see Walter et al. (2006).

Water samples for $\delta^{15}\text{N}$ nitrate and nitrite analysis were collected in 125 ml HDPE bottles and kept frozen prior to analysis. For logistical reasons, samples from the M77 cruise that contained low to negligible levels of nitrite ($[\text{NO}_2^-] < 0.1 \mu\text{mol l}^{-1}$) were acidified and stored at room temperature, whereas samples with significant $[\text{NO}_2^-]$ were kept frozen prior to the $\delta^{15}\text{N}\text{-NO}_2^-$ analysis. Aliquots of these samples were treated in the laboratory with sufficient sulfanilic acid to remove $[\text{NO}_2^-]$ prior to $\delta^{15}\text{N}\text{-NO}_3^-$ analysis with any remaining sample stored at room temperature.

The isotopic composition of dissolved nitrate ($\delta^{15}\text{N}\text{-NO}_3^-$) and nitrite ($\delta^{15}\text{N}\text{-NO}_2^-$) was measured using the Cd-reduction/azide method (McIlvin and Altabet, 2005) with addition of NaCl as described by Ryabenko et al. (2009). All the samples from the Atlantic study region and 50 % of the Pacific samples were analyzed at the IFM-GEOMAR in Germany, while c. 50 % of the Pacific samples were analyzed at SMAST in the USA, using the same method. The only difference was that at SMAST N_2O produced by this method was analyzed isotopically, whereas at IFM-GEOMAR N_2O

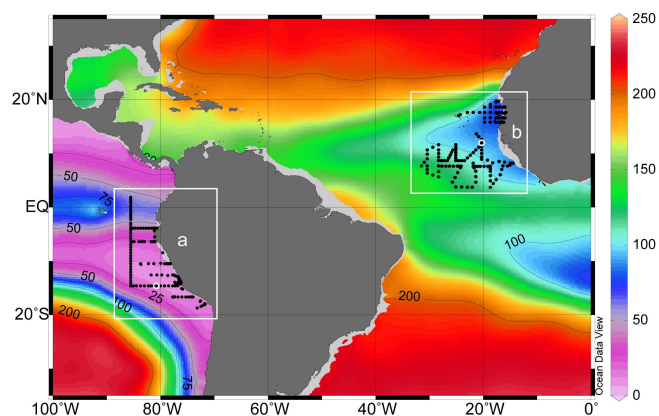


Fig. 1. Oxygen distribution at 200 m (Schlitzer, R., Ocean Data View, World Ocean Atlas 2005, http://odv.awi.de/en/data/ocean/world_ocean_atlas_2005/) with CTD station locations in the Pacific (a) and Atlantic (b) study regions referred to in the text. White circles indicate station 84 (a) and station 5 (b).

was converted on-line to N_2 for isotopic analysis. The detection limit at IFM-GEOMAR was $0.2 \mu\text{mol l}^{-1}$ of nitrate or nitrite with the precision of the $\delta^{15}\text{N}$ measurements being $\pm 0.2 \text{‰}$. The detection limit at SMAST was slightly higher, $0.5 \mu\text{mol l}^{-1}$, with the same precision of ^{15}N measurements.

The analyses of the Pacific deep water samples ($> 1500 \text{ m}$) from both labs gave near identical values of $\delta^{15}\text{N}\text{-}([\text{NO}_2^-] + [\text{NO}_3^-])$ of $5.69 \pm 0.7 \text{‰}$ (IFM-GEOMAR; $n = 31$) and $5.62 \pm 0.4 \text{‰}$ (SMAST; $n = 8$) respectively. The Fisher test showed that we can merge the two data sets with a confidence level $> 95 \%$. The resulting mean value of $5.64 \pm 0.7 \text{‰}$ ($n = 39$) lies between previously published values of 6.5‰ Voss (2001) and 4.5‰ Sigman (1997) for the deep North Pacific Ocean. Deep waters of the Atlantic showed very similar values as those of the Pacific ($5.3 \text{‰} \pm 0.5$ for $> 2000 \text{ m}$, see Supplementary material, Table 1).

3 Hydrographic setting of the two study regions

In the North Equatorial Atlantic region, the eastward flow of the North Equatorial Counter Current (NECC) and North Equatorial Under Current (NEUC) supplies oxygen rich waters to the Atlantic OMZ (Glessmer et al., 2009). The water mass distribution in this Atlantic OMZ study region (Fig. 1b) is affected by the Cape Verde Frontal Zone, which marks the boundary between North and South Atlantic Central Waters (NACW, SACW). This separates well-ventilated waters of the subtropical gyre in the north from less-ventilated waters to the south. Our CTD data (Fig. 2) show water mass properties $< 500 \text{ m}$ intermediate between those of NACW and SACW. Antarctic Intermediate Water (AAIW: $3\text{--}5 \text{ °C}$, $S = 34.5$) is found at $\sim 1000 \text{ m}$ with North Atlantic Deep Water (NADW) filling the depth range between ~ 1000 and

Table 1. Predicted surface water $\delta^{15}\text{N-NO}_3^-$ under different scenarios. $F_{\text{total}} = F_{\text{dust}} + F_{\text{mixing}} - F_{\text{assimilation}}$. The end members for $\delta^{15}\text{N}$ surface water calculation were: $\delta^{15}\text{N-dust} = -7\text{‰}$, $\delta^{15}\text{N-mixing} = 5\text{‰}$ and $\delta^{15}\text{N-assimilation} = -5\text{‰}$.

scenario	$\delta^{15}\text{N-NO}_3^-$ surface water	$F_{\text{dust}}/F_{\text{total}}$, %	$F_{\text{mixing}}/F_{\text{total}}$, %	$F_{\text{assimilation}}/F_{\text{total}}$, %
1	-5.8	90	10	0
2	-1	50	50	0
3	1	33 %	33 %	33 %

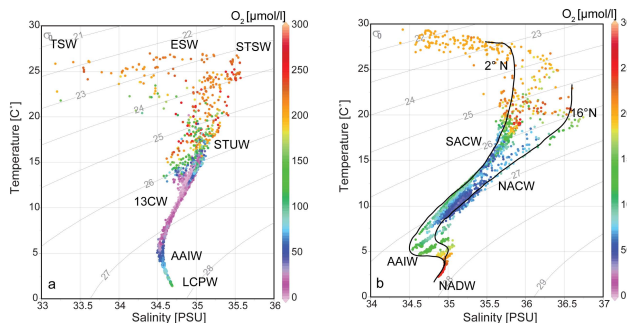


Fig. 2. T-S diagrams with O_2 color coded for the Pacific (a) and the Atlantic (b) study regions from CTD data collected during the M77, M80 and *L'Atalante* cruises.

