We report measurements of isotopic composition of nitrogen (Δ15N) of particulate organic nitrogen (PON) at eighteen sampling locations in the north-eastern and central Arabian Sea during the waning phase of the summer monsoon. This season is ideal to detect signatures of upwelling and denitrification in the Arabian Sea. Our observations indicate significant spatial variability in the Δ15N as a result of the upper ocean response to the monsoonal forcing that triggers upwelling and thus supplies sub surface nitrate to the surface. An increasing (decreasing) trend has been found in the Δ15N (PON) from the upwelling zone to the open ocean, which tracks the progressive utilization of advected nitrate from the coast. Monsoon-driven mixing and supply of nitrate and/or PON with lower Δ15N from the west through advection are mainly confined to the upper 50 m, however, at some locations advection imprints its signature in the deeper layers as well. The results have implications to the interpretation of sedimentary Δ15N record from this region and deciphering the role of monsoonal forcing over the nitrogen utilization by plankton.

Introduction

Nitrogen isotopic composition (Δ15N, expressed as deviation in parts per thousand (‰) from atmospheric air standard) of particulate organic nitrogen (PON) provides an insight into various biogeochemical transformations occurring in the marine nitrogen cycle (e.g., Gandhi et al., 2011a). The Δ15N of phytoplankton varies as a result of biologically mediated isotopic discrimination and primarily depends on the Δ15N of the N source and the biological isotopic fractionation during uptake and assimilation of the nutrient source. Under a nitrogen replete environment, phytoplankton preferentially assimilate 14N relative to 15N resulting in the lower Δ15N of phytoplankton relative to that of the nitrogen source. On the other hand, under nitrogen limiting conditions, phytoplankton utilize available nitrogen completely and Δ15N of phytoplankton closely reflects that of the nitrogen source (Altabet and McCarthy, 1985). Cynobacteria lowers the Δ15N (~ 0.6‰; Emerson et al., 1991) of PON by converting atmospheric N2 (Δ15N H= 0‰) into organic nitrogen. Further, nitrogen recycling also lowers the Δ15N of PON, because of isotopic fractionation during heterotrophic processes. The low-Δ15N ammonium released by zooplankton is assimilated by phytoplankton leading to a lower Δ15N of surface PON (Altabet, 1988). Further, the Δ15N of PON also depends on phytoplankton species, physiology and the rate and phase of growth of phytoplankton (Montoya and McCarthy, 1995). Sinking particulate matter likely to propagate these surface generated signals to the sea floor and thus, nitrogen isotopic compositions of sediments are being used to decipher the information on long-term variation in surface nitrogen utilization and critical oceanic N cycle processes (Altabet and Francois, 1994). In this context, measurements of the Δ15N of plankton and dissolved inorganic nitrogen are critical to the interpretation of sedimentary Δ15N records as well as in quantifying the sources of nitrogen that support production in contemporary oceanic ecosystems (Montoya, 2008).

A variety of geochemical and biological
processes are known to be active in the Arabian Sea; e.g., higher primary productivity during the winter and summer monsoons due to the entrainment of nutrients into the mixed layer by convective overturning (Madhupratap et al., 1996; Gandhi et al., 2011b) and coastal upwelling (Barber et al., 2001), respectively. Such episodic events of higher productivity result in oxygen deficiency in middle layers of the water column (Naqvi, 1987). Loss of oxidized form of nitrogen to the atmosphere by intense denitrification and anaerobic ammonium oxidation is also observed (Bange et al., 2005; Nicholls et al., 2007). The Arabian Sea, with its well-developed oxygen minimum zone (OMZ) is one of the major regions of water column denitrification in the world ocean (Naqvi, 1987). However, the basin gains new nitrogen from the atmosphere by the occurrence of N$_2$-fixing cyanobacteria, mainly Trichodesmium bloom during inter-monsoon every year (Devassy et al., 1978; Gandhi et al., 2010; 2011a). All the above processes affect the $\delta^{15}$N of the inorganic nitrogen pool and hence the average $\delta^{15}$N of PON and sinking particles. Study of $\delta^{15}$N of surface PON may elucidate the strength of certain water column processes.

Here, we discuss the vertical profiles of $\delta^{15}$N of PON in the north-eastern and central Arabian Sea during the waning phase of the summer monsoon (June-September). Surface temperature, nutrients and chlorophyll data from the same cruise are presented elsewhere (Naqvi et al., 2010) and referred to for details.

**Methodology**

Sampling was performed along the cruise track shown in the Fig. 1 during 4-25 Sep 2004. Samples were collected for nitrogen isotopic composition of natural PON at eighteen Stations using Niskin bottles, mounted on a CTD rosette from various depths, mostly up to ~100 m, however, at two Stations (1 and 2) up to 1500 m. Further, at four Stations (8-10, 13, and 15) Station depths were shallower, so samples were collected only up to ~50 m depth. 2L of sea water was collected from each depth. After collection, sample bottles were closed immediately to avoid any atmospheric contamination. Immediately after the collection, all samples were filtered through pre-combusted (4 hrs at 400°C) 47 mm diameters and 0.7 μm pore size Whitman GF/F filters. Care was taken to minimize atmospheric contamination by opening sample bottles sequentially. After filtration, filters were dried in an oven at 50°C overnight and stored for further mass spectrometric analysis.

For the present study, a CarloErba elemental analyzer interfaced via Conflo III to a Finnigan Delta Plus mass spectrometer, which was used to measure PON and atom% $^{15}$N in the samples. The technique for sub-microgram level $^{15}$N determination (Owens and Rees, 1989) was followed. Two standards USGS32 (KNO$_3$) and IAEA-N-2 ([NH$_4$]$_2$SO$_4$, #342) were used to check the accuracy of the measurements. Precision for the $\delta^{15}$N determination was ±0.1‰. The average uncertainty associated with the determination of PON was less than 6%. $\delta^{15}$N is defined as:

$$\delta^{15}N = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

Where, R is the ratio of $^{15}$N to $^{14}$N. All values of $\delta^{15}$N presented are relative to the $^{15}$N/$^{14}$N ratio of atmospheric N$_2$. 

![Fig. 1: Sampling locations (filled stars) in the central and western Arabian Sea during 4-25 Sep 2004. Samples were collected at eighteen Stations (rectangles) for measurement of PON and $\delta^{15}$N of PON. Dotted line shows the cruise track and the direction shown with arrows. See the text for details about the four different Sections (1 to 4).](image-url)
As mentioned earlier, $\delta^{15}N$ of PON at a particular location is a function of several processes such as remineralization, vertical mixing, and lateral advection; therefore the mean $\delta^{15}N$, weighted with PON was calculated to decouple and identify different processes. The weighted $\delta^{15}N$ of PON is then calculated (Altabet and McCarthy, 1986) as:

$$\text{Weighted } \delta^{15}N = \frac{\sum_i n_i \delta^{15}N_i \times PON_i}{\sum_i PON_i}$$

Here ‘n’ represents different depths at a given sampling location.

In the present study, the whole cruise track has been subdivided into four Sections; Section 1 (north central Arabian Sea) includes Stations 1 and 2, Section 2 includes Oman shelf region (Stations 4, 6, 8-11, 13-15), Section 3 includes Oman shelf to offshore Stations which retreating the southern limit of the US JGOFS up to 15°N (Stations 16, 18, 20), and the Section 4 includes Stations along the 15°N latitude, (south central Arabian Sea) (Stations 22, 24, 26, 28). The other intermediate Stations marked by stars were not sampled for $\delta^{15}N$. For the study period, surface wind data derived from the QuikSCAT scatterometer are available at http://apdrc.soest.hawaii.edu/dods/public_data/satellite_product. Effect of upwelling observed using the sea surface height anomaly data are derived from the weekly merged data from multi-satellite (TOPEX/Poseidon, ERS and Jason), which has a spatial resolution of 1/3 degree. Level 3 weekly grided (0.5°×0.5°)

