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Paired N and O isotopic analysis of nitrate and nitrite in the Arabian Sea oxygen deficient zone

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ABSTRACT

The Arabian Sea is home to one of the three main oceanic oxygen deficient zones (ODZs). We present paired nitrogen (N) and oxygen (O) isotope measurements of nitrate (NO_3^-) and nitrite (NO_2^-) from the central Arabian Sea in order to understand the effects of N biogeochemistry on the distribution of these species in the low oxygen waters. Within the ODZ, NO_2^- accumulated in a secondary NO_2^- maximum (SNM), though the shape and magnitude of the SNM, along with the isotopic composition of NO_3^- and NO_2^-, were highly dependent on the location within the ODZ. We also explored water mass mixing within the Arabian Sea as an explanatory factor in the distribution of NO_2^- in the SNM. The intrusion of Persian Gulf Water at depth may influence the shape of the NO_2^- peak by introducing small amounts of dissolved oxygen (O_2), favoring NO_2^- oxidation. There was also evidence that vertical mixing may play a role in shaping the top of the SNM peak. Finally, we present evidence for NO_2^- oxidation and NO_2^- reduction co-occurring within the ODZ, as has been previously suggested in the Arabian Sea, as well as in other ODZs. The decoupling of the N and O isotopes of NO_3^-, deviating from the expected 1:1 ratio for dissimilatory NO_3^- reduction, indicates that NO_2^- oxidation has a significant influence on the isotopic composition of NO_3^-. Additionally, the N isotopes of NO_2^- were generally fit well by Rayleigh curves for NO_2^- oxidation. However, the removal of dissolved inorganic nitrogen (DIN) within the domain reflects the importance of NO_2^- reduction to N_2.

1. Introduction

Nitrogen (N) is a critical component of all life on Earth, and is a limiting nutrient in a significant portion of the surface ocean (Moore et al., 2013). The global inventory of fixed N, largely composed of nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+), is controlled by its production and removal processes. New fixed N is introduced largely through biological nitrogen fixation, whereby nitrogen gas (N_2) from the atmosphere is converted into a form that is usable by marine fauna. The main loss processes of fixed N are denitrification and anammox, which result in the production of gaseous N forms that are eventually released back to the atmosphere. Denitrification is the stepwise reduction of NO_3^- and NO_2^- to gaseous nitric oxide (NO), nitrous oxide (N_2O), and N_2. The anammox process uses both NO_2^- and NH_4^+ to generate N_2.

An important feature of denitrification and anammox is that they are inhibited in the presence of oxygen (O_2), with O_2 thresholds estimated to be between 0.2 and 20 μM O_2 (Jensen et al., 2008; Kalvelage et al., 2011; Babbin et al., 2014; Dalsgaard et al., 2014). Low O_2 conditions allowing for these N loss processes are found in permanent oxygen deficient zones (ODZs) throughout the world's oceans. There are three main ODZs, located in the Eastern Tropical North Pacific, Eastern Tropical South Pacific, and the Arabian Sea. These ODZs, though they account for only 0.1% of total ocean volume, are theorized to be responsible for 30–50% of total N loss from the oceans (Gruber and Sarmiento, 1997; Codispoti et al., 2001).

As a result of the O_2 sensitivity of N loss processes, unique N distribution features are observed within ODZs that are not seen throughout the rest of the world's oceans. The most prominent of these features is the secondary NO_2^- maximum (SNM), where NO_2^- accumulates above 0.2 μM (Naqvi, 1991). Coincident with the SNM, there also appears a deficit of dissolved inorganic nitrogen ($DIN=NO_3^-+NO_2^-+NH_4^+$) relative to phosphate (PO_4^{3-}) that is indicative of N loss. This deficit of DIN, represented by a minimum in the tracer N*, where $N^*=DIN-16*PO_4^{3-}+2.9$ μmol/kg (Gruber and Sarmiento, 1997; Deutsch et al., 2001) is corroborated by accumulation of excess dissolved N_2 (Chang et al., 2010, 2012). Thus, in ODZs, NO_2^- appears to be produced by dissimilatory NO_3^- reduction (NAR) and

Abbreviations: ODZ, oxygen deficient zone; SNM, secondary nitrite maximum; ASHSW, Arabian Sea High Salinity Water; ICW, Indian Central Water; PGW, Persian Gulf Water; RSW, Red Sea Water

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consumed by NO_2^- reduction (NIR) to N_2 via denitrification and anammox.

