# Atmospheric Deposition of N, P and Fe to the Northern Indian Ocean

### A THESIS

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In the

**Faculty of Science** 

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# **DECLARATION**

I, **Bikkina Srinivas**, S/o Mr. Bikkina Bhishmudu, resident of E-202, PRL residences, Navrangpura, Ahmedabad – 380009, hereby declare that the research work incorporated in the present thesis entitled *"Atmospheric Deposition of N, P and Fe to the Northern Indian Ocean"* is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required.

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Date: 9<sup>th</sup> July 2012

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# CERTIFICATE

I feel great pleasure in certifying that the thesis entitled "Atmospheric Deposition of N, P and Fe to the Northern Indian Ocean" embodies a record of the results of investigations carried out by Bikkina Srinivas under my guidance.

He has completed the following requirements as per Ph.D. regulations of the University

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(d) Published/accepted minimum of one research paper in a referred research journal.

I am satisfied with the analysis of data, interpretation of results and conclusions drawn.

I recommend the submission of thesis.

lin

Date:9<sup>th</sup> July 2012

Name and designation of supervisor Manmohan Sarin, Senior Professor

*Countersigned by* Head of the Department Dedicated to My parents, brother and my mentors'

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## ABSTRACT

The continental outflow from south and south-east Asia to the Northern Indian Ocean is a conspicuous feature during the late NE-monsoon (January-April). The prime focus of this thesis is to assess spatio-temporal variability in the atmospheric abundances of chemical constituents over the Bay of Bengal (BoB) and the Arabian Sea (ARS). This thesis also addresses on the air-sea deposition of nutrients, their dry-deposition fluxes, fixation rates and contribution to the Primary Production (PP). Relatively high concentrations of nutrients (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>,  $N_{Org}$ ,  $PO_4^{3-}$  and  $Fe_{ws}$ ) over the BoB suggest that impact of anthropogenic sources is significantly pronounced over this oceanic region. The concentration of  $N_{\text{Inorg}}$ (mainly as  $NH_4^+$ -N over the BoB and  $NO_3^-$ -N over the ARS) dominates (> 80 %) the N<sub>Tot</sub> (N<sub>Inorg</sub>+N<sub>Org</sub>). However, deposition of N<sub>Org</sub> near coastal regions can be significant as projected by the models. Significant linear relationship among P<sub>Inorg</sub>, nss-K<sup>+</sup>, Fews, OC and EC together with analysis of air mass back trajectories suggest their contribution from biomass burning emissions in the Indo-Gangetic Plain. The fractional solubility of aerosol-Fe (Fe<sub>ws</sub> (%) = Fe<sub>ws</sub> / Fe<sub>Tot</sub>\*100) over the BoB and the ARS varied from 1.4-24 and 0.02-0.4 %, respectively during the study period. The large variability in Fe solubility over the BoB is attributed to the type of mineral dust and contribution from combustion sources. The drydeposition fluxes are relatively high over the BoB (N<sub>Tot</sub>, P<sub>Inorg</sub> and Fe<sub>ws</sub> are 2-167, 0.5-4.8 and 0.02-1.2  $\mu$ mol m<sup>-2</sup> d<sup>-1</sup>, respectively) compared to those over the ARS (N<sub>Tot</sub> and P<sub>Inorg</sub>: 0.2–18.6 and 0.3-0.9  $\mu$ mol m<sup>-2</sup> d<sup>-1</sup>, respectively; Fe<sub>ws</sub>: 0.7-15.3 nmol  $m^{-2} d^{-1}$ ). The air-sea deposition of N and P is of comparable magnitude with their supply via rivers. The high enrichment factors of Pb, Cd and Cu over the BoB reemphasize the dominance of anthropogenic sources.

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Introduction

#### **1.1. Introduction**

Atmospheric particulate matter is ubiquitous in the Earth system and affecting the radiation budget of the atmosphere (via direct and indirect effect), visibility degradation, health effects, and providing nuclei for the condensation of water vapour, thus, results in cloud formation [Lawrence and Lelieveld, 2010; Ramanathan et al., 2001a; Ravishankara, 1997]. Apart from these, the long-range atmospheric transport of continental aerosols to remote oceanic regions can provide nutrients (N, P and Fe) to the seawater and, thus, influencing the biogeochemistry of surface ocean [Duce et al., 1991; Jickells et al., 2005; Mahowald et al., 2011and references therein]. Figure 1.1 depicts the typical nutrient deposition across air-sea interface and its subsequent role in the biogeochemistry of the surface ocean. It has been suggested that the availability of nutrients (N, P and Fe) to the surface seawater is a crucial factor that controls the strength of Oceanic Biological Pump, thereby, influencing the partial pressure of  $CO_2$  in the atmosphere [*Gruber*, 2004]. In this context, it is important to study the atmospheric deposition of nutrients and their relevance to the ocean surface biogeochemistry.

#### 1.1.1. Significance of atmospheric input of N

Nitrogen is an essential nutrient for terrestrial and marine ecosystems. The atmospheric transport and deposition of anthropogenic nitrogen is a topic of significant interest as it can perturb surface water productivity and thereby influences the marine biogeochemistry of nitrogen species. Atmospheric deposition of soluble nitrogen to neritic (coastal) waters can cause Eutrophication, trigger phytoplankton blooms which in turn can lead to oxygen depletion in deep waters and sediments [*Howarth*, 2008; *Nixon*, 1995; *Paerl and Whitall*, 1999; *Paerl et al.*, 2002]. Likewise, atmospheric anthropogenic nitrogen (AAN) deposition to oligotrophic gyres can enhance the oceanic productivity; can be a major source to the open ocean [*Duce et al.*, 2008; *Jickells*, 2006; *Spokes et al.*, 2000]. In addition, a recent study has emphasized the role of atmospheric N (and S) deposition on ocean acidification and its influence on the inorganic carbon system [*Doney et al.*, 2007]. Their study suggest that, on a global scale, the oceanic uptake of CO<sub>2</sub> by the deposition of soluble nitrogen can lead to increase

in dissolved inorganic carbon (DIC) levels and alkalinity in the surface waters. Furthermore, the effect is N deposition on ocean acidification is only a few percent relative to its contribution from the anthropogenic  $CO_2$  uptake and is particularly important only in the downwind oceanic regions affected by pollution sources. Revised marine budget of N cycle has suggested the significant role of atmospheric source [*Duce et al.*, 2008; *Jickells*, 2006; *Seitzinger et al.*, 2002].

The abundance of reactive nitrogen in the atmosphere has increased significantly in recent years due to the growing anthropogenic activities, including fossil-fuel combustion, biomass burning and fertilizer production [*Galloway and Cowling*, 2002]. By combining the inorganic aerosol thermodynamic equilibrium model with a three dimensional chemical transport model, Luo et al., [2007] have concluded that atmospheric deposition of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> is increased by a factor of two (globally) in 1990s compared to that observed for pre-industrial scenario.



Figure 1.1: Biogeochemistry of nutrient species (N, P and Fe) in the marine environment.

In addition, there is a growing concern that with rapid increase in anthropogenic activities from south and south-east Asia, the atmospheric transport and subsequent deposition of nitrogen can have adverse impact on surrounding oceanic waters [*Duce et al.*, 2008 and references therein].

The growing number of evidences suggest that in the absence of significant input of P and Fe, deposition of AAN can shift the ecosystem towards other limiting nutrients (P or Fe) via changes in the Redfield stoichiometry (N:P = 16:1) of surface ocean [*Duce et al.*, 2008; *Jickells*, 2006]. In addition, recent studies have highlighted the importance of atmospheric deposition of organic nitrogen and further emphasizes its bioavailability in the surface ocean [*Bronk et al.*, 2007; *Cornell et al.*, 2003; *Cornell*, 2010; *Mace et al.*, 2003; *Nixon*, 1995; *Russell et al.*, 1998; *Scudlark et al.*, 1998; *Spokes et al.*, 2000]. There is not much information available with regard to various sources, transport pathways and deposition process of organic nitrogen [*Cornell*, 2010; *Duce et al.*, 2008; *Seitzinger and Sanders*, 1999]. Therefore, there is a need to study the various forms of atmospheric nitrogen species in terms of their abundances; transport and deposition to the surface ocean in order to better constrain their effect on the biogeochemistry of the surface ocean [*Dentener et al.*, 2006; *Duce et al.*, 2008; *Jickells*, 2006; *Lesworth et al.*, 2010].

#### 1.1.2. Significance of atmospheric input of P

Phosphorous is one of the essential major nutrient for Primary Productivity in both terrestrial and marine ecosystems [*Chester*, 2002; *Fang*, 2004]. Due to its association with C and N fixed by the marine phytoplankton, defined as Redfield ratio (C: N: P = 106:16:1), any changes in the supply of phosphorous would lead to significant changes in the biogeochemical cycles of nutrients [*Mahowald et al.*, 2008; *Schlesinger*, 1997]. In addition, it has been suggested that marine productivity over geological time scale is regulated by the availability of phosphorous [*Tyrrell*, 1999]. Recent observations suggest that Productivity in some of the oligotrophic oceanic regions (Mediterranean Sea and Sargasso Sea) and in marine basins, fed by large quantity of freshwater, is limited by the availability of phosphorus [*Paytan and McLaughlin*, 2007 and references there in]. Atmospheric input to these remote oceanic regions, is suggested to be an important source and, thus, enhancing the carbon sequestration. Until recently, atmospheric mineral dust is considered as a major source of phosphorous to the surface ocean [*Nenes et al.*, 2011] due to the fact that phosphorous comprises 0.07 % of the upper continental crust [*Taylor and McLennan*, 1985] and desert regions account for almost ~33 % of land area. In this regard, several studies investigated the atmospheric transport of mineral dust ( $P_{dust}$ ) to the oceanic regions [*Anderson et al.*, 2010; *Bergametti et al.*, 1992; *Mahowald et al.*, 2008; *Nenes et al.*, 2011]. However, recent studies have highlighted the importance of biomass burning emissions (agricultural-waste residue) as a significant source of phosphorous [*Anderson et al.*, 2010 and references there in]. It has also been suggested that the global atmospheric cycle of phosphorous is significantly perturbed due to extensive use of fertilizers and mining of phosphate rocks [*Jahnke*, 2000].

Owing to the paucity of data, earlier studies suggested the minor role of aeolian input of P compared to its riverine supply [*Froelich et al.*, 1982; *Graham and Duce*, 1979]. Recent studies have documented that the magnitude of atmospheric input of phosphorous may attain comparable levels with respect to its riverine supply [*Compton et al.*, 2000; *Paytan and McLaughlin*, 2007]. These estimations included the perturbations related to global P cycle and contribution from other anthropogenic sources. With the rapid increase in anthropogenic activities from south and south-east Asia, it also essential to assess the atmospheric abundances of this macronutrient in marine regions that are influenced by the continental air masses (viz., downwind of south and south-east Asia, North America,) with relevance to Primary Production in the surface waters. These contrasting views demand further investigation in this regard.

#### 1.1.3. Significance of atmospheric input of Fe

Aeolian supply of iron has been suggested as a dominant source to the open ocean [*Duce and Tindale*, 1991; *Jickells and Spokes*, 2001; *Mahowald et al.*, 2005a]. In vast area of the open ocean waters (Subarctic Pacific, Equatorial Pacific and Southern Ocean: High Nutrient Low Chlorophyll regions), productivity is limited by the availability of one of the key essential micro nutrient, Fe [*Martin and Fitzwater*, 1988; *Martin et al.*, 1989]. In-vitro (glass

bottle) addition of soluble Fe to the aliquots of sea water from these regions resulted in enhanced chlorophyll levels [*Martin and Fitzwater*, 1988]. This led to the hypothesis that productivity in HNLC waters is limited by the availability of Fe and supply of this micro nutrient can stimulate phytoplankton blooms. Subsequently, mesoscale insitu iron fertilization experiments further demonstrate the Fe limitation in HNLC regions [*Boyd et al.*, 2000; *Boyd et al.*, 2007; *Coale et al.*, 1996; *Martin et al.*, 1994].

Since then, most of the research has been carried out on the availability of iron to these regions [*Jickells et al.*, 2005; *Luo et al.*, 2005; *Mahowald et al.*, 2005b]. It has also been suggested that dust transport during glacial times is an order of magnitude higher than that in the present-day [*Boyd and Ellwood*, 2010 and references therein]. This argument has been further strengthened by a long-term record of Fe (dust) deposition, retrieved from a marine sediment core from the sub-Antarctic Atlantic region (ODP Site 1090), that extends up to 4 Myrs (i.e., entire Pliocene and Pleistocene). This record clearly demonstrates the long-term coupling between mineral dust and climate over the past 4 Myrs [*Martinez-Garcia et al.*, 2011]. In addition, the observed anti correlation between concentration of mineral dust and CO<sub>2</sub> in the Vostok ice core record (that extends up to 120 kyrs), suggesting the enhanced supply of Fe (dust) during the glacial time to the southern Ocean results in sequestration of atmospheric CO<sub>2</sub>[*Martin*, 1990].

The studies conducted in HNLC regions have highlighted the dust mediated glacial-interglacial CO<sub>2</sub> changes [*Petit et al.*, 1999; *Ridgwell et al.*, 2003; *Sigman and Boyle*, 2000] and emphasize the need to further understand the atmospheric transport and deposition of this micronutrient to the open ocean [*Boyd et al.*, 2000; *Coale et al.*, 1996; *Jickells et al.*, 2005; *Mahowald et al.*, 2009]. Apart from the primary productivity, deposition of iron-bearing minerals to the North Atlantic could stimulate N<sub>2</sub> fixation [*Falkowski*, 1997]. Their study also suggests that enhanced supply of mineral dust could lead to greater amount of N<sub>2</sub> fixation during glacial times.

Ever since, numerous studies have focussed on the dust transport to these oceanic regions [*Duce et al.*, 1991; *Duce and Tindale*, 1991; *Jickells and Spokes*, 2001; *Jickells et al.*, 2005]. In this regard, previous studies and models suggested

that the mineral dust transport from arid-semi arid regions is a dominant source of soluble iron to the open ocean [*Duce and Tindale*, 1991; *Hand et al.*, 2004; *Jickells and Spokes*, 2001; *Mahowald et al.*, 2005a]. Although, Fe comprises the third most abundant element (3.5%) in the upper continental crust (UCC), it is very scarce in surface seawater (i.e., often observed in the concentration range of < 1 nM).

The poor solubility in surface waters is due to the precipitation of Fe in oxygenated sea water as oxy-hydroxides at circum-neutral pH (~ 8.1). Recent observations from the North Atlantic suggest the pronounced atmospheric control of dissolved iron concentration in the surface waters as evident from the coherent coupling between high dust loading in marine aerosols and corresponding high concentration of dissolved Fe [*Sedwick et al.*, 2005]. This observation clearly emphasizes the fact that atmospheric input indeed can be a major controlling factor for the dissolved iron concentration in the surface ocean.

Despite of its low concentration in surface seawater, studies within the source region of mineral aerosols have documented the poor solubility of iron, less than a percent [*Jickells and Spokes*, 2001]. However, aerosols collected over the remote North Pacific Ocean show enhanced Fe-solubility compared to that from the source regions of mineral dust [*Hsu et al.*, 2010; *Solmon et al.*, 2009; *Zhuang et al.*, 1992a; *Zhuang et al.*, 1992b]. The observed variability has been explained in terms of uptake of acidic species (viz., H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> etc.,) by mineral dust during long-range transport. Subsequent studies have shown that factors such as particle-size, dust concentration, mineralogy, presence of organic compounds and solar irradiation can also play a vital role in Fe solubility [*Baker and Jickells*, 2006; *Baker et al.*, 2010b; *Mahowald et al.*, 2009 and references therein; *Paris et al.*, 2010].

More recently, the importance of combustion sources (biomass burning and fossil-fuel combustion) has been suggested as a potential source of soluble iron to open ocean waters [*Chuang et al.*, 2005; *Guieu et al.*, 2005; *Kumar and Sarin*, 2010; *Luo et al.*, 2008; *Paris et al.*, 2010; *Schroth et al.*, 2009; *Sedwick et al.*, 2007; *Sholkovitz et al.*, 2009b]. Although meteoritic debris (cosmic dust) and

volcanic ash have been considered as a significant source of Fe, these estimates are not well constrained due to their episodic fallout nature. These observations stress the need for regional scale studies on the control for iron solubility in ambient aerosols.

Apart from the deposition of nutrients (viz. N, P and Fe), supply of other anthropogenic trace metals such as Cu can have severe impact on ecosystem health. Recent modelling study suggest the effect of Cu deposition to the low nutrient low chlorophyll (LNLC) areas (viz., Bay of Bengal), located in the downwind regions of pollution sources from south and south-east Asia, with relevance to changes in marine community structure [*Paytan et al.*, 2009]. Therefore, it is pre-requisite to assess their atmospheric abundances and drydeposition fluxes (viz., Cu, Pb and Cd etc.,) for the marine regions that are influenced by polluted continental outflow.

#### 1.2. Rationale

The Northern Indian Ocean, comprises Bay of Bengal (BoB) and Arabian Sea (ARS), is an ideal site to study the impact of continental outflow on the marine atmospheric boundary layer (MABL). Based on the measurement of optical and chemical properties of aerosols during the late NE-monsoon (January-April), earlier studies have documented the downwind transport of airborne pollutants up to the equatorial Indian Ocean [*Jayaraman et al.*, 1998; *Lelieveld et al.*, 2001; *Mayol-Bracero et al.*, 2002; *Ramanathan et al.*, 2001b; *Satheesh*, 2002; *Satheesh and Srinivasan*, 2002]. Furthermore, comparative study by Kumar et al., [2008b] has demonstrated the large anthropogenic influence of continental aerosols in the Bay of Bengal compared to that in the Arabian Sea [*Kedia et al.*, 2010; *Nair et al.*, 2007].

It has been documented by several studies that the continental outflow from the Indo-Gangetic Plain causes the widespread dispersal of pollutants over the Bay of Bengal during the late NE-monsoon [*Nair et al.*, 2007; *Rajput et al.*, 2011; *Ram et al.*, 2008; *Ram et al.*, 2010; *Rengarajan et al.*, 2007]. In addition, recent studies have highlighted the impact of outflow from south and south-east Asia on aerosol composition in the MABL of Bay of Bengal during the late NEmonsoon [*Kumar and Sarin*, 2010; *Sarin et al.*, 2011]. However, there is no such
attempt to assess the impact of nutrients in the continental outflow over the Northern Indian Ocean. In this context, a systematic study has been undertaken to study the impact of continental outflow on the atmospheric abundances of nutrients (N, P and Fe), dry-deposition fluxes and to assess their effect on surface waters of the Northern Indian Ocean.

## 1.3. Work Plan

With the above rationale, aerosols samples were collected from the marine atmospheric boundary layer of Bay of Bengal (BoB) and Arabian Sea (ARS) during the continental outflow (January-April). All samples were collected on preweighed tissuquartz filters (pre-combusted, PALLFLEX<sup>®TM</sup>) and analyzed for water-soluble inorganic constituents (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sup>4+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>), total soluble nitrogen (N<sub>Tot</sub> = N<sub>Inorg</sub> + N<sub>Org</sub>), PO<sub>4</sub><sup>3-</sup>, crustal elements (Al, Fe, Ca and Mg), trace metals (Pb, Cd, Cu and Mn), soluble iron (Fe<sub>ws</sub>) and carbonaceous aerosols (EC and OC). Water-soluble inorganic constituents (WSIC) were analyzed on Dionex-500 Ion-chromatograph; N<sub>Tot</sub> is on Schimadzu TN-analyzer; P<sub>Inorg</sub> is on LWCC (from WPI) connected USB-4000 spectrophotometer (from Ocean Optics); crustal elements (Al, Fe, Ca and Mg) on ICP-AES; trace metals (Pb, Cd, Cu and Mn) and Fe<sub>ws</sub> is on GF-AAS (AAnalyst-100; Perkin Elmer; HGP-800) and carbonaceous species on Sunset-EC-OC analyzer.

#### 1.4. Objectives

- 1) To assess the spatial and temporal variability in the abundances of nutrients (N, P and Fe) and selected trace elements in the MABL.
- To assess the relative contribution of anthropogenic vis-à-vis natural sources of selected constituents.
- 3) To assess the deposition fluxes of N, P and Fe to Northern Indian Ocean.
- 4) To quantify the fractional solubility of aerosol iron and to assess the environmental factors affecting its solubility.

#### 1.5. Structure of Thesis

**Chapter 1** provides a brief introduction of ambient aerosols with major emphasis on soluble nutrient species (N, P and Fe), their long-range transport to marine environment and deposition to the surface waters and, hence, its pivotal role in biogeochemistry of nutrient cycles. A review of previous research work carried out over the Northern Indian Ocean and other marine regions is presented in this chapter. Furthermore, this chapter also includes the rationale and objectives of the thesis work.

**Chapter 2** presents a brief description about the sampling locations, aerosol collection and analytical procedures developed and adopted for the analysis of nutrient species (N, P and Fe) and other supporting chemical constituents (viz, carbonaceous aerosols, water soluble ionic constituents, crustal and trace elements) used in this study.

**Chapter 3** presents the results regarding the spatio-temporal abundance pattern of chemical constituents (i.e., water-soluble inorganic ions, crustal elements, trace metals and carbonaceous species) in ambient aerosols collected from the Bay of Bengal during the continental outflow (January-April). In addition, causes for the observed relative difference in the abundances between the seasons (Winter and Spring-intermonsoon) have been discussed in brief.

**Chapter 4** presents the results regarding the spatio-temporal abundance pattern of soluble nitrogen species  $[N_{Tot} = N_{Inorg} + N_{Org}]$ ; where  $N_{Inorg}$  is  $(NH_4^++NO_3^-)$  and  $N_{Org}$  is organic nitrogen] in ambient aerosols collected from the BoB, ARS and the IGP-outflow during the continental outflow (January-April). In addition, causes for the observed relative difference in the abundances of soluble nitrogen species over the sampling sites have been discussed in brief.

**Chapter 5** presents the results regarding the spatio-temporal abundance pattern of soluble inorganic phosphorous ( $P_{Inorg}$ ) in the ambient aerosols collected from the BoB, ARS and the IGP-outflow. This chapter also highlights the importance of natural vis-à-vis anthropogenic sources of this macro nutrient over the two oceanic regions. Furthermore, the role of acid uptake by mineral dust during the long-range atmospheric transport in supplying  $P_{Inorg}$  to the surface waters has also been discussed in this chapter.

**Chapter 6** presents the results regarding the spatio-temporal abundance pattern of water-soluble iron (Fe<sub>ws</sub>) in the ambient aerosols collected from the BoB, ARS and the IGP-outflow. This chapter also highlights the importance of natural vis-à-vis anthropogenic sources of this micro nutrient over the two oceanic regions. Furthermore, the role of chemical processing of mineral dust during the

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long-range atmospheric transport in enhancing the aerosol iron solubility  $Fe_{ws}$  to the surface waters has also been discussed in this chapter.

**Chapter 7** presents the dry-deposition of nutrient species (N, P and Fe) to the Northern Indian Ocean in comparison with other oceanic regions. Further, the relevance of soluble Fe and P-deposition in C- and N-fixation in the surface waters of BoB and ARS has also been discussed in this chapter. In addition, marine geochemical budget of nutrients (includes the comparison of aeolian input with riverine supply, Primary and New production in the sea water) is also presented in this chapter.

**Chapter 8** presents the atmospheric abundances of trace metals to the Bay of Bengal in comparison with other oceanic regions. The spatio-temporal and seasonal variability has been discussed. The dry-deposition fluxes of trace-metals (viz., Cd, Pb, Cu and Mn etc.,) and their surface seawater residence times were also estimated in this chapter.

**Chapter 9** summarizes the key findings of the present study and their implications to biogeochemistry of the Northern Indian Ocean. This chapter also includes the scope of future research work, is presented in brief.

# Chapter 2

**Materials and Methods** 

### 2.1. Introduction

The marine atmospheric boundary layer (MABL) of the Northern Indian Ocean is influenced by the continental outflow from south and south-east Asia during the late NE-monsoon (January-April). The prevailing meteorological conditions (NE-monsoon: land to sea winds) during this period facilitates the continental transport. A typical synoptic wind pattern over the Northern Indian Ocean is shown in Figure 2.1. Arabian Sea (ARS) and Bay of Bengal (BoB) comprises the two limbs of the Northern Indian Ocean. Owing to geographical differences between these two marine basins can lead to differences in their nutrient inputs (N, P and Fe). It is essential to mention here that ARS is relatively less influenced by the continental outflow compared to BoB [*Kumar et al.*, 2008b].

The precipitation events are rather unlikely over the Northern Indian Ocean during the continental outflow (January-April). Therefore, atmospheric dry-deposition represents the total deposition to the study region (BoB and ARS). To assess the impact of continental outflow on the chemical composition of MABL, a systematic and stringent sampling strategy is designed for the collection of aerosol samples from the ARS and BoB during the continental outflow to achieve the specified objectives (Chapter 1). The present thesis includes an overall of 152 aerosol samples collected from various research cruises and from the continental outflow site in the Indo-Gangetic Plain (Table 2.1). For the present study, aerosol samples were collected from the MABL of ARS and BoB during three research cruises (SK-223A, B and SK-254) onboard ORV Sagar Kanya as a part of National programme, Integrated Campaign of Aerosols and trace gases Radiation Budget (ICARB-2006; ICARB-2009).

Table 2.1: The sampling period, duration and the no of samples (N) collected from the MABL ofNorthern Indian Ocean during the continental outflow (January-April).

Study area	Sampling period	Duration	Cruise	Sampler	N
Arabian Sea	Spring-intermonsoon	April-May'06	SK-223B	TSP	19
Bay of Bengal	Spring-intermonsoon	Mar-April'06	SK-223A	TSP	23
Bay of Bengal	Winter season	Dec'08-Jan'09	SK-254	PM <sub>2.5</sub>	31
Bay of Bengal	Winter season	Dec'08-Jan'09	SK-254	$PM_{10}$	33
IGP-outflow	Winter & Spring	Nov'09-Mar'10	-	PM <sub>2.5</sub>	46



Figure 2.1: The synoptic wind pattern over the Northern Indian Ocean during the NE-(January-April) and SE-monsoon (June-September).

(NCEP reanalysis data (u-wind;v-wind) is used for obtaining the surface level winds; source: http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.pressure.html)

Samples were also collected from a rural continental site, Kharagpur, in the Indo-Gangetic Plain (IGP) during November'09-March'10. Necessary details regarding sampling sites, collection of aerosol samples and analytical procedures developed for the measurement of chemical constituents are described briefly in the following sections.

#### 2.2. Site description

#### 2.2.1: Arabian Sea

Arabian Sea (ARS) is geographically well situated in the western part of the northern Indian Ocean (Figure 2.2), receiving ample amount of mineral dust from the surrounding desert regions (Oman, Arab regions on the west; Thar on the east). The region is characterized by high biological productivity during June-September (summer or SW-monsoon) due to intense upwelling by strong monsoonal winds [*Prasanna Kumar and Narvekar*, 2005]. Likewise, the convective mixing during NE-monsoon (December-February) results in bringing the nutrient rich subsurface water to the surface [*Madhupratap et al.*, 1996], thus, making this region more productive. However, ARS receives aeolian input during NE-monsoon only.

The input of nutrients from peninsular rivers to the ARS is relatively small compared to the BoB. Therefore, to assess the impact of continental outflow on the abundances of nutrients, a cruise has been undertaken during April-May'06. The sampling period is a transition between NE-monsoon and SW-monsoon. Relevant meteorological details and sampling protocol for the collection of aerosols is given elsewhere [*Kumar et al.*, 2008b]. During JGOFS programme, ARS is relatively well studied in terms of atmospheric abundances of nutrients and other pollutants [*Johansen et al.*, 1999; *Johansen and Hoffmann*, 2003; *Siefert et al.*, 1999; *Tindale and Pease*, 1999]. However, there was no such attempt to understand the effect of atmospheric input on the biogeochemistry of surface waters of the BoB.

## 2.2.2: Bay of Bengal

Bay of Bengal (BoB), situated at the eastern side of the Indian peninsula (Figure 2.2), characterized by relatively low productivity as compared to that in the Arabian Sea (ARS). There are various factors (viz., immense fresh water

discharge from peninsular rivers, cloud cover, huge suspended load etc), that are responsible for the observed low biological productivity in the BoB. However, the biological productivity in the Bay region during winter months (December-February) and spring-intermonsoon period (March-April) is relatively high (i.e., due to less stratification, eddy pumping) compared to the SW- monsoon [*Gauns et al.*, 2005; *Kumar et al.*, 2007; *Madhupratap et al.*, 2003]. Earlier studies have documented the downwind transport of pollutants to the MABL which extended up to the equatorial Indian Ocean [*Lelieveld et al.*, 2001; *Mayol-Bracero et al.*, 2002; *Ramanathan et al.*, 2001b].



Figure 2.2: Map of India, showing the sampling sites: Kharagpur, Arabian Sea and Bay of Bengal.

Furthermore, a comparative study has shown the relatively large impact of continental outflow on the MABL of Bay of Bengal compared to that over the Arabian Sea [*Kumar et al.*, 2008b]. Therefore, aeolian input can be a significant source of nutrients to the BoB during January-April. It is essential to mention here that relative to MABL of the ARS, Bay region is impacted by the continental outflow from Indo-Gangetic Plain and south-east Asia. Therefore, to assess the

impact of continental outflow on the abundances of nutrients, aerosols were collected from two research cruises (onboard ORV Sagar Kanya), during March-April'06 and January'09. Relevant meteorological details and sampling protocol for the collection of aerosols is given briefly in the section 2.3.

## 2.2.3: Kharagpur

Kharagpur is a rural site, located in the Indo-Gangetic Plain (Figure 2.2), a few kilometres away from the north-west coast of the Bay of Bengal. Earlier studies have documented the downward transport of atmospheric pollutants from the Indo-Gangetic Plain to the Bay of Bengal during the late north east (NE-monsoon: January-April) monsoon [*Kumar et al.*, 2010; *Ram and Sarin*, 2010; *Ram et al.*, 2010; *Rengarajan et al.*, 2007]. Therefore, sampling site represents the outflow catchment of pollutants that enter into the Bay region.

#### 2.3. Aerosol Sample Collection

Aerosol samples were collected from the marine atmospheric boundary layer of Arabian Sea and Bay of Bengal, as a part of Integrated Campaign for Aerosols and trace gases Radiation Budget (ICARB). The cruise tracks of ICARB-Campaign conducted in the ARS and BoB during January-April is shown in Figure 2.3.

## 2.3.1. Arabian Sea

A total of 19 bulk aerosol (TSP) samples were collected on PALLFLEX<sup>®TM</sup> tissuquartz filters using a high volume sampler. Aerosol samples were collected onboard ORV Sagar Kanya (Cruise SK-223B; Figure 2.3) during spring-intermonsoon (April-May'06) as a part of National Programme, Integrated Campaign of Aerosols and trace gases Radiation Budget (ICARB-2006). The sampling period is a transition between NE--monsoon (winds from land to ocean) to SW-monsoon (winds from ocean to land). More detailed description about the prevailing meteorological conditions, aerosol sample collection and analysis of supporting chemical constituents (viz., water-soluble inorganic constituents, crustal elements and carbonaceous species) were mentioned briefly elsewhere [*Kumar et al.*, 2008b]. These aerosol filters have been further used in the present study to assess the abundances of nutrients (viz., relative abundances of organic vis-à-vis inorganic nitrogen, water-soluble inorganic phosphorous and water-

soluble iron and the fractional solubility of aerosol iron). The chemical composition data published in Kumar et al., [2008] has been used to infer about the source characteristics of nutrients, role of chemical processing of dust during long-range atmospheric transport in the present work and relevant information is appropriately cited in the text.

## 2.3.2. Bay of Bengal

A total of 23 bulk (TSP) aerosol samples were collected onboard ORV Sagar Kanya (Cruise SK-223A; Figure 2.3) during Spring-intermonsoon (March-April'06) as a part of National Programme, Integrated Campaign of Aerosols and trace gases Radiation Budget (ICARB-2006). During initial part of the cruise, winds were north-easterly and changed to south-westerly at later time of the sampling period. Like mentioned in the earlier section, aerosol filters were analyzed for nutrient abundances and other chemical composition data from Kumar et al., [2008b] has been used to infer about source characteristics and atmospheric processing of mineral dust.



Figure 2.3: Cruise tracks in the Bay of Bengal and the Arabian Sea during the continental outflow (January-April).

More detailed description about the meteorological parameters, aerosol sampling and analysis of chemical composition is found elsewhere [*Kumar et al.*, 2008b]. Based on the analyses of chemical composition of water-soluble inorganic ionic constituents (WSIC), crustal elements and carbonaceous species, earlier study by Kumar et al., [2008b] has inferred the more anthropogenic influence from continental air-masses on the MABL of BoB than over ARS.

As mentioned earlier, aerosol samples collected in the ICARB-2006 campaign over BoB and ARS is mainly during spring-intermonsoon. However, the impact of continental outflow persists during the late NE-monsoon (December-April) and source strength varies (decreases) from Winter (December-February) to Spring-intermonsoon (March-April). Therefore, further to assess the chemical composition of ambient particulate matter during winter months, aerosols ( $PM_{2.5}$ ,  $PM_{10}$ ) were collected in two size-fractions ( $PM_{2.5}$  and  $PM_{10}$ : particulate matter less than 2.5 and 10 µm aerodynamic diameter, respectively;  $PM_{2.5}$  conventionally referred as fine mode) during January'09 from the MABL of BoB.

Overall, 31 PM<sub>2.5</sub> and 33 PM<sub>10</sub> samples were collected (Figure 2.4), on pre-combusted PALLFLEX®TM tissuquartz filter using high-volume sampler (Thermo Anderson Inc.,) by operating simultaneously at a nominal flow rate of ~1.13 m<sup>3</sup> min<sup>-1</sup>, during January'09 as part of National Programme, Winter-Integrated Campaign of Aerosols and trace gases Radiation Budget (W-ICARB). These filters are reported to have a collection efficiency of 99.99 % for the particles above 0.3  $\mu$ m. The sampler inlets were designed to have a 50 % cut-off diameter for 2.5 and 10  $\mu$ m particles at the operating flow rate with 5 % uncertainty. Aerosol samplers were calibrated before and after the cruise to check the variation in the flow rate (if any). After collection, aerosol filters were sealed zip-lock bags and stored at -19°C till the time of analysis. The gravimetric mass concentrations were obtained by measuring the filter weight before and after the collection. Prior to their weighing, samples were equilibrated for ~24 hrs and balance (Saratorius<sup>®TM</sup>, Aerosol balance) is maintained at constant relative humidity (35-40%) and temperature (21-23°C). Based on the repeat measurement of filter weights, an overall uncertainty of  $\pm 1 \text{ mg}$  (that corresponds to an overall error of ~15 %) is associated with the particulate mass loading.

Aerosol samples were subsequently analyzed for the mass concentrations of water-soluble inorganic and total nitrogen ( $N_{Inorg}$  and  $N_{Tot}$ ), phosphorous ( $P_{Inorg}$ =  $PO_4^{3-}$ ) and iron (Fe<sub>ws</sub>). In addition, other water-soluble inorganic ions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>), crustal elements (Al, Fe, Ca and Mg), trace metals (Pb, Cd, Cu and Mn) and carbonaceous species (EC and OC) were also measured as supporting parameters. For all chemical analyses, filters were handled under the clean laminar hood flow bench (Class-100).

## 2.3.3: Kharagpur

A total of 46 PM<sub>2.5</sub> samples were also collected from the Kharagpur (IGPoutflow) using a high volume sampler (Thermo Anderson, Mass flow controller), operated at a flow rate of 1.13 m<sup>3</sup> min<sup>-1</sup> and is calibrated periodically to check the variation, if any. All aerosol samples were collected on PALLFLEX<sup>®TM</sup> tissuquartz (2500QAT-UP, 25.4 cm x 20.0 cm) filters during November'09-March'10. As mentioned in the earlier section (2.2.3), sampling site is located downwind of the Indo-Gangetic Plain (IGP) and only, a few kilometres away from the north-west coast of the Bay of Bengal. The relative humidity, temperature and mean surface level wind speed were obtained from the NCEP reanalysis data.



Figure 2.4: Aerosol Sample collection onboard ORV Sagar Kanya, as part of national Programme, Integrated Campaign of Aerosols and trace gases Radiation Budget during 27<sup>th</sup> December, 2008-31<sup>st</sup> January, 2009.

The relative humidity and ambient temperature values varied from 38 to 58 % and 21.5 to 30.4°C, respectively. Likewise, the mean wind speed varied from 0.5 -3.8 m.s-1 during the sampling at Kharagpur.

Samples were equilibrated under the laminar flow bench (Class-100) prior to their gravimetric weight measurement. In addition, aerosol balance is maintained at constant RH (%) and temperature (as mentioned above).  $PM_{2.5}$ mass concentrations were obtained by the difference in weights of quartz filters (i.e., before and after the aerosol collection). Subsequently these filters were analyzed for other chemical constituents (viz, water-soluble inorganic ionic constituents, crustal and trace elements, carbonaceous aerosols etc).

#### 2.4. Analytical Methods

The brief outline of the analytical scheme adapted for the analysis of chemical composition of water-soluble nutrient species (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, N<sub>Org</sub>, P<sub>Inorg</sub> and Fe<sub>ws</sub>) and other supporting parameters (viz., Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>; crustal (Al, Fe, Ca and Mg) and trace (Pb, Cd, Cu and Mn) elements; carbonaceous species (EC, OC)), is given in Figure 2.5. For all the chemical analyses, aerosol filters were handled under the clean-laminar hood flow bench (Class-100). The subsequent sections will describe briefly about the methods adapted/developed for the individual chemical constituents.

## 2.4.1. Water soluble inorganic nitrogen (N<sub>Inorg</sub>)

To measure the water soluble inorganic nitrogen ( $N_{Inorg} = NO_3^- + NH_4^+$ ), one fourth of aerosol filter (in a pre-cleaned Savillex bombs) is extracted with 50.0 ml Milli-Q (specific resistivity > 18.2 M $\Omega$  cm, Millipore Co.,) water by repeated ultrasonication for near about 30 min (3 x 10 min cycle). Water extracts were analyzed for inorganic constituents on Dionex–500 Ion Chromatograph equipped with a conductivity detector (ED-50). Typical chromatogram for cations and anions, obtained from the Dionex-500 Ion Chromatograph is depicted in Figure 2.6. The water soluble cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) were separated on CS-12A 4 mm column connected in line with CSRS-ULTRA<sup>®</sup>-II 4 mm cation suppressor (in recycle mode; isocratic elution with a flow rate of 1.0 ml min<sup>-1</sup>); 20 mM methane sulphonic acid (MSA) is used as a mobile phase. Anions (Cl<sup>-</sup>, NO<sub>3</sub> and SO<sub>4</sub><sup>2-</sup>) were separated on AS-14A 4 mm column in

conjunction with ASRS<sup>®</sup>-ULTRA-II 4 mm suppressor (connected in recycle mode; isocratic elution with a flow rate of 1.0 ml min<sup>-1</sup>) using carbonatebicarbonate mixture (100 mM NaHCO<sub>3</sub> + 800 mM Na<sub>2</sub>CO<sub>3</sub>) as an eluent.

For the Ion chromatographic measurements, stock solution standards (~1000 ppm) for cations were prepared gravimetrically by dissolving the analytical grade salts (NaCl for Na<sup>+</sup>; NH<sub>4</sub>Cl for NH<sub>4</sub><sup>+</sup>; KNO<sub>3</sub> for K<sup>+</sup>; CaCO<sub>3</sub> for Ca<sup>2+</sup>; Pure Mg metal is dissolved in 1N HCl and diluted with Milli-Q water), whereas commercial Merck<sup>®</sup> standard (~1000 ppm) is used for the measurement of anions. These stock solutions were suitably diluted for the Ion-chromatographic analysis and the Merck<sup>®</sup> standards were cross-calibrated with gravimetrically prepared ones, to check the analytical accuracy.

The analytical precision between the two standards is within 5 %. Along with the samples, filter blanks were also analyzed and sample concentrations are suitably corrected for blanks. The procedural method detection limits (MDL), defined as three times the standard deviation of the concentration of measured water-soluble inorganic ions normalized with average filtered volume of air (~1200 m<sup>3</sup>), for the Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are 11.3, 6.8, 6.5, 0.8, 3.0, 15.2, 8 and 30 ng m<sup>-3</sup>, respectively. Based on the analysis of repeat samples and standards, the analytical precession was better than 5 % for all the cations and anions (Figure 2.7).

## 2.4.2. Water-soluble Organic Nitrogen (Norg)

To measure the water soluble organic nitrogen ( $N_{Org}$ ), circular filter punches (6-8 pieces; ca. 2.0 dia) are extracted with Milli-Q water (in a pre-cleaned Savillex bombs) by repeat ultrasonication (~30 min as 3 x 10 min cycle) and analyzed for the total soluble nitrogen ( $N_{Tot}$ ) on Shimadzu total nitrogen (TN-7) analyzer equipped with a chemi-luminescence detector (CLS). The generation of nitric oxide (NO) by the decomposition of total nitrogen compounds at a high temperature (~ 680<sup>o</sup>C) catalytic oxidation (HTCO) using Pt-Al<sub>2</sub>O<sub>3</sub> (as a catalyst), are detected by a chemi-luminescence (CLS) detector and thus quantifying the amount of total soluble nitrogen [*Koike and Tupas*, 1993; *Maita and Yanada*, 1990; *Nakamura et al.*, 2006; *Ogawa et al.*, 1999].



Figure 2.5: Analytical scheme for the analysis of water-soluble inorganic ionic constituents, crustal and trace and elements; carbonaceous species and water-soluble iron in aerosols.



Figure 2.6: Typical (real-time) chromatogram obtained for the measurement of cations  $(Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+})$ , and anions (CI,  $NO_3^-$  and  $SO_4^{-2-})$  using DIONEX-500 Ion-chromatograph.

The amount of soluble organic nitrogen ( $N_{Org}$ ) is then obtained by subtracting the inorganic nitrogen ( $N_{Inorg}$ ) contribution from total soluble nitrogen ( $N_{Tot}$ ). Standards for total soluble nitrogen is prepared from the analytical grade NaNO<sub>3</sub> (~10000 µM) and suitably diluted for the instrument calibration. Based on the repeat analyses, the overall precision for the measurement of  $N_{Tot}$  is about 10 % [*Srinivas et al.*, 2011b].

## 2.4.3. Water-soluble inorganic phosphorous (P<sub>Inorg</sub>)

Water-soluble inorganic phosphorous ( $P_{Inorg} = PO_4^{3-}$ ) is measured using 2 m-long liquid core waveguide capillary cell [LWCC, from world precession instruments (WPI)] connected to USB-4000 spectrophotometer (from Ocean Optics). The increase in path length from 1 to 200 cm is allowed to achieve the measurement of low concentration of  $P_{Inorg}$  in aerosols. For the determination of  $P_{Inorg}$  using LWCC, conventional molybdenum blue method of Murphy and Riley [1951] is modified; the reagents and standard preparations are similar to that described in [*Li. and Hansell.*, 2008]. The mixed reagent is prepared by dissolving 1.2 g of ammonium hepta molybdate in 5N H<sub>2</sub>SO<sub>4</sub> (~70 ml of Reagent grade sulphuric acid is diluted to 500 ml with Mill-Q) and then made the final volume to 500ml with Milli-Q water.

The use of ascorbic acid as a reducing agent and potassium antimonytartrate as a catalyst for fast colour development in the conventional Murphy and Riley molybdenum blue method is replaced by the use of Hydrazine sulphate (prepared by dissolving analytical grade salt of 1.0 g in 200 ml of Milli-Q water) as a reducing agent. These modifications are intended to reduce LWCC wall coating effect from the reagents and to achieve stable baseline signal thereby improving signal to noise ratio. The conventional method has an absorption maximum at wavelength 885 nm [Strickland and Parsons, 1972] for the determination of orthophosphate by Murphy and Riley method. Owing to the absoption of far red wavelength by water in the LWCC (Liquid Core Wave guide Capillary Cell), by water in the LWCC (Liquid Core Wave guide Capillary Cell), the transmission of light at 880 nm or 885 nm is negligible. As a result, the use of LWCC spectrophotometer with aqueous solutions beyond 750 nm is not recommended due to severe transmission loss of light intensity.



Figure 2.7: Repeat measurement of water-soluble inorganic ionic constituents ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $C\Gamma$ ,  $NO_3^-$  and  $SO_4^{-2}$ ; are expressed in ppm; and n is the number of repeat measurements) in aerosol samples.

Therefore, earlier studies measured the absorbance of phospho-molybdenum blue complex at a slightly less intense absorption wavelength of 710 nm for phosphate determination in natural waters and open ocean oligotrophic water [*Patey et al.*, 2008; *Patey et al.*, 2010; *Zhang and Chi*, 2002] and hence used the same wavelength for our phosphate determination in aerosol water extract.

The stock solution (~ 2000  $\mu$ M) for the phosphate measurement is prepared by dissolving the analytical grade KH<sub>2</sub>PO<sub>4</sub> (oven dried for two hours, at 110<sup>o</sup>C). Standards prepared from the Commercial Merck<sup>®</sup> (1000 ppm) solution, were used to cross-validate the calibration graph obtained with gravimetrically prepared standards, to ascertain the analytical accuracy of the method. The results indicate that both standards are consistent within 5 %. Based on the repeat check standards, independent check standard (Merck), and repeat aerosol sample extracts (Figure 2.8), the reproducibility in the measurement is about 10 % (Table.2.2).

## 2.4.4. Water-soluble iron (Fews)

For the determination of water-soluble iron (Fe<sub>ws</sub>), 8-10 circular filter punches (ca. 2.0 cm dia.) were extracted with 10 ml Milli-Q by ultrasonication for about ~10 min. These extracts were filtered through 0.45  $\mu$ m Millipore filters using syringe filter cartridge (ca. 25 mm dia.) and acidified to pH ~2 with double distilled HNO<sub>3</sub>. These sample solutions were subsequently analyzed for watersoluble iron (Fe<sub>ws</sub>) on graphite furnace atomic absorption spectrophotometer (GF-AAS, Perkin Elmer model).

Due to the analytical difficulties of sampling of seawater (for soluble iron), and quite difficult to reproduce the in- situ seawater conditions (organic ligands, pH etc.,) within the laboratory, Milli-Q water is chosen as a leach solution for the soluble iron measurement. The choice of ultra pure de-ionized water (specific resistivity  $\approx 18.2 \text{ M}\Omega$ -cm) as a leach solution is to be consistent and compare with other studies of soluble iron in aerosols [*Buck et al.*, 2006; *Kumar and Sarin*, 2010; *Sedwick et al.*, 2007; *Srinivas et al.*, 2011a] and resembles the wet deposition of aerosols. Since the pH of the de-ionized water is about  $\sim 5.6$ (slightly acidic), our estimate of soluble iron in aerosols will be the upper estimate for seawater (pH  $\sim 8.1$ , alkaline), in which the solubility is lower compared to the Milli-Q water. Based on the repeat extacts of aerosols and repeat measurements, the analytical reproducibility of  $Fe_{ws}$  is better than 10 % (Figure 2.8). The method detection limits, which are defined as three times the standard deviation of procedural blanks normalized with average filtered volume of air, of  $N_{Tot}$ ,  $PO_4^{3-}$  and  $Fe_{ws}$  were 5.1, 0.013 and 0.003 nmol m<sup>-3</sup>, respectively.

#### 2.4.5. Crustal and trace metals

To measure trace metals, 8 - 10 (ca. 2.0 cm dia or  $1/16^{th}$  area) filter punches were digested using 0.5 ml distilled HF, 5.0 ml distilled 8N HNO<sub>3</sub> and 3.0 ml Milli-Q (18.2 M $\Omega$ -cm specific resistivity) in Teflon digestion vessels using a high pressure (~100 bar, Temp: 210°C; 1hr cycle) Microwave digestion system (Milestone, Figure 2.9). These digested solutions were made to suitable volume (~30 ml) and subsequently analyzed for crustal elements (Al, Fe, Ca and Mg) on ICP-AES (HORIBA, Jobin Yvon–ULTIMA 2) and trace metals ( Pb, Cd, Cu and Mn) on GF-AAS (Perkin Elmer model, HGA-500 coupled to AAnalyst-100 autosampler). The accurate and reproducible analytical measurements on Graphite Furnace-Atomic Absorption Spectrophotometer are achieved by optimizing the temperature conditions (viz., drying, ashing/charring and atomization cycles) and are described in Table 2.3 and Table 2.4.



Figure 2.8: Repeat measurement of water-soluble inorganic phosphorous ( $P_{Inorg}$ ; are expressed in  $\mu M$ ) and iron ( $Fe_{ws}$ ; are in  $ng/cm^2$ ) in aerosol samples and n is the number of repeat measurements.



Figure 2.9: A snapshot of Microwave digestion chamber (Model: Milestone), used for the trace metal analysis.

Commercial Merck<sup>®</sup> (23 trace metal) standard (~ 1000 ppm) is used for the analysis of crustal and traces elements. Analytical accuracy of the measurement is ascertained by analyzing commercial rock standard (W1, certified basaltic rock). Based on the repeat measurements (Figure 2.10) and extracts, the overall analytical reproducibility for most of the metals is found to be within 10 % (see Table 2.2).

Table 2.2: Atomic absorption and emission wavelengths ( $\lambda$ ) used for various elemental analyses by GF-AAS and ICP-AES, and LWCC-Spectrophotometer, the precision of analyses.

Element	Tech.	$\lambda_{max}(nm)$	CV (%)	Element	Tech.	$\lambda_{max}$ (nm)	CV (%)
Al	ICP-AES	396.152	8.7	Fe <sub>ws</sub>	GF-AAS	248.3	5.5
Ca	ICP-AES	393.366	9.7	Pb	GF-AAS	283.3	4.7
Fe	ICP-AES	259.940	8.7	Cd	GF-AAS	228.8	4.4
Mg	ICP-AES	279.543	9.9	Cu	GF-AAS	324.8	5.7
Р	LWCC	710	8.1	Mn	GF-AAS	279.5	5.8

Based on a number of repeat measurements, the precision of measurement is given by the coefficient of variation (CV) as:

 $CV(\%) = [\{\Sigma (d_i/X_m)^2\}/2n]^{1/2} * 100$ 

Here,  $d_i$  = difference between the repeats,  $X_m$  = mean of the repeats

N = no. of repeat pairs measured.

Other trace metals (V, Cr, Co, Ni) were analyzed in aerosols collected from the MABL during January'09 and March-April'06 by ICP-MS (Model: Thermo X-series II). Along with the aerosol samples, blank filter were also digested with the reagents (HF+HNO<sub>3</sub>) and analyzed for the crustal and trace elements. Filter blanks (field and procedural) were also analyzed for the crustal constituents and trace metals, and sample concentrations were suitably corrected. The method detection limits are defined as three times the standard deviation of procedural blanks normalized to the average volume of air sampled through the aerosol filter. Detection limits for Al, Ca, Mg, Fe, Cu, Mn, Pb, Cd, V, Cr, Co and Ni were about 80.0, 15.1, 10.8, 11.0, 0.28, 0.59, 0.13, 0.04, 0.45, 1.09, 0.03 and 0.42 ng m<sup>-3</sup>, respectively.



Figure 2.10: Repeat measurements of Crustal elements (Al, Fe, Ca and Mg; are expressed in ppm) in aerosol samples. Solid line represents the 1:1 line and 'n' represents the number of repeat measurements

#### 2.4.6. Carbonaceous Species (EC and OC)

Carbonaceous species in the aerosol filters are measured on Sunset EC-OC analyzer that uses the thermo-optical transmittance (TOT) method to quantify the relative proportions of organic versus elemental carbon. Typical EC-OC analyzer consists of three basic components, sample oxidizing oven (also called front oven),  $MnO_2$  oxidizing oven (i.e., back oven) and a methanator. For the analysis of EC and OC, a rectangular punch (ca. area =  $1.5 \text{ cm}^2$ ) is placed on a quartz boat and kept in the front oven. The concentrations of organic and elemental carbon (OC and EC) were then measured on Sunset EC-OC analyzer using NIOSH-5040 (National Institute of Occupational Safety and Health) protocol. For one complete analysis, the defined run time is approximately of 12.55 min.

During the initial stage, organic and carbonate carbon (if present) from the aerosol filter are volatilized in the inert (He) atmosphere at a programmed temperature of  $820^{\circ}$ C (achieved in 3-4 steps). These vapours are carried into a MnO<sub>2</sub> Oxidizing oven (at a temperature of  $900^{\circ}$ C), where OC is oxidized to CO<sub>2</sub>. This CO<sub>2</sub> gas subsequently combined with H<sub>2</sub> and reduced to CH<sub>4</sub> in the methanator (at a temperature of  $450^{\circ}$ C).The resultant CH<sub>4</sub> gas is fed to Flame Ionization Detector (FID) and ion current is measured, is proportional to the amount of OC present in the sample. During the second stage, temperature of the front oven is reduced to  $630^{\circ}$ C and increased to  $900^{\circ}$ C in various steps under the He/O<sub>2</sub> atmosphere, during which carbon (elemental) from the sample filter is volatalized and entered into the back oven.

Element	Wavelength λ <sub>max</sub> (nm)	Drying Temp ( <sup>°</sup> C)	Pyrolysis Temp (°C)	Atomization Temp (°C)
Fe <sub>ws</sub>	248.3	120	1400	2400
Pb	283.3	120	700	1800
Cd	228.3	120	700	1600
Cu	324.8	120	1000	2300
Mn	279.5	120	1400	2200

Table 2.3: Optimized temperature conditions used for the measurement of water-soluble iron and trace metals on GF-AAS.

Evolved  $CO_2$  from EC in the back oven is converted to  $CH_4$  in the methanator. The resultant response of the FID is proportional to EC present in the sample. However, it has been observed that during the initial stage of combustion, a part of the OC is converted to EC and will be evolved during the second stage of heating (He-O<sub>2</sub> atmosphere). Therefore, correction is necessary for the pyrolyzed carbon (PC), without which it leads to underestimation of OC and over estimation of EC. This can be corrected using a diode (He-Ne) laser whose transmittance can be measured after the passing through filter (placed in the quartz boat). Typical (real-time) thermograph obtained from the Sun Set EC-OC analyzer during the analysis of carbonaceous species (EC and OC) is depicted in Figure 2.11.



Figure 2.11: Typical (real-time) thermograph obtained from the Sun Set EC-OC analyzer during the analysis of carbonaceous species (EC and OC).

Element	Sample id	Sample Vol. (ml)	Reagents Volume (ml)	final Vol. ( ml)	Meas. (ppb)	Expect. (ppb)	% dev
KGP-31		0.1	1.0 ml MQ	1.1	14.8	-	
ГĊ <sub>ws</sub>	KGP-31S	0.1	1.0 ml-10 ppb	1.1	23.6	23.9	1.3
Dh	AS-848 - No dilution		-	12.3	-		
AS-848 S		0.5	0.5 ml-20 ppb + 0.5 ml sample		15.5	16.2	4.0
Cd	AS-409	-	No dilution	-	2.09	-	
Cu	AS-409 S	0.5	0.5 ml-5 ppb + 0.5 ml sample	1.0	3.55	3.6	2.8
Cu	AS-417	0.5	0.5 ml MQ	1.0	2.09	-	
Cu	AS-417 S	0.5	0.5 ml-10 ppb + 0.5 ml sample	1.0	15.5	15.7	1.0
Mn	AS-418	0.1	1.0 ml MQ	1.1	7.54	-	
	AS-418 S	0.1	0.5 ml-5 ppb + 0.5 ml MQ	1.1	9.78	9.81	0.3

Table 2.4: Standard additions performed to check the accuracy of the measurement of trace elements.

(Note: *S* = *Spiked Samples;* 

 $MQ = Milli-Q (> 18.2 M\Omega-cm)$  water;

*Meas.* = *Measured Concentration;* 

*Expect.* = *Expected Concentration*)



Figure 2.12: Repeat measurements of OC and EC ( $\mu g/cm^2$ ) in aerosol samples; 'n' represents the number of repeat measurements.

Owing to the property of light absorbing nature of EC, OC-EC split line is defined as the point at which transmittance of EC is reached to its initial value (i.e., as a result of pyrolitically converted EC, transmittance through filter decreases than actual EC present in the sample. However, in the He-O<sub>2</sub> atmosphere, pyrolitically formed EC will be first volatilized during which transmittance is increased and reached to initial transmittance value of true EC concentration present in the sample, referred as EC-OC split point). At the end of each analysis, fixed volume of calibration gas (5 % CH<sub>4</sub> in He gas as an internal standard) is injected into the instrument to monitor the efficiency of FID.

In addition, potassium hydrogen phthalate is used as an external standard to ascertain the accuracy of the measurement. For detailed analytical procedures reference is made to the following publications [*Srinivas et al.*, 2011b; *Srinivas et al.*, 2011a]. Repeat measurements of carboanaceous species in aerosol samples are depicted in Figure 2.12. Based on the replicate analysis, the analytical precision for the measurement of EC and OC is better than 5 %.

## Chapter 3

Chemical characterization of atmospheric aerosols over Bay of Bengal during the continental outflow: Spatio-temporal Variability

#### **3.1. Introduction**

Suspended particulate matter, ubiquitous in the Earth's climate system, has potential to perturb radiation budget of the atmosphere directly by scattering and absorbing the incoming solar radiation or indirectly by acting as cloud condensation nuclei (CCN) [*Charlson et al.*, 1991; *Ramanathan et al.*, 2001a; *Ramanathan et al.*, 2001b; *Twomey*, 1977]. In addition, they provide the substrate for various chemical reactions occurring in the atmosphere which results in the change in surface properties (hydrophobic to hydrophilic) and eventually leads to the changes in their size-distribution and hence life time of the aerosols [*Andreae and Crutzen*, 1997; *Dentener et al.*, 1996]. All these factors lead to a large degree of uncertainty in the evaluation of climate change (Intergovernmental Panel on Climate Change (IPCC), 2001) which has been further constrained by having large number of real time measurements of chemical and physical properties of aerosols in different environments (e.g. marine, urban, remote) (IPCC, 2007).

The densely populated south Asian region is undergoing rapid industrialization leading to enhanced emission of a variety of air pollutants including anthropogenic aerosols making this region climatically sensitive in the global perspective [Lawrence and Lelieveld, 2010 and references therein]. The dominance of anthropogenic sources over Indo-Gangetic Plain, during Wintertime have been confirmed based on several field experiments in recent years [Ram and Sarin, 2010; Ram et al., 2010; Rengarajan et al., 2007; Tare et al., 2006] as well as their significant impact on the radiative forcing [Nair et al., 2007; Ramachandran et al., 2006]. The long-range transport of continental aerosols from natural and anthropogenic sources to the remote marine environment has been recognized as a major source for many bio-geochemically important trace metals and nutrients to the oceanic regions [Arimoto et al., 2003; Duce, 1986; Duce et al., 1991; Duce et al., 2008; Jickells, 1999; Jickells et al., 2005; Martin et al., 1989; Prospero, 1981a]. These nutrients may perturb the phytoplankton productivity and subsequently can have impact on the climate [Doney et al., 2007; Jickells et al., 2005; Mahowald et al., 2005b; Spokes et al., 2000].

The Bay of Bengal (BoB; situated in the eastern part of northern Indian Ocean) is one of the ideal location, confined by land from three side, to study the

impact of continental aerosols transported to the marine environment. This region is largely affected by the winds originating from north/north-eastern region of Indian subcontinent as well as from south-east Asian countries (Burma, Thailand, Bangladesh and China) during the late NE-monsoon. Some of the recent studies (e.g., INDOEX; Integration Campaign for Aerosols, gases and Radiation Budget, ICARB) over this region have documented the transport of natural (mineral dust) as well as anthropogenic aerosols from Indian subcontinent and south-Asian region [*Ganguly et al.*, 2005; *Kaskaoutis et al.*, 2010; *Kumar et al.*, 2010; *Moorthy et al.*, 2008; *Moorthy et al.*, 2010; *Ramanathan et al.*, 2001a].

One of the previous studies, during spring inter-monsoon season, had shown that air flow influences both the abundance and composition of the particulate matter over the BoB using the chemical composition of bulk (TSP) aerosols [*Kumar et al.*, 2008a; *Kumar et al.*, 2008b]. However, the abundances and atmospheric reactivity of major pollutants (nitrate, sulphate, ammonia) and their removal processes depend critically on their size dependent distribution [*Song and Carmichael*, 2001]. Thus, one of the major limitations of current models relates to the lack of real-time data on size dependent chemical composition of atmospheric aerosols and the associated spatio-temporal variability. The measurements based on bulk-aerosols are inadequate to constrain the model scenario made in recent years. It is thus essential to have a comprehensive study on the size-dependent chemical composition of aerosols over this region.

In the present study, a cruise was undertaken in the Bay of Bengal during the national programme "Integrated campaign of aerosols, trace gases and radiation budget-Winter" (ICARB-W) in the month of January'09. This study provides a comprehensive and unique data set for water-soluble constituents, crustal elements and carbonaceous species in  $PM_{2.5}$  and  $PM_{10}$  (particulate matter less than 2.5 and 10 µm aerodynamic diameter, respectively) and hence the continental influence over the Bay of Bengal. Furthermore, a comparison is made between the chemical composition data from the present cruise with that of Kumar et al., [2008b] to identify the prominent seasonal differences within the Bay of Bengal during *Winter* (December-February) and *Spring-inter monsoon*  (March-April). The collection and analysis of aerosols during the cruises undertaken in the Bay of Bengal were presented briefly in Chapter 2.

#### 3.2. Cruise Track and Meteorological Conditions

Aerosol samples were collected over the Bay of Bengal (BoB), onboard ORV Sagar Kanya (SK254), during January'09. The cruise initiated on 27<sup>th</sup> December'08 from Chennai and terminated on 30<sup>th</sup> January'09 at Kochi, by making several transects between 4 to 22°N and 76 to 98°E and hence covering the entire BoB (Chapter 2). The dots along the cruise track show the position of the ship at 05:30 UTC on each day. During first half (27<sup>th</sup> December to 10<sup>th</sup> January) of SK 254, prevailing winds were north-westerly, i.e. winds are originating from north and north-eastern part of India as well as from Bangladesh.

However, a change in wind pattern is observed during later part of the cruise (11<sup>th</sup> to 28<sup>th</sup> January'09) such that the typical air mass originated over eastern Asian region e.g. Burma, Thailand and as far as from China. It has been observed that the continental outflow persists for short span of four months, starting from January to April. During the rest of period (i.e., June-September: SW-monsoon), prevailing meteorology does not favour the transport of land derived pollutants to the MABL.



Figure 3.1: Typical Air mass back trajectory ensemble of the air masses associated with the IGP- and SEA-outflow during January'09 and IGP-outflow during March-April'06. (source: http://ready.arl.noaa.gov/HYSPLIT.php)

The meteorological parameters such as wind speed, relative humidity, and air temperature were measured onboard, during both cruises at a height of 15 m from the sea level on hourly basis. The relative humidity varied from 49.1 to 79.8 %, with mean of about 64.2 % during the campaign period. The prevailing winds were corrected for the ship's motion and found in the range of 1.2 to 6.3 m s<sup>-1</sup>, whereas surface-level pressure variations were recorded between 1007 to 1017 mb. For more detailed description regarding the meteorological parameters during January'09 reference is made to earlier publication [*Kumar et al.*, 2010]. Likewise, detailed meteorological information during the spring-intermonsoon (March-April) cruise has been provided in earlier publications [*Alappattu*, 2007].

#### 3.3. Results

#### 3.3.1. Air mass back trajectory analysis

To identify the potential sources contributing to aerosol chemical composition over the Bay of Bengal, seven days air-mass back trajectories (AMBT) were computed using HYSPLIT-Model [*Draxler*, 2002] from the NOAA Air Resource Laboratory (GADS data set), at different arrival heights (100, 500 and 1000m). The back-trajectory analyses suggest the dominance of air-masses from Indo-Gangetic Plains (IGP) during initial period (27<sup>th</sup> December'08 to 10<sup>th</sup> January'09). However, during later part of the cruise (i.e. in south Bay of Bengal), most of the air-masses were originating from south-east Asia.

Likewise, the computed AMBTs at an arrival height of 1000 m during March-April'06 have shown their origin from Thar Desert and then passing over the Indo-Gangetic Plain (IGP) before it enters into the BoB. Therefore, in this study, different air masses sampled from the marine atmospheric boundary layer (MABL) during Winter (January'09) and Spring-intermonsoon (March-April'06) have been characterized based on their distinct chemical signatures between the IGP- and SEA-outflow. Typical AMBTs computed at an arrival height of 500 m during cruises undertaken in the Bay of Bengal (BoB) is depicted in Figure 3.1.

## 3.3.2. Spatio-temporal variability of mass concentrations

The mean mass concentration and standard deviation of measured chemical composition in aerosols collected from the IGP- and SEA-outflow during January'09; and those sampled from the IGP-outflow during MarchApril'06 [*Kumar et al.*, 2008b] is presented in Table 3.1. Statistical test (one-way ANOVA) has been performed to identify the significant differences in their mass concentrations between the outflows. The particulate mass loading exhibit a pronounced temporal variability, with systematically high mass concentrations in N-BoB (16.2 - 108  $\mu$ g m<sup>-3</sup>) as compared to that in S-BoB (6.0 - 60.7  $\mu$ g m<sup>-3</sup>). The high concentration in N-BoB is attributed to the proximity of sampling locations near to the continents. It is noteworthy that the decrease in magnitude of mass concentration from N-to S-BoB is also reflected in all the measured chemical constituents.

High mass loading of  $PM_{10}$  in N-BoB is mainly attributed to the proximity of sampling locations near to the continents. However, the  $PM_{10}$  mass was found 2-3 times higher than the mass loading (total suspended particulate) observed during inter-monsoon period (March - April) in BoB [*Kumar et al.*, 2008a; *Kumar et al.*, 2008b]. The average wind patterns observed during the Winter cruise (Chapter 2) were originating from continents compared to the mixed wind-pattern found (land to sea vis-à-vis sea to land) during the Spring-intermonsoon cruise [*Kumar et al.*, 2008b]. During Winter months (December-February), the prevailing meteorological conditions favour the downwind transport of pollutants from the IGP to the Bay of Bengal. However, the magnitude of transport of pollutants decreases during the intermonsoon period (March-April) due to weakening of NE-monsoon and, hence, a subsequent shift in meteorological conditions (as evident from the AMBTs during March-April'06).

A very significant correlation is observed between  $PM_{2.5}$  and  $PM_{10}$  in N-BoB ( $r^2 = 0.93$ ; P < 0.05) as well as in S-BoB ( $r^2 = 0.84$ ; P < 0.05) indicating the similar sources (i.e. continental outflow) for fine and coarse mode aerosols. During the study period, the percent contribution of PM<sub>2.5</sub> mass to PM<sub>10</sub> found to vary from 46 to 96 % (Av. = 67 %) and 34 to 88 % (Av. = 63 %) in N-BoB and S-BoB respectively. On an average, PM<sub>2.5</sub> contributes significantly (~ 65 % of PM<sub>10</sub>) to ambient aerosol over the Bay of Bengal. Earlier studies have suggested the predominance of fine mode aerosols over the Bay of Bengal, based on the higher Angstrom exponent values [*Kedia and Ramachandran*, 2008; *Moorthy et al.*, 2008]. This argument further supports the findings in the present study based

on chemical composition of aerosols from the MABL of BoB in two size-fractions  $(PM_{2.5}, PM_{10})$ .

Table 3.1: Mean  $(\pm 1\sigma)$  concentration (in  $\mu g m^{-3}$ ) of chemical constituents in aerosols collected from the IGP- and SEA-outflow during the late NE-monsoon (January-April) over the Bay of Bengal

	Janua	<sup>\$</sup> March-April'06		
Species	IGP-outflow	SEA-outflow	IGP-outflow	
		$Av \pm sd$		
PM	$57.8\pm30.6$	$32.2 \pm 15.1$	$22.5 \pm 13.0$	
Na+	$0.9\pm\ 0.9$	$2.4 \pm 1.1$	$0.86\pm0.62$	
$\mathrm{NH_4}^+$	$5.1 \pm 3.8$	$1.4 \pm 1.4$	$0.90\pm0.63$	
$K^+$	$0.7\pm\ 0.3$	$0.6 \pm 0.3$	$0.24\pm0.11$	
$Mg^{2+}$	$0.1\pm~0.1$	$0.3\pm0.13$	$0.16\pm0.08$	
Ca <sup>2+</sup>	$0.3 \pm 0.1$	$0.2 \pm 0.1$	$0.68\pm0.35$	
Cl	$0.3\pm~0.4$	$0.5 \pm 0.3$	$0.01\pm0.01$	
NO <sub>3</sub> -	$1.0\pm~0.8$	$0.8 \pm 0.4$	$0.07\pm0.09$	
$SO_4^{2-}$	$15.2 \pm 9.3$	$8.9 \pm 4.2$	$6.0 \pm 2.5$	
OC	$9.1 \pm 6.0$	$3.9 \pm 2.8$	$1.9 \pm 1.6$	
EC	$2.7 \pm 1.7$	$1.1 \pm 0.5$	$0.4 \pm 0.2$	
Al	$1.8 \pm 1.1$	$0.6 \pm 0.2$	$0.9 \pm 0.5$	
Ca	$0.4 \pm 0.2$	$0.2 \pm 0.1$	$0.7\pm0.4$	
Fe	$0.8 \pm 0.5$	$0.2 \pm 0.1$	$0.6 \pm 0.3$	
Mg	$0.3 \pm 0.1$	$0.3 \pm 0.1$	$0.3 \pm 0.2$	
Dust	$21.2\pm0.3$	$6.9\pm0.2$	$11.5 \pm 6.8$	
Sea-Salt	$1.6 \pm 1.6$	$3.9 \pm 1.9$	$1.3 \pm 0.9$	
POM	$14.6\pm9.5$	$6.2 \pm 4.5$	$3.0 \pm 2.5$	
TCA	$17.2 \pm 11.1$	$7.0 \pm 4.9$	$3.4 \pm 2.7$	

**Note:** PM denotes particulate mass; Dust = Al\*100/8 (Taylor and McLennan, 1984); Sea-Salt =  $Cl+1.47*Na^+$  (Quinn et al., 2007); POM = Particulate Organic Matter = OC\*1.6; TCA = Total Carbonaceous Mass concentration = POM + EC; S Mass concentrations were obtained from Kumar et al., (2008b).

## 3.3.3. Size-distribution

The fractional abundance ratio of  $PM_{2.5}/PM_{10}$  for all the measured chemical constituents is used to assess their size-distribution (Table 3.3). From this table, it is implicit that fine particulate matter dominates (~ 67 and 63 % in the IGP- and SEA-outflow, respectively) the aerosol chemical composition of

MABL during the study period. Among the WSIC, comparison of mass concentration in  $PM_{2.5}$  to  $PM_{10}$  suggests the predominant fine mode occurrence of  $SO_4^{2-}$ ,  $NH_4^+$  and  $K^+$  in the continental outflow (IGP- and SEA-). In contrast,  $NO_3^-$  shows a bimodal distribution with relatively high ratio in the IGP-outflow (Av:  $0.42 \pm 0.26$ ), suggesting their association with both fine (eg: as  $NH_4NO_3$ ) and coarse mode aerosols (i.e., as a result of reaction with mineral dust and sea-salts). However, their mass ratio in south Bay region (Av:  $0.14 \pm 0.09$ ) indicate its predominant association with coarse mode aerosols (eg: reaction of HNO<sub>3</sub> with mineral dust and sea-salts).

The neutralization of anthropogenic nitrates by sea-salts and/or alkaline dust is one of the possible reasons for occurrence of nitrate in  $PM_{10}$ . Likewise, comparison of mass ratio of ions in  $PM_{2.5}$  to  $PM_{10}$  for water-soluble crustal elements ( $Ca^{2+}$  and  $Mg^{2+}$ ) and that derived from the sea-salts ( $Na^+$ ,  $Mg^{2+}$  and  $Cl^-$ ) suggests their dominance in coarse mode. The EC shows a predominant fine mode distribution in both the outflows (IGP- and SEA-; See Table 3.3). In contrast, OC exhibit a bimodal distribution over N- and S-BoB as evident from their mass fraction of PM2.5/PM10 (Av:  $0.67 \pm 0.09$  in the IGP-Outflow; Av:  $0.52 \pm 0.18$  in the SEA-outflow). In this study, comparison is made between PM10 (January'09) and bulk (TSP) aerosols (March -April'06) to infer about seasonal trends in the aerosol chemical composition. Subsequent sections provide brief discussion about significant differences in the chemical composition of aerosols, distinguished based on their origin of air-masses (IGP- and SEA-type) sampled over the Bay of Bengal during the continental outflow (January-April).

## 3.3.4. Chemical composition of aerosols in the IGP- and SEA-outflow

The various components of ambient aerosols were calculated based on chemical proxies, have been discussed in this section. These constituents include water-soluble inorganic component (Sea-salts and anthropogenic species), mineral dust and carbonaceous species. An attempt has been made to achieve chemical mass closure by summing up the measured chemical species and matching it with gravimetrically measured mass loading in  $PM_{10}$  (this study) and TSP (obtained from *Kumar et al.*, [2008b]) at the end of this section.
	Janua	ury'09	March-April'06	<b>One-way</b>	
Ratio	<sup>1</sup> IGP-	<sup>2</sup> SEA-	<sup>3</sup> IGP-	ANOVĂ	
	outflow	outflow	outflow	F(2,52) 12.7	
$Na^{+}/\Sigma WSIC$ (%)	< 0.052	< 0.051	> 0.051	F(2, 53) = 12.7;	
	> 0.053	< 0.053	< 0.052	P < 0.05	
NH. <sup>+</sup> /SWSIC (%)	< 0.052	< 0.051	> 0.052	F(2, 53) = 12.6;	
14114 /2 WBIC (70)	< 0.053	> 0.053	< 0.051	P < 0.05	
$K^{+}/\Sigma WSIC(0/2)$	> 0.052	> 0.051	< 0.052	F(2, 53) = 12.0;	
K /2 W SIC (70)	> 0.053	< 0.053	> 0.051	P < 0.05	
$M\alpha^{2+}/SWSIC(0/2)$	< 0.052	< 0.051	< 0.051	F(2, 53) = 14.6;	
wig /2 w SiC (70)	< 0.053	> 0.053	> 0.052	P < 0.05	
$C_{2}^{2+}/\Sigma WSIC(9/2)$	> 0.052	> 0.051	< 0.051	F (2, 53) = 92.6;	
	< 0.053	< 0.053	< 0.052	P < 0.05	
$C^{1}/\Sigma WSIC(0/)$	> 0.052	> 0.051	> 0.051	F (2, 48) = 6.6;	
C1/2WSIC(%)	> 0.053	< 0.053	< 0.052	P < 0.05	
NO <sup>2</sup> /SWSIC (%)	> 0.052	> 0.051	< 0.051	F(2, 52) = 16.8;	
110372WBIC (70)	< 0.053	< 0.053	< 0.052	P < 0.05	
$SO^{2}$ /SWSIC (%)	> 0.052	> 0.051	< 0.052	F(2, 53) = 9.0;	
504 /2 WBIC (70)	> 0.053	< 0.053	> 0.051	P < 0.05	
SWSIC/DM (%)	< 0.052	< 0.051	> 0.051	F(2, 52) = 2.6;	
2 w SIC/1 W (70)	> 0.053	> 0.053	> 0.052	P < 0.05	
Dust/PM $(%)$	< 0.052	< 0.051	< 0.051	F(2, 52) = 27.1;	
Dust/1 Ivi (70)	< 0.053	< 0.053	< 0.052	P < 0.05	
OC/PM (%)	< 0.052	< 0.051	< 0.051	F(2, 52) = 19.9;	
OC/1 W1 (70)	< 0.053	> 0.053	> 0.052	P < 0.05	
EC/DM (%)	> 0.052	> 0.051	< 0.051	F(2, 52) = 27.9;	
EC/FIVI (70)	< 0.053	< 0.053	< 0.052	P < 0.05	

Table 3.2: One-way ANOVA results for the mass concentrations of water-soluble inorganic ions (WSIC), mineral dust, Organic carbon and EC between the IGP- and SEA-outflow during January'09 and March-April'06.

# 3.3.5. Water-soluble ionic composition

The percentage contribution of an individual ionic component to the WSIC is shown as pie-charts (Figure 3.2) for the aerosols collected from the MABL of Bay of Bengal during January'09 and March-April'06. For this calculation, the percent contribution of individual ion concentration to  $\Sigma$ WSIC has been estimated for each sample and then computed the average for all samples. From this figure ,

it is obvious that the  $SO_4^{2-}$  and  $NH_4^+$  are the major contributors to WSIC with minor contributions of Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> in the IGP-outflow during January'09 and March-April'06. In contrast, WSIC in SEA-outflow follows the order,  $SO_4^{2-}$ Na<sup>+</sup>> NH<sub>4</sub><sup>+</sup>> NO<sub>3</sub><sup>-</sup>> K<sup>+</sup>> Cl<sup>-</sup>> Mg<sup>2+</sup>> Ca<sup>2+</sup>. In S-BoB (i.e., affected by the SEAtype air masses), there is an increase in the contribution from Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> in PM<sub>10</sub>. Overall,  $SO_4^{2-}$  is the dominant contributor to the ionic budget of aerosols over the Bay of Bengal during both cruises (January'09 and March-April'06).

IGP-outflow SEA-outflow		Mode
Mean	Mode	
$0.67\pm0.13$	$0.63\pm0.12$	fine
$0.29\pm0.20$	$0.14\pm0.04$	coarse
$0.91\pm0.14$	$1.02\pm0.05$	fine
$0.75\pm0.17$	$0.72\pm0.11$	fine
$0.27\ \pm 0.21$	$0.19\ \pm 0.09$	coarse
$0.28\ \pm 0.14$	$0.34 \pm 0.21$	coarse
$0.42\ \pm 0.32$	$0.43\ \pm 0.28$	coarse
$0.42\ \pm 0.26$	$0.14\ \pm 0.09$	bimodal
$0.76 \pm 0.11$	$0.73 \pm 0.09$	fine
$0.21\pm0.18$	$0.25\pm0.16$	coarse
$0.19\pm0.18$	$0.21\pm0.08$	coarse
$0.25\pm0.33$	$0.27\pm0.09$	coarse
$0.23\pm0.15$	$0.17\pm0.04$	coarse
$0.67\pm0.09$	$0.52\pm0.18$	bimodal
$0.77\pm0.16$	$1.02\pm0.21$	fine
	IGP-outflowMean $0.67 \pm 0.13$ $0.29 \pm 0.20$ $0.91 \pm 0.14$ $0.75 \pm 0.17$ $0.27 \pm 0.21$ $0.28 \pm 0.14$ $0.42 \pm 0.32$ $0.42 \pm 0.26$ $0.76 \pm 0.11$ $0.21 \pm 0.18$ $0.19 \pm 0.18$ $0.25 \pm 0.33$ $0.23 \pm 0.15$ $0.67 \pm 0.09$ $0.77 \pm 0.16$	IGP-outflowSEA-outflowMean $\pm 1 \sigma$ 0.67 $\pm$ 0.130.63 $\pm$ 0.120.29 $\pm$ 0.200.14 $\pm$ 0.040.91 $\pm$ 0.141.02 $\pm$ 0.050.75 $\pm$ 0.170.72 $\pm$ 0.110.27 $\pm$ 0.210.19 $\pm$ 0.090.28 $\pm$ 0.140.34 $\pm$ 0.210.42 $\pm$ 0.320.43 $\pm$ 0.280.42 $\pm$ 0.260.14 $\pm$ 0.090.76 $\pm$ 0.110.73 $\pm$ 0.090.21 $\pm$ 0.180.25 $\pm$ 0.160.19 $\pm$ 0.150.17 $\pm$ 0.040.67 $\pm$ 0.090.52 $\pm$ 0.180.77 $\pm$ 0.161.02 $\pm$ 0.21

Table 3.3: The mass ratio of  $PM_{2.5}/PM_{10}$  for the measured constituents in aerosols sampled from the IGP- and SEA-outflow during January'09.

The non-sea-salt (nss) components of K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> have been calculated by using the following equations : nss-K<sup>+</sup> = K<sup>+</sup> - 0.037 \* Na<sup>+</sup>; nss-Ca<sup>2+</sup>= Ca<sup>2+</sup>- 0.038 \* Ca<sup>2+</sup>; nss-Mg<sup>2+</sup> = Mg<sup>2+</sup>- 0.12 \* Na<sup>+</sup>; nss-SO<sub>4</sub><sup>2-</sup> = SO<sub>4</sub><sup>2-</sup> - 0.25 \* Na<sup>+</sup>; where 0.037, 0.038, 0.12, 0.25 are weight ratios of K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> to Na<sup>+</sup> in seawater [*Keene et al.*, 1986] and considering Na<sup>+</sup> as a reference element for the correction of sea-salt contribution. On an average, nss-SO<sub>4</sub><sup>2-</sup> and nss-K<sup>+</sup> constitutes greater than 90 and 80 % of total SO<sub>4</sub><sup>2-</sup> and K<sup>+</sup>, respectively in

the IGP- and SEA-outflow, sampled during January'09 and March-April'06, suggesting their anthropogenic dominance in the MABL (Table 3.4). Although nss-Ca<sup>2+</sup> accounts for almost ~ 85 and 95 % of total water-soluble calcium in the IGP-outflow during January'09 and March-April'06, it accounts for only 50 % in the MABL of S-BoB (Table 3.4). This is attributed to the relative increase in magnitude of sea-salt contribution over the southern Bay region during January'09.

The sum of cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>) and anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) constitute the water-soluble ionic composition (WSIC expressed in  $\mu$ g m<sup>-3</sup>) which varied from 6.6 to 50.3  $\mu$ g m<sup>-3</sup> ( $\Sigma$ WSIC/PM<sub>10</sub>:24 -50 %) and 4.3 to 26.4  $\mu$ g m<sup>-3</sup> ( $\Sigma$ WSIC/PM<sub>10</sub>: 39 -76 %) in the IGP- and SEA-outflow, respectively during the cruise undertaken in January'09. Likewise, water-soluble inorganic constituents ( $\Sigma$ WSIC) account for almost 44 % of TSP mass during March-April'06. However, the contribution of  $\Sigma$ WSIC to total particulate mass loading is more or less consistent in the IGP-outflow sampled from the MABL during January'09 (~42%) and March-April'06 (~ 44%).

#### 3.3.6. Sea-Salts

Sea-Salt concentrations were estimated using the following relation [Quinn, 2004].

Sea Salt = Cl<sup>-</sup> ( $\mu$ g.m<sup>-3</sup>) + 1.47 x Na<sup>+</sup> ( $\mu$ g.m<sup>-3</sup>)

Here, 1.47 is the ratio of  $(Na^+ + K^+ + Mg^{2+} + Ca^{2+} + SO_4^{2-} + HCO_3^-)/Na^+$ . This approach of calculating sea salt is solely based on the assumption that Na<sup>+</sup> and Cl<sup>-</sup> are mainly derived from sea water and hence excluding the contribution from non sea salt (nss)-components such as K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> thereby allowing for the Cl<sup>-</sup> loss from sea salt through chemical reactions with acidic constituents of the ambient particulate matter. This approximation is fairly good enough in the present study because of the fact that collected aerosol samples are of marine region. On an average, estimated sea salt concentrations account for almost 4 and 6 % of particulate mass loading in aerosols sampled from the IGP-outflow during January'09 and March- April'06. Surprisingly, relatively high concentrations (~ 15 %) were obtained for the aerosols collected from the south Bay of Bengal during the January'09 cruise. This argument has been further strengthened by the relative increase in mean wind speed over the S-BoB which results in high concentration of sea salts [*Kaskaoutis et al.*, 2010].





Figure 3.2: Fractional contribution of individual water-soluble inorganic constituents to the  $\Sigma WSIC$  (i.e., sum of all cations and anions) in air masses sampled from the IGP- and SEA-outflow during January'09; and from the IGP-outflow during March-April'06

The equivalent mass ratio of Mg/Na<sup>+</sup> in aerosols collected from the MABL during January'09 cruise averages about  $0.19 \pm 0.09$  and  $0.11\pm0.02$  for Nand S-BoB, respectively. The equivalent ratio of Mg<sup>+</sup>/Na<sup>+</sup> in the S-BoB is of similar to that derived from the composition of seawater (0.12), suggests their common source. However, the high equivalent ratio observed over the northern Bay region can be explained by its contribution from crustal source apart from the sea salts.

# 3.3.7. Crustal elements and mineral dust

The mass concentrations of crustal elements (Al, Fe, Ca and Mg) show pronounced spatial and temporal variability. In addition, a strong inter correlation (p-value < 0.001) between these species suggest their common source, mineral dust. Likewise, a significant linear correlation (p-value < 0.05) between these crustal elements with nss-SO<sub>4</sub><sup>2-</sup>, indicate their common long-range atmospheric transport. In the N-BoB, significant correlation ( $r^2 = 0.53$ ; p-value < 0.01) observed in PM<sub>10</sub> fraction between Ca and NO<sub>3</sub><sup>-</sup> further confirms the acid uptake by mineral aerosol. No such significant linear relationship is observed over the south Bay, where the dust levels are significantly low, in comparison to that over N-BoB. In contrast, a strong linear correlation found between nss-SO<sub>4</sub><sup>2-</sup>, water soluble Ca<sup>2+</sup> and total aerosol Ca in PM<sub>10</sub> for the entire BoB, also supports aciduptake by mineral aerosols.

In both size fractions (PM<sub>2.5</sub> and PM<sub>10</sub>), the mean elemental ratio of Fe/Al in PM<sub>2.5</sub> is about 0.51 ( $\pm$  0.30), whereas in PM<sub>10</sub> it is about 0.40 ( $\pm$  0.09). In PM<sub>10</sub>, Fe/Al ratio is close to the reported value of upper continental crust (UCC value of Fe/Al = 0.43; [*Taylor and McLennan*, 1985]. The relative enrichment of Fe in PM<sub>2.5</sub>, which contains fine mode aerosols, can be attributed to the anthropogenic combustion sources [*Kumar et al.*, 2010]. Likewise, the mass ratio of Ca/Al and Mg/Al in PM<sub>10</sub> fraction were also close to the UCC values (Ca/Al = 0.37, Mg/Al = 0.17) reported by Taylor and McLennan, [1985]. Surprisingly in some aerosol samples collected from the S-BoB, depleted values of Fe/Al, Ca/Al, Mg/Al ratios (lower than the UCC value reported by Taylor and McLennan, [1985]), were observed. However, AMBTs computed at an arrival height of 100, 500 and 1000m for these sampling dates have shown localized pattern (recirculating within

the MABL), suggesting the background dust. The variability of Ca/Al, Fe/Al and Mg/Al is quite larger in PM<sub>2.5</sub> because of low dust concentrations. However, it is also likely that the particulate mass loading for these samples are very low ( $\leq 10 \ \mu g \ m^{-3}$ ) and, hence, can have more uncertainty in the measurement of these crustal elements.

Assuming that the mineral dust comprises 8.04 % of Al and it has no other anthropogenic sources, dust concentrations were estimated, which accounts for almost 30 and 10 % of PM<sub>10</sub> and PM<sub>2.5</sub> mass, respectively. The estimated mass concentration of mineral dust during January'09 accounts for near about 30 % in PM<sub>10</sub> and 10 % in PM<sub>2.5</sub> mass fraction. However, the dust concentrations in PM<sub>10</sub> samples were of comparable magnitude with that observed during March-April'06 (~ 50 %) over the Bay of Bengal. Though, the dust levels were of comparable magnitude during the two sampling periods (January'09 and March-April'06), they significantly differ in their source. The former sampling period (January) receives mineral dust from the Indo-Gangetic Plain (as evident from the AMBTs, Figure 3.1), whereas it originates from Thar Desert during March-April. Furthermore, the aerosols collected during these sampling periods (January'09 and March-April'06), have shown characteristic source signatures, that differ in terms of their elemental ratios of Fe/Al, Ca/Al and Mg/Al.

A comparison of elemental ratios of Fe/Al, Ca/Al and Mg/Al in aerosols collected from the MABL during January'09 and March-April'06 is presented in Table 3.4. Significant differences were observed between these ratios in both the outflows (IGP- and SEA-) and one-way ANOVA analyses have been shown in Table 3.5. From this table, it has been observed that Ca/Al ratios were significantly different between the IGP- and SEA-outflow sampled from the MABL during January'09. However, no such significant differences were observed for Fe/Al (P > 0.05; Figure 3.3).

The observed difference in the Ca/Al ratio between IGP- and SEA-outflow during January'09 cruise could be due to the relative increase in contribution of Sea-Salts over the south Bay region (as evident from the mass ratio of nss- $Ca^{2+}/Ca^{2+}$ : 0.50 ± 0.23 and  $Ca^{2+}/Ca$ : 0.80 ± 0.25; Figure 3.3). The elemental ratios of Fe/Al, Ca/Al and Ca<sup>2+</sup>/Ca in the IGP- and SEA-outflow sampled from

the MABL during January'09 and March-April'06 is presented as histogram (Figure 3.3). In contrast, C/Al and Fe/Al ratio during March-April'06 is significantly different (P < 0.05) compared to that in the January'09 cruise. It is noteworthy that the observed mass concentrations of total aerosol Ca during January'09 is far less compared to the water soluble Ca<sup>2+</sup> in March-April'06. The water-soluble Ca<sup>2+</sup>/Ca during the two sampling periods were significantly different (p < 0.05).

# 3.3.8. Carbonaceous Species

The concentration of carbonaceous species (EC, OC) shows progressive decreasing trend, consistent with the particulate loading, with relatively high concentrations observed over the N-BoB compared to that in the S-BoB.

	Janu	March-April'06	
<b>Characteristic Ratio</b>	IGP-outflow	SEA-outflow	IGP-outflow
		$Av \pm sd$	
nss-SO4 <sup>2-</sup> /SO4 <sup>2-</sup>	$0.97\pm0.04$	$0.92\pm0.04$	$0.96\pm0.02$
$nss-K^+/K^+$	$0.94\pm0.05$	$0.83\pm0.09$	$0.87\pm0.08$
$nss-Ca^{2+}/Ca^{2+}$	$0.85\pm0.13$	$0.50\pm0.23$	$0.95\pm0.04$
Ca <sup>2+</sup> /Ca	$0.75\pm0.10$	$0.80\pm0.25$	$0.92\pm0.05$
NO <sub>3</sub> <sup>-</sup> /nss-SO <sub>4</sub> <sup>2-</sup>	$0.10 \pm 0.11$	$0.11\pm0.07$	$0.01\pm0.02$
nss-SO4 <sup>2-</sup> /nss-Ca <sup>2+</sup>	$60 \pm 21$	$105 \pm 52$	$10.4\pm~4.0$
nss-K <sup>+</sup> /nss-Ca <sup>2+</sup>	$3.0 \pm 0.6$	$6.5 \pm 3.1$	$0.36\pm\ 0.10$
<sup>#</sup> NH <sub>4</sub> <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup>	$0.78\pm0.28$	$0.35\pm0.26$	$0.40\pm0.20$
$^{\#}NH_{4}^{+}/(SO_{4}^{-2} + NO_{3}^{-})$	$0.74\pm0.28$	$0.33\pm0.24$	$0.40\pm\ 0.20$
$^{\#}(NH_{4}^{+}+Ca^{2+})/SO_{4}^{2}$	$0.84\pm0.24$	$0.40\pm0.26$	$0.67\pm0.20$
$(NH_4^+ + Ca^{2+})/(SO_4^{2-} + NO_3^-)$	$0.80\pm0.25$	$0.38\pm0.25$	$0.66\pm\ 0.20$
Fe/Al	$0.42\pm0.07$	$0.36\pm0.11$	$0.72\pm0.37$
Ca/Al	$0.27\pm0.12$	$0.43\pm0.11$	$0.86\pm0.17$
Mg/Al	$0.24\pm0.19$	$0.65\pm0.27$	$0.35\pm0.12$
OC/EC	$3.4 \pm 1.1$	$3.2 \pm 2.0$	$4.3 \pm 2.4$
TC/EC	$4.4 \pm 1.1$	$4.0 \pm 2.0$	$5.3 \pm 2.4$
nss-K <sup>+</sup> /EC	$0.29\pm0.09$	$0.47\pm0.15$	$0.55\pm\ 0.14$
nss-K <sup>+</sup> /OC	$0.09\pm0.03$	$0.20\pm0.13$	$0.16\pm\ 0.07$
nss-SO <sub>4</sub> <sup>2-</sup> /EC	$6.1 \pm 3.5$	$7.9 \pm 2.8$	$15.5 \pm 5.7$

 Table 3.4: Diagnostic ratios of chemical composition in the IGP- and SEA-outflow during

 January'09 and March-April'06

# Equivalent ratio

However, spatial distribution was similar (decreasing trend from north to south) to the present study during the cruise undertaken in March-April'06.The statistical description of carbonaceous species mass concentration in aerosols sampled from the MABL of Bay of Bengal during January'09 (IGP-and SEA-outflow) and March-April'06 (IGP-outflow) is presented in Table 3.1.

Statistical analysis (One-way ANOVA) reveals the significant differences (P < 0.05; See Table 3.2) between the outflows (IGP and SEA) with regard to their percentage contribution of OC, EC towards particulate mass loading. It is noteworthy that, EC contribution towards the particulate mass is more or less constant (~ 4%) in the IGP- and SEA-outflow during January'09. However, significantly (P < 0.05) lower concentrations (2 %) were observed for the IGP-outflow sampled from the Bay of Bengal during March-April'06 [*Sudheer and Sarin*, 2008]. In contrast, the percentage contribution of OC towards mass loading is significantly higher (P < 0.05) for the IGP- air masses sampled over the Bay of Bengal during January'09 compared to that for the SEA- and IGP- outflow during January'09 and March-April'06, respectively (See Table 3.2).

Particulate organic matter (POM) concentrations, estimated from the measured OC multiplied by a factor of 1.6, contribute significantly to  $PM_{2.5}$  (25 % and 14 %) and  $PM_{10}$  (24 % and 16 %) over N-BoB and S-BoB respectively. This factor 1.6 is the ratio of average organic molecular weight per carbon weight suggested by Turpin and Lim, [2001]. Using the similar factor, the POM estimated during ICARB-2006 was averaged around 11 % of total mass loading [*Sudheer and Sarin*, 2008] almost two times lower than that during Winter monsoon.

#### **3.4. Discussions**

#### 3.4.1: Seasonal variability of WSIC

The mass concentrations of anthropogenic water-soluble inorganic constituents (ANTH =  $NO_3^-$  + nss- $SO_4^{2-}$  +  $NH_4^+$  + nss- $K^+$ ) are relatively high during the cruise in "Winter" as compared to that in "Spring-intermonsoon". The high concentration of chemical constituents is attributed to relatively large impact of continental outflow during the Winter cruise (January'09). The prevailing meteorological conditions during Winter months (December-February) favour the

downwind transport of pollutants from the Indo-Gangetic Plain to the Bay of Bengal.



Figure 3.3: Comparison of characteristic ratios of mass concentrations between the IGP- and SEA-outflow during the cruises in January'09 and March-April'06

However, their magnitude decreases during the intermonsoon period (March-April) due to weakening of NE-monsoon. In addition, due to the prevailing low ambient temperatures and shallow boundary layer height during Winter season results in high concentration of chemical constituents in the MABL compared to that in the intermonsoon period. In contrast, an increase in the boundary layer height during Spring-intermonsoon together with the weak NE-monsoonal winds is responsible for the observed low concentration of chemical constituents, the mineral dust concentrations were relatively high during the Spring-intermonsoon. Seasonal variability of aerosol chemical composition is also evident from the statistically significant differences in the characteristic mass ratios between

Winter and Spring-intermonsoon (Table 3.2 and Table 3.5). The mass ratios of nss-SO<sub>4</sub><sup>2-</sup>/nss-Ca<sup>2+</sup> and nss-K<sup>+</sup>/nss-Ca<sup>2+</sup> in aerosols (See Table 3.4) collected from the IGP-outflow during January'09 and March-April'06 are significantly different (P-value < 0.05). The relatively high mass ratios of nss-SO<sub>4</sub><sup>2-</sup>/nss-Ca<sup>2+</sup> and nss-K<sup>+</sup>/nss-Ca<sup>2+</sup> during January'09 compared to that in March-April'06 is attributed to elevated abundances of anthropogenic water-soluble inorganic constituents and low concentrations of nss-Ca<sup>2+</sup>, which is a characteristic of IGP-outflow.

Table 3.5: One-way ANOVA analyses (at  $\alpha = 0.05$ ) of comparison of mean scores between the outflows sampled from the Bay of Bengal during January'09 and March-April'06 (Note: Subscript number below the p-value (0.05) denotes comparison between the outflows).

	Janu	ary'09	March-April'06	One-way
Ratio	<sup>1</sup> IGP- outflow	<sup>2</sup> SEA- outflow	<sup>3</sup> IGP- outflow	ANOVA
$nss - SO \cdot 2^{-}/EC$	> 0.052	> 0.051	< 0.051	F(2, 53) = 25.8;
1135-504 /EC	< 0.053	< 0.053	< 0.052	P < 0.05
$nss-SO_4^{2-}/nss-Ca^{2+}$	< 0.052	< 0.051	< <b>0.05</b> <sub>1</sub>	F(2, 52) = 47.2;
1155 504 /1155 Ou	< 0.053	< 0.053	< 0.052	P < 0.05
nss-K <sup>+</sup> /nss-Ca <sup>2+</sup>	< 0.052	< 0.051	< 0.051	F(2, 52) = 57.8;
	< 0.053	< 0.053	< 0.052	P < 0.05
nss-K <sup>+</sup> /FC	< 0.052	< 0.051	< <b>0.05</b> <sub>1</sub>	F(2, 53) = 57.8;
	< 0.053	> 0.053	> 0.052	P < 0.05
nss-K <sup>+</sup> /OC	< 0.052	< 0.051	< 0.051	F (2, 52) = 6.6;
	< 0.053	> 0.053	> 0.052	P < 0.05
OC/EC	> 0.052	> 0.051	> 0.051	F (2, 52) = 1.8;
	> 0.053	> 0.053	> 0.052	P > 0.05
$NO_2^{-}/nss-SO_4^{2-}$	> 0.052	> 0.051	< 0.051	F(2, 52) = 10.6;
	< 0.053	< 0.053	< 0.052	P < 0.05
$NH_4^+/SO_4^{2-}$	< 0.052	< 0.051	< <b>0</b> .05 <sub>1</sub>	F(2, 53) = 15.6;
	< 0.053	> 0.053	> 0.052	P < 0.05
$(NH_4^+ + Ca^{2+})/SO_4^{2-}$	< 0.052	< 0.051	> 0.051	F(2, 53) = 15.3;
	> 0.053	< 0.053	< 0.052	P < 0.05
Ca <sup>2+</sup> /Ca	> 0.052	> 0.051	< 0.051	F(2, 52) = 9.9;
	< 0.053	< 0.053	< 0.052	P < 0.05
Ca/Al	< 0.052	< 0.051	< 0.051	F(2, 53) = 91.8;
	< 0.053	< 0.053	< 0.052	P < 0.05
Fe/A1	> 0.052	> 0.051	< 0.051	F(2, 53) = 12.8;
1 0/ / 11	< 0.053	< 0.053	< <b>0.0</b> 5 <sub>2</sub>	P < 0.05

However, during March-April'06, owing to shift in the boundary layer height and the transport of mineral dust from the Thar Desert to the Bay of Bengal (as also evident from the AMBTs, see Figure 3.1) are responsible for the low mass ratios.

## 3.4.2. Seasonal variability of mineral dust

It has been observed that the solubility of Ca in aerosols sampled from the IGP-outflow during Winter and Spring-intermonsoon is significantly different (P < 0.05; Table 3.4). The solubility is relatively high during Spring-intermonsoon (Ca<sup>2+</sup>/Ca: 0.92  $\pm$  0.05; Figure 3.3) compared to that in Winter (Ca<sup>2+</sup>/Ca: 0.75  $\pm$  0.10; Figure 3.3). The relatively low solubility of aerosol-Ca observed during Winter months (December-February) is mainly due to the difference in soil dust (as evident from the Ca/Al ratio) together with the availability of neutralizing species (NH<sub>4</sub><sup>+</sup> + Ca<sup>2+</sup>) for acidic anthropogenic species (nss-SO<sub>4</sub><sup>2-</sup>).

The equivalent ratio of  $NH_4^+/SO_4^{2-}$  for the IGP-outflow sampled over the Bay of Bengal (Winter:  $0.78 \pm 0.28$ ; Spring-intermonsoon:  $0.40 \pm 0.20$ ; Figure 3.3) during the two sampling periods suggest the availability of excess acid for the reactive uptake by the alkaline dust. Furthermore, the equivalent mass ratio of  $(NH_4^+ + Ca^{2+})/SO_4^{2-}$  during January'09 and March-April'06 centred on  $0.84 \pm 0.24$  and  $0.67 \pm 0.20$ , respectively. It is noteworthy that the mineral dust concentration during Spring-intermonsoon (~50%) is considerably higher as compared to that in Winter (~30 %). It is, thus, inferred that during Winter months NH<sub>3</sub> becomes the major neutralizing species, suggesting the minor role of Ca<sup>2+</sup>. In contrast, Ca<sup>2+</sup> also becomes the important neutralizing species for excess acidity (defined as the left over acid after reacting with NH<sub>3</sub>) in the MABL during March-April'06. From the above observations, it is implicit that the presence of calcareous mineral dust together with the availability of excess acid over the Bay of Bengal during Spring-intermonsoon can explain the high solubility of aerosol-Ca.

Another notable feature lies in the data that higher abundance of calcium during Spring-intermonsoon is also characterized by the high ratios of Ca/Al (0.86  $\pm$  0.17; Figure 3.3). In contrast, relatively low ratios were observed in aerosols sampled from the IGP-outflow during January'09 (Ca/Al: 0.27  $\pm$  0.12; Figure 3.3). Earlier studies have suggested that desert soils from the Thar region

(Rajasthan, located in the north western part of the India) are enriched in calcareous minerals [*Tindale and Pease*, 1999; *Yadav and Rajamani*, 2004] and are characterized by high abundance ratio of Ca/Al in ambient aerosols [*Rastogi and Sarin*, 2009]. From Table 3.4, it is inferred that the elemental ratio of Ca/Al, Fe/Al and Mg/Al are distinctly different (P < 0.05, see Table 3.5) in aerosols collected from the IGP-outflow during January'09 and March-April'06. Based on the origin of AMBTs, it has been suggested that dust from the Thar Desert is a source of mineral aerosols to the MABL during March-April'06. This argument is further supported by their characteristic high Ca/Al (0.79-2.19) [*Kumar and Sarin*, 2009].

In contrast, AMBTs during January'09 were originated from the Indo-Gangetic Plain. Therefore, it is inferred that alluvial mineral dust from the IGP is a dominant source to the MABL during Winter months. Interestingly, the low Ca/Al ratio in fine mode aerosols sampled from the Bay region  $(0.27 \pm 0.20)$  is somewhat consistent with that sampled from the IGP  $(0.23 \pm 0.11)$  during the continental outflow. Based on the above observations, it has been inferred that the mineral aerosols in the MABL during Winter and Spring-intermonsoon season distinctly differ in term of their source composition with regard to the abundance and solubility of aerosol Ca, Ca/Al during the continental outflow.

#### 3.4.3. Source apportionment of carbonaceous aerosols

The carbonaceous species (EC and OC) also show high concentrations during January'09 (Winter) compared to that in March-April'06 (Spring-intermonsoon). In order to understand the spatial distribution of carbonaceous species during both cruises (January'09 and March-April'06) in a more detailed way, a suite of characteristic mass ratios (OC/EC, TC/EC, nss-K<sup>+</sup>/EC, nss-K<sup>+</sup>/OC and nss-SO<sub>4</sub><sup>2-</sup>/EC) have been studied to infer about their sources. The statistical description regarding their range, mean and standard deviation of these mass ratios were presented in Table 3.4.

Significant differences (P < 0.05) were observed between the IGP-and SEA-outflow, sampled during January'09 and March-April'06 in terms of their mass ratios of nss-K<sup>+</sup>/EC, nss-K<sup>+</sup>/OC and nss-SO<sub>4</sub><sup>2-</sup>/EC (Table 3.5). Relatively high ratios were observed in aerosols sampled from the SEA-outflow (January'09)

and those collected from the MABL during March-April'06 (Figure 3.3). However, no such significant differences (P > 0.05) were observed in the mass ratios of OC/EC and TC/EC between the outflows (IGP and SEA). The spatial distribution of carbonaceous species show progressive decrease in OC and EC concentration from N- to S-BoB during the cruise undertaken in January'09. However, the spatial distribution of OC/EC shows an increase from 11<sup>th</sup> January'09 to 17<sup>th</sup> January'09. This observation suggests the relatively high contribution of organic carbon caused by the biomass burning emissions during S-BoB transects when winds were from south-east Asia.

In addition, the high nss-K<sup>+</sup>/EC and nss-K<sup>+</sup>/OC ratio over the S-BoB (see Table 3.4) reflects the impact of biomass burning emissions during the study period. It has been further observed that during transect in the S-BoB, notable fire emissions were detected by MODIS-TERRA satellite. In addition, more prominent fire emissions have been detected during March-April'06 over the IGP and SEA. Figure 3.4 depicts the MODIS- images of open biomass burning emissions during the cruise undertaken in Winter and Spring-intermonsoon (http://rapidfire.sci.gsfc.nasa.gov/cgi-bin/imagery/firemaps.cgi). The evidence for biomass burning as a dominant source of OC is further illustrated from the significant linear relationship between OC and nss- $K^+$  (P < 0.05) in aerosols collected from the IGP and SEA outflow during January'09 and March-April'06 [Srinivas et al., 2011a; Srinivas et al., 2011b]. Therefore, observed differences in nss-K<sup>+</sup>/EC and nss-K<sup>+</sup>/OC ratios during March-April'06 and January'09 could be due to their contribution from biomass burning emissions. In this study, a suite of diagnostic ratios (TC/EC and  $nss-K^+/EC$ ) have been used to decipher the relative contribution of carbonaceous species from biomass and fossil fuel burning emissions.

The TC/EC ratio (where TC is total carbon defined as the sum of EC and OC) has been used by several investigators in order to identify and quantify the source characteristics (i.e. emissions from biomass and fossil-fuel combustion) [*Andreae and Merlet*, 2001; *Novakov et al.*, 2005]. For this, mixing model approach has been adopted similar on the line of Mayol-Bracero et al., [2002], in which biomass burning and fossil fuel combustion are considered as two end

members. The TC/EC value for biomass burning from a diverse vegetation and wood fuel (bio fuel) is averaged around 9.1 [*Andreae and Merlet*, 2001] and that for fossil fuel combustion sources is about 2.0 [*Mayol-Bracero et al.*, 2002; *Novakov et al.*, 2000]. Assuming these are representative of two end members (viz. 2.0 for fossil fuel and 9.1 for biomass burning), TC/EC ranges from 2.5 - 6.1 and 2.7 - 7.5 in the IGP- and SEA-outflow, during January'09, indicates that 7 - 58 % and 10 - 77 % of carbonaceous species contribution from biomass burning emissions, respectively. Such observation point towards mixed contribution from both sources contrary to the previous study by Sudheer and Sarin [2008], reporting the dominant (> 80 %) contribution from biomass burning emissions

# WINTERSPRING-INTERMONSOONImage: spring spri

Figure 3.4: MODIS-fire images of open biomass burning emissions during the cruise undertaken in "Winter" and "Spring-intermonsoon" (source: http://rapidfire.sci.gsfc.nasa.gov/cgi-bin/imagery/firemaps.cgi).

over the Bay of Bengal during spring inter-monsoon (March-April'06). From these calculations, it is apparent that in the study region, carbonaceous species contribution is from the combined sources (viz. fossil-fuel and bio-mass burning sources). However, these calculations can be biased due to the underlying assumption of representative TC/EC value for the two end members. More recent study by Habib et al., [2008], had shown a lower TC/EC ratio for diverse vegetation (biomass) burning.

In addition, the condensation of VOCs can also account for high OC concentration during the long-range atmospheric transport. Although, TC/EC ratio has been used to decipher the relative contribution of biomass source versus fossil-fuel combustion, this ratio may not represent the source signature due to the partitioning of OC viz., evaporative loss of VOCs away from the source region and their oxidative loss during long-range atmospheric transport. EC is refractory and inert in nature, does not undergo chemical reaction unlike OC [*Lim et al.*, 2003]. Therefore, qualitative estimation of carbonaceous aerosol contribution from anthropogenic combustion sources based on TC/EC ratio may yield uncertainty.

Several recent studies have shown that biomass burning is a dominant source of carbonaceous aerosols in the IGP [*Badarinath et al.*, 2006; *Venkataraman et al.*, 2006]. A recent study by Gustafson et al., [2009], has also shown that emission inventories in the Indo-Gangetic Plain are dominated by the biomass burning source. In addition, enriched concentrations of K<sup>+</sup> have been observed in aerosols sampled from the forest fires over the Amazonian region and over the Western Africa during ground based and aircraft sampling [*Guazzotti et al.*, 2003; *Paris et al.*, 2010]. Likewise, higher abundance of potassium has been observed in biomass burning aerosols over the IGP during agricultural crop-waste residue burning [*Pal*, 2009; *Ram et al.*, 2008]. Therefore, nss-K<sup>+</sup>/EC ratio has been used to assess the relative contribution of carbonaceous species from the combustion sources (Biomass vis-à-vis fossil-fuel combustion) during the study period. According to Andreae and Merlet, [2001], K<sup>+</sup>/EC ratio in the biomass burning emissions lies in between 0.1 to 0.63. The mass ratio of nss-K<sup>+</sup>/EC during January'09 averages about 0.29  $\pm$  0.09 and 0.47  $\pm$  0.15 in the IGP- and SEA- outflow, respectively. Likewise, the mean ratio during March-April'06 is centered on  $0.55 \pm 0.14$ . The relatively high ratio over the Bay of Bengal during January'09 and March-April'06 signifies the source of K<sup>+</sup> and carbonaceous aerosol from biomass burning emissions as fossil fuel combustion produces insignificant amount of K<sup>+</sup> [*Andreae*, 1983; *Park et al.*, 2007].

In order to quantify the relative contribution of carbonaceous species from two sources, K<sup>+</sup>/EC ratio from fossil-fuel combustion sources is taken as zero and that from biomass burning sources as 0.63. Based on the average K<sup>+</sup>/EC ratio, estimated contribution of EC from biomass burning is more than 70 % in both SEA- and IGP-outflow sampled during January'09 and March-April'06, respectively. However, the contribution of EC from biomass source is somewhat lower in aerosols sampled from the IGP-outflow over the Bay of Bengal during January'09. This observation emphasizes the dominance of biomass burning sources over the Bay of Bengal. Except one study by Sudheer and Sarin [2008], previous studies (INDOEX) have attributed the carbonaceous mass concentration over the northern Indian Ocean is mainly from fossil-fuel combustion sources. This study, together with high concentrations of nss-K<sup>+</sup> and EC in PM<sub>2.5</sub> aerosols further suggests the significant contribution of carbonaceous aerosol mass concentration is from biomass burning during January'09.

# 3.4.4. Evidence of Cl depletion over of Bay of Bengal

Chloride depletion in marine aerosols collected over a polluted marine region is a common phenomenon and is investigated by several researchers [*Hsu et al.*, 2007; *Zhuang et al.*, 1999b]. The reaction of sea salt with acidic pollutants such as  $H_2SO_4$  and  $HNO_3$  can replace chloride from the sea salt and thus leads to the formation of nitrate and sulphate. These reactions further shift  $NO_3^-$  and  $SO_4^{2^-}$  aerosols from the fine mode to coarse mode thereby increasing the dry deposition velocities and scavenging efficiency of these particles. As a result of chloride depletion, the Cl<sup>-</sup>/Na<sup>+</sup> ratio can be much lower in marine aerosols than their actual mass ratio from seawater (Cl<sup>-</sup>/Na<sup>+</sup> sea-water ratio is 1.8) [*Pakkanen*, 1996; *Yao et al.*, 2003; *Zhuang et al.*, 1999a; b]. The chloride deficit (%) is calculated for all samples by the following equation.

 $Cl^{-} defect (\%) = ([Cl_{sw} - Cl_{meas}]/[Cl_{sw}]) * 100$ 

=  $[(1.16 * Na^{+}_{meas} - Cl^{-}_{meas})/(1.16 * Na^{+})] * 100$ 

In this equation, Na<sup>+</sup><sub>meas</sub> and Cl<sup>-</sup><sub>meas</sub> are expressed in equivalent concentrations. Here, factor 1.16 is the ratio of equivalent concentrations of chloride and sodium in seawater. This approach is very much similar to that of earlier studies in the literature [Pakkanen et al., 1996; Yao et al., 2003; Zhuang et al., 1999b]. The calculation is based on the assumption that  $Na^+$  in aerosol samples is solely derived from seawater and doesn't have significant anthropogenic source. In the present study, large chloride deficit have been observed ranging from 39-100 and 13-100 % over the Bay of Bengal with a mean value of  $86 \pm 20$  and  $89 \pm 20\%$  in PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. The magnitude of Cl-deficit exhibits a linear increase with the excess-nss- $SO_4^{2-}$  (excess over  $NH_4^+$ ); suggesting that displacement of HCl from sea-salt particles by H<sub>2</sub>SO<sub>4</sub> is a dominant reaction mechanism for the chloride-depletion [Sarin et al., 2011]. It is thus suggested that sea-salts could serve as potential sink for anthropogenic SO<sub>2</sub> in the downwind polluted marine environment. The emergence of hydrogen chloride from the deficit process is a source of reactive chlorine and has implications to the oxidation of hydrocarbons and dimethyl sulphide (DMS) in the MABL.

# 3.4.5: Dry-deposition of particulate carbon

The long-range atmospheric transport of particulate carbon to the marine atmospheric boundary layer (MABL) and its subsequent deposition to seawater, can contribute significantly to the organic carbon input to the deep sea sediments [*Duce and Duursma*, 1977]. It has been shown by earlier studies that for the seasalt aerosols (particles greater than 3  $\mu$ m and are of marine origin), the mean mass ratio of C/Na for seawater is very low (~ 0.05 \* 10<sup>-3</sup>; [*Buat-Menard et al.*, 1989]). However, it has been suggested that the C/Na in aerosols for the marine regions which are affected by the downwind transport of pollutants from continental outflow can be much higher and hence, in those environments it is important to study about the input of particulate carbon to the seawater (SEAREX studies).

In this regard, earlier studies suggested that the detailed description of atmospheric particulate carbon cycle requires a prior knowledge of its sources, its transformation process during long-range transport to the MABL [*Duce et al.*,

1983]. In the present study, the mass ratio of total carbon to sodium in the  $PM_{10}$  fraction for N-BoB ranges from 2.4 - 87.3 (Av: 27.5 ± 28.1) and it varies from 0.5-3.5 (Av: 2.2 ± 1.6) for S-BoB. This ratio is three orders of magnitude higher as compared to that observed for sea-salt aerosols, suggests the impact of continental outflow in the study region.

In addition, dry-deposition fluxes of C (i.e., flux = Conc. \*  $V_d$ ; where  $V_d$ = dry-deposition velocity) to the Bay of Bengal have been estimated during the study period. For PM<sub>2.5</sub>, the dry-deposition flux is estimated using a deposition velocity of 0.1 cm s<sup>-1</sup>. In case of PM<sub>10</sub> fraction, a deposition velocity of 1.0 cm s<sup>-1</sup> for the fraction of OC present in the coarse mode (PM<sub>10-2.5</sub>). Similarly, 0.1 cm s<sup>-1</sup> is used as a deposition velocity for EC, and for the fraction of OC present in fine mode to estimate the fluxes in PM<sub>10</sub>. The mean atmospheric dry-deposition of OC is about 207 µmol-C m<sup>-2</sup> d<sup>-1</sup> (range: 26 – 674 µmol-C m<sup>-2</sup> d<sup>-1</sup>). By integrating to the whole study area (~ 2.2 \* 10<sup>12</sup> m<sup>2</sup>), this flux corresponds to 2 Tg-C yr<sup>-1</sup> input to the Bay region. Likewise, the mean dry-deposition flux of EC is ~14 µmol-C m<sup>-2</sup> d<sup>-1</sup> (range: 1.4 – 48 µmol-C m<sup>-2</sup> d<sup>-1</sup>), which corresponds to 0.13 Tg-C yr<sup>-1</sup> deposition to the Bay of Bengal. A comparison of these deposition fluxes with global input to the ocean (OC: 11 Tg yr<sup>-1</sup>; EC = 2 Tg y<sup>-1</sup>; [*Jurado et al.*, 2008]) suggest that aeolian supply can account for 18 and 7 % of OC and EC respectively.

# 3.4.6: Source apportionment

In order to infer about the sources that contribute to the chemical composition of aerosols of both size fractions (PM<sub>10</sub> and PM<sub>2.5</sub>), factor analysis has been performed using principal component analysis (PCA-varimax) technique using STATISTICA<sup>®</sup> (i.e., a *stat soft*). The rotated factor loading of chemical constituents in PM<sub>10</sub> and PM<sub>2.5</sub> fractions were given in Table 3.6. In PM<sub>10</sub> fractions, PCA results in two factors that are accounting for 86 % of the total variance in the data. Factor 1 had high loadings for NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, OC, EC, Al, Ca, Fe, Pb and Cd which explained 63 % of the total variance. The contributing chemical species to this factor has been identified as a mixed source of mineral dust and pollutants, suggest their common atmospheric transport pattern to the MABL of Bay of Bengal (continental origin). Likewise, near about

23 % of the total variance is explained by the factor 2 in  $PM_{10}$  fraction and the contributing chemical constituents were  $Na^+$ ,  $Mg^{2+}$  and Mg, suggesting their marine origin (i.e., sea salts).

	<b>PM</b> <sub>10</sub>			PM <sub>2.5</sub>		
Variable	Factor (1)	Factor (2)	Factor (1)	Factor (2)	Factor (3)	Factor (4)
Na <sup>+</sup>	-0.28	0.94	-0.23	0.05	0.92	-0.04
$\mathrm{NH_4}^+$	0.91	-0.34	0.86	0.22	-0.24	0.30
K <sup>+</sup>	0.92	0.25	0.85	0.05	-0.01	0.39
Mg <sup>2+</sup>	-0.09	0.97	0.14	0.20	0.91	-0.11
Ca <sup>2+</sup>	0.92	0.21	0.68	0.41	0.31	-0.18
NO <sub>3</sub> -	0.56	0.46	0.23	0.01	-0.09	0.90
SO4 <sup>2-</sup>	0.93	-0.08	0.89	0.23	-0.16	0.23
OC	0.94	-0.09	0.66	0.14	-0.16	0.63
EC	0.90	0.05	0.64	0.06	-0.06	0.70
Al	0.89	-0.32	0.29	0.89	-0.07	-0.03
Ca	0.97	0.12	-0.08	0.81	0.35	0.09
Fe	0.92	-0.22	0.16	0.93	0.09	0.11
Mg	0.26	0.93	-0.12	0.67	0.65	-0.09
Expl.Var	9.43	3.41	5.48	3.11	2.45	2.12
Prp.Totl	0.63	0.23	0.37	0.21	0.16	0.14
source	continental	marine	bb	dust	sea-salt	ff-comb

Table 3.6: Principal Component Analysis (PCA) of chemical constituents in  $PM_{10}$  and  $PM_{2.5}$  fractions.

**Note:** *bb* = *bio-mass burning; ff-comb* = *fossil-fuel combustion; Expl.Var* = *Explained variance; Prp. Totl* = *proportion of total variance.* 

In case of  $PM_{2.5}$  fraction, the PCA analysis results in four factors that explained almost 88 % of the total variance. Factor 1 had a high loading of  $NH_4^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $SO_4^{2-}$ , OC, EC, Pb and Cd which account for 37 % of the total variance. This factor has been identified as mixed sources such as secondary formation process, emission products from biomass burning and fossil-fuel combustion. Similarly, factor 2 explained almost 21 % of the total variance in the data with contributing chemical species was Al, Ca, Fe and Mg.

The strong inter correlation between the crustal constituents and the corresponding principal component (factor 2) suggests that this could of crustal

origin [*Almeida et al.*, 2005; *Song et al.*, 2006]. The high loadings of Na<sup>+</sup>, Mg<sup>2+</sup> and Mg in factor 3 explained near about 16 % of the total variance of data and suggesting their common source, sea salt [*Harrison et al.*, 1996]. In PM<sub>2.5</sub> fraction, the mass ratio of Mg<sup>+</sup> to Na<sup>+</sup> is about 0.15, which is slightly higher than the seawater ratio (i.e., ~ 0.15). This further suggests that significant contribution of Mg<sup>2+</sup> is not only from sea salt but also from continental transport (i.e., may be derived from the mineral dust). Similarly, factor 4 accounts for ~ 14 % of the total variance and correlated with high loadings of NO<sub>3</sub><sup>-</sup>, OC and EC. This could be due to contribution from secondary nitrates, volatile organic compounds (VOCs).



Figure 3.5: Air mass back trajectory cluster for the sampling site (Kharagpur), located downwind of outflow from the Indo-Gangetic Plain.

#### 3.4.7: Chemical Characterization of fine mode aerosols in the IGP-outflow

As mentioned in the earlier sections, continental outflow from the Indo-Gangetic Plain (IGP) is a source of pollutants in the MABL of the Bay of Bengal during Winter (December-February) and Spring intermonsoon (March-April). Therefore, to characterize the chemical composition of aerosols in the IGPoutflow, fine mode ( $PM_{2.5}$ ) aerosols were collected during November'09-March'10. These samples were studied for water soluble ionic constituents (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>), crustal elements (Al, Fe, Ca and Mg) and carbonaceous species (EC, OC).

Air mass back trajectory (AMBTs) analysis at the sampling site shows the downwind transport of pollutants from the IGP to the BoB (Figure 3.5). The mass loading varies from 23.1 to 177.2  $\mu$ g m<sup>-3</sup> with high concentrations observed for early Winter samples (December-January) compared to later time period (February-March). Table 3.7 presents the chemical composition of fine mode aerosols, sampled from the IGP-outflow during November'09-March'10 with regard to their range, mean and standard deviation. Among the water soluble ions, SO<sub>4</sub><sup>2-</sup> (61 %), NH<sub>4</sub><sup>+</sup> (22 %), K<sup>+</sup> (8.5 %) and NO<sub>3</sub><sup>-</sup> (6.4 %) account for ~ 98 % of  $\Sigma$ WSIC. During the study period,  $\Sigma$ WSIC and mineral dust accounts for ~ 31 and 19 % of PM<sub>2.5</sub> mass, respectively.



Figure 3.6: A comparison of water-soluble inorganic constituents in  $PM_{2.5}$  samples collected from the IGP-outflow and the Bay of Bengal. (includes those samples whose AMBTs originate from Indo-Gangetic Plain).

Higher abundance of OC and nss- $K^+$  together with significant (p-value < 0.01) linear relation between them suggests their common source, emissions from biomass burning. A comparison of chemical composition of aerosols from the IGP-outflow with that from the Bay of Bengal (whose AMBTs are from the Indo-Gangetic Plain) clearly demonstrates the source signatures of IGP-outflow (Figure 3.6). From this comparison, it is obvious that the IGP-outflow, indeed, responsible for the observed chemical composition of Water-soluble inorganic constituents over the Bay of Bengal.

A noteworthy feature of the data is evident from the ratio of Ca/Al and Fe/Al that are consistent for both the IGP-outflow and the Bay of Bengal, suggests their common source, alluvial mineral dust (Figure 3.7). Based on the nss-K<sup>+/</sup>EC, nss-K<sup>+/</sup>OC, OC/EC and TC/EC ratios, it is inferred the dominant contribution of biomass burning emissions in the IGP-outflow and over the Bay of Bengal. The prevalent similarity between the IGP-outflow and North Bay of Bengal, suggest their characteristic source signature of the mineral dust. This observation is also supported by the AMBTs (Figure 3.5).



Figure 3.7: Histogram, showing the comparison of characteristic ratios in aerosols collected from the IGP-outflow (November'09-March'10) and the North Bay of Bengal (January'09).

#### 3.4.8. Mass closure

Mass concentrations were estimated from the measured constituents in aerosol samples and compared with the gravimetrically obtained  $PM_{10}$  and TSP mass concentrations. In the present study, particulate mass concentration ( $PM_x$ ) in aerosols is calculated as follows.

 $PM_X$  = Mineral dust + Sea Salt + Anthropogenic water-soluble ions (ANTH) + Particulate Organic Matter (POM) + EC

$$= (A1 * 12.5) + (Cl- + 1.47 * Na+) + (NH4+ + NO3- + nss-SO42 + nss-K+) + (1.6 * OC) + EC$$

Here, x = 2.5 or 10 respectively.

The relative contribution of chemical species to the average particulate mass for aerosols collected from the IGP- and SEA-outflow over the Bay of Bengal during January'09 (this study) and March-April'06 [*Kumar et al.*, 2008b] were shown as pie diagrams (Figure 3.8).

Table 3.7: Statistical	description of data	regarding their rang	ge, mean and	standard	deviation j	for
the aerosols collected	from the IGP-out	flow during Novembe	er'09 to Marc	ch'10.		

Statistic	Min	Max	Mean	stdev
PM <sub>2.5</sub>	23.1	177.2	89.7	33.1
Cl	BDL	0.1	BDL	BDL
NO <sub>3</sub> <sup>-</sup>	0.1	11.4	1.9	2.5
$SO_4^{2-}$	7.0	29.4	15.3	5.4
$Na^+$	0.1	0.4	0.2	0.1
$\mathrm{NH_4}^+$	3.1	20.6	6.5	2.9
$K^+$	0.7	3.8	2.0	0.6
$Mg^{2+}$	BDL	0.20	0.06	0.04
Ca <sup>2+</sup>	BDL	1.3	0.2	0.2
Al	0.4	2.2	1.3	0.4
Ca	0.1	1.2	0.3	0.2
Fe	0.1	1.8	0.7	0.4
Mg	0.1	0.4	0.2	0.1
EC	1.2	8.9	4.5	1.6
OC	5.7	54.6	30.7	12.1
TC	6.9	60.1	35.1	13.1

**Note:** All mass concentrations were in  $\mu$ g m<sup>-3</sup>. BDL is below detection limit.



IGP-outflow (March-April'06)

Figure 3.8: Fractional contribution of anthropogenic water-soluble inorganic constituents  $(ANTH = NO_3^- + nss-SO_4^{2-} + NH_4^+)$ , mineral dust (Al\*12.5), Sea-Salt, particulate organic matter and EC to the particulate mass in air masses sampled from the IGP- and SEA-outflow during January'09; and from the IGP-outflow during March-April'06

The anthropogenic components constitute the significant fraction during Winter and Spring-intermonsoon. The anthropogenic fraction of water-soluble inorganic ionic constituents (ANTH) account for near about 35 % in aerosols sampled from the IGP- and SEA-outflow over the Bay region during Winter and Spring-intermonsoon. Likewise, the fractional contribution of organic matter to particulate mass is significantly high (P < 0.05) during Winter (IGP-outflow: ~ 24 %; SEA-outflow: ~ 16 %) compared to that in Spring-intermonsoon (IGP-outflow: ~11 %).

# 3.5. Summary and conclusions

The present study encompasses chemical characterization of water-soluble ionic species, mineral dust, sea-salts and carbonaceous species in ambient aerosols (with regard to their abundances, sources, size-distribution and spatio-temporal variability), collected over the Bay of Bengal during Winter (January'09) and Spring-intermonsoon (March-April'06). A strong spatio-temporal variability has been observed for mass loading of PM<sub>2.5</sub> and PM<sub>10</sub> with relatively higher concentration in the northern Bay and dominated by fine (PM<sub>2.5</sub>) mode aerosols constituting ~65 % of PM<sub>10</sub> during wintertime. Comparison of abundances between the PM<sub>2.5</sub> and PM<sub>10</sub> fraction reveals their size-distribution. The watersoluble ionic constituents such as nss-SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup> and nss-K<sup>+</sup> show a predominant fine mode nature. In contrast, NO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and Cl<sup>-</sup> have shown coarse mode distribution.

Likewise, predominance of crustal elements (Al, Fe, Ca and Mg) in PM<sub>10</sub> fraction rather than in PM<sub>2.5</sub>, suggest its association with the coarse mode aerosols mineral dust. In contrast, OC exhibit a bimodal distribution. Unlike OC, EC show a predominant fine mode distribution over the Bay of Bengal during the continental outflow. Significant differences were observed between the two sampling seasons with relatively high concentration of anthropogenic constituents (nss-SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, nss-K<sup>+</sup>, EC and OC) observed during the Winter cruise as compared to that for Spring-intermonsoon, suggests their dominance during the former sampling period. Sea-Salts contribution towards the mass loading is relatively low compared to that from anthropogenic constituents and mineral dust during Winter and Spring-intermonsoon.

On an average, mineral dust accounts for  $\sim 30$  and 50 % of particulate mass during Winter and Spring-intermonsoon, respectively; distinctly differ in terms of their source. The alluvial soil from the Indo-Gangetic Plain is a major source of mineral dust during Winter. In contrast, transport from the Desert regions (eg: Thar, Arabian etc.,) contributes significantly to mineral aerosol loading in the MABL of Bay of Bengal during Spring-intermonsoon. The evidence for this is constrained from the differences in the abundance and solubility of aerosol-Ca, Ca/Al ratio between the two seasons.

The fractional contribution of WSIC (i.e., water-soluble ionic constituents) to particulate mass loading was more or less similar (~ 45 %) throughout Bay of Bengal during both seasons, with dominant contribution from sulphate to the ionic budget. On an average, nss-SO<sub>4</sub><sup>2-</sup> constitutes ~ 65 % of the total water-soluble ionic species and is primarily associated with the fine mode (PM<sub>2.5</sub>) aerosols. The spatial distribution of carbonaceous species (EC and OC) exhibit a similar pattern as that of mass loading in both cruises, showing a decreasing trend in the EC and OC concentration towards S-BoB. The mixed contribution of fossil-fuel and biomass burning sources has been observed towards carbonaceous species in N-BoB where as S-BoB is more influenced by biomass combustion sources. Relatively high mass ratio of nss-K<sup>+/</sup>EC, nss-K<sup>+</sup>/OC in air masses, originate from the south-east Asia during January'09 and from the Indo-Gangetic Plain during March-April'06, suggesting the impact of biomass burning emissions.

The impact of continental outflow on the atmospheric chemistry of aerosols in the MABL of Bay of Bengal is evident from a variety of processes discussed in this chapter. The transport of continental aerosols to the oceanic region has implication in the biogeochemistry of various elements due to the atmospheric deposition as well as in the climate forcing which needs further consideration.

# Chapter 4

Atmospheric abundances of Water-soluble Inorganic and Organic Nitrogen over the Bay of Bengal and the Arabian Sea

#### 4.1. Introduction

Nitrogen is an essential nutrient for terrestrial and marine ecosystems. The abundance of reactive nitrogen in the atmosphere has increased significantly in recent years due to the growing anthropogenic activities, including fossil-fuel combustion, biomass burning and fertilizer production [*Galloway and Cowling*, 2002]. The impact of transport and deposition of anthropogenic nitrogen is a topic of significant interest as it can perturb surface water productivity and thereby influences the marine biogeochemistry of nitrogen species and other nutrients. Recent studies have highlighted the importance of anthropogenic atmospheric nitrogen deposition to open ocean as a major source and its potential to enhance primary production particularly in the oligotrophic waters [*Duce et al.*, 2008]. Similarly, atmospheric deposition of reactive nitrogen to estuarine and coastal waters can increase eutrophication, trigger phytoplankton blooms which in turn can lead to oxygen depletion in deep waters and sediments [*Howarth*, 2008; *Nixon*, 1995; *Paerl and Whitall*, 1999; *Paerl et al.*, 2002].

On a global scale, it is estimated that the atmospheric supply of reactive nitrogen to the ocean is of the same order as its riverine supply [*Jickells*, 2006] and is susceptible to further increase in the near future with rapidly changing global emission scenario. The magnitude of atmospheric deposition of reactive nitrogen across the air-sea interface is dependent on its aerosol mass concentration. Therefore, in order to assess its deposition fluxes, it is essential to assess the mass concentrations of nitrogen in the marine atmospheric boundary layer (MABL).

The water-soluble reactive nitrogen in aerosols comprises of both inorganic and organic forms. The water-soluble inorganic nitrogen ( $N_{Inorg}$ ) is the sum of the mass concentrations of nitrate and ammonia ( $NO_3^- + NH_4^+$ ). In the atmosphere, nitrate is produced from its precursor gases ( $NO_x = NO + NO_2$ ) through gas phase photochemical reactions [*Seinfeld and Pandis*, 2006]. In urban (source) regions,  $NO_3^-$  predominantly exists as  $NH_4NO_3$  in fine mode aerosol as a result of its reaction with  $NH_3$ . Nitrate also exists in coarse mode as a result of reaction with other neutralizing species in the atmosphere such as mineral aerosols viz calcareous dust (CaCO<sub>3</sub>) and sea salts [*Pakkanen*, 1996]. Particulate

 $NH_4^+$  is derived from gaseous  $NH_3$ , which is supplied to the atmosphere as a result of agricultural activities viz. fertilizer use.

Until recently, the principal focus of air-sea exchange studies (eg: SEAREX) of reactive nitrogen to the surface ocean dealt with the deposition of soluble inorganic nitrogen. Some of these studies had also highlighted that all forms of soluble reactive nitrogen species including organic nitrogen ( $N_{Org}$ ), are bio-available [*Bronk et al.*, 2007; *Duce et al.*, 2008; *Jickells*, 2006; *Seitzinger and Sanders*, 1999; *Spokes et al.*, 2000]. As a result, recent studies on atmospheric deposition are extended to organic nitrogen ( $N_{Org}$ ) in atmospheric aerosols. The soluble organic nitrogen in aerosols comprises of different chemical species that include secondary organic nitrates, reduced amines or urea and terrestrial (land) derived organic nitrogen [*Neff et al.*, 2002; *Russell et al.*, 1998]. In spite of the significance of soluble organic nitrogen ( $N_{Org}$ ), detailed information on its sources, size distribution, transport and deposition processes is rather limited [*Duce*, 1998].

The abundances of both inorganic and organic nitrogen, studied based on the size-segregated ( $PM_{2.5}$ ,  $PM_{10}$ ) and bulk (TSP) aerosols collected from the MABL of the Bay of Bengal (BoB), Arabian Sea (AS) and from the IGP-outflow during the late NE-monsoon (January-April) to identify the sources, size distribution, and to assess the spatio-temporal variability in mass concentrations of inorganic and organic nitrogen over Bay of Bengal. A summary of comparison of results obtained from earlier cruises undertaken in the BoB, during January-April) is presented in the Table 4.1 in order to make the data set representative for this region.

# 4.2. Results and Discussions

## 4.2.1. Air mass back trajectory analysis

Air mass back trajectories (AMBTs) have been used to trace the possible source regions of aerosols at the sampling site along with the cruise track (Figure 4.1a). 7-days air mass back trajectories are computed from the National Oceanic and Atmospheric Administration (NOAA) air resources laboratory GDAS database using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (<u>http://ready.arl.noaa.gov/HYSPLIT.php;</u> HYSPLIT program, version- 4.0) at arrival heights of 500, 1000 m [*Draxler*, 2002].



Figure 4.1: (a) Cruise tracks undertaken during March-April'06 and January'09 in the Bay of Bengal. The air mass back trajectory cluster, at arrival height of 500 m during January'09 is also shown. Sampling stations along the cruise track are indicated by dots. (b). Similar cruise tracks undertaken during same time period in 2001 and 2003 are also shown.  $N_{Inorg}$  and  $N_{Org}$  are measured only in the latter two cruises (2006, 2009). Indo-Gangetic Plain is shown as an inset in (a).

AMBTs indicate that, during the period 27<sup>th</sup> December-2008 to 10<sup>th</sup> January'09, the source region of aerosols is from the Indo Gangetic Plain (IGP). A temporal shift in the AMBTs during the period of 11- 28<sup>th</sup> January'09 points to the regional source from south-east Asia (SEA). In addition, some of the back trajectories show traverse over the Bay. The AMBTs (Figure 4.1a) over Bay of Bengal have formed the basis to group the analytical data into three categories as IGP-outflow, SEA-Outflow and Marine Air Parcel (MAP, air masses within the Bay region). The sampling tracks conducted during earlier cruises (February-March'01, February'03 and March-April'06) for the collection of TSP samples are shown in Figure 4.1b and relevant data from these cruises is presented in Table 4.1.

#### 4.2.2. Error propagation in $N_{Org}$

As mentioned in Chapter 2, N<sub>Org</sub> is assessed by taking the difference of measured concentrations of N<sub>Tot</sub> and N<sub>Inorg</sub>; and, thus, leading to cumulative error in Norg [Cornell et al., 2003; Mace and Duce, 2002]. Depending on the dominance of N<sub>Inorg</sub>, N<sub>Org</sub> is associated with relatively large uncertainty and in some cases yields a negative concentration. A large uncertainty and the potential biasness arising due to rounding negative numbers to zero and, hence, leading to the overestimation of N<sub>Org</sub> has been discussed by earlier studies [González Benítez et al., 2009; Mace and Duce, 2002; Mace et al., 2003]. The negative values of N<sub>Org</sub> have been discarded similar to the approach adopted by Lesworth et al., [2010]. The criterion adopted in this study deals with excluding samples in which the propagated error of N<sub>Org</sub> is comparable or more than the estimated concentration by taking the difference of N<sub>Tot</sub> and N<sub>Inorg</sub>. This criterion also emphasizes that large negative values result from the error associated with estimate of N<sub>Tot</sub> rather than samples with low N<sub>Org</sub> concentration [Lesworth et al., 2010]. The negative value of N<sub>Org</sub> arises only in those samples wherever the ratio of N<sub>Inorg</sub> to N<sub>Tot</sub> is greater than or equal to 0.90. This approach does not introduce biasness in the remaining data-set.

#### 4.2.3. Spatio-temporal variability

The mass concentration of  $PM_{2.5}$  averages nearly 65% of  $PM_{10}$ , suggesting its dominance over Bay of Bengal. The mass concentrations of soluble reactive nitrogen species ( $NH_4^+$ ,  $NO_3^-$  and  $N_{Org}$ ) show significant temporal variability in size segregated (PM<sub>2.5</sub>, PM<sub>10</sub>) aerosols (Figure 4.2). In PM<sub>2.5</sub>, mass concentrations of nitrogen species varied as 16 - 561 nmol m<sup>-3</sup> for NH<sub>4</sub><sup>+</sup>,  $\leq 0.13 - 22.3$  nmol m<sup>-3</sup> for NO<sub>3</sub><sup>-</sup> and 7 - 173 nmol m<sup>-3</sup> for water soluble organic nitrogen (N<sub>Org</sub>). However, dominance of NO<sub>3</sub><sup>-</sup> in the coarse mode is evident from its average concentration cantered on 16 nmol m<sup>-3</sup> over North Bay of Bengal.

The spatio-temporal variability studied for both inorganic and organic nitrogen, based on air mass back trajectory analysis, suggest that chemical composition of aerosols over north-Bay of Bengal (N-BoB, dominated by the continental outflow from IGP) exhibit higher abundance of nitrogen species. In contrast, southern Bay region (S-BoB) influenced by the outflow from south-east Asia (SEA), show characteristic low concentrations of N<sub>Inorg</sub> and N<sub>Org</sub> (Figure 4.2). On an average, N<sub>Inorg</sub>/N<sub>Tot</sub> ratio in PM<sub>2.5</sub> over N-BoB and S-BoB is 0.85 ± 0.11 and 0.91 ± 0.12 respectively. A comparison of the soluble nitrogen species from all cruises (February-March'01, February'03, March-April'06, January'09) is presented in Table 4.1. It is evident that mass concentration of NH<sub>4</sub><sup>+</sup> dominates the N<sub>Inorg</sub> (NH<sub>4</sub><sup>+</sup>/ N<sub>Inorg</sub>> 0.8, see Table 4.1).

Although  $N_{Tot}$  is not measured in February-March'01, February'03 cruises and measured only in March-April'06, January'09; it is reasonable to infer that water soluble inorganic nitrogen (mainly in the form of  $NH_4^+$ ) dominates the total nitrogen ( $N_{Tot}$ ). It is relevant to restate that all cruises were conducted during the same time (January-April). In PM<sub>2.5</sub>, mass concentration of  $N_{Org}$  over N-BoB is significantly higher (23 - 173 nmol m<sup>-3</sup>) compared to S-BoB (0 - 43 nmol m<sup>-3</sup>). Aerosol mass concentrations of soluble nitrogen species collected from different oceanic regions have been summarized in Table 4.2. These data suggest that, on an average, contribution of  $N_{Org}$  to  $N_{Tot}$  in fine and coarse mode aerosols is 17 and 15 % respectively (Table 4.2). A similar ratio has been also reported from the Gulf of Aqaba [*Chen et al.*, 2006]. As stated earlier,  $NH_4^+$  mass concentration dominates and accounts for as much as 98% of  $N_{Inorg}$  in both PM<sub>2.5</sub> and PM<sub>10</sub>.

The continental outflow from the Indo-Gangetic Plain (IGP) and southeast Asia dominates the widespread dispersal of pollutants over the Bay of Bengal. In IGP, biomass burning emissions (post-harvest burning of agriculturalwaste) is a dominant source of pollutants. In addition, large-scale application of fertilizers (ammonia and urea based) in the agricultural fields represent a major source of  $NH_4^+$  to the atmosphere. Zhang and Anastasio [2003a] had proposed that water-soluble  $N_{Org}$  is converted into  $N_{Inorg}$  (as  $NH_4^+$ - N) during the long-range transport of continental aerosols (cycling in the atmosphere and fog waters).

Furthermore, relatively high concentration of  $NH_4^+$  in rainwater and aerosolwater-extract could arise due to the hydrolysis of urea and amino-acid containing compounds [*Cornell et al.*, 1998]. Therefore, the conversion of  $N_{Org}$  to  $NH_3$  could explain high mass concentrations of  $NH_4^+$  in this study, and hence leading to low contribution of  $N_{Org}$  to  $N_{Tot}$  over remote oceanic regions (away from source region). The contribution of  $N_{Org}$  to  $N_{Tot}$  in  $PM_{2.5}$  and  $PM_{10}$  ranges from 12 to 38 % and 12 to 44 %, respectively. The relatively high concentration of  $N_{Org}$  (as much as 40 %) is observed along the coastal locations (Figure 4.3). It is noteworthy that the contribution of  $N_{Org}$  to  $N_{Tot}$  associated with the AMBTs originating from IGP (from 27<sup>th</sup> December'08-10<sup>th</sup> January'09) ranges from 12.4 to 38.4 %.



Figure 4.2: Temporal variability of water soluble nitrogen species in the MABL of Bay of Bengal over a span of 30 days is associated with the temporal shift in the wind-regimes, from Indo-Gangetic Plain (during early part of the cruise) to outflow from south-east

Constituent	<sup>#</sup> Feb-Mar'01	<sup>#</sup> Feb'03	<sup>#</sup> March-April'06	<sup>\$</sup> January'09	<sup>£</sup> January'09
	(n = 26)	( n = 24)	(n = 23)	(n = 31)	(n = 33)
$\mathrm{NH_4}^+$	7.2 - 57.8	0.6 - 126	0.6 - 127	16 - 561	3.4 - 678
NO <sub>3</sub> -	0.1 - 17.0	0.8 - 48.2	≤0.13 -5.6	≤0.13 - 22	≤0.13 - 42.5
$N_{Inorg}$	0.23 - 58.4	2.9 -130	2.3 - 128	18 - 565	7 - 693
$N_{Org}$	n.a.	n.a.	0 - 65	0 - 173	0 - 202
N <sub>Tot</sub>	n.a.	n.a.	9 -152	24 - 738	7 -786
NH4 <sup>+</sup> /NInorg	0.37 - 1.0	0.01 - 0.99	0.28 - 1.0	0.81 - 1.0	0.22 - 1.0
$N_{Inorg}/N_{Tot}$	n.a.	n.a.	0.06 - 1.09	0.62 - 1.22	0.56 -1.04
$N_{\text{Org}}/N_{\text{Tot}}$	n.a.	n.a.	0.0 - 0.94	0.0 - 0.38	0.0 - 0.44
NH4 <sup>+</sup> /SO4 <sup>2-</sup>	0.05 - 0.44	0.01 - 0.62	0.01 - 0.65	0.58 -1.12	0.05 - 1.08
$*NH_4^{+/}\Sigma WSIC$	0.01 - 0.12	0.001 - 0.17	0.001-0.17	0.003 -0.17	0.01- 0.26
$*SO_4^2 / \Sigma WSIC$	0.26 - 0.78	0.36 - 0.73	0.62 - 0.73	0.54 -0.71	0.33 - 0.70

Table 4.1: Range of concentrations of  $N_{Inorg}$  and  $N_{Org}$  in aerosols over the Bay of Bengal.

Note: Concentrations are expressed in nmol  $m^{-3}$  and  $NH_4^+/SO_4^{-2-}$  ratio is expressed in equivalent units.

\* Weight ratio of  $NH_4^+$  and  $SO_4^{2-}$  to total water soluble inorganic constituents (WSIC). # Data for bulk aerosols (TSP), \$ refers to  $PM_{2.5}$  (n = 31), £ refers to  $PM_{10}$  (n = 33). n.a. = not analyzed

In contrast, contribution of  $N_{Org}$  to  $N_{Tot}$  associated with south-east Asian outflow (as evident from the AMBTs from  $11^{th} - 28^{th}$  January'09) is relatively low (range: 0 – 27.4 %, Figure 4.3). The post-harvest burning of agricultural waste in the IGP has been well documented in some of the recent studies [*Badarinath et al.*, 2006; *Rajput et al.*, 2011; *Ram et al.*, 2010]. Therefore, the observed high concentrations of N<sub>Org</sub> can be attributed to biomass burning emissions from the Indo-Gangetic Plain.

# 4.2.4. Size distribution of Nitrogen Species

The scatter plot of mass concentrations of nitrogen species in  $PM_{2.5}$  and  $PM_{10}$ , show the predominance of  $NH_4^+$  and  $N_{Org}$  in  $PM_{2.5}$  (Figure 4.4c, e); whereas  $NO_3^-$  (Figure 4.4d) exists mainly in  $PM_{10}$  fraction. The dominant contribution of  $N_{Inorg}$  to total nitrogen ( $N_{Tot}$ ) in  $PM_{2.5}$  is also evident from Figure 4.4a. In bulk (TSP) aerosols collected during March-April'06, the mass ratio of  $NH_4^+$  to  $N_{Inorg}$  averages about  $0.91 \pm 0.21$  (range: 0.28 to 1.0), suggest that soluble inorganic nitrogen abundance is dominated by  $NH_4^+$  and contributes to almost 90% of  $N_{Inorg}$ . Relatively high mass concentration of  $NO_3^-$  in  $PM_{10}$  aerosols suggests its preferential association with coarse mode dust as  $Ca(NO_3)_2$ . A significant linear relation ( $R^2 = 0.62$ ; n = 15; p-value < 0.001; Figure 4.5b) between  $Ca^{2+}$  and  $NO_3^-$  over north Bay of Bengal (N-BoB) further attests to the above hypothesis.



Figure 4.3: Contribution (%) of water soluble organic nitrogen ( $N_{Org}$ ) to total soluble nitrogen ( $N_{Tot}$ ) in (a) PM<sub>2.5</sub> and (b) PM<sub>10</sub> over Bay of Bengal during January'09.

Location	Duration	NInorg	Norg	N <sub>Tot</sub>	%(N <sub>Org</sub> /N <sub>Tot</sub> )	Reference
Bay of Bengal	Jan-09	226	46	272	17	Present study (PM <sub>2.5</sub> )
Bay of Bengal	Jan-09	203	35	237	15	Present study (PM <sub>10</sub> )
Bay of Bengal	March-April-2006	47	11	58	19	Present study (TSP)
Yellow Sea	5-Mar	945	204	1149	17	Shi et al., 2010 (TSP)
Yellow Sea	6-Mar	490	87	577	17	Shi et al., 2010 (TSP) Cornell et al., 2001
Hawaii	Jan-Jun-1998	7.6	3.3	10.9	31	(rain & fine, coarse)
South China Sea	5-May	131	65	196	33	Shi et al., 2010 (TSP) Mace et al., 2003
Mediterranean Sea	Mar-May-2000	85	26	111	26	(rain & bulk) Lesworth et al., 2010
North Atlantic Ocean	Sep-Oct-Nov	-	-	-	24	(fine and Coarse)
Gulf of Aqaba	Aug-03 to Nov-04	65	10	75	13	Chen et al., 2006 (TSP) Nakamura et al., 2006
East china sea	Sep-Oct-2002	170	54	224	24	(fine and coarse)
N. California (Davis)	Aug-97 to July-98	-	15.6	-	20	Zhang et al., 2002 (PM <sub>2.5</sub> ) Miyazaki et al., 2010
North Pacific Ocean	Jul-Aug-2008	-	-	-	73	(sub micron aerosols) Miyazaki et al., 2010
North Pacific Ocean	Jul-Aug-2009	-	-	-	84	(super micron aerosols)
Western North Pacific	Aug-Sep-2008				67	Miyazaki et al., 2010 Violoki and Mihalopoulos., 2010
Crete (Greece)	Jan-05 to Dec-06	-	-	-	13	(fine and coarse)
Chapel hill, USA	Jan-Jun-2007	-	-	-	33	Lin et al., 2010 (PM <sub>2.5</sub> )

Table 4.2: Concentration (nmol m<sup>-3</sup>) of soluble nitrogen species in aerosols from different oceanic regions.

Note:  $N_{Org}$  to  $N_{Tot}$  is calculated for only those samples in which the propagated error of  $N_{Org}$  is comparable or more than the estimated concentration by taking the difference of  $N_{Tot}$  and  $N_{Inorg}$  (see Chapter-2).
This linear relationship has been explained in terms of chemical reaction of mineral aerosols with gas phase HNO<sub>3</sub> [*Harrison and Kitto*, 1990; *Matsumoto et al.*, 2009; *Pakkanen*, 1996; *Wolf*, 1984; *Zhuang et al.*, 1999b]. However, similar relationship among Ca<sup>2+</sup> and NO<sub>3</sub><sup>-</sup> is not valid for the data from southern Bay of Bengal, where mineral aerosols and NO<sub>3</sub><sup>-</sup> concentrations are relatively low. These results further support NO<sub>3</sub><sup>-</sup> existence in the coarse mode over Bay of Bengal. Although water soluble organic nitrogen (N<sub>Org</sub>) predominantly occurs in the fine mode over Bay of Bengal, a significant fraction also exists in the coarse mode. Similar to this observation over Bay of Bengal, bimodal distribution of N<sub>Org</sub> has also been documented over north-Pacific [*Miyazaki et al.*, 2010].



Figure 4.4: Scatter plot (a)  $N_{Inorg}$  versus  $N_{Tot}$  in  $PM_{2.5}$ , (b)  $N_{Inorg}$  and  $N_{Tot}$  for TSP (March-April'06);  $NH_4^+$ ,  $NO_3^-$  and  $N_{Org}$  in  $PM_{2.5}$  versus  $PM_{10}$  (c, d & e), suggesting dominance of  $NH_4^+$ , organic nitrogen ( $N_{Org}$ ) in the fine mode and coarse mode  $NO_3^-$ . Dominant contribution of  $N_{Inorg}$  to total nitrogen ( $N_{Tot}$ ) is very evident from the plot shown in (a) & (b).

In this study, there is an evidence for meaningful relationship of  $N_{Org}$  with nss-Ca<sup>2+</sup> (R<sup>2</sup> = 0.32; n = 19; p-value < 0.01) and total aerosol Ca (R<sup>2</sup> = 0.86; n = 33; PM<sub>10</sub>; p-value < 0.001), suggesting occurrence of  $N_{Org}$  in the coarse mode. Condensation of volatile organic nitrogen compounds on pre existing mineral

aerosols and sea salt particles (or that derived from soil organic matter) can lead to its coarse mode fraction. A similar relationship is reported between nss-Ca<sup>2+</sup> and soluble organic nitrogen in marine aerosols collected over remote Atlantic ocean [*Lesworth et al.*, 2010] and over eastern Mediterranean Sea [*Violaki et al.*, 2010]. These studies have argued that association of N<sub>Org</sub> with mineral aerosols is due to scavenging of organic nitrogen compounds on dust during its long-range transport from source regions. Therefore, the observed linear relationship between water soluble organic nitrogen and nss-Ca<sup>2+</sup> can explain the organic nitrogen fraction in the coarse mode.

#### 4.2.5. Source apportionment

In order to identify potential sources of water soluble  $N_{Org}$  over Bay of Bengal, regression analysis has been carried out among concentrations of  $N_{Org}$ ,  $N_{Tot}$ , OC, EC,  $NH_4^+$ , nss-K<sup>+</sup> and nss-SO<sub>4</sub><sup>2-</sup> (Figure 4.6). It is evident that nss-K<sup>+</sup> and  $N_{Org}$  exhibit a significant linear relation ( $R^2 = 0.61$ ; n = 18; p- value < 0.05), suggesting their biogenic source. Likewise, a strong linear correlation exists between nss-K<sup>+</sup> and EC ( $R^2 = 0.73$ ; n = 31; p-value < 0.01); and OC ( $R^2 = 0.76$ ; n = 31; PM<sub>2.5</sub>; p-value < 0.01). These interrelationships bring out the significant role of biomass burning emissions in contributing to aerosol  $N_{Org}$  (Figure 4.6). As stated earlier, samples from N-BoB show dominant influence of continental outflow from the Indo-Gangetic Plain. These observations suggest a common source for soluble organic nitrogen ( $N_{Org}$ ) and nss-K<sup>+</sup> from biomass burning.



Figure 4.5: Scatter plot between (a)  $NH_4^+$  and nss-SO<sub>4</sub><sup>2-</sup> (equivalent units); (b)  $Ca^{2+}$  and  $NO_3^-$  over the Bay of Bengal during January'09

The temporal variability in the abundances of  $N_{Org}$  and  $NH_4^+$  (Figure 4.2) and a significant linear relation between them also suggest their common source and/or common atmospheric transport process (Figure 4.6). The decomposition of urea in rain water to  $NH_3$  can be a potential cause for the linear relation of  $NH_4^+$ with soluble organic nitrogen (N<sub>Org</sub>). Atmospheric abundance of urea is associated with the suspension of dust from agricultural fields and/or from the sea salt production [Cornell et al., 1998]. Urea is extensively used as a fertilizer in the Indo-Gangetic Plain and hence could serve as a significant source of soluble organic nitrogen. A recent study by [Altieri et al., 2009] has shown that atmospherically derived organic nitrogen in precipitation is dominated by the reduced forms of nitrogen. Similarly, the conversion of organic nitrogen to  $NH_4^+$ in atmospheric condensed phases (in fog water and aerosol extracts) has been reported during exposure to sunlight and ozone [Zhang and Anastasio, 2003b]. Furthermore, dissolved amino acids are shown to be a significant source of NH<sub>4</sub><sup>+</sup> in PM2.5 samples [Zhang and Anastasio, 2003a]. Therefore, the observed linear relation of soluble organic nitrogen with  $\mathrm{NH_4^+}$  in marine aerosols indicates their common source from urea or amino compounds.

A comparison of mass concentrations of  $N_{Inorg}$  from the present study and data from the earlier cruises conducted in the Bay of Bengal (See Table 4.1); suggest an increasing trend in the mass ratio of  $NH_4^+/\Sigma WSIC$  (from 0.07 to 0.13). A possible explanation for the increase in contribution of  $N_{Inorg}$  ( $NH_4^+$ ) is attributed to increase in emission of  $NH_3$  from fertilizer use in the Indo-Gangetic Plain [*Singh and Singh*, 2008].

A recent study has measured the total particulate nitrogen at a coastal site (Chennai) along the west coast of Bay of Bengal [*Pavuluri et al.*, 2010]. Their study has reported that the abundance  $NH_4^+$  and  $NO_3^-$  account for almost 78 and 6 % of the total nitrogen. This observation further supports the major findings in the present study related to the dominance of inorganic nitrogen (as  $NH_4^+$ - N) over the Bay of Bengal. Owing to predominance ( $\geq 85$  %) of water-soluble inorganic nitrogen within the MABL of Bay of Bengal during the continental out flow, only  $N_{Inorg}$  has been measured in aerosols collected from the IGP-outflow. As mentioned in Chapter 2, the sampling site (Kharagpur) is influenced by the

downwind transport of pollutants from the Indo-Gangetic Plain and then entering into the Bay of Bengal (as evident from the AMBTs). Therefore, a comparison is made between the molar ratios of  $NH_4^+/\Sigma WSIC$  and  $NH_4^+/N_{Inorg}$ ; equivalent ratio of  $NH_4^+/SO_4^{2-}$  in aerosols collected from the IGP-outflow during December'09 to February'10 and those sampled from the N-BoB (i.e., a region which is influenced by the origin of air masses from the IGP) during January'09.

	N <sub>Org</sub>	0.7	9	0.82	0.92	0.88	0.78	0.90
600 600	м. Р.	•	C	0.88	0.88	0.86	0.85	0.82
508 250			•	EC	0.83	0.79	0.85	0.77
800 400	e i		:		N <sub>Tot</sub>	0.99	0.87	0.98
600 300	2. 		:		A. A.	<b>NH</b> <sub>4</sub> <sup>+</sup>	0.87	0.99
32 16	(r.	J.4.	•	 ۲	sti <sup>r i</sup>	* inter	nss-K <sup>+</sup>	0.88
328 160	er.		•		pro e .	, sri	je in i	$\boxed{\begin{array}{c} \text{nss -} \\ \text{SO}_4^{2-} \end{array}}$

Figure 4.6: Linear regression analysis of  $N_{Org}$  with  $N_{Tob}$  EC, OC,  $NH_4^+$ , nss-K<sup>+</sup> and nss -SO<sub>4</sub><sup>2-</sup> in PM<sub>2.5</sub> from the Bay of Bengal during January'09. (All concentrations are expressed in nmol m<sup>-3</sup>).

It is noteworthy that the NH<sub>4</sub><sup>+</sup> mass concentration dominates (Av: 94 ± 7 %) the water-soluble inorganic nitrogen (N<sub>Inorg</sub>) within the IGP-outflow and contributes to almost ~ 22 % of  $\Sigma$ WSIC (i.e., sum of concentrations of all cations and anions). This is in well agreement with that observed from the MABL of N-BoB during January'09 (NH<sub>4</sub><sup>+</sup>/ $\Sigma$ WSIC:~ 23 %; SO<sub>4</sub><sup>2-</sup>/ $\Sigma$ WSIC = 67 %; NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup> : 0.92 ± 0.15). The mass concentration of SO<sub>4</sub><sup>2-</sup> accounts for 63% of  $\Sigma$ WSIC and the equivalent ratio of NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup> averages about 0.92 ± 0.11 in the fine mode aerosols collected from the IGP-outflow. It is therefore inferred that IGP-outflow

can be a significant source of water-soluble nitrogen species from to the MABL during the continental outflow.

In contrast to the Bay of Bengal, the mass concentration of  $NO_3^-$  dominates (> 95 %) the water-soluble inorganic nitrogen (N<sub>Inorg</sub>) over the Arabian Sea. The analysis of N<sub>Tot</sub> in the aerosols collected from the MABL of Arabian Sea, reveal the negligible contribution of water-soluble organic nitrogen (N<sub>Inorg</sub>/N<sub>Tot</sub>: ~1.0). In all the aerosol samples (N = 19), N<sub>Inorg</sub> and N<sub>Tot</sub> concentrations are not significantly different (P < 0.05). Therefore, it is inferred that N<sub>Inorg</sub> (as NO<sub>3</sub><sup>-</sup> - N) dominates the N<sub>Tot</sub> over the Arabian Sea. In the present study, dry-deposition of soluble nitrogen were estimated from the mass concentrations and compared with the water column primary production in order to assess its contribution over the Bay.

## 4.2.6. Dry-deposition fluxes

The mass concentrations of soluble reactive nitrogen species were used to estimate their dry-deposition fluxes. This can be represented by the following equation.

Dry-deposition flux =  $f_{dry} = C_{meas} * V_{dry}$ 

Since, the scatter plot of  $NH_4^+$ ,  $NO_3^-$  between  $PM_{2.5}$  and  $PM_{10}$  aerosols indicating the fine mode existence of  $NH_4^+$  and coarse mode existence of  $NO_3^-$ , drydeposition velocity ( $V_{dry}$ ) for  $NH_4^+$ ,  $NO_3^-$  are taken as 0.1 and 1.0 cm sec<sup>-1</sup>. Similar dry-deposition velocities have been used in numerous studies reported in the literature [*Baker et al.*, 2003; *Chen et al.*, 2006; *Chen et al.*, 2007; *Duce et al.*, 1991]. Though, the soluble organic nitrogen in marine aerosols exists in both fine and coarse mode with almost ~80 % in fine fraction, its  $f_{dry}$  is calculated by applying the measured mass concentration in this ratio. The dry-deposition flux of total soluble nitrogen ( $N_{Tot}$ ) is estimated as the sum of deposition fluxes of  $NO_3^-$ ,  $NH_4^+$  and  $N_{Org}$ .

In PM<sub>10</sub>, the dry-deposition flux of soluble inorganic nitrogen (N<sub>Inorg</sub>) varies from 2 to 83  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup> with a mean of 27 ± 20  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup>, while the deposition fluxes of N<sub>Org</sub> vary from 0 – 123  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup> (average: 17 ± 29  $\mu$ mol-N m<sup>-2</sup> day<sup>-1</sup>. Similarly, in PM<sub>2.5</sub> aerosols, the average dry-deposition flux of N<sub>Inorg</sub> is about 16 ± 12  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup> (range: 2.0 - 49  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup>), whereas

the mean dry-deposition flux of soluble organic nitrogen (N<sub>Org</sub>) is about  $2.6 \pm 3.3$  µmol m<sup>-2</sup> d<sup>-1</sup> (range: 0 -15 µmol-N m<sup>-2</sup> d<sup>-1</sup>).



Figure 4.7: Dry-deposition fluxes ( $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup>) of aerosol water-soluble inorganic ( $N_{Inorg} = NH_4^+ + NO_3^-$ ) and organic ( $N_{Org}$ ) nitrogen from the Bay of Bengal during January'09.

The spatial variability in dry-deposition fluxes of soluble inorganic ( $N_{Inorg}$ ) and organic nitrogen ( $N_{Org}$ ) in aerosols collected during the study period is shown in Figure 4.7. These surfacial contours were generated by the interpolation of measured mass concentrations using Ocean Data View software [*Schlitzer*, 2002]. As explained earlier, relatively high contribution of  $N_{Org}$  to  $N_{Tot}$  is associated with the IGP outflow (as high as 40 %) with most of the values centred on 20 % (Figure 4.3). This is in sharp contrast with the south-east Asian outflow. Likewise, the high contribution of  $N_{H_4}^+$  (a dominant species of  $N_{Inorg}$ ) in the IGP outflow can be explained due to its emissions from agricultural fields and subsequent transport to the study area.

Therefore, the observed high concentrations of  $NH_4^+$  and  $N_{Org}$  are mainly attributed to their source from biomass burning emissions and application of fertilizers. It is evident from these contours that during January'09 marine boundary layer of Bay of Bengal is significantly impacted by the soluble reactive nitrogen species and their subsequent deposition to seawater can have substantial impact on surface biogeochemistry.

## 4.2.7. Impact on ocean surface biogeochemistry

It is relevant to reemphasize that Bay of Bengal is influenced by the continental outflow only during 4 months (January-April). It is, therefore, pertinent to argue that air-sea deposition can be extrapolated for the entire year. In order to assess the impact of atmospheric deposition of soluble nitrogen to the surface Bay of Bengal, dry-deposition flux of N<sub>Tot</sub> is compared with water column Primary Productivity (PP) during the late NE-monsoon (January-March). Although water column productivity is not measured in this study, data reported in the literature exhibit a large range of Primary Production, 99-566mgCm<sup>2</sup>d<sup>1</sup> [*Gauns et al.*, 2005]. The column integrated primary production in the surface waters of Bay of Bengal is summarized in Table 4.3. Therefore, a comparison of the atmospheric deposition with water column productivity provides only a rough estimate of the contribution of air-sea input. The dry-deposition fluxes of soluble nitrogen (N<sub>Tot</sub>) is 5 to 167  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup> (Av: 66  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup>) and 2 to 94  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup> (Av: 24  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup>) over the north Bay of Bengal and the south Bay of Bengal, respectively.

Assuming Redfield stoichiometry (C:N:P = 106:16:1) and that all atmospheric input of soluble nitrogen is completely utilized during primary production, the average flux of  $N_{Tot}$  (43 µmol-N m<sup>-2</sup> d<sup>-1</sup>) corresponds to an equivalent carbon of 3.5 mg m<sup>-2</sup> d<sup>-1</sup> fixed in the surface waters. This corresponds to no more than 5 % of the in-situ Primary Production (PP) during January. Nevertheless, deposition of N<sub>Tot</sub> varies from 2-167 µmol-N m<sup>-2</sup> d<sup>-1</sup>, which can support up to 13 % of the Primary Production (99-566 mg-C m<sup>-2</sup> d<sup>-1</sup>, a typical range of PP during January-March) in the surface waters of the Bay of Bengal.

Using N<sup>15</sup> as a tracer, Kumar et al., [*Kumar et al.*, 2004] have derived a fratio of about 0.5 for the Bay of Bengal, which suggests that almost half of the PP is exported to deep ocean in the Bay of Bengal. Therefore, on an average, atmospheric dry-deposition of  $N_{Tot}$  can support no more than 10 % of the new production during winter time (January-February) and spring (March-April). Nevertheless, on annual seasonal cycle, Primary Production and f-ratio also vary over a wide range. Therefore, quantitative estimate of contribution of atmospheric deposition to new production is not strictly appropriate for this region.

A comparison of atmospheric dry-deposition of total soluble nitrogen (range: from 2 - 167  $\mu$ mol - N m<sup>-2</sup>d<sup>-1</sup>), with that from riverine supply (214  $\mu$ mol-N m<sup>-2</sup> d<sup>-1</sup>; [*Kumar et al.*, 1996]), suggest that the two sources tend to be of comparable order in the changing scenario of increasing anthropogenic activities. The upper limit of atmospheric supply of N<sub>Tot</sub> along the coastal areas is reasonable to compare with the riverine supply.

A recent study by Dentener et al., [2006], has evaluated 23 models for the global annual estimates of nitrogen and sulphur deposition. They recognized that deposition fluxes of  $NH_4^+$  from Indian region are over estimated and that of nitrate are underestimated. Likewise, study by Duce et al., [2008] has projected a three-to-four fold increase in atmospheric nitrogen deposition in the marine regions around south-east Asia. Thus, real time data (this study) from Bay of Bengal is essential to evaluate the models.

Time	Region	ŧРР	Reference	
Dec-2001	Dec-2001 W-BoB		Jyothibabu et al. 2008	
Dec-2005-Jan-2006	C-BoB	375	Ramaiah et al., 2010	
Dec-2005-Jan-2006	W-BoB	280	Ramaiah et al., 2010	
Nov-Dec-2000	Coastal & Open Ocean	99 - 566	Gauns et al., 2005	
Sept-Oct-2002	Coastal	280	Kumar and Ramesh, 2005	
Sept-Oct-2002	Open Ocean	360	Kumar and Ramesh, 2005	
Sept-Oct-2002	W-BoB	196-350	Prasanna Kumar et al., 2007	
Sept-Oct-2002	C-BoB	182-513	Prasanna Kumar et al., 2007	
April-May-2003	W-BoB	250 - 469	Prasanna Kumar et al., 2007	
April-May-2003	C-BoB	155 - 427	Prasanna Kumar et al., 2007	

 Table 4.3: Reported columnar integrated Primary Production in the Bay of Bengal.

W-BoB = Western Bay of Bengal, C-BoB = Central Bay of Bengal

£ Column integrated Primary Production in mg-C m<sup>-2</sup> d<sup>-1</sup>.

As stated earlier, based on cruise undertaken in January'09, atmospheric deposition of  $N_{Tot}$  ranges from 2 - 167 µmol-N m<sup>-2</sup> d<sup>-1</sup> (equivalent to 10-853 mg-N m<sup>-2</sup> yr<sup>-1</sup>). The upper limit of estimated flux is of comparable magnitude to the projection (800-1200 mg-N m<sup>-2</sup> yr<sup>-1</sup>) made by Duce et al., [2008]. Considering the associated uncertainties, estimated flux is within the range estimated by Duce et al., [2008]. Therefore, region scale studies can provide a better insight and such data therefore is essential to evaluate the impact of continental outflow on the MABL.

## 4.3. Conclusions

This study presents the first comprehensive data set on inorganic and organic nitrogen in size segregated (PM<sub>2.5</sub>, PM<sub>10</sub>) aerosols from the Bay of Bengal during the continental outflow (January-April). The concentration of soluble nitrogen ( $N_{Tot} = N_{Inorg} + N_{Org}$ ) shows large spatio-temporal variability; relatively high over North Bay of Bengal (N-BoB) as compared to southern Bay (S-BoB). The soluble inorganic nitrogen ( $N_{Inorg} = NH_4^+ + NO_3^-$ ) abundance is dominated by  $NH_4^+$  (~ 98 %) and existing in the fine mode (PM<sub>2.5</sub>), whereas  $NO_3^-$  exists mainly in coarse mode. The soluble organic nitrogen also exists mostly in fine mode aerosols, albeit small fraction in the coarse mode.

A linear relation between  $NH_4^+$  and soluble organic nitrogen (N<sub>Org</sub>) over the marine boundary layer of Bay of Bengal, indicate their common source (i.e., urea or amino compounds hydrolysis to  $NH_3$  can explain the observed relation). This reaction could explain their fine mode existence. The dry-deposition flux of soluble reactive nitrogen ranges from 2-167 µmol-N m<sup>-2</sup> d<sup>-1</sup> and can support up to 13 % of the primary production in the Bay of Bengal (assuming Redfield ratio, C: N: P = 106:16:1).

# Chapter 5

Atmospheric pathways of Phosphorous to the Bay of Bengal and the Arabian Sea: Contribution from anthropogenic sources and mineral dust

#### 5.1. Introduction

Phosphorous is one of the limiting nutrients for the Primary Productivity in both terrestrial and marine ecosystems [*Chester*, 2002; *Fang*, 2004]. Since long, it has been suggested that the marine Primary Productivity over the geological time scale was limited by the availability of phosphorous [*Tyrrell*, 1999]. Recent observations also suggest that Productivity in some of the oceanic regions (Mediterranean Sea and Sargasso Sea) and in marine basins, fed by large quantity of freshwater, is limited by the availability of phosphorous [*Paytan and McLaughlin*, 2007 and references therein].

The role of phosphorus limitation in nitrogen fixation has been also emphasized for open ocean waters of the Atlantic and Pacific [*Mills et al.*, 2004; *Moutin*, 2008; *Sanudo-Wilhelmy et al.*, 2001]. In this context, atmospheric mineral dust is considered as a major source of phosphorous to the ocean surface [*Anderson et al.*, 2010; *Herut et al.*, 1999; *Krom et al.*, 2004; *Nenes et al.*, 2011; *Ridame and Guieu*, 2002]. However, present-day increase in the supply of phosphorous from anthropogenic sources would lead to significant changes in the marine biogeochemical cycle of nutrients [*Mahowald et al.*, 2008; *Schlesinger*, 1997]. It is also argued that the global atmospheric cycle of phosphorous is significantly perturbed due to the extensive use of fertilizers and mining of phosphate rocks [*Jahnke*, 2000]. The importance of biomass burning emissions has been suggested as a significant source of phosphorous [*Anderson et al.*, 2010 and references there in; *Mahowald et al.*, 2008; *Mahowald et al.*, 2005a].

Recent studies have documented that the magnitude of atmospheric input of phosphorous may attain comparable levels with respect to its riverine supply [*Compton et al.*, 2000; *Paytan and McLaughlin*, 2007]. Therefore, atmospheric transport and air-sea deposition of phosphorous demand further investigation in the regional context. This study presents the first comprehensive data set on the concentration of water-soluble inorganic phosphorus (P<sub>Inorg</sub>) in ambient aerosols, its sources, size distribution and dry-deposition to the Bay of Bengal and the Arabian Sea during the continental outflow (January-April). Although, wet deposition is considered as a major source of nutrients to the ocean surface, precipitation events over the study region during January-April are very uncommon. Therefore, atmospheric dry-deposition represents the total deposition to the Bay of Bengal and the Arabian Sea.

## 5.2. Results and discussions

## 5.2.1. Air mass back trajectory (AMBT) analyses

The isentropic AMBTs were computed (for seven days) from the HYSPLIT Model (Version - 4, [Draxler, 2002]) by reanalysis of NCEP data set (GDAS, global data set from 2006 to present, http://ready.arl.noaa.gov/hysplitbin/trajasrc.pl). AMBTs computed at an arrival height of 1000 m (and above) suggest that origin of air masses during January'09 cruise is mainly from the Indo-Gangetic Plain and south-east Asia (Figure 5.1). In contrast, air masses originate from Desert regions of Sahara, Arab, Oman, Somali and Thar during cruises undertaken from March to May 2006 (Figure 5.1). The advective transport of mineral dust from the Middle East, Arabian Peninsula, Oman, Iran, Thar and Somalia to the MABL of Arabian Sea has been well recognized [Middleton, 1986; Prospero et al., 2002; Tindale and Pease, 1999]. A detailed description on the transport pathways of aerosols to the Arabian Sea and Bay of Bengal, during January to April, has been reported in earlier publications [Badarinath et al., 2010; Dey et al., 2004; Siefert et al., 1999; Srinivas et al., 2011a]. Based on LIDAR studies, an evidence for high altitude dust transport (~ 3-3.5 km), during March-April'06, has been provided by Raj et al., [2008]. Likewise, high aerosol loading over the Arabian Sea during INDOEX field experiment was explained by invoking high-altitude transport of mineral dust from Desert (viz., Arabia, Thar, Iranian, Somalia) regions [Lelieveld et al., 2001; Ramanathan et al., 2001b].

## 5.2.2. Statistical analyses

A summary of the chemical data (Mean with  $\pm 1\sigma$ ) from cruises in the Bay of Bengal (March-April'06 and January'09) and the Arabian Sea (April-May'06) is presented in Tables 5.1 and Table 5.2. A comparison among abundances of P<sub>Inorg</sub> and chemical constituents is presented in terms of their statistical significance. Multiple linear regression analysis is also performed among the measured chemical constituents to infer about the provenance of aerosol phosphorus. Furthermore, ANOVA analysis (including post-hoc tests) has been carried out to evaluate the seasonal variability in the molar ratios of  $nss-K^+/nss-Ca^{2+}$ ,  $nss-SO_4^{2-}/nss-Ca^{2+}$  and  $P_{Inorg}/nss-Ca^{2+}$  for the data (Table 5.2) from all cruises (March-April'06, April-May'06 and January'09).



Figure 5.1: Cruise tracks undertaken onboard ORV Sagar Kanya: (a) Bay of Bengal (SK-223A: March-April'06) and Arabian Sea (SK-223B: April-May'06); (b) Bay of Bengal (SK-254: January'09). 7-day Air Mass Back Trajectories (AMBTs) computed at an arrival height of 1000 m is also shown.

Parameter	Bay	Arabian Sea				
	<sup>\$</sup> January'09	*March-April'06	*April-May'06			
<sup>\$</sup> P <sub>Inorg</sub>	$1.3 \pm 0.5$	$1.1 \pm 0.3$	$0.3 \pm 0.1$			
$Na^+$	$75 \pm 35$	$37 \pm 27$	$83\pm106$			
$\mathrm{NH_4}^+$	$171\pm182$	$50 \pm 35$	BDL			
$\mathbf{K}^+$	$17 \pm 7$	$6 \pm 3$	$3\pm 2$			
$Mg^{2+}$	$9\pm 6$	$7 \pm 3$	$8 \pm 11$			
Ca <sup>2+</sup>	$6 \pm 3$	$17 \pm 9$	$21 \pm 14$			
Cl	$9\pm10$	$0.4 \pm 0.3$	$62 \pm 110$			
NO <sub>3</sub> <sup>-</sup>	$14 \pm 10$	$1.2 \pm 1.4$	$8\pm7$			
$\mathrm{SO_4}^{2-}$	$123\pm79$	$62 \pm 26$	$35 \pm 12$			
Al	$41 \pm 35$	$34 \pm 20$	32 ±17			
Ca	$8 \pm 4$	$18 \pm 9$	$22 \pm 15$			
Fe	$8\pm8$	$11 \pm 6$	$8 \pm 5$			
Mg	$13 \pm 5$	$12 \pm 6$	$20 \pm 11$			
OC	$542\pm434$	$157 \pm 132$	$18 \pm 13$			
EC	$159 \pm 119$	33 ± 13	$7 \pm 3$			
\$ This Study; * From Kumar et al., (2008).						

Table 5.1: Chemical constituents (Mean  $\pm 1\sigma$ ) in aerosols from the Bay of Bengal and the Arabian Sea. (All concentrations are in nmol m<sup>-3</sup>)

### 5.2.3. P<sub>Inorg</sub> Concentration over Bay of Bengal

The mass concentration of water-soluble inorganic phosphorous ( $P_{Inorg} = PO_4^{3-}$ ) in TSP ranged from 0.7 to 2.1 nmol m<sup>-3</sup> (Av = 1.1 ± 0.3 nmol m<sup>-3</sup>) during March-April'06 (Table 5.1). During sampling in January'09,  $P_{Inorg}$  varied from 0.1 to 0.8 nmol m<sup>-3</sup> in PM<sub>2.5</sub> (Av = 0.3 ± 0.2 nmol m<sup>-3</sup>) and 0.3 to 2.8 nmol m<sup>-3</sup> in PM<sub>10</sub> (Av = 1.3 ± 0.5 nmol m<sup>-3</sup>), respectively. A comparison of the temporal data (Average with ±1 $\sigma$ ) suggests that  $P_{Inorg}$  concentrations in TSP and PM<sub>10</sub> are not significantly different during March-April'06 and January'09 (Table 5.1). Despite this similarity in the abundance pattern, evidence for different sources of  $P_{Inorg}$  is discernible from the analytical data. The abundances of water-soluble calcium (Ca<sup>2+</sup>) and  $P_{Inorg}$  in two size-fractions (PM<sub>2.5</sub>, PM<sub>10</sub>), collected during January'09, suggest their dominant occurrence in the coarse mode (Figure 5.2; see Table 5.1). The mass ratio of PM<sub>2.5</sub> to PM<sub>10</sub> for Ca<sup>2+</sup> and P<sub>Inorg</sub> is computed for each sample and then averaged for all samples. The corresponding ratio centers on 0.31 ± 0.18





Figure 5.2: Water-soluble calcium ( $Ca^{2+}$ ) and inorganic phosphorous ( $P_{Inorg} = PO_4^{3-}$ ) plotted for  $PM_{2.5}$  and  $PM_{10}$  collected during January'09 from the Bay of Bengal; suggest dominant occurrence of  $P_{Inorg}$  and  $Ca^{2+}$  in the coarse mode aerosols.

The contribution of  $P_{Inorg}$  from mineral dust has been investigated based on the chemical data presented in Tables 5.1 and 5.2. The mass concentration of  $SO_4^{2-}$  (with nss- $SO_4^{2-}/SO_4^{2-} \ge 90$  %) accounts for ~ 67 and 60 % of  $\Sigma$ WSIC in March-April'06 and January'09, respectively (where WSIC refers to watersoluble inorganic constituents and taken as sum of concentrations of all cations and anions). During these two sampling campaigns in the BoB, the equivalent ratio of  $NH_4^+/SO_4^{2-}$  and  $(NH_4^++Ca^{2+})/SO_4^{2-}$  is far less than one (Table 5.2), suggesting chemical uptake of excess acid by mineral dust. This is also evident from the significant (P-value < 0.05) linear correlation between nss-Ca<sup>2+</sup> and nss- $SO_4^{2-}$  (Figure 5.3a) and among aerosol-Ca and nss-Ca<sup>2+</sup> (Figure 5.3b). The dominant contribution of nss- $SO_4^{2-}$  in the MABL of Bay of Bengal is clearly evident from the steep slope of its linear regression lines with nss-Ca<sup>2+</sup> for data from January'09 (m = 23; R<sup>2</sup> = 0.75; P < 0.05) and March-April'06 (m = 2.3; R<sup>2</sup> = 0.62; P < 0.05; Figure 5.3a). This is in sharp contrast to the lower slope of linear regression for data from the Arabian Sea (m = 0.83;  $R^2 = 0.67$ ; Figure 5.3a). It is noteworthy that the solubility of aerosol-Ca (defined as nss-Ca<sup>2+</sup>/Ca) in March-April'06 is relatively high compared to that in January'09 (Table 5.2).

Another notable observation relates to significantly high  $Ca^{2+}$  concentration (range: 172 to 1425 ng m<sup>-3</sup>; Av: 675 ± 348 ng m<sup>-3</sup>) during March-April'06 compared to January'09 (range: 17 to 518 ng m<sup>-3</sup>; Av: 230 ± 116). Furthermore, on an average mineral dust concentration (assessed based on measured Al concentration and assuming Al content of 8.0 % in the mineral dust) accounts for ~ 33 and 50 % of the aerosol mass in January'09 and March-April'06, respectively. The relatively high solubility (Av: 92 ± 5 %) of aerosol-Ca together with high abundance of mineral dust (Av: 49 % of Particulate mass) during March-April'06 is attributed to differences in the source regions of mineral dust and chemical processing during the long-range transport.



Figure 5.3: The scatter plots between (a) nss-Ca<sup>2+</sup> and nss-SO<sub>4</sub><sup>2-</sup> and (b) aerosol Ca and nss-Ca<sup>2+</sup> suggest reactive uptake of acidic species ( $H_2SO_4$ ) by the mineral dust during long-range atmospheric transport.

Based on the above reasoning, temporal trend and significant role of chemical processing of mineral dust has been suggested for the aerosols sampled during March-April'06 compared to that in January'09. These differences in the chemical composition of aerosols are attributed to the varying type of mineral dust over the Bay of Bengal during the two seasons. The air-mass back trajectories (AMBTs), during March-April'06, were from Desert regions (Thar Desert) in

western India; whereas air masses during January'09 over the Bay of Bengal show dominant influence from the Indo-Gangetic Plain. The elemental ratio of Ca/Al in aerosols associated with these air masses averages around  $0.81 \pm 0.16$  for March-April'06 [*Kumar et al.*, 2008b] and  $0.35 \pm 0.14$  for January'09 [*Kumar et al.*, 2010].

Daramatar	Bay	Arabian Sea	
	January'09	*March-April'06	*April-May'06
P <sub>Inorg</sub>	$1.3 \pm 0.5$	$1.1 \pm 0.3$	$0.3 \pm 0.1$
<sup>\$</sup> P <sub>Dust</sub>	$0.3 \pm 0.3$	$0.3 \pm 0.2$	$0.2 \pm 0.1$
${}^{\#}\mathbf{P}_{Anth}$	$1.0 \pm 0.5$	$0.8 \pm 0.2$	$0.1 \pm 0.1$
$P_{Dust}/P_{Inorg}$	$0.2 \pm 0.2$	$0.2 \pm 0.1$	$0.7 \pm 0.3$
${}^{\$}P_{Anth}/P_{Inorg}$	$0.8\pm0.2$	$0.8 \pm 0.1$	$0.3 \pm 0.3$
${}^{\$}P_{Inorg}/nss-Ca^{2+}$	$0.54\pm0.54$	$0.09\pm0.05$	$0.03\pm\ 0.02$
<sup>§</sup> nss-K <sup>+</sup> /nss-Ca <sup>2+</sup>	$5.0 \pm 3.9$	$0.4 \pm 0.1$	$0.07\pm0.08$
§nss-SO4 <sup>2-</sup> /nss-Ca <sup>2+</sup>	$35.1 \pm 19.0$	$4.3 \pm 1.7$	$2.1 \pm 1.1$
$^{\$}$ nss-Ca <sup>2+</sup> /Ca <sup>2+</sup>	$0.66\pm0.26$	$0.95 \pm 0.04$	$0.89 \pm 0.12$
<sup>§</sup> Ca <sup>2+</sup> /Ca	$0.76 \pm 0.16$	$0.92 \pm 0.05$	$0.95 \pm 0.14$
<sup>£</sup> NH <sub>4</sub> <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup>	$0.55 \pm 0.34$	$0.40 \pm 0.20$	-
$^{t}(NH_{4}^{+}+Ca^{2+})/SO_{4}^{2-}$	$0.60 \pm 0.33$	$0.67 \pm 0.20$	$0.59 \pm 0.23$
<sup>£</sup> (Na <sup>+</sup> +NH <sub>4</sub> <sup>+</sup> +Ca <sup>2+</sup> )/SO <sub>4</sub> <sup>2-</sup>	$1.07 \pm 0.17$	$0.97 \pm 0.06$	$1.8 \pm 1.2$

Table 5.2: Diagnostic mass ratios in aerosols collected from the Bay of Bengal and the Arabian Sea.

P<sub>Inorg</sub>, P<sub>Dust</sub> and P<sub>Anth</sub> are in nmol m<sup>-3</sup> (This study).

 $P_{Dust}$  is estimated by multiplying the P/Al ratio in the Upper Continental Crust (~ 0.008; McLennan, 2001) and measured Al concentration in the ambient aerosols (i.e.,  $P_{dust} = 0.008*Al_{meas}$ ).

# Anthropogenic fraction of water soluble inorganic phosphorous ( $P_{Anth} = P_{Inorg} P_{Dust}$ ).

§ Molar ratio.

£ Equivalent ratio.

\* From Kumar et al., 2008.

The relatively high ratio of Ca/Al is consistent with that reported over the Arabian Sea, attributable to the source of dust from the Desert region in western India [*Rastogi and Sarin*, 2009; *Yadav and Rajamani*, 2004]. In contrast, the lower ratio of Ca/Al over Bay of Bengal (during January'09) is largely dictated by the outflow from the Indo-Gangetic Plain (Ca/Al =  $0.23 \pm 0.11$ , as measured at downwind site in the Gangetic Plain).

A significant correlation between nss-Ca<sup>2+</sup> and P<sub>Inorg</sub> (R<sup>2</sup> = 0.64; n = 23; pvalue < 0.001; Figure 5.3a) for the data from March-April'06 suggests their common source from the mineral dust. The contribution of dust derived phosphorous has been traced by the linear relation (P < 0.05) between nss-Ca<sup>2+</sup> and P<sub>Inorg</sub> [*Herut et al.*, 1999; *Markaki et al.*, 2003]. These studies have shown that the air masses originating from the Arabian Peninsula exhibit a linear relation among nss-Ca<sup>2+</sup> and total inorganic phosphorous [*Markaki et al.*, 2003]. Higher abundance of P and Ca in the desert dust (from Thar Desert) has been documented by Yadav and Rajamani, [2004]. These desert soils are reported to be rich in Ca which is reflected from the characteristic high elemental ratio of Ca/Al [*Kumar and Sarin*, 2009; *Rastogi and Sarin*, 2006; *Yadav and Rajamani*, 2004].

Several studies have documented the uptake of anthropogenic species (eg: nss-SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>) by Ca-rich mineral aerosols during the long-range transport [*Rastogi and Sarin*, 2006; *Saliba and Chamseddine*, 2012; *Wolf*, 1984]. The chemical uptake of acidic species enhances the solubility of Ca-rich minerals such as carbonates, apatite (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>), represented by following equations; and, hence, mineral dust is considered as a significant source of P<sub>Inorg</sub> from ambient aerosols.

$$Ca_{3}(PO_{4})_{2} + H_{2}SO_{4} \rightarrow CaSO_{4} + H_{3}PO_{4}$$
$$Ca_{3}(PO_{4}) + HNO_{3} \rightarrow Ca(NO_{3})_{2} + H_{3}PO_{4}$$

Therefore, the observed linear relation between nss-Ca<sup>2+</sup> and P<sub>Inorg</sub> during March-April'06 (Figure 5.3a) over the Bay of Bengal is attributed to their common source (as evident from the AMBTs originating from the Thar Desert; Figure 5.1). In contrast, relatively high concentrations of P<sub>Inorg</sub> associated with extremely low concentrations of Ca<sup>2+</sup> during January'09 (Figure 5.3a), suggest the dominance of anthropogenic sources (biomass burning emissions and use of fertilizers).

## 5.2.4. P<sub>Inorg</sub> over Arabian Sea

The concentration of  $P_{Inorg}$  in aerosol samples collected from the Arabian Sea during April-May'06 (Cruise SK-223B), varied from 0.2 to 0.5 nmol m<sup>-3</sup> (Av:  $0.3 \pm 0.1$  nmol m<sup>-3</sup>). This concentration is significantly lower than that observed over the Bay of Bengal, which is dominated by anthropogenic sources and acid processing of mineral dust (Figure 5.3a). A significant difference in the P<sub>Inorg</sub>/nss-

Ca<sup>2+</sup> ratio in aerosols over the Arabian Sea and Bay of Bengal is noteworthy (Table 5.2). The P<sub>Inorg</sub>/nss-Ca<sup>2+</sup> ratio varied from 0.01 – 0.11 (Av: 0.03 ± 0.02) over the Arabian Sea during April-May'06. In contrast, P<sub>Inorg</sub>/nss-Ca<sup>2+</sup> ratio averages around 0.09 ± 0.05 (range: 0.04 – 0.23) over the Bay of Bengal during March-April'06, and the ratio is one order of magnitude higher (Av: 0.54 ± 0.54, range: 0.12 – 2.4) during January'09 (Table 5.2). Relatively high P<sub>Inorg</sub>/nss-Ca<sup>2+</sup> ratio over the Bay of Bengal during January'09 is attributed to the enhanced supply of P<sub>Inorg</sub> from fertilizers and biomass burning emissions with relatively low Ca<sup>2+</sup> content. The reactive uptake of acidic species (nss-SO<sub>4</sub><sup>2-</sup>) by mineral dust is also evident from the mass ratio of water-soluble Ca<sup>2+</sup> to total aerosol Ca (Figure 5.2b) varying from 0.63 to 1.05 (Av: 0.95 ± 0.14); with average nss-Ca<sup>2+</sup>/Ca<sup>2+</sup> ratio centering on 0.89 ± 0.12 (Table 5.2). However, abundance of nss-SO<sub>4</sub><sup>2-</sup> in the MABL of Arabian Sea is significantly lower than that over the Bay of Bengal (Figure 5.2a).

## 5.2.5. Anthropogenic source of P<sub>Inorg</sub> vis-à-vis mineral dust

A characteristic high abundances of anthropogenic constituents (nss-K<sup>+</sup> and  $nss-SO_4^{2-}$ ) within the MABL of Bay of Bengal, during January'09, are evident based on relatively high ratios of  $nss-SO_4^{2-}/nss-Ca^{2+}$  (Figure 5.3a) and  $nss-K^+/nss-$ Ca<sup>2+</sup>(Figure 5.4b). These characteristic ratios in January'09 over the Bay of Bengal are relatively high compared to those observed during March-April'06 and over the Arabian Sea (April-May'06). The difference in the slopes of the regression lines (Figure 5.3a and Figure 5.4b) reflect the seasonal variability in the chemical composition of aerosols associated with the outflow from the Indo-Gangetic Plain (from December to February) and from Desert regions during March-May. Also, a statistical test has been performed in order to ascertain differences in the ratios of  $nss-K^+/nss-Ca^{2+}$ ,  $nss-SO_4^{2-}/nss-Ca^{2+}$  and  $P_{Inorg}/nss-Ca^{2+}$  for the data from January'09, March-April'06 (Bay of Bengal); April-May'06 (Arabian Sea). ANOVA analyses (along with post-hoc's test) suggest that PInorg concentration and ionic ratios (nss-K<sup>+</sup>/nss-Ca<sup>2+</sup>, nss-SO<sub>4</sub><sup>2-</sup>/nss-Ca<sup>2+</sup> and P<sub>Inorg</sub>/nss-Ca<sup>2+</sup>) are significantly different (P < 0.05) for seasonal data from all cruises (January'09, March-April'06 and April-May'06). A significant difference is evident between P<sub>lnorg</sub>/nss-Ca<sup>2+</sup> for winter (January'09) and spring-intermonsoon (March-April'06,

April-May'06) cruises [F (2, 71) = 15.782, P-value < 0.05]. Likewise, significant difference (P-value < 0.05) is observed for nss-K<sup>+</sup>/nss-Ca<sup>2+</sup> [F(2,71) = 11.56; P < 0.05) and nss-SO<sub>4</sub><sup>2-</sup>/nss-Ca<sup>2+</sup> [F(2, 71) = 50.6; P < 0.05] (Table 5.2, data from January'09, March-April'06 and April-May'06).



Figure 5.4: Scatter plots: (a) nss-Ca<sup>2+</sup> versus  $P_{Inorg}$ . Data plotted with symbol ( $\checkmark$ ) provides evidence for the acid processing of mineral dust. The dotted line plotted through symbol ( $\bigcirc$ ) with high  $P_{Inorg}/nss-Ca^{2+}$  ratio, exhibits steep slope, suggesting dominant supply of  $P_{Inorg}$  from anthropogenic sources. For comparison, data from the Arabian Sea ( $\blacksquare$ ), with high abundance of dust represents exceptionally lower  $P_{Inorg}/nss-Ca^{2+}$  ratios. Likewise, scatter plot in Figure 5.3b between nss-Ca<sup>2+</sup> and nss-K<sup>+</sup> exhibits similar slope and variability as in Figure 5.3a, with higher abundance of nss-K<sup>+</sup> (relative to nss-Ca<sup>2+</sup>) during January'09 compared to March-April'06 (BoB) and April-May'06 (ARS).

The relatively high concentrations of anthropogenic constituents (nss- $SO_4^{2-}$ & nss-K<sup>+</sup>) together with the low abundance of nss-Ca<sup>2+</sup> within the MABL of Bay of Bengal, during the winter time (January-March), is a characteristic feature of the outflow from the Indo-Gangetic Plain [*Kumar et al.*, 2010; *Sarin et al.*, 2011; *Srinivas et al.*, 2011a]. The high ratios of nss-SO<sub>4</sub><sup>2-</sup>/nss-Ca<sup>2+</sup>, nss-K<sup>+</sup>/nss-Ca<sup>2+</sup> and P<sub>Inorg</sub>/nss-Ca<sup>2+</sup> during January'09 (Table 5.2) are attributed to dominance of pollution sources. In contrast, the relative decrease in the source strength of the continental outflow during the spring-intermonsoon (March-April), together with higher abundance of water soluble Ca<sup>2+</sup>, is a dominant cause for the low ratios of nss-SO<sub>4</sub><sup>2-</sup>/nss-Ca<sup>2+</sup>, nss-K<sup>+</sup>/nss-Ca<sup>2+</sup> and P<sub>Inorg</sub>/nss-Ca<sup>2+</sup>, nss-K<sup>+</sup>/nss-Ca<sup>2+</sup>, is a dominant cause for the low ratios of nss-SO<sub>4</sub><sup>2-</sup>/nss-Ca<sup>2+</sup>, nss-K<sup>+</sup>/nss-Ca<sup>2+</sup> and P<sub>Inorg</sub>/nss-Ca<sup>2+</sup>, nss-K<sup>+</sup>/nss-Ca<sup>2+</sup> and P<sub>Inorg</sub>/nss-Ca<sup>2+</sup>, nss-K<sup>+</sup>/nss-Ca<sup>2+</sup> and P<sub>Inorg</sub>/nss-Ca<sup>2+</sup> (Figure 5.3a, Figure 5.4a, Figure 5.4b). The high concentration of Ca<sup>2+</sup> mainly results from seasonal shift in

the source regions of mineral dust during March-April'06, as evident from the AMBTs which originates from the Thar Desert. The enhanced solubility of aerosol Ca and the linear relation of  $P_{Inorg}$  with nss-Ca<sup>2+</sup> during March-April'06, suggest that significant fraction of water soluble inorganic P is derived from the chemical processing of mineral dust.

The mass concentration of  $P_{Inorg}$  in the MABL of Bay of Bengal is significantly higher than that derived from the mineral dust as its only source. A significant linear-relationship of  $P_{Inorg}$  and nss-K<sup>+</sup> (p-value< 0.05) suggests their common anthropogenic source from fertilizers and/or biomass burning emissions. A recent study by Singh and Singh [2008], has shown significant increase in the use of fertilizers (rich in N, P and K) in the Indo-Gangetic Plain during the past few decades. Therefore, atmospheric transport of dust from disturbed soils and agricultural fields could serve as a dominant source of  $P_{Inorg}$ . Furthermore, biomass burning emissions (burning of agricultural crop-waste residue) has been suggested as a significant source of aerosol-P, similar to aerosol-K<sup>+</sup> [*Izquierdo et al.*, 2012; *Mahowald et al.*, 2008 and references therein; *Mahowald et al.*, 2005a]. Thus, a linear correlation between nss-K<sup>+</sup> and P<sub>Inorg</sub> is attributed to their contribution from both biomass burning emissions and fertilizers.

The P<sub>Inorg</sub>/EC ratio in the fine mode aerosols (P<sub>Inorg</sub>) over the Bay of Bengal, during January'09, averages about  $0.003 \pm 0.002$  (also evident from the slope of regression line between EC and P<sub>Inorg</sub>; m = 0.001; R<sup>2</sup> = 0.54; Figure not shown in this manuscript). A similar ratio of P<sub>Inorg</sub> to BC (0.0029± 0.0001) has been reported for the biomass burning emissions over the Amazonian region [*Mahowald et al.*, 2008]. Therefore, significant contribution of K<sup>+</sup> and P<sub>Inorg</sub> from fertilizers associated with the large-scale agricultural activity and biomass burning emissions (crop-waste residue burning) in the Indo-Gangetic Plain can explain their higher abundances over the Bay of Bengal during the continental outflow.

The phosphorous contribution from dust ( $P_{Dust}$ ) is subtracted from the total  $P_{Inorg}$  in order to obtain the anthropogenic component ( $P_{Anth}$ ). In Figure 5.4a, three distinct relationships among  $P_{Inorg}$  and nss-Ca<sup>2+</sup> are identified. The line with steep slope (high  $P_{Inorg}$  and low nss-Ca<sup>2+</sup>) is dominated by the anthropogenic phosphorous ( $P_{Anth}$ ). The line with flat slope (Figure 5.4a; low  $P_{Inorg}$  and high nss-

 $Ca^{2+}$ ) for the Arabian Sea is dominated mainly by  $P_{Inorg}$  derived from the mineral dust. The 3<sup>rd</sup> relationship with an intermediate slope for the data from the Bay of Bengal (during March-April'06) is dictated by varying contribution from dust and anthropogenic sources.

In this study,  $P_{Dust}$  concentrations were estimated by multiplying P/Al ratio of 0.008 [from the revised composition of Upper Continental Crust (UCC); [*McLennan*, 2001]; P = 700 ppm; Al = 8.04 %] with the measured Al concentration in aerosol samples. In this calculation, it is assumed that Al is solely derived from the Continental Crust. A ratio of 0.012 for P/Al has been suggested for Saharan dust by Guieu et al., [2002]. Similarly, Herut et al., [1999] had suggested a ratio of about 0.011 for the Saharan aerosols. However, there are no available data for dust composition from the Thar Desert. For this study, P/Al ratio of UCC from Taylor and McLennan [1985] subsequently revised by McLennan, [2001] has been used to estimate the P<sub>Dust</sub>. The mass concentrations of P<sub>Inorg</sub>, P<sub>Dust</sub>, P<sub>Anth</sub> and the corresponding ratios of P<sub>Dust</sub>/P<sub>Inorg</sub>, P<sub>Anth</sub>/P<sub>Inorg</sub> and P<sub>Inorg</sub>/nss-Ca<sup>2+</sup> within the MABL of Bay of Bengal and Arabian Sea are summarized in Table 5.2. Over the Bay of Bengal, P<sub>Anth</sub> contributes significantly, varying from 61–94 % (Av: 77 ± 10 %) during March-April'06 and from 24 – 96 % (Av. 76 ± 18%) during January'09.

It is implicit in this approach that mobilization of  $P_{Inorg}$  by acid processing of mineral dust is also a part of  $P_{Anth}$ . In contrast,  $P_{Inorg}$  over the Arabian Sea is mainly dominated by Desert dust ( $P_{Dust} = ~70\%$ ). The spatio-temporal variability of percentage contribution of  $P_{anth}/P_{Inorg}$  to the study region is depicted in Figure 5.5. From this Figure , it is inferred that the contribution of  $P_{Inorg}$  from anthropogenic sources (viz., biomass burning emissions and fertilizers etc) dominates over the Bay of Bengal during the continental outflow.

## 5.2.6. Atmospheric dry-deposition of P<sub>Inorg</sub>

The dry-deposition flux of  $P_{Inorg}$  is estimated by using the following equation.

Dry-deposition flux,  $F_{dry} = V_{dry} * C_{meas}$ 

Here,  $V_{dry}$  and  $C_{meas}$  refer to the dry-deposition velocity and the measured mass concentration respectively. For the flux computation, 2.0 cm s<sup>-1</sup> is used as a

deposition velocity to estimate the dry flux. A similar dry-deposition velocity has been used by several studies reported in the literature to estimate deposition fluxes [*Baker et al.*, 2006b; *Chen et al.*, 2006; *Chen et al.*, 2007; *Duce et al.*, 1991; *Herut et al.*, 1999a; *Markaki et al.*, 2003]. Based on experimental data and modelled results, deposition velocity of 0.1 and 2.0 cm s<sup>-1</sup> has been suggested for fine and coarse mode aerosols by Spokes [2000]. Due to the dominant occurrence of P<sub>Inorg</sub> in PM<sub>10</sub> (as evident from the mass ratio of PM<sub>2.5</sub>/PM<sub>10</sub>, Av: 0.25) suggest its association in the coarse mode. Therefore, V<sub>d</sub> of 2.0 cm s<sup>-1</sup> is used for estimating the deposition flux in this study.

The dry-deposition flux of  $P_{Inorg}$  to the Bay of Bengal ranges from 1.1-3.6 (Av:1.9 ± 0.6) µmol-P m<sup>-2</sup> d<sup>-1</sup> during March-April'06 and from 0.5 - 4.8 (Av: 2.3 ± 0.9) µmol-P m<sup>-2</sup> d<sup>-1</sup> during January'09 (assuming dry-deposition velocity of  $P_{Inorg}$  as 2.0 cm s<sup>-1</sup>); whereas to the Arabian Sea it varies from 0.3 - 0.9 (Av: 0.6 ± 0.2) µmol-P m<sup>-2</sup> d<sup>-1</sup> during April-May'06. These fluxes have been compared with the model based estimates [*Mahowald et al.*, 2008; *Okin et al.*, 2011]. The atmospheric deposition of  $P_{Inorg}$  to the Bay of Bengal (this study) is ~ 0.022 Tg-P yr-1 (0.024 for January'09 and 0.019 Tg-P yr<sup>-1</sup> for March-April'06) and to the Arabian Sea is ~0.014 Tg-P yr<sup>-1</sup> for April-May'06 (Area of BoB and ARS are taken as 2.2\*10<sup>12</sup> m<sup>2</sup> and 4.93\*10<sup>12</sup> m<sup>2</sup>, respectively; and dry-deposition is integrated only for 150 days when continental outflow is dominant). Thus, the total dry-deposition flux of  $P_{Inorg}$  (~0.036 Tg-P yr<sup>-1</sup>) over these two oceanic regions can be considered as representative of the annual deposition of  $P_{Inorg}$  to the Northern Indian Ocean (NIO).



Figure 5.5: Fractional contribution of anthropogenic water-soluble inorganic phosphorous ( $P_{Anth}$ ) towards  $P_{Inorg}$  over the Bay of Bengal and the Arabian Sea

A comparison of dry-deposition of  $P_{\text{Inorg}}$  to the Northern Indian Ocean (this study) with the model based estimates (reported in the literature) is presented in Table 5.3. Furthermore, comparison is also made between the Northern Indian Ocean with that of other oceanic regions. These estimates are of comparable magnitude with the model based results for the Northern Indian Ocean (0.04 Tg-P yr<sup>-1</sup> by [*Okin et al.*, 2011] and 0.014 Tg-P yr<sup>-1</sup> by [*Mahowald et al.*, 2008]).

Reference	N-Indian Ocean	N-Atlantic	N-Pacific		
This study	0.036	-	-		
<sup>\$</sup> Duce et al., [1991]	0.070	0.154	0.336		
<sup>\$</sup> Prospero et al., [1996]	0.014	0.154	0.067		
<sup>\$</sup> Ginoux et al., [2001]	0.097	0.123	0.064		
Zender et al., [2003]	0.040	0.190	0.030		
<sup>s</sup> Luo et al., [2003]	0.079	0.161	0.025		
<sup>\$</sup> Tegen et al., [2004]	0.043	0.181	0.039		
<sup>§</sup> Jickells et al.,[2005]	0.083	0.141	0.050		
Mahowald et al., [2008]	0.014	0.028	0.022		
Okin et al., [2011]	0.043	0.020	0.026		
\$ P <sub>Inorg</sub> is estimated from the abundance of mineral dust and P concentration in UCC					

Table 5.3: Comparison of  $P_{Inorg}$  Fluxes (Tg yr<sup>-1</sup>) from the North Indian Ocean with other oceanic regions (viz., Atlantic and Pacific).

#### 5.2.7: Comparison with Riverine Supply

The global riverine input of  $P_{Inorg}$  via major rivers is about 0.8 - 1.4 Tg-P yr<sup>-1</sup> [*Compton et al.*, 2000 ] and the fresh water influx from the global rivers is about 37.4 \* 10<sup>12</sup> m<sup>3</sup> yr<sup>-1</sup> [*Kumar et al.*, 1996; *Martin and Whitfield*, 1983]. It has been reported that Bay receives approximately 1.625 \* 10<sup>12</sup> m<sup>3</sup> yr<sup>-1</sup> of freshwater [*Prasanna Kumar et al.*, 2004; *Sarin et al.*, 1990]. Thus, the riverine input of P<sub>Inorg</sub> to the BoB is estimated to be 35 - 61 Gg-P yr<sup>-1</sup>. Since, P<sub>Inorg</sub> abundance is relatively high during January'09 compared to that in March-April'06 (Spring-intermonsoon), it is relevant to compare the atmospheric input with the riverine supply in order to estimate the maximum contribution via air-sea deposition to the Bay of Bengal. The concentration of P<sub>Inorg</sub> in MABL of the Bay of Bengal, during January'09, ranged from 0.32 – 2.76 nmol m<sup>-3</sup>. Therefore, dry-deposition of P<sub>Inorg</sub> to the BoB ranges from 0.5 - 4.8 µmol-P m<sup>-2</sup> d<sup>-1</sup> (5 - 50 Gg-P yr<sup>-1</sup>). A comparison

of these estimates suggests that the atmospheric deposition of  $P_{Inorg}$  is of comparable magnitude to its supply via rivers; and that atmosphere is a significant source of  $P_{Inorg}$  to surface waters of the Bay of Bengal.

### 5.3. Conclusion and implications

The spatio-temporal variability in the concentration of water-soluble inorganic phosphorous (P<sub>Inorg</sub>) has been studied over the Bay of Bengal and the Arabian Sea during the continental outflow (January-April). This study provides the first field-evidence for the acid processing of mineral dust during atmospheric transport and, hence, enhanced solubility of PInorg. Therefore, it has been suggested that high concentrations of sulphate, persisting in the continental outflow from the Indo-Gangetic Plain, provides most conducive environment for acid mobilization of phosphorous (and other nutrients) from dust-laden air masses. Nevertheless, contribution from anthropogenic sources (fertilizers and biomass burning emissions) is overwhelming and account for nearly 75 % of P<sub>Inorg</sub>. In contrast, P<sub>Inorg</sub> concentrations are 4 to 5 times lower over the Arabian Sea and anthropogenic fraction contributes no more than  $\sim 30$  % of P<sub>Inorg</sub>. The atmospheric dry-deposition of phosphorous (0.4-3.8 Gmol-P yr<sup>-1</sup>) is comparable to its supply via rivers (1.1-2.0 Gmol-P yr<sup>-1</sup>) draining into the Bay of Bengal. In the present-day scenario of growing anthropogenic activities, these results have implications to significant impact on biogeochemistry of coastal waters downwind of pollution sources. Estimate of dry-deposition of P<sub>Inorg</sub> to the Northern Indian Ocean is of comparable magnitude with the model based results.

## Chapter 6

Impact of anthropogenic sources on aerosol iron solubility over the Bay of Bengal and the Arabian Sea

#### **6.1. Introduction**

Atmospheric deposition of mineral dust, considered as a major source of Fe to the open ocean, has potential to enhance the primary productivity; which in turn influences the atmospheric CO<sub>2</sub> budget and, hence, climate [*Duce and Tindale*, 1991; *Jickells et al.*, 2005; *Mahowald et al.*, 2009]. The atmospheric supply of Fe also has an impact on surface ocean biogeochemistry and on the production of dimethyl sulphide [*Cooper et al.*, 1996; *Jickells and Spokes*, 2001; *T. D. Jickells*, 2001; *Turner et al.*, 1996; *Zhuang et al.*, 1992b].

A number of studies carried out in high nutrient-low chlorophyll (HNLC) regions (Subarctic Pacific, Equatorial Pacific and Southern ocean) have highlighted the role of atmospheric deposition of mineral dust in mediating glacial-interglacial CO<sub>2</sub> changes and have emphasized the need to understand the atmospheric transport and deposition of soluble Fe to open ocean [*Boyd et al.*, 2000; *Boyd*, 2000 ; *Coale et al.*, 1996; *Jickells et al.*, 2005; *Mahowald et al.*, 2009; *Martin and Fitzwater*, 1988; *Martin*, 1990]. In this context, modelling approaches have suggested the transport of mineral dust from semi-arid and arid regions of the world as the dominant source of soluble iron to the open ocean [*Luo et al.*, 2005; *Mahowald et al.*, 2005b].

Studies on the solubility of mineral dust suggest that, in general, the fractional solubility of Fe is very poor, less than ~ 1 % [*Jickells and Spokes*, 2001]. Recently, aerosols collected over the remote north Pacific Ocean show enhanced Fe-solubility compared to that from the source regions of mineral dust [*Zhuang et al.*, 1992b]. This variation in solubility has been explained as the uptake of acidic anthropogenic species by mineral aerosols during transport. However, particle-size and concentration of mineral dust, mineralogy, presence of organic compounds and solar irradiation can also play a vital role in Fesolubility [*Zhuang et al.*, 1992b]. More recently, the importance of combustion sources (biomass-burning and fossil-fuel combustion) has been suggested as a potential source of soluble iron [*Chuang et al.*, 2005; *Guieu et al.*, 2005; *Kumar and Sarin*, 2010; *Kumar et al.*, 2010; *Luo et al.*, 2008; *Schroth et al.*, 2009]. Although meteoritic debris (cosmic dust) and volcanic ash have been considered as a significant contributor of Fe to seawater, these estimates are not well

constrained due to their episodic fallout nature. These observations stress the need for regional scale studies on the control for iron solubility in ambient aerosols.

This manuscript addresses the issue of fractional solubility of aerosol-Fe over the Bay of Bengal and the Arabian Sea. Based on the optical and chemical properties of aerosols, it has been demonstrated that marine atmospheric boundary layer (MABL) of the northern Indian Ocean is significantly influenced by the continental outflow from the south and south-east Asia during winter and spring seasons [*Lelieveld et al.*, 2001; *Ramanathan et al.*, 2001a]. Therefore, these two oceanic regions provide an ideal location to study the impact of continental outflow on fractional solubility of aerosol-Fe from mineral dust entering the MABL.

#### 6.2. Results and discussion

#### 6.2.1. Aerosol iron solubility

The mass concentration of total aerosol iron (Fe<sub>Tot</sub>) in the MABL of Bay of Bengal (BoB) and the Arabian Sea (ARS) during the study period (Table 6.1), overlap within the spread of the data (BoB, range: 31 -1651 ng m<sup>-3</sup>; ARS, range: 92 -1010 ng m<sup>-3</sup>). However, the fractional solubility of aerosol iron (Fe<sub>ws</sub> %) is significantly different over ARS (0.02 - 0.4 %) and BoB (1.4 – 24.0 %). Table 6.1 presents the concentrations of total aerosol Fe (Fe<sub>Tot</sub>) and fractional solubility of aerosol iron (Fe<sub>ws</sub> %) for the two study regions. The significant difference in Fe<sub>ws</sub> (%) between the two oceanic regions is attributed to differences in the chemical characteristics of mineral dust. The Arabian Sea receives coarse dust from the surrounding desert regions (Saharan and Arab Deserts on the western side, Thar Desert on the eastern side), whereas transport of fine alluvial dust from the Indo-Gangetic Plain is a dominant source to the Bay of Bengal.

The mineralogical composition of soils adjoining the Thar Desert, situated in the north-western part of India, suggests that quartz is the most abundant mineral followed by K-feldspar, mica, calcite, chlorite and plagioclase [*Yadav and Rajamani*, 2004]. In addition, some heavy minerals (garnet, amphibole, titanite and zircon) have also been identified. In contrast, the Indo-Gangetic Plain is characterized by alluvial soils (in the flood plains of major rivers), mostly granitic in nature with 84-85 % quartz, 8-11 % of feldspars and 4-7 % of mica [*Tripathi et al.*, 2007].

Despite the mineralogical differences, physical size of the mineral dust is responsible for the high Fe<sub>ws</sub> (%) over the Bay of Bengal. Based on the chemical characterization of aerosols, earlier studies [*Kumar et al.*, 2008a; *Kumar et al.*, 2008b; *Lelieveld et al.*, 2001; *Sudheer and Sarin*, 2008] have highlighted the impact of continental outflow on the MABL of the Bay of Bengal during late NEmonsoon (January-April). In addition, during long-range transport, atmospheric processing of mineral dust by anthropogenic acidic species (HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) can enhance the fractional solubility of aerosol iron [*Meskhidze et al.*, 2003; *Solmon et al.*, 2009]. The enhanced fractional solubility of aerosol-Fe over the Bay of Bengal, as compared to that over the Arabian Sea, can also be attributed to the chemical processing of fine alluvial dust. In PM<sub>10</sub>, Fe<sub>Tot</sub> and Fe<sub>ws</sub> show pronounced and similar temporal variability, suggesting a common source.

The scatter plot of mass concentrations of  $Fe_{Tot}$  and  $Fe_{ws}$  in PM<sub>2.5</sub> against PM<sub>10</sub> suggests the coarse mode nature of  $Fe_{Tot}$  and fine mode existence of  $Fe_{ws}$  (Figure 6.1). Furthermore, both  $Fe_{ws}$  and  $Fe_{Tot}$  show spatial variability with systematically high concentrations over N-BoB compared to that over S-BoB. The relatively high concentrations of  $Fe_{Tot}$ ,  $Fe_{ws}$  are consistent with the high aerosol loading over N-BoB due to closer proximity of the continental sources. The relatively low fractional solubility of aerosol iron (Fe<sub>ws</sub> %) over the Arabian Sea is consistent with earlier studies Siefert et al., [1999]. In the coarse mode (>3µm) aerosols over the Arabian Sea, Siefert et al. [1999] have shown that the contribution of Fe(II) to total aerosol iron (Fe<sub>Tot</sub>) is no more than 2 % during spring-intermonsoon (May-1995).

The low iron solubility over the Arabian Sea, as documented in the present study, can be explained due to lack of atmospheric processing of coarser desert dust (quartz as the abundant mineral) with anthropogenic acidic species. Furthermore, acid mobilization of iron from mineral aerosols is not favoured due to relatively high abundance of mineral dust enriched in Ca. It has been reported that CaCO<sub>3</sub> is the major neutralizing constituent over the Arabian Sea [*Kumar et al.*, 2008a; *Kumar et al.*, 2008b].

Ara	abian S	ea	Bay of Bengal					
<sup>@</sup> TSP (N = 19, April-May 2006)			<sup>@</sup> TSP (N = 23, March-April 2006)			PM <sub>10</sub> (N = 33, January'09)		
Sample id	<sup>\$</sup> Fe <sub>Tot</sub>	Fews %)	Sample id	<sup>\$</sup> Fe <sub>Tot</sub>	Fews (%)	Sample id	<sup>S</sup> Fe <sub>Tot</sub>	Fe <sub>ws</sub> (%)
AS-501	1010	0.05	AS-402	807	5.3	AS-802	909	7.6
AS-503	976	0.02	AS-403	1116	4.3	AS-804	667	5.8
AS-504	648	0.08	AS-405	799	6.2	AS-806	430	6.8
AS-506	315	0.04	AS-406	938	4.3	AS-808	773	4.3
AS-507	364	0.11	AS-408	1010	6.6	AS-810	1317	6.0
AS-508	381	0.03	AS-409	1221	4.2	AS-812	1651	3.6
AS-510	434	0.09	AS-410	946	7.0	AS-814	1649	3.3
AS-511	450	0.02	AS-412	706	3.2	AS-816	493	2.5
AS-512	953	0.04	AS-413	546	3.8	AS-818	198	4.7
AS-513	452	0.22	AS-414	600	3.8	AS-820	127	9.4
AS-517	232	0.04	AS-416	421	12.0	AS-822	254	6.9
AS-518	92	0.43	AS-417	420	7.2	AS-824	1270	6.2
AS-520	327	0.08	AS-418	272	6.8	AS-826	898	7.3
AS-521	298	0.12	AS-420	242	5.6	AS-828	461	1.4
AS-522	255	0.03	AS-421	245	13.6	AS-830	213	5.2
AS-524	153	0.03	AS-422	668	2.9	AS-832	339	7.5
AS-525	296	0.19	AS-424	184	5.2	AS-834	382	14.6
AS-527	432	0.07	AS-425	150	11.1	AS-836	355	8.6
AS-528	372	0.02	AS-426	309	13.1	AS-838	329	5.7
			AS-428	294	3.5	AS-840	306	12.7
			AS-429	527	2.6	AS-842	260	9.3
			AS-430	547	2.3	AS-844	254	7.1
			AS-431	595	2.6	AS-846	230	10.4
						AS-848	31	3.2
						AS-850	95	23.9
						AS-852	210	11.9
						AS-854	196	3.5
						AS-856	220	2.7
						AS-858	169	6.9
						AS-860	96	6.6
						AS-862	113	3.1
						AS-863	159	5.2
						AS-864	91	3.5

Table 6.1: Aerosol iron and its fractional solubility over the Arabian Sea and the Bay of Bengal

\$ Concentration (ng m<sup>-3</sup>).  $Fe_{ws}$ %: fractional solubility of total aerosol-Fe (Fe<sub>Tot</sub>) defined as  $Fe_{ws}/Fe_{Tot}$ \*100 and  $Fe_{ws}$  is water soluble Fe; @ FeTot is obtained from Kumar et al., (2008b).

#### 6.2.2. Evidence for chemical processing of mineral dust

The fractional solubility of aerosol iron (Fe<sub>ws</sub> %) in PM<sub>10</sub>, during January'09, varied from 1.4 to 9.4 % and 2.7 to 23.9 % over N-BoB and S-BoB, respectively. In addition, results from this study show a linear relationship between Fe<sub>ws</sub> (%) and Fe<sub>Tot</sub> ( $R^2 = 0.40$ ; n = 17; p-value = 0.006) and nss-SO<sub>4</sub><sup>2-</sup> ( $R^2 = 0.53$ ; n = 17; p-value = 0.001; Figure 6.5) over S-BoB, suggesting the role of acid uptake by mineral aerosols in enhancing the fractional solubility of aerosol iron. Note that one outlier (aerosol sample collected on 20<sup>th</sup> January'09) was excluded from this analysis. In contrast, no such significant correlation is evident for the chemical data from N-BoB (Figure 6.5).

This would constrain the availability of acidic species (H<sub>2</sub>SO<sub>4</sub>) to mobilize iron from mineral dust. The total aerosol iron (Fe<sub>Tot</sub>) and water soluble iron (Fe<sub>ws</sub>) over the Arabian Sea and the Bay of Bengal are plotted on a logarithmic scale with 0.01 %, 1 %, 5 %, 10 %, 25 % and 50 % solubility (Figure 6.4). This plot shows that the solubility over the Arabian Sea and the Bay of Bengal is in the range of 0.01 to 1% and 1 to 50 %, respectively. The linear relationship over S-BoB can therefore be explained in terms of mixing state of aerosols.



Figure 6.1: Scatter plots for aerosol-iron ( $Fe_{Tot}$ ) and water soluble iron ( $Fe_{ws}$ ) indicating their relative distribution in  $PM_{2.5}$  and  $PM_{10}$  over the Bay of Bengal (January'09). Close and open circles represent samples collected from N-BoB and S-BoB respectively.



Figure 6.2: Total aerosol-Fe ( $Fe_{Tot}$ ) and water soluble-Fe ( $Fe_{ws}$ ), over the Arabian Sea (ARS) and the Bay of Bengal (BoB), on logarithmic scale with 0.01, 0.1, 1, 5, 10, 25 and 50 percent solubility lines.

Although direct information on the mixing state of aerosols over the Bay of Bengal is not available from our field campaign, it has been suggested that the extent of internal mixing is enhanced with the aging of aerosol population [*Baker and Croot*, 2010]. The aging of aerosols can be invoked for the air-masses associated with the outflow from south-east Asia (Figure 6.2). This hypothesis is further supported by the average equivalent ratio of  $(NH_4^+ + Ca^{2+})/nss-SO_4^{2-}$ , which is about  $0.86 \pm 0.23$  for N-BoB and  $0.43 \pm 0.26$  for S-BoB, suggesting relatively high acidity over S-BoB. Likewise, a significant linear relation between total acidity (TA = nss-SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>, in neq m<sup>-3</sup>) and Fe<sub>ws</sub> % (R<sup>2</sup> = 0.40; n = 17; p-value < 0.001) over S-BoB provides further support to the hypothesis that acid processing of mineral dust would enhance the fractional solubility of aerosol iron. It is noteworthy that the mass concentration of mineral dust was relatively high

over N-BoB owing to the close proximity of continental sources. The contribution of Fe from anthropogenic combustion sources is not expected to be significant in  $PM_{10}$  mass fraction. This is also evident from the data that  $PM_{10}$  contains 65 % of  $PM_{2.5}$  mass. Therefore, in order to investigate the fractional solubility of aerosol iron, Fe<sub>ws</sub> in PM<sub>2.5</sub> samples has been measured during January'09. In PM<sub>2.5</sub>, the fractional solubility of aerosol iron (Fe<sub>ws</sub> %) varied from 3.5 to 49.7 % over BoB. It is noteworthy that the solubility in the fine (PM<sub>2.5</sub>) mode approaches 50 %, emphasizing the dominant role of combustion sources in enhancing the fractional solubility of iron. Earlier studies have suggested that inter-relationship among soluble Fe, nss-K<sup>+</sup>, OC and EC in fine mode aerosols provide an evidence for their common source signature in the continental outflow [*Chuang et al.*, 2005; *Kumar et al.*, 2010; *Paris et al.*, 2010].

### 6.2.3. Evidence for biomass-burning source

In PM<sub>10</sub>, nss-K<sup>+</sup> contributes to ~3 % of the total water soluble ion concentration ( $\Sigma$ WSIC) and ranged from 0.1 – 1.3 (Avg = 0.60 ± 0.30) µg m<sup>-3</sup> during January'09 over BoB. Similarly, bulk aerosols collected from the MABL of the Bay during March-April'06 have concentration of nss-K<sup>+</sup> varying from 0.1 – 0.4 µg m<sup>-3</sup>. In contrast, the contribution of nss-K<sup>+</sup> to  $\Sigma$ WSIC is insignificant over Arabian Sea during April-May'06. The nss-K<sup>+</sup> is used as a diagnostic tracer of biomass burning, its concentration is reported to be high in biomass derived aerosols. Evidence for this is constrained in the emission of K<sup>+</sup> EC and OC during biomass-burning emissions [*Andreae*, 1983].

In addition to mineral aerosols, biomass burning is also identified as a potential source of soluble iron to sea water [*Guieu et al.*, 2005; *Paris et al.*, 2010]. In this study, the significant linear correlations between nss-K<sup>+</sup> and OC during March-April'06 ( $R^2 = 0.82$ ; n = 23; p-value < 0.01) and January'09 ( $R^2 = 0.85$ ; p-value < 0.001 for n = 33; Figure 6.3a) over the Bay of Bengal suggest a significant contribution of biomass burning. In addition, significant correlations between Fe<sub>ws</sub> and OC ( $R^2 = 0.63$ ; p-value < 0.001; n = 33) and nss-K<sup>+</sup> ( $R^2 = 0.61$ ; p-value < 0.001; n = 33; Figure 6.3b) during January'09 further supports biomass burning emissions as a possible source of soluble iron. Similar evidence is also reflected for the analytical data from March-April'06.

In PM<sub>2.5</sub> and PM<sub>10</sub> size fractions, the nss-K<sup>+</sup>/Fe<sub>Tot</sub> concentration averages to 6.8  $\pm$  2.5 and 2.0  $\pm$  1.3, respectively. These values are significantly high compared to those reported for the upper continental crust (0.49; [*Wedepohl*, 1995]) and for the other oceanic regions (Mediterranean Sea: 0.63  $\pm$  0.12; Guieu et al., 2005). The biomass burning emissions from agricultural crop waste (rice & wheat straw), associated with the outflow from IGP, are responsible for the high nss-K<sup>+</sup> concentration and thus high nss-K<sup>+</sup>/Fe<sub>Tot</sub>.

Furthermore, rice straw contains nearly 65% of soluble K<sup>+</sup>, thus providing evidence for biomass burning as a potential source [Pal, 2009]. In contrast, nss-K<sup>+</sup>/Fe<sub>Tot</sub> in samples collected during March-April'06 is relatively low (average:  $0.39 \pm 0.11$ ) compared to the ones measured in January'09. The presence of high mineral dust during March-April'06 would also lead to low ratio of nss-K<sup>+</sup>/Fe<sub>Tot</sub>. Comparison of the data from the March-April'06 and January'09 cruises, suggest that the latter time period of the cruise is characterized by high concentrations of nss-K<sup>+</sup>, nss-SO<sub>4</sub><sup>2-</sup>, Fe<sub>ws</sub> and OC. The impact of biomass burning emissions is dominant during winter time in the Indo-Gangetic Plain and hence long-range transport of chemical constituents is important over the Bay of Bengal.



Figure 6.3: Scatter plot of (a)  $nss-K^+$  vs. OC (b)  $nss-K^+$  and  $Fe_{ws}$  in  $PM_{10}$  and  $PM_{2.5}$  samples collected over the Bay of Bengal during Januar'09 indicate that significant contribution of soluble iron is derived from biomass burning emissions.

The high  $Fe_{ws}$  (%) in PM<sub>2.5</sub> over the Bay of Bengal is associated with fine nature of dust, with high surface area to volume ratio together with mixing of acidic species. In addition, the contribution from biomass burning sources is discernible

based on linear relation among nss-K<sup>+</sup>, OC and Fe<sub>ws</sub>. Although, the magnitude of Fe<sub>ws</sub> from combustion sources (biomass-burning and fossil-fuel combustion) is not significant compared to that from mineral aerosols, the enhanced fractional solubility of aerosol iron (Fe<sub>ws</sub> %) is an important issue for the global models. The spatial variability in the fractional solubility of aerosol iron over the Bay of Bengal and the Arabian Sea is presented in Figure 6.4. These contours are generated using Ocean Data View software [*Schlitzer*, 2002] and are representative for the entire sampling period. This plot shows relatively low solubility of iron over the eastern Arabian Sea compared to that over western Arabian Sea.

A comparison of the fractional solubility of aerosol iron from different oceanic and continental regions is presented in Table 6.2. The fractional solubility of aerosol iron over the Bay of Bengal is relatively high compared to North Atlantic and Pacific Ocean. The atmospheric processing of mineral dust during long-range transport in the presence of high abundance of anthropogenic acidic species and contribution from combustion sources are likely factors governing the high fractional solubility of aerosol-Fe. In contrast, the fractional solubility over Arabian Sea is relatively low compared to the other oceanic regions.



Figure 6.4: Spatial variability of fractional solubility of aerosol iron ( $Fe_{ws}$  %) over the Bay of Bengal and the Arabian Sea

#### 6.2.4. Mixing model for fractional solubility

In PM<sub>2.5</sub>, the fractional solubility of aerosol iron varied from 3.5 to 21.2 % and 11.4 to 49.7 % over N-BoB and S-BoB, respectively. It is noteworthy that N-BoB is characterized by high aerosol iron (Fe<sub>Tot</sub>) concentration but low fractional solubility (Fe<sub>ws</sub> %), representing one end member with the contribution from
mineral dust. In contrast, aerosols over S-BoB are characterized by higher  $Fe_{ws}$  (%) associated with low concentration of aerosol iron ( $Fe_{Tot}$ ). The scatter plot (Figure 6.1) of  $Fe_{Tot}$  between  $PM_{2.5}$  and  $PM_{10}$  suggest the predominant existence of total aerosol iron in the coarse mode (i.e. contribution from mineral dust).



Figure 6.5: (a) Fractional solubility of aerosol iron ( $Fe_{ws}$  %) in  $PM_{2.5}$  and  $PM_{10}$  plotted against total aerosol-Fe ( $Fe_{Tot}$ ). Modeled data points (this study) and hyperbolic relationship (dash line) is obtained by a two end member mixing, (1) Dust: with high  $Fe_{Tot}$  with low  $Fe_{ws}$  %; and (2) Combustion sources: low  $Fe_{Tot}$  with high  $Fe_{ws}$  (%). (b) Linear increase of  $Fe_{ws}$  % with  $1/Fe_{Tot}$ further establishes that fractional solubility of aerosol-Fe can be explained by two end-member mixing (mineral dust and anthropogenic combustion sources).

The abundance of mineral dust in  $PM_{10}$  can account for 33 % of the average particulate mass concentration; whereas its contribution to  $PM_{2.5}$  is relatively low. Therefore, anthropogenic sources can contribute significantly to  $Fe_{Tot}$  in the fine mode. In this regard, the inverse relationship observed between  $Fe_{ws}$  (%) and  $Fe_{Tot}$  (Figure 6.5) can be explained by the mixing of the two end member (mineral dust and combustion sources). A similar inverse relationship has been used in the North Atlantic to explain the fractional solubility of aerosol iron ( $Fe_{ws}$  %), where advection of Saharan desert dust and air mass from North America contribute significantly to the particulate loading [*Sedwick et al.*, 2007]. Likewise, two end-member mixing approach has been used to explain the observed fractional solubility of aerosol-Fe from a high altitude site (Mt. Abu) in

Region	Туре	Duration	Fe <sub>Tot</sub>	Fe <sub>ws</sub>	Fe <sub>ws</sub> (%)	Reference
Bay of Bengal	PM <sub>2.5</sub>	Jan'09	98	16.9	23.4	Present study
Bay of Bengal	$PM_{10}$	Jan'09	459	27.4	6.9	Present study
Bay of Bengal	TSP	Mar-April'06	590	31.1	6.0	Present study
Arabian Sea	TSP	April-May'06	444	0.3	0.1	Present study
North Atlantic Ocean	TSP	July-Aug'03	653	-	1.4	[Sholkovitz et al., 2009b]
North Atlantic Ocean	TSP	April-June'04	49	-	11.6	[Sholkovitz et al., 2009b]
North Pacific Ocean	TSP	May-June'02	95	6.5	9.0	[Buck et al., 2006]
<sup>\$</sup> Mt.Abu (India)	PM <sub>2.5</sub>	Mar-May'07	431	4.6	1.7	Kumar and Sarin, 2010
<sup>§</sup> Mt.Abu (India)	PM <sub>2.5</sub>	Oct-Nov'07	150	11.0	8.0	Kumar and Sarin, 2010

Table 6.2: Comparison of fractional solubility of aerosol iron over the Ocenic regions and high altitude sites.

A continental site in western India-source region of mineral dust to Arabian Sea. Fe<sub>ws</sub> % = fractional solubility of total aerosol-Fe (Fe<sub>Tot</sub>) and Fe<sub>ws</sub> is the water-soluble iron.

western India [Kumar and Sarin, 2010].

A scatter plot and linear relation between  $1/\text{Fe}_{\text{Tot}}$  and  $\text{Fe}_{ws} \%$  (r = 0.66; p-value < 0.001; except for two outliers excluded for low PM<sub>10</sub> concentration  $\le 6 \ \mu\text{g}$  m<sup>-3</sup>), provide further support for the existence of two end members in the study area (see Figure 6.5). The mixing curve is generated by assuming that one end member is characterized by Fe<sub>Tot</sub> concentration of 1651 ng m<sup>-3</sup> with fractional solubility of 3.6 % (high Fe<sub>Tot</sub>, low Fe<sub>ws</sub> %; representative of dust) and other end member is characterized by 95 ng m<sup>-3</sup> with a solubility of 24.0 % (low Fe<sub>Tot</sub>, high Fe<sub>ws</sub> %, representative of combustion sources).

#### 6.3. Aerosol iron solubility in the IGP-outflow

It has been observed that the MABL of North Bay of Bengal (N-BoB) is influenced by the continental air masses that originate from the Indo-Gangetic Plain (IGP) during the cruise in January'09. Therefore, in order to investigate the role of chemical processing of mineral dust and anthropogenic combustion sources on aerosol iron solubility within the Indo-Gangetic Plain, the fractional solubility iron and other supporting chemical constituents (viz., nss-SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, nss-K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, EC and OC) have been studied in the fine mode (PM<sub>2.5</sub>) aerosols, collected from the IGP-outflow during 21<sup>st</sup> November'09 to 25<sup>th</sup> March'10.

# 6.3.1. Temporal variability

The mass concentrations of both the water soluble and total aerosol iron (Fe<sub>ws</sub> and Fe<sub>Tot</sub>) show pronounced temporal variability during the study period (Figure 6.6). This pattern is consistent with its particulate mass loading and hence reflected in the individual chemical species. The mass concentrations of mineral dust, Fe<sub>Tot</sub>, Fe<sub>ws</sub>, Fe<sub>ws</sub> (%), nss-SO<sub>4</sub><sup>2-</sup>, nss-K<sup>+</sup>, OC and EC over the sampling site, Kharagpur has been given in Table 6.3. During the study period, Fe<sub>ws</sub> mass concentration varied from 11.5 - 144.3 ng m<sup>-3</sup> (Avg ± stdev: 59.8 ± 39.5), whereas the total aerosol iron (Fe<sub>Tot</sub>) mass concentration ranged between 93 -1780 ng m<sup>-3</sup> (Avg ± stdev: 673 ± 355 ng m<sup>-3</sup>). The fractional solubility of aerosol iron [Fe<sub>ws</sub> (%) = Fe<sub>ws</sub>/Fe<sub>Tot</sub> \*100] varies from 4.3 -17.1 % (Avg ± stdev: 9.4 ± 3.2 %). It has been suggested that the PM<sub>2.5</sub> samples collected from the Bay of Bengal during January'09 is also influenced by the continental outflow from the IGP, as evident from the AMBTs [*Srinivas et al.*, 2011a]. Therefore, in order to relate the air

masses that are sampled from the Bay of Bengal during January'09 and from the receptor site (Kharagpur during the present study), comparison is made between the elemental ratios of Fe/Al and Ca/Al. Though, samples were not collected at the same time, it was assumed that continental outflow from the IGP during the late NE-monsoon has the same chemical composition, as it is also supported by the AMBT cluster (Chapter 3).

#### 6.3.2. Elemental ratios of crustal constituents

The mean elemental ratio of Fe/Al and Ca/Al is centered on  $0.51 \pm 0.22$  and  $0.21 \pm 0.03$  for the aerosols collected from the IGP-outflow (Kharagpur). During January'09, the mean elemental ratio of Fe/Al and Ca/Al over the northern Bay region averages about  $0.52 \pm 0.31$  and  $0.27 \pm 0.20$ . Table 6.4 presents the comparison of elemental ratios of Fe/Al and Ca/Al in the study region (Kharagpur, IGP) with that observed over the Bay of Bengal during January'09 in fine mode aerosols. From this comparison, it is clearly evident that the source for fine alluvial dust observed over the Bay region during January'09 is the Indo-Gangetic Plain. It is interesting to note that the elemental ratio of Ca/Al is relatively low compared to that from upper continental crustal value (0.35, [*Taylor and McLennan*, 1985]). In contrast, the elemental ratio of Fe/Al has shown enrichment compared to that of crustal value (0.44, [*Taylor and McLennan*, 1985]). This observation emphasizes the characteristic nature of the mineral dust within the IGP.

#### 6.3.3. Evidence for the chemical processing of alluvial dust

A significant co-variability is observed between the mass concentrations of mineral dust (estimated based on the measured Al concentration and Al comprises 8.04 % of the mineral dust),  $Fe_{Tot}$  and  $Fe_{ws}$  (Figure 6.6). Likewise, the fractional solubility of aerosol iron ( $Fe_{ws}$  %) is mimicking the temporal abundance pattern of nss-SO<sub>4</sub><sup>2-</sup> (Figure 6.6; also further confirmed by 3 point moving average, Figure not shown here). It is discernible from the Figure 6.2 that variability of nss-SO<sub>4</sub><sup>2</sup> and  $Fe_{ws}$  (%) are in phase. This hints the chemical processing of alluvial fine dust during the late NE-monsoon season by acidic species ( $H_2SO_4$ ) in the atmosphere. The role of acid processing on aerosol iron solubility has been assessed by a recent study based on the prevalent linear relation between  $nss-SO_4^{2-}$  and  $Fe_{ws}$  (%) in PM<sub>2.5</sub> and PM<sub>10</sub> samples, collected from the MABL of BoB during January'09 [*Kumar et al.*, 2010; *Srinivas et al.*, 2011a].

As mentioned earlier, during January'09, AMBTs computed for the sampling dates suggests the influence of continental air-masses from the IGP on the MABL of Bay of Bengal. Albeit, no such significant linear relation between nss- $SO_4^{2-}$  and Fe<sub>ws</sub> (%) is evident (due to more scatter), the co-variability between these parameters signifies the potential role of chemical processing of alluvial dust from the Indo-Gangetic Plain which enters into the Bay of Bengal during the late NE-monsoon (January-April). In addition, there exists a strong linear correlation of Fe<sub>Tot</sub> with Al and Fe<sub>ws</sub> for the aerosols collected from the continental outflow from the Indo-Gangetic Plain (Figure 6.7). This relation further attests to the point that during the study period significant fraction of Fe<sub>ws</sub> is derived from crustal source (i.e., mineral dust).

Parameter	Min	Max	Mean	Median	Stdev
PM <sub>2.5</sub>	23.1	177.2	89.7	93.6	33.1
$\mathrm{SO_4}^{2-}$	7.0	29.4	15.3	14.4	5.4
$Na^+$	0.1	0.4	0.2	0.2	0.1
$K^+$	0.7	3.8	2.0	2.0	0.6
nss-SO4 <sup>2-</sup>	6.9	29.3	15.3	14.4	5.4
$nss-K^+$	0.7	3.8	2.0	2.0	0.6
Al	0.4	2.2	1.3	1.3	0.4
Ca	0.1	0.4	0.3	0.3	0.1
Fe	0.1	1.8	0.7	0.6	0.4
Dust	4.7	28.1	16.0	15.7	4.5
OC	5.7	54.6	30.7	32.5	12.1
EC	1.2	8.9	4.5	4.3	1.6
*Fe <sub>WS</sub>	11.5	144.3	59.3	56.6	31.6
$Fe_{WS}/Fe_{Tot}*100$	4.3	17.1	9.4	9.2	3.3

Table 6.3: Statistical description of data regarding their range, mean, median and standard deviation of the fine mode aerosols from the IGP-outflow (Kharagpur).

Note: All concentrations were expressed in  $\mu g m^{-3}$ , except for Fe<sub>ws</sub> which is in ng m<sup>-3</sup>.

#### 6.3.4. Impact of anthropogenic combustion sources

In this study, observed scatter in the linear relation of  $Fe_{ws}$  (%) with nss-SO<sub>4</sub><sup>2-</sup> in the source region may be due to its contribution from other anthropogenic combustion sources (fossil-fuel and bio-mass burning). The intensive agricultural crop-waste residue, biomass and bio-fuel burning over the Indo-Gangetic Plain has been reported by several studies [*Badarinath et al.*, 2006; *Ram et al.*, 2010; *Venkataraman et al.*, 2006]. From these studies, it is evident that source region is characterized by the biomass burning emissions. The potential role of soluble iron supply from biomass burning has been highlighted recently by several studies [*Guieu et al.*, 2005; *Kumar et al.*, 2010; *Paris et al.*, 2010]. Therefore, one can expect a significant contribution of soluble iron (Fe<sub>ws</sub>) from biomass source over the IGP-out flow which enters to the Bay of Bengal during the late NE-monsoon.

Table 6.4: Comparison of elemental ratios of Ca/Al and Fe/Al with that observed over the Bay of Bengal during the late NE-monsoon (December-April).

Region	Duration	Statistic	Mean ± Stdev	Reference
KGP (IGP)	Nov'09-Mar'10	Ca/Al	$0.21\pm0.03$	Present study
N-BoB	Dec'08-January'09	Ca/Al	$0.27\pm0.20$	Srinivas et al., 2011
S-BoB	Dec'08-Jan'10	Ca/Al	$0.51\pm0.30$	Srinivas et al., 2011
BoB	March-April'06	Ca/Al	$0.81\pm0.16$	Kumar et al., 2008b
KGP (IGP)	Nov'09-Mar'10	Fe/Al	$0.51\pm0.22$	Present study
N-BoB	Dec'08-January'09	Fe/Al	$0.52\pm0.31$	Srinivas et al., 2011
S-BoB	Dec'08-Jan'10	Fe/Al	$0.50\pm0.30$	Srinivas et al., 2011
BoB	March-April'06	Fe/Al	$0.72\pm0.37$	Kumar et al., 2008b
BoB	March-April'06	Fe/Al	$0.72\pm0.37$	Kumar et al., 2008b

In the present study, a significant linear relation of organic carbon (OC) with non sea salt potassium (nss-K<sup>+</sup>; n = 46; p-value < 0.001; Figure 6.8a) and water soluble iron (Fe<sub>ws</sub>; n = 46; p-value < 0.001; Figure 6.8b) is observed. The presence of enriched nss-K<sup>+</sup> and its significant relationship with carbonaceous species in the atmosphere (OC, EC) has been attributed to biomass source by numerous studies [*Andreae*, 1983; *Gaudichett et al.*, 1995]. Therefore, from this observation, it is likely that the sampling site is influenced by biomass burning source. Similar linear relation is observed between nss-K<sup>+</sup>, OC, Fe<sub>ws</sub> in fine (PM<sub>2.5</sub>) mode aerosols during January'09 over the Bay of Bengal [*Kumar et al.*,

2010]. Based on the above observations, it is inferred that significant fraction of soluble iron is derived biomass source over the IGP and hence reflected in the continental outflow from IGP during the late NE-monsoon



Figure 6.6: Temporal variability of the mass concentrations of mineral dust,  $Fe_{Tot}$ ,  $nss-SO_4^2$ ,  $Fe_{ws}$  and  $Fe_{ws}$  (%) in the IGP-outflow (Kharagpur).

### 6.3.5. Effect of particle size on the aerosol iron solubility

The fractional solubility of aerosol iron (Fe<sub>ws</sub> %) is plotted against the mineral dust concentrations over the sampling site, Kharagpur (Figure 6.9).

Likewise, it has also been compared with the data from the Bay of Bengal during March-April'06 (TSP samples, n = 23) and January'09 (31 PM<sub>2.5</sub> and 33 PM<sub>10</sub> aerosol samples). In all samples, there exists an inverse moderate linear relationship between mineral dust mass concentration and the fractional solubility of aerosol iron (Figure 6.9). This further emphasizes the importance of size sorting effect, as finer particles have more surface area to volume ratio as compared to the coarse particles.

It is clearly evident from the Figure 6.9 that the Fews (%) in  $PM_{10}$  and TSP aerosols (sampled during January'09 and March-April'06) is relatively low compared to that in fine ( $PM_{2.5}$ ) mode. It is noteworthy that the Fews (%) in  $PM_{2.5}$  samples collected during November'09-March'10 (4.3 - 17.1 %) within the source region (Indo-Gangetic Plain) is relatively low compared that for aerosols collected from the BoB during January'09 (3.5 - 49.7 %). Based on the above observations, it is inferred that during long-range transport, the size distribution of aerosol population alters from coarse to fine mode and this relation holds even in the fine fraction (viz., fine quartz to clays).



Figure 6.7: The scatter plot of (a) Fe and Al (b) Fe and Fe<sub>ws</sub> at Kharagpur (IGP), suggests that significant contribution of soluble iron is derived from Crustal sources (i.e., fine alluvial dust).

Therefore, it is relevant to state that the fine mode aerosols over the source region has a different solubility compared to that in the long-range transport as is evident from the present study. However, the enhanced fractional solubility of aerosol iron within the fine mode ( $PM_{2.5}$ ) aerosols over the Bay region is attributed to its increase in surface area to volume ratio together with chemical processing of fine dust (possible surface reaction with anthropogenic acidic species).



Figure 6.8: The scatter plot of (a) nss- $K^+$  and OC (b) Fe<sub>ws</sub> and OC, suggest the significant contribution of soluble iron from Biomass burning source in the IGP-outflow (Kharagpur).

In addition, the contribution of soluble iron from combustion sources can also be a significant factor for the enhanced fractional solubility of aerosol iron. Owing to the impact of IGP-outflow (as evident from the AMBTs), the observed variability between the sampling site and the Bay of Bengal cannot be solely explained based on its contribution from combustion sources. Besides this, a recent study has emphasized the minor role of physical size-sorting effect on the fractional solubility of aerosol iron [*Shi et al.*, 2011]. The high  $Fe_{ws}$  (%) in fine mode (PM<sub>2.5</sub>) aerosols over the BoB is attributed to chemical processing of alluvial dust. However, the low iron solubility over the source region (IGP) can be explained by their relative increase in particle size from the Bay of Bengal to Indo-Gangetic Plain even in the fine mode aerosols. Therefore, present study highlights the importance of various factors (viz, size sorting of particles, combustion sources and chemical processing of mineral dust) on the aerosol iron solubility in the continental outflow from the Indo-Gangetic Plain.

#### 6.4. Deposition flux of Fews

The air-sea deposition of soluble iron is estimated from the soluble component (Fe<sub>ws</sub>) of aerosol-Fe (Fe<sub>Tot</sub>) multiplied by the dry-deposition velocity; assuming that the fractional solubility after deposition of mineral dust and/or combustion derived products is comparable with the solubility derived from laboratory studies. This can be expressed by the following equation. The deposition flux (f<sub>d</sub>) = Fe<sub>ws</sub> \* V<sub>d</sub>; Here V<sub>d</sub> = dry-deposition velocity, which is assumed as 1.0 cm sec<sup>-1</sup> in the present study [*Jickells and Spokes*, 2001]. The soluble iron flux varied from 8.2 to 57.5 µg m<sup>-2</sup> day<sup>-1</sup> over the BoB and 0.04 to 0.9 µg m<sup>-2</sup> d<sup>-1</sup> over the ARS for the campaign in March-May'06. Likewise, during January'09, the dry-deposition of soluble iron (Fe<sub>ws</sub>) in PM<sub>10</sub> aerosols ranged from 0.9 - 68.4 (23.7 ± 19.9) µg m<sup>-2</sup> day<sup>-1</sup> over the Bay of Bengal.



Figure 6.9: Scatter plot of mineral dust mass concentrations versus fractional solubility of aerosol iron (from the present study and earlier studies) over the Bay of Bengal, exhibits an inverse linear relation suggesting the control of mineral aerosol particle size on aerosol iron solubility.

Although, the fractional solubility of aerosol iron over Arabian Sea is low, the amount of dust input to the surface waters from surrounding desert regions compensate for the poor solubility. Results from this study indicate that the regional-scale studies can provide a better insight in understanding the relative importance of different sources. The air-sea deposition of soluble iron associated with high fractional solubility of dust and/or combustion derived products can increase the total pool of iron in seawater with a potential stimulating effect on primary production.

# 6.5. Conclusions

This study reveals that the fractional solubility of aerosol iron is 1 to 2 orders of magnitude higher in the MABL of the  $\$  as compared to that over the Arabian Sea. This difference is attributed to chemical characteristics of the mineral dust reaching the two oceanic regions. The Arabian Sea receives coarse dust from the desert regions; whereas transport of alluvial dust from the Indo-Gangetic Plain is a dominant source to the Bay of Bengal. A significant correlation of Fe<sub>ws</sub> % with Fe<sub>Tot</sub> and nss-SO<sub>4</sub><sup>2-</sup> provides evidence for the chemical processing of alluvial dust by atmospheric acidic constituents (H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) during long-range transport, and, thus enhances the solubility of aerosol-Fe. In addition, supply of soluble iron from combustion sources (agricultural crop waste redidue & biomass-biofuel burning) is identified as another source of soluble iron. These results have implications to the ocean surface biogeochemistry.

# Chapter 7

Atmospheric deposition of N, P and Fe to the Northern Indian Ocean: Implications to C- and N- fixation

#### 7.1. Introduction

In the present-day scenario of growing anthropogenic activities, air-sea deposition of nutrients (N, P and Fe) can have profound impact on the ocean surface biogeochemistry. Past estimates have shown that atmospheric supply of nutrients to the surface waters is a significant source [*Duce et al.*, 1991; *Prospero et al.*, 1996]. Likewise, recent studies have highlighted the importance of atmospheric anthropogenic nitrogen (AAN) deposition to oligotrophic oceanic gyres in supporting the Primary Production [*Duce et al.*, 2008; *Jickells*, 2006; *Spokes et al.*, 2000]. The atmospheric supply of AAN to nitrogen limited estuarine and coastal waters can increase the phytoplankton biomass and can lead to hypoxia [*Paerl et al.*, 2002; *Whitall et al.*, 2007].

The growing number of evidences suggest that in the absence of significant input of phosphorous and iron, deposition of AAN can shift the ecosystem towards other limiting nutrients (P or Fe) via changes in the Redfield stoichiometry (N/P = 16:1) of surface ocean [*Duce et al.*, 2008; *Jickells*, 2006]. It is well recognized that atmospheric supply of soluble iron is a dominant source to the open ocean [*Duce and Tindale*, 1991; *Jickells and Spokes*, 2001; *Mahowald et al.*, 2005a]. Existing studies from high-nutrient low-chlorophyll (HNLC) regions have highlighted the dust mediated glacial-interglacial CO<sub>2</sub> changes and emphasize the need to further understand the atmospheric transport and deposition of soluble Fe to the open ocean [*Boyd et al.*, 2000; *Coale et al.*, 1996; *Jickells et al.*, 2005; *Mahowald et al.*, 2009; *Martin et al.*, 1989]. In this context, several recent studies have addressed the need to quantify the atmospheric deposition of nutrients to the oceanic regions located downwind of the pollution sources.

The Northern Indian Ocean is an ideal site to study the impact of continental outflow on the marine atmospheric boundary layer (MABL) during the late NE-monsoon (January-April). Recent studies have documented the impact of outflow from south and south-east Asia on aerosol composition in the MABL of Arabian Sea (ARS) and Bay of Bengal (BoB) [*Kumar et al.*, 2010; *Lelieveld et al.*, 2001; *Ramanathan et al.*, 2001b; *Srinivas et al.*, 2011a; *Srinivas et al.*, 2011b; *Srinivas and Sarin*, 2012]. The main objective of this study is to assess the spatiotemporal variability in the dry-deposition fluxes of N, P and Fe; their fixation

rates and contribution to the Primary Production. The study on atmospheric drydeposition is most relevant, as wet precipitation events are very rare when continental outflow persists over the Northern Indian Ocean (BoB and ARS) during the period of late NE-monsoon (January-April).

# 7.2. Dry-deposition fluxes

The dry-deposition fluxes of nutrient species to the Bay of Bengal and the Arabian Sea have been assessed based on their aerosol concentrations across the air-sea interface. The statistical description comprising of range, mean and standard deviation of nutrient abundances is summarized in Table 7.1. As discussed in the previous chapters, the relative abundances of chemical constituents over the BoB and the ARS have been explained in terms of differences in the source strength of anthropogenic constituents and source regions of mineral dust. Furthermore, it has been suggested that within the Bay region, the impact of continental outflow decreases from winter months (December-February) to spring-intermonsoon (March-April). Hence, relatively high mass concentrations of nutrients occur in the MABL of BoB during January'09 compared to those in March-April'06 [*Srinivas et al.*, 2011a; *Srinivas et al.*, 2011b].

The mass concentration of nutrient species ( $N_{Inorg}$ ,  $N_{Org}$ ,  $N_{Tot}$ ,  $P_{Inorg}$  and Fe<sub>ws</sub>) during January'09, show strong spatial gradient; with higher concentrations over N-BoB and relatively low values over S-BoB [*Srinivas et al.*, 2011b]. This is attributed to proximity of N-BoB to the continental sources. The mass concentrations of nutrients in PM<sub>2.5</sub> and PM<sub>10</sub> reveal dominant occurrence of NH<sub>4</sub><sup>+</sup>, N<sub>Org</sub> and Fe<sub>ws</sub> in the fine mode (PM<sub>2.5</sub>); whereas NO<sub>3</sub><sup>-</sup> and P<sub>Inorg</sub> are relatively abundant in PM<sub>10</sub> [*Srinivas et al.*, 2011a; *Srinivas et al.*, 2011b; *Srinivas and Sarin*, 2012]. The dry-deposition fluxes of nutrients (N<sub>Inorg</sub>, N<sub>Org</sub>, PO<sub>4</sub><sup>3-</sup> and Fe<sub>ws</sub>) are calculated from their aerosol concentrations and the dry-deposition velocity of an individual species, expressed by the following equation.

Dry deposition flux  $f_{dry} = C_{meas} * V_{dry}$  (1)

Here,  $C_{meas}$  is the measured mass concentration of nutrient (N, P and Fe) in aerosols and  $V_{dry}$  is the dry deposition velocity. Earlier study by Duce et al., (1991), had suggested dry-deposition velocity for fine (< 1.0µm particles) and coarse mode aerosols (> 1.0  $\mu$ m particles) as 0.1 and 1.0 cm s<sup>-1</sup> respectively. In the present study, the dry deposition velocity (DDV) of NH<sub>4</sub><sup>+</sup> is taken as 0.1 cm s<sup>-1</sup> due to its predominant occurrence in the fine mode [*Baker et al.*, 2003; *Chen et al.*, 2006; *Chen et al.*, 2007]. The dry-deposition velocity for NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and Fe<sub>ws</sub> is taken as 1.0, 2.0 and 1.0 cm sec<sup>-1</sup>, respectively, due to their association with the coarse mode aerosols [*Chen et al.*, 2006; *Duce et al.*, 1991; *Jickells and Spokes*, 2001].

Due to the abundance of  $N_{Org}$  in the fine mode, dry-deposition flux is estimated by multiplying its respective concentration and deposition velocity in two size fractions (PM<sub>2.5</sub> and PM<sub>10</sub>). As dry-deposition velocities are difficult to measure and poorly constrained, flux estimates of nutrients (this study) have inherent uncertainty (of about a factor of three). Sarin et al., [1999], had measured dry-deposition velocity of NO<sub>3</sub><sup>-</sup>, in bulk aerosol collected from the MABL of Arabian Sea, as ~ 0.9 cm sec<sup>-1</sup>. For P<sub>Inorg</sub>, dry-deposition velocity of 2.0 cm sec<sup>-1</sup> has been used for coarse mode aerosols by [*Spokes et al.*, 2000; *Yeatman et al.*, 2001]. A dry-deposition velocity of 2.3 - 2.7 cm s<sup>-1</sup> has been also suggested for P<sub>Inorg</sub> by earlier studies [*Bergametti et al.*, 1992; *Markaki et al.*, 2003].

Table 7.1: Statistical description of nutrients in aerosols collected from the MABL of the Bay of Bengal and Arabian Sea.

	Arabian Sea		<b>Bay of Bengal</b>		<b>Bay of Bengal</b>	
	April-May'06		March-April'06		January'09	
Parameter	range	$Av \pm sd$	range	$Av \pm sd$	range	$Av \pm sd$
$\mathrm{NH_4}^+$	≤0.38	≤0.38	0.6 -127	$33 \pm 35$	3.4 - 678	82 ± 182
NO <sub>3</sub> <sup>-</sup>	≤0.2 - 21.6	$6.5\pm6.5$	0.1 - 5.6	$0.8 \pm 1.4$	≤0.2 - 43	$10\ \pm 10$
N <sub>Inorg</sub>	0.9 - 21.6	$6.9\pm6.6$	2.3 - 128	$38\pm34$	7.4 - 693	$105\ \pm 185$
N <sub>Tot</sub>	≤5.1 - 32.0	$5.8 \pm 8.4$	9.5 - 152	$45\pm~40$	≤5.1 - 786	$115 \pm 229$
$\mathbf{P}_{\mathrm{Inorg}}$	0.2 - 0.5	$0.4 \pm 0.1$	0.6 - 2.2	$1.1\pm0.4$	0.3 - 2.8	$1.3 \pm 0.5$
Fe <sub>ws</sub>	*0.8 - 17.7	$*5.6 \pm 4.2$	0.2 - 1.2	$0.6 \pm 0.3$	0.02 - 1.4	$0.5\ \pm 0.4$
Note: All mass concentrations are expressed in nmol m <sup>-3</sup> (* is in pmol m <sup>-3</sup> ).						

The dry-deposition fluxes of nutrients during January'09 show pronounced spatial variability, with high fluxes over the N-BoB and decreasing towards the S-BoB. In PM10, the dry-deposition fluxes of NInorg, PInorg and Fews over the N-

BoB varied as 4.8 - 82.5, 1.4 - 3.3 and  $0.1 - 1.2 \mu mol m-2 d-1$ , respectively; whereas over S-BoB, they ranged between 2.1 - 31.5, 0.5 - 4.8 and  $0.02 - 0.9 \mu mol m-2 d-1$ , respectively. The dry-deposition flux of NTot ranged from 2 to 167  $\mu$ mol m-2 d-1 with an average of about  $43\mu$ mol m-2 day-1 over the BoB during January'09 [Srinivas et al., 2011b]. A comparison of dry-deposition fluxes from the two sampling campaigns, January'09 and March-April'06, suggests strong anthropogenic influence during the winter time (January-February).

In January'09, the dry-deposition fluxes of  $N_{Inorg}$ ,  $P_{Inorg}$  and  $Fe_{ws}$  centered on 26.6 ± 20.3, 2.3 ± 0.9 and 0.4 ± 0.4 µmol m<sup>-2</sup> d<sup>-1</sup>; whereas the mean drydeposition fluxes in March-April'06 are  $5.3 \pm 2.7$ ,  $1.8 \pm 0.6$  and  $0.5 \pm 0.3$  µmol m<sup>-2</sup> d<sup>-1</sup>, respectively. The dry-deposition fluxes of  $N_{Inorg}$ ,  $P_{Inorg}$  and  $Fe_{ws}$  over the Arabian Sea average around  $8.5 \pm 5.4$ ,  $0.6 \pm 0.2$  µmol m<sup>-2</sup> day<sup>-1</sup> and  $4.9 \pm 3.7$  nmol m<sup>-2</sup> day<sup>-1</sup>, respectively (Table 7.2). The spatial distribution of dry-deposition fluxes of  $N_{Tot}$ ,  $P_{Inorg}$  and Fe<sub>ws</sub> in aerosols collected from the Bay of Bengal (January'09 and March-April'06) and Arabian Sea (April-May'06) are given in Figure 7.1.

Location	NInorg	PInorg	Fews	Reference			
Bay of Bengal	$26.6\pm20.3$	$2.3\pm0.9$	$0.4 \pm 0.4$	This Study			
Bay of Bengal	$5.3 \pm 2.7$	$1.9\pm0.7$	$0.5 \pm 0.3$	This Study			
Arabian Sea	$8.5\pm5.4$	$0.6\pm0.2$	$4.9\pm3.7^{\#}$	This Study			
Eilat, Israel	$36 \pm 16$	$0.3\pm0.2$	$0.2 \pm 0.2$	Chen et al., [2007]			
<sup>\$</sup> Eilat, Israel	$38 \pm 17$	$0.2\pm0.2$	$0.02\pm0.02$	Chen et al., [2007]			
<sup>\$</sup> Israeli Mediterranean	*18	0.9	-	Herut et al. [1999]			
Crete Island	32	-	-	Kouvarakis et al. [2001]			
<sup>\$</sup> Erdemli	120	0.5	-	Markaki et al. [2003]			
<sup>\$</sup> Crete Island	32	0.3	-	Markaki et al. [2003]			
Central North Pacific	0.6 – 3	0.08 - 0.4	0.004 - 0.02	Chen, [2004]			
Tropical North Atlantic $1-5$ $0.1-0.3$ $0.06-0.2$ Chen and Siefert, [2004]							
\$ Nutrients were extracted with sea water; $\#$ in nmol m <sup>-2</sup> d <sup>-1</sup> ; * is 1/3 of wet-deposition							

Table 7.2: Dry-deposition fluxes of nutrients ( $\mu$ mol m<sup>-2</sup> day<sup>-1</sup>) to the Bay of Bengal, Arabian Sea and other oceanic regions

These contours are made by the interpolation of data within the study region using ocean data view software (Schlitzer et al., 2002; <u>http://odv.awi.de</u>). It is evident that dry-deposition fluxes to the ARS are relatively low compared to

BoB (Figure 7.1). The spatial variability in the dry-deposition fluxes is attributed to the relative dominance of continental outflow over the BoB. The model estimates of atmospheric deposition fluxes (Tg yr<sup>-1</sup>) of N, P and Fe to the BoB and ARS are of comparable magnitude with the present study (Table 7.4).



Figure 7.1: Spatial distribution of dry-deposition fluxes of nutrients during (a) January'09 (b) March-April'06 (c) April-May'06 over the northern Indian Ocean

# 7.3. Marine budget of N and P - role of atmospheric input

# 7.3.1. Comparison of with riverine supply

The global riverine water discharge is estimated as ~  $37.4*10^{12}$  m<sup>3</sup> yr<sup>-1</sup> [*Kumar et al.*, 1996; *Martin and Whitfield*, 1983]. The Bay of Bengal receives large quantity of fresh water discharge (1.625 \*  $10^{12}$  m<sup>3</sup> yr<sup>-1</sup>) from Peninsular rivers (Ganga, Brahmaputra, Godavari, Krishna; *Prasanna Kumar* et al., [2004], *Sarin et al.*, [1990]). The riverine supply of freshwater discharge to the Arabian Sea is ~  $0.34 * 10^{12}$  m<sup>-3</sup> yr<sup>-1</sup> (238 \*  $10^9$  m<sup>-3</sup> yr<sup>-1</sup> by Indus; 47, 19, 12, 4, 1 and 16 \*

 $10^9$  m<sup>3</sup> yr<sup>-1</sup> by Narmada, Tapi, Mahi, Sabarmati, Vishwamitiri and Mandovi). Seitzinger et al. [2002], had estimated the global riverine flux of inorganic nitrogen to the coastal waters as ~21 Tg-N yr<sup>-1</sup> based on 1990 inventory data. Their study further emphasizes that riverine input may increase to 47 Tg-N yr<sup>-1</sup> by 2050 as a result of growing anthropogenic activities (increase in fertilizer production and consumption; increase in fossil-fuel combustion). Therefore, fluvial supply of N<sub>Inorg</sub> to the study region (BoB and ARS) has been estimated based on minimum flux of 21 Tg-N yr<sup>-1</sup>in 1990 and maximum input of 47 Tg-N yr<sup>-1</sup> in 2050 as contribution to the World Rivers. Hence, the estimated flux of N<sub>Inorg</sub> to the BoB and ARS via rivers is about 0.9 - 2.0 Tg-N yr<sup>-1</sup> and 0.2 - 0.4 Tg-N yr<sup>-1</sup>, respectively.

The area-weighted atmospheric dry-deposition flux (i.e. assuming that continental outflow persists only for a period of 5 months, December-April, flux is integrated for 150 days for estimating the annual input) of  $N_{Inorg}$  to the BoB and ARS is about 0.01 - 0.38 Tg-N yr<sup>-1</sup> and 0.01- 0.19 Tg-N yr<sup>-1</sup>, respectively. As stated earlier, occurrence of precipitation events during the continental outflow is very rare. A comparison of riverine supply with estimated atmospheric deposition of  $N_{Inorg}$  suggests that they are of comparable magnitude and, hence, highlights the role of aeolian supply.

The atmospheric supply of phosphorous to the ocean accounts for less than 10 % of the riverine input and considered as an insignificant source [*Froelich et al.*, 1982]. These estimations were due to inadequate measurements of aerosol-P compared to those from the peninsular rivers. However, recently revised budget of P addresses the significance of atmospheric source [*Mahowald et al.*, 2008; *Mahowald et al.*, 2005a; *Paytan and McLaughlin*, 2007]. These studies have highlighted the importance of anthropogenic sources of phosphorous (viz, mining of phosphate rocks, increase in production of fertilizers and increased erosional input, biomass burning and fossil-fuel combustion etc).

Based on the data from major rivers, Compton et al., [2000], have estimated the global riverine input of dissolved inorganic phosphorous (0.8 - 1.4 Tg-P yr<sup>-1</sup>). In this study, the riverine input of dissolved inorganic phosphorous to



the BoB and ARS is estimated to be 35 - 60 Gg-P yr<sup>-1</sup>[*Srinivas and Sarin*, 2012] and 7-13 Gg-P yr<sup>-1</sup>, respectively.

Figure 7.2: Marine geochemical budget of nitrogen and phosphorous to the (a) Bay of Bengal and (b) Arabian Sea.

The concentration of  $P_{Inorg}$  in ambient aerosols over the Bay of Bengal during January'09 ranges from 0.3-2.8 nmol m<sup>-3</sup>. Therefore, drydeposition of  $P_{Inorg}$  to the BoB is estimated to be 0.5-4.8 µmol-P m<sup>-2</sup> d<sup>-1</sup>. Likewise, the mass concentration of  $P_{Inorg}$  over the Arabian Sea ranges from 0.20-0.53 nmol-P m<sup>-3</sup>, which corresponds to air-sea deposition of 0.3-0.9 µmol-P m<sup>-2</sup> d<sup>-1</sup>. Therefore, the area-weighted dry-deposition fluxes of  $P_{Inorg}$  to the Bay of Bengal and the Arabian Sea are about 6-50 Gg-P yr<sup>-1</sup> and 8-21 Gg-P yr<sup>-1</sup>, respectively. Therefore, a comparison of atmospheric supply with the riverine inputs of  $P_{Inorg}$ suggests that both are of comparable magnitude (Figure 7.3); suggesting atmospheric deposition as a significant source of  $P_{Inorg}$  to the surface waters of Northern Indian Ocean.

The global riverine input of dissolved Fe to the coastal regions is estimated to be 1.5 Tg yr<sup>-1</sup> [*Jickells et al.*, 2005]. Estimated riverine fluxes of dissolved-Fe to the Bay of Bengal and the Arabian Sea are 0.065 and 0.013 Tg yr<sup>-1</sup>, respectively. The area-weighted atmospheric flux of soluble iron to the surface waters of the Bay of Bengal and the Arabian Sea are averaged around 0.009 and 0.0002 Tg yr<sup>-1</sup>, respectively; indicating that atmospheric deposition of Fe is only 13 and 2 % of the contribution from rivers.

# 7.3.2. Comparison with Primary Production

During the late NE-monsoon (January-April), the Bay of Bengal is relatively less stratified compared to the large influx of fresh water during the SW-monsoon (June-September). Primary production is reported to be high during the winter time (December-February) and spring inter-monsoon (March-April) [*Gauns et al.*, 2005; *Prasanna Kumar et al.*, 2002]. It is noteworthy that during these seasons, the MABL of Bay of Bengal is significantly influenced by the continental outflow from south and south-east Asia [*Kumar et al.*, 2010; *Lelieveld et al.*, 2001]. The column integrated Primary Production (PP) in the BoB during winter months (December-February) varies from 99 - 566 mg-C m<sup>-2</sup> d<sup>-1</sup> [*Gauns et al.*, 2005]. A comparison of atmospheric deposition of N<sub>Tot</sub> (2 – 167 µmol-N m<sup>-2</sup> d<sup>-1</sup>) with the water column Productivity (assuming Redfield stoichiometry of C/N (= 6.625) and upon deposition N<sub>Tot</sub> is completely utilized by marine phytoplankton) suggests that air-sea deposition can account for no more than 13 % of PP in the surface waters of BoB (Figure 7.3). Since, most of the PP is recycled within the surface waters; it is reasonable to compare the estimate of atmospheric deposition with the new production (NP). The f-ratio of 0.5 has been reported in the BoB suggesting that almost half of the primary production is exported from the surface waters [*Kumar et al.*, 2004]. This comparison suggests that atmospheric deposition of N<sub>Tot</sub> can support up to 25 % of new production (NP). It is relevant to state that the Primary Production in the Bay of Bengal varies over a wide range. Therefore, contribution from atmospheric deposition to PP estimated in this study could be of lower order as the contribution from gas phase HNO<sub>3</sub> has not been included in this study.

In contrast, Arabian Sea is characterized by relatively high PP during the summer (by intense upwelling) and winter (by convective mixing). The column integrated PP in the ARS during the late NE-monsoon (January-April) varies from 65-202 mmol-C m<sup>-2</sup> d<sup>-1</sup> ( $\approx$  0.8-2.4 g-C m<sup>-2</sup> d<sup>-1</sup>; [*Barber et al.*, 2001]). However, it has been suggested that the open ocean waters of the Arabian Sea are characterized by high PP (> 0.5g - C m<sup>-2</sup> d<sup>-1</sup>) throughout the year [*Madhupratap et al.*, 2001]. During April-May'06, the dry-deposition of N<sub>Inorg</sub> varies from 1.3-18.6 µmol-N m<sup>-2</sup> d<sup>-1</sup>. Comparison of the atmospheric deposition of N<sub>Inorg</sub> with water column PP can account for no more than 1 % of PP (assuming Redfield stoichiometry). It is, thus, inferred that atmospheric deposition is a significant source of nutrients (N, P and Fe) to the surface waters of the Bay of Bengal during the study period (January-April), whereas atmospheric contribution to the Arabian Sea is relatively insignificant.

# 7.4. C- and N- fixation by atmospheric input

# 7.4.1. Potential C-fixation

In this study, potential carbon and nitrogen 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 Indian Ocean (BoB and ARS) are replete in P (a non-limiting nutrient) and atmospheric deposition of Fe and N could support additional Primary Production. Since, continental outflow dominates the widespread dispersal of airborne pollutants (nutrients) in the MABL during the late NE-monsoon (January-April),

it is relevant to estimate the nitrogen and carbon fixation fuelled by the atmospheric input during this period only. The spatial distribution of potential Cand N- fixation (supported by atmospheric deposition) in the study region is shown in Figure 7.3.

Table 7.3: Comparison of atmospheric deposition fluxes ( $Tg yr^{-1}$ ) of N, P and Fe (this study) with model based estimates to the Indian Ocean.

Study Region	N <sub>dep</sub>	P <sub>dep</sub>	Fe <sub>dep</sub>	Reference
Bay of Bengal	0.12	0.021	0.009	Present study
Arabian Sea	0.15	0.014	0.0002	Present study
N. Indian Ocean	0.27	0.035	0.009	Present study
N. Indian Ocean	4.10	0.043	0.040	Okin et al., 2011
N. Indian Ocean	1.76	-	-	Duce et al., 2008
N. Indian Ocean	-	0.014	0.046	Mahowald et al., 2008;2009

In the Bay of Bengal, during winter (December-February) and spring intermonsoon (March-May), the phytoplankton community is dominated by the abundance of diatoms (80-90 %), dinoflagellates [*Madhu et al.*, 2006]. In the Arabian Sea, diatoms (~ 86%), cyano bacteria (7%) and dinoflagellates (~ 6%) constitute major phytoplankton assemblages [*Sawant and Madhupratap*, 1996]. Since diatoms are one of the abundant phytoplankton species both in the BoB and ARS; potential C- fixation rates were estimated based on the following equation.

$$C_{dia}^{Fix} = Fe_{dep}^{atm} * [Fe_{ws}\%] * \left[\frac{C}{Fe}\right]_{dia}$$
(2)

Here,  $Fe_{dep}^{atm}$  and Fe<sub>ws</sub> % are atmospheric deposition flux of total aerosol iron and the fractional solubility of aerosol iron within the MABL, respectively. The cellular uptake ratio of Fe: C by diatoms is about 8µmol/mol (i.e. C:Fe = 1,25,000; [*Moore et al.*, 2002]). Therefore, the amount of carbon fixed by diatoms can be calculated by Equation 2. The average mass concentration of total aerosol iron (~ 460 ng m<sup>-3</sup>) during January'09 could corresponds to a drydeposition flux of 0.13 Tg yr<sup>-1</sup> to the Bay of Bengal (V<sub>dry</sub> = 0.01 m s<sup>-1</sup>; area = 2.2 \* 10<sup>12</sup> m<sup>2</sup>). Using average fractional solubility of aerosol iron (~ 7 %) during this period, the dry-deposition of soluble iron to the Bay of Bengal is about 0.009 Tg yr<sup>-1</sup>. Therefore, atmospheric input can account for ~1.1 Pg-C yr<sup>-1</sup> (from equation 2) fixed during Primary Production (~ 2 % of global PP, 50 Pg-C yr<sup>-1</sup>[*Carr et al.*, 2006]). Using a similar concept, the dry-deposition of total aerosol iron to the Arabian Sea is 0.28 Tg yr<sup>-1</sup> (V<sub>dry</sub> = 0.01 m s<sup>-1</sup>; conc. = 444 ng m<sup>-3</sup>; Area = 4.93 x  $10^{12}$  m<sup>2</sup>; [*Bange et al.*, 2000]). However, the fractional solubility of aerosol iron is no more than 0.5 % in the Arabian Sea (mean: 0.09 %; range: 0.02-0.43 %, [*Srinivas et al.*, 2011a]). This is consistent with earlier findings over the Arabian Sea [*Johansen and Hoffmann*, 2003; *Siefert et al.*, 1999]. Therefore, dry-deposition of soluble iron is ~ 0.00025 Tg yr<sup>-1</sup> and can account for no more than 0.03 Pg-C yr<sup>-1</sup> carbon (Figure 7.3) fixed during the Primary Production (less than 1 % of global PP).



Figure 7.3: Estimated potential carbon (Pg-C  $yr^{-1}$ ) and nitrogen fixation rates (Tg-N  $yr^{-1}$ ), supported by atmospheric deposition of Fe.

#### 7.4.2. Potential N- fixation

The marine diazotrophs require high abundance of Fe and their occurrence is limited to tropics, due to temperature limitation [*Capone et al.*, 1997; *Carpenter and Capone*, 1992]. With this concept, recent studies have estimated the potential N-fixation by diazotrophs with regard to atmospheric deposition [*Berman-Frank et al.*, 2001; *Okin et al.*, 2011]. Earlier study by Berman-Frank et al., 2001 suggests that the availability of iron limits the N-fixation in almost 75 % of the world ocean. In addition, their study also shows that oceanic regions such as tropical north Atlantic and Indian Ocean are conducive for N-fixation by *Trichodesmium* species.

Due to the close proximity of Desert regions, the transport of mineral aerosols from this dust sources to the surrounding oceanic regions facilitates N-fixation in the eastern North Atlantic and Western Arabian Sea. In contrast, relatively low N-fixation in the tropical north-east Pacific Ocean (a HNLC region) is attributed to the non-availability of iron in these waters. However, the model simulations clearly demonstrate the potential N-fixation along the tropics [*Berman-Frank et al.*, 2001; *Capone et al.*, 1997; *Okin et al.*, 2011]. A recent study has suggested the potential role of atmospherically derived P and Fe regulation for N-fixation [*Monteiro et al.*, 2011]. Therefore, potential N- fixation rates have been estimated with respect to atmospheric input by assuming Fe and P limitation in the BoB and ARS (Figure 7.3). This approach is adapted from a recent study by Okin et al., [2011], represented by the following equations.

$$N_{fix}^{atm} = \left(Fe_{ws}\right)_{dep}^{atm} \times \left[\frac{N}{Fe}\right]_{diaz}; \text{ (assuming Fe limitation)}$$
(3)

$$N_{fix}^{atm} = P_{dep}^{atm} \times \left[\frac{N}{P}\right]_{diaz}; \quad \text{(assuming P limitation)} \tag{4}$$

In this equation,  $N_{fix}^{atm}$  is N-fixation supported by the atmospheric deposition of Fe and P. In the literature, cellular uptake ratio of N/Fe by diazotrophic organisms varies almost one order of magnitude, from 50 to 1050 g/g [*Okin et al.*, 2011 and references therein]. Therefore, the estimates of N-fixation supported by atmospheric deposition of Fe to the study region (BoB and ARS) are computed from the extreme values. Similarly, the N/P ratio of marine diazotrophs

varies only by a factor 3, from 18 to 56 g/g [*Okin et al.*, 2011 and the references therein]. Assuming a mean N/P ratio of 37g/g (applicable to marine diazotrophs; [*Okin et al.*, 2011 and references therein], nitrogen fixation rates were assessed based on the assumption that surface waters are depleted in P.

It is noteworthy that N-fixation in the ARS ranges from 0.001- 0.03 Tg-N yr<sup>-1</sup> with an N/Fe ratio of about 50. Likewise, nitrogen fixation rate varies from 0.03 - 0.67 Tg-N yr<sup>-1</sup> with an N/Fe of 1050. As *Trichodesmium* species (a marine diazotrophs that require high abundance of iron) are identified both in the ARS and BoB, the higher end value (0.03 - 0.67 Tg-N yr<sup>-1</sup>) is compared with the other estimates reported in the literature. This comparison suggests that N-fixation rates, assessed in this study are somewhat consistent with the earlier estimates of 3.3 Tg-N yr<sup>-1</sup> [*Bange et al.*, 2000], 1.5 Tg-N yr<sup>-1</sup> [*Somasundar et al.*, 1990], 1.0 Tg-N yr<sup>-1</sup> [*Capone et al.*, 1997] and 3.5 Tg-N yr<sup>-1</sup> [*Brandes et al.*, 1998]. Similarly, assuming P-limitation, the estimated N-fixation rate for Arabian Sea corresponds to ~ 0.5 Tg-N yr<sup>-1</sup>. In both these approaches, the N-fixation rate is quite similar and is comparable with the literature studies. However, the estimated N-fixation rate may vary by a factor of 3 to 5.

Recently, the N-fixation rate of ~ 15.6 Tg yr<sup>-1</sup> has been reported for the *Trichodesmium* species in the Arabian Sea during spring bloom [*Gandhi et al.*, 2011]. This estimate is somewhat higher compared to other studies for this region [*Bange et al.*, 2000 and references therein; *Capone et al.*, 1997]. The modelling study by Krishnamurthy et al., [2010], suggests that an increase in the atmospheric input of N to the tropics could result in decrease in N-fixation by diazotrophs due to competition with other diatoms and picoautotrophs. Although, estimated N-fixation rate (Figure 7.3) in the present study is relatively low compared to that reported in the bloom conditions of *Trichodesmium* species [*Gandhi et al.*, 2011], it is reasonable to argue that the atmospheric supply of iron from desert regions is likely to be an important factor responsible for observed nitrogen fixation.

The N-fixation rate in the BoB, supported by atmospheric deposition of soluble Fe, is about 0.4 Tg-N yr<sup>-1</sup> (for N: Fe = 50) and 8.2 Tg-N yr<sup>-1</sup> (for N: Fe = 1050). Assuming P limitation in the surface waters of Bay of Bengal (area of 2.2

\*10<sup>12</sup> m<sup>2</sup>), average N-fixation rate is 0.9 Tg-N yr<sup>-1</sup>. Due to the lack of measurements of N-fixation rate for this region (BoB), an upper estimate of 1.0 Tg-N yr<sup>-1</sup> has been suggested based on a mass balance approach by Naqvi, [2011]. This is somewhat of comparable with the estimate in this study (0.4 and 0.9 Tg-N yr<sup>-1</sup> by assuming Fe and P limitation respectively). Their study also suggests that the N- fixation rate in the BoB is of comparable magnitude with that in ARS. Therefore, the upper estimate for N-fixation rate (~8.2 Tg-N yr<sup>-1</sup>) is very unlikely. Hence, N-fixation rate of 0.5 Tg-N yr<sup>-1</sup> for the Northern Indian Ocean has been suggested as a conservative estimate (assessed based on the soluble Fe fluxes). These calculations can be biased due to the underlying assumption that surface waters in the study region (BoB and ARS) are limited by the availability of Fe and P. However, our approach provides a reasonable estimate for the N- fixation rate that is somewhat comparable with the earlier estimates.

#### 7.5. Ecological impact

The molar dry-deposition flux ratio of N<sub>Inorg</sub> to phosphorous (N/P ratio) to the BoB is relatively high during January'09 (Range: 2-35; Av  $\pm$  sd: 12  $\pm$  8) compared to March-April'06 (Range: 1 - 6; Av  $\pm$  sd: 3  $\pm$  1). The high N/P ratio is attributed to the impact of continental outflow during winter months (December-February) compared to the spring-intermonsoon (March-May). The low N/P ratio over BoB during March-April'06 is due to decrease in the source strength of continental outflow. In contrast, the high N/P ratio (range: 3 – 37; Av  $\pm$  sd: 14  $\pm$ 9) over the ARS is attributed to high concentrations of nitrate (resulted from the continental transport) relative to phosphorous (supply from desert regions).

Spatial variability of N/P ratios in the atmospheric dry-deposition fluxes over the Bay of Bengal and the Arabian Sea are presented in Figure 7.4. The high N/P ratios in the atmospheric dry-deposition were also reported from the North Atlantic Ocean [*Baker et al.*, 2003] and Gulf of Aqaba [*Chen et al.*, 2007]. Although, mean ratios are comparable to the Redfield ratio (N/P = 16), the observed high ratios in the air-sea deposition to the BoB (in January'09) and the ARS (in April-May'06), have implications to pronounced temporal biogeochemical response in the surface ocean. It is suggested that the enhanced atmospheric supply of reactive nitrogen (compared to phosphorous) can affect the Redfield ratio in the surface waters through more N and less P deposition [*Duce et al.*, 2008]. Therefore, the high N/P ratio in the atmospheric dry-deposition fluxes can have significant impact on the biogeochemistry of surface waters of the northern Indian Ocean.



*Figure 7.4: Molar N/P ratio in the air-sea deposition during (a) January'09 (b) March-April'06 (c) April-May'06* 

# 7.6. Conclusions

Based on real-time measurements, this study provides a comprehensive data set on atmospheric dry-deposition of nutrient species (N, P and Fe) to two important regions (Bay of Bengal and Arabian Sea) of the Northern Indian Ocean. The mass concentrations and dry-deposition of nutrient species show pronounced spatio-temporal variability. The dry-deposition fluxes over the Bay of Bengal, associated with the continental outflow, are relatively high compared to those over the Arabian Sea. The continental transport to the Arabian Sea is relatively dominated by the mineral dust from Desert regions, with poor fractional solubility for nutrients.

The relatively high deposition fluxes over the Bay of Bengal during January'09 compared to those in March-April'06 are attributable to the temporal shift in wind regimes and decrease in the source strength of the continental outflow during the Spring-intermonsoon. The N/ P ratio in the dry-deposition to the two oceanic regions is significantly higher than the Redfield ratio (N/P = 16), suggesting the dominant impact of atmospheric source on surface Primary Productivity. A comparison of results from the present study with model-based estimates for the Northern Indian Ocean suggests that except for P and Fe, N-deposition fluxes are grossly over-estimated. Assuming P- and Fe-limitation in the surface waters, the N-fixation rate by diazotrophs in the Arabian Sea and Bay

of Bengal is about 0.5 Tg yr<sup>-1</sup>, consistent with the JGOFS data for the Arabian Sea. It is noteworthy that in the Fe-limited Arabian Sea, the contribution of atmospheric input is insignificant to the Primary Production. The cause for this is attributed to the poor fractional solubility of Fe from the mineral dust entering the Arabian Sea.

An overall mismatch with the experimentally measured atmospheric deposition fluxes requires reassessment of the model parameters with respect to the projected increase in the potential-emission sources, incorporating temporal variability in the continental outflow and fractional solubility of aerosol-Fe. Nevertheless, further increase in the air-sea deposition fluxes of nutrients has potential to augment C-fixation rate in the Northern Indian Ocean.

# Chapter 8

Atmospheric deposition of toxic metals to the Bay of Bengal: Implications to surface biogeochemistry

### 8.1. Introduction

Atmospheric deposition has been long recognized as a major source of trace metals to the marine environment [Chester et al., 1999; Duce et al., 1991; Duce and Tindale, 1991; Gao et al., 2002; Hsu et al., 2010; Koçak et al., 2005; Migon et al., 1997; Spokes et al., 2001; Witt et al., 2010]. High concentrations of Al, Mn and Pb in surface seawater are often attributed to their atmospheric input [Bruland, 1983; Patterson and Settle, 1987]. In addition, recent studies have highlighted that atmospheric supply of Fe to high nutrient low chlorophyll regions (HNLC) can enhance primary production and, hence, increase the drawdown of atmospheric CO<sub>2</sub> [Jickells et al., 2005; Mahowald et al., 2005; Martin, 1990; Martin and Fitzwater, 1988]. On the contrary, atmospheric deposition of trace metals such as Cu can have a toxic effect on marine phytoplankton and inhibit their growth. In the present day scenario of growing anthropogenic activities, knowledge of atmospheric input of trace metals to the sea water is, thus, essential to understand their impact on ocean surface biogeochemistry. Recent studies have emphasized the importance of deposition of toxic metals to the oceanic regions (example: Bay of Bengal), located downwind of the polluted air masses from south and south-east Asia, which in turn can alter the marine phytoplankton community structure [Paytan et al., 2009; Sholkovitz et al., 2009a].

The magnitude of atmospheric deposition of trace metals across the air-sea interface depends on their aerosol mass concentrations from which it is derived [*Chester et al.*, 1999]. Upon deposition to the ocean surface, the impact of trace metals is governed by its fractional solubility in sea water. The solubility of a trace metal and its residence time in surface seawater depends on several factors such as source composition (eg: crustal or non crustal, anthropogenic), mode of removal from the atmosphere (via dry or wet deposition), solution pH, (wet scavenging, i.e., acidic or alkaline or neutral), aging of aerosol in the atmosphere during long-range transport, and in-cloud dissolution [*Aguilar-Islas et al.*, 2010; *Bonnet and Guieu*, 2004; *Buck et al.*, 2010b; *Chester et al.*, 1993; *Desboeufs et al.*, 2005; *Guieu et al.*, 1994; *Guieu et al.*, 1997; *Guieu et al.*, 2005; *Measures et al.*, 2010; *Sedwick et al.*, 2007; *Spokes et al.*, 2001]. A wide range of data has emerged owing to different analytical protocols adopted to assess the fractional

solubility of trace metals [*Chester et al.*, 1999; *Spokes et al.*, 1994; *Spokes and Jickells*, 1996; *Srinivas et al.*, 2011a]. Several studies have shown that anthropogenic fractions of Cu, Pb, V and Fe are more soluble in seawater as compared to the components associated with mineral dust [*Hal*, 1989; *Maring and Duce*, 1989; *Schroth et al.*, 2009; *Sholkovitz et al.*, 2009a].

This chapter presents a comprehensive study carried out over the Bay of Bengal (BoB), a semi-enclosed basin located in the eastern side of the North Indian Ocean, influenced by the semi-annual reversing monsoonal wind pattern. Based on the measurement of optical and chemical properties of aerosols, earlier studies have highlighted that the entire Bay region is impacted by continental outflow from south and south-east Asia during the *Winter* (December-February) and Spring-intermonsoon (March-April) [Kumar et al., 2010; Lelieveld et al., 2001; Ramanathan et al., 2001a]. The impact of anthropogenic acidic species has been documented through wide-spread depletion of chloride from sea-salt aerosols [Sarin et al., 2011]. Likewise, role of biomass burning emissions and fossil-fuel combustion as a dominant source of enhancing the fractional solubility of Fe over the Bay of Bengal has been reported by Kumar et al., [2010]. A comparative study of the fractional solubility of aerosol Fe over the Bay of Bengal and the Arabian Sea has provided evidence for the chemical processing of mineral dust in the presence of a highly acidic environment (dominated by sulphate) [Srinivas et al., 2011a]. Therefore, the Bay of Bengal is an ideal oceanic region to study the impact of anthropogenic trace metals on the biogeochemistry of the surface waters.

In order to assess the impact of atmospheric deposition of trace metals on surface waters, it is prerequisite to quantify their fluxes across the air-sea interface. Wet deposition is considered as a significant source of trace metals to the surface ocean. However, occurrence of rain events is very rare over the Bay of Bengal during the late NE-monsoon (January-April). Therefore, dry-deposition fluxes of trace metals, reported in this study, represent nearly the total atmospheric input to the Bay of Bengal. The sources, size distribution, and spatio-temporal variability in the mass concentrations of crustal elements (Al, Ca, Fe and Mg) and trace metals (Pb, Cd, Cu, Mn, V, Cr, Co and Ni) have been studied through  $PM_{2.5}$ ,  $PM_{10}$  (particle sizes less than 2 µm and less than 10 µm, respectively) and bulk (TSP) aerosols collected from the marine atmospheric boundary layer (MABL) during two research cruises undertaken in the BoB as a part of the National Programme on Integrated Campaign of Aerosols, gasses and Radiation Budget (ICARB-2006 & ICARB-2009). The study on atmospheric drydeposition is most relevant, as wet precipitation events are very scarce when continental outflow persists over the Bay of Bengal during the late NE-monsoon (January-April).

#### 8.2. Results

# 8.2.1 Mass concentrations

The mass concentrations of  $PM_{2.5}$  and  $PM_{10}$  show pronounced temporal variability, and range from 2.0 – 76.7 and 6.0 – 108.4 µg m<sup>-3</sup> respectively. On an average, fine mass ( $PM_{2.5}$ ) accounts for ~ 65% of  $PM_{10}$  during January'09. Although  $PM_{2.5}$  samples were analyzed for trace metals (Pb, Cd, Cu, Mn, V, Cr, Co and Ni), comparison is made between  $PM_{10}$  samples and bulk (TSP) aerosols collected during March-April'06 to infer the seasonal trends. The measured trace metals exhibited a strong spatial (North- and South-BoB) and temporal (*Winter* and *Spring-intermonsoon*) variability during the sampling period (Figure 8.1 and Figure 8.2). A statistical description of the data from each cruise is presented in Table 8.1.

No statistically significant difference (P > 0.05) in the abundances of certain metals (Al, Fe, Mg, V, Co and Ni) is observed between the data from January'09 and March-April'06. In contrast, mass concentration of Ca, Pb, Cd, Cu, Mn and Cr show significantly different concentrations (P < 0.05) during the two seasons (January'09 and March-April'06; Table 8.2). Relatively high concentrations of Pb, Cd and Mn were observed during January'09 compared to those in March-April'06. In addition to the seasonal variability, characteristic differences were observed between the air masses sampled from the N- and S-BoB (i.e., influenced by the IGP and SEA-outflow, respectively) during January'09 with regard to the abundance ratios of Pb/nss-SO<sub>4</sub><sup>2-</sup>, Cd/nss-SO<sub>4</sub><sup>2-</sup>, Pb/EC and Cd/EC (Figure 8.3). Likewise, the seasonal shift in the AMBTs that was observed for the cruises conducted in the Bay of Bengal during January'09

and March-April'06 may have contributed to the measured differences in the mass ratios of crustal elements (Ca/Al, Fe/Al, Mg/Al and Ca<sup>2+</sup>/Ca; Figure 8.4).

Furthermore, a comparison is made between the mass concentrations of trace metals from the Bay of Bengal with those reported for other oceanic regions (Table 8.3). The mean Al concentration over the Bay of Bengal is similar to that reported over the Arabian Sea,the Mediterranean Seaand the Gulf of Aquaba, whereas it is greater than that reported for the North Atlantic, the East-China Sea, and the North and North-east Irish Sea. Likewise, the concentration of Fe over the Bay of Bengal is similar to that over the Arabian Sea and the East-China Sea, but slightly lower than concentrations reported for the Gulf of Aquaba and the Mediterranean Sea (Table 8.3). It is further observed that the concentrations of Pb, Cd, Cu, Cr, Co and Ni in the BoB are similar to those from other oceanic regions (Atlantic, Mediterranean etc.), whereas the reported concentrations of Mn and V are higher in the BoB (Table 8.3). This is attributed to the impact of continental outflow from Indo-Gangetic Plain and south-east Asia during the study period (January-April).

Table 8.1: Statistical description of concentration of trace metals data in the Bay of Bengal during the "Winter" (January'09;  $PM_{10}$ ; N = 33) and "Spring-intermonsoon" (March-April'06; TSP; N = 23).

	Winter		<sup>#</sup> Spring-int	termonsoon
Element	range	$Av \pm sd$	range	$Av \pm sd$
Al	205-3468	$1107 \pm 949$	185 - 1892	$923\pm540$
Fe	31-1651	$459\pm444$	150 -1221	$590\pm312$
Ca	41-732	$305\ \pm 158$	196 - 1419	$733\pm362$
Mg	71-580	$312\pm129$	74 - 540	$296 \pm 151$
Pb	2.7-70	$29.5\pm18.8$	3.2 - 13.5	$8.1\pm3.3$
Cd	0.03-2.8	$1.1\pm0.8$	0.1 - 1.6	$0.3\pm0.3$
Cu	0.5 - 21	$4.6\pm3.9$	3.2 - 27.9	$9.3\pm 6.3$
Mn	2.2 -102.9	$39.9\pm29.4$	4.6 - 42.7	$19.4\pm10.6$
V	1.9 - 158	$33.5\pm41.8$	5.4 - 61.7	$28.3\pm18.2$
Cr	$\leq$ 1.1 - 20	$5.9 \pm 5.3$	0.2 - 7.2	$2.2 \pm 1.7$
Co	0.1 - 1.5	$0.4\pm0.4$	0.3 - 0.6	$0.4\pm0.1$
Ni	$\leq$ 0.42- 10	$2.0 \pm 2.0$	0.7-2.4	$1.4 \pm 0.5$

Note: All mass concentrations were expressed in ng  $m^{-3}$ 

# concentration of crustal elements were obtained from Kumar et al., (2008b)

Element	t-test	Difference (IGP- & SEA- outflow)	P- Value
Al	4.7	Significant	< 0.05
Fe	2.8	Significant	< 0.05
Са	4.4	Significant	< 0.05
Mg	1.4	Not Significant	> 0.05
V	4.2	Significant	< 0.05
Cu	1.9	Not Significant	> 0.05
Pb	0.3	Not Significant	> 0.05
Cd	1.6	Not Significant	> 0.05
Mn	0.9	Not Significant	> 0.05
(b)			
Element	t-test	Difference (Winter&Spring-intermonsoon)	P- Value
Al	0.9	Not Significant	> 0.05
Fe	1.3	Not Significant	> 0.05
Са	5.3	Significant	< 0.05
Mg	0.4	Not Significant	> 0.05
V	4.2	Significant	< 0.05
Cu	1.9	Not Significant	> 0.05
Pb	0.3	Not Significant	> 0.05
Cd		$\mathbf{N} + \mathbf{G}^* + \mathbf{G}^*$	> 0.05
Ca	1.6	Not Significant	> 0.05

Table 8.2: Two-tailed t-test results for identifying the significant differences between the (a)IGP- and SEA-outflow (b) Winter and Spring-intermonsoon over the Bay of Bengal.

#### 8.2.3. Enrichment factors

**(a)** 

In this study, the enrichment factors of trace metals were estimated in order to assess their relative increase in supply from non-crustal (i.e., anthropogenic) sources over the study region during the period of continental outflow (January-April). The abundance of trace metals in ambient aerosols is generally normalized with Al concentration and compared with the corresponding elemental ratios in the upper crust to estimate the fraction of each trace metal that is of crustal origin. The enrichment factors of trace metals are calculated as follows.
$$EF_{crust} = \frac{\left(\frac{X}{Al}\right)_{aerosol}}{\left(\frac{X}{Al}\right)_{crust}}$$

Here, X is the mass concentration of the metal of interest measured in aerosols and expressed in ng m<sup>-3</sup>. In this regard, Chester et al., [1993] have defined the trace metals as non enriched elements (NEE) whose crustal enrichment factors are less than 10 and as anomalously enriched elements (AEE) whose enrichment factors are more than 10, suggesting that substantial portion of element is of non-crustal origin.

Average crustal enrichment factors in  $PM_{2.5}$ ,  $PM_{10}$  and bulk (TSP) aerosols collected from the MABL of Bay of Bengal during the period of continental outflow are shown in Figure 8.5. Anomalous enrichment factors, indicative of an anthropogenic source, were observed for Pb, Cu, V, Cd and, possibly, for Mn. For Pb and Cd, the enrichment was greater during the spring intermonsoon period.

### 8.2.4. Dry depositional fluxes

Dry deposition fluxes of trace metals (Figure 8.6) were estimated by multiplying their abundances with an appropriate dry deposition velocity, which can be represented by the following equation:

Dry deposition flux =  $C_{aero} \times V_{dry}$ ;

Here,  $C_{aero}$  is the measured mass concentration of trace metal and  $V_{dry}$  is the dry deposition velocity. The dry deposition velocity is difficult to measure and depends mostly on particle size and meteorological parameters (such as wind speed, relative humidity, surface roughness and atmospheric stability). Therefore, for the present study, deposition velocities were adopted from earlier studies [*Arimoto et al.*, 2003; *Duce et al.*, 1991]. In this study, the deposition velocity for Pb, Cd and Cu is taken as 0.1 cm s<sup>-1</sup>, whereas a deposition velocity of 1.0 cm s<sup>-1</sup> is used for Al, Fe, Mn, V, Cr, Co and Ni. Owing to their predominant origin from high temperature combustion processes, certain trace metals such as Pb, Cd and Cu mostly exists in the fine particle size mode; therefore, a deposition velocity of 0.1 cm s<sup>-1</sup> for these metals is thought to be valid.



Figure 8.1: Spatio-temporal variability of crustal elements (Al, Fe and Ca), trace metals (V, Cu, Pb, Cd and Mn) for the cruise undertaken in the Bay of Bengal during January'09

A dry deposition velocity of 1.0 cm s<sup>-1</sup> for Al, Fe, Mn, V, Mn Cr, Co and Ni has been used elsewhere by several researchers [*Chen et al.*, 2008; *Chester et al.*, 2000; *Gao et al.*, 2002; *Hsu et al.*, 2010].

An inherent uncertainty of about a factor of 2 to 3 associated with the  $V_{dry}[Duce et al., 1991]$  is propagated to the estimated fluxes. Dry deposition fluxes were interpolated and contoured using Ocean Data View software (ODV V.4.0) [Schlitzer, 2002].



Figure 8.2: Spatio-temporal variability of crustal elements (Al, Fe and Ca), trace metals (V, Cu, Pb, Cd and Mn) for the cruise undertaken in the Bay of Bengal during March-April'06.

Region	Al	Fe	Pb	Cd	Cu	Mn	V	Cr	Со	Ni	Reference
Bay of Bengal (2006)	923	590	8.1	0.3	9	19	28	2.2	0.4	1.4	Present study
Bay of Bengal (2009)	1107	459	30	1.1	5	40	34	5.9	0.4	2.0	Present study
Arabian Sea (2006)	855	444	-	-	-	-	-	-	-	-	Kumar et al., 2008
East china sea	615	410	17	0.5	58	16	4	3.7	0.3	1.5	(Hsu et al., 2010)
Mediterranean sea	952	724	25	0.2	6	17		2.3			(Koçak et al., 2004)
Gulf of Aquaba	1081	683	7	0.1	3	17	5	3.0	0.3	2.8	(Chen et al., 2008)
North Sea	285	292	50	-	9	11	-	1.9	-	3.3	(Chester et al., 2000)
West.Mediterrenean sea	383	304	55	-	6	12	-	2.2	-	3.5	(Chester et al., 2000)
North-east Irish Sea	297	363	43	-	15	11	-	5.6	-	7.6	(Chester et al., 2000)

Table 8.3: Comparison of mean concentrations of crustal and trace metals in aerosols from different oceans.

Note: All trace metal concentrations are expressed in ng m<sup>-3</sup>; mass concentrations of Al, Fe in the MABL of Bay of Bengal during March-April'06 were adopted from Kumar et al., [2008].

### 8.3. Discussions

### 8.3.1. Characteristic differences in the IGP- and SEA- Outflow

As stated in Section 8.2.1, based on air mass back trajectories (AMBTs) analyses, a temporal shift in the wind regimes was a conspicuous feature observed over the Bay of Bengal during the cruise in January'09. During 27<sup>th</sup> December'08 - 10<sup>th</sup> January'09, AMBTs represent the outflow from the Indo-Gangetic Plain (IGP); whereas impact of the continental outflow from south-east Asia (SEA) is evident during 11<sup>th</sup> January - 28<sup>th</sup> January'09. The chemical composition of aerosols associated with the IGP- and SEA- outflow are significantly (P < 0.05) different in terms of Al, Fe, and Ca abundances (Table 8.2). It is noteworthy that the concentrations of these crustal elements (Al, Ca and Fe) exhibit similar pattern of temporal variability (Figure 8.2) and north-south gradient, with relatively high levels occurring over the N-BoB (associated with IGP outflow).

In contrast, concentrations of Cu, Cd, Pb and V do not vary significantly (P > 0.05; two tailed t-test; Table 8.2) with the IGP- and SEA-outflow (Figure 8.2). However, characteristic differences between the IGP- and SEA- outflow can be seen from diagnostic ratios of Pb/nss-SO<sub>4</sub><sup>2-</sup>, Cd/nss-SO<sub>4</sub><sup>2-</sup>, Pb/EC and Cd/EC. The relatively high ratios are associated with the SEA-outflow (Figure 8.4), suggesting significant impact of anthropogenic combustion sources (from fossil-fuel combustion and biomass burning).

The trace metals, Mn, Cr, Co and Ni, do not show significant enrichment with respect to their crustal abundances (Figure 8.6). In contrast, Pb, Cd, V and Cu show significant enrichment (Figure 8.6). Based on high enrichment factors of Cu ( $\text{EF}_{\text{crust}} = \sim 50$ ), Pb ( $\text{EF}_{\text{crust}} = \sim 150$ ), Cd ( $\text{EF}_{\text{crust}} = \sim 1000$ ), these metals are categorized as AEE type (anomalously enriched elements,  $\text{EF}_{\text{crust}} > 10$ ). The  $\text{EF}_{\text{crust}}$ of V during January'09 and March-April'06 corresponds to  $18.0 \pm 7.4$  and  $23.0 \pm$ 4.4, respectively. Relatively low enrichment is observed during the winter (January'09) compared to that in the inter-monsoon cruise (March-April '08). The high  $\text{EF}_{\text{crust}}$  of V merits some discussion as it exhibits temporal variability similar to that of Al, suggesting its dominant source from mineral dust. A comparison of the mass concentration of V in  $\text{PM}_{2.5}$  with  $\text{PM}_{10}$  also suggests its occurrence in the coarse mode ( $\text{PM}_{2.5}/\text{PM}_{10}$ :  $0.22 \pm 0.13$ ).

	Al	Ca	Fe	Mg	Pb	Cd	Cu	Mn	V	Cr	Со	Ni
Al	1.00											
Ca	0.93	1.00										
Fe	0.93	0.85	1.00									
Mg	-0.41	-0.44	-0.06	1.00								
Pb	0.73	0.71	0.68	-0.34	1.00							
Cd	0.25	0.22	0.14	-0.28	0.27	1.00						
Cu	-0.20	-0.08	-0.06	0.24	0.01	-0.08	1.00					
Mn	0.96	0.90	0.91	-0.41	0.75	0.19	-0.13	1.00				
V	0.96	0.91	0.94	-0.33	0.74	0.15	-0.05	0.96	1.00			
Cr	0.70	0.52	0.78	-0.03	0.40	0.02	-0.20	0.75	0.75	1.00		
Со	0.72	0.88	0.68	-0.36	0.64	0.14	0.16	0.74	0.76	0.37	1.00	
Ni	0.47	0.53	0.50	-0.22	0.55	-0.02	0.37	0.60	0.61	0.43	0.71	1.00
					Jar	uary'0	9					
	AL	Ca	Fe	Mg	Pb	Cd	Cu	Mn	V	Cr	Со	Ni
AL	1.00											
Ca	0.84	1.00										
Fe	0.98	0.90	1.00									
Mg	0.00	0.39	0.09	1.00								
Pb	0.42	0.69	0.48	0.41	1.00							
Cd	0.69	0.81	0.72	0.22	0.83	1.00						
Cu	0.49	0.51	0.50	0.12	0.48	0.69	1.00					
Mn	0.44	0.34	0.44	0.03	0.04	0.23	0.05	1.00				
V	0.97	0.85	0.99	0.05	0.41	0.66	0.46	0.47	1.00			
Cr	0.64	0.53	0.67	0.02	0.27	0.42	0.17	0.54	0.71	1.00		
Со	0.93	0.77	0.94	0.04	0.34	0.63	0.51	0.45	0.96	0.74	1.00	
Ni	0.53	0.51	0.57	0.10	0.34	0.54	0.41	0.29	0.58	0.92	0.62	1.00

Table 8.4: Binary correlation matrixes for the measured crustal constituents (Al, Ca, Fe andMg) trace metals during March-April'06 and January'09.

Chester et al., [1991] had shown that V is primarily of crustal origin ( $EF_{crust} < 6$ ) based on sampling in the Arabian Sea during the NE-monsoon. However, a recent study by Chen et al., [2008] has attributed the high enrichment factor of V in the air masses over the Arabian Sea to specific type of anthropogenic emissions such as fuel burning.

Although mineral dust is a major source of V (abundance of V in UCC is taken as 0.011 %; [*McLennan*, 2001]), the enrichment of V in ambient aerosols could mainly arise from combustion products of heavy oil rich in V-porphyrins [*Rahn*, 1981; *Zoller et al.*, 1973]. During March-April'06, AMBTs originate from the Desert regions (Thar, Arabia and Oman), subsequently pass over the polluted regions in the Indo-Gangetic Plain before entering into the MABL of Bay of Bengal. Therefore, high enrichment factor of V (Figure 8.5) could be attributed to the anthropogenic mineral dust enriched in V.

The high enrichment factors of Pb, Cd and Cu (Figure 8.5) and their significant correlation with non-sea salt sulphate (nss-SO<sub>4</sub><sup>2-</sup>) suggests their contribution from anthropogenic sources (coal fired power plants, metal smelting and fossil-fuels). Emissions from coal-fired power plants and pyro-metallurgical industries in the IGP have been reported leading to high concentrations of Pb, Cu and other trace metals in the lake sediments [*Donahue et al.*, 2006]. In addition, the unpaired two-tailed t-test reveal significant differences in the enrichment factors (with respect to crust) of trace metals for AMBTs representing IGP- and SEA- outflow (Table 8.2). The enrichment factors (i.e.,  $EF_{crust}$ ) of Pb and Cd are relatively high over the S-BoB (influenced by air masses from south-east Asia) compared to the IGP-outflow, suggesting the long-range transport of trace metals in the fine-mode.

### 8.3.2. Seasonal variability

A comparison of atmospheric abundances of trace metals during the "*Winter*" (January'09) and "*Spring-intermonsoon*" (March-April'06) suggests relatively high concentrations during former time period (Figure 8.1 and Figure 8.2). No significant difference (P > 0.05; two tailed t-test; Table 8.2) is evident for data on Al, Fe, Mg, V, Co and Ni from cruises in January'09 and March-April'06. In contrast, Ca, Pb, Cd, Cu, Mn and Cr show distinctly different concentrations (P < 0.05) during the two seasons, with higher concentrations of Pb, Cd and Mn observed during January'09. This is attributed to dominant impact of pollutants associated with the continental outflow from the Indo-Gangetic Plain in winter months (December-February). The relatively shallow atmospheric boundary layer during winter time and regional meteorology favours trapping of

aerosols in the lower atmosphere and their advective transport to the MABL of the Bay of Bengal. In contrast, strong convective mixing during the springintermonsoon leads to lower columnar concentration of pollutants over the Gangetic Plain.



Figure 8.3: Characteristic differences in the mass ratios of Pb/nss-SO<sub>4</sub><sup>2-</sup>, Cd/nss-SO<sub>4</sub><sup>2-</sup>, Pb/EC and Cd/EC between IGP- and SEA-outflow during the cruise in January'09

The characteristic differences between winter and spring- inter monsoon season are not only evident from the trace metal abundances but are also reflected in terms of the mass ratios of crustal elements (Ca/Al and Fe/Al), which were significantly different (P < 0.05; two tailed t-test) during the two seasons. The ratio of Ca/Al, Mg/Al and Fe/Al during January'09 averaged about  $0.35 \pm 0.14$ ,  $0.46 \pm 0.3$  and  $0.39 \pm 0.10$  respectively, whereas during March-April'06, these ratios were about  $0.86 \pm 0.17$  for Ca/Al,  $0.35 \pm 0.12$  for Mg/Al,  $0.72 \pm 0.37$  for Fe/Al (Figure 8.4). The observed variability in the elemental ratios of crustal constituents (Al, Ca, Fe and Mg) is attributed to seasonal differences in the source of mineral dust. Based on the AMBT analyses, it has been inferred that Bay receives mineral dust input from the Indo-Gangetic Plain (IGP) during winter. The soils (alluvial) in these plains are depleted in Ca and Mg. Mineral dust derived

from these soils is responsible for the observed low Ca/Al and Mg/Al. This is further supported by the low Ca/Al ratio ( $0.21 \pm 0.03$ ) in fine (PM<sub>2.5</sub>) aerosols collected during November'09-March'10 from a rural site in the IGP, characterized by the downwind transport of pollutants to the Bay of Bengal.

In contrast, high elemental ratios of Ca/Al and Mg/Al over the Bay of Bengal during March-April'06 are due to the presence of calcareous mineral dust (as inferred from the back trajectory analyses) originating from the Thar Desert. It has been shown that the advective dust plume sampled from the Arabian Sea, whose AMBTs originated from the Thar Desert region, are enriched in Ca [*Tindale and Pease*, 1999]. In addition, a characteristic high Ca/Al ratio of 0.91 has been reported for the aerosols collected from Thar Desert [*Rastogi and Sarin*, 2009; *Yadav and Rajamani*, 2004]. Therefore, the observed high Ca/Al ratio during the spring intermonsoon can be explained by a source of dust in the Thar Desert.

The mass ratio of Cd/Pb during the two sampling periods (March-April'06 and January'09) is not significantly different (P > 0.01), pointing towards a common source. The ratio of Cd/Pb range from 0.02 - 0.24 (Av: 0.03; sd: 0.01; one extreme outlier is excluded) during March-April'06, whereas during January'09, the ratio ranges from 0.01 - 0.06 (Av: 0.03; sd: 0.01). However, the mass concentrations of Pb and Cd were higher during January'09 (Pb: 29.5 ± 18.8 ng m<sup>-3</sup>; Cd:  $1.1 \pm 0.7$  ng m<sup>-3</sup>) compared to March-April'06 (Pb:  $8.1 \pm 3.3$  ng m<sup>-3</sup>; Cd:  $0.3 \pm 0.3$  ng m<sup>-3</sup>). The higher concentrations of Pb and Cd during January'09, therefore, clearly demonstrate a stronger anthropogenic impact during winter months.

### 8.3.3. Sources and Size distribution

In order to investigate inter-element relationships between the measured trace metals, linear regression analysis was performed and the binary correlation matrix is computed for  $PM_{10}$  (January'09; Table 8.4a) and TSP (March-April'06; Table 8.4b) samples. From this analysis, it is observed that Fe, Ca, Mg, Mn, V, Cr, Co and Ni have significant (p < 0.01; r > 0.80) correlations with Al, suggesting an origin from crustal mineral aerosols. Similarly Pb, Cd and Cu are correlated among themselves, suggesting their common source (i.e., non crustal).



Figure 8.4: Elemental ratios of Ca/Al, Mg/Al and Fe/Al over the Bay of Bengal during March-April'06 (Kumar et al., 2008b) and January'09(this study); and over the Arabian Sea (Kumar et al., 2008a).

The significant linear relation of Pb and Cd with nss-SO<sub>4</sub><sup>2-</sup> during the study period (January'09 & March-April'06), also suggests a common anthropogenic source or transport pattern from the continents. In addition, comparison of mass concentrations in  $PM_{2.5}$  with  $PM_{10}$  suggests that Pb, Cd and Cu exist mostly as fine mode aerosols whereas Al, Ca, Mg, Fe, Mn, V, Cr, Co and Ni exist in coarse mode. Furthermore, prevalent strong correlations among Al, Ca, Fe, Mn, V, Cr, Co and Ni together with coarse mode existence of these metals suggest their crustal source (i.e., mineral dust). The fine mode Pb, Cd and Cu may result from anthropogenic sources (such as high temperature combustion sources).

### 8.3.4. Dry-deposition fluxes

The estimated dry-deposition fluxes (Figure 8.6) have a large inherent uncertainty due to the assumption of representative dry-deposition velocities (V<sub>dry</sub>). As mentioned earlier, V<sub>dry</sub> is difficult to measure owing to its complex coupling with several meteorological parameters such as wind speed, relative humidity and surface roughness etc. The mean and variability of wind speed are similar during winter (range: 0.3-12.4 m s<sup>-1</sup>; Av: ~ 5.5 m s<sup>-1</sup>) and spring-intermonsoon (range: 0.3-13.3 m s<sup>-1</sup>; Av: ~ 4.8 m s<sup>-1</sup>). Likewise, the relative humidity during both cruises was not significantly different (winter: 41-99 %; spring-intermonsoon: 51-95 %). Earlier studies have suggested that at low wind speed (~5 m s<sup>-1</sup>) there is not a considerable enhancement in the particle deposition

velocity due to dependency of sea spray production on wind speed by bursting bubbles [*Pryor and Sørensen*, 2002; *Pyror and Sørensen*, 2000]. However, it has been suggested that at higher wind speeds of about 10-15 m s<sup>-1</sup> the deposition velocity of sub-micrometer particles (i.e., > 0.2-1.0  $\mu$ m) can increase significantly to about 30 % [*Pyror and Sorensen*, 2000].

By assuming the predominant fine mode occurrence of anthropogenic trace metals (eg: Pb, Cd and Cu;  $V_{dry}$  of 0.1 cm sec<sup>-1</sup>), their dry-deposition fluxes to the study region can be underestimated during the sampling period if the mean wind speeds are greater than 5 m s<sup>-1</sup>. Consequently, estimated fluxes from this approach are likely to be lower bounds for the Bay of Bengal. Similarly, the sensitivity of  $V_{dry}$  to hygroscopic growth of particles has been studied by Pyror and Sorensen [2000], who suggested the enhanced deposition of larger particles at higher RH (%). Therefore, in this scenario, the estimated dry-deposition fluxes of crustal major elements (Al, Ca , Fe and Mg) and related trace metals (V, Cr, Co and Ni) are lower than the actual fluxes. However, it is important to note that the hygroscopic growth of particles depends on the amount of water-soluble species in a composite material.



Figure 8.5: Mean enrichment factors of trace metals within the MABL of Bay of Bengal during January'09 and March-April'06.

(AEE = anomalously enriched elements; NEE = non-anomalously enriched elements).

A comparison of the contribution of  $\Sigma$ WSIC (i.e., sum of concentrations of all cations and anions) to particulate mass in the winter (Av:  $45 \pm 9$  %) and spring intermonsoon (Av:  $44 \pm 12$  %) suggests that the difference between the means is not significant (P > 0.05; two-tailed t-test; t = 0.2647). From this observation, it is inferred that there were no substantial changes in the dry-deposition velocity due to hygroscopic growth of particles. A comparison of dry-deposition fluxes from the present study with that carried out over other oceanic regions is summarized in Table 8.5.

### 8.3.5. Mineral dust input

The abundance of Al in aerosols is used to estimate the mineral dust concentration based on the assumption that Al comprises approximately 8 % of mineral dust and is solely originated from the upper crust [*McLennan*, 2001; *Taylor and McLennan*, 1985]. On an average, mineral dust concentration accounts for 33 % of PM<sub>10</sub> mass during January'09 and varied between 2.6 - 43.4  $\mu$ g m<sup>-3</sup> (Av: 13.8 ± 11.9  $\mu$ g m<sup>-3</sup>). Similarly, during March-April'06, the estimated mass concentration of mineral dust (49 % TSP mass) ranged from 2.3 - 23.7  $\mu$ g m<sup>-3</sup> with a mean (± stdev) of ~ 11.5 ± 6.8  $\mu$ g m<sup>-3</sup>. These concentrations were converted into mineral dust flux to the study region. The calculated dry-deposition fluxes varied from 0.7 - 14 g m<sup>-2</sup> yr<sup>-1</sup> during the winter cruise, and from 0.7 to 7 g m<sup>-2</sup> yr<sup>1</sup> during the spring intermonsoon.

In the literature, model based estimates for mineral aerosol flux has been provided for the entire northern Indian Ocean (area:  $7.1 \times 10^{12} \text{ m}^2$ ). From this, the mineral dust input to the Bay of Bengal (area:  $2.2 \times 10^{12} \text{ m}^2$ ) has been deduced to compare with fluxes estimated in the present study (see paragraph above). An average dust flux of ~20 Tg yr<sup>-1</sup> (i.e., equivalent to ~9 g m<sup>-2</sup> yr<sup>-1</sup>) to the Bay of Bengal was estimated by Goldberg and Griffin, [1970]. Likewise, a recent study by Jickells et al., [2005] provided a composite estimate of mineral dust input to the Bay region gave values between 1 and 10 g m<sup>-2</sup> yr<sup>-1</sup> [*Mahowald et al.*, 2005b]. From the DEAD (Dust Entrainment and Deposition ) model, the mineral dust input to the Northern Indian Ocean is about 36 Tg yr<sup>-1</sup>, which yields a total flux of ~ 11 g m<sup>-2</sup> yr<sup>-1</sup> [*Zender et al.*, 2003]. Similarly, an

estimate of ~20 Tg yr<sup>-1</sup>has been given by Prospero [1996] for the Northern Indian Ocean, which corresponds to a mineral dust input of ~ 6 g m<sup>-2</sup> yr<sup>-1</sup>.

However, substantially larger estimates have also been provided for the Northern Indian Ocean: ~ 100 Tg yr<sup>-1</sup> by Duce et al. [1991] and ~ 138 Tg yr<sup>-1</sup> by Ginoux et al. [2001]. Based on the Al concentration in surface waters, Han et al., [2008] estimated a dust deposition of ~ 1-5 g m<sup>-2</sup> yr<sup>-1</sup> to the southern Bay of Bengal. A more recent estimate of ~  $0.66 \pm 0.07$  g m<sup>-2</sup> yr<sup>-1</sup> dust input to the Bay of Bengal has been provided by Hatta et al., [2008, AGU fall meeting abstract; CLIVAR REPEAT HYDROGRAPHY, March-April 2007] based on the surface seawater dissolved Al concentration.

The estimated dust input to the Bay of Bengal from the present study  $(0.7 - 14 \text{ g m}^{-2} \text{ yr}^{-1} \text{ during the winter and from 0.7-7 g m}^{-2} \text{ yr}^{-1} \text{ during the spring intermonsoon}) is in agreement with the model-based estimates [$ *Jickells et al.*, 2005;*Mahowald et al.*, 2005b;*Prospero*, 1996;*Zender et al.*, 2003] as well as with the estimates based on surface water Al concentrations. Therefore, despite the larger estimates provided by Duce et al. [1991] and by Ginoux et al. [2001], it has been concluded that mineral aerosol fluxes, estimated in this study, are generally consistent with those obtained by previous studies.

### 8.3.6. Residence time of trace metals

In this study, atmospheric dry-deposition fluxes of trace metals are compared with the metal concentrations in seawater in order to assess their residence time in the water column of the Bay of Bengal. The calculation of residence time is made based on the literature data of trace metals in surface waters of the Bay of Bengal [*Rejomon et al.*, 2008; *Rejomon et al.*, 2010; *Solai et al.*, 2010]. These studies have shown that dissolved concentrations of Fe, Cu, Cd and Pb in the Bay of Bengal differ by a factor of 2 during summer (June-September) and winter (November-February) months. Therefore, metal concentrations in the surface waters are assumed to be same during the study period. The residence time of a trace metal is calculated by dividing its inventory within the surface mixed layer with the atmospheric deposition flux. Furthermore, the fractional solubility of trace metal in aerosols is accounted for in estimating the total atmospheric deposition (dry- and wet-deposition).

As stated in Section 2.1, the impact of continental outflow on the MABL of Bay of Bengal persists only during the late NE-monsoon (January-April). During this period, the precipitation events are very rare. However, in order to constrain the wet-deposition flux, hourly precipitation data over the study region have been used from the TRMM data (<u>http://gdata1.sci.gsfc.nasa.gov/daac-bin/G3/execute.cgi</u>; See the Figure in the supporting material). For this, an upper estimate of 0.5 mm/hr has been assumed as a representative mean hourly rainfall over the Bay of Bengal. The wet-deposition flux of an individual trace metal is then calculated by using the following equation.

$$f_{wet} = P * C_{rain} * \rho_{air}^{-1} * \rho_{water};$$

where P,  $C_{rain}$ ,  $\rho_{air}^{-1}$  and  $\rho_{water}$  represent the wet precipitation amount (i.e., 0.5 x 24 mm/day), metal concentration in rain water (ng m<sup>-3</sup>) (assumed similar to its fractional solubility multiplied by concentration in aerosol, density of air (i.e., ~1.2 kg m<sup>-3</sup>) and water (i.e., 1000 kg m<sup>-3</sup>) respectively. Finally, the residence time of dissolved metals in the mixed layer has been estimated by assuming a solubility of metals in aerosols of either 10 or 100 % in seawater. Although, the residence times estimated in this study have a larger uncertainty, they provide first-order estimates for the study region (Table 8.6).

For PM<sub>10</sub>, dry deposition flux of Fe averages ~ 397  $\mu$ g m<sup>-2</sup> d<sup>-1</sup>. Using this, an estimate of dissolved Fe flux to the Bay is obtained by multiplying the average fractional solubility of iron (Fe<sub>ws</sub>/Fe<sub>Tot</sub> \* 100; Fe<sub>ws</sub>& Fe<sub>Tot</sub> are the water-soluble and total aerosol iron respectively; solubility is 6.9 % for PM<sub>10</sub> sampled during January'09) with dry-deposition flux of total aerosol Fe. This calculation yields a dissolved iron flux of 27.3  $\mu$ g m<sup>-2</sup> d<sup>-1</sup>. By assuming the dissolved concentration of Fe in rain water to be same as its fractional solubility in de-ionized water times the aerosol concentration, and using daily precipitation rate of 12 mm/day, the estimated wet-deposition flux is about 0.46  $\mu$ g m<sup>-2</sup> d<sup>-1</sup>, less than a factor of 5 times to that of its dry-deposition. The combined estimate of atmospheric deposition of dissolved Fe is about 28  $\mu$ g m<sup>-2</sup> d<sup>-1</sup>, which yields a residence time of 6.8 yrs that is

	Bay of Bengal			<sup>1</sup> Gulf of Aqaba		<sup>2</sup> East China Sea		<sup>3</sup> NE.	Atlantic Ocean	<sup>4</sup> W.Mediterrenean	
		January'09 Mar-April'06		Aug'03-Sept'05		2005 -2007		Ju	n'96; May'97	Sep-Oct'88;Feb-July'89	
Metal	V <sub>dry</sub>	<b>f</b> <sub>dry</sub>	$\mathbf{f}_{dry}$	V <sub>dry</sub>	$\mathbf{f}_{dry}$	V <sub>dry</sub>	<b>f</b> <sub>dry</sub>	V <sub>dry</sub>	<b>f</b> <sub>dry</sub>	V <sub>dry</sub>	<b>f</b> <sub>dry</sub>
Al	1.0	$1.0 \pm 0.8$	$0.8 \pm 0.5$	1.0	0.9	2.0	$0.04\pm0.07$	1.3	0.014	1.0	0.4
Fe	1.0	$0.4\pm0.4$	$0.5\ \pm 0.3$	1.0	0.6	2.0	$0.04\pm0.05$			1.0	0.3
V	1.0	29.0±36.1	$24.5 \pm 15.7$	1.0	4.7	1.0	$1.5 \pm 4.0$				
Mn	1.0	34.5±25.4	$16.7 \pm 9.1$	1.0	14.5	1.0	6.7±14.3	1.3	2.2	1.0	10.8
Cu	0.1	$0.4\ \pm 0.3$	$0.8\ \pm 0.3$	0.4	1.1	0.5	$12 \pm 14$			0.1	0.6
Pb	0.1	$2.6\ \pm 1.6$	$0.7 \pm 0.3$	0.4	2.2	0.5	$2.5\pm6.7$	0.5	3.4	0.1	5.8
Cd	0.1	$0.1\ \pm 0.1$	$0.03\pm0.03$	0.4	0.03	0.5	$0.2\pm0.4$				-
Ni	1.0	$1.8 \pm 1.7$	$1.2 \pm 0.5$	0.4	0.9	1.0	$0.2\pm0.3$			1.0	2.9
Cr	1.0	$5.1\pm4.6$	$1.9 \pm 1.5$	1.0	2.6	1.0	$0.2 \pm 0.2$			1.0	2.3
Co	1.0	$0.4\ \pm 0.4$	$0.4\ \pm 0.1$	1.0	0.3	1.0	$0.07\pm0.09$			1.0	0.2

Table 8.5: Comparison of dry-deposition fluxes of metals from the MABL of Bay of Bengal with other Oceanic regions.

<sup>1</sup> Chen et al., [2008]: Gulf of Aqaba, Red Sea; <sup>2</sup>Hsu et al., [2010]: East China Sea; <sup>3</sup>Spokes et al., [2001]: North-east Atlantic Ocean; <sup>4</sup>Chester et al., [1999]: Western Mediterranean Sea.

**Note:** dry-deposition fluxes of Pb, Cu and Mn were in  $\mu g m^{-2} d^{-1}$ ; Al, Fe are in mg m<sup>-2</sup> d<sup>-1</sup> and Cd which is in ng m<sup>-2</sup> d<sup>-1</sup>.

of comparable magnitude with the estimated residence time of 4.8 yrs by assuming 10 % solubility (Table 8.6).

The estimated residence time of Fe in the surface waters of the Bay of Bengal could be higher than that expected for a bio-limiting micronutrient. The high value for the estimated residence time is mainly due to the high dissolved Fe concentration (~ 2.34  $\mu$ g /litre) measured by Rejomon et al., [2008] in the coastal shelf waters. In contrast, a recent study has reported a dissolved Fe concentration of 1.34 nM in the surface waters of the south Bay region as a part of "CLIVAR-II repeat hydrography" during March-April'07 [*Hatta et al.*, 2008].

Table 8.6: Estimates of residence times (years) of trace metals in the surface waters of Bay of Bengal.

Element	۴Fe	<sup>€</sup> Mn	٤Cu	٤Cd	٤Pb	٤Co	٤Ni
conc ( $\mu$ g l <sup>-1</sup> )	2.34	13	0.9	0.03	0.31	0.076	0.046
MLD (m)	30	30	30	30	30	30	30
Metal conc (ng m <sup>-3</sup> )	459	39.9	4.6	1.1	29.5	0.4	2.0
10 % solubility	45.9	4.0	0.46	0.11	2.95	0.042	0.2
V <sub>dry</sub> (cm sec <sup>-1</sup> )	1.0	1.0	0.1	0.1	0.1	1.0	1.0
<sup>#</sup> dry-deposition ( $\mu g m^{-2} d^{-1}$ )	397	34.5	0.4	0.1	2.5	0.4	1.7
<sup>\$</sup> dry-deposition ( $\mu g m^{-2} d^{-1}$ )	39.7	3.45	0.40	0.10	2.55	0.04	0.17
<sup>#</sup> Wet-deposition ( $\mu g m^{-2} d^{-1}$ )	4.6	0.40	0.046	0.011	0.295	0.004	0.020
<sup>\$</sup> Wet-deposition ( $\mu g m^{-2} d^{-1}$ )	0.46	0.04	0.005	0.001	0.030	0.0004	0.002
<sup>#</sup> Tot. deposition ( $\mu g m^{-2} d^{-1}$ )	401	35	0.44	0.11	2.84	0.37	1.75
<sup>\$</sup> Tot. deposition ( $\mu g m^{-2} d^{-1}$ )	40.1	3.5	0.40	0.10	2.58	0.04	0.17
<sup>#</sup> Residence Time (yrs)	0.5	31.7	166	20.2	8.8	17.0	2.2
<sup>\$</sup> Residence Time (yrs)	4.8	317	183	22	10	170	22

\$ Déposition fluxes by assuming 10 % solubility of metals ; # Deposition fluxes by assuming 100 % solubility. ;MLD (m) = mixed layer depth [*Narvekar and Prasanna Kumar*, 2006].

Concentration of metals in sea water are from <sup>1</sup>Rejomon et al., (2008) and <sup>2</sup>Solai et al., (2010).

By using this concentration, a residence time of about  $\sim 0.2$  yrs for Fe has been obtained, in which case indicates the importance of atmospheric supply as a significant source to surface waters of the Bay of Bengal. However, in this study, the concentration measured at off shore waters of Sri Lanka, where the fluvial input is not significant. In contrast, fluvial contribution along with heavy



Figure 8.6: Spatial variability in dry-deposition fluxes of crustal elements and trace metals in aerosols from the Bay of Bengal. (Dry-deposition fluxes of Al & Fe are in mg m<sup>-2</sup>  $d^{-1}$ ; Pb, Cu and Mn are in  $\mu g m^{-2} d^{-1}$ ; Cd is in ng m<sup>-2</sup>  $d^{-1}$ ).

suspended load can account for the observed high concentration of dissolved Fe in seawater, reported by Rejoman et al., [2008] was measured along the West coast of Bay of Bengal. However, the range of values for the Fe residence time estimated here is consistent with estimates for the Sargasso sea (0.7 yrs, [*Jickells*, 1999]), Gulf of Aqaba (0.4 - 1.5 yrs, [*Chase et al.*, 2006]; 4.9 yrs, [*Chen et al.*, 2008]) and North-Pacific (0.5 yrs, [*Boyle et al.*, 2005]. However, relatively longer residence times have been suggested by Landing and Bruland [1987] for dissolved Fe and Mn (DFe = 8.2-56 yrs; DMn = 180-920 yrs) in the open ocean waters.

As noted above, certain metals such as Cu, Cd and Pb have high enrichment factors, suggesting their significant contribution from anthropogenic sources. It has been suggested that the fractional solubility of anthropogenic trace metals is relatively high compared to that originating from crustal sources [*Sholkovitz et al.*, 2009a]. Therefore, residence times for anthropogenic trace metals calculated by assuming 10 % solubility could be overestimated, and actual residence times may be substantially smaller. For those metals such as Mn, Co and Ni that are assumed to be derived mostly from upper continental crust (EF<sub>crust</sub> < 10), residence time is calculated by assuming 10 % solubility; may be more reasonable. In view of the large contribution of anthropogenic trace metals to aerosols within the marine atmospheric boundary layer of Bay of Bengal during the winter and spring intermonsoon seasons, their air-sea deposition can have a substantial effect on marine biogeochemical cycles of these elements.

### 8.4. Conclusions

This study presents the first comprehensive data set on Al, Fe, Pb, Cd, Cu, and Mn in aerosols collected from the marine boundary layer of Bay of Bengal during January'09 and March-April'06. Comparison of mass concentrations in PM<sub>2.5</sub> with PM<sub>10</sub> suggests that Al, Ca, Mg, Fe and Mn exist in coarse mode, associated with mineral dust. In contrast, Pb, Cd and Cu exist in fine mode aerosols, suggesting their anthropogenic source (i.e., emissions from combustion derived sources, industrial emissions). The abundance of air-borne trace metals within the marine boundary layer of the southern Bay of Bengal region indicates the impact of anthropogenic sources on this remote oceanic region. The mass concentrations (ng m<sup>-3</sup> of air) of trace metals such as Pb, Cd, Cu, Cr, Co and Ni were similar to those reported from the other oceanic regions (Atlantic, Mediterranean etc.), whereas the measured concentrations of Mn and V are higher in the Bay of Bengal. This is attributed to impact of continental outflow from Indo-Gangetic Plain and south-east Asia during the study period (January-April). Mineral dust input to the study region based on inferred dry deposition velocities are consistent with estimates based on models. Dry-deposition fluxes are compared with seawater concentrations to estimate their water column residence time in the Bay of Bengal. These results indicate that for most of the metals, residence time is less than 25 yrs except for Mn, Cu and Co.

## Chapter 9

Synthesis and Future Directions

### 9.1. Synthesis

The impact of continental outflow on the oceanic waters is essential to evaluate their role in surface biogeochemistry. Very few systematic studies with regard to chemical composition of aerosols over the oceanic regions, down wind of the pollution sources are available. Apart from the chemical composition, atmospheric abundances of nutrient species (N, P and Fe), their sources, transport pathways, deposition fluxes and their impact on open ocean water are poorly constrained and, hitherto, lacking in the literature. Subsequently, owing to paucity of data, atmospheric components in the global biogeochemical models are often poorly represented.

In the present-day scenario of growing anthropogenic activities, it has been further suggested that the impact is much more prominent in oceanic waters around the south and south-east Asia due to rapid industrialization, urbanization and increase in use of fertilizers. The present study investigates the impact of continental outflow on the surface waters of the Northern Indian Ocean. This study provides a unique data set of size-segregated aerosol samples (PM<sub>2.5</sub>, PM<sub>10</sub> and TSP), collected from the Arabian Sea and Bay of Bengal. These samples were analyzed for the water-soluble inorganic constituents (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>), crustal elements (Al, Fe, Ca and Mg) and trace metals (Pb, Cd). In addition, fractional solubility of iron (Fe<sub>ws</sub> % = Fe<sub>ws</sub>/Fe<sub>Tot</sub> \*100; Fe<sub>ws</sub> = water-soluble iron and Fe<sub>Tot</sub> = total aerosol iron), and the factors affecting its solubility has been assessed during the long-range atmospheric transport of continental aerosols to the marine atmospheric boundary layer (MABL).

The present study encompasses chemical characterization of nutrient species (N, P and Fe) over the Northern Indian Ocean during the continental outflow (Winter: January'09 and Spring-intermonsoon: March-April'06). In addition, chemical characterization of aerosols in the MABL through their atmospheric abundances of water-soluble ionic species, mineral dust, sea-salts and carbonaceous species have also been studied (i.e., to assess to their abundances, sources, size-distribution and spatio-temporal variability) during the continental outflow. The study area comprises Bay of Bengal (BoB) and the Arabian Sea (ARS). The continental impact from south and south-east Asia dominates the wide

spread dispersal of pollutants during the late NE-monsoon (January-April). Furthermore, it has been shown that the impact is much more prominent over the Bay of Bengal compared to the Arabian Sea.

A strong spatio-temporal variability has been observed for mass loading of  $PM_{2.5}$  and  $PM_{10}$  with relatively higher concentration in the northern Bay and dominated by fine ( $PM_{2.5}$ ) mode aerosols constituting ~ 65 % of  $PM_{10}$  during wintertime. Comparison of abundances between the  $PM_{2.5}$  and  $PM_{10}$  fraction reveals their size-distribution. The water-soluble ionic constituents such as nss- $SO_4^{2-}$ ,  $NH_4^+$  and nss- $K^+$  show a predominant fine mode nature. In contrast,  $NO_3^-$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $CI^-$  have shown coarse mode distribution. Likewise, the predominance of crustal elements (Al, Fe, Ca and Mg) in  $PM_{10}$  rather than in  $PM_{2.5}$  is suggesting their association with coarse mode mineral dust. In contrast, OC exhibit a bimodal distribution. Unlike OC, EC show a predominant fine mode distribution over the Bay of Bengal during the continental outflow.

Significant differences were observed between the two sampling seasons with relatively high concentration of anthropogenic constituents (nss-SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, nss-K<sup>+</sup>, EC and OC) observed during the *Winter* (December-February) cruise as compared to that for *Spring-intermonsoon* (March-May) suggests their dominance during the former sampling period. Sea-Salts contribution towards mass loading is relatively low compared to that from anthropogenic constituents and mineral dust during *Winter* and *Spring-intermonsoon*. On an average, mineral dust accounts for ~30 and 50 % of particulate mass during Winter and Spring-intermonsoon; respectively with distinctly differ in terms of their source.

The alluvial soil from the Indo-Gangetic Plain is major source of mineral dust during *Winter* whereas the transport from the desert regions (eg: Thar, Arab etc.,) is a significant contributor of aerosols to the MABL. The evidence for this constrained from the differences in the abundance and solubility of aerosol-Ca, Ca/Al ratio between the two seasons. The fractional contribution of WSIC (i.e., water-soluble ionic constituents) to particulate mass loading was more or less similar (~ 45 %) throughout Bay of Bengal during both seasons, with dominant contribution from sulphate to the ionic budget. On an average, nss-SO<sub>4</sub><sup>2</sup>

constitutes ~ 65 % of the total water-soluble ionic species and is primarily associated with the fine mode ( $PM_{2.5}$ ) aerosols.

The spatial distribution of carbonaceous species (EC and OC) exhibit a similar pattern as that of mass loading in both cruises, showing a decreasing trend in the EC and OC concentration towards S-BoB. The mixed contribution of fossil-fuel and biomass burning sources has been observed towards carbonaceous species in N-BoB where as S-BoB is more influenced by biomass combustion sources. Relatively high mass ratio of nss-K<sup>+/</sup>EC, nss-K<sup>+</sup>/OC in air masses, originate from the south-east Asia during January'09 and from the Indo-Gangetic Plain during March-April'06, suggesting the impact of biomass burning emissions.

The relative abundance of chemical constituents over the BoB and the ARS have been explained in terms of differences in the source strength of anthropogenic constituents and source regions of mineral dust. Relatively higher abundances of nutrients observed BoB compared to that over the ARS. Furthermore, within the Bay region, the impact of continental outflow decreases from winter months (December-February) to spring-intermonsoon (March-April). Hence, relatively high mass concentrations of nutrients occur in the MABL of BoB during Winter months compared to those in Spring-intermonsoon season. The mass concentration of water-soluble inorganic nitrogen (N<sub>Inorg</sub>: NH<sub>4</sub><sup>+</sup>+ NO<sub>3</sub><sup>-</sup>, range: 18 to 565 nmol m<sup>-3</sup>) dominates the total soluble nitrogen (N<sub>Tot</sub> = N<sub>Inorg</sub> + N<sub>Org</sub>) in the fine mode (PM<sub>2.5</sub>), and occurs mainly as NH<sub>4</sub><sup>+</sup> (range: 16 to 561 nmol m<sup>-3</sup>) over the Bay of Bengal.

Likewise, the mass concentrations of  $N_{Tot}$  is dominated  $N_{Inorg}$  (mainly as  $NO_3^- - N$ ) over the Arabian Sea. The mass-ratio of  $N_{Inorg}$  in  $PM_{2.5}$  to  $PM_{10}$  centers around 85 %, suggesting that contribution of coarse mode  $NO_3^-$  is relatively insignificant over the Bay of Bengal. The dominant contribution of  $N_{Inorg}$  (as  $NH_4^+$ ) to  $N_{Tot}$  is also evident based on the data from earlier cruises (February-March'01, February'03 and March-April'06) conducted in the Bay of Bengal. Water-soluble  $N_{Org}$  also dominates the fine fraction and accounts for no more than 38 % of  $N_{Tot}$ , with relatively high concentrations along the coastal region. A significant linear relationship among  $N_{Org}$ ,  $NH_4^+$ , nss-K<sup>+</sup> and EC (p-value < 0.001)

suggest their common source from biomass burning emissions and large-scale application of fertilizers (urea).

The spatio-temporal variability of inorganic phosphorous ( $P_{Inorg} = PO_4^{3-}$ ) in the MABL and dry-deposition flux to the surface waters has been studied during the continental outflow (January-April). A comparison of  $P_{Inorg}$ concentration in  $PM_{2.5}$  (0.1-0.8 nmol m<sup>-3</sup>) and  $PM_{10}$  (0.3 -2.8 nmol m<sup>-3</sup>), reveal its dominant occurrence in the coarse mode ( $D_a \ge 2.5\mu$ m). The analytical data also provide an evidence for the chemical processing of mineral dust by atmospheric acidic species and mobilization of  $P_{Inorg}$  during long-range atmospheric transport. However, significantly high  $P_{Inorg}/nss-Ca^{2+}$  ratios over the Bay of Bengal relative to that over Arabian Sea suggest dominant contribution of anthropogenic sources (fertilizers and biomass burning emissions). In contrast,  $P_{Inorg}$  concentration over the Arabian Sea is about 4 to 5 times lower and primarily associated with mineral dust from Desert regions. The dry-deposition of  $P_{Inorg}$  to the Bay of Bengal varies by one order of magnitude (0.5 – 5.0 µmol-P m<sup>-2</sup> d<sup>-1</sup>; Av: 0.02 Tg yr<sup>-1</sup>) and is of comparable magnitude with the model-based estimates.

Ambient aerosols collected from the marine atmospheric boundary layer (MABL) of the Bay of Bengal and the Arabian Sea have been studied to assess the fractional solubility of aerosol iron, defined as  $Fe_{ws}$  (%) =  $Fe_{ws}/Fe_{Tot}$  \* 100; where  $Fe_{Tot}$  is total aerosol iron and  $Fe_{ws}$  is water-soluble iron. The mass concentration of  $Fe_{Tot}$  over the two oceanic regions is not significantly different. However, the fractional solubility is 1 to 2 orders of magnitude higher over the Bay of Bengal (1.4 – 24 %) compared to that over the Arabian Sea (0.02 - 0.4 %). The spatio-temporal variability in  $Fe_{ws}$  (%) is attributed to differences in the nature of the mineral dust over the two oceanic regions.

The Arabian Sea receives coarse dust from desert regions; whereas transport of alluvial dust from the Indo-Gangetic Plain is a dominant source to the Bay of Bengal. The poor fractional solubility (<1%) of Fe from mineral dust, hitherto overestimated in the literature, is documented for the Arabian Sea. A significant linear relationship (p-value < 0.001) among Fe<sub>ws</sub> (%), Fe<sub>Tot</sub> and nss- $SO_4^{2-}$  over the Bay of Bengal provides unequivocal evidence for the chemical processing of mineral dust. Furthermore, the role of anthropogenic sources

(biomass burning and fossil-fuel combustion) in enhancing the  $Fe_{ws}$  (%) is discernible from the chemical composition of fine mode (PM<sub>2.5</sub>) aerosols over the Bay of Bengal.

The occurrence of wet precipitation events over the study region (BoB and ARS) during the continental outflow is very rare and, hence, wet-deposition is not significant. The dry-deposition fluxes exhibit spatio-temporal variability and are relatively high over the BoB ( $N_{Tot}$ : 2 – 167 µmol m<sup>-2</sup> d<sup>-1</sup>; P<sub>Inorg</sub>: 0.5 – 4.8 µmol m<sup>-2</sup> d<sup>-1</sup>; Fe<sub>ws</sub>: 0.02 - 1.2 µmol m<sup>-2</sup> d<sup>-1</sup>, where N<sub>Tot</sub> is (N<sub>Inorg</sub> + N<sub>Org</sub>) and Fe<sub>ws</sub> refers to water-soluble fraction of aerosol-Fe) compared to those over the ARS (N<sub>Tot</sub>: 0.2 – 18.6 µmol m<sup>-2</sup> d<sup>-1</sup>; P<sub>Inorg</sub>: 0.3-0.9 µmol m<sup>-2</sup> d<sup>-1</sup>; Fe<sub>ws</sub>: 0.7-15.3 nmol m<sup>-2</sup> d<sup>-1</sup>).

The atmospheric source of N and P is of comparable magnitude with their supply via rivers. Assuming Redfield stoichiometry and complete utilization of N<sub>Tot</sub> by marine phytoplankton, atmospheric input can account for no more than 13 and 1 % of Primary Production in the BoB and ARS, respectively. Using atmospherically derived P- and Fe-fluxes, C-fixation rate in the BoB (1.1 Pg yr<sup>-1</sup>) is considerably higher than that in the ARS (0.03 Pg yr-1). However, N-fixation rate in the two ocean basins is somewhat similar (~ 0.5 Tg yr<sup>-1</sup>). The growing anthropogenic activities and a further increase in the air-sea deposition fluxes of nutrients have potential to augment C-fixation rates in the Northern Indian Ocean.

#### 9.2. Scope of future research

The work carried out in this thesis provides comprehensive information regarding the atmospheric abundances of nutrients (N, P and Fe), transport pattern, transformation processes, deposition fluxes and their impact on ocean surface biogeochemistry. In addition, aerosol iron solubility and the factors affecting its solubility has also been studied over the two basins (Bay of Bengal and Arabian Sea). However, there are considerable challenging issues pertaining to the dust transport to the remote oceanic regions in terms of their supply of soluble iron through atmospheric processing and contribution from combustion sources.

### 9.2.1. Stable isotopic composition of Fe

It has been suggested that atmospheric supply of soluble Fe is a dominant source to the open ocean. Since one third of the land masses are covered by desert sources, global chemical transport models and emission inventories of dust sources suggest arid and semi-arid regions of the world as a major source of Fe to the open ocean waters. However, it has been shown that these desert soils are characterized by poor solubility (< 1 % only accessible for biology). In addition, anthropogenic sources have been identified as a significant contributor of aeolian iron input. In specific, recent studies have argued that the fractional solubility of aerosol iron form combustion sources (viz., fossil-fuel combustion and biomass burning emissions) are relatively high ( $\leq 80$  %) and, thus, suggested that their supply controls the bio-available iron in the open ocean waters, particularly in the downwind of pollution sources. Recent studies have demonstrated that stable isotopic composition of Fe can be used to de-convolute contribution from natural versus anthropogenic sources. Therefore, the combined chemical and isotopic investigation of source specific aerosols, and those transported to marine boundary layer can give a better handle to understand the major sources and their transport pathways of this micro nutrient to the surface waters.

### 9.2.2. Mineralogy of dust in the MABL

Despite the differences in the sources of Fe, mineralogy is a key factor that solely dictates the solubility of iron and other metals in open ocean waters. It has been suggested that the fractional solubility of iron in clay (eg: illite, chlorite and montimorlinite etc.,) minerals is relatively high compared to that for quartz, feldspar and other minerals. Therefore, brief knowledge about mineralogical differences in the soil (alluvial versus desert) can give vital information regarding their relative importance of dominant contributing mineral during the long-range atmospheric transport of continental aerosols to the remote oceanic regions.

### 9.2.3. Mixing state of aerosols

The mixing state of aerosols has gained considerable attention in the recent years. The role internal versus external mixture of mineral dust with other anthropogenic acidic species ( $H_2SO_4$ ,  $HNO_3$ ) is essential to understand the atmospheric processing of mineral dust during the long-range transport. This has implications to the supply of soluble iron to the open ocean waters. So far, over the oceanic region, very limited measurements were available in this respect. Therefore, combined knowledge of chemical composition of aerosols together

with its mixing state can ascertain the presence/absence of atmospheric processing of mineral dust during the long-range transport.

### 9.2.4. Modelling the effects of aeolian input on the Ocean Biogeochemistry

In order to well understand the role of atmospheric input on the biogeochemistry of the surface ocean, regional scale estimates has to be included in the biogeochemical models. In this regard, limited number of studies has focussed on the aeolian supply to the Arabian Sea and the Bay of Bengal. The transport and the deposition of pollutants during the late NE-monsoon, can lead to changes in the net community production in the surface waters of the Bay of Bengal. In addition to the nutrient inputs, the deposition of toxic metals can affect the phytoplankton taxa. Therefore, the effect of combined nutrient and toxic species deposition should be better represented in order to constrain the role of aeolian supply in biogeochemical cycles of C and other elements.

# 9.2.5. Long-term characterization of dust transport and regional mapping of fractional solubility of aerosol iron

Long term chemical characterization of dust transport has not been assessed for the Northern Indian Ocean. Unlike the other oceanic regions, there were no such measurements available for the study region to understand the dust transport pattern, their seasonal trends and long-term variability. The studies so far existing in the literature, is only based on the limited seasonal sampling at few high altitude sites and through national field campaigns over the Bay of Bengal and the Arabian Sea. Therefore, it is important to study the long-term of variability of dust fluxes for this oceanic region. This will provide the changes in the mineral dust input as a result of increase in emissions from land-use practices, increase in droughts and other anthropogenic emissions (eg: re-suspended urban dust etc). In addition, high resolution regional mapping of aerosol iron solubility has to be studied from the downwind oceanic region of pollution sources to better represent this parameter in the global chemical transport model, thus, assessing the realistic impact on open ocean waters via the supply of key micro nutrient.

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7) Bikkina Srinivas and M. M. Sarin 2012, "Dry deposition of Toxic metals to the Bay of Bengal: Implications to surface Biogeochemistry", Revision submitted to *Journal of Marine Systems (Revision Submitted)*.

## Manuscripts Under preparation:

 Bikkina Srinivas and M. M. Sarin, 2012, "Atmospheric dry-deposition N, P and Fe to the Northern Indian Ocean: Implications to C- and N-fixation", under submission to "*Tellus B*"

- 9) Bikkina Srinivas, M. M. Sarin and R. Rengarajan, 2012, "Chemical Characterization of aerosols during the continental outflow: Seasonal and Temporal trends", under submission to "*Environmental Research Letters*"
- 10) Bikkina Srinivas and M. M. Sarin, 2012, "Chemical characterization of fine aerosols in the continental outflow from the Indo-Gangetic Plain: Evidence for long-range atmospheric transport", under submission to "Journal of Geophysical Research-Atmospheres"
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- 2) Ashwini Kumar, M.M.Sarin, Bikkina Srinivas, A.K. Sudheer, and N. Rastogi, "Large-scale chloride-depletion in sea-salt aerosols over Bay of Bengal: Implications to climate forcing" Asia Oceania Geosciences Society-2010, 5-9 'July, Hyderabad, India.
- 3) Bikkina Srinivas, M. M. Sarin, A. Kumar, "Impact of anthropogenic sources on iron mobilization from mineral aerosols", 5<sup>th</sup> International symposium on biological and environmental chemistry DMS (P) and related compounds 19-22<sup>nd</sup> October'2010, Goa, India.
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