4000 m (Fig. 2b). A summary of the water masses properties found in both study regions is presented in Supplementary material, Table 1.

In the South Pacific, the Equatorial Undercurrent (EUC), Southern Subsurface Counter Currents (SCCs), and the Southern Intermediate Counter Currents (SICC) supply 13°C Equatorial Water (13CW, $25.8 < \sigma_\theta < 26.6$) to the eastern Pacific OMZ (Stramma et al., 2010). The westward flowing South Equatorial Current (SEC) may recirculate some 13° water from the OMZ by returning eastward as the South Subsurface Counter Current at $3\text{--}5^\circ\text{S}$ (Schott et al., 2004). The origin of 13CW is remote from the equator (Qu et al., 2009) mostly as Subantarctic Mode Water (SAMW; (Toggweiler et al., 1991)) and transports very oxygen depleted waters to the OMZ, due to its relative old age. The South Pacific Subtropical Underwater (STUW) is a likely O_2 source from the south which is centered on the $\sigma_\theta = 25.0$ isopycnal and is well-ventilated across nearly the full width of the subtropical gyre (O'Connor et al., 2002). The low-salinity water ($S < 34.5$) found between c. 500 and 1000 m southward of 10°S is Antarctic Intermediate Water (AAIW). South Pacific Deep Water ($1.2\text{--}2^\circ\text{C}$) is found between c. 1500–3000 m and is underlain by Lower Circumpolar Water (LCPW) (Fiedler and Talley, 2006) (Fig. 2a).

Because of the differences in hydrography and significantly lower oxygen supply, the Pacific OMZ is much

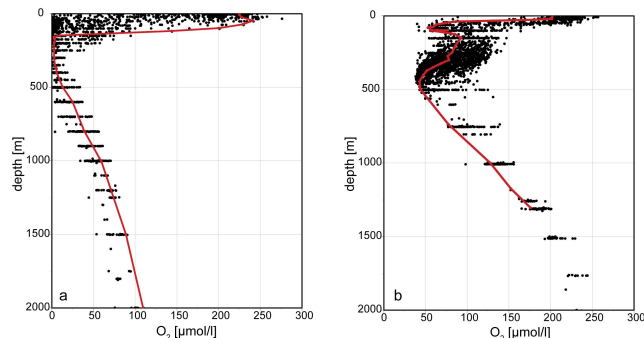


Fig. 3. Oxygen distribution in the Pacific (a) and the Atlantic (b) study regions, as measured on the cruises M77, M80 and *L'Atalante*. The red lines show the water-column profiles for M77 station 84 in the Pacific and M80 station 5 in the Atlantic

more intense as compared to the Atlantic (Karstensen et al., 2008). The resulting very low oxygen concentrations favor metabolic pathways that convert nitrogen from biologically reactive “fixed” forms (for example nitrate, nitrite or ammonium) to N_2 via denitrification and/or anammox.

4 Results and discussion

4.1 Vertical distribution of nitrogen species and isotopes

4.1.1 General

Dissolved O_2 varies considerably in its depth distribution between the Atlantic and Pacific study regions as shown in Fig. 3. Figure 4 presents typical water column profiles for oxygen and several nitrogen related properties from both study regions (outside of the upwelling zones). Stations 5 (Atlantic, M80) and 84 (Pacific, M77) were chosen due to synoptic availability of N_2O , $\delta^{15}\text{N}$ and $[\text{NO}_2^-]$ data. The geographic positions of the stations are indicated on Fig. 1 by white circles.

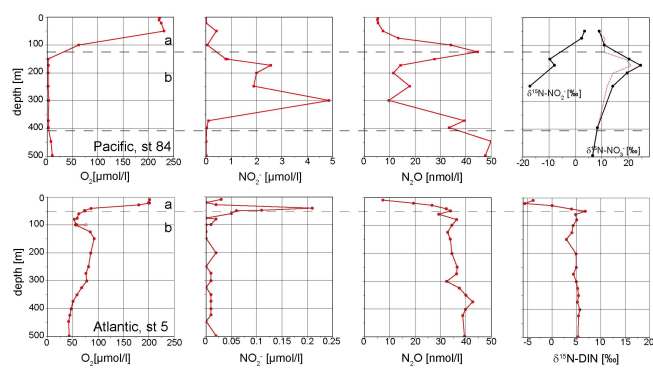


Fig. 4. Typical water column profiles from the SE Pacific OMZ (st. 84, 81° W/14° S) from the M77 cruise (upper panels) and the NE Atlantic OMZ (st. 5, 20.5° W/12.3° N) from the M80 cruise (lower panels). Black lines in the Pacific indicate $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NO}_2^-$, and the red line indicates $\delta^{15}\text{N-DIN}$ (calculated as the concentration weighed average of the NO_3^- and NO_2^- $\delta^{15}\text{N}$ values). Note the different of scales for $\delta^{15}\text{N}$: -20 to $+20$ ‰ in the Pacific and -5 to $+20$ ‰ in the Atlantic.

4.1.2 Pacific study region

In the Pacific study region, the OMZ contains mostly 13CW, with oxygen concentrations $< 2 \mu\text{mol l}^{-1}$ at depths as shallow as ~ 50 m and as deep as ~ 550 m. The Pacific station (Fig. 4, upper panels) is also characterized by a broad oxygen minimum with $[\text{O}_2] < 2 \mu\text{mol l}^{-1}$ (170–400 m). We divide the Pacific profile into layers (a) and (b) to focus the discussion of nitrogen transformations at the upper OMZ boundary and its core.

