

Accumulation of dissolved organic carbon and nitrogen in the photic zone in the nitrogen-depleted waters of the Bay of Bengal.

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Abstract

Dissolved organic matter (DOM) accumulates in the upper ocean for several days to years and supports both autotrophic and heterotrophic activities. To examine the source of DOM and its role in plankton metabolic processes, 18 stations were sampled in the Bay of Bengal (BoB) during June 2019. The concentration of DOC in the upper ocean exhibited a significant relationship with Chlorophyll-a (Chl-a), particulate organic carbon (POC) and DOC exudation rates, suggesting possible sources through *in situ* biological processes. The mean DOC: DON ratio (8.3 ± 2) and isotopic composition of carbon in DOC ($\delta^{13}\text{C}_{\text{DOC}}$ of $-21.2 \pm 1\%$) indicates a marine origin in the BoB during the study period. On the other hand, dissolved organic nitrogen (DON) exhibited a significant weak inverse relationship with salinity in the northern BoB indicating some contribution from the riverine source. Phytoplankton uptake rates of amino acids (glycine or aspartic acid) were 10 times lower than dissolved inorganic nitrogen (DIN). The accumulation time of semi-labile DOC, produced by phytoplankton, in the upper ocean varied between 2.5 and 7.5 months in the BoB with the longer rate in the anticyclonic (ACE; 5.6 ± 1 months) than cyclonic eddy (CE; 3.6 ± 0.5 months) regions. This study suggests that DOM is produced through *in situ* processes and supports phytoplankton biomass in the BoB than hitherto hypothesized as river-borne sources and refractory in nature.

1. Introduction

The oligotrophic regions of the open ocean are characterized by strong stratification with a lower amplitude of seasonal variability in temperature and biogeochemical properties than in the temperate region. Since these regions represent about 60% of the global oceanic area, the biogeochemical processes that occur in these regions have global significance (Karl, 2002). In the oligotrophic regions, the concentration of inorganic nutrients is low, and often below detection limits of conventional methods (McCarthy, 1980), resulting in the dominance of microbial food web involving dissolved organic matter (DOM) as a substratum (e.g. Azam et al. 1983, Legendre and Le Fèvre 1995; Legendre and Rassoul-zadegan 1995). Several processes, such as cell lysis (e.g. Agustí et al. 1998), grazing (e.g. Nagata and Kirchman, 1992), and release of DOM from the cells of recently photosynthesized organic matter, contribute to the DOM pool (eg: Nagata, 2000; Thornton, 2014) in the upper ocean. Since DOM released by phytoplankton is labile in nature, it may enter to food web through the microbial loop to support higher trophic level organisms (Fogg, 1966; 1983).

The Bay of Bengal (BoB) is a tropical basin and receives a significant amount of freshwater through major rivers, such as Ganges, Brahmaputra, Irrawady and Salween riverine systems, leading to strong salinity stratification (Ittekkot et al., 1991; Madhupratap et al., 2003). Most of the nutrients brought by the rivers are consumed within the estuary itself and a small fraction is fluxed to the coastal BoB (Krishna et al., 2015a), hence oligotrophic conditions prevail throughout the year in the BoB with inorganic nutrients under detection limits (Sarma et al., 2018; 2020; Sherin et al., 2019). Recently Sarma et al. (2019) suggested that organic nutrients (dissolved organic nitrogen (DON) and phosphorus (DOP)) supports phytoplankton biomass and primary production in the BoB in the absence of inorganic nutrients. Recently, Rao et al. (2021) observed that $\sim 45 \pm 5\%$ of the primary production is released as DOC into the surrounding waters from the phytoplankton cells that may contribute to an increase in DOC pool in the BoB. Shah et al. (2018) also reported a high concentration of DOC in the BoB and attributed it to possible contribution from the river discharge and primary production. Krishna et al. (2015b) estimated that ~ 1.82 Tg of riverine DOC is fluxed annually to the BoB. Since the influence of river discharge decreases from north to south, the high concentration of DOC in the central and southern BoB may be contributed by *in situ* processes and both riverine and *in situ* processes in the north.

It is hypothesized that a significant fraction of the DOC in the upper ocean is contributed by labile/semi-labile, produced by *in situ* processes, and supports heterotrophic carbon demand through the microbial loop in the BoB. This would explain the potential source of carbon supporting almost equal biomass of mesozooplankton in the BoB (974 ± 474 mg C m⁻²; Ramaiah et al., 2010) and the

Arabian Sea (1080 ± 50 mg C m⁻²; Smith et al., 1998) despite 2-3 times lower primary production in the former than latter basin (Gauns et al., 2005). This would also further explain the export of a small fraction of primary production (<5%; Anand et al., 2017) to the twilight zone in the BoB due to the accumulation of a significant fraction of organic matter as DOC in the surface layers. If this hypothesis is correct, the accumulation time of the DOC in the surface layer may be faster than anticipated from river-borne DOC, which is expected to be refractory. To test this hypothesis, we fixed the objectives of this study were to estimate: 1) source of DOC using stable isotopic composition of carbon ($\delta^{13}\text{C}_{\text{DOC}}$), 2) the role of organic nutrients in supporting phytoplankton biomass/production and 3) the accumulation time of DOC and POC in the photic zone in the BoB.

2. Material and methods

2.1. Sampling

Water in the upper 100 m of the water column was sampled onboard ORV Sagar Nidhi (Cruise No. SN142) in the western BoB during 11-29 June 2019 (Fig. 1). In this cruise, 18 stations were occupied and deck incubation experiments were conducted at 14 stations (see Fig.1). Seawater samples from different depths were collected using 12 five litre Niskin bottles connected to the rosette. Physical properties, such as temperature, conductivity and depth, were measured using sensors (19 Plus, Sea-Bird Electronics, USA) attached to the rosette. Phytoplankton biomass, as chlorophyll-a, was measured using a fluorescence sensor (Wet Laboratories, USA). The detection limits for temperature, salinity, pressure and fluorescence were 0.001°C, 0.001, 0.1m and 0.01 µg/l respectively. Samples for nutrients were collected in 100 ml plastic bottles and were kept in the refrigerator and analysed within 2-3 hours after sampling. Samples for dissolved organic carbon (DOC) and total nitrogen (TN) were collected by passing samples from Niskin bottle through pre-combusted GF/F filter and collected the filtrate in pre-acid cleaned (3 N HCl) glass bottles (30 ml) with Teflon tap and HCl was added to bring pH to 3 and stored in the room temperature.

2.2 Hydrographic measurements

The concentration of nutrients (nitrate, nitrite, ammonium, phosphate, organic phosphate) were measured, soon after collection on-board, following the colourimetric procedure of Grasshoff et al. (1983) using Eco-Lab autoanalyzer. The precision of nitrate+nitrite, nitrite, ammonium, and phosphate measurements were ± 0.05 , 0.04, 0.03, and 0.03 µM respectively by repeated measurement of the same sample (n=10). The concentration of total phosphate was measured following Grasshoff et al. (1983) in which potassium persulphate and sulphuric acid were added and placed in an autoclave for 30 minutes to convert to inorganic phosphate and measured using the autoanalyzer. The concentration of

dissolved organic phosphate (DOP) was estimated as a difference between total phosphate and inorganic phosphate. The precision of the dissolved organic phosphate was $\pm 0.08 \mu\text{M}$ based on repeated measurement of the same sample ($n=10$). Fluorescence data, obtained by the sensor, were calibrated with chlorophyll *a* (Chl *a*) measured at discrete depths using High-Pressure Liquid Chromatography (HPLC) following Roy et al. (2015).

