

**An eddy-stimulated  
hotspot for fixed  
nitrogen-loss**

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# An eddy-stimulated hotspot for fixed nitrogen-loss from the Peru oxygen minimum zone

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Received: 30 May 2012 – Accepted: 5 June 2012 – Published: 2 July 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

Fixed nitrogen (N) loss to biogenic  $N_2$  in intense oceanic  $O_2$  minimum zones (OMZ) accounts for a large fraction of the global N sink and is an essential control on the ocean's N budget. However, major uncertainties exist regarding microbial pathways as well as net impact on the magnitude of N-loss and the ocean's overall N budget. Here we report the discovery of a N-loss hotspot in the Peru OMZ associated with a coastally trapped mesoscale eddy that is marked by an extreme N deficit matched by biogenic  $N_2$  production, high  $NO_2^-$  levels, and the highest isotope enrichments observed so far in OMZ's for the residual  $NO_3^-$ . High sea surface chlorophyll (SSC) in seaward flowing streamers provides evidence for offshore eddy transport of highly productive, inshore water. Resulting pulses in the downward flux of particles likely stimulated heterotrophic dissimilatory  $NO_3^-$  reduction and subsequent production of biogenic  $N_2$ . The associated temporal/spatial heterogeneity of N-loss, mediated by a local succession of microbial processes, may explain inconsistencies observed among prior studies. Similar transient enhancements of N-loss likely occur within all other major OMZ's exerting a major influence on global ocean N and N isotope budgets.

## 1 Introduction

Extensive oxygen minimum zones (OMZ's, also known as  $O_2$  deficient zones – ODZ's) are found at intermediate depths in the Arabian Sea, off Western Mexico, and off Peru and Northern Chile. They arise regionally from poor ventilation of source waters and high downward fluxes of organic matter (OM) supporting subsurface respiration. In these regions, the lack of  $O_2$  requires microbial heterotrophy to rely on oxidants other than  $O_2$  and include those that result in the biogenic production of  $N_2$  gas from chemically combined forms of N. These processes also occur in anoxic marine sediments and in sum account for almost the entire N-loss from the oceans (Codispoti, 2007; Gruber, 2008) and thereby are essential terms in the ocean's N budget. The balance with

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N sources (from biologically mediated  $N_2$  fixation, rivers and the atmosphere) controls the oceanic fixed-N inventory (primarily as  $NO_3^-$ ) which being an essential nutrient is a major control on marine productivity. The overall magnitude of N-loss from OMZ's is under debate and is a key determinant of whether the ocean's inventory of fixed-N is currently in steady-state or declining (Codispoti, 2007). Recent decadal-scale expansion of OMZ's, a possible consequence of global warming (Stramma et al., 2008, 2009), suggests that oceanic N-loss could be increasing, underscoring the need to understand the present state of the ocean's N budget and the processes that control it.

A number of interlinking microbial pathways contribute to N-loss in OMZ's and control the corresponding production of biogenic  $N_2$ . Whereas heterotrophic denitrification (HDN;  $NO_3^- \rightarrow N_2$  via  $NO_2^-$ ) was canonically viewed as dominant, important roles are now ascribed to the chemosynthetic anammox process (ANM;  $NO_2^- + NH_4^+ \rightarrow N_2$ ; Kuypers et al., 2003) as well as dissimilatory nitrate reduction to ammonia (DNRA;  $NO_3^- \rightarrow NH_4^+$  via  $NO_2^-$ ; Lam et al., 2009). Recent studies disagree as to whether HDN or ANM is the dominant process for producing biogenic  $N_2$  (Ward et al., 2009; Bulow et al., 2010; Hamersley et al., 2007) and it remains unclear if these differences are the result of regional contrasts, time/space heterogeneity, or methodology (Voss and Montoya, 2009). Coupling these pathways can result in variable stoichiometry between  $NO_3^-$  removal and  $N_2$  production provided there is an allochthonous supply of  $NH_4^+$ . However, recent comparison between  $NO_3^-$  deficits and biogenic  $N_2$  in several OMZ's are consistent with traditional stoichiometries (Chang et al., 2010). These microbial processes do vary in their environmental sensitivities such as threshold  $O_2$  concentration (Kalvelage et al., 2011), so that knowledge of variability in their presence and activity is required for modeling and prediction of response to future global change.

Stable N isotope distributions in the ocean are also greatly influenced by N-loss processes (variations in  $^{15}N/^{14}N$  are expressed in the  $\delta^{15}N$  notation as ‰ difference from the ratio for atmospheric  $N_2$ ). Dissimilatory  $NO_3^-$  reduction to  $NO_2^-$  is known to produce both strong N as well as O isotopic fractionation (Granger et al., 2008) leaving residual seawater  $NO_3^-$  isotopically enriched. and the product  $NO_2^-$  isotopically

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depleted (Casciotti and McIlvin, 2007; fractionation factor,  $\epsilon \sim 25\%$ ). Presumably because isotopically-light  $N_2$  gas is ultimately produced via preferential loss of  $^{14}N$ , this process is responsible for enriching the oceanic fixed-N inventory in  $^{15}N$  ( $\delta^{15}N \sim 5\%$  relative to atmospheric  $N_2$ ; Sigman et al., 2009) as compared to sources (e.g.  $-1$  to  $-2\%$  for  $N_2$  fixation; Carpenter et al., 1997).

Regionally high  $\delta^{15}N$  values for residual  $NO_3^-$  ( $\delta^{15}NO_3^-$ ) in OMZ's produce a corresponding signal in underlying sediments via upwelling and phytoplankton assimilation and downcore records reveal that OMZ N-loss has been highly sensitive to past climate change (Altabet et al., 2002). These isotopic effects have also been used to quantitatively constrain the modern ocean's N budget. Due to physical transport limitation of substrates into and through sediments, benthic N-loss produces little isotopic fractionation as compared to water column N-loss in OMZ's. This distinction allows isotopic mass balances and the average oceanic  $\delta^{15}NO_3^-$  to be used to estimate the relative importance of N-loss in sediments vs. the water column, as well as the magnitude of the overall oceanic N sink (Brandes and Devol, 2002). However such calculations are highly dependent on the choice of effective fractionation factors, which can be influenced by a number of environmental factors (Altabet, 2007) in addition to microbial pathways.

