

Atmospheric Deposition of Inorganic and Organic Nitrogen to the Bay of Bengal: Impact of Continental Outflow

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Abstract

The continental outflow from south and south-east Asia, persisting during January to March, dominates the widespread dispersal of pollutants over tropical Bay of Bengal. With a view to assess the impact of anthropogenic sources on surface ocean biogeochemistry, concentrations of water-soluble inorganic and organic nitrogen (N_{Inorg} , N_{Org}), their spatial variability and dry-deposition fluxes have been studied in size-segregated ($PM_{2.5}$ and PM_{10}) aerosols collected during Jan-2009 from MABL of Bay of Bengal. The mass concentration of N_{Inorg} (NH_4^+ + NO_3^- , range: 18 to 565 $nmol\ m^{-3}$) dominates the total soluble nitrogen ($N_{\text{Tot}} = N_{\text{Inorg}} + N_{\text{Org}}$) in the fine mode ($PM_{2.5}$), and occurs mainly as NH_4^+ (range: 16 to 561 $nmol\ m^{-3}$). 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. The dominant contribution of N_{Inorg} (as NH_4^+) to N_{Tot} is also evident based on the data from earlier cruises (Feb-Mar-2001, Feb-2003 and Mar-Apr-2006) 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^+ , $nss-K^+$ and EC (p-value < 0.001) suggest their common source from biomass burning emissions and large-scale application of fertilizers (urea). The dry-deposition flux of nitrogen ($N_{\text{Inorg}} + N_{\text{Org}}$) to the Bay of Bengal ranges from 2 to 167 $\mu mol\ m^{-2}\ d^{-1}$. The upper estimate of N-deposition is somewhat comparable with the model based fluxes, and can support up to 13 % of the Primary Production in the Bay of Bengal.

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 growing anthropogenic activities, including fossil-fuel combustion, biomass burning and fertilizer production (Galloway and Cowling, 2002). The atmospheric transport and subsequent deposition of anthropogenic nitrogen is of significant interest as it can perturb ocean surface Primary Productivity, thereby influencing the marine biogeochemistry of nitrogen species and other nutrients. Recent studies have highlighted the importance of atmospheric anthropogenic nitrogen (AAN) deposition to the open ocean and its potential to enhance Primary Production particularly in the oligotrophic waters (Duce et al., 2008). Likewise, deposition of AAN to estuarine and coastal waters can increase eutrophication, trigger phytoplankton bloom, which in turn can lead to oxygen depletion in the water column and sediments (Howarth, 2008; Nixon, 1995; Paerl et al., 2002; Paerl and Whitall, 1999).

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 the deposition fluxes, it is essential to quantify mass concentrations of nitrogen species in the marine atmospheric boundary layer (MABL). The water-soluble reactive nitrogen in aerosols comprises of both inorganic and organic forms. The inorganic nitrogen (N_{Inorg}) is a sum of mass concentrations of nitrate and ammonia ($\text{NO}_3^- + \text{NH}_4^+$). In urban (source) regions, NO_3^- exists predominantly as NH_4NO_3 in the fine mode aerosols due to 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 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.

Until recently, the principal focus of air-sea exchange studies (eg: SEAREX) on reactive nitrogen to the ocean surface had 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, studies on atmospheric deposition needs to be extended to measure 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).

We report here systematic measurements of both inorganic and organic nitrogen based on the size-segregated ($PM_{2.5}$, PM_{10}) aerosols collected during Jan-2009 from the MABL of Bay of Bengal. Our main objective is to identify the sources, and to assess the spatio-temporal variability and depositional fluxes of inorganic and organic nitrogen when continental outflow persists over the Bay of Bengal. We have also summarized results from our earlier cruises undertaken in the Bay of Bengal, during the same time period (January-April), in order to make the data set representative for this region.

2. Experimental methods

2.1. Site description

The Bay of Bengal, a semi enclosed basin of northern Indian Ocean, is influenced by the semi-annual pattern of complete reversal of winds. During June- November, monsoonal winds from sea to land do not favor the continental outflow to the marine atmospheric boundary layer (MABL). However, with complete reversal of winds from south-westerly to north-easterly (land to sea) in the wintertime (December-February) and spring-intermonsoon (March-April), downwind transport of pollutants from the Indo-Gangetic Plain and south-east Asia is dominant. Earlier studies carried out during INDOEX programme on the optical properties of aerosols in the MABL of Bay of Bengal have addressed the importance of continental outflow influencing the radiative forcing over this oceanic region (Jayaraman et al., 1998; Ramanathan et al., 2001; Satheesh, 2002). Recent studies on chemical characteristics of aerosols over Bay of Bengal, during winter and spring-intermonsoon, have demonstrated strong impact of anthropogenic sources on the atmospheric chemistry (Kumar et al., 2008; Lelieveld et al., 2001; Sudheer and Sarin, 2008). Although wet deposition is also considered as a dominant pathway for the atmospheric supply of nutrients to the ocean surface, occurrence of precipitation events over Bay of Bengal are rare during the time of continental outflow (January-April). Nevertheless, our sampling carried out during the wet-phase (SW-monsoon) suggests the dominance of sea-salts in the ambient aerosols. Thus, our study on dry-deposition of inorganic and organic nitrogen associated with continental outflow to the Bay of Bengal is most relevant.

2.2. Cruise track and Meteorological conditions

As a part of the Indian national ICARB programme (Integrated Campaign of Aerosols and trace gases Radiation Budget), cruise track undertaken in Jan-2009, onboard ORV Sagar Kanya, is shown in Fig 1a. Along with, relevant meteorological parameters were measured at an interval of every hour. The

relative humidity ranged from 50 – 80 % with an average of 65 %. The winds during the study period were predominantly north-easterly and the relative wind speed varied from 1.2 to 6.3 m sec⁻¹. More specific details and meteorological conditions have been described elsewhere (Kumar et al., 2010).

2.3. Sample collection and analysis

The size segregated aerosols (PM_{2.5} & PM₁₀) were collected using high volume samplers (HVS-PM_{2.5}, PM₁₀; Thermo Anderson) during Jan-2009. Samplers were calibrated before and after the cruise and the flow rate varied between 1.10 to 1.17 m³ min⁻¹ for the two samplers. A total of 64 samples (31 samples for PM_{2.5} and 33 for PM₁₀) were collected on pre-combusted (at 250⁰c) PALFLEX[®]™ tissuquartz filters (28 cm x 20 cm). After sample collection, filters were sealed in zip- lock bags and stored in the deep freezer at - 19⁰C until the time of analysis. The mass concentrations of PM_{2.5} and PM₁₀ were obtained gravimetrically by measuring the weight of the filters, before and after the collection. All samples were handled under a clean laminar-flow bench (Class-100) for chemical analysis. The sampling tracks conducted during earlier cruises (Feb-Mar-2001, Feb-2003 and Mar-Apr-2006) for the collection of TSP samples are shown in Fig.1b and the relevant data from these cruises is presented in Table 1.

The filter aliquots (one-fourth filter) were treated with 50.0 ml of milli-Q water and extracts were analyzed for water soluble anions (Cl⁻, NO₃⁻ and SO₄²⁻) and cations (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) on Dionex-500 Ion chromatograph equipped with suppressed conductivity detector. A detailed description of the analytical procedures has been provided in earlier publications from our Lab (Kumar et al., 2010; Rengarajan et al., 2007). The non-sea-salt fraction of SO₄²⁻, K⁺ and Ca²⁺ was calculated from the total concentrations using following equations (Keene et al., 1986).

$$\text{Nss-SO}_4^{2-} = \text{SO}_4^{2-} (\mu\text{g m}^{-3}) - 0.252 * \text{Na}^+ (\mu\text{g m}^{-3})$$

$$\text{Nss-K}^+ = \text{K}^+ (\mu\text{g m}^{-3}) - 0.037 * \text{Na}^+ (\mu\text{g m}^{-3})$$

$$\text{Nss-Ca}^{2+} = \text{Ca}^{2+} (\mu\text{g m}^{-3}) - 0.038 * \text{Na}^+ (\mu\text{g m}^{-3})$$

The constants 0.252, 0.037 and 0.038 in the above relations are the ratios of SO₄²⁻/Na⁺, K⁺/Na⁺ and Ca²⁺/Na⁺ similar to the composition of seawater.

For the determination of the water soluble organic nitrogen (N_{Org}), water extracts were filtered through pre-combusted glass-fiber filters (Whatmann GF/F) and analyzed for total nitrogen (N_{Tot}) using Shimadzu (TN-7) analyzer equipped with a chemi-luminescence's detector (Koike and Tupas, 1993; Maita and Yanada, 1990; Nakamura et al., 2006; Ogawa et al., 1999). The soluble organic nitrogen (N_{Org}) is then obtained by subtracting the inorganic nitrogen (N_{Inorg} = NH₄⁺+NO₃⁻) from the total

nitrogen (N_{Tot}). Mass concentrations of all constituents were corrected for procedural blanks (involving a number of blank filters, $n = 7$). The detection limits for NO_3^- , NH_4^+ and N_{Tot} , ascertained as three times the standard deviation of procedural blanks and normalized to the volume of filtered air ($\sim 1400 \text{ m}^3$), are 0.13, 0.38 and 5.1 nmol m^{-3} respectively. The overall precision of the measurements for N_{Inorg} is $\pm 5 \%$ or better, whereas that for N_{Tot} is less than 10% .

2.3.1. Error propagation in N_{Org} mass concentration

As stated earlier, water-soluble N_{Org} is assessed by taking the difference of measured mass concentrations of N_{Tot} and N_{Inorg} ; and, thus, leading to cumulative error in N_{Org} (Cornell et al., 2003; Mace and Duce, 2002). Depending on the dominance of N_{Inorg} , N_{Org} 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_{Org} has been discussed by earlier studies (González Benítez et al., 2009; Mace et al., 2003a; Mace and Duce, 2002).

In this study, we have discarded any of the large negative values of N_{Org} , similar to the approach adopted by Lesworth et al., (2010). The criterion adopted by us deals with excluding the 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} . This criterion also emphasizes that large negative values of N_{Org} result from error associated with estimate of N_{Tot} rather than aerosol samples with low N_{Org} concentration (Lesworth et al., 2010). The negative value of N_{Org} arises only in those samples wherever the ratio of N_{Inorg} to N_{Tot} is greater than or equal to 0.90. We, therefore, suggest that our approach does not introduce biasness in the remaining data-set.

2.3.2 Supporting Chemical parameters

Concentrations of elemental carbon (EC) and organic carbon (OC) in the filters were measured using NIOSH protocol on Sunset EC-OC analyzer (Ram et al., 2008; Rengarajan et al., 2007; Sudheer and Sarin, 2008). For crustal elements (Al and Ca), circular punches (8-10 punches; ca. $r = 1.0 \text{ cm}$ dia) drawn from the filters, were digested with Teflon distilled HF, HNO_3 in a microwave digestion system. After sample digestion, the solutions were made to known volume and analyzed for Al, Ca on ICP-AES. The detailed description for the measurements of trace metals and carbonaceous species has been described in earlier publications (Rengarajan et al., 2007).

3. Results and Discussions

3.1. 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 (Fig. 1a). Seven-day 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 (HYSPLIT program, version- 4.0, <http://ready.arl.noaa.gov/HYSPLIT.php>) at arrival heights of 500, 1000 m (Draxler, 2002). The AMBTs indicate that, during the period 27th Dec-2008 to 10th Jan-2009, the source region of aerosols is from the Indo Gangetic Plain (IGP). A temporal shift in the AMBTs during the period of 11- 28th Jan-2009 points to the regional source from south-east Asia. In addition, some of the back trajectories show traverse over the Bay. The AMBTs (Fig.1) over Bay of Bengal have formed the basis to group the analytical data into three categories as IGP outflow (air masses originating from Indo Gangetic Plain), outflow from south-east Asia (air mass trajectories from south-east Asia) and Marine Air Parcel (MAP, air masses within the Bay region).

3.2. Spatio-temporal variability

The mass concentration of PM_{2.5} averages nearly 65 % of PM₁₀, suggesting its dominance over Bay of Bengal. The mass concentrations of soluble reactive nitrogen species (NH₄⁺, NO₃⁻ and N_{Org}) show significant temporal variability in size segregated (PM_{2.5}, PM₁₀) aerosols (Fig 2). In PM_{2.5}, mass concentrations of nitrogen species varied as 16 - 561 nmol m⁻³ for NH₄⁺, ≤ 0.13 – 22.3 nmol m⁻³ for NO₃⁻ and 7 - 173 nmol m⁻³ for water soluble organic nitrogen (N_{Org}). However, dominance of NO₃⁻ in the coarse mode is evident from its average concentration centered on 16 nmol m⁻³ 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_{Inorg} and N_{Org} (Fig. 2). On average, N_{Inorg}/N_{Tot} ratio in PM_{2.5} 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 (Feb-Mar-2001, Feb-2003, Mar-Apr-2006, Jan-2009) is presented in Table 1. It is evident that mass concentration of NH₄⁺ dominates the N_{Inorg} (NH₄⁺/ N_{Inorg} > 0.8, see Table 1). Although N_{Tot} is not measured in Feb-Mar-2001, Feb-2003 cruises and measured only in Mar-Apr-2006, Jan-2009; 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 (Jan-April). In $\text{PM}_{2.5}$, mass concentration of N_{Org} over N-BoB is significantly higher (range: 23-173 nmol m^{-3}) compared to S-BoB (range: 0 - 43 nmol m^{-3}). Aerosol mass concentrations of soluble nitrogen species collected from different oceanic regions have been summarized in Table-2. These data suggest that, on average, contribution of N_{Org} to N_{Tot} in fine and coarse mode aerosols is 17 and 15 % respectively (Table-2). A similar ratio has been also reported from the Gulf of Aquaba (Chen et al., 2006). As stated earlier, NH_4^+ mass concentration dominates and accounts for as much as 98% of N_{Inorg} in both $\text{PM}_{2.5}$ and PM_{10} . The continental outflow from the Indo-Gangetic Plain (IGP) and south-east Asia dominates the wide-spread dispersal of pollutants over the Bay of Bengal. In IGP, biomass burning emissions (post-harvest burning of agricultural-waste) is a dominant source of pollutants. In addition, large-scale application of fertilizers (ammonia and urea based) in the agricultural dominated region 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 aerosol-water-extract could arise due to the hydrolysis of urea and amino-acid containing compounds (Cornell et al., 1993). 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 $\text{PM}_{2.5}$ 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 (Fig.3). It is noteworthy that the contribution of N_{Org} to N_{Tot} associated with the AMBTs originating from IGP (from 27th Dec'2008-10th Jan'2009) ranges from 12.4 to 38.4 %. In contrast, contribution of N_{Org} to N_{Tot} associated with south-east Asian outflow (as evident from the AMBTs from 11th - 28th Jan'2009) is relatively low (range: 0 - 27.4 %, Fig.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_{Org} can be attributed to biomass burning emissions from the IGP.

3.3. Size distribution of Nitrogen Species

The scatter plot of mass concentrations of nitrogen species in PM_{2.5} and PM₁₀, show the predominance of NH₄⁺ and N_{Org} in PM_{2.5} (Fig. 4c, 4e); whereas NO₃⁻ (Fig. 4d) exists mainly in PM₁₀ fraction. The dominant contribution of N_{Inorg} to total nitrogen (N_{Tot}) in PM_{2.5} is also evident from Fig. 4a. In bulk (TSP) aerosols collected during March-April'2006, the mass ratio of NH₄⁺ to N_{Inorg} averages about 0.91 ± 0.21 (range: 0.28 to 1.0), suggest that soluble inorganic nitrogen abundance is dominated by NH₄⁺ and contributes to almost 90% of N_{Inorg}. Further, moderately tight correlation observed between N_{Tot} and N_{Inorg} (R² = 0.80; m = 0.77; p-value < 0.0001; n = 23; Fig. 4b) together with the average mass ratio of N_{Inorg}/N_{Tot} (i.e., 0.86) over Bay of Bengal suggest that during Mar-April'2006 N_{Inorg} account for ~ 85% of N_{Tot}. In PM_{2.5}, the strong correlation (R² = 0.98; n = 31; p-value < 0.001) between NH₄⁺ and nss-SO₄²⁻ (Fig.5a) together with the equivalent ratio of NH₄⁺/SO₄²⁻ (Av: 0.84 ± 0.15), suggest near complete neutralization of NH₃ with H₂SO₄ over Bay of Bengal, resulting in the formation of NH₄HSO₄.

Relatively high mass concentration of NO₃⁻ in PM₁₀ aerosols suggests its preferential association with coarse mode dust as Ca(NO₃)₂. A significant linear relation (R² = 0.62; n = 15; p-value < 0.001; Fig 5b) between Ca²⁺ and NO₃⁻ over north Bay of Bengal (N-BoB) further attests to the above hypothesis. This linear relationship has been explained in terms of chemical reaction of mineral aerosols with gas phase HNO₃ (Harrison and Kitto, 1990; Matsumoto et al., 2009; Pakkanen, 1996; Wolf, 1984; Zhuang et al., 1999). However, similar relationship among Ca²⁺ and NO₃⁻ is not valid for the data from southern Bay of Bengal, where mineral aerosols and NO₃⁻ concentrations are relatively low. These results further support NO₃⁻ existence in the coarse mode over Bay of Bengal.

Although water soluble organic nitrogen (N_{Org}) predominantly occurs in the fine mode over Bay of Bengal, a significant fraction also exists in the coarse mode. Similar to our observation over Bay of Bengal, bimodal distribution of N_{Org} has also been documented over north-Pacific (Miyazaki et al., 2010). In this study, there is an evidence for meaningful relationship of N_{Org} with nss-Ca²⁺ (R² = 0.32; n = 19; p-value < 0.01) and total aerosol Ca (R² = 0.86; n = 33; PM₁₀; 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-Ca²⁺ 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_{Org} 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^{2+} can explain the organic nitrogen fraction in the coarse mode.

3.4. 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^+ and nss-SO_4^{2-} (Fig 6). It is evident that nss-K^+ 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^+ and EC ($R^2 = 0.73$; $n = 31$; p -value < 0.0001); and OC ($R^2 = 0.76$; $n = 31$; $\text{PM}_{2.5}$; p -value < 0.001). These interrelationships bring out the significant role of biomass burning emissions in contributing to aerosol N_{Org} (Fig 6). As stated earlier, samples from N-BoB show dominant influence of continental outflow from the Indo-Gangetic Plain. Intense biomass burning and agricultural crop waste burning in the Indo-Gangetic Plain (Badarinath et al., 2006; Venkataraman et al., 2006) have been reported based on linear trend between soluble K^+ and EC (Ram and Sarin, 2010; Ram et al., 2010; Rengarajan et al., 2007). These observations suggest a common source for soluble organic nitrogen (N_{Org}) and nss-K^+ from biomass burning.

The temporal variability in the abundances of N_{Org} and NH_4^+ (Fig.2) and a significant linear relation between them also suggest their common source and/or common atmospheric transport process (Fig 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_{Org}). 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, 2003a). Furthermore, dissolved amino acids are shown to be a significant source of NH_4^+ in $\text{PM}_{2.5}$ samples (Zhang and Anastasio, 2003b). Therefore the observed linear relation of soluble organic nitrogen with NH_4^+ in marine aerosols indicates their common source from urea or amino compounds.

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.

3.5. 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.

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

Since the scatter plot of NH_4^+ , NO_3^- between $\text{PM}_{2.5}$ and PM_{10} aerosols indicating the fine mode existence of NH_4^+ and coarse mode existence of NO_3^- , dry-deposition velocity (V_{dry}) for NH_4^+ , NO_3^- are taken as 0.1 and 1.0 cm sec^{-1} . Similar dry-deposition velocities have been used in numerous studies reported in the literature (Baker et al., 2003; Chen et al., 2007; Chen et al., 2006; 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_{10} , the dry-deposition flux of soluble inorganic nitrogen (N_{Inorg}) varies from 2 to 83 $\mu\text{mol-N m}^{-2} \text{d}^{-1}$ with a mean of $27 \pm 20 \mu\text{mol-N m}^{-2} \text{d}^{-1}$, while the deposition fluxes of N_{Org} vary from 0 – 123 $\mu\text{mol-N m}^{-2} \text{d}^{-1}$ (average: $17 \pm 29 \mu\text{mol-N m}^{-2} \text{day}^{-1}$). Similarly, in $\text{PM}_{2.5}$ aerosols, the average dry-deposition flux of N_{Inorg} is about $16 \pm 12 \mu\text{mol-N m}^{-2} \text{d}^{-1}$ (range: 2.0 - 49 $\mu\text{mol-N m}^{-2} \text{d}^{-1}$), whereas the mean dry-deposition flux of soluble organic nitrogen (N_{Org}) is about $2.6 \pm 3.3 \mu\text{mol m}^{-2} \text{d}^{-1}$ (range: 0 -15 $\mu\text{mol-N m}^{-2} \text{d}^{-1}$). 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 Fig 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 centered on 20 % (Fig. 3). This is in sharp contrast with the south-east Asian outflow. Likewise, the high contribution of NH_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 Jan-2009 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.

3.6. Impact on ocean surface biogeochemistry

It is relevant to reemphasize that Bay of Bengal is influenced by the continental outflow only during 4 months (Jan-Apr). 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_{Tot} 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 - 566 mg-C $m^{-2} d^{-1}$ (Gauns et al., 2005). The column integrated primary production in the surface waters of Bay of Bengal is summarized in Table-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_{Tot}) is 5 to 167 $\mu mol-N m^{-2} d^{-1}$ (Av: 66 $\mu mol-N m^{-2} d^{-1}$) and 2 to 94 $\mu mol-N m^{-2} d^{-1}$ (Av: 24 $\mu mol-N m^{-2} d^{-1}$) over north Bay of Bengal and 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 $\mu mol-N m^{-2} d^{-1}$) corresponds to an equivalent carbon of 3.5 mg $m^{-2} d^{-1}$ 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_{Tot} varies from 2-167 $\mu mol-N m^{-2} d^{-1}$, which can support up to 13 % of the Primary Production (99-566 mg-C $m^{-2} d^{-1}$, a typical range of PP during Jan-Mar) in the surface waters of the Bay. Using N^{15} as a tracer, (Kumar et al., 2004) have derived a f-ratio 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 average, atmospheric dry-deposition of N_{Tot} can support no more than 10 % of the new production during winter time (Jan-Feb) 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 $\mu mol - N m^{-2} d^{-1}$), with that from river supply (214 $\mu mol-N m^{-2} d^{-1}$; 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_{Tot} 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. As stated earlier, based on cruise undertaken in Jan 2009, atmospheric deposition of N_{Tot} ranges from 2 - 167 $\mu\text{mol-N m}^{-2} \text{d}^{-1}$ (equivalent to 10 - 853 $\text{mg-N m}^{-2} \text{yr}^{-1}$). The upper limit of estimated flux is of comparable magnitude to the projection (800-1200 $\text{mg-N m}^{-2} \text{yr}^{-1}$) made by (Duce et al., 2008). Considering the associated uncertainties, estimated flux is within the range estimated by Duce et al., 2008. Furthermore, a comparison of mass concentrations of N_{Inorg} data in Table-1, suggest an increasing trend in the mass ratio of $\text{NH}_4^+ / \Sigma\text{WSIC}$ (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).

Although, in the present study, we have measured only total soluble nitrogen (dominated by NH_4^+), recent study by (Pavuluri et al., 2010) have also measured the total particulate nitrogen at a coastal site (Chennai) along the west coast of Bay of Bengal. 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 our findings on the dominance of inorganic nitrogen (as $\text{NH}_4^+ - \text{N}$) over Bay of Bengal. Therefore, dry-deposition flux of nitrogen estimated in this study is representative for this oceanic region. 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. Conclusions

This study presents the first comprehensive data set on inorganic and organic nitrogen in size segregated ($\text{PM}_{2.5}$, PM_{10}) aerosols from the Bay of Bengal during the period of late northeast monsoon (Jan-April) when the continental transport over the Bay is dominant. The mass concentrations of soluble nitrogen ($N_{\text{Tot}} = N_{\text{Inorg}} + N_{\text{Org}}$) show large spatio-temporal variability. The concentration of soluble reactive nitrogen (organic + inorganic) is relatively high over North Bay of Bengal compared to southern Bay (S-BoB). The soluble inorganic nitrogen ($N_{\text{Inorg}} = \text{NH}_4^+ + \text{NO}_3^-$) abundance is dominated by NH_4^+ (~ 98 %) and existing in the fine mode ($\text{PM}_{2.5}$), 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_{Org}) 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 $\mu\text{mol-N m}^{-2} \text{d}^{-1}$ and can support up to 13% of the primary production in the Bay of Bengal (assuming Redfield ratio (C:N:P = 106:16:1)).

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Table 1: Mass concentrations of N_{Inorg} ($\text{NH}_4^+ + \text{NO}_3^-$) and N_{Org} in ambient aerosols over Bay of Bengal.

Constituent	[#] Feb-Mar-2001 (n = 26)	[#] Feb -2003 (n = 24)	[#] Mar-April 2006 (n = 23)	^{\$} Jan-2009 (n = 31)	[£] Jan-2009 (n = 33)
Range					
NH_4^+	7.2 - 57.8	0.6 - 126	0.6 - 127	16 - 561	3.4 - 678
NO_3^-	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_{Tot}	n.a.	n.a.	9 -152	24 - 738	7 -786
$\text{NH}_4^+/\text{N}_{\text{Inorg}}$	0.37 - 1.0	0.01 - 0.99	0.28 - 1.0	0.81 - 1.0	0.22 - 1.0
$\text{N}_{\text{Inorg}}/\text{N}_{\text{Tot}}$	n.a.	n.a.	0.06 - 1.09	0.62 - 1.22	0.56 -1.04
$\text{N}_{\text{Org}}/\text{N}_{\text{Tot}}$	n.a.	n.a.	0.0 - 0.94	0.0 - 0.38	0.0 - 0.44
$\text{NH}_4^+/\text{SO}_4^{2-}$	0.05 - 0.44	0.01 - 0.62	0.01 - 0.65	0.58 -1.12	0.05 - 1.08
$\text{NH}_4^+/\Sigma\text{WSIC}$	0.01 - 0.12	0.001 - 0.17	0.001-0.17	0.003 - 0.17	0.01- 0.26
$\text{SO}_4^{2-}/\Sigma\text{WSIC}$	0.26 - 0.78	0.36 - 0.73	0.62 - 0.73	0.54 -0.71	0.33 - 0.70

Concentrations are expressed in nmol m^{-3} and $\text{NH}_4^+/\text{SO}_4^{2-}$ 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 $\text{PM}_{2.5}$ (n = 31), £ refers to PM_{10} (n = 33). n.a. = not analyzed

Note: For organic nitrogen, we have excluded those samples in which the propagated error (uncertainty) is equal to more than the estimated N_{Org} ($N_{\text{Tot}} - N_{\text{Inorg}}$).

Table 2. Concentration (nmol. m⁻³) of soluble nitrogen species in aerosols from different oceanic regions.

Location	Duration	N _{Inorg}	N _{Org}	N _{Tot}	%(N _{Org} /N _{Tot})	Reference
Bay of Bengal	Jan-09	226	46	272	17	Present study (PM _{2.5} aerosols)
Bay of Bengal	Jan-09	203	35	237	15	Present study (PM ₁₀ aerosols)
Bay of Bengal	Mar-April-2006	47	11	58	19	Present study (TSP aerosols)
Yellow Sea	Mar-05	945	204	1149	17	(Shi et al., 2010 TSP aerosols)
Yellow Sea	Mar-06	490	87	577	17	(Shi et al., 2010 TSP aerosols)
Hawaii	Jan-Jun-1998	7.6	3.3	10.9	31	(Cornell et al., 2001(rain & fine,coarse))
South China Sea	May-05	131	65	196	33	(Shi et al., 2010 TSP aerosols)
Mediterranean Sea	Mar-May-2000	85	26	111	26	Mace et al., 2003 (rain & bulk aerosols)
North Atlantic Ocean	Sep-Oct-Nov	-	-	-	24	Lesworth et al., 2010 (fine and Coarse)
Gulf of Aqaba	Aug-03 to Nov-04	65	10	75	13	Chen et al., 2006 (TSP aerosols)
East china sea	Sep-Oct-2002	170	54	224	24	Nakamura et al., 2006 (fine and coarse)
N. California (Davis)	Aug-97 to July-98	-	15.6	-	20	(Zhang et al., 2002 ,PM2.5 aerosols)
North Pacific Ocean	Jul-Aug-2008	-	-	-	73	Miyazaki et al., 2010 (sub micron aerosols)
North Pacific Ocean	Jul-Aug-2009	-	-	-	84	Miyazaki et al., 2010 (super micron aerosols)
Western North Pacific	Aug-Sep-2008	-	-	-	67	Miyazaki et al., 2010
Crete (Greece)	Jan-05 to Dec-06	-	-	-	13	(Violaki et al., 2010, (fine and coarse))
Chapel hill, USA	Jan-Jun-2007	-	-	-	33	(Lin et al., 2010, PM2.5 aerosols)

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 the experimental methods).

Table 3. Column integrated Primary Production ($\text{mg-C m}^{-2} \text{ day}^{-1}$) in the Bay of Bengal.

Time	Region	£PP	Reference
Dec-01	W-BoB	245 ± 86	(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)

W-BoB = Western Bay of Bengal, C-BoB = Central Bay of Bengal
£ Column integrated Primary Production in $\text{mg-C m}^{-2} \text{ d}^{-1}$.

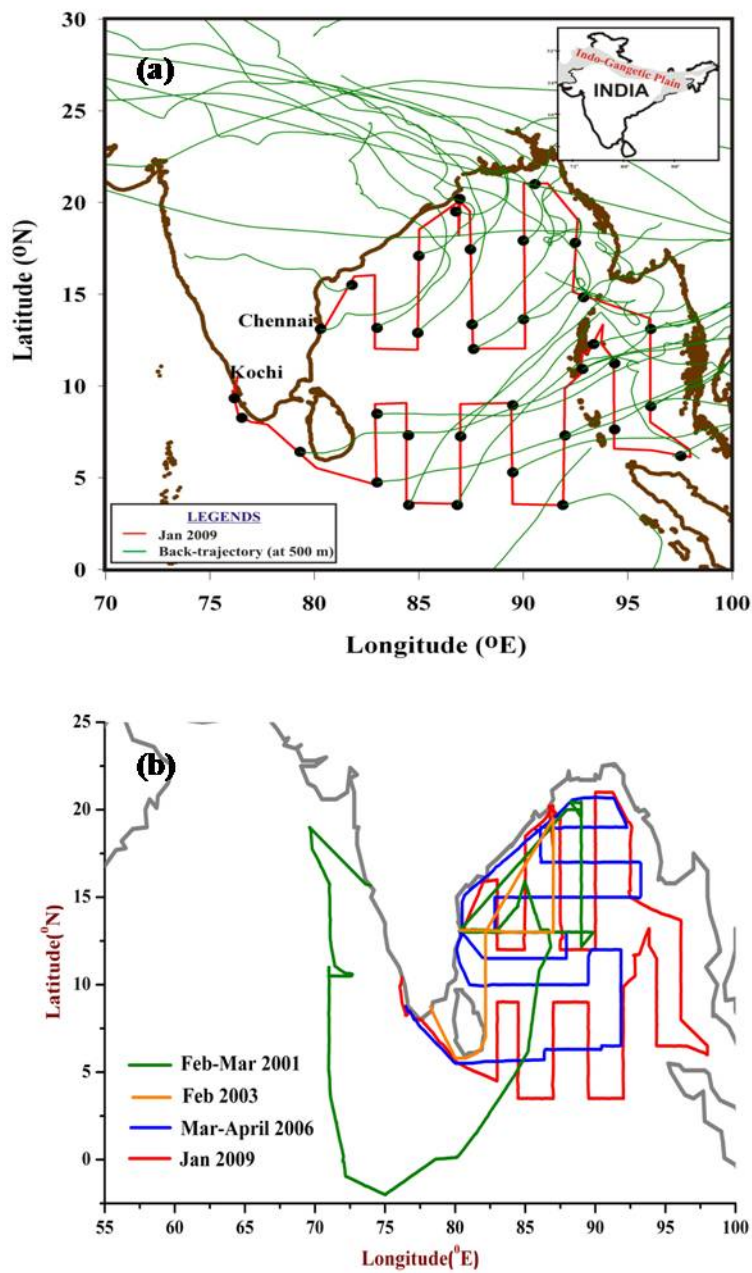


Fig.1: (a) Cruise tracks undertaken during Mar-April 2006 (blue line) and Jan-2009 (red line) in the Bay of Bengal. The air mass back trajectory cluster, at arrival height of 500 m during Jan-2009 is also shown. Sampling stations along the cruise track are indicated by dots. (b). Similar cruise tracks 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).