The Arabian Sea is the largest ODZ by volume (Helly and Levin, 2004). In the Arabian Sea, N loss appears to occur through both denitrification (Nicholls et al., 2007; Ward et al., 2009; Bulow et al., 2010; Gaye et al., 2013) and anammox (Jensen et al., 2011). Estimates of water column denitrification rates within the Arabian Sea have been made using a variety of techniques to understand to what extent the Arabian Sea contributes to global N loss. Naqvi (1987) estimated a loss of 29.5 Tg N/yr based on advective and diffusive transport of NO_3^- deficit out of the ODZ. Devol et al. (2006) used N_2 gas measurements to extrapolate a denitrification rate of 41 ± 18 Tg N/yr. DeVries et al. (2012) modeled excess N_2 to estimate a total N loss of 12–16 Tg N/yr in the Arabian Sea. Furthermore, some incubation-based studies indicate that significant N loss may not only be occurring where NO_2^- accumulates within the Arabian Sea, as significant N loss was observed over the Omani shelf in the western Arabian Sea with no associated NO_2^- accumulation (Jensen et al., 2011). As such, there remains an open question of whether NO_2^- observed in the SNM is consistently being produced and consumed there or whether it signifies a lack of N_2-production activity (Jayakumar et al., 2009; Lam et al., 2011). These studies yield different views on the magnitudes and mechanisms of N loss in the Arabian Sea; however, most assume that NO_3^- reduction is coupled to NO_2^- reduction, by denitrification and/or anammox, rather than NO_2^- oxidation.

In addition to the N loss pathways, however, NO_2^- can also be produced and consumed via nitrification, which entails the oxidation of ammonia (NH_3) to NO_2^- and the oxidation of NO_2^- to NO_3^-. Although ODZs are now thought to be functionally anoxic (Thamdrup et al., 2012), there has been significant evidence for NO_2^- oxidation (NXR) occurring within ODZs, including the Arabian Sea (Casciotti et al., 2013; Gaye et al., 2013; Buchwald et al., 2015). The O_2 affinity of NH_4^+ oxidation and NO_2^- oxidation appear to allow them to proceed below 1 μM O_2 (Füssel et al., 2012; Kalvelage et al., 2013; Ji et al., 2015; Peng et al., 2015; Bristow et al., 2016; Peng et al., 2016). Furthermore, a diffusive flux of O_2 from the oxycline may support a significant amount of oxic respiration near the top of the ODZ (Peters et al., 2016). In this study we present an analysis of paired stable N and O isotope measurements of NO_3^- and NO_2^- to further our understanding of the fate of NO_2^- within the Arabian Sea ODZ.

2. Materials and methods

2.1. Study site

The Arabian Sea is a semi-enclosed, poorly-ventilated ocean basin located in the northwest Indian Ocean. This region experiences seasonal climate and productivity variability due to seasonally reversing monsoons (Wyrtki, 1971; Shetye et al., 1994; Schott and McCreary, 2001). There are two phytoplankton blooms driven by the monsoons, one during the summer southwest monsoon and one during the winter northeast monsoon (Wiggert et al., 2005; Lévy et al., 2007). During the southwest monsoon, Ekman divergence along the western edge of the Arabian Sea drives upwelling along the Omani shelf and to some extent within the central Arabian Sea (Wiggert et al., 2005). This upwelling supplies nutrients to the surface and results in a phytoplankton bloom. During the northeast monsoon, deep convective mixing due to strong, cooler winds drives a bloom in the northeast Arabian Sea (McCarthy et al., 1999; Wiggert et al., 2005). The sinking of detritus depletes O_2 in the water column as the organic matter is remineralized. However, the areas of highest surface production are separate from the region of persistent denitrification (Naqvi, 1991). Advection and turbulent diffusion of O_2 due to mesoscale circulation features play important roles in determining the distribution of O_2 within the Arabian Sea (Resplandy et al., 2012; McCreary et al., 2013).

The bulk of the water in the Arabian Sea ODZ consists of Indian Central Water (ICW), which is an old water mass, low in O_2, that flows northward from the southern Indian Ocean (You and Tomczak, 1993). Flowing into the central Arabian Sea are several surface-derived water masses that are higher in O_2 and salinity: Persian Gulf Water (PGW), Red Sea Water (RSW), and Arabian Sea High Salinity Water (ASHSW). PGW is a warm water mass that flows southward into the Arabian Sea at depths of 200–400 m (Kumar and Prasad, 1999; Prasad et al., 2001). RSW flows from the Gulf of Aden eastward into the Arabian Sea at depths of 400–800 m (Kumar and Prasad, 1999). ASHSW is a shallow water mass that forms in the northern reaches of the Arabian Sea and mixes southward (Kumar and Prasad, 1999). However, limited ventilation of the basin (Naqvi, 1991) and the inflow of already O_2-depleted water (Olson et al., 1993; Böning and Bard, 2009) are also contributing factors to the permanent ODZ located in the northeast Arabian Sea (Fig. 1).

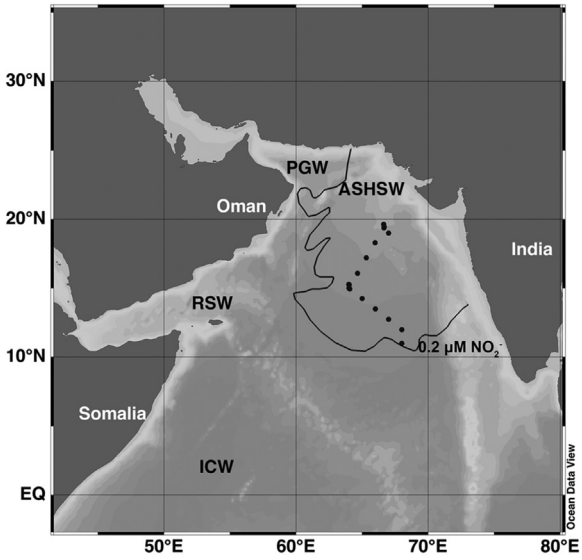

Fig. 1. Stations sampled during the 2007 cruise. The black outline shows the canonical extent of the permanent Arabian Sea ODZ, which is considered to be the region where more than 0.2 μM of nitrite accumulates in the secondary nitrite maximum (Naqvi, 1991). Approximate regions of water mass definitions used in this study are also indicated (PGW=Persian Gulf Water, RSW=Red Sea water, ICW=Indian Central Water, and ASHSW=Arabian Sea High Salinity Water).

2.2. Cruise sampling

Water samples were collected on the R/V *Roger Revelle* in September-October 2007 during the late monsoon/intermonsoon transition period. The cruise track (Fig. 1) was designed to sample stations along a gradient in intensity of the ODZ (Fig. S1). Samples were collected from Niskin bottles on a conductivity-temperature-depth (CTD) rosette. O_2 measurements were taken using a Seabird O_2 sensor calibrated to onboard micro-Winkler titrations using a method for improved measurement performance at low O_2 concentrations (Broenkow and Cline, 1969; Bulow et al., 2010). NO_3^- and PO_4^{3-} concentrations were determined using an onboard segmented flow autoanalyzer (SKALAR Analytical). NO_2^- concentrations were determined using a Shimadzu UV–visible spectrophotometer following protocols outlined by Strickland and Parsons (1972). Samples for NO_3^- isotopic measurement were filtered (0.2 μm pore size) and stored frozen at −20 °C until analysis. Samples for NO_2^- isotopic measurement were prepared at sea, as described below.

2.3. Isotope measurements

Both NO_3^- and NO_2^- samples were analyzed for $\delta^{15}N$ and $\delta^{18}O$, where: