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N-Cycling and Balancing of the N-Deficit Generated in the Oxygen Minimum Zone over the Namibian Shelf – an Isotope-based Approach

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Abstract

The northern Benguela upwelling system is a nutrient-replete region with high plankton biomass production and a seasonally changing oxygen minimum zone. Nitrate:phosphate ratios in fresh upwelling water are low due to denitrification in the near-seafloor oxygen minimum zone and phosphate efflux from sediments. This makes the region a candidate for substantial dinitrogen fixation, for which evidence is scarce. Nutrient and oxygen data, N isotope data of nitrate, nitrogen isotope ratios of particulate matter, particulate organic carbon content and suspended matter concentrations on a transect across the shelf and upper slope at 23°S illustrate N-cycling processes and are the basis for estimating the contribution of N-sources and N-sinks to the reactive nitrogen pool. It appears that N-removal due to denitrification exceeds N gain by N₂ fixation and physical mixing processes by a factor of >6, although inorganic N:P ratios again increase as surface water is advected offshore. Nitrate and

ammonium regeneration, nutrient assimilation with N:P < 16, shelf break mixing, atmospheric input and N₂ fixation all contribute to the restoration of inorganic N:P ratios back to Redfield conditions, but in seasonally changing proportions. The Benguela upwelling system thus is a nutrient source for the oceanic mixed layer where N-sources and N-sinks are not in balance and Redfield conditions can only re-adjust by advection and mixing processes integrated over time.

1. Introduction

Upwelling systems are the largest marine source of CO₂ to the atmosphere and their immense primary production fueled by upwelled nutrients far outweighs their modest regional extent (Watson, 1995; Wetzel *et al.*, 2005). Productivity eventually re-captures the outgassed CO₂ by phytoplankton assimilation. But it is questionable if CO₂ outgassing and uptake are in direct balance in individual upwelling systems. Because they often tap oxygen-deficient intermediate water masses, upwelling shelves are prone to oxygen deficiency aggravated by very high oxygen demand generated by remineralization of sinking organic matter (Monteiro *et al.*, 2006). Oxygen-deficient coastal upwelling often does not supply nutrients into the euphotic zone in Redfield ratios, but with surplus of phosphate over nitrate (termed P* by Deutsch *et al.* 2007), because either is nitrate used to oxidize organic matter in the absence of dissolved O₂ (Lipschultz *et al.*, 1990), or phosphate is added from anoxic sediments high in organic carbon and phosphorus overlying the shelf (Bailey, 1991). In the case that inorganic N:P ratios of upwelled waters are smaller than 16, current understanding is that there will be a zone at the fringes of the high productivity belt where nitrate is depleted by assimilation, and phosphate remains in aged upwelling waters, triggering the “Redfield homeostat” of diazotrophic N₂ fixation until the nitrate deficit is filled (Rixen *et al.*, 2005; Rixen *et al.*, 2009; Tyrrell, 1999). If this basic concept is true, the CO₂ budget of an upwelling system remains

constant on time scales of years to decades and on spatial scales far beyond the immediate coastal upwelling area, since the N deficits produced in hypoxic water masses are balanced by N₂ fixation at the fringes of the upwelling region and the hemipelagic ocean.

One example of such a system is the Benguela upwelling system (BUS) where several upwelling cells exist along the Namibian and South African coast due to the interaction of trade winds with coastal topography (*Shannon and Nelson, 1996*). The northward component of the Southeast Trades drives upwelling and causes offshore Ekman transport in the surface mixed layer. Near-seafloor onshore transport and upwelling from 50 to 200 m water depth compensate for the wind-driven water deficit. The BUS is part of the eastern boundary current system of the south Atlantic. Off central and northern Namibia, the confluence of the northward flowing Benguela Current and the poleward Angola current form a transition zone between central water of tropical and subtropical origin. Eastern South Atlantic Central Water (ESACW; Fig. 1a) is advected within the Benguela current from the Agulhas region equatorwards as far as the Angola Benguela Frontal Zone at 17°S (*Mohrholz et al., 2001*). The Angola current and its subsurface extension, the poleward undercurrent (PU), transport nutrient-rich and oxygen-depleted South Atlantic Central Water (SACW) from the Angola Gyre along the shelf break (Fig. 1a). Its proportion in the upwelling water controls the intensity of the oxygen minimum zone (OMZ), which is most pronounced on the northern Benguela shelf (*Inthorn et al., 2006; Mohrholz et al., 2008; Monteiro et al., 2006*). Upwelling mainly occurs at the coast (*Mohrholz et al., 2008*), but also over the shelf due to a belt of negative wind stress curl (*Fennel et al., 2012*). Also shelf break upwelling was observed (*Barange and Pillar, 1992*).

Water mass composition and thus oxygenation on the shelf vary throughout the year owing to seasonal changes in the wind-driven Ekman regime. High SACW contributions (80 to 100%) are found along the 23°S transect off Walvis Bay in austral summer (February/March) when the PU is most active and the cross-shelf circulation is weak, so that

ventilation of the bottom water is impeded (*Mohrholz et al.*, 2008). The cross-shelf circulation is strongest in the peak upwelling season in August/September and brings oxygen-rich ESACW from the shelf break onto the shelf (*Mohrholz et al.*, 2008). Hypoxia and anoxia on the shelf are thus mainly controlled by the water mass composition, but oxygen demand from high organic matter fluxes and degradation reduce original O₂ concentrations (*Monteiro et al.*, 2006) and create conditions conducive for anaerobic pathways of organic matter degradation. Oxygen concentrations below 10 μM and ~5 μM stimulate anammox and heterotrophic denitrification, respectively (*Cline and Kaplan*, 1975; *Jensen et al.*, 2008), and cause nitrate deficits over phosphate in OMZs that are transferred into surface waters by upwelling (*Tyrrell and Lucas*, 2002).

Nitrate reduction in the water column – the first step of heterotrophic denitrification - and presumably also anammox are associated with kinetic fractionation of stable N isotopes causing an enrichment of the heavier ¹⁵N isotope in the residual nitrate pool (*Konovalov et al.*, 2008; *Sigman et al.*, 2005). The fractionation factor (ε) is the difference between the isotopic composition of the source and the product (*Mariotti et al.*, 1981). Heterotrophic denitrifying bacteria and nitrate assimilating phytoplankton discriminate against the heavier ¹⁵N isotope with a fractionation factor of 25‰ and 5‰, respectively (*Granger et al.*, 2004; *Granger et al.*, 2008). Although large reactive nitrogen deficits over phosphate occur in upwelling water, there is no experimental evidence for significant N₂ fixation in the BUS (*Sohm et al.*, 2011; *Wasmund*, pers. comm., 2011). This is puzzling, because inorganic N:P ratios are evidently restored to Redfield ratios in modified upwelling water advected offshore (*Wasmund et al.*, 2005) and seem to exemplify the P*-concept (*Deutsch et al.*, 2007) that links N₂ fixation in time and space to the denitrification zones of the ocean. In the absence of evidence for N₂ fixation several alternative processes have been invoked, such as shelf break upwelling in a second upwelling cell (*Barange and Pillar*, 1992; *Emeis et al.*, 2009), or non-Redfield assimilation stoichiometry (*Weber and Deutsch*, 2010).

Here, we use data of oxygen and nutrient concentrations as well as stable isotope compositions of nitrogen in nitrate ($\delta^{15}\text{N}_{\text{NO}_3}$) and $\delta^{15}\text{N}$ ratios of particulate nitrogen ($\delta^{15}\text{N}_{\text{PN}}$) as well as particulate organic carbon content (POC) to investigate N-cycling processes in the BUS and the isotopic composition of nitrate as a fingerprint of its origin. With the data, we quantify the nitrate deficit generated by denitrification and phosphate release, estimate how much denitrification contributes to the regional nitrate deficit, and identify mechanisms that restore the inorganic N:P ratios in the mixed layer of the adjacent South Atlantic.

2. Materials and Methods

2.1. Sampling

Water samples were taken with a CTD/rosette sampler during cruises M76-2 (May/June 2008), D-356 (August/September 2010) and MSM17-3 (February/March 2011) and were filtered over pre-combusted GF/F Filters onboard. Filtrates were stored frozen in acid-washed polypropylene bottles for nutrient analysis and isotope analysis. Since the main focus of all cruises was on the 23°S transect and sampling was most detailed there, we concentrate on this transect.

Particulate matter sampling was carried out by filtration onboard. Water was filtered over pre-weight and pre-combusted (450°C) GF/F Filters (Whatman). Filters were dried immediately after filtration at 40°C for 48h.

2.2. Analytical Methods

Nutrients of M76-2 samples were measured with a BRAN & LUEBBE autoanalyser in the home laboratory in Hamburg by applying standard methods. Nutrient analyses of D-356 were carried out onboard and samples of MSM17-3 were measured in the home laboratory in Bremen. Standard methods and a SKALAR autoanalyser were used for the samples of D-356

and MSM17-3. Oxygen concentrations in discrete samples were measured by using Winkler methods and were further used to calibrate oxygen data obtained from the CTD.

Particulate organic carbon (POC) was measured using a Thermo Flash EA 1112. Briefly, homogenized samples were weighed into silver capsules and inorganic carbon was removed by adding 1M HCl suprapur prior to analyses. All POC data are given in weight-%.

