

Atmospheric deposition of macro and micro-nutrients to the Northern Indian Ocean

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DOCTOR OF PHILOSOPHY

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Declaration

I, **Prema Piyusha Panda** hereby declare that this thesis represents work entitled “**Atmospheric deposition of macro and micro-nutrients to the Northern Indian Ocean**” which has been carried out by me and that it has not been submitted, either in part or full, to any other University or Institution for the award of any research degree.

Place: Goa University,
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Prema Piyusha Panda

Certificate

Certificate This is to certify that the work presented in this thesis entitled “**Atmospheric deposition of macro and micro-nutrients to the Northern Indian Ocean**” submitted by **Prema Piyusha Panda** to the Goa University for the degree of Doctor of Philosophy is based on his original studies carried out by him under my supervision. The thesis or any part of this work has not been previously submitted for any other degree or diploma in any university or institution.

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**Om Maa Gadachandi
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Om Namaha Sivaya**

*I dedicated my thesis to all
those who dare to follow
their dreams.*

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ABSTRACT:

Atmospheric aerosols are potential sources of nutrients to the remote marine environment and oligotrophic region which can modulate ocean biogeochemical cycles. The aerosol emission and subsequent deposition on the surface water are highly dependent upon mineral dust production, wind pattern as well as atmospheric emissions. The prime focus of this thesis is to understand the spatial-seasonal variation of dust and nutrient species over a wide area of the North Indian Ocean (the Arabian Sea, Bay of Bengal and Indian Ocean up to 13°S latitude) and estimate their depositional flux. The fractional solubility of trace elements along with the factors affecting the fractional are evaluated which are crucial information to constrain regional as well as global biogeochemical models. The dust and nutrient species show highly spatial and seasonal variability owing to geographical location as well as favorable meteorological conditions. Northern Indian Ocean receives the highest amount of dust during the Monsoon season while the equatorial and central Indian Ocean region receives the least amount of dust. The post-monsoon season shows higher fractional solubility due to the least dust and higher atmospheric processing via acidic species emitting from biomass burning and other anthropogenic emission activities. Similar to the post-monsoon season winter season also shows the second-highest fractional solubility owing to higher anthropogenic emission as well as the presence of the highest amount of acidic species. The continental outflow of anthropogenic aerosol and dust during these two seasons enhances the atmospheric processing of dust and also increases the soluble nutrient flux to the North Indian Ocean compared to the summer and monsoon seasons. The least amount of fractional solubility as well as soluble nutrient flux is observed during the monsoon season while dust and associated trace element production are the highest. The lack of atmospheric acidic species leads to lower atmospheric processing of dust and results reduction in fractional solubility.

(Keywords: Aerosol, Atmospheric Nutrients, Mineral dust, Trace elements, Fractional Solubility, Dry depositional fluxes, Marine atmosphere, Arabian Sea, Bay of Bengal, Indian Ocean)

Chapter 1

Introduction

1.1 Introduction:

Atmospheric aerosols (Solid and liquid particles suspended in ambient air) play a vital role in modulating the Earth's radiation budget. Aerosols show a large size range from submicron size to 100µm, create haze and fog, act as cloud condensation nuclei (CCN) and ice condensation nuclei (ICC), cause melting of snow and ice (Seinfeld and Pandis, 2016; Tomasi and Lupi, 2017).

The Primary aerosol originates from soil or dust (mineral dust), volcanic eruption and Sea salts are called natural aerosols and other aerosols such as NO_x, SO_x, Carbonaceous aerosols (Organic carbon (OC), Elemental Carbon (EC), non sea-salt potassium (nss-K⁺), etc are anthropogenic aerosols (Seinfeld and Pandis, 2016; Tomasi and Lupi, 2017). Other than these primary aerosols secondary aerosols are formed in the atmosphere from gas-to-particle conversion via nucleation, liquid to particle or particle-to-particle conversion by Aitken mode and chemical uptake /condensation/ coagulation of gas, liquid and particles by accumulation mode made the atmospheric chemistry complex (Pöschl, 2005; Seinfeld and Pandis, 2016; Tomasi and Lupi, 2017).

Atmospheric mineral dust accounts for ~35% of total aerosol mass ranging from submicron to 100µm aerodynamic diameter and also has a significant impact on the radiation budget, CCN, ICN also acts as an active site for condensation of liquid, uptake of other chemical species like SO_x, NO_x (Pöschl, 2005; Kumar et al., 2008a, 2008b, 2010; Seinfeld and Pandis, 2016; Tomasi and Lupi, 2017). Long-range transport of these dust and subsequent deposition in the remote marine environment act as nutrients to the surface ocean (Fig-1.1). These atmospheric nutrients enhance primary productivity, which increases the CO₂ fixation rate. Half of the global photosynthetic carbon fixation is governed by marine primary producers (Field et al., 1998; Morel et al., 2003; Jickells et al., 2005; Kumar et al., 2008a, 2008b, 2010; Moore et al., 2013), which will help to mitigate current Anthropocene climate change. Hence atmospheric nutrients or land-derived dust and other aerosols can help to fulfill the marine organisms' (primary producers) nutrient requirements.

In this chapter, I summarise the primary productivity in the ocean, its source of nutrients, the importance of dust as a nutrient source and the impact of aerosol as a nutrient in marine ecosystems.

Half of the global photosynthetic carbon fixation is being governed by marine primary producers (Field et al., 1998; Moore et al., 2013). These marine primary producers (phytoplankton) use dissolved reactive nitrogen species (NO₃⁻, NH₄⁺), phosphate, silica and

calcium as major nutrients/essential nutrients for their growth (Reldfield, 1958; De Baar, 1994; Sterner and Elser, 2003; Moore et al., 2013 and references therein). Other than these major nutrients Phytoplankton requires minor nutrient/TEs like Fe, Mn, Cu, Co, Cd, Zn. for different biogeochemical processes such as activations of enzymes, Carbon fixation, photosynthesis ... (Table-1.1) derived from SCOR Working group (2007). Depending upon the availability some of the nutrients are considered as limiting (Fe) or co-limiting nutrients (Mn, Cu...) (Boyd et al., 2007; SCOR working group, 2007; Moore et al., 2013; Browning et al., 2021). For example, regions like high nutrient/nitrate low chlorophyll (HNLC) zone Fe acts as limiting nutrients and Mn as a co-limiting nutrient covering 25% of the Global Ocean (De Baar et al., 2005; Jickells et al., 2005; Moore et al, 2013; Browning et al., 2021). In contrast, 60% of the world's oceans considered as low nitrate low chlorophyll (LNLC) region, where the unavailability of nitrogen species restricts the new production Steinacher et al., 2010; Achtureberg et al., 2017).

Table 1.1 Important biogeochemical processes in the Ocean and the trace metals thought to be fundamental to their action. derived from Morel and Price (2003)

Biogeochemical process	Important trace elements
Carbon fixation	Fe, Mn
N ₂ fixation	Fe, Mo (V)
Denitrification	Cu, Fe, Mo
Nitrification	Cu, Fe, Mo
Methane oxidation	Cu
Organic N utilisation	Fe, Cu, Ni
Formation of volatile species	Fe, Cu, V
Synthesis of photopigments	Fe and others
Toxicity	Cu, As (Cd, Pb)

In some cases, within the phytoplankton community, these TEs behave differently for example *Prochlorococcus* is the most common and abundant species affected by Cu toxicity however, a closely related species like *Synechoccus* thrives in Cu-enriched water (Mann et al., 2002; SCOR Working group 2007). Improving our understanding of the source and supply of these nutrients will help better constrain our biogeochemical models.

Photic zone (0-200m depth) of surface seawater fuel by nutrients from 1. Oceanic crust (hydrothermal process and magmatic activity), 2. Continental runoff (riverine and other freshwater flux), 3. Sediment-water boundary process (diagenesis, resuspension, coastal upwelling), 4. Atmospheric supply (Fig-1.1) (SCOR Working group, 2007 and references therein). These nutrient sources such as hydrothermal activity, continental runoff and upwelling

are area-specific and restricted to a few hundred kilometers from the coast or a specific part of the ocean however atmospheric deposition has no such limitations due to the long-range transport of dust it can travel up to thousands of kilometers for example the Saharan dust traveled all across the Atlantic Ocean and fertilize the Amazon rain forest and the Caribbean islands (Okin et al., 2004; Abouchami et al., 2013; Kumar et al., 2014; Rizzolo et al., 2017). Additionally, stratified and/or oligotrophic regions of the world ocean receive nutrients majorly from atmospheric deposition (Jickells et al., 2005; Jickells and Moore 2015; Pabortsava et al., 2017).

In the last three decades, studies have indicated a link between atmospheric aerosols (particularly aeolian dust) and biological productivity, which in turn has implications for carbon export and other biogeochemical processes discussed previously (Martin et al., 1989; Jickells et al., 2005; Moffett et al., 2015; Banerjee and Prasanna Kumar, 2014; Guieu et al., 2019).

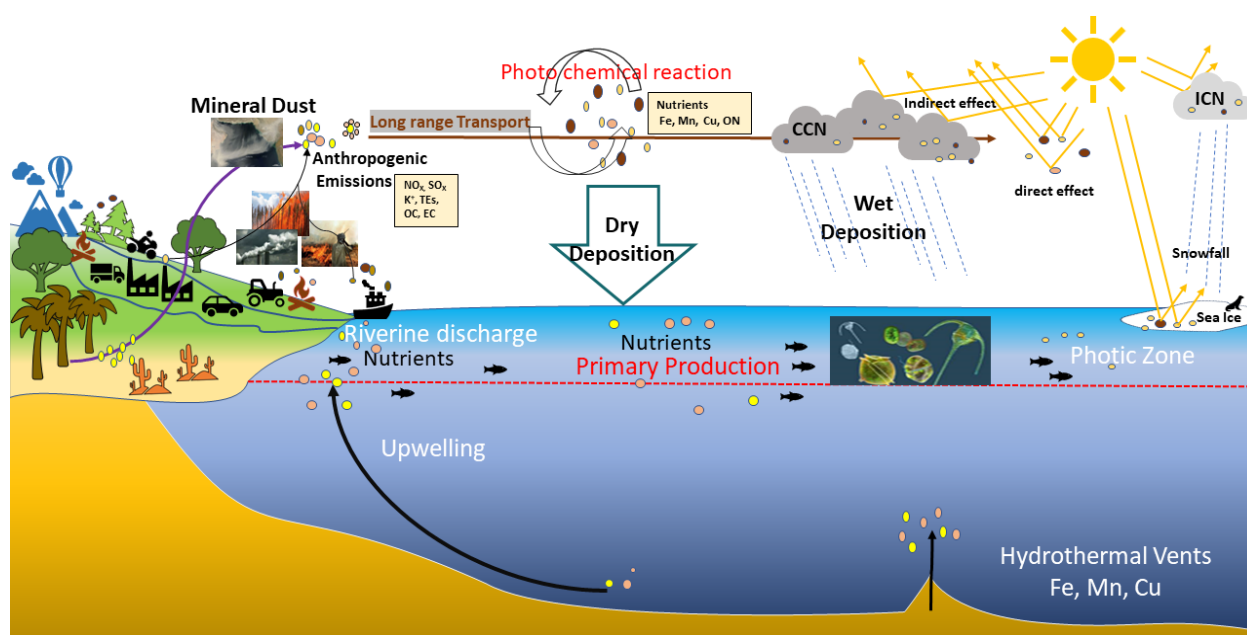


Fig-1.1 Significance of Aerosol as a nutrient source, as well as other sources of nutrients to the surface ocean and the role of aerosol in climate change.

In the present-day scenario of growing industrial/vehicular emissions, the anthropogenic emissions (constituting acidic gases e.g. SO_2 and NO_x) are bound to alter the pristine natural mineral dust from refractory to more labile/readily soluble (Laskin et al., 2005; Liao and Seinfeld, 2005; Kumar and Sarin, 2009; Riemer et al., 2019; Goel et al., 2020). For example, the enhancement in iron solubility has been linked to the chemical processing (in the presence of SO_2 and its oxidation products) of mineral dust particles during long-range atmospheric

transport. Additionally, recent studies have suggested anthropogenic emissions (biomass burning and fossil-fuel combustion) as a significant source of these nutrients including labile/soluble trace metals in aerosols in contrast to its supply from natural mineral dust (Fig-1.1) (Barkley et al., 2019; Ito et al., 2019; Wang et al., 2021; Hamilton et al., 2022). Observational and modeling studies have demonstrated that external (atmospheric) nutrient input can stimulate primary productivity, enhance nitrogen fixation, alter the phytoplankton size distribution, and potentially increase the carbon sequestration by the biological pump in the ocean (Mills et al., 2004; Duce et al., 2008; Maranon et al., 2007; Liu et al., 2013). In addition, a rapid increase in aerosol optical depth (AOD) is reported over Asia (mainly over the North Indian Ocean) leading to an increase in ocean acidification (Doney et al. 2011; Campbell et al., 2013; Sarma et al., 2015) and may also enhance coastal primary production (Yadav et al., 2016). The transportation and deposition (over the surface ocean) of these macro and micro nutrients associated with natural/anthropogenic aerosols display large spatial as well as temporal variability owing to their short residence time (Boyd and Doney, 2003; Baker et al., 2010; Mahowald et al., 2018 and 2019; Pease et al., 1998). It is thus, important to quantify their fluxes which will be helpful in constraining their role and impact on surface water biogeochemical processes (Grand et al., 2014; Mills et al., 2004; Moore et al., 2013).

1.1 Scope and Objective of Study:

1.1.1 Scope of study:

The North Indian Ocean (NIO), being one of the most productive regions, mainly constitutes of two basins; the Bay of Bengal (BoB) and Arabian Sea (AS). These basins are vulnerable, due to its geographical location and atmospheric outflow from surrounding continental emissions (Kumar et al, 2008 a, b; Kumar et al., 2010; Srinivas et al., 2012, 2014; Banerjee et al., 2019; Ramaswamy et al., 2017; Kumar et al., 2020), to atmospheric nutrient deposition (Fig-1.2). The Indian Ocean is surrounded by major desert-like the Australian deserts (Great Victoria, Great Sandy, Tanami deserts. Etc.), African deserts (Sahara, Kalahari, Nubian, Danakil and Grand Bara deserts, etc.), Middle Eastern deserts (Syrian desert, Rub -al-Khali, Wahiba Sand Sea deserts...), the South Asian deserts (Dasht-E-Kavir, Kharan, Registan, Thar desert...) are the major source of mineral dust contributing 230 Tg per year equivalent to Indian Ocean equivalent central Atlantic Ocean (Léon and Legrand, 2003; Kok et al, 2021,2023; Kumar et al., 2022). These mineral dust sources remain active at different times; recently Suresh et al. (2021) and Singh et al. (2023) highlighted within the monsoon season different dust sources remain active during different periods like the beginning of the monsoon the Middle

East region is a major contributor of mineral dust, while the end monsoon Thar and other south Asian region are the major contributor of mineral dust and during mid-monsoon northeastern Africa dominate mineral dust supply to the Arabian Sea. The nutrient/TEs contained in mineral dust highly depend upon the mineralogy of the dust (Journet et al., 2008; Formenti et al., 2014; Desboeufs et al., 2024) and recently Suresh et al. (2022) explained variation in dust mineralogy and source over the Arabian Sea. Other than the dust source the Indian Ocean is also surrounded by highly urbanized and industrial regions and active biomass-burning regions like Indo Gangetic Plain (IGP), South East Asia (SEA) and forest fires recurring at places like the Australian region (Kumar et al., 2010,2022, 2024; Hamilton et al., 2022).

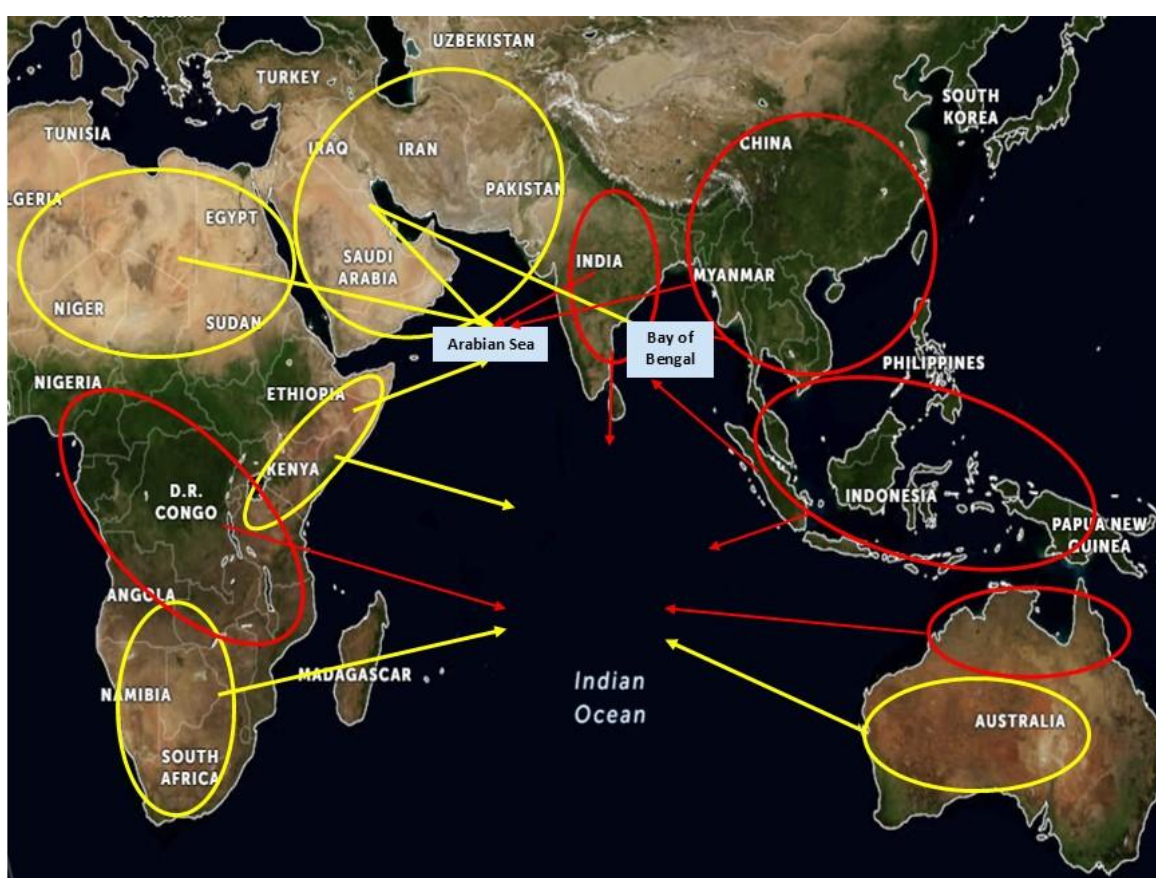


Fig-2.1 Potential dust (Yellow circles/ellipse) and anthropogenic emission (Red circles/ellipse) source surrounding the Indian Ocean.

Aerosol (mineral dust/anthropogenic) transport and their deposition are largely governed by well-known annual reversal of the prevailing wind regimes wherein, south-westerly winds are dominant at the onset of the summer monsoon (June–September) and north-easterly winds during winter months (December–February) episodic activation of other wind

systems like the Shamal wind and Leevard wind provide the additional complexity nutrient transport to the NIO (Schott and Mc-Creary, 2001; Ramaswamy et al., 2017; Kumar et al., 2020).

Previously various studies highlighted regional oceanographic processes such as wind-driven coastal upwelling and mixed-layer deepening enhance primary up to 300% (Nair et al., 1989; Barber et al., 2001; Goes et al., 2005) and convective mixing during winter in the Arabian Sea (Madupratap et al., 1996; Barber et al., 2001; Prasanna Kumar et al., 2001; Gupta et al., 2016). Goes et al., 2005 speed highlighted the warming of Eurasian land mass increases the wind speed during the monsoon in the Arabian Sea, while the convective mixing during winter decreases due to the same (Goes et al., 2020). Corollary to this increase in wind speed will also increase the mineral dust transport from land to the Oceanic environment. Additionally, some model-based studies explained atmospheric mineral dust plays a significant role in primary productivity in the Arabian Sea (Wiggert and Murtugudde, 2007; Banerjee and Kumar, 2014; Guieu et al., 2019) and the transport of anthropogenic aerosols/ Pollutants (based on AOD data) from Indian subcontinent strengthen the convective mixing and phytoplankton blooms (Sridevi and Sarma, 2022). Siefert et al. (1999) and Johansen and Hoffmann (2003) tried to measure atmospheric aerosol samples collected from the Arabian Sea during the Monsoon and Winter seasons respectively, but these two studies were restricted to the western Arabian Sea. Other than these two studies ICARB campaigns tried to explain dust and nutrients over the Arabian Sea but it was restricted to the summer season only (Kumar et al., 2008a, 2008b; Srinivas et al., 2012). Therefore, a basin-wide study focusing on the Monsoon and Winter seasons is needed to understand the influence of atmospheric aerosol on the biogeochemical cycle over the Arabian Sea. Pease et al. (1998) and Tindale and Pease (1999) have collected dust over the north/northwestern part of the Arabian Sea to estimate dust from Al concentration, which is high during Winter and Summer Season due to transport of dust at high latitude is the reason. Ramaswamy et al. (2017) and Kumar et al. (2020) explain strong wind during the monsoon (SW monsoon) can potentially transport more mineral dust compared to winter (NE monsoon) when the wind is not strong enough to raise the mineral dust. These observations need to be validated via more basin-wide observation during the respective season.

Atmospheric outflow from surrounding continental emissions consists of the unique blend of processed aerosols which are the potential supplier of essential macro and micronutrients to surface waters of both basins (Kumar and Sarin, 2009; Kumar et al., 2010; Srinivas et al., 2012 and 2014). The availability of these nutrients depends on the chemical processing of aerosols during long-range transport on spatial and seasonal scale (Kumar et al., 2010; Baker and Croot, 2010; Meshkhidze et al., 2019; Baker et al., 2020). Anthropogenic

emissions from biomass burning and fossil fuel combustions are, also, a significant source of soluble/bioavailable iron and other trace metals to the Bay of Bengal (Kumar et al., 2010; Srinivas and Sarin, 2012; 2013). These described studies over the Bay of Bengal are restricted to Winter and Summer seasons, Tiwari et al. (2016), (2018) highlighted the post-monsoon (October and November) biomass burning over the IGP produces an ample amount of anthropogenic aerosol which transported to the Bay of Bengal and Arabian Sea. These anthropogenic aerosols can alter the TEs solubility and surface biogeochemistry but there is no study that highlights the nutrient supply to the Bay of Bengal during the monsoon season.

The input of nutrients via atmospheric outflow can significantly modulate the various biogeochemical processes within NIO, including primary productivity (Guieu et al., 2019). Alteration of the biogeochemical processes in NIO has a significant impact on the food chain and eventually on our marine bio-resources, including fisheries, which is a major contribution toward the annual revenue of our nation. It is thus important to quantify the nutrients associated with aerosols and their spatial as well as temporal distribution over the two oceanic basins to better constrain their impact on surface water biogeochemical processes.

As shown above, several studies were attempted to identify the dust source and quantify them as well as nutrients over the NIO but these studies are restricted to particular regions and/or seasons, a comprehensive study over the NIO is much needed to fulfill the knowledge gap existing in atmospheric nutrient supply to the NIO. This thesis presents a detailed description on the dust and associated nutrient concentration, their seasonal variability, and nutrient flux to the north Indian Ocean. Apart from dust and nutrient flux geochemical characteristics, fractional solubility of TEs in Aerosol samples collected from the boundary layer of the Arabian Sea, Bay of Bengal and Indian Ocean are discussed and also highlighted their global biogeochemical significance. Thus, the proposed thesis study aims to address the contribution of macro and micro-nutrients to the NIO following these objectives:

1.2.2 Objective of study:

- 1. To quantify the spatial and temporal distribution of macro and micro-nutrients over the NIO.*
- 2. To estimate atmospheric depositional fluxes of dust and associated nutrients to the NIO.*
- 3. To assess various factors controlling the solubility of trace metals over the NIO.*

For accomplishing the above objectives, aerosol sample were collected over the NIO

during 7 different cruise campaigns to quantify nutrient concentrations and fluxes. In addition, other chemical species were analysed to assess the factors controlling nutrient availability. These analytical data are further complemented with the air mass back trajectory (AMBT) analyses for different seasons over the NIO region to understand the emission and transport of aerosols from the continental outflow. The cruises undertaken in this study are strategically planned to cover all seasons including summer, monsoon, post-monsoon and winter. Attempts have been made to cover the wider span of both basins (the Bay of Bengal and the Arabian Sea) as well as the region up to 13°S latitude of the Indian Ocean. The samples were analysed for major nutrients (reactive N- species such as NO_3^- , NH_4^+ and Total nitrogen) and trace metals/TEs Such as (Fe, Mn and Cu) along with the chemical composition to achieve the proposed objectives.

1.3 Thesis Structure:

The Thesis is divided into six chapters. All these chapters are briefly described as follows **Chapter 1** provides a birds-eye view of atmospheric aerosol and its importance in modulating different physical, chemical and biogeochemical processes of the earth. It also highlights the previous studies and current knowledge gaps in the Indian Ocean along with detailed objectives and structure of the thesis.

Chapter 2 provides a birds-eye view of the study area's geography and meteorological variations. It also describes the details of analytical procedures followed in this study along with a highlight of different instruments used with other technical details.

Chapter 3 provides a detailed discussion of Seasonal variability in atmospheric nutrient distribution and their deposition fluxes over the Arabian Sea.

Chapter 4 highlights our current work on Atmospheric nutrient distribution and their deposition fluxes over the Bay of Bengal: Seasonal variability and factors affecting their bio-availability

Chapter 5 describes in detail on Sources of atmospheric nutrients and factors controlling their distribution over the Indian Ocean.

Chapter 6 summarizes the results of this thesis and briefly outlines the future perspectives.

Chapter 2
Materials and Methods

2.1 Introduction:

To achieve the specified objectives (Chapter 1), a systematic sampling strategy was designed for the collection of aerosol samples from the North Indian Ocean (NIO), which includes the Arabian Sea (AS), Bay of Bengal (BoB) and Indian Ocean (IO). These oceanic regions represent very diverse meteorological conditions and receive aerosol from different active sources during different seasons (Kumar et al., 2020). A well-designed analytical protocol was an integral part of this study wherein aerosol samples were collected onto tisuquartz filters using high-volume air samplers. The NIO also acts as a natural laboratory for studying the dust and associated nutrients, the western and northwestern side of NIO is surrounded by major deserts and dry regions like northeast Africa, the Middle East (Egypt, Oman, Yemen, Saudi Arabian, Iran), Pakistan and Thar desert of the India. Other than these regions dust from the Australian desert and eastern Africa can entrain in the Indian Ocean and fertilize surface biogeochemistry. Similar to dust sources the NIO is also surrounded by major urbanized and industrialized areas (India, Southeast Asia) where biomass-burning activity is often seen during post-harvesting seasons and continental outflow of these emissions can transport ample nutrients along with toxicants to the oceanic region. This transported nutrient before being deposited in the surface ocean undergoes atmospheric mixing which processes more pristine refractory dust into labile form which can easily be uptake by the primary producer. Hence to understand the atmospheric nutrients over the NIO this study was undertaken. A detailed description of the sampling region, sampling periods, meteorological conditions and analytical protocols adopted for the measurements of mineral dust-associated trace elements (TEs) and chemical species in collected aerosol samples have been described in the following sections:

2.2 Study Area:

2.2.1 Indian Ocean:

The samples have been collected on-board the research vessel Sindhu Sadhana (SSD) in the year 2018 and 2019 during boreal summer, which can be subdivided into summer/northern spring inter-monsoon (April and May) and Indian summer monsoon (ISM) or SW-Monsoon (June-August) periods respectively. Hence forth, for simplicity, The cruise period of 2018 define as summer and that of 2019 as Monsoon months. The cruise track followed for sample collection is shown in Fig-2.2. In 2018, cruise was undertaken from 01 April 2018 to 04

May in 2018 (SSD-048) and from 18 July to 23 July in 2019 (SSD-062). The SSD-48 cruise started from Chennai port (13.06 °N, 80.18 °E) in the western Bay of Bengal (BoB) and moved toward southeast up to (6.55 °N, 82.30 °E), then it turned toward the southwest and up to Central Indian Ocean Basin (CIOB) (13.75 °S, 74.68 °E). While returning to Chennai port, ship followed similar meridional track parallel to previous but with an offset of 10-15 km. The SSD-62 started from Mourmugao port, Goa (15.37 °N, 73.84 °E) located in the eastern Arabian Sea, sailed in the southeast direction along the east Arabian sea coast up to 75.5 °E then it headed south up to CIOB (13.56 °S, 75.56 °E) then return to Mourmugao port. Up to Kochi (9.93 °N, 76.26 °E), it followed a parallel track with an offset of 15-20 km; after that, it moved along the shelf of the Indian subcontinent up to Goa. I could not collect aerosol samples while heading back to Goa after the equator due to heavy monsoon rain till Goa. The Indian coast is an urbanized and heavily industrialized zone comprising of petrochemical refineries, chemical industries, mineral processing plants, and busy seaports, making it a potential emission source of anthropogenic pollutants to the ambient atmosphere throughout the year. During the campaign meteorological data was collected by AWS. During both campaigns air temperature was almost similar, which was 27° C and 28° C for Summer and Monsoon respectively and average relative humidity was ~80% during both the season. However, Wind speed was relatively higher during monsoon average wind speed was 9.89 m/s while during Summer it was 7.5 m/s.

2.2.2 Arabian Sea:

The Arabian Sea (Fig. 2.1) is one of the ideal locations to understand dust and associated nutrients, landlocked on three sides out of which two sides are surrounded by major deserts (western and northern) and the eastern side is surrounded by major settlements and the populated cities like Mumbai, Kochi, Karachi, etc. This region gets an ample amount of dust when the wind blows from the south-southwest or northern region (Summer and Monsoon Season, Fig- 2.2), while northeast wind or easterly (Post monsoon and Winter Season, Fig- 2.2) wind can bring anthropogenic emissions in the form of continental outflow. The basin gets a unique blend of dust and anthropogenic aerosol. The aerosol sampling was carried out onboard RV Sindhu Sadhana (cruise No. SSD-40, SSD-55, SSD-68). SSD-40 and SSD-55 cover a large area of the Arabian Sea during the monsoon season and SSD-68 during the Winter season, all three cruises followed the same cruise track (Fig-2.1) more details were provided in Table 2.1. It is important to note that all cruises were planned with an aim to capture biogeochemical features of the Arabian Sea during SWM similar to those covered during the Joint Global Ocean

Flux Studies (JGOFS) experiment to compare possible changes in the last two decades with respect to the present-day scenario. Both cruises were started from Goa (73.79°E, 15.46°N) to the southern Arabian Sea down to 8°N through the coastal region of Goa, Karnataka, and Kerala. Subsequently, it sailed towards the northern Arabian Sea, following the coastal waters from Kerala up to Gujarat (21°N). From the northern Arabian Sea (21°N, 69.13°E), the cruise moved towards the west and sailed up to 64°E, then towards south continuing up to 11.5°N. Subsequently, the ship went eastward and returned to the Goa port (Fig- 2.1).

Aerosol samples were collected onboard research vessel Sindhu Sadhana (SSD) in the years 2017 and 2018 during August month. In 2017, a cruise was undertaken from 05-31 August (SSD-040) and another during 02-30 August in 2018 (SSD-055) following a similar cruise track shown in Fig. 1. 22 and 21 aerosol samples (total suspended particulate (TSP)) were collected during SSD-40 and SSD-55, respectively, along the cruise track (shown in Fig. 1a,b). The meteorological parameters were measured onboard with the help of AWS (Autonomous weather station) in every 2 minutes. The relative humidity during monsoon season was $\geq 90\%$ while the average wind speed was $> 10\text{ m/s}$. The air temperature average was $\sim 27^\circ\text{C}$ and the average surface level pressure was 1004 mb during both the monsoon cruises (SSD-40 and SSD-55). During the Winter season (SSD-68), A drop in relative humidity (Avg= 70.6%) and wind speed (6.6 m/s) was observed. The average air temperature was 26.3°C and surface pressure was 1010.2 mb. During the monsoon other than a low-level jet (LLJ)/ monsoon wind system occurs over the Arabian (Red color high-speed wind Fig- 2.2) two more wind systems the Shamal wind (enter the Arabian from the Northwest direction) and the lever wind (enter the Arabian from the North) responsible for synoptic transport of ample amount of dust to the Arabian Sea (detail description in Goudie and Middleton, 2006; Kumar et al., 2020; Aswini et al., 2021; Panda et al., 2022).

2.2.3 Bay of Bengal:

Aerosol samples were collected onboard RV-Sindhu Sadhana during SSD-015 ($n = 11$) and SSD-019 ($n = 11$) (Table 2.1) conducted during October 2015 (Post monsoon, transition from southwest monsoon to northeast monsoon) and February 2016 (winter, end of northeast monsoon), respectively. Sampling took place during the aforementioned expeditions, primarily limited to the coastal region covering a latitudinal stretch between 13°N and 21°N during post-

monsoon. However, the Winter cruise encompassed a border geographic scope, spanning the open oceanic sector of the BoB between 13–21°N and 80–90°E (Fig-2.1). Sampling occurred exclusively during periods when the cruise maintained a speed of 10 knots or higher, ensuring wind directionality from the ship's fore and mitigating contamination from exhaust emissions. The marine atmospheric boundary layer of the BoB is strongly influenced by the continental outflow during our study period. It experiences a sharp seasonal reversal of winds due to a strong land-ocean thermal gradient (Beegum et al., 2012).

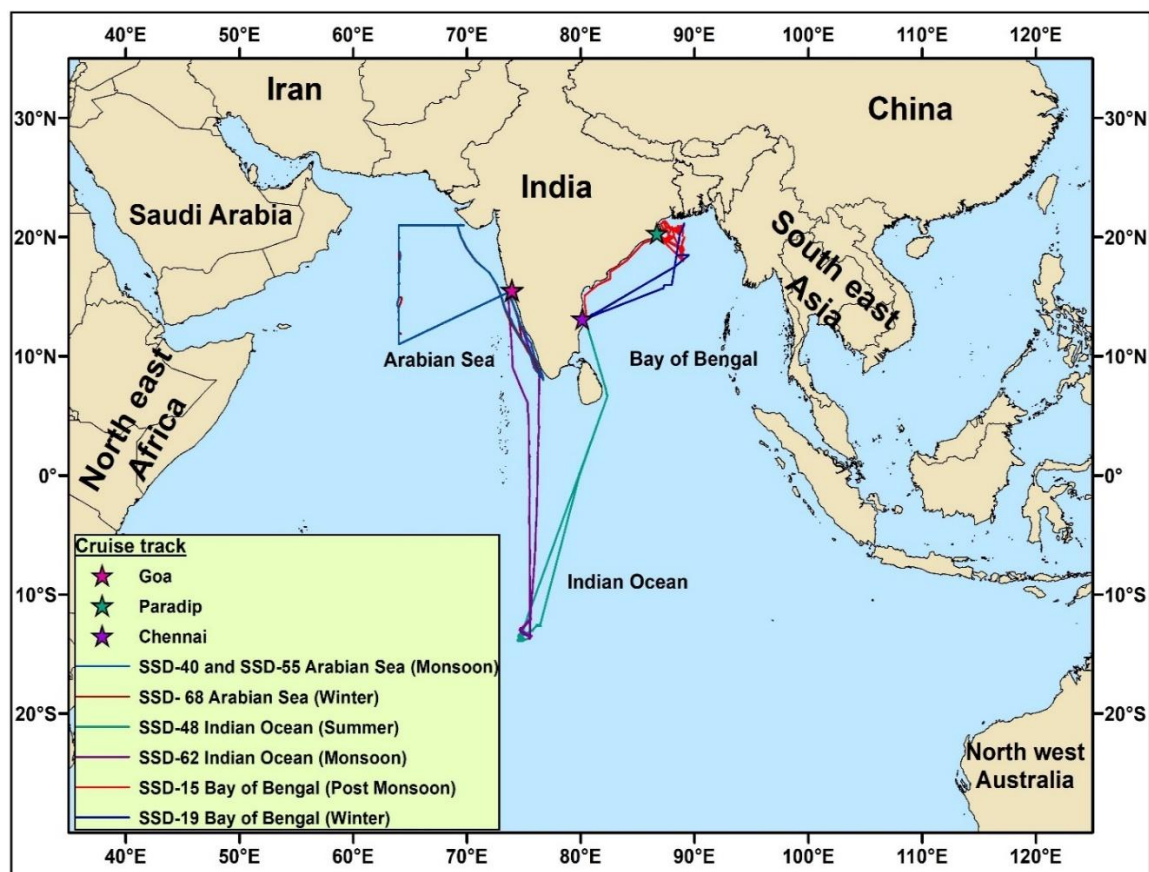


Fig-2.1 Study area map showing cruise transects in the Indian Ocean (IO), Arabian Sea (AS) and Bay of Bengal (BoB) during different seasons.

The wind system changes from south-westerlies during the southwest monsoon to predominantly north-easterlies during the northeast monsoon. The SSD-015 cruise campaign was conducted during October (Post monsoon), which was a transitioning month and experienced relatively weaker winds compared to the rest of the season. These winds transport a complex mixture of aerosols that contains biomass and fossil fuel-burning products, mineral dust, sea salt, and secondary particles such as sulfate, nitrate, and ammonium salts (Kumar et al., 2008b). The crop residue burning is prominent in North India during late October and early

November (Tiwari et al., 2018), and has significant potential to impact the aerosol loading in this region (Tiwari et al., 2016; Nayak et al., 2022). The SSD-019 cruise campaign was conducted during the northern winter month of February, during which the prevailing airflow over the Indian subcontinent is predominantly north-easterly/northerly. North-easterlies, blowing towards the ocean from polluted continental landmass during wintertime, transport a significant amount of aerosols over the BoB. Meteorological parameter such as Relative humidity (RH), air temperature, surface pressure, and wind speed were monitored periodically by AWS at a height of 20 m above sea level. During both the campaign RH shows a large variability 31- 100% and 56-96% during the post-monsoon and winter respectively. However, the mean values were comparable $73 \pm 12\%$ during post-monsoon and $77 \pm 7\%$ in winter. A relatively calmer winds 3.6 ± 2.9 m/s and 2.7 ± 1.7 m/s was experienced during the post-monsoon and winter seasons respectively. The surface pressure showed very low variability (1005–1013 mb), whereas, the temperature varied from 23°C to 32°C. Detail meteorological conditions were described in (Nayak et al., 2022).

2.2.4 Wind Pattern:

Wind pattern plays a vital role for transport of dust and associated nutrients to remote marine locations. The north Indian Ocean experiences strong LLJ also called Findlater jet (FLJ) or southwest monsoonal wind during June- September (Fig-2.2), northeast monsoon wind during December-February (Fig-2.2) and transition of these two wind systems occurs during Summer (March-May) and post-monsoon (October- November) (Fig-2.2) (Schott and McCreary Jr, 2001; Shankar et al., 2002; Vinayachandran et al., 2021). However, low-pressure and small-scale weather phenomena can affect the source region of the wind on a day-to-day basis, which can affect aerosol transport. For a better understanding of wind mass and its sources of origin NOAA Air Resources Laboratory (ARL), HYSPLIT transport and dispersion model (<http://www.ready.noaa.gov>) was used to estimate seven days' air mass back trajectories (AMBTs) corresponding to the sampling track at different heights and the result of this model are discussed in each following chapter (Stein et al., 2015).

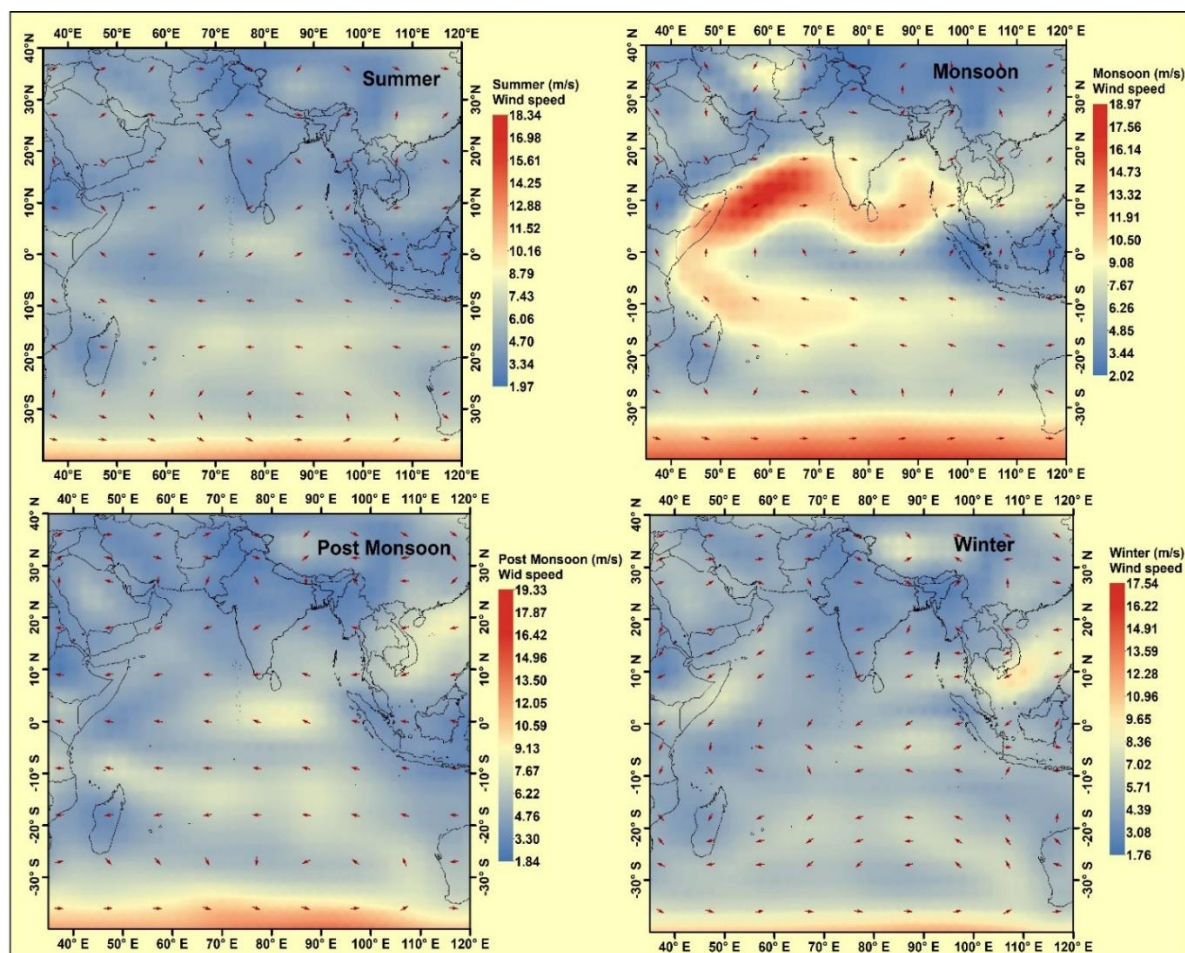


Fig-2.2 Map showing seasonal wind direction (shown in red arrows) and 5-year average wind speed over the study area. Southwesterly winds dominate during Jun-Sep while northeasterly winds prevail during Dec-Feb. During Mar-May and Oct-Nov, the transition between the major wind patterns takes place. (Data adapted from <ftp://ftp.cpc.ncep.noaa.gov/wd51we/reanalysis-1/6hr/rotating/>)

2.2.5 Aerosol Sampling:

Aerosol samples were collected on board the research vessel Sindhu Sadhana (SSD). All samples were collected while the ship was sailing at a speed of >8 knots, ensuring that the winds were from the foreside of the ship and contamination from the ship's exhaust did not affect the particulate sampling. PM_{10} samples were collected in all seasons other than monsoon season (SSD-40 and SSD-55) using a high-volume sampler (ENVIROTECH Model APM-430) with a flow rate of $1.1 \text{ m}^3 \text{ min}^{-1}$. During SSD-40 and SSD-55 TSP (total suspended particles) samples were collected using a sampler without PM_{10} module (ENVIROTECH Model APM-430). In the SSD-68 cruise along with PM_{10} , $PM_{2.5}$ samples were collected using TISCH-HVS- $PM_{2.5}$ sample with an average flow rate $1.1 \text{ m}^3 \text{ min}^{-1}$.

Table 2.1: Details of samples collected from the North Indian Ocean (NIO) during different seasons.

Cruise Name	Region	Season	Sampling Period (DD/MM/YYYY)		Sample Number (n)
			Start	End	
SSD-15	Bay of Bengal	Post Monsoon	14/10/2015	29/10/2015	11
SSD-19		Winter	6/2/2016	20/02/2016	11
SSD-40	Arabian Sea	Monsoon	5/8/2017	31/08/2017	22
SSD-55		Monsoon	2/8/2018	30/08/2018	21
SSD-68		Winter	7/12/2019	5/1/2019	46
SSD-48	Indian Ocean	Summer	1/4/2018	3/5/2018	20
SSD-62		Monsoon	18/06/2019	21/07/2019	12

Aerosol sampler was placed on the bridge deck (~16 m above MSL (Mean Sea Level)] at an optimized position where maximum wind from ship's bow reach to the sampler. All samples were collected on daily basis on PALLFLEX™ Tissue-quartz filter (8" x 10") with varying sampling time (range :20-24 hours) depending on the on-board operations, wind speed and wind direction. All filters were pre-combusted at 200 °C prior to sampling. Post collection, samples were packed in ziplock bags and preserved in a deep freezer at -19 °C till further analyses in a clean lab. Along with samples, several field blanks were collected by placing filters on the sampler for few hours without running it. This was done to assess level of contamination while handling and storage of the samples After the cruise, all samples were transferred to CSIR-National Institute of Oceanography and stored in -19 °C until further analyses. Cruise-wise sample details are provided in Table 2.1.

2.3 Analytical Techniques:

2.3.1 Sample Preparation:

Filter (~1/8 of sampled area) was cut, using a ceramic scissor, under a clean laminar flow bench for water-soluble as well as total trace metal analysis. Filters were transferred in 50 mL Savillax vials and leached with ultrapure deionized water/Milli-Q water (resistivity=18.2 MΩ) for 30 minutes with 15 min of ultrasonication. Post-leaching, supernatant parts were transferred to precleaned polypropylene bottles via filtration (0.2 µm Watmann PVDF syringe filters). An aliquot (10 mL) of extracted leachate was acidified for water-soluble trace metal analyses, and another aliquot was stored in a deep freezer (-20°C) till its analysis for cations and anions.

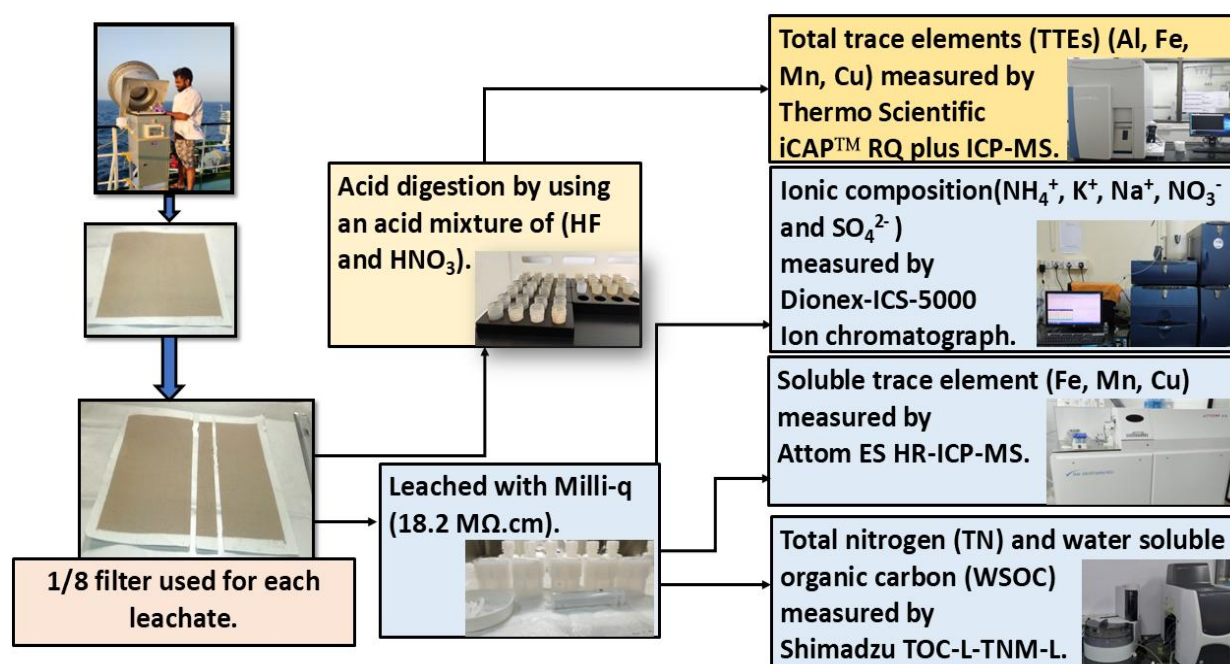


Fig-2.3 Analytical scheme for the sampling and analysis of aerosol samples

For total metal analyses, filters 1/8 part were cut and transferred to acid-precleaned 15 ml Savillex vials along with a mixture of suprapure acids (HF and HNO₃). Post transfer, all vials were kept on a hot plate at 110°C for 24 hours to ensure complete digestion. Subsequently, samples were dried, and 2mL suprapure concentrated HNO₃ was added again and kept on the hot plate for open digestion. Subsequently, the addition of 0.5 mL (twice), suprapure HNO₃ was done, and open digestion was continued to ensure complete digestion of samples by visually getting a clear solution. Dried samples were leached with 2 % HNO₃ solution and transferred to a precleaned polypropylene bottle, and the final solution was made to 50 mL.

2.3.2 Analysis of water-soluble ions:

Dissolve anions (Cl⁻, NO₃⁻, SO₄²⁻) were measured with Ion Chromatograph (Thermo-Fisher Scientific Dionex-ICS-5000) with a suppressed conductivity detector. The anions were separated by using the analytical column IonPac AS-16 (4 × 250 mm), guard column IonPac AG16 (4 × 50 mm) column, 22mM, NaOH as eluent at a flow rate 0.9 mL min⁻¹ in the isocratic elution mode using ASRS 300 as a suppressor. Similarly, cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) were analysed by using analytical column IonPac CS12A (4 × 250 mm), Ion Pac CG12A (4 × 50 mm) used as guard column, and CSRS 300 used as a suppressor. Methyl sulfonic acid has been used as an eluant for cation analysis with a run time of 15 min. Thermo Scientific Dionex six cation-II and Dionex five anion standards were used for instrument calibration. Procedural

blank concentrations for both cations and anions are provided in Table 2.2. The precision of measurements for all dissolved ions by ion chromatography was assessed and results are shown in Fig. 2.4.

2.3.3 Analysis of trace elements:

Post digestion, a clear solution was obtained which was used for analysis of total TEs. total Al (Al_T) and total Fe (Fe_T), total Mn (Mn_T) and total Cu (Cu_T) were measured using Q-ICP MS (Thermo Scientific iCAP™ RQ plus ICP-MS). The instrument was calibrated with Merck 23-element multi-element standard. 12 calibration standard was used to get a linear correlation ($R^2 > 0.99$). Rhodium (2ppb) was used as an internal standard which helps to understand the stability of the instrument. The Procedural blank for TTEs are given in Table 2.2. Few samples and standards were analysed repeatedly to determine the precision of analysis; these replicate measurements show analytical reproducibility of 5 % or less for all TEs. To assess the accuracy of these measurements, international standards NIST (SRM 2710a Montana soil) was used as certified reference materials and accuracy was found to be better than 5% for all TEs. In addition, total TEs in digested Arizona Test Dust (ATD) was analysed following a similar procedure as used for samples. Our result (Table 2.3) compared well with previously reported data by Shelly et al. (2015) and recovery for reported TEs are within 3% uncertainty (as compared with Shelly et al. 2015).

Table 2.2 Procedural blank concentrations (including contribution from chemical reagents and filter blank) of different ionic species and trace elements are normalised to average air volume filtered (~850 m³).

Ionic species	Concentration (in µg/m³)	Metal species	Concentration (in ng/m³)
Na ⁺	0.07	Al _T	0.63
NH ₄ ⁺	0.06	Fe _T	0.79
K ⁺	0.113	Mn _T	0.0005
Ca ²⁺	0.01	Cu _T	0.0007
Mg ²⁺	0.01	Fe _s	BDL
Cl ⁻	0.15	Mn _s	BDL
NO ₃ ⁻	0.1	Cu _s	BDL
SO ₄ ²⁻	0.062		

For water soluble TEs analysis, samples leached with Milli-q were acidified with suprapure HNO₃ following the method described in section 2.3.1 and used for soluble Fe (Fe_s), soluble Mn (Mn_s) and soluble Cu (Cu_s) measurements using HR-ICP-MS (Nu Instruments, Attom ES). The instrument was calibrated using a similar procedure as Q-ICP-MS described earlier in this section. Procedural blank concentration is given in Table 2.2. Reproducibility of repeat sample of total and soluble TEs are shown in Fig-2.5.

Table 2.3 Concentration of different elements present in Arizona test dust and their comparison with previously published data.

			Al	Ti	Mn	Fe	Cu
Shelly et al. (2015)	Value	µg g ⁻¹	69,600	3220	764	33,600	NA
	STD.	µg g ⁻¹	1870	50	12	600	NA
Buck et al. (2019)	Value	µg g ⁻¹	73240	3492	1230	40610	67.3
	STD.	µg g ⁻¹	799	43	130	474	3.1
Current Study	Value	µg g ⁻¹	68072	3300	790	32860	46
	STD.	µg g ⁻¹	878	33	8	420	1
Recovery % compare with Shelly et al. (2015)		%	98	102	103	98	NA

2.3.4 Total nitrogen (TN) and water-soluble organic carbon (WSOC) analysis:

A Shimadzu TOC-LCPH-TN analyser was used to determine TN as well as water-soluble organic carbon (WSOC) concentrations (Shetye et al., 2019). TN was analysed at 720 °C following the chemiluminescence method, where 300 µL of the sample was injected into the furnace packed with Pt catalyst at a temperature of 720 °C. The evolved Nitric Oxide (NO) was measured using a non-dispersive infrared (NDIR) detector to assess (TN) content. Standardization was achieved using potassium nitrate solution. A 5-point calibration curve was generated before each batch. Blank concentration of TN was below the detection limit, when the detection limit of the instrument was 4 ng mL⁻¹, so no blank correction was required for TN. ON was estimated by subtracting total inorganic nitrogen (N content in NH₄⁺ and NO₃⁻) from total nitrogen. The reproducibility of TN analysis is shown in Fig-2.4.

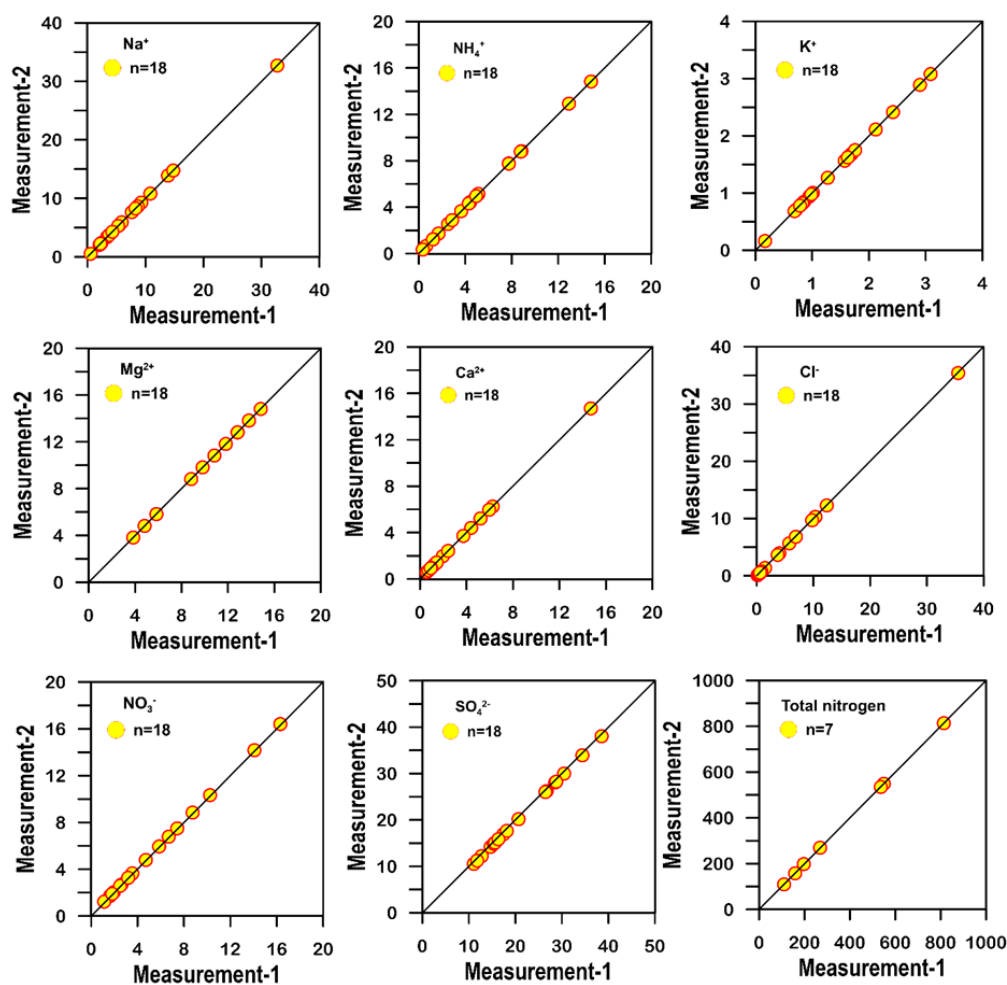


Fig-2.4 Repeat measurements of the chemical species (mg L^{-1}) in Milli-q leach of aerosol samples. Solid lines represent 1:1 correspondence between the data.

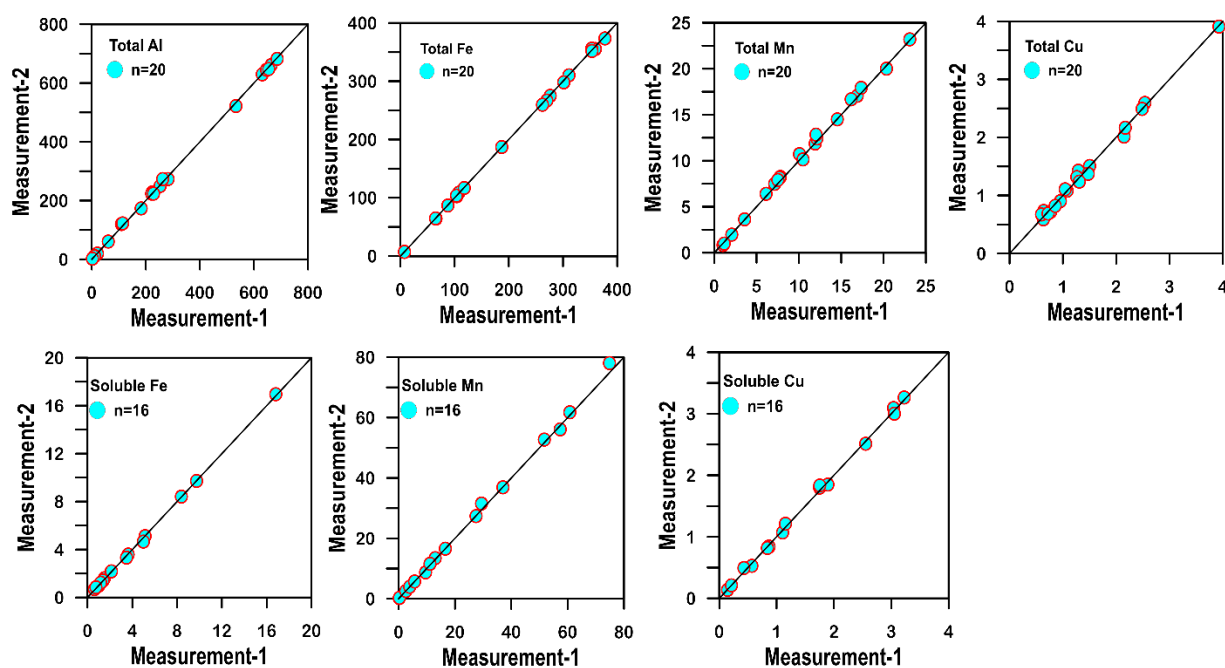


Fig-2.5 Repeat measurements of the Trace elements (ng mL^{-1}) in aerosol samples. Solid lines represent 1:1 correspondence between the data.

For WSOC measurement standardization was achieved using potassium hydrogen phthalate. A 5-point calibration curve was generated before each batch. WSOC was analyzed at 680°C following combustion catalytic oxidation method. Triplicate analysis was done for each sample. CRM (Deep Sea TOC standard; 41–44 µM) procured from the University of Miami was run in each batch, and the accuracy of the analysis was ± 1 µM. 25 µL of water extract was injected into the furnace packed with Pt catalyst at a temperature of 680 °C. The evolved CO₂ was measured using a non-dispersive infrared (NDIR) detector to assess total carbon (TC) content. Another aliquot of the solution (100 µL) was acidified with 25% phosphoric acid (25% H₃PO₄, vol/vol), and the evolved CO₂ was considered as inorganic carbon (IC). WSOC concentration was obtained by subtracting IC values from TC.

2.4 Calculations:

2.4.1 Dust estimation:

In this study, mineral dust concentration was calculated using Al concentration, presuming Al content is 8.04 % (wt %) similar to those in the upper continental crust (UCC) (McLennan,2001)

2.4.2 Enrichment factor:

In order to further substantiate the contribution of anthropogenic sources to the trace metal concentration during our study period, enrichment factor (EF)^{30,34} is calculated for all three metals. This is calculated by normalizing the ratio of the concentration of trace metals with respect to Al by their corresponding ratio in the crust (upper continental crust or UCC composition is used for normalization)⁷⁰ following the relation given as:

$$EF_{UCC} = (C_x / C_{Al})_{aerosol} / (C_x / C_{Al})_{UCC}$$

Here C_x is the concentration of element of interest other than Al. Typically any metal with EF ≥ 10 indicates a contribution from the pollution sources, however, those with EF <10 are considered mainly derived from continental sources.

2.4.3 Fractional solubility:

Fractional solubility (i.e. X% = [Xs/X.T.] x 100; X = Fe, Mn, and Cu) of trace metals vary significantly over space and time and depend on physicochemical processing during transport

as well as on the dust emission source

2.4.4 Dry deposition flux:

Bulk aerosol deposition is the sum of the dry deposition flux and wet deposition flux. We witnessed precipitation events (particularly during SSD-62) and wet deposition could be significant during monsoon months, thus, the dry deposition flux can be considered as a lower limit for the estimation of bulk deposition.

Dry deposition flux of different N-species, Fe, Mn, Cu are calculated along with total dust supply by using the relation given as:

$$F_{\text{dry}} = C_X * V_{\text{dx}}$$

Where C_X = concentration of element of interest X, V_{dx} = dry depositional velocity associated with respective element/trace elements (Buck et al., 2019; Panda et al., 2022). A previous study by Sarin et al., (1999) has given an upper limit for $V_d = 1 \text{ cm s}^{-1}$ based on the ^{210}Pb data over the Arabian Sea. Srinivas and Sarin (2013) collected size-segregated samples viz. PM_{10} and $\text{PM}_{2.5}$ over the BoB and used depositional velocity 1 cm s^{-1} and 0.1 cm s^{-1} respectively. For mineral dust and associated TEs like Fe and Mn, I used $V_d = 1 \text{ cm s}^{-1}$. However, presuming the dominance of Cu in fine fraction considering its major source from anthropogenic emissions, I used $V_d = 0.1 \text{ cm s}^{-1}$. The, nitrates are mostly associated with coarse fraction, however, ammonium and organic nitrogen being dominant in fine mode. Thus, I used 1 cm s^{-1} and 0.1 cm s^{-1} as V_d for coarse and fine mode nitrogen species, respectively.

2.5 Inter-calibration of soluble trace element analysis:

2.5.1 Brief Overview of difference in leaching protocol used for Milli-q/ultrapure water leach:

In order to access the differences in different ultrapure batch leaching techniques a well-designed stepwise evaluation procedure was planned and the same samples were divided into 5 subsamples and processed as per the following procedures.

Subsample 2a was leached using the protocol usually employed by the lab at Guangzhou Institute of Geochemistry (GIG) (Li et al., 2023; Zhang et al., 2022; Zhang et al., 2023). In brief,

the subsample was shredded and then immersed in 20 mL ultrapure water for 2 h, stirred using an orbital shaker; after that, the solution was filtered through a poly-ether-sulfone membrane syringe filter (with a pore size of 0.22 μm), acidified with a small volume of high-purity HNO_3 to contain 1% HNO_3 , and then analyzed using ICP-MS to determine dissolvable trace elements. Subsample 2b was leached using the same protocol as subsample 2a, and the purpose was to examine whether aerosol particles were homogeneously distributed on different subsamples and to assess the repeatability of the GIG leaching protocol.

Subsamples 3a, 3b and 3c were leached using the protocols typically used by ZJU (Zhejiang University, China), OUC (Ocean University of China, China) and NIO (National Institute of Oceanography, India), respectively, in order to compare solubilities determined by at GIG (Subsample 2a, Table-2.4) with those reported by the other three labs. Please note that subsamples 3c were leached and analyzed by NIO, while subsamples 3b and 3c were leached and analyzed at GIG (using the ZJU and OUC protocols, respectively).

Subsample 3a was leached at GIG using the ZJU protocol (Liu et al., 2021; Zhu et al., 2020). In brief, each subsample was shredded and immersed in 20 mL ultrapure water, and the aqueous mixture was sonicated for 1 h during which the water bath temperature was kept below 30 $^{\circ}\text{C}$; after that, the aqueous mixture was filtered using a poly-ether-sulfone membrane syringe filter (pore size: 0.22 μm) and acidified for later ICP-MS analysis. Subsample 3b was leaching at GIG using the OUC protocol (Shi et al., 2020), which is very similar to the ZJU method: the only difference is that the filter pore size was 0.45 μm for the OUC protocol and 0.22 μm for the ZJU protocol.

Subsample 3c was leached and analyzed at NIO using the NIO protocol (Panda et al., 2022). In brief, each subsample was shredded and placed into a pre-cleaned Savillex vial (50 mL); after that, the vial was filled with 20 mL ultrapure water, capped, and ultrasonicate for 30 minutes to agitate the aqueous mixture (but in 2 cycles with 15 min for each cycle, in order to maintain the water bath at room temperature). The aqueous mixture was then filtered through a Whatman PVDF syringe filter (pore size: 0.2 μm), and then acidified with HNO_3 (2%) for later high-resolution ICP-MS analysis (Nu Instruments, Attom ES). These details already discussed in section 2.3.3.

Table 2.4 Overview of protocols used to digest and leach subsamples examined. GIG: Guangzhou Institute of Geochemistry (China); ZJU: Zhejiang University (China); OUC: Ocean University of China (China); NIO: CSIR-National Institute of Oceanography (Goa, India).

Subsample code	Agitation	Contact time (h)	Filter pore size (µm)	Lab	References
1	digestion			GIG	Total trace metal
2a	shaking	2	0.22	GIG	Zhang et al. (2022)
3a	sonication	1	0.22	ZJU	Liu et al. (2021)
3b	sonication	1	0.45	OUC	Shi et al. (2020)
3c	sonication	0.5	0.2	NIO	Panda et al. (2022)

GIG: Guangzhou Institute of Geochemistry (China)

ZJU: Zhejiang University (China)

OUC: Ocean University of China (China)

NIO: CSIR-National Institute of Oceanography (Goa, India).

2.5.2 Outcome of inter-calibration study:

To summarize, although the four ultrapure water batch leaching protocols examined differ in agitation method, contact time and/or filter pore size (GIG: shaking, 2 h contact time, 0.22 µm filter pore size; ZJU: sonication, 1 h contact time, 0.22 µm filter pore size; OUC: sonication, 1 h contact time, 0.45 µm filter pore size; NIO: sonication, 1 h contact time, 0.22 µm filter pore size), for the nine elements (including Fe, Al, As, Cr, Cu, Mn, Pb, V and Zn) examined in this intercomparison study, their solubilities determined using the four protocols in general show good agreement. Ultrapure water/Milli-q batch leaching is widely used in atmospheric research to determine aerosol trace element solubilities, and the specific leaching protocols used in different labs can still vary in agitation methods, contact time, and filter pore size. It is yet unclear to what extent the difference in these experimental parameters would affect the reported aerosol trace element solubilities; in other words, it remains to be examined whether solubilities reported by previous studies which used different ultrapure water batch leaching protocols are comparable.

the effects of agitation methods, filter pore size and contact time on the reported solubilities of nine aerosol trace elements, including Fe, Al, As, Cr, Cu, Mn, Pb, V and Zn was examined. It was found that the difference in agitation methods (shaking vs. sonication), filter pore size (0.22 vs. 0.45 µm), and contact time (1 vs. 2 h) only led to the small and sometimes insignificant difference in the reported solubilities. The aerosol trace element solubilities were determined using four widely used ultrapure water leaching protocols which differ in agitation methods,

filter pore size and/or contact time, and in general, the solubilities determined using the four protocols were found to be in good agreement. Therefore, aerosol trace element solubilities determined in previous studies using ultrapure water batch leaching may be comparable.

Aerosol trace element solubility is an operationally defined term (Baker and Croot, 2010; Meskhidze et al., 2019), and strongly depends on the leaching protocol employed. A number of leaching protocols have been used in previous studies to extract dissolvable trace elements, making it very challenging to compare solubilities reported in different studies (Perron et al., 2024). In order to reduce uncertainties in aerosol trace element solubilities, it is necessary to formulate standard operating procedures for frequently used aerosol leaching protocols. The current work suggests that although ultrapure water batch leaching protocols used by different labs vary in specific experimental parameters, the determined aerosol trace element solubilities show good agreement; furthermore, ultrapure water batch leaching is operationally simple and does not introduce any other chemical species which may interfere analysis of water-soluble inorganic ions and organics. Therefore, It was recommend ultrapure water batch leaching to be one of the reference leaching schemes. Before a standard operating procedure can be formulated for ultrapure water batch leaching, the community will need to reach a consensus on agitation methods, contact time and filter pore size, and further intercomparison studies, preferentially with more labs involved, will be very helpful.

Chapter 3

*Seasonal variability in atmospheric nutrient
distribution and their deposition fluxes over
the Arabian Sea*

3.1 Introduction:

Atmospheric aerosols serve as a potential nutrient source for remote open oceans and oligotrophic waters outside of upwelling zones, substantially modulating primary productivity (Jickells et al., 2005, Boyd et al., 2010; Mahowald et al., 2018; Hamilton et al., 2023). Recent scenarios of global warming have led to increased emissions of mineral dust and anthropogenic aerosols, driven by urbanization and desertification (Ginoux et al., 2012). These changes have resulted in higher atmospheric aerosol concentrations and dust emissions, as evidenced by the increased aerosol optical depth (AOD) (Krishna Moorthy et al., 2013; Srivastava, 2017). Mineral dust is one of the largest components of atmospheric aerosol derived from the continent, with an annual emission of 1000 to 2150 Tg (Choobari et al., 2014; Mahowald et al., 2005; Zender et al., 2004; Kok et al., 2021). Deposition (via wet and dry) of mineral dust is an important pathway for the supply of a variety of trace elements and associated nutrients to the coastal as well as open oceanic regions (Mahowald et al., 2005; Luo et al., 2008; Kumar et al., 2010; Schulz et al., 2012; Baker et al., 2020). Among these metals, a set of bio-active trace metals/trace elements (Fe, Mn, Cu) are essential for marine microbial metabolism (Martin et al., 1990; Morel and Price, 2003; Jickells et al., 2005; Mahowald et al., 2005 and 2018; Tagliabue et al., 2017; Lohan and Tagliabue, 2018), which contribute to phytoplankton abundance and proliferation, however sometimes they act as toxicants if the concentration is higher than optimum requirement (Paytan et al., 2009). Thus, dust deposition is one of the key controlling factors for phytoplankton primary productivity and hence biogeochemical cycling of carbon (Anderson, 2020; Guieu et al., 2019; Jickells et al., 2005; Mahowald et al., 2018). In addition to dust, anthropogenic emissions from biomass burning and industrial emissions are significant suppliers of trace elements as well as nutrient species like nitrate and ammonium (Kumar et al., 2010; Srinivas et al., 2012; Mahowald et al., 2018; Hamilton et al., 2021; Perron et al., 2022; Panda et al., 2024). Hence, it is important not only to quantify dust and associated trace elements but also all trace elements present in aerosols.

The soluble fraction of trace elements (TEs) can be considered as bio-available fractions in aerosols because this is readily available for cellular processes of microorganisms (Morel and Price, 2003; Shelley et al., 2018; Perron et al., 2020). The quantification of fractional solubility of trace elements in aerosol is crucial to constrain their impact on the surface water biogeochemical processes. Atmospheric nutrient and their fractional solubility are widely studied and reported from Atlantic (Baker et al., 2006a, 2006b, 2013 and 2020; Trapp et al., 2010; Buck et al., 2010; Powell et al., 2015; Chance et al., 2015), Pacific (Buck et al., 2006 and

2013; Hsu et al., 2010; Gao et al., 2014; Baker et al., 2016), as well as from the North Indian Ocean (relatively few as compared to other oceans Siefert et al., 1999; Johansen and Hoffmann, 2003; Kumar et al., 2010; Srinivas et al., 2012; Srinivas et al., 2014; Panda et al., 2022, 2024). Out of all trace elements, Fe receives special attention due to its behavior as a limiting nutrient in oligotrophic as well as high nutrient low chlorophyll region (Martin et al., 1991; Moore et al., 2001; Moffett et al., 2007; Browning et al., 2017; Holmes et al., 2019; Zhang et al., 2020). A large variability (in the range of 0.01 to 90 %) have been reported for fractional solubility of Fe over the Globe (Sholkovitz et al., 2012; Mahowald et al., 2018) mainly attributed to variability in mineral dust composition and concentration, particle size, chemical processing during long-range transport, different leaching protocol (Zhuang et al., 1992; Spokes and Jickells, 1995; Meskhidze et al., 2003; Bonnet and Guieu, 2004; Baker and Jickells, 2006; Buck et al., 2006 and 2013; Solmon et al., 2009; Aguilar-Islas et al., 2010; Kumar et al., 2010; Trapp et al., 2010; Shi et al., 2011; Sholkovitz et al., 2012; Srinivas et al., 2012; Gao et al., 2014; Chance et al., 2015; Baker et al., 2017 and 2020; Perron et al., 2020; Zhang et al. 2022). In contrast to Fe solubility, a very limited study is reported for fractional solubility of Cu (Paytan et al., 2009; Hsu et al., 2010; Sholkovitz et al., 2010; Gao et al., 2014; Jordi et al., 2012; Shelley et al., 2018), Mn (Baker et al., 2006b; Jickells et al., 2016; Shelley et al., 2018) and other trace metals (Baker et al., 2020) over the oceanic regions.

Arabian Sea (AS), located in the western part of the North Indian Ocean, is strongly impacted by dust deposition during southwest monsoon (Monsoon; Tindale and Pease, 1999; Pease et al., 1998; Nair, 2006; Ramaswamy et al., 2017; Aswini et al., 2020; Suresh et al., 2021) months. The transported dust from the Arabian Peninsula (Ramaswamy et al., 2017) and Northeast African regions (Léon and Legrand, 2003; Suresh et al., 2021), can supply significant amounts of trace elements to the surface waters of the Arabian Sea, particularly during Monsoon. In contrast to the southwest monsoon, the northeast monsoon remains active from December to February every year inducing wind-driven mixing over the northern Arabian Sea which enhances primary productivity along with episodic dust storm events that provide suitable conditions for *Noctiluca scintillans* and phytoplankton blooms (Madhupratap et al., 1996; Patra et al., 2007; Banerjee and Prasanna Kumar, 2014; Gomes et al., 2014). North-east monsoon winds flowing from the Indian subcontinent towards the Arabian Sea could potentially transport winter-time emissions from biomass burning and other anthropogenic activities that occur over the Indo-Gangetic Plain (IGP). The anthropogenic emission can be a possible source of nutrients during the winter period additionally the acid processing of dust during long-range transport

from IGP to AS can potentially alter the bioavailability of TEs. In support of this a recent model-based study by Sridevi and Sarma (2022) explained higher AOD over Arabian sea due to anthropogenic emission and significantly strengthening convective mixing. Still, today the contribution of atmospheric nutrients over the Arabian Sea is the least studied.

Information on trace element composition and their bioavailability in atmospheric aerosols are important to understanding their impact on surface water post-deposition (Baker and Croot, 2010; Baker et al., 2020). So far, very few studies have been reported on trace metal composition (Chester et al., 1991; Pease et al., 1998) and their fractional solubility (Siefert et al., 1999; Johansen and Hoffmann, 2003; Srinivas et al., 2012) over the Arabian Sea. In particular, Siefert et al., (1999), have reported on total and soluble/labile Fe (II) during monsoons and Johansen and Hoffmann, (2003) during winter. These studies were restricted to the western and central Arabian Sea. In addition, several model-based studies have highlighted the significance of dust deposition and its impact on primary productivity during Monsoon (Wiggert and Murtugudde, 2005; Wiggert et al., 2007; Liao et al., 2016; Guieu et al., 2019). Very recently, Guieu et al., (2019), have shown a decrease in net primary productivity by 30 % in the absence of dissolved Fe deposition on an annual scale, which further decreases to 50 % during the upwelling period. Considering their role and importance of atmospheric nutrients in the marine region, aerosol samples were collected from AS during the Monsoon and Winter seasons and measured inorganic nitrogen species (macro-nutrients) and micro-nutrients/TEs composition (Fe, Mn and Cu) associated with transported mineral dust. We tried to understand their spatial distribution as well as their fractional solubility over a wider area of the Arabian Sea during Monsoon months of the year 2017 and 2018 and Winter of 2019. We further assess variation in fractional solubility of these bioactive metals/TEs in relevance to the dust source region and their chemical processing during long-range transport. We have also quantified the deposition fluxes of these trace elements to the Arabian Sea which have an important implication on the primary productivity during the study period.

3.2 Results and Discussion:

3.2.1 Cruise tracks and wind patterns during the study Period:

Aerosol samples were collected onboard the research vessel Sindhu Sadhana (SSD) in the years 2017 and 2018 during August, representing monsoon samples and December 2019 representative samples of winter. In 2017, the cruise was undertaken from 05-31 August (SSD-

040), from 02-30 August in 2018 (SSD-055) and from 7 December 2019 to 5 January 2020 (SSD-068) following similar cruise tracks shown in Fig-3.1a,b. It is important to note that both cruises were planned with the aim of capturing biogeochemical features of the AS during Monsoon and Winter, similar to those covered during the Joint Global Ocean Flux Studies (JGOFS) experiment, to compare possible changes in the last two decades to the present day scenario. All 3 cruises started from Goa (73.79 °E, 15.46 °N) to the southern Arabian Sea down to 8°N through the coastal region of Goa, Karnataka and Kerala. Subsequently, it sailed toward the northern Arabian Sea following the coastal waters from Kerala up to Gujarat (21°N). From the northern Arabian Sea (21°N, 69.13°E), the cruise moved towards the west and sailed up to 64°E, then towards the south, continuing up to 11.5°N. Subsequently, the ship took an eastward direction and returned to the Goa port (Fig-3.1a, b). During the monsoon, 22 and 21 aerosol samples (total suspended particulates (TSP) were collected, during SSD-40 and SSD-55 respectively 22 Size segregated PM₁₀ and PM_{2.5} samples were collected during SSD-68, along the cruise track (shown in Fig. 1a,b) (Table 3.1).

This study, aimed to assess the spatial distribution of aerosol composition and thus we divided our samples based on the geographical location along which samples were collected. The AS experiences a strong monsoon wind reversal, which changes the dust source during different seasons (Kumar et al., 2020). During the SW monsoon (monsoon) axis of Findlater Jet (FLJ) remains within 18-16°N over the AS (Chowdhury et al., 2023) and in NE monsoon (winter) AS experiences wind-driven convective mixing which intensifies mixed layer depth (MLD) from 22-15°N (Madhupratap et al., 1996). To understand the atmospheric nutrient supply and its importance in biogeochemistry, the AS is divided into two regions 1- Northern Arabian Sea (above 16°N latitude), where wind-driven convective mixing is high in winter and experiences excessive wind stress due to FLJ during monsoon. 2- Southern Arabian Sea (below 16°N latitude) where winter MLD is shorter and lies below FLJ axes. These two divisions are shown in Fig-3.1a and 1b where the blue polygon represents the northern AS and the yellow polygon represents the southern Arabian Sea. In Fig-3.1a Air mass back trajectory at 500m height is shown in red lines along the summer Shamal wind and Levar wind, these wind systems potentially carry mineral dust from NE Africa and the Middle East region (Suresh et al., 2021, Singh et al., 2023) during monsoon seasons. However, in winter time, the majority of the wind is from southern Asia (Fig-3.1b). These winter NE-Monsoon winds can transport winter-time anthropogenic emissions from IGP, coastal plains of India and Pakistan and some wind also showed their origin from south east Asia (Fig-3.1b).

