Non-Redfieldian C:N:P ratios in the inorganic and organic pools of the northern Indian Ocean

A thesis submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

by

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Discipline of Earth Sciences Indian Institute of Technology Gandhinagar, India 2021

Dedicated to my family.

Declaration

I, Deepika Sahoo, declare that this written submission represents my ideas in my own words, and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above can cause disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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Abstract

Availability of nitrogen (N) and phosphorus (P) determine the strength of the ocean's carbon (C) uptake, and variation in the N:P ratio in inorganic nutrients is key to phytoplankton growth. A similarity between C:N:P ratios in the plankton and deep water inorganic nutrients was observed by Alfred C. Redfield around 85 years ago, who suggested that biological processes in the surface ocean are controlled by deep ocean chemistry. This notion of similarity in the ratios has been a tenet in ocean biogeochemistry until a phytoplankton physiology model and an empirical data set suggested that the Redfield Ratio is not a universally optimal value rather it merely reflects the average stoichiometry of phytoplankton. Recent studies revealed that the C:N:P ratios in organic matter and inorganic nutrients deviate from the Redfield Ratio. At present, however, understanding of the (environmental) factors governing the C:N:P stoichiometry remains poor. The northern Indian Ocean due to its geographic setting and monsoonal wind forcing offers a natural biogeochemical laboratory to explore the effect of environmental and physical factors on C:N:P stoichiometry.

A handful of studies on the C:N:P ratios in phytoplankton, particulate organic matter (POM), dissolved organic matter (DOM), and nutrients have been reported from the Atlantic Ocean, and to a lesser extent from the Pacific Ocean with a few studies in the Indian Ocean. Despite the fact that the northern Indian Ocean is distinct from other oceans in terms of the biogeochemical and physical phenomena, particularly due to the reversal in monsoonal wind forcing, not much emphasis has been given to the region to understand the mechanisms regulating the elemental proportions.

This thesis reports the results on C:N:P ratios in nutrients, POM and DOM in three depth layers (top: surface to the depth of chlorophyll maximum, subsurface: depth of chlorophyll maximum to ~ 300 m, and deep layers: 300 m to a maximum of 3000 m) in the northern Indian Ocean, i.e., the Bay of Bengal and the Arabian Sea. The role

of physical processes – eddies, convective mixing, riverine discharge, and biogeochemical processes – N_2 fixation and denitrification, in changing the elemental ratios is discussed in this thesis.

We observed that the elemental ratios deviated greatly from the Redfield Ratio in both the northern Indian Ocean basins. Our observations of low N:P ratio (< 16:1) in the top layer nutrients indicate the N stressed productivity in these tropical basins. C:N:P ratios in particulate organic matter (POM) in the Bay of Bengal were 232:25:1 during summer and 249:39:1 during spring. Although the Bay of Bengal receives large riverine influx, but its influence in changing the C:N:P ratios was small during spring. In the Arabian Sea, the C:N:P ratios were 245:32:1 in the top layer POM during winter. The elemental ratios in nutrient and POM in the top layer were affected by the winter convective mixing in the northern Arabian Sea. Comparatively high nutrient concentrations and low POM elemental ratios were observed in the northern Arabian Sea. Overall the high C:N:P ratios in POM in the top layers was mostly driven by the preferential remineralisation of ratios in the subsurface and deep layers was mostly driven by the preferential remineralisation of organic P over N and C.

The Bay of Bengal is often prevailed by mesoscale eddies. Anticyclonic eddies, mode water eddy and non-eddy regions were identified in this basin during summer. The eddy and non-eddy stations exhibited a mixed effect on C:N:P ratios of nutrients and POM in the top layer. However, comparatively low N and P nutrients were observed at the anticyclonic eddy regions during spring. A similar effect of anticyclonic eddy on the nutrient concentrations and their ratios was observed in the southeastern Arabian Sea during winter.

In the Bay of Bengal, the elemental ratios (357:30:1) of DOM in the top layer were higher than the Redfield Ratio during summer but less than the global average of elemental ratios (640:44:1) for the surface bulk DOM. The ratios (2338:146:1) were higher than the global average during spring in the Bay of Bengal. However, the top layer DOM elemental ratios (635:47:1) in the Arabian Sea were similar to the global average values during winter.

Contrary to our hypothesis, N_2 fixation does not seem to have a role in changing the N:P ratios in the top layer POM pool and subsurface nutrients in the Bay of Bengal. But the role of N_2 fixation should be interpreted with caution as our N_2 fixation rates were

low during the observational period. Denitrification in hypoxic waters of the Arabian Sea leads to lowering of the N:P ratio of nutrients in its subsurface and deep layers. The data generated for this thesis might be useful for ocean biogeochemistry modellers who have begun to represent a variable elemental stoichiometry of phytoplankton and nutrients.

Keywords: Redfield Ratio, Bay of Bengal, Arabian Sea, Particulate organic matter, Dissolved organic matter, Nutrients, Biological nitrogen fixation, Denitrification, Mesoscale eddy, Picoplankton.

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List of Abbreviations

$\delta^{13}\mathbf{C}$	Carbon isotope composition of POC and DIC with V-PDB as standard
$\delta^{15}{ m N}$	Nitrogen isotope composition of PON with air as standard
%0	per mil (or parts per thousand)
ACE	Anticyclonic Eddy
Anammox	Anaerobic Ammonium Oxidation
AOU	Apparent Oxygen Utilisation
ATP	Adenosine Triphosphate
AWS	Automatic Weather Station
BWE	Boundary Water Eddy
С	Carbon
Chl a	Chlorophyll a
CO ₂	Carbon Dioxide
CTD	Conductivity Temperature Depth
DCM	Deep Chlorophyll Maximum
DIC	Dissolved Inorganic Carbon
DIM	Dissolved Inorganic Matter
DIN	Dissolved Inorganic Nitrogen
DIP	Dissolved Inorganic Phosphorus
DNA	Deoxyribonucleic Acid
DNRA	Dissimilatory Nitrate Reduction to Ammonia
DO	Dissolved Oxygen

DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
DOP	Dissolved Organic Phosphorus
EA	Elemental Analyzer
EICC	East India Coastal Current
Fe	Iron
IAEA	International Atomic Energy Agency
INCOIS	Indian National Centre for Ocean Information Services
IRMS	Isotope Ratio Mass Spectrometer
MLD	Mixed Layer Depth
MPA	Molybdophosphoric Acid
MWE	Mode Water Eddy
Ν	Nitrogen
NDIR	Non Dispersive Infra-Red
NE	Non-Eddy
\mathbf{NH}_4^+	Ammonium
NO_3^-	Nitrate
NO	Nitric Oxide
NO_2^-	Nitrite
NO_2	Nitrogen Dioxide
\mathbf{NO}_{x}	Oxides of Nitrogen
NPOC	Non-Purgeable Organic Carbon
O ₂	Oxygen
ORV	Oceanographic Research Vessel
Р	Phosphorus

PCA	Principal Component Analysis
PMB	Phosphomolybdenum Blue
PO_{4}^{3-}	Phosphate
POC	Particulate Organic Carbon
РОМ	Particulate Organic Matter
PON	Particulate Organic Nitrogen
РОР	Particulate Organic Phosphorus
PRL	Physical Research Laboratory
RNA	Ribonucleic Acid
SMC	Summer Monsoon Current
SSHA	Sea Surface Height Anomaly
тнс	Total Hydrocarbon
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
V-PDB	Vienna-Pee Dee Belemnite
WICC	West India Coastal Current
WMC	Winter Monsoon Current

Chapter 1

Introduction

1.1 Background

Carbon (C), nitrogen (N) and phosphorus (P) are the key elements to life and their cycling affects the Earth's climate. These elemental cycles are interlinked through various metabolic pathways. Therefore, any change in one elemental cycle will introduce the change in other elemental cycles (*Falkowski et al.*, 2008; *Finzi et al.*, 2011). For example, photosynthesis is a fundamental process responsible for sustaining life on the Earth. During this process, autotrophs (primary producers) utilise light energy and nutrients such as N and P to fix inorganic C to organic matter:

$$106 \operatorname{CO}_2 + 16 \operatorname{HNO}_3 + \operatorname{H}_3 \operatorname{PO}_4 + 78 \operatorname{H}_2 \operatorname{O} \xrightarrow{\operatorname{Sunlight}} \operatorname{C}_{106} \operatorname{H}_{175} \operatorname{O}_{42} \operatorname{N}_{16} \operatorname{P} + 150 \operatorname{O}_2$$
(1.1)

Marine primary producers fix atmospheric carbon dioxide (CO_2) into organic forms that account for nearly 50% of the global primary production $(111-117 \text{ Pg C y}^{-1})$ (*Behrenfeld et al.*, 2001). A part of this fixed C is sequestered to the deep ocean through biological pump. The efficiency of the biological pump is driven by the availability of nutrients in the euphotic zone. The concentrations of bioavailable N, P, silicon (Si), zinc (Zn) and iron (Fe) are low relative to phytoplankton demand in the sunlit ocean. Elements such as Zn and Fe are present in trace amounts (nM levels), thereby known as the micronutrients, while N, P, and Si are considered as the macronutrients as they are present in higher amounts (μ M levels). Furthermore, N and P are classified as the proximate and ultimate limiting nutrients for ocean productivity, respectively (*Tyrrell*, 1999). The proximate limiting nutrient represents the localized limitation. An increase in the proximate limiting nutrient's concentration may enhance productivity within hours or days. But the ultimate limiting nutrient represents the nutrient whose supply triggers productivity at the ecosystem level over a long time scale, somewhat over thousands of years for the global ocean.

C, N, and P are present in a certain proportion in the phytoplankton structural molecules as illustrated in equation (1.1). Therefore, the elemental composition of marine phytoplankton is central to ocean biogeochemistry as it links the global C cycle with the cycling of other elements, such as nitrogen (N) and phosphorus (P) (*Galbraith and Martiny*, 2015).

These elements are present in inorganic and organic forms in seawater. The inorganic form of these elements include aqueous CO_2 ($\text{CO}_2(\text{aq})$), carbonic acid (H_2CO_3), carbonate (CO_3^{2-}), bicarbonate (HCO_3^{-}), nitrate (NO_3^{-}), nitrite (NO_2^{-}), ammonium (NH_4^+) and phosphate (PO_4^{3-}). These inorganic forms of elements serve as nutrients to the primary producers and we recognize these forms as dissolved inorganic matter (DIM) pool. Organic matter such as carbohydrate, protein, lipid, nucleic acid, phospholipid and many more forms produced during the photosynthesis are considered as the total organic matter pool. This pool is further divided into two pools: particulate organic matter (POM) and dissolved organic matter (DOM). By definition, the organic matter of size < 0.45 µm is considered DOM and > 0.45 µm is considered POM. For practical purposes, we have considered the organic matter that does not pass through a 0.7 µm pore size filter as POM during our experiments. The functional difference between these two pools is that the DOM is too small to sink through the water column on its own, and mainly transported with ocean currents, while POM is large enough to sink.

C constitutes $\sim 24-80\%$ of dry weight in organic molecules, hence it is a major component in all classes of organic macromolecules particularly in lipids and carbohydrates where N and P are notably absent (Figure 1.1). The major organic N rich molecules are protein, nucleic acids, chlorophyll *a*, *b*, *c* and amino acids, while RNA is the major P rich biomolecule, followed by phospholipid, DNA and ATP.



Figure 1.1: Major inorganic (dark colors) and organic (light colors) molecules of carbon, nitrogen and phosphorus in the ocean.

1.2 Marine biogeochemical cycling of elements

1.2.1 Marine carbon cycle

The marine C cycle is mainly mediated by the solubility and biological pumps. C cycling by the solubility pump is governed by the global differences in seawater temperature. CO_2 is more soluble in cold water. The sinking of cold and dense water at high latitude regions leads to transport of CO_2 to deep ocean, that is transported through the thermohaline circulation to the low latitude regions where warming of the upwelled water leads to the release of CO_2 .

When CO₂ dissolves in seawater, it reacts with water and form H₂CO₃, which subsequently dissociates to HCO₃⁻ and CO₃²⁻ ions (equation (1.2)). CO₂(aq), HCO₃⁻ and CO₃²⁻ are the inorganic forms of C and hence categorised as dissolved inorganic C (DIC). The most abundant inorganic C species under current oceanic pH conditions are HCO₃⁻ (91%), followed by CO₃²⁻ (8%) with a very low fraction of CO₂(aq) (1%) (*Marchitto*, 2013).

$$\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \to \mathrm{H}_2\mathrm{CO}_3 \to \mathrm{HCO}_3^- + \mathrm{H}^+ \to \mathrm{CO}_3^{2-} + 2\,\mathrm{H}^+ \tag{1.2}$$

Biological pump, by which plankton sequester C from the surface to the deeper ocean includes the soft-tissue pump and carbonate pump. In the soft-tissue pump, phytoplankton convert DIC into particulate organic C (POC) during photosynthesis and release dissolved organic C (DOC). A major fraction of organic matter (~90%) is remineralised to CO_2 in the surface ocean, while a small fraction (~10%) is exported from the photic zone to the deeper ocean (known as export production) and further around 1% into the deep sea sediments where it can be stored for centuries (*Broecker*, 1974). This fraction of organic C is effectively sequestered from the active C cycle in the ocean (Figure 1.2). In the carbonate pump, some of the calcifying phytoplankton, such as coccolithophores, drive the carbonate pump by precipitating C in the form of calcium carbonate (CaCO₃). Upwelling of the deep water and re-equilibration of seawater with atmosphere drives the CO₂ uptake.

1.2.2 Marine nitrogen cycle

Bioavailable forms of N in seawater are NO_3^- , NO_2^- , and NH_4^+ . These inorganic species of N are grouped into dissolved inorganic N (DIN), which is directly accessible to phytoplankton. Molecular N (N₂) is present in ~1 mM concentration in the surface water but can only be directly utilised only by a specific group of organisms called diazotrophs (*Tyrrell*, 1999). The organic components of N include particulate organic N (PON) and dissolved organic N (DON).

Coastal ocean receives N through riverine inputs, upwelling and atmospheric deposition. In the open ocean, biological N₂ fixation is a major source of bioavailable N. It is a microbially mediated process, by which N₂ gets converted to NH_4^+ . In the absence of reactive N and at sufficient availability of PO_4^{3-} and Fe, diazotrophs utilize N₂ by breaking the triple bond between the N atoms. Diazotrophs subsequently convert N₂ into NH_4^+ by nitrogenase enzyme. The new N produced by N₂ fixation fuels primary productivity, which ultimately plays an important role in driving net CO₂ sequestration from the atmosphere.

During the nitrification process, NH_4^+ converts to NO_2^- and finally to NO_3^- by the *Nitrosomonas* and *Nitrobacter* organisms, respectively. Phytoplankton utilise DIN to photosynthesize organic matter. A major fraction of the organic matter gets decomposed to regenerate nutrients in the photic zone, while a small fraction sinks below the photic zone. In subsurface oxygen depleted waters, NO_3^- serves as oxidant for the organic matter decomposition. Thereby NO_3^- is reduced to N_2O and further to N_2 in a multistep process: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$. This heterotrophic reduction of NO_3^- is known as denitrification, which is a major remineralisation process in oxygen minimum zones responsible for the removal of bioavailable N from the ocean.

More recently, the anaerobic ammonium oxidation (anammox) and dissimilatory nitrate reduction to ammonia (DNRA) were discovered as important processes responsible for bioavailable N removal in the oxygen depleted regions. Anammox is a chemolithoautotrophic process that involves the fixation of DIC and simultaneous generation of N₂ from the reaction between NH_4^+ and NO_2^- . DNRA is an anaerobic process by which $NO_3^-/NO_2^$ reduces to NH_4^+ (Figure 1.2).

1.2.3 Marine phosphorus cycle

Riverine influx is a significant source of P to the ocean. Atmospheric deposition through aerosols and mineral dust is also an important source of P particularly in the open ocean. PO_4^{3-} is the inorganic form of P which is also referred to as dissolved inorganic P (DIP). Particulate organic P (POP) and dissolved organic P (DOP) constitute the organic form of P. P is one of the fundamental elements constituting structural biomolecules such as DNA, RNA, ATP and phospholipids. In fact, DIP is considered as the proximate limiting nutrient that limits marine primary productivity and its availability can influence the phytoplankton species distribution. Therefore, P plays a key role in photosynthesis, where phytoplankton consume DIP to produce organic matter. A major fraction of the organic matter undergoes decomposition and releases DIP within the photic zone, while only a small fraction of organic P reaches to the deep ocean and buried in marine sediments (Figure 1.2). Upwelling of seawater is a major source of P to the photic zone. The annual upward flux of P from subsurface waters accounts for $\sim 90\%$ of total P influx to the photic zone (*Hashihama et al.*, 2021).



Figure 1.2: A brief schematic representing the marine biogeochemical cycling of C, N, and P. Blue, green, and pink colors represent C, N, and P cycling, respectively. Black color refers to the integrated cycling of C, N, and P.

1.3 Linking the three elemental cycles - The Redfield Ratio

In 1934, Alfred C. Redfield noticed that the C:N:P ratio of surface plankton was similar to that of the major nutrients in deep water in the Sargasso Sea (*Redfield*, 1934). Thereafter Redfield started analysing R. H. Fleming's 1940 data set and estimated a C:N:P ratio of 106:16:1 for surface plankton. For deep ocean nutrients, Redfield analysed L. H. N. Cooper's 1937 and F. A. Richards's 1956 and 1957 data set, which yielded a C:N:P ratio of 105:15:1. Based on these observations, Redfield concluded that the average elemental composition of marine plankton and that in the deep water nutrients is statistically consistent at 106C:16N:1P in the global ocean (*Redfield*, 1958). This ratio is widely known as the Redfield Ratio in marine biogeochemistry. Equation (1.1) is based on Redfield's observations.

Redfield provided three explanations for the fixed C:N:P ratios: (1) it is a mere geochemical coincidence, (2) microorganisms adapt to oceanic nutrient stoichiometry, which means phytoplankton have the ability to change their elemental composition and (3) biogeochemical processes regulate the elemental ratios (*Redfield*, 1958).

The Redfield Ratio defines the C:N:P ratios of photosynthesis and remineralisation reactions; later Anderson (1995) extended it to oxygen (O_2). During photosynthesis, phytoplankton acquire nutrients from seawater at approximately 106C:16N:1P and simultaneously liberate 150 moles of O_2 molecules to seawater for every mole of P consumption. This leads the $-O_2$:C:N:P ratio to -150:106:16:1.

1.4 Evolution of the Redfield Ratio concept

The Redfield Ratio has been a tenet in ocean biogeochemistry until a phytoplankton physiology model and an empirical data set suggested that the Redfield Ratio is not a universally optimal value rather it merely reflects the average stoichiometry of marine phytoplankton. From the empirical and theoretical results, *Klausmeier et al.* (2004a) concluded that the N:P ratio in POM can vary over time in response to changes in the ecological balance between exponential growth and equilibrium phases or in N and P availability. Competitive equilibrium growth results in high N:P ratio, while exponential growth leads to low N:P ratio in the phytoplankton. The phytoplankton physiology and resource competition model studies predicted that the optimal N:P ratio typically varies from 8.2 to 45.0, depending on the ecological conditions (*Klausmeier et al.*, 2004a).

Deviations of the N:P ratio from 16:1 in nutrients are used to infer the N or P limitation to phytoplankton growth, because the ratio can be easily compared with the cellular N:P ratio of phytoplankton. Furthermore, the excess NO_3^- relative to PO_4^{3-} , i.e., $N^* = [NO_3^-] - 16 [PO_4^{3-}]$, is used to study the net effect of various biogeochemical processes such as N₂ fixation (increase in N^{*}) and denitrification (decrease in N^{*}) in the water column (*Tyrrell*, 1999; *Deutsch and Weber*, 2012).

Studying the variation of elemental ratios unravels biogeochemical processes. Most of the marine biogeochemical concepts are often based on the assumption of temporally and seasonally static elemental ratios of phytoplankton. Nutrient demand of phytoplankton, nutrient limitation of productivity and the link between nutrient supply, primary
productivity and C export are generally studied using the elemental composition of phytoplankton. The organic matter that is exported from the photic zone further contributes to the subsurface nutrients and their elemental ratios. Therefore, the inclusion of varying elemental ratios in biogeochemical models could be beneficial in assessing the accurate shifting of primary productivity, C export and changes on subsurface nutrient pool in changing environmental conditions.

Nearly all climate models predict that the ongoing warming and elevating nutrient deficient conditions may lead to decrease in primary productivity and C export in open ocean regions (*Bopp et al.*, 2013). Considering a fixed C:P ratio of POM pool, one would interpret that the reduced primary productivity in more stratified and nutrient limited regions will lead to a low C export from the photic zone. On the contrary, the flexible stoichiometric concept suggests that the C:P ratio in POM pool will increase and so the C export. Therefore, the C export will not decrease as that inferred from the static stoichiometric concept in nutrient deficient oceans in future (Tanioka and Matsumoto, 2017). This could be because of the increasing abundance of picoplankton such as Prochlorococcus, Synechococcus and picoeukaryotes in nutrient deficient regions which possess high cellular elemental ratios (Martiny et al., 2013a). The regions such as the subtropical North Atlantic Ocean, where > 60% of POC is contributed by the picoplankton alone, the increased C:P ratio of photic zone POM supports a large increase in C export (*Casey*) et al., 2013; Matsumoto et al., 2020). Thus the incorporation of flexible elemental ratios in global biogeochemical models will enable us to improve the predictive ability and more importantly the estimation of accurate future levels of primary and export production. The interdependence of marine plankton composition on the environmental factors particularly temperature and nutrients is an integral part to our understanding of the interlinking of physical, biological and chemical components of the ocean ecosystem.

1.5 Variation of elemental ratios in global ocean

Recent findings highlighted a global latitudinal variation of C:N:P ratios from the canonical Redfield Ratio (*Martiny et al.*, 2013a,b). The variation in environmental parameters, such as temperature and nutrient concentrations, and biological parameters, such as cell physiology and community structure, could explain the variation in elemental ratios in POM (*Martiny et al.*, 2013a). Ocean exhibits a strong latitudinal gradient of environmental parameters, e.g., the high latitude regions experience low temperature and high nutrient concentrations; however, the low latitude regions experience high temperature and low nutrient concentrations. Equatorial regions experience an intermediate set of environmental parameters due to upwelling. The variation in N:P and C:P in POM ratios seems to mimic the pattern of environmental parameters over the latitudinal intervals. High latitude nutrient rich basins exhibit low elemental ratios (less than the Redfield Ratio) and the low latitude nutrient deficient region exhibit high elemental ratios (above the Redfield Ratio), however, the elemental ratios in equatorial basins are close to the Redfield Ratio.

The elemental ratios in POM particularly N:P and C:P also exhibit seasonal variation with elevated ratios in summer and fall and decreased ratios in the winter and spring seasons (*Martiny et al.*, 2016). The ratios vary between 5 to 40 for N:P, 50 to 500 for C:P and 5 to 10 for C:N. N:P and C:P ratios generally exhibit large variation from the Redfield Ratio than the C:N ratio.

1.5.1 Hypotheses responsible for the variation of elemental ratios

Several modelling, observational and laboratory studies have suggested different mechanisms to explain the non-Redfieldian behaviour of C:N:P ratios among marine plankton communities. Three mechanisms that are most important in explaining the varying elemental ratios are the growth rate hypothesis, nutrient supply hypothesis and allometric diversity hypothesis.

1.5.1.1 Growth rate hypothesis

The growth rate hypothesis states that the differences in C:N:P ratios in organic matter are governed by the allocation changes of resource acquisition and growth machinery in the cellular structure (*Arrigo*, 2005). Resource acquisition machinery includes protein, ribosomes and chlorophyll which are N rich and possess high C:P and N:P ratios. Growth machinery includes P rich RNA having low C:P and N:P ratios. As these constituents make up a large portion of cellular material, changes in their relative proportions have a marked effect on the bulk cellular elemental composition.

In a nutrient scarce environment, the slow growing small phytoplankton dominate the phytoplankton community by synthesizing additional resource acquisition machinery such as proteins (high N:P and C:P ratios) and are called the "survivalist". On the contrary, the large phytoplankton prevail in the nutrient rich environment by synthesizing more growth machinery such as RNAs (low N:P and C:P ratios) in order to maintain a high growth rate. These fast growing large phytoplankton are called as the "bloomer". Picoplankton such as *Prochlorococcus*, *Synechococcus* and picoeukaryotes possess high C:P and N:P ratios, while eukaryotes such as diatoms have low elemental ratios. Thereby, the oligotrophic regions such as subtropical ecosystems where picoplankton constitute a major fraction of phytoplankton community exhibit a higher elemental ratios than the Redfield Ratio, while lower elemental ratios are observed in the polar region.

Furthermore, the hypothesis explains the higher N:P ratio in diazotrophs. Diazotrophs often have a higher N:P ratio than non-N₂ fixers, for e.g., the *Trichodesmium* blooms possess high N:P ratio ranging from 42 to 125 (*Karl et al.*, 1992; *Letelier and Karl*, 1996). *Trichodesmium* reportedly grows slowly with a maximum growth rate of ~0.14 d⁻¹, favouring the growth rate hypothesis (*LaRoche and Breitbarth*, 2005). High cellular N content in diazotrophs is attributed to their exclusive and inexhaustible N supply. Since the process is energetically costly, diazotrophs allocate more P-poor light-harvesting machinery in the cellular structure to power N₂ fixation (*Klausmeier et al.*, 2004a). Therefore, the basins where diazotrophs account for a significant percent of phytoplankton population may lead to an overall increase in the N:P ratio in the POM.

1.5.1.2 Nutrient supply hypothesis

This hypothesis is based on the classic "resource competition theory". It is proposed that the resource competition among algal species is the central mechanism for controlling the elemental composition of the phytoplankton community (*Tilman et al.*, 1982). The element, which is present in low concentration in seawater, the phytoplankton community will be dominated by the organisms that can adapt to a low cellular content of that element (*Klausmeier et al.*, 2004a). When the concentration is high, fast growing organisms dominate the phytoplankton community having high uptake rate of that element.

Based on this concept, the nutrient supply hypothesis states that the absolute concentration of nutrients, such as DIN and DIP, determines the POM elemental ratios. Therefore, the expected C:N:P ratios in oligotrophic basins are higher than the Redfield Ratio, and the reverse holds for nutrient rich basins (*Galbraith and Martiny*, 2015). This happens because slow growing cyanobacteria such as *Prochlorococcus* and *Synechococcus*, with a high N:P and C:P ratios in their biomass/nutrient uptake requirements, prevails in oligotrophic waters whereas fast growing microorganisms such as diatoms (with a low N:P and C:P ratios) flourish in nutrient rich waters (*Singh et al.*, 2017; *Sharoni and Halevy*, 2020).

1.5.1.3 Allometric diversity hypothesis

This hypothesis states that the taxonomic composition of a community influences its elemental stoichiometry. Small phytoplankton such as cyanobacteria possess high elemental ratios, while the large eukaryotic phytoplankton possess low elemental ratios (*Klausmeier et al.*, 2004a; *Arrigo*, 2005). Even in the same phylum, the elemental compositions vary with different genus. For example, in cyanobacteria, the genus *Prochlorococcus* (0.5–0.7 µm) has comparatively high C:N:P ratios (234:33:1) than the genus *Synechococcus* (0.8–1.5 µm) (181:33:1) (*Martiny et al.*, 2013a; *Singh et al.*, 2015a).

1.5.2 Variation in elemental ratios in different pools

The three elemental pools: DIM, POM and DOM — are interlinked through processes such as POM export, upward flux of nutrients, and exchange of DOM between the depth layers (*Pujo-Pay et al.*, 2011). In the photic zone, DIM and DOM are diffused to POM through biological consumption (*Pujo-Pay et al.*, 2011). A part of POM gets recycled to DOM by excretion or lyses of organic matter; subsequently, DOM (and POM) remineralises to DIM, completing the cycle. In the subsurface and deep waters, POM and DOM are largely recycled to DIM (*Krom et al.*, 2010).

1.5.2.1 Dissolved inorganic matter (nutrient) pool

Multiple studies have proposed that the deep water DIN:DIP ratio is maintained near the Redfield Ratio by physical ocean mixing despite the non-Redfieldian ratios in the surface plankton communities (e.g., *Mills and Arrigo* (2010)). However, the DIN:DIP ratio in the photic zone remains much less than the Redfield Ratio in most of the subtropical oceans. The severe N deficiency in the photic zone is attributed to the uptake of nutrients by the phytoplankton. Typically, in subtropical oligotrophic ecosystems such as the Indian Ocean and subtropical North Pacific Ocean, the phytoplankton community is mainly populated by the slow growing small phytoplankton that have high biomass N:P requirement, leaving the low residual DIN:DIP ratio in surface waters. On the contrary, the depressed uptake ratio of N:P of the Southern Ocean surface plankton leads to the elevated residual DIN:DIP in surface water (*Lee et al.*, 2021). Although the most pervasive processes such as physical mixing and remineralisation of organic matter contribute to the surface water DIN:DIP ratio.

In the Pacific Ocean, the DIN:DIP ratio decreases from 13:1 in the subsurface to near zero in the surface water. Therefore, the N^{*} is negative throughout the water column and decreases more in the deep waters (*Deutsch and Weber*, 2012). Unlike the other subtropical oceans, the photic zone DIN:DIP ratio in the North Atlantic Ocean is \sim 30:1, almost twice the Redfield Ratio (*Wu et al.*, 2000). Although the non-Redfieldian uptake of phytoplankton affects the surface water DIN:DIP ratio, the variations are also attributed to the N budget processes such as N₂ fixation and denitrification (*Deutsch and Weber*, 2012). High N₂ fixation rates in the subtropical North Atlantic Ocean cause elevated DIN concentration thereby increasing the DIN:DIP ratio in the surface water.

Global N^{*} minima in subsurface waters are mainly observed in the Arabian Sea and the central and the eastern tropical Pacific (*Hupe and Karstensen*, 2000; *Deutsch and Weber*, 2012; *Hamasaki et al.*, 2018). Denitrification and anammox processes in these basins are responsible for a substantial loss of DIN from the subsurface water under hypoxic conditions. The denitrifying heterotrophic bacteria utilise NO_3^- as an oxidant during the organic matter remineralisation and the autotrophic anammox bacteria produce N₂ from NO_2^- and NH_4^+ in the anoxic subsurface waters. These processes result in depletion of DIN and thereby lowering the DIN:DIP ratio in the subsurface waters.

N^{*} maxima in the tropical and subtropical North Atlantic infers the N inputs to the basin. Theoretically, sinking of biomass having high N:P ratio may produce N^{*} maxima upon its remineralisation. But several studies have attributed the maxima to the remineralisation of diazotrophs. In addition, some studies emphasized the decomposition of DON and DOP and atmospheric N deposition in increasing N^{*} values (*Gruber and Sarmiento*, 1997; *Deutsch and Weber*, 2012).

1.5.2.2 Particulate organic matter pool

C:P and N:P ratios are usually more variable than the C:N ratio in POM, as P has more plasticity than N. Marine phytoplankton can reduce their cellular P requirement by substituting non-P membrane lipids such as sulfur and N containing membrane lipids (devoid of P) for phospholipids during P scarcity in the ocean, which leads to the C:P ratio more variable than the other ratios (*Van Mooy et al.*, 2009).

The elemental ratios of POM vary spatially with changing phytoplankton communities in response to the changing environmental conditions. Subtropical regions exhibit high elemental ratios while the polar regions exhibit low elemental ratios. In fact, the variation follows a clear latitudinal pattern in the global ocean. The average C:N:P ratios are 195:28:1 in nutrient depleted, warmer low latitude regions, 137:18:1 in equatorial regions and 78:13:1 in the high latitude cold and nutrient rich regions (*Martiny et al.*, 2013a). The average C:N:P ratios of 210:36:1 and 172:25:1 are observed in subtropical North Atlantic Ocean and subtropical North Pacific Ocean, respectively (*Martiny et al.*, 2013a; *Singh et al.*, 2015a).

Variation of POM elemental ratios in the water column is driven by the production and differential remineralisation of organic matter. In the photic zone, the abundance of phytoplankton community decides the overall C:N:P ratio in POM. However, in the subsurface and deep waters, remineralisation of organic matter alters the elemental ratios. POP undergoes preferential remineralisation, followed by PON and POC (*Loh and Bauer*, 2000). Thereby the C:N, N:P and C:P ratios in POM attain their highest in the photic zone, and further decreases in the subsurface and deep waters. C:P ratio varies the most, while C:N ratio varies the least from the Redfield Ratio in the water column.

1.5.2.3 Dissolved organic matter pool

DOM in the ocean is one of the largest reservoirs of organic matter holding approximately as much C (~662 Pg C) as in the atmospheric CO₂ reservoir (~750 Pg C) (*Siegenthaler* and Sarmiento, 1993; Hansell et al., 2009). DOC represents the second largest reservoir of the bioreactive C after DIC (~38,000 Pg C) (Hansell and Carlson, 1998), while DON and DOP exceed by an order of magnitude from the concentration of inorganic nutrients in the ocean (*Church et al.*, 2002). They can be substrate to the autotrophic and heterotrophic plankton, and particularly DOC act as a sink to the fixed atmospheric C.

DOM is produced by several mechanisms such as extracellular release by phytoplankton during grazing, via cell lysis, solubilisation of particles, and bacterial degradation (*Collos et al.*, 1992; *Smith et al.*, 1992). Heterotrophic bacterial uptake, direct phytoplankton assimilation, photochemical decomposition, and sorption onto sinking particles decrease the DOM elemental concentrations (*Palenik and Morel*, 1990; *Keil and Kirchman*, 1994; *Chari et al.*, 2016).

The bulk DOM pool consists of compounds of varying biological lability, from refractory compounds, turning over of century to millennia time scales to very labile compounds turning over on time scales of minutes to days (*Bauer et al.*, 1992). The refractory DOM pool is uniformly distributed throughout the water column and represents approximately 70% of surface DOC in stratified basins (*Druffel et al.*, 1992; *Cherrier, J. et al.*, 1996). In deep water (> 1000 m), DOC is mostly refractory with an average age of 4000 to 6000 years in the North Atlantic and the North Pacific Oceans, respectively (*Williams and Druffel*, 1987; *Bauer et al.*, 1992).

Considerable knowledge has been gained on the C:N:P stoichiometry of the POM and DIM pool in the ocean, but little is known about the DOM pool elemental stoichiometry. The vertical gradient of elemental ratios in DOM is mainly driven by the heterotrophic consumption and the preferential remineralisation of labile fraction of DOM. Variations in DON:DOP and DOC:DOP ratios in the water column are attributed to the preferential remineralisation of labile DOP relative to semi-labile and refractory DON and DOC (*Letscher and Moore*, 2015). In the water column, labile fractions readily remineralise and the semi-labile fractions with a relatively long turnover time (than labile components) degrades slowly during their export from the upper ocean towards the deep water, and thus, responsible for the observed gradient in the elemental ratios.

The C:N:P ratios in the refractory DOM pool deviate substantially from the Redfield Ratio and even higher than that of the labile, semi-labile, and bulk DOM in surface water (*Pan*, 2007). The global average C:N:P ratio of the surface water bulk DOM pool is 640:44:1, however, the individual ratios exhibit a large range of variation, which could be attributed to the components of DOM with different turnover time and due to the assimilation of results from biogeochemically distinct basins.

1.6 The northern Indian Ocean

Several studies on the C:N:P ratios in phytoplankton and nutrients have been reported from the Atlantic Ocean, and to an extent from the Pacific Ocean with a few studies in the Indian Ocean (*Copin-Montegut and Copin-Montegut*, 1983; *Karl et al.*, 2001; *Martiny et al.*, 2013a,b, 2014; *Singh et al.*, 2015a). In the Indian Ocean, these studies are mostly confined to the eastern (*Garcia et al.*, 2018; *Baer et al.*, 2019), northwestern (*Martiny et al.*, 2013a,b) and southwestern tropical regions (*Copin-Montegut and Copin-Montegut*, 1983). Furthermore, the bulk DOM pool elemental ratios were studied only in the western Arabian Sea (*Letscher and Moore*, 2015).

Despite the fact that the northern Indian Ocean is distinct from other oceans in terms of the extent and intensity of biogeochemical processes, particularly due to the reversal in monsoonal wind forcings, less is known about the mechanisms regulating the elemental stoichiometry. Due to its unique biogeochemical possessing of intense diazotrophic and denitrification activity, the region provides a natural laboratory to understand the effect of the biogeochemical processes on the C:N:P ratios in various oceanic pools.

The northern Indian Ocean consists of the Arabian Sea and the Bay of Bengal at its western and eastern sides, respectively. Being landlocked by the Asian landmass in its north, it is influenced by the seasonally reversing monsoon system. Winds are stronger during summer than that during the winter monsoon (November–February), and weak winds prevail during the transition months: March–May and October in both the basins. These monsoonal winds over the northern Indian Ocean force seasonal reversing of upper ocean circulation in these basins during the summer and winter monsoons (*Schott and McCreary*, 2001).

Surface ocean boundary currents change their direction from clockwise during the summer monsoon and anticlockwise during the winter monsoon. During the summer monsoon, the major current along the west coast of India called the West India Coastal Current (WICC) moves from the north to equatorward in the Arabian Sea and joins the current along the east coast of India i.e., the East India Coastal Current (EICC), that travels equator to northward in the Bay of Bengal and reverses during the winter monsoon (*Schott and McCreary*, 2001). Apart from these coastal currents, the large scale open ocean monsoonal currents: the Summer Monsoon Current (SMC) and Winter Monsoon Current (WMC) also undergo seasonal reversal in the northern Indian Ocean (*Shankar et al.*, 2002). These monsoon currents flow across the Laccadive high (winter monsoon) and low (summer monsoon) in the south-eastern Arabian Sea, link the surface water circulation in the Bay of Bengal and the Arabian Sea (*Bruce et al.*, 1994; *Shankar and Shetye*, 1997). During the summer monsoon, the SMC flows from the eastern boundary of the Bay of Bengal to the western Arabian Sea during the winter monsoon.

Even though the Arabian Sea and Bay of Bengal are situated at the same latitudinal regions, the basins are biogeochemically distinct and influenced by several physical processes. The Bay of Bengal receives high freshwater influx via high rainfall and riverine influx exceeding evaporation. On the contrary, the high saline waters in the Arabian Sea witness high evaporation over rainfall and riverine influx into the basin. The low saline water is transported by EICC from the Bay of Bengal to the south-eastern Arabian Sea and further carried northward by the WICC during winter (*Wyrtki*, 1973; *Schott and Mc-Creary*, 2001). The high saline water (Arabian Sea High Salinity Water) from the Arabian Sea transports to the eastern Bay of Bengal by WICC during the summer monsoon (*Han et al.*, 2001).

High rates of N_2 fixation and denitrification have been reported from the Arabian

Sea, while these processes are comparatively less intense in the Bay of Bengal (*Ward* et al., 2009; Gandhi et al., 2011b; Saxena et al., 2020). Additionally, physical processes such as mesoscale eddies are prominent particularly in the Bay of Bengal in almost all the seasons, and convective mixing during winter and deep water upwelling during summer in the Arabian Sea may play a significant role in altering the elemental chemistry of the basins.

1.6.1 The Bay of Bengal

The eastern part of the northern Indian Ocean is influenced by the precipitation and freshwater influx from several river channels fed by the monsoonal and Himalayan glacier rivers (*Subramanian*, 1993). Riverine discharge is at its peak during the summer monsoon in the Bay of Bengal (*Unger et al.*, 2003). A large freshwater influx $(1.6 \times 10^{12} \text{ m}^3 \text{ yr}^{-1})$ is received from the Ganges-Brahmaputra river system into the Bay of Bengal (*Subramanian*, 1993). High riverine discharge in the northern Bay of Bengal makes the water relatively less saline than the southern Bay of Bengal (*Vinayachandran and Kurian*, 2007).

The large flux of freshwater in the basin generates vertical density and temperature gradient leading to surface water stratification. The surface water stratification and weak winds have a capping effect on the nutrient rich deep water upwelling to the photic zone (*Gauns et al.*, 2005). This makes the Bay of Bengal less productive as compared to the Arabian Sea (*Prasanna Kumar et al.*, 2010). Although riverine discharge transports terrestrial sediments, organic matter and nutrients to the Bay of Bengal, but most of them get consumed within the estuarine ecosystem (*Singh and Ramesh*, 2011; *Dutta et al.*, 2019). Therefore, the open ocean region remains nutrient limited, particularly in N for primary productivity. The suspended sediment discharge into the basin is ~1.4 × 10^9 tonnes, imposes a ballast effect on the organic matter export to the deeper ocean (*Madhupratap et al.*, 2003).

The mesoscale eddies are frequent in this basin, emerging from the baroclinic and barotropic instabilities related to the shearing of horizontal currents. These mesoscale features affect the vertical transport of water by upwelling and downwelling associated with the cyclonic and anticyclonic eddies, respectively and lateral transport by advection of the eddy core.

1.6.2 The Arabian Sea

The Arabian Sea is located in the western part of the northern Indian Ocean, and encompasses an area around $6.2 \times 10^6 \text{ km}^2$ (*Burkill et al.*, 1993). The basin exhibits high salinity due to excess evaporation over precipitation and continental runoff (*Rao et al.*, 1981). Most importantly, the basin is biologically one of the most productive regions due to the monsoon driven strong seasonal supply of nutrients to the surface (Madhupratap et al., 1996; Smith, 2001; Prakash et al., 2008). The average primary productivity in the Arabian Sea is more than a factor of two higher than that in the Bay of Bengal (Madhupratap et al., 2003). During the summer monsoon, the strong south-westerly winds $(\sim 18 \text{ m s}^{-1})$ induce deep water upwelling along the Somalia coast due to Ekman transport of surface water (*Bauer et al.*, 1991). The enhanced supply of deep water nutrients roots for high productivity in this region during the summer season. Likewise, during the winter monsoon, north-easterly winds induce convective mixing in the northern and to some extent in the north-eastern Arabian Sea (Kumar and Prasad, 1996). Cold and dry winds from the Himalaya region enhance evaporative cooling and increase the density of surface water, which further subsides and leads to vertical mixing, called convective mixing. Convective mixing enhances the nutrient supply to the sunlit layer by uplifting the nutricline to shallower depths and thereby enhances the primary productivity during winter (Madhupratap et al., 1996; Kumar et al., 2001).

High seasonality in biological production and its subsequent export lead to oxygen depletion in subsurface waters which constitute one of the most intense open ocean oxygen minimum zones in the global ocean (*Codispoti*, 2007). Intense oxygen minimum zone (< 6 µM dissolved oxygen concentration) is normally observed in the intermediate depths (150–1200 m) north of 12°N and east of 56°E in the Arabian Sea (*Naqvi*, 1987). Subsurface hypoxic conditions lead to the occurrence of several N removal processes such as denitrification and anammox (*Ward et al.*, 2009; *Bandekar et al.*, 2018)

1.6.3 Previous studies on the C:N:P proportions

Only in recent years, a few studies have been reported in the northern Indian Ocean but were confined to the Bay of Bengal. There is no study on the elemental ratios in the Arabian Sea, which experiences a myriad of physical and biological processes that might affect the elemental dynamics and their ratios. A paucity of concurrent observations of biogeochemical processes and elemental concentrations have barred us to understand the veracity of elemental ratios and the exact role of biogeochemical and physical parameters on the C:N:P ratios in the global ocean in general, and in the northern Indian Ocean in particular.

Garcia et al. (2018) reported the first study on the dynamics of the elemental ratios in the eastern Indian Ocean during spring. Their study highlighted the variation of C:N:P ratios in surface POM along the southern Indian Ocean gyre (31°S to 12°S), equatorial Indian Ocean (10°S to 5°N) and the Bay of Bengal (5°N to 19°N). *Baer et al.* (2019) reported the concurrent nutrients (DIN and DIP) concentration and ratios in the upper 200 m during spring. A significant regional variation in the nutrient and POM elemental concentrations and ratios were found in the eastern Indian Ocean region. Nutrients and POM concentrations were low in the southern Indian Ocean gyre and high northwards. In the Bay of Bengal, the elemental concentrations decreased from 9°N to 15°N due to the increasing surface water stratification that causes restricted deep water nutrient supply to the sunlit layer. POM elemental ratios followed a similar pattern with high ratios in the southern Indian Ocean gyre and decreased ratios in the north; however, the ratios at the equatorial Indian Ocean were slightly above the Redfield Ratio. On the contrary, N:P ratio in nutrients showed an opposite trend with low (9 to 11.5) values in the southern Indian Ocean gyre and higher (13 to 15) values in the equatorial Indian Ocean and the Bay of Bengal region. Higher nutrient (N, P, and Fe) supply and warm temperature (29.1 to 32.6 °C) were observed in the Bay of Bengal region. Nutrient supply was a driving factor for the variation of POM elemental ratios in the eastern Indian Ocean particularly in the Bay of Bengal. Overall the average C:N:P ratios for the eastern Indian Ocean region are 135:19:1, and the ratios are 151:20:1 in the Southern Indian Ocean Gyre, 131:19:1 in the equatorial Indian Ocean and 127:18:1 in the Bay of Bengal.

Although DOM forms one of the largest reservoirs of C and N in the ocean (*Ogawa* and *Tanoue*, 2003) and contributes 20–25% in global export production, the elemental ratios in DOM are not well studied. Only a few studies such as *Letscher and Moore* (2015) reported that the C:N ratio of the non-refractory DOM pool varied from 8.3 to 10.0 in the western Arabian Sea.

1.7 Scope of the present work

The main objective of the present study is to understand the variation of C:N:P ratios in POM, DOM and nutrient pools in the ocean in general and in the northern Indian Ocean in particular. We studied the variation of elemental ratios in three different layers (top, subsurface and deep layers) in the water column. The top layer extends from the surface to the depth of chlorophyll maximum (DCM) where maximum photosynthetic activity prevails. The successive subsurface layer is considered from the depth of chlorophyll maximum up to 300 m (at ACE2), which is characterised by lowest dissolved oxygen concentration due to respiration of sinking organic matter from the top layer. The layer below the subsurface layer to the deepest sampling depth (maximum up to 3000 m) is classified as the deep layer, which is affected by the mixing of various water masses and remains rich in nutrients. Additionally, various physical (eddies) and biogeochemical (N₂ fixation) processes are studied to understand their role in varying elemental ratios. Specifically, focus of the present study is to:

- i. Estimate the C:N:P proportions in POM, DOM and DIM pools and their variation from the Redfield Ratio in the Bay of Bengal. The elemental ratios in the top, subsurface and deep layers are studied during summer (July 2018) and spring (April 2019).
- ii. Investigate the effect of mesoscale eddies on elemental ratios in the Bay of Bengal. The variation of elemental ratios of POM, DOM and nutrients in anticyclonic eddy (ACE), mode water eddy and non-eddy regions are studied during summer and spring.

- iii. Investigate the influence of riverine influx on the elemental concentrations and ratios during spring in the Bay of Bengal. For this, conservative mixing calculations are carried out for DIC and δ^{13} C of DIC during spring. Furthermore, the top layer POC:Chlorophyll *a* and POC:PON ratio at the coastal stations are compared with those from the previous studies in typical coastal regions receiving high riverine discharge.
- iv. Understand the role of N₂ fixation in regulating the N:P ratio in export flux and subsurface layer nutrients in the Bay of Bengal. The contribution of N₂ fixation in varying N:P ratio of export flux is estimated by applying a simple two-component N source model by (*Karl et al.*, 1997).
- v. To test the nutrient supply and growth rate hypotheses for the varying elemental ratios in POM in the Bay of Bengal. For this, the contribution of picoplankton (*Prochlorococcus* and *Synechococcus*) to the total POC biomass in the top layer are estimated during spring.
- vi. Investigate the role of convective mixing in regulating the elemental ratios of POM, DOM and DIM and their variation from the Redfield Ratio in the Arabian Sea. The elemental ratios and their distribution are studied during the winter monsoon (December 2019 to January 2020) in the Arabian Sea. The findings of this study will help biogeochemical modelling in the Indian Ocean region.
- vii. Investigate the effect of denitrification on N:P ratio in the subsurface water nutrients in the Arabian Sea. For this, the N:P ratio in subsurface layer nutrients is calculated and its deviation from the Redfield Ratio is investigated in the hypoxic waters (dissolved $O_2 < 6 \mu$ M).

1.8 Outline of the thesis

The thesis is divided into six chapters.

This chapter gives a brief introduction to the fundamental elements of organic compounds: C, N and P and their biogeochemical cycling in the ocean. The canonical Redfield Ratio is discussed. The evolution of the Redfield concept with varying C:N:P ratios in organic and inorganic pools and the possible mechanisms that drive their variation are highlighted. Additionally, this chapter gives a summary of the previous studies on elemental ratios in the northern Indian Ocean region and the scope of the present work.

Chapter 2

This chapter contains all the details of our sampling in the northern Indian Ocean. Details and precautionary measures taken during seawater sampling and measurement are presented. The measurement procedures of nutrients, POM and isotopic (δ^{15} N of PON and δ^{13} C of POC and DIC) values are provided. The procedure adopted for the analysis of TP and POP is explained in detail.

Chapter 3

This chapter presents the results of C:N:P ratios in organic and inorganic pool in the Bay of Bengal during the summer monsoon. The variation of elemental ratios in the water column is explained and a global comparison of our results is presented.

Chapter 4

The role of mesoscale ACEs and N_2 fixation in varying elemental ratios in the Bay of Bengal during spring is presented in this chapter. Additionally, the influence of the riverine influx on C:N:P ratios is included in this chapter.

Chapter 5

This chapter discusses the pattern of variation of elemental ratios in organic and inorganic pools in the Arabian Sea. The role of convective mixing on the variation of C:N:P ratios is studied in this chapter.

Chapter 6

This chapter highlights the significant findings of the present thesis work and suggests the scope for future potential research works.

Chapter 2

Materials and Methods

2.1 Background

This thesis presents the results from three different research expeditions conducted in the Bay of Bengal and the Arabian Sea. We sampled the Bay of Bengal during the summer (12 July to 2 August 2018) and spring (5 April to 15 April 2019) onboard oceanographic



Figure 2.1: Sampling stations in the Bay of Bengal and the Arabian Sea during three different research cruises: *Sagar Nidhi* (SN#132), *Sindhu Sankalp* (SSK#127), and *Sagar Kanya* (SK#364)

research vessel (ORV) Sagar Nidhi (SN#132), and ORV Sindhu Sankalp (SSK#127), respectively (Figure 2.1). The northeastern and central Arabian Sea was sampled during winter (17 December 2019 to 5 January 2020) onboard ORV Sagar Kanya (SK#364). The results include elemental concentrations and ratios in POM, DOM, and DIM (nutrients) at different depths (up to 14) from the surface to about 3000 m water depth (varied from station to station) (Table 2.1). δ^{13} C values of POC, δ^{15} N values of PON and δ^{13} C values of DIC were also measured. Concurrent stable isotope tracer based C and N₂ fixation rates data were obtained from the literature and unpublished studies. This chapter contains different methods used for data collection and experiments during this study.

2.2 Environmental parameters

The data for temperature, salinity, density, dissolved oxygen (DO) and fluorescence during the expeditions were collected using a Sea-Bird conductivity-temperature-depth (CTD) rosette sampler fitted with Niskin bottles (Figure 2.2). Samples for nutrients (nitrate (NO_3^-) , nitrite (NO_2^-) , and phosphate (PO_4^{3-})) analyses were collected in 60 mL high density polyethylene bottles in duplicates and frozen at -20 °C until analysis in the onshore laboratory.

Nutrients were measured using an autoanalyzer (SKALAR, The Netherlands) at PRL, Ahmedabad. Samples were taken out from the freezer in ambient temperature till they melted completely and then shaken gently before the measurement. Reliability of the nutrients data was obtained daily by measuring certified reference materials, such as MOOS-3 (NO_x (NO₃⁻ + NO₂⁻): 26.6 ± 0.3 µM, NO₂⁻: $3.54 \pm 0.05 \mu$ M, and PO₄³⁻: $1.60 \pm 0.15 \mu$ M) from National Research Council, Canada (*Clancy et al.*, 2014). The detection limits for NO₂⁻, NO_x, and PO₄³⁻ were 0.06 µM, 0.16 µM, and 0.02 µM, respectively. The instrument and analytical procedures used during the analysis are discussed in section 2.2.1.



Figure 2.2: CTD sensors and Niskin bottles mounted on a rosette sampler during the *Sindhu Sankalp* (SSK#127) cruise in the Bay of Bengal. (Photo Credit: Anima Tirkey)

2.2.1 Autoanalyzer

Autoanalyzer works on the principle of segmented flow analysis. This is a continuous flow method of wet chemistry, which involves a stream of samples and reagents, segmented with bubbles, pumped through a manifold for reactions to take place before entering a flow cell for detection. The autoanalyzer consists of an autosampler, chemistry unit, detectors

1 0			1 1 0
Date of sampling (dd.mm.yyyy)	Latitude (°N)	Longitude (°E)	Maximum sampling depth (m)
Cruise No SN#132			
12.07.2018	07°29.99′	88°14.23′	2000
16.07.2018	08°47.66′	88°13.44′	2000
18.07.2018	12°29.60′	88°06.52′	2000
19.07.2018	14°13.64′	88°03.63′	2000
24.07.2018	16°30.49′	88°00.42′	2000
29.07.2018	16°28.19′	87°05.02′	2000
31.07.2018	15°42.30′	85°28.94′	2000
02.08.2018	14°10.33′	85°05.32′	2000
Cruise No SSK#127			
05.04.2019	13°05.58′	80°73.21′	200
07.04.2019	16°30.09′	83°50.88′	2000
08.04.2019	18°32.61′	85°46.12′	530
09.04.2019	19°49.84′	87°00.13′	1000
10.04.2019	19°49.91′	88°59.11′	1000
12.04.2019	14°26.69′	87°23.85′	1500
13.04.2019	13°05.47′	$87^{\circ}00.08'$	2000
14.04.2019	13°04.49′	84°13.42′	1000
Cruise No SK#364			
17.12.2019	15°56.81′	73°09.22′	50
19.12.2019	19°59.16′	69°30.61′	140
21.12.2019	19°59.99′	64°59.98′	3000
22.12.2019	17°59.57′	64°59.77′	2000
23.12.2019	15°59.99′	64°59.96′	2000
24.12.2019	$14^{\circ}00.14'$	$64^{\circ}59.87'$	3000
26.12.2019	11°59.65′	64°59.96′	2000
27.12.2019	09°59.65′	65°00.22′	2000
29.12.2019	07°59.91′	65°00.03′	2000
30.12.2019	06°00.19′	65°00.32′	2000
31.12.2019	03°59.96′	64°59.79′	2000
	Date of sampling (dd.mm.yyyy) 12.07.2018 16.07.2018 18.07.2018 19.07.2018 24.07.2018 29.07.2018 31.07.2018 02.08.2018 05.04.2019 07.04.2019 09.04.2019 10.04.2019 112.04.2019 12.04.2019 13.04.2019 14.04.2019 12.2019 22.12.2019 23.12.2019 24.12.2019 24.12.2019 24.12.2019 25.12.2019 30.12.2019 31.12.2019	Date of sampling (dd.mm.yyyy) Latitude (°N) Cruise No SN#1 12.07.2018 07°29.99' 16.07.2018 08°47.66' 18.07.2018 12°29.60' 19.07.2018 14°13.64' 24.07.2018 16°30.49' 29.07.2018 16°28.19' 31.07.2018 15°42.30' 02.08.2018 14°10.33' Cruise No SSK# 05.04.2019 13°05.58' 07.04.2019 16°30.09' 08.04.2019 18°32.61' 09.04.2019 19°49.84' 10.04.2019 19°49.91' 11.0.04.2019 13°05.54' 11.0.04.2019 13°05.47' 12.04.2019 13°05.47' 13.04.2019 13°05.47' 14.04.2019 13°05.47' 15°56.81' 1 19.2.019 13°05.47' 13.04.2019 13°05.47' 14.04.2019 13°05.41' 19.12.2019 13°05.41' 19.12.2019 19°59.91' 11°12.2019 19°59.95'	Date of sampling (dd.mm.yyyy)Latitude (°N)Longitude (°E)Cruise No SN#13212.07.201807°29.99'88°14.23'16.07.201808°47.66'88°13.44'18.07.201812°29.60'88°06.52'19.07.201814°13.64'88°03.63'24.07.201816°30.49'88°00.42'29.07.201816°28.19'88°05.32'29.07.201816°28.19'85°05.32'31.07.201815°42.30'85°05.32'02.08.201814°10.33'85°05.32'Cruise No SSK#107.04.201916°30.09'83°50.88'08.04.201918°32.61'85°46.12'09.04.201919°49.84'87°00.13'10.04.201919°49.91'88°59.11'12.04.201913°05.47'87°00.08'13.04.201913°05.47'87°00.08'14.04.201913°04.49'84°13.42'15°56.81'73°09.22'19.12.201919°59.96'66°59.96'22.12.201915°59.99'64°59.96'23.12.201915°59.99'64°59.96'26.12.201911°59.57'64°59.96'26.12.201911°59.57'64°59.96'26.12.201911°59.59'65°00.22'29.12.201911°59.59'65°00.32'29.12.201909°59.55'65°00.32'29.12.201909°59.56'65°00.32'29.12.201907°59.91'65°00.32'29.12.201906°00.19'65°00.32'29.12.201906°59.96'65°00.32'29.12.2019

Table 2.1: Sampling locations with date and maximum depth of sampling.

and data handling unit (Figure 2.3). The chemistry unit consists of individual channels for the measurement of NO_2^- , NO_X and PO_4^{3-} .

07°59.79'

11°01.99'

13°30.47'

68°25.00'

71°02.50'

72°19.92'

2000

2000

1000

Measurement of NO_2^- , NO_x , and PO_4^{3-} in seawater samples were carried out by automated procedures. The procedure for NO_2^- measurement is based on the reaction of diazonium compounds (formed by diazotizing of sulphanilamide by NO_2^- in water under acid conditions) with N-(1-naphthyl) ethylene diamine dihydrochloride. The reaction produces a reddish-purple colour complex which is measured at 540 nm.

SK12

SK13

SK14

02.01.2020

04.01.2020

05.01.2020

 NO_x measurement is based on the cadmium reduction method. In this method, the sample is buffered at pH 8.2 and is passed through a column containing granulated copper-cadmium to reduce NO_3^- to NO_2^- . The total NO_2^- , i.e., originally present plus reduced from NO_3^- , is measured as in NO_2^- determination at 540 nm.

The determination of PO_4^{3-} is based on the reaction of a mixed reagent of ammonium heptamolybdate and potassium antimony (III) oxide tartrate in an acidic medium with diluted solutions of PO_4^{3-} to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue coloured complex by ascorbic acid and measured at 880 nm.



Figure 2.3: SKALAR autoanalyzer at PRL, Ahmedabad. (Photo Credit: Deepika Sahoo)

2.3 Dissolved inorganic carbon concentration and its isotopic composition analysis

Seawater samples for DIC and its isotopic composition (δ^{13} C) were collected in exetainers (Labco, UK) in duplicates and preserved with saturated mercuric chloride (100% HgCl₂) solution to cease microbial activity. We filled the exetainers completely to avoid air bubbles inside.

DIC was measured using a Coulometer (UIC's Model 5012, USA) with an analytical precision of $\pm 2\%$. Isotopic compositions are denoted by δ notation and expressed in $\%_0$

unit:

$$\delta(\%_0) = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000$$
(2.1)

where, R is the ratio of the heavier isotope to the lighter isotope. Final values are reported with respect to the international standards, i.e., Vienna-Pee Dee Belemnite (V-PDB) for δ^{13} C.

For δ^{13} C values of DIC, septum vials containing 0.1 mL of 100% orthophosphoric acid were flushed with He gas in GasBench II attached to a continuous flow isotope ratio mass spectrometer (IRMS, Thermo Scientific MAT253) (discussed in section 2.3.2). After flushing, ~1 mL of the seawater samples was injected into the septum vials using a gas tight syringe and kept at 28 °C for 18 hours to allow complete reaction of samples with orthophosphoric acid in order to release CO₂. The CO₂ gas measured for its isotopic composition in the IRMS connected to GasBench II. Sodium bicarbonate (NaHCO₃) of known C isotopic composition (δ^{13} C = -11.4 ± 0.1‰) was used as the lab standard. The precision of δ^{13} C measurement was better than 0.10‰. The instruments used in the analysis and their working principles are discussed below.

2.3.1 Coulometer

The instrument consists of two units: an acidification unit and a coulometer. After acidification of samples in the acidification unit, the released CO_2 gets measured in the coulometer (Figure 2.4). The coulometer measures the absolute mass of CO_2 evolved from sample acidification following Faraday's law of electrolysis. Sodium carbonate (Na₂CO₃) is used as standard to verify the absolute values of DIC.

Atmospheric air is used as the carrier gas during the analysis. However, atmospheric air may contaminate DIC measurements. Therefore, the atmospheric air is made to pass through a pre air scrubber. The scrubber consists of a potassium hydroxide (KOH) solution, prepared by dissolving 45 g of KOH in 100 mL of deionised water.

First, the seawater sample (~ 20 mL volume) gets acidified with orthophosphoric acid to convert DIC into CO₂ in the acidification unit. After acidification, the CO₂ gas carries through the air (devoid of CO_2) via a silica gel scrubber to the coulometeric cell. The coulometeric cell has cathode and anode solutions. The cathode solution consists of monoethanolamine and a colour indicator. Inside the coulometeric cell, CO_2 first purge into the cell cathode compartment, where CO_2 gets absorbed, then reacts with monoethanolamine to form a titratable acid i.e., hydroxyethylcarbamic acid.

This acid causes the cathode solution to fade and the percent of transmittance of the solution increases. A photodetector monitors the change in the percent of transmittance. As transmittance increases, the titration current gets activated. At anode, silver (Ag) electrolyses to produce electrons (Ag⁰ \rightarrow Ag⁺ + e⁻). These electrons move to the cathode, where water in the cathode solution electrolyses to H₂ and OH⁻ as: 2H₂O + 2e⁻ \rightarrow H₂ (g) + 2OH⁻. The OH⁻ ions neutralizes the hydroxyethylcarbamic acid solution at cathode. When the solution returns back to its original colour, cell current stops. The coulometer then measures the exact amount of electric current that was needed to generate OH⁻ ions to neutralize the acid formed by C in the sample. This amount of current is directly proportional to the amount of CO₂ in the cell. By using Faraday's law, the coulometer calculates the exact weight of C.



Figure 2.4: Flow diagram of UIC CO₂ Coulometer.

2.3.2 GasBench

GasBench is a peripheral connected to the IRMS to inject the CO₂ gas released from the sample for measuring δ^{13} C of DIC in water samples (Figure 2.5). The CO₂ gas released from the septum vials after a complete reaction of samples with orthophosphoric acid is transferred to the Gasbench. However, the released gas might also contain the water vapour along with the sample gas. This water vapour is removed by passing the sample stream through a hygroscopic gastight Nafion tubing. A resulting dry gas (such as CO₂ + He) is transferred to the Gas Chromatograph (GC) column. The GC column separates different gas compounds released from the sample. The compounds released from the GC are transferred to IRMS for isotopic measurement.



Figure 2.5: GasBench connected with MAT253–IRMS. (Photo Credit: Deepak Kumar Rai)

2.4 Particulate organic carbon and nitrogen: Concentrations and compositions

Samples for POC and PON were collected by filtering seawater on precombusted (at 400 °C for 4 hours) Whatman glass microfiber filters (GF/F, 47 mm (SN#132), and 25 mm diameter (SSK#127 and SK#364), 0.7 μ m pore size) using a manifold filtration unit connected to vacuum pump. During the SN#132 expedition, ~3.7 to 4.7 L seawater for depths up to 500 m and 5 to 8 L of seawater for depths from 1000 to 2000 m were filtered for POC and PON combined. In SSK#127, 2 to 4.7 L seawater for depths up to 200 m and 2.35 to 5.7 L for depths from 300 to 2000 m were filtered for POC and PON. During SK#364, 2.35 L seawater for depth up to 300 m and 4.7 to 6 L for depths from 500 to 2000 m were filtered for POC and PON. The filters, secured in sterile petri dishes, were dried overnight at 50 °C in an oven onboard and stored for further analysis in mass spectrometer.

POC and PON amount and their isotopic compositions (δ^{13} C and δ^{15} N) were measured using an Elemental Analyzer (EA) (FLASH 2000) coupled with IRMS (Thermo Delta V Plus, Bremen, Germany) connected via Conflo IV interface following *Bhavya et al.* (2016a) and *Bhavya et al.* (2016b) (Figure 2.6). For POC and δ^{13} C measurements, samples were decarbonated by exposing the GF/F filters containing POM to acid fumes (HCl, 37%) prior to the measurement. Samples for PON and δ^{15} N were not treated with the acid fumes. The analytical precision for both POC and PON for duplicate measurements were < 10%, while δ^{13} C and δ^{15} N had analytical precision of < 0.1‰ and 0.3‰, respectively. IAEA-N-2 ((NH₄)₂SO₄, 21.21%, 20.3‰) for N and IAEA-CH-3 (Cellulose, 44.40%, -24.7‰) for C were used as standards in addition to the internal laboratory standards. The δ^{13} C values are reported with respect to the international standards, i.e., V-PDB for δ^{13} C and Air-N₂ for δ^{15} N. Some examples of calibration plots, which were constructed to estimate the amount of C and N in the sample filters are shown in Figure 2.7. The instruments used during the measurements and their working principles are discussed below.



Figure 2.6: FLASH 2000 EA connected to Thermo Delta V Plus-IRMS at PRL, Ahmedabad. (Photo Credit: Deepak Kumar Rai)



Figure 2.7: Examples of calibration plots for the estimation of POC (a and b) and PON (c and d) concentration on different dates.

2.4.1 Elemental Analyzer

EA is a peripheral connected to the IRMS. POC and PON in the samples get converted to CO₂ and N₂ for the measurement of their amounts and isotopic compositions (δ^{13} C and δ^{15} N) (Figure 2.6).

EA uses a high temperature flash combustion method, which involves the complete conversion of all organic and inorganic compounds by instantaneous and complete oxidation of the sample. It consists of an oxidation and a reduction reactor, a water trap and a GC. The reactors are made up of quartz tubes. The oxidation column was prepared by filling silver cobaltous oxide (3 cm) and chromium oxide (12 cm), separated (1 cm) and bracketed (5 cm) by quartz wool layers. The reduction column was prepared by filling copper granules (20 cm) and bracketed by quartz wool layers (5 cm) on both sides of the copper granule layer. The water trap tube has a length of 12 cm and an outer diameter of 1.5 cm was filled with magnesium perchlorate granules in between quartz wool layers (1 to 2 cm).

Samples filtered on GF/F filters packed in tin capsules were dropped through an autosampler into the oxidation chamber at 1020 °C furnace temperature for combustion in presence of oxidising agents such as chromium oxide and silver cobaltous oxide. Upon combustion, carbon dioxide (CO₂), oxides of N (NO_x), and water (H₂O) are carried by Helium to the reduction column maintained at 680 °C. NO_x reduced to N₂ in the reduction chamber and a combination of gases including N₂, CO₂, and H₂O come out as the final output. H₂O was trapped in the magnesium perchlorate column. A mixture of gases (N₂ and CO₂) is then passed through the GC column, where each gas is separated based on its retention time inside the column. The separated gases are introduced in the Delta-V plus IRMS through Conflo IV (Figure 2.6).

2.4.2 Isotope Ratio Mass Spectrometer

IRMS consists of the three main components: source, analyzer, and detector (Figure 2.8). Sample gets singly ionised in the source by the thorium coated tungsten filament. The filament emits electrons upon heating at 1.5 A current. The emitted electrons collide with sample gas (CO₂ and N₂) and ionise them. In the analyzer, a magnetic field is applied to increase the ionisation efficiency which makes the path of ionized molecules spiral. A high voltage ($\sim 2.5 \text{ kV}$) potential difference is applied to accelerate the positively ionized gas molecules, which enters the magnetic sector. Gas molecules with charge (q) accelerate under voltage (V) as:

$$qV = \frac{1}{2}mv^2 \tag{2.2}$$

where m is the mass of the molecule and v is the velocity with which it escapes the ion source. In the analyzer, the charged molecules are separated based on their mass to charge ratio. For CO₂ ions, the beams with masses 44, 45, and 46 atomic mass unit (corresponding to ${}^{12}C^{16}O_2$, ${}^{12}C^{16}O^{17}O$, ${}^{13}C^{16}O_2$, ${}^{12}C^{17}O^{17}O$, ${}^{13}C^{16}O^{17}O$ and ${}^{12}C^{16}O^{18}O$) are produced. For N₂, beams with 28, 29, and 30 atomic mass units (corresponding to ${}^{14}N_2$, ${}^{14}N^{15}N$, and ${}^{15}N_2$, respectively) are produced. These ions follow curvilinear paths owing to the Lorentz force, which is balanced by the centripetal force on the ion beam



Figure 2.8: A schematic showing components of IRMS and its principle.

entering perpendicular to the magnetic field (B) direction (equation (2.3)):

$$q(v \times B) = \frac{mv^2}{r} \tag{2.3}$$

Combining equations (2.2) and (2.3),

$$r^2 = \frac{2mV}{qB^2} \tag{2.4}$$

Lighter molecules deflect more than heavier molecules with a small radius of curvature (r) (equation (2.4)). The detector consists of Faraday cups connected to resistors ($\sim 10^9 \Omega$). Faraday cups where ions neutralize by colliding inside the metal cups and giving up their positive charges and kinetic energies. This produces currents that are passed through the external high resistance resistors. Finally, the voltage across the resistance produced by ions is measured in IRMS, proportional to the number of ions entering into the Faraday cup per unit time.

2.5 Particulate organic phosphorus and total phosphorus analysis

For POP, samples were collected by filtering seawater on pre-combusted (at 400 °C for 4 hours) Whatman glass microfiber filters (GF/F, 47 mm (SN#132 and SK#364) and 25 mm (SSK#127) diameter, 0.7 µm pore size). During the SN#132 expedition, 2.35 L seawater for depths up to 500 m, and 3 to 4 L for depths from 1000 to 2000 m were filtered. In SSK#127, 2 to 4.7 L seawater for depths up to 200 m and 2.35 to 5.7 L for depths from 300 to 2000 m were filtered. During, SK#364, 2.35 L seawater up to 300 m and for depths from 500 to 2000 m, 4.7 to 10 L seawater were filtered. Filtration was followed by rinsing of the GF/F filters with 5 mL of 0.17 M sodium sulphate (Na₂SO₄) solution to drain out the adsorbed particles with POP. The filters, secured in sterile petri dishes, were dried overnight at 50 °C in an oven onboard and stored for further analysis in the PRL laboratory. Seawater samples for TP were collected in 60 mL high density polyethylene

bottles and frozen at -20 °C until analysis.

