

Variability of organic nitrogen and its role in regulating phytoplankton in the eastern Arabian Sea

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Abstract:

The relative importance of organic nitrogen (ON) and inorganic nitrogen (IN) as nitrogen sources for the phytoplankton communities were studied through a seasonal time series of nitrogen species in the eastern Arabian Sea. Seasonal data on nitrogen species showed that ON dominates the system throughout the year and account for >90% of the total nitrogen (TN) during north east monsoon (NEM). The average ON concentration in the study region was 11.5 μM during NEM as compared to 7.2 μM during south west monsoon (SWM). The contribution of picoplankton to the total phytoplankton pool (f_{pico}) increased from 19% during SWM to 36% in NEM. Along with cyanobacteria, the diatoms *Thalassionema nitzschoides* and *Thalassiosira sp.* and among the dinoflagellates *Pronoctiluca sp.* were found to proliferate in ON rich waters. We suggest atmospheric deposition, riverine-input, resuspension of bottom sediment and ground water intrusion as the possible sources of ON in the study region.

Keywords: organic nitrogen, eastern Arabian Sea, phytoplankton, cyanobacteria, diatoms

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1. Introduction

Nitrogen is a limiting nutrient for algal growth over 70% of the global ocean (Duce et al., 2008) affecting the oceanic biological productivity (Ward et al., 2009; Moore et al., 2013; Gruber 2016). The synthetic nitrogen fertilizer usage has almost increased another tenfold from 1960 to 2013 (Battye et al., 2017; Jickells et al., 2017). Nitrogen enters the oceans through rivers, groundwater and direct waste discharges, atmospheric deposition, N_2 fixation (Jickells et al., 2017) and from sediment (Scheffer, 2001), while it is lost from the ocean through denitrification and anammox processes (Ward et al., 2009; Gruber 2016). Recent reports show that Northern Indian Ocean (NIO) is a high and increasing nitrogen deposition region (Jickells et al., 2017). The increasing nitrogen inputs (riverine and atmospheric deposition) may lead to intensification of hypoxic conditions and increased fluxes of N_2O , a potent green house gas (Naqvi et al., 2010).

Recently, Battye et al. (2017) raised a question “Is Nitrogen the next Carbon”, and showed that nitrogen is following similar increasing trends like carbon, with associated adverse environmental consequences. Anthropogenic nitrogen supply will have first impact in the coastal waters as they alone receive 24% of the TN through atmospheric deposition (Vet et al., 2014), and are most susceptible to ecological changes (Bhavaya et al., 2016). In order to understand the impact of such processes on phytoplankton composition, it is necessary to monitor the concentrations of various nitrogen species.

Phytoplankton species tend to prefer a particular type of nitrogen, which can affect energy transfer to higher trophic levels and benthic-pelagic coupling (Bronk et al., 2007). Few studies also suggest that cyanobacteria and dinoflagellates are associated with higher NH_4^+ and ON, compared to NO_3^- (Berg et al., 1997, 2003; Lomas and Glibert, 1999). Glibert et al. (2004) gave evidences for dissolved organic nitrogen (DON) uptake during a cyanobacterial bloom in Florida Bay. Among all the nitrogen species, the DON comprises the largest component (60–69%) of total dissolved nitrogen in rivers, estuaries, coastal and open oceanic surface waters (Bronk 2002, Sipler and Bronk 2015), and could drive ecological shift. Previously, Parab et al. (2006) have reported a seasonal community shift in the eastern Arabian Sea from diatoms (SWM) to dinoflagellates (fall inter monsoon (FIM)) to cyanobacteria (NEM) associated with IN species. This would also have a profound effect on the oceanic CO_2 sequestration capacity as the composition of the phytoplankton community affects the

magnitude and efficiency of carbon export (Durkin et al., 2016). Here we hypothesize that ON plays an important role in the seasonal phytoplankton community shift in the Arabian Sea coastal waters (ASCW). We present for the first time, the seasonal variation of ON in the ASCW, its possible sources and role in phytoplankton diversity. This study also identifies the phytoplankton that might flourish in ON rich waters in the future.

Methodology

2.1 Sample collection

Time series measurements were carried out at the Candolim Time Series (CaTS) transect off Goa covering four stations (G3, G4, G5 and G6) in the eastern Arabian Sea (Fig. 1). The maximum depth at these stations varied from 12m to 38m. Sampling was done using fishing trawlers during different seasons; January (NEM), May (SIM), September (SWM) and November (FIM) of 2015 and SWM of 2016. Sea bird CTD was used for measuring temperature and salinity. Sampling was done at discrete depths (1, 6, 12 m for G3; 1, 9, 18 m for G4; 1, 9, 18, 27 m for G5; 1, 9, 18, 27, 38 m for G6) using Niskin sampler (5 L). Salinity and temperature data were acquired using a portable Sea-Bird Electronics CTD (conductivity-temperature-depth) system. During SIM conductivity sensor was non-functional; hence salinity was not measured during this season. Subsamples for nutrients, phytoplankton pigments and their speciation were collected and preserved for subsequent analyses in the CSIR-National Institute of Oceanography (NIO) laboratory. Additionally, ON was measured in groundwater samples from nine wells across Goa, very close to the Mandovi and Zuari estuaries (Fig.1).

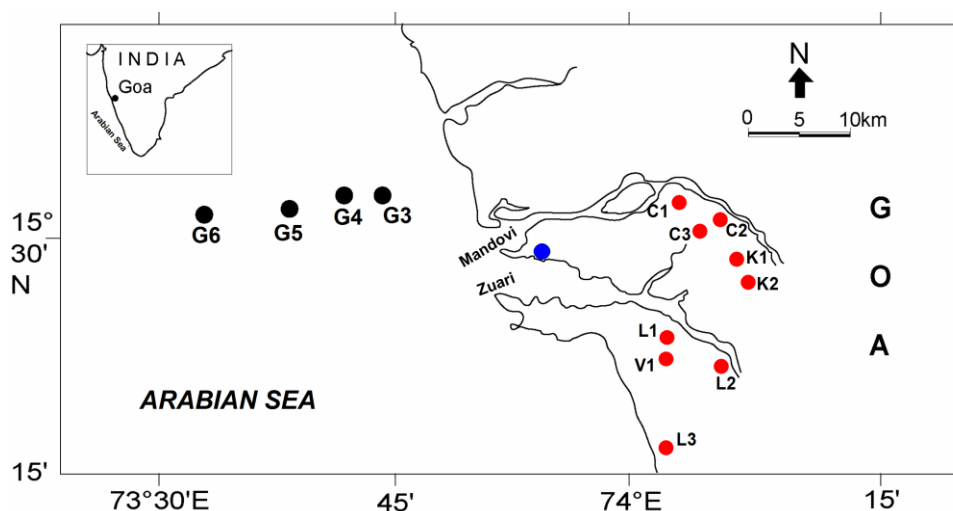


Figure 1: Map showing locations of CaTS stations (G3 to G6) off Goa, Ground water sampling locations (C1-C3, K1,K2,L1-L3 and V1), and atmospheric sampling point (marked as blue). Mandovi and Zuari estuaries are also marked.

2.2 Nutrient and Dissolved Oxygen analyses

Samples for inorganic nutrients were collected in 60 ml plastic bottles and preserved with HgCl_2 for subsequent analysis in laboratory. Upon, reaching the laboratory (after 2 to 3 hours from the time of collection) inorganic nutrients were analyzed using an Auto analyzer (SKALAR) with a precision of ± 0.06 , ± 0.006 , ± 0.01 , ± 0.003 and ± 0.06 μM for NO_3^- , NO_2^- , NH_4^+ , PO_4^{-3} and SiO_4^{-2} respectively (Grasshoff et al., 1983). Dissolved oxygen (DO) was estimated following the Winkler titrimetric method (Grasshoff et al., 1983) with a precision of <1 μM .

2.3 ON

Seawater for ON was collected into acid-cleaned 30 mL glass vials and immediately frozen upright at -20 °C. A Shimadzu Total nitrogen analyzer was used to determine TN concentrations (Dickson et al., 2007) which comprises of IN (NO_3^- , NO_2^- and NH_4^+) and ON. TN was analyzed at 720°C following chemiluminescence method, wherein the nitrogen oxidation product nitric oxide (NO) is quantified by reaction with ozone and detection of the resulting chemiluminescence (Badr et al., 2003; Letscher et al., 2013). Standardization was achieved using potassium nitrate and a 5 point calibration curve was generated before each batch of analyses. ON was calculated as a difference between TN and IN. Triplicate analysis was done for each sample. CRM (Deep Sea standard 33 μM for TN) procured from University of Miami was run in each batch, and the accuracy of the analysis was ± 1 μM . Apart from the ON measurements, Particulate Organic Nitrogen (PON) was measured at station G5. For PON analysis, seawater samples were taken in acid-washed plastic carboys and filtered through precombusted (450°C for hours) GF/F filters (0.7 μm pore size). The filtration volume varied from 0.5 to 4 litres depending on the suspended load. The filters were exposed to acid-fumes (36% HCl) to remove carbonates and air dried in a clean laminar flow. A 12 mm diameter sub-section of the filter was packed tightly in tin cups and analyzed using a elemental analyzer (THERMO). DON was calculated as the difference between ON and PON.

2.4 Aerosol analysis

Bulk aerosols (total suspended particulate matter) were collected using a high volume sampler located at CSIR-NIO, Goa (15.45 °N, 73.80 °E) during NEM and SIM. A total of 18 samples were analysed for water soluble ON. The procedure followed is briefly described here. A portion of filter (one-fourth filter) was leached with 50 mL of milli-Q water and extracts were filtered through

Puradisc 25 syringe filters (0.2 µm PVDF). An aliquot of filtrate was analyzed for water soluble anions (Cl⁻, NO₃⁻ and SO₄²⁻) and cations (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) on Dionex-500 Ion Chromatograph equipped with suppressed conductivity detector. A detailed description of the analytical procedure has been provided in earlier publications (Rengarajan et al., 2007; Kumar et al., 2010). For the determination of the water soluble TN, water extracts were analyzed using Shimadzu TN analyzer. ON was calculated as the difference between TN and IN. The overall precision of the measurements for IN and TN is ± 5% or better.

2.5 Phytoplankton pigment analysis

For the pigment analysis, 1 L of water sample was immediately filtered using a GF/F filter (0.7 µm) avoiding exposure to direct light. Phytoplankton pigments were extracted and analyzed by HPLC following the modified method of Van Heukelem (2002) as described in Kurian et al. (2012). Calibration standards were procured from DHI, Denmark. Marker pigments zeaxanthin (Zea), fucoxanthin (Fuco) and peridinin (Per) were considered to represent cyanobacteria, diatoms and dinoflagellates, respectively. We also reconstructed the proportion of various phytoplankton size classes (f_{micro} , f_{nano} and f_{pico}) following Uitz et al. (2006). In the present study, we used seven pigments (Fuco, Per, alloxanthin, 19'-Hexanoyloxyfucoxanthin (19'HF), 19'-Butanoyloxyfucoxanthin (19'BF), Zea and TChlb (Chlb+divinyl chlorophyllb (DivChlb)) as markers of phytoplankton taxa (diagnostic pigments; DP). Size fractionated contributions of phytoplankton (f_{micro} , f_{nano} and f_{pico}) were calculated as follows:

$$f_{micro} = 100 \times (1.41[\text{Fuco}] + 1.41[\text{Per}]) / \sum \text{DP} \quad (>20 \mu\text{m})$$

$$f_{nano} = 100 \times (0.60[\text{alloxanthin}] + 0.35[19'\text{BF}] + 1.27[19'\text{HF}]) / \sum \text{DP} \quad (2 \text{ to } 20 \mu\text{m})$$

$$f_{pico} = 100 \times (0.86[\text{Zea}] + 1.01[\text{TChlb}]) / \sum \text{DP} \quad (<2 \mu\text{m})$$

2.6 Phytoplankton microscopic counts

A subsample of 250 ml water was fixed with Lugol's iodine (1 % final concentration) for phytoplankton counts. All the samples were stored in the dark at room temperature until enumeration. A settling and siphoning procedure (using 11µm nylon mesh) was followed to concentrate the samples which were then examined microscopically in a Sedgewick-Rafter plankton counting chamber (Structure Probe, Inc., West Chester, PA, USA) under an inverted microscope (Olympus IX 51; 4009) at 200X magnification. Phytoplankton taxa were identified following Tomas (1997) and Subramanyan (1946, 1968). In addition, cyanobacterial (*Synechococcus*) abundance was measured by flow cytometry. Samples were fixed with glutaraldehyde (0.2% final concentration) and were frozen in liquid nitrogen and stored at -80°C until analysis. The analysis was carried out using a

Flow cytometer (BD FACS Calibur) equipped with blue (488 nm) and red (633 nm) lasers, and absolute counts of were obtained following *Marie et al.* (1997).

3. Results

3.1 Hydrography and Dissolved Oxygen (DO)

Sea surface temperature (SST) was low during NEM reaching a minimum of 27.1°C; whereas the highest SST (31.6 °C) was observed in SIM (Fig. 2a,b,c,d). Sea surface salinity (SSS) was high during SWM at deeper depths (Fig. 2e,f,g,h). Also, the CTD profiles showed deeper mixed layer during NEM as observed in Kerala coast by Gupta et al. (2016). DO concentrations were high during SIM reaching up to 207 μM (Fig. 2i,j,k,l) at the surface. The waters below 20m were suboxic during SWM ($\sim 3.2 \mu\text{M}$) and FIM ($0.7 \mu\text{M}$).

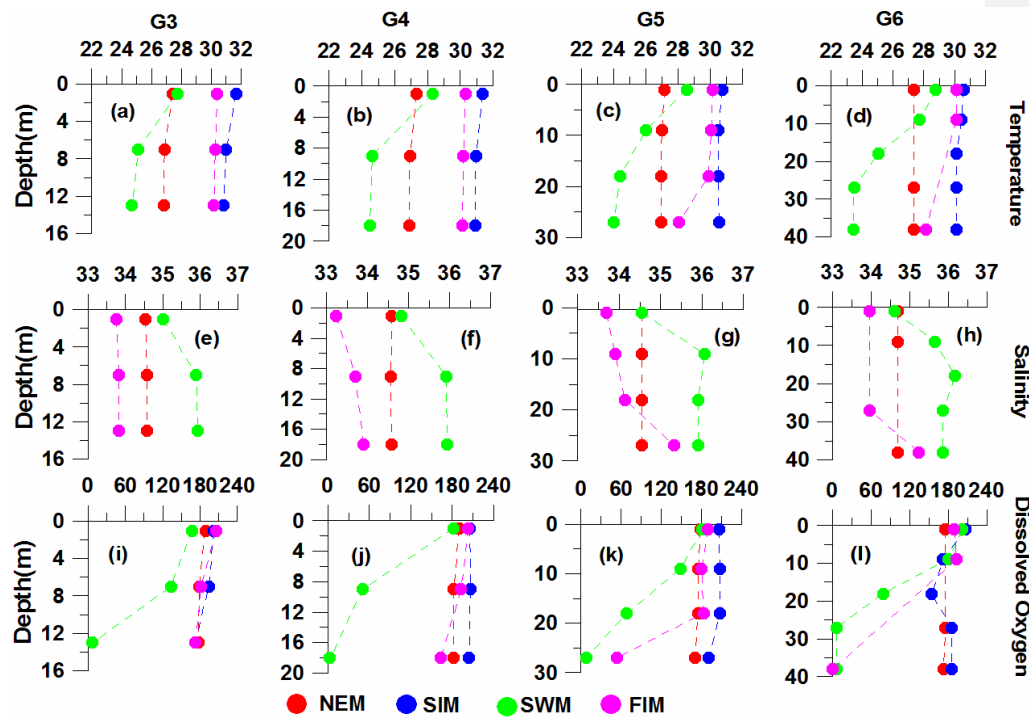


Figure 2: Seasonal variations in Temperature (°C), Salinity (psu) and Dissolved Oxygen (μM) in the ASCW during 2015.

3.2 Seasonal variation of nitrogen species

NH_4^+ concentrations were as high as 6 μM during SWM at the bottom of the innermost station G3 (Fig. 3). Minimum concentrations of NH_4^+ were seen during NEM. The water column NO_3^- was <0.5 μM during NEM and SIM; however, the concentrations increased during SWM reaching upto 16.5 μM in bottom waters of G6 (Fig. 3). The average water column NO_3^- concentrations were 0.24 μM , 0.18 μM , 5 μM and 2 μM during NEM, SIM, SWM, and FIM. NO_2^- also showed higher concentration (up to 3 μM) during SWM, especially at G5 (Fig. 3). High ON concentrations (15.5 μM) were observed during the FIM and NEM. ON concentrations were comparatively lower during SIM and SWM with the lowest concentration (<7 μM) in the surface waters at stn G5 during SWM (Fig.3). The average concentration of ON during NEM was 11.5 μM as compared to 7.2 μM in SWM. ON comprised 94% of the TN during NEM, 83% during SIM, 81% during FIM and 50% during SWM. The high ON during NEM (January) was observed for other sampling of NEM 2015 (December), and also for other years (2014, 2016 and 2017; supplementary Fig. 1). Based on the above mentioned nitrogen concentrations, each season represented a particular type of nutrient condition. NEM=Low IN & High ON, SIM= Low IN & Low ON, SWM= High IN & Low ON, FIM= High IN & high ON.

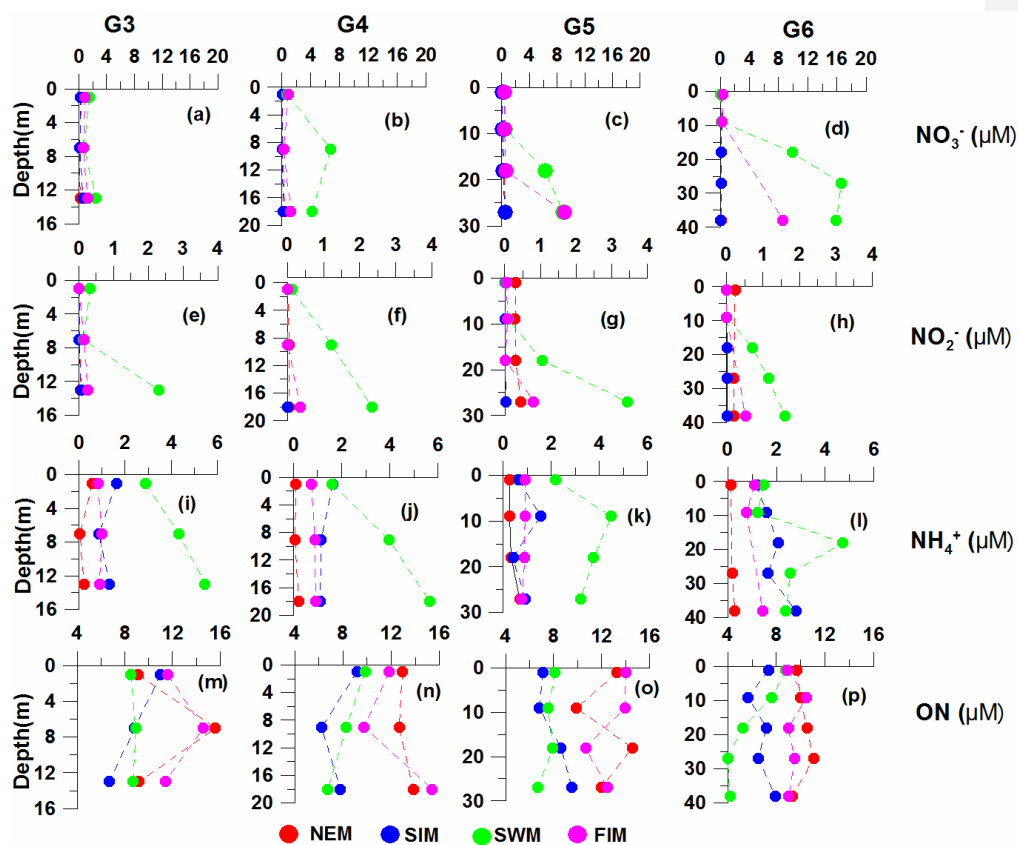


Figure 3: Seasonal variations in N species (NO_3^- (a,b,c,d), NO_2^- (e,f,g,h), NH_4^+ (i,j,k,l) and ON (m,n,o,p)) in the ASCW during 2015.

In addition, the PON analysis indicates that ON was mostly dominated by the DON, while PON constituted a smaller fraction (Fig. 4). DON followed ON trend and was high during NEM and FIM, while PON was high during SWM and FIM, with higher concentrations in the bottom waters.

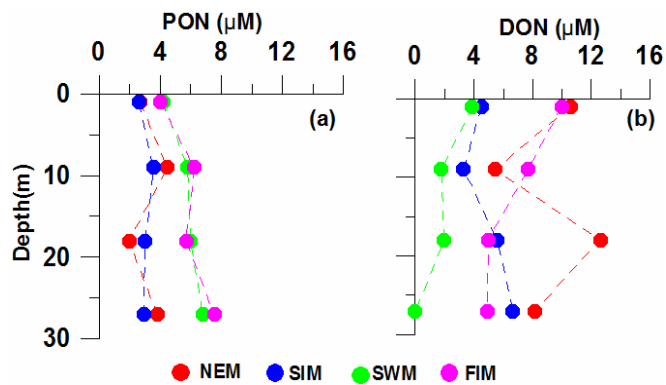


Figure 4: Seasonal variations in PON and DON at station G5 in the ASCW during 2015.

3.2 Variations in SiO_4^{2-} and PO_4^{3-}

SiO_4^{2-} varied from 4.7 to 11 μM , 2.36 to 7.1 μM , 2.8 to 39 μM , and 3.66 to 22.7 μM during NEM, SIM, SWM, and FIM respectively (Fig 5a). PO_4^{3-} varied from 0.28 to 0.64 μM , 0.07 to 0.27 μM , 0.55 to 2.1 μM and 0.19 to 1.1 μM during NEM, SIM, SWM, and FIM respectively (Fig 5b). As PO_4^{3-} is one of the key requirements for N_2 fixers, we calculated P^* ($P^* = [\text{PO}_4^{3-}] - [\text{NO}_3^-]/16$) that indicates deviation of PO_4^{3-} concentration from the Redfield ratio (N:P = 16).

Positive P^* indicates PO_4^{3-} concentrations in excess compared to NO_3^- (Deutsch et al., 2007, Kumar et al., 2017). P^* values in the surface waters were in excess throughout the study period, and varied from 0.055 during SIM to 1.956 during SWM (Supplementary **Table 1**). Mean P^* values were in the following order SIM < FIM < NEM < SWM. Such low P^* values during SIM were also observed by Kumar et al. (2017) and were attributed to the consumption of PO_4^{3-} by diazotrophs.

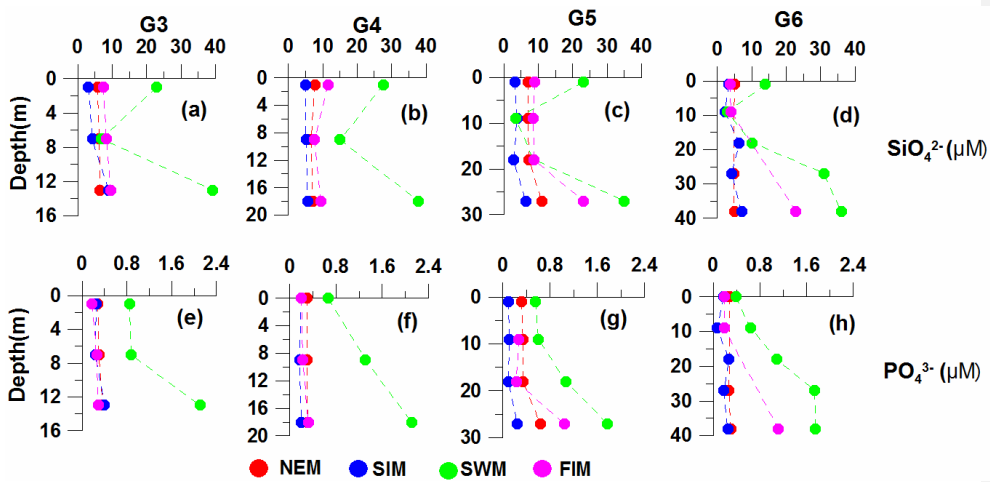


Figure 5: Seasonal variations in SiO_4^{2-} (a,b,c,d) and PO_4^{3-} (e,f,g,h) in the ASCW during 2015.

3.4 Phytoplankton pigments

The analysis of the phytoplankton marker pigments showed that the seasonal changes were driven by the proportion of the dominant groups: diatoms, dinoflagellates and cyanobacteria. Chl *a* was high during SWM and FIM mainly contributed by diatoms and dinoflagellates as seen by the marker pigments Fuco and Per (Fig. 6). Zea was comparatively higher during FIM and NEM (Fig. 6). The f_{micro} decreased from 74% during SWM to 55% during NEM; whereas the f_{pico} increased from 19% during SWM to 36% during NEM.

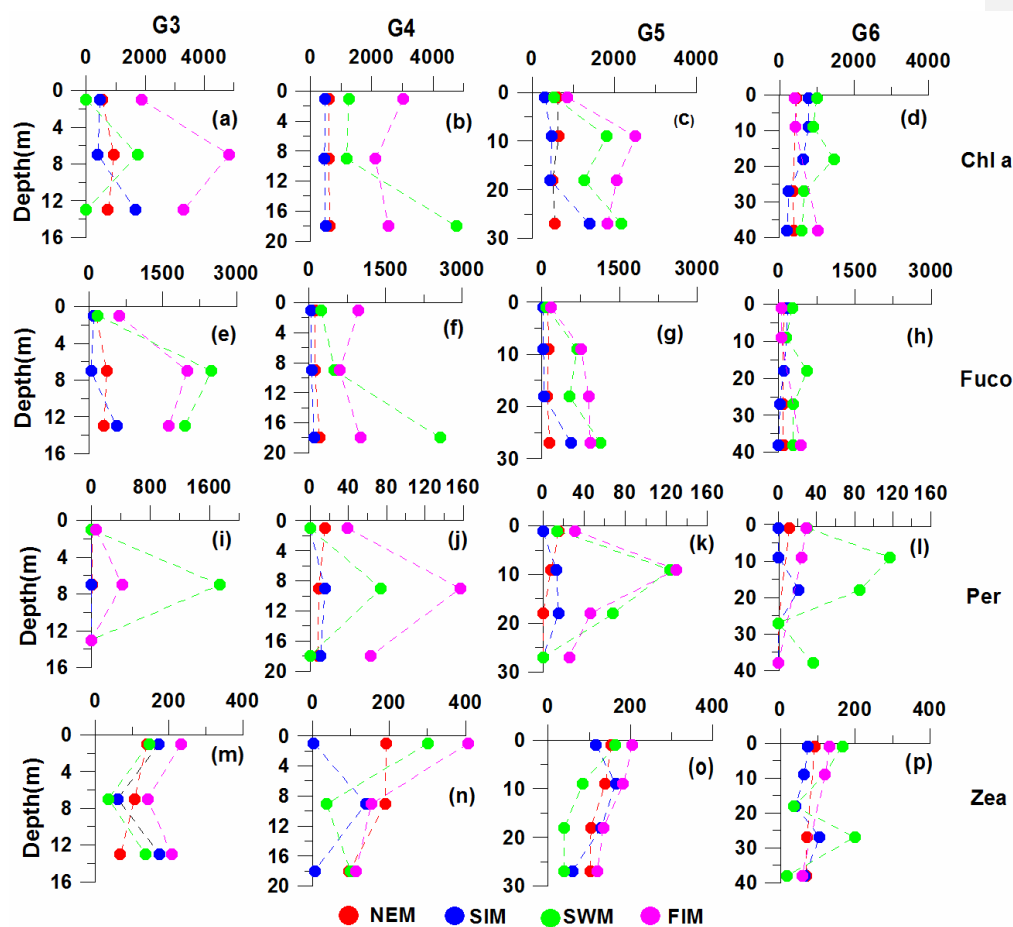


Figure 6: Seasonal variations in phytoplankton pigments (ngL^{-1}) (Chl a, Fuco, Per, and Zea) in the ASCW during 2015.

3.5 Phytoplankton abundance

Consistent to the marker pigments, light microscopic observation also showed high phytoplankton density during SWM and FIM. It was dominated by diatoms followed by dinoflagellates. In this study we found 41 species of diatoms belonging to 35 genera and 26 species of dinoflagellates belonging to 20 genera, while nitrogen fixing cyanobacterium *Trichodesmium sp.* were found during SIM (Tables 1 & 2). The Shannon diversity index was relatively high during SIM ($H' = 3.4$ to 4.6) and SWM ($H' = 3.9$ to 4.5) (as compared to FIM ($H' = 3.2$ to 4.1) and NEM (2.3 to 4.2)). The

diatoms were represented mainly by *Chaetoceros sp.*, *Navicula sp.*, *Coscinodiscus sp.*, *Thalassiosira sp.*, *Thalassionema nitzchoides*. Among the dinoflagellates, *Scrippsiella sp.*, *Alexandrium sp.*, *Gyrodinium sp.*, *Pronoctulica sp.*, were the dominant genus present. *Chaetoceros sp.*, was high during FIM, while *Thalassionema nitzchoides*, *Thalassiosira sp.*, and *Pronoctulica sp.* were high during the NEM (Fig 7). Diatom *Coscinodiscus sp.*, was high in bottom waters, while dinoflagellate *Scrippsiella sp.* was not found in bottom waters.

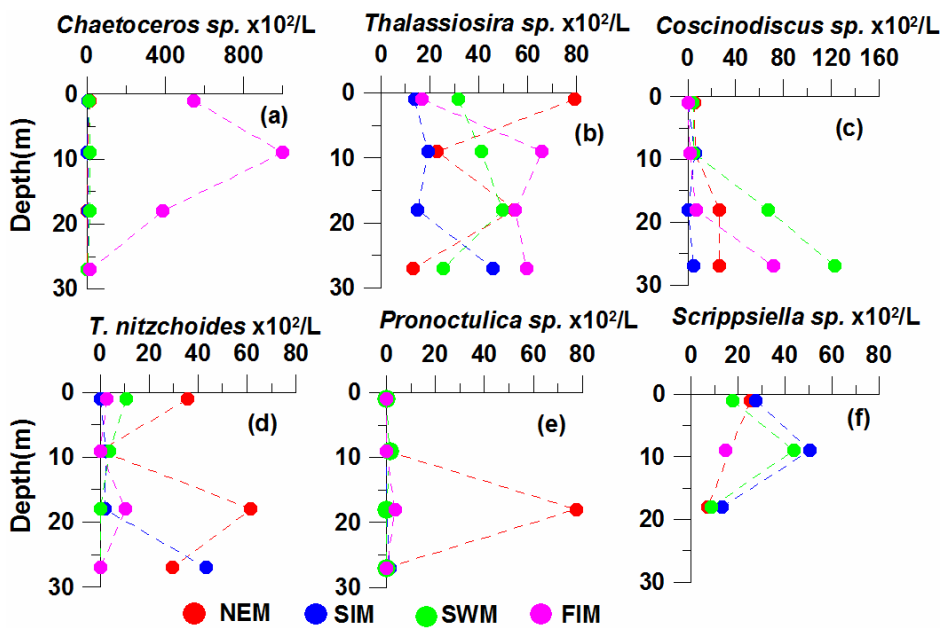


Figure 7: Seasonal variations in distribution of phytoplankton species (cells L⁻¹) in the ASCW during 2015 (a) *Chaetoceros sp.*, (b) *Thalassiosira sp.*, (c) *Coscinodiscus sp.*, (d) *Thalassionema nitzchoides*., (e) *Pronoctulica sp.*, (f) *Scrippsiella sp.*

Table 1: Depth integrated seasonal distribution of diatoms at G5 station.

	NEM	SIM	SWM	FIM
Phytoplankton composition	Cells x 10 ² / L	Cells x 10 ² / L	Cells x 10 ² / L	Cells x 10 ² / L
<i>Actinoptychus spp.</i>	X	11	8	21
<i>Amphora spp.</i>	X	55	X	127
<i>Asterionella japonica</i>	X	11	X	X
<i>Asterionellopsis glacialis</i>	X	X	X	129
<i>Asteromphalus spp.</i>	103	X	X	X
<i>Bacteriastrum furcatum</i>	X	X	X	33
<i>Bacteriastrum hyalinum</i>	X	X	12	72
<i>Cerataulina spp.</i>	X	11	12	X
<i>Chaetoceros spp.</i>	71	99	341	15007
<i>Cocconeis spp.</i>	X	X	12	86
<i>Coscinodiscus spp.</i>	438	76	1221	400
<i>Cyclotella spp.</i>	12	17	19	42
<i>Dactyliosolen fragilissimus</i>	127	17	352	14034
<i>Dactyliosolen spp.</i>	X	22	X	X
<i>Ditylum brightwellii</i>	X	6	69	32
<i>Diploneis spp.</i>	165	17	X	X
<i>Ethmodiscus spp.</i>	12	X	X	123
<i>Entomoneis spp.</i>	15	6	X	X
<i>Eucampia spp.</i>	X	X	108	31
<i>Fragillaria spp.</i>	59	103	401	32
<i>Guinardia flaccida</i>	337	6	890	148
<i>Guinardia striata</i>	X	62	139	264
<i>Gyrosigma sp.</i>	59	112	X	11
<i>Hemiaulus spp.</i>	X	29	23	12
<i>Leptocylindrus mediterraneus</i>	X	X	166	X
<i>Leptocylindrus spp.</i>	X	66	69	X
<i>Licmophora spp.</i>	X	X	23	X
<i>Lioloma pacificum</i>	X	33		X
<i>Meuniera membranacea</i>	X	X	19	X
<i>Meuniera membranacea</i>	X	X	12	X
<i>Navicula spp.</i>	643	239	327	137
<i>Nitzschia spp.</i>	41	313	2752	391
<i>Odontella mobiliensis</i>	X	X	X	113
<i>Odontella sinensis</i>	X	16	X	32
<i>Planktoniella sol</i>	X	X	19	X
<i>Pleurosigma clevei</i>	X	246	X	X
<i>Pleurosigma spp.</i>	139	645	19	193
<i>Rhizosolenia spp.</i>	X	136	2787	139
<i>Surirella spp.</i>	50	22	50	X

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<i>Synedra spp.</i>	27	50	X	21
<i>Thalassionema nitzschooides</i>	847	234	82	105
<i>Thalassionema spp.</i>	X	X	46	93
<i>Thalassiosira spp.</i>	1113	576	1073	1428

Table 2: Depth integrated seasonal distribution of dinoflagellates and cyanobacteria at G5 station.

	NEM	SIM	SWM	FIM
Phytoplankton composition	Cells x 10 ² /L	Cells x 10 ² /L	Cells x 10 ² /L	Cells x 10 ² /L
<i>Amphisolenia bidentata</i>	X	6	X	X
<i>Amylax triacantha</i>	X	X	19	X
<i>Ceratium biceps</i>	X	6	19	12
<i>Ceratium furca</i>	12	22	X	45
<i>Ceratium tripose</i>	X	6	55	X
<i>Chattonella spp.</i>	X	X	243	X
<i>Dicroerisma psiloneriella</i>	X	11	X	X
<i>Dictyocha fibula</i>	X	X	X	11
<i>Dictyocha spp.</i>	X	X	X	31
<i>Dictyocha octonaria</i>	X	34	X	X
<i>Dinophysis caudata</i>	X	X	12	31
<i>Gonyaulax polygramma</i>	X	X	39	111
<i>Gymnodinium spp.</i>	X	46	X	X
<i>Gyrodinium spp.</i>	X	28	550	33
<i>Noctiluca spp.</i>	X	22	46	X
<i>Ornithocercus spp.</i>	X	X	X	33
<i>Oxytoxum nanum</i>	24	27	19	29
<i>Oxytoxum scolopax</i>	12	X	X	X
<i>Pronoctiluca spp.</i>	697	6	12	31
<i>Prorocentrum micans</i>	36	X	12	66
<i>Protoperidinium spp.</i>	71	62	55	29
<i>Pyrocystis fusiformis</i>	X	X	12	X
<i>Pyrocystis noctiluca</i>	59	X	4	X
<i>Pyrophacus sp.</i>	X	28	262	261
<i>Scrippsiella spp.</i>	176	695	549	131
<i>Cyanobacteria spp.</i>	12	51	X	X

3.6 Sources of ON

3.6.1 Influence of freshwater runoff

To assess the impact of riverine discharge on ASCW, the SWM of 2015 and 2016 were compared as the rainfall during both years were very distinct. Sea surface salinity (SSS) was higher during 2015 (34.5) than 2016 (32.5). ON input from freshwater was less in SWM of 2015 as compared to during

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2016 (Fig 6). This high ON during 2016 was also associated with high concentration of marker pigment Zea as compared to SWM of 2015 (Fig. 8).

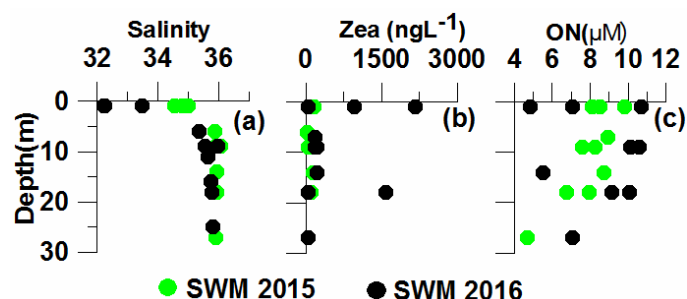


Figure 8: Variations in Salinity, ON, and Zea in the ASCW during SWM of 2015 and 2016.

3.6.2 Aerosol analysis

Aerosol analysis revealed that ON ranged between 9.5% and 32% of the total N during NEM with an average of 15%, whereas the ON decreased during SIM and ranged from 0.8% to 7.5% with an average of 5.3%. Atmospheric ON concentration ranged from 16 to 65 (μMm^{-3}) during NEM and was from 1.3 to 17.8 (μMm^{-3}) during SIM.

3.6.3 Groundwater investigation

In addition to the coastal waters, we carried out investigations on ground waters in Goa. High ON concentrations ($>100 \mu\text{M}$) were observed at 4 sites (C2, C3, V1 and L2; Fig.1) which are very close to the Mandovi and Zuari estuaries which drain to the coastal region. Among the 9 sampling sites (Fig. 1), the maximum concentration of ON was found at station C3 (140 μM). ON concentrations below 10 μM were observed at C1, K1, L1 and L3.

3.7 Canonical correspondence analysis (CCA)

The dynamics of chemotaxonomic pigments and their relation to the environmental variables was studied using CCA. Figure 9(a-d) shows that the first and the second ordination axes in the CCA analysis of individual variables are associated with different chemotaxonomic pigments. During the NEM, Zea and Per were influenced by DO, and ON, whereas Fuco was influenced by salinity, NO_3^- , NH_4^+ and PO_4^{3-} (Fig. 9a). During SIM, Zea and Fuco were influenced by ON, DO, and NO_3^- (Fig. 9b). In SWM, Zea and Per were influenced by ON (Fig.9c). During FIM, Zea and Chl *a* were influenced by temperature and DO, whereas Per was influenced by ON and NH_4^+ (Fig.9d). In

general, ON and DO are the major environmental variables influencing the distribution of chemotaxonomic pigments (Zea, Fuco and Per) during all the seasons.

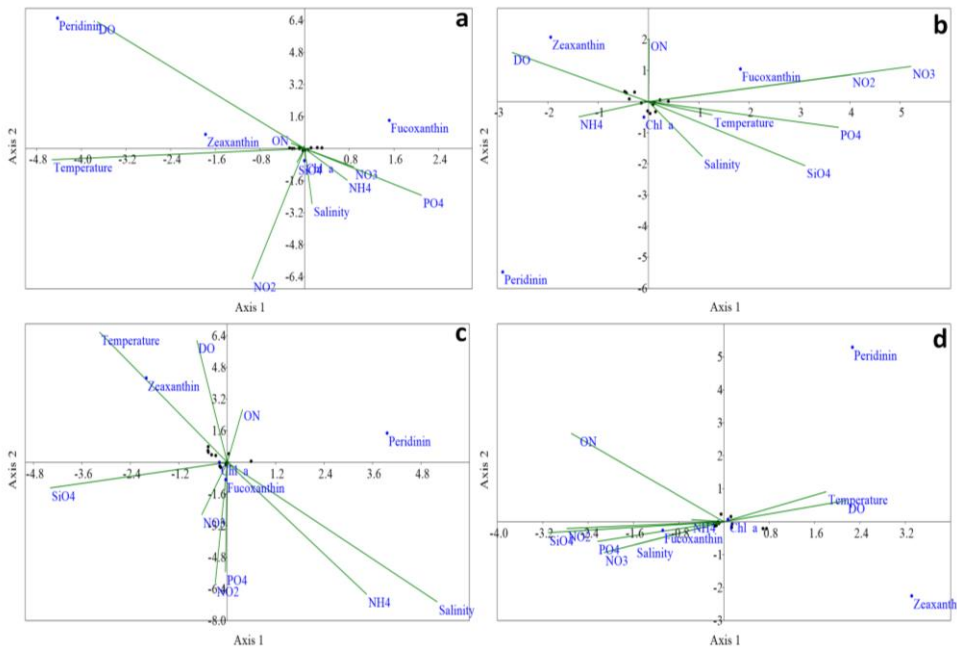


Fig. 9

4. Discussion

The study region is known to be strongly influenced by land driven nitrogen sources (Naqvi et al., 2006), however the impact of excess nitrogen on the phytoplankton communities is less studied. The seasonal ON data showed high concentrations during NEM and FIM as compared to SIM and SWM and were positively correlated with DO (Fig. 9). Comparable ON concentrations (up to 15.3 μM) have been reported from other regions as well (for e.g., Akkeshi Bay, eastern Hokkaido, Japan [Hasegawa et al., 2000], on the shelf waters of Black Sea [Ducklow et al., 2007], and in the Belgian coastal waters [Suratman et al., 2008]).

In the present study, ON comprised 94% of the TN during NEM, 83% during SIM, 81% during FIM and 50% during SWM. This probably associated with the rates of ON turnover during different seasons. High productivity in early SWM season (as seen from Chl *a*) which leading to hypoxia (high heterotrophic activity) in the latter part of SWM might have resulted in higher biological consumption of ON and hence contribute 50% to TN. The high biological production during SWM

results in organic matter storage in surface layers facilitating microbial loop in FIM. Therefore, turnover rates of ON in different seasons assumes significance to assess its contribution to overall biological production and nitrogen cycling. In the following sections, we try to explore the impact of ON towards the phytoplankton diversity and its possible sources in the ASCW.

4.1 Phytoplankton communities under varying nitrogen species

From figure 3, it is clear that nitrogen species concentrations change with seasons as follows. NEM=Low IN & High ON, SIM= Low IN & Low ON, SWM= High IN & Low ON and FIM=High IN & High ON. We tried to understand the phytoplankton preferences for nitrogen species during these seasons. During NEM (Low IN & High ON), the diatoms abundance was low and were dominated by *Thalassiosira spp.* (1113×10^2 Cells / L), *Thalassionema nitzschooides* (847×10^2 Cells / L), *Navicula spp.* (643×10^2 Cells / L), and *Coscinodiscus spp.* (438×10^2 Cells / L, Table 1), while dinoflagellates were dominated by *Pronoctiluca spp.* (697×10^2 Cells / L; Table 2). The low diatom abundance could be due to deeper silicicline, as compared to other seasons (fig. 6). In SIM, when the system had low IN & ON, the diatoms abundance was low and were dominated by *Pleurosigma spp.* (889×10^2 Cells / L) and *Thalassiosira spp.* (576×10^2 Cells / L), while dinoflagellates were dominated by *Scrippsiella spp.* (695×10^2 Cells / L). Nitrogen fixing cyanobacteria *Trichodesmium sp.* (51×10^2 Cells / L) abundance was also maximum during this season. The nitrogen fixing cyanobacteria would have utilized excess phosphate as seen from P* (supplementary Fig. 1). During SWM with high IN & low ON conditions, the diatoms abundance was high, and were dominated by *Rhizosolenia spp.* (2787×10^2 Cells / L) and *Nitzschia spp.* (2752×10^2 Cells / L), while dinoflagellates were dominated by *Gyrodinium spp.* (550×10^2 Cells / L) and *Scrippsiella spp.* (550×10^2 Cells / L). In FIM, when the system had high IN & ON, the diatoms were dominated by *Chaetoceros spp.* (15007×10^2 Cells / L) and *Dactyliosolen fragilissimus* (14034×10^2 Cells / L), while dinoflagellates were dominated by *Pyrophacus sp.* (261×10^2 Cells / L).

In the present study, the contribution of picophytoplankton to the total phytoplankton (f_{pico}) increased from 19% during SWM to 36% during NEM, whereas it was 22% during FIM (Fig. 9). Although highest contribution of picophytoplankton was 41% during SIM, it was associated with nitrogen fixing cyanobacteria such as *Trichodesmium sp.* in the ASCW (Gandhi et al., 2011; Parab et al., 2012; Ahmad et al., 2017; Kumar et al., 2017) as also seen from their maximum abundance during this season (Table 2). From the CCA analysis and calculated excess phosphate, it is clear that PO_4^{3-} is not the limiting factor for cyanobacteria in ASCW. The high ON during NEM correlates with high cyanobacteria as seen from the marker pigment Zea (Fig. 3, 6 and 9), and are known for ON

utilization as a nitrogen source (Billen 1984; Zubkov et al., 2003; Glibert et al., 2004). Although phytoplankton prefer NH_4^+ over other N sources, however under IN-limited conditions as seen from present study during NEM, N availability, rather than N preference, can regulate uptake (Tamminen and Irmisch, 1996). Many marine cyanobacteria, including *Synechococcus* spp., are known to possess ureC genes and can utilize ON such as urea as a sole N source (Collier et al., 1999; Moore et al., 2002).

In the present study also, abundance of *Synechococcus* spp., was high during FIM (high ON) as compared to SIM (low ON) (supplementary Fig 2).

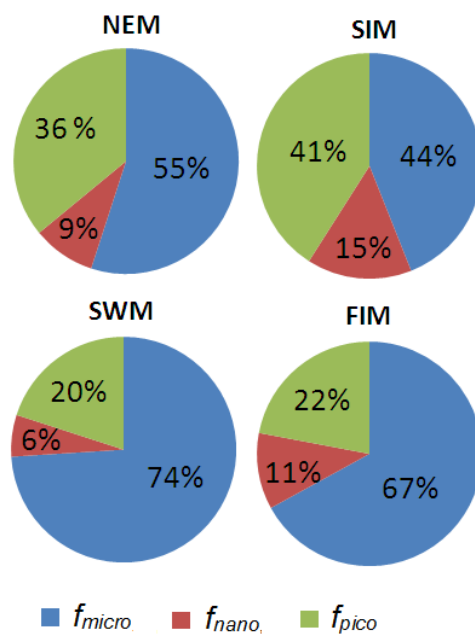


Figure 10: Percentage contribution of various phytoplankton groups (f_{micro} , f_{nano} , and f_{pico}) during NEM, SIM, SWM and FIM in the ASCW

The f_{micro} decreased from 74% during SWM to 55% during NEM (Fig.10). Diatoms are known to be associated with SiO_4^- and IN sources as seen from their high abundance during SWM and FIM when the system had ample SiO_4^- and IN (Fig. 3,5&6). Deeper silicicline during NEM would prevent pumping of SiO_4^- to upper layers (Fig. 5), contributing in low diatom abundance. Though diatoms generally prefer IN (Tamminen and Irmisch, 1996), few species like *Thalassionema nitzschoides* and

Thalassiosira sp. seem to be flourishing during NEM under ON replete conditions (Fig. 7). Our results are consistent with Armbrust et al. (2004) who gave evidences through genomic sequencing that *Thalassiosira pseudonana* can uptake and utilize ON such as amino acids and purines by possessing plasma membrane amino acid transporters. Past autoradiography studies also demonstrated diatom uptake of ¹⁴C-labeled amino acids (Wheeler et al., 1974, 1977). Apart from the two genus mentioned above, *Coscinodiscus sp.* also proliferated in ON rich waters. Among the dinoflagellates, our data suggests that *Pronoctiluca sp.* were higher in ON rich waters (Fig. 7) Among all the phytoplankton, diatom *Thalassiosira sp.* and dinoflagellate *Scrippsiella spp.* were abundant during all seasons, indicating that these species can utilize both IN and ON. Such phytoplankton species capable of utilizing ON will have competitive advantage over other phytoplankton (Bronk et al., 2007) in future ON rich scenarios. Considering the future projections of increase in ON deposition over the Asia and Indian Ocean (Kanikadou et al., 2016; Jickells et al., 2017), the ON enhancement might alter the phytoplankton community in the ASCW.

4.2. Possible sources of ON in the coastal waters, off Goa

4.2.1. Riverine influx

The global riverine nitrogen fluxes to the oceans have probably doubled since 1860 (Moore et al., 2013; Beusen et al., 2016) and are expected to increase by 2030 (Seitzinger et al., 2010). The global riverine flux estimate at fresh/saltwater boundary for DON is 11 TgN yr⁻¹ (Seitzinger et al., 2005, 2010). Riverine nitrogen fluxes to the Arabian Sea depend on the fresh water discharge, which is directly linked to the SW monsoon. For instance, the rainfall during SWM of 2015 was low (2265 mm) compared to 2016 (2845 mm). Freshwater runoff is also reflected in sea surface salinity with higher values during 2015 (34.5) compared to 2016 (32.5). The freshwater runoff resulted in additional 3 μM ON during SWM of 2016 highlighting riverine influx as a source of ON. This excess ON might have resulted in high abundance of cyanobacteria (as seen from the marker pigment Zea) during SWM of 2016 (Fig. 8)

4.2.2 Atmospheric sources

Atmospheric input is an important source of ON in the coastal waters (Vet et al., 2014). Air mass trajectories for various seasons indicate a strong probability of polluted air masses passing over the central Indian Peninsula to the ASCW in NEM and FIM. Rengarajan et al. (2011) reported the formation of secondary organic aerosols during NEM over the western India. Our aerosol measurements showed significant variations in ON during NEM (9.5 to 32 % of the TN) and SIM (0.8 to 7.5% of the TN). These aerosols would have deposited on the surface waters through wet

and/or dry deposition processes, thus contributing towards high ON concentrations in the water column during NEM. This is important as ON such as urea supports most of the phytoplankton nitrogen requirement in the surface waters (Bradley et al., 2010). ON compounds represent both a nitrogen and an energy source for heterotrophic microorganisms in the sea (Billen 1984). The understanding of aerosol ON contribution is also important because recently, Mao et al. (2014) reported that the mean aerosol optical depth (AOD) over the Indian Ocean has increased in the last ten years. In addition, based on modeling study Kanakidov et al. (2016) predicted higher ON deposition in the future over the northern Indian Ocean.

4.2.3. Resuspension of bottom sediments

ON concentrations were high in the bottom waters which also reflected high concentration of NH_4^+ (Fig. 3). High NH_4^+ at the CaTS transect was earlier reported by Naqvi et al. (2000, 2006), however no previous data on ON is available from the study site. High ON concentrations in the bottom waters were reported earlier in Belgian coast (De Galan et al., 2004; Van der Zee and Chou 2005). Basford et al. (1993) suggested that the high concentrations in the bottom waters may be a result of resuspension of bottom sediments with high organic carbon. Bottom sediments off Goa are moderately rich in organic matter with C_{org} varying between 2 and 3.5% in the study region (Pratihary et al., 2014, Naik et al., 2016). High PON concentrations in bottom waters (Fig. 4) indicate that resuspension of bottom sediments could be a source of ON. In addition, a high resolution bottom water sampling also confirms high ON, especially at stations G3 and G4 (supplementary Fig. 3) Hence, resuspension of bottom sediment could be a possible reason for high ON in the bottom waters in the ASCW.

4.2.4. Groundwater contribution

Our measurements in few ground water samples suggest high ON concentrations ($>100 \mu\text{M}$) at 4 sites which are very close to the Mandovi and Zuari estuaries draining to the coastal region (C2, C3, V1 and L2; Fig.1). The highest concentration of ON was $140 \mu\text{M}$ in the ground water (at C3), which is ~ 10 times higher than that seen in the coastal waters off Goa. These high ON waters could possibly reach Mandovi or Zuari estuaries through groundwater intrusion and can result in high ON in the coastal waters. Additionally, ground water intrusion may take place directly at the coastal region through submarine groundwater discharge (SGD) (Rengarajan and Sarma 2015). The high ON concentrations in the shallow stations (G3 and G4) during FIM and NEM may be due to submarine ground water discharge, however SGD data is not available at the study site.

Conclusions

Our study on nitrogen species in the ASCW clearly shows that the region is dominated by ON throughout the year and accounts for >90% of the total nitrogen during NEM. The nitrogen species changes seasonally in the ASCW with Low IN & High ON during NEM, Low IN & Low ON during SIM, High IN & Low ON during SWM and High IN & High ON during FIM. During NEM and FIM, air mass that passes over the land into coastal sea carrying sizeable ON (15%) act as source of ON to the surface waters in the ASCW. Diatom abundance was high during high IN conditions, while cyanobacteria and some species of diatoms (*Thalassionema nitzchoides* and *Thalassiosira sp.*) and dinoflagellates (*Pronoctiluca sp.*) were dominant during high ON conditions. Diatom *Thalassiosira sp.* and dinoflagellate *Scrippsiella sp.* abundance was high during all seasons, indicating that these species can utilize both IN and ON. Our results indicate that phytoplankton capable of utilizing ON may possess competitive advantage over other phytoplankton in future ON rich waters. Atmospheric deposition, riverine input, resuspension of bottom sediment and ground water intrusion could be the possible sources of ON in the ASCW. The answers to open ended questions in Section 4 on the source strengths of ON to coastal waters need immediate attention.

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Table 1: Seasonal variations in P* in the ASCW during 2015.

Station	Depth	NEM	SIM	SWM	FIM
<u>G6</u>	<u>1</u>	<u>0.271</u>	<u>0.173</u>	<u>0.389</u>	<u>0.167</u>
<u>G6</u>	<u>9</u>	<u>-</u>	<u>0.055</u>	<u>0.632</u>	<u>0.171</u>
<u>G6</u>	<u>18</u>	<u>-</u>	<u>0.263</u>	<u>0.473</u>	<u>-</u>
<u>G6</u>	<u>27</u>	<u>0.261</u>	<u>0.170</u>	<u>0.704</u>	<u>-</u>
<u>G6</u>	<u>38</u>	<u>0.289</u>	<u>0.245</u>	<u>0.761</u>	<u>0.578</u>
<u>G5</u>	<u>1</u>	<u>0.298</u>	<u>0.097</u>	<u>0.529</u>	<u>-</u>
<u>G5</u>	<u>9</u>	<u>0.321</u>	<u>0.107</u>	<u>0.568</u>	<u>0.251</u>
<u>G5</u>	<u>18</u>	<u>0.321</u>	<u>0.088</u>	<u>0.673</u>	<u>0.194</u>
<u>G5</u>	<u>27</u>	<u>0.608</u>	<u>0.223</u>	<u>1.220</u>	<u>0.476</u>
<u>G4</u>	<u>1</u>	<u>0.294</u>	<u>0.198</u>	<u>0.623</u>	<u>0.145</u>
<u>G4</u>	<u>9</u>	<u>0.295</u>	<u>0.163</u>	<u>0.891</u>	<u>0.208</u>
<u>G4</u>	<u>18</u>	<u>0.283</u>	<u>0.190</u>	<u>1.845</u>	<u>0.241</u>
<u>G3</u>	<u>1</u>	<u>0.258</u>	<u>0.234</u>	<u>0.752</u>	<u>0.124</u>
<u>G3</u>	<u>7</u>	<u>0.295</u>	<u>0.233</u>	<u>0.831</u>	<u>0.220</u>
<u>G3</u>	<u>13</u>	<u>0.359</u>	<u>0.360</u>	<u>1.956</u>	<u>0.213</u>

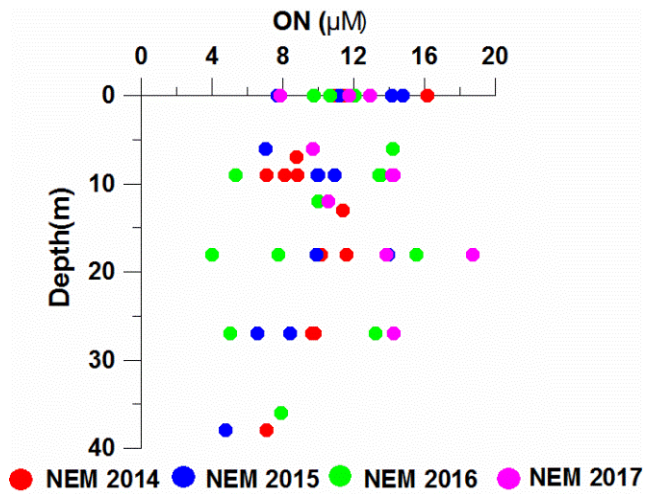
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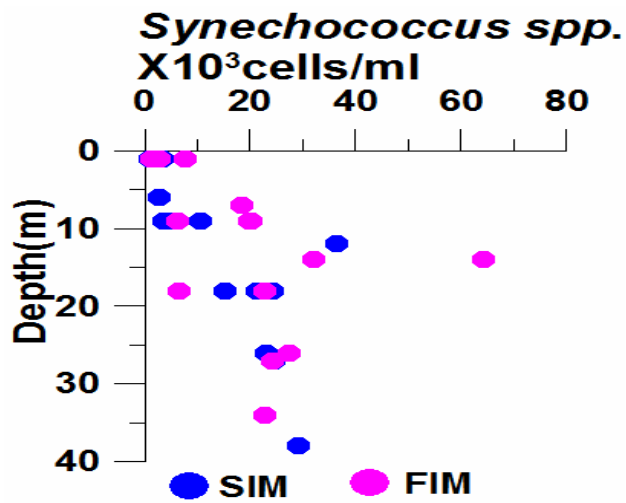
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SUPPLEMENTARY FIGURE 1: Spatial variations in ON concentrations during NEM of 2014 to 2017.

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SUPPLEMENTARY FIGURE 2: Seasonal distribution of cyanobacteria *Synechococcus* sp. along G3 to G6.



SUPPLEMENTARY FIGURE 3: Spatial variations in ON concentrations during NEM of 2019.