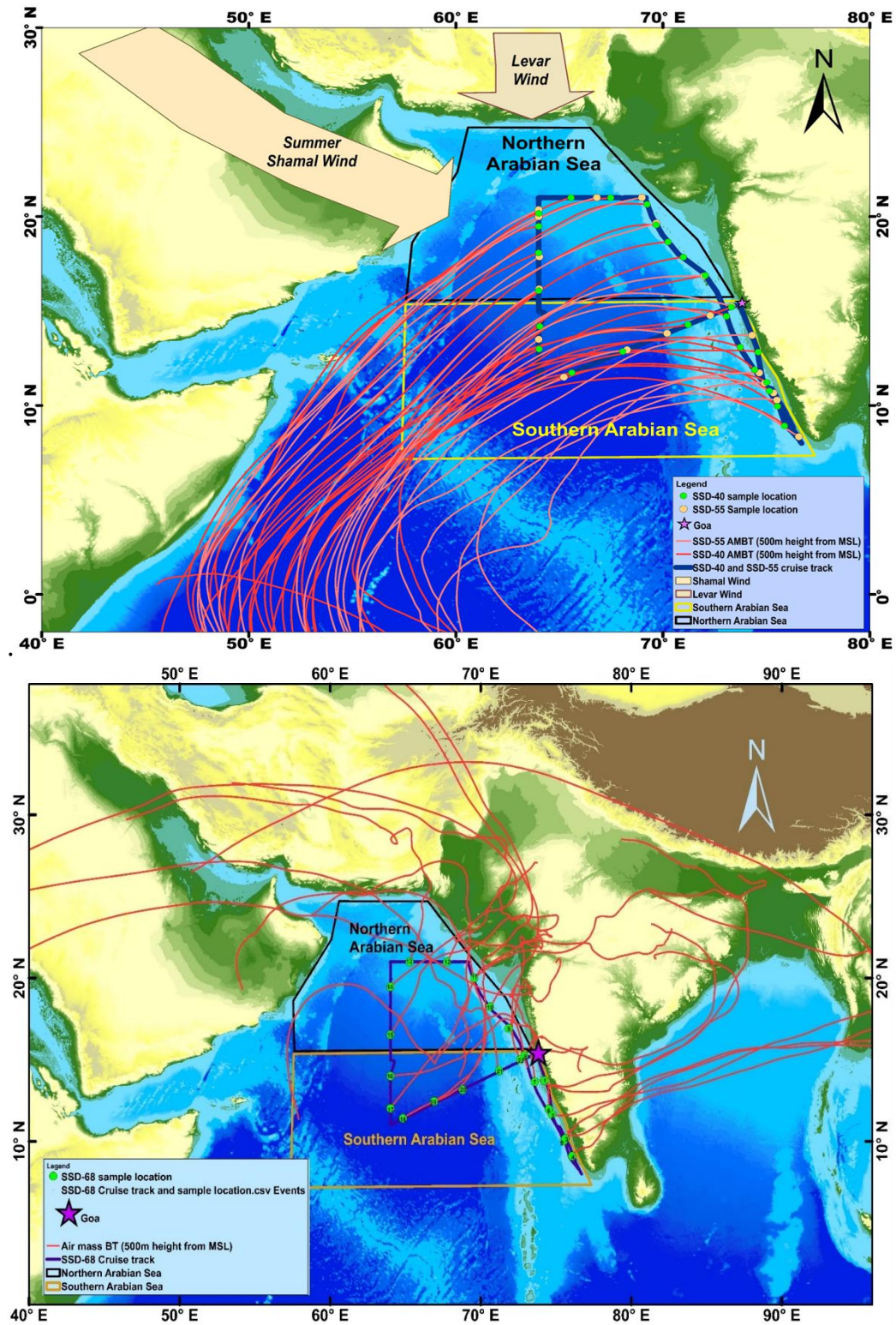


Fig-3.1 Cruise tracks undertaken in the Arabian Sea (a) SSD-40 and SSD-55 (Monsoon cruises) and midpoints of sample locations green and yellow respectively (b) SSD-68 (Winter Season) and midpoints of sample location green. Red lines in both the figures represent AMBT at 500m height. Solid blue and yellow polygons represent the northern and southern Arabian Sea respectively (details in the main text Section 3.2.1).

Table 3.1 Sampling dates, start and end locations of each sample over the Arabian Sea during SSD-40, SSD-55 and SSD-68.

SSD-40						
Sample-Id	Sampling Dates (DD/MM/YYYY)		Latitude (in °N)	Longitude (in °E)	Latitude (in °N)	Longitude (in °E)
	Start Date	End Date	Start		End	
SSD-40-B-T-01	05/08/2017	05/08/2017	13.36	74.43	12.29	74.65
SSD-40-B-T-02	05/08/2017	06/08/2017	12.26	74.66	10.63	75.39
SSD-40-B-T-03	07/08/2017	08/08/2017	8.47	76.36	9.37	75.28
SSD-40-B-T-04	08/08/2017	08/08/2017	9.39	75.79	10.52	75.28
SSD-40-B-T-05	08/08/2017	09/08/2017	10.52	75.28	11.00	75.00
SSD-40-B-T-06	10/08/2017	10/8/2017	11.41	74.73	12.35	74.13
SSD-40-B-T-07	10/08/2017	11/8/2017	12.49	74.04	13.68	73.44
SSD-40-B-T-08	11/08/2017	12/8/2017	13.69	73.43	15.74	72.11
SSD-40-B-T-09	12/08/2017	13/8/2017	16.77	72.12	17.00	71.98
SSD-40-B-T-10	13/08/2017	14/08/2017	17.46	71.41	18.24	70.57
SSD-40-B-T-11	14/08/2017	14/08/2017	18.28	70.53	19.03	69.97
SSD-40-B-T-12	14/08/2017	15/08/2017	19.03	69.97	19.93	69.51
SSD-40-B-T-13	15/08/2017	16/08/2017	19.94	69.49	21.00	69.10
SSD-40-B-T-14	17/08/2017	18/08/2017	20.99	68.34	21.00	66.62
SSD-40-B-T-15	18/08/2017	19/08/2017	21.00	66.62	21.00	64.51
SSD-40-B-T-16	19/08/2017	20/08/2017	20.36	63.99	19.97	64.02
SSD-40-B-T-17	20/08/2017	21/08/2017	19.97	64.02	18.99	63.99
SSD-40-B-T-18	21/08/2017	22/08/2017	18.99	63.99	17.16	64.00
SSD-40-B-T-19	22/08/2017	23/08/2017	17.16	64.00	14.99	64.00
SSD-40-B-T-20	24/08/2017	25/08/2017	14.37	64.11	14.00	64.00
SSD-40-B-T-21	25/08/2017	26/08/2017	14.00	64.00	11.97	64.05
SSD-40-B-T-22	27/08/2017	28/08/2017	11.31	64.69	12.16	66.52
SSD-40-B-T-23	28/08/2017	29/08/2017	12.16	66.52	13.55	69.61
SSD-40-B-T-24	29/08/2017	30/08/2017	13.55	69.61	15.00	72.83
SSD-40-B-T-25	30/08/2017	31/08/2017	15.00	72.83	15.41	73.79
SSD-55						
Sample-Id	Sampling Dates (DD/MM/YYYY)		Latitude (in °N)	Longitude (in °E)	Latitude (in °N)	Longitude (in °E)
	Start Date	End Date	Start		End	
SSD-55-B-TQ-01	02/08/2018	03/08/2018	15.37	73.67	12.06	75.03
SSD-55-B-TQ-02	03/08/2018	04/08/2018	12.20	75.04	8.71	76.49
SSD-55-B-TQ-03	04/08/2018	05/08/2018	8.69	76.51	8.00	76.69
SSD-55-B-TQ-04	05/08/2018	06/08/2018	10.28	75.51	10.29	75.51
SSD-55-B-TQ-05	06/08/2018	08/08/2018	10.26	75.5	13.21	73.81
SSD-55-B-TQ-06	08/08/2018	09/08/2018	11.18	74.99	11.19	74.98
SSD-55-B-TQ-07	09/08/2018	10/08/2018	17.35	71.56	16.36	72.41
SSD-55-B-TQ-08	10/08/2018	12/8/2018	18.36	70.50	21.00	69.19

SSD-55-B-TQ-09	13/08/2018	15/08/2018	21.00	69.14	21.01	68.84
SSD-55-TQ-10	15/08/2018	17/08/2018	21.01	68.51	21.01	65.11
<i>Table 3.1 continue</i>						
SSD-55-TQ-11	17/08/2018	18/08/2018	21.01	65.06	20.00	64.00
SSD-55-TQ-12	18/08/2018	19/08/2018	20.00	64.00	18.37	64.14
SSD-55-TQ-13	19/08/2018	20/08/2018	18.36	64.14	17.37	64.05
SSD-55-TQ-14	20/08/2018	22/08/2018	17.34	64.05	15.00	64.00
SSD-55-TQ-15	22/08/2018	25/08/2018	15.00	64.00	12.00	64.00
SSD-55-TQ-16	25/08/2018	27/08/2018	12.00	64.00	12.11	66.44
SSD-55-TQ-17	27/08/2018	28/08/2018	12.12	66.46	13.77	70.09
SSD-55-TQ-18	28/08/2018	28/08/2018	13.29	69.03	14.35	71.37
SSD-55-TQ-19	28/08/2018	29/08/2018	14.36	71.39	14.35	71.37
SSD-55-TQ-20	29/08/2018	29/08/2018	14.49	71.68	15.04	72.9
SSD-55-TQ-21	29/08/2018	30/08/2018	15.05	72.92	15.46	73.72
SSD-68*						
Sample-Id	Sampling Dates (DD/MM/YYYY)		Latitude (in °N)	Longitude (in °E)	Latitude (in °N)	Longitude (in °E)
	Start Date	End Date	Start		End	
SSD-68-T-01	07/12/2019	08/12/2019	15.09	12.35	73.54	74.31
SSD-68-T-02	08/12/2019	09/12/2019	12.28	11.02	74.35	75.10
SSD-68-T-03	09/12/2019	09/12/2019	10.92	9.16	75.19	75.87
SSD-68-T-04	09/12/2019	10/12/2019	9.16	9.97	75.86	75.97
SSD-68-T-05	12/10/2019	11/12/2019	8.94	9.26	75.98	76.15
SSD-68-T-06	11/12/2019	12/12/2019	9.33	11.00	76.10	75.12
SSD-68-T-07	12/12/2019	13/12/2019	11.14	12.82	75.02	74.00
SSD-68-T-08	13/12/2019	13/12/2019	12.82	14.49	74.00	73.18
SSD-68-T-09	13/12/2019	15/12/2019	14.50	15.99	73.17	72.62
SSD-68-T-10	15/12/2019	16/12/2019	16.21	17.63	72.48	71.21
SSD-68-T-11	16/12/2019	16/12/2019	17.66	18.83	71.17	70.08
SSD-68-T-12	16/12/2019	18/12/2019	19.01	21.00	70.01	69.12
SSD-68-T-13	18/12/2019	20/12/2019	21.01	20.98	69.06	66.47
SSD-68-T-14	20/12/2019	21/12/2019	20.98	21.00	66.43	64.10
SSD-68-T-15	22/12/2019	23/12/2019	20.94	18.00	64.00	64.00
SSD-68-T-16	24/12/2019	25/12/2019	17.96	15.10	64.00	64.00
SSD-68-T-17	26/12/2019	27/12/2019	15.00	13.00	64.00	64.00
SSD-68-T-18	29/12/2019	30/12/2019	13.00	11.03	64.00	64.00
SSD-68-T-19	01/12/2019	01/01/2020	11.00	11.83	64.01	65.64
SSD-68-T-20	01/01/2020	01/01/2020	11.83	13.06	65.66	68.14
SSD-68-T-21	01/01/2020	02/01/2020	13.07	14.85	68.17	68.94
SSD-68-T-22	02/01/2020	03/01/2020	14.21	14.85	70.47	71.75
SSD-68-T-23	02/01/2020	05/01/2020	15.00	15.00	72.02	73.21

*During SSD-68 both PM₁₀ and PM_{2.5} sample collected parallelly.

3.2.2 Macro-nutrient over the Arabian Sea:

The inorganic nitrogen species over the Arabian Sea show wide ranges during both seasons.

Mass concentrations of inorganic nitrogen species varied as 3.3-207.6 nmol m⁻³ and 8.7-232.6 nmol m⁻³ for NO₃⁻, 0.2 – 43.0 nmol m⁻³ for NH₄⁺ during monsoon and winter seasons respectively. The average concentration of NO₃⁻ for monsoon and winter were 28.3 ± 36.4 nmol m⁻³ and 61.6 ± 52.8 nmol m⁻³ respectively (Table 3.2). The North Arabian Sea receives higher nitrate than the southern AS during both seasons (Fig-3.2a). This may be due to anthropogenic emissions from the surrounding continental region, which includes a mega-city like Mumbai, but the correlation between nss-SO₄²⁻ and NO₃⁻ (Fig-3.3b) shows a poor correlation indicating both originated from different sources, unlike previous observations over the Indian Ocean (Panda et al., 2024).

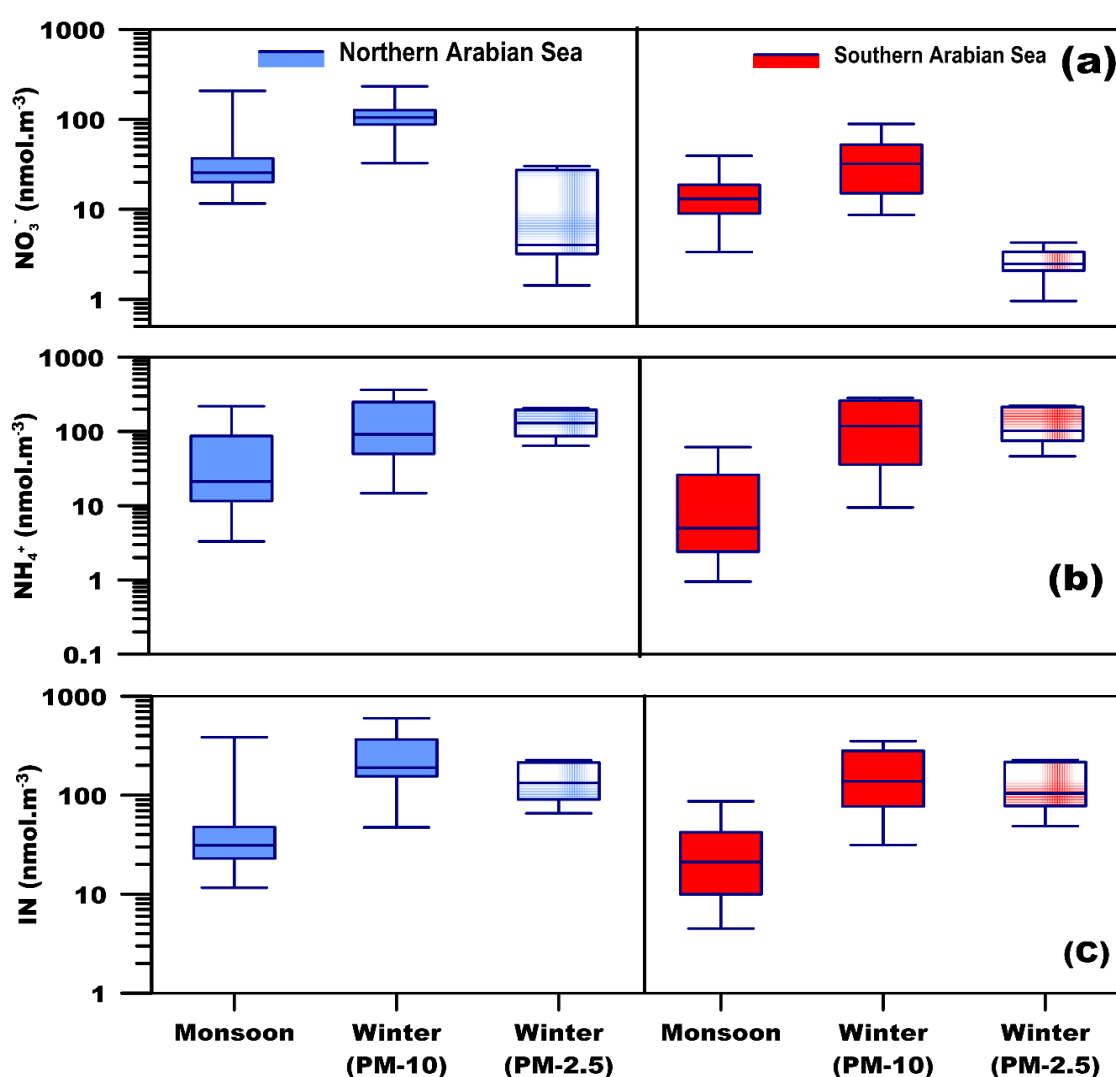


Fig-3.2 Spatial and seasonal variation of inorganic nitrogen species (a) Nitrate, (b) Ammonium, (c) Inorganic nitrogen over the Arabian sea.

Aswini et al. (2022) highlighted marine nitrate emission during the monsoon season over AS, which might be an additional source of nitrate during the monsoon, while Bikkina et al.

(2021) suggested the possibility of heterogeneous reactive uptake of nitrate by dust during winter. Like nitrate, NH_4^+ shows a higher concentration of $138.8 \pm 107.0 \text{ nmol m}^{-3}$ in winter and $26.8 \pm 43.7 \text{ nmol m}^{-3}$ (Table 3.2) in monsoon, indicating the dominance of continental influence or biomass burning during winter causing a multifold increase in NH_4^+ supply. This observation is also supported by the correlation between nss-K^+ (an indicator of biomass burning) and NH_4^+ (Fig-3.3a) similar to previous observations over the Indian Ocean (Panda et al., 2024) and Arabian Sea (Bikkina et al., 2021). In winter the widespread use of fertilizer, animal livestock and burning is prominent in North India during October (Rastogi et al., 2014; Bikkina et al., 2021) and has significant potential to impact the aerosol loading, which could be responsible for high NH_4^+ concentration in aerosol (Bhuvaneshwari et al., 2019; Pohl et al., 2023). During the winter season impact of aerosol size on nutrient species was also assessed, It was observed that nitrate mainly existed in coarse mode (PM_{10}) but NH_4^+ dominated derived from fine aerosol ($\text{PM}_{2.5}$) (Fig-3.2a,b).

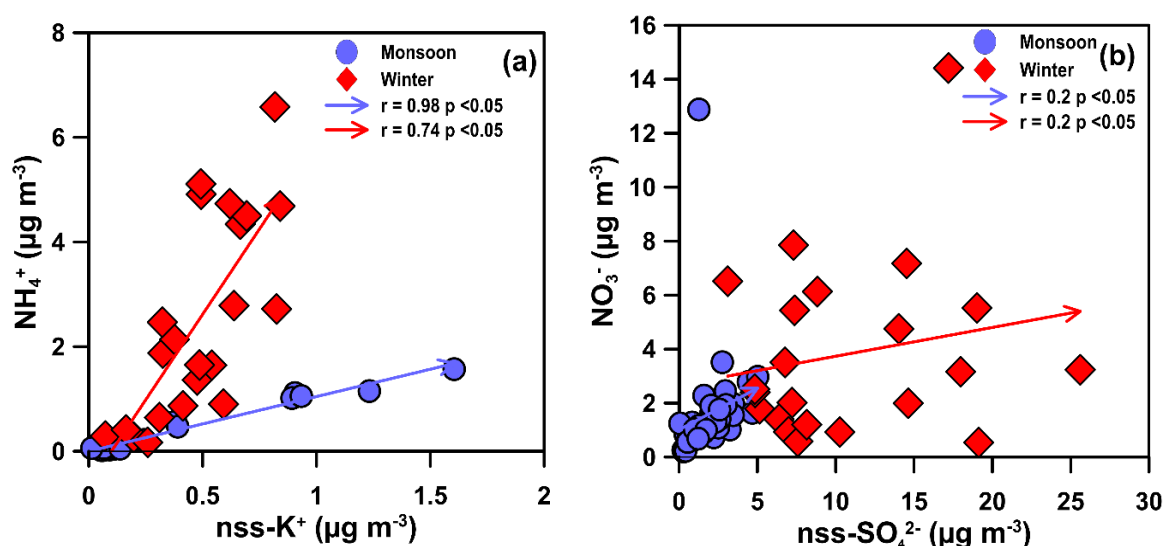


Fig-3.3 Correlation plot between (a) non sea-salt potassium and ammonium, (b) non sea-salt sulphate and nitrate.

Inorganic nitrogen ($\text{IN} = \text{NH}_4^+ + \text{NO}_3^-$) shows a relatively higher concentration of $200.4 \pm 138.8 \text{ nmol m}^{-3}$ during winter in contrast to the monsoon $45.2 \pm 67.9 \text{ nmol m}^{-3}$. The NH_4^+ is a major contributor to IN accounting for >50% during winter but accounts for up to 37% in the monsoon, which makes NO_3^- a major contributor to IN species. The dominance of NH_4^+ in winter indicates that inorganic nitrogen is primarily influenced by nitrogen input from human activities, such as the biomass burning large-scale application of fertilizers (ammonia and urea-based).

3.2.3 Dust and other Trace Elements over the Arabian Sea:

The Arabian Sea receives $16.3 \pm 13.3 \mu\text{g}/\text{m}^3$ and $12.9 \pm 6.2 \mu\text{g}/\text{m}^3$ dust during the monsoon and winter seasons respectively (Fig-3.4, Table 3.2). During the winter season, two dust storms were encountered whose concentrations were 5 times higher than the average concentration. These dust storm concentrations are not included in the current data average calculation and flux discussed in the upcoming section. The North Arabian Sea receives higher dust compared to southern AS during both the season (Fig-3.4a) proximity from the source and favourable wind patterns transport ample amounts of dust from the Middle East, Iran and Thar regions to the study area. Similar to the current observation, Tindale and Pease also observed higher dust transport from the western continent of AS via low-level jet to northern AS (which is partly considered as central AS by Tindale and Pease) during the Monsoon. Suresh et al. (2021) and Singh et al. (2023) also identified the western Arabian Sea region (NE-Africa, Oman, and Iran) as the major source of dust during the Monsoon season by using Sr-Nd isotope as a proxy. In addition to spatial variation, fine aerosol samples ($\text{PM}_{2.5}$) were also collected during the winter season.

The fine dust contribution to PM_{10} over AS varies from 2.2-32.8% and interestingly the lowest fine dust contribution was observed over the northern Arabian Sea and the highest fine dust contribution was observed over the southern Arabian Sea. As discussed previously in this section, NE-monsoon transports an ample amount of dust to the AS. However, due to the atmospheric removal of coarse dust (PM_{10}) in the northern Arabian Sea and long-range transport of fine dust ($\text{PM}_{2.5}$) the total dust concentration decreases over southern AS, while the relative abundance of fine dust increases.

The mass concentrations of Fe_T over the study periods ranged from $1.6 - 50.7 \text{ ng m}^{-3}$ with a mean value of $15.7 \pm 13.0 \text{ nmol m}^{-3}$ in monsoon and $16.1 \pm 10.4 \text{ nmol m}^{-3}$ in winter similar to dust (Fig-3.4; Table 3.2). The observed mean Fe_T concentrations in this study are much higher than other marine atmospheres, ranging from 28.4 ng m^{-3} over the Pacific Ocean (Buck et al., 2013) and lower compared to the Atlantic Ocean (Fe_T range = $0.185\text{--}5650 \text{ ng m}^{-3}$) especially sample collected over the eastern Atlantic (Shelley et al., 2018) and over the East China Sea (410 ng m^{-3} , Hsu et al., 2010). However, it shows lower values with previously reported Fe_T concentration over the Arabian Sea BDL to $> 7000 \text{ ng m}^{-3}$ during monsoon (Siefert et al., 1999) but higher than the study conducted during winter $0.19\text{--}0.89 \text{ ng m}^{-3}$ by Johansen and Hoffmann (2003) and summer $92\text{--}1010 \text{ ng m}^{-3}$ Srinivas et al. (2012). Winter season Fe_T concentration in

this study matches well with US JGOFS 1995 cruises data (Tindale and Pease 1999) where Fe_T values vary $0.15\text{--}2.64\ \mu\text{g m}^{-3}$ (mean: $0.88\ \mu\text{g m}^{-3}$) but are higher than summer (June–September which referred as the monsoon in this study). In both seasons, the northern Arabian Sea receives higher Fe_T compared to the southern Arabian Sea (Fig-3.4b). In the context of particle size, the northern Arabian Sea is dominated by coarse particles, while the southern Arabian Sea is dominated by fine aerosol particles similar to dust (Fig-3.4b).

Table 3.2 Seasonal range and mean $\pm$ standard deviation of dust, trace elements and other chemical species.

	Units	Monsoon		Winter	
		Range	Mean $\pm$ SD	Range	Mean $\pm$ SD
Dust	$\mu\text{g/m}^3$	2.7-67.7	16.3 ± 13.3	5.2-81.7 *	12.9 ± 6.2
NO_3^-	nmol/m^3	3.3-207.6	28.3 ± 36.4	8.7-232.6	61.6 ± 52.8
NH_4^+		0.9-218.3	26.8 ± 43.7	9.5-365.0	138.8 ± 107.0
IN		4.5-384.3	45.2 ± 67.9	31.4-597.6	200.4 ± 138.8
nss-K^+		0.1-112.1	16.8 ± 24.0	1.9-21.5	12.3 ± 5.6
nss- SO_4^{2-}		0.3-73.0	21.4 ± 14.9	32.3-266.5	112.1 ± 62.5
Total Acid		6.8-312.0	69.3 ± 57.1	136.0-590.6	285.8 ± 145.0
Fe_T		1.6-50.7	15.7 ± 13.0	2.9-45.0	16.1 ± 10.4
Mn_T	pmol/m^3	71.1-3283.4	818.2 ± 734.4	146.5-1601.3	556.9 ± 381.8
Cu_T		22.7-231.5	88.5 ± 58.8	40.0-588.0	136.8 ± 122.8
Fe_s		0.6-587.1	114.6 ± 166.1	88.1-1853.8	840.5 ± 571.8
Mn_s		23.9-1236.0	286.3 ± 267.8	61.3-1551.7	383.4 ± 311.2
Cu_s		2.2-125.9	20.1 ± 20.8	14.2-199.0	72.3 ± 54.0
Fe%	%	0.01-3.6	0.8 ± 0.9	0.4-13.9	5.8 ± 3.3
Mn%		6.2-87.5	42.9 ± 24.4	37.2-97.1	69.0 ± 16.0
Cu%		4.1-78.0	26.1 ± 19.5	20.4-94.1	56.3 ± 18.9

*Winter dust concentration **range** includes two dust storm samples but is not included in the average dust concentration calculation.

Unlike Fe_T , Mn_T concentration was higher during monsoon season $818.2 \pm 734.4\ \text{pmol m}^{-3}$ than in winter $556.9 \pm 381.8\ \text{pmol m}^{-3}$ (Fig-3.4, Table 3.2). Interestingly, Mn_T shows an EF >10 during the monsoon but <10 during winter. Mn_T is primarily derived from natural sources (Mahowald et al., 2018). It was found that carbonates present in northeastern Africa and the Arabian Peninsula are naturally enriched with Mn_T (Taylor et al., 2005), but those from the Thar desert are devoid of such naturally enriched Mn-bearing carbonates (Yadav and Rajamani, 2004). The prevailing southwest winds during monsoon transport the naturally enriched Mn_T to

the AS (Panda et al., 2022). The observed Mn_T concentration is also similar to the previous Srinivas et al. (2013) over the Bay of Bengal and Powell (2015) observation over the eastern Atlantic region (median = >700 pmol m^{-3} when winds are derived from the Sahara). Other remote locations, like the Southern Atlantic Ocean, Pacific Ocean and East China Sea, receive much lower Mn in comparison to the BoB irrespective of season (Chance et al., 2015; Buck et al., 2013; Hsu et al., 2010).

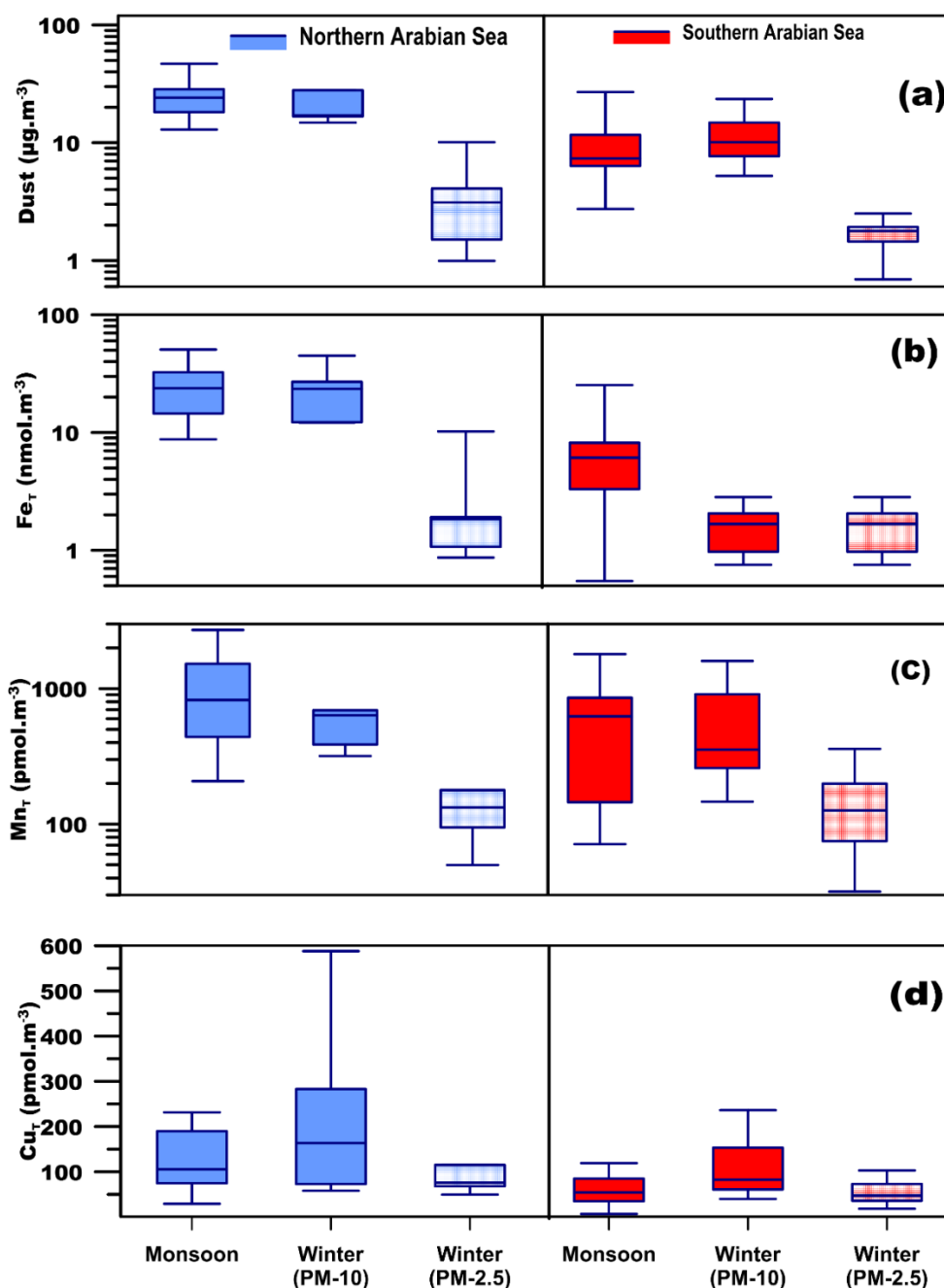


Fig-3.4: Spatial and seasonal variation of (a) dust, (b) total Fe (Fe_T), (c) total Mn (Mn_T), (d) total Cu (Cu_T) over the Arabian Sea.

Cu_T also shows a higher contribution during winter and $136.8 \pm 122.8 \text{ pmol m}^{-3}$ than monsoon $88.5 \pm 58.8 \text{ pmol m}^{-3}$ but earlier shows a wider range of 40.-588.0 pmol m^{-3} than later 22.7-231.5 pmol m^{-3} (Fig-3.4c, Table 3.2). The North Arabian Sea receives higher like other trace elements (Fig-3.4c). Unlike Fe and Mn, Cu_T is mainly derived from anthropogenic emission which is evident from EF>10 irrespective of season (Fig-3.5) (panda et al., 2022; 2024). Winter is characterized as a continental outflow period due to a favorable wind increase in anthropogenic activity (Kumar et al., 2010; Srinivas and Sarin, 2013) which leads to a higher concentration of Cu_T in winter than in the wet monsoon period during winter Cu_T. The AS receives a higher average Cu_T than the Bay of Bengal, which might be due to the high dust supply (including natural Cu and emissions from mining activity in Iran and SW-India) along with anthropogenic emissions (biomass burning and fossil fuel burning) leading to high Cu_T over AS. As per particle size, the northern Arabian Sea receives $7.7 \pm 3.7\%$, $17.8 \pm 6.2\%$ and $52.7 \pm 25.1\%$ of Fe, Mn, and Cu respectively from fine aerosols while southern AS receives $16.2 \pm 11.5\%$, $33.5 \pm 12.0\%$ and $52.3 \pm 21.5\%$ of Fe, Mn, and Cu respectively.

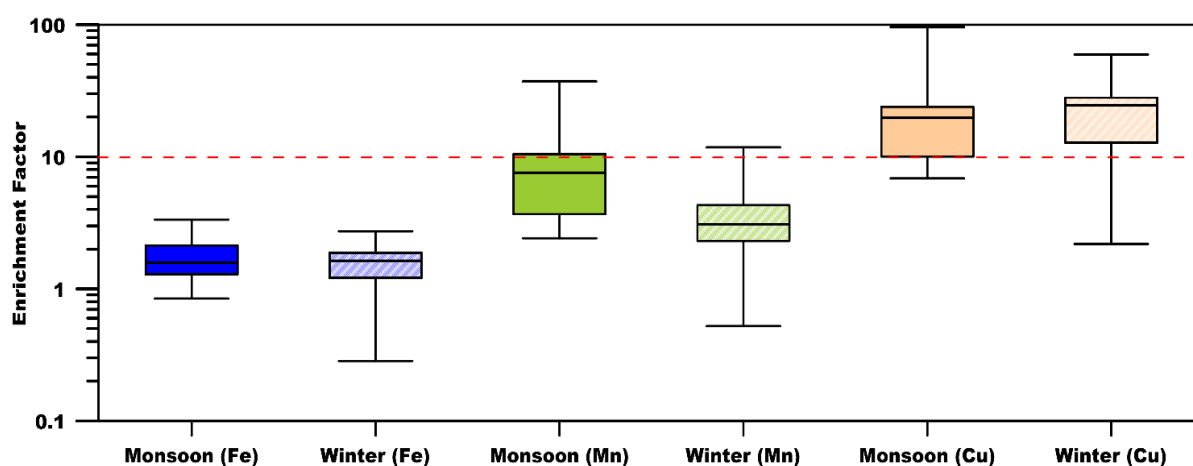


Fig-3.5 Box plot of enrichment factor for Fe (blue), Mn (green) and Cu (yellow) as per season. The dashed red line is considered to be the Enrichment line >10 times of crustal average.

3.2.4 Soluble TEs over the Arabian Sea:

Soluble TEs over AS show the opposite pattern of dust, mean soluble TEs higher during winter $840.5 \pm 571.8 \text{ pmol m}^{-3}$, $383.4 \pm 311.2 \text{ pmol m}^{-3}$, $72.3 \pm 54.0 \text{ pmol m}^{-3}$ and $114.6 \pm 166.1 \text{ pmol m}^{-3}$, $286.3 \pm 267.8 \text{ pmol m}^{-3}$, $20.1 \pm 20.8 \text{ pmol m}^{-3}$ during monsoon for Fe, Mn and Cu respectively (Fig-3.6, Table 3.2). Higher acidic species during winter along with anthropogenic emissions observed from high EF led to atmospheric processing during long-

range transport of dust causing relatively higher soluble TEs. Similarly, southern AS receives less dust and total TEs but due to atmospheric processing during long-range transport shows comparable soluble TEs (Fig-3.6) to the northern Arabian Sea. The TEs over AS are higher compared to IO due to their distal location and limited acidic supply, the TEs remain in their refractory form in later regions (Panda et al., 2024). The observed Arabian Sea means soluble Fe and Cu during winter is higher than BoB, whereas soluble Mn over the BoB is higher than AS. This might be due to dust supply from different sources and their mineralogy could be a controlling factor over the BoB which easily gets processed.

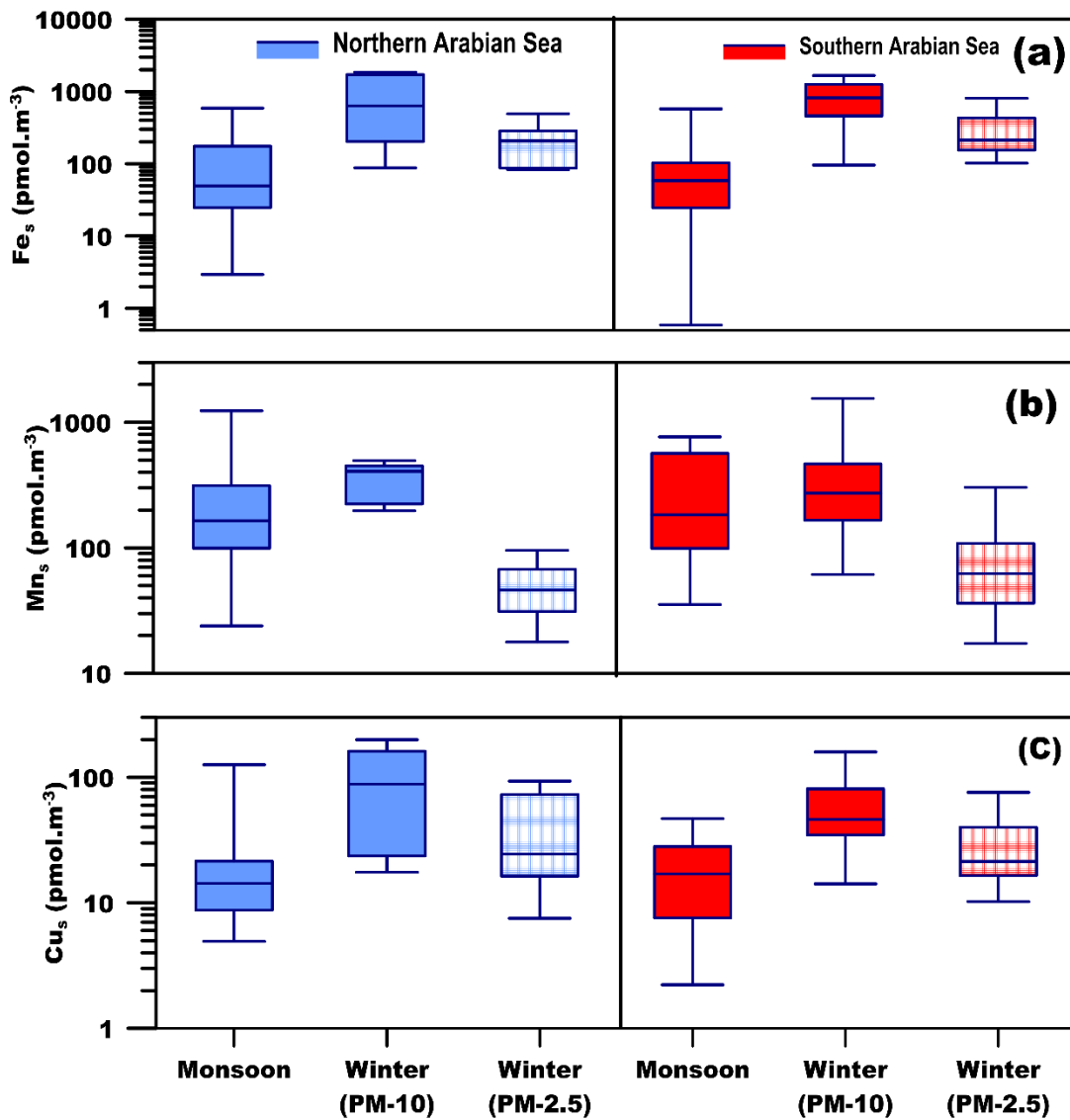


Fig-3.6 Spatial and seasonal variation of (a) soluble Fe (Fe_s), (b) soluble Mn (Mn_s), (c) soluble Cu (Cu_s) over the Arabian Sea.

3.2.5 Fractional solubility and factor-controlling fractional solubility over the Arabian Sea:

During winter, relatively higher fractional solubility was observed (Fe%: 5.8 ± 3.3 %; Mn%: 69.0 ± 16.0 %; Cu%: 56.3 ± 18.9 %) compared to the monsoon season (Fe%: 0.8 ± 0.9 %; Mn%: 42.9 ± 24.4 %; Cu%: 26.1 ± 19.5 %) (Table-3.2) indicating a possibility of relatively higher atmospheric processing of dust and associated TEs in contrast to monsoon months. In the previous section, it was discussed that the northern Arabian Sea receives higher dust as well as all TEs, but the observed fractional solubility over the southern Arabian Sea is higher irrespective of seasons (Fig-3.7). Interestingly, northern Arabian receives a relatively higher amount of total acid (TA= nitrate + 2* non-sea salt sulphate) (TA in winter = $309.2 \text{ nmol m}^{-3}$; TA in monsoon = 94.5 nmol m^{-3}) compared to the southern Arabian Sea (TA in winter = $274.8 \text{ nmol m}^{-3}$; TA in monsoon = 51.6 nmol m^{-3}) but long-range transport of dust during winter and turbulent mixing of dust LLJ during monsoon enhance atmospheric processing resulting higher solubility over southern AS. The atmospheric processing of dust is also evident from the correlation between total TEs and fractional solubility (Fig-3.8). This indicates an increase in total TEs fractional solubility decreases while the increase in fine particles (which is caused due to the gravitational settling of coarse particles; Mahowald et al., 2014; Toth III et al., 2020) fractional solubility increases.

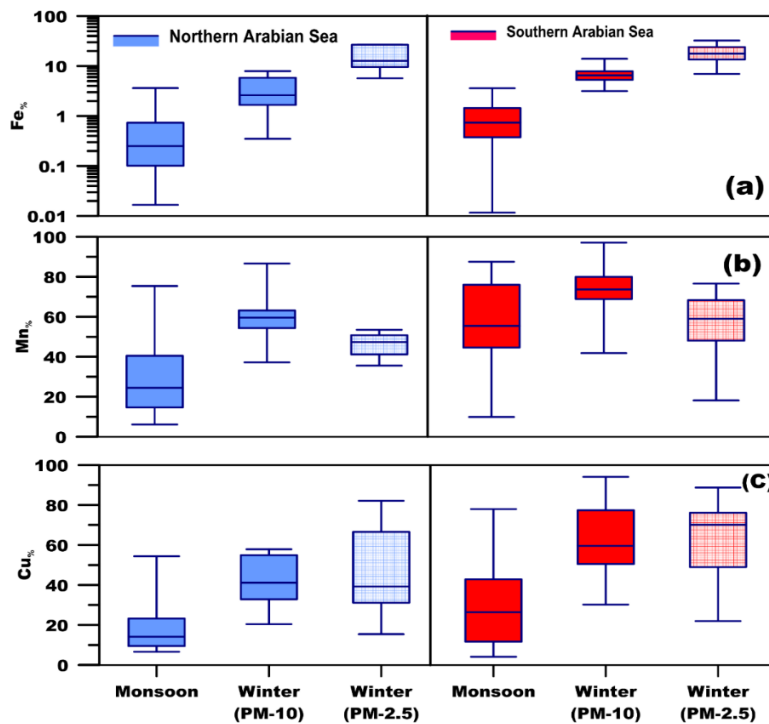


Fig-3.7 Spatial and seasonal variation fractional solubility of (a) Fe%, (b) Mn%, (c) Cu% over the Arabian Sea.