$\delta^{15}\text{N}$ of nitrate was determined using the “denitrifier method” (Casciotti *et al.*, 2002; Sigman *et al.*, 2001a) and are reported in ‰ using the delta-notation

$$\delta^{15}\text{N}_{\text{sample}} = ((^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{reference}} - 1) * 1000 \quad (1)$$

with air N_2 as reference for $^{15}\text{N}/^{14}\text{N}$. The values were calibrated using IAEA-N3 ($\delta^{15}\text{N}_{\text{NO}_3} = +4.7\text{‰}$) and USGS-34 ($\delta^{15}\text{N}_{\text{NO}_3} = -1.8\text{‰}$; Böhlke *et al.*, 2003). A potassium nitrate standard was measured twice within each run for quality assurance. Isotope values were corrected using the single point correction referring to IAEA-N3 for $\delta^{15}\text{N}_{\text{NO}_3}$. The standard deviation for IAEA-N3 was 0.3‰, which is within the same specification for $\delta^{15}\text{N}_{\text{NO}_3}$ for at least duplicate measurements of the samples. Since nitrite was not removed prior to isotope analyses and since *Pseudomonas aureofaciens* used for the “denitrifier method” consume both nitrate and nitrite, we have to perform a nitrite correction of $\delta^{15}\text{N}$ values in samples with significant nitrite concentrations (more than 1 μM). The correction was done using the equation:

$$\delta^{15}\text{N}_{\text{NO}_2} = ((\text{NO}_3 + \text{NO}_2) * \delta^{15}\text{N}_{\text{NO}_3+\text{NO}_2}) - (\text{NO}_3 * \delta^{15}\text{N}_{\text{NO}_3}) / \text{NO}_2 \quad (2)$$

for samples from the bottom water of station #206 and #252. Because we lack genuine nitrite $\delta^{15}\text{N}$ values for the BUS, we have to resort to literature data. In the Arabian Sea OMZ $\delta^{15}\text{N}_{\text{NO}_2}$ values are calculated from equation (2) to average -18.1‰ (Gaye, B., B. Nagel, K. Dähnke, T. Rixen, and K.-C. Emeis, Evidence of coupled denitrification and nitrification in the ODZ of the Arabian Sea from paired stable isotopes of nitrate and nitrite, resubmitted to *Global Biogeochemical Cycles.*) which is in accordance with nitrite isotope data from the Eastern Tropical North Pacific OMZ (Casciotti & McIlvin, 2007).

$\delta^{15}\text{N}_{\text{PN}}$ ratios were measured using a Thermo Delta Plus XP mass spectrometer after combustion in a Thermo Flush EA 1112. A single-point calibration was performed with IAEA-N1 standard (*Bahlmann et al.*, 2010). Within each run IAEA-N2 and IVA Sediment standards have been measured to assure measurement quality and to assess the laboratories long-term measurement performance. The standard deviation for IAEA-N1 was less than 0.2 ‰ and duplicate measurements of suspended matter samples differ less than 0.3‰ due to inhomogeneous particle coverage of filters.

3. Results

We concentrate on the data obtained for the sampling period in May/June 2008, when the shelf was partially anoxic, and use nutrient data from D-356 and MSM17-3 to demonstrate the high seasonal variability on the Namibian shelf. In May/June 2008 moderate coastal upwelling of water from 100 to 150 m water depth occurred at 23°S. On the shelf, the subsurface SACW contribution (Fig. 1b) was highest (< 85%, 50 m) on the inner shelf in the coastal upwelling region and decreased towards the outer shelf (< 65%, 200 m). A patch of low SACW fraction (<40%) was found above the bottom at the shelf break (station #202). A distinct thermocline was present within the upper 50 m above the shelf break and further offshore. We found suboxic conditions (< 20 μM) in the bottom water of the inner shelf at 23°S and even surface waters near the coast were oxygen depleted (O_2 < 80 μM ; Fig. 2a). The subsurface OMZ spread into the hemipelagic ocean where minimum O_2 concentrations ranged between 40 and 60 μM .

Nitrate concentrations (Fig. 2b) in the mixed layer were lowest near the coast and at the offshore station #201 (< 2 μM). A “nitrate plume” above the shelf break with significantly elevated concentrations by > 5 μM compared to the adjacent stations lifted the nitracline up into the thermocline. A similar pattern was observed for phosphate (Fig. 2c): elevated concentrations occurred above the shelf break, but differing from nitrate, highest

concentrations ($> 1.5 \mu\text{M}$) were found near the coast. Nitrite concentrations (Fig. 2d) above $1 \mu\text{M}$ were restricted to suboxic bottom water on the inner shelf with a maximum of $4.4 \mu\text{M}$ at 60 cm above the seafloor at station #252. Ammonium concentrations (Fig. 2e) were above $1 \mu\text{M}$ throughout the inner shelf, with maximum values in coastal surface water between 6 and $7 \mu\text{M}$, and above $8 \mu\text{M}$ at the seafloor (#206).

Suspended matter concentrations (SPM, see supplement S1) and particulate organic carbon content (POC, see supplement S2) correlated near the seafloor. Both increased in bottom water towards the inner shelf from 4.9 mg/l to $\sim 30 \text{ mg/l}$ in the bottom nepheloid layer and from 2.8% to 6.0%, respectively. SPM concentrations were high in surface water near the coast ($\sim 19 \text{ mg/l}$) at co-occurring low POC concentrations of 2.7% to 2.9%. SPM concentrations decreased in surface water in offshore direction to 4.2 mg/l at the most offshore station. POC content in surface water was high at stations #206 and #198. Further offshore, high POC contents in surface waters were observed at co-occurring low SPM concentrations and vice versa. At offshore station #201 a pronounced deep surface SPM maximum (18 mg/l) occurred at 17 m water depth at a remarkably low POC content of 1.2%. Bottom waters at the shelf break were rich in SPM (12.5 mg/l at 5 m above seafloor) and POC (4%) compared to the surrounding waters.

Bottom waters at the shelf break had excess reactive nitrogen with respect to phosphate. DIN/P ratios (see supplement S3) were calculated as $(\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+)/\text{PO}_4^{3-}$ and ranged between 21 and 16 at the outer shelf stations. DIN/P ratios decrease on the inner shelf down to 3.4 in coastal surface water.

The $\delta^{15}\text{N}_{\text{NO}_3}$ of water at the shelf edge – the source for upwelling waters over the shelf – ratios ranged from 5.7‰ to 6.7‰ (Fig. 3a). These values are slightly higher than deep ocean nitrate originating from subduction around the polar front (5.5‰; Sigman *et al.*, 2001b). By contrast, bottom water nitrate on the inner shelf OMZ was most enriched in ^{15}N ($\delta^{15}\text{N}_{\text{NO}_3}$ values between 28 and 29.6‰) at station #252. The nitrite correction (eq. 2) was performed

for these samples because nitrite content was 32% of the combined $\text{NO}_2^- + \text{NO}_3^-$ pool. High $\delta^{15}\text{N}_{\text{NO}_3}$ values ($< 13.9\text{‰}$) were also found within the mixed layer at the most distal station #201 on the 23°S transect, where nitrate concentrations dropped below $2 \mu\text{M}$. Stable nitrogen isotope ratios of particulate nitrogen ($\delta^{15}\text{N}_{\text{PN}}$) ratios ranged between 3.0‰ in the surface water at the most distal station (#201) and 11.0‰ in intermediate water (50 m) at nearshore station #252 (Fig. 3b). $\delta^{15}\text{N}_{\text{PN}}$ were low ($< 5.5\text{‰}$) in surface waters at the outer shelf and upper slope. High $\delta^{15}\text{N}_{\text{PN}}$ ($> 7\text{‰}$) characterised all suspensions in intermediate and bottom water with the exceptions of shelf break bottom water (6.2‰) and bottom water at station #206 (6.7‰).

4. Discussion

N-loss processes such as heterotrophic denitrification and anammox are known to occur in the Benguela OMZ (*Kuypers et al.*, 2005; *Tyrrell and Lucas*, 2002), but there is only little experimental evidence for N_2 fixation balancing the N-loss, and the rates observed were too low to compensate the N-loss (*Sohm et al.*, 2011). Despite a pronounced N-deficit on the inner Namibian shelf, however, we find a balanced inorganic N:P ratio ($(\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+)/\text{PO}_4^{3-}$) of ~ 16 in surface water offshore the shelf break in May/June 2008. This suggests a source of inorganic N in surface water advected from the shelf to the open ocean. Below we address the question if the BUS is a closed system in which N-losses are compensated by N-supply restoring Redfield conditions. If this is not the case and N-losses exceed N-supply, the BUS would be a sink of fixed N, thus weakening the CO_2 uptake capacity of the regional biological pump. We then investigate seasonal variability linked to water mass and oxygen dynamics, and attempt to quantify the deficit of inorganic N transferred into the adjacent hemipelagic ocean.

4.1. Processes of N-Cycling on the Namibian Shelf

Our discussion of data and transformations of reactive N follows mainly a 2D cross shelf circulation model view. This is applicable to the circulation on the shelf, but has some weaknesses for the shelf break and adjacent oceanic stations. *Mohrholz et al.* (2008) have shown that the cross shelf circulation on the shelf is controlled by upwelling dynamics with offshore Ekman transport in the mixed layer and an onshore compensation flow below the thermocline. Offshore of the shelf edge and below the surface layer the circulation is dominated by meridional currents, namely the Benguela current and the poleward undercurrent. Although the meridional flow on the shelf is prominent (*Monteiro and van der Plas, 2006; Monteiro et al., 2008*), one can interpret the conditions observed on the transect off Walvis Bay as a projection of the 3D picture onto a 2D transect. This is because the meridional extent of the upwelling area is large compared to the shelf width. Further assuming that processes are uniform along the coast, a 2D transect depiction is mainly controlled by cross shelf dynamics. This assumption is also applicable for the surface mixed layer beyond the shelf edge, because the Ekman offshore transport dominates the flow on longer time scales.

Phosphate and ammonium concentrations (Fig. 2c and 2e) increase in bottom water from the outer shelf towards the coast. The increase is caused by intense remineralisation of organic matter in sediments of the inner shelf. Ammonium and phosphate diffuse out of the sediments under low oxygen conditions (*Neumann, 2012*). The benthic ammonium supply is entrained into the cross shelf flow and wells up near the coast.

Significant amounts of nitrate in sub-thermocline water on the shelf are consumed within the OMZ on the inner shelf (Fig. 2b) as soon as decreasing oxygen concentrations reach the threshold of $\sim 5\text{-}10 \mu\text{M}$ for heterotrophic denitrification and anammox (*Cline and Kaplan, 1975; Jensen et al., 2008*). In sub-thermocline water on the outer shelf and at station #206 $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ (data not shown) change in parallel. This pattern is consistent with nitrate reduction (the first step of heterotrophic denitrification; *Granger et al., 2008*), which

was detected in the bottom nepheloid layer throughout the OMZ in low rates (*Füssel et al.*, 2011). The $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values continue to rise towards the inner shelf while the nitrate deficit (N_{def} ; see supplement S4) increases. This indicates progressive nitrate consumption by nitrate reduction. Other nitrate and nitrite consuming processes which could account for the evolving nitrate deficit in the deep water over the shelf at 23°S are anammox and dissimilative nitrate reduction to ammonium (DNRA). Anammox is possibly the dominant reason for the N-deficit on the Namibian shelf (*Kuypers et al.*, 2005) and anammox rates exceed nitrate reduction rates at station #252 (*Füssel et al.*, 2011). Nitrate ammonifiers were not evident at station #252 (*Füssel et al.*, 2011) and not responsible for decreasing nitrate concentrations in waters of the OMZ. From our data we cannot definitely state which process is the most effective in eliminating reactive N before the water upwells into the euphotic mixed layer.