Results

Hydrographic Condition

Upwelling at the Omani coast is evidenced by the lower sea surface temperature (~22°C; SST). Upwelling in the western Arabian Sea is driven by strong southwesterly winds and is very vigorous. During end of the monsoon season also winds were southwesterly in the region (Fig. 2). Consequently low SST and higher nitrate signatures observed up to a distance of ~1000 km from the Omani coast (Naqvi et al., 2010). SST increased from ~22°C at the Oman coast in the western Arabian Sea to ~28°C at the central and eastern Arabian Sea. Following winds, the upwelled water moves towards central Arabian Sea as evident by the higher sea surface height anomaly (Fig. 2). Upwelling also occurs at the west coast of India as evidenced by the lower SST (~23°C) but its effect remains limited to the coastal region (Naqvi et al., 2010). Upwelling in the eastern Arabian Sea is remotely forced, and much less energetic (McCreary et al., 1993). Nitrate pattern shows an opposite trend from SST; nitrate is maximum (~10µM) at the Oman coast and gradually decreases to near detection limit in the central Arabian Sea (Naqvi et al., 2010). There is a large variation (< 8µM to >16µM) in the surface nitrate within the Omani coast, with the higher values in the south-eastern part, where high nitrate-low chlorophyll (HNLC) conditions develop due to Fe limitation (Naqvi et al., 2010), causing under-utilization of nitrate. Surface chlorophyll is higher at Station 7 (> 5 mg m$^{-3}$; situated in the north-eastern part of the Omani coast) than that at Station 16 (< 0.1 mg m$^{-3}$; situated in the south-eastern part of the Omani coast). Fe limitation in the south-eastern part promotes under-utilization of nitrate. As the upwelled water in the western Arabian Sea spreads eastward, it retains its high nitrate content far away from its origin (~1000 km). Diatoms dominate the plankton community along the western Arabian Sea (Brown et al., 2002), whereas plankton community shifts towards smaller autotrophic types due to the depletion of silicate offshore during this season (Garrison et al., 1998).

Nitrogen Isotopic Composition of PON

Central Arabian Sea

Surface values of PON and its $\delta^{15}N$ along with the Station locations are given in Table 1. Section 1 includes Stations 1 and 2. Although both the Stations lie in the central Arabian Sea a large difference is found in the surface values of PON: 1.9 and 5.8µM at Stations 1 and 2, respectively. Such a difference is observed in surface $\delta^{15}N$ values as well, 12.3 and 6.6‰ at Stations 1 and 2, respectively (Table 1). Station 1 lies within the area influenced by the upwelled water at the Omani coast but not Station 2. This is could be the reason for the large difference in PON and its $\delta^{15}N$ values at both the locations. PON weighted $\delta^{15}N$ values for different depth intervals are shown in Fig. 3a. PON weighted $\delta^{15}N$ is generally higher at Station 1 than at Station 2, except at the 500-2500 depth interval (Fig 3a). A progressive
increase in PON weighted $\delta^{15}N$ from 10.2 to 16.1% was observed up to 250 m at Station 2, whereas, at Station 1 a sudden increase (from 14.8 to 27.6%) was found at 50-100m from 0-50m. PON weighted $\delta^{15}N$ decreased after 500 m at Station 1, whereas, it increased after 500 m at Station 2 (Fig. 3a). No clear trend has been observed in PON weighted $\delta^{15}N$ at both these Stations.

Oman Shelf Region

This Section includes Stations from the Oman shelf region. PON varied from 3.9 to 13.2 $\mu$M (with an average of 7.5 $\mu$M). PON was relatively very high (more than 12 $\mu$M) at two Stations (6 and 15) (Table 1). The average PON in the shelf region became 5.9 $\mu$M by excluding both the Stations. $\delta^{15}N$ values in the surface varied from 8.2 to 12.8% (with an average 10.8%), excluding Station 4 at which $\delta^{15}N$ was 1.8% (Table 1). The average value decreased to 9.8% by including Station 4. PON weighted $\delta^{15}N$ up to 50 m and below 50 m values for the representative Stations (4, 6, 8, 11 and 14) which cover the whole region across the coast are plotted in Fig. 3b. PON weighted $\delta^{15}N$ for upper 50 m values were lower than that of below 50 m at all the Stations. PON weighted $\delta^{15}N$ for upper 50 m ranged from 6.0 to 11.8%, whereas it varied from 8.6 to 28.8% below 50 m. PON weighted $\delta^{15}N$ values in the upper 50m are comparable at all

Fig. 2: Sea Surface height anomaly (legend on the right, in cm) images overlaid with surface winds (source: http://apdrc.soest.hawaii.edu/dods/public_data/satellite_product) showing different periods (A) 29 August-04 September, (B) 05-11 September, (C) 12-18 September, (D) 19-25 September, (E) 26 September-02 October 2004 in the Arabian Sea.
the locations, except at the northern most location (Station 4). Station 4 also shows the lowest value for 50-100 m depth interval.

**Oman Coast to South Central Arabian Sea**

Here surface PON and δ¹⁵N of PON ranged from 3.1 to 7.4 µM (with an average of 5.5 µM) and 6.0 to 13.0‰ (with an average of 9.1‰), respectively (Table 1). A general decreasing trend was observed in the surface δ¹⁵N from the Oman coast to off-shore, whilst the trend reversed for surface PON. PON weighted δ¹⁵N for upper 50m decreased from the Omani coast to offshore range from 9.6 to 14.7‰, whereas, it remained comparable for 50-100m depth interval at all the locations (Fig. 3c).

**South Central Arabian Sea**

This Section includes Stations along the 15°N transect. Surface PON ranged from 1.8 to 4.3 µM (with an average of 2.9 µM) and δ¹⁵N of surface PON varied from 8.7 to 25.4‰ (with an average of 17.1‰) for this Section (Table 1). Generally, surface PON decreased from the west to the east, whereas δ¹⁵N of surface PON increased (Table 1). There was a progressive increase observed in PON weighted δ¹⁵N for upper 50 m from the west to the east (Fig. 3d). Overall, PON weighted δ¹⁵N for upper 50 m varied from 10.0 to 24.2‰, whereas it varied from 22.7 to 32.0‰ for 50-100 m. Generally, PON weighted δ¹⁵N for upper 50 m was lower than that for 50-100 m depth, except at Station 26 (Fig. 3d).

**Longitudinal Variation**

Figure 4 shows the longitudinal variation of the surface PON and δ¹⁵N of PON. An opposite trend has been observed for PON and its nitrogen isotopic composition from the east to the west. The highest PON value is found near the Oman coast whereas the lowest value is observed near to the west coast of India. In contrast, the latter region has the highest δ¹⁵N of PON and the lowest is found in the former. The region near to the Oman coast (56°E to 60°E) shows a large variation in the PON, varied from 3.1 to 13.2 µM, whereas spread is comparatively less in the δ¹⁵N of PON, it varies from 8.2 to 13.0‰ (barring Station 4).

**Discussion**

**Vertical Patterns**

A large variation in the PON and δ¹⁵N of PON has been found in the in the central AS (Station 1 and 2) which indicates that several processes are acting together in the region. Station 2 is certainly influenced by upwelling at the Omani coast. The upwelling supplies sub-surface nitrate to the surface and this water mass advects towards central Arabian Sea. Such a supply of water mass of lower δ¹⁵N and/or nitrate of lower δ¹⁵N imparts its effect throughout the water column in the central Arabian Sea as seen in the observed δ¹⁵N values. No regular pattern has been seen in the δ¹⁵N values from surface towards the deep at Station 2. Lower values of δ¹⁵N are observed in deeper samples too. Remineralization and mixing of laterally advected water mass decides the overall variation of δ¹⁵N at this location. In contrast, Station 1 lies within the area of intense denitrification.

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**Table 1. Station number, sampling position, surface particulate organic nitrogen (PON) and its δ¹⁵N data at different Stations**

<table>
<thead>
<tr>
<th>Station No.</th>
<th>Latitude (ºN)</th>
<th>Longitude (ºE)</th>
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<th>δ¹⁵N (‰)</th>
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and out of the influence of upwelling water mass of the Omani coast (Naqvi, 1991). At Station 1, a steady increase in the PON weighted $\delta^{15}$N from surface-50 m to 100-200 m suggests the progressive remineralization of organic matter. A large variation of PON weighted $\delta^{15}$N for different depths between Station 1 and 2 could be because of the variability in the vertical scale of mineralization in the different parts of the Arabian Sea (Naqvi et al., 2010).

In most of the locations, value of weighed $\delta^{15}$N below 50 m is more than that of upper 50 m (Fig. 3). Though higher values of $\delta^{15}$N are associated with lower PON values there is no strong linear relationship which suggests the involvement of other processes in governing the $\delta^{15}$N of PON. Further, no gradient has been observed in the surface $\delta^{15}$N values from shelf region towards off-shore. However, weighted values of $\delta^{15}$N for upper 50 m show a steady increase from open to coastal locations (Fig. 3), whereas such effects diminishes below 50 m due to the remineralization and mixing. In general, in most of the Stations, weighed $\delta^{15}$N below 50 m is more than that of upper 50 m, except at the Station 28 (close to the coast and could have terrestrial inputs).

Two parameters viz., $\Delta \delta^{15}$N and ‘$F$’ have been used Altabet and McCarthy (1986) to point out the role of different processes occurring in the warm-core eddies and the Sargasso Sea on the PON and its $\delta^{15}$N.

Here, $\Delta \delta^{15}$N is the difference between the maximum $\delta^{15}$N value and $\delta^{15}$N value associated with the maximum PON and $F = (1- (\text{PON at max } \delta^{15}\text{N/ PONmax})).$
Natural Isotopic Composition of Particulate Organic Nitrogen

Indicates the degree of degradation of organic matter. If degradation were the only process controlling PON, there should be a relationship between $F$ and the observed increase in $\delta^{15}N$. A plot between $\ln F$ and $\Delta \delta^{15}N$ provides information about the effect of degradation over observed $\delta^{15}N$. Any scatter in the plot hints towards the involvement of other processes controlling the variation in $\delta^{15}N$ of PON. Fig. 5 presents a plot of $\ln F$ vs. $\Delta \delta^{15}N$. There is a trend toward a greater range in $\Delta \delta^{15}N$ with decreasing $\ln F$ suggesting that the lower amount of remineralization can result in larger $\delta^{15}N$ values (Fig. 5). However, large degree of scatter and lack of a linear relationship indicate that the assumption that degradation is the only process controlling PON and its $\delta^{15}N$ is too simplistic. The plot indicates that processes in addition to particle decomposition control the concentration of PON and its $\delta^{15}N$. Wind driven mixing and advection from the West are the plausible factors for the deviation from linear relationship between $\ln F$ and $\Delta \delta^{15}N$.

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Spatial Variation

Measurements of $\delta^{15}N$ of surface PON in the Arabian Sea suggest that advection plays a critical role in the $\delta^{15}N$ of PON values in the off-shore Oman and the central AS during late SW monsoon. Relatively low scatter in the $\delta^{15}N$ values (Fig. 4) near the Oman coast suggests a supply of nitrate of similar isotopic composition from below which supports the plankton bloom in the region. As the unutilized $^{15}N$ enriched nitrate moves towards the central AS due to the wind forcing, it shows a progressive enrichment in the $\delta^{15}N$ of surface PON (Fig. 4). Similarly, PON values show a progressive decline from the Omani coast to offshore (Fig. 4) suggests a progressive depletion of nutrients towards central AS. However, a large scatter in the PON values near to the coast of Oman has been found. Similarly, a large scatter is also observed in the surface chlorophyll a values (Naqvi et al., 2010). This could be due to the varying supply and/or underutilization of nutrient or patchiness of plankton. As said earlier, Fe limitation could be a plausible reason for the under-utilization of nitrate in the south-eastern part of the Omani coast which results in the large scatter in the PON and chlorophyll a values. The effect of Fe limitation diminishes in the offshore region by the supply of Fe through atmospheric deposition (Naqvi et al., 2010). Therefore, the unutilized nitrate moves toward offshore region and is being utilized while progressing eastward. The $\delta^{15}N$ of the remaining nitrate pool is enriched by this utilization and so is its $\delta^{15}N$ in the eastward direction.
Conclusions

No clear linear trend exists between PON and its $\delta^{15}$N as the combined effects of remineralization, supply of nitrate, and/or PON of lower $\delta^{15}$N from the Oman coast through advection mainly govern these parameters. Mixing by winds further modified the $\delta^{15}$N of PON in the surface. Our observations suggest that the mixing and advection dominates the remineralization effect during the season particularly in upper 50 m. Though remineralization overcomes the other effects and causes enrichment in the $\delta^{15}$N in the deeper samples, yet at some locations, lateral advection imprints its signature in the deeper water too e.g. Station 2. A linear trend has been found in the surface PON and its $\delta^{15}$N from the Oman coast to the central AS. This trend supports the inference that the unutilized upwelled nitrate in the Oman coast advects towards central AS by winds and imparts its signature in the $\delta^{15}$N of PON.

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