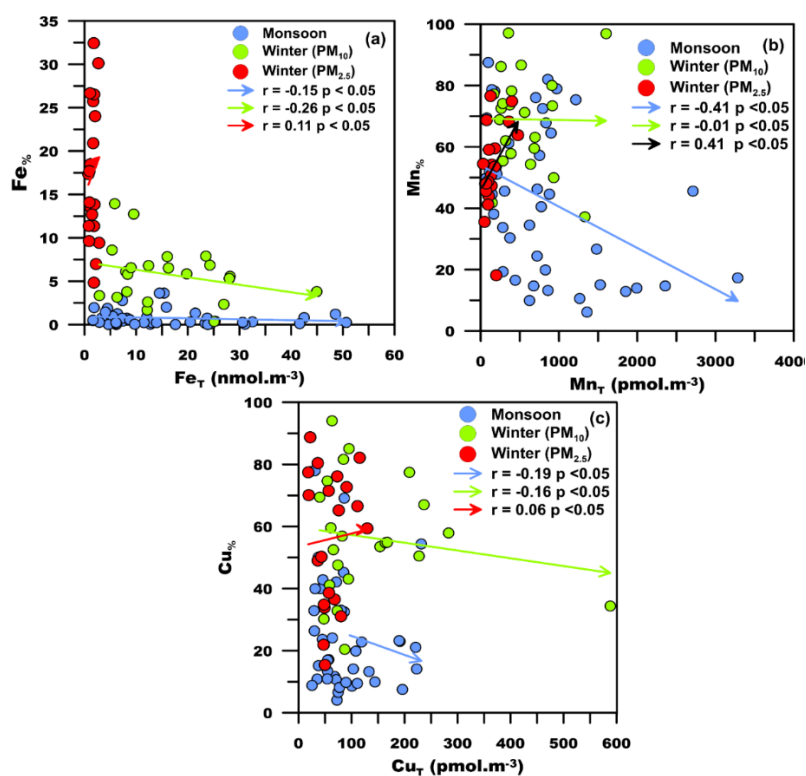


Fig-3.8 Correlation plot between (a) total Fe (Fe_T) with $Fe\%$, (b) total Mn (Mn_T) with $Mn\%$ (c) total Cu (Cu_T) with $Cu\%$.

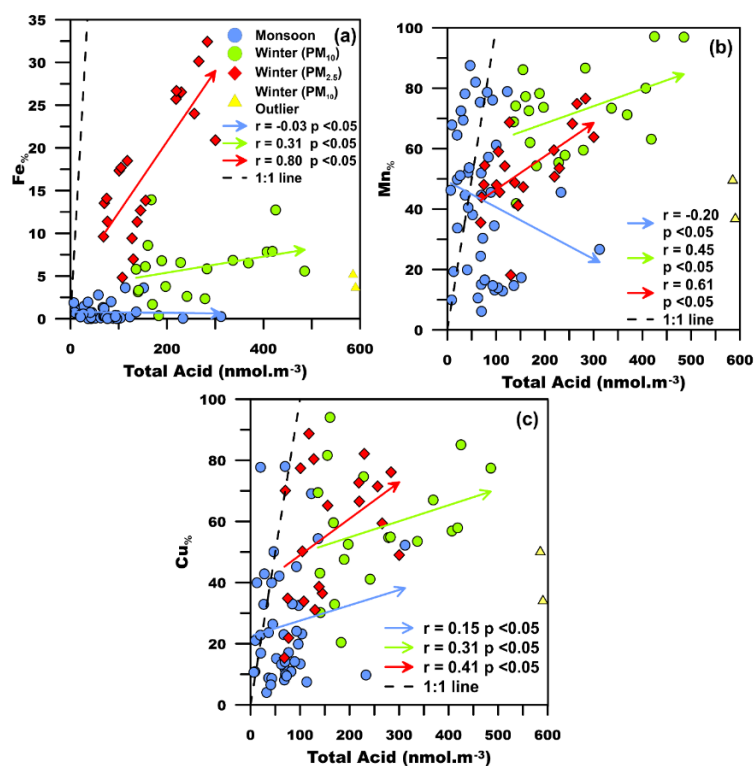


Fig-3.9 Correlation plot between Total Acid (TA) with $Fe\%$, $Mn\%$ and $Cu\%$ in (a), (b) and (c) respectively.

Due to the abundance of acidic species and active atmosphere in winter fractional solubility increases during winter which is absent in monsoons evident from the linear correlation plot between TA and fractional solubility in the winter (Fig-3.10). The linear and positive relation between fractional solubility and non-sea salt potassium (tracer for biomass burning) provides evidence of TEs contribution from the biomass burning during the winter season only which is absent during monsoon -ve correlation.

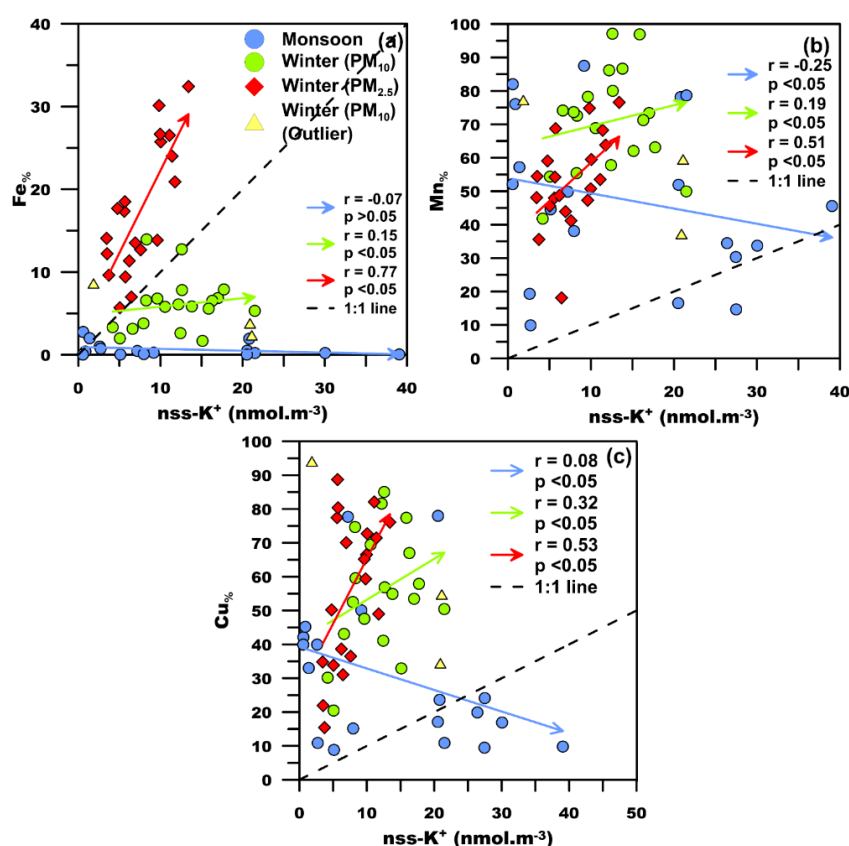


Fig-3.10 Correlation plot between $nss-K^+$ with $Fe\%$, $Mn\%$ and $Cu\%$ in (a), (b) and (c) respectively.

3.2.6 Dry depositional flux over the Arabian Sea:

Dry deposition flux (DF) of dust and TEs depends upon deposition velocity (V_{dx}), which can introduce significant uncertainty in flux estimation (Srinivas and Sarin 2013). The estimated amount of dust flux during the monsoon season averages around $14.0 \pm 11.5 \text{ mg m}^{-2} \text{ d}^{-1}$ and in the winter season $13.3 \pm 9.2 \text{ mg m}^{-2} \text{ d}^{-1}$ (excluding dust storm samples), which is relatively low (almost half) as compared to those reported in the model-based study by Zender et al. (2004).

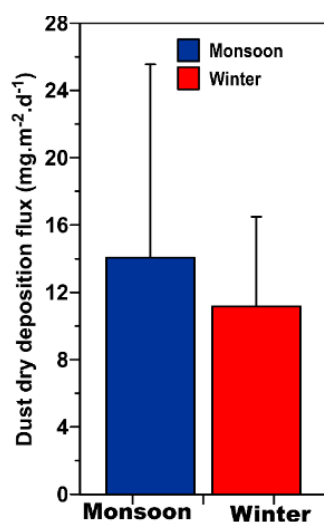


Fig-3.11 Dry deposition flux of dust over AS during the Monsoon and Winter seasons.

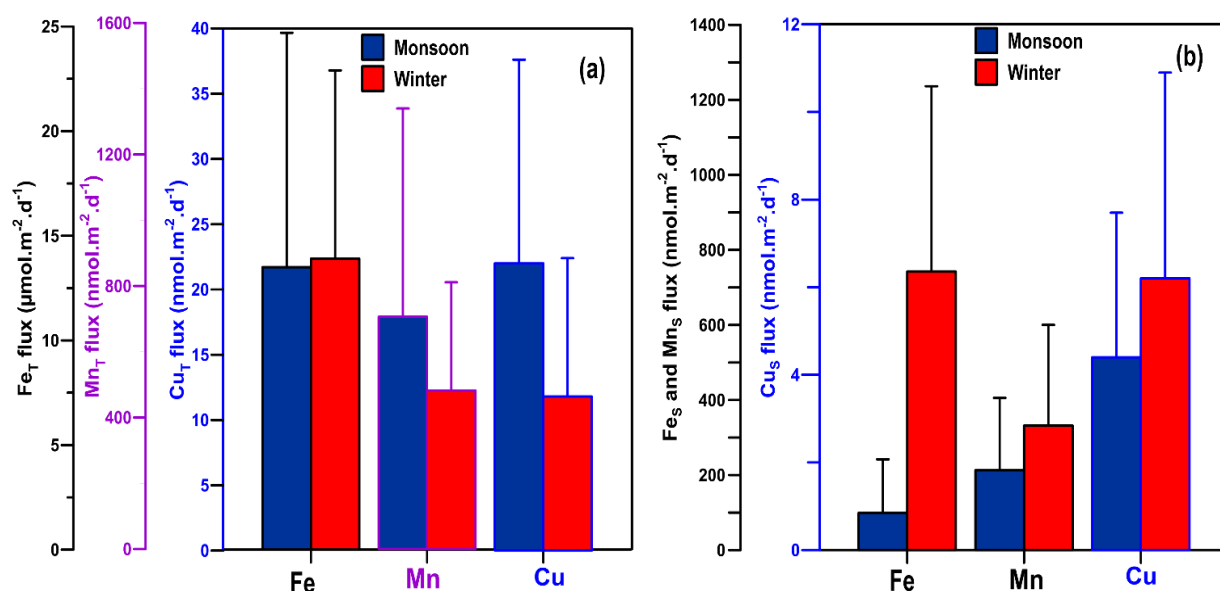


Fig-3.12 Dry deposition flux of (a) total trace elements (b) soluble trace elements over AS during the Monsoon and Winter seasons.

In this study, it was found AS receives higher Fe_T flux (monsoon: $13.5 \pm 11.2 \mu\text{mol m}^{-2} \text{d}^{-1}$; winter: $13.3 \pm 9.2 \mu\text{mol m}^{-2} \text{d}^{-1}$)(Fig-3.12a). Previous studies by Kumar et al. (2008) have reported DF of Al_T and Fe_T as 0.66 and 0.39 mg m⁻²d⁻¹ during the spring inter-monsoon months, which are lower than our observed values of 1.1 and 0.8 mg m⁻² d⁻¹ in monsoon season for Al and Fe respectively. Increased frequency of dust storms, as well as high dust activity, have been reported from the Arabian Peninsula during the July-September months in contrast to other seasons as well as episodic dust storms during winter (Tindale and Pease,1999;

Banerjee and Prasana Kumar, 2014; Ramaswamy et al., 2017; Suresh et al., 2021). The favorable meteorological conditions (particularly strong SW monsoon winds) could potentially bring significant dust to the AS (Aswini et al., 2020). This may lead to relatively higher DF for Fe and Al over the AS during this study. DF of Mn_T (monsoon: $706.1 \pm 633.8 \text{ nmol m}^{-2} \text{ d}^{-1}$; winter: $481.2 \pm 329.9 \text{ nmol m}^{-2} \text{ d}^{-1}$) and Cu_T (monsoon: $22.0 \pm 15.6 \text{ nmol m}^{-2} \text{ d}^{-1}$; winter: $11.8 \pm 10.6 \text{ nmol m}^{-2} \text{ d}^{-1}$) (Fig-3.12a) is found to be relatively higher than those reported by Srinivas and Sarin (2013) over the Bay of Bengal. The higher DF of Cu_T in monsoon is due to a higher depositional velocity of 0.3 cm s^{-1} while during winter due to lower wind speed $V_d = 0.1 \text{ cm s}^{-1}$ was assumed (Panda et al., 2022).

The AS receives higher F_{es} flux, on average 5.5 (range 0.03-28) $\text{nmol m}^{-2} \text{ d}^{-1}$ during monsoon as compared to those reported by Srinivas et al. 68 during Summer ($0.04\text{-}0.9 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$) months, which is intriguing considering the relatively higher contribution of anthropogenic emission in summer compared to monsoon months. In contrast, Kumar et al. (2008) have reported a very high soluble Fe flux ($40 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$), presuming 10% fractional solubility of Fe. This clearly highlights the role and importance of real-time sampling of aerosols and their analyses. Soluble Fe supply to the AS is relatively higher ($5.5 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$), than those reported from high-productive oceanic regions like the Peruvian coast (DF of $F_{es} = 0.8 \text{ ng m}^{-2} \text{ d}^{-1}$) (Baker et al., 2016) or those observed at HNLC regions of South Atlantic (DF $F_{es} = 0.1 \text{ ng m}^{-2} \text{ d}^{-1}$). Recently, Chinni and Singh (2022) have used soluble iron aeolian flux range between $0.01\text{-}0.05 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ (by considering fractional solubility of Fe (Fe%) as 0.1%) to assess the relative contribution of dissolved Fe from various sources. This is highly underestimated in contrast to this study. Thus, real-time measurements of nutrients associated with aerosols are important for constraining the nutrient biogeochemical cycling in the Ocean. While comparing the deposition flux data from other parts of the world, we observed higher dust as well as TEs fluxes over the Arabian Sea except those reported over the Mediterranean Sea. The higher flux could be due to the high depositional velocity ($V_{dx} = 1.48\text{-}1.8 \text{ cm s}^{-1}$) considered for the calculation (Kocak et al., 2005). The dry deposition flux of soluble Mn and Cu to the Arabian Sea during winter (Fe: $726.2 \pm 494.0 \text{ nmol m}^{-2} \text{ d}^{-1}$; Mn: $331.3 \pm 268.9 \text{ nmol m}^{-2} \text{ d}^{-1}$; Cu: $6.2 \pm 4.7 \text{ nmol m}^{-2} \text{ d}^{-1}$) is higher compared to monsoon season (Fe: $98.7 \pm 143.1 \text{ nmol m}^{-2} \text{ d}^{-1}$; Mn: $212.6 \pm 192.8 \text{ nmol m}^{-2} \text{ d}^{-1}$; Cu: $4.4 \pm 3.3 \text{ nmol m}^{-2} \text{ d}^{-1}$) (Fig-3.11b) and other regions of the Indian Ocean contributing significantly to the surface biogeochemical cycle during winter.

3.2.7 Role in Carbon Fixation

Anthropogenic Fe deposition was established as the most important factor for carbon uptake in many recent studies (Krishnamurthy et al., 2010; Okin et al., 2011; Ito et al., 2021; Hamilton et al., 2022), mainly due to its positive effect on productivity. Based on the information at hand, atmospheric nitrogen and iron inputs are significant contributors for oceanic productivity, supporting around 5% and 10–20%, respectively, of the global export of organic material from the surface ocean (Moore et al., 2013). Krishnamurthy et al., (2009) also suggested that the simultaneous anthropogenic N and Fe deposition can increase oceanic productivity by $\sim 1.3 \text{ Pg C yr}^{-1}$ in the current era compared to the pre-industrial conditions. Assuming, however, complete assimilation of anthropogenic nitrogen by carbon fixation, a new marine biological production of up to 0.3 Pg C yr^{-1} could be supported (Duce et al., 2008). In this study, potential carbon fixation rates, supported by atmospheric deposition, have been estimated following the approach of (Okin et al., 2011). In AS, the phytoplankton community is dominated by the abundance of diatoms (86%) (Gauns et al., 2005). Since diatoms are one of the abundant phytoplankton species in the AS; the C-fixation is estimated by atmospheric input of Fe.

$$C_{\text{Fix}}^{\text{Atm}} = \text{Fe}_{\text{Dep}}^{\text{Atm}} \times \text{Fe}_{\%} \times \left(\frac{C}{\text{Fe}} \right)_{\text{dia}}$$

In this equation $\text{Fe}_{\text{Dep}}^{\text{Atm}}$ and $\text{Fe}_{\%}$ are the dry-deposition flux and the fractional solubility of aerosol iron in BoB, respectively. The cellular uptake ratio by diatoms is about $8 \mu\text{mol/mol}$ (i.e. C: Fe = 1,25,000) (Moore et al., 2002). Using the average fractional solubility of aerosol iron ($\sim 0.8\%$ in PM and $\sim 5.8\%$ in winter), the dry-deposition of Fe_s to the AS (considering 210 days as continental emission days) is about 0.040 Tg yr^{-1} and 0.004 Tg yr^{-1} in winter and monsoon respectively. The atmospheric input of Fe_s can account for $0.5 \pm 0.8 \text{ Pg -C yr}^{-1}$ in monsoon and $5.0 \pm 3.7 \text{ Pg-C yr}^{-1}$ in winter. Therefore, atmospheric input of Fe_s can account for $\sim 10\%$ and 1% of global PP (50 Pg-C yr^{-1} ; Carr et al., 2006) during winter and monsoon respectively. In previous studies, it was highlighted that wind-driven convective mixing enhances mixed layer depth which supplies nutrients to the surface layer of AS during winter (Madhupratap et al. 1996; Kumar et al., 2001). A recent study by Sridevi and Sarma (2021) highlighted due to increased anthropogenic emissions, winter convective mixing gets strengthened, causing phytoplankton to bloom. From this study, it seems during winter time anthropogenic emissions not only strengthen convective mixing but also increase

atmospheric processing of TEs, which acts as an additional but vital source of limiting nutrients (N and Fe) and increasing primary production in the Arabian Sea.

3.3 Summary

The concentration of inorganic nitrogen species, mineral dust and associated soluble and total TEs (Fe, Mn, and Cu) were measured in the atmospheric aerosols collected over the AS during three oceanographic campaigns two in consecutive monsoon seasons (2017 and 2018) and one during winter season (2019). The major outcomes of this study are summarized below:

1. Atmospheric dust is one of the potential suppliers of macro and micronutrients to the AS during the study period and shows large spatial variability. The northern sector of the AS receives the maximum amount of mineral dust owing to its geographical location as well as favorable meteorological conditions.
2. Fe, Mn abundance over the AS is associated with the dust during monsoon; however, significant influence of anthropogenic emissions is observed during winter. Cu is largely associated with anthropogenic sources showing large variability during both seasons. The Arabian Sea receives higher dust-associated total TEs during monsoon but due to the dominance of anthropogenic emission higher amount of total Cu is observed during the winter season.
3. The northern Arabian Sea receives higher dust and nutrients (macro and micro) with an abundance of coarse particles, while southern AS receives relatively less. Due to the long-range transport of fine particles and atmospheric removal of coarse particles, dominance of fine particles was observed over southern AS during the winter season.
4. Due to anthropogenic emissions along with the atmospheric processing of dust via acidic species increased fractional solubility of TEs during the winter season compared to monsoon season. A significant correlation between fractional solubility and biomass-burning tracers like nss-K^+ suggests a significant contribution of soluble TEs from biomass burning during winter which is absent during monsoon.
5. The dry deposition fluxes estimated for dust TEs were relatively high compared to those reported from other oceanic regions. The atmospheric Fe flux to the Arabian Sea has a

significant impact on biogeochemistry. Soluble Fe flux accounts for up to 10% of primary productivity during the winter season.

These data sets on soluble and total TEs composition have implications for atmospheric sources and supply of nutrients triggered by the large-scale dust and anthropogenic activities occurring in the surrounding region of the AS. This data will provide an important input to global biogeochemical models.

Chapter 4

*Atmospheric nutrient distribution and their
deposition fluxes over the Bay of Bengal:
Seasonal variability and factors affecting
their bio-availability*

4.1 Introduction:

The earth's atmosphere has been enormously altered and impacted by the rapid extension of anthropogenic emissions in recent years, leading to the "Anthropocene era". The overall effect of future emissions changes is projected to be a decrease in the acidity of aerosols, cloud water, aerosol chemical composition and distribution (Allen et al., 2016). These changes are expected to affect not only impact on continental pollution and human health but also the atmospheric nutrient delivery to the oceans through altered atmospheric lifetimes and changes in deposition mode (Pechony and Shindell, 2010; Martino et al., 2014; Zhang et al., 2016). Atmospheric deposition is considered to be the major pathway by which substances from the atmosphere enter into terrestrial and aquatic ecosystems (Morera-Gómez et al., 2019). The environmental consequences of these processes can be both harmful and beneficial (Pacyna, 2008). On one side, acidification and eutrophication of various ecosystems may be a consequence of the excess deposition of sulfur and nutrients (Bouwman et al., 2002). In addition, the long-range transport of natural and anthropogenic continental aerosols is recognized as a significant source of micro and macro nutrients to the marine ecosystem and can impact phytoplankton productivity in the surface ocean (Jickells et al., 2005; Behrenfeld et al., 2006; Srinivas and Sarin, 2013; Jickells et al., 2017; Yadav et al., 2016). In a global change scenario, anthropogenic acids could have an impact on certain atmospheric minerals and their chemistry (Zhu et al., 2020). Aerosol acidic species (SO_4^{2-} and NO_3^-) play a key role in the dissolution of inorganic elements and increase their bioavailability and deposition in the ocean (Kumar et al., 2010).

In recent years, the dominant source of reactive nitrogen species has been derived from anthropogenic sources, including biomass, fossil fuel combustion sources, and agricultural emissions (Baker et al., 2021). Atmospheric aerosol nitrogen includes the contribution from both inorganic (NH_4^+ and NO_3^-) and organic nitrogen species (Jickells, 2006; Srinivas et al., 2011a; Jickells et al., 2013; Srinivas and Sarin, 2013; Sarma et al., 2022). In the atmosphere, the global organic nitrogen (N_{Org}) cycle has been demonstrated to have a strong ($\sim 45\%$) anthropogenic component (Kanakidou et al., 2012). The marine phytoplankton community can easily access this extra inorganic N supply, which has a positive impact on phytoplankton biomass and marine productivity (Duce et al., 2008; Jickells et al., 2017). To assess the short-term response of phytoplankton communities to aerosol deposition, (Sharma et al., 2022), performed an experimental study demonstrating the effects of atmospheric dust input from winter monsoon samples on natural phytoplankton communities from the Arabian Sea. The

authors established that the external input of inorganic nitrogen and iron (from dust) were the primary factors responsible for promoting growth, irrespective of the ambient CO₂ levels. Many previous studies in open ocean (Jickells, 2006; Duce et al., 2008) suggested that deposition of atmospheric anthropogenic nitrogen could shift the ecosystem towards other limiting nutrients like Fe, Mn etc (Ito et al., 2021; Hamilton et al., 2022; Lu et al., 2024).

Trace elements (TEs) like Fe, Mn and Cu are mainly introduced into the atmosphere by desert dust, but biomass combustion, industrial and ship emissions are predicted to become a major source of TEs in the oceans in the next century. It has been suggested in many studies that biomass burning is a significant source of pollutants in the global troposphere and nutrients to the remote ocean (Krishnamurthy et al., 2009; Schill et al., 2020; Ito et al., 2021; Hamilton et al., 2022). TEs bioavailability is a common limitation for phytoplankton in warm and oligotrophic regions, although the larger community may also be limited by nitrogen or phosphorus. Recent studies suggest Fe and Mn depositions are responsible for ocean carbon and N₂-fixation which could influence ocean biological pumps (Okin et al., 2011; Moore et al., 2013) and hence iron deposition modulates ocean biogeochemistry (Boyd et al., 2019). Previous observations (Nenes et al., 2011; Takahashi et al., 2011) suggested that the labile fractions of elements like Fe, Mn, and Cu increase during atmospheric long-range transport due to exposure to acidic (i.e., low pH) conditions in aerosol and cloud fluids.

The purpose of the present study is to evaluate the impact of a comprehensive representation of atmospheric inputs on surface water biogeochemical process of the Bay of Bengal (BoB). BoB is classically reported to be a low productive region due to weak nutrient supply caused by strong salinity stratification (Prasanna Kumar et al., 2002). However, the effects of riverine inflows have been extensively studied, and they are primarily restricted along the coasts or in marginal shelf basins (Krishna et al., 2015). Hence, atmospheric deposition plays an important role for the external supply of nutrients that can reach distal open-ocean regions far remote from land. The BoB is one of the ideal regions, confined by land from three sides, to study the impact of continental aerosols transported to the marine environment and reported higher levels of aerosol optical depth (AOD) than other oceanic regions (Zhang and Reid, 2010; Sarma et al., 2021). This region is largely affected by the winds originating from the north/north-eastern region of the Indian subcontinent as well as from Southeast Asian countries (Burma, Thailand, Bangladesh and China) during the late NE monsoon/Winter monsoon. Winter monsoons (December to March) are considered the season for continental outflows and the effects of continental outflows on atmospheric composition have been studied previously (Srinivas et al., 2011a, b, 2014; Aryasree et al., 2015; Rastogi et al., 2020).

(Srinivas and Sarin, 2012) suggest that during the rest of the year, prevailing wind regimes and meteorological conditions do not favor the atmospheric transport of continental products. But in the post-monsoon (PM) period (October to November, beginning of northeast monsoon), when the switchover from summer monsoon to winter monsoon (WM) occurs, this time is also very crucial to observe anthropogenic effects as most of the biomass burning is happening in this time period (Nayak et al., 2022; Tiwari et al., 2018). This present work is a comprehensive study to examine the combined impacts of both seasons (PM and WM) on atmospheric labile nutrient deposition to the oceans and their effects on marine biogeochemistry corresponding to anthropogenic activities. Thus, in this study, water-soluble inorganic, organic nitrogen and other TEs deposition flux were estimated to assess the role of biogeochemical processes like nitrogen and carbon fixation associated with long-range transport and anthropogenic activity. Further, time series comparisons of nutrient ion deposition over BoB were also evaluated to observe the magnitude of anthropogenic influence.

4.2 Result and Discussions:

4.2.1 Cruise Track and Wind Patterns during the Study Period:

Aerosol samples were collected onboard the RV-Sindhu Sadhana SSD-015 (n = 11) and SSD-019 (n = 11) conducted during October 2015 (PM, transition from southwest monsoon to northeast monsoon) and February 2016 (WM, end of northeast monsoon), respectively. Sampling took place during the aforementioned expeditions, primarily limited to the coastal region covering a latitudinal stretch between 13°N and 21°N during PM. However, the WM cruise encompassed a border geographic scope, spanning the open oceanic sector of the BoB between 13–21°N and 80–90°E (Fig-4.1a) (Table 4.1). The marine atmospheric boundary layer of the BoB is strongly influenced by the continental outflow during our study period. It experiences a sharp seasonal reversal of winds due to a strong land-ocean thermal gradient (Begum et al., 2012). The wind system changes from south-westerlies during the southwest monsoon to predominantly north-easterlies during the northeast monsoon

The SSD-015 cruise campaign was conducted during October (PM), which was a transitioning month and experienced relatively weaker winds compared to the rest of the season. These winds transport a complex mixture of aerosols that contain biomass and fossil fuel-burning products, mineral dust, sea salt, and secondary particles such as sulfate, nitrate, and ammonium salts (Kumar et al., 2008b). Crop residue burning is prominent in northern India during late October and early November (Tiwari et al., 2018), and has significant potential to

impact aerosol loading in the region (Tiwari et al., 2016; Nayak et al., 2022). The SSD-019 cruise campaign was conducted during the northern winter month of February, during which the prevailing airflow over the Indian subcontinent is predominantly north-easterly/northerly. North-easterlies, blowing towards the ocean from polluted continental landmass during wintertime, transport a significant amount of aerosols over the BoB. Detailed meteorological conditions like relative humidity (RH), wind speed, and temperature during the two campaigns were described in (Nayak et al., 2022). The Bay of Bengal is a closed basin compared to the Arabian Sea and our study area is mainly restricted to the eastern and central parts (Fig-4.1a) for a detailed understanding of the basin instead of categorizing as per geographical location which we did in the previous chapter, we categorize them as per the origin of wind mass. The wind pattern and wind speed is the primary factor for the transport of aerosols/nutrients to the remote oceanic environment. To understand the origin and nature of air mass back trajectories, we used a hybrid single-particle Lagrangian integrated trajectory model (HYSPLIT-version 4; GDAS data set) from the National Oceanic and Atmospheric Administration (NOAA) air resources laboratory as outlined by Stein et al., 2015 and Rolph et al., 2017. Air mass back trajectories (AMBT) were computed for seven days at an altitude 500 m above sea level. Each computed trajectory ended at the midpoint of the transect used for the collection of each sample (Fig-4.1b). Based on the analysis of wind-drive back trajectories, three major air parcels were identified: (1) Continental air parcels (CAP), those originating from land and traversing less than a day over the ocean before reaching the sampling transect., (2) Marine air parcels (MAP), characterized by trajectories predominantly over the ocean for over one day prior to intersecting the sampling transects; and (3) A combination of CAP and MAP trajectories (CAP + MAP), representing air parcels traveling over both ocean and land for more than two days before reaching the sampling transect (Fig-4.1b) (Table 5.1).

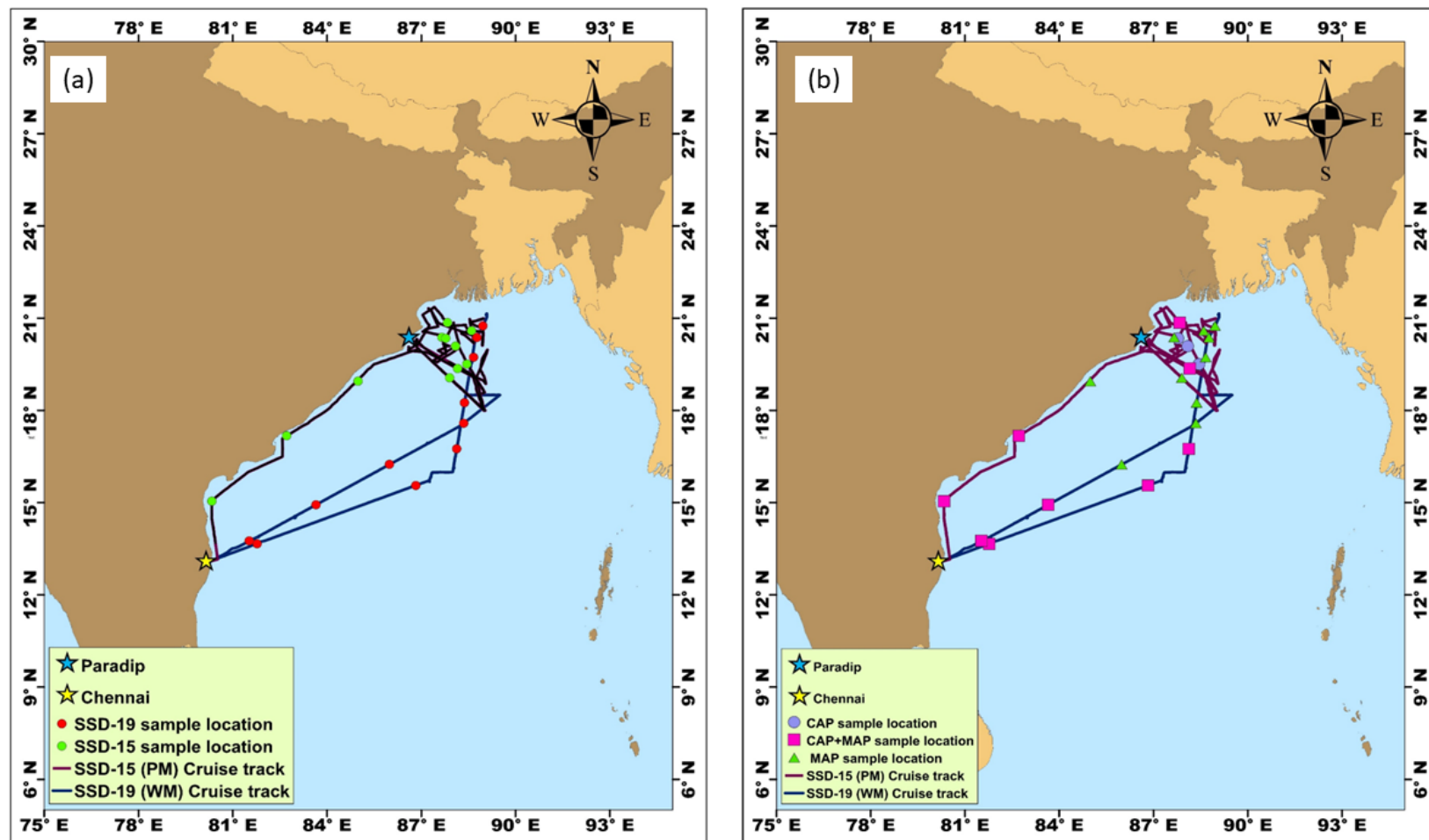


Fig-4.1 Cruise tracks undertaken in the Bay of Bengal (a) SSD-15 and SSD-19 and midpoints of sample location green and red respectively (b) sample classified into CAP, MAP and CAP+ MAP based upon AMBT at 500m height (details in main text Section 4.2)

Table 4.1 Sampling dates, start and end locations of each sample over the Bay of Bengal during SSD-15 and SSD-19.

Sample	Date		Lat		Lon		Wind Parcel
	Start	End	Start	End	Start	End	
SSD-15							
BSD-15-10-01	10/14/2015	10/15/2015	13.82	16.27	80.43	82.1	CAP +MAP
BSD-15-10-02	10/15/2015	10/16/2015	16.3	18.05	82.16	84.05	CAP +MAP
BSD-15-10-03	10/16/2015	10/17/2015	18.06	19.84	84.05	86.47	MAP
BSD-15-10-04	10/17/2015	10/18/2015	19.86	18.00	86.51	89.00	MAP
BSD-15-10-05	10/18/2015	10/19/2015	18.00	20.19	89.00	86.86	CAP +MAP
BSD-15-10-06	10/19/2015	10/20/2015	20.19	20.57	86.90	88.48	MAP
BSD-15-10-07	10/21/2015	10/22/2015	20.22	20.96	88.67	88.53	MAP
BSD-15-10-08	10/23/2015	10/24/2015	20.46	21.25	88.58	87.32	CAP +MAP
BSD-15-10-09	10/26/2015	10/27/2015	19.85	20.84	87.77	88.03	CAP
BSD-15-10-10	10/27/2015	10/28/2015	20.14	20.04	88.17	88.01	CAP
BSD-15-10-11	10/28/2015	10/29/2015	19.98	19.03	88.24	88.66	CAP
	SSD-19						
BSD-19-B-1	2/6/2016	2/7/2016	13.14	14.18	80.39	83.16	CAP +MAP
BSD-19-B-2	2/8/2016	2/9/2016	15.12	15.99	85.66	87.99	CAP +MAP
BSD-19-B-3	2/9/2016	2/10/2016	16.01	17.49	88.00	88.25	CAP +MAP
BSD-19-B-4	2/10/2016	2/11/2016	17.50	19.00	88.42	88.50	MAP
BSD-19-B-5	2/11/2016	2/12/2016	19.02	20.43	88.60	88.8	MAP
BSD-19-B-6	2/12/2016	2/13/2016	20.46	21.04	88.78	89.09	MAP
BSD-19-B-7	2/13/2016	2/14/2016	21.04	19.7	89.09	88.65	MAP
BSD-19-B-8	2/16/2016	2/17/2016	18.24	16.92	89.17	87.18	MAP
BSD-19-B-9	2/17/2016	2/18/2016	16.92	15.57	87.18	84.79	MAP
BSD-19-B-10	2/18/2016	2/19/2016	15.57	14.29	84.79	82.51	CAP +MAP
BSD-19-B-11	2/19/2016	2/20/2016	14.28	13.23	82.49	80.56	CAP +MAP

CAP: Continental Air Parcel; MAP:
Marine Air Parcel
CAP+ MAP: Mixture of Continent and
Marine Air Parc

4.2.2 Macro-nutrient (N- Species) and source characterization over the Bay of Bengal:

The variation of total aerosol mass loading (M_L) and/or the mass concentration ($\mu\text{g m}^{-3}$) of different water-soluble ionic compositions (WSIC) in the aerosol samples (collected and analyzed during the two cruises in BoB). The mean value of total mass load of WSIC within aerosol samples collected in October 2015 (PM) was observed $23.81 \pm 7.91 \mu\text{g m}^{-3}$, which exhibits a good agreement with the findings of Nair et al. (2014), wherein a range of $21\text{--}53 \mu\text{g m}^{-3}$ in proximity to the Indian sub-continent was reported. The cruise track during October 2015 was mostly confined to the coastal region covering a latitudinal stretch between 13°N and 21°N , whereas the February 2016 (WM) cruise covered a larger area in the open oceanic region of BoB between $13\text{--}21^\circ \text{N}$ and $80\text{--}90^\circ \text{E}$ (Fig-4.1a). In WM M_L of WSIC shows a range of $26.70 \pm 6.59 \mu\text{g m}^{-3}$. With this being a transitioning month, the PM experiences relatively weaker winds compared to the rest of the season. The elevated aerosol mass loading observed in WM compared to the PM corroborates the hypothesis that during the former, prevailing winds exhibited a north-easterly direction, facilitating the transport of aerosols and other minor species from continental sources to oceanic domains (Beegum et al., 2012; Aryasree et al., 2015; Rastogi et al., 2020). This could also be partially attributed to the generation of sea-spray aerosols due to the action of strong gusts (Nair et al., 2004). This trend is also supported by the contribution of CAP, CAP+MAP and MAP observed for the overall sampling period. The Mean M_L values were $23.32 \pm 7.36 \mu\text{g m}^{-3}$, $24.75 \pm 9.33 \mu\text{g m}^{-3}$ and $26.28 \pm 5.55 \mu\text{g m}^{-3}$ for CAP, CAP+MAP and MAP respectively, where the highest average M_L of WSIC was found in MAP. Higher M_L in MAP sample attributed high sea salt loading $15.10 \pm 15.66 \%$ of M_L , where CAP and CAP+MAP shows lower sea salt contribution $2.88 \pm 1.69 \%$ and $10.34 \pm 9.96 \%$ respectively. Abundance of the major ions in bulk deposition showed a trend as $\text{SO}_4^{2+} > \text{NO}_3^- > \text{Cl}^-$ for anions in both sampling period and $\text{NH}_4^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+}$ and $\text{Na}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ for cations respectively in PM and WM (Fig-4.2). Throughout the both campaigns SO_4^{2+} contributed maximum, that is 71.86% and 60.17% total WSICs followed by NH_4^+ (20.68%) and K^+ (2.50%) in PM and Na^+ (11.85%) and NH_4^+ (10.12%) in WM. The contribution of different inorganic ions in CAP, CAP+ MAP and MAP are presented in Fig-4.2. Kurokawa and Ohara, (2020) suggested that in recent years, Asian countries have emitted large amounts of SO_2 and NO_x . The oxidation of SO_2 and NO_x can contribute to high levels of secondary ions, such as SO_4^{2-} and NO_3^- .