Prior approaches to the study of OMZ N-loss processes have tacitly assumed a relatively stationary and homogeneous interior-ocean environment. This was also once the case for studies of the near-surface ocean with respect to plankton productivity and community ecology. It is now well recognized that physical forcing of temporal/spatial heterogeneity not only produces physical patchiness but results in higher average oceanic productivity (McGillicuddy and Robinson, 1997; McGillicuddy et al., 1998). This physical forcing and patchiness often occurs in the form and at the scale of mesoscale eddies. Here we show the first evidence for analogous interactions between eddies and OMZ N-loss.

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## 2 Sampling and analytical methods

The physical, chemical, and biological dynamics of the Peru OMZ were studied in a series of cruises carried out as part of the German-led Climate–Biogeochemistry Interactions in the Tropical Ocean Program (<http://www.sfb754.de>) of the German Research Foundation. In January and February of 2009, total of 121 stations were occupied between 1° N and 18° S and from the coast out to 85° 50' W providing detailed spatial coverage of biogeochemical properties relevant to N-loss processes (Fig. 1a). At each station, water samples were collected using 12 l Niskin bottles on a CTD rosette system equipped with temperature, pressure, conductivity and oxygen sensors. Nutrients and oxygen were determined according to Grasshoff et al. (1999). The isotopic composition of dissolved  $\text{NO}_3^-$  was measured using Cd-reduction to  $\text{NO}_2^-$  followed by reaction with azide to produce  $\text{N}_2\text{O}$  (McIlvin and Altabet, 2005). NaCl was added to ensure consistent quantitative yield (Ryabenko et al., 2009). Pre-existing  $\text{NO}_2^-$  was removed at the time of collection by addition of sulfanilic acid. For  $\text{NO}_2^-$  isotopic analysis, a separate sample set was collected and preserved frozen and only the azide treatment was applied. Samples were analyzed in both Germany (GEOMAR) and in the USA (SMAST) using a purge-trap isotope ratio mass spectrometer (PT-IRMS) system. High precision  $\text{N}_2/\text{Ar}$  for detection of biogenic  $\text{N}_2$  and  $\delta^{15}\text{N}-\text{N}_2$  were determined on septum sealed samples using on-line gas extraction system coupled to a multicollector IRMS (Bristow et al., 2012). These data were produced by removing  $\text{O}_2$  in the samples prior to introduction into the mass spectrometer to avoid artifacts associated with varying  $\text{N}_2/\text{O}_2$  (Devol et al., 2006).  $\delta^{15}\text{N}-\text{N}_2$  data were acquired during the same analytical sessions. Publicly available satellite data for sea surface chlorophyll (SSC) are from the NASA Giovanni website (<http://gdata1.sci.gsfc.nasa.gov>) and sea level anomaly (SLA) are from the AVISO website (<http://www.aviso.oceanobs.com>).

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### 3 Results

#### 3.1 Properties maps of Peru OMZ

For context, relevant biogeochemical properties are mapped along a constant density (isopycnal) surface to highlight the effects of non-conservative, N-cycling processes (Fig. 1). The chosen isopycnal density corresponding to  $\sigma_\theta = 26.3 \text{ kg m}^{-3}$  varied between 100 and 170 m depth and was located vertically near the top of the minimum  $\text{O}_2$  layer of the water column. South of 7 to 10° S,  $\text{O}_2$  concentrations on this isopycnal surface were generally low enough to enable N-loss processes ( $< 5 \mu\text{mol kg}^{-1}$ ; Fig. 1a) consistent with prior observations (Codispoti and Christensen, 1985). Southward intensification of the OMZ along its northern boundary is associated with the poleward flow of the Peru Undercurrent (PUC) partly sourced in the lower equatorial undercurrent (Strub et al., 1987), comprising both the OMZ's core and the source of upwelled waters in this region. Onset of dissimilatory  $\text{NO}_3^-$  reduction in the OMZ is marked by the pronounced appearance of  $\text{NO}_2^-$ , which is both an intermediate for HDN and DNRA, as well as a substrate for ANM (Fig. 1b). For most of the open ocean portion of the Peru OMZ, maximal  $[\text{NO}_2^-]$  is  $< 5 \mu\text{mol kg}^{-1}$ . Net N-loss as a consequence of  $\text{NO}_3^-$  conversion to  $\text{N}_2$  gas has been previously estimated using N-deficit calculations based on anomalies in the oxidized forms of N relative to the Redfield proportionality with  $\text{PO}_4^{3-}$  (Devol et al., 2006);

$$N' = \text{NO}_3^- + \text{NO}_2^- - 16 \times \text{PO}_4^{3-} \quad (1)$$

The N-deficit,  $N'$ , is similar to the  $N^*$  formulation (Gruber and Sarmiento, 1997) but without the latter's constant offset (Appendix A).  $\text{NH}_4^+$  is not included as its concentration has almost always been observed to be very low to non-detectable in our study area, particularly seaward of the shelf. South of 7 to 10° S,  $N'$  decreases from  $-5$  to  $-30 \mu\text{mol kg}^{-1}$  along  $\sigma_\theta = 26.3 \text{ kg m}^{-3}$  confirming substantial N-loss correlated with the

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O<sub>2</sub> and NO<sub>2</sub><sup>-</sup> observations (Fig. 1c). Consistent with N loss via dissimilatory NO<sub>3</sub><sup>-</sup> reduction, δ<sup>15</sup>N values for residual NO<sub>3</sub><sup>-</sup> are inversely correlated with N' (Fig. 1d).

### 3.2 An N-loss hotspot

Our biogeochemical maps reveal one highly anomalous offshore station (12° S 82° W, Station 7) characterized by extreme values for N-loss indicators with respect to the background geographic gradients. We believe a 2nd hotspot is evident in these maps (Station 29, 16° S 76° 27' W) but is not discussed further due to a less comprehensive dataset available for this site. Station 7 is marked by strongly elevated [NO<sub>2</sub><sup>-</sup>] of up to 10 μmol kg<sup>-1</sup>, high δ<sup>15</sup>NO<sub>3</sub><sup>-</sup>, as well as very negative N' signature (Fig. 2a) in comparison with surrounding stations (Fig. 1). The highest measured values of δ<sup>15</sup>N and δ<sup>18</sup>O for OMZ NO<sub>3</sub><sup>-</sup> that we are aware of, are also observed at this station reaching 40‰ and 34‰ (Fig. 2b). In contrast, ocean-wide δ<sup>15</sup>NO<sub>3</sub><sup>-</sup> averages are near 5 and 2‰, respectively (Sigman et al., 2009). At our other Peru OMZ stations, maximal δ<sup>15</sup>NO<sub>3</sub><sup>-</sup> is typically ~15‰ and values as high as 24‰ have been reported from other OMZ's (Altabet et al., 1999). Although the extrema are relatively shallow (100 m), these N-loss indicators extend broadly over the water column down to 400 m depth, corresponding to the layer of lowest O<sub>2</sub> concentration (Figs. 2, 3). Sections for N' and [NO<sub>2</sub><sup>-</sup>] on a E–W transect at 12° S also confirm Station 7 to be distinct as compared to neighboring stations particularly with respect to the greater vertical extent of maxima. In contrast, the adjacent section at 14° S shows no evidence for an offshore N-loss hotspot (Fig. 3).

Dissimilatory NO<sub>3</sub><sup>-</sup> reduction to NO<sub>2</sub><sup>-</sup> is known to produce N and O isotopic fractionation with a characteristic slope near 1 (Granger et al., 2008). Deviations from this relationship are a common feature of the limited available data set available for OMZ's and have been interpreted as evidence for co-occurrence of other N transformation processes including NO<sub>2</sub><sup>-</sup> oxidation and contributions from N<sub>2</sub> fixation (Casciotti and McIlvin, 2007; Sigman et al., 2005). In contrast at Station 7, co-variation between NO<sub>3</sub><sup>-</sup>

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$\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  is indistinguishable from a slope of 1, implying dominance of  $\text{NO}_3^-$  reduction at this site (Fig. 2c). A Rayleigh fractionation model (Fig. 2d) can be used to estimate an “apparent” fractionation factor ( $\epsilon$ ) for N-loss assuming approximation to a closed system as done in prior studies (e.g., Voss et al., 2001). For Station 7,  $\epsilon$  is found to be lower ( $\sim 17\%$ ; Fig. 2d) than previously considered typical for OMZ N-loss but similar to recent observations of the average behavior for the Peru OMZ (Ryabenko et al., 2012).

### 3.3 Biogenic $\text{N}_2$

The amount of biogenic  $\text{N}_2$  production resulting from N-loss processes (HDN or ANM) can be estimated from high precision  $\text{N}_2/\text{Ar}$  determinations (Chang et al., 2010). Biogenic  $\text{N}_2$  production increases the measured  $\text{N}_2/\text{Ar}$  ratio over the value predicted from equilibration with the atmosphere at in situ temperature and salinity. Deviations from equilibrium  $\text{N}_2/\text{Ar}$  ratios are also known to arise from physical processes such as bubble injection in water mass formation regions. Our data are adjusted as previously described to account for this (Chang et al., 2010), allowing estimation of an “excess”  $\text{N}_2$  concentration due to biological processes. Biogenic  $\text{N}_2$  concentrations below the oceanic mixed layer can also be predicted using Richards stoichiometry (Richards, 1965) which takes into account nitrogen originating from the breakdown of OM that does not appear as  $\text{NH}_4^+$  and is assumed to be also converted to  $\text{N}_2$  (Appendix A);

$$\text{N}_2 \text{ biogenic (as } \mu\text{mol kg}^{-1} \text{N}_2) = (\text{N}'_{\text{source waters}} - \text{N}'_{\text{OMZ}}) \cdot 0.5 \quad (2)$$

Measured biogenic  $\text{N}_2$  concentrations throughout the OMZ at Station 7 (80 to 400 m) closely follows concentrations predicted from the  $\text{N}'$  data (Fig. 4a) suggesting that  $\text{NO}_3^-$  removal is well balanced by biogenic  $\text{N}_2$  production. However, measured biogenic  $\text{N}_2$  concentrations in the oxycline of Station 7, above the core of the OMZ (50 to 80 m), are twice as high as the values predicted from  $\text{N}'$ . Our observations at other “normal” offshore stations, as well as recently published data (Chang et al., 2010), do not show

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this unusual feature. Creation of this biogenic  $N_2$  maximum thus required a significant allochthonous source of biogenic  $N_2$  decoupled from local dissimilatory  $NO_3^-$  reduction.

Our method for  $N_2/Ar$  determination, allows the  $\delta^{15}N$  of dissolved  $N_2$  to be measured at very high precision (better than  $\pm 0.05\text{‰}$ ), which provides further information concerning the source of biogenic  $N_2$ . Such high precision is needed to detect the isotopic ratio of the biogenic  $N_2$  above the large background of atmospheric  $N_2$ . We calculate predicted  $\delta^{15}N$   $N_2$  anomalies relative to the atmospheric background based on an isotope mass balance with  $NO_3^-$  and  $NO_2^-$ . We assume that the mass-weighted difference between  $\delta^{15}N$  of source and OMZ waters must be reflected in biogenic  $N_2$  (Appendix A). As with biogenic  $N_2$  concentration, the predicted anomalies in the  $\delta^{15}N$  of total  $N_2$  (atmospheric background plus biogenic) are in agreement with the measured values throughout most of the OMZ (Fig. 4b). Together these data are consistent with a simple mass balance between  $NO_3^-$  removal and biogenic  $N_2$  production. However, large discrepancies between measured and predicted isotopic ratios are observed within the oxycline where a 0.25 ‰ higher than expected signal is observed at the biogenic  $N_2$  maximum (Fig. 4b). Whereas the predicted  $\delta^{15}N$  of the biogenic  $N_2$  component alone ranges from  $-5$  to  $+3\text{‰}$  (also from  $NO_3^-$  and  $NO_2^-$  isotope mass balance), the measurements imply that the  $\delta^{15}N$  of the biogenic  $N_2$  at this depth is substantially higher,  $\sim +5\text{‰}$ . This implies that the allochthonous biogenic  $N_2$  found in the oxycline was produced from  $NO_3^-$  (or  $NH_4^+$ ) with little isotope fractionation and is distinct from the apparent autochthonous source within the OMZ below it.

### 3.4 Eddy impacts

Previously, patches of high  $[NO_2^-]$  along the Peru margin were found to be associated with seaward current jets (Friederich and Codispoti, 1987). Understanding the N-loss hotspot status of Station 7 therefore likely requires consideration of any synoptic mesoscale variability. As observed from satellite images, both anticyclonic and cyclonic eddies are important and persistent features of the circulation of this coastal upwelling

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system as well as of the Eastern tropical South Pacific as a whole (Chaigneau et al., 2008). Off Peru, coherent eddies are typically formed along the coast and propagate westward at 3 to 6 km d<sup>-1</sup> and have a mean eddy lifetime of ~1 month. Their mean radius is 80 km, increasing equatorward due to the increasing Rossby Radius of Deformation. Eddies are most frequently observed off Chimbote (9° S) and south of San Juan (15° S), north and south of Station 7. As detected by satellite sea-surface chlorophyll (SSC; phytoplankton concentration) and satellite sea level anomaly (SLA; mesoscale circulation), Station 7 was located on the seaward flank of a large eddy trapped near the coast and centered near 11° S and 80.5° W (Fig. 5). Further evidence of Station 7's having been located within the edge of an anticyclonic eddy is seen in the O<sub>2</sub> section at 12° S which shows this station to be located at the periphery of a "bowl"-like distribution (Fig. 3). The region inshore of Station 7 with deepening oxycline on this section corresponds to part of the eddy's interior. Note that Station 7 was occupied on 5 January 2009, whereas the SSC map is an average for the entire month. However, the SLA data represent a 1-day snapshot for 7 January 2009 and the overlay between the current vectors and SSC suggest that the eddy was relatively stationary in this location throughout the observation period. In fact, SSC images for December 2008 and February 2009 also show the eddy to be in the same location.

The SSC imagery reveals low phytoplankton concentrations at the eddy's center and high values around most of its periphery. To the northwest, a high SSC filament appears to have been pulled offshore from the highly productive inshore upwelling region perhaps through interaction between the eddy's circulation and the equatorward mean-flow at the surface in this region. Very high inshore productivity is associated with intense upwelling of nutrient-rich (NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>, and silicate) waters on the shallow shelf coupled with Fe release from the sediment that relieves Fe limitation (Bruland et al., 2005). SLA reflects current structures superimposed on the mean flow. When overlaid on the SSC map, current vectors derived from the satellite SLA data confirm the eddy to be a strong anticyclonic feature as well as the offshore motion of the Northwestern SSC filament (Fig. 5). Given the observed eddy size and an estimated swirl velocity of

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$\sim 20 \text{ km d}^{-1}$  estimated from the SLA data and on board ADCP measurements, it took approximately 20 days to transport coastal water to the location of Station 7. Thus there is sufficient time for this and other eddies to impact offshore waters as also shown by the observed offshore flowing SSC filament.

## 4 Discussion

We have identified a “hotspot” for N-loss in the Peru OMZ based on the distribution of  $\text{N}'$ ,  $\text{NO}_2^-$ , and  $\delta^{15}\text{NO}_3^-$ . Mass balance considerations and isotope analysis furthermore supports in situ stimulation of the conversion of  $\text{NO}_3^-$  to  $\text{N}_2$  in the OMZ through a combination of HDN, DNRA, and/or ANM without extraneous  $\text{NH}_4^+$  sources for the latter. This stimulation, in turn, appears to be the result of Station 7's being located near or within the seaward edge of a coastally trapped, anticyclonic eddy (Fig. 5). A particular role for eddies in producing N-loss hotspots in association with seaward flowing streamers can account for the uniqueness of this observation (aside from possibly Station 29) as the station grid (Fig. 1) was not designed to resolve synoptic eddy features. It was happenstance that Station 7 was positioned at the seaward flank of a large coastal eddy.

The eddy likely produced the N-loss hotspot through offshore transport of highly productive inshore waters in the form of a high SSC streamer in its northwestern quadrant. We hypothesize that the subsequent downward pulse of OM in the form of sinking particles stimulates localized N-loss given the heterotrophic nature of HDN and DNRA processes (Bulow et al., 2010; Thamdrup et al., 2006). While ANM is autotrophic, it is also dependent on  $\text{NH}_4^+$  and  $\text{NO}_2^-$  supplied by heterotrophic denitrification, DNRA, or other  $\text{NO}_3^-$  reducers. Thus dissimilatory  $\text{NO}_3^-$  reduction and concomitant production of biogenic  $\text{N}_2$  is likely controlled by the OM flux, which if episodic, would produce subsurface N-loss hotspots. Although high SSC was not found directly at Station 7, a modest temporal/spatial displacement would be expected between near-surface phytoplankton

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blooms, bloom collapse, the subsequent downward organic flux, and the appearance of N-loss indicators.

Since shelf water was clearly advected offshore in the eddy streamer, it is possible that some of Station 7's N-loss hotspot characteristics have been exported from the inner shelf. However the N-loss hotspot characteristics within the OMZ at Station 7 generally lie too deep, with most of the corresponding isopycnal surfaces intersecting the upper slope (Figs. 2, 3) so that N-loss indicators in this depth range must have been generated locally in offshore waters. The biogenic  $N_2$  maximum within the oxycline, however, is shallow enough to have originated from the inner shelf. Accordingly, we suggest that the high biogenic  $N_2$  peak in the oxycline 5 at 50 m is likely a feature that has been advected from the shelf. It is almost 3 times higher than expected from coincident  $N'$  and best explained by either biogenic  $N_2$  production in shelf sediments and/or  $NH_4^+$  release from sediments that is subsequently consumed by ANM in the water column. As such, the high biogenic  $N_2$  feature is in itself evidence of direct eddy streamer influence at Station 7 despite a lack of locally high SSC. The high  $\delta^{15}N$  value for the biogenic  $N_2$  maximum is also consistent with a sediment source, where complete removal of fixed-N produces  $N_2$  with little or no isotope fractionation (Brandes and Devol, 1997).

An implication of our observations is that coastally trapped eddies can increase the magnitude of regional N-losses. Offshore transport of highly productive inshore waters inject large pulses of OM into the deep OMZ that would otherwise be respired in near surface oxygenated waters or sequestered by inner shelf sediments. By providing fuel for deep-ocean microbial N-loss processes, eddies thereby enhance the OMZ's overall N-loss relative to OM production. Assuming conventional Redfield (1958) and Richards (1965) stoichiometry, photoautotrophic conversion of  $30 \mu\text{mol kg}^{-1}$  of  $\text{NO}_3^-$  in the upper 30 m of upwelled water would produce enough OM to deplete  $20 \mu\text{mol kg}^{-1}$  of  $\text{NO}_3^-$  from the upper 250 m of the offshore OMZ. Eddy lifetime and swirl velocity appear sufficient for this OM to be both produced within the streamers and to sink into the OMZ. When added to the "background"  $\text{NO}_3^-$  removal observed throughout the Peru

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OMZ (Fig. 1), the extreme magnitudes of the N-loss indicators observed at Station 7 are readily explained.

A second implication is that coastal eddies create previously unrecognized spatial as well as temporal variability in deep OMZ biogeochemistry. Hence, apparently inconsistent results among prior studies with respect to the rates of dominant pathways (Thamdrup et al., 2006; Ward et al., 2009; Bulow et al., 2010; Hamersley et al., 2007; Lam et al., 2009) may be explained by station positions that varied relative to the eddy field. Pulses of OM from eddy streamers would also produce temporal succession in the underlying OMZ microbial community. In the oxycline and above, remineralization of OM, production of  $\text{NH}_4^+$ , and nitrification (and perhaps  $\text{N}_2\text{O}$  production) would be transiently enhanced as suggested by earlier observations (Friederich and Codispoti, 1987). Subsequent sinking of OM into the OMZ would stimulate heterotrophic processes supported by  $\text{NO}_3^-$  reduction leading to the observed accumulation of  $\text{NO}_2^-$  and N deficits. Pulses of HDN (“stop and go denitrification”) may also lead to  $\text{N}_2\text{O}$  production (an intermediate in the biochemistry for HDN; Naqvi et al., 2000).  $\text{NH}_4^+$  produced directly from OM and/or DNRA would in turn stimulate ANM. Overall, the Peru OMZ should be viewed as a dynamic system impacted by episodic physical forcing of OM flux that increases N-loss via microbial transformations to biogenic  $\text{N}_2$ . This perspective is critical for the design of future field programs.

Finally, the observed extreme enrichments of  $\text{NO}_3^-$   $^{15}\text{N}$  and  $^{18}\text{O}$  imply that important revisions to global ocean fixed-N and N isotope budgets may be required. Because sedimentary denitrification produces little N-isotopic fractionation (Brandes and Devol, 1997), the ratio of the average  $^{15}\text{N}$  enrichment in the whole ocean ( $\sim 7\text{‰}$  compared to sources) to the OMZ denitrification effect ( $\sim 25\text{‰}$ ) has been used to estimate the relative contribution of OMZ to sedimentary N-loss (Brandes and Devol, 2002). It has been suggested though, that the effective OMZ fractionation effect has been overestimated and consequently its proportion of global marine N-loss has been underestimated (Altabet, 2007). Since the global rate of N-loss in OMZ’s is considered to be better constrained than for N-loss in sediments, too high a fractionation factor would also lead

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to overestimation of total oceanic N-loss and a budget that would imply that N sinks exceed sources. Here we show an apparent fractionation factor for N-loss lower than canonical for OMZ's (17 vs. 25 ‰). Further, the extreme  $\text{NO}_3^-$  drawdown observed has important implications for the  $\delta^{15}\text{N}$  of biogenic  $\text{N}_2$ , the term that directly impacts overall the N isotope budget. Extreme  $\text{NO}_3^-$  removal produces the extreme  $\delta^{15}\text{NO}_3^-$  observed at Station 7 and requires, by mass balance, a less isotopically depleted biogenic  $\text{N}_2$  product. Indeed, the calculated depth integrated average  $\delta^{15}\text{N}$  for biogenic  $\text{N}_2$  within the OMZ at Station 7 is  $\sim -1$  ‰ and thus only 6 ‰ less than the oceanic average  $\delta^{15}\text{NO}_3^-$ . When applied to global N isotope budgets, the resulting lower effective fractionation effect for OMZ N-loss also implies that OMZ's account for a larger portion of overall oceanic N-loss than previously thought (Altabet, 2007) as well as an oceanic fixed-N budget closer to balance.

The impact of coastal mesoscale eddies on OMZ N-loss processes reported here is unlikely to be restricted to the waters off Peru, especially as the number of eddies can be greater in the other large OMZ's, off Mexico and in the Arabian Sea (Chelton et al., 2011). However, OMZ's also extend geographically far beyond the region of direct influence of coastal eddies, especially the one off Mexico (Codispoti and Richards, 1976). In oligotrophic open ocean regions, mesoscale eddies in particular are recognized as enhancing the vertical flux of nutrients and primary productivity (McGillicuddy and Robinson, 1997; McGillicuddy et al., 1998). Since most mesoscale eddies have recently been characterized as “non-linear” and capable of advecting water parcels, they have even greater potential for biogeochemical impact on the subsurface ocean (Chelton et al., 2011). Open-ocean eddies may thus produce similar “hotspots” for microbially mediated N-loss even in portions of OMZs that are distant from productive coastal waters.

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## Appendix A

### Use of $N'$ to estimate $\text{NO}_3^-$ removal and production of biogenic $\text{N}_2$

Outside of OMZ's,  $\text{NO}_3^-$  generally varies in stoichiometric proportion with  $\text{PO}_4^{-3}$  and  $\text{O}_2$  as originally observed by Redfield (Redfield, 1958). Negative deviations in  $[\text{NO}_3^-]$  from values expected from these proportions has been termed the  $\text{NO}_3^-$  deficit and is used to estimate net removal and production of biogenic  $\text{N}_2$  in OMZ's (Devol et al., 2006). The commonly used  $N^*$  ( $= [\text{NO}_3^-] - 16 \cdot [\text{PO}_4^{-3}] + 2.9$ ; Gruber and Sarmiento, 1997) assumes  $\text{NO}_3^-$  as the only form of dissolved inorganic N, uses the Redfield N:P ratio, and applies an offset of 2.9 that allows for global average  $N^*$  to be 0. We have used a modification of  $N^*$  ( $N' = \text{NO}_3^- + \text{NO}_2^- - 16 \cdot \text{PO}_4^{-3}$ ), which takes into account  $\text{NO}_2^-$ , which can be found at significant concentrations in OMZ's, and forgoes the global offset as not being relevant regionally.  $N'$  slightly overestimates actual  $\text{NO}_3^-$  removal because of  $\text{PO}_4^{-3}$  release from organic matter breakdown by about 16 % (Devol et al., 2006). Accordingly, biogenic  $\text{N}_2$  ( $\text{N}_2$  biogenic) assuming equivalence with  $\text{NO}_3^-$  removal as well as Richards' stoichiometry (1.71  $\text{NO}_3^-$ :1  $\text{N}_2$ ; Richards, 1965) and taking into account conversion of organic N to  $\text{N}_2$ , can be calculated as:

$$\text{N}_2 \text{ biogenic (as } \mu\text{mol N}_2) = (N'_{\text{source}} - N'_{\text{OMZ}}) \cdot 0.86 / 1.71 \quad (\text{A1})$$

$$\text{N}_2 \text{ biogenic} \sim (N'_{\text{source}} - N'_{\text{OMZ}}) \cdot 0.5 \quad (\text{A2})$$

Because the corrections for  $\text{PO}_4^{-3}$  production and  $\text{N}_2$  produced from organic N breakdown assume the same elemental stoichiometry for organic matter, they effectively cancel each other.

The  $N'_{\text{source}}$  term accounts for source waters not necessarily having zero N anomaly. It was measured at stations upstream from the OMZ on isopycal surfaces corresponding to those bounding the Peru OMZ and is about  $-5 \mu\text{mol kg}^{-1}$  in this system.

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Figure 3a compares biogenic  $N_2$  calculated in this fashion ( $N'$  derived) with measured values (from  $N_2/Ar$ ).

### Anomaly in the $\delta^{15}N$ of $N_2$

The  $\delta^{15}N$ - $N_2$  anomaly reported is the difference between the measured value and the value expected at atmospheric equilibrium at in situ temperature and salinity (between 0.6 and 0.8‰). For the measured anomaly, the difference between measured  $\delta^{15}N$ - $N_2$  and the equilibrium value is reported (Fig. 3b). For the expected anomaly, the  $\delta^{15}N$  of biogenic  $N_2$  is first calculated from isotope mass balance between source  $NO_3^-$  and OMZ  $NO_3^-$  and  $NO_2^-$  assuming differences are accounted for by production of biogenic  $N_2$ :

$$\delta^{15}N\text{-}N_2 \text{ biogenic} = (\delta^{15}N\text{-}NO_3^-_{\text{source}} \cdot [NO_3^-]_{\text{source}} - [NO_3^-]_{\text{OMZ}} \cdot \delta^{15}N\text{-}NO_3^-_{\text{OMZ}} - [NO_2^-]_{\text{OMZ}} \cdot \delta^{15}N\text{-}NO_2^-_{\text{OMZ}}) / [N_2 \text{ biogenic}] \quad (A3)$$

$$[NO_3^-]_{\text{source}} = 16 \cdot PO_4^{-3}_{\text{OMZ}} + N'_{\text{source}} \quad (A4)$$

As for  $N'_{\text{source}}$ ,  $\delta^{15}N\text{-}NO_3^-_{\text{source}}$  is measured at stations upstream of the Peru OMZ and is about 7‰. Not included is the isotopic signal from the small amount of biogenic  $N_2$  produced from organic N which would be expected to produce a modest increase in its  $\delta^{15}N$  value in this system.

The expected  $\delta^{15}N$ - $N_2$  anomaly is calculated by addition of the biogenic  $N_2$  signal with the background  $N_2$  of atmospheric origin ( $N_{2 \text{ atm}}$ ; calculated assuming equilibrium at in situ temperature and salinity) with zero  $\delta^{15}N$  anomaly;

$$\delta^{15}N\text{-}N_2 \text{ anomaly} = ([N_{2 \text{ atm}}] + [N_2 \text{ biogenic}] \cdot \delta^{15}N\text{-}N_2 \text{ biogenic}) / ([N_{2 \text{ atm}}] + [N_2 \text{ biogenic}]) \quad (A5)$$

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*Acknowledgements.* Enrique Montes aided in sample collection and Jen Larkum and Laura Bristow provided critical technical assistance. Funding to MAA was provided by the US National Science Foundation. Funding to ER, LS, DW, MF, PG and GL was provided by the Deutsche Forschungsgemeinschaft-supported project SFB-754 ([www.sfb754.de](http://www.sfb754.de)). The RV Meteor M77/3 and M77/4 Pacific cruises were granted by the DFG and the crews and captain of “RV Meteor” are thanked for their help during cruises M77/3 and M77/4.

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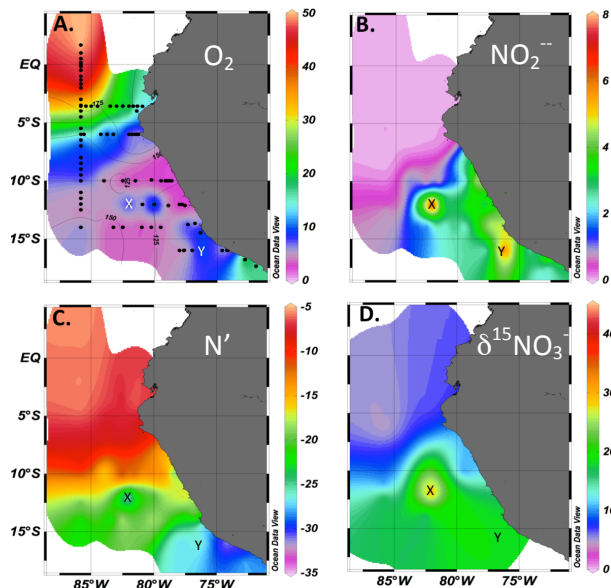
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**Fig. 1.** Biogeochemical maps of the Peru OMZ from a series of stations constituting 6 transects normal and 1 transect parallel to the coast occupied during cruises M77/3 and M77/4 of the German research vessel “RV Meteor” in January and February of 2009. Properties are shown along a constant density surface ( $\sigma_{\theta} = 26.3 \text{ kg m}^{-3}$  within the upper portion of the OMZ corresponding to a depth range of 100 to 170 m. **(A)**  $\text{O}_2$  concentration ( $\mu\text{mol kg}^{-1}$ ), station locations, and density of  $\sigma_{\theta} = 26.3 \text{ kg m}^{-3}$ . **(B)**  $\text{NO}_2^-$  concentration ( $\mu\text{mol kg}^{-1}$ ). **(C)** Nitrogen anomaly –  $N'$  ( $\mu\text{mol kg}^{-1}$ ) calculated as  $[\text{NO}_3^-] + [\text{NO}_2^-] - 16 \cdot [\text{PO}_4^{3-}]$ . **(D)** The  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$ . When southward intensification of suboxic conditions reaches  $[\text{O}_2] < 5 \mu\text{mol kg}^{-1}$ , the onset of N-loss processes is evident. Location of Station 7, a hotspot for N-loss, is marked by an “X”. Data smoothing to produce this visualization diminishes somewhat the extrema found at Station 7 (see Fig. 2). A second hotspot (Station 29) was also detected (marked by a “Y”), but is not discussed in the text due to a less comprehensive data set for this site.

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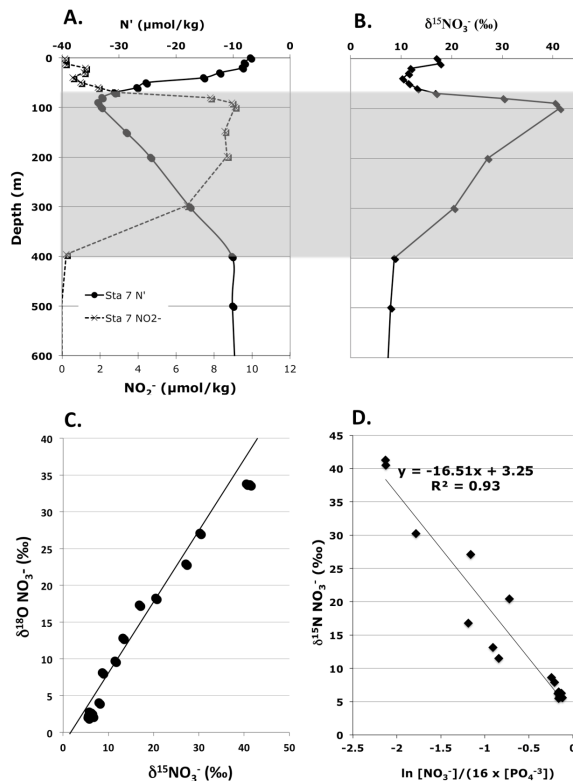
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Interactive Discussion



## An eddy-stimulated hotspot for fixed nitrogen-loss

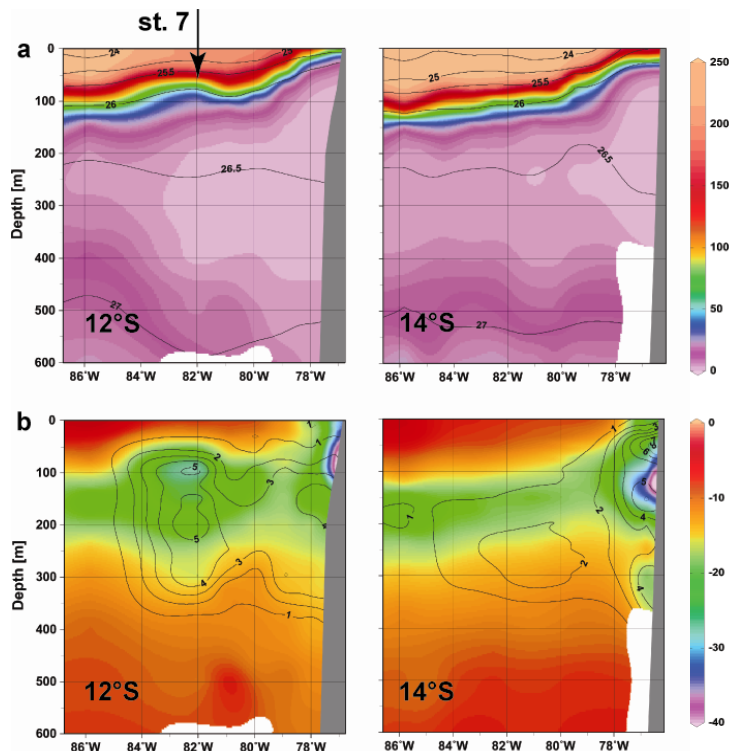
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**Fig. 2.** Depth profiles for N-loss indicators at Station 7 showing extreme values. OMZ indicated as a shaded depth interval (see also Fig. 3). **(A)**  $\text{NO}_2^-$  and N deficit ( $N'$ ) concentration profiles ( $\mu\text{mol kg}^{-1}$ ). **(B)** Profiles for  $\delta^{15}\text{NO}_3^-$  (‰ relative atmospheric  $\text{N}_2$ ) for station 7. **(C)** Crossplot of the  $\delta^{18}\text{O}$  vs the  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$ . **(D)** Rayleigh plot of  $\delta^{15}\text{NO}_3^-$  vs. the  $\ln$  of the residual  $\text{NO}_3^-$  fraction assuming the  $\text{NO}_3^-$  concentration prior to removal is approximated as  $16 \cdot [\text{PO}_4^{3-}]$ . The inverse slope estimates the fractionation effect ( $\epsilon$ ) at  $\sim 17\%$ .

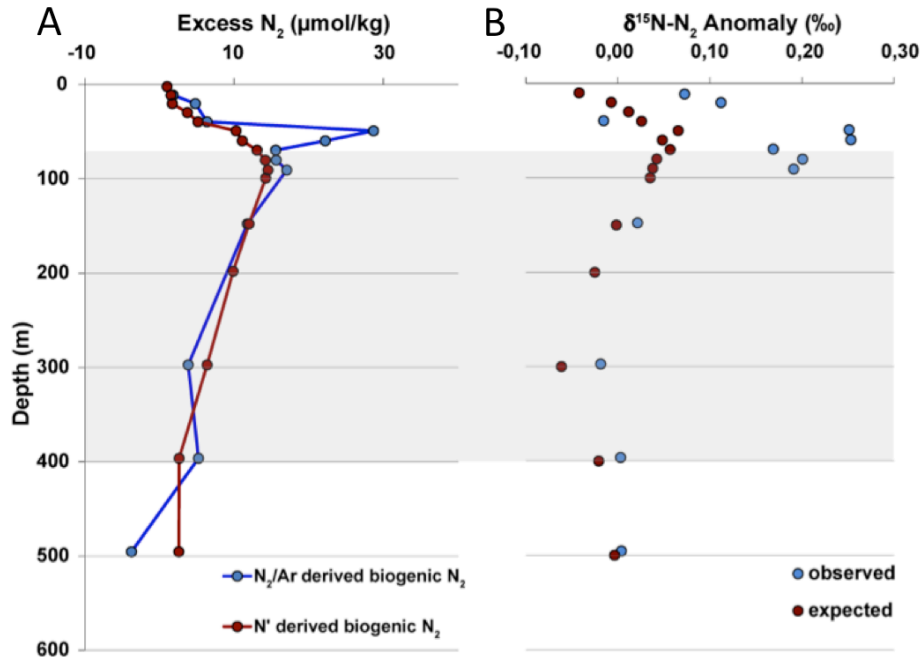
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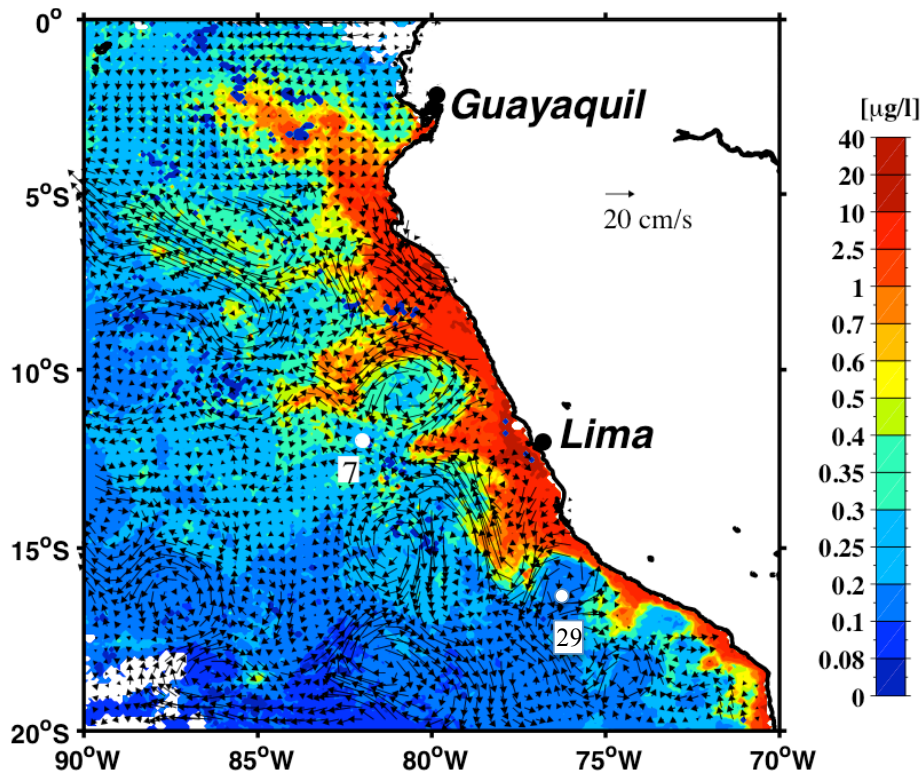


**Fig. 3.** Property distribution section off the Peru coast. **(A)**  $O_2$  concentration ( $\mu\text{mol kg}^{-1}$ ; color shading) and  $\sigma_\theta$  (contour lines) sections at  $12^\circ\text{S}$  and  $14^\circ\text{S}$  latitude (see station positions in Fig. 1). Station 7 is part of the  $12^\circ\text{S}$  section and its position is marked. **(B)** Corresponding  $N'$  (color shading) and  $\text{NO}_2^-$  concentration (contour lines) sections at  $12^\circ\text{S}$  and  $14^\circ\text{S}$ . Units are in  $\mu\text{mol kg}^{-1}$ . Data smoothing to produce this visualization diminishes somewhat the extrema found at Station 7 (see Fig. 2).





**Fig. 4.** Biogenic  $N_2$  depth profiles at Station 7. **(A)** Measured and expected excess  $N_2$  (biogenic) concentration ( $\mu\text{mol kg}^{-1}$ ). **(B)** The measured and expected  $\delta^{15}\text{N}$  anomaly for  $N_2$ . OMZ indicated as a shaded depth interval. Expected biogenic  $N_2$  is derived from the nitrogen anomaly ( $N'$ ) assuming Richards stoichiometry (Richards, 1965) after taking into account  $N'$  for water masses upstream of the OMZ (Appendix A). Measured biogenic  $N_2$  is calculated from deviations in  $N_2/\text{Ar}$  ratio from values expected at saturation with the atmosphere at in situ temperature and salinity and adjusted for physical sources of  $N_2/\text{Ar}$  anomaly by comparison with stations outside the OMZ (Chang et al., 2010). The expected  $\delta^{15}\text{N}$  anomaly for  $N_2$  is based on isotopic mass balance between the system's source  $\text{NO}_3^-$  and OMZ  $\text{NO}_3^-$  and  $\text{NO}_2^-$  (Appendix A).



**Fig. 5.** Satellite observations for the period when Station 7 was occupied (location as indicated). Sea surface chlorophyll (SSC;  $\mu\text{g l}^{-1}$ ) for January 2009 is overlaid by current vectors derived from sea level anomaly (SLA) for 7 January 2009. SSC reflects surface ocean phytoplankton concentration and productivity and was available from the NASA Giovanni website (<http://gdata1.sci.gsfc.nasa.gov>) as a monthly average. SLA and related current vectors varies in response to barotropic velocity variation from the mean state and is available from the AVISO website ([www.aviso.oceanobs.com](http://www.aviso.oceanobs.com)) representing the sea state for a given day.

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