As the upwelled water moves across the shelf, the $\delta^{15}\text{N}_{\text{NO}_3}$ values in surface waters decrease from the stations closest the coast to roughly the shelf break. Near the coast, particulate matter that is apparently produced in the surface layer by phytoplankton has higher $\delta^{15}\text{N}_{\text{PN}}$ values than $\delta^{15}\text{N}$ of the ambient nitrate. This suggests that a relatively ^{15}N -enriched N-source is assimilated by phytoplankton, whereas a relatively ^{15}N -depleted source adds to the dissolved nitrate pool. For both, the branching of high ambient ammonium concentrations into either biomass (ammonium assimilation) or nitrate (nitrification) is a good candidate (*Wankel et al.*, 2007).

High ammonium concentrations (Fig. 2e) in coastal surface water most likely originate from two sources. The first is benthic remineralisation of organic matter, because both ammonium and phosphate concentrations are elevated in freshly upwelled waters near the coast. In addition to the benthic source, an ammonium source from ammonification of particulate nitrogen in the water column is indicated by a vertical decrease of SPM concentrations from the mixed layer (~ 10 mg/l) to 50 m water depth (~ 5 mg/l; see

supplement S1). Additionally, POC content decreases in the upper 50 m of station #252 (see supplement S2). At the same time, the average $\delta^{15}\text{N}_{\text{PN}}$ ratio of the sinking material increases from 7.8‰ in the mixed layer to 9.5‰ at 50 m water depth (Fig. 3b), indicating a preferential release of ^{15}N depleted ammonium during ammonification. The ammonium mixture produced is partly assimilated and causes the mismatch between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{15}\text{N}_{\text{PN}}$ seen at station #252. Here, particles in the surface water have higher $\delta^{15}\text{N}$ ratios than ambient nitrate ($\delta^{15}\text{N}_{\text{PN}} = 8.3\text{‰}$ versus $\delta^{15}\text{N}_{\text{NO}_3} = 7.5\text{‰}$ and 7.8‰), whereas biomass from assimilation of that nitrate should have a $\delta^{15}\text{N}_{\text{PN}}$ that is 5‰ more negative than ambient $\delta^{15}\text{N}_{\text{NO}_3}$ (Granger *et al.*, 2004). This implies that assimilation of isotopically enriched ammonium – associated with a fractionation factor of 6 to 27‰ (Hoch *et al.*, 1992; Wankel *et al.*, 2007; Waser *et al.*, 1998) – raises the $\delta^{15}\text{N}_{\text{PN}}$.

Additions from nitrification of ammonium on the other hand decrease the $\delta^{15}\text{N}$ of the nitrate pool, because marine nitrification discriminates strongly against ^{15}N ($^{15}\epsilon$ between 14 and 19‰: Casciotti *et al.*, 2003). The branching of ammonium fluxes to either nitrification or ammonium assimilation, associated with different fractionation factors, thus leads to nitrate that is more ^{15}N -depleted than the suspended matter produced by ammonium assimilation of the residual (Wankel *et al.*, 2007).

$\delta^{15}\text{N}_{\text{PN}}$ ratios (Fig. 3b) decrease in offshore direction from 7.2‰ at station #206 to values between 5.5‰ and 3.8‰ at the shelf break (station #198) coincident with decreasing ammonium concentrations (Fig. 2e). Nitrate rather than ammonium is the predominant N-source for primary production offshore of station #206 and low $\delta^{15}\text{N}_{\text{PN}}$ ratios mimic low $\delta^{15}\text{N}_{\text{NO}_3}$ ratios of newly produced nitrate (see also Granger *et al.*, 2011). The production of nitrate in the oxygen gradient of OMZs is a typical feature also known from the Eastern Tropical North Pacific (Ward and Zafiriou, 1988), the Eastern Tropical South Pacific (Lipschultz *et al.*, 1990; Ward *et al.*, 1989) and from the Arabian Sea (Gaye, B., B. Nagel, K. Dähnke, T. Rixen, and K.-C. Emeis, Evidence of coupled denitrification and nitrification in

the ODZ of the Arabian Sea from paired stable isotopes of nitrate and nitrite, resubmitted to *Global Biogeochemical Cycles*.). As surface water moves offshore with the Ekman transport, decreasing primary production at decreasing nitrate concentrations causes decreasing SPM concentrations (see supplement S1). A contribution of N₂ fixation is seen in the oceanic end member (station #201), where nitrate is almost completely consumed (Fig. 2b), but SPM concentration is high and has a low $\delta^{15}\text{N}_{\text{PN}}$ value of 3.0‰ (Fig. 3b). Nitrate in surface water of station #201 is almost consumed (0.14 μM at 11 m water depth) and $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{15}\text{N}_{\text{PN}}$ at 17 m water depth are 13.9‰ and 3.0‰, respectively. Beyond the shelf break, *Trichodesmium* occasionally occurs and one to ten *Trichodesmium* colonies per m³ were encountered in plankton nets in February 2011 in the northern BUS (H. Auel, pers. comm., 2011).

4.2. Seasonal Variability of Water Masses and Nutrient Composition on the Namibian Shelf

Nutrient concentrations and nutrient ratios in the northern BUS are highly variable due to the seesaw of two distinct water masses caused by physical processes. Nutrient-depleted and oxygenated ESACW mixes on the shelf with nutrient-rich and oxygen-depleted SACW between the Lüderitz upwelling cell (26°S) and the Angola-Benguela-Frontal-Zone at 17°S (*Mohrholz et al.*, 2008). Since ESACW and SACW have completely different oxygen and nutrient concentrations (as well as differing nitrate/phosphate ratios), prevailing upwelling conditions control oxygenation and nutrient conditions over the shelf. This is illustrated in Fig. 4 that depicts two different situations on the 23° transect. In August/September 2010 (cruise D356), DIN/P ratios on the shelf ranged between 13.6 and 22.8 (Fig. 4b) when intense upwelling occurred in the northern BUS. In this season, a weak poleward undercurrent and strong cross-shelf compensation currents transported waters with high ESACW proportions onto the shelf (*Mohrholz et al.*, 2008). This mixture had high inorganic N/P ratios. *Poole and Tomczak* (1999) propose low N:P ratios of ~ 9 for the ESACW in their water mass definitions

of the Atlantic Ocean. But they define the core depth of ESACW between 350 and 600 m, which is below our sampling depths. Because oxygen concentrations on the shelf are $> 30 \mu\text{M}$ (Fig. 4a) denitrification and release of ammonium and phosphate from sediments were inhibited so that the high inorganic N:P ratios of upwelling source waters reached the surface. Bottom water DIN/P ratios increased from the outer to the inner shelf, where sulphur bacteria abundantly inhabiting the benthic boundary layer take up phosphate during oxic periods to store it within the cells as polyphosphate (*Brock and Schulz-Vogt, 2011*). Consequently, arriving high DIN:P ratios further increase and are transported into surface water by upwelling and Ekman transport. By contrast a weak cross-shelf compensation current and strong poleward undercurrent activity controlled the water mass composition in the northern BUS during cruise MSM17-3 in February/March 2011. ESACW had retracted to the South and the dominance of oxygen-poor SACW (with DIN:P ratios around 16:1) promoted the development of suboxic conditions on the shelf (Fig. 4c). This stimulated heterotrophic denitrification and anammox and created an N-deficit by either denitrification or phosphate release from sediments leading to lowered DIN/P ratios (Fig. 4d). Phosphate can be released from the seafloor under anoxic conditions from internal sources from the inner-shelf organic-rich diatomaceous mud (*Bailey, 1991*). Under changing oxic/anoxic conditions, phosphate-sequestering bacteria play a role in generating recent concretionary phosphorites on the landward flank of the diatomaceous mudbelt and in releasing mediate phosphorous from sediments (*Nathan et al., 1993*). This source likely contains a contribution from large sulphur bacteria inhabiting the diatomaceous mud on the inner shelf: Under anoxic conditions and sulphide exposure, intracellular polyphosphate stored under oxic conditions is decomposed and released to pore water (*Brock and Schulz-Vogt, 2011*). Because sediment pore water and ambient bottom water are in isotopic disequilibrium regarding oxygen isotopes of phosphate ($\delta^{18}\text{O}_\text{P}$), the imprint of regenerated phosphate is evident under anoxic conditions (*Goldhammer et al., 2011*) and further decreases the DIN:P ratio in the water column on the

inner shelf. Phosphate concentrations in pore water of the diatomaceous mud reach up to < 500 μM in 10 to 20 cm below seafloor (*Goldhammer et al.*, 2011) and increase to > 1000 μM during prolonged suboxic periods over the central Namibian shelf (*Bartholomae and van der Plas*, 2007; *van der Plas et al.*, 2007).

4.3. Quantification of the Nitrate Deficit and Denitrification

N loss or P gain both affect the local deficit of inorganic N (N_{def}) in the system. *Devol et al.*, 2006 defined N_{def} as the difference between the preformed N:P conditions (N^{pref}) and the measured inorganic N-pool (NO_3^- , NO_2^- and NH_4^+):

$$N_{\text{def}} = N^{\text{pref}} - N^{\text{meas}} \quad (3),$$

To estimate the local N^{pref} we plotted DIN ($[\text{NO}_3^-] + [\text{NO}_2^-] + [\text{NH}_4^+]$) versus $[\text{PO}_4^{3-}]$ from water samples that were not affected by denitrification and phosphate release ($\text{O}_2 > 65 \mu\text{M}$) nor by assimilation processes (50 – 500 m water depth). The slope of the regression in Fig. 5 is 18.22 and the intercept on the PO_4^{3-} -axis is 0.01, so that:

$$N^{\text{pref}} = 18.22 * (\text{PO}_4^{3-} - 0.01) \quad (4).$$

Offshore of the shelf break N_{def} (see supplement S4) is negative between 100 and 650 m water depth and mirrors a slight N excess over phosphate. N_{def} increases towards the mixed layer and laterally towards the shelf, to maximum values in coastal surface water at station #192 (27.2 μM) and within the bottom nepheloid layer at #252 (28.6 μM).