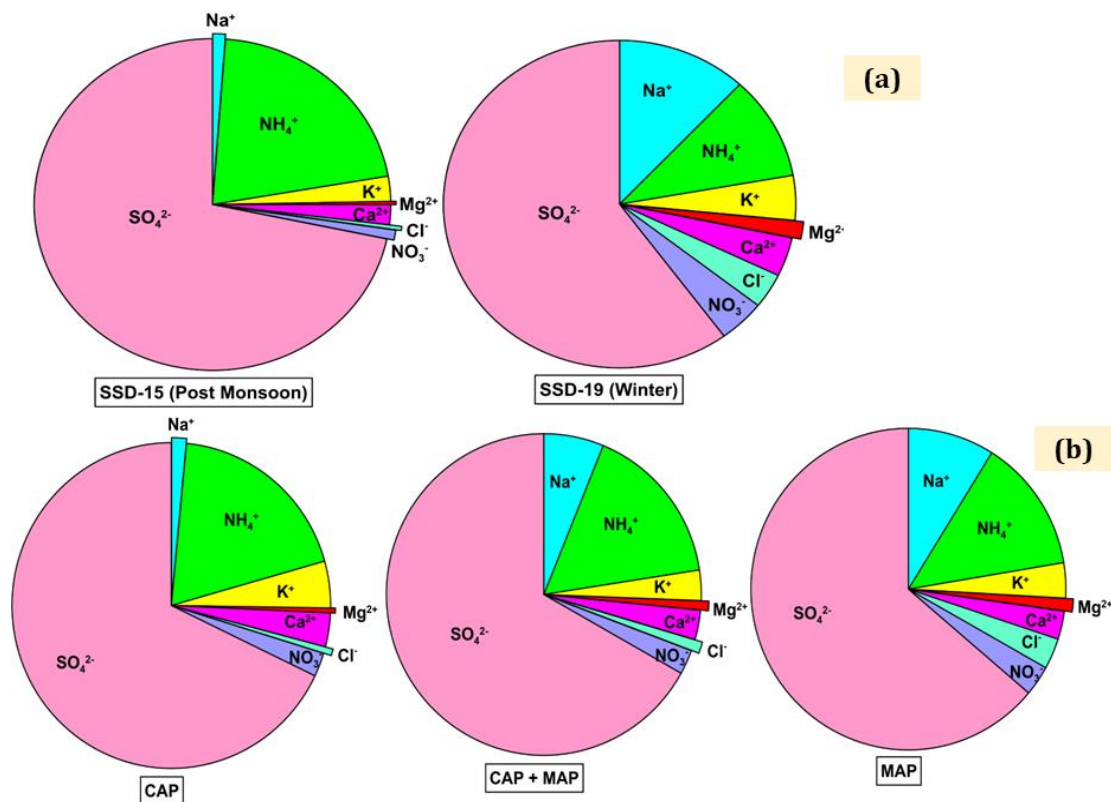


Fig-4.2 Pie chart representing chemical composition aerosol samples collected over the BoB (a) represents seasonal variation during the PM (SSD-15) and the WM (SSD-19) (b) Chemical composition air mass specific aerosol samples.

It is also noteworthy that NO_3^- concentrations are higher in WM than PM and the region of maximum concentration is farther from the coast. It shows the maximum values in MAP ($0.80 \pm 0.70 \mu\text{g m}^{-3}$) samples followed by CAP+MAP ($0.61 \pm 0.83 \mu\text{g m}^{-3}$) and CAP ($0.55 \pm 0.50 \mu\text{g m}^{-3}$), which indicates that it is not caused by direct outflow from the land. Similar incidents were also observed by (Nair et al., 2014). The correlation of coefficients between NO_3^- and Na^+ , Mg^{2+} , and Ca^{2+} for PM were 0.50, 0.78, and 0.91 (Fig-4.3a) respectively. Thus, NO_3^- in PM existed as compounds of Na^+ , Mg^{2+} , and nss-Ca^{2+} indicating the marine and continental sources simultaneously. However, in WM we only found a correlation of NO_3^- with Na^+ (0.74) and Mg^{2+} (0.69) (Fig-4.3b), which indicates the influence of marine sources only.

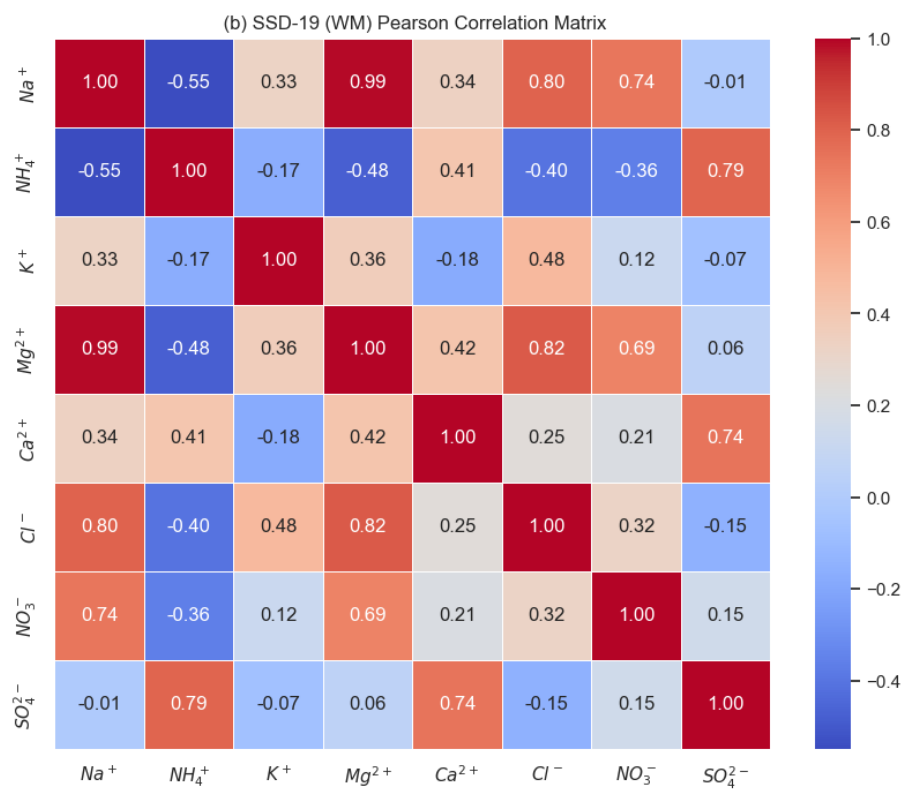
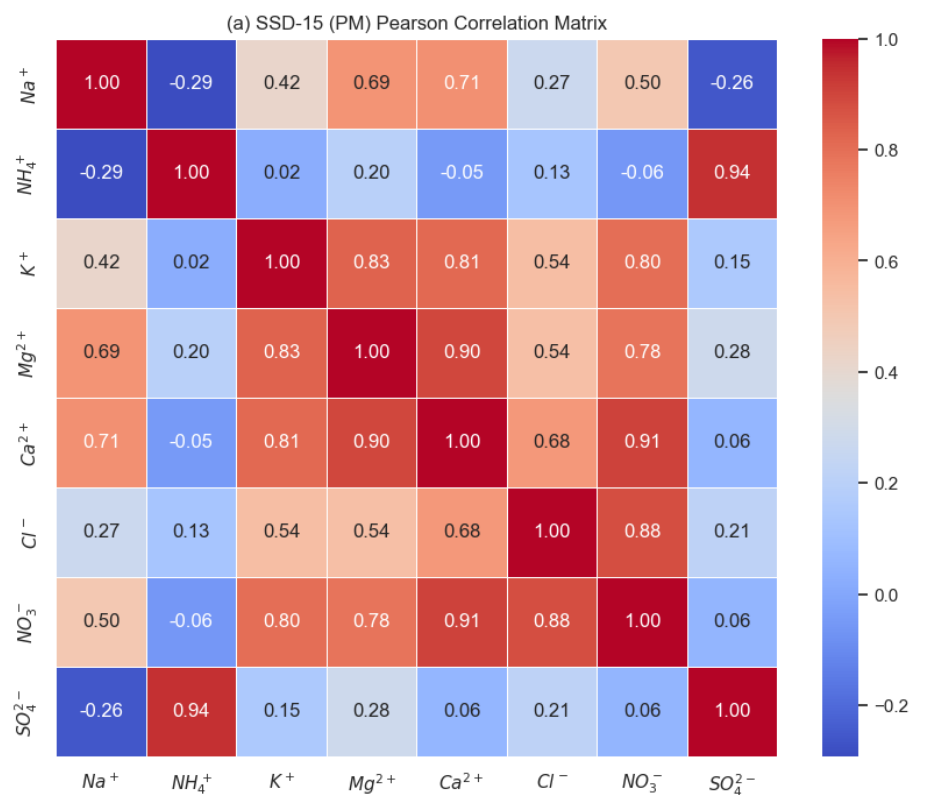


Fig-4.3 Pearson Correlation matrix for major chemical composition (a) SSD-15 or Post Monsoon and (b) SSD-19 or Winter Monsoon.

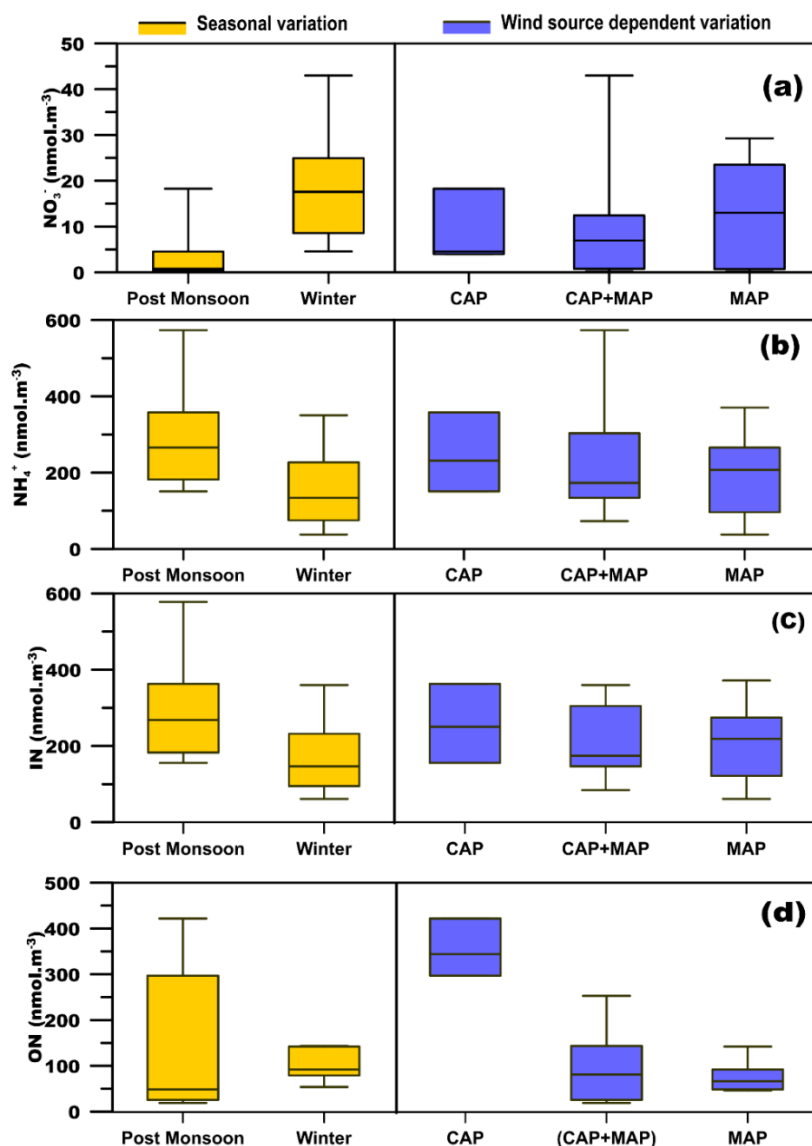


Fig-4.4 Seasonal variation and wind parcel-wise concentration of all reactive N-Species (a) Nitrate, (b) Ammonium, (c) Inorganic Nitrogen, (d) Organic Nitrogen.

Mass concentrations of nitrogen species for the overall sampling period varied as 37.5 – 573.36 nmol m⁻³ for NH_4^+ , 0.2 – 43.0 nmol m⁻³ for NO_3^- over the BoB. The average concentration of NO_3^- for PM and WM were 3.7 ± 5.5 nmol m⁻³ and 18.50 ± 11.31 nmol m⁻³ respectively (Table 4.2; Fig-4.4). A higher concentration of NO_3^- in WM supports the addition of NO_3^- from marine sources in WM previously. The correlation between nss- SO_4^{2-} and NO_3^- (Fig-4.5b) shows a poor correlation indicating both originated from different sources, unlike our previous observation over

the Indian Ocean (Panda et al., 2024). In contrast, NH_4^+ shows higher concentrations of $278.4 \pm 122.4 \text{ nmol m}^{-3}$ in PM and $151.4 \pm 95.4 \text{ nmol m}^{-3}$ (Table 4.2) in WM, which indicates the dominance of continental influence or biomass burning. This observation is also supported by the correlation between nss-K^+ (an indicator of biomass burning) and NH_4^+ (Fig-4.5a) similar to our observation over the Indian Ocean (Bikkina et al., 2022; Panda et al., 2024). In PM, crop residue burning is prominent in northern India during October (Tiwari et al., 2016; Nayak et al., 2022) and has significant potential to impact the aerosol loading, which could be responsible for high NH_4^+ concentration in aerosol (Bhuvaneshwari et al., 2019; Pohl et al., 2023). Mass concentration of N-NH_4^+ dominates N_{Inorg} ($\text{N-NH}_4^+ / \text{N}_{\text{Inorg}}$ more than 0.8 in both PM and WM. The ratio indicates that inorganic nitrogen is primarily influenced by nitrogen input from human activities, such as the large-scale application of fertilizers (ammonia and urea-based).

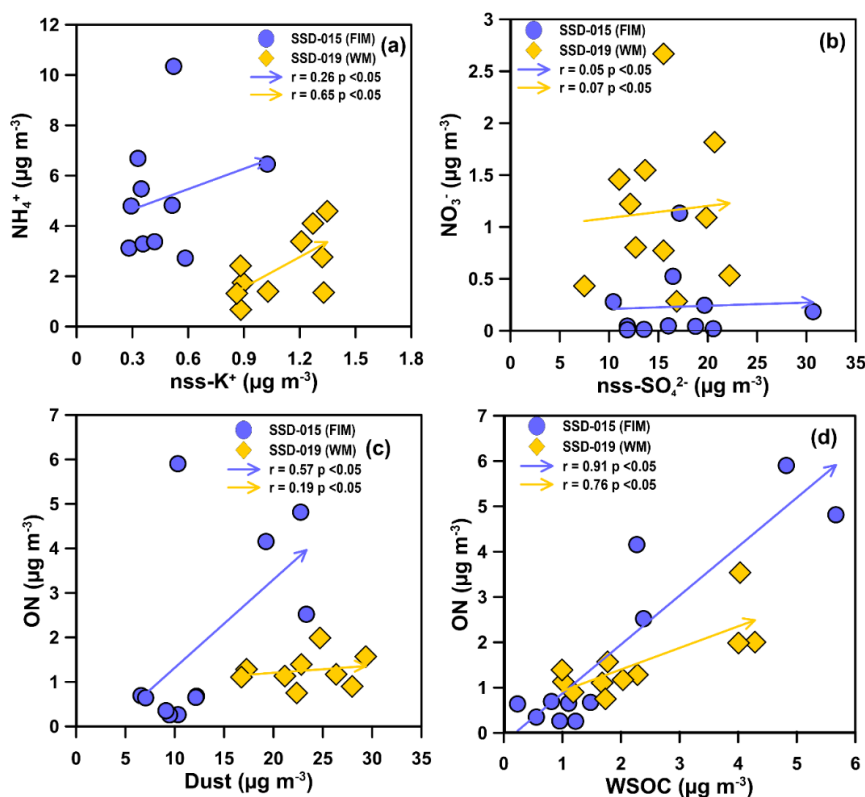


Fig-4.5 Correlation plot between (a) nss-K^+ and NH_4^+ , (b) nss-SO_4^{2-} and NO_3^- , (c) Dust and $\text{Organic nitrogen (ON)}$, (d) $\text{water-soluble organic carbon (WSOC)}$ and ON .

In addition, Mass concentrations of N_{Inorg} and N_{Org} in ambient aerosols over BoB is $170.2 \pm 92.1 \text{ nmol m}^{-3}$ and $109.3 \pm 55.4 \text{ nmol m}^{-3}$ (Table 4.2) in WM respectively. The observed N_{Inorg} values show good agreement with the previous study in the Bay of Bengal (Srinivas et al., 2011a;

Srinivas and Sarin, 2013) while the N_{Org} shows a higher range which is similar to other anthropogenic-influenced regions (Spokes et al., 2000; Shi et al., 2010). In the overall sampling period, CAP ($59.1 \pm 6.0\%$) shows a major contribution than CAP+MAP ($29.9 \pm 22.8\%$) and MAP ($29.7 \pm 18.0\%$) (Table 4.3) in N_{Org} concentration. Similar to our previous observations over the Indian Ocean, ON over the BoB originated from the same source of WSOC which is mostly soil organic nitrogen evident from a strong correlation with dust (Fig-4.5c) and WSOC(Fig-4.5d).

Table 4.2 Seasonal range and mean $\pm$ standard deviation of dust, trace elements and other chemical species.

	Units	SSD-15 (Post Monsoon)		SSD-19 (Winter)	
		Range	Mean $\pm$ SD	Range	Mean $\pm$ SD
Dust	$\mu\text{g}/\text{m}^3$	6.6-23.3	13 ± 6	3.8-29.4	20.6 ± 7.4
NO_3^-	nmol/m^3	0.2-18.3	3.7 ± 5.5	4.6-43.0	18.5 ± 11.3
NH_4^+		150.9-573.4	278.4 ± 122.4	37.5-350.4	151.4 ± 95.4
IN		155.7-577.6	282.8 ± 122.5	61.1-359.7	170.2 ± 92.1
ON		18.7-421.7	136.0 ± 149.6	53.6-252.8	109.3 ± 55.4
TN		193-784.4	418.8 ± 209.5	153-423.9	279.6 ± 83.5
nss-K^+		7.5-40.8	14.6 ± 10.2	15.8-34.5	27.1 ± 6.3
nss- SO_4^{2-}		108.6-319.1	176.8 ± 58.8	77.9-231.0	158.6 ± 46.4
Total Acid		221.7-641.2	357.4 ± 118	162.7-470.5	335.6 ± 94.3
Fe_T		3.3-25.6	7.9 ± 6.3	4.8-19.7	14.9 ± 4.5
Mn_T	pmol/m^3	285.5-3919	1246.7 ± 1001.7	391.8-1537.1	795.7 ± 311.1
Cu_T		11.2-240	55.3 ± 66.0	15-127.7	57.0 ± 27.8
Fe_S		277.7-1201.6	762.7 ± 323.5	315.2-1431.3	713.5 ± 361.0
Mn_S		147.2-3027.5	827.9 ± 771.5	176.8-786.2	480.9 ± 175.7
Cu_S		7.7-101.7	28.9 ± 25.7	13.7-56.1	27.7 ± 13.5
$\text{Fe}\%$	$\%$	4.7-26.1	12.2 ± 6.5	1.9-13.6	5.5 ± 3.8
$\text{Mn}\%$		50.3-77.3	65.0 ± 10.4	45.1-73.3	60.6 ± 8.4
$\text{Cu}\%$		30.7-98	67.4 ± 23.1	29-91.5	52.5 ± 20.1
ON%		5.8-65.6	26.4 ± 21.7	15.1-75	41.2 ± 18.5

Table 4.3 Wind parcel-wise range and mean $\pm$ standard deviation of dust, trace elements and other chemical species.

	unit	CAP	CAP+MAP	MAP
Dust	$\mu\text{g}/\text{m}^3$	17.4 ± 6.4	15.7 ± 8.3	17.5 ± 8.0
Nitrate (NO_3^-)	nmol/m^3	8.9 ± 8.1	9.8 ± 13.4	12.9 ± 11.3
Ammonium (NH_4^+)	nmol/m^3	246.8 ± 104.4	225.0 ± 160.4	196.3 ± 102.6
IN	nmol/m^3	256.2 ± 103.6	235.3 ± 155.3	209.7 ± 96.5
ON	nmol/m^3	354.2 ± 63.0	98.2 ± 80.66	75.3 ± 32.8
Fe_T	nmol/m^3	15.0 ± 9.2	9.3 ± 5.7	12.3 ± 6.3
Mn_T	pmol/m^3	2169.2 ± 1522.7	856.6 ± 410.5	825.0 ± 415.3
Cu_T	pmol/m^3	119.2 ± 105.3	54.6 ± 36.7	38.6 ± 19.2
Fe_S	pmol/m^3	843.4 ± 317.1	787.8 ± 308.8	661.8 ± 377.9
Mn_S	pmol/m^3	1574.9 ± 1258.1	518.0 ± 239.0	501.1 ± 199.1
Cu_S	pmol/m^3	50.1 ± 44.8	30.3 ± 13.4	20.1 ± 9.7
nss-K^+	nmol/m^3	27.3 ± 13.0	17.9 ± 8.9	21.6 ± 11.2
Total Acid	nmol/m^3	336.6 ± 101.3	346.2 ± 139.4	349.7 ± 77.6
$\text{Fe}_\%$	%	6.2 ± 1.8	11.9 ± 7.6	6.8 ± 4.8
$\text{Mn}_\%$	%	70.1 ± 10.4	60.5 ± 9.5	62.6 ± 9.1
$\text{Cu}_\%$	%	43.5 ± 13.4	66.3 ± 21.7	59.2 ± 24.3
$\text{ON}_\%$	%	59.1 ± 6.0	29.9 ± 22.8	29.7 ± 18.0

4.2.3 Dust and associated total trace elements (TEs) over the Bay of Bengal:

Bay of Bengal receives $13 \pm 6 \mu\text{g}/\text{m}^3$ and $20.6 \pm 7.4 \mu\text{g}/\text{m}^3$ dust during the PM and WM respectively (Fig-4.6, Table 4.2). The observed average dust is much higher than the dust received by the Indian Ocean as discussed in Chapter 5. The dust received during PM is comparable with the Arabian Sea discussed in Chapter 3 but average dust received during WM is much higher than the Arabian Sea (AS) and the Indian Ocean (IO). The higher dust might be due to episodic emission and a smaller number of samples compared to the AS and IO. If we correlate with the range of dust concentration we can find that the highest amount of dust ($3.8\text{-}29.4 \mu\text{g}/\text{m}^3$) received during the WM is almost a similar range during monsoon over the Indian Ocean ($2.8\text{-}25.1 \mu\text{g}/\text{m}^3$)

and much lower compare to the Arabian Sea (Table 4.2), Multiple samples show $>30 \mu\text{g}/\text{m}^3$ dust over the Arabian Sea during the Monsoon and WM Season, however broader geographical coverage episodic nature of dust emission lower the overall average over the AS. Additionally, episodic higher dust emission from IGP can increase dust concentration over the BoB during WM, similar to our observation Srinivas et al., 2013 observed $>40 \mu\text{g}/\text{m}^3$ dust during WM which was absent during Summer. The favourable wind during WM and higher wind speed compared to PM can transport more dust to BoB. When we classify dust concentration as per wind mass source, we observe that CAP and MAP carried a similar amount of dust $\sim 17.5 \mu\text{g}/\text{m}^3$ (Table 4.3) and during mixing they might lose some dust still CAP+MAP receives a comparable amount of dust $15.7 \pm 8.3 \mu\text{g}/\text{m}^3$ (Fig-4.6) indicating well mixing of different wind mass.

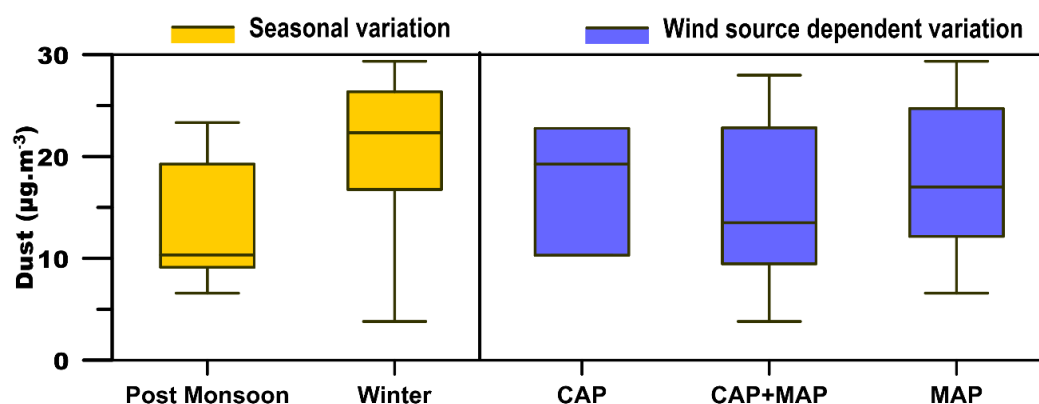


Fig-4.6 Seasonal and wind mass-dependent variations of dust over the Bay of Bengal.

The mass concentration of Fe_{Tot} over the two study periods ranged from $186.74 - 1427.64 \text{ ng m}^{-3}$ with a mean value of $7.9 \pm 6.3 \text{ nmol m}^{-3}$ in PM and $14.9 \pm \text{nmol m}^{-3}$ in WM similar to dust (Fig-4.7; Table 4.2). The observed mean Fe_T concentrations in this study are much higher than other marine atmospheres, ranging from 28.4 ng m^{-3} over the Pacific Ocean (Buck et al., 2013) and lower compared to the Atlantic Ocean (Fe_T range = $0.185-5650 \text{ ng m}^{-3}$) especially sample collected over the eastern Atlantic (Shelley et al., 2018). However, it shows similar values to previously reported Fe_T concentration over the Bay of Bengal ($31-1651 \text{ ng m}^{-3}$, Kumar et al., 2010 and Srinivas et al., 2012), and over the East China Sea (410 ng m^{-3} , Hsu et al., 2010). Winter monsoon in this study showed a higher mean value ($833.83 \pm 249.18 \text{ ng m}^{-3}$) than in previous studies (Kumar et al., 2010; Srinivas et al., 2012). Higher average Fe_T during WM is attributed to a higher average dust supply ($20.55 \pm 7.40 \mu\text{g m}^{-3}$) compared to previous studies (Average dust = $13.81 \pm 11.90 \mu\text{g m}^{-3}$ Kumar et al., 2010).

This study observed that the average Fe_T in CAP, MAP and CAP + MAP are 15.0 ± 9.2 $nmol\ m^{-3}$, 12.3 ± 6.3 $nmol\ m^{-3}$ and 9.3 ± 5.7 $nmol\ m^{-3}$ respectively (Fig-4.7a), which showed the dominance of continental influence. Fe/Al ratio in PM and WM was found to be 0.43 ± 0.20 (range: 0.13 – 0.78) and 0.54 ± 0.14 (range: 0.34 – 0.87), which were similar to the reported UCC Fe/Al (0.44) value (McLennan, 2001). Many previous and recent studies have also reported Fe/Al values (Buck et al., 2006; Kumar et al., 2010; Srinivas et al., 2012) showing localized patterns within the marine boundary layer and influence of MAP. Previous studies by Kumar et al., (2010) and Srinivas et al. (2012) also reported similar Fe/Al ratios over the BoB. Enrichment factor for $Fe \ll 10$ but still higher enrichment factor 1.2 ± 0.3 during WM compared to 1 ± 0.4 in PM (Fig-4.8a) indicates a contribution from anthropogenic emission in both the season and CAP shows >1 EF indicate CAP samples (Fig-4.8b) are more influenced by anthropogenic emission/biomass burning.

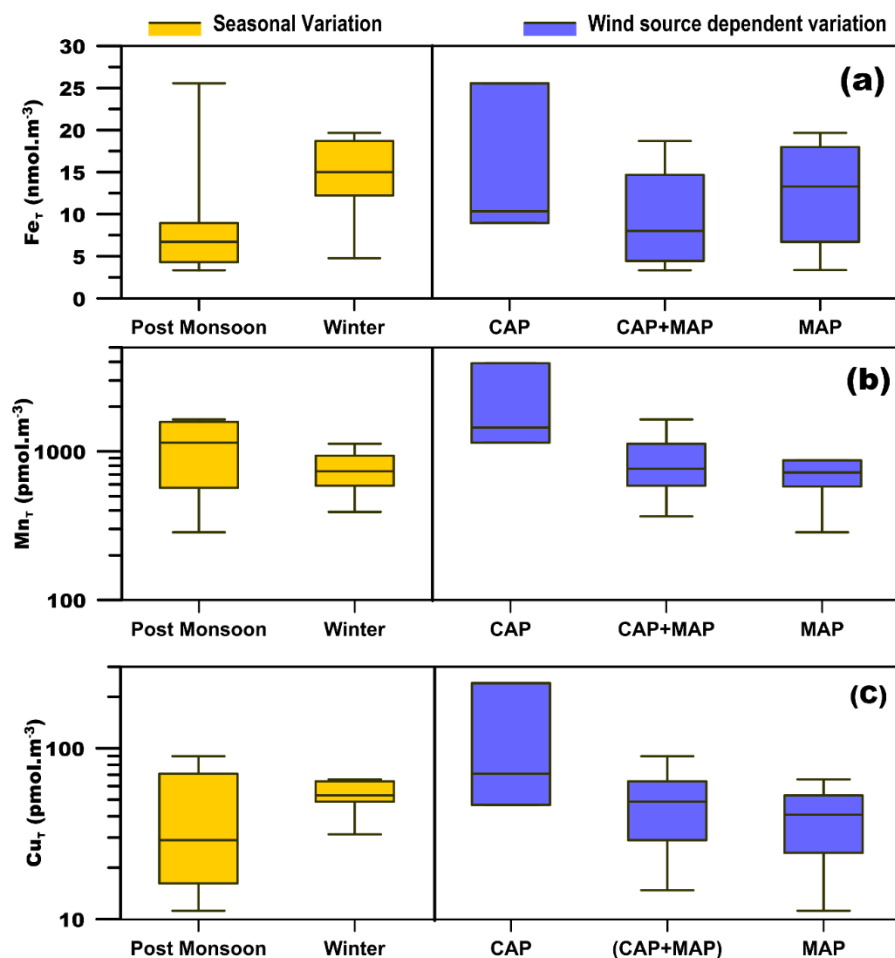


Fig-4.7 Seasonal and wind dependent variation of (a) total Fe (Fe_T), (b) total Mn (Mn_T), (c) total Cu (Cu_T) over the Bay of Bengal.

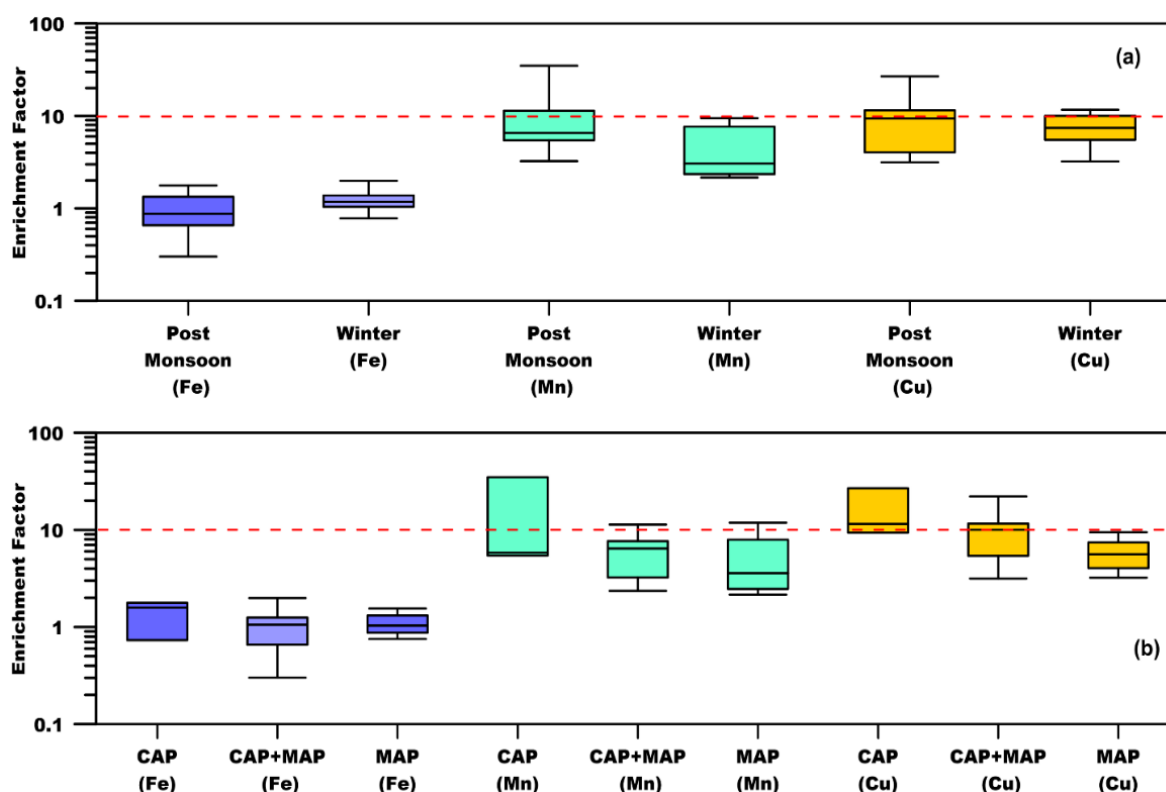


Fig-4.8 Box plot of enrichment factor for Fe (blue), Mn (green) and Cu (yellow) (a) as per season (b) as per wind mass. The red line is considered to be the Enrichment line >10 times of crustal average.

Unlike Fe_T , Mn_T concentration was higher during PM $1246.7 \pm 1001.7 \text{ pmol m}^{-3}$ than WM $795.7 \pm 311.1 \text{ pmol m}^{-3}$ (Fig-4.7, Table 4.2). The observed higher Mn_T concentration was due to the Mn-rich (3919 pmol m^{-3} , Table 4.2) Continental Air Parcel (CAP) derived from the Middle East region, which brought ample Mn to the study location. Previously, Panda et al. (2022) explained mineral dust derived from Middle Eastern deserts was enriched in Mn. Due to this enriched Mn sample CAP sample shows a higher mean Mn concentration $2169.2 \pm 1522.7 \text{ pmol m}^{-3}$, whereas MAP and CAP+ MAP samples show almost similar concentrations of Mn $825.0 \pm 415.3 \text{ pmol m}^{-3}$, $856.5 \pm 410.5 \text{ pmol m}^{-3}$ respectively (Table 4.3). This observation is also supported by EF (Fig-4.8a) where few PM samples are >10 enriched and most of the samples originate from continental wind parcels (Fig-4.8b). In the case of other air parcels, they remain on or below the enrichment line. Observed WM, Mn_T concentration is also similar to the previous Srinivas et al. (2013) over the Bay of Bengal and Powell (2015) observation over the eastern

Atlantic region (median = $>700 \text{ pmol m}^{-3}$ when wind are derived from the Sahara). Other remote locations like the Southern Atlantic Ocean, Pacific Ocean and East China Sea receive much lower in comparison to the BoB irrespective of season (Chance et al., 2015; Buck et al., 2013; Hsu et al., 2010).

Cu_T also shows a similar contribution during PM and WM $57.0 \pm 27.8 \text{ pmol m}^{-3}$ and $55.3 \pm 66.6 \text{ pmol m}^{-3}$ but earlier shows a wider range of $11.2 - 246.8 \text{ pmol m}^{-3}$ than later $15-127.7 \text{ pmol m}^{-3}$ (Fig-4.7, Table 4.2). The observed higher Cu_T concentration during PM was due to wind parcels coming from IGP. This is also supported by higher Cu_T concentrations in CAP samples $119.2 \pm 105.3 \text{ pmol m}^{-3}$, which is almost twice as high as mixed air parcels (CAP+MAP) $54.6 \pm 36.7 \text{ pmol m}^{-3}$ and thrice higher than MAP ($38.6 \pm 19.2 \text{ pmol m}^{-3}$) (Fig-4.7). Several studies explained that enormous biomass burning/stubble burning over the biomass burning during post-harvesting season i.e., PM season can bring ample amounts of anthropogenic Cu to BoB, this is the case of elevated Cu in CAP samples during PM (Srinivas and Sarin, 2013; Nayak et al., 2022). However, the unlikely Mn_T observed mean Cu_T over BoB was $\sim$ twice lower than the previous observation by Srinivas and Sarin (2013) and more than 10 times lower than the East China Sea observation by Hsu et al. (2010). The observed mean Cu_T was also lower than our previous observation during the Summer over the Bay of Bengal Indian Ocean Sector (discussed in Chapter 5) and also lower than the Arabian Sea irrespective of seasons (discussed in Chapter 3).

4.2.4 Soluble TEs over the Bay of Bengal:

Soluble TEs over BoB show the opposite pattern of dust, mean soluble TEs higher during PM $762.7 \pm 323.5 \text{ pmol m}^{-3}$, $827.9 \pm 771.5 \text{ pmol m}^{-3}$, $28.9 \pm 25.7 \text{ pmol m}^{-3}$ and $713.5 \pm 361.0 \text{ pmol m}^{-3}$, $480.9 \pm 175.7 \text{ pmol m}^{-3}$, $27.7 \pm 13.5 \text{ pmol m}^{-3}$ during WM for Fe, Mn and Cu respectively (Fig-4.9, Table 4.2). Higher acidic species along with anthropogenic emission observed from high EF lead to atmospheric processing during long-range transport of dust causing relatively higher soluble TEs during PM. Similarly, CAP samples showed higher soluble TEs (Fig-4.9) due to the combined effect of anthropogenic emission and atmospheric processing. Whereas CAP+MAP shows lower soluble TEs due to the dominance of atmospheric processing/mixing during their long-range transport and the least soluble TEs are found in MAP Samples (Fig-4.9). The observed soluble TEs over BoB is higher compared to IO and AS (monsoon) than Cu discussed in previous chapters. The observed mean soluble Fe and Cu during WM over BoB is lower than AS, whereas

soluble Mn over BoB is higher during WM.

4.2.5 Fractional solubility and factors controlling fractional solubility over the Bay of Bengal:

Overall average fractional solubility of iron ($\text{Fe}_\%$) was observed with the mean value of 12.2 ± 6.5 in PM and 5.5 ± 3.8 in WM (Fig-4.10a). The fractional solubility of iron ($\text{Fe}_\%$) in PM is 2 times greater than WM in this study and also with previously observed data in the Bay of Bengal, which was 6.9% (Srinivas et al., 2012). This observation could be supported by the higher acidic species range in PM ($221.7 - 641.2 \text{ nmol m}^{-3}$) than WM ($162.7 - 470.5 \text{ pmol m}^{-3}$) over BoB (Table 4.2).

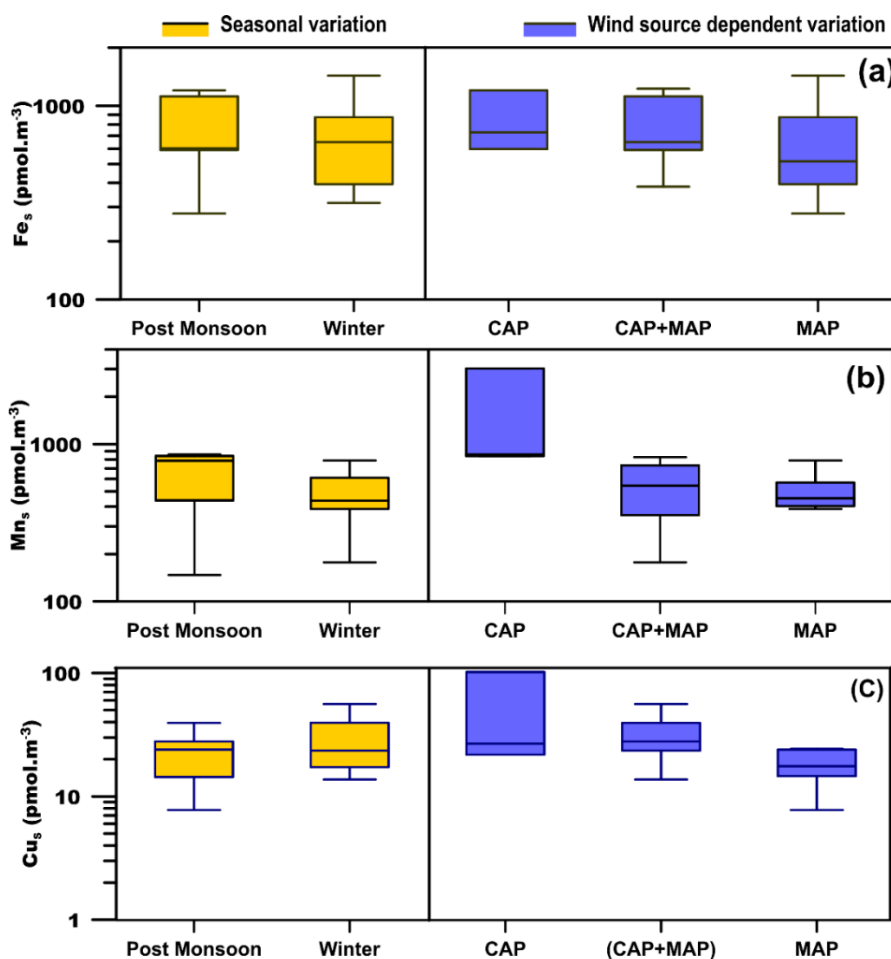


Fig-4.9 Seasonal and wind-dependent variation of (a) soluble Fe (Fes), (b) soluble Mn (Mns), (c) soluble Cu (Cus) over the Bay of Bengal.

The average $\text{Fe}_\%$ was found to be the maximum in MAP+CAP ($11.9 \pm 7.6\%$) followed by MAP

($6.8 \pm 4.8\%$) and CAP ($6.2 \pm 1.8\%$) which indicates that acid processing during long-range transport of Fe-containing particles significantly increases the Fe% in the aerosol. A number of studies indicate that during long-range transport, atmospheric processing of mineral dust by anthropogenic acidic species (HNO_3 and H_2SO_4) can enhance the fractional solubility of aerosol iron (Kumar et al., 2010; Buck et al., 2013; Shelley et al., 2018; Baker et al., 2021). Field-based studies found that aerosol Fe solubility was positively correlated with sulfate and/or nitrate (Kumar et al., 2010; Shi et al., 2020), indicating enhancement of Fe solubility through atmospheric acid processing.

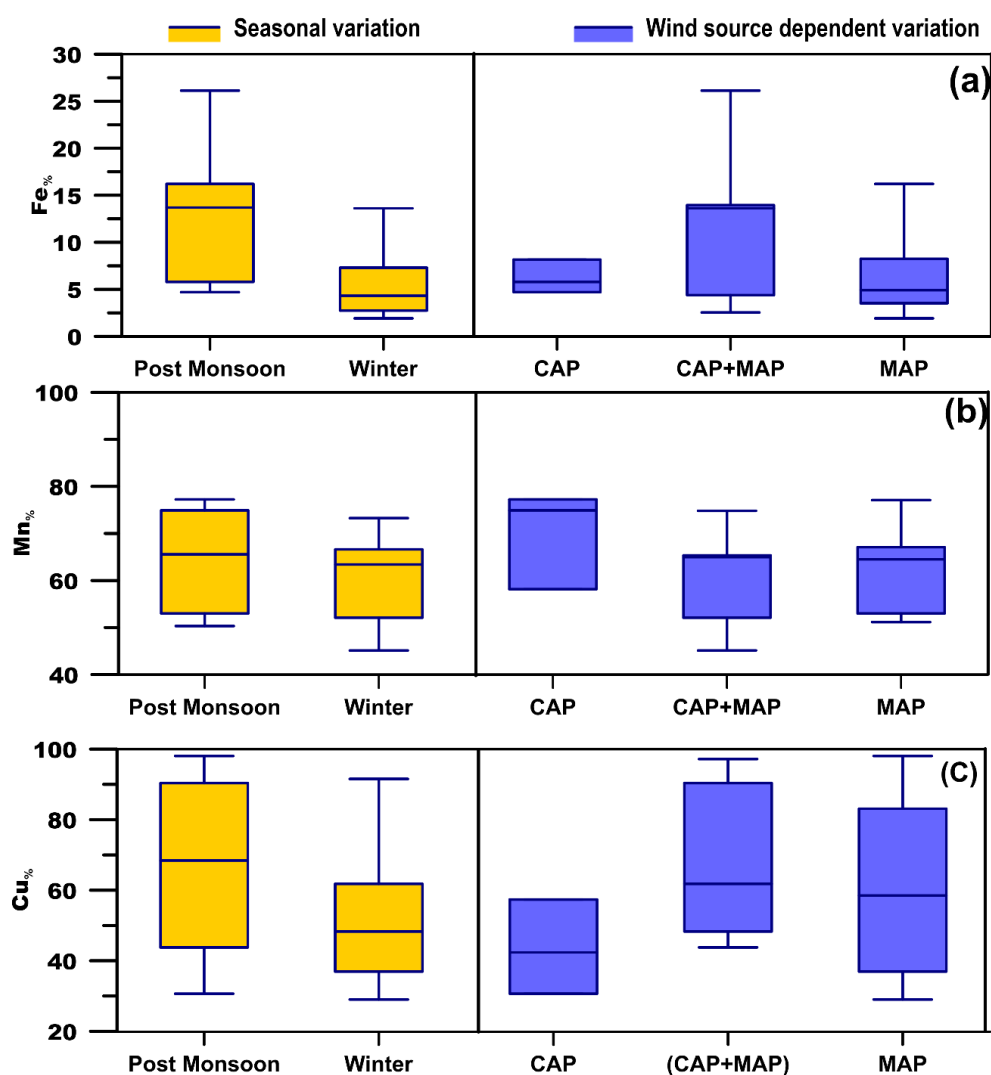


Fig-4.10 Seasonal and wind-dependent fractional solubility of (a) Fe%, (b) Mn%, (c) Cu% over the Bay of Bengal.

The correlation between Fe% and the molar equivalent of two major acidic species (SO_4^{2-} ,

NO_3^-) known as total acid ($\text{TA} = \text{NO}_3^- + 2\text{SO}_4^{2-}$ in nmol m^{-3}) in aerosol particles was examined in this study (Buck et al., 2006). In both seasons $\text{Fe}_\%$ showed a significant correlation with total acid (Fig-4.12a). In the present study, the RH was about 70% on average, and total acid/ Fe_{Tot} was about $61.21 \pm 35.19 \text{ nmol nmol}^{-1}$ in PM and $23.32 \pm 4.64 \text{ nmol nmol}^{-1}$ in WM, indicating high aerosol acidification due to the catalysis of soluble Fe and, consequently, substantial production of soluble acid. In a recent study, Shi et al., (2020) reported the feedback between aerosol acidification and Fe catalysis as a major reason for high Fe solubility in aerosols. This observation was also supported by a significant correlation $r = 0.50$ between TA and $\text{Fe}_\%$ during PM suggesting a higher degree of acid processing of Fe-bearing minerals compared to WM $r = 0.38$. Additionally, an inverse relation between Fe_T and $\text{Fe}_\%$ (Fig-4.11a) suggests in WM higher Fe_T -bearing dust, low TA leads to lower fractional solubility inferred from a relatively -ve value of (0.65) compared to the PM ($r = -0.54$). The nss-K^+ being a tracer for biomass burning correlated with $\text{Fe}_\%$ (Kumar et al., 2010; Srinivas et al., 2012; Panda et al., 2024). $\text{Fe}_\%$ concentration shows a significant correlation with nss-K^+ in PM ($r = 0.68$) and in WM ($r = 0.33$) (Fig-4.13a) indicating biomass burning is a potential source for soluble Fe during both seasons. Kumar et al. (2010) also observed a significant correlation between nss-K^+ and $\text{Fe}_\%$ during WM, when continental outflow prevails over the BoB. The IGP region experiences an ample amount of biomass burning during PM and BoB receives a significant amount of aerosol from IGP during this period (discussed in the previous section) this indicates biomass burning is an important source of Fe during PM, when the crop burning is a main influence as previously discussed. Observed outliers (Fig-4.13a) in PM are CAP samples of ample amounts of dust (discussed previously) along with anthropogenic emissions that alter the relationship and these samples follow different correlation trends.

The Mn also shows higher mean fractional solubility of $65 \pm 10.4 \%$ during PM and $60.6 \pm 8.4 \%$ during WM which is comparable with our previous winter season observation over the AS but higher compared to the monsoon and all observations over the Indian Ocean. But unlike the AS and IO, $\text{Mn}_\%$ over BoB varies within a narrow range, observed wider fractional solubility in earlier basins is due to the change in dust source these two basins receive dust from enriched Mn sources frequently depending upon the geographical location and wind direction. Due to the same region, episodic active wind from Iran and the Middle East brings enriched Mn during PM, which shows higher fractional solubility with a higher amount of total Mn (showed as an outlier in Fig-4.11b) instead of low TA (showed as an outlier in Fig-4.12b) also increase the mean $\text{Mn}_\%$ in CAP samples $70.1 \pm 10.4 \%$ compare to MAP samples $62.6 \pm 9.1 \%$ and CAP+MAP samples $60.5 \pm 9.5 \%$

(Fig-4.10b).

Mineral dust is the primary contributor to Mn (Mahowald et al., 2018), and atmospheric processing of these plays a significant role in determining fractional solubility along with mineralogy (Panda et al., 2022, 2024). So unlike Fe, we did get a strong inverse relation between Mn% and Mn_T (Fig-4.11b). Due to differences in dust sources mineralogy of Mn changes over the BoB, so as acid processing, which is reflected in Fig- 4.12b, where TA and Mn% show a relatively poor correlation compared to the AS winter (discussed in previous chapter). Over the BoB, significant correlation between nss-K⁺ and Mn% suggests Mn over the BoB is affected by biomass burning emission (Fig-4.13b). The WM season receives relatively more anthropogenic Mn ($r = 0.51$) than PM ($r = 0.35$).

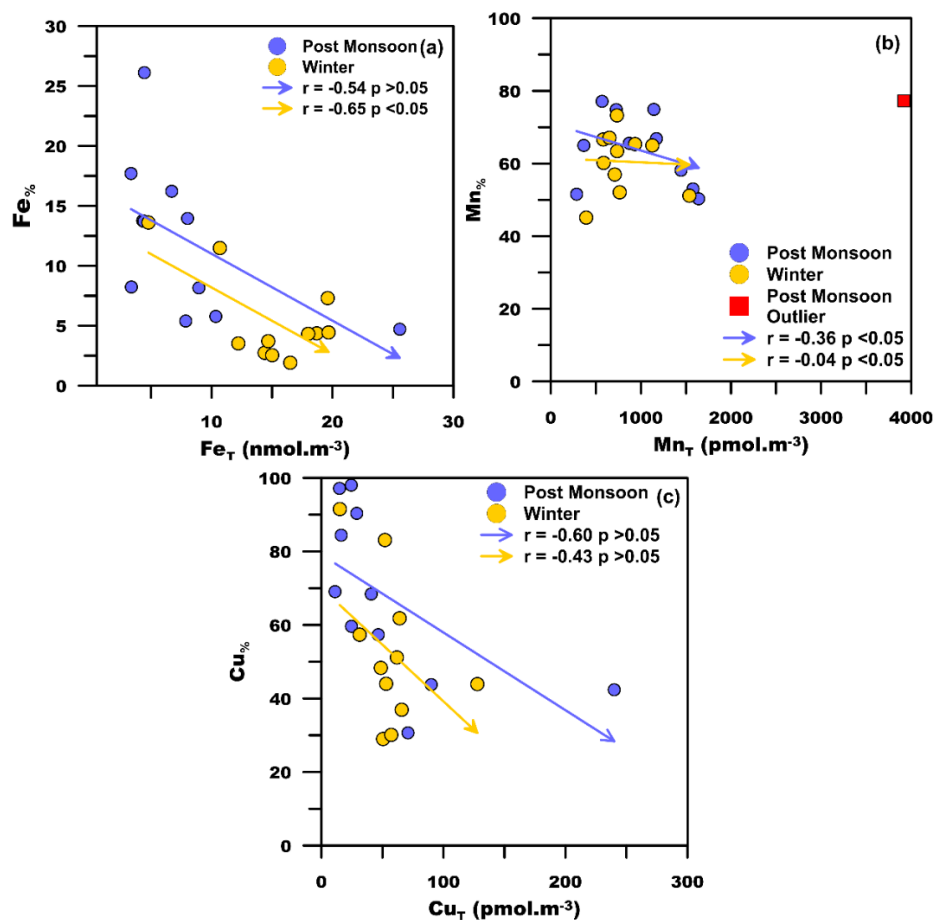


Fig-4.11 Correlation plot between (a) total Fe (Fe_T) with Fe%, (b) total Mn (Mn_T) with Mn% (c) total Cu (Cu_T) with Cu%.

Similar to Fe and Mn, Cu also shows higher mean fractional solubility during PM 67.4 ± 23.1

% compared to WM 52.5 ± 20.1 %. The observed seasonal mean Cu% is higher compared to the Indian Ocean and Arabian Sea for Summer and Monsoon Seasons but WM AS and BoB show similar Cu%. Cu is mainly derived from anthropogenic sources like biomass burning, fossil fuel burning shows higher fractional solubility compared to Fe. CAP+MAP samples show higher Cu% (66.3 ± 21.7 %) compared to CAP and MAP sample which receives 43.5 ± 13.4 and 59.2 ± 24.3 % respectively similar to Fe. Although Cu is derived from anthropogenic emission, the significant contribution from dust can't be ignored, this observation is supported by strong inverse relation between Cu% and Cu_T (Fig-4.11c) and atmospheric processing of these Cu during long-range transport increases the fractional solubility inferred from (Fig-4.12c). We observed a few outlier samples in Cu% and total acid correlation plot (Fig-4.12c), samples (3 nos) specifically have higher TA but low solubility and also contained a higher amount of dust content, while the outlier sample (1nos marked in red) with lower TA with higher fractional solubility contained the least amount of dust from WM.

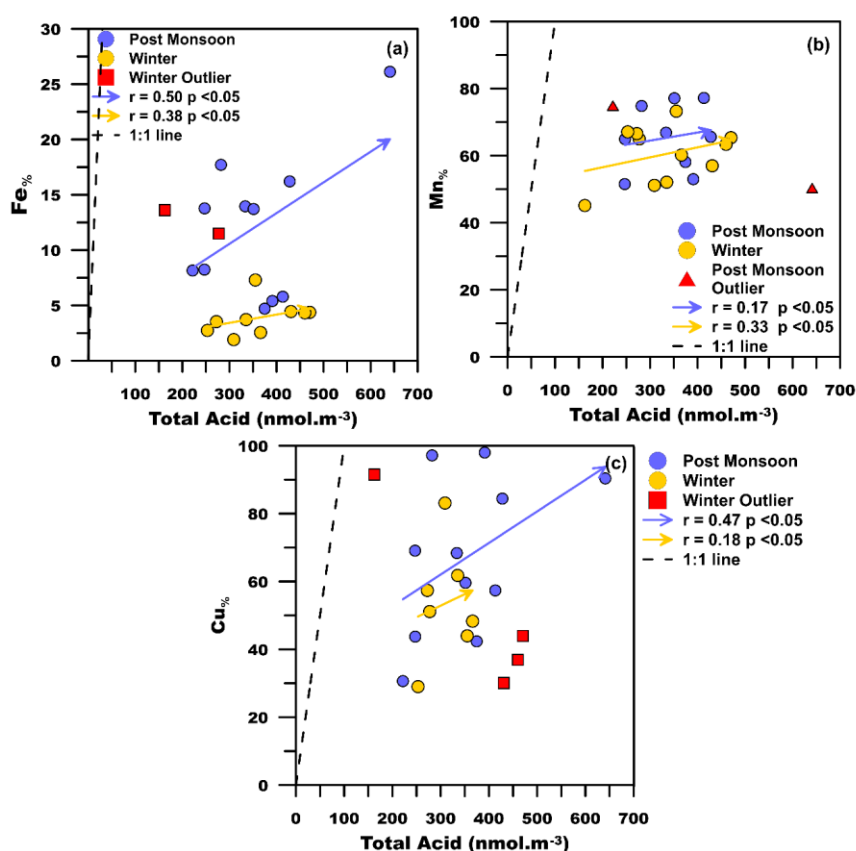


Fig-4.12 Correlation plot between Total Acid (TA) with Fe%, Mn% and Cu% in (a), (b) and (c) respectively.

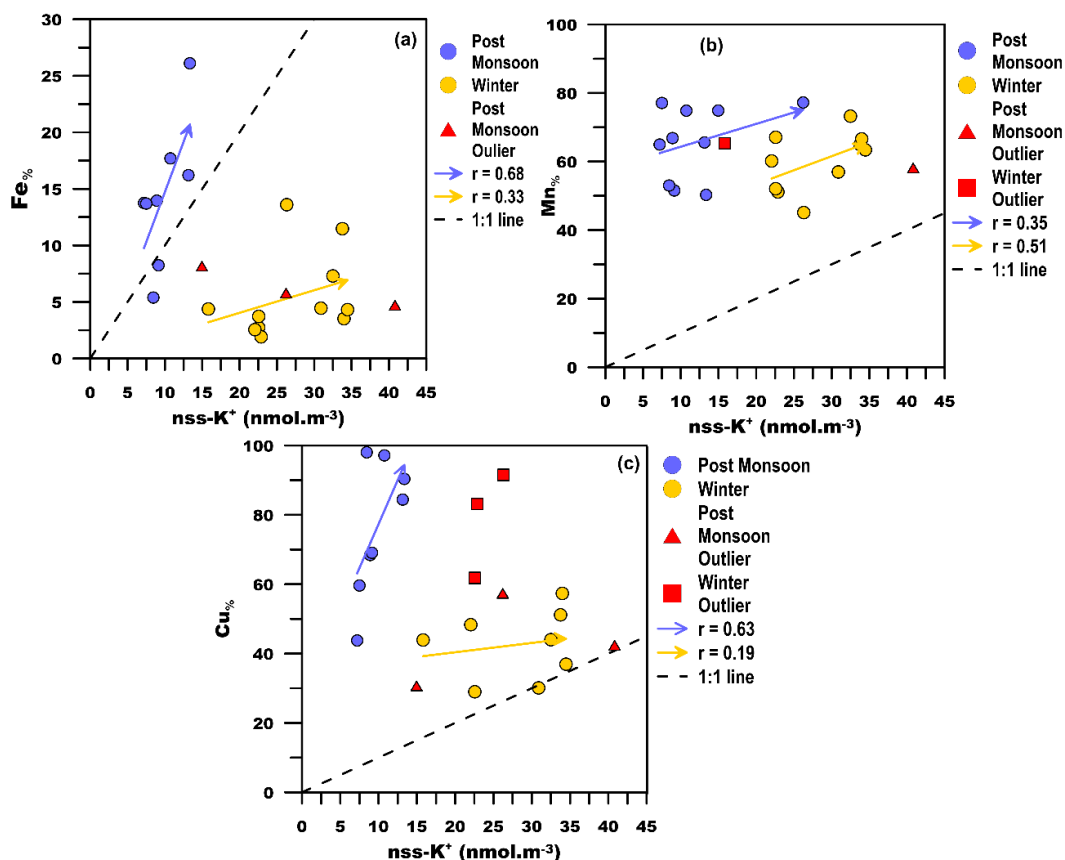


Fig-4.13 Correlation plot between $nss-K^+$ with Fe%, Mn% and Cu% in (a), (b) and (c) respectively.

Due to these conditions, the WM sample shows an r -value of 0.18 compared to the PM ($r = 0.47$). Similar to Fe CAP sample of PM samples and high dust sample of WM exists as an outlier in $nss-K^+$ and Cu% correlation (Fig-4.13c marked in red) these samples might be spiked by the additional Cu source such as fossil fuel emission or from ore smelters. Other than these outlier samples, both seasons show the contribution of Cu from biomass burning while in PM biomass burning emissions are the major contributor of Cus inferred from $r = 0.63$ (Fig-4.13c).

4.2.6 Dry depositional flux over the Bay of Bengal:

The estimated mean dry deposition flux of dust over the BoB is $11.2 \pm 5.2 \text{ mg m}^{-2}\text{d}^{-1}$ during PM which is lower compared to WM $17.8 \pm 6.4 \text{ mg m}^{-2}\text{d}^{-1}$ (Fig-4.14). Overserved higher dust flux during WM is also higher compared to a previous study by Srinivas and Sarin (2013) who observed $12 \pm 10 \text{ mg m}^{-2}\text{d}^{-1}$ during WM and $10 \pm 6 \text{ mg m}^{-2}\text{d}^{-1}$ during Summer. The observed dust flux during WM is also higher compared to our previous observations over the IO and AS. The observed high dust during WM may be due to episodic high dust flow during this period or

due to the relatively narrow geographical/spatial coverage of cruises (restricted to western BoB) compared to Srinivas Sarin (2013) where the geographical coverage was much wider than the current study and favorable wind transport more dust to coastal region compared to distal open ocean region. This is a proposed hypothesis for our observation but to better constrain this observation we need to do more dust flux measurements over the BoB during different seasons including WM. The MADCOW estimation ($0.5 \pm 0.08 \text{ g.m}^{-2} \cdot \text{year}^{-1}$) dust over the IO by Grand et al. (2015) is one to fold lower than our current observations as well as the previous observations. overall mean total N flux in dry deposition is $39.08 \pm 20.21 \text{ } \mu\text{mol m}^{-2}\text{d}^{-1}$ in PM and $38.54 \pm 9.04 \text{ } \mu\text{mol m}^{-2}\text{d}^{-1}$ in WM. In the two sampling periods, the mean flux values did not differ significantly. The range of observed data is greater than that of previous studies (Srinivas et al., 2011a; Singh et al., 2012). Day-wise variations in different nutrient ions (IN, ON) are presented in Fig-4.15. Area-weighted atmospheric dry-deposition flux (i.e. Assuming that anthropogenic influence persists for a period of 7 months, PM (October- November) and WM (December–April), flux is integrated for 210 d for estimating the annual input and total area of BoB = $2.2 * 10^{12} \text{ m}^2$) of IN were $0.18 \pm 0.07 \text{ Tg N yr}^{-1}$ in PM and $0.19 \pm 0.07 \text{ Tg N yr}^{-1}$ in WM consecutively. The observed IN flux is comparable to the riverine supply of inorganic N flux $0.9\text{--}2.0 \text{ Tg-N yr}^{-1}$ (Srinivas and Sarin, 2013), which indicates the increasing importance of atmospheric deposition to ocean surface water. In earlier studies, Srinivas and Sarin (2013) estimated $0.01\text{--}0.38 \text{ Tg-N yr}^{-1}$ atmospheric flux for IN considering only the WM period.

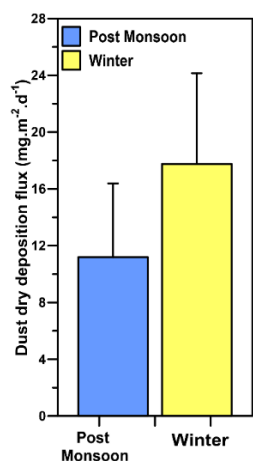


Fig-4.14 Dry deposition flux of dust over BoB during Post-monsoon (PM) and Winter monsoon (WM).

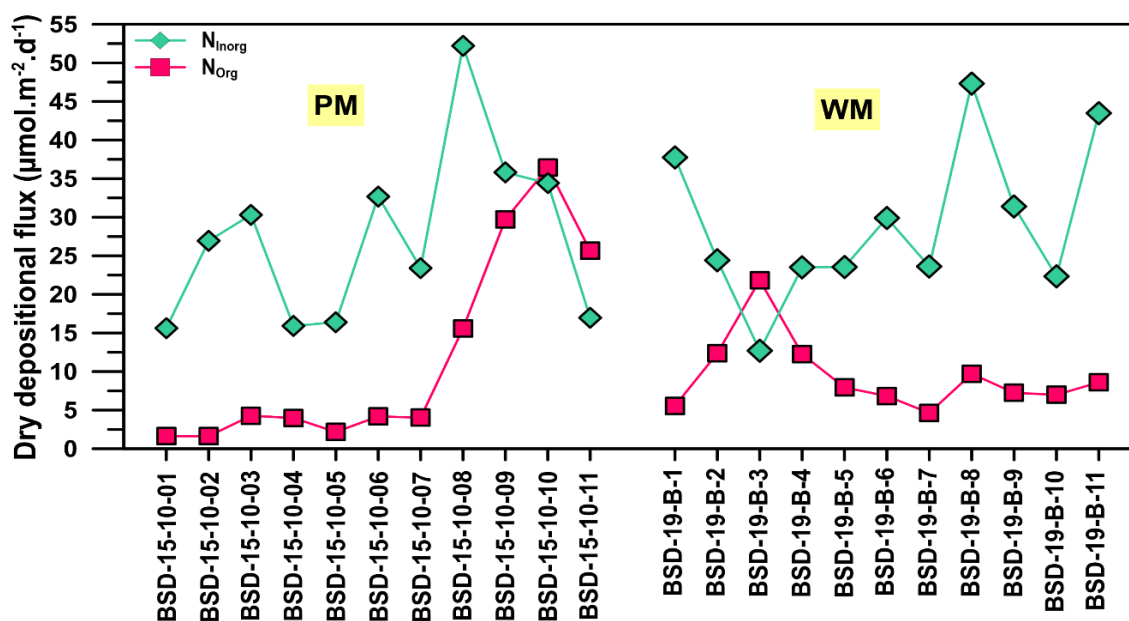


Fig-4.15 Daily dry deposition flux of reactive nitrogen species IN and ON over BoB during Post-monsoon (PM) and Winter monsoon (WM).

The present study observed similar IN depositional flux during both seasons, which indicates the importance of deposition in PM and also indicates the significance of anthropogenic influence through recent times. The observed N deposition flux over the marine boundary layer of BoB is significantly influenced by the soluble reactive nitrogen species and their subsequent deposition to seawater can have a substantial impact on surface biogeochemistry, which is discussed in later sections.

The estimated mean dry depositional flux of the total TEs are $\text{Fe} = 6.9 \pm 5.5 \mu\text{mol m}^{-2}\text{d}^{-1}$ during PM lower compared to WM $12.9 \pm 3.9 \mu\text{mol m}^{-2}\text{d}^{-1}$ (Fig-4.16a) but Mn follows the opposite trend with higher flux during PM $1077 \pm 865.5 \text{ nmol m}^{-2}\text{d}^{-1}$ compare to WM $687.5 \pm 268.8 \mu\text{mol m}^{-2}\text{d}^{-1}$ (Fig-4.16a) and Cu shows almost similar flux during both the season $4.8 \pm 5.7 \text{ nmol m}^{-2}\text{d}^{-1}$ during PM and $4.9 \pm 2.8 \text{ nmol m}^{-2}\text{d}^{-1}$ in WM (Fig-4.16a). Similar to dust, Fe_T flux during WM is higher than in previous observations, but PM flux is within the range of previous observations. In the case of Mn we observe a higher flux during PM compared to previous observations by Srinivas and Sarin (2013) $627 \pm 462 \text{ nmol m}^{-2}\text{d}^{-1}$ during WM which is comparable to our current observation. The estimated Cu flux in the current study is lower compared to Srinivas and Sarin (2013) observation. In all their element cases deposition velocity are also the same but observed

variation in elemental flux due to the activity of different sources during different times. To understand the TEs variation more observations is required, specifically long-term observation will help us understand interannual variations and activity of different sources during different times.

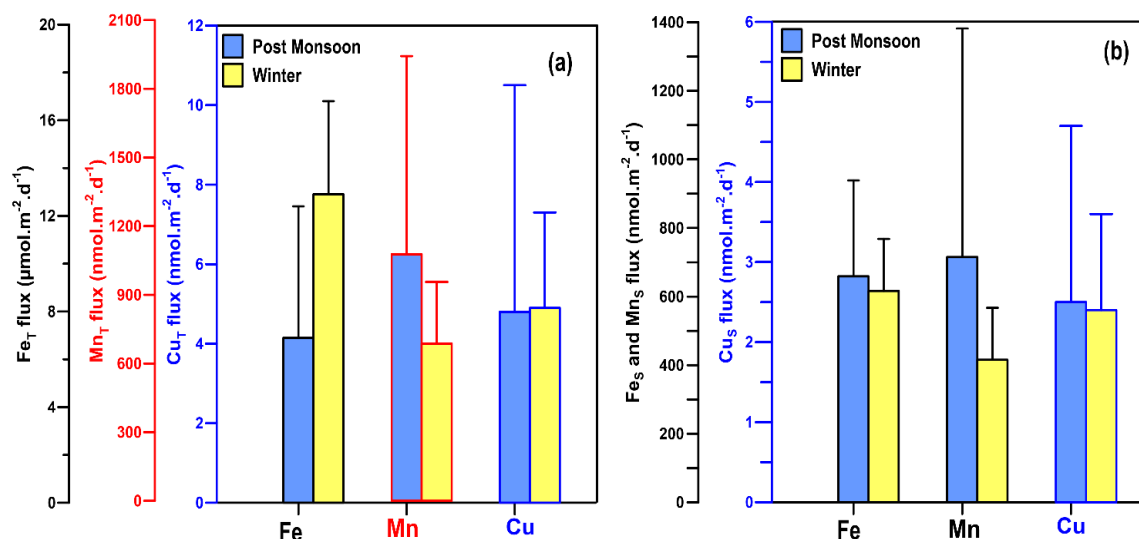


Fig-4.16 Dry deposition flux of (a) total trace elements (b) soluble trace elements over BoB during Post-monsoon (PM) and Winter monsoon (WM).

The mean dry-deposition fluxes of Fe_S over BoB observed $0.66 \pm 0.28 \mu\text{mol m}^{-2} \text{d}^{-1}$ in PM and $0.62 \pm 0.31 \mu\text{mol m}^{-2} \text{d}^{-1}$, which is comparable to previous studies in continental outflow period over BoB (Srinivas et al., 2012). Recent studies suggest that anthropogenic combustion and biomass-burning processes can contribute significantly to the atmospheric inputs of soluble Fe into the ocean (Kumar et al., 2010; Matsui et al., 2018; Ito et al., 2021; Hamilton et al., 2022). The significance of atmospheric Fe deposition in ocean biogeochemistry is discussed in later sections. Srinivas et al., 2013, estimated riverine fluxes of dissolved-Fe to the BoB were 0.065 Tg yr^{-1} . The estimated atmospheric Fe_S fluxes from this study are 0.017 and 0.016 Tg yr^{-1} which is 26% and 25% of the riverine flux in PM and WM respectively, which is almost 2 times greater than previous studies (13% in WM, Srinivas et al., 2013), the result indicates increasing anthropogenic influence in atmospheric depositions. The estimated Fe_{ws} flux is also comparable to the present-day global atmospheric Fe_S flux range into the ocean, which is $0.2\text{--}0.4 \text{ Tg Fe yr}^{-1}$ (Mahowald et al., 2009). Similar to Fe_S, Mn_S is higher during PM $715.3 \pm 666.6 \text{ nmol m}^{-2} \text{d}^{-1}$ and $415.5 \pm 151.8 \text{ nmol m}^{-2} \text{d}^{-1}$ in WM (Fig-4.16b). This is the first observation of soluble Mn over BoB so we didn't have any previous reference over the BoB but compared to our observation over

IO and AS, BoB receives higher soluble Mn flux during both seasons. The dominance of atmospheric processing over BoB was discussed previously resulting in high Mns deposition compared to other basins. Whereas Cu, which is majorly derived from anthropogenic activity and anthropogenic, shows almost equal dry deposition flux $\sim 2.4 \text{ nmol m}^{-2} \text{ d}^{-1}$ (Fig-4.16b) during both seasons, both lower than our observations over AS and IO.

4.3 Impact on Biogeochemistry:

4.3.1 Role of Atmospheric N in New Production:

The atmospheric deposition of soluble inorganic nitrogen could apparently fuel the new primary production of the BoB ecosystem. It is assumed in previous observations that inorganic nitrogen is fully bio-available and in the case of organic nitrogen it has 20–80% lower bioavailability (Yan and Kim, 2015). For the calculation of new production, Redfield ratio C: N of 6.625, and N_{Org} utilization rates (assumed to be 80%), was used to calculate the new production in surface water (Chen and Huang, 2021). Equation is as follows

$$\text{New production (NP)} = [(\text{DF IN} + \alpha \text{ DF ON})] \times 6.625$$

Where, DF is the deposition flux determined for IN and ON, and α is the ON bioavailability parameter, which varies from 0.2 to 0.8. In this study, the bioavailability of ON was assumed maximum of 80% (0.8). Using a Redfield C / N ratio of 6.625, the total nitrogen flux was converted to $1.57 - 6.00 \text{ mg C m}^{-2} \text{ d}^{-1}$ ($3.41 \pm 1.67 \text{ gm C m}^{-2} \text{ d}^{-1}$) fixed by marine phytoplankton in PM. In WM it was estimated $5.2 - 15 \text{ mg C m}^{-2} \text{ d}^{-1}$ ($3.40 \pm 0.84 \text{ gm C m}^{-2} \text{ d}^{-1}$). According to earlier studies, the typical range of column-integrated primary productivity in PM for BoB was accounted for $184 - 512 \text{ mg C m}^{-2} \text{ d}^{-1}$ in PM and in WM it was found to be $99 - 566 \text{ mg C m}^{-2} \text{ d}^{-1}$ (Gauns et al., 2005). This would account for 0.9-3.3% and 2.6-5.2% primary production in the surface water of BoB for FIM and WM respectively, which were found to be in good agreement with the previous study where Srinivas et al. (2011), reported up to 13% of the Primary Production could be supported by atmospheric deposition of nitrogen. In comparison, other studies reported 12–14% in the southern East China Sea (Yan and Kim, 2015), 0.3–6.7% in the Yellow Sea (Qi et al., 2013), 5.6–8.7% in the northern South China Sea (Chen and Huang, 2018). Duce et al., (2008) reported 1.5–6.9% on average for oceans worldwide. Accordingly, for marginal seas near densely populated areas like BoB are subjected to constant observation and further research on

atmospheric deposition as they can substantially affect the growth of phytoplankton in the ocean and affect the entire ecosystem.

4.3.2 Role in Nitrogen fixation:

Nitrogen fixation is globally acknowledged as an important pathway for bioavailable nitrogen inputs in the marine ecosystem by altering primary production in nitrogen (N) limited marine environments (Elser et al., 2007; Sohm et al., 2011). This process is most often limited by iron (Fe) (Moore et al., 2013). This present study estimated the potential N-fixation with respect to atmospheric deposition by assuming Fe limitation in the BoB by the following equations (Okin et al., 2011).

$$N_{\text{Fix}}^{\text{Atm}} = Fe_s^{\text{Atm}} \times \left(\frac{N}{Fe} \right)_{\text{diaz}}, \text{ where Fe is limiting}$$

In this equation, $N_{\text{Fix}}^{\text{Atm}}$ is N-fixation supported by the atmospheric deposition of Fe (Baker et al., 2007); Fe_s^{Atm} dry deposition flux of and Fe_s Okin et al. (2011) reported that the N:Fe ratio of diazotrophic organisms spans more than an order of magnitude (from 50 to 1050 g/g). In this study for estimations of $N_{\text{Fix}}^{\text{Atm}}$, the extreme values of the N:Fe ratio were used. The values derived using an N:Fe ratio of 1050 should be considered as the maximum possible rates of N fixation. These maximum rates of nitrogen fixation (using an N:Fe ratio of 1050) due to atmospheric Fe deposition in the BoB are $691.90 \pm 293.51 \mu\text{mol N m}^{-2}\text{d}^{-1}$ ($\sim 6.50\text{--}28.13 \text{ Tg yr}^{-1}$) in PM and $647.26 \pm 327.49 \mu\text{mol N m}^{-2}\text{d}^{-1}$ ($\sim 7.38\text{--}33.50 \text{ Tg yr}^{-1}$) in WM. In contrast, using a N: Fe ratio of 50, the maximum rate of N fixation in this region is $32.95 \pm 13.98 \mu\text{mol m}^{-2}\text{d}^{-1}$ ($\sim 0.31\text{--}1.34 \text{ Tg yr}^{-1}$) in PM and $30.82 \pm 15.59 \mu\text{mol N m}^{-2}\text{d}^{-1}$ ($\sim 0.35\text{--}1.60 \text{ Tg yr}^{-1}$) in WM. This comparison argues that the N fixation rates in this region are closer to the lower range of N: Fe (50 g/g) and N: P ratio used here. An upper estimate of 1.0 Tg-N yr^{-1} ($80 \mu\text{mol m}^{-2}\text{d}^{-1}$) has been suggested based on a mass balance approach by (Naqvi et al., 2011) which is also in the same order as our estimate in this study that is (Avg $\pm$ SD, $0.82 \pm 0.37 \text{ Tg-N yr}^{-1}$) by assuming Fe limitation in overall study period. This measurement suggests that in this region the lower N: Fe value may be applicable and a higher estimate for N-fixation rate $\sim 691.90 \mu\text{mol N m}^{-2} \text{ d}^{-1}$ is very unlikely with respect to the in-situ N fixation of this region. The observed N fixation rate from atmospheric Fe deposition is found to be slightly higher than the previous studies for this

region (Srinivas and Sarin, 2013) and is in good agreement with other ocean basins (Deutsch et al., 2001; Karl and Letelier, 2008; Okin et al., 2011). It is also comparable to the global nitrogen fixation is estimated in the range of $\sim 111\text{--}164 \text{ Tg N yr}^{-1}$ in recent times (Krishnamurthy et al., 2009; Jickells et al., 2017).

4.3.3 Role in Carbon fixation:

In this study, potential carbon fixation rates, supported by atmospheric deposition, have been estimated following the approach of (Okin et al., 2011). The underlying assumption is that the surface waters of the northern BoB are replete in P (a non-limiting nutrient) and atmospheric deposition of Fe and N could support additional primary production. In the Bay of Bengal, during winter, the phytoplankton community is dominated by the abundance of diatoms (80–90%) (Gauns et al., 2005). Since diatoms are one of the abundant phytoplankton species in the BoB; the C-fixation is estimated by atmospheric input of Fe. The cellular uptake ratio by diatoms is about $8 \mu\text{mol/mol}$ (i.e. C:Fe = 1,25,000) (Moore et al., 2002). Using the average fractional solubility of aerosol iron ($\sim 12\%$ in PM and $\sim 5\%$ in WM), the dry-deposition of soluble iron to the Bay of Bengal is about 0.017 Tg yr^{-1} and 0.016 Tg yr^{-1} in both seasons respectively. The atmospheric input of Fe_{ws} can account for $2.13 \pm 0.90 \text{ Pg -C yr}^{-1}$ in PM and $1.99 \pm 1.01 \text{ Pg-C yr}^{-1}$ in WM. Therefore, atmospheric input of Fe_{ws} can account for $\sim 4\%$ of global PP (50 Pg-C yr^{-1} ; Carr et al., 2006) in both periods, while the C fixation rate in PM was slightly higher than WM. Kumar and Ramesh (2005), reported that the f- ratios (new production) found to be very high in PM, ranging from 0.1 to 0.8 (mean ~ 0.5) regardless of proximity to the coast, which is much higher than the other highly productive regions. This high f ratio indicates the capacity to remove and remove the anthropogenic excess CO_2 from the atmosphere during the PM. Hence, PM plays an important role in terms of atmospheric nutrient supply to BoB. This present study shows a 2 times higher C-fixation rate than earlier study by Srinivas and Sarin (2013), which may be attributed to the incorporation of PM months in nutrient flux estimation. However, further extensive studies are required to estimate the amount of fixed carbon by atmospheric deposition exports and sequester in the Deep Ocean.

4.4 Summary:

The transport pattern of continental substances and pollutants from adjacent continents to the Bay of Bengal (BoB) has drawn more attention as it can considerably impact the surface ocean's biogeochemical cycles. In this study, to quantify the atmospheric dry deposition of selected species (IN, ON, TEs such as Fe, Mn and Cu), their simultaneous measurements along with the other ionic composition and fractional solubility of TEs in bulk aerosol samples from the MABL over the Bay of Bengal in Post-Monsoon (PM) and Winter-Monsoon (WM) have been carried out. The contribution of different air masses (CAP, CAP+MAP and MAP) were also observed for the overall sample during two sampling periods. The observations have resulted in the following conclusions:

- The reactive nitrogen species like NH_4^+ and ON concentrations were relatively higher than NO_3^- due to the contribution of anthropogenic aerosol sources. Aerosol ammonium and ON exhibited the highest concentration during PM but the highest nitrate concentration during WM. NH_4^+ dominates the IN concentration (NH_4^+/IN more than 0.8 in both PM and WM) indicating anthropogenic influence. TN flux in dry deposition is $39.08 \pm 9.04 \mu\text{mol m}^{-2}\text{d}^{-1}$ in PM and $38.51 \pm 9.04 \mu\text{mol m}^{-2}\text{d}^{-1}$ in WM. Using the Redfield ratio, TN flux can account for $1.57 - 6.00 \text{ C m}^{-2}\text{d}^{-1}$ and $2.53\text{-}5.11 \text{ mg C m}^{-2}\text{d}^{-1}$ fixed by marine phytoplankton in PM and WM, respectively, which can support up to 3.3% and 5.3% primary productivity in two respective seasons.
- The Bay of Bengal receives the highest dust and Fe_T during WM which is higher compared to other seasons similar to M_L owing to high wind activity during WM able to transport more continental material from land to sea. Observed high M_L , dust and total TEs during WM in CAP samples compared to the other two categories owing to the proximity of sampling location and favorable wind conditions. Higher Mn_T during PM due to episodic wind from the Middle East is able to transport Mn-enriched mineral dust up to BoB.
- Soluble TEs show higher concentration during PM owing to low mass load and relatively high anthropogenic supply of acidic species and TEs from biomass burning enable atmospheric processing of TEs during long-range transport resulting in high labile TEs during this period.
- Fractional solubility of TEs over BoB is higher during PM compared to WM. The CAP+MAP samples show higher fractional solubility for Fe and Cu compared to MAP and CAP shows the least. This observation explains the importance of atmospheric processing during the long-range transport of dust. Mixing and photochemical reaction of acidic species leads to higher fractional

solubility in CAP+ MAP samples. The sampling period is during continental outflow periods which include an ample amount of anthropogenic emission coming to the BoB during both the seasons. The BoB exhibits a beautiful relationship between dust and atmospheric processing along with anthropogenic emission. The observed solubility is much higher than our previous observation over the IO and the AS (Monsoon). But within the basin, we observe a good correlation between biomass trace and fractional solubility, source dependence/mineralogy dependent correlation with atmospheric processing and their impact on solubility. All these controlling parameters interplay with each other which determines the solubility of the corresponding element.

- Ecological effects of atmospheric deposition of nutrients on the BoB ecosystem are evaluated. The estimated N fixation in this region was found to be $\sim 0.31\text{--}1.34 \text{ Tg yr}^{-1}$ in PM and $\sim 0.35\text{--}1.60 \text{ Tg yr}^{-1}$ in WM (assuming N: Fe ratio of 50). Our estimation was in good agreement with the upper estimate value of 1.0 Tg-N yr^{-1} suggested by Naqvi et al., 2011.
- The potential C-fixation by atmospheric input of Fe was also estimated. The atmospheric input of soluble Fe can account for $2.13 \pm 0.90 \text{ Pg -C Yr}^{-1}$ in PM and $1.99 \pm 1.01 \text{ Pg-C Yr}^{-1}$ in WM. Therefore, atmospheric input can account for $\sim 4\%$ of global PP (50 Pg-C yr^{-1} ; Carr et al., 2006) and 20% of Indian Ocean PP (9.9 Pg-C yr^{-1}) in both periods. The observed nutrient ion deposition in this present study suggests the gradual increase in nutrient ion deposition like NH_4^+ , ON and Fe through the years, compared with previously available data from BoB due to anthropogenic influence

From our study, we understand that the BoB is an ideal site to understand the impact of anthropogenic emissions on atmospheric nutrients and their subsequent impact on primary productivity. To mitigate the growing global warming scenario, we need long-term monitoring of atmospheric nutrients and concordant monitoring of BoB seawater biogeochemistry will help to improve our knowledge and better constrain biogeochemical models.

Chapter 5

*Sources of atmospheric nutrients and factors
controlling their distribution over the Indian
Ocean*

5.1 Introduction:

Atmospheric aerosol deposition can supply bio-essential nutrient, like nitrate, phosphate, silicate, and trace elements (TEs), to the remote oceanic environment (Pöschl et al., 2005; Jickells et al., 2005, 2016; Ventura et al., 2021). Nutrients from atmospheric supply can modulate surface water biogeochemical processes which include enhancement of ocean primary productivity (PP) (Krishnamurthy et al., 2009; Banerjee and Prasanna Kumar, 2015; Hamilton et al., 2021 reference there in). Regional meteorological condition affects atmospheric aerosol composition and concentration to a greater extent, for example, the Bay of Bengal (BoB) receives anthropogenic aerosol during winter season due to IGP (Indo Gangetic Plain) outflow whereas relatively lower values of anthropogenic aerosols have been reported in the Arabian Sea (AS), despite of its location on same latitude (Kumar et al., 2008; Srinivas et al., 2014; Budhavant et al., 2018). Apart from the meteorological condition, land use and land cover can significantly alter nature and composition of aerosol and its distribution (Mahowald et al., 2006; Ginoux et al., 2012; Ward et al., 2014). During SEAREX (Sea Air Exchange) campaign, zonal and meridional variation of nitrate and dust and its spatiotemporal variation was explained based on different geographic and climatological variations (Duce, 1989; Duce and Tindale, 1991; Duce et al., 1991; Chobari et al., 2014).

Due to these large variabilities and uncertainties, it is important to understand spatial and temporal variation of dust and associated nutrient species. Secondary atmospheric processing of these aerosol, which involves gas to particle conversion, photochemical reaction, scavenging and other such process alters the primary nature of aerosol. Desboeufs et al. (2005) have demonstrated the role of atmospheric processing in altering the primary nature of dust. Supply of atmospheric dust are episodic and short lived and associated trace metals (Fe, Mn, Co, Cu) with these dust can act as an important source of nutrient in remote marine locations, particularly in the oligotrophic and high nitrate low chlorophyll (HNLC) regions, which is roughly 25% of the world ocean (de Baar et al., 2005; Jickells et al., 2005; Boyd and Ellwood, 2010; Taglibue et al., 2012). Atmospheric dust supplies ~3 times higher dissolve Fe/ bioactive Fe to surface ocean compare to riverine flux (Duce and Tindale, 1991; Jickells et al., 2005). Recent studies indicate 60% of world ocean are becoming low nitrate low chlorophyll (LNLC) zone which is further getting accelerated due to increasing global warming (Steinacher et al., 2010; Achterberg et al., 2014). Atmospheric supply of reactive nitrogen consists of both inorganic active nitrogen (IN; $\text{NO}_3^- + \text{NH}_4^+$) and

organic nitrogen (ON) which can act as key regulator of PP in these LNLC region (Guieu et al., 2014; Louis et al., 2015; Ridame et al., 2014). Furthermore, increasing pollution and use of fertilizer in agriculture and increase in biomass burning activities over land can enhance contribution of reactive nitrogen and TEs to the atmosphere and their subsequent transport to the oceanic region can modulate surface marine ecosystem (Alteri et al., 2021; Bikkina et al., 2021; Jickells., 2017; Krishnamurthy et al., 2009). In order to assess the role and impact of these nutrients to surface water biogeochemical processes, it is important to understand and quantify spatial and temporal variation of these atmospheric nutrient (reactive nitrogen, dust and associated TEs)

North Indian Ocean (NIO) experiences seasonal reversal of surface currents as well as winds and being land locked with presence of major desert in western, north-western side, highly populated and urbanised region in north and eastern side, provides a natural laboratory for researcher to understand and assess the impact of atmospheric deposition to surface water biogeochemical processes (Naqvi et al., 2005; Wiggert et al., 2005). Over the Indian Ocean (IO), PP decreases from north to south which is associated poor supply of nutrient to equatorial and Central Indian Ocean Basin (CIOB). Irrespective of its uniqueness, biogeochemical and climatological significance, unlike the Pacific and the Atlantic, the Indian Ocean is one of the least studied Ocean, not in terms of atmospheric chemistry but also marine nutrient cycling and its ecological aspect are least explored (Hood et al., 2008; Hermes et al., 2019).

In past three decades, number of efforts undertaken to understand and quantify atmospheric nutrient supply to the Indian Ocean which includes JGOFS programme during early nineties (Pease et al., 1998; Tindale and Pease, 1999; Johansen et al., 1999, 2003, 2004; Siefert et al., 1999), ICARB-2006 and 2018, WICARB-2008-09 (Aswini et al., 2020; Kumar et al., 2008a, b, 2010; Srinivas et al., 2012, 2013a, b). Apart from these, there were episodic campaigns, mostly covering the Arabian Sea and Bay of Bengal, (Kumar et al., 2012; Aswini et al. 2022; Bikkina et al., 2021; Panda et al., 2022; Sarma et al., 2022 and references therein) leaving a large knowledge gap in the Equatorial and southern part of the Indian Ocean.

Considering the role and importance of these nutrients in the marine region, in this study, we present the spatial distribution of water-soluble total nitrogen (TN; which comprises of (IN) and water-soluble organic nitrogen (ON)), mineral dust and associated trace elements as well as their

solubility in the aerosols collected during two cruise campaigns SSD-48 and SSD-62 (Table 5.1) over the equatorial IO along similar meridional transits.

5.2 Result and Discussions:

5.2.1 Wind pattern during the study period:

The seven days Air Mass Back Trajectory (AMBTs) corresponding to the sampling track in every 6-hour interval are shown in Fig-5.1 along with the midpoint of each sample. Sample location details of SSD-48 (Summer) are shown in Table 5.1 and SSD-62 (Monsoon) are shown in Table 5.1. AMBTs are measured in three different heights from MSL, which are 500m, 1000m and 2000m, respectively which are shown in Fig-5.1 with three different colors (Stein et al., 2015). In this study, our aim is to assess the spatial distribution of aerosol composition and thus we divided our samples based on the location of transects along which samples were collected and wind pattern. Though our cruises were along Meridional transit, We divided our cruise track into four different North -South Sectors depending upon the oceanic region and dominating Air mass namely (1) Bay of Bengal Indian oceanic sector (BIOS) which covered the Bay of Bengal and extend up to 5°N latitude of North Indian Ocean(NIO); (2) Equatorial Indian Ocean Sector (EIOS) which started from 5°N latitude and Ends at 5°S latitude; (3) Central Indian Ocean Sector (CIOS), which was from 5°S to 13.75°S southernmost end of cruise; (4) Arabian sea Indian Ocean Sector(AIOS) which Arabian Sea and extend up to 5°N latitude of NIO. Samples collected on these transects are grouped and named accordingly. We will be using this classification onwards to interpret and discuss our data. BIOS sector receives wind from the Indian subcontinent including the Thar desert, Indo- Gangetic plain and the Middle East along with wind from the Arabian sea and Bay of Bengal also contribute significantly. During Monsoon, the AIOS sector receives maximum wind from the Arabian sea along with wind from NE Africa and the Arabian desert. Unlikely BIOS, it does not have any influence from BOB during the study period. The wind parcels in the EIOS sector are of Marine origin with a very low contribution from Indonesia and other South Asian islands during both the cruise period. CIOS receives wind from the Southern Ocean sector of the Indian Ocean. A significant amount of wind parcels are coming from the Australian and Indonesian islands during SSD-48, while during SSD-62 marine wind parcels are dominant compared to wind derived from the wind Australia. From AMBTs, we can

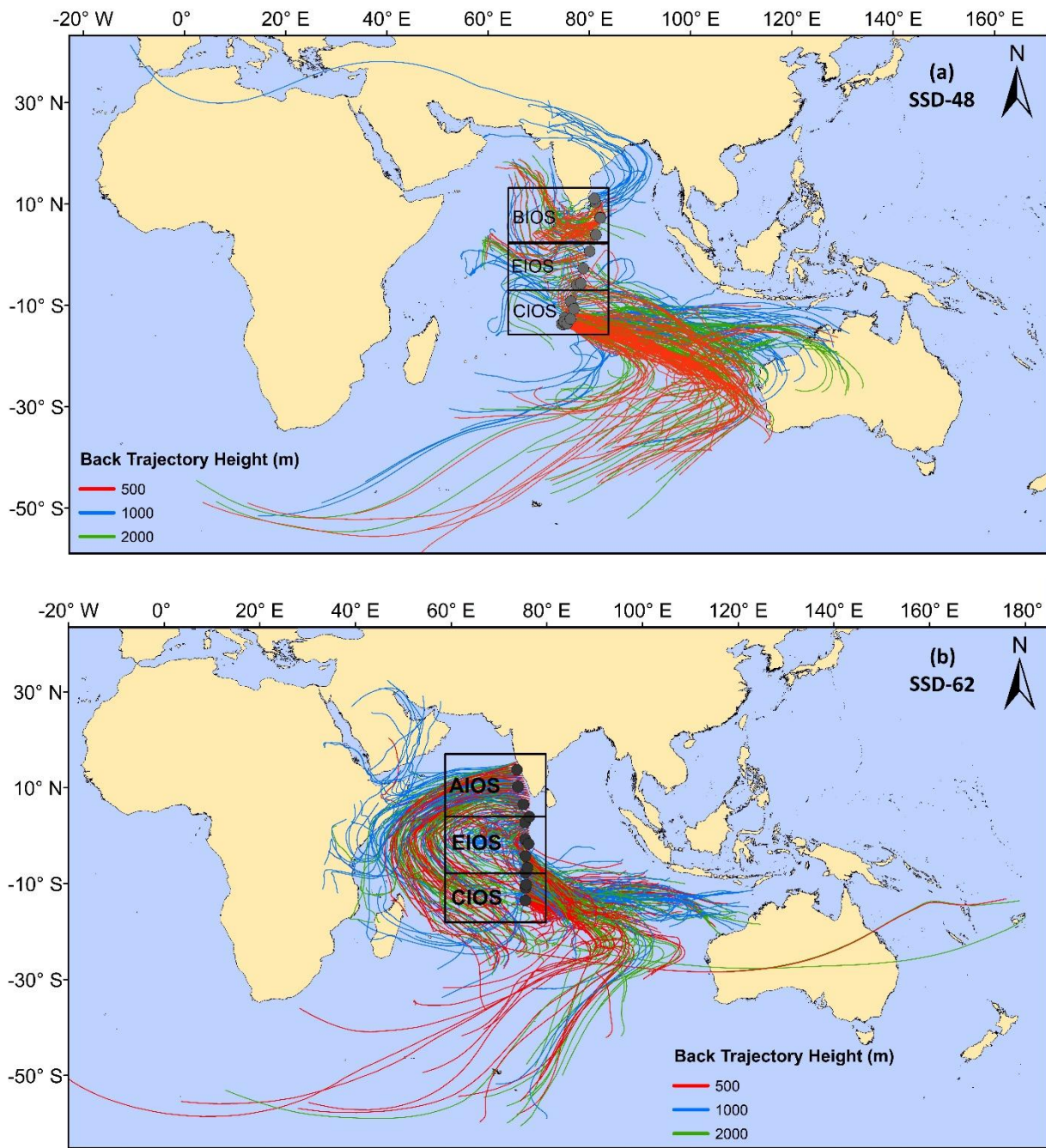


Fig-5.1 Cruise tracks undertaken in the Indian Ocean (a) SSD-48 (1st April - 5th May 2018) and (b) SSD-62 (18th June - 23rd July 2019). The red, blue and green lines represent Air mass back trajectory at 500,1000- and 2000-meters height respectively above mean sea level. Black dots represent the mid-point of each sample.

Table 5.1 SSD-48 (summer) and SSD-62 (monsoon) Sample location details

SSD-48						
SAMPLE ID	Sampling Date (DD/MM/YYYY)		Start Location		End Location	
	From	To	Latitude	Longitude	Latitude	Longitude
SSD-48-T-01	1/4/2018	2/4/2018	11.19 N	80.98 E	8.00 N	82.00 E
SSD-48-T-02	2/4/2018	3/4/2018	8.00 N	82.00 E	5.00 N	82.00 E
SSD-48-T-03	3/4/2018	4/4/2018	5.00 N	82.00 E	1.00 N	80.00 E
SSD-48-T-04	4/4/2018	5/4/2018	1.00N	80.00 E	2.00S	79.00 E
SSD-48-T-05	5/4/2018	6/4/2018	2.00 S	79.00 E	5.00 S	78.00 E
SSD-48-T-06	6/4/2018	7/8/2018	5.00 S	78.00 E	8.00 S	77.00 E
SSD-48-T-07	7/4/2018	8/4/2018	8.00 S	77.00 E	11.60 S	75.42 E
SSD-48-T-08	8/4/2018	9/4/2018	11.62 S	75.41 E	13.75 S	74.68 E
SSD-48-T-09	9/4/2018	10/4/2018	13.74 S	74.89 E	13.74 S	74.93 E
SSD-48-T-10	10/4/2018	11/4/2018	13.74S	74.93 E	13.68 S	74.75 E
SSD-48-T-11	11/4/2018	13/04/2018	13.68 S	74.75 E	13.62 S	74.68 E
SSD-48-T-12	13/04/2018	15/04/2018	13.62 S	74.68 E	13.56 S	74.75 E
SSD-48-T-13	16/04/2018	20/04/2018	13.43 S	74.5 E	13.25 S	74.81 E
SSD-48-T-14	20/04/2018	22/04/2018	13.25 S	74.81 E	13.56 S	75.5 E
SSD-48-T-15	22/04/2018	24/04/2018	13.56 S	75.5 E	13.59 S	74.70 E
SSD-48-T-16	25/04/2018	27/04/2018	13.56 S	75.79 E	12.43 S	76.46 E
SSD-48-T-17	27/04/2018	28/04/2018	12.39 S	76.47 E	8.78 S	77.47 E
SSD-48-T-18	28/04/2018	30/04/2018	8.78 S	77.47 E	0.66 N	80.13 E
SSD-48-T-19	2/5/2018	3/5/2018	5.66 N	81.99 E	9.18 N	81.59 E
SSD-48-T-20	3/5/2018	4/5/2018	9.22 N	81.58 E	12.2 N	80.86 E
SSD-62						
SAMPLE ID	Sampling Date (DD/MM/YY)		Start Location		End Location	
	From	To	Latitude	Longitude	Latitude	Longitude
SSD-62-T-01	18/06/19	19/06/19	15.42 N	73.78 E	11.99 N	73.84 E
SSD-62-T-02	19/06/19	20/06/19	11.99 N	73.84 E	8.49 N	74.26 E
SSD-62-T-03	20/06/19	21/06/19	8.35 N	74.32 E	4.668 N	75.41 E
SSD-62-T-04	21/06/19	22/06/19	4.65N	75.41 E	0.94 N	75.47 E
SSD-62-T-05	22/06/19	23/06/19	0.94 N	75.49 E	2.387 S	75.5 E
SSD-62-T-06	23/06/19	24/06/19	2.54 S	75.49 E	5.96 S	75.52 E
SSD-62-T-07	24/06/19	25/06/19	5.96 S	75.52 E	9.45 S	75.54 E
SSD-62-T-08	25/06/19	26/06/19	9.45 S	75.54 E	12.06 S	75.56 E
SSD-62-T-09	28/06/19	29/06/19	12.94 S	74.68 E	12.07 S	75.56 E

Table-5.1 Continue

SSD-62-T-10	30/06/19	1/7/2019	11.98 S	75.57 E	75.82 E	8.29 S
SSD-62-T-11	15/07/19	17/07/19	4.55 S	76.05 E	76.23 E	1.49 N
SSD-62-T-12	17/07/19	19/07/19	2.22 N	76.22 E	76.31 E	5.73 N

5.2.2 Dust Supply:

In this study, mineral dust concentration was calculated using Al concentration, presuming Al content is 8.04 % (wt %) similar to those in the upper continental crust (UCC) (McLennan, 2001). A decreasing, north to south, trend was observed for mineral dust (Fig- 5.2) with average higher values in the AIOS ($14.6 \pm 9.7 \mu\text{g m}^{-3}$) and BIOS ($10.2 \pm 9.7 \mu\text{g m}^{-3}$), which are located within similar latitudinal belt in the NIO. Among these sectors, aeolian dust is relatively higher over the AIOS (SSD-62) in comparison to BIOS (SSD-48), which is due to the impact of air parcels derived from the Arabian Peninsula and northeast African desert (Fig-5.1) during the sampling months. Similar dust concentrations have been reported by Panda et al. (2022) during the monsoon period over the AS. During active southwest monsoon months (July-August), regional wind systems over the AS including western disturbance, summer Shamal winds, and Levar winds have the potential to lift and transport dust from the Middle-east and NE –African desert region (Ramaswamy et al., 2017). During summer months (April-May), although, high dust emissions have been observed over the sources in the Western part of the AS (Goudie and Middleton, 2006; Prosper, 2002), winds are not as conducive and strong compared to those during Monsoon leading to relatively lower dust levels over the BIOS. Moreover, BIOS is relatively far away from the dust sources as compared to AIOS which can further cause lower dust concentration during SSD-48. The role of regional winds in dust supply is further evident from the study reported by Aswini et al. (2020), wherein, average dust over the NIO was found to be $3.6 \pm 0.7 \mu\text{g m}^{-3}$ (almost 5 times lower than this study) during winter months (January- February) when majority of winds are derived from Indian landmass where relatively lower dust emissions have been reported (Prospero, 2002).

Average dust concentration was found to decrease sharply from EIOS ($8 \pm 5.8 \mu\text{g m}^{-3}$) to CIOS ($1.8 \pm 1 \mu\text{g m}^{-3}$) during SSD-48. However, almost similar dust concentrations were seen in EIOS ($3.6 \pm 0.4 \mu\text{g m}^{-3}$) and CIOS ($3.7 \pm 1 \mu\text{g m}^{-3}$) during SSD-62. Relatively high dust values in the EIOS during summer (SSD-48), as compared to the monsoon period (SSD-62), can be attributed to the influence of continental-derived wind parcels (particularly from the Northwest Australian

Desert) in the equatorial region which can carry a significant amount of mineral dust. However, the majority of the air parcels were found to be of marine origin (Fig-5.1), during monsoon (SSD-62). The absence of a prominent wind pattern and active dust sources around the CIOB region led to low dust supply to this region.

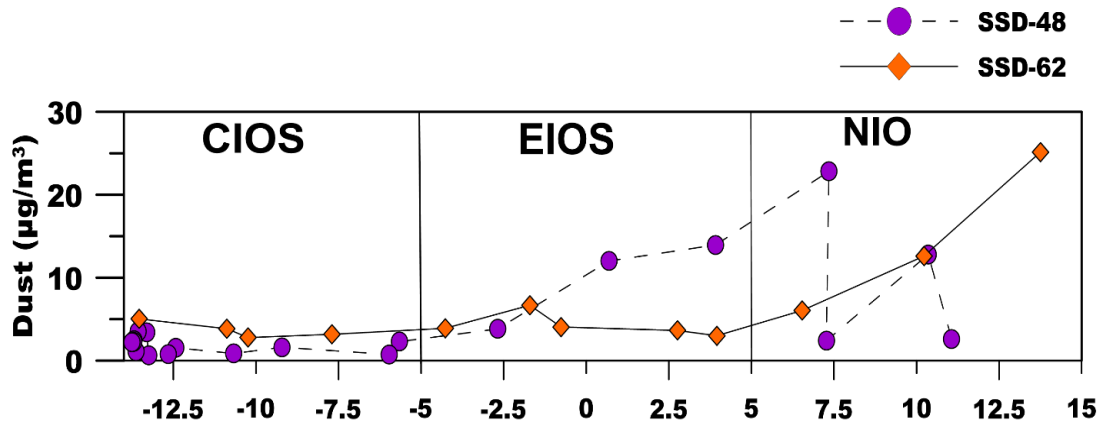


Fig-5.2 Spatial variation of Dust (in $\mu\text{g}/\text{m}^3$) during SSD-48 and SSD-62. In X-axis latitudes are marked -ve sign from southern hemisphere latitude and +ve sign for northern hemisphere latitude.

Witt et al. (2006) have reported mineral dust concentration averaging around $4 \mu\text{g m}^{-3}$ around west Australian coast. However, this ought to decrease in the open oceanic region and/or CIOB, due to physical removal during transport. Higher dust concentrations over the CIOB during this study is possibly due to higher dust emissions over the Australian desert and strong conducive winds carrying larger amounts of dust towards CIOB.

5.2.3 Macro-nutrient (atmospheric reactive-N species) over the Indian Ocean:

Reactive nitrogen is comprised of Inorganic nitrogen (in NH_4^+ and NO_3^-) and organic nitrogen (estimated from the difference between TN and inorganic N; see section 2.2). A significant difference was seen in NH_4^+ concentration ($0.2\text{--}26.5 \text{ nmol m}^{-3}$; $4.6 \pm 7.6 \text{ nmol m}^{-3}$) during summer (SSD-48) in contrast to monsoon (SSD-62), wherein it was found below the detection limit (Fig-5.3a) (Table 5.2). During SSD-48, a large spatial variation in NH_4^+ values were observed with a very higher average values in BIOS ($14.6 \pm 11 \text{ nmol m}^{-3}$) region, as compared to CIOB ($1.1 \pm 0.9 \text{ nmol m}^{-3}$) and EIOB ($2.5 \pm 2.5 \text{ nmol m}^{-3}$) region (Fig-5.3a). Higher NH_4^+ over BIOS compared to other sectors can be due to the influence of continental outflow in this region, which is also supported by back trajectory analyses (Fig-5.1). In contrast to NH_4^+ , almost similar NO_3^- concentrations were observed during summer ($0.8\text{--}23.3 \text{ nmol m}^{-3}$; $9.2 \pm 7.6 \text{ nmol m}^{-3}$) and

monsoon ($3.3\text{--}30.7\text{ nmol m}^{-3}$; $8.9 \pm 7.5\text{ nmol m}^{-3}$) campaigns (Table 5.2 and Fig-5.3b). However, a gradual north to south decrease in nitrate was observed during the monsoon except few higher values were seen in CIOS during SSD-62 (Fig-5.3b).

The average IN was found to be higher during summer ($5.1 \pm 6.6\text{ nmol m}^{-3}$) than monsoon ($2.0 \pm 0.7\text{ nmol m}^{-3}$) during these campaigns (Fig-5.3c). However, these values were less than those reported earlier from the IO, particularly in the NIO. Previously Johansen et al. (1999) reported $36 \pm 13\text{ nmol m}^{-3}$ during summer and $10 \pm 3\text{ nmol m}^{-3}$ during monsoon over the AS. In recent years, Srinivas et al. (2015) observed $182 \pm 142\text{ nmol m}^{-3}$ of IN over BoB during Dec- Jan months, and $140 \pm 83\text{ nmol m}^{-3}$ during winter months over the open ocean and coastal region of the AS (Bikkina et al., 2021). In another recent work by Aswini et al. (2020), IN was averaged around ~ 219 and $\sim 25.3\text{ nmol m}^{-3}$, during winter months, over the eastern Arabian sea and equatorial Indian ocean respectively. IN value observed by Aswini et al. (2020) over equatorial IO is higher than these campaigns (Avg = $4.7 \pm 3.5\text{ nmol m}^{-3}$). The higher IN value during winter months were attributed to higher IN supply from Indian sub-continent mainly due to continental outflow wherein, air-parcels are enriched in emissions from biomass burning over the Indo-Gangetic Plains (IGP) and under favourable wind (NE- Monsoon) which can efficiently transport these IN to marginal seas of the IO. However, lower IN in this study could be due to distal sampling locations from the emission source region (see Fig-5.1) as well as unfavourable meteorological conditions. Lower IN over IO could be also attributed to wet season over Indian subcontinent and south-east Asia region, when heavy monsoonal rain and low biomass burning produce lower amount of IN.

A similar spatial distribution is seen for Organic nitrogen (ON), during both campaigns. A north to south decreasing trend is seen for summer ($0.9\text{--}43.7\text{ nmol m}^{-3}$; $10.9 \pm 12\text{ nmol m}^{-3}$) and Monsoon ($1.7\text{--}25.8\text{ nmol m}^{-3}$; $7.8 \pm 7\text{ nmol m}^{-3}$) campaigns (Fig-5.3d) (Table 5.2). Similar to IN, ON observed in these campaigns were significantly lower than those reported earlier from the Bay of Bengal ($59 \pm 54\text{ nmol m}^{-3}$; Bikkina et al., 2010), and the AS ($86 \pm 81\text{ nmol m}^{-3}$; Bikkina et al., 2021). However, these ON values are comparable with those reported from other remote oceanic regions like the Pacific Ocean ($16 \pm 19\text{ nmol m}^{-3}$; Nakamura et al., 2006) and Atlantic Ocean (9.8 nmol m^{-3} ; Lesworth et al., 2011). Interestingly, in our current study, the ON contributed $70 \pm 8\%$ and $76 \pm 4\%$ (Table 5.2) during summer and monsoon respectively of TN inventory,

which indicates organic nitrogen is a dominant among total active nitrogen over the IO. Lower concentration all N- species and different measuring techniques used to measure different N- species (discussed in previous section) can lead to introduce a significant amount of error (Bikkina et al., 2021).

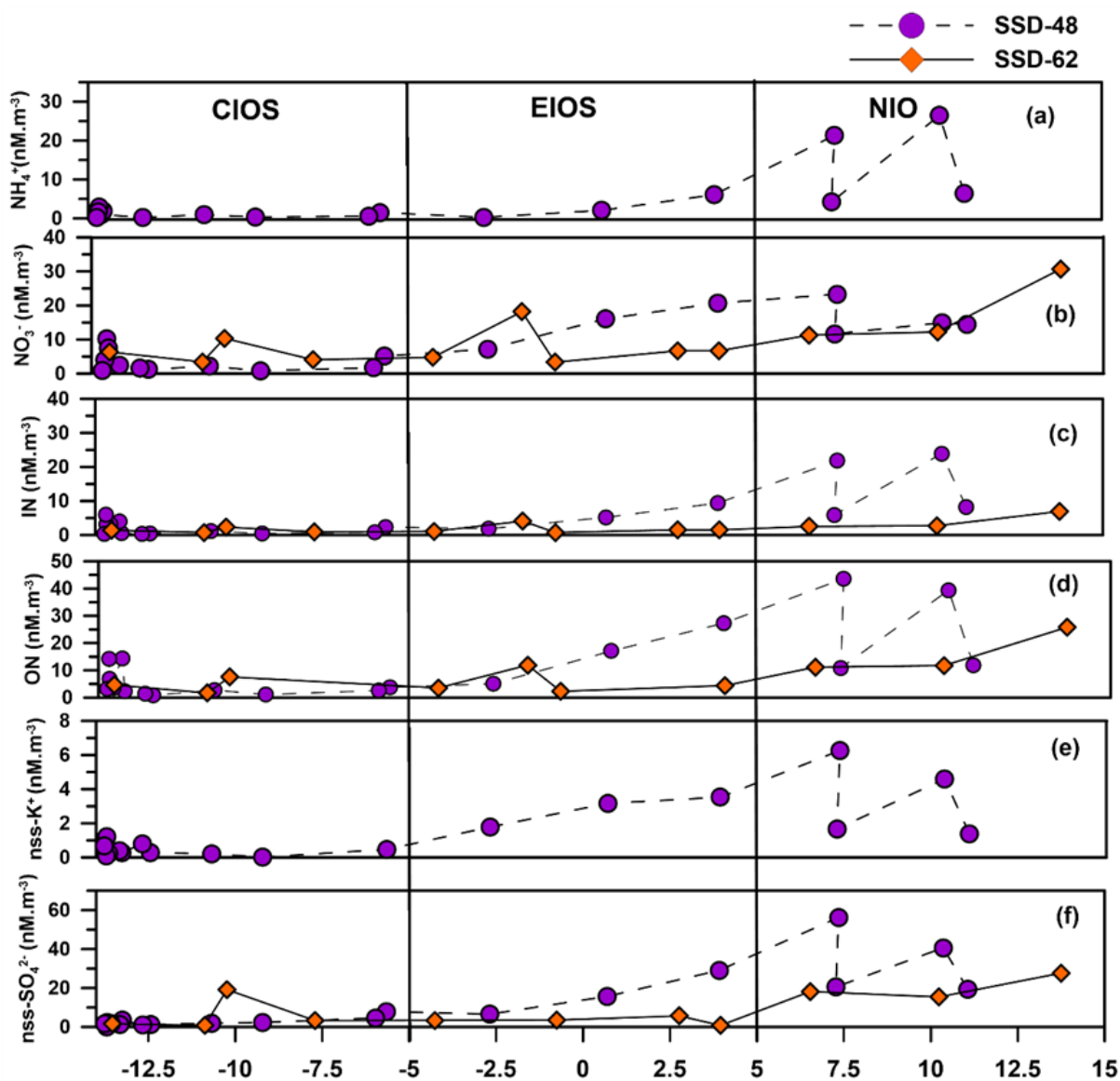


Fig-5.3 Spatial variation of chemical species (a) Ammonium (NH_4^+), (b) Nitrate (NO_3^-), (c) Inorganic nitrogen (IN), (d) Organic nitrogen (ON), (e) non-sea salt potassium (nss-K^+), (f) non-sea salt sulphate (nss-SO_4^{2-}) during SSD-48 and SSD-62.

Apart from the quantification, we also attempted to assess the sources of reactive nitrogen by correlating with different chemical species of natural and anthropogenic origin, such as nss-K^+ , nss-SO_4^{2-} which are also showing a similar latitudinal gradient as per reactive nitrogen (Fig-

5.3a-f). A strong correlation between NH_4^+ and nss-K^+ was seen during the summer months ($R^2 = 0.70$; $p < 0.05$). However, for SSD-62, nss-K^+ was also found to be below detection limits (Fig-5.3e). This clearly indicates NH_4^+ over the IO was mainly derived from biomass-burning emission sources. Fossil fuel combustion, biomass burning and processing contribute to significant emission of NO_x ; later on, oxidation of the NO_x produces an ample amount of NO_3^- species in the atmosphere, which was transported to the marine region with dust. The absence of nss-K^+ (biomass burning tracer) during the monsoon period and its strong correlation with nss-SO_4^{2-} ($R^2 = 0.69$; $p < 0.05$) (Fig-5.4b) indicate fossil fuel burning is a possible source of NO_3^- during monsoon and transported to the marine region.

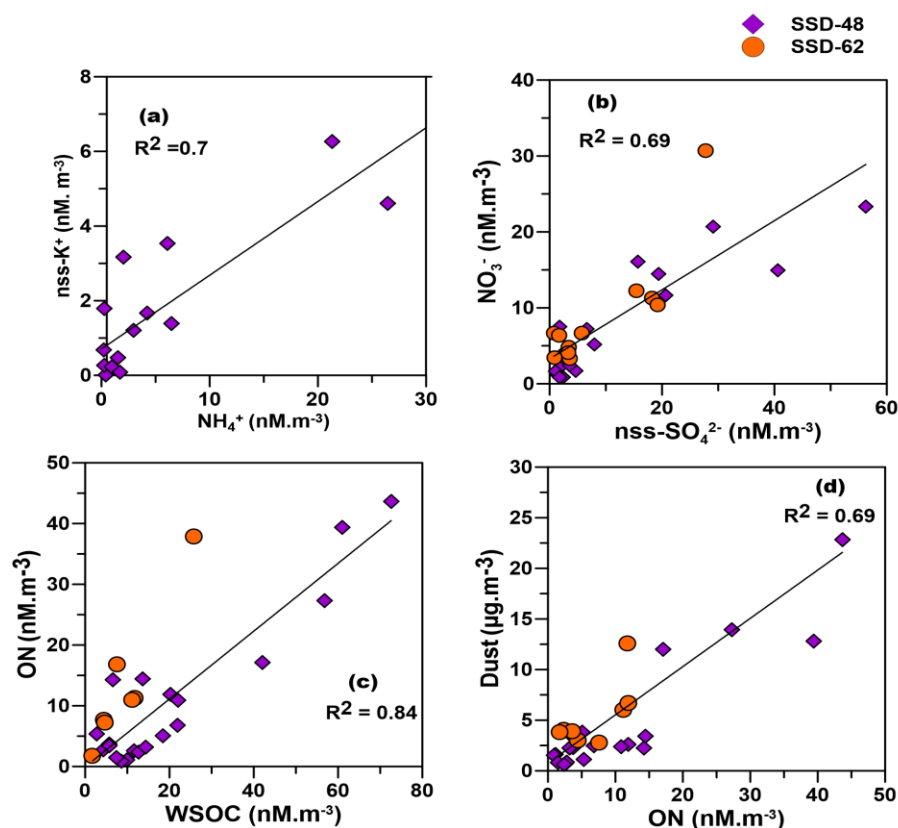


Fig-5.4 Correlation plot between (a) Ammonium (NH_4^+) and non-sea salt potassium(nss-K^+), (b) non-sea salt sulphate (nss-SO_4^{2-}) and nitrate (NO_3^-), (c) water soluble organic carbon (WSOC) and organic nitrogen (ON), (d) ON and Dust.

Table 5.2: Concentration range and mean of different chemical compositions. IN and ON stand for water soluble inorganic nitrogen, water-soluble organic nitrogen respectively. Fractional solubility of Fe, Mn and Cu also mentioned along with ON% out of total Nitrogen.

	Units	SSD-48 (Summer)		SSD-62 (Monsoon)	
		Range	Mean	Range	Mean
Dust	µg/m ³	0.6-22.8	4.7	2.8-25.1	6.4
Nitrate (NO₃⁻)	nmol/m ³	0.8-23.3	9.2	3.3-30.7	8.9
Ammonium (NH₄⁺)		0.2-26.5	4.6	BDL	BDL
IN		0.35-23.9	5.1	0.75-7.5	2
ON		0.9-43.7	10.9	1.7-25.8	7.8
TN		1.4-65.5	16	2.5-32.7	9.85
nss-K⁺		0.01-6.3	1.5	BDL	BDL
nss- SO₄²⁻		0.04- 56.27	11.5	0.8-27.7	8.6
Fe_T		0.09-16.42	3.4	1.5-17.85	8.62
Mn_T	pmol/m ³	16-1807	559	280-6062	2210
Cu_T		3-763	168	8.6-88.6	28
Fe_S		0.7-43	16	0.13-24.1	7
Mn_S		5-354	118	4.8-393	88.6
Cu_S		Feb-95	24	0.8-8	3.8
Fe%	%	0.04-3.86	0.99	0.002-0.23	0.09
Mn%		Sep-64	31	1.2-31	6
Cu%		Apr-92	31	4.4-37	16.7
ON%		52-90	70	68.5-81	76

The strong correlation between ON and WSOC (Fig-5.4c) with $R^2 = 0.84$ demonstrate a major role of secondary processes during transport, to the air-parcel. Previously some researcher explained soil organic matter can be significant contributor of ON, especially soil derived from dry arid region like the Saharan desert and northern Africa contribute significant amount of ON to the Mediterranean Sea (Mace et al.,2003; Jickells et al.2013). A significant correlation between ON with dust with $R^2 = 0.69$ (Fig-5.4d) indicates a possible relationship of ON with desert dust which is also supported by a previous study by Mace et al. (2003), which had indicated ON can be derived from soil organic matter. The air-mass back trajectory analyses also show a significant

amount of air masses were derived from eastern Africa and northern Australia, which are mainly dry and arid throughout the year. This study, possibly, provides first dataset of reactive nitrogen covering large area of the Indian Ocean. However, long-term data is necessary to get a more robust picture of reactive nitrogen and to assess their impact on modulating surface water biogeochemical processes.

5.2.4 Dust associated total trace elements over the Indian Ocean:

Typically, atmospheric Fe and Mn are mainly associated with natural dust with a partial influence from anthropogenic sources, however, Cu is mostly derived from anthropogenic emissions like vehicular activity, coal fire-plant and other industrial action with a minimal contribution from natural dust (Panda et al., 2022). In this study, higher Fe_T ($8.3 \pm 6 \text{ nmol m}^{-3}$) was seen during monsoon compared to summer ($3.4 \pm 4.7 \text{ nmol m}^{-3}$) campaign (Table 5.2, Fig-5.5). Similarly, higher Mn_T ($1914 \pm 1751 \text{ pmol m}^{-3}$) was found during monsoon compared to summer ($559 \pm 538 \text{ pmol m}^{-3}$) months over the Indian Ocean. The spatial distribution of both TEs are distinct in monsoon and summer campaigns, wherein the Fe_T follow a decreasing trend with highest average in the NIO ($16.5 \pm 2.1 \text{ nmol m}^{-3}$), ($8.2 \pm 7 \text{ nmol m}^{-3}$) followed by EIOS ($6.2 \pm 2.8 \text{ nmol m}^{-3}$), ($6 \pm 5.2 \text{ nmol m}^{-3}$) and CIOS ($3.5 \pm 3.1 \text{ nmol m}^{-3}$), ($0.9 \pm 0.7 \text{ nmol m}^{-3}$) during monsoon and summer, respectively, similar to the mineral dust (Table 5.2). However, higher Mn_T was observed in the EIOS ($2477 \pm 2332 \text{ pmol m}^{-3}$) samples as compared to those collected in the CIOS ($1461 \pm 1302 \text{ pmol m}^{-3}$) and NIO ($1070 \pm 1175 \text{ pmol m}^{-3}$) sector during monsoon and no significant differences during summer NIO ($570 \pm 131 \text{ pmol m}^{-3}$), EIOS ($468 \pm 293 \text{ pmol m}^{-3}$), CIOS ($586 \pm 685 \text{ pmol m}^{-3}$). This highlights the influence of distinct dust types is impacting the EIOS with high Mn content, particularly during monsoon period. AMBTs reaching to EIOS during SSD-62 were mostly derived from the northeast African desert region which are enriched in Mn-bearing carbonates (Taylor et al., 2005), which can also contribute to the higher soluble fraction of Mn. In contrast to Fe and Mn, higher concentration of Cu_T was observed in aerosols collected during summer ($168 \pm 249 \text{ pmol m}^{-3}$) than those in the monsoon ($34 \pm 31 \text{ pmol m}^{-3}$) months. While assessing the spatial distribution of Cu_T , almost comparable values were observed in all sectors except for significantly higher values in the NIO ($358 \pm 386 \text{ pmol m}^{-3}$) and EIOS ($297 \pm 274 \text{ pmol m}^{-3}$) during summer. These sectors were impacted by continental outflow (see Fig. 1) during the campaign period and can have anthropogenic impacts. To further assess the anthropogenic influence, we calculated enrichment factor (EF) using the formula described in Panda et al. (2022).

Except one sample over the NIO, higher EF (>80) for Cu is seen in the two sectors during summer (Fig-5.6), which corroborate to the contribution of Cu from anthropogenic sources. Furthermore, it is interesting to observe higher EF (>80) for Cu in the CIOS sector, particularly during Summer.

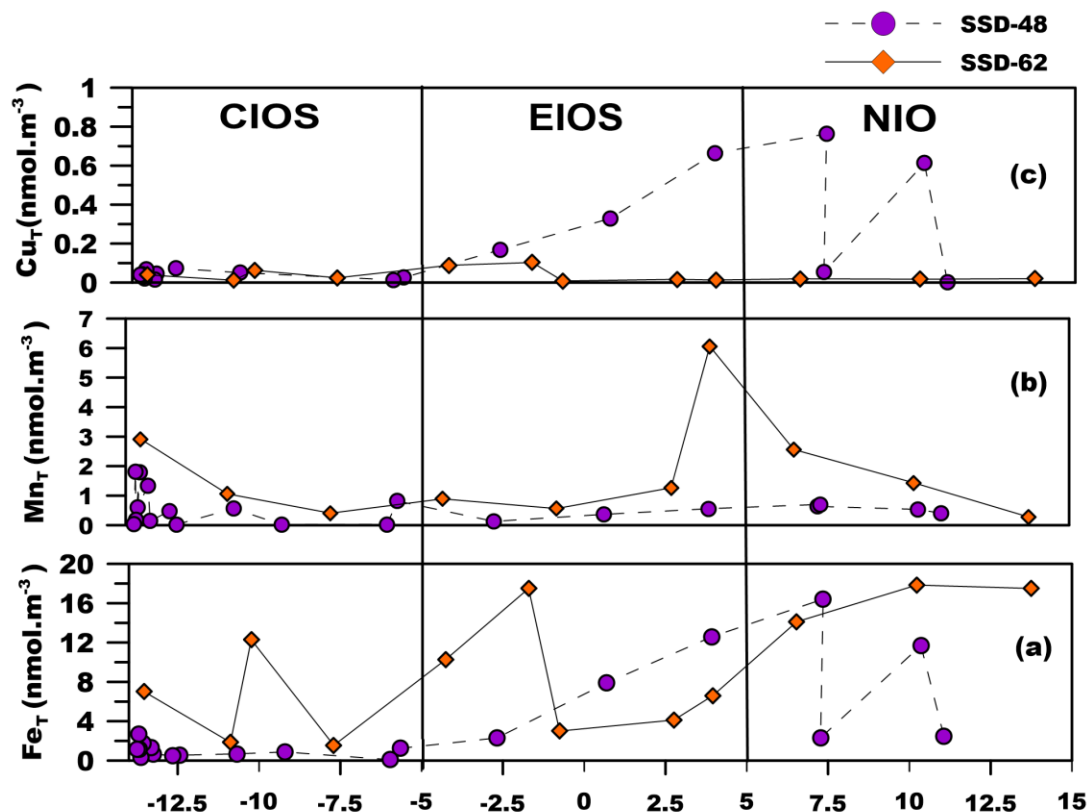


Fig-5.5 Spatial variation of total trace element (a) Fe_T , (b) Mn_T and (c) Cu_T during SSD-48 and SSD-62.