A high temperature oxidation method was adopted to estimate POP and TP concentrations (*Murphy and Riley*, 1962). Potassium persulfate ($K_2S_2O_8$) was used as an oxidising agent for digestion of the organic matter. Potassium di-hydrogen phosphate (KH_2PO_4) standard was used for the calibration and adenosine-5'-triphosphate disodium (ATP-Na₂) standard was used as laboratory standard to estimate the recovery percentage (80-85%). All the working standards for calibration and the laboratory standards were prepared in artificial seawater (ASW, prepared at laboratory with salinity \sim 33) in order to avoid any possible matrix effect. Two reagents such as ascorbic acid and mixed reagent were prepared fresh on the day of measurement:

- i. For acidic ascorbic acid solution, 10 g ascorbic acid was dissolved in 50 mL of deionised water, and then added with 50 mL sulphuric acid (4.5 M).
- ii. For mixed reagent, 12.5 g of ammonium heptamolybdate tetrahydrate dissolved in 125 mL deionized water. 0.5 g of potassium antimony tartrate was dissolved separately in 20 mL deionized water. Then the molybdate solution was added to 350 mL sulphuric acid (4.5 M), while stirring continuously. Then the tartrate solution was added, mixed well and stored in the refrigerator.

For TP, 25 mL of seawater sample in narrow mouth borosil glass vials was added with 2 mL of 5% of acidic $K_2S_2O_8$ solution and then digested in an Equitron autoclave at 121 °C, 1.055 kg cm⁻² (5 psi) for 80 minutes. The digested samples were allowed to cool down up to room temperature. Subsequently, 1 mL of ascorbic acid and 0.5 mL of mixed reagents were added to each sample and shaken properly. After 30 min, the samples were analysed in a spectrophotometer (Shimadzu Spectrophotometer UV-1800) using a 50 mm cuvette at a wavelength of 880 nm.

For POP, the sample containing GF/F filter kept in narrow mouth borosil glass vial was added with 20 mL of 3% $K_2S_2O_8$ solution and then autoclaved at 121 °C for 80 minutes. After cooling down to room temperature, the digested solution was filtered using a 0.45 µm syringe filter in order to avoid unnecessary scattering due to the suspended particles during measurement. The filtered solution then diluted to 1.5% $K_2S_2O_8$ with deionised water, because > 2% $K_2S_2O_8$ inhibits colour development during reaction. Dilution was followed by the addition of 2 mL of ascorbic acid and 1 mL of mixed reagent prior to the measurement. The analysis of POP was performed in a 100 mm cuvette in the spectrophotometer.

The detection limit of the measurements was 0.1 nM. This procedure is based on the spectrophotometric detection of phosphomolybdenum blue (PMB) complex, which is formed by a sequence of reactions (*Murphy and Riley*, 1962). First, PO_4^{3-} in the sample reacts with acidified molybdate to produce 12- molybdophosphoric acid (12-MPA) (equation (2.5)), which is subsequently reduced to PMB by ascorbic acid (equation (2.6)).

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^+ \rightarrow H_3PO_4(MoO_3)_{12} + 12H_2O$$
 (2.5)

$$\mathrm{H}_{3}\mathrm{PMo}(\mathrm{VI})_{12}\mathrm{O}_{40} + \mathrm{Ascorbic} \operatorname{acid} \rightarrow [\mathrm{H}_{4}\mathrm{PMo}(\mathrm{VI})_{8}\mathrm{Mo}(\mathrm{V})_{4}\mathrm{O}_{40}]^{3-}$$
(2.6)

2.5.1 Calibration and correction

The concentrations of P in seawater samples were calculated using the equations obtained from the calibration curve (Figure 2.9). The recovery percent of laboratory standards were between 80 to 85% during the measurements. Therefore, 15 to 20% of correction was incorporated on each sample value.



Figure 2.9: Examples of calibration plots for the estimation of TP (a and b) and POP (c and d) concentration on different dates.

2.5.2 Spectrophotometer

The spectrophotometer measures the amount of light that a sample absorbs. It works by passing a light beam through a sample to measure the light intensity of a sample. Spectrophotometer measures near-ultraviolet (200–400 nm), visible (400–700 nm), and near-infrared (700 nm–3 μ m) rays of electromagnetic radiation.

It consists of two instruments: a spectrometer and a photometer. The spectrometer produces light, while the photometer measures the intensity of light. The spectrophotometer is designed in a way that a sample is placed between spectrometer and photometer, the amount of light that passes through the sample is measured in the photometer and delivers a voltage signal to the display.

The spectrophotometer has a light source, a monochromator, a sample compartment, a photoelectric detector, an amplifier, and a digital display (Figure 2.10). We used a double beam configured spectrophotometer. This optical configuration divides the monochromatic light into two beams, the reference beam and sample beam using a rotating, semi-transparent mirror. When the reference cell with solvent in it is placed for the reference beam and the sample cell with sample in it is placed for the sample beam in the sample compartment, each transmitted light enters the detector. The transmittance and absorbance are measured from sample sign I and the reference sign I_o .

Spectrophotometer follows Bouguer-Beer's law for quantitative analysis, which is also known as Lambert-Beer's law. This law states that the transmittance (T) is:

$$T = I/I_o = 10^{-kcl} (2.7)$$

$$A = log(1/T) = log(I_o/I) = kcl$$
(2.8)

where I_o is the light intensity passed through a sample and I is the intensity of the transmitted light, where k stands for proportional constant, c for concentration and l is the path length of light. $(I/I_o) \times 100$ is the percent transmittance (%T) and A denotes the absorbance. The absorbance of light is proportional to the concentration of the sample (Beer's law) and the path length of light (Bouguer's law) (equation (2.7) and (2.8)).



Figure 2.10: Double beam configured spectrophotometer.

2.6 Total organic carbon and total nitrogen analysis

For TOC and TN measurements, seawater samples were collected in 50 mL sterile centrifuge tubes (Tarsons, India) in duplicates. The centrifuge tubes were rinsed three times with deionized water and later rinsed twice with the sample aliquot to avoid any possible contamination. The samples were frozen immediately at -20 °C until analysis in the onshore laboratory at PRL, Ahmedabad.

The TOC measurements were performed using a high temperature catalytic oxidation method in the TOC analyzer (TOC-L-CPH, Shimadzu Corporation, Japan) (*Knap et al.*, 1993; *Suratman et al.*, 2009; *Pujo-Pay et al.*, 2011). Inorganic carbon was removed by acidifying the sample with 2N HCL through purging of carrier gas prior to the TOC measurement. Ultrapure zero gas with 99.9995% purity was used as the carrier gas. The zero gas contains 0.5 ppm carbon monoxide (CO), 2 ppm CO₂, 1 ppm nitrogen dioxide (NO₂) and 0.2 ppm total hydrocarbon (THC) and was manufactured and supplied by Vinay Air Products, Ahmedabad, India.

System blank was checked and maintained at zero before analysis. The TOC analyzer was rinsed with deionized water before and after every sample measurement to remove the salt accumulation and clean the system. The non-purgeable organic carbon was oxidised to CO₂ and measured using Non Dispersive Infra-Red (NDIR) detector (discussed in section 2.6.1). Sucrose was used for calibration and laboratory standard for TOC measurement. 237 mg of sucrose was dissolved in 100 mL of deionized water to prepare a standard solution of 1000 ppm C concentration. An intermediate solution of 10 ppm C concentration was prepared from the standard solution. Using the autodilution feature,

the instrument performed multiple point calibration with working standards of 0.4, 0.8, 1.2, 1.6 and 2.0 ppm C concentrations.

TN concentrations were measured simultaneously in a TN analyzer (TNM-L-CPH, Shimadzu Corporation, Japan) by oxidising dissolved N to nitric oxide (NO) into the combustion tube at 720 °C. The resultant NO was detected in the chemiluminescence detector (discussed in section 2.6.1).

Potassium nitrate (KNO₃) was used for calibration and laboratory standard in the TN measurement. 7.22 g of KNO₃ was dissolved in 1 L deionized water to prepare a standard solution of 1000 ppm N concentration. An intermediate solution of 10 ppm N concentration was prepared from the standard solution. Using the autodilution feature, the instrument performed multiple point calibration with working standards of 0.25, 0.5, 0.75, 1.0 and 1.25 ppm N concentrations.

The accuracy of the results was ensured by routinely measuring a certified reference material (Batch 18, Lot#08-18 for deep seawater) provided by the University of Miami, USA (*Hansell*, 2005). The analysis was performed at the absolute deviation within 5% of the standard value. The coefficient of variation was 2% for TON and TN measurements.

2.6.1 Total organic carbon and total nitrogen analyzer

The instrument consists of three units including autosampler (ASI-L), TOC (TOC-L) and TN (TNM-L) units and a data handling unit (Figure 2.11). The TOC-L unit consists of a combustion chamber and NDIR detector. The combustion tube was prepared by inserting two sheets of platinum mesh in the bottom of the tube, and a layer (5 mm) of quartz wool on it, which was followed by the filling of TOC standard catalyst (platinum coated Al-Si oxide) in the combustion tube to a height of 140 mm from the top end of the tube. A layer (10 mm) of ~0.2 g ceramic fiber was placed uniformly over the catalyst. The furnace temperature of the combustion chamber was maintained at 720 °C during the simultaneous measurement of TOC and TN concentration in seawater samples.

NPOC (Non-Purgeable Organic Carbon) method was used for TOC analysis, which removes inorganic C from the sample and the remaining C is measured as TOC. The



Figure 2.11: Shimadzu TOC-TN analyzer at PRL, Ahmedabad. (Photo Credit: Deepika Sahoo)

autosampler takes the samples from the vials to the TOC unit through Hamilton syringe, where the sample is acidified with 5% of 2N HCL for ~10 mins. After acidifying the seawater sample to pH 2 to 3, sparge gas was bubbled through the sample to eliminate the inorganic C component. The sample was then introduced into the combustion tube, which was filled with Al-Si oxide as oxidation catalyst and heated to 720 °C. During combustion, the remaining TOC in the sample is converted to CO₂. The carrier gas, which flows at a rate of 150 mL min⁻¹ to the combustion tube, carries the sample combustion products to an electronic humidifier, where the gas is cooled and dehydrated. The gas then carries the sample combustion products through a halogen scrubber to remove chlorine and other halogens. Finally, the carrier gas delivers the combustion products to the cell of NDIR gas analyzer, where CO₂ is detected. The NDIR outputs an analog detection signal that forms a peak and the peak area is measured by the TOC-Control L software.

The NDIR detector consists of a light source, cell and detection portion. The detector uses a diaphragm type of detection system called Luft detectors. The diaphragm connected to an opposing electrode in a parallel circuit, which further connected to a high-value resistor and an amplifier. Light passes through the cell compartment and the detector. Depending on the concentration of CO_2 generated from the sample, an amount of light passes through the quartz window into the detection portion. The movement of the trapped CO_2 within the detector compartment causes the diaphragm to flex. Upon flexing, the distance between the diaphragm and electrode changes and creates an electrical signal corresponding to the concentration of TOC in the sample.

For TN measurement, the sample was introduced into the combustion tube at 720 °C furnace temperature. Zero gas was used as the carrier gas that provides oxygen to support combustion and to the ozone generator inside the TN detector. During combustion, N containing compounds in the sample thermally decomposes to NO. The zero gas containing NO was cooled in a thermoelectric cooler and dehumidified by the electronic dehumidifier immediately after exiting the combustion tube. The cooled gas then enters the chemiluminescence gas analyser, where the NO reacts with ozone (O₃) and converts into a combination of NO₂ and excited NO₂ (NO₂^{*}). As NO₂^{*} returns to the ground state, it emits radiation, which was measured photo-electrically. The detector signal generates a peak that is proportional to the N concentration in the sample. The peak area and the TN concentrations were measured by the TOC-Control L software.

2.7 Elemental concentrations in dissolved organic matter

TON and TOP were estimated by subtracting inorganic matter from its total elemental pool as [TN] - [DIN] and [TP] - [DIP], respectively. The DOC, DON, and DOP concentrations were estimated as the difference between TOC and POC, TON and PON, and TOP and POP, respectively. This method has limitations for DOP measurements in samples having < 10% of total dissolved P.

2.8 Statistical analyses

Linear regression analyses (significance level, p < 0.05) were performed among C, N, and P concentrations in different pools. One-way ANOVA was done to test the significant (p < 0.05) difference in ratios in the different pools using the SigmaPlot 14.0 software. Shapiro-Wilk test was performed to check the normality in data for ANOVA analysis. Linear regression and ANOVA analyses were performed for analysing the results from the SN#132 study in the Bay of Bengal during the summer monsoon 2018 (Chapter 3).

The influence of environmental variables on the concentration of elements and their elemental ratios in three different pools was investigated using Principal Component Analysis (PCA) in R programming language. Pearson's correlation coefficient at p < 0.05 was used to estimate the strength of the relationships. The PCA analysis showed that the first two principal axes (PC1 and PC2) explained the highest percent of the variability. The PCA is used to highlight the relationships between variables projected in a multidimensional space. Each arrow represents a variable as mentioned near their heads. Arrows' distance from the origin and their closeness to each other is proportional to correlation, i.e., when arrows are far from the center and close to each other, they are positively correlated. When arrows are symmetrically opposite, they are anticorrelated. If the arrows are orthogonal, there is no correlation. If the variables are close to the origin, the relationship among these variables is inconclusive. PCA analysis was used in the SN#132 and SSK#127 study in the Bay of Bengal during the summer 2018 (Chapter 3) and spring 2019 (Chapter 4), respectively.

Spearman's correlation coefficient at $\alpha < 0.05$ was used to estimate the strength of the relationships between parameters in the top, subsurface, and deep layers. The statistical significance of the differences between the mean values of a parameter (elemental concentrations and ratios in nutrients and organic matter) measured at coastal and open ocean stations were tested following *Chao* (1974). Two mean values (say μ_1 and μ_2) are considered to be significantly different from each other at $\alpha < 0.05$, if $\mu_1 - \mu_2 \ge$ $1.645\sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}$, where σ_1 and σ_2 are the standard deviations around the mean values μ_1 and μ_2 calculated from data points n_1 and n_2 , respectively. Spearman's correlation test and the significance testing following *Chao* (1974) were performed in SSK#127 and SK#364 studies in the Bay of Bengal and the Arabian Sea during spring 2019 (Chapter 4) and winter 2019–2020 (Chapter 5), respectively.
Chapter 3

C:N:P proportions in the Bay of Bengal during the summer monsoon

3.1 Introduction

The Bay of Bengal is an economically, ecologically, and culturally important basin as it forms a long coastline with the Indian subcontinent. It is surrounded by the Indian subcontinent in the north and north-west, and the Andaman and Nicobar Islands in the east. The prevalence of eddies are typical characteristics of this basin (*Mukherjee et al.*, 2019). Frequently occurring mesoscale eddies in this basin are associated with advective transfer of riverine water offshore. The Bay of Bengal experiences semi-annual seasonality of the Asian monsoon system (*Gadqil*, 2003). Strong southwesterly winds lead to high rainfall over the Indian subcontinent from June to September, whereas between December to February, northeasterly winds lead to heavy rainfall in the southern states of India. Large freshwater influx $(1.625 \times 10^{12} \text{ m}^3 \text{ year}^{-1})$ from the Ganges-Brahmaputra river system drives strong vertical density gradient leading to higher sea surface temperature than usual in the Bay of Bengal (Subramanian, 1993; Shetye et al., 1991). The influx of nutrients through riverine discharge, surrounding mangroves, and wetlands enhance the productivity in the coastal regions (*Choudhury and Pal*, 2010; *Dutta et al.*, 2019) and leads to a considerable C export in the deeper Bay of Bengal (*Ittekkot et al.*, 1991; *Singh* and Ramesh, 2015; Kumar et al., 2004a).

The Bay of Bengal witnesses high concentration of DOC \sim 75–100 µM in the surface waters due to high riverine flux (*Shah et al.*, 2018). In addition, DON and DOP constitute about 70–99% of the total dissolved nutrients in the waters above the thermocline (*Sarma et al.*, 2019b). At the same time, the water column remains stratified restricting the upward nutrient flux due to strong halocline (*Prasanna Kumar et al.*, 2010). In such cases, recycling processes and frequent eddies observed over the Bay of Bengal could be of considerable importance for primary production (*Gomes et al.*, 2000; *Kumar et al.*, 2004b; *Singh et al.*, 2015b). In fact eddies are known to enhance the primary production in the Bay of Bengal (*Prasanna Kumar et al.*, 2010; *Singh et al.*, 2015b).

These physical (e.g., stratification and eddy driven mixing), and biogeochemical phenomena such as (e.g., N_2 fixation) might have a control on C:N:P ratios in the Bay of Bengal. However, paucity of data lacks our knowledge of the elemental ratios in the basin. To enhance our understanding on the C:N:P ratios in the Bay of Bengal, we sampled the water column at eight stations in the basin during the summer monsoon. The purpose of this study was to:

- (i) Estimate the C:N:P ratios in POM, DOM and DIM pools in the water column (surface to 2000 m depth)
- (ii) Understand the impact of mesoscale eddies and N₂ fixation on the elemental ratios.

3.2 Methods

Sampling was performed in the Bay of Bengal during the peak of summer monsoon (12 July to 2 August 2018) on-board ORV Sagar Nidhi (SN#132) (Figure 3.1, Table 3.1). Water samples were collected using a Sea-Bird CTD rosette sampler from 12 different depths (10 m, 25 m, 50 m, 75 m, 100 m, 150 m, 200 m, 300 m, 500 m, 1000 m, 1500 m, and 2000 m) at each station. At times, one of the two subsurface sampling depths (i.e., 50 m or 75 m) was changed to match the DCM. To analyse the variability in elemental concentrations and ratios in the water column, we have categorized our observations into three depth segments on the basis of biogeochemical processes as explained in Chapter 1: (1) top layer (surface to DCM), (2) subsurface layer (DCM to 300 m), and (3) deep

layer (300 m to 2000 m). The DCM varied between 25 m and 78 m. For calculation purposes, we have considered the DCM depth in both the top and subsurface layers, and similarly 300 m depth in both the subsurface and deep layers. MLD was calculated by 0.2 °C decrease in temperature from that at the 10 m reference depth (*de Boyer Montégut et al.*, 2004; *Holte and Talley*, 2009).



Figure 3.1: Daily sea surface height anomaly overlaid by geostrophic currents on 12 July 2018. The eddies remained in the same position throughout the sampling period. Circles: sampling locations.

The measurement of elemental concentrations of DIM, POM, and DOM, and δ^{13} C and δ^{15} N of POM were discussed in Chapter 2. The nutricline was estimated as the depth where NO₃⁻ increased to 1 µM. The N₂ fixation and C uptake rates were taken from a concurrent study performed on the same cruise (*Saxena et al.*, 2020) to assess the role of these two biogeochemical processes on C:N:P ratios.

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Station	Date of sampling (dd.mm.yyyy)	Latitude (°N)	Longitude (°E)	SST (°C)	SSS	Chl $a \ (\mathrm{mg \ m^{-3}})^\dagger$	DCM (m)	MLD (m)	Nutricline (m)	N_2 fixation (µmol N m ⁻² d ⁻¹)*	Primary production (mmol C $m^{-2} d^{-1}$)*
ACE1	12.7.2018	07° 29.99′	88° 14.23′	28.8	34.19	0.29 ± 0.04	75	64	58	11 ± 5	30 ± 8
MWE	16.7.2018	08°47.66'	88°13.44'	28.1	34.39	0.89 ± 0.59	25	49	10	6 ± 6	87 ± 11
NE1	18.7.2018	12°29.60'	88°06.52'	28.8	33.11	0.38 ± 0.41	57	52	58	27 ± 16	39 ± 4
NE2	19.7.2018	14°13.64'	88°03.63'	28.5	32.78	0.23 ± 0.16	55	48	45	20 ± 4	24 ± 2
ACE2	24.7.2018	16°30.49'	88°00.42'	28.2	33.48	0.42 ± 0.21	47	43	51	4 ± 4	69 ± 5
ACE3	29.7.2018	16°28.19'	87°05.02'	28.7	33.44	0.20 ± 0.18	76	77	33	12 ± 8	58 ± 13
BWE	31.7.2018	15°42.30'	85°28.94'	28.7	33.62	0.23 ± 0.09	55	41	32	75 ± 98	81 ± 12
ACE4	02.8.2018	14°10.33'	85°05.32'	29.1	33.04	0.25 ± 0.28	78	66	66	41 ± 6	45 ± 4

Table 3.1: Details of environmental parameters at the eight sampling locations during summer 2018.

[†]Chlorophyll a (Chl a) values are averaged over the top layer, *Column integrated (up to 75 m) N₂ fixation rates and primary production data are taken from Saxena et al. (2020)

Processed Automatic Weather Station (AWS) data for wind speed was provided by Indian National Centre for Ocean Information Services (INCOIS), India (*Harikumar et al.*, 2013). To categorize the sample locations based on the sea surface height anomaly (SSHA), geostrophic current data were obtained from the Copernicus Marine Environmental Monitoring Service (https://resources.marine.copernicus.eu/; data retrieved on 17 August 2019). Cyclonic eddies were identified by the anticlockwise geostrophic currents with < -0.2 m SSHA. Anticyclonic eddies (ACEs) were identified by the clockwise circulation with > 0.2 m SSHA. Features having increased SSHA accompanied by lens shaped isopycnals were characterized as mode water eddy (MWE) (*Sweeney et al.*, 2003). Station located along the boundary area of cyclonic and ACE was categorised as boundary water eddy (BWE). Stations with no significant SSHA were considered as non-eddy(NE) stations. We sampled four ACE (1–4), two NE (1–2) and one each MWE and BWE.

3.3 Role of environmental factors on C, N, and P concentrations and their ratios

Variations in elemental ratios are driven by environmental factors such as temperature, salinity, and nutrient concentrations (*Körtzinger et al.*, 2001; *Frigstad et al.*, 2011). Sea surface temperature ranged from 28 to 29 °C while sea surface salinity varied from 32 to 34 (Figure 3.2).



Figure 3.2: Vertical section of (a) temperature, (b) salinity, (c) density, and (d) chlorophyll *a*. Section distance starts from station ACE1 (50 km) and ends at ACE4 (1500 km).

Nutrients (DIN, DIP, and DIC) concentration showed anticorrelation with temperature in PCA analysis (Figure 3.3). This suggests that temperature might not play a direct role on nutrient concentration. Rather this indicate that the nutrient concentrations are high in deep (cold) waters, but influx of cold waters during physical processes (such as eddies) might enhance the nutrient concentration in the surface waters in the Bay of Bengal. Additionally, positive correlation between nutrients and salinity indicate that the nutrients are of marine origin (Figure 3.3). This is not surprising as terrestrial nutrients are largely consumed within the estuarine ecosystem in the basin (*Singh and Ramesh*, 2011; Dutta et al., 2019). Correlations between elemental ratios with temperature and salinity should be interpreted with caution as both of these parameters are not known to directly affect the elemental ratios. However, change in temperature affects nutrient uptake and other biogeochemical processes (such as respiration/decomposition), in turn influencing the elemental stoichiometry (Lomas et al., 2002; Spackeen et al., 2018). In addition, salinity gradient has been shown to change N uptake rates in mesocosm experiments (*Kumar et al.*, 2018). In theory, temperature and salinity related influences could be both physiological and taxonomic (Barton and Yvon-Durocher, 2019; Hernando et al., 2020). The N uptake potential is a part of physiological change of phytoplankton driven by salinity and temperature (Kaur-Kahlon et al., 2016; Kumar et al., 2018; Barton and Yvon-Durocher, 2019; Hernando et al., 2020). Since our data are spatially distributed, these influences are likely to be taxonomical. Anticorrelation of salinity with POM concentrations could be attributed to the increase of elemental uptake potential due to the freshening of water at elevated temperature (*Hernando et al.*, 2020) or relatively higher consumption (mineralisation) of POM at higher salinity condition. However, these need to be experimentally verified in the Bay of Bengal.

Overlapping of the PON:POP and POC:POP vectors suggest that the ratios are driven by variation in POP through similar processes, such as the POP remineralisation. Additionally, no significant correlations of PON:POP and POC:POP with PON and POC, respectively, confirms the variation of these ratios to be due to oscillations in POP (Figure 3.3).



Figure 3.3: PCA analysis of depth, temperature, salinity, fluorescence, dissolved inorganic nutrients, POM, DOM, elemental ratios, δ^{13} C, and δ^{15} N of POM.

3.4 The C:N:P ratios in DIM, POM and DOM

3.4.1 Dissolved inorganic matter

The low N:P ratio in nutrients (varied from 3 to 12 < 16:1, Figure 3.4) in the top layer indicates N stressed primary production in the Bay of Bengal. This is confirmed from the negative intercept between DIN and DIP (Figure 3.5), which suggests that DIN gets exhausted before DIP. Unlike N:P ratio, C:N and C:P ratios in DIM of the top layer were thousand and hundred times higher than the Redfield Ratio, respectively. $HCO_3^$ and CO_3^{2-} are the alkalinity species accounts for 99% of DIC pool (~2000 µM) in ocean. These species reside thousands of years in the ocean, higher than the average mixing time of ocean. Additionally, only a small fraction of HCO_3^- and CO_3^{2-} is utilized by phytoplankton for photosynthesis and calcifying organisms for carbonate precipitation. Therefore the DIC pool is so large it cannot be easily exhausted and is considered here as unutilised. It present almost 2–3 orders of magnitude higher that the other macronutrients such as NO_3^- and PO_4^{3-} . Therefore, when one looks at the change in DIC:DIN or DIC:DIP over time (i.e., consumption rate ratios), these ratios are likely to be close to Redfield. However, ratios in the static set of concentrations at a given time, as presented here, are roughly order of magnitudes higher.

A large spatial variation in DIC:DIN and DIC:DIP ratios in the top and subsurface layers was observed across the stations with higher values at ACE and NE stations (Table 3.2). However, DIC:DIN and DIC:DIP ratios were similar in the deeper layers across stations. The DIN:DIP ratios increased with depth with no significant spatial variability.



Figure 3.4: Box-whiskers plots showing C:N, N:P and C:P ratios in top layer, subsurface water, and deep water. Pink dotted lines represent mean, whereas blue (POM, DOM) and green (DIM) solid lines represent median. Black solid brackets represent significantly different groups (p < 0.05) obtained from One way ANOVA test. Whiskers account for 10 and 90% of distribution, whereas box accounts for 25 and 75%.

Parameter		ACE			MWE			NE		BWE		
	Тор	Subsurface	Deep	Тор	Subsurface	Deep	Тор	Subsurface	Deep	Тор	Subsurface	Deep
POC (µM)	4.91 ± 1.59	2.52 ± 0.42	2.14 ± 0.73	8.24 ± 3.65	2.94 ± 1.76	2.67 ± 0.82	3.52 ± 0.53	2.08 ± 0.32	1.85 ± 0.02	4.03 ± 1.16	1.80 ± 0.63	1.88 ± 0.88
PON (µM)	0.58 ± 0.32	0.30 ± 0.16	0.16 ± 0.05	0.86 ± 0.06	0.43 ± 0.35	0.17 ± 0.03	0.37 ± 0.02	0.19 ± 0.05	0.15 ± 0.01	0.40 ± 0.11	0.14 ± 0.08	0.11 ± 0.05
POP (µM)	0.021 ± 0.010	0.009 ± 0.003	0.004 ± 0.002	0.044 ± 0.004	0.011 ± 0.014	0.003 ± 0.0004	0.016 ± 0.003	0.006 ± 0.002	0.002 ± 0.0004	0.02 ± 0.01	0.005 ± 0.003	0.003 ± 0.002
DOC (µM)	76.86 ± 5.77	65.69 ± 6.01	49.86 ± 7.17	75.96 ± 1.15	63.31 ± 7.57	49.79 ± 5.62	93.44 ± 5.10	71.23 ± 7.32	62.90 ± 18.49	63.94 ± 2.95	49.71 ± 9.92	42.11 ± 8.11
DON (µM)	5.34 ± 1.00	7.09 ± 3.41	7.33 ± 7.70	8.42 ± 0.80	12.24 ± 5.09	19.54 ± 0.22	8.18 ± 0.30	15.35 ± 1.91	19.49 ± 2.34	5.09 ± 0.94	3.71 ± 1.74	7.73 ± 7.48
DOP (µM)	0.36 ± 0.13	0.43 ± 0.19	0.40 ± 0.23	0.36 ± 0.48	0.52 ± 0.44	0.25 ± 0.31	0.29 ± 0.03	0.29 ± 0.003	0.29 ± 0.08	0.28 ± 0.13	0.33 ± 0.16	0.53 ± 0.22
DIC (µM)	1910.25 ± 77.33	2108.35 ± 58.89	2246.50 ± 37.06	1973.13 ± 6.37	2103.31 ± 105.42	2242.36 ± 17.48	1969.65 ± 102.24	2217.15 ± 118.29	2360.83 ± 106.01	1916.56 ± 29.39	2074.37 ± 79.82	2317.87 ± 109.66
DIN (µM)	0.29 ± 0.13	15.84 ± 2.36	33.87 ± 1.49	1.96 ± 0.49	14.86 ± 11.29	34.98 ± 2.79	0.56 ± 0.35	20.79 ± 0.74	36.10 ± 0.37	1.68 ± 2.47	20.77 ± 9.44	30.69 ± 6.98
DIP (µM)	0.15 ± 0.04	1.45 ± 0.20	2.75 ± 0.12	0.38 ± 0.04	1.36 ± 0.82	2.75 ± 0.23	0.18 ± 0.02	1.76 ± 0.09	2.80 ± 0.01	0.29 ± 0.27	1.75 ± 0.67	2.56 ± 0.44
POC:PON	9.98 ± 2.04	12.49 ± 3.89	16.21 ± 6.29	9.76 ± 5.04	9.34 ± 2.59	15.64 ± 3.59	9.80 ± 1.34	12.98 ± 0.56	12.81 ± 1.18	9.96 ± 0.89	14.05 ± 2.59	17.15 ± 1.75
POC:POP	238.91 ± 37.84	408.73 ± 31.18	828.40 ± 156.45	187.94 ± 77.85	407.82 ± 183.11	951.26 ± 293.39	241.71 ± 62.03	584.50 ± 32.16	1294.49 ± 179.35	226.75 ± 20.50	447.57 ± 108.04	877.16 ± 645.84
PON:POP	26.98 ± 11.35	30.28 ± 9.68	63.11 ± 35.50	19.89 ± 2.71	37.83 ± 13.95	61.41 ± 16.94	24.57 ± 3.12	43.04 ± 0.68	105.73 ± 3.51	22.81 ± 1.76	31.64 ± 4.84	52.08 ± 37.28
DOC:DON	15.08 ± 1.64	12.55 ± 5.50	12.32 ± 8.26	9.09 ± 0.95	6.05 ± 2.44	2.55 ± 0.26	11.71 ± 0.72	5.71 ± 0.99	3.35 ± 0.33	12.88 ± 2.73	20.62 ± 18.01	10.46 ± 6.90
DOC:DOP	274.73 ± 105.10	231.49 ± 102.16	172.84 ± 50.54	784.38 ± 764.19	441.08 ± 649.98	698.43 ± 819.98	349.55 ± 38.42	288.64 ± 29.52	242.37 ± 131.72	275.50 ± 170.51	202.71 ± 153.48	88.38 ± 34.42
DON:DOP	18.62 ± 9.26	17.79 ± 2.04	19.30 ± 13.35	82.40 ± 73.95	96.17 ± 123.08	291.84 ± 353.74	30.61 ± 6.03	57.08 ± 2.81	73.04 ± 27.22	20.29 ± 8.09	15.26 ± 9.46	11.40 ± 7.57
DIC:DIN	7289.80 ± 3043.03	1054.31 ± 1225.65	65.04 ± 1.07	1058.79 ± 305.94	368.88 ± 516.97	64.30 ± 5.24	9905.74 ± 2954.69	435.02 ± 260.08	65.47 ± 2.30	5134.73 ± 4215.76	148.19 ± 139.24	78.48 ± 16.48
DIC:DIP	14546.90 ± 5520.35	4225.68 ± 2306.26	822.10 ± 31.60	5304.01 ± 659.89	2360.36 ± 1932.53	817.20 ± 71.45	13984.41 ± 391.88	2145.07 ± 241.45	842.85 ± 36.25	10273.59 ± 6132.11	1450.87 ± 885.53	925.58 ± 136.69
DIN:DIP	2.62 ± 2.06	9.20 ± 1.32	12.28 ± 0.13	5.15 ± 0.75	9.62 ± 2.99	12.71 ± 0.08	2.34 ± 1.10	10.57 ± 0.32	12.87 ± 0.10	3.74 ± 3.24	11.30 ± 1.94	11.94 ± 1.08

Table 3.2: C, N and P and their ratios in different reservoirs at three depth layers at ACE, MWE, NE, and BWE stations.



Figure 3.5: Correlation between (a) POC and PON, (b) PON and POP, (c) POC and POP, (d) DIC and DIN (e) DIN and DIP, (f) DIC and DIP, (g) DOC and DON, (h) DON and DOP, and (i) DOC and DOP. Straight lines are drawn for the correlations significant at p < 0.05.

On average, the C:N:P ratios in dissolved inorganic nutrients were 12717:3:1, 3126:10:1, and 840:12:1 in the top, subsurface, and deep layers, respectively.

3.4.2 Particulate organic matter

The N:P, and C:P ratios in POM were invariably higher than the Redfield Ratio in the top layer and increased further with depth (Figure 3.4). Average POC:PON ratio in the top layer showed little variability (~9) and remained largely fixed in the water column. The increase in the POC:POP and PON:POP ratios from the top to the subsurface layer suggests the preferential remineralisation of POP in sinking organic matter (*Loh and Bauer*, 2000; *Letscher and Moore*, 2015). In addition, strong correlation (r = 0.5 and 0.7 and p < 0.05) of PON:POP and POC:POP ratios with nutrients confirms the recycling of POP. Overall, the C:N:P ratios in POM were 232:25:1, 457:35:1, and 966:72:1 in the

top, subsurface, and deep layers, respectively.

During remineralisation, preferential removal of ¹³C enriched molecules such as protein and nucleic acids and retention of ¹³C depleted lipid rich residual organic matter results in decrease in δ^{13} C (~1.6‰) of POM from the top layer to the subsurface and deep layers (*Post et al.*, 2007) (Figure 3.6). On the other hand, removal of ¹⁴N rich biomolecules during degradation might have resulted in the increase in δ^{15} N (6‰ in the subsurface, and 7.5‰ in the deep water) of POM (*Macko et al.*, 1994). Usually δ^{13} C in POC varies from -24‰ to -18‰ (*Fry and Sherr*, 1989; *Middelburg and Nieuwenhuize*, 1998) and δ^{15} N in PON from 5 to 8‰ in marine phytoplankton (*Minagawa et al.*, 2001). Although the Bay of Bengal receives enormous terrestrial influx (33 to 51.2 g m⁻² y⁻¹) (*Ittekkot et al.*, 1991; *Unger et al.*, 2003), mean C:N ratio (~10), δ^{13} C (-21.5 to -26.2‰, average -24.6 ± 1.2‰), and δ^{15} N (0.9 to 8.3‰, average 4.4 ± 1.9‰) of POM in the top 100 m in our study indicate that the POM in the sunlit layer of the Bay of Bengal is largely derived from *in situ* production rather than external supply.



Figure 3.6: Depth profile of δ^{13} C (green dashed line) and δ^{15} N (blue solid line) of POM at (a) ACE1, (b) MWE, (c) NE1, (d) NE2, (e) ACE2, (f) ACE3, (g) BWE, and (h) ACE4 stations.

3.4.3 Dissolved organic matter

The POM and DIM elemental ratios are primarily controlled by nutrient uptake and remineralisation processes. The remineralisation process of POM to dissolved nutrients involves cycling through the DOM pool (Johnson et al., 2013; Singh et al., 2015a). Therefore, the DOM serves as an important intermediary link between POM and nutrients during remineralisation. In the NO_x deficient top layer of the Bay of Bengal, DON is an order of magnitude higher than DIN (Figure 3.7), suggests DON might be an alternative source of bioavailable N for phytoplankton in these waters (*Church et al.*, 2002; *Zubkov* et al., 2003; Aldunate et al., 2020). A previous study in the Bay of Bengal suggested a link between primary productivity and high DON and DOP concentrations during the spring inter-monsoon 2018 (Sarma et al., 2019b), but no such correlation was observed in our study. The absence of correlation between primary production and DON in our study can be explained by the coupling between DON production and uptake, leading to lack of DON accumulation. The seasonal change in phytoplankton community composition is possibly another cause for no-correlation. DON-consuming phytoplankton (cyanobacteria) are most abundant during summer in oligotrophic oceans (*Huisman et al.*, 2018). Given that use is one of the important sources of N for autotrophs in the surface water of the Bay of Bengal (*Baer et al.*, 2019), a study focused on DON uptake in different seasons is desirable to quantify the importance of DON as an alternative N source for phytoplankton in the Bay of Bengal.

During this study, the DOC concentrations were higher in the top layer with lower concentrations measured in the subsurface and deep layers (Figure 3.7). The opposite vertical trend was observed for DON and DOP concentrations with highest concentrations found in the subsurface and deep layers. DOC is freshly produced in the sunlit surface ocean via phytoplankton degradation and food web processes (grazing by microzooplankton) and the labile components are generally rapidly consumed by heterotrophic prokaryotes (*Calleja et al.*, 2019). The semi labile portion of DOC escapes rapid microbial consumption and accumulates in surface waters during strong stratification (*Calleja et al.*, 2019). On the contrary, the low concentrations of DON and DOP in the top layer may be attributed to the photochemical breakdown of organic matter (*Chari et al.*, 2016) and



Figure 3.7: Depth distribution of elemental concentration in (a) POC, (b) PON, (c) POP, (d) DOC, (e) DON, (f) DOP, (g) DIC, (h) DIN, and (i) DIP. Please note the y axis is stretched up to upper 300 m for better visualization.

faster remineralisation of DOP and DON over DOC (*Church et al.*, 2002; *Letscher and Moore*, 2015). Therefore, the accumulation of DOC and low concentrations of DON and DOP in the top layer might have resulted in high C:P \sim 357, and C:N ratio \sim 13 in DOM (*Ogawa and Tanoue*, 2003) (Figure 3.4).

In the subsurface and deep layers, the C:N and C:P ratios in DOM were lower than that in the top layer (Figure 3.4). This could be attributed to the remineralisation of DOC by heterotrophic communities in subsurface waters. Typically, DON is more resistant to remineralisation than DOP. The downward transport of refractory DON (> 50% of DON; (*Roussenov et al.*, 2006; *Vidal et al.*, 2018)) results in an enhanced accumulation below the

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top layer of the ocean. Overall, this might have resulted in decreased C:N and C:P ratios along with increased N:P ratio in DOM in the subsurface and deep layers. On average, C:N:P ratios in DOM were 357:30:1, 268:37:1, and 245:66:1 in the top, subsurface, and deep layers, respectively.

3.5 The role of strong winds and eddies on the C:N:P ratios

Strong southwesterly winds (up to 24.5 m s⁻¹) and eddies were identified in our sampling area during the study period. Relatively deep mixed layer (41–77 m) and shallow nutricline (10–66 m) were observed, which might be due to the strong winds and eddy induced mixing of the water column. At ACE stations, the nutricline was relatively deep, while shallow nutricline with relatively high POM concentrations was observed at MWE station. Average δ^{15} N of POM varied between 5‰ and 6‰ at ACE1, ACE2, MWE, and BWE stations in the upper 100 m (Figure 3.6), mimicking the isotopic composition (5.5‰) of the deep water NO₃⁻ in the same region (*Bristow et al.*, 2017). This suggests the supply of new N from the subsurface waters to the sunlit layer, in turn leading to increased primary production at these stations.

In this study the DIM and POM elemental concentrations were different at the eddy and NE stations. Mean DIC, DIN and DIP concentrations were 1910.3 \pm 77.3 µM, 0.3 \pm 0.1 µM and 0.1 \pm 0.04 µM, respectively, in the top layer at ACE stations (Table 3.2). However, high DIN and DIP concentrations were observed in the top layer at MWE and BWE stations (Table 3.2, Figure 3.7). The mean DIC, DIN and DIP concentrations were 1973.1 \pm 6.4 µM, 2.0 \pm 0.5 µM and 0.4 \pm 0.04 µM, respectively, at MWE station and 1916.6 \pm 29.4 µM, 1.7 \pm 2.5 µM and 0.3 \pm 0.3 µM, respectively, at BWE in the top layer. At NE stations, mean DIC, DIN, and DIP concentrations in the top layer were higher than those observed at ACE stations but lower than that at MWE station. The MWE stations also exhibited high POM elemental concentrations in the top layer than the other stations (Table 3.2). The mean concentrations for POC, PON, and POP were 8.2 \pm 3.7, 0.9 \pm 0.1, and 0.04 \pm 0.004 µM, respectively, in the top layer at the MWE station. Overall, eddies showed a mixed effect on C:N:P ratios in the top layer. Although there were differences in DIM and POM concentrations, little variability in C:N:P ratios of POM between eddy and NE stations was observed.

Comparatively low DOC and DON concentrations and slightly high DOP concentration at ACEs lead to the low DOC:DOP and DON:DOP ratios in ACE stations compared to the NE stations (Table 3.2). A study by *Sarma et al.* (2019a) during spring 2018 reported higher POC and PON concentrations than our study but the C:N ratio in POM remained the same. Similarly, primary production estimates reported in a concurrent study (288–1044 mg C m⁻² d⁻¹; *Saxena et al.* (2020)) are consistent with that (758 ± 220 mg C m⁻² d⁻¹) reported by *Sarma et al.* (2019a). These primary productivity estimates are much higher than an earlier estimate of primary productivity conducted during N stressed conditions during April 2016 (primary productivity: 3–7 nmol C L⁻¹ h⁻¹; N:P flux ratio < 14; *Baer et al.* (2019)). Overall, these studies suggest the role of eddies in supplying nutrients to the photic layer and consequently increased primary production leading to elevated elemental ratios in POM (*Sarma et al.*, 2019a,b).

3.6 Impact of biogeochemical processes on C:N:P ratios

Marine biogeochemical processes have the potential to change the plankton and nutrient elemental ratios and vice versa (*Klausmeier et al.*, 2004b; *Mills and Arrigo*, 2010; *Jabir et al.*, 2020). Despite PO_4^{3-} excess (N:P ~3) in the top layer with adequate dry deposition flux of Fe (0.02-1.2 µmol m⁻² d⁻¹ (*Srinivas and Sarin*, 2013), low N₂ fixation rates (4-75 µmol N m⁻² d⁻¹) were observed in the Bay of Bengal (*Saxena et al.*, 2020). Assuming photoautotrophs require 1 mole N to fix 6.6 mole C (*Redfield*, 1958), the contribution of N₂ fixation to autotrophic C fixation remains below 1% (*Saxena et al.*, 2020). Apart from the low N₂ fixation in surface waters during our study, heterotrophic N₂ fixation rates are also low in the oxygen minimum zone of the Bay of Bengal (*Löscher et al.*, 2020). Such low contribution is unlikely to change the elemental ratios. No correlation between N₂ fixation rates and different elemental ratios confirms the same (Figure 3.8).

The N:P ratios in nutrients act as a proxy for biogeochemical processes leading to N loss (such as denitrification and anammox) in the subsurface low oxygenated waters.

The inorganic nutrients N:P ratio (< 16:1) in the water column suggest the occurrence of N loss processes in the Bay of Bengal. Low but detectable rates of anammox (5.5 nM N d^{-1}) and denitrification (0.9 nM N d^{-1}) are measured in the oxygen minimum zone by *Bristow et al.* (2017). However, an extensive study is required to understand the effect of N loss processes of this magnitude on nutrient stoichiometry of the Bay of Bengal.



Figure 3.8: Correlation between (a) DON and primary productivity, (b) DOP and primary productivity, (c) N₂ fixation and DIP, (d) N₂ fixation and DOP, (e) DIN:DIP and N₂ fixation, and (f) PON:POP and N₂ fixation. Lines are not drawn as none of the correlations are significant at p < 0.05.

3.7 Testing nutrient supply hypothesis in the Bay of Bengal

Considering the observed deviations in C:N:P ratio from the Redfield Ratio in the dissolved and particulate matter pools, we examined whether the Bay of Bengal supports nutrient supply hypothesis for tropical ecosystems proposed by *Rhee* (1978). This hypothesis states that the absolute concentration of nutrients such as DIN and DIP, rather than their ratio, determine the POM stoichiometry. Based on this hypothesis, expected C:N:P ratios in oligotrophic basins are higher than the Redfield Ratio and reverse holds for the nutrientrich basins (*Galbraith and Martiny*, 2015; *Klausmeier et al.*, 2004a). This happens as slow growing cyanobacteria with high N:P ratio in their biomass/nutrient uptake requirements grow in oligotrophic waters, whereas fast growing microorganisms (with low N:P ratio) flourish in nutrient-rich waters (*Arrigo*, 2005; *Singh et al.*, 2017; *Sharoni and Halevy*, 2020). Poor supply of nutrients due to stratification makes the Bay of Bengal oligotrophic during most of the seasons (*Prasanna Kumar et al.*, 2010; *McCreary et al.*, 2013). We observed that the C:N, C:P, and N:P ratios in the POM at surface waters are higher than the Redfield Ratio and seems to be favouring the nutrient supply hypothesis for tropical systems.

3.8 Putting the Bay of Bengal elemental ratios in the global ocean perspective

The average C:N:P ratio (232:25:1) of POM in the top layers of the Bay of Bengal is in a similar range to observations in other tropical oceans, such as the subtropical North Atlantic Ocean (210:36:1) (*Singh et al.*, 2015a) and subtropical North Pacific Ocean (172:25:1) (*Martiny et al.*, 2013a). The subtropical North Atlantic is considered as P limited (DIN:DIP ~30) basin and witnesses high C:N:P ratio in the POM (*Wu et al.*, 2000). However, the Bay of Bengal and the subtropical North Pacific Ocean (*Karl et al.*, 2001) are N limited, and both possess high N:P ratio (25) in POM and low N:P (< 16) in subsurface nutrients. Our overall analysis suggests that the nutrient availability in the Bay of Bengal and the subtropical North Pacific Ocean is likely governed by the N loss processes (such as denitrification), whereas N gain processes (such as N₂ fixation) exert control in the subtropical North Atlantic Ocean (*Deutsch and Weber*, 2012). The average C:N:P ratio in the DOM in the top layer is 357:30:1 in the Bay, lower than the global average 640:44:1 for bulk DOM in the surface ocean (*Letscher and Moore*, 2015).

3.9 Conclusion

We presented a comprehensive study of C:N:P ratio in the inorganic and organic pools of the Bay of Bengal water column covering depths from the surface to 2000 m. Overall, C:N:P ratios deviated greatly from the Redfield Ratio (C:N:P = 106:16:1) in all the biogeochemical pools and at all depths. In the POM, C:N:P ratios were 232:25:1, 457:35:1 and 966:72:1 in the top, subsurface and deep water layer, respectively. Our estimated C:N:P ratios in POM are comparable to that observed in other tropical basins such as the North Pacific Ocean and North Atlantic Ocean. On the other hand, C:N:P ratio in the DOM in the top layer (357:30:1) is relatively lower than the global average of 640:44:1 for bulk DOM in surface water.

Despite being a peak summer monsoon period, relatively low concentration of nutrients with low N:P ratio suggests that primary production was limited by bioavailable N. Concurrently estimated low N_2 fixation rates suggest that diazotrophic organisms had a minimal impact on nutrient or POM stoichiometry. Instead, non-diazotrophic cyanobacteria along with low supply of nutrients governed higher N:P ratio in the POM. Overall, higher C:N:P ratio than the Redfield Ratio in POM in surface waters support the nutrient supply hypothesis for tropical oceans with low inorganic nutrient concentrations. Low N:P ratio in nutrients in the subsurface waters suggest a potential role of nitrogen loss processes in regulating the nutrient stoichiometry.

Eddies have mixed effects on C:N:P ratios in the top layer. DIM concentrations are lower in ACE stations compared to that in the NE stations. On the contrary, POM concentrations are higher in ACE stations compared to that in the NE stations. However, there is not much change in C:N:P ratios of DIM and POM at eddy and NE stations.

Chapter 4

C:N:P ratios in the Bay of Bengal during spring: Role of eddies and N₂ fixation

4.1 Introduction

Recent observations and numerical simulations have profoundly established that the C:N:P ratios in the ocean deviate from the canonical Redfield Ratio (106:16:1). Physical and biogeochemical processes have been hypothesized to be responsible for this deviation. However, a paucity of concurrent observations on biogeochemical and physical parameters have barred us to understand their exact role on the C:N:P ratios. The Bay of Bengal remains highly understudied in this regard, but the basin can provide an ideal realm to explore the integrated effect of eddies, N₂ fixation and many more processes on its marine chemistry.

Cyclonic and anticyclonic mesoscale (10–500 km diameter) eddies are a major part of the water circulation in the Bay of Bengal. Cyclonic eddies are the areas of divergence which are associated with upwelling of nutrient-rich subsurface water, and ACEs are the convergence areas where downwelling dominates. In the Bay of Bengal, cyclonic eddies increase primary productivity, while low nutrient concentrations result in low primary productivity at ACE regions (*Singh et al.*, 2015b; *Sarma et al.*, 2019a). Phytoplankton community composition is different in different type of eddies, e.g., microplankton flourish in nutrient rich cyclonic eddies while picoplankton dominate in the nutrient depleted ACEs (*Sarma et al.*, 2020b). Apparently, 50–60% of phytoplankton abundance in the Bay of Bengal is of the picoplankton alone, while nanoplankton are the second most abundant species (*Sarma et al.*, 2020b). At ACE regions, picoplankton constitute a major fraction of phytoplankton owing to their hypothesized potential to consume dissolved organic nutrients in depleted inorganic nutrient regimes (*Sarma et al.*, 2020b).

In our study during summer, monsoonal winds and mesoscale eddies were suggested to have a mixed effect on the elemental proportions of organic and nutrient pools in the top layer (*Sahoo et al.*, 2020). Nutrients were lower in ACEs compared to those in the NE stations. On the contrary, POM concentrations were higher in ACEs compared to that in the NE stations. However, there was not much difference in the elemental ratios in nutrients and POM at eddy and NE stations. During spring, the surface Bay of Bengal experiences high temperature and salinity owing to heat gain by the sea and excess evaporation, respectively (*Narvekar and Kumar*, 2006). Weaker winds and prolonged ACEs hinder the supply of subsurface nutrients to the euphotic zone, which leads to ultra-oligotrophy in the Bay of Bengal (*Jyothibabu et al.*, 2021). These changing environmental conditions can affect the phytoplankton growth and thereby their elemental stoichiometry during spring. For example, increased temperature and the reduced availability of nutrients lead to increase in C:N and C:P ratios in POM (*Matsumoto et al.*, 2020).

Three reasons spurred us to revisit the Bay of Bengal to study the elemental dynamics during spring. First, in a previous study during summer, we sampled only open ocean stations where the influence of river water was negligible (*Sahoo et al.*, 2020). In this study, we have sampled coastal as well as open ocean regions in the Bay of Bengal. We hypothesize that the elemental proportions, particularly in the coastal Bay of Bengal, might have been influenced by a combination of processes including river water intrusion in addition to *in situ* primary production and remineralisation. Second, during spring the Bay of Bengal experiences severe N limitation than during summer (*Narvekar and Kumar*, 2014). The changing environmental conditions and associated biogeochemical processes such as N₂ fixation might affect the elemental stoichiometry. Third, ACEs prevail dominantly during spring (*Jyothibabu et al.*, 2021). Furthermore, the age of an eddy is another aspect to look at in biological context as a time lag always exists between ocean physical process and its manifestation on productivity. Prolonged ACEs might affect the organic and nutrient pools in the Bay of Bengal. For this purpose, we conducted this study in the basin during April 2019.

4.2 Methods

We participated in ORV Sindhu Sankalp expedition (SSK#127) that cruised from Chennai (13°N, 80.3°E) along the eastern coast of India, turned to the open ocean at ~19.9°N and moved southwards in the Bay of Bengal from 5 April to 15 April 2019 (Figure 4.1a and b). We sampled eight stations during this expedition: five stations including NE1, ACE1, NE2, NE3, and NE4 were situated along the east coast of India, were considered as the coastal stations, and the rest including NE5, NE6, and ACE2 were considered as the open ocean stations. Water samples were collected using a Sea-Bird CTD rosette sampler at a maximum of 10 different depths (5, 25, 50, 85, 200, 300, 500, 1000, 1500, and 2000 m). Based on the biogeochemical processes, we divide our analysis into three different depth segments: top, subsurface, and deep layer as explained in Chapter 1. The top layer extends from the surface to the DCM. The successive subsurface layer is considered from the DCM up to < 360 m. The layer below the subsurface layer to the deepest sampling depth is classified as deep layer.

Apparent oxygen utilisation (AOU) was calculated as the difference between the measured DO concentration and its temperature and salinity dependent saturation concentration (*Murray and Riley*, 1969).

Following the methods described in Chapter 2, the elemental concentrations of DIM, POM, and DOM, and δ^{13} C value of DIC were measured. For Chl *a* concentrations, samples were collected by filtering 1 L seawater onto Whatman glass microfiber filters (GF/F, 25 mm diameter, 0.7 µm pore size) followed by extraction in 90% acetone and kept for 24 h in a refrigerator. The Chl *a* concentrations were measured in HPLC (Agilent, USA) at Space Applications Centre, Ahmedabad. Nutricline depth was considered as the depth where DIN concentration increased to 1 µM (*Richardson and Bendtsen*, 2017; *Garcia et al.*, 2018). The vertical diffusive fluxes of DIN from subsurface waters were calculated following *King and Devol* (1979) and the vertical diffusion coefficient used in



this calculation was taken from *Nozaki and Alibo* (2003).

Figure 4.1: Geostrophic currents overlaid on the sea surface height anomaly (m) during (a) 5–10 April, and (b) 10–14 April 2019. The surface water (c) DIN and (d) DIP concentrations. The coastal (NE1, ACE1, NE2, NE3, and NE4) and open ocean (NE5, NE6, and ACE2) stations are shown with filled and open circles, respectively. BDL: below detection limit.

Several eddy features were identified based on the SSHA and geostrophic current during the sampling period. Cyclonic eddies were identified by anticlockwise geostrophic currents with < -0.2 m SSHA. ACEs were identified by the clockwise circulation with > 0.2 m SSHA. We sampled two ACE stations and categorised them as ACE1 and ACE2, while no significant SSHA values at the rest six stations led to categorize them as NE stations (NE1–NE6; Figure 4.1, Table 4.1).

The N₂ fixation rates and abundance data of picoplankton such as *Prochlorococcus* and *Synechococcus* obtained from Saxena et al. (2021) (under preparation). The C amount of *Prochlorococcus* and *Synechococcus* was calculated by multiplying their abundances (cell counts L^{-1}) with their C content per cell values. The C content per cell values of the photic zone *Prochlorococcus* and *Synechococcus* were taken from *Casey et al.* (2013).

Station	Date of sampling (dd.mm.yyyy)	Latitude (°N)	Longitude (°E)	SST (°C)	SSS	MLD (m)	DCM (m)	Nutricline (m)	Chl $a \ (\mu g \ L^{-1})^*$	$\delta^{13}{ m C}$ of DIC $(\%_0)^\dagger$	POC:Chl a^{\dagger}
NE1	05.04.2019	13° 05.58′	80° 73.21′	29.1	34.3	12	22	8	0.27	-	80 - 508
ACE1	07.04.2019	16° 30.09′	83° 50.88′	29.0	33.2	30	83	84	0.10	0.2 - 0.4	67 - 458
NE2	08.04.2019	18° 32.61′	85° 46.12′	27.6	33.1	20	55	41	0.21	-0.6 - 0.2	82 - 376
NE3	09.04.2019	19° 49.84′	87° 00.13′	28.4	33.0	24	69	39	0.16	-0.5 - 0.3	82 - 249
NE4	10.04.2019	19° 49.91 ′	88° 59 .11′	28.0	32.8	34	71	56	0.19	-0.3 - 0.4	81 - 269
NE5	12.04.2019	14° 26.69′	87° 23.85′	30.0	32.1	12	61	53	0.24	-0.20.001	132 - 667
NE6	13.04.2019	13° 05.47′	87° 00.08′	30.3	32.3	20	87	54	0.10	-0.4 - 0.3	332
ACE2	14.04.2019	13° 04.49′	84° 13.42′	30.2	33.3	27	86	87	0.08	0.1 - 0.2	85 - 457

Table 4.1: Environmental parameters at the eight sampling locations during spring 2019.

*Surface (5 m) Chl *a* values are presented, $^{\dagger}\delta^{13}$ C of DIC and POC:Chl *a* values in the top layer. Due to logistic issues, samples for δ^{13} C of DIC could not be collected at NE1.

Further, the contribution of *Prochlorococcus* and *Synechococcus* biomass to the total POC pool was calculated.

4.3 Estimation of riverine flux contribution at the coastal stations

In order to estimate the riverine contribution into the Bay of Bengal, we assumed the salinity remains conserved during the mixing of river (r) and seawater (s). Therefore, the measured salinity of samples (Salinity_{sample}) can be expressed using a mass balance concept:

$$Salinity_{sample} = Salinity_r f_r + Salinity_s (1 - f_r)$$

$$(4.1)$$

The subscripts r and s stand for river water and seawater, respectively. f_r and $(1 - f_r)$ represent the river and seawater fraction in conservative mixing. f_r is calculated as:

$$f_r = \frac{Salinity_s - Salinity_{sample}}{Salinity_s - Salinity_r}$$
(4.2)

We considered mean values of the parameters from the open ocean stations in our study locations to be representative of seawater end members. Seawater end member values of salinity (Salinity_s), DIC (DIC_s), and δ^{13} C (δ^{13} C_s) are 33.79, 1.83 mM, and 0.13%₀, respectively. River water end member values of salinity (Salinity_r), DIC (DIC_r), and δ^{13} C (δ^{13} C_r) are 0.19, 2.35 mM, and -4%₀, respectively (taken from *Samanta et al.* (2015) for pre-monsoon period).

Similar to equation (4.1), we write mass balance equation for DIC and δ^{13} C for conservatively mixed sample having DIC_{CM} and δ^{13} C_{CM} as:

$$DIC_{CM} = DIC_r f_r + DIC_s (1 - f_r)$$
(4.3)

 $\delta^{13}C_{CM}g_{CM} = \delta^{13}C_rg_r + \delta^{13}C_sg_s$ (4.4)

$$g_{CM} = g_r + g_s \tag{4.5}$$

where g_r is the fraction of DIC of river water (DIC_rf_r), and g_s is the fraction of DIC in seawater (DIC_s (1-f_r)). The total fraction of DIC in mixture (g_{CM}) = DIC_{CM}. Deviations (Δ DIC and $\Delta \delta^{13}$ C) of measured DIC concentrations and δ^{13} C from the respective conservative mixing values were estimated by following *Alling et al.* (2012). Equation (4.4) can be written as

$$\delta^{13}C_{CM} = \frac{\delta^{13}C_r DIC_r f_r + \delta^{13}C_s DIC_s (1 - f_r)}{DIC_{CM}}$$
(4.6)

Equation (4.6) can be written by combining equations (4.2) and (4.6) as:

$$\delta^{13}C_{CM} = \frac{Salinity_{sample} \left(DIC_r \,\delta^{13}C_r - DIC_s \,\delta^{13}C_s \right) + Salinity_r DIC_s \,\delta^{13}C_s - Salinity_s DIC_r \,\delta^{13}C_r}{Salinity_{sample} \left(DIC_r - DIC_s \right) + Salinity_r DIC_s - Salinity_s DIC_r}$$

$$(4.7)$$

Deviations of measured DIC concentrations (Δ DIC) and δ^{13} C ($\Delta\delta^{13}$ C) from the respective conservative mixing values (DIC_{CM} and δ^{13} C_{CM}) were estimated as:

$$\Delta DIC = \frac{DIC_{sample} - DIC_{CM}}{DIC_{CM}}$$
(4.8)

$$\Delta \delta^{13} C = \delta^{13} C_{sample} - \delta^{13} C_{CM} \tag{4.9}$$

The trend of conservative mixing lines are linear for salinity-DIC and salinity- δ^{13} C (Figure 4.2a and b). However, according to equation (4.7), the conservative mixing line trend for salinity- δ^{13} C should be hyperbolic in nature. But the variation in salinity at the coastal stations was minimal, therefore the trend for salinity- δ^{13} C looks linear in Figure 4.2b. In the Figure 4.2c, origin represents the conservative mixing of river and seawater. All the DIC and δ^{13} C values have deviated from the conservative mixing line in Figure 4.2a and b, which suggests that the variation of DIC is least accounted by the mixing of seawater and river water. Furthermore, the Δ DIC and $\Delta\delta^{13}$ C values were scattered into quadrants away from the origin (Figure 4.2c), reconfirms that the coastal stations were influenced by the marine processes. Additional processes such as *in situ* primary production, degradation of organic matter, and calcite dissolution might have impacted the DIC pool.



Figure 4.2: Variation of (a) DIC, (b) δ^{13} C of DIC with salinity in top layer, and (c) Δ DIC vs. $\Delta\delta^{13}$ C of DIC in the Bay of Bengal, where $\Delta\delta^{13}$ C and Δ DIC are deviations from the values expected from conservative mixing calculations. Black solid lines in (a) and (b) represent conservative mixing of freshwater and seawater.

4.4 Processes affecting elemental concentrations and proportions

The river water fraction was negligible (< 0.05) at our stations. Sea surface temperature varied from 27.6 to 30.3 °C with warmer (\geq 30 °C) waters at the open ocean stations (Table 4.1). But the sea surface salinity at the coastal stations was not much different from those at the open ocean stations (Table 4.1). It varied from 32.1 to 34.3 with the highest value at NE1. The δ^{13} C values of DIC at the Hooghly river system ranged from -11.4 to -1.6% (*Samanta et al.*, 2015). During our sampling, the δ^{13} C values in the top layer at the coastal stations (-0.6 to 0.4%) also showed typical marine range and were higher than the reported riverine values by Samanta et al. (2015). It ranged from -0.6 to 0.4‰ and -0.4 to 0.3‰ in the top layer at the coastal and open ocean stations, respectively. In fact, the DIC and δ^{13} C values at the coastal stations showed significant deviation from the conservative mixing line of river and seawater (Figure 4.2). The nonzero values of Δ DIC and $\Delta\delta^{13}$ C such as negative Δ DIC and positive $\Delta\delta^{13}$ C values indicate that the *in situ* primary production certainly accounts for a significant variation in DIC. Positive Δ DIC and negative $\Delta\delta^{13}$ C values reinforce the idea that DIC primarily inherited from the degradation of organic matter. Moreover, positive Δ DIC and $\Delta\delta^{13}$ C values indicate that carbonate dissolution is also an important process prevalent in the coastal regions and responsible for the generation of DIC.

DIC values and the lack of significant difference in nutrients at the coastal and open ocean stations altogether confirmed that the elemental chemistry at the coastal stations was not substantially influenced by the riverine influx. But we caution that our coastal sampling sites may not possess typical characteristics (e.g., strong upwelling, high nutrient concentration) of coastal areas in other oceanographic regions and it is likely that the river influence is limited to within a short distance from the river mouths.

Although the elemental concentrations in POM at the coastal stations were significantly different from that at the open ocean stations, no significant difference was reflected in their elemental ratios. As expected from the mixing calculation, POC:PON ratio in the top layer was 7.6 \pm 2.5 at the coastal and 6.6 \pm 1.0 at open ocean stations, suggesting that *in situ* primary production contributed significantly to the POM pool in the top layer, as terrestrially derived POM possess high C:N ratio (> 10) (*Hedges et al.*, 1986). POC:Chl *a* ratio, a proxy to identify the source of organic matter in aquatic systems (*Bentaleb et al.*, 1998), is typically low in the freshly produced organic matter than in terrestrial organic matter. POC:Chl *a* ratio normally ranges from ~40 (*Montagnes et al.*, 1994) to 200 (*Cifuentes et al.*, 1988; *Bentaleb et al.*, 1998) for *in situ* produced organic matter (*Geider et al.*, 1998). *Sarma et al.* (2019a) estimated the mean POC:Chl *a* ratio of 1123 \pm 389 at the sampling stations along the east coast in the Bay of Bengal. They attributed the POC:Chl *a* ratio to the faster degradation of Chl *a*, and a possible contribution of heterotrophs (bacteria and zooplankton) and terrestrial organic matter (*Sarma et al.*, 2019a). On the contrary, the POC:Chl *a* ratio at our sampling stations (ranged from 67 to 667, mean 245 ± 177) was lower than that observed by *Sarma et al.* (2019a), reconfirming no influence of riverine influx at our sampling stations.

The δ^{13} C of POC values varied from -25.5 to -22.9% (mean = -24.2%) at the coastal stations in the top layer, close to that of the marine isotope signature of carbon (mean = -23.9%) (*Sahoo et al.*, 2021). One of our coastal stations i.e., NE3 was close to the Mahanadi River. We have calculated the contribution of riverine influx of organic matter at NE3 using the mass balance concept as in equation (4.10).

$$\delta^{13}C_{sample} = \delta^{13}C_r f_r + \delta^{13}C_s (1 - f_r)$$
(4.10)

In this equation δ^{13} C referes to the δ^{13} C values of POC. The δ^{13} C values of POC are $-24.3\%_0$ at NE3, $-26.8\%_0$ at the Mahanadi River, and $-23.9\%_0$ at our open ocean station (*Sarma et al.*, 2014; *Sahoo et al.*, 2021). The Mahanadi River contributes 13.8% organic matter at NE3, which suggests that the organic matter at our coastal stations were profoundly affected by the marine processes.

DIC, DIN, and DIP concentrations ranged from 1591 to 2155 µM, BDL to 12.5 µM, and 0.2 to 1.2 µM, respectively in the top layer (Figure 4.3). The average DIC:DIN, DIC:DIP, and DIN:DIP ratios were 3458 ± 4251 (3362 ± 4643 at coastal and 1133 at open ocean), 8437 ± 3339 (8288 ± 3284 at coastal and 9934 ± 2205 at open ocean), and 8.9 ± 2.5 (7.1 ± 4.1 at coastal and 7.9 ± 4.3 at open ocean), respectively in the top layer (Figure 4.4). High DIC concentration at the coastal stations led to a higher DIC:DIN ratio in the top layer. Likewise, the low concentration of DOP in open ocean stations led to high DON:DOP and DOC:DOP ratios in the top layer. The average DOC:DON (22.3 \pm 19.1 at coastal and 10.2 ± 5.3 at open ocean), DOC:DOP (1194 \pm 1113 at coastal and 7603 \pm 8077 at open ocean), and DON:DOP (61.5 ± 73.0 at coastal and 482 at open ocean) ratios were 21.2 ± 17.9 , 2337.8 \pm 4060.1, and 146.0 \pm 201.6, respectively in the top layer (Figure 4.4).

POC, PON, and POP concentrations ranged from 2.1 to 12.3 μ M, 0.3 to 2.0 μ M, and 0.01 to 0.1 μ M, respectively, in the top layer with the highest at NE1. The mean POC:PON, POC:POP, and PON:POP ratios were 7.1 \pm 2.2 (7.6 \pm 2.5 at coastal and 6.6 \pm 1.0 at open ocean), 249.4 \pm 58.0 (245 \pm 62 at coastal and 247 \pm 48 at open ocean),



Figure 4.3: Vertical section of (a) DIC, (b) DIN, (c) DIP, (d) POC, (e) PON, (f) POP, (g) DOC, (h) DON, and (i) DOP concentration. Section distance starts from NE1 (50 km) and ends at ACE2 (2370 km).

and $38.6 \pm 17.6 (35.1 \pm 14.0 \text{ at coastal and } 37.5 \pm 4.7 \text{ at open ocean})$, respectively in the top layer (Figure 4.4).

The POC:PON, and PON:POP ratios ranged higher in the top layer at the coastal stations, where high POM concentrations were also observed. Below the top layer, degradation of organic matter profoundly contributed to the nutrient dynamics in the coastal and open ocean stations. Labile POP and PON degrade faster than POC, resulting in an increased POC:POP and POC:PON ratios in the subsurface and deep layer (*Loh and Bauer*, 2000) (Figure 4.4). The mean ratios increased to 8.0 ± 4.0 (7.8 ± 3.9 at coastal and 8.2 ± 4.2 at open ocean), 327.6 ± 111.7 (327 ± 91 at coastal and 318 ± 141 at open ocean), and 47.5 ± 21.8 (50.6 ± 26.6 at coastal and 41.3 ± 10.0 at the open ocean) for POC:PON, POC:POP, and PON:POP, respectively in the subsurface layer. However, the variation in the mean elemental ratios in the deep layer was less than that in the subsurface layer. The mean POC:PON, POC:PON, POC:PON, POC:POP, and PON:POP, and PON:POP ratios were 10.3 ± 3.4 (9.7 ± 3.0 at coastal 10.9 ± 3.9 at open ocean), 369.3 ± 106.5 (342 ± 79 at coastal and 400 ± 128 at open ocean), and 39.3 ± 16.5 (40.8 ± 21.0 at coastal and 37.6 ± 9.4 at open ocean), respectively in the deep layer.

Large variability in the elemental concentrations and ratios was evident in this study. However, there was no significant difference in the elemental concentrations (except in POM) at the coastal and open ocean stations in the top layer. Likewise, all the elemental ratios were also similar at both the regions in the top layer. The coastal stations had larger range of elemental concentrations and ratios than the open ocean stations, which led to the overall large variability in elemental ratios in the top layer.



Figure 4.4: Box-whiskers plots showing C:N, N:P and C:P ratios in DIM, POM, and DOM pools in the top, subsurface, and deep layers. Pink dotted lines represent the mean. Whiskers account for 5% and 95% of distribution, whereas boxes account for 25% and 75%. Dots within the boxes represent 50% of the distribution. Blue boxes represent the coastal and black represent the open ocean stations. Boxes are not shown when the number of data points is less than 2.

4.5 Impact of eddies on elemental proportions

Mesoscale eddies influence ocean biogeochemistry by modulating the supply of nutrients to the photic zone (*Sarma et al.*, 2019a). The Nutricline was deeper (84 and 87 m) at ACE1 and ACE2 compared to NE stations where it reached maximum up to 56 m. Deeper nutricline at ACEs indicate that the downwelling of surface water resulted in decreasing nutrients (DIN and DIP) in the top layer at ACE1 and ACE2 (Figure 4.1c and d). In the top layer, concentrations of DIN and DIP were low, particularly DIN concentration was below the detection limit in surface water at all stations but NE4 (Figure 4.1c and d). Furthermore, the DIN concentration was still below the detection limit up to 85 m at ACE1 and ACE2, and 51 m at NE1, NE2, NE3, NE5, and NE6 (Figure 4.3). At ACE1 and ACE2, DIN (BDL at both the stations) and DIP (mean DIP: $0.2 \pm 0.04 \mu$ M at ACE1 and $0.2 \pm 0.1 \,\mu\text{M}$ at ACE2) concentrations were lower than that at the NE stations (mean DIN: $5.5 \pm 4.9 \ \mu\text{M}$ and DIP: $0.4 \pm 0.3 \ \mu\text{M}$) in the top layer. Being situated at the periphery of a cyclonic eddy, high vertical diffusive flux of DIN might have resulted in relatively high primary productivity (19.5 \pm 3.7 mmol C m⁻² d⁻¹, Saxena et al. 2021, under preparation) at NE2 (Table 4.2). The elemental concentrations and ratios in POM and DOM were not much distinct at ACE1, ACE2 and NE stations.

Table 4.2: Vertical diffusive flux of DIN, N_2 fixation and its contribution in N:P ratios of export flux from the top layer during spring 2019.

Station	Vertical diffusive flux of DIN (mmol N $m^{-2} d^{-1}$)	N ₂ fixation (µmol N m ⁻² d ⁻¹)*	Contribution of N_2 fixation to N:P export flux (%)
NE1	1.7	-	-
ACE1	4.3	16.5	0.4
NE2	8.6	6.8	0.1
NE3	4.1	6.7	0.2
NE4	2.1	5.5	0.3
NE5	1.1	BDL	-
NE6	3.0	5.3	0.2
ACE2	4.1	-	-

*Column integrated N_2 fixation rates are taken from Saxena et al. (2021) (under preparation).

N₂ fixation experiment was not performed at NE1 and ACE2 due to logistic issues.

4.6 Role of picoplankton in varying elemental ratios in POM

In the Bay of Bengal, nutrient availability plays a bigger role than the temperature in driving the microbial community composition (*Angelova et al.*, 2019). The temperature did not vary much and also not correlated to the elemental ratios of POM in the top layer during this study (Figure 4.5). The nutrient availability might influence the phytoplankton distribution. The eddies can entrain nutrient-rich shelf waters and advect them offshore, thereby playing a key role in the phytoplankton community distribution (*Gomes et al.*, 2016). No coherent pattern of picoplankton (*Prochlorococcus* and *Synechococcus*) distribution was observed in ACE and NE stations in our study (Saxena et al. 2021, under preparation).

Recently Sarma et al. (2020a) have reported that the picoplankton contributed up to 80% and the micro and nanoplankton contributed between 10 to 30% to the total phytoplankton biomass in the Bay of Bengal during June 2019 (Sarma et al., 2020a). The total phytoplankton biomass (autotrophic) reportedly constitutes up to 27% of the total POC pool in the basin (Baer et al., 2019). The detrital matter and heterotrophs also constitute a large fraction (~50%) of plankton biomass (Garcia et al., 2018). In this study, Prochlorococcus and Synechococcus together constituted a maximum up to 29% of the total POC pool in the top layer, which is a significant fraction of the total phytoplankton biomass.

Prochlorococcus and Synechococcus are slow-growing and small-sized phytoplankton, capable to adapt in nutrient-deficient conditions, and possess high C:P and N:P ratios than the Redfield Ratio following the growth rate hypothesis (*Klausmeier et al.*, 2004a; Arrigo, 2005). The growth rate hypothesis suggests that the nutrient scarce environment normally favours the growth of slow-growing phytoplankton that can synthesize more resource acquisition machinery such as proteins that have high N:P ratio. The nutrient replete environment supports the fast-growing large phytoplankton by synthesizing more growth machinery such as RNAs that have low N:P ratio.

Overall, the C:P (coastal: 254 ± 38 , open ocean: 244 ± 34) and N:P (coastal: 39 ± 12 , open ocean: 37 ± 3) ratios in POM were higher than the Redfield Ratio. Since



Figure 4.5: Spearman correlation matrix of environmental parameters (temperature (T), salinity (S), and nutrients), abundance of picoplankton (*Prochlorococcus* (Pro), and *Syne-chococcus* (Syn)) and elemental ratios in inorganic and organic matter in the top layer at $\alpha = 0.05$.

Prochlorococcus and *Synechococcus* constituted only up to 29% of the total POC, a major fraction of the POM pool is likely constituted by dead and detrital matter. But this dead and detrital matter may also have its origin in the picoplankton in the oligotrophic waters. Therefore, the higher elemental ratios in POM suggests that the Bay of Bengal support the growth rate hypothesis (Figure 4.6).

The existence of prolonged (originated roughly two months before sampling) ACEs throughout the sampling area associated with substantial downwelling of surface water could have transformed the Bay of Bengal into an oligotrophic region. Deep nutricline accompanied with shallow mixed layer during the study was indicative of the increased oligotrophic conditions as compared to that in the previous study in the Bay of Bengal during summer (*Sahoo et al.*, 2020). Overall, the top layer was nutrient-depleted and



Figure 4.6: Integrated picoplankton abundance (data obtained from Saxena et al. (2021), under preparation) in log scale, POC:POP, and PON:POP ratios in POM in the top layer.

showed high elemental ratios in POM during spring than during summer (Sahoo et al., 2020). The static oligotrophic environment reasonably supports the growth of picoplankton ton (Agawin et al., 2000). Sarma et al. (2020a) observed high abundance of picoplankton at ACE, while the low microplankton abundance at ACE was due to the unavailability of DIN and DIP during June 2019 in the Bay of Bengal. In the present study, picoplankton constituted up to 29% of the POC pool, due to their ability to thrive in the low nutrient concentrations. Particularly, Prochlorococcus can adapt to oligotrophic conditions through gene gains and losses (Ustick et al., 2021). Prochlorococcus and Synechococcus showed a significant correlation with DIP and DIN concentrations, respectively in this study. Furthermore, Synechococcus was significantly correlated to the POM elemental concentrations in the top layer (Figure 4.5). Therefore, the low nutrient availability and thereby the distribution of picoplankton appeared to regulate the variation of elemental ratios of POM in the top layer.

4.7 Role of N_2 fixation on the elemental proportions

In oligotrophic basins where primary productivity is N limited, biological N₂ fixation is considered to be a major source of new N to the photic zone and may account for $\sim 50\%$ of the organic carbon export (*Karl et al.*, 1997). Favourable environmental conditions including weaker winds, warm sea surface temperature (> 28 °C) and clear sky in addition to an adequate supply of PO_4^{3-} and Fe suggest the possibility of diazotrophic activity in the basin (*Mills et al.*, 2004; *Singh et al.*, 2017). Diazotrophs increase the DIN pool at the cost of consuming DIP. Therefore, DIN:DIP ratio is expected to increase due to the diazotrophic activity in the photic zone.

Previous studies reported low N₂ fixation rates (4 to 75 µmol N m⁻² d⁻¹ during July 2018 and 53.3 to 194.1 µmol N m⁻² d⁻¹ during June 2019) in the Bay of Bengal (*Sarma et al.*, 2020c; *Saxena et al.*, 2020). Yet, the upper bound of the measured N₂ fixation rates in the Bay of Bengal is comparatively higher than many of the other ocean regimes (*Saxena et al.*, 2020). In the present study, the concurrently measured N₂ fixation rates were even lower and varied from below detection limit to 17 µmol N m⁻² d⁻¹ (Saxena et al. 2021, under preparation).

The mean DIN:DIP ratio in the top layer was lower (8.9 ± 2.5) than the Redfield Ratio. The influence of N₂ fixation on the top layer DIN:DIP ratio is elusive due to the occurrence of concurrent biological processes such as nutrient uptake by phytoplankton. The low DIN:DIP ratio might be attributed to the excessive competitive consumption of N relative to P by the slow-growing, smaller phytoplankton (*Klausmeier et al.*, 2004a).

In the subsurface layer, the low DIN:DIP ratio (10.9 ± 1.9) indicates the possible occurrence of denitrification and anammox in the Bay of Bengal. However, low rates of anammox (5.5 nM N d⁻¹) and patchy distribution of denitrification (0.9 nM N d⁻¹) in this basin suggest that the processes were less likely to change the subsurface DIN:DIP ratio (*Bristow et al.*, 2017). Then what caused the mean subsurface DIN:DIP ratio to decrease to 10.9?

In the subsurface layer, the DIN:DIP ratio reflects the integrated effect of remineralisation of sinking organic matter and various N loss processes. Remineralisation of organic matter significantly contributes to the subsurface nutrients, especially the regions where diazotrophs dominate the phytoplankton community. Diazotrophs normally possess a high cellular N:P ratio (42 to 125) (*Karl et al.*, 1992; *Letelier and Karl*, 1996). The remineralisation of diazotrophs (sinking from the top layer) with a high biomass N:P ratio, increases the subsurface DIN:DIP ratio (*Michaels et al.*, 1996). But the contribution of
diazotrophs to the subsurface nutrients in the Bay of Bengal is not known.

Therefore, we have estimated the contribution of N_2 fixation in varying N:P ratio of export flux by applying a simple two-component N source model by *Karl et al.* (1997):

$$\frac{N_{fix}}{N_{fix} + N_{up}} = \frac{(N:P)_{export} - (N:P)_{up}}{(N:P)_{export}}$$
(4.11)

where N_{fix} and N_{up} denote the N_2 fixation rate and vertical eddy diffusive flux of DIN, respectively. $(N:P)_{export}$ and $(N:P)_{up}$ are the N:P ratio of the export flux from the top layer and vertical eddy diffusive nutrient flux, respectively. The assumption is that the vertical diffusion is the only source of new P as DIP and that this process and N_2 fixation are the two potential sources of new N as DIN in the top layer. We have considered the DIN:DIP ratio of the subsurface water layer as $(N:P)_{up}$ in this study. The left-hand side of equation (4.11) represents the contribution of N_2 fixation in the N:P ratio of export flux, which ranged from ~0.1 to 0.4%. The exported organic matter further contributes to the subsurface nutrient pool upon remineralisation. But this low contribution in the export flux indicates no role of N_2 fixation in changing the subsurface DIN:DIP ratio.

The mean (N:P)_{export} calculated from equation (4.11) is 11.1, which corresponds to the mean N:P ratio in subsurface nutrients (11.0). It infers that the remineralisation of exported organic matter considerably contributed to the nutrients in the subsurface layer. The elemental ratio in export flux generally corresponds to that in POM in the euphotic zone. However, a discrepancy in the N:P ratio was observed between the POM in the top layer and the export flux (Figure 4.7). In particular, the mean (N:P)_{export} was approximately four times lower than the mean N:P ratio in the top layer POM. The dominance of picoplankton leads to a high N:P ratio in POM in the top layer, but possesses a low export efficiency compared to microplankton (*Fu et al.*, 2016). The organic matter of small phytoplankton is likely to be recycled within the upper water column. The microplankton, having low N:P ratio, are highly efficient in sinking and thereby possibly contribute largely to the export flux (*Aumont and Bopp*, 2006). Although the microplankton (such as diatoms) abundance is reportedly low in the Bay of Bengal during spring (*Sarma et al.*, 2020b), their accumulation in the export flux might have resulted in a low (N:P)_{export} than the N:P ratio in POM in the top layer.



Figure 4.7: A schematic representing N:P ratio in the Bay of Bengal during spring 2019.

4.8 Putting the C:N:P ratios in the global ocean perspective

Overall, the mean C:N:P ratios of POM was 249:39:1 in the top layer. The POC:PON and PON:POP ratios in the top layer are statistically different from those in the previous study in the Bay of Bengal during the summer monsoon (232:25:1) (*Sahoo et al.*, 2020). Likewise, the POC:PON and POC:POP ratios are statistically different from the observations made in the subtropical North Atlantic Ocean (210:36:1) (*Singh et al.*, 2015a). Our mean C:P and N:P ratios (2338 \pm 4060 and 146 \pm 201, respectively) in the DOM in the top layer. Refractory DOM have elevated global average C:N:P ratios of 1370:60:1 and the non-refractory DOM have 317:39:1 (*Letscher and Moore*, 2015). During this study the ratios in DOM appeared to be more refractory in nature. Therefore, these values are higher than the global average C:N:P ratios (640:44:1) for bulk DOM in surface water (*Letscher and Moore*, 2015).

4.9 Conclusion

This study enumerates the effect of physical and biogeochemical processes on the elemental ratios in the top layer of the Bay of Bengal. The C:N:P ratios in the organic (except C:N ratio in POM) and nutrient pools deviated greatly from the Redfield Ratio in the top layer during spring. Mean C:N:P ratios were 249:39:1, 2338:146:1, and 8437:9:1 in POM, DOM, and DIM, respectively in the top layer. The C:N and N:P ratios in POM in this study are slightly different from those obtained during summer 2018 (232:25:1) in the Bay of Bengal. The elemental ratios are statistically different from those in the subtropical North Atlantic Ocean (210:36:1). Riverine influx appeared to have no influence on C:N:P ratios in our coastal locations in the Bay of Bengal.

 N_2 fixation contributed negligibly (< 0.5%) to the N:P ratio of export flux, suggesting no role of it in changing DIN:DIP ratio in the subsurface layer. Mesoscale eddies have a significant effect on the nutrient concentrations in the top layer. Low concentration of nutrients was measured in the top layer of ACE stations. On the contrary, no significant influence was observed in the organic matter pool in ACE stations. So the ACEs do not seem to influence the elemental ratios.

In this study, we have examined the role of eddies and N_2 fixation in varying elemental proportions in the Bay of Bengal, but other causes also need to be explored. An in-depth understanding of these processes will help to improve the biogeochemical models based on flexible elemental proportions.

Chapter 5

Role of winter convective mixing in changing C:N:P ratios in the Arabian Sea

5.1 Introduction

Several studies have reported variation in elemental ratios in POM and DOM, and nutrients in the Atlantic Ocean, the Pacific Ocean, the Bay of Bengal and southern parts of the Indian Ocean (*Copin-Montegut and Copin-Montegut*, 1983; *Karl et al.*, 2001; *Martiny et al.*, 2013a,b, 2014; *Singh et al.*, 2015a; *Garcia et al.*, 2018; *Sahoo et al.*, 2020). Despite being biogeochemically important, the Arabian Sea has been overlooked, with no studies on elemental ratios at present from the region.

The Arabian Sea is in the western part of the northern Indian Ocean and is characterised by a unique seasonal monsoon reversal. Strong summer monsoonal winds cause intense upwelling of cold and nutrient rich deep water along the coasts of Somalia and Oman (*Bauer et al.*, 1991). Consequently, this enhanced supply of upwelled nutrients sustains high primary productivity (> 1.0 g C m⁻² d⁻¹) in the western Arabian Sea (*Brock et al.*, 1991; *Brock and McClain*, 1992; *Veldhuis et al.*, 1997). In contrast, during the winter monsoon, cold (< 23 °C) and dry northeasterly winds cause strong evaporative cooling in the northern Arabian Sea and drive convective mixing.

Convective mixing is a characteristic process of the northern Arabian Sea during the winter monsoon. This phenomenon causes deepening (100 m) of the mixed layer result-

ing in the entrainment of nutrients from the subsurface water (*Kumar and Prasad*, 1996; *Prasad*, 2004). Thereby nutrient concentrations in the euphotic zone increase in response to the convective mixing. Change in optical and physicochemical properties of the euphotic zone further triggers high primary productivity, elevated elemental concentrations in POM, and regulates the size distribution of phytoplankton in the northern Arabian Sea (*Madhupratap et al.*, 1996; *Kumar et al.*, 2001).

Elemental ratios of POM reflect the elemental composition of the plankton type that constitute the organic matter pool. The dominance of small-sized (0.2 to 2 μ m) phytoplankton lead to high elemental ratios (average 195:28:1) in the POM pool than the larger phytoplankton (*Klausmeier et al.*, 2004a; *Arrigo*, 2005). Regions influenced by winter mixing having elevated nutrient supply favour the growth of larger phytoplankton such as diatom, and certain picoplankton such as *Synechococccus* in the northern and central Arabian Sea (*Madhupratap et al.*, 1996; *Bemal et al.*, 2017). Thereby, the POM pool in the northern and central Arabian Sea might have relatively low elemental ratios than the other part of the ocean during the winter monsoon.

The spatial distribution of seasonal blooms in the Arabian Sea is also modulated by mesoscale structures such as eddies and filaments, which populate the basin throughout the year (*Resplandy et al.*, 2011). During winter, although convective mixing is identified as the primary trigger of winter blooms, it is observed that vertical and horizontal advection by mesoscale eddies and filaments are responsible for 40 to 50% of nutrient supply to the euphotic zone (*Resplandy et al.*, 2011). Cyclonic eddies associated with the subsurface water upwelling amplify the nutrient supply to the euphotic zone. On the contrary, ACE deepen the nutricline due to surface water downwelling and decrease the nutrient concentrations in the euphotic zone. Preponderance of prolonged eddies might transform the N:P ratio of nutrients in the sunlit ocean.

High seasonality in biological production in the Arabian Sea and its subsequent export leads to O_2 depletion in subsurface waters, which constitute one of the most intense open ocean oxygen minimum zones (*Codispoti*, 2007). O_2 deficient conditions result in depletion of bioavailable N (NO₃⁻ and NO₂⁻) through denitrification and anammox and thereby lowering the N:P ratio in the nutrient pool in subsurface water (*Hupe and Karstensen*, 2000). Convective mixing and eddies might influence the elemental ratios in the euphotic layer, and N loss might considerably change the elemental ratios of nutrients in the subsurface water. Therefore, we sampled the water column at 14 stations in the Arabian Sea during the winter monsoon to understand the

- i. C:N:P ratios and their variation in organic and inorganic pools in the water column
- ii. Influence of winter convective mixing, eddy, and N removal processes on elemental ratios
- iii. Role of the phytoplankton community in changing the C:N:P ratio.

5.2 Methods

Sampling was conducted aboard ORV Sagar Kanya (SK#364) in the Arabian Sea from 16 December 2019 to 6 January 2020. We sampled 14 stations (SK1 to SK14) using a Sea-Bird CTD rosette sampler mostly at 14 different depths (5, 25, 50, 75, 100, 150, 200, 300, 500, 1000, 1500, 2000, 2500 and 3000 m) (Figure 5.1, Table 5.1). SK1, SK2, and SK12 to SK14 were categorised as the eastern stations, SK3 to SK7 as the northern stations, and SK8 to SK11 as the southern stations. We present our analysis into three different depth segments: top, subsurface, and deep layers as explained in Chapter 1. The top layer extends from the surface to \sim 75 m. The successive subsurface layer is considered from \sim 75 m to 300 m. The layer below the subsurface layer to the deepest sampling depth up to 3000 m is classified as deep layer.

The measurement of elemental concentrations of DIM, POM and DOM are discussed in Chapter 2. The depth at which the NO_3^- concentration increased to 1 µM was considered as the nutricline depth (*Garcia et al.*, 2018). The vertical diffusive flux of DIN from subsurface waters was calculated following *King and Devol* (1979). The vertical diffusion coefficients used in the diffusive flux estimation at the coastal and open ocean stations were taken from *Gandhi et al.* (2011a).

The MLD was calculated as 0.2 °C decrease from the temperature at 10 m depth (*de Boyer Montégut*, 2004). Microbial hypoxia and denitrifying conditions were identified

based on the DO concentration < 20 and 6 μ M, respectively (*Rixen et al.*, 2020). Surface chl *a* concentrations were obtained from the Copernicus Marine Environmental Monitoring Service (https://resources.marine.copernicus.eu/; data retrieved on 21 April 2021).



Figure 5.1: Surface Chl *a* concentrations and sampling locations in the Arabian Sea during the winter 2019–20.

The abundance of *Prochlorococcus* and *Synechococcus* were obtained from Nazirahmed et al. (2021) (under preparation). The biomass of *Prochlorococcus* and *Synechococcus* was calculated by multiplying their abundances (cell counts L^{-1}) with their C content per cell value. The C content per cell of *Prochlorococcus* and *Synechococcus* were taken from *Casey et al.* (2013). Based on this, we estimated the contribution of *Prochlorococcus* and *Synechococcus* biomass to the total POC pool.

ACEs were identified based on the SSHA and geostrophic current. ACEs were identified at S9, S12, and S13 by the clockwise circulation of geostrophic current with > 0.2 m SSHA.

5.3 Role of convective mixing on the elemental ratios

A combination of evaporation due to the dry northeasterly winds and reduction in solar insolation leads to cooling and subsequent densification of surface water during the winter monsoon in the northern Arabian Sea (north of 15°N) (*Kumar and Prasad*, 1996; *Madhupratap et al.*, 1996). This further leads to convective mixing that propels nutrients to the euphotic layer and fuels high primary production in the region.

Changes in the hydrological and surface meteorological parameters such as low atmospheric (24.5–25.3 °C except S7) and sea surface temperature (25.9–27.4 °C) accompanied with the deepening of mixed layer at the northern stations witnessed that the stations were influenced by convective mixing (Figure 5.2). Furthermore, the evaporative cooling of surface water led to comparatively high salinity particularly in the northern stations. Salinity varied from 36.1 to 36.6 at the northern stations, S2, and S8.

Concurrently, the surface water convective mixing was accompanied by an increased diffusive flux of DIN to the top layer from the thermocline region, as evident from the shoaling of nutricline (< 10 m) at the northern stations except S7. The diffusive flux of DIN across the mixed layer was higher at S3 (2.34 mmol N m⁻² d⁻¹) and S5 (2.12 mmol

Station	Date of sampling (dd.mm.yyyy)	Latitude (°N)	Longitude (°E)	SST (°C)	SSS	SSHA (cm)	MLD (m)
SK1	17.12.2019	15°57′	73°09′	28.6	34.7	15	51
SK2	19.12.2019	19° 59 ′	69°31′	26.9	36.1	11	58
SK3	21.12.2019	19°60′	64°60′	26.3	36.3	3	57
SK4	22.12.2019	17°60′	64°60′	25.9	36.1	4	48
SK5	23.12.2019	15°60′	64°60′	26.8	36.2	4	66
SK6	24.12.2019	14°00′	64°60′	27.2	36.4	0	42
SK7	26.12.2019	11°60′	64°60′	27.5	36.2	0	48
SK8	27.12.2019	09°60′	65°00′	28.2	36.6	7	48
SK9	29.12.2019	07°60′	65°00′	29.1	35.4	15	44
SK10	30.12.2019	06°00′	65°00′	29.1	35.2	12	45
SK11	31.12.2019	03°60′	64°60′	29.4	35.3	9	26
SK12	02.01.2020	07°60′	68°25′	29.1	35.6	19	71
SK13	04.01.2020	11°02′	71°03′	29.1	36.1	11	48
SK14	05.01.2020	13°31′	72°20′	28.9	36.2	7	42

Table 5.1: Details of environmental parameters at the fourteen (S1–S14) sampling locations during winter 2019–20.

N m⁻² d⁻¹) than that at the other stations and even higher than that during the spring in the Arabian Sea (*Gandhi et al.*, 2011a).



Figure 5.2: Hydrological characteristics along the cruise track: (a) Atmospheric temperature, SST and SSS, and (b) Chl *a* concentration, MLD and SSHA.

Furthermore, the 2 μ M DIN contour which was seen at or deeper than 50 m at S6, S7, the southern and eastern stations, surfaced at some of the northern stations (S3 to S5). Concurrently the 0.5 μ M DIP contour was observed at or deeper than 50 m at the southern and eastern stations (except S2), while shoaled at S2 and the northern stations (Figure 5.3). Concurrently high chl *a* (0.15–0.42 μ g L⁻¹) and the top layer POM concentrations were observed at S1, S2, and the northern stations (Figure 5.3). Superposition of the chl *a* distribution with DIN and DIP concentrations confirms that the convective mixing driven increased nutrient supply led to high POM concentrations in the northern stations.

Increased supply of nutrients led to low DIC:DIP ratio in the northern stations than other stations. DIC:DIP ratio was statistically low at the northern stations (3555 \pm 1274) than the southern and eastern stations (6330 \pm 2156) in the top layer (Figure 5.4). However, no significant differences were observed for the top layer DIC:DIN and DIN:DIP ratios between the northern, and the southern and eastern stations. The increased supply of nutrients triggred high top layer POM concentrations but low elemental ratios at the northern stations. The POC:PON (7 \pm 2) and POC:POP (207 \pm 43) ratios were significantly low at the northern stations than that at the southern and eastern stations (POC:PON (8 \pm 2) and POC:POP (266 \pm 61)) in the top layer. Additionally, the PON:POP ratio was comparatively higher at S7, the southern (except S11) and eastern (except S1 and S2) stations in the top layer.

The increase in elemental ratios particularly POC:POP at the southern and eastern



Figure 5.3: Vertical section up to 220 m of (a) DIC, (b) DIN, (c) DIP, (d) POC, (e) PON, (f) POP, (g) DOC, (h) DON, and (i) DOP concentration.



Figure 5.4: Vertical section up to 220 m of (a) DIC:DIN, (b) DIN:DIP, (c) DIC:DIP, (d) POC:PON, (e) PON:POP, (f) POC:POP, (g) DOC:DON, (h) DON:DOP, and (i) DOC:DOP concentration.

stations could be due to the prevalence of small-sized phytoplankton. The small-sized phytoplankton possess high C:P ratio as they allocate more C-rich carbohydrate and N-rich protein-pigment complexes at a very low expense of P nutrient in their cellular structure under nutrient deficient environment (*Klausmeier et al.*, 2004a; *Arrigo*, 2005). The role of picoplankton distribution in varying the POM elemental ratios is discussed in section 5.4. Altogether, the variation of the elemental ratios in nutrients and POM in the top layer at the northern, and the southern and eastern stations appeared to be influenced by convective mixing. The mean POC:PON, PON:POP, and POC:POP ratios were 8.0 ± 1.7 , 31.7 ± 9.5 , and 245.3 ± 62.0 , respectively, in the top layer, higher than



the Redfield Ratio (Figure 5.5).

Figure 5.5: Box-whiskers plots showing elemental ratios in DIM, POM, and DOM in three depth layers. Pink dotted lines represent mean. Whiskers account for 5 and 95% of distribution, whereas box accounts for 25 and 75%. Dots within the boxes represent 50% of the distribution.

5.4 Role of picoplankton in elemental ratios in POM

A value of 5 μ M for DIN and 0.5 μ M for DIP is considered as the threshold concentrations for N and P limitation for phytoplankton growth (*Mousing et al.*, 2018). During this study, DIN and DIP concentrations at all the stations (except in 5 and 50 m depth at S3 and S4 for DIP) were below their threshold values in the upper 50 m. In the nutrient limiting environment, the competitive acquisition of nutrients is an important mechanism for controlling the community size structure of phytoplankton because the large surface area to volume ratio and a small diffusive boundary layer lend smaller species a competitive advantage over larger species (*Tilman et al.*, 1982). Therefore, the picoplankton community favourably prevails in the oligotrophic systems, while diatoms and other large eukaryotes associate with high nutrient environments such as in upwelling regions.

Previous studies in the Arabian Sea have reported that the basin is dominated mostly by picoplankton such as *Prochlorococcus*, *Synechococcus*, picoeukaryotic algae and heterotrophic bacteria during the winter monsoon (*Campbell et al.*, 1998; *Roy and Anil*, 2015). A high abundance of *Prochlorococcus* was observed at stable oligotrophic warm waters and low surface NO_3^- concentration (< 1 µM) (*Campbell et al.*, 1998).

During this study, the abundance of *Prochlorococcus* was slightly higher at the southern stations and S12 and S13, while the abundance of *Synechococcus* was dropped at these stations and S14 (Nazirahmed et al. 2021, under preparation) (Figure 5.6). Although the concentrations of DIN and DIP in the surface water were below their threshold values (5 and 0.5 μ M), the northern stations had relatively increased nutrient concentrations in the top layer due to the convective mixing, which might favour the growth of *Synechococcus*.



Figure 5.6: Distribution of integrated picoplankton abundance (data obtained from Nazirahmed et al. 2021, under preparation) in log scale, DIP concentration and C:P, and N:P ratios in particulate organic matter (POC:POP and PON:POP) in the top layer.

Prochlorococcus showed a negative correlation with DIP, while *Synechococcus* exhibited a positive correlation with DIP and POM elemental concentrations (Figure 5.7a). It infers that *Synechococcus* constituted high biomass in the northern stations. However, the smaller phytoplankton, *Prochlorococcus* constituted comparatively high POM biomass in the southern stations and at S12, S13, and S14 due to their more efficient nutrient diffusion capacity at decreased ambient nutrient concentrations. Furthermore, a negative relationship between *Synechococcus* and temperature suggests that temperature variation could also be one of the reasons for the reduced *Synechococcus* abundance in the southern and eastern (except S1 and S2) stations (Figure 5.7a).

A negative correlation of PON:POP and POC:POP ratio with *Synechococcus* and positive correlation with *Prochlorococcus* abundance suggest that the competitive dominance of *Prochlorococcus* over *Synechococcus* in the nutrient-deficient waters in the southern and some of the eastern stations might have led to a comparatively higher elemental ratios (Figure 5.6 and 5.7a). *Prochlorococcus* possess high elemental ratios followed by *Synechococcus*, and picoeukaryotes (*Martiny et al.*, 2013a; *Singh et al.*, 2015a).

This study was performed during the beginning of the winter monsoon, when the picoplankton biomass decreases owing to intense microzooplankton grazing (*Bemal et al.*, 2017). On average, *Prochlorococcus* and *Synechococcus* together constituted 16% (ranged from 0.5 to 92%) of the total POC biomass in the top layer during this study. Therefore, the variability in POM elemental ratios could not be explained only by the *Prochlorococcus* and *Synechococcus* communities, the abundances of large phytoplankton and microzooplankton also need to be studied. At present limited information on marine plankton distribution left our speculation unresolved and demands a detailed study of the taxon-specific elemental ratios in the Arabian Sea.



Figure 5.7: Spearman's correlation matrices of the concentrations and ratios in the (a) top (b) subsurface, and (c) deep layer. Values in coloured boxes are different from 0 at $\alpha = 0.05$.



Figure 5.8: Sea surface height anomaly overlaid by geostrophic currents during (a) 17–21 December 2019, (b) 22–26 December 2019, (c) 27–31 December 2019, and (d) 1–5 January 2020. The sampling locations are shown with blue circles.

0

-0.2

75°E

10°N -0.1

8°N

65°E

6°N

4°N

SK10

65°E

K11

70°E

SK13

75°E

70°E

0

-0.1

-0.2

5.5 Impact of anticyclonic eddies on elemental ratios in the top layer

A large ACE is normally observed in the southeast Arabian Sea during the winter monsoon (*Bruce et al.*, 1994; *Shankar and Shetye*, 1997). It grows rapidly from late November to late December at about 10°N over the Laccadive Islands, and hence named as Laccadive High. In January, it can be seen moving westward where it dies in the mid basin. The eddy expands \sim 500–800 km spatially and 300–400 m vertically.

We observed a large ACE in the south-eastern Arabian Sea (Figure 5.8). S12, S9, and S13 were situated at the periphery of the ACE. The concomitant lowering of nutrients particularly DIN at these stations might be due to the surface water downwelling associated with the ACE, which ultimately deepens the nutricline. The southern and eastern stations were comparatively nutrient poor, as evident from the deepening of contour representing DIN:DIP ratio: 2, than that in the northern stations (Figure 5.4). The occurrence of ACE further lowered the nutrient levels at S9, S12, and S13. The contour representing DIN:DIP ratio: 2, deepened the most (~ 100 m) at S12.

5.6 Variation of elemental ratios in the subsurface and deep layers

The DIN:DIP ratio was less than the Redfield Ratio throughout the water column and the lowest value was observed in the top layer (5.6 ± 3.8) (Figure 5.5). Low DIN:DIP ratio in the subsurface and deep layer $(10.7 \pm 2.9 \text{ and } 12.7 \pm 1.2, \text{ respectively} < 16)$ implies N removal in the oxygen minimum zones (*Deutsch and Weber*, 2012). Upon upwelling of the such N deficient subsurface water to the top layer, the DIN:DIP ratio further decreases due to the preferential uptake of N nutrients by small-sized phytoplankton.

Intense oxygen minimum zone (< 6 μ M dissolved oxygen concentration) is normally observed in the intermediate depths (150–1200 m) north of 12°N and east of 56°E in the Arabian Sea, which is one of the largest denitrification zones in the global ocean (*Naqvi*, 1987; *Fauzi et al.*, 1993). The Arabian Sea oxygen minimum zone harbours a less diverse assemblage of anammox bacteria in addition to largely diverse denitrifying bacteria (*Ward et al.*, 2009). During this study, the oxygen minimum zone was intense within the subsurface layer at the northern stations (Figure 5.9a). The low DIN:DIP ratio (9–10) at most depths in this layer is indicative of the occurrence of denitrification. The denitrifying heterotrophic bacteria utilise NO₃⁻ as an oxidant during the remineralisation of organic matter leads to N loss from the subsurface waters. Moreover, a notable departure in DIN



Figure 5.9: (a) DO concentration (y axis is stretched in the middle) (b) DIP versus DIN concentrations in the water column. Solid line represents the Redfield Ratio (16:1).

concentration from the traditional Redfield Ratio in the subsurface layer at the northern stations confirms our theory on the effect of N loss processes on elemental concentrations (*Deutsch and Weber*, 2012) (Figure 5.9b).

The elemental ratios of POM showed an increase below the top layer. In the subsurface layer, the mean POC:PON, PON:POP, and POC:POP ratios were 9.1 ± 3.1 , 35.6 ± 13.1 , and 308.6 ± 104.4 , respectively (Figure 5.5). The mean POC:PON, PON:POP, and POC:POP ratios were 11.0 ± 3.5 , 40.5 ± 14.8 , and 424.6 ± 160.3 , respectively, in the deep layer. Differential remineralisation of organic matter generally leads to most of the variation in elemental ratios in the subsurface and deep layers. In the POM pool, POP undergoes preferential remineralisation followed by PON and POC (*Loh and Bauer*, 2000). An increase in the POC:PON ratio in the subsurface and deep layers could be attributed to the faster remineralisation of PON compared to POC (Figure 5.7b and c). The strong anticorrelation between POC:PON ratio and PON concentration confirmed the differential remineralization theory. Likewise, the increasing PON:POP and POC:POP ratios in the subsurface and deep layers were due to the preferential remineralisation of POP in the sinking organic matter (*Loh and Bauer*, 2000), supported by a negative relationship between the ratios and POP concentration (Figure 5.7b and c).

Unlike the POM pool, C:P ratio in the DOM pool decreased in the subsurface and deep layers, while no such uniform increasing or decreasing behaviour was seen in C:N and N:P ratios. The mean DOC:DON, DON:DOP, and DOC:DOP ratios were 12.2 ± 6.1 , 47.4 ± 54.4 , and 635.5 ± 690.5 , respectively, in the top layer (Figure 5.5). In subsurface water, the DOC:DON, DON:DOP, and DOC:DOP ratios were 14.4 ± 31.1 , 36.2 ± 43.4 , and 309.1 ± 507.9 , respectively. The mean ratios in the deep layer were 16.0 ± 37.5 , 47.8 ± 139.6 , and 269.1 ± 786.4 for DOC:DON, DON:DOP, and DOC:DOP, respectively. This variation of DOC:DOP ratio might be attributed to the increasing DOP concentration in the subsurface and deep layers, further confirmed from the negative relationship between the ratio and DOP concentration (Figure 5.7b and c).

5.7 Role of N_2 fixation on the elemental ratios

 N_2 fixation plays a vital role in supplying new N to the euphotic zone of oligotrophic basins. It may account for ~50% of the organic matter export to the deep ocean (*Karl et al.*, 1997). Like in the euphotic layer, N_2 fixation also contributes to the subsurface layer nutrient pool upon remineralisation of the N-rich biomass of N_2 fixers. The N_2 fixation rates during the study were below the detection limit at most of the depths in the top layer at all stations but at S10 and the eastern stations (except S2) (Saxena et al. 2021, under preparation). Therefore, the low N_2 fixation rates do not seem to affect the elemental ratios of POM in the top layer and that of nutrients in subsurface layer during the winter monsoon.

5.8 Putting the Arabian Sea elemental ratios in the global ocean perspective

Overall, the mean C:N:P ratios in POM in the top layer: 245:32:1 is statistically different from those estimated in the Bay of Bengal during summer (232:25:1) (*Sahoo et al.*, 2020) and spring (249:39:1) (*Sahoo et al.*, 2021). Our C:N:P observations in the POM are marginally different from the observations in the subtropical North Atlantic Ocean (210:36:1) (*Singh et al.*, 2015a). Our mean elemental ratio in DOM is 635:47:1 in the top layer, which is close to the global mean C:N:P ratio (640:44:1) for DOM in surface water (*Letscher and Moore*, 2015). Altogether, the elemental ratios have greatly deviated from the traditional Redfield Ratio and witnessed the influence of winter convective mixing in regulating their variation.

5.9 Conclusion

We analysed C:N:P ratios in the inorganic and organic pools from the surface to 3000 m water depth in the Arabian Sea during the winter monsoon. The mean C:N:P ratios in POM were 245:32:1 in the top layer, higher than the Redfield Ratio. This ratio is significantly different from that in the subtropical North Atlantic Ocean (210:36:1). The elemental ratios in DOM were 635:47:1 in the top layer, consistent with the global value for bulk DOM (640:44:1).

Convective mixing resulted in decreased C:P ratio in the nutrients and C:P and C:N ratios in POM in the top layer at the northern stations. However, higher C:N and C:P ratios in POM were observed in the top layer at the southern and eastern stations. The variation in POM elemental ratios is attributed to the distribution of picoplankton. *Prochlorococcus* dominated the phytoplankton community at the southern and some of the eastern stations that might have led to the high elemental ratios in POM. However, an extensive study on taxon specific elemental stoichiometry is necessary to unravel the role of phytoplankton community on elemental ratios in the basin.

Furthermore, the prevalence of ACE in the southeastern Arabian Sea during winter might have caused DIN and DIP deficiency in the surface waters at the southern and eastern stations. Lower DIN:DIP and higher DIC:DIP ratios were observed in the top layer at these stations. Low N_2 fixation rates do not seem to affect the elemental ratios during the winter monsoon. Relatively decreased subsurface layer DIN:DIP ratio at the northern stations indicates the influence of denitrification on the nutrient pool.

Chapter 6

Summary and scope for future works

6.1 Summary

Even though the northern Indian Ocean is characterized by a myriad of physical and biogeochemical processes, the paucity of data precluded our understanding of the variation of elemental ratios in organic and inorganic pools in this region. The present study is attempted to understand the variation of C:N:P ratios from the canonical Redfield Ratio in the northern Indian Ocean. The oceanic processes including mesoscale eddies, convective mixing and N_2 fixation were examined to understand their role in varying elemental ratios. In addition, the coastal stations in the Bay of Bengal were studied to analyse the influence of riverine influx on the elemental ratios. An in-depth understanding of these processes will help to improve the biogeochemical models of this region based on flexible elemental proportions. The major findings of this study are as follows:

6.2 C:N:P proportions in the the Bay of Bengal during the summer monsoon

i. The elemental ratios greatly deviated from the Redfield Ratio. The average N:P ratio $\sim 3:1$ in the top layer nutrients coupled with reported low primary production rates in the basin suggested that the production was N limited.

- ii. The average C:N:P ratio of POM in the top layers of the Bay of Bengal was 232:25:1, similar to observations in other tropical oceans, such as the subtropical North Atlantic Ocean (210:36:1) and subtropical North Pacific Ocean (172:25:1) (*Martiny et al.*, 2013a; *Singh et al.*, 2015a). The average C:N:P ratio in the DOM in the top layer was estimated as 357:30:1 in the basin, lower than the global average 640:44:1 for bulk DOM in the surface ocean (*Letscher and Moore*, 2015). The increase in PON:POP and POC:POP ratios from the top layer to the deep layer are governed by the preferential remineralisation of POP and PON than POC.
- iii. Higher C:N:P ratios than the Redfield Ratio in POM in surface water suggests that the basin supports the nutrient supply hypothesis for tropical oceans with low inorganic nutrient concentrations.
- iv. Relatively deep mixed layer (41–77 m) and shallow nutricline (10–66 m) were observed during the sampling period, which might be due to the strong winds and eddy-induced mixing of the water column. Eddies showed a mixed effect on the C:N:P ratios in the top layer. Although there were differences in DIM and POM concentrations, but only little variability in C:N:P ratios of POM was observed between the eddy and non-eddy stations.
- v. Low autotrophic N₂ fixation rates in photic zone suggest that diazotrophs had a minimal impact on nutrient or POM ratios in the basin. The low N:P ratio in nutrients in the subsurface waters suggests a potential role of N loss processes in regulating nutrient stoichiometry.

6.3 C:N:P ratios in the Bay of Bengal during spring: Role of eddies and N₂ fixation

i. The C:N:P ratios in the organic (except C:N ratio in POM) and nutrient pools deviated greatly from the Redfield Ratio in the top layer during spring. Average C:N:P ratios were 249:39:1, 2338:146:1, and 8437:9:1 in POM, DOM, and DIM, respectively in the top layer. The C:N and N:P ratios in POM in this study are slightly different from those obtained during summer 2018 (232:25:1) in the Bay of Bengal (*Sahoo et al.*, 2020).

- ii. Conservative mixing of river and seawater calculation, C:N ratio (average 7.6 ± 2.5) of POM, and POC:Chl *a* ratio in the top layer (average 225 ± 153) suggest that the elemental ratios in our coastal locations were not influenced by the riverine influx to the basin.
- iii. No significant differences were observed in the parameters (except POM concentrations) at the coastal and open ocean regions. This was due to the coastal region had larger range of elemental concentrations and ratios than the open ocean region.
- iv. Prolonged ACEs had a significant influence on the DIN and DIP concentrations than the NE stations during spring. Deep nutriclines (84 m at ACE1 and 87 m at ACE2) at ACE stations indicate that the surface water downwelling resulted in the decreasing DIN and DIP concentrations in the top layer. On the contrary, no significant influence was observed in the organic matter pool at ACE stations. Hence the ACEs do not seem to influence the elemental ratios.
- v. *Prochlorococcus* and *Synechococcus* together constituted only up to 29% of the total POC pool in the top layer, a major fraction of the POM pool is likely constituted by dead and detrital matter. But this dead and detrital matter may also have its origin in the picoplankton in the oligotrophic waters. Therefore, the higher elemental ratios in POM suggests that the Bay of Bengal support the growth rate hypothesis.
- vi. N₂ fixation contributed 0.1 to 0.4% to the N:P ratio of export flux, suggesting no role of it in changing DIN:DIP ratio in the subsurface layer.
- vii. The average (N:P)_{export} corresponded to the average N:P ratio in subsurface nutrients (11.0), inferring that the remineralisation of exported organic matter considerably contributed to the nutrients in the subsurface layer.
- viii. A discrepancy in the N:P ratio was observed between the POM in the top layer and the export flux, which suggests that the accumulation of microplankton might lead to low (N:P)_{export} than that in the top layer POM.

6.4 Role of winter convective mixing in changing C:N:P ratios in the Arabian Sea

- i. The elemental ratios have greatly deviated from the traditional Redfield Ratio and witnessed the influence of winter convective mixing in regulating their variation. Convective mixing of the surface water at the northern stations led to comparatively higher DIN and DIP concentrations in the top layer. Concurrently, the top layer DIC:DIP, POC:POP ratios were statistically lower in the northern stations.
- ii. A large ACE was spotted in the southern and eastern stations, which normally occurs during winter in the south-eastern Arabian Sea. Deeper nutricline associated with the ACE resulted in the concomitant lowering of DIN, and DIP concentrations, and DIN:DIP ratio in the top layer at these stations.
- iii. Low DIN:DIP ratio in the subsurface and deep layer (10.7 ± 2.9 and 12.7 ± 1.2, respectively < 16) implies the influence of N removal processes in the suboxic waters in the basin.
- iv. The increased POC:PON, POC:POP and PON:POP ratios from the top to deep layers was due to the preferential remineralisation of POP and PON.
- v. The varying elemental ratios were observed to be driven by both the nutrient availability and temperature in the Arabian Sea.
- vi. The elemental ratios of POM in the top layer varied with the picoplankton species that dominate the phytoplankton population. Higher C:P and N:P ratios of POM were observed in the southern and some of the eastern stations where *Prochlorococcus* dominated the POM pool, while low ratios were observed in the northern and some of the eastern stations where *Synechococcus* dominated the POM pool.
- vii. Overall, the mean C:N:P ratios in POM in the top layer: 245:32:1 is statistically different from those estimated in the Bay of Bengal during summer (232:25:1) (Sahoo et al., 2020) and spring (249:39:1) (Sahoo et al., 2021). Our C:N:P observations in

the POM are marginally different from the observations in the subtropical North Atlantic Ocean (210:36:1) (*Singh et al.*, 2015a).

viii. The average elemental ratio in DOM was 635:47:1 in the top layer, which is close to the global mean C:N:P ratios (640:44:1) for DOM in surface water (*Letscher and Moore*, 2015).

6.5 Scope for future works

This thesis work presented significant findings but more work needs to be done on this topic for improving our understanding of the non-Redfieldian elemental ratios. We suggest to carry the following work in future studies:

- i. The thesis work presented the C:N:P ratios in the organic and inorganic matter in the northern Indian Ocean and the role of physical and biogeochemical processes in controlling the ratios. However, the effect of deep water upwelling during the summer monsoon on the elemental ratios in the Arabian Sea could not be explored during this thesis work. We believe that the phenomenon must have a significant effect on the elemental ratios which need to be studied.
- ii. The riverine influence on the elemental ratios can be better examined at coastal stations receiving high terrestrial input during the peak discharge period such as in the summer monsoon.
- iii. We suggested that the C:N:P ratios in POM were higher than the Redfield Ratio with the supposition that the phytoplankton community is mostly populated by picoplankton in the nutrient deficient tropical waters. But the taxon specific C:N:P ratios were not established for this region, which needs to be studied to provide a better understanding of varying elemental ratios of plankton.
- iv. A major fraction of POM is contributed by heterotrophs and detrital matter. Therefore, the elemental ratios in heterotrophs and detrital matter also need to be examined.

- v. The contribution of N₂ fixation in controlling elemental ratios can be estimated for the Arabian Sea in fall when *Trichodesmium* blooms appear in the basin. This estimation will help to understand its effect on changing elemental ratios in subsurface nutrients.
- vi. The northern Indian Ocean is an emerging hub for tropical cyclones. Cyclonic activities increase nutrient concentrations and primary productivity in the sunlit layer. Therefore, the effect of cyclonic activities on the elemental ratios in the northern Indian Ocean can be studied.
- vii. Changing hydrographic conditions such as temperature, salinity and nutrient concentrations may indirectly affect the elemental ratios of phytoplankton by regulating their growth and nutrient assimilation. Mesocosm experiments are suggested to test this hypothesis.

"No this is not the beginning of a new chapter in my life; this is the beginning of a new book! That first book is already closed, ended and tossed into the seas; this new book is newly opened, has just begun! Look, it is the first page! And it is a beutiful one!"

C. JoyBell C.

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List of Publications

Publications in Journals

- Sahoo, D., Saxena, H., Tripathi, N., Khan, M.A., Rahman, A., Kumar, S., Sudheer, A.K., Singh, A. (2020). Non-Redfieldian C:N:P ratio in the inorganic and organic pools of the Bay of Bengal during the summer monsoon. Marine Ecology Progress Series, 653:41–55. https://doi.org/10.3354/meps13498
- Saxena, H., Sahoo, D., Khan, M.A., Kumar, S., Sudheer, A.K., Singh, A. (2020). Dinitrogen fixation rates in the Bay of Bengal during summer monsoon. Environmental Research Communications, 2:051007. https://doi.org/10.1088/2515-7620/ ab89fa
- Sahoo, D., Saxena, H., Nazirahmed, S., Kumar, S., Sudheer, A.K., Bhushan, R., Sahay, A., Singh, A. (2021). Role of eddies and N₂ fixation in regulating C:N:P proportions in the Bay of Bengal. Biogeochemistry, 155:413-429. https://doi. org/10.1007/s10533-021-00833-4
- Varna, M., Singh, A., Sahoo, D., Sengupta, D. (2021). Strengthening of winter coastal currents drive salinity decline in the eastern Arabian Sea. Geophysical Research Letters, 48. https://doi.org/10.1029/2021GL094516
- Khan, M.A., Rahman, A., Sahoo, D., Saxena, H., Singh, A., Kumar, S. (2021). Nitrous oxide in the central Bay of Bengal during the summer monsoon. Regional Studies in Marine Science (Under review).
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Presentations at Conferences

- Sahoo, D., Saxena, H., Tripathi, N., Khan, M.A., Rahman, A., Kumar, S., Sudheer, A.K., Singh, A., "Understanding of C:N:P stoichiometry in the northern Indian Ocean" at National Space Science Symposium (NSSS) on 29 January 2019. [Poster]
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- Sahoo, D., Saxena, H., Nazirahmed, S., Kumar, S., Sudheer, A.K., Bhushan, R., Sahay, A., and Singh, A. (2021). Role of eddies and N₂ fixation in regulating C:N:P proportions in the Bay of Bengal. Biogeochemistry, 155:413-429. https: //doi.org/10.1007/s10533-021-00833-4

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Non-Redfieldian C:N:P ratio in the inorganic and organic pools of the Bay of Bengal during the summer monsoon

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ABSTRACT: Nitrogen (N) and phosphorus (P) determine the strength of the ocean's biological carbon (C) pump, and variation in the N:P ratio is key to phytoplankton growth. A fixed C:N:P ratio (106:16:1) in organic matter and deep-water nutrients was observed by Alfred C. Redfield. However, recent studies have challenged the concept of the Redfield Ratio, and its veracity remains to be examined in oceanic basins like the Bay of Bengal. For this purpose, we sampled the water in the Bay of Bengal for C, N, and P content in the organic and inorganic pools from the surface to 2000 m. Overall, the C:N:P ratio deviated greatly from the Redfield Ratio. The C:N:P ratio in particulate organic matter varied from 232:25:1 in the top layer (surface to the depth of the chlorophyll maximum) to 966:72:1 in the deep water (300-2000 m). In dissolved organic matter, the ratio varied from 357:30:1 in the top layer to 245:66:1 in the deep water. The N:P ratio in nutrients varied from 3 in the top layer to 12 in the deep water. The nutrient-depleted top layer (average $NO_3^- + NO_2^- \sim 0.7 \mu mol l^{-1}$) with a low N:P ratio coupled with reported low primary production rates in the Bay suggested that the production was N limited. Concurrent N_2 fixation rates were not sufficient to alter the observed C:N:P ratio. Eddies showed a mixed effect on the C:N:P ratio. Our C:N:P ratios in particulate organic matter are comparable to other tropical basins and supports the nutrient supply hypothesis for low latitude ecosystems.

KEY WORDS: Northern Indian Ocean \cdot Elemental stoichiometry \cdot Organic matter \cdot Nitrogen limitation

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1. INTRODUCTION

Until recently, it was believed that the molar carbon:nitrogen:phosphorus (C:N:P) ratio in phytoplankton (inferred from bulk organic matter) and deep ocean nutrients remained statistically uniform at 106:16:1—a coincidence discovered by Alfred C. Redfield and thereafter known as the Redfield Ratio (Redfield 1934). Redfield provided 3 explanations for a fixed C:N:P ratio: (1) it is a mere geochemical coincidence, (2) microorganisms adapt to oceanic nutrient stoichiometry, and (3) biogeochemical processes regulate the ratio (Redfield 1958). However, a phytoplankton physiology model and an empirical data set suggested that the Redfield Ratio is not a universally optimal value; rather, it is the average stoichiometry of phytoplankton in the ocean (Klausmeier et al. 2004a). In addition, recent findings highlighted a global latitudinal variation in the C:N:P ratio from the canonical Redfield Ratio (Martiny et al. 2013a,b).

Elemental ratios of phytoplankton and nutrients are of paramount importance to our understanding of their biogeochemical cycling in the oceans (Weber & Deutsch 2012, Wang et al. 2019). Biologically, C is the backbone of all biomolecules, while N and P are proximate and ultimate limiting nutrients, respecAuthor copy

tively, for oceanic primary production (Tyrrell 1999). The C:N:P stoichiometry in particulate and dissolved pools of the ocean has been fundamental to our understanding of marine biogeochemistry, as it allows us to estimate the approximate concentration of one nutrient through the knowledge of the other, leading to ease in calculations of various rate processes, such as export production and nutrient-based flux rate calculations (Geider & La Roche 2002, Tyrrell 2019). Deviations from the N:P ratio of 16:1 in nutrients are used to infer the net effect of various biogeochemical processes such as N₂ fixation (>16:1) and denitrification

to infer the net effect of various biogeochemical processes such as N_2 fixation (>16:1) and denitrification (<16:1) in the water column (Gruber & Sarmiento 1997, Tyrrell 1999, Lenton & Watson 2000, Deutsch & Weber 2012, Zehr & Capone 2020). Most marine elemental stoichiometry studies are confined to particulate organic matter (POM) and dissolved inorganic matter (DIM) (Copin-Montegut & Copin-Montegut 1983, Martiny et al. 2013a, Singh et al. 2015a, Baer et al. 2019). Although dissolved organic matter (DOM) forms one of the largest reservoirs of C and N in the ocean (Ogawa & Tanoue 2003) and contributes 20–25% in global export production, the elemental ratios in DOM are not well

studied. A globally compiled data set on marine C:N:P ratio (810:48:1) in DOM, with little data from the Indian Ocean, suggested that it deviates greatly from the Redfield Ratio (Letscher & Moore 2015).

Several studies on the C:N:P ratio in phytoplankton and in nutrients have been reported from the Atlantic Ocean, and to an extent from the Pacific Ocean with limited studies in the Indian Ocean (Copin-Montegut & Copin-Montegut 1983, Karl et al. 2001, Martiny et al. 2013a,b, 2014, Singh et al. 2015a). In the Indian Ocean, these studies are mostly confined to the northwestern (Martiny et al. 2013b) and southwestern tropical regions (Copin-Montegut & Copin-Montegut 1983). Despite the fact that the northern Indian Ocean is distinct from other oceans in terms of the extent and magnitude of biogeochemical processes, particularly due to monsoonal wind forcing, less is known about mechanisms regulating elemental stoichiometry in this part of the Indian Ocean.

The Bay of Bengal (hereafter the Bay), the northeastern part of the Indian Ocean, is an economically¹, ecologically, and culturally important basin as it forms a long coastline with the Indian subcontinent. It is surrounded by the Indian subcontinent in the north and northwest, and the Andaman Nicobar Islands in the east. The prevalence of eddies are typical characteristics of this basin (Mukherjee et al. 2019); frequently occurring mesoscale eddies are associated with advective transfer of riverine water offshore. The Bay experiences semi-annual seasonality of the Asian monsoon system (Gadgil 2003). Strong southwesterly winds lead to high rainfall over the Indian subcontinent from June to September, whereas between December and February, northeasterly winds lead to heavy rainfall in the southern states of India. Large freshwater influx $(1.625 \times 10^{12} \text{ m}^3 \text{ yr}^{-1})$ from the Ganges-Brahmaputra river system drives a strong vertical density gradient leading to higher sea surface temperature than usual in the Bay (Subramanian 1993, Shetye et al. 1991). The influx of nutrients through riverine discharge, surrounding mangroves and wetlands enhances productivity in the coastal regions (Dutta et al. 2019) and leads to a considerable organic C export to the deeper Bay (Ittekkot et al. 1991, Kumar et al. 2004, Singh & Ramesh 2015).

The Bay shows high concentrations of dissolved organic C (DOC) ~75-100 μ mol l⁻¹ in the surface waters due to high riverine flux (Shah et al. 2018). In addition, dissolved organic N (DON) and dissolved organic P (DOP) constitute about 70-99% of the total dissolved nutrients in the waters above the thermocline (Sarma et al. 2019a). At the same time, the water column remains stratified, restricting the upward nutrient flux due to a strong halocline (Prasanna Kumar et al. 2010). In such cases, recycling processes and frequent eddies observed over the Bay could be of considerable importance for primary production (Prasanna Kumar et al. 2004, Singh et al. 2015b). In fact, eddies are known to enhance the primary production in the Bay (Prasanna Kumar et al. 2010, Singh et al. 2015b).

These hydrographic (e.g. riverine influx), physical (e.g. stratification and eddy-driven mixing), and biogeochemical (e.g. N₂ fixation) variables might have an influence on the C:N:P ratio in the Bay. However, there are only a few studies from the basin, and these are limited only to POM stoichiometry. The C:N ratio in POM was higher (8.0–17.2) in the coastal Bay during spring 2018 (Sarma et al. 2019b) than that (7.1) in the offshore Bay during spring 2016 (Garcia et al. 2018). In order to comprehensively explore the interplay of biogeochemical and physical processes on the C:N:P ratio, we sampled the water column at 8 locations in the Bay during the summer monsoon (July 2018). Our major objectives during this study were to (1) estimate the C:N:P ratio in organic and inorganic pools in the water column (surface to

¹The Bay of Bengal Initiative for Multi-Sectoral Technical and Economic Cooperation (BIMSTEC) supports international trade among India, Bangladesh, Bhutan, Myanmar, Thailand, Sri Lanka, and Nepal.

2. MATERIALS AND METHODS

Sampling was performed in the Bay during the peak of the summer monsoon (12 July to 2 August 2018) on-board ORV 'Sagar Nidhi' (SN#132) (see Table 1). We sampled 8 different stations; 5 of which were along an 88° E transect while the rest were located from 85–87° E longitudinal range (Fig. 1). Water samples were collected using a Sea-Bird CTD rosette sampler from 12 different depths (10, 25, 50, 75, 100, 150, 200, 300, 500, 1000, 1500, and 2000 m) at each station. At times, one of the 2 subsurface sampling depths (i.e. 50 or 75 m) was changed to match the depth of the deep chlorophyll maximum (DCM). The CTD sensors provided data on water temperature, salinity, and density. Fluorescence data were obtained from a well-calibrated sensor mounted on the



Fig. 1. Daily sea surface height anomaly overlaid by geostrophic currents on 12 July 2018. The eddies remained in the same position throughout the sampling period. Circles: sampling locations. Station abbreviations: ACE: anticyclonic eddy; MWE: mode water eddy; NE: non-eddy; BWE: boundary water eddy

CTD rosette sampler. Mixed layer depth was calculated using a 0.2°C deviation in potential temperature from the surface water (de Boyer Montégut 2004, Holte & Talley 2009).

For total organic C (TOC) and total N (TN) measurements, seawater samples were collected in 50 ml sterile centrifuge tubes. The samples were frozen immediately at -20°C until analysis in the onshore laboratory. The TOC measurements were performed using a high temperature catalytic oxidation method in a TOC analyser (TOC-L-CPH, Shimadzu Corporation) (Suratman et al. 2009, Pujo-Pay et al. 2011). Inorganic C was removed by acidifying the sample with 2 N HCl through purging of a carrier gas (zero gas, ultra-pure, 99.9995% purity) prior to the TOC measurement. The non-purgeable organic C was oxidised to CO2 and measured using a Non Dispersive Infra-Red detector. TN concentrations were measured on a TN analyser (TNM-L-CPH, Shimadzu Corporation) by oxidising dissolved nitrogen to nitric oxide (NO) into the combustion tube at 720°C. The resultant NO was detected in a chemiluminescence detector (Chaichana et al. 2019). The accuracy of the results was ensured by routinely measuring a certi-

> fied reference material (Batch 18, Lot#08-18 for deep seawater) provided by the University of Miami (Hansell 2005). Analysis was performed after ensuring that the absolute deviation of the measured value from the known value was within 5%. The coefficient of variation was 2% for total organic C (TOC) and TN measurements.

> Samples for nutrients (NO3-, NO2-, and phosphate $[PO_4^{3-}]$) analysis and total phosphorous (TP) were collected in 60 ml high density polyethylene bottles and frozen at -20°C. Nutrients were measured using an autoanalyser (SKA-LAR). The detection limits for NO_x (NO_3^- + NO_2^{-}), NO_2^{-} , and PO_4^{3-} were 0.16, 0.06, and 0.02 $\mu mol~l^{-1},$ respectively. NO_x and PO_4^{3-} are referred to as dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP), respectively. The depth at which the NO₃⁻ concentration reached 1 µmol l⁻¹ was considered the nutricline, which was used to infer the nutrient supply rate to the surface layer (Garcia et al. 2018). Dissolved inorganic C (DIC) samples were collected in 12 ml Exetainers (Labco) followed by addition of 0.2 ml

Sea surface height anomaly (m)

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mercuric chloride (100% HgCl₂). DIC was measured using a coulometer (UIC; Model 5012) with an analytical precision of $\pm 2\%$.

Samples for particulate organic C (POC), N (PON), and P (POP) were collected by filtering seawater on precombusted (at 400°C for 4 h) Whatman glass microfiber filters (GF/F, 47 mm diameter, 0.7 µm pore size). Around 3.7-4.7 l of water for depths up to 500 m and 5-8 l of water for depths from 1000-2000 m were filtered for POC and PON combined. For POP, 2.35 l of seawater was filtered for depths up to 500 m, whereas 3–4 l was filtered for depths from 1000-2000 m. Concentrations and isotopic compositions (δ^{13} C and δ^{15} N) for POC and PON were measured using an elemental analyzer (FLASH 2000; Thermo Scientific) coupled with an isotope ratio mass spectrometer (Thermo Delta V Plus; Thermo Scientific) connected via Conflo interface. The analytical precision for both POC and PON for duplicate measurements was <10 %, while δ^{13} C and δ^{15} N had analytical precision of <0.1 and 0.3%, respectively. IAEA-N-2 ((NH₄)₂SO₄; 20.3‰) for N and IAEA-CH-3 (cellulose, -24.7‰) for C were used as standards in addition to the internal laboratory standards.

A high temperature oxidation method was adopted to estimate POP (Murphy & Riley 1962). Potassium persulfate $(K_2S_2O_8)$ was used as an oxidising agent for digestion of the organic matter. Potassium dihydrogen phosphate (KH_2PO_4) standard was used for the calibration and adenosine-5'-triphosphate disodium (ATP-Na₂) standard was used to estimate the recovery percentage (80-85%). Samples were digested in an autoclave at 1.055 kg cm^{-2} (15 psi) for 80 min in the presence of $K_2S_2O_8$. Digested samples were analysed spectrophotometrically (Shimadzu Spectrophotometer UV-1800) at a wavelength of 880 nm. The detection limit of the measurements was 0.1 nmol l⁻¹. TON and total organic P (TOP) were estimated by subtracting inorganic matter from its total elemental pool as [TN] - [DIN] and [TP] - [DIP], respectively. DOC, DON, and DOP concentrations were quantified as the difference between TOC and POC, TON and PON, and TOP and POP, respectively. This method has limitations for DOP measurements in samples having <10% of total dissolved P. Our samples, however, had slightly higher than 10% DOP in the total dissolved P pool. Nonetheless, the UV oxidation method is encouraged for the precise measurement of DOP in such waters (Foreman et al. 2019). All ratios were estimated in units of mol mol^{-1} .

We used published N_2 fixation and C uptake rates from a concurrent study performed on the same cruise (Saxena et al. 2020) to assess the role of these

2 biogeochemical processes on C:N:P ratios. Processed Automatic Weather Station data for wind speed was provided by the Indian National Centre for Ocean Information Services, India (Harikumar et al. 2013). To categorize the sample locations based on sea surface height anomaly, daily meridional and zonal geostrophic current $(0.25^{\circ} \times 0.25^{\circ})$ along with sea surface height anomaly $(0.25^{\circ} \times 0.25^{\circ})$ data were obtained from the Copernicus Marine Environmental Monitoring Service (https://resources.marine.copernicus.eu/; data retrieved on 17 August 2019). Cyclonic eddies were identified by anticlockwise geostrophic currents with <-0.2 m sea surface height anomaly. Anticyclonic eddies (ACE) were identified by a clockwise circulation with >0.2 m sea surface height anomaly. Features having increased sea surface height anomaly accompanied by lens shaped isopycnals were characterized as a mode water eddy (MWE) (Sweeney et al. 2003). Stations located along the boundary area of cyclonic and ACEs were categorised as a boundary water eddy (BWE). Stations with no significant sea surface height anomaly were considered non-eddy (NE) stations. We sampled 4 ACE (1-4), 2 NE (1-2) and one each MWE and BWE stations.

Linear regression analyses (significance level: α < 0.05) were performed among C, N, and P concentrations in the different pools. One-way ANOVA was used to test the significant (p < 0.05) difference in the ratios of the different pools, using SigmaPlot 14.0 software. The Shapiro-Wilk test was performed to check the normality of the data for ANOVA analysis. Influence of environmental variables on the concentration of elements and their elemental ratios in the 3 different pools was investigated using principal component analysis (PCA) in R (R Core Team 2019). Elemental ratios, $\delta^{13}C$, and $\delta^{15}N$ of POM were considered as dependent variables while others, such as the environmental parameters (temperature, salinity) and individual elemental concentrations in DIM, DOM, and POM were considered independent variables. Pearson's correlation coefficient at $\alpha < 0.05$ was used to estimate the strength of the relationships.

3. RESULTS

3.1. Hydrographic properties

Several eddy features were evident in the Bay during the study period. We observed strong southwesterly winds (average wind speed ~11.5 m s⁻¹ with a maximum ~24.5 m s⁻¹) throughout the sampling Table 1. Details of environmental parameters at the 8 sampling locations during summer 2018 (error values: SD). See Fig. 1 for station locations. SST: sea surface temperature; SSS: sea surface salinity. Chl *a* values are averaged over the top layer; column-integrated (up to 75 m) N₂ fixation rates and primary production data are taken from Saxena et al. (2020)

Serial no.	Stn	Lat (°N)	Long (°E)	Date of sampling (dd-m-yyyy)	SST (°C)	SSS	Chl <i>a</i> (mg m ⁻³)	Depth of chl max (m)	Mixed layer (m)	Nutri- cline (m)	$egin{array}{l} N_2 \mbox{ fixation} \ (\mu mol \ N \ m^{-2} \ d^{-1}) \end{array}$	Primary production (mmol C m ⁻² d ⁻¹)
1	ACE1	07°29.99'	88°14.23′	12-7-2018	28.8	34.19	0.29 ± 0.04	75	64	58	11 ± 5	30 ± 8
2	MWE	08°47.66′	88°13.44′	16-7-2018	28.1	34.39	0.89 ± 0.59	25	49	10	6 ± 6	87 ± 11
3	NE1	12°29.60'	88°06.52'	18-7-2018	28.8	33.11	0.38 ± 0.41	57	52	58	27 ± 16	39 ± 4
4	NE2	14°13.64′	88°03.63'	19-7-2018	28.5	32.78	0.23 ± 0.16	55	48	45	20 ± 4	24 ± 2
5	ACE2	16°30.49'	88°00.42′	24-7-2018	28.2	33.48	0.42 ± 0.21	47	43	51	4 ± 4	69 ± 5
6	ACE3	16°28.19'	87°05.02′	29-7-2018	28.7	33.44	0.20 ± 0.18	76	77	33	12 ± 8	58 ± 13
7	BWE	15°42.30'	85°28.94′	31-7-2018	28.7	33.62	0.23 ± 0.09	55	41	32	75 ± 98	81 ± 12
8	ACE4	14°10.33'	85°05.32′	02-8-2018	29.1	33.04	0.25 ± 0.28	78	66	66	41 ± 6	45 ± 4



Fig. 2. Vertical section of (a) temperature, (b) salinity, (c) density, and (d) chl *a*. Section distance starts from Stn ACE1 (50 km) and ends at ACE4 (1500 km)

period. Sea surface temperature ranged from 28–29°C, while sea surface salinity varied from 33–34 (Table 1, Fig. 2). Sea surface salinity was the highest (34.39) at MWE and the lowest (32.78) at NE2. The mixed layer was deep (77 m) at ACE3 and shallow (41 m) at BWE. The nutricline varied between 10 m (at MWE) and 66 m (at ACE4) (Table 1).

3.2. Concentrations and ratios in the POM

To analyse the variability in elemental concentrations and ratios in the water column, we categorised our observations into 3 depth segments: (1) top layer (surface to DCM) where primary production is high, (2) subsurface layer (DCM to 300 m) where mineralisation is high, and (3) deep layer (300–2000 m). The DCM varied between 25 m (MWE) and 78 m (ACE4). For calculation purposes, we considered the DCM depth in both the top and subsurface layers, and similarly 300 m depth in both the subsurface and deep layers.

POC, PON, and POP concentrations decreased with depth at all stations (Fig. S1 in the Supplement at www.int-res.com/articles/suppl/m653p041_supp.pdf). The concentrations for POC, PON, and POP ranged from 3.5-6.5, 0.3-0.9, and $0.01-0.03 \mu mol l^{-1}$, respectively, in the top layer at the ACE stations. High POC and POP concentrations were observed at ACE2, while POC and POP concentrations were low at ACE4. Among the ACE locations, the highest PON was at ACE1 and the lowest at ACE4. The MWE showed high POC, PON, and POP concentrations in the top layer compared to that at the other stations.

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Table 2. Average concentration (µmol l^{-1} , ±1 SD; 8 stations), and % contribution of particulate organic C, N, and P (POC, PON, POP, respectively) from each pool to their respective total pools

	POC	PON	РОР
Particulate organic p	ool		
Top layer	4.87 ± 1.83	0.54 ± 0.26	0.022 ± 0.011
	0.24	7.03	4.04
Subsurface water	2.37 ± 0.47	0.27 ± 0.14	0.008 ± 0.003
	0.11	0.98	0.40
Deep water	2.10 ± 0.55	0.15 ± 0.04	0.003 ± 0.001
	0.09	0.33	0.10
	DOC	DON	DOP
Dissolved organic po	ol		
Top layer	79.28 ± 10.67	6.40 ± 1.68	0.33 ± 0.09
	3.93	83.35	59.69
Subsurface water	64.78 ± 8.26	9.38 ± 4.95	0.39 ± 0.15
	2.95	34.45	20.11
Deep water	52.14 ± 11.05	11.95 ± 8.09	0.37 ± 0.18
	2.23	25.82	11.99
	DIC	DIN	DIP
Dissolved inorganic	pool		
Top layer	1933.75 ± 70.74	0.74 ± 0.70	0.20 ± 0.09
	95.83	9.62	36.27
Subsurface water	2130.68 ± 80.41	17.57 ± 3.11	1.56 ± 0.22
	96.94	64.57	79.49
Deep water	2283.48 ± 71.38	34.17 ± 1.98	2.74 ± 0.11
	97.68	73.85	87.91

(Table S1). Overall, POC, PON, and POP constituted about 0.2, 7, and 4% of their total elemental pools in the top layer (Table 2).

The C:N, N:P, and C:P ratios in POM were in every case higher than the Redfield Ratio in the top layer and increased further with depth (Figs. 3 & S2). Average POC:PON ratios in the top layers (~9) showed little variability, but showed deviations among stations in the deeper layer (Table S1). In the top layer, average POC:PON and PON:POP ratios were higher at ACE stations compared to most stations, whereas the POC:POP ratio was higher at NE stations in the subsurface and deeper layers. Overall, the C:N:P ratios in POM were 232:25:1, 457:35:1, and 966:72:1 in the top, subsurface, and deep layers, respectively (Fig. 4).

3.3. Concentration and ratios in the DOM

The DOC concentrations were higher in the top layer, with lower concentra-



Fig. 3. Vertical section of (a) POC:PON, (b) PON:POP, (c) POC:POP, (d) DOC:DON, (e) DON:DOP, (f) DOC:DOP, (g) DIC:DIN, (h) DIN:DIP, and (i) DIC:DIP ratios. Section distance starts from Stn ACE1 (50 km) and ends at ACE4 (1500 km). POC, PON, POP: particulate organic C, N, P, respectively; DOC, DON, DOP: dissolved organic C, N, P, respectively; DIC, DIN, DIP: dissolved inorganic C, N, P, respectively



Fig. 4. C:N, N:P, and C:P ratios in top layer, subsurface water, and deep water. Pink dotted lines: mean; blue (POM, DOM: particulate organic, dissolved organic matter, respectively) and green (DIM: dissolved inorganic matter) solid lines: median. Black solid brackets: significantly different groups (p < 0.05) obtained from 1-way ANOVA; whiskers account for 10 and 90% of distribution; box accounts for 25 and 75%. Other abbreviations as in Fig. 3

tions measured in subsurface and deeper waters. The opposite vertical trend was observed for DON and DOP concentrations, with highest concentrations found in subsurface and deep waters (Table 2). Average DOC, DON, and DOP concentrations were 76.9 ± 5.8, 5.3 \pm 1.0, and 0.4 \pm 0.1 µmol l⁻¹, respectively, in the top layer of the ACE stations (Table S1). At MWE, the DOC, DON, and DOP concentrations were $76.0 \pm$ 1.1, 8.4 \pm 0.8, and 0.4 \pm 0.5 µmol l⁻¹, respectively, in the top layer. The average concentrations of DOC, DON, and DOP in the top layers were 93.4 ± 5.1 , 8.2 \pm 0.3, and 0.3 \pm 0.03 µmol l⁻¹, respectively, at the NE stations, while these values were 63.9 ± 2.9 , 5.1 ± 0.9 , and $0.3 \pm 0.1 \mu$ mol l⁻¹, respectively, at the BWE. DOC, DON, and DOP constituted about 4, 83, and 60%, respectively, of their total elemental pools in the top layers, while in the deeper waters their respective contributions were 2, 26, and 12% (Table 2).

All the ratios in the DOM pool deviated greatly from the Redfield Ratio. In the top layer, the average DOC:DON ratio was higher at the ACE stations than others (Table S1). In contrast, DOC:DOP and DON: DOP ratios were the lowest in the top layer of the ACE stations. The C:N and C:P ratios in DOM were lower in the subsurface and deep waters than in the top layer (Fig. 4). On average, C:N:P ratios in DOM were 357:30:1, 268:37:1, and 245:66:1 in the top, subsurface, and deep waters, respectively (Fig. 4).

3.4. Concentration and ratios in the dissolved inorganic pool

Average DIC, DIN, and DIP concentrations were 1910.3 \pm 77.3, 0.3 \pm 0.1, and 0.15 \pm 0.04 µmol l⁻¹, respectively, in the top layer at the ACE stations (Table S1). DIN and DIP concentrations were high in the top layer at MWE and BWE (Table S1, Fig. S1). The average DIC, DIN, and DIP concentrations were 1973.1 \pm 6.4, 2.0 \pm 0.5, and 0.38 \pm 0.04 µmol l⁻¹, respectively, in the top layer at the MWE station. At the NE stations, average DIC, DIN, and DIP concentrations in the top layer were higher than those observed at the ACE stations but lower than that at the MWE station. DIC, DIN, and DIP concentrations were 1916.6 \pm 29.4, 1.7 \pm 2.5, and 0.3 \pm 0.3 µmol l⁻¹,



Fig. 5. Depth profile of δ^{13} C (green dashed line) and δ^{15} N (brown solid line) of POM at (a) ACE1, (b) MWE, (c) NE1, (d) NE2, (e) ACE2, (f) ACE3, (g) BWE, and (h) ACE4 stations. See Fig. 1 for abbreviations

respectively, in the top layer of the BWE. DIC, DIN, and DIP constituted about 96, 10 and 36%, respectively, of their total elemental pools in the top layer (Table 2). There was large spatial variation in DIC: DIN and DIC:DIP ratios in the top and subsurface layers across the stations, with higher values at the ACE and NE stations (Table S1). However, DIC:DIN and DIC:DIP ratios were similar in the deeper layers across stations. The DIN:DIP ratios increased with depth with no significant spatial variability (Fig. 3). On average, the C:N:P ratios in dissolved inorganic nutrients were 12717:3:1, 3126:10:1, and 840:12:1 in the top, subsurface, and deep waters, respectively (Fig. 4).

3.5. Isotopic composition (δ^{15} N and δ^{13} C) of POM

The δ^{15} N of POM was positive throughout and increased with depth (Fig. 5). δ^{15} N ranged from 0.9– 6.5‰ in the top, 1.2–9.4‰ in the subsurface, and 7–9.5‰ in the deep layers at the ACE stations. In the top layer, average δ^{15} N was 4.5 ± 0.7, 2.7 ± 0.4, and 3.6 ± 0.7‰ at the MWE, NE, and BWE stations, respectively. The ¹⁵N enrichment in POM was higher in the deep waters of ACE and NE than that at the BWE station. Contrary to δ^{15} N, δ^{13} C decreased with depth. It varied between -22.1 and -26.1‰ in the ACE, and remained around -24.3 ± 0.1‰ in the top layer of the NE and -24.1 ± 0.9‰ in the top layer of the BWE stations. Comparatively less depleted ¹³C signatures (-22.3 ± 0.8‰) in POM were observed at the top waters of the MWE.

3.6. Statistical analysis

The POC concentrations were positively correlated with PON ($r^2 = 0.59$, p < 0.05) and POP ($r^2 = 0.71$, p < 0.05) (Fig. S3). In addition, PON concentrations were positively correlated with POP concentrations ($r^2 = 0.66$, p < 0.05). However, no significant correlations were detected between DOC and DON, DON and DOP, and DOC and DOP concentrations. The DIN and DIP concentrations were strongly correlated ($r^2 = 0.99$, p < 0.05) with a slope of 13.18 and negative intercept—suggesting N nutrients were exhausted before PO₄³⁻. Although the generation of DIP and DIN through organic matter remineralisation is faster than DIC in the ocean, DIC was strongly correlated with DIN ($r^2 = 0.75$, p < 0.05) and DIP ($r^2 = 0.78$, p < 0.05).

The PCA analysis showed that the first 2 principal axes (PC) explained a total of ~60% of the variability, with 49% accounted by PC1 (Fig. 6). PCA is used to highlight the relationships between variables projected in a multidimensional space. We have shown only PC1 and PC2, as they explain the most variability among parameters. Each arrow in Fig. 6 represents a variable (as mentioned near the arrowheads); the distance of the arrows from the origin and their closeness to each other is proportional to correlation, i.e. when arrows are far from the centre and close to each other, they are positively correlated. When arrows are symmetrically opposite, they are anticorrelated. If the arrows are orthogonal, there is no correlation. If the variables are close to the origin, the relationship among these variables is inconclusive. The vectors for POC:POP and PON:POP were identical, and anticorrelated with POP (r = -0.5). DOC:DON was anticorrelated with DON (r = -0.7), while DOC:DOP was anticorrelated with DOP (r =-0.6). DIN:DIP was strongly correlated with both DIN and DIP (r = 0.9). Likewise, DIC:DIN was anticorrelated with DIC and DIN (r = -0.7). DIC:DIP was anticorrelated with DIC and DIP (r = -0.7). δ^{13} C was positively correlated with POC (r = 0.7) and negatively with DIC (r = -0.6), while δ^{15} N was positively correlated with DIN (r = 0.7). DOC:DOP and DON:DOP



Fig. 6. Principal component analysis of depth, temperature, salinity, fluorescence, dissolved inorganic nutrients, particulate organic matter (POM), dissolved organic matter, elemental ratios, $\delta^{13}C$, and $\delta^{15}N$ of POM. Abbreviations as in Fig. 3

were negatively correlated with DOP. DIC, DIN, and DIP were negatively and positively correlated with *in situ* temperature and salinity, respectively.

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4. DISCUSSION

This comprehensive study on the elemental stoichiometry in the particulate and dissolved pools of the poorly studied Bay revealed significant deviations from the Redfield Ratio. This deviation is far more pronounced in the deeper than the upper layers, with variable role of eddies and biogeochemical processes such as N_2 fixation. Below, we examine the role of physical and biogeochemical influences in shaping the ecological stoichiometry in the Bay.

4.1. Role of environmental factors on C, N, and P concentrations and their ratios

Variations in elemental ratios are driven by environmental factors such as temperature, salinity, and nutrient concentrations (Körtzinger et al. 2001, Frigstad et al. 2011). Nutrients (DIN, DIP, and DIC) were anticorrelated with temperature in our PCA analysis (Fig. 6). This suggests that temperature might not play a direct role in nutrient concentration. Rather, it suggests that nutrient concentrations are high in deep (cold) waters, and the influx of cold waters through physical processes (such as eddies) might enhance the nutrient concentration in the surface Bay. Additionally, the positive correlation between nutrients and salinity indicates that the nutrients are of marine origin (Fig. 6). This is not surprising, as terrestrial nutrients are largely consumed within the Bay's estuarine ecosystem (Singh & Ramesh 2011, Dutta et al. 2019). Correlations between elemental ratios and temperature and salinity should be interpreted with caution, as neither of these parameters are known to directly affect the elemental ratios. However, temperature changes affect nutrient uptake and other biogeochemical processes (such as respiration/decomposition), in turn influencing elemental stoichiometry (Lomas et al. 2002, Spackeen et al. 2018). In addition, salinity gradients have been shown to change N uptake rates in mesocosm experiments (Kumar et al. 2018). In theory, temperatureand salinity-related influences could be both physiological and taxonomic (Barton & Yvon-Durocher 2019, Hernando et al. 2020). The N-uptake potential is a part of physiological change of phytoplankton driven by salinity and temperature (Kaur-Kahlon et Author copy

al. 2016, Kumar et al. 2018, Barton & Yvon-Durocher 2019, Hernando et al. 2020). Since our data are spatially distributed, these influences are likely to be taxonomical. The anticorrelation of salinity with POM concentrations could be attributed to the increase in elemental uptake potential due to the freshening of water at elevated temperatures (Hernando et al. 2020) or the relatively higher consumption (mineralisation) of POM at higher salinities. However, these mechanisms need to be experimentally verified in the Bay.

The overlapping of the PON:POP and POC:POP vectors suggest that these ratios are driven by variations in POP through similar processes, such as the POP remineralisation. Additionally, that there was no significant correlations of PON:POP and POC:POP with PON and POC, respectively, confirms that the variation of these ratios is due to oscillations in POP (Fig. 6).

4.2. Interlinking between the C:N:P ratios in POM, DOM, and DIM

The 3 elemental pools are interlinked among the depth layers through processes such as POM export, upward flux of nutrients, and exchange of DOM between the layers (Pujo-Pay et al. 2011). In the top layer, DIM and DOM are diffused to POM through biological consumption (Pujo-Pay et al. 2011). A part of POM gets recycled to DOM by excretion or lyses of organic matter; subsequently, DOM (and POM) remineralises to DIM, completing the cycle. In the subsurface and deep layers, POM and DOM are largely recycled to DIM (Krom et al. 2010).

The POC:PON ratio remains largely fixed in the water column, while increase in the C:P and N:P ratios in POM from the top to the subsurface layer (Fig. 3) suggests the preferential remineralisation of POP in sinking organic matter (Loh & Bauer 2000, Letscher & Moore 2015). In addition, the strong correlation (r = 0.5 and 0.7 and p < 0.05) of PON:POP and POC:POP ratios with nutrients confirms the recycling of POP (Fig. 6). During remineralisation, preferential removal of ¹³C-enriched molecules such as protein and nucleic acids, and retention of ¹³Cdepleted, lipid-rich residual organic matter results in a decrease in δ^{13} C (~1.6‰) of POM from the top layer to the subsurface and deep waters (Fig. 5) (Post et al. 2007). On the other hand, removal of N-rich biomolecules during degradation might have resulted in the increase in $\delta^{15}N$ (6‰ in the subsurface, and 7.5‰ in the deep water) of POM (Macko et al. 1994).

The very low N:P ratio in nutrients (<<16:1) in the top layer indicates N-stressed primary production in the Bay. This is confirmed from the negative intercept between DIN and DIP (Fig. S3e), which suggests that DIN gets exhausted before DIP. Unlike the N:P ratio, C:N and C:P ratios in DIM of the top layer were a thousand and a hundred times higher than the Redfield Ratio, respectively. The DIC pool is so large that it cannot be easily exhausted, and is considered here as unutilised. Therefore, when one looks at the change in DIC:DIN or DIC:DIP over time (i.e. consumption rate ratios), these ratios are likely to be close to the Redfield Ratio. However, the ratios in a static set of concentrations at a given time, as presented here, are roughly order of magnitudes higher.

The POM and DIM elemental proportions are primarily controlled by nutrient uptake and remineralisation processes. The remineralisation of POM to dissolved nutrients involves cycling through the DOM pool (Johnson et al. 2013, Singh et al. 2015a). Thus, DOM serves as an important intermediary link between POM and nutrients during remineralisation. In the NO_x-deficient top layer of the Bay, DON is an order of magnitude higher than DIN (Fig. S1e,h), suggesting that DON might be an alternative source of bioavailable N for phytoplankton in these waters (Church et al. 2002, Zubkov et al. 2003, Aldunate et al. 2020). A previous study in the Bay suggested a link between primary productivity and high DON and DOP concentrations during the spring intermonsoon of 2018 (Sarma et al. 2019a), but no such correlation was observed in our study (Fig. S4a,b). The absence of a correlation between primary production and DON in our study might be explained by the coupling between DON production and uptake, leading to a lack of DON accumulation. Another potential cause for no correlation may be the seasonal change in phytoplankton community composition. DON-consuming phytoplankton (cyanobacteria) are most abundant during summer in oligotrophic oceans (Huisman et al. 2018). Given that urea is one of the important sources of N for autotrophs in the surface water of the Bay (Baer et al. 2019), a study focused on DON uptake in different seasons is desirable to quantify the importance of DON as an alternative N source for phytoplankton in the Bay.

Low concentrations of DON and DOP in the top layer may be attributed to the photochemical breakdown of organic matter (Chari et al. 2016) and faster remineralisation of DOP and DON over DOC (Church et al. 2002, Letscher & Moore 2015, Chaichana et al. 2019). DOC is freshly produced in the sunlit surface ocean via phytoplankton degradation and food web processes (grazing by microzooplankton), and the labile components are generally rapidly consumed by heterotrophic prokaryotes (Calleja et al. 2019). The semi-labile portion of DOC escapes rapid microbial consumption and accumulates in surface waters during high stratification. The accumulation of DOC in the top layer might have resulted in a high C:P ratio of ~357, and a C:N ratio ~13 in DOM (Ogawa & Tanoue 2003). Bacteria (mostly heterotrophs) use DOM as a substrate (Granéli et al. 1999). They require more N per unit biomass (C:N = 3-7; Nagata 1986) than phytoplankton (C:N = 6-20). In the present study, DOM had a high C:N ratio (13.2) in the top layer, thus bacteria may retain the same DOM proportion. Bacteria also consume more N than P compared to the Redfield Ratio (Bertilsson et al. 2003), hence they might also change DOM stoichiometry at the surface if DOM concentrations are low.

Accumulated semi-labile DOM in the surface water can be transported down by vertical mixing and by ballasting of terrestrially derived lithogenic matter in sinking particles, thereby increasing the organic C export to the deep sea (Rixen et al. 2019). This subducted fraction of DOC can be remineralised by subsurface heterotrophic communities (Calleja et al. 2019), thereby decreasing the DOC concentration in the subsurface and deep waters. The depth profile of DOC in this study is consistent with observations elsewhere in tropical regions (Santinelli et al. 2006). DON is more resistant to remineralisation than DOP. The downward transport of refractory DON (>50 %of DON; Roussenov et al. 2006, Vidal et al. 2018) results in an enhanced accumulation below the surface layer of the ocean. Overall, this may have resulted in decreased C:N and C:P, along with increased N:P ratio in DOM in the subsurface and deep waters. These observations are consistent with the negative correlation of DON:DOP with DOP (Fig. 6). The average C:N:P ratio in the DOM in the top layer is 357:30:1 in the Bay, lower than the global average 640:44:1 for bulk DOM in the surface ocean (Letscher & Moore 2015). However, the DON:DOP ratio in the top 100 m ranged from 5-237 among stations, higher than that (1.1-16.6) reported for the coastal Bay during spring 2018 (Sarma et al. 2019a).

Usually δ^{13} C in POC varies from -24 to -18‰ (Fry & Sherr 1989, Middelburg & Nieuwenhuize 1998) and δ^{15} N in PON from 5–8‰ in marine phytoplankton (Minagawa et al. 2001). Although the Bay receives enormous terrestrial influx (33–51.2 g m⁻² yr⁻¹) (Ittekkot et al. 1991, Unger et al. 2003), the mean C:N ratio (~10), δ^{13} C (-21.5 to -26.2‰, average -24.6 ± 1.2‰), and δ^{15} N (0.9–8.3‰, average 4.4 ± 1.9‰) of

POM in the top 100 m in our study indicates that the POM in the surface layer of the Bay is largely derived from *in situ* production rather than external supply.

4.3. The role of strong winds and eddies on the C:N:P ratios

Overall, eddies showed a mixed effect on the C:N:P ratios in the top layer. Strong southwesterly winds (up to 24.5 m s^{-1}) and eddies were identified in our sampling area during the study period. A relatively deep mixed layer (41-77 m) and shallow nutricline (10-66 m) (Table S2) were observed during the sampling period, which might be due to the strong winds and eddy-induced mixing of the water column. Although there were differences in DIM and POM concentrations, little variability in C:N:P ratios of POM between eddy and non-eddy stations was observed. DOC and DON concentrations were lower at the ACE compared to that at the NE stations, while DOP was slightly higher at the ACE stations in the top layer. Due to this difference, the DOC:DOP and DON:DOP ratios were lower in the ACE locations compared to the NE locations. A study conducted to understand the influence of eddies on nutrients and POM during spring 2018 (Sarma et al. 2019b) reported POC and PON concentrations higher than our study, but the C:N ratio in POM remained the same. Similarly, primary production estimates reported in a concurrent study (288–1044 mg C $m^{-2} d^{-1}$; Saxena et al. 2020) are consistent with that (758 \pm 220 mg C m⁻² d⁻¹) reported by Sarma et al. (2019a). These primary productivity estimates are much higher than an earlier estimate of primary productivity conducted during N-stressed conditions in April 2016 (primary productivity: 3-7 nmol C l⁻¹ h⁻¹; N:P flux ratio <14; Baer et al. 2019). Overall, these studies suggest a role of eddies in supplying nutrients to the photic layer and consequently increasing primary production leading to an elevated elemental ratio in POM (Sarma et al. 2019a,b). On an average, the C:N:P ratio in POM in the top layer is higher than reported earlier in the Bay during spring inter-monsoon (Garcia et al. 2018) (Table S2).

4.4. Impact of biogeochemical processes on the C:N:P ratio

Marine biogeochemical processes have the potential to change the plankton and nutrient elemental ratios, and vice versa (Klausmeier et al. 2004b, Mills Author copy

& Arrigo 2010, Jabir et al. 2020). Despite PO_4^{3-} excess (N:P ~3) in the top layer with adequate dry deposition flux of Fe (0.02–1.2 μ mol m⁻² d⁻¹; Srinivas & Sarin 2013), low N_2 fixation rates were observed in the Bay (Saxena et al. 2020). Assuming photoautotrophs require 1 mol N to fix 6.6 mol C (Redfield 1958, Orcutt et al. 2001), the contribution of N_2 fixation to phototrophic C fixation remains below 1% (Saxena et al. 2020). Apart from the low N_2 fixation in surface waters during our study, heterotrophic N2 fixation rates are below detection limits in the oxygen minimum zone of the Bay (Löscher et al. 2020). Such low rates of N₂ fixation are unlikely to change the C:N:P ratios. No correlation between N2 fixation rates and different elemental ratios confirms the same (Fig. S4e,f).

The observed PON:POP ratio (~25) could be attributed to the presence of smaller non-diazotrophic cyanobacteria, such as *Prochlorococcus* and *Synechococcus*, which are ubiquitous in the surface waters (Bertilsson et al. 2003, Martiny et al. 2013a, Baer et al. 2019). *Prochlorococcus* tend to be dominant in high-temperature and low-nutrient waters.

The N:P ratios in nutrients act as a proxy for biogeochemical processes leading to N loss (such as denitrification and anammox) in the subsurface low oxygenated waters. The N:P ratio of dissolved inorganic nutrients in the water column (<16:1) suggests the occurrence of N loss processes in the Bay, with low but detectable rates of anammox (5.5 nM N d⁻¹) and denitrification (0.9 nM N d⁻¹) measured in the oxygen minimum zone (Bristow et al. 2017). However, an extensive study is required to understand the effect of N loss processes of this magnitude on nutrient stoichiometry of the Bay.

Considering the observed deviations in the C:N:P ratio from the Redfield Ratio in the dissolved and particulate matter pools, we examined whether the Bay supports the nutrient supply hypothesis for tropical ecosystems proposed by Rhee (1978). This hypothesis states that the absolute concentration of nutrients such as DIN and DIP, rather than their ratio, determines the POM stoichiometry. Based on this hypothesis, expected C:N:P ratios in oligotrophic basins are higher than the Redfield Ratio, and the reverse holds for nutrient-rich basins (Galbraith & Martiny 2015). This happens because slow growing cyanobacteria, with a high N:P ratio in their biomass/nutrient uptake requirements, grow in oligotrophic waters whereas fast growing microorganisms (with a low N:P ratio) flourish in nutrient-rich waters (Singh et al. 2017, Sharoni & Halevy 2020). Poor supply of nutrients due to stratification makes the Bay oligotrophic during most seasons (Prasanna Kumar et al. 2010, Mc Creary et al. 2013). We observed that the C:N, C:P, and N:P ratios in the POM at surface waters are higher than the Redfield Ratio, and this seems to favour the nutrient supply hypothesis for tropical systems.

The average C:N:P ratio (232:25:1) of POM in the top layers of the Bay is similar to observations in other tropical oceans, such as the subtropical North Atlantic Ocean (210:36:1) (Singh et al. 2015a) and subtropical North Pacific Ocean (172:25:1) (Martiny et al. 2013a). The subtropical North Atlantic is considered a P-limited (DIN:DIP ~30) basin, and exhibits a high C:N:P ratio in the POM (Wu et al. 2000). However, the Bay and the subtropical North Pacific Ocean are N-limited, and both possess high N:P ratios (25) in POM and low N:P ratios (<16) in subsurface nutrients. Our overall analysis suggests that the nutrient availability in the Bay is likely governed by N loss processes (such as denitrification), whereas N gain processes (such as N₂ fixation) exert control in the subtropical North Atlantic Ocean (Deutsch & Weber 2012).

5. CONCLUSIONS

We presented a comprehensive study of C:N:P ratios in the inorganic and organic pools of the Bay water column covering depths from the surface to 2000 m. Overall, C:N:P ratios deviated greatly from the Redfield Ratio (C:N:P = 106:16:1) in all the biogeochemical pools and at all depths. In the POM, C:N:P ratios were 232:25:1, 457:35:1 and 966:72:1 in the top, subsurface, and deep water layers, respectively. Our estimated C:N:P ratios in POM are comparable to that observed in other tropical basins such as the North Pacific Ocean and North Atlantic Ocean. On the other hand, the C:N:P ratio in the DOM in the top layer (357:30:1) is lower than the global average of 640:44:1 for bulk DOM in surface water.

Despite being a peak summer monsoon period, relatively low concentrations of nutrients with a low N:P ratio suggest that primary production was limited by bioavailable N. Concurrently estimated low N₂ fixation rates suggest that diazotrophic organisms had a minimal impact on nutrient or POM stoichiometry. Instead, a low supply of nutrients governed the observed higher N:P ratio in the POM. The POC: PON ratio and δ^{13} C of POM in the top 100 m of the Bay indicate that the POM was mostly derived from *in situ* processes, and that there is a relatively small influence of terrestrial influx in the open Bay. Overall, the higher C:N:P ratio than the Redfield Ratio in POM in surface waters supports the nutrient supply hypothesis for tropical oceans with low inorganic nutrient concentrations. The low N:P ratio in nutrients in the subsurface waters suggests a potential role of N loss processes in regulating nutrient stoichiometry.

Eddies have mixed effects on C:N:P ratios in the top layer. DIM concentrations are lower in ACE locations compared to that in the NE locations. Conversely, POM concentrations are higher in ACE locations compared to that in the NE locations. However, there is not much difference in the C:N:P ratios of DIM and POM at eddy and non-eddy stations. This study provides a detailed insight of elemental dynamics in organic and inorganic pools during the summer monsoon in the Bay, which can be used in biogeochemical models for this region.

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Role of eddies and N₂ fixation in regulating C:N:P proportions in the Bay of Bengal

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Abstract Recent observations and numerical simulations have profoundly established that the C:N:P ratios in the ocean deviate from the canonical Redfield Ratio (106:16:1). Physical and biogeochemical processes have been hypothesized to be responsible for this deviation. However, a paucity of concurrent observations on biogeochemical and physical parameters have barred us to understand their exact role on the C:N:P ratios. For this purpose, we have sampled the Bay of Bengal for its C, N, and P contents in the organic and inorganic pools from 5 to 2000 m depth at eight stations (five coastal and three open ocean) during boreal spring 2019. Mesoscale anticyclonic eddies were identified at two of the sampling stations,

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A. Sahay Space Applications Centre, Ahmedabad, Gujarat 380015, India where nutrient concentrations were lower in the top layer (5 m to the depth of chlorophyll maximum) compared to those at the non-eddy stations. Mean $(NO_3^{-}+NO_2^{-})$:PO₄³⁻ ratio was lower at the anticyclonic eddy stations compared to that at the non-eddy stations in the top layer. Yet C:N:P ratios in the particulate and dissolved organic matter in the top layer were the same at anticyclonic eddy and non-eddy stations. Overall the mean C:N:P ratios were 249:39:1 in particulate organic matter and 2338:146:1 in dissolved organic matter in the top layer. Biological N₂ fixation was not a driver in controlling the N:P ratio of the export flux and the subsurface water nutrient ratios during spring. Although the Bay of Bengal receives large riverine influx, its influence in changing the C:N:P ratios was small during this study.

Keywords Northern Indian Ocean · Elemental proportion · Mesoscale eddy · Picoplankton · Redfield Ratio · Dissolved organic matter

Introduction

Marine phytoplankton play a crucial role in regulating the carbon dioxide concentration in the Earth's atmosphere (Farquhar et al. 2000). The growth and community structure of phytoplankton are mainly controlled by the ambient physicochemical factors such as temperature and nutrient ratios (Geider and La Roche 2002). In fact, nutrient ratios are key to phytoplankton growth (Klausmeier et al. 2004). A similarity in the elemental proportion of carbon:nitrogen:phosphorus (C:N:P) of plankton and macronutrients in the ocean was first discussed by Alfred C. Redfield (Redfield 1934), who proposed that the average elemental proportion of plankton and the deep water nutrients remain statistically uniform at 106 C:16 N:1P. Thereafter this ratio became a cornerstone of ocean biogeochemistry and referred as the Redfield Ratio (Redfield 1934, 1958). However, phytoplankton physiology model studies established that the N:P ratio is not universally constant at 16 rather it merely reflects the average stoichiometry of phytoplankton in ocean. The ratio can vary over time in response to changes in the ecological balance between exponential growth and equilibrium phases, and with the availability N and P nutrients (Klausmeier et al. 2004). It is shown that the nutrient availability in the sunlit ocean governs the phytoplankton distribution and latitudinal patterns of elemental proportions of particulate organic matter (POM) in the global ocean (Martiny et al. 2013a, b; Tanioka et al. 2020).

Until now, several C:N:P stoichiometric studies have been performed in the Atlantic Ocean, the Pacific Ocean, and southern parts of the Indian Ocean (Martiny et al. 2013a, b; Singh et al. 2015a; Garcia et al. 2018). However, only a couple of such studies have been reported from the Bay of Bengal (hereafter the Bay) (Garcia et al. 2018; Sahoo et al. 2020). The Bay, situated in the northeastern Indian Ocean, receives a high freshwater influx $(1.6 \times 10^{12} \text{ m}^3 \text{ year}^{-1})$ (Subramanian 1993). The basin experiences seasonal reversal of monsoonal winds, cyclones and mesoscale eddies (Mukherjee et al. 2019). These processes might affect the elemental proportions of the Bay (Sahoo et al. 2020).

Cyclonic and anticyclonic mesoscale (10–500 km diameter) eddies are a major part of the water circulation in the Bay. Cyclonic eddies are the areas of divergence which are associated with upwelling of nutrient-rich subsurface water, and anticyclonic eddies (ACE) are the convergence areas where downwelling dominates. Cyclonic eddies increase primary productivity, while low nutrient concentrations result in low primary productivity at ACE regions (Singh et al. 2015b; Sarma et al. 2019).

Phytoplankton community composition is different in the different type of eddies, e.g., microplankton flourish in nutrient rich cyclonic eddies while picoplankton dominate in the nutrient depleted ACEs (Sarma et al. 2020a). Apparently, 50–60% of phytoplankton abundance in the Bay is of the picoplankton alone, while nanoplankton are the second most abundant species (Sarma et al. 2020a). At ACE regions, picoplankton constitute a major fraction of phytoplankton owing to their hypothesized potential to consume dissolved organic nutrients in depleted inorganic nutrient regimes (Sarma et al. 2020a).

In a previous study in the Bay during summer, monsoonal winds and mesoscale eddies were suggested to have a mixed effect on the elemental proportions of organic and nutrient pools in the top layer (Sahoo et al. 2020). Nutrients were lower in ACEs compared to those in the non-eddy (NE) stations. On the contrary, POM concentrations were higher in ACEs compared to that in the NE stations. However, there was not much difference in the elemental ratios in nutrients and POM at eddy and NE stations. During spring, the surface Bay experiences high temperature and salinity owing to heat gain by the sea and excess evaporation, respectively (Narvekar and Kumar 2006). Weaker winds and prolonged ACEs hinder the supply of subsurface nutrients to the euphotic zone, which leads to ultraoligotrophy in the Bay (Jyothibabu et al. 2021). These changing environmental conditions can affect the phytoplankton growth and thereby their elemental stoichiometry during spring. For example, increased temperature and the reduced availability of nutrients lead to increase in C:N and C:P ratios in POM (Matsumoto et al. 2020).

Three reasons spurred us to revisit the Bay to study the elemental dynamics during spring. First, in a previous study during summer, we sampled only open ocean stations where the influence of river water was negligible (Sahoo et al. 2020). In this study, we have sampled coastal as well as open ocean regions in the Bay. We hypothesize that the elemental proportions, particularly in the coastal Bay, might have been influenced by a combination of processes including river water intrusion in addition to in situ primary production and remineralisation. Second, during spring the Bay experiences severe N limitation than summer (Narvekar and Kumar 2014). The changing conditions associated environmental and

biogeochemical processes such as N_2 fixation might also affect the elemental stoichiometry. Third, ACEs prevail dominantly during spring (Jyothibabu et al. 2021). Furthermore, the age of an eddy is another aspect to look at in biological context as a time lag always exists between ocean physical process and its manifestation on productivity. Prolonged ACEs might affect the organic and nutrient pools in the Bay. To test the above hypotheses, we conducted this study in the Bay during April 2019.

Methods

We participated in ORV Sindhu Sankalp expedition (SSK 127) that cruised from Chennai (13° N, 80.3° E) along the eastern coast of India, turned to the open ocean at $\sim 19.9^{\circ}$ N and moved southwards in the Bay from 5 April to 15 April 2019 (Fig. 1a and b). We sampled eight stations during this expedition: five stations - NE1, ACE1, NE2, NE3, and NE4 situated along the east coast of India- were considered as the coastal stations, and the rest including NE5, NE6, and ACE2 were considered as the open ocean stations. Water samples were collected using a Sea-Bird CTD rosette sampler at a maximum of 10 different depths (5, 25, 50, 85, 200, 300, 500, 1000, 1500, and 2000 m). Water temperature, salinity and dissolved oxygen data were obtained from calibrated sensors mounted on the CTD rosette sampler. Mixed layer depth was calculated as 0.2 °C decrease from the water temperature at 10 m depth (de Boyer Montégut 2004). Apparent oxygen utilisation was calculated as the difference between the measured dissolved oxygen concentration and its temperature and salinity dependent saturation concentration (Murray and Riley 1969). For Chlorophyll a (Chl a) concentration, 1 L seawater samples were filtered onto Whatman glass microfiber filters (GF/F, 25 mm diameter, 0.7 µm pore size) followed by extraction in 90% acetone and kept for 24 h in a refrigerator. The Chl a concentrations were measured in HPLC (Agilent, USA).

TOC measurements were performed using high temperature catalytic oxidation method in Shimadzu TOC analyser (TOC-L-CPH, Japan) and TN measurements were performed in Shimadzu TN analyser (TNM-L-CPH, Japan) as detailed in Sahoo et al. (2020). The accuracy of TOC and TN results was ensured by routinely measuring certified reference material (Batch 18, Lot#08–18 for deep seawater) provided by the University of Miami, USA (Hansell 2005). The absolute deviation of measured values was maintained within 5% of the standard value of reference material during the entire analysis. The coefficient of variation was 2% for TOC and TN measurements.

Nutrients (nitrate (NO₃⁻), nitrite (NO₂⁻), and phosphate (PO_4^{3-})) were measured using autoanalyzer (SKALAR, The Netherlands). Reliability of the nutrients data was obtained daily by measuring certified reference material: MOOS-3 from National Research Council, Canada (Clancy et al. 2014). The detection limits for NO_x (NO₃⁻ + NO₂⁻) and PO₄³⁻ were 0.16 and 0.02 $\mu M,$ respectively. NO_x and ${PO_4}^{3-}$ are referred to as dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorous (DIP), respectively. Nutricline was considered as the depth where DIN concentration increased to 1 µM (Richardson and Bendtsen 2017). The vertical diffusive fluxes of DIN from subsurface waters were calculated following King and Devol (1979) and the vertical diffusion coefficient used in this calculation was taken from Nozaki and Alibo (2003). Dissolved inorganic carbon (DIC) was measured using Coulometer (UIC's Model 5012, USA) with an analytical precision of $\pm 2\%$. δ^{13} C values of DIC were measured using GasBench II attached to an Isotope Ratio Mass Spectrometer (Thermo Scientific MAT 253) with a precision better than 0.10 %.

Samples for particulate organic C (POC), N (PON) and P (POP) were collected by filtering seawater on pre-combusted (at 400 °C for 4 h) Whatman glass microfiber filters (GF/F, 25 mm diameter, 0.7 μ m pore size). POC and PON concentrations were measured using an Elemental Analyzer (FLASH 2000; Thermo Scientific) coupled with an Isotope Ratio Mass Spectrometer (Delta V Plus; Thermo Scientific) connected via conflo interface. IAEA-N-2 ((NH₄)₂SO₄) for N and IAEA-CH-3 (Cellulose) for C were used as standards in addition to the internal laboratory standards. The analytical precision for both POC and PON measurements were < 10%.

High temperature oxidation method was adopted to estimate total P (TP) and POP (Murphy and Riley 1962). Potassium dihydrogen phosphate (KH₂PO₄) standard was used for calibration and Adenosine-5'-Triphosphate Disodium (ATP-Na₂) standard was used to estimate recovery percentage. Samples were


20°N 1 m/s NE3 0.3 a. NE2 0.2 18°N 0.1 ACE 16°N 0 Data View / DIVA -0.1 ONE5 14°N -0.2 O ACE2 ONE6 ő 0.3 12°N 80°E 82°E 84°E 86°E 88°E 90°E DIN (µM) 0.18 20°N C. NE4 NE3 18°N NE2 0.17 16°N ACE1 NE5 0.16 0 Data View 14°N BDL 0 0 ACE2 NE6 12°N 0.15

Sea surface height anomaly (m)

Fig. 1 Geostrophic currents overlaid on the sea surface height anomaly (m) during a 5-10 April, and b 10-14 April 2019. The surface water c DIN and d DIP concentrations. The coastal

86°E

88°E

90°E

84°E

82°E

80°E

digested at 15 psi for 80 min, followed by their analysis in Shimadzu Spectrophotometer (UV-1800, Japan). The detection limit of the measurements was 0.1 nM. Total organic N (TON) and total organic P (TOP) were estimated by subtracting inorganic matter from its total elemental pool such as [TN]–[DIN] and [TP]–[DIP], respectively. Dissolved organic C (DOC), N (DON), and P (DOP) concentrations were quantified as the difference between TOC and POC, TON and PON and TOP and POP, respectively.

Abundances of picoplankton, such as *Prochlorococcus* and *Synechococcus*, were obtained from Saxena et al. (2021) (under preparation). The biomass of *Prochlorococcus* and *Synechococcus* was calculated by multiplying their abundances (cell counts L^{-1}) with their carbon content per cell values. The carbon content per cell values of the euphotic zone

(NE1, ACE1, NE2, NE3, and NE4) and open ocean (NE5, NE6, and ACE2) stations are shown with filled and open circles, respectively. *BDL* below detection limit

Prochlorococcus and *Synechococcus* were taken from Casey et al. (2013). Further, the contribution of *Prochlorococcus* and *Synechococcus* biomass to the total POC pool was calculated.

Several eddy features were identified based on the sea surface height anomaly and geostrophic current during the sampling period. The sea surface height anomaly along with geostrophic current $(0.25^{\circ} \times 0.25^{\circ})$ data was obtained from the Copernicus Marine Environmental Monitoring Service (https://resources.marine.copernicus.eu/; data retrieved on 24 February 2020). Cyclonic eddies were identified by anticlockwise geostrophic currents with < -0.2 m sea surface height anomaly. ACEs were identified by the clockwise circulation with > 0.2 m sea surface height anomaly. We sampled two ACE stations and categorised them as ACE1 and ACE2, while no significant

sea surface height anomaly values at the rest six stations led to categorize them as NE stations (NE1–NE6; Fig. 1; Table 1).

We performed Principal Component Analysis (PCA) between elemental concentrations and environmental variables. Pearson's correlation coefficient at $\alpha < 0.05$ was used to estimate the strength of the relationships.

The statistical significance of the differences between the mean values of a parameter (elemental concentrations and ratios in nutrients and organic matter) measured at coastal and open ocean stations were tested following Chao (1974). Two mean values (say μ_1 and μ_2) are considered to be significantly different from each other at $\alpha < 0.05$, if $\mu_1 - \mu_2 \ge 1.645 \sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}$, where σ_1 and σ_2 are the standard deviations around the mean values μ_1 and μ_2 calculated from data points n_1 and n_2 , respectively.

Results

Hydrological characteristics

Sea surface temperature varied from 27.6 to 30.3 °C with warmer (> $30 \,^{\circ}$ C) waters at southeastern stations (NE5, NE6, and ACE2; Table 1). Sea surface salinity varied from 32.1 to 34.3 with the highest value at NE1. The mixed layer depth was shallow (12 m) at NE1 and NE5 and deep (34 m) at NE4. Nutricline was deeper (> 80 m) at ACE1 and ACE2 compared to NE stations where it reached to 56 m. Surface Chl a concentration varied from 0.08 to 0.27 μ g L⁻¹ with the highest at NE1 and the lowest at ACE2. The depth of chlorophyll maximum varied from 22 to 87 m, deeper at ACE1, NE6, and ACE2 and shallower at NE1. The POC:Chl a (weight: weight) varied from 67 to 667 in the top layer at the sampling stations (Table 1). The vertical diffusive flux of DIN varied from 1.1 to 8.6 mmol N $m^{-2} d^{-1}$, the highest flux observed at NE2 and the lowest at NE5 (Table 2).

Biogeochemical parameters

Based on the biogeochemical processes, we divide our analysis into three different depth segments: top,

Station	Latitude (°N)	Longitude (°E)	Date of sampling (dd.mm.yyyy)	SST (°C)	SSS	MLD (m)	DCM (m)	Nutricline (m)	Chl $a (\mu g L^{-1})^a$	δ ¹³ C of DIC (‰) ^b	POC:Chl a ^b
NE1	13° 05.58′	80° 73.21′	05.04.2019	29.1	34.3	12	22	8	0.27	_	80–508
ACE1	16° 30.09′	83° 50.88′	07.04.2019	29.0	33.2	30	83	84	0.10	0.2 to 0.4	67–458
NE2	18° 32.61′	85° 46.12′	08.04.2019	27.6	33.1	20	55	41	0.21	- 0.6 to 0.2	82–376
NE3	19° 49.84′	87° 00.13′	09.04.2019	28.4	33.0	24	69	39	0.16	- 0.5 to 0.3	82–249
NE4	19° 49.91′	88° 59.11′	10.04.2019	28.0	32.8	34	71	56	0.19	- 0.3 to 0.4	81–269
NE5	14° 26.69′	87° 23.85′	12.04.2019	30.0	32.1	12	61	53	0.24	- 0.2 to - 0.001	132–667
NE6	13° 05.47′	87° 00.08′	13.04.2019	30.3	32.3	20	87	54	0.10	- 0.4 to 0.3	332
ACE2	13° 04.49′	84° 13.42′	14.04.2019	30.2	33.3	27	86	87	0.08	0.1 to 0.2	85–457

 Table 1
 Environmental parameters at the eight sampling locations during spring 2019

SST-sea surface temperature, SSS-sea surface salinity, MLD-mixed layer depth, DCM-depth of chlorophyll maximum, DIC-dissolved inorganic carbon, POC-particulate organic carbon, Chl-Chlorophyll

^aSurface (5 m) Chl *a* values are presented, ^b δ^{13} C of DIC and POC:Chl *a* values in the top layer. Due to logistic issues, samples for δ^{13} C of DIC could not be collected at NE1

2019								
Station	Vertical diffusive flux of DIN (mmol N m ^{-2} d ^{-1})	N_2 fixation (µmol N m ⁻² d ⁻¹) ^a	Contribution of N ₂ fixation N:P export flux (%)					
NE1	1.7	_	-					
ACE1	4.3	16.5	0.4					

Table 2. Vertical diffusive flux of DIN. N2 fixation and its contribution in N:P ratios of export flux from the top layer during spring

6.8

6.7

5.5

5.3

BDL

0.1

0.2

0.3

_ 0.2

DIN-dissolved inorganic nitrogen and BDL-below detection limit

^aColumn integrated N₂ fixation rates are taken from Saxena et al. (2021) (under preparation). N₂ fixation experiment was not performed at NE1 and ACE2 due to logistic issues

subsurface, and deep layer. The top layer extends from the surface to the depth of chlorophyll maximum where maximum photosynthetic activity prevails. The successive subsurface layer is considered from the depth of chlorophyll maximum to < 360 m, which is characterised by low dissolved oxygen concentration due to respiration of sinking organic matter from the top layer. The layer below the subsurface layer to the deepest sampling depth is classified as deep layer, which is affected by the mixing of various water masses and remains rich in nutrients.

Dissolved inorganic pool

In the top layer, concentrations of DIN and DIP were low; particularly DIN concentration was below the detection limit in surface water at all the stations but NE4 (Fig. 1c and d). The DIN concentration was below the detection limit up to 51 m at NE1, NE2, NE3, NE5, and NE6 and continued to be below the detection limit up to 85 m at ACE1 and ACE2 (Fig. 2). Overall, the DIC, DIN, and DIP concentrations ranged from 1591 to 2155 µM, below detection limit to 12.5 μ M, and 0.2 to 1.2 μ M, respectively in the top layer (Fig. 2). At ACE1 and ACE2, DIN (below detection limit at both the stations) and DIP (mean DIP: $0.2 \pm 0.04 \ \mu\text{M}$ at ACE1 and $0.2 \pm 0.1 \ \mu\text{M}$ at ACE2; standard deviation values are $\pm 1\sigma$) concentrations were lower than that at the NE stations (mean DIN: $5.5 \pm 4.9 \,\mu\text{M}$ and DIP: $0.4 \pm 0.3 \,\mu\text{M}$) in the top layer. Below this layer, we observed a steep increase in DIN and DIP concentrations. In the subsurface layer, DIC, DIN, and DIP concentrations ranged from 1840 to 2284 μ M, below detection limit to 34.1 μ M, and 0.2 to 2.7 µM, respectively. These concentrations ranged from 2042 to 2499 µM, 33.5 to 38.7 µM, and 2.6 to 3.1 µM, respectively in the deep layer. The subsurface layer DIC concentration was relatively low at NE4, NE5, NE6 and ACE2. Low deep layer DIC concentration was observed at NE4 and ACE2.

Mean DIC:DIN, DIC:DIP, and DIN:DIP ratios were 3458 \pm 4251 (3362 \pm 4643 at coastal and 1133 at open ocean), 8437 ± 3339 (8288 ± 3284 at coastal and 9934 \pm 2205 at open ocean), and 8.9 \pm 2.5 $(7.1 \pm 4.1 \text{ at coastal and } 7.9 \pm 4.3 \text{ at open ocean}),$ respectively in the top layer (Fig. 3). As the top layer DIN concentration was below detection limit at all the stations except at NE1 and NE4, the DIN:DIP ratios were calculated only for NE1 (8.3 \pm 1.8) and NE4 (3.7 ± 3.6) . We observed a sharp increase in DIN:DIP ratio in the subsurface water followed by a gradual increase in the deep layer. In the subsurface layer, the mean ratios were 173 ± 255 (144 \pm 127 at coastal and 222 ± 402 at open ocean), 2064 ± 2184 $(2016 \pm 2276 \text{ at coastal and } 2223 \pm 2570 \text{ at open}$ ocean), and 10.9 ± 1.9 (10.8 \pm 1.6 at coastal and 11.1 ± 2.5 at open ocean) for DIC:DIN, DIC:DIP, and DIN:DIP ratios, respectively. In the deep layer, the mean DIC:DIN, DIC:DIP, and DIN:DIP ratios were $62.0\pm3.3~(63.0\pm2.9$ at coastal and 61.5 ± 3.5 at open ocean), 786 ± 53 (797 ± 41 at coastal and 786 ± 52 at open ocean), 13.0 ± 0.4 (12.6 ± 0.5 at

NE2

NE3

NE4

NE5

NE6

ACE2

8.6

4.1

2.1

1.1

3.0

4.1





Fig. 2 Vertical section of a DIC, b DIN, c DIP, d POC, e PON, f POP, g DOC, h DON, and i DOP concentration. Section distance starts from NE1 (50 km) and ends at ACE2 (2370 km)

coastal and 12.8 ± 0.3 at open ocean), respectively. Overall, the DIN:DIP ratios were less than the Redfield Ratio throughout the column.

Particulate organic matter

The elemental concentrations in POM decreased with depth at all the stations (Fig. 2). POC, PON, and POP concentrations ranged from 2.1 to 12.3 μ M, 0.3 to 2.0 μ M, and 0.01 to 0.1 μ M, respectively, in the top layer. The coastal stations exhibited higher concentrations (highest at NE1) than the open ocean stations. In the subsurface layer, POC, PON, and POP concentrations ranged from 0.7 to 3.7 μ M, 0.1 to 1.0 μ M, and 0.002 to 0.02 μ M, respectively. The concentrations decreased further in the deep layer. The POC, PON, and POP concentrations ranged from 0.6 to 2.1 μ M, 0.1 to 0.3 μ M, and 0.002 to 0.005 μ M, respectively in the deep layer.

All the elemental ratios in POM deviated from the Redfield Ratio. Mean POC:PON ratio was 7.1 ± 2.2 (7.6 \pm 2.5 at coastal and 6.6 \pm 1.0 at open ocean) in the top layer, close to the Redfield Ratio (6.6). POC:POP, and PON:POP ratios were 249 ± 58 (245 \pm 62 at coastal and 247 \pm 48 at open ocean), and 38.6 ± 17.6 (35.1 \pm 14.0 at coastal and 37.5 ± 4.7 at open ocean), respectively in the top layer (Fig. 3). Variability in the elemental ratios in the

top layer was more in the coastal Bay than in the open ocean stations. In the subsurface layer, the mean ratios increased to 8.0 ± 4.0 (7.8 \pm 3.9 at coastal and 8.2 ± 4.2 at open ocean), 323 ± 112 (327 ± 91 at coastal and 318 ± 141 at open ocean), and $47.5 \pm 21.8 \ (50.6 \pm 26.6 \ {\rm at\ coastal\ and\ } 41.3 \pm 10.0$ at the open ocean) for POC:PON, POC:POP, and PON:POP, respectively. However, the variation in the mean elemental ratios in the deep layer was less than that in the subsurface layer. The mean POC:PON, POC:POP, and PON:POP ratios were 10.3 ± 3.4 $(9.7 \pm 3.0 \text{ at coastal and } 10.9 \pm 3.9 \text{ at open ocean}),$ 369 ± 107 (342 ± 79 at coastal and 400 ± 128 at open ocean), and 39.3 ± 16.5 (40.8 ± 21.0 at coastal and 37.6 ± 9.4 at open ocean), respectively in the deep layer.

The contribution of the *Prochlorococcus* and *Synechococcus* biomass ranged from 2 to 29% to the total POC pool in the top layer during this study.

Dissolved organic matter

DOC concentration was high in the top layer and decreased in the subsurface and the deep layer (Fig. 2). On the contrary, DON concentration was low in the top layer and increased in the deep layer (except at NE3 and NE4). DOP concentration was relatively low in the open ocean stations. In the top



Fig. 3 Box-whiskers plots showing C:N, N:P and C:P ratios in DIM, POM, and DOM pools in the top, subsurface, and deep layers. Pink dotted lines represent the mean. Whiskers account for 5 and 95% of distribution, whereas boxes account for 25 and

layer, DOC, DON, and DOP concentrations ranged from 48.4 to 170.9 μ M, 2.4 to 11.1 μ M, and 0.5 to 0.01 μ M, respectively. In the subsurface layer, DOC, DON, and DOP concentrations ranged from 47.4 to 170.9 μ M, 2.1 to 22.7 μ M, and 0.02 to 0.5 μ M, respectively. The concentrations ranged from 39.1 to 85.5 μ M, 0.4

75%. Dots within the boxes represent 50% of the distribution. Blue boxes represent the coastal and black represent the open ocean stations. Boxes are not shown when the number of data points is less than 2

to 16.7 μ M, and 0.06 to 0.46 μ M for DOC, DON, and DOP, respectively in the deep layer. DON concentration was high in all the three depth layers at NE5, while a similar pattern was observed at NE2 for DOP concentration.

All the ratios in the DOM pool deviated greatly from the Redfield Ratio. The DOC:DON ratio was higher at the coastal stations than open ocean stations in the top layer. Mean DOC:DON, DOC:DOP, and DON:DOP ratios were 21.2 ± 17.9 (22.3 ± 19.1 at coastal and 10.2 ± 5.3 at open ocean), 2338 ± 4060 $(1194 \pm 1113 \text{ at coastal and } 7603 \pm 8077 \text{ at open}$ ocean), and 146 \pm 202 (61.5 \pm 73.0 at coastal and 482 at open ocean), respectively in top layer (Fig. 3). DOC:DON ratio was high in the top layer than in the subsurface and deep layer at all the stations except at NE2 and NE3. In the subsurface layer, the mean ratios were 13.3 ± 12.5 (17.0 ± 15.2 at coastal and 8.2 ± 3.9 at open ocean), 861 ± 1302 (635 ± 1123 at coastal and 3119 at open ocean), and 78.5 \pm 142.9 $(33.7 \pm 18.3 \text{ at coastal and } 482 \text{ at open ocean})$ for DOC:DON, DOC:DOP, and DON:DOP, respectively. The mean ratios were $12.5 \pm 22.6 (20.6 \pm 31.4 \text{ at})$ coastal and 5.1 ± 0.9 at open ocean), 374 ± 301 $(429 \pm 332 \text{ at coastal and } 209 \pm 103 \text{ at open ocean}),$ $58.0 \pm 52.6~(67.0 \pm 60.7~{\rm at~coastal}~{\rm and}~35.5 \pm 20.7$ at open ocean) for DOC:DON, DOC:DOP, and DON:DOP, respectively in deep layer.

Isotopic composition ($\delta^{13}C$) of DIC

The δ^{13} C values of DIC were positive in the surface water at the coastal stations and ACE2, while the values were negative at NE5 and NE6. ACE1 and NE4 showed the highest δ^{13} C values in the top layer (Table 1). The values were more negative in the subsurface and deep layers compared to that in the top layer. δ^{13} C ranged from -0.6 to 0.4 %, -0.7 to 0.2 % and -0.5 to -0.2 % in the top, subsurface and deep layer, respectively.

Statistical analysis

The interrelationships of environmental variables (nutrients, apparent oxygen utilisation, temperature, and salinity) and elemental concentrations in organic matter pool with the elemental proportions are performed using PCA. The two principal axes accounted for $\sim 64\%$ of the total variability among parameters (Fig. 4). The vectors represent individual parameters and their direction of increase. Closely placed vectors away from origin represent positive correlation, while vectors directed in opposite direction represent anticorrelation among parameters.

Parameters with orthogonal vectors are not correlated. The interrelationship among parameters and their statistical significance are presented in Table S1. POC:PON and POC:POP ratios were anticorrelated to PON (r = -0.5) and POP (r = -0.5), respectively. DON:DOP and DOC:DOP ratios were strongly anticorrelated to DOP (r = -0.6, and -0.7). DOC:DON ratio was anticorrelated to DON (r = -0.8). No significant difference observed between elemental ratios at the coastal and open ocean stations.

River water contribution

Considering salinity as a conservative tracer and an ideal indicator for river and seawater mixing mechanism, river water fraction (f_r) was calculated as:

$$f_{r} = \frac{Salinity_{s} - Salinity_{sample}}{Salinity_{s} - Salinity_{r}}$$
(1)

The subscripts r and s stand for river water and seawater, respectively. For open ocean observations in this study, we considered the mean top layer salinity (33.79) at ACE2 as the seawater end-member as this was one of the open ocean stations that had the highest salinity. The river water end-member value of salinity (Salinity_r = 0.19) was taken from Samanta et al. (2015) for the pre-monsoon period. At coastal stations, f_r ranged from 0.001 to 0.03, suggesting the water to be of completely marine origin (see supplementary file for more details).

Discussion

Processes affecting elemental concentrations and their proportions

The river water fraction was negligible (< 0.05) at our stations. The sea surface salinity at the coastal stations was not much different from those at the open ocean stations (Table 1). The δ^{13} C values of DIC at the Hooghly river system ranged from -11.4 to -1.6 % (Samanta et al. 2015). During our sampling, the δ^{13} C values in the top layer at the coastal stations (-0.6 to 0.4 ‰) also showed typical marine range and were higher than the reported riverine values by Samanta et al. (2015). It ranged from -0.6 to 0.4 ‰ and -0.4 to 0.3 ‰ in the top layer at the coastal and open ocean



Fig. 4 PCA analysis of temperature (T), salinity (S), apparent oxygen utilisation (AOU), nutrients, elemental concentrations and ratios in particulate organic matter, dissolved organic matter, represented by vectors

stations, respectively. In fact, the DIC and δ^{13} C values at the coastal stations were deviated from the conservative mixing line of river and seawater (Fig. S1). DIC values and the lack of significant difference in nutrients at the coastal and open ocean stations further confirmed that the elemental chemistry at the coastal stations was not substantially influenced by the riverine influx. But we caution that our coastal sampling sites may not possess typical characteristics (e.g., strong upwelling, high nutrient concentration) of coastal areas in other oceanographic regions and it is likely that the river influence is limited to within a short distance from the river mouths.

Although the elemental concentrations in POM at the coastal stations were significantly different from that at the open ocean stations, no significant difference was reflected in their elemental ratios. As expected from the mixing calculation, POC:PON ratio in the top layer was 7.6 ± 2.5 at the coastal and

 6.6 ± 1.0 at open ocean stations, suggesting that in situ primary production contributed significantly to the POM pool in the top layer, as terrestrially derived POM possess high C:N ratio (> 10) (Hedges et al. 1986). POC:Chl a ratio, a proxy to identify the source of organic matter in aquatic systems (Bentaleb et al. 1998), is typically low in the freshly produced organic matter than in terrestrial organic matter. POC:Chl a ratio normally ranges from ~ 40 (Montagnes et al. 1994) to 200 (Cifuentes et al. 1988; Bentaleb et al. 1998) for in situ produced organic matter (Geider et al. 1998) Sarma et al. (2019) estimated the mean POC:Chl a ratio of 1123 ± 389 at the sampling stations along the east coast in the Bay. They attributed the POC:Chl a ratio to the faster degradation of Chl a, and a possible contribution of heterotrophs (bacteria and zooplankton) and terrestrial organic matter (Sarma et al. 2019). On the contrary, the POC:Chl a ratio at our sampling stations (ranged from 67 to 667,

mean 245 ± 177) was lower than that observed by Sarma et al. (2019), reconfirming no influence of riverine influx at our sampling stations.

High DIC concentration at the coastal stations led to a higher DIC:DIN ratio in the top layer. Likewise, the low concentration of DOP in open ocean stations led to high DON:DOP and DOC:DOP ratios in the top layer. The POC:PON, PON:POP, and PON:POP ratios ranged higher in the top layer at the coastal stations, where high POM concentrations were also observed. Below the top layer, degradation of organic matter profoundly contributed to the nutrient dynamics in the coastal and open ocean stations. Labile POP and PON degrade faster than POC, resulting in an increased POC:POP and POC:PON ratios in the subsurface and deep layer (Loh and Bauer 2000) (Figs. 3 and 4).

Large variability in the elemental concentrations and ratios was evident in this study. There were no significant difference in the elemental concentrations (except in POM) at the coastal and open ocean stations in the top layer. Likewise, all the elemental ratios were also similar at both the regions in the top layer. The coastal stations had larger range of elemental concentrations and ratios than the open ocean stations, which led to the overall large variability in elemental ratios in the top layer.

Impact of eddies on elemental proportions

Mesoscale eddies influence ocean biogeochemistry by modulating the supply of nutrients to the euphotic zone (Sarma et al. 2019). At ACE1 and ACE2, the deep nutriclines (84 and 87 m) indicate that the downwelling resulted in decreasing nutrients (DIN and DIP) in the top layer (Fig. 1c). Being situated at the periphery of a cyclonic eddy, high vertical diffusive flux of DIN might have resulted in relatively high primary productivity (19.5 \pm 3.7 mmol C m⁻² d⁻¹, Saxena et al. 2021, under preparation) at NE2. The elemental concentrations and ratios in POM and DOM were not much distinct at ACE1, ACE2 and NE stations.

In the Bay, nutrient availability plays a bigger role than the temperature in driving the microbial community composition (Angelova et al. 2019). The temperature did not vary much and also did not correlate to the elemental ratios of POM in the top layer during this study (Fig. S2). The nutrient availability might have influenced the phytoplankton distribution. The eddies can entrain nutrient-rich shelf waters and advect them offshore, thereby playing a key role in the phytoplankton community distribution (Gomes et al. 2016). No coherent pattern of picoplankton (*Prochlorococcus* and *Synechococcus*) distribution was observed in ACE and NE stations in our study (Saxena et al. 2021, under preparation).

Recently Sarma et al. (2020a) have reported that the picoplankton contributed up to 80% and the micro and nanoplankton contributed between 10 to 30% to the total phytoplankton biomass in the Bay during June 2019. The total phytoplankton biomass reportedly constitutes up to 27% of the total POC pool in the Bay (Baer et al. 2019). The detrital matter and heterotrophs constitute a large fraction (\sim 50%) of plankton biomass (Garcia et al. 2018). In this study, *Prochlorococcus* and *Synechococcus* together constituted a maximum up to 29% of the total POC pool in the total phytoplankton biomass.

Prochlorococcus and *Synechococcus* are slowgrowing and small-sized phytoplankton that thrives in nutrient-deficient conditions, and possess higher C:P and N:P ratios than the Redfield Ratio following the growth rate hypothesis (Klausmeier et al. 2004; Arrigo 2005). The growth rate hypothesis suggests that the nutrient scarce environment normally favours the growth of slow-growing phytoplankton that can synthesize more resource acquisition machinery such as proteins that have high N:P ratio. The nutrient replete environment supports the fast-growing large phytoplankton by synthesizing more growth machinery such as RNAs that have low N:P ratio.

Overall the C:P (coastal: 254 ± 38 , open ocean: 244 ± 34) and N:P (coastal: 39 ± 12 , open ocean: 37 ± 3) ratios in POM were higher than the Redfield Ratio. Since *Prochlorococcus* and *Synechococcus* constituted only up to 29% of the total POC, a major fraction of the POM pool is likely constituted by dead and detrital matter. But this dead and detrital matter may also have its origin in the picoplankton in the oligotrophic waters. Therefore, the higher elemental ratios in POM suggests that the Bay support the growth rate hypothesis (Fig. 5).

The existence of prolonged (originated roughly two months before the sampling) ACEs throughout the sampling area associated with substantial downwelling of surface water could have transformed the Bay into an oligotrophic region. Deep nutricline



Fig. 5 Integrated picoplankton abundance (data obtained from Saxena et al. (2021), under preparation) in log scale, POC:POP, and PON:POP ratios in particulate organic matter in the top layer

accompanied with shallow mixed layer during the study was indicative of the increased oligotrophic conditions as compared to that in the previous study in the Bay during summer (Sahoo et al. 2020). Overall, the top layer was nutrient-depleted and showed high elemental ratios in POM during spring than during summer (Sahoo et al. 2020).

The static oligotrophic environment reasonably supports the growth of picoplankton (Agawin et al. 2000) Sarma et al. (2020a) observed high abundance of picoplankton at ACE, while the low microplankton abundance at ACE was due to the unavailability of DIN and DIP during June 2019 in the Bay. In the present study, picoplankton constituted up to 29% of the POC pool. Particularly, Prochlorococcus can adapt to oligotrophic conditions through gene gains and losses (Ustick et al. 2021). Prochlorococcus and Synechococcus showed a significant correlation with DIP and DIN concentrations, respectively, in this study. Synechococcus abundance was significantly correlated to the POM elemental concentrations in the top layer (Fig. S2). Therefore, the low nutrient availability and thereby the distribution of picoplankton seemed to regulate the variation of elemental ratios of POM in the top layer.

Role of N₂ fixation on the elemental proportions

In oligotrophic basins where primary productivity is N limited, biological N_2 fixation is considered to be a

major source of new N to the euphotic zone and may account up to 50% of the organic carbon export (Karl et al. 1997). Favourable environmental conditions including weaker winds, warm sea surface temperature (> 28 °C) and clear sky in addition to an adequate supply of PO_4^{3-} and Fe suggest the possibility of diazotrophic activity in the Bay (Mills et al. 2004; Singh et al. 2017). Diazotrophs increase the DIN pool at the cost of consuming DIP. Therefore, DIN:DIP ratio is expected to increase due to the diazotrophic activity in the euphotic zone.

Previous studies reported low N₂ fixation rates (4–75 μ mol N m⁻² d⁻¹ during July 2018 and 53.3–194.1 μ mol N m⁻² d⁻¹ during June 2019) in the Bay (Sarma et al. 2020b; Saxena et al. 2020). Yet, the upper bound of the measured N₂ fixation rates in the Bay is comparatively higher than that in many of the other ocean regimes (Saxena et al. 2020). In the present study, the concurrently measured N₂ fixation rates were even lower than that during the summer and varied from below detection limit to 17 μ mol N m⁻² d⁻¹ (Saxena et al. 2021, under preparation).

The mean DIN:DIP ratio in the top layer was lower (8.9 ± 2.5) than the Redfield Ratio. The influence of N₂ fixation on the top layer DIN:DIP ratio is subtle due to the occurrence of concurrent biological processes such as nutrient uptake by non-diazotrophic phytoplankton. The low DIN:DIP ratio might be attributed to the excessive competitive consumption of N

relative to P by the slow-growing, smaller phytoplankton (Klausmeier et al. 2004).

In the subsurface layer, the low DIN:DIP ratio (10.9 ± 1.9) indicates the possible occurrence of denitrification and anammox in the Bay. However, low rates of anammox (5.5 nM N d⁻¹) and patchy distribution of denitrification (0.9 nM N d⁻¹) in this basin suggest that the processes were less likely to influence the subsurface DIN:DIP ratio (Bristow et al. 2017). Then what caused the mean subsurface DIN:DIP ratio to decrease to 10.9?

In the subsurface layer, the DIN:DIP ratio reflects the integrated effect of remineralisation of sinking organic matter and various N loss processes. Remineralisation of organic matter significantly contributes to the subsurface nutrients, especially the regions where diazotrophs dominate the phytoplankton community. Diazotrophs normally possess a high cellular N:P ratio (42 to 125) (Karl et al. 1992; Letelier and Karl 1996). The remineralisation of diazotrophs (sinking from the top layer) with a high biomass N:P ratio, increases the subsurface DIN:DIP ratio (Michaels et al. 1996). But the contribution of diazotrophs to the subsurface nutrients in the Bay is not known.

Therefore, we have estimated the contribution of N_2 fixation in varying N:P ratio of export flux by applying a simple two-component N source model by Karl et al. (1997):

$$\frac{N_{\text{fix}}}{(N_{\text{fix}} + N_{\text{up}})} = \frac{\left[(N : P)_{\text{export}} - (N : P)_{\text{up}} \right]}{(N : P)_{\text{export}}}$$
(2)

where N_{fix} and N_{up} denote the N_2 fixation rate and vertical eddy diffusive flux of DIN, respectively. $(N:P)_{export}$ and $(N:P)_{up}$ are the N:P ratio of the export flux from the top layer and vertical eddy diffusive nutrient flux, respectively. The assumption is that the vertical diffusion is the only source of new P as DIP and that this process and N_2 fixation are the two potential sources of new N as DIN in the top layer. We have considered the DIN:DIP ratio of the subsurface water layer as $(N:P)_{up}$ in this study. The left-hand side of Eq. (2) represents the contribution of N_2 fixation in the N:P ratio of export flux, which ranged from ~ 0.1 to 0.4%. The exported organic matter further contributes to the subsurface nutrient pool upon remineralisation. But this low contribution in the export flux indicates no role of N_2 fixation in changing the subsurface DIN:DIP ratio.

The mean (N:P)_{export} calculated from Eq. (2) is 11.1, which corresponds to the mean N:P ratio in subsurface nutrients (11.0). It infers that the remineralisation of exported organic matter considerably contributed to the nutrients in the subsurface layer. The elemental ratio in export flux generally corresponds to that in POM in the euphotic zone. However, a discrepancy in the N:P ratio was observed between the POM in the top layer and the export flux (Fig. 6). In particular, the mean (N:P)export was approximately four times lower than the mean N:P ratio in the top layer POM. The picoplankton and detrital matter lead to a high N:P ratio in POM in the top layer, but possess a low export efficiency compared to microplankton (Fu et al. 2016). The organic matter of small phytoplankton is likely to be recycled within the upper water column. The microplankton, having low N:P ratio, are highly efficient in sinking and thereby possibly contribute largely to the export flux (Aumont and Bopp 2006). Although the microplankton (such as diatoms) abundance is reportedly low in the Bay during spring (Sarma et al. 2020a), their accumulation in the export flux might have resulted in a low (N:P)_{export} than the N:P ratio in POM in the top layer.

Overall, the mean C:N:P ratios of POM was 249:39:1 in the top layer. The POC:PON and PON:POP ratios in the top layer are statistically different from those in the previous study in the Bay during the summer monsoon (232:25:1) (Sahoo et al. 2020). Likewise, the POC:PON and POC:POP ratios are statistically different from the observations made in the subtropical North Atlantic Ocean (210:36:1) (Singh et al. 2015a). Our mean C:P and N:P ratios of DOM were 2338 ± 4060 and 146 ± 201 , respectively, in the top layer. Refractory DOM have elevated global average C:N:P ratios of 1370:60:1 and the nonrefractory DOM have 317:39:1 (Letscher and Moore 2015). During this study the ratios in DOM appeared to be more refractory in nature. Therefore, these values are higher than the global average C:N:P ratios (640:44:1) for bulk DOM in surface water (Letscher and Moore 2015).



Fig. 6 A schematic representing N:P ratio in the Bay of Bengal during spring 2019

Conclusions

This study enumerates the effect of physical and biogeochemical processes on the elemental ratios in the top layer of the Bay of Bengal. The C:N:P ratios in the organic (except C:N ratio in POM) and nutrient pools deviated greatly from the Redfield Ratio in the top layer during spring. Mean C:N:P ratios were 249:39:1, 2338:146:1, and 8437:9:1 in POM, DOM, and DIM, respectively in the top layer. The C:N and N:P ratios in POM in this study are slightly different from those obtained during summer 2018 (232:25:1) in the Bay of Bengal. The elemental ratios are statistically different from those in the subtropical North Atlantic Ocean (210:36:1). Riverine influx appeared to have no influence on C:N:P ratios in our coastal locations in the Bay of Bengal.

 N_2 fixation contributed negligibly (< 0.5%) to the N:P ratio of export flux, suggesting no role of it in changing DIN:DIP ratio in the subsurface layer. Mesoscale eddies have a significant effect on the nutrient concentrations in the top layer. Low concentration of nutrients measured in the top layer at ACE stations. On the contrary, no significant influence was observed in the organic matter pool at ACE stations. So the ACEs do not seem to influence the elemental ratios. In this study, we have examined the role of eddies and N_2 fixation in varying elemental proportions in the Bay of Bengal, but other causes also need to be explored. An in-depth understanding of these processes will help to improve the biogeochemical models based on flexible elemental proportions.

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Data availability It will be archived in PANGAEA upon publication.

Declarations

Conflict of interest Authors declared no conflict of interest.

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