Layer a (0–120 m) includes a ~ 70 m deep mixed layer and the 50 m deep euphotic zone (Chavez and Messie, 2009), and contains water with the highest oxygen concentrations as well as a very sharp oxycline at 80–120 m in which $[\text{O}_2]$ drops from ~ 150 to $20 \mu\text{mol l}^{-1}$. The primary nitrite maximum lies close to the base of the euphotic zone and can be a consequence of two processes (Lomas and Lipschultz, 2006): light-limited, incomplete assimilatory reduction of nitrate by phytoplankton and microbial ammonium oxidation to nitrite (i.e. the first step of nitrification). Near-surface N_2O is close to saturation and increases within the oxycline from ~ 12 to $\sim 45 \text{ nmol l}^{-1}$. The observed increase in nitrous oxide within the oxycline can be associated with ammonia oxidation (Codispoti, 2010), which leads to an efflux of N_2O from the mixed layer to the atmosphere via gas exchange. The concentrations of $[\text{NO}_3^-]$ and $[\text{NO}_2^-]$ above 80 m in layer a at this station were below our detection limit for $\delta^{15}\text{N}$ measurement ($0.2 \mu\text{mol l}^{-1}$). Higher near-surface DIN concentrations were observed at other stations along the 86° W transect and the corresponding $\delta^{15}\text{N-NO}_3^-$ values were as high as 20 ‰. High surface $\delta^{15}\text{N-NO}_3^-$ is likely the result of incomplete nutrient utilization and fractionation during nitrate assimilation (Granger et al., 2004).

$\delta^{15}\text{N-NO}_2^-$ is generally much lower than $\delta^{15}\text{N-NO}_3^-$ and the difference between the two increases from layer a to layer b. Relative ^{15}N depletion in nitrite can be explained by isotopic fractionation during nitrate reduction to nitrite. A smaller difference between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NO}_2^-$ observed in the oxycline is likely due to nitrification as the fractionation effect of the process is significantly smaller (~ 13 ‰) (Casciotti, 2009; Casciotti and McIlvin, 2007) than the one expected for denitrification (~ 25 ‰) (Barford, 1999; Granger, 2006). Thus there is evidence for a clear switch from nitrification to denitrification with depth.

Layer b (120 m to 400 m). O_2 concentrations in this layer drop below $5 \mu\text{mol l}^{-1}$ and there is a strong increase in $[\text{NO}_2^-]$ towards a “secondary” maximum at the core of OMZ. N_2O concentrations drop sharply within the OMZ core to $\sim 10 \text{ nmol l}^{-1}$ and increase again only towards the lower border of the layer. Denitrification is the only N-removal process which is known to consume N_2O , hence it is likely that both the increase in $[\text{NO}_2^-]$ and the increase and decrease in $[\text{N}_2\text{O}]$ within this layer can be attributed to different stages of canonical denitrification ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$) (Bange, 2008). The vertical profiles, especially the minimum in N_2O within the OMZ’s core, provide strong evidence that all stages of canonical denitrification influence nitrogen speciation in this layer. The observed increase in $\delta^{15}\text{N-NO}_3^-$ and decrease in $\delta^{15}\text{N-NO}_2^-$ at the base of the layer B are also consistent with denitrification, which leaves $[\text{NO}_2^-]$ depleted in ^{15}N . Interestingly, the difference between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NO}_2^-$ values are higher (~ 30 ‰) than fractionation factor calculated for N-loss process within OMZ (~ 11.4 ‰, see below) but close to the expected value for pure culture studies (28.6 ‰) (i.e. Barford et al., 1999). The reason for this could be the nitrite oxidation, which has an inverse isotopic fractionation effect, leaving $\delta^{15}\text{N-NO}_2^-$ depleted in ^{15}N (Casciotti, 2009). Nitrite oxidation can appear in nitrification-denitrification coupled systems or in anammox as a side-reaction (i.e. Straus 1998, van de Graaf 1996). The deep $[\text{NO}_2^-]$ maximum can support anammox, which has been observed in several previous studies of this region (Galan et al., 2009; Hamersley et al., 2007; Lam et al., 2009).

4.1.3 Atlantic study region

In the Atlantic study region, the oxygen profile has two minima at ~ 70 m and ~ 400 m (Fig. 3b). The shallow minimum is strongest between Senegal and the Cape Verde Islands and is probably caused by enhanced subsurface remineralization associated with high biological productivity and a shallow mixed layer (Karstensen et al., 2008). The deeper minimum is more prominent south of Cape Verde and is associated with the water mass boundary between Central Water and AAIW (Stramma et al., 2005). The double oxygen minimum (Fig. 3) is therefore caused by the mixing of two water masses from the North and South (NACW and SACW) of the Atlantic region.

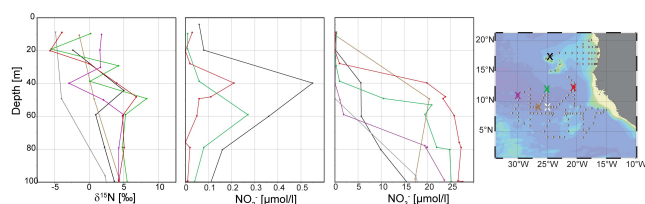


Fig. 5. Shallow vertical profiles of M80 stations south to Cape Verde islands in the Atlantic. Stations: 1 (TENATSO) and 5, 67, 76, 81 and 87 located between 12° N and 9° N.

The profiles from the Atlantic station (Fig. 4, lower panels) are considerably simpler, with fewer subsurface features. Once again, two layers have been distinguished based on oxygen concentration and its influence on dominant nitrogen cycle processes.

Layer a (0–50 m) includes the surface mixed layer which extends to c. 30 m. This layer includes the steepest part of the oxycline, a strong increase in N_2O with depth, and a primary nitrite maximum which lies at the base of this layer. The $\delta^{15}N$ of DIN increases steadily throughout this layer and reaches a maximum at a depth close to the primary nitrite maximum. These features can be attributed to a combination of remineralization of organic matter, nitrite excretion by phytoplankton after nitrate reduction and nitrification. In contrast to the Pacific study region, the surface layer has minimum values of $\delta^{15}N$ in DIN, with some values being strongly negative (e.g. -5.6‰ at 20 m).

Examination of near-surface profiles from the Atlantic (Fig. 5) reveals negative values of $\delta^{15}N$ in DIN within the surface mixed layer at stations located South of Cape Verde and at the TENATSO station. There is a tendency for the values to be most negative at the shallowest depths (20 m) with extremely low $\delta^{15}N$ values almost always observed in this depth range. Generally below 20 m, both NO_3^- $\delta^{15}N$ and concentration increase with depth. We argue that the source of nitrate at the very surface of stations with low $\delta^{15}N$ NO_3^- is from atmospheric deposition (see below, Sect. 4.2.5). Nitrite concentration was below the detection limit of $0.02\text{ }\mu\text{mol l}^{-1}$, while $[NO_3^-]$ concentrations in the region are about $0.1\text{--}0.5\text{ }\mu\text{mol l}^{-1}$. Thus contamination via nitrite cannot be the reason for low $\delta^{15}N$ values. In regions more influenced by upwelled waters, the near-surface values were higher in the range $+4\text{--}+7\text{‰}$ and more consistent with an isotopic signal from upwelled NO_3^- . Even though these concentration levels lie close to our detection limit for $\delta^{15}N$ measurements ($0.2\text{ }\mu\text{mol l}^{-1}$), all surface water samples were measured 5 times and gave reliable values with $>95\%$ reliability and $\pm 0.3\text{‰}$ standard deviation. Further, laboratory tests with dilutions of $\delta^{15}N$ standards showed no suggestion of any systematic change of measured $\delta^{15}N$ values with decreasing $[NO_3^-]$ concentrations.

Apparent exceptions are found at stations 87 at 25° W and 67 at 30° W (marked with white and purple crosses in Fig. 5) where low $\delta^{15}N$ of -4 and -3‰ are observed at 50 and 40 m respectively. Corresponding nitrate concentrations are 0.25 and $0.20\text{ }\mu\text{mol l}^{-1}$, respectively, and nitrite concentration is below the detection limit. While these values appear to be too deep to be influenced by atmospheric input, in fact the mixed layer is indeed deeper at these stations: 40–50 m instead of 20 m. Thus, we believe, that the low $\delta^{15}N$ signal at these stations could also originate from atmospheric deposition. To be conservative, we only considered the upper 20 m water column for our calculations of nitrogen fluxes in the Table 1 (see Sect. 4.2.5).

At station 1 (TENATSO, marked with black cross in Fig. 5) between 40–60 m isotope signature lay $0 < \delta^{15}N < 5$ with nitrate concentrations increasing up to $6\text{ }\mu\text{mol l}^{-1}$ and nitrite up to $0.55\text{ }\mu\text{mol l}^{-1}$. Elevated nitrate and nitrite concentrations having a $\delta^{15}N$ signature of only few per mil is here likely due to N-fixation, which was observed in this region during other studies (i.e. Bourbonnais 2009).

Layer b (below 50 m) includes the core of the Atlantic OMZ. In contrast to the Pacific OMZ, the Atlantic profiles had no secondary nitrite maximum, and $\delta^{15}N$ values and N_2O concentrations remained relatively constant with depth. The N_2O profiles show no evidence for consumption as was seen in the Pacific. This is a clear indication for the absence of significant denitrification in this region. A slight increase in N_2O with depth below 50 m can be explained by nitrification (Walter et al., 2006).

4.2 Property-property distributions

4.2.1 Nitrate to Phosphate

Figure 6 presents the NO_3^- to PO_4^{3-} relationship (with dissolved oxygen concentrations as the color code) for the Atlantic and Pacific study regions. According to Redfield stoichiometry, the average ocean ratio of N:P is 16:1. Deviations from this ratio can be an indicator for which nutrient sink/source processes are dominating in the ocean region of interest. Waters in the Pacific study region are highly N-deficient ($N:P < 16$), with the highest deficits found in oxygen minimum waters (purple coloring, Fig. 6a) and associated with the N-removal processes denitrification and/or anammox (Deutsch et al., 2001). Data from the Atlantic study region show strong positive deviations from the 16:1 Redfield stoichiometry, which can be a result of N_2 -fixation (Hansell et al., 2004; Michaels et al., 1996; Gruber and Sarmiento, 1997) and/or nutrient uptake and/or remineralization with non-Redfield stoichiometry (Monteiro and Follows, 2006). Positive deviations from Redfield stoichiometry can also, potentially, be caused by atmospheric deposition of nitrogen (Duce et al., 2008). Note that our treatment of deviations in $[NO_3^-]:[PO_4^{3-}]$ does not include the nitrite (NO_2^-) produced under low oxygen. Including NO_2^- in the calculation,

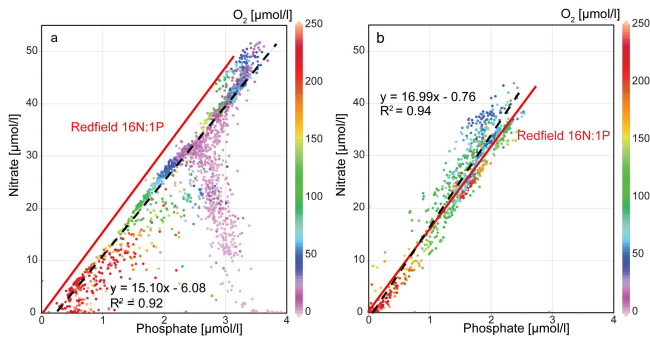


Fig. 6. $[\text{NO}_3^-]:[\text{PO}_4^{3-}]$ relationships in the Pacific (a) and the Atlantic (b) study regions. The data are color-coded by oxygen concentration. Note that the average $[\text{NO}_3^-]:[\text{PO}_4^{3-}]$ relationship in the Pacific was calculated for $[\text{O}_2] > 50 \mu\text{mol l}^{-1}$.

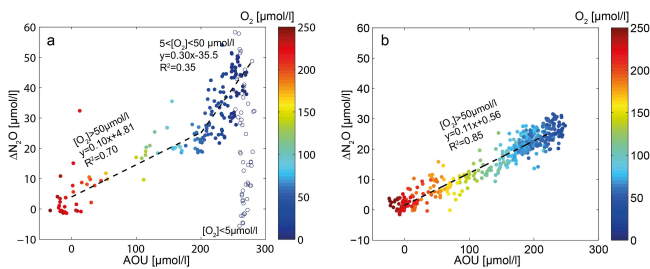


Fig. 7. $\Delta\text{N}_2\text{O}$ vs. AOU at upper oxycline (350 m in the Pacific (a) and 500 m the Atlantic (b) study areas) with oxygen concentration as color code. Black dashed lines show the correlation between $\Delta\text{N}_2\text{O}$ and AOU, empty circles indicate the samples with $[\text{O}_2] < 5 \mu\text{mol l}^{-1}$.

however, does not change the ratios significantly (average $\text{DIN}:[\text{PO}_4^{3-}] = 15.04$ in the Pacific and 16.92 in the Atlantic regions).