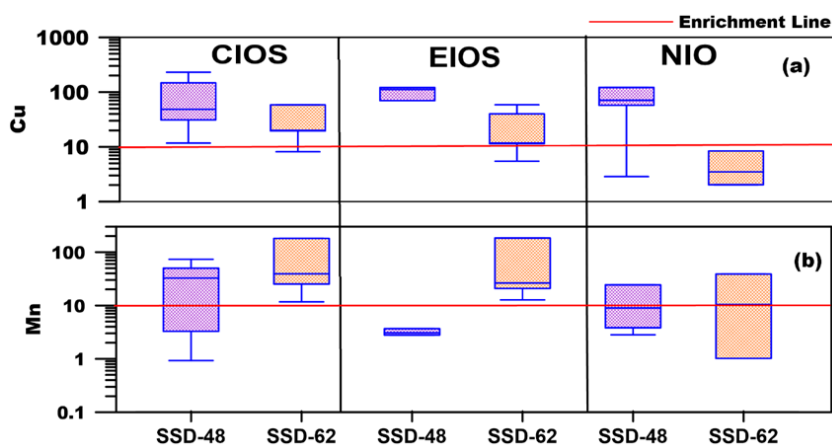


Fig-5.6 Box plot of enrichment factor for (a) Mn and (b) Cu in three sectors. The red line is considered as the Enrichment line >10 times of crustal average.

This is intriguing as the total concentration of Cu is relatively low in the CIOS and may be attributed to contribution from a different source. The AMBTs arriving at the CIOS, particularly during summer months were mostly derived from the south-east Asia and north-western Australian region. Interestingly, we find a moderate correlation between nss-K⁺ and total Cu (Fig-5.7) for the samples collected in CIOS indicating contribution of Cu from the anthropogenic emissions from Australia and south-east Asia (Desservettaz et al., 2017; Milic et al. 2017). Similar to Cu, higher EF is observed for Mn in CIOS suggesting, its possible contribution Australian and south-east Asian anthropogenic emissions (Perron et al.2022).

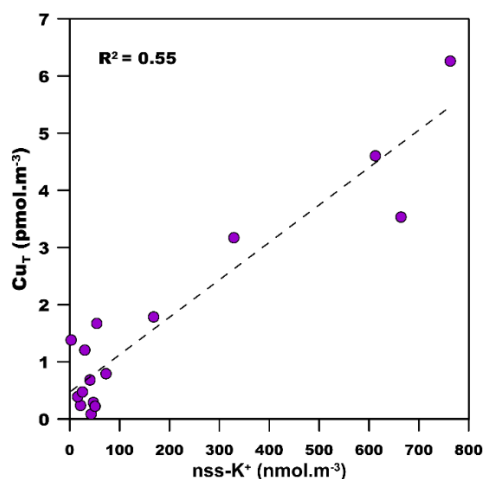


Fig-5.7 Correlation plot between nss-K⁺ and total Cu (Cu_T).

5.2.5 Soluble TEs over the Indian Ocean:

The average soluble TE (Fe, Mn and Cu) concentration and its range are provided in Table 5.2 and its spatial variability is shown in Fig-5.8. There are no significant spatial trends were seen for soluble TEs, however, their higher average values were observed in each sector, from the summer (SSD-48) campaign compared to monsoon (SSD-62) months. In contrast to this, relatively higher average soluble Fe (average= 71.3 pmol.m⁻³) have been reported from the Pacific Ocean along a similar meridional transit (Buck et al., 2013). However, unlike Fe_s, Mn_s concentration over the Pacific Ocean were on lower side (0.1-35.7 pmol.m⁻³ average= 4.4 pmol.m⁻³) which have been attributed to regional geology source region and wind pattern. Similarly, higher Fe_s have been reported by Buck et al. (2006) and Chance et al. (2015) over the southern Atlantic Ocean region. Kumar et al. (2010) reported 557±321 pmol.m⁻³ of Fe_s over the Bay of Bengal during summer while the Arabian Sea receives lower Fe_s 5.5 ± 4.2 pmol.m⁻³. Such varying

soluble concentrations from the North Indian Ocean clearly demonstrate the role of regional meteorology and proximity from the source region is an important factor contributing to the soluble TEs in the aerosols.

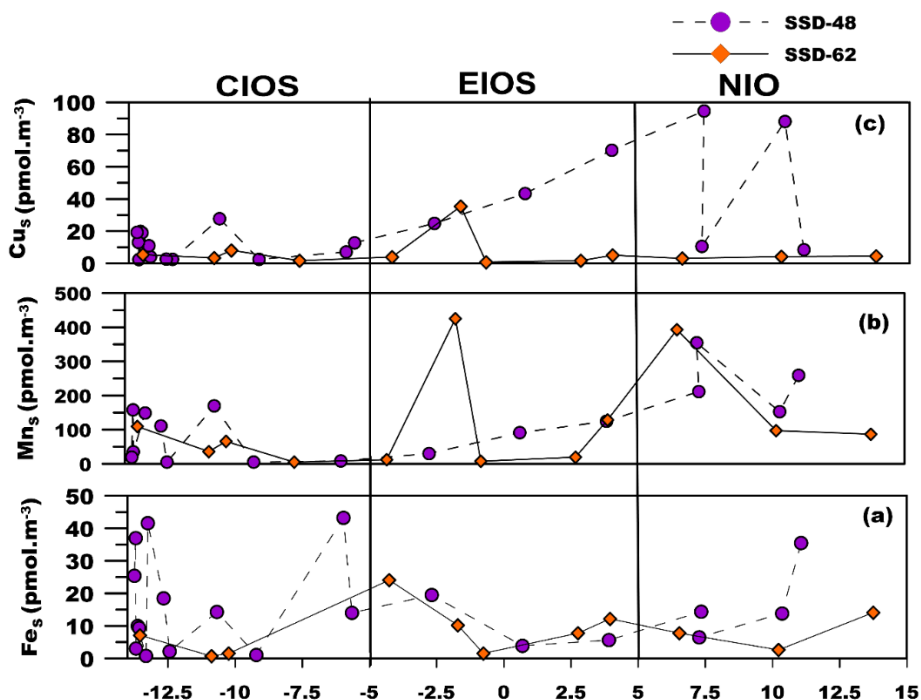


Fig-5.8 Spatial variation of Soluble trace metal (a) Fe_s , (b) Mn_s and (c) Cu_s over the Indian Ocean.

5.2.6 Fractional Solubility and factors controlling fractional solubility over the Indian Ocean:

The fractional solubility is the percentage of soluble TEs w.r.t. total TEs present in aerosol and it can be referred as “operational” solubility as compared to absolute solubility (Kumar and Sarin, 2009). In this study, the fractional solubility of Fe ($Fe\%$) was significantly higher during summer (range= 0.04-3.86, Mean=0.99) months, particularly in CIOs ($1.8 \pm 1.9\%$), and shows a wider range compared to monsoon (range = 0.002-0.23 %) (Fig-5.9). These fractional solubilities are order of magnitude lower than those reported by Kumar et al. (2010) in the Bay of Bengal and are comparable with those reported in the Arabian Sea (Panda et al., 2022 and references therein). Similarly, Srinivas et al., (2011) reported $Fe\%$ in the range of 2.6-13.6% over the Bay of Bengal during the summer months (March- April 2009) and attributed it to localized recirculation of air mass in the southern Bay of Bengal. In case of CIOs, which shows higher solubility during

summer months (average=1.18% range = 0.06-3.86%) may be attributed to more labile Fe-rich dust from central arid Australia and south-east Asia.

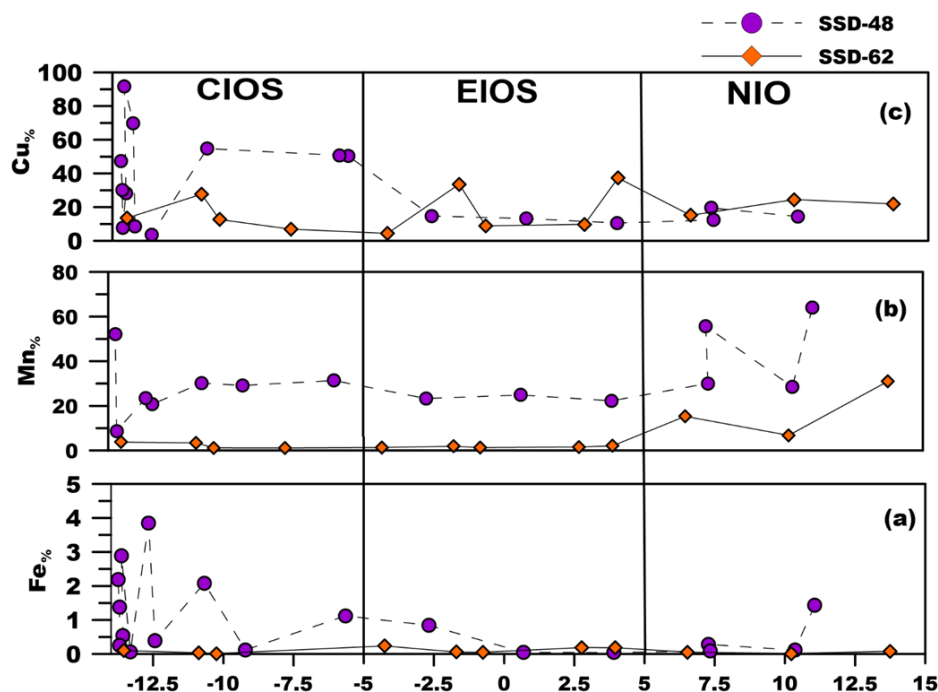


Fig-5.9 Spatial variation of Fractional solubility of (a) Fe%, (b) Mn% and (c) Cu% over Indian ocean.

This observation also supported by wind mass back trajectory (Fig-5.1a) which shows during summer maximum wind coming to CIOS region are from mentioned region. A similar higher fractional solubility has been reported by Perron et al. (2020) which observed ~ 4% of Fe% over the northern and north-west Australian region which they attribute to Fe-laden dust emission from central Australia. Similar to our current observation. Baker et al. (2013) observes mean Fe% of ~ 2.4% over south-east Atlantic region (off Africa) and explained lower solubility in Fe, < 5% over Atlantic Ocean was due to the influence of Saharan dust. During monsoon, we observe much lower Fe% compare to other regions of Indian Ocean. Overall, Fe% over Indian Ocean during both summer and monsoon depend upon the dust source. We also observed a hyperbolic relation between Fe_T and Fe% (Fig-5.10a) which indicate contribution from two end-members defined as higher dust/total Fe with lower solubility and lower dust/total Fe with higher solubility. A similar inverse relationship between total Fe and their solubility have been observed by multiple researchers at different oceanic regions (Buck et al., 2006; Sholkovitz et al., 2012 and references within; Baker et al., 2013; Chance et al., 2015).

Another important factor which can contribute to enhanced Fe_s is the chemical processing of dust mediated by acidic species during long range transport (Baker and Croot, 2010). Total acidic species (TA) was calculated as molar concentration of Nitrate added with twice the concentration of non-sea salt sulphate (Buck et al., 2006, Panda et al., 2022) and compared with the soluble Fe concentration. Similar to Buck et al. (2006), a linear relation between nitrate and nss-sulphate (Fig-5.4b) and no significant correlation between Fe_s and TA (Fig-5.10b). Instead of getting a linear relation between Fe_s with TA, a decreasing trend is seen in (Fig-5.10b), suggesting the increase in TA has no impact on the fractional solubility of Fe. Thus, it can be argued that, mineralogy of dust might be playing a significant role for lower solubility of Fe over Indian Ocean. Fe bounded in compact crystal lattice like haematite and goethite shows lower solubility compare to kaolinite and illite like clay mineral and earlier mineral group remain unaffected or partially affected compared to later group (Journet et al., 2008; Marcotte et al., 2020). Thus, the chemical processing has a minimal contribution to Fe_s compared to the varying emission source regions.

During both campaigns, relatively higher fractional solubility of Mn ($31 \pm 15\%$) and ($6 \pm 9\%$) in summer and monsoon respectively was observed in contrast to Fe. However, higher Mn_s was displayed in NIO ($45 \pm 18\%$), EIOS ($23.5 \pm 1.3\%$) and CIOS ($27 \pm 13\%$) during SSD-48 than SSD-62 (NIO ($18 \pm 12\%$), EIOS ($2 \pm 0.6\%$) and CIOS ($2.4 \pm 1.4\%$), similar to Fe_s).

The Mn_s over the Indian Ocean was found to be lower than those reported from the Arabian Sea ($\text{Mn}_s = 43\%$; Panda et al., 2022) irrespective of the season. Mn_s observed during summer was comparable with those observed over the remote south east Atlantic Ocean region by Chance et al. (2015) with a range of 1-82% and mean value $\sim 20\%$. However, relatively lower solubility is seen when compared with the Atlantic (Backer et al., 2013 mean $\text{Mn}_s = 50\%$); and South China sea (Hsu et al., 2010; mean $\text{Mn}_s = 49\%$). A correlation plot between soluble Mn with TA is shown in Fig-5.10d, which shows a positive correlation and provides a hint of contribution of soluble Mn from chemical processing. Unlike Fe, Mn (as oxide) bearing common minerals like the Todorokite and Birnessite have layered crystal structure and can readily undergo oxidative reduction which make them more labile (Post et al., 1999). Other than Mn-oxide, Mn bearing carbonates and desert varnishes (formed by Mn- oxidizing microbes) on hard rock surface and their subsequent weathering and subsequent transport to the atmosphere can leads to high EF Mn

over remote marine location (Bullard et al.,2004, Chance et al.,2015). This further underscore to the need of detailed study on the understanding of mineralogy of dust and their controls on the solubility.

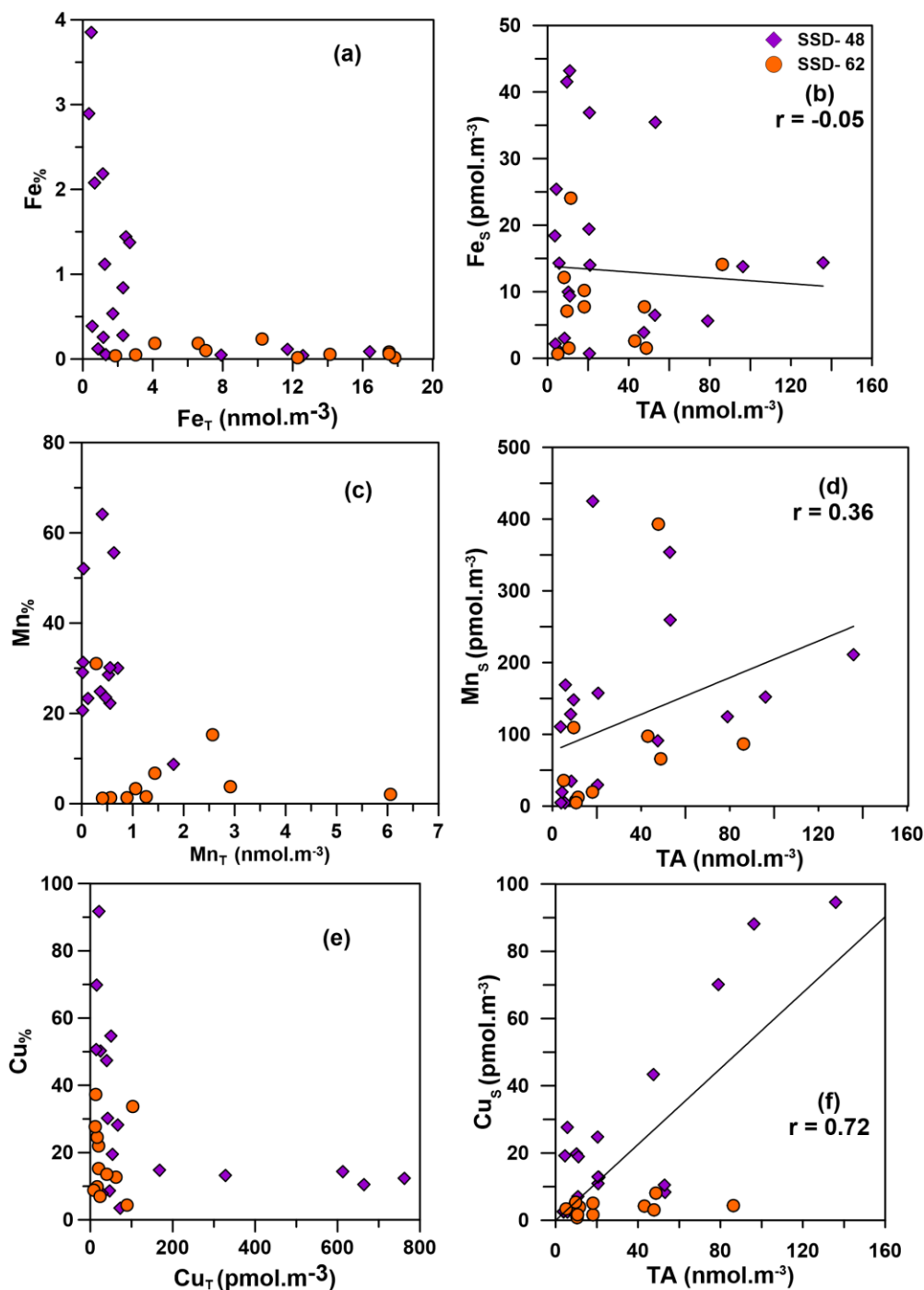


Fig-5.10 Correlation plot between (a) total Fe (Fe_T) with $Fe\%$, (c) total Mn (Mn_T) with $Mn\%$ (e) total Cu (Cu_T) with $Cu\%$, Total Acid (TA) with Fe_S , Mn_S and Cu_S in (b), (d) and (f) respectively.

Similar to Fe and Mn, Cu showed higher solubility during summer with a much wider range 4-92% with a mean of 31% (Table 5.2). While during monsoon, it shows comparatively narrow range of 4.4-37% with a mean of 16.7% (Table 5.2). Cu% also show similar trend like Fe% during summer and CIOS sector shows higher Cu% ($39 \pm 29\%$) followed by EIOS ($22 \pm 19\%$) and NIO ($15 \pm 4\%$). However, during monsoon Cu% almost equal in all sectors NIO ($21 \pm 5\%$), EIOS ($16 \pm 13\%$), CIOS ($15 \pm 9\%$). Cu% over the Indian Ocean were found lower during monsoon campaign, however, comparable with those reported by Panda et al. (2022) over the Arabian Sea during Monsoon months. Our current observation Cu% over the Indian Ocean is also lower compare with previous studies from different ocean basin like north Pacific (Buck et al., 2019), South China Sea (Hsu et al., 2010) and Atlantic Ocean (Sholkovitz et al., 2010). Correlation between Cu% and total Cu (Fig-5.10e) shows a hyperbolic relationship like Fe. However, linear relation between C_{us} and TA (Fig-5.10f) indicate the role of acid processing in contributing soluble Cu and possibly playing an important role to the fractional solubility of Cu.

5.2.7 Dry depositional flux over the Indian Ocean:

Atmospheric dry deposition flux (DF) was calculated by using formula described in section- 2.4.4 and given in Table 5.3. Mean estimated DF of dust was found to be similar for both summer ($4.1 \pm 5.1 \text{ mg.m}^{-2}.\text{day}^{-1}$) and monsoon ($5.5 \pm 5.6 \text{ mg.m}^{-2}.\text{day}^{-1}$) campaigns. These values are 2-3 times lower than those reported previously from the Arabian Sea and Bay of Bengal (Table 5.3), mainly due to the proximity of dust source region from the sampling locations. Instead of calculating basin wide average, sector wise dust flux was estimated for NIO; which averaged around $3.2 \pm 3 \text{ g.m}^{-2}.\text{year}^{-1}$ during summer and is falling in the range ($0.3\text{-}6 \text{ g.m}^{-2}.\text{year}^{-1}$) estimated previously by Srinivas and Sarin (2013). The estimated dust flux over the NIO also shows a good agreement with previously model based flux estimation by Grand et al. (2015) ($2.5 \pm 0.5 \text{ g.m}^{-2}.\text{year}^{-1}$), Jickells et al., (2005) ($2\text{-}5 \text{ g.m}^{-2}.\text{year}^{-1}$) and Mahowald et al., (2005) ($3 \pm 1 \text{ g.m}^{-2}.\text{year}^{-1}$). In contrast to NIO, dust flux over the EIOS region is overestimated by 5 times ($2.5 \pm 1.8 \text{ g.m}^{-2}.\text{year}^{-1}$) for summer and twice ($1.1 \pm 0.1 \text{ g.m}^{-2}.\text{year}^{-1}$) for monsoon from MADCOW estimation ($0.5\pm 0.08 \text{ g.m}^{-2}.\text{year}^{-1}$) as well as from other models. The MADCOW model introduces uncertainty, while considering composition of aerosol and its solubility; these parameters change on the basis of space and time (Grand et al., 2015). This clearly highlights the need for real-time measurement points to re-evaluation of model-based outputs particularly for the Indian Ocean.

DF of reactive nitrogen species NH_4^+ , NO_3^- and ON over the Indian Ocean during summer varied from 0.02 to 2.3 $\mu\text{mol m}^{-2}\text{d}^{-1}$ ($0.4 \pm 0.65 \mu\text{mol m}^{-2}\text{d}^{-1}$), 0.73 to 20.15 $\mu\text{mol m}^{-2}\text{d}^{-1}$ ($8 \pm 6.6 \mu\text{mol m}^{-2}\text{d}^{-1}$), and 0.1 to 3.8 $\mu\text{mol m}^{-2}\text{d}^{-1}$ ($0.9 \pm 1 \mu\text{mol m}^{-2}\text{d}^{-1}$), respectively. During monsoon, NO_3^- ($7.7 \pm 6.5 \mu\text{mol m}^{-2}\text{d}^{-1}$) and ON ($0.55 \pm 0.6 \mu\text{mol m}^{-2}\text{d}^{-1}$) was comparable with summer, however, NH_4^+ was negligible as their concentration were found below detection limit during the summer campaign. While, comparing our current data with the Arabian Sea (Bikkina et al., 2021) and Bay of Bengal (Srinivas et al., 2013a), the Indian Ocean receive ≤ 3 times reactive nitrogen. Equatorial Indian Ocean receives lower reactive nitrogen species compare to equatorial eastern Atlantic Ocean irrespective of any season (Powell et al., 2015).

Similar to reactive nitrogen species, DF of trace element over the Indian Ocean is also lower than the Arabian and Bay of Bengal irrespective of any season (Table 5.3). However, inter-basinal comparison of our current data (Arithmetic mean of DF) (Table 5.3) with previous study from remote Atlantic Ocean (Baker et al., 2013; Chance et al., 2015), the Indian Ocean receives higher amount of Fe_T and Mn_T irrespective of any season but similar to equatorial Atlantic Ocean (Powell et al., 2015). Saharan outflow brings higher amount of dust and associated TEs to the equatorial Atlantic region which enhance the DF but such active dust sources are absent over southern and northern Atlantic Ocean which causes lower DF flux over the later regions. If we consider sector wise DF of TEs and dust CIO sector also receives a comparable amount with remote Atlantic oceanic region discussed earlier.

Unlike total trace element, the Indian Ocean receives considerable amount of soluble Fe flux (Table 5.3). Arabian Sea also receives similar amount soluble Fe during monsoon (Table 5.3), while Bay of Bengal receives relatively higher FeS (~4 times higher than the Indian Ocean and Arabian Sea) during winter and summer seasons observed previously (Kumar et al., 2010; Srinivas and Sarin, 2013b). Atmospheric processing/ acid processing of dust over the Bay of Bengal is responsible for its higher soluble Fe flux, which is less significant over the Arabian Sea and Indian Ocean region during study period. Previously model based flux calculation by Grand et al. (2015) estimated higher soluble Fe flux as ($290 \pm 70 \mu\text{mol.m}^{-2}.\text{yr}^{-1}$) for the southern Bay of Bengal (5-10°N) which also fall within our current study area. In this model Grand et al. (2015) consider Fe% as 18% (Kumar et al., 2010), which could be valid for the northern Bay of Bengal,

Table 5.3 Average Dry deposition Flux of dust and other chemical species over Indian Ocean (Current study) and peripheral oceanic basins. a. Panda et al.,2022; b. Srinivas et al., 2012; c. Bikkina et al., 2021; d. Srinivas and Sarin, 2013b.

Species	Unit	Indian Ocean				Arabian Sea					Bay of Bengal		
		Summer-2018		Monsoon-2019		Monsoon-2017 & 2018 ^a		Summer-2006 ^b	Winter 2018 ^c		Dec-2008 & Jan-2009 (Winter) ^d		Mar-2006 (Summer) ^d
		Vdry	DF	DF		Vdry	DF	DF	DF		Vdry	DF	DF
Dust	mg day ⁻¹ m ⁻²	1	4.1 ± 5.1	5.5 ± 5.6		1	13.8 ± 10.6	-	-		1	12 ± 10	10 ± 6
Nitrate	μmol day ⁻¹ m ⁻²	1	8 ± 6.6	7.7 ± 6.5		1	-	-	27 ± 11		1	-	-
Ammonium		0.1	0.4 ± 0.65	-		0.1	-	-	9.4 ± 7.1		0.1	-	-
ON		0.1	0.9 ± 1	0.55 ± 0.6		0.1	-	-	7.4 ± 7.0		0.1	-	-
Fe _T	nmol day ⁻¹ m ⁻²	1	3 ± 4.1	7 ± 5		1	13.5 ± 11	-	-		1	7 ± 7	9 ± 5
Mn _T		1	26 ± 25	105 ± 93.1		1	706 ± 634	-	-		1	627 ± 462	304 ± 165
Cu _T		0.1	0.8 ± 1.3	0.2 ± 0.13		0.3	22 ± 16	-	-		0.1	6 ± 5	12 ± 5
Fe _S		1	14 ± 12	112 ± 103		1	98.7 ± 143	0.7 - 16	-		1	423 ± 355 ^b	-

where atmospheric aerosol is highly influenced by anthropogenic emissions. However, the southern Bay of Bengal is devoid of such impact which is visible from lower Fe% (0.5%). Similar to NIO other two sectors (EIOS, CIOS) of our current study receives lower soluble Fe compare to model data.

5.3 Summary:

The concentrations of mineral dust, associated macro (N- species) and micro nutrients (Fe, Mn, and Cu) were measured in atmospheric aerosols collected over the IO during two on-board cruise campaigns in summer and monsoon months of 2018 and 2019, respectively. Major outcomes of this study are:

1. The North Indian Ocean receives the maximum amount of dust irrespective of season in contrast to the equatorial and central Indian Ocean owing to its geographical location and prevailing meteorological conditions.
2. Macro nutrients (reactive N species) were found lower in the Indian Ocean compared to the Arabian Sea and Bay of Bengal. Major anthropogenic tracers such as ammonium and nss-K^+ were found below the detection limit during monsoon months indicating negligible influence of anthropogenic emissions in the remote sectors of the Indian Ocean.
3. Micronutrients (Fe, Mn and Cu) were considerably low over the Indian Ocean. While, Fe is majorly associated with dust but high EF of Mn and Cu indicate these species highly influenced by either enriched sources (Mn) or anthropogenic activity. A positive correlation between total acid and soluble Mn and Cu indicate the role of chemical processing in contributing to their fractional solubility.
4. Inverse hyperbolic relation between fractional solubility and total TEs observed over the Indian Ocean and interestingly monsoon sample mainly lies towards natural dust end members while during summer towards end member with high solubility and low dust.
5. Dry depositional flux of dust as well as nutrients were found lower than the Arabian Sea and Bay of Bengal. In addition, we observe significant differences in concentration of TEs measured in this campaign as compared to model-based estimations which may be attributed to the unavailability of fractional solubility data from this region.

This study provides first trans-equatorial observation of the mineral dust and nutrient supply over the Indian Ocean. Such data set are essential to full fill scientific knowledge gap for the understanding of nutrient biogeochemical cycling in the Indian Ocean.

Chapter 6
Summary, conclusions and future direction

6.1 Summary:

The regional scale studies of vital nutrient species present in atmospheric aerosol over the marine region are important to understand and assess their impact on ocean surface biogeochemical cycles and carbon cycles which have direct and indirect effects on climate and environmental changes. However, there is a scarcity of field measurements of atmospheric nutrient species and dust across the Indian Ocean region. Real-time field observations offer the most direct insights into aerosol properties. This study provides comprehensive and unique data on seasonal and spatial variation of atmospheric nutrient species and their depositional flux over a wide area of the Indian Ocean, including the Arabian Sea (AS) and the Bay of Bengal (BoB) up to 13°S latitude Indian Ocean. Along with the estimation of macro and micro-nutrient species, the fractional solubilities of trace elements (TEs) like Fe, Mn and Cu were determined and the factors influencing/controlling these TEs solubilities were evaluated. The chapter-wise or geographic location-wise major outcomes of this study are summarized below

Over the Arabian Sea, the inorganic nitrogen ($\text{IN} = \text{NH}_4^+ + \text{NO}_3^-$) shows a relatively higher concentration of $200.4 \pm 138.8 \text{ nmol m}^{-3}$ during winter in contrast to the monsoon $45.2 \pm 67.9 \text{ nmol m}^{-3}$. The NH_4^+ is a major contributor to IN accounting for >50% during winter but accounts for up to 37% in the monsoon, which makes NO_3^- a major contributor to IN species. From this study, it was observed that the AS receives higher dust flux during monsoon ($15.9 \pm 13.2 \text{ } \mu\text{g m}^{-3}$) compared to winter ($12.9 \pm 6.2 \text{ } \mu\text{g m}^{-3}$). This data excludes samples collected during the dust storm events. The northern AS received higher dust compared to the southern AS during the study period. To understand the effect of particle size on dust and TEs, size-segregated aerosol samples (PM_{10} and $\text{PM}_{2.5}$) were collected during winter, with fine dust contributing $12.7 \pm 8.5 \%$ to total dust. Similar to dust, Fe and Mn were also observed to show relatively higher concentrations in the northern AS during both seasons. Enrichment factor (EF) was estimated for all TEs and Fe shows similar EF (~ 1.5) during both seasons. Interestingly, Mn shows an EF >10 during the monsoon but <10 during winter. It was found that carbonates present in northeastern Africa and the Arabian Peninsula are naturally enriched with Mn, but those from the Thar desert are devoid of such naturally enriched Mn-bearing carbonates. The prevailing southwest winds during monsoon transport the naturally enriched Mn to the AS. Atmospheric Cu concentration was higher during the winter ($136.8 \pm 122.8 \text{ pmol m}^{-3}$) mainly due to continental outflow throughout NE monsoon wind, which can transport anthropogenic Cu (which is also evident from higher enrichment factor (EF) >10) possibly from the Indian subcontinent. All soluble TEs concentrations were higher in winter compared to monsoon season. The effect of particle size on trace element concentration was

also assessed during the winter season. It was found that the total Fe present in fine aerosol (PM_{2.5}) accounts for ~13% of the total Fe present in PM₁₀. Interestingly, for soluble Fe, fine aerosol contributes ~42% of the soluble Fe present in PM₁₀. In the case of Cu, fine aerosols (PM_{2.5}) contribute ~50% to both total and soluble Cu present in PM₁₀. During winter, relatively higher fractional solubility was observed (Fe%: 5.8 ± 3.3 %; Mn%: 69.0 ± 16.0 %; Cu%: 56.3 ± 18.9 %) compared to the monsoon season (Fe%: 0.8 ± 0.9 %; Mn%: 42.9 ± 24.4 %; Cu%: 26.1 ± 19.5 %) indicating a possibility of relatively higher atmospheric processing of dust and associated TEs in contrast to monsoon months. This is also supported by the inverse relation between the fractional solubility and total TEs as well as a significant correlation between fractional solubility and total acid during winter. The linear and positive relation between fractional solubility and non-sea salt potassium (tracer for biomass burning) also provides evidence of TEs contribution from the biomass burning during the winter season only. The dry deposition flux of soluble TEs to the Arabian Sea during winter (Fe: 726.2 ± 494.0 nmol m⁻² d⁻¹; Mn: 331.3 ± 268.9 nmol m⁻² d⁻¹; Cu: 6.2 ± 4.7 nmol m⁻² d⁻¹) is higher compared to monsoon season (Fe: 98.7 ± 143.1 nmol m⁻² d⁻¹; Mn: 212.6 ± 192.8 nmol m⁻² d⁻¹; Cu: 4.4 ± 3.3 nmol m⁻² d⁻¹) and other regions of the Indian Ocean contributing significantly to the surface biogeochemical cycle during winter. Soluble Fe flux to the AS can impact up to 10% of Primary productivity with the highest impact during the winter season.

Over the Bay of Bengal, the reactive nitrogen species like NH₄⁺ and organic nitrogen concentrations were relatively higher than NO₃⁻ due to the contribution of anthropogenic aerosol sources during the study period. NH₄⁺ dominates the inorganic nitrogen (IN) concentration (NH₄⁺/ IN > 0.8 in both post-monsoon and winter seasons) indicating anthropogenic influence in both seasons. Total nitrogen (TN) dry deposition flux is 39.08 ± 9.04 μmol m⁻² d⁻¹ in PM and 38.51 ± 9.04 μmol m⁻² d⁻¹ in winter. Using the Redfield ratio, TN flux accounts for 1.57 – 6.00 C m⁻² d⁻¹ and 2.53-5.11 mg C m⁻² d⁻¹ carbon fixation by marine phytoplankton in the post-monsoon and winter seasons respectively which can support up to 3.3% and 5.3% net primary productivity of the BoB in two respective seasons. The Bay of Bengal receives higher dust (20.6 ± 7.4 μg m⁻³) and Fe (14.9 ± 4.5 nmol m⁻³) during winter compared to post-monsoon (dust: 13.0 ± 6.0 μg m⁻³; Fe: 7.9 ± 6.3 nmol m⁻³). The active NE monsoon wind in winter is able to transport more continental material from land to sea compared to the post-monsoon season. High dust and total TEs were observed in CAP samples compared to the other two categories due to the sampling location's proximity to the source (continent) and favorable wind conditions. The relatively higher average Mn (1.25 ± 1.00 nmol/m³) was observed during post-monsoon mainly due to episodic wind from the Middle

East, which transported Mn-enriched mineral dust up to BoB. This event was largely absent during the winter months. This observation was also supported by a higher enrichment factor of Mn during post-monsoon. The soluble TEs show higher concentration during post-monsoon owing to low mass load and relatively higher supply of acidic species along with a significant amount of TEs from biomass burning enabling atmospheric processing of TEs during long-range transport. The fractional solubility of TEs over BoB is higher during post-monsoon (Average Fe%: 12.2 ± 6.5 %; Mn%: 65.0 ± 10.4 %; Cu%: 67.4 ± 23.1 %) compared to winter (Average Fe%: 5.5 ± 3.8 %; Mn%: 60.6 ± 8.4 %; Cu%: 52.5 ± 20.1 %). The lower dust supply in post-monsoon and a higher total acid (TA): dust ratio facilitate enhanced atmospheric processing compared to the winter season. Linear relation between fractional solubility and nss-K^+ suggests a notable amount TEs contribution from biomass burning in both seasons. The dry depositional flux of dust and TEs to the BoB has increased in recent years evident from this work compared to previous observations. The estimated N fixation in this region was found to be $\sim 0.31\text{--}1.34 \text{ Tg yr}^{-1}$ in post-monsoon and $\sim 0.35\text{--}1.60 \text{ Tg yr}^{-1}$ in winter (assuming N: Fe ratio of 50). Our estimation was in good agreement with the upper estimate value of 1.0 Tg-N yr^{-1} suggested by Naqvi et al. (2011). The potential C-fixation by atmospheric input of Fe was also estimated. The atmospheric input of soluble Fe can account for $2.13 \pm 0.90 \text{ Pg -C yr}^{-1}$ in post-monsoon and $1.99 \pm 1.01 \text{ Pg-C yr}^{-1}$ in winter. Therefore, atmospheric input can account for ~ 4 % of global PP (50 Pg-C yr^{-1} ; Carr et al., 2006) and 20% of Indian Ocean PP (9.9 Pg-C yr^{-1}) in both seasons.

The current study over the Indian Ocean is the 1st meridional observation of atmospheric nutrients over the region covering both sides of the equator. This study presents precious unexplored information on atmospheric nutrients such as reactive nitrogen species (Nitrate, Ammonium, Organic nitrogen), micro-nutrients (e.g. Fe, Mn and Cu) concentration along with mineral dust in the aerosol samples collected from the Indian Ocean over summer (April–May 2018) and monsoon (June–July 2019) months. A significant spatial variation of dust was observed during summer ($0.6\text{--}22.8 \mu\text{g m}^{-3}$) and monsoon ($2.8\text{--}25.1 \mu\text{g m}^{-3}$) months with a decreasing trend from north to south. Dust as well as other nutrient species shows a general north-to-south decreasing trend, however, no such trend was seen in the soluble trace elements (TEs) concentration. Anthropogenic species like NH_4^+ and nss-K^+ were found below the detection limit during the monsoon campaign. The fractional solubility of Fe, Mn and Cu were estimated by measuring their concentration in ultrapure water leach which averaged around 0.99 ± 1.12 %, 31.0 ± 14.9 % and 31.1 ± 25.4 %, respectively during summer and 0.09 ± 0.08 %, 6.0 ± 8.9 %, 16.7 ± 9.6 %, respectively, during the monsoon period. The correlation of

soluble Fe with total Fe and total acidic species suggests varying dust sources is an important controlling factor for the fraction solubility of Fe with negligible contribution from the chemical processing. However, a significant correlation was observed between total acid and fractional solubility of Mn and Cu suggesting the role of chemical processing in enhancement of their solubility. Dry deposition flux of aeolian dust was estimated for both campaigns using Al concentration and relatively higher fluxes were observed for summer ($12.6 \pm 8.4 \text{ mg m}^{-2} \text{ d}^{-1}$) and monsoon ($8.7 \pm 8.4 \text{ mg m}^{-2} \text{ d}^{-1}$) months as compared to model-based estimates reported in the literature. Contrastingly, the estimated deposition flux of soluble Fe from both campaigns displays relatively lower values as compared to model-based results which underscores a need for re-evaluation of biogeochemical models with real-time data.

6.2 Future scope of research:

The research carried out as part of this thesis has addressed the spatial-seasonal variation in the dust and nutrient species present in aerosol and their depositional fluxes to the Indian Ocean. The fractional solubility of TEs along with factors impacting their fractional solubility over the Indian Ocean also discussed. Although the present work was carried out to reveal many interesting aspects of the mineral dust and nutrient species over this region, however, there exist numerous knowledge gaps related to the atmospheric nutrient flux in the region which need further research.

- Estimation of dry deposition velocity and possible seasonal variation by using isotopes like ^{10}Be and ^{210}Pb over the North Indian Ocean.
- Estimation of anthropogenic aerosols like V, Cd, Zn, Pb, etc and determination of their fractional Solubility.
- Estimation and flux calculation of other atmospheric major nutrients like Phosphate and Silicate along with their dependency on particle size over the Indian Ocean.
- Source identification of dust (via using Sr and Nd isotopes) as well as for nutrient species like nitrogen, iron and copper via their respective stable isotopes.

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List of Publication and Conferences:

List of Publication from Thesis:

1. Panda, P. P., Aswini, M. A., Bhatt, P., Srimuruganandam, B., Peketi, A., & Kumar, A. (2022). Bioactive Trace Elements' Composition and Their Fractional Solubility in Aerosols from the Arabian Sea during the Southwest Monsoon. *ACS Earth and Space Chemistry*, 6(8), 1969-1981.
2. Panda, P. P., Shukla, G., Kumar, A., Aswini, M. A., Kaushik, A., Nayak, G., & Matta, V. M. (2024). Atmospheric deposition of mineral dust and associated nutrients over the Equatorial Indian Ocean. *Science of The Total Environment*, 915, 169779.
3. Li, R., Panda, P. P., Chen, Y., Zhu, Z., Wang, F., Zhu, Y., ... & Tang, M. (2024). Aerosol trace element solubility determined using ultrapure water batch leaching: an intercomparison study of four different leaching protocols. *Atmospheric Measurement Techniques Discussions*, 2024, 1-25.

List of Publication other than Thesis:

1. Kaushik, A., Kumar, A., Aswini, M. A., Panda, P. P., Shukla, G., & Gupta, N. C. (2021). Seasonal variation in chemical composition of size-segregated aerosols over the Northeastern Arabian Sea. *Frontiers in Environmental Science*, 8, 619174.
2. Badesab, F., Mascarenhas-Periera, M. B. L., Gaikwad, V., Dewangan, P., Panda, P. P., Deenadayalan, K., ... & Lakshmi, B. V. (2021). Rock magnetic evidence of tectonic control on the sedimentation and diagenesis in the Andaman Sea over~ 1 million years. *Marine and Petroleum Geology*, 130, 105150.
3. Sharma, D., Biswas, H., Panda, P. P., Chowdhury, M., Silori, S., Pandey, M., ... & Kumar, A. (2022). Atmospheric dust addition under elevated CO₂ restructured phytoplankton community from the Arabian Sea: A microcosm approach. *Marine Chemistry*, 247, 104183.
4. Yogi, D. S., Naik, A., Panda, P. P., Yadav, R., Desai, A., & Nanajkar, M. (2023). Ontogenetic dietary shift in megabenthic predatory elasmobranchs of a tropical estuarine bay. *Estuaries and Coasts*, 46(1), 279-291.

List of Conferences:

1. IIOSC-2022 (14-18 March 2022, CSIR-NIO, Goa). (Poster Presentation)
2. SOLAS Open Science Conference-2022 (25-29 September 2022, Hybrid in Cape Town, South Africa). (Oral Presentation)
3. Samudra Manthan'23 (28-30 September 2023, CSIR-NIO, Goa). (Presentation and Poster).
4. IASTA-2023(12-14 December, Mumbai, India). (Poster Presentation)