During the expedition M76-2 in May/June 2008, upwelling source water at the shelf break had DIN:P ratios ~20:1 (see supplement S3) that correspond to a N_{def} of ~ -2 μM . This is in accordance with nutrient data for SACW of *van der Plas et al.* (2007). During onshore advection with the cross-shelf compensation current, O_2 concentrations decrease from 70 μM to 0 μM in inner shelf bottom water. Assuming a threshold for heterotrophic denitrification of ~5 μM and of ~10 μM for anammox (*Cline and Kaplan*, 1975; *Jensen et al.*, 2008) both processes are feasible on the inner shelf below 70 m water depth. There, heterotrophic

denitrification, anammox, and phosphate release decrease the inorganic N:P ratio to 7.1 (see supplement S3) and cause a N_{def} of 28.6 μM in the bottom water of station #252 (see supplement S4). Integrated over the water column at 23°S and at O_2 concentrations below 10 μM a cumulative N_{def} of 3 M N per m^2 is generated by all three processes. Taking into account that the OMZ is roughly situated above the diatomaceous mud belt, which has an extension of 18 000 km^2 (Emeis *et al.*, 2004), we calculate an N_{def} amounting 0.75 Tg N for that area in May/June 2008. Water on the shelf moves eastward at a rate of 550 km per annum (Mohrholz *et al.*, 2008), so that water in the OMZ is completely exchanged 4.5 times a year. Assuming that the lower 30 m of the water column are suboxic for 9 months per year (Bartholomae and van der Plas, 2007; Joubert, 2006) our estimate for the inorganic N deficit relative to phosphate amounts 2.5 Tg N per annum for the water column above the diatomaceous mud belt. This is in the same range of calculations by Kuypers *et al.* (2005) who attributed a loss of fixed N of 1.4 ± 1 Tg on an area of 100,000 km^2 to anammox.

To calculate the contribution of heterotrophic denitrification to N_{def} , we use the stable nitrate isotope data set. Heterotrophic denitrification is associated with a fractionation factor of 25‰ for stable N and O isotopes of nitrate (Granger *et al.*, 2004; Sigman *et al.*, 2009a; Voss *et al.*, 2001), leaving the residual nitrate isotopically enriched. In an upwelling system nitrate is supplied constantly to the OMZ so that heterotrophic denitrification follows the “open system model” rather than the “Rayleigh closed system” model (Sigman *et al.*, 2009b).

Using the equation:

$$\delta^{15}\text{N}_{\text{reactant}} = \delta^{15}\text{N}_{\text{initial}} + \varepsilon (1-f) \quad (5)$$

for nitrate N isotopes, we calculated the contribution of denitrification to the N_{def} . Source nitrate at the shelf break had a $\delta^{15}\text{N}_{\text{NO}_3}$ of 6.1‰, and f was calculated according to (Mariotti *et al.*, 1981):

$$f = (\text{NO}_3^-) / (\text{NO}_3^- + N_{\text{def}}) \quad (6).$$

The observed depth-integrated and nitrite-corrected average $\delta^{15}\text{N}_{\text{NO}_3}$ of 18.1‰ within the OMZ requires that ~ 48% of the nitrate arriving at the core of the OMZ have to be eliminated by heterotrophic denitrification. Looking at the nitrate concentrations (Fig. 2b), we find that this isotope-based calculation underestimates the nitrate elimination due to heterotrophic denitrification: water enters the OMZ containing ~18 μM nitrate and lowest nitrate concentrations in the core of the OMZ are 7.0 μM . Annual heterotrophic water column denitrification above the diatomaceous mud belt amounts 0.25 Tg N assuming an average suboxic depth interval of 30 m ($\text{O}_2 < 10 \mu\text{M}$) for nine months per year and a mean residence time of water of 80 days. According to this calculation only 10% of the total N_{def} were due to heterotrophic denitrification during M76-2 in May/June 2008. Other candidates causing the N_{def} are phosphate release from sediments and anammox that is thought to eliminate the majority of reactive N within the northern BUS (*Füssel et al.*, 2011; *Kuypers et al.*, 2005).

4.4. Restoration of Surface Water N:P Ratio

The N-deficit in surface water is advected offshore from the coast by the Ekman transport and decreases successively from 27.2 μM to 0.2 μM at station #201 (see supplement S4). Possible N-sources for filling the N-deficit in the Benguela region are: (1) atmospheric or land input, (2) N_2 fixation, (3) assimilation of nutrients with N:P ratio <16, (4) nitrification or (5) shelf break upwelling or mixing.

Atmospheric dry deposition in the Atlantic Ocean between 30°S and 10°S has N:P ratios much above 16 and therefore is a potential N-source. The atmospheric nitrate input in the open Atlantic Ocean between 25 and 17°S is relatively low ($< 20 \mu\text{M m}^{-2} \text{d}^{-1}$; *Baker et al.*, 2003). Many arid environments have highly alkaline soils where ammonia is emitted to the atmosphere (*McCalley and Sparks*, 2008). Dry deposition of ammonium is unlikely since NH_4^+ and organic N are associated with fine mode aerosols ($< 1\mu\text{m}$; *Baker et al.*, 2003) but fine sands dominate the sediments immediately along the Namibian coast where elevated

ammonium concentrations occur. Ammonium concentrations in coastal surface water range between $< 7 \mu\text{M}$ in May/June 2008 (Fig. 2e) and $0.7 \mu\text{M}$ in February/March 2011 (data not shown) during times of weak trade wind and upwelling activity. We attribute changing ammonium concentrations in surface water to remineralisation processes at the sediment-water interface and the upwelling intensity rather than to atmospheric inputs.

N_2 fixation rates in the BUS or the adjacent South Atlantic Gyre are generally low. Highest N_2 fixation rates ($< 8 \text{ nmol N l}^{-1} \text{ d}^{-1}$) were found within or near the BUS where high nitrate concentrations did not exclude N_2 fixation (Sohm *et al.*, 2011). This agrees with our data from May/June 2008 where patches of negative $\delta^{15}\text{N}_{\text{PN}}$ (-1.8‰) occurred on the Namibian shelf at 20°S (data not shown). We find no isotopic indication of N_2 fixation in surface water above the shelf at 23°S in either $\delta^{15}\text{N}$ of nitrate or in $\delta^{15}\text{N}_{\text{PN}}$. Over the continental slope at the most offshore station #201, however, we find balanced N:P ratios where nitrate is almost completely consumed in the mixed layer (Fig. 2b) and organic matter is isotopically enriched in ^{15}N (13.9‰ ; Fig. 3a). Suspended matter concentrations in the deep mixed layer (17 m water depth) are high and comparable to those in surface water near the coast (18 mg/l ; see supplement S1). This indicates stimulated phytoplankton activity in surface water. Intense remineralisation reduces POC content (see supplement S2) from surface water (4.3%) to the deep mixed layer (1.2%). Summarizing, we find nutrient-depleted surface water at station #201 (Fig. 2), a deep-surface SPM maximum, and low $\delta^{15}\text{N}_{\text{PN}}$ values of 3.0‰ at co-occurring high $\delta^{15}\text{N}_{\text{NO}_3}$ values of 13.9‰ . This pattern is consistent with N_2 fixation. If it is indeed present, this is likely a small contribution, because the N_{def} in surface water (0-20 m) drops by only 0.05 M/m^2 between stations #202 and #201. The corresponding N-supply by fixation to the BUS at 23°S is 6 times less than the N-loss estimated from nitrate isotopes.

Another mechanism for N:P ratio restoration is the consumption of nutrients with N:P < 16 under nutrient-replete conditions (Geider and La Roche, 2002; Weber and Deutsch,

2010). In our study area, diatoms dominate phytoplankton on the inner shelf and nutrient-replete conditions favour nutrient assimilation with N:P <16..

Even if organic matter N:P ratios are below Redfield, remineralisation releases nutrients with proportional N:P of ~16 and thus helps to increase the initially low inorganic N:P ratio at the coast. Nitrification of ammonium from benthic and water-column sources plays an important role in the surface water of the inner shelf (see discussion above). Although the supply of preformed nitrate in upwelling systems is large, evidence for quantitatively significant nitrification within OMZs is accumulating (*Füssel et al.*, 2011; *Lam et al.*, 2011; *Gaye, B., B. Nagel, K. Dähnke, T. Rixen, and K.-C. Emeis*, Evidence of coupled denitrification and nitrification in the ODZ of the Arabian Sea from paired stable isotopes of nitrate and nitrite, resubmitted to *Global Biogeochemical Cycles.*), and recycling of ammonium from particles and sediments contributes to the increase of N:P ratios offshore.

Finally, shelf break upwelling and turbulent mixing across the thermocline are episodic processes that dilute and mask the N-deficit in modified upwelling water because inorganic N:P ratios in subsurface waters at the shelf break are above 16. Shelf break upwelling is reported to be active during high wind speed periods (*Barange and Pillar*, 1992; *Pichevin et al.*, 2005) and is caused by negative wind stress curl that roughly coincides with the shelf break. Using an analytical model *Fennel and Lass* (2007) and *Fennel et al.* (2012) have shown that the structure of the wind field off Namibia forces curl-driven upwelling on the entire shelf. This process supplies nutrients from the subsurface layers into the euphotic zone. Additionally, the breaking of internal waves and tides at the shelf edge increases the turbulent diapycnal mixing and also contributes to the entrainment of nutrients into the upper layer (*Mohrholz and Heene*, 2011). Elevated SPM concentrations (supplement S1) and high $\delta^{15}\text{N}_{\text{PN}}$ ratios (Fig. 3c) in warm stratified surface water at the 23°S transect image a recent shelf break upwelling phase and a late stage plankton bloom due to an uplift of the nitracline (Fig. 2b) and $\delta^{15}\text{N}_{\text{NO}_3}$ isolines (Fig. 3a). Shelf break mixing thus is an episodic phenomenon,

but elevated biomass concentrations in surface water above the shelf break have been encountered on other cruises (N. Wasmund, pers. comm., 2011). The water mass analysis (Fig. 1b) illustrates a dominating ESACW-portion at station #201. As shown above, ESACW imports nutrients with elevated inorganic N/P ratios and thus contributes to balance the N_{def} .

The N-deficit generated in the OMZ cannot always be balanced as suggested by inorganic N/P ratios in surface water encountered during expeditions D356 and MSM17-3 (Fig. 4). During late austral summer (MSM17-3; February/March 2011), when the OMZ spreads over the entire shelf (Fig. 4c), DIN/P ratios in surface water were constantly < 7.5 at nitrate concentrations offshore the inner shelf break $< 1.5 \mu\text{M}$. Even surface water temperatures around 20.5°C apparently did not stimulate N_2 fixation anywhere on the transect. DIN/P ratios in surface water from September 2010 (expedition D356; Fig. 4b) drop from ~ 22 to ~ 6 in offshore direction at surface water temperatures of 16.6°C at the most offshore station. This implies that the modified upwelling water still hosted the N-deficit generated during times when the water parcel was situated in the OMZ weeks to months before.