4.2.2 N_2O vs. AOU

Property-property plots of $\Delta\text{N}_2\text{O}$ to apparent oxygen utilization (AOU) (with $[\text{O}_2]$ as the color code) are presented in Fig. 7, where AOU is the difference between the measured dissolved oxygen concentration and its equilibrium concentration in water with the same physical and chemical properties.

$\Delta\text{N}_2\text{O}$ is the excess nitrous oxide and is defined as the difference between the measured N_2O and the equilibrium N_2O concentration at the time when a water parcel had its last contact with the atmosphere. Because the atmospheric N_2O mixing ratios have been increasing since 1800, the calculation of excess N_2O has to take into account the age of the water parcel at the time of the measurement. Freing et al. (2009) showed that the difference in the slopes of $\Delta\text{N}_2\text{O}$ vs. AOU associated with different ways of calculating excess N_2O can be as much as 17 %. The methods used include the transit

time distribution (TTD) approach, where CFC-12 and SF_6 data are used to calculate a mean-age of a water parcel. Alternatively, a “layer” method (Walter et al., 2004) uses different equilibrium N_2O concentrations for mixed layer and deep waters. For the sake of simplicity we used here the “contemporary” approach, where the $[\text{N}_2\text{O}]_{\text{eq}}$ in the upper 500 m is calculated based on the contemporary atmospheric dry mole fraction of N_2O (N_2O of 322×10^{-9} for Pacific data and 323×10^{-9} for Atlantic data, <http://agage.eas.gatech.edu/>) (Nevison et al., 2003; Yoshinari, 1976). Although the contemporary method may lead to underestimations of $\Delta\text{N}_2\text{O}$ vs. AOU slopes of up to 17 % (Freing et al., 2009), it does not affect the qualitative comparison of the Atlantic and Pacific study regions given below. An overall linear relationship of $\Delta\text{N}_2\text{O}$ to AOU (Fig. 7) was observed previously in both regions (Oudot et al., 1990; Elkins et al., 1978; Nevison et al., 2003).

However, the Pacific relationship has two different slopes for oxygen concentrations below and above $50 \mu\text{mol l}^{-1}$ (which corresponds here to an AOU of c. $208 \mu\text{mol l}^{-1}$). For $5 < [\text{O}_2] < 50 \mu\text{mol l}^{-1}$ the slope of the $\Delta\text{N}_2\text{O}$ to AOU relation is 0.30 ± 0.050 which is significantly higher than that for $[\text{O}_2] > 50 \mu\text{mol l}^{-1}$ (0.10 ± 0.009). This is suggestive of a higher yield of N_2O per mole NO_3^- produced by nitrification at low oxygen levels (Goreau et al., 1980; Stein and Yung, 2003). In Pacific waters with $[\text{O}_2] < 5 \mu\text{mol l}^{-1}$ (AOU of c. $248 \mu\text{mol l}^{-1}$), $\Delta\text{N}_2\text{O}$ concentrations decrease again to near-zero values, indicative of the consumption of N_2O at very low oxygen levels mentioned above. Corresponding changes in slope are not visible in the Atlantic data, likely because there are so few data with $[\text{O}_2] < 50 \mu\text{mol l}^{-1}$. The slopes of the $\Delta\text{N}_2\text{O}$ vs. AOU relationships for $[\text{O}_2] > 50 \mu\text{mol l}^{-1}$ are remarkably similar in both regions: 0.10 ± 0.009 and 0.11 ± 0.003 in the Pacific and Atlantic, respectively. These values lie close to the value of 0.107 reported for the tropical Atlantic by Walter et al. (2006) but lower than the value of 0.211 reported by Oudot (2002). The values from the Oudot (2002) paper, however, should be taken with particular care as the mean atmospheric mixing ratio of N_2O presented in their paper (316×10^{-9}) seems to be unrealistically high in comparison to the mean atmospheric background dry mole fraction of N_2O at the time of their measurements (308×10^{-9} , <http://agage.eas.gatech.edu/>).

This higher yield of N_2O under reduced concentrations of oxygen was observed earlier (Goreau et al., 1980) and was attributed to increasing N_2O yield when ammonia oxidizing microbes become O_2 stressed. This view was challenged by Frame and Casciotti (2010), who showed that ammonia-oxidizing bacteria do not have increased N_2O yield under low O_2 conditions under environmentally relevant culture conditions. The most recent findings from both the Atlantic and Pacific oceans indicate however that archaeal ammonia-oxidizers (AOA) rather than bacteria may be key organisms for the production of oceanic nitrous oxide and

can exhibit higher production rates under low oxygen conditions (Löscher et al., 2011).

Regarding the Pacific observations at very low O_2 , N_2O removal provides strong evidence for the occurrence of denitrification given its specificity for this process (Bange et al., 2005). However, the amount of N_2O removed (c. 50 nmol l^{-1}) is an order of magnitude lower than the observed amount of NO_3^- removal. Hence it gives no indication of the quantitative significance of this process for overall fixed nitrogen removal (e.g. compared to anammox).

Additional insight into N-loss processes is gained here from nitrogen isotope ($\delta^{15}\text{N-NO}_3^-$) and fixed nitrogen deficit (N') data.