2.3. Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) measurements

DOC and total nitrogen (TN) were measured using DOC/TN analyser (IsoTOC; M/s Elementar analytics, Germany) following the high-temperature catalytic combustion method. The seawater samples were first acidified with supra-pure hydrochloric acid and purged with high purity helium to remove inorganic carbon. About $50 \mu\text{l}$ of the acidified sample was injected and converted DOC and DON into CO_2 and N_2 respectively and their signals were measured using a Non-Dispersive Infra-Red (NDIR) detector. The instrument was calibrated using high purity glutamic acid. The precision of the DOC measurements was $<3\%$ based on repeat injections of the same sample ($n=10$). The DON is estimated by subtracting dissolved inorganic nitrogen (DIN) from TN. The precision of the DON is dependent on the ratio of DON/TDN and it was estimated following Saunders et al. (2017). The precision of DON was $\pm 0.9 \mu\text{M}$ in the upper 25m of the water column, where DIN concentrations were low, and $\pm 1.6 \mu\text{M}$ at depth below 25 m depth, where DIN concentrations were high especially in the CE regions.

2.4. Measurements of the isotopic composition of carbon in DOC

Isotopic composition of DOC was measured by carrying the CO_2 , after DOC oxidation in the IsoTOC, to the Isotope Ratio Mass Spectrometer (IRMS; Isoprime, UK) in online mode. The high purity CO_2 tank was calibrated with IAEA standards and laboratory standards such as glutamic acid, and alanine. The isotopic composition of the DOC was measured with reference to the tank CO_2 . The isotopic composition of carbon in DOC was reported in PDB (Pee Dee Belemnite). The precision of the measurements was 0.3% based on repeated measurements ($n=10$) of the same sample.

2.5. Uptake rate measurements of DIN and amino acids

The DIN and DON uptake rates were measured in the upper 50 m of the water column at different light depths 100, 75, 50, and 25% of the incident radiation at the surface using neutral screens. At each depth about 5 L of water filtered through pre-combusted (400°C , 12h) GF/F filter and natural nitrogen isotopic composition of particulate organic nitrogen (PON) was measured. About one litre of the sample was collected in a Nalgene bottle and 99% $\text{Na}^{15}\text{NO}_3$, $^{15}\text{NH}_4\text{Cl}$, glycine ($\text{C}_2\text{H}_5^{15}\text{NO}_2$) and aspartic acid ($\text{C}_4\text{H}_7^{15}\text{NO}_4$) (Sigma Aldrich, USA) enriched tracer was added to the sample and

incubated in 3 sets for 4 hours interval each (0600 to 1000h, 1000 to 1400h and 1400-1800h). The daily uptake rates were estimated as the sum of rates of three incubations. The concentration of the tracer was added as 10% of the ambient concentration of NO_3 , NH_4 and DON following Watts and Owens (1999). All the samples were incubated in triplicate in light and duplicate bottles in dark conditions. The temperature in the incubator was maintained to *in situ* temperature. After the incubation period, the sample was filtered through pre-combusted (at 400°C for 12 h) GF/F (Whatman) filters and dried at 50°C for 24 h. The content and atomic ratios of the nitrogen were measured using an Elemental analyser (Isocube; Elementaar analytics, Germany) coupled to the IRMS (Isoprime, UK). The uptake rates of enriched inorganic and organic nitrogen were estimated following Dugdale and Wilkerson (1986) after removing the uptake in the dark.

3. Results

3.1. *Spatial Variability in hydrographic properties*

In this study, two cyclonic (CE) and one anticyclonic eddy (ACE) were sampled in the eastern and central BoB (Fig. 1). The path of eddies and hydrographic structure of the eddies were presented elsewhere (Sarma et al., 2020), however, we presented briefly here. The temperature in the upper 50 m of the water column was warmer in the ACE region whereas cooler waters were observed in the CE region (Fig. 2a). Cooler waters were also observed between stations 8 and 11 associated with high local winds and mixing. Similarly, the entire upper 50 m of the water column was 33.5 salinity whereas salinity increased by 0.5 below the depth of 40 m, except in the ACE region (Fig. 2b). Occurrence of low saline (<32-33) water was noticed in the northern BoB (stns. 11 to 14) (Fig. 2b). Overall salinity in the western BoB was lower than that of the eastern. The phytoplankton biomass (as Chl-a) varied between 0.1 and 0.7 mg m^{-3} with prominent subsurface Chl-a maxima at the depth below 40 m in the entire study region (Fig. 2c). The surfacing of subsurface Chl-a maxima was noticed at stations between 8 and 11 associated with high local winds (Fig. 2c).

3.2. *Spatial variations in dissolved inorganic and organic nutrients*

The concentration of nitrate varied between <0.1 and 0.2 μM in the upper 50 m of the water column in the ACE region and it was >0.5 μM in the CE and no eddy regions (Fig. 3a). A significant increase in nitrate (>0.5 μM) concentration was noticed in the CE region. Higher Chl-a concentration was noticed in the stations between 8 and 11 associated with low concentrations of nitrate (Fig. 3a, and 2c). Low concentrations of phosphate (<0.1 μM) were observed in the upper 50 m of the water column in the ACE region and a significant increase was noticed at the depth below 20 to 40 m in the CE region (Fig. 3b). A higher concentration of phosphate was noticed at stations between 8 and 11 associated

with an increase in Chl-a (Fig. 3b). The concentration of silicate was mostly higher ($>1.5 \mu\text{M}$) in the upper 50 m of the water column in the entire study region (Fig. 3c). A significant increase in silicate concentration was observed in the CE region associated with phosphate and nitrate. The concentration of ammonium was low ($<0.05 \mu\text{M}$) in the entire water column in the ACE and upper 20 m of the water column in the CE region but increased up to $0.2 \mu\text{M}$ at the depth below 40 m.

The concentrations of DON varied between 7.5 and $18 \mu\text{M}$ in the BoB, higher in the upper 40 m than those at depths below (Fig. 4a). The concentration of DON was about 100 to 150 times higher than DIN in the study region (Fig. 3a). A higher concentration of DON was observed in the western (stns. 14-18) than eastern BoB associated with higher nitrate concentrations in the former than latter (Fig. 3a and 4a). The concentration of DON was decreased to $<8 \mu\text{M}$ at 50 m depth. The concentration of DOP varied between 0.2 and $1.5 \mu\text{M}$ with higher concentrations in the eastern than western BoB (Fig. 4b). The concentration of DOP was 5 to 7 times higher than inorganic phosphate. Due to the low concentration of inorganic nitrogen and phosphorus in the mixed layer, the contribution of DON and DOP to total nitrogen and phosphorus comes to 85 and 95% in the study region respectively. The DON/DOP ratio varied between 10 and 60 in the BoB with lower (<30) in the eastern than western BoB (40-60).