5. Summary and Conclusions

The northern BUS is a highly variable system, because it depends on the seasonally changing water-mass mixture over the shelf. This creates conditions leading to rapidly changing nutrient supply to surface waters over the shelf and in the adjacent hemipelagic ocean, to highly variable nutrient ratios in the modified upwelling waters, and to seasonally changing oxygenation on the shelf. Owing to the seesaw of two distinct water masses, N-cycling processes change or shift spatially. In May/June 2008 denitrification occurred in the moderately extended OMZ. Ammonium produced during benthic remineralisation and during ammonification of organic matter in the water column accumulates in the OMZ and welled up

near the coast. The branching of ammonium to either ammonium assimilation or nitrification leads to ^{15}N -enriched particulate matter and replenishes the nitrate pool. Nitrate assimilation dominated primary production above the outer shelf.

In the BUS we calculate that the total N-deficit of 2.5 Tg N per year is created in the oxygen deficient water column overlying the shelf. Using the isotope-based “open system model” from *Sigman et al. (2009b)*, we calculate that only 0.05 Tg N of this deficit is generated by denitrification of preformed nitrate. The global annual N-loss due to water-column denitrification matches 150 Tg (*Codispoti et al., 2001*). About one half of reactive N is removed in the three major OMZs located in the Arabian Sea (about 50 Tg N a⁻¹; *Devol et al., 2006*), in the Eastern Tropical North Pacific and in the Eastern Tropical South Pacific (25 to 50 Tg a⁻¹ in each region; *Codispoti et al., 2001; Devol, 2008*). Compared to these large-volume OMZs the Benguela OMZ is only a minor sink of oceanic reactive N.

The P*-concept of *Deutsch et al. (2007)* links oceanic N₂ fixation with zones of reactive N removal in time and space. Possibly due to the intense seasonal variability, the BUS N₂ fixation rate is low and differs from other upwelling areas (e.g., *Fernandez et al., 2011; Deutsch et al., 2007*), although conditions of modified upwelling water advected into the adjacent hemipelagic ocean are conducive for N₂ fixation. Our isotope-based estimate and mass-balanced calculation illustrate that denitrification in the OMZ exceeds N₂ fixation offshore by a factor of 6. In spite of this, the N-deficit generated in the OMZ was filled in offshore surface waters in May/June 2008 most probably due to physical mixing of sub-thermocline water with surface water at the shelf-break that diluted the N deficit. The BUS is a dynamic system where N-loss and N-supply are temporally and spatially decoupled. The associated variability in nutrient ratios exported to the hemipelagic ocean may be the reason why diazotrophic N₂ fixation is a sporadic and subordinate N-source in the system

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Figures

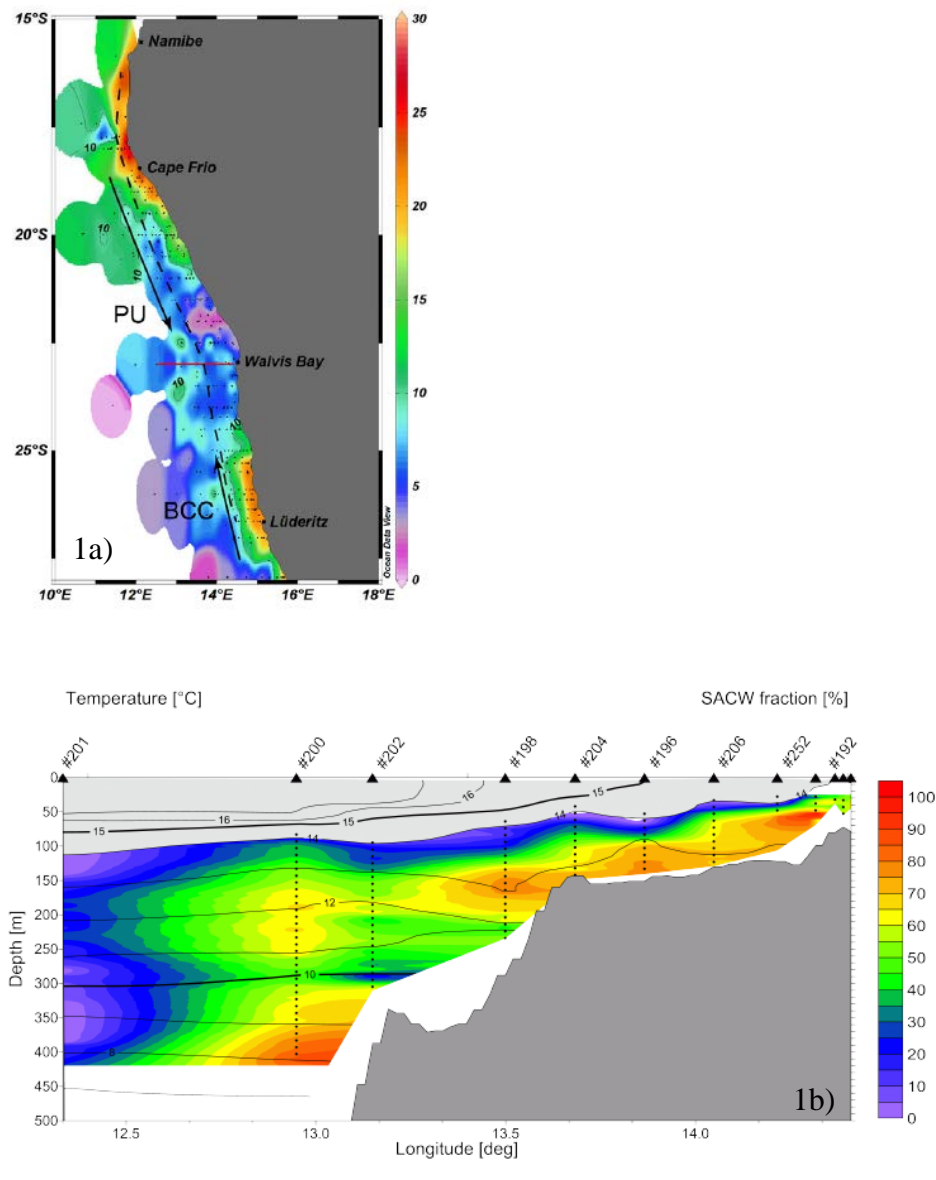
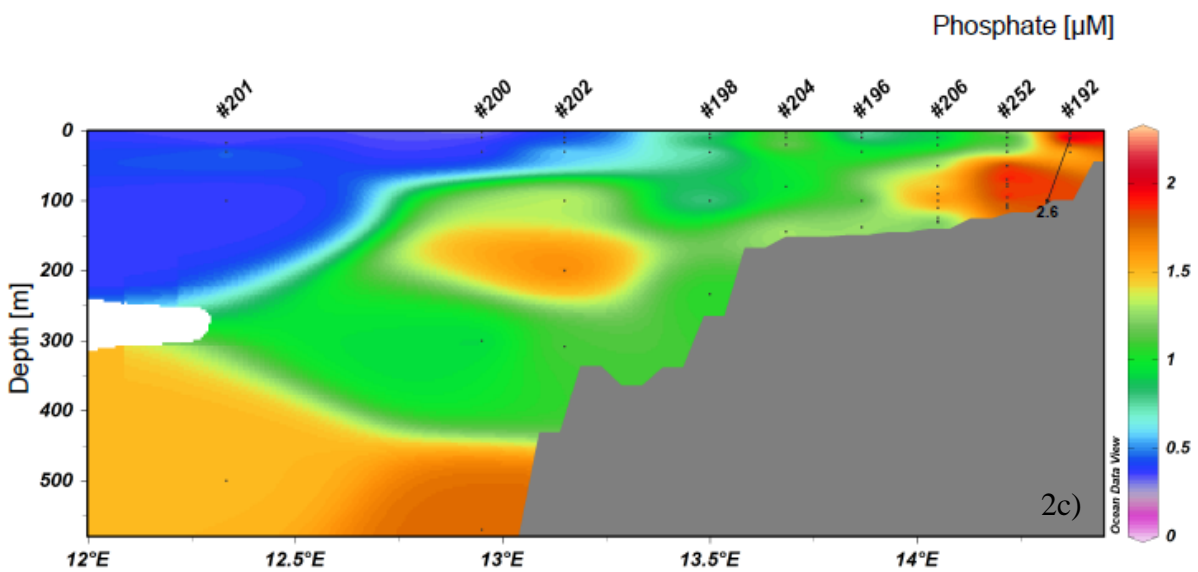
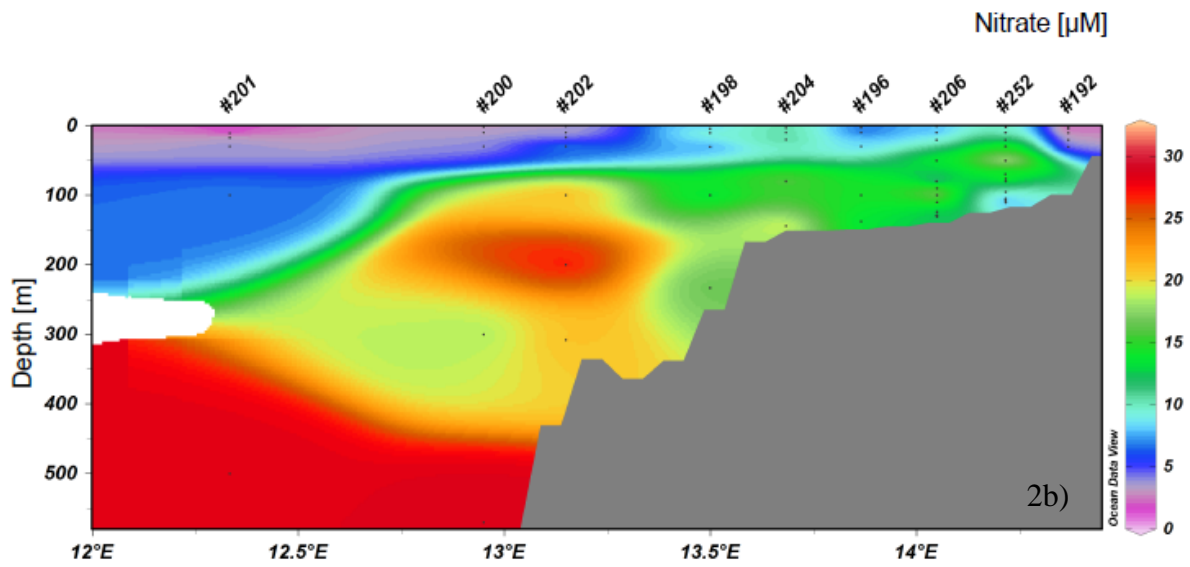
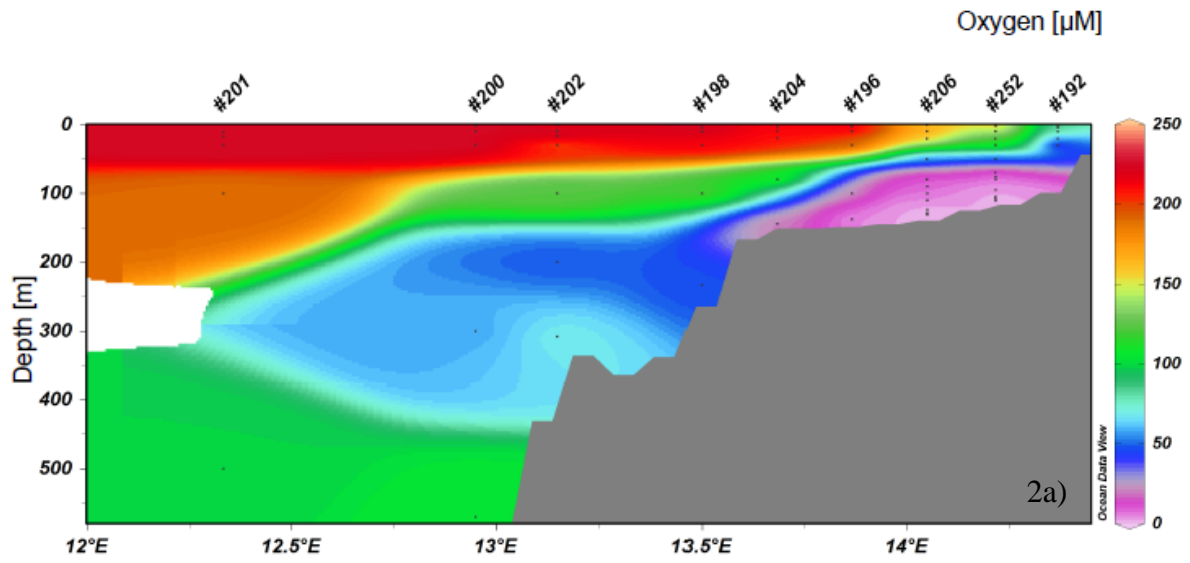


Fig. 1: a) Map of the study area showing nitrate concentrations in surface water (0-5 m) from data available in the Namibian collection of bottle data. The red line marks the 23°S-transect where detailed sampling was carried out during the three cruises in 2008, 2010 and 2011. The dashed line indicates the shelf break and arrows mark the Benguela Coastal Current (BCC) and the Poleward Undercurrent (PU) that supply ESACW (Eastern South Atlantic Central Water) and SACW (South Atlantic Central Water), respectively. b) Water mass distribution (% SACW, colours) and temperature (contours) on the transect at 23°S during expedition M76-2 (May-June 2008)



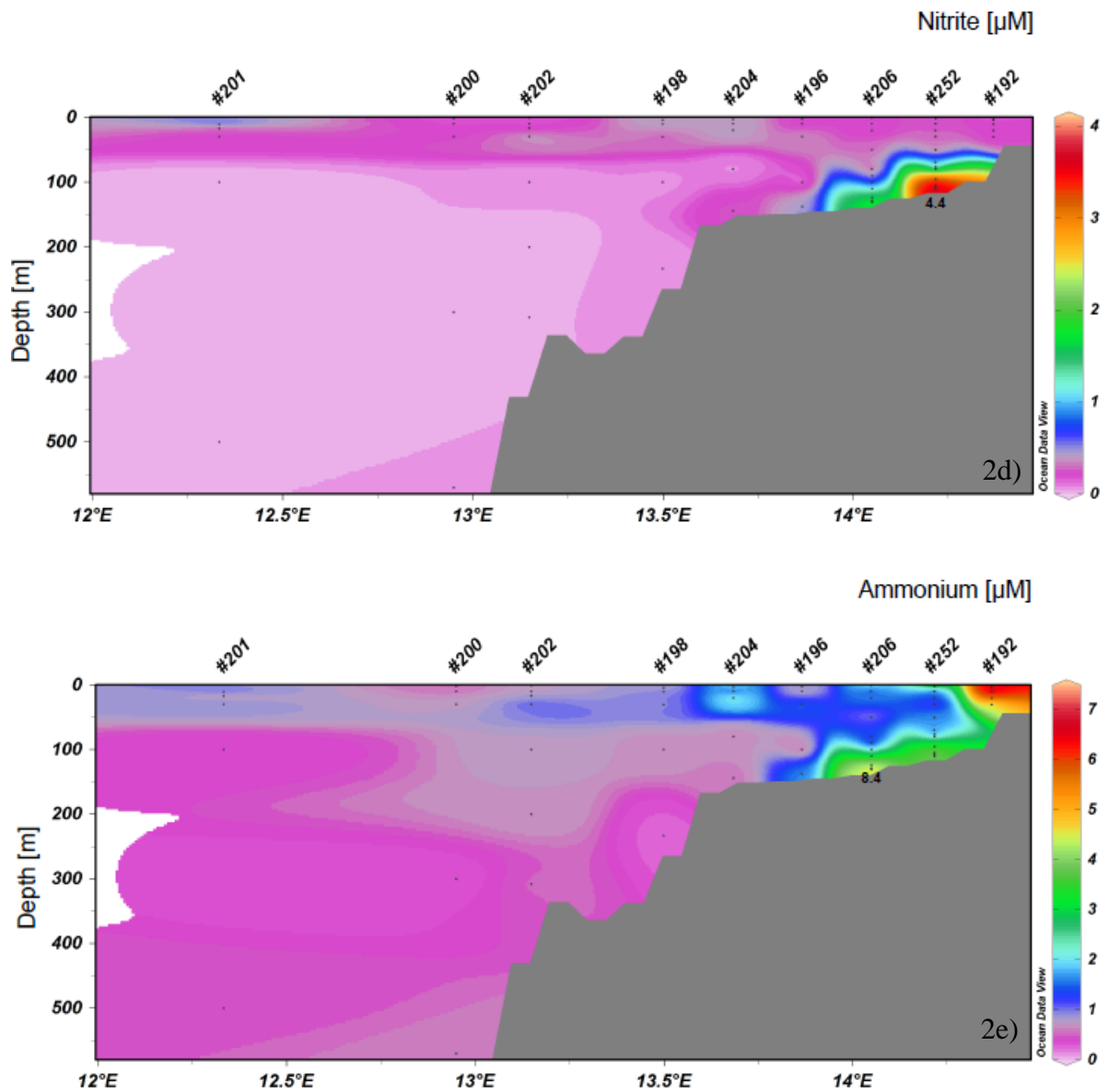


Fig. 2: Interpolated concentrations during M76-2 (May-June 2008) on the 23°S transect normal to the coast. a) oxygen; b) nitrate; c) phosphate; d) nitrite and e) ammonium. Numbers mark individual concentrations that deviate from the colour code due to steep concentration gradients.

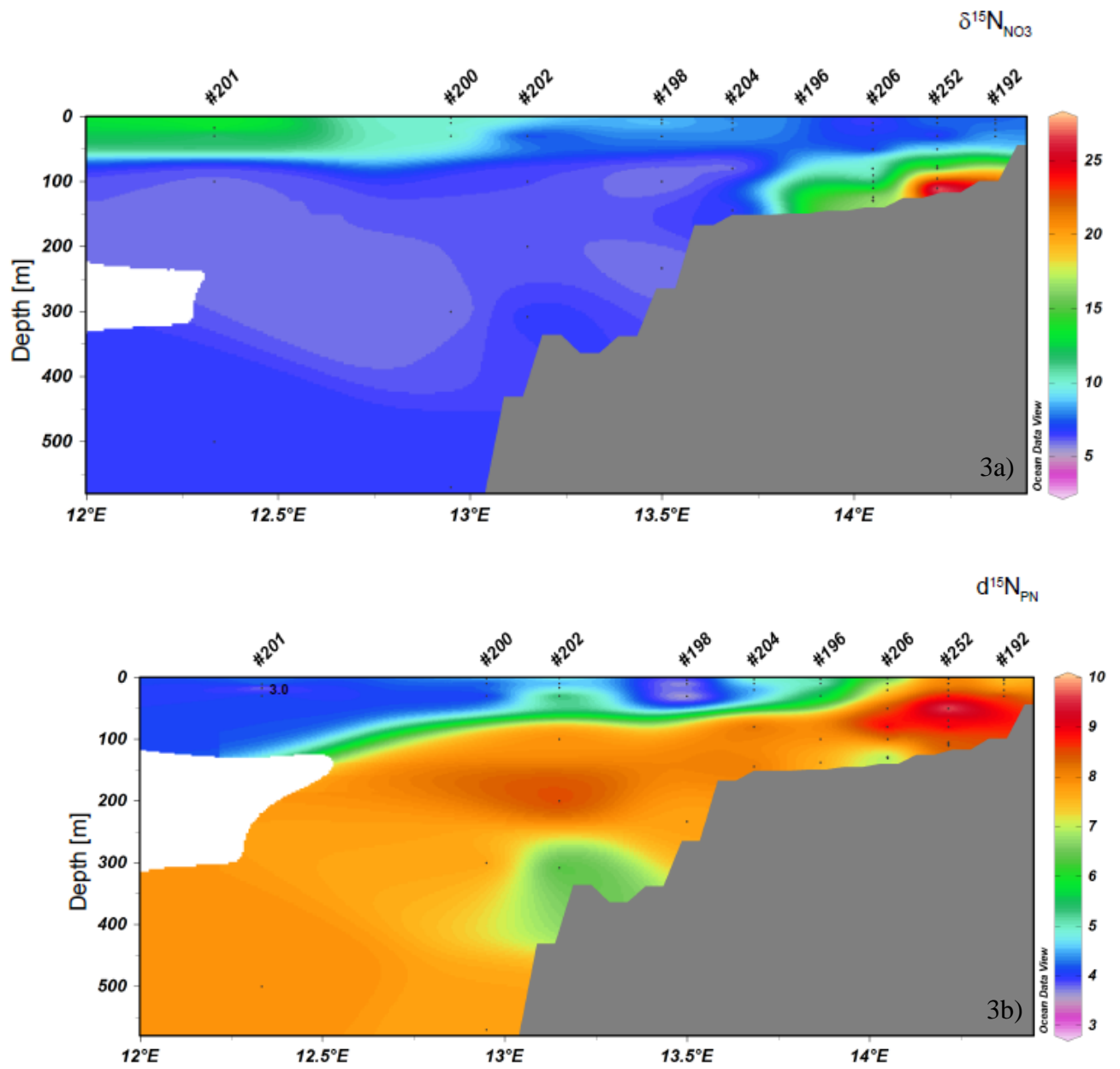
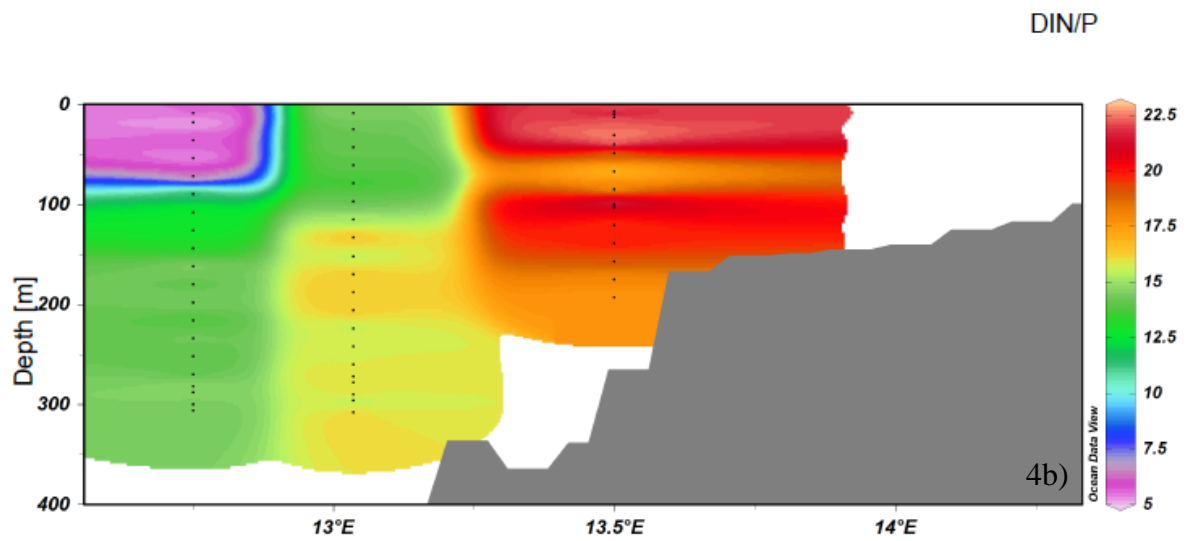
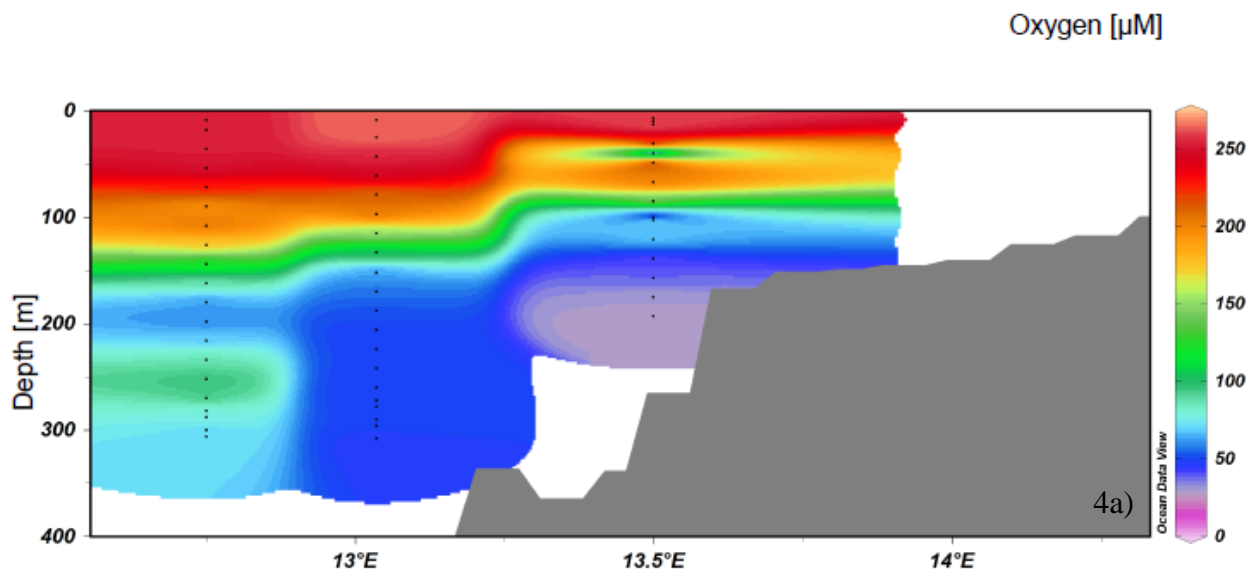


Fig. 3: Interpolated isotopic compositions in ‰ during M 76-2. a) $\delta^{15}\text{N}_{\text{NO}_3}$; b) $\delta^{15}\text{N}_{\text{PN}}$



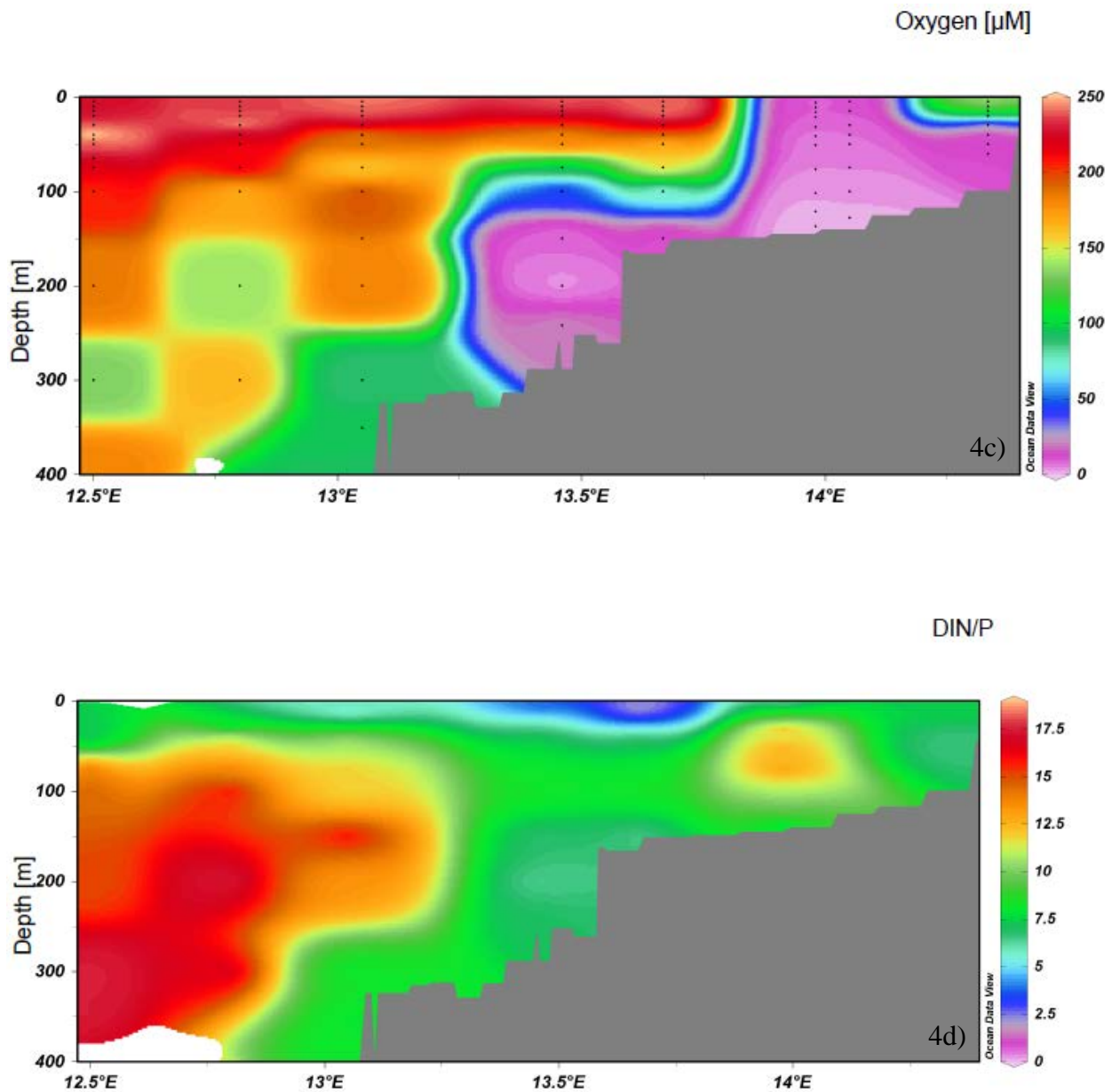


Fig. 4: a) O_2 concentrations on the 23°S transect show enhanced oxygenation during August/September 2010 that was caused by strong upwelling and cross-shelf currents transporting ESACW with elevated molar DIN/P ratios (Fig. 4b) onto the shelf. In February/March 2011 the OMZ (Fig. 4c) covered almost the entire shelf and molar DIN/P ratios (Fig. 4d) decreased from 17.5 above the upper slope to 5 in coastal surface water.

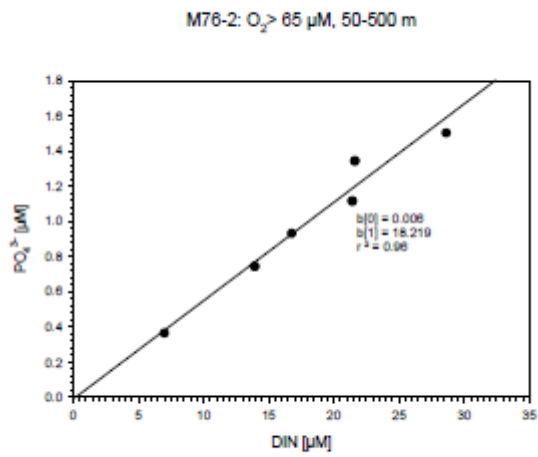


Fig. 5: Linear correlation between dissolved inorganic nitrogen ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$) and phosphate of sampling sites from M76-2 on the 23 °S-transect between 50 and 500 m water depth and $\text{O}_2 > 65 \mu\text{M}$.

Supplement

Samples were taken during expedition M76-2 in May/June 2008.

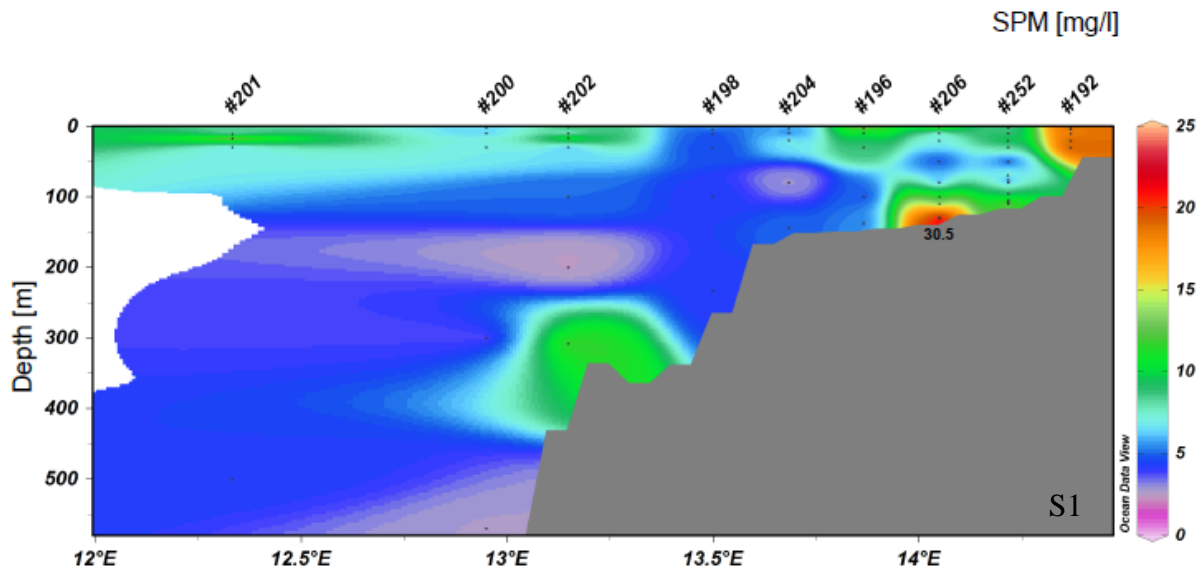


Fig. S1: Interpolated suspended matter concentrations (SPM) shown in mg/l.

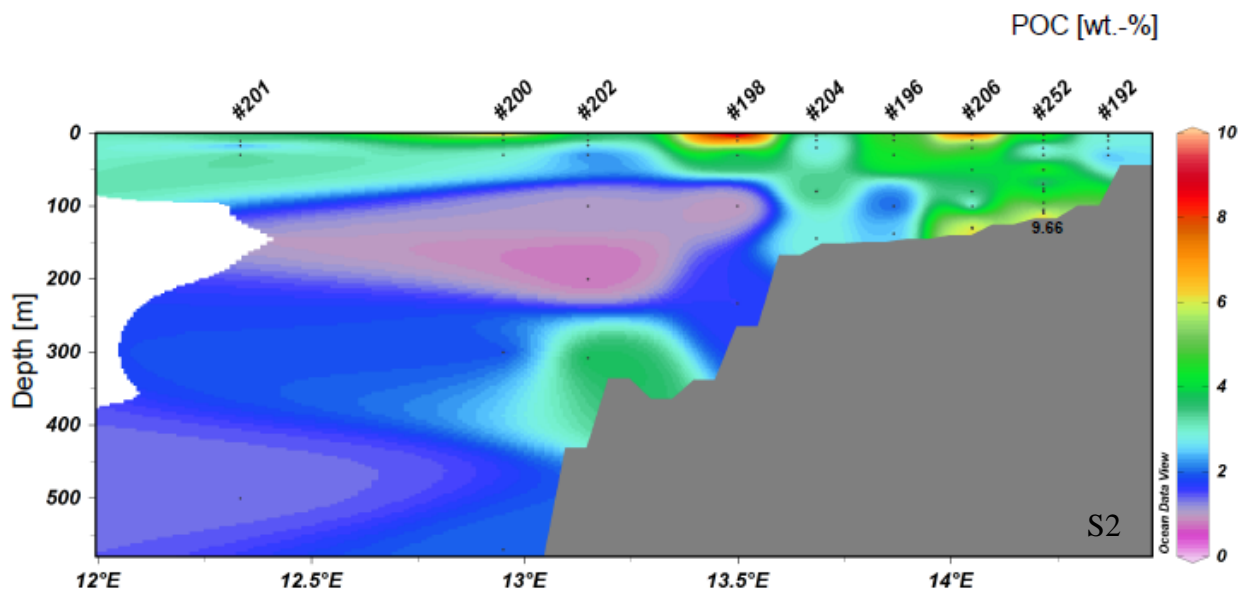


Fig. S2: Interpolated particulate organic matter content (POC) shown in weight-%.

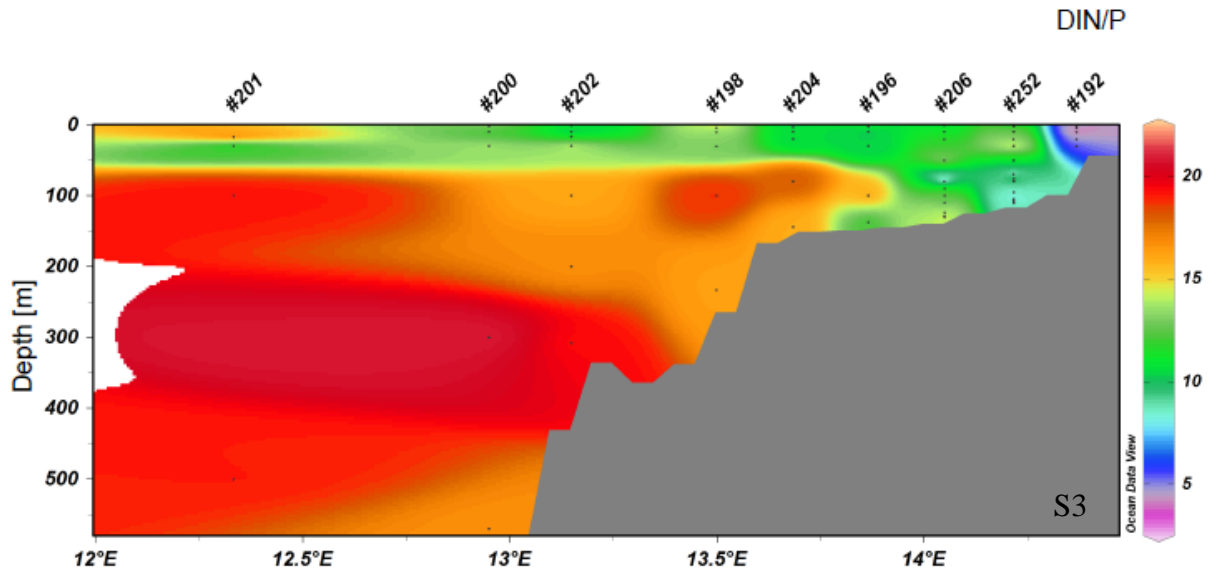


Fig. S3: Interpolated molar DIN/P ratio calculated as $(\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+) / \text{PO}_4^{3-}$.

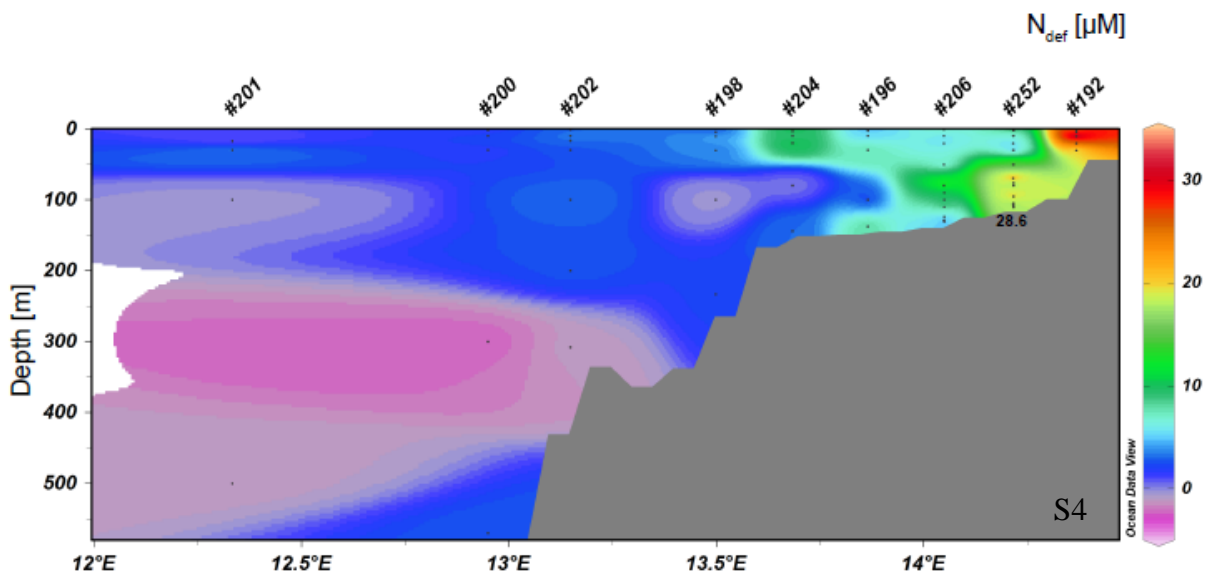


Fig. S4: Interpolated N-deficit was defined as the difference between the preformed inorganic N/P conditions and the measured inorganic N-pool (NO_3^- , NO_2^- , and NH_4^+).