4.2.3 $\delta^{15}\text{N-NO}_3^-$ vs. N_2O and N'

Figure 8 shows ΔN_2O vs. $\delta^{15}\text{N-NO}_3^-$ (with color coding indicating oxygen concentration) in the two study regions, which helps to reveal processes responsible for the production or consumption of nitrous oxide. In the Atlantic, the profiles and property-property plots show no evidence of N_2O consumption and the nitrogen isotope values stay close to the oceanic average of 5‰, which is also consistent with a lack of denitrification. As discussed above, the dominant process affecting N_2O in the Atlantic study region is production due to nitrification. For Pacific oxygenated waters ($[O_2] > 5 \mu\text{mol l}^{-1}$) the ΔN_2O vs. $\delta^{15}\text{N-NO}_3^-$ relationship is similar to that found in the Atlantic. The reason for some very low $\delta^{15}\text{N-NO}_3^-$ values in Atlantic surface water is discussed below. A trend towards high $\delta^{15}\text{N-NO}_3^-$ values in the Pacific study region (Fig. 8a) can be associated with denitrification at lower O_2 concentrations ($[O_2] < 5 \mu\text{mol l}^{-1}$, purple coloring) or with nitrate assimilation in near surface waters ($[O_2] > 200 \mu\text{mol l}^{-1}$, red coloring). These two processes cannot be distinguished in figure 8a as the ΔN_2O is close to zero both for waters with $[O_2] < 5 \mu\text{mol l}^{-1}$ (due to denitrification), and for waters with $[O_2] > 200 \mu\text{mol l}^{-1}$ (due to N_2O equilibration with the atmosphere). In order to differentiate between these two processes the correlation between $\delta^{15}\text{N-NO}_3^-$ and the N-deficit was calculated (Fig. 8c).

In the core of the OMZ, the $\delta^{15}\text{N}$ of DIN is inversely correlated with N' (mainly negative values) and hence with N-removal, whereas in high-oxygen, near-surface waters, $\delta^{15}\text{N-NO}_3^-$ increases independent of N' , reflecting fractionation during NO_3^- assimilation by phytoplankton in the euphotic zone (Granger et al., 2004).

4.2.4 Isotope fractionation and N-loss in the Pacific OMZ

The reduction of nitrate to nitrite is the first step of the denitrification process and is also an essential source of NO_2^- for fuelling anammox (Lam et al., 2009). We will next examine the isotope fractionation signal associated with this reduction step. The kinetic isotope fractionation factor can

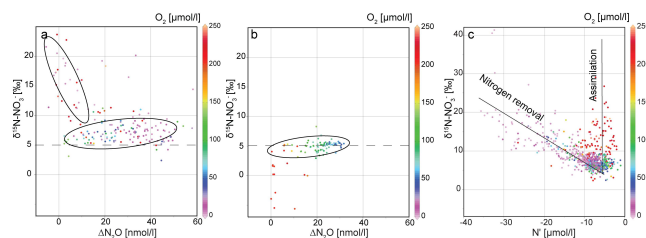


Fig. 8. $\delta^{15}\text{N-NO}_3^-$ vs. ΔN_2O in the Pacific (a) and in the Atlantic (b) study areas and (c) the $\delta^{15}\text{N}$ vs. N' distribution in the Pacific. The data are color-coded by oxygen concentration. The nitrogen deficit in the figure 8c was calculated as $N' = [NO_3^-] + [NO_2^-] - 16 \times [PO_4^{3-}]$. $\delta^{15}\text{N}$ vs. N' data reveal two clear trends in the Pacific study region.

be represented as either $\alpha_r = {}^{15}\text{R}/{}^{14}\text{R}$ or $\varepsilon_r = (1-\alpha) \times 1000$, where ${}^{15}\text{R}$ and ${}^{14}\text{R}$ are the rates of denitrification for ${}^{15}\text{NO}_3^-$ and ${}^{14}\text{NO}_3^-$, respectively. An effective or “apparent” value for the fractionation factor for nitrate reduction (ε_r) can be calculated through application of the Rayleigh model to the field data or “diffusive” model of Brandes (1998), where diffusive transport is included. Model of Brandes (1998) require knowledge or estimations of denitrification rates and coefficient of eddy diffusivity for fractionation factor calculation. For the Peruvian OMZ neither of those two parameters are known however, thus we calculation ε^* with the Rayleigh model. This model assumes removal from a closed pool of nitrate with constant isotopic fractionation. Hence:

$$\delta^{15}\text{N-NO}_3^-(f) = \delta^{15}\text{N-NO}_3^-(f=1) - \varepsilon^* \times \ln(f), \quad (1)$$

where f is the fraction of consumed NO_3^- , $f = [NO_3^-]/(16 \times [PO_4^{3-}])$, the ε^* is an “apparent” fractionation factor, in this case for a nitrogen removal process. Least squares fitting of all data from the Pacific OMZ (i.e. $[O_2] < 50 \mu\text{mol l}^{-1}$) is shown in Fig. 10a, with the “apparent” isotopic enrichment factor (ε^*) estimated to be +11.4‰ (standard error of the fit is 0.7, Fig. 10). The data are scattered between relationships defined by $\varepsilon^* = 5$ and 25‰ (assuming a common initial value for $\delta^{15}\text{N}_{\text{initial}}$ of 5.2‰). This value of ε^* of +11.5‰ is significantly lower than values estimated from data from the Eastern Tropical North Pacific (22.5–30‰) and Arabian Sea (22–25‰) (Brandes et al., 1998; Sigman et al., 2003; Voss et al., 2001) and from denitrifier cultures (28.6‰) (Barford et al., 1999). However the value lies close to a values determined 30 years ago for 2 stations off southern Peru using much less sensitive analytical techniques (13.8‰) (Liu, 1979).

Separating data for shelf and offshore stations (Fig. 9b) results in fits with significantly different values of ε^* of 7.6‰ and 16.0‰, respectively. Similar observations of low ε_d have been made in Santa Barbara Basin as compared to the open ETNP (Sigman et al., 2003). This was attributed to a larger contribution from sedimentary denitrification input

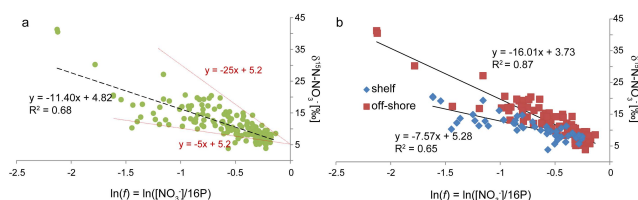


Fig. 9. (a) Application of Rayleigh model to assess fractionation in the Pacific OMZ for all waters with $[O_2] < 50 \mu\text{mol l}^{-1}$. Dashed lines indicate relationships calculated for $\epsilon_d = 5$ and 25‰. The average calculated or “apparent” fractionation factor for the entire region is 11.4‰. (b) Apparent fractionation factors calculated separately for shelf (stations shallower than 200m) and off-shore (stations deeper than 200m) stations. The shelf stations show a lower apparent fractionation factor of 7.6‰, while the value for off-shore stations is 16.0‰.

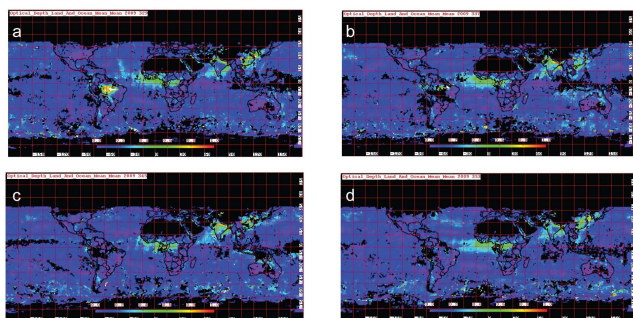


Fig. 10. Satellite images of Aerosol Optical Depth at different time periods of 2009.: (a) 25 Oct–2 Dec; (b) 3 Dec–10 Dec; (c) 11 Dec–18 Dec; (d) 19 Dec–26 Dec (http://ladsweb.nascom.nasa.gov/browse_images/13-browser.html)

into the water column in the Basin, which has a significantly smaller fractionation effect of 0–5‰ due to control of overall NO_3^- removal rate by transport through the sediments (Brandes and Devol, 2002, Lehmann et al., 2007).

4.2.5 Dust deposition signal in the surface waters south of Cape Verde

In marked contrast to the Pacific study region, most $\delta^{15}\text{N-NO}_3^-$ values from the Atlantic (Fig. 8b) stay close to the ocean average value of 5.2‰ (Supplementary material, Table 1 (Sigman et al., 2009)). In part this can be explained by the absence of significant fixed-N removal in this region (N' values remain positive, data not shown (Gruber and Sarmiento, 1997)). Notable also was the complete absence of any trend towards higher values associated with partial nitrate utilization in fully-oxygenated, near-surface waters on the M80 samples (stations south to Cape Verde). Significant increases of $\delta^{15}\text{N}$ (up to 12‰) in surface waters were only observed at shallow stations very close to the African coast (data from *L'Atalante* cruise in 2008, not shown) that

are likely associated with partial phytoplankton uptake of upwelled NO_3^- (Altabet, 2001; Altabet and Francois, 1994).

Decreasing values of $\delta^{15}\text{N}$ of DIN towards the surface have been reported previously for Monterey Bay (Wankel et al., 2007), and for near-surface samples collected close to the Azores Front (30–35° N) (Bourbonnais et al., 2009) and at Bermuda (Knapp et al., 2010). The lowest values published from this general region (Bourbonnais et al., 2009) were ~ 3.5 ‰ at a depth of 100 m. Our data indicate very similar values at this depth. The relatively low values of 3.5‰ were attributed by Bourbonnais et al. (2009) to the effects of nitrogen fixation, which can result in remineralised DIN with typical values of -1 ‰ (-2 ‰ to $+2$ ‰) (Carpenter et al., 1997; Montoya et al., 2002). The strongly negative $\delta^{15}\text{N}$ values measured in surface waters south of Cape Verde (e.g. down to -5.5 ‰, Fig. 5) have not been observed before in oceanic surface waters and cannot be explained by ammonification and nitrification of organic nitrogen produced by nitrogen fixers. On the other hand, very low values of $\delta^{15}\text{N}$ (~ -7 ‰) of aerosol nitrate have been measured in samples of atmospheric dust from this region (Baker et al., 2007; Morin et al., 2009). Similarly low, negative values have been measured in samples of atmospheric dust originating in the Sahara that were collected from the eastern Mediterranean (Wankel et al., 2010). Recent work (Knapp et al., 2010) shows that the wet deposition flux of fixed-N at Bermuda can be comparable to estimates of biological N_2 fixation rates in surface waters. The $\delta^{15}\text{N-NO}_3^-$ in wet deposition at Bermuda was significantly lower (-4.5 ‰) than $\delta^{15}\text{N}$ added by oceanic N_2 fixation (-2 to 0‰) (Hastings et al., 2003; Knapp et al., 2010). For our study region, dry deposition of dust from the Sahara is likely to dominate the N-flux (Duarte et al., 2006).

The N-flux due to diapycnal mixing of NO_3^- from below in the eastern Atlantic (28°30' N, 23° W) has been estimated to be $140 \mu\text{mol/m}^2/\text{day}$ and was statistically indistinguishable from the integrated rate of nitrate assimilation (Lewis et al., 1986). Later studies in the oligotrophic north Atlantic and at Cape Verde region come to values of about $7 \text{ mg N m}^{-2} \text{ d}^{-1}$ (or $\sim 500 \mu\text{mol/m}^2/\text{day}$) (Klein and Siedler, 1995) and at region close to Mauretania to almost double value of about $1037 \mu\text{mol/m}^2/\text{day}$, calculated from the cruises data during high upwelling season (Schafstall et al., 2010). According to Baker et al. (2007) the dry deposition N flux of soluble aerosol at 20° W in the Atlantic ocean is $80\text{--}120 \mu\text{mol/m}^2/\text{day}$, while wet deposition is $50\text{--}70 \mu\text{mol/m}^2/\text{day}$. Duarte (2006), for example, estimated a dry deposition N flux of $280 \pm 70 \mu\text{mol/m}^2/\text{day}$ in tropical Atlantic region, which is significant in comparison to the diapycnal flux. This deposition flux is sufficient to supply the observed DIN inventory of the top 20 m ($0.2 \mu\text{mol l}^{-1}$) within two weeks.

The most negative $\delta^{15}\text{N}$ values in surface water were observed at stations south of the Cape Verde Islands, which

is also the region with the highest Saharan dust deposition (Schepanski et al., 2009; Tanaka and Chiba, 2006). A few days before our samples were collected on M80, an intensive dust event took place, and this may have influenced the $\delta^{15}\text{N}$ values observed. Satellite imagery from November and December 2009 are shown in Fig. 10 and indicate a significant dust event in the region over the period immediately prior to our samples being collected (between 26 November and 12 December 2009).

Under these conditions, the nitrogen loading to the surface layer cannot be considered to be in a steady state. We therefore examined extreme scenarios with dry deposition N flux dominating and for balance with diapycnal mixing and assimilation (Table 1). Total N flux (F_{total}) is the sum of two sources from atmospheric deposition (F_{dust} , initial value of $\delta^{15}\text{N-dust} = -7\text{‰}$) and diapycnal mixing (F_{mix} , initial value of $\delta^{15}\text{N-mixing} = 5\text{‰}$) and one nitrogen sink from assimilation ($F_{\text{assimilation}}$). The fractionation factor for assimilation can vary with environmental conditions and dominant phytoplankton species. In oligotrophic waters, however, observed isotope fractionation will be close to zero due to complete NO_3^- utilization. Assuming that utilized NO_3^- has an ocean-average value of $\delta^{15}\text{N} = 5\text{‰}$ and fractionation factor close to zero, the assimilation will decrease nitrate concentration but increase $\delta^{15}\text{N}$ of it in ambient waters by 5‰ , thus $\delta^{15}\text{N-}$ assimilation = -5‰ .

In the first scenario, 90 % of total nitrogen derives from dust deposition and only 10 % is from diapycnal mixing. This scenario results in a $\delta^{15}\text{N}$ value of -5.8‰ , very close to observations. The second scenario assumes equal contribution from those two nitrogen sources resulting in a $\delta^{15}\text{N}$ of -1‰ , while the third includes assimilation as a nitrogen sink and result in $\delta^{15}\text{N}$ of $+1\text{‰}$ (Table 1).

These scenarios do not take into consideration an isotopic signal from N_2 fixation. They do show, however, that under non-steady state conditions, such as shortly after dust deposition events, the $\delta^{15}\text{N}$ for NO_3^- in surface waters can decrease to -5.8‰ . Thus, atmospheric dust N deposition should be taken into account, together with the oceanic N_2 fixation, in explaining the low $\delta^{15}\text{N}$ NO_3^- pool observed in subtropical thermoclines (Brandes et al., 1998; Karl et al., 2002; Knapp et al., 2005; Wannicke et al., 2010).

5 Summary and conclusions

In this paper we have presented an extensive amount of new data for nitrogen isotope and key nitrogen species, such as N_2O , collected from OMZ regions in the eastern tropical North Atlantic and eastern tropical South Pacific. These regions have strongly contrasting O_2 concentrations and N cycling processes. Measurements with near identical techniques in both oceans, reveal that whereas deep waters ($> 2000\text{ m}$) share near-identical values of $\delta^{15}\text{N-DIN}$ ($5.3 \pm 0.4\text{‰}$), there are significant to major differences between the two OMZs in both surface and intermediate

waters. The same AAIW water mass, for instance, has in the Pacific $\delta^{15}\text{N-DIN}$ average value of $6.7 \pm 0.8\text{‰}$ and in the Atlantic of $5.5 \pm 0.6\text{‰}$ (Supplementary material, Table 1). According to a Student t-test, the difference is highly significant ($p < 0.01$). This difference can be due to N-loss in the Pacific, increasing $\delta^{15}\text{N}$ signal of the water mass, and/or nitrogen fixation in the Atlantic, driving $\delta^{15}\text{N}$ signal in the opposite direction. Strongest differences in $\delta^{15}\text{N-DIN}$ in the two study regions are located in depth 100–500 m in the OMZs. In the Pacific $\delta^{15}\text{N}$ values tend towards strongly positive values as a result of N-loss processes within the OMZ and partial NO_3^- utilization in surface waters, while in the Atlantic the values stay close to $\sim 5.4\text{‰}$ on average.

Co-located measurements of N_2O and stable N-isotopes in waters with $[\text{O}_2] < \sim 5\ \mu\text{mol l}^{-1}$ reveal a clear signal of canonical denitrification, although its quantitative significance for overall N-loss, relative to anammox, cannot be assessed. The correlations of N_2O with $\delta^{15}\text{N-NO}_3^-$ and AOU for waters with $[\text{O}_2] > 50\ \mu\text{mol l}^{-1}$ are similar in both OMZs, reflecting similar N_2O yields during nitrification. However, waters with $5 < [\text{O}_2] < 50\ \mu\text{mol l}^{-1}$ in the Pacific exhibit correlations that are suggestive of a 300 % higher relative N_2O yield.

Whereas $\delta^{15}\text{N-NO}_3^-$ values in surface waters of the Pacific OMZ region are strongly positive, being controlled by partial nutrient utilization and a ^{15}N -enriched NO_3^- supply affected by subsurface denitrification, the oligotrophic surface waters south of Cape Verde in the Atlantic exhibit negative values of $\delta^{15}\text{N}$ (-5 to $+2\text{‰}$). The negative values are too low to be explained by N-fixation and we show that they are most likely the result of a transient input of NO_3^- associated with atmospheric deposition of Saharan dust. This implies that atmospheric dust input as well as nitrogen fixation should be considered in budgets and explanations of upper ocean stable N isotope data, especially in the Atlantic region.

Within the Pacific OMZ, correlation of $\delta^{15}\text{N}$ with measures of N-loss gives a calculated apparent fractionation factor for $\delta^{15}\text{N-NO}_3^-$ ($\epsilon_r = 11.4 \pm 0.3\text{‰}$) which is low compared to canonical values, but close to a value estimated by the only prior study in this region (Liu, 1979). Sub-division of the data into shelf and offshore stations resulted in improved correlations and very different apparent fractionation factors for the two depth-regimes ($\epsilon_{\text{d-offshore}} = 16 \pm 0.5\text{‰}$; $\epsilon_{\text{d-shelf}} = 7.6 \pm 0.6\text{‰}$). Whereas the offshore value lies close to the $\sim 20\text{‰}$ fractionation factor of denitrification (Brandes et al., 1998; Granger et al., 2008), the much lower apparent fractionation factor for shelf waters likely reflects a larger contribution from sedimentary denitrification (fractionation factor of 1.5‰ ; (Brandes and Devol, 2002). We note that the fractionation effect from the complete set of stations ($\epsilon^* = 11.4 \pm 0.3\text{‰}$) lies reasonably close to an apparent global fractionation factor for OMZ denitrification of 12‰ which was calculated for a steady state 50:50 balance between water column and sedimentary denitrification (Altabet, 2007).

Supplementary material related to this article is available online at:
<http://www.biogeosciences.net/9/203/2012/bg-9-203-2012-supplement.pdf>.

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