3.3. Spatial variations in dissolved organic carbon and its isotopic composition

The concentration of DOC varied between 75 and $120 \mu\text{M}$ in the BoB and exhibited patchy maximum in the upper 20 m of the water column and decreased with depth. The DOC concentrations were slightly lower in the ACE than in other regions. A higher concentration of DOC (100 - $120 \mu\text{M}$) was observed in the upper 20 m of water column associated with low salinity (stns 12-13) in the northern BoB (Fig. 4c). The concentrations of DOC was higher in the eastern than western BoB in the upper 50 m of the water column. The DOC: DON ratio varied between 5.5 and 13 in the study region and higher ratios (12-13) were observed in the low salinity region in the northern BoB with the mean ratio of 8.3 ± 2 in the study region. The $\delta^{13}\text{C}_{\text{DOC}}$ varied between -23.3 and -19.5% in the BoB in the study region with lighter values of $-22.9 \pm 0.5\%$ in the low salinity region (Fig. 4d). Relatively lighter values were observed in the western than eastern BoB. The mean $\delta^{13}\text{C}_{\text{DOC}}$ in the study region comes to $-21.1 \pm 1\%$.

3.4. Spatial variations in inorganic and organic nitrogen utilization rates

DIN uptake rates in the photic layer varied between 0.025 and $0.06 \mu\text{mole l}^{-1} \text{d}^{-1}$ in the study region (Fig. 5a). Lower uptake rates were observed in the south compared to northern BoB. Lower DIN uptake rates were observed in the ACE region ($\sim 0.03 \mu\text{mole l}^{-1} \text{d}^{-1}$) than CE and no eddy regions ($\sim 0.05 \mu\text{mole}$

$l^{-1} d^{-1}$). The amino acids (glycine and aspartic acid) uptake rates in the photic layer varied between 0.002 and 0.006 $\mu\text{moles } l^{-1} d^{-1}$ in the study region (Fig. 5b). The amino acid uptake rates were about 10 times lower than DIN uptake rates in the BoB. Relatively higher uptake rates of amino acids are noticed in the ACE (0.005 $\mu\text{moles } l^{-1} d^{-1}$) than CE (0.003 $\mu\text{moles } l^{-1} d^{-1}$) region.

4. Discussion

4.1. Evaluation of source of DOC in the BoB

The concentrations of DOC in the mixed layer of the BoB were higher than that in other oceanic regions and consistent with earlier reports (Fernandes et al., 2008; Hansell et al., 2009; Shah et al., 2018). The higher concentrations of DOC in the BoB is attributed to the river discharge and primary production (Shah et al., 2018). The higher concentrations of DOC (100-120 μM) was observed in the northern BoB associated with low salinity (~ 31.5), suggesting the possible riverine source of DOC. The inverse relation observed between salinity and DOC concentration further confirms the possible source of river discharge in the northern BoB (Fig. 7a). On the other hand, if the data from the low salinity region (Station 11) is excluded, the remaining data did not display a significant relationship between DOC and salinity ($r^2=0.09$). The concentration of DOC decreased towards the south to 80 to $<100 \mu\text{M}$ and it may probably be due to a decrease in river discharge influence as indicated by increasing salinity. The higher concentrations of DOC by 10-20% are reported in the oligotrophic region in the North and South Pacific Ocean (Church et al., 2002; Raimbault et al., 2008) and North Atlantic (Kepkay and Wells, 1992). The elevated DOC concentrations at the surface are reported to associate with high primary production (Raimbault and Garcia, 2007). The strong linear relationship between Chl-a and DOC indicates a possible source of DOC through *in situ* production including in the low salinity region (Fig. 7b).

To examine the potential source of DOC, the elemental ratios of DOC, DON and DOP and isotopic composition of carbon in DOC is examined. The DOC/DON ratio of dissolved organic matter varied between 5.5 and 19 in the study region with higher values in the low salinity region (12-19) in the northern BoB with a mean of 9.4 ± 2 and it is close to that of the global mean upper ocean DOM (13.6 ± 3 ; Benner, 2002). The higher DOC/DON ratio suggests that N is relatively depleted in DOM in the surface waters as mean marine plankton is 6.6 (Redfield et al., 1963) but it is lower than terrestrial source (21-25; Pocklington and Leonard, 1979; Louchouart et al., 1997; Stonge and Hillaire-Marcel, 2001). On the other hand, DON/DOP ratio varied between 2 and 49 with a mean ratio of 21 ± 9 suggesting that enriched DON over the DOP than Redfield value of 16. In general, higher DOC/DON and DON/DOP ratios are reported in the upper ocean and attributed to selective remineralization of N

and P containing compounds relative to carbon. The photic layer contains some fraction of the recalcitrant DOC and DON. Assuming the deepwater DOC and DON are recalcitrant (Berner, 2002), which is about 43 and 3 μM respectively at 1000 m in the BoB (deep water data was not presented), and the same concentration of recalcitrant DOC may be present in the upper ocean as well. This may be the potential reason for a relatively higher C/N ratio (9.4 ± 2) than the classical Redfield ratio of 6.6. Excluding old calcitrant DOM, the DOC/DON ratio of the freshly formed DOM (excess DOM in the photic zone relative to deep water) was around 7.2 ± 1.5 suggests *in situ* processes contributed to the DOC and DON in the photic zone.

The isotopic composition of DOC ($\delta^{13}\text{C}_{\text{DOC}}$) varied between -19.5 and -24.5‰ with relatively depleted values were noticed (-23.5 to -22.5‰) in the low salinity region in the northern BoB whereas it was varied between -19.5 and -22.5‰ with a mean of $-21.2\pm 1\%$ (Fig. 4d), which suggests typical marine signatures (Druffel et al., 2017; Barber et al., 2017). The typical marine planktonic organic matter contains $\delta^{13}\text{C}_{\text{DOC}}$ signatures of -19 to -24‰ compared to terrestrial organic matter of ~ -28 to -25‰ (Peterson and Fry, 1987; Krishna et al., 2014; Sarma et al., 2014). Therefore both $\delta^{13}\text{C}_{\text{DOC}}$ and DOC/DON ratios suggest that *in situ* processes contribute to the DOC pool in the BoB during the study period. The bulk DOC (as well DON and DOP) is typically assumed to be origin in the surface ocean via phytoplankton excretion, cell lysis or solubility of living and detrital POM, sloppy feeding at various trophic levels (Williams, 1975). Therefore, the DOC exudated by the phytoplankton may contribute significantly to the DOC pool in the upper ocean in the BoB.

4.2. Role of phytoplankton exudation on DOC accumulation in the upper ocean

Phytoplankton releases about 5-10% of photosynthetic carbon under rapid growth in nutrient-replete conditions and it is higher in the nutrient-limited growth, but it can vary between 4.5% and 65% in different basins in the global ocean (Carlson, 2002). Recently Rao et al. (2021) measured that about $45\pm 5\%$ of the primary production is released as DOC to the surrounding waters in the BoB due to the existence of oligotrophic conditions. The concentration of DOC displayed strong linear relation with Chl-a, POC and DOC exudation rates in the BoB (Fig 7b,d) suggesting that a significant fraction of the DOC may be contributed by *in situ* productions in the upper ocean. In addition, DOC release is greatly increased by grazing of protists and copepods (Strom et al., 1997) and its contribution is unknown in the BoB. Zweifel et al. (1993) found the promotion of DOC breakdown in the nutrient replete system and preservation in the nutrient deplete conditions. Bacteria are unable to utilize carbon-rich organic matter, such as carbohydrates, under nutrient-deficient conditions (Cauwet et al., 2002) resulting in accumulation of DOC in the surface waters that indicates long-term malfunctioning of the

microbial loop and also competition for inorganic nutrients for decomposition of DOC (Thingstad et al., 1997; Tanaka and Rassoulzadegan, 2002). The accumulation of DOC in the upper ocean is also caused by the nature of the DOC. Carbon-rich carbohydrates are released to the surface ocean through phytoplankton extracellular release. High molecular weight DOM, contributed by polysaccharides (>1000 Da) (Benner et al., 1992; McCarthy et al., 1996; Skoog and Benner, 1997), is difficult to degrade microbially resulting in the accumulation of DOC in the surface ocean for some period. The amount of recalcitrant DOM production in the upper ocean is dependent on the phytoplankton community structure (Aluwihare and Repeta, 1999). The strong relationship between DOC and exudation rate of DOC (Fig. 7d) indicates that a significant fraction of DOC is produced through the release of DOC from the phytoplankton cells leading to its accumulation in the surface ocean. Due to the lack of inorganic nutrients in the surface ocean, DOC degradation will be slower resulting in accumulation. In addition to this, the quality of organic matter and its composition also contributes to its accumulation and it is unclear in the BoB.

4.3. Fate of DOC in the upper ocean in the BoB

Seasonal accumulation of DOC during the stratified period and mixed with the subsurface water during winter mixing was reported in several oceanic environments (Copin-Montegut and Avril, 1993; Carlson et al., 1994). Perennial occurrence of stratification and absence of winter-overturning lead to accumulation of DOC that acts as a large and long-term reservoir of biological carbon in the upper ocean. The other way of transport of DOC is via diffusion or lateral transport to the south Indian Ocean. The diffusive flux of the DOC, DON and DOP can be computed as $F = K_z \delta_{OM}/\delta_z$ where K_z is the diffusion coefficient and δ_{OM}/δ_z is the concentration gradient of DOC, DON and DOP in and out of the mixed layer. K_z is rarely experimentally measured in oceanic waters. Sarma et al. (2019) estimated K_z using the relationship between $\partial SiO_4/\partial z$ and vertical stability ($N^2 = g(\partial\rho/\partial z)/\rho$) to be $3.7 \pm 1.2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ in the BoB. Using the estimated K_z and concentration gradient between within and below the mixed layer, the diffusive fluxes for DOC, DON and DOP were estimated as 0.74, 0.29 and 0.03 $\text{mmol m}^{-2} \text{ d}^{-1}$ respectively. Anand et al. (2017) measured particle flux at 100 m using the Thorium-234 scavenging method in the BoB and found it to vary between 0.1 and 1.6 (mean of 0.8 ± 0.3) $\text{mmol C m}^{-2} \text{ d}^{-1}$ and it is consistent with the DOC diffusive fluxes. Anand et al. (2017) found that <5% of the primary production is exported to the subsurface waters in the BoB and it has been attributed to consumption of primary production by heterotrophs in the upper ocean before it sinks to subsurface layers. The low sinking carbon fluxes may also be caused by the release of a significant amount of primary production as DOC and conversion of this DOC and its accumulation in the surface water over

some time. A significant relationship between POC and DOC in the photic layer (Fig. 7c) indicates possible conversion between these two pools through bacterial uptake and transfer to zooplankton via microbial food web. In addition to this, DOC may be transported by surface currents to the south Indian Ocean where it may support heterotrophic activity.

4.4. *Organic matter accumulation time in the upper ocean*

Ogawa and Tanoue (2002) explained that deepwater contains refractory DOC, which is quite resistant to microbial degradation with an average age of several thousands of years. The mean concentration of deepwater DOC was $\sim 43 \mu\text{M}$ (compiled by Ogawa and Tanoue, 2002). The higher concentrations of DOC in the upper ocean (mainly photic zone) is contributed by labile, semi-labile and refractory DOC (Kirchman et al., 1993; Carlson and Ducklow, 1995; Cherrier et al., 1996; Romera-Castillo et al., 2016). Assuming refractory DOC is uniformly distributed in the entire water column, the semi-labile DOC can be estimated as excess DOC over deep water value. The mean excess DOC in the photic layer comes to $47 \pm 10 \mu\text{M}$ during the study period in the BoB. Rao et al. (2021) measured the DOC exudation rates (DOC production) during the same cruise (SN142) of this study and found them to vary between 0.002 and 1.3 (mean 0.4 ± 0.1) $\mu\text{M}/\text{d}$ in the study region. Assuming that the estimated semi-labile DOC is produced by the phytoplankton, the accumulation time was estimated as a product of mean photic zone semi-labile DOC divided by mean DOC production rates in the photic zone. The estimated accumulation time varied between 4.5 to 18 months in the photic zone with higher ACE (11.5 ± 2 months) than CE (6 ± 1 months) during the study period. Similarly, the POC accumulation time is estimated as a product of the mean concentration of POC in the photic layer and the mean POC production rate. The POC production time varied between 0.07 to 1.7 (mean 0.4 ± 0.1) $\mu\text{M}/\text{d}$ (Sarma et al., 2020) whereas POC concentration ranged between 1.9 to 19 (mean 5 ± 1) μM in the study region. The POC accumulation time varied between 9 and 34 days with higher rates in the ACE (20 ± 3 days) and lower in the CE region (15 ± 2 days) (Fig. 6b). Rao et al. (2021) found that a higher contribution of picophytoplankton and DOC release is measured in the ACE whereas higher microplankton biomass was observed in the CE region (Sarma et al., 2020). Since the concentration of inorganic nutrients is low, more time is taken for microbial decomposition leading to a longer period of accumulation of semi-labile DOC in the ACE than CE, where some amount of nutrients is brought to the surface due to divergence at the centre of eddy.

The elevated DOC concentrations have been reported mainly in the surface waters and were attributed to biological processes mainly by elevated primary production (Raimbault and Garcia, 2007). The DOC concentrations, integrated into the mixed layer of 25m, displayed linear relation with an

accumulation time of particulate organic carbon in the BoB ($r^2=0.42$; $p<0.001$) suggesting that recycling of POC contributes to DOC accumulation in the upper ocean. Since $>90\%$ of the phytoplankton biomass is contributed by picophytoplankton in the ACE region (Sarma et al., 2020) the export flux is low (Anand et al., 2017) resulting in more accumulation of DOC than in the CE region (Fig. 6a).

4.5. Source and fate of dissolved organic nitrogen in the BoB

The higher DON concentrations ($>10 \mu\text{M}$) were found in the upper 40 m of the water column and decreased with depth below. The concentrations of DON in the upper ocean were higher than many regions in the world ocean (1.2 to $7.3 \mu\text{M}$; Bronk, 2002) but close to that of in the equatorial Atlantic (15°S - 25°N ; Vidal et al., 1999). Relatively higher concentrations of DON were noticed in the western than eastern BoB (Fig. 4a) associating with low salinity (Fig. 2c) suggesting that river water may be a significant source of DON. The DON contributed $\sim 90\%$ of the total dissolved nitrogen in the upper ocean in the BoB. The strong inverse relationship observed between salinity and DON ($r^2=0.46$; $p<0.001$) suggests a possible source from the rivers. The concentration of DON in the estuaries opened to the BoB varied between 40 and $160 \mu\text{M}$ and the estimated annual fluxes of DON to the BoB is 0.3 Tg (Krishna et al., 2015a). The DON: DOP ratios varied between 15 and 55 in the BoB and lower values <30 were found in the southern BoB and higher in the northern and western BoB associated with lower salinity. The ranges of DON: DOP ratios found in the BoB are consistent with the same found elsewhere in the world (14 - 55) in the North Pacific, North Central Pacific gyre, Southern Ocean, Georges Bank and central Atlantic Ocean (Loh et al., 2000; Hopkinson et al., 1997; Vidal et al., 1999). The higher DON: DOP ratios strongly suggest that preferential remineralization of DOP relative to DON in the BoB. Clark et al. (1998) found a high concentration of high molecular weight fraction of DOM in the Equatorial Pacific with high DON: DOP ratios. The DIN: DIP ratios in the mixed layer (9.2 ± 2) were significantly lower than the Redfield ratio, while DIN+DON and DIP+DOP ratios (18.0 ± 3) were close to the Redfield ratio. Similar results were obtained in the Pacific Ocean (Jackson and Williams, 1985) and Hawaii Ocean Time-series in the subtropical North Pacific (Karl et al., 1993) suggesting that inorganic and organic nitrogen and phosphorus must be considered to balance the budget.

The major sources of DON to the upper ocean is the release of DON by phytoplankton through passive diffusion or overflow of excess produced in the cells, sloppy feeding during grazing of zooplankton or bacterivory, cell rupture due to viral infections (Fogg, 1966; Bjornsen, 1988; Capone et al., 1994; Glibert and Bronk, 1994; Berman et al., 1999; Nagata, 2000). Hasegawa et al. (2000) provided

experimental evidence for the more efficient release of DON by smaller than larger planktons. Since smaller cells have a larger surface to volume ratio, more DON can be diffused through their cell wall into the surrounding water. Sarma et al. (2020) found that 80-90% of the phytoplankton biomass is contributed by picophytoplankton in the BoB resulting in more release of DON. In addition to that zooplankton sloppy feeding (Dagg, 1974; Lampert, 1978) and cell lysis due to viral infection (Fuhrman, 1999 and references therein) also contributes a significant amount of DON release. Sellner (1992) found that *Trichodesmium* contributes to DON release both directly through the release of DON and indirectly through regeneration of DIN and DON by bacteria and grazers living in association with the colonies. Capone et al. (1994) reported that half of the fixed N₂ by *Trichodesmium* in the Atlantic Ocean and the Caribbean Sea is released as DON, primarily as dissolved free amino acids. Perennial occurrence of *Trichodesmium* spp. was reported in the BoB (Jyothibabu et al., 2006; Paul et al., 2007; Hedge et al., 2008; Mulholland and Capone, 2009; Shetye et al., 2013; Sahu et al., 2017) and occurrence of N₂ fixation was also reported in the BoB (Sarma et al., 2020; Sexana et al., 2020). Therefore, a significant fraction of the DON may be released from phytoplankton into the upper ocean. The mean DOC: DON ratio (10.4±2) are typically found in the marine regions (Ogawa et al., 1999; Hopkinson et al., 1997) than rivers and estuaries (18-65; Bronk et al., 1998; Stepanauskas et al., 1990; 2000; Alberts and Takacs, 1999) indicates the significant fraction of DON may possible originated through *in situ* processes. Nevertheless, due to the lack of isotopic composition of DON, the exact source could not be confirmed.

DON exists in several forms in the marine environment including proteins, free amino acids, amino sugars, nucleic acids, excretion productions such as urea and methylamine and high molecular weight compounds such as lignin and chitin (Berman, 2003; Osburn et al., 2016). Bioavailability of low molecular weight compounds such as urea, amino acids and sugar amines, for phytoplankton are reported (Berman and Chava, 1999; Flynn and Butler, 1986) in the aquatic environment. Algae can uptake organic nutrients either directly or indirectly after microbial remineralization of DOM (Wetzel, 2001). Utilization of organic nutrients by phytoplankton are reported in the absence of or low concentration of dissolved inorganic nitrogen and phosphorus (Butler et al., 1979; Berg et al., 1997), however mechanism of uptake may vary and depends on the environmental conditions and phytoplankton composition (Mackay et al., 2020). Palenik and Morel (1990) reported that an enzyme on the cell surface of some marine phytoplankton (such as coccolithophores) oxidizes amino acids and produces several compounds along with ammonium. This ammonium is subsequently taken up by phytoplankton and used for their growth. Berg et al. (1997) found that remineralization of DON by bacteria and subsequent release of inorganic nitrogen is thought to be the mechanism of DON uptake

by phytoplankton. Zubkov et al. (2004) experimentally found that *Prochlorococcus* uptake amino acids (leucine and methionine) with higher turnover rates in the upper 80 m of water column than depth below. The mixotrophic phytoplanktons, such as dinoflagellates, cyanobacteria, can take up directly DON, when inorganic nutrients are poor, through heterotrophic mode. Mitbavkar et al. (2020) reported that cyanobacteria are dominant in the BoB, in which *Synechococcus* abundance is higher in the coastal and *Prochlorococcus* in the open sea region. Since *Prochlorococcus* is mixotrophic plankton and turns to heterotrophic in the absence of inorganic nutrients, it can uptake DON directly in the heterotrophic mode.

To examine the role of DIN and DON to support phytoplankton biomass in the BoB, the uptake rates of DIN (nitrate and ammonium) and DON (amino acids-glycine and aspartic acid) were compared in the BoB. The mixed layer means DIN uptake rates varied between 0.03 and 0.065 mmol N m⁻³ d⁻¹ whereas it was ranged from 0.002 to 0.006 mmol N m⁻³ d⁻¹ for amino acids in the BoB. The uptake rates of amino acids were about 10 times lower than DIN uptake rates. The amino acid uptake rates in the BoB were consistent with the same measured elsewhere in the world (0.001 to 0.16 mmol m⁻³ d⁻¹; Rich et al., 1997; Gilbert et al., 1991; Berg et al., 1997; Jorgensen et al., 1994; 1999) and higher uptake rates were measured in the Thames Estuary (0.01 to 0.25 mmol m⁻³ d⁻¹; Middelburg and Nieuwenhuize, 2000). Typically the contribution of amino acid uptake rate to total dissolved nitrogen uptake (nitrate+ ammonium+ amino acid) rate contributed between 1.1 to 16% and it was ~10% in the case of BoB. Lower DIN uptake rates were noticed in the ACE than other regions, in contrast, higher amino acid uptake rates were observed in the former than the latter region in the BoB. Lower DIN uptake rates in the ACE was associated with under detection limits of DIN concentrations (<0.1 μM) suggesting that phytoplankton may be adopted to uptake amino acids in the absence of DIN in the ACE region and also possibly dominance of mixotrophic cyanobacteria. Kumar (2013) observed that about 20% of the DON is contributed by dissolved free amino acids and proteins in the BoB. It is more likely that amino acids may be degraded to ammonium first by bacteria and subsequently, the degraded product may be taken up by phytoplankton. Though our data cannot confirm the possible uptake mechanism, utilization of DON (autotrophs through microbial degradation and uptake in inorganic form or heterotrophs direct uptake of DON by bacteria and transform to microzooplankton through the microbial loop) may support the food web in the BoB. More experiments are required in future to evaluate the composition of DON, uptake mechanisms and its contribution to support auto and heterotrophs in the BoB.

Based on the present study, the bulk DOC, DON and DOP in the BoB have fundamentally originated in the surface ocean via processes such as phytoplankton excretion, lysis, solubilization of POM and sloppy feeding in the food web. Therefore the high DOC and DON observed in the BoB largely

resulted from biological activity involving production, consumption and transformation processes within the upper ocean during the study period than contributed by external sources (Williams, 1975; Raimbault et al., 2008) and supported food web dynamics within the Bay. Therefore the contribution of organic matter on primary production and its impact on secondary and tertiary production needs more attention in the BoB, which is severely neglected.

5. Summary and Conclusion

To examine the source of DOC and DON and their role in the biological processes, 18 stations were occupied in the BoB during June 2019. The concentrations of DOC was higher in the BoB by 10-20% than in other regions in the Indian Ocean. Though relatively higher concentrations of DOC and significant inverse region suggests the contribution of riverine source in the northern Bay it is insignificant in the central and southern Bay. The strong relationship of DOC with Chl-a, POC and DOC exudation rates, DOC: DON, DON: DOP ratios and $\delta^{13}\text{C}_{\text{DOC}}$ suggested *in situ* production is the major source of DOC and DON in the BoB. The accumulation time of labile/semi-labile DOC in the upper ocean varied between 4.5 and 18 months with a longer rate in the ACE (11.5 ± 2 months) than CE (6 ± 1 months) during the study period. The lower sinking carbon fluxes at the 100 m and high mesozooplankton biomass and in the BoB can be explained by the accumulation of primary production as DOC in the surface layer and supporting through microbial loop respectively. The amino acid uptake rates are 10 times lower than DIN uptake rates in the BoB. Possible support of phytoplankton biomass through degradation of part of DON by bacteria and subsequent uptake is anticipated. However, the mechanism of uptake of organic nutrients, their composition and contribution to overall primary production and plankton biomass needs further evaluation. Nevertheless, our study suggests that DOM acts as an energy source to the plankton and contributes to the food web dynamics and more attention is needed to be paid to understand the carbon cycle in the BoB.

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Legend to figures

Figure 1: The map showing the station locations with the background of sea level anomaly (negative is cyclonic eddy CE) and positive is anticyclonic eddy (ACE)) and surface ocean currents. The stations circled were represents where incubation experiments for primary production, nutrients (inorganic and organic) uptake rates and DOC exudation rates were measured.

Figure 2: Spatial variability in a) temperature ($^{\circ}\text{C}$), b) salinity and c) Chlorophyll-a (mg m^{-3}) along the cruise track with reference to distance from station 1. The station numbers were depicted on the upper axis. The location of CE and ACE were also noted.

Figure 3: Spatial variability in a) nitrate (μM), b) phosphate (μM), and c) silicate (μM) along the cruise track with reference to distance from station 1. The station numbers were depicted on the upper axis. The location of CE and ACE were also noted.

Figure 4: Spatial variability in a) DON (μM), b) DOP (μM), c) DOC (μM) and $\delta^{13}\text{C}_{\text{DOC}}$ ($\%$) (μM) along the cruise track with reference to distance from station 1. The station numbers were depicted on the upper axis. The location of CE and ACE were also noted.

Figure 5: Spatial variability in photic zone mean uptake rates of a) DIN ($\mu\text{mole l}^{-1} \text{d}^{-1}$), and b) DON ($\mu\text{mole l}^{-1} \text{d}^{-1}$) in the BoB.

Figure 6: Spatial variability in photic zone mean turnover rates of a) DOC (in months) and b) POC (in days) in the BoB.

Figure 7: The relation of DOC with a) salinity, b) Chl-a (mg m^{-3}), c) POC (μM) and d) DOC exudation rates in the BoB.

Figure 1:

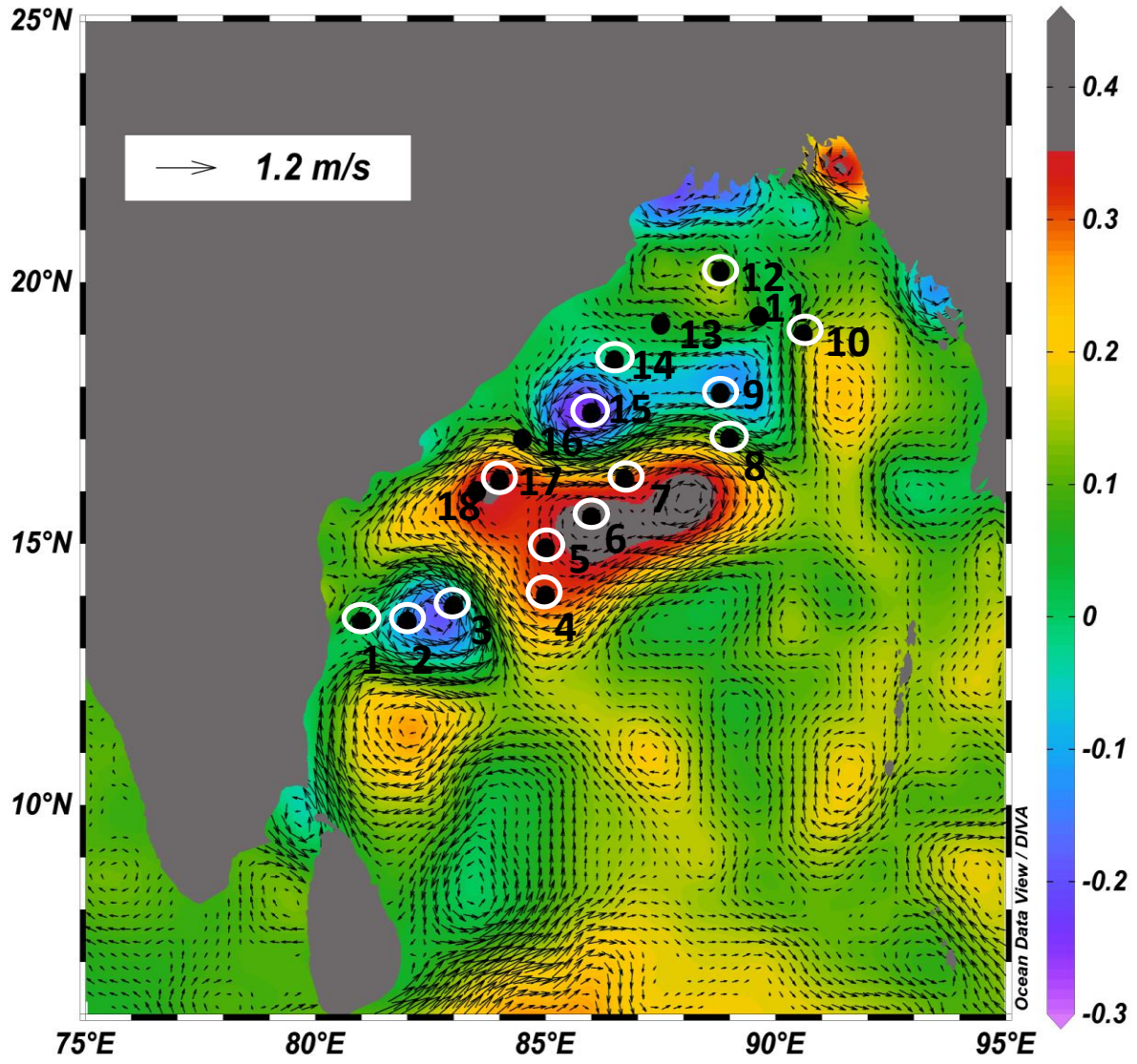


Figure 2:

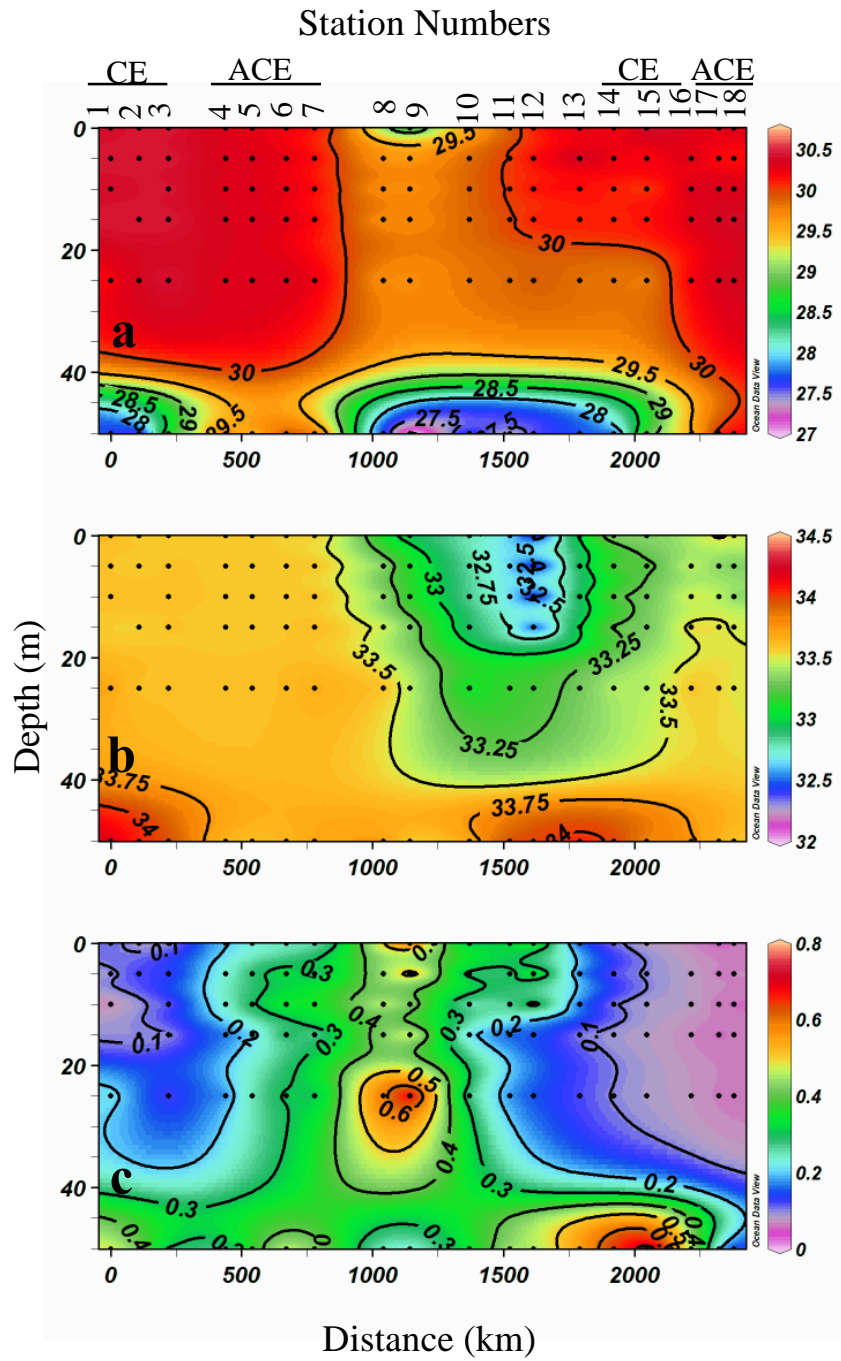


Figure 3:

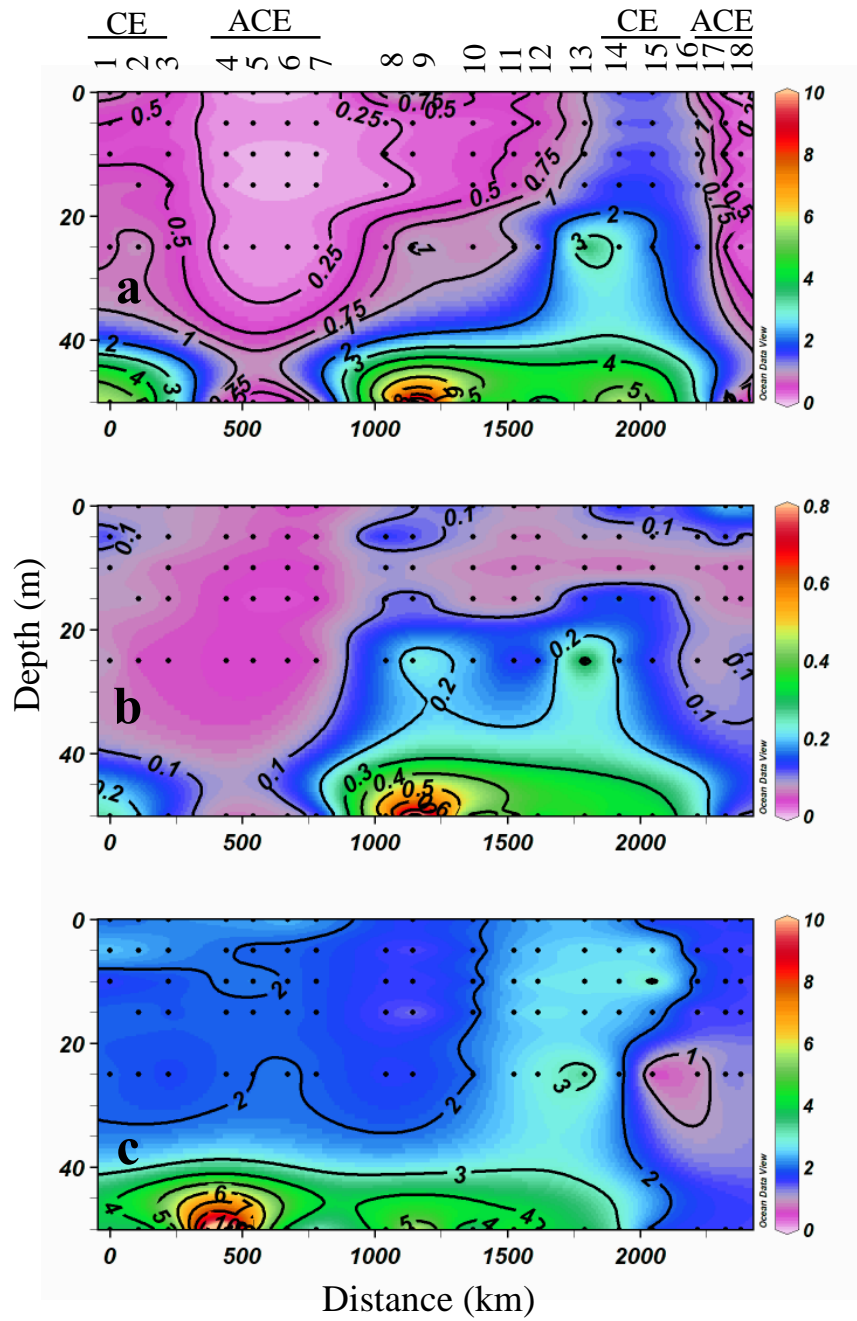


Figure 4:

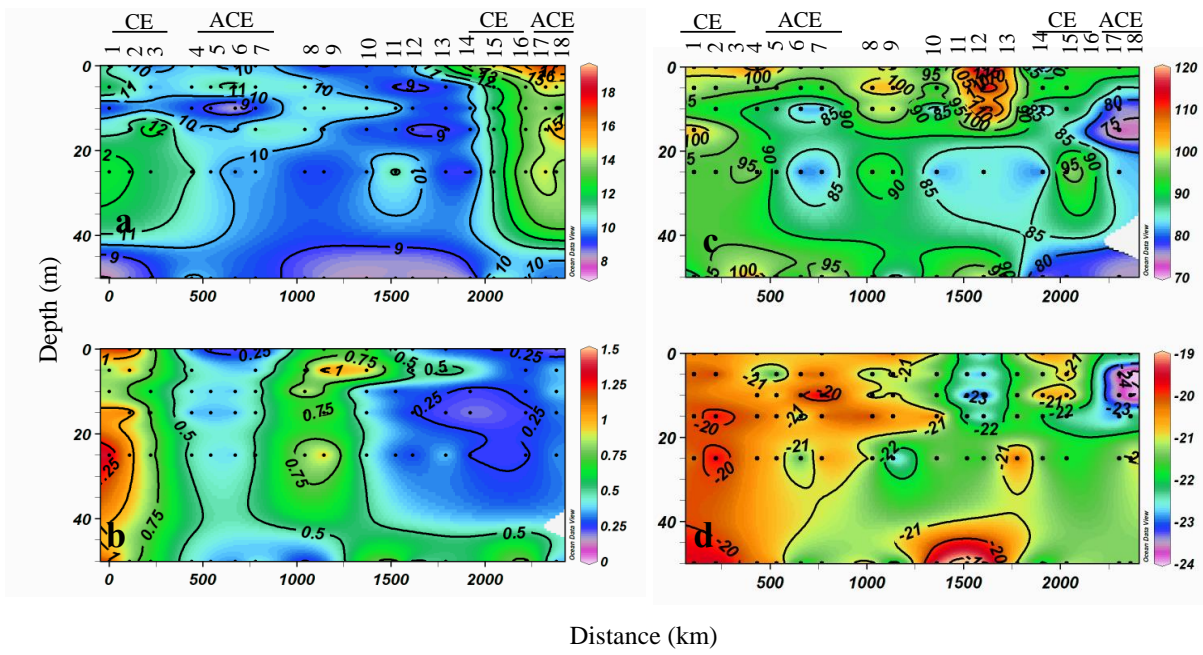


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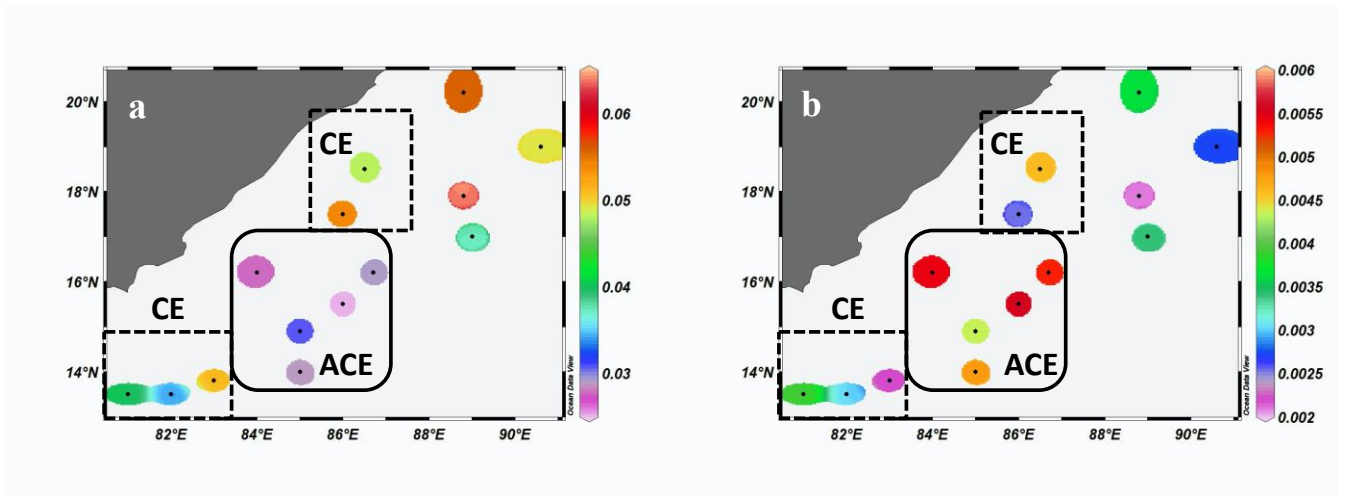


Figure 6:

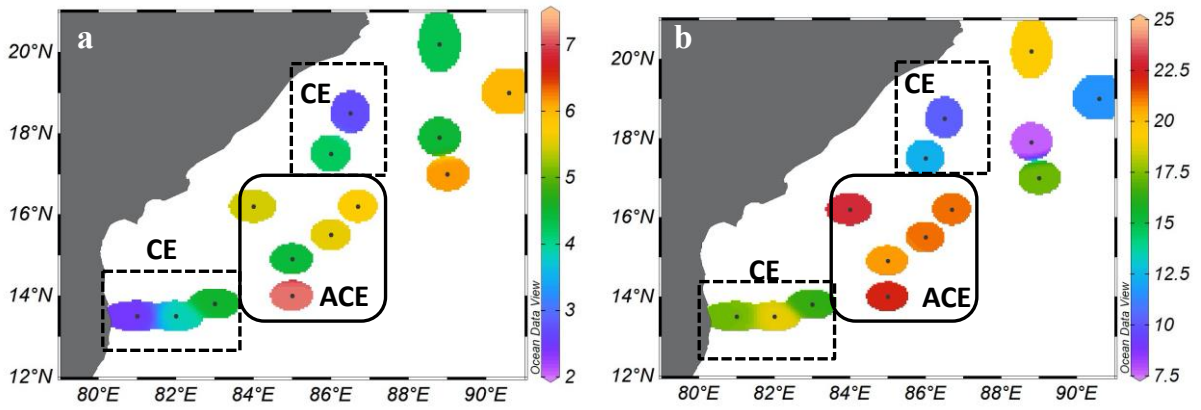


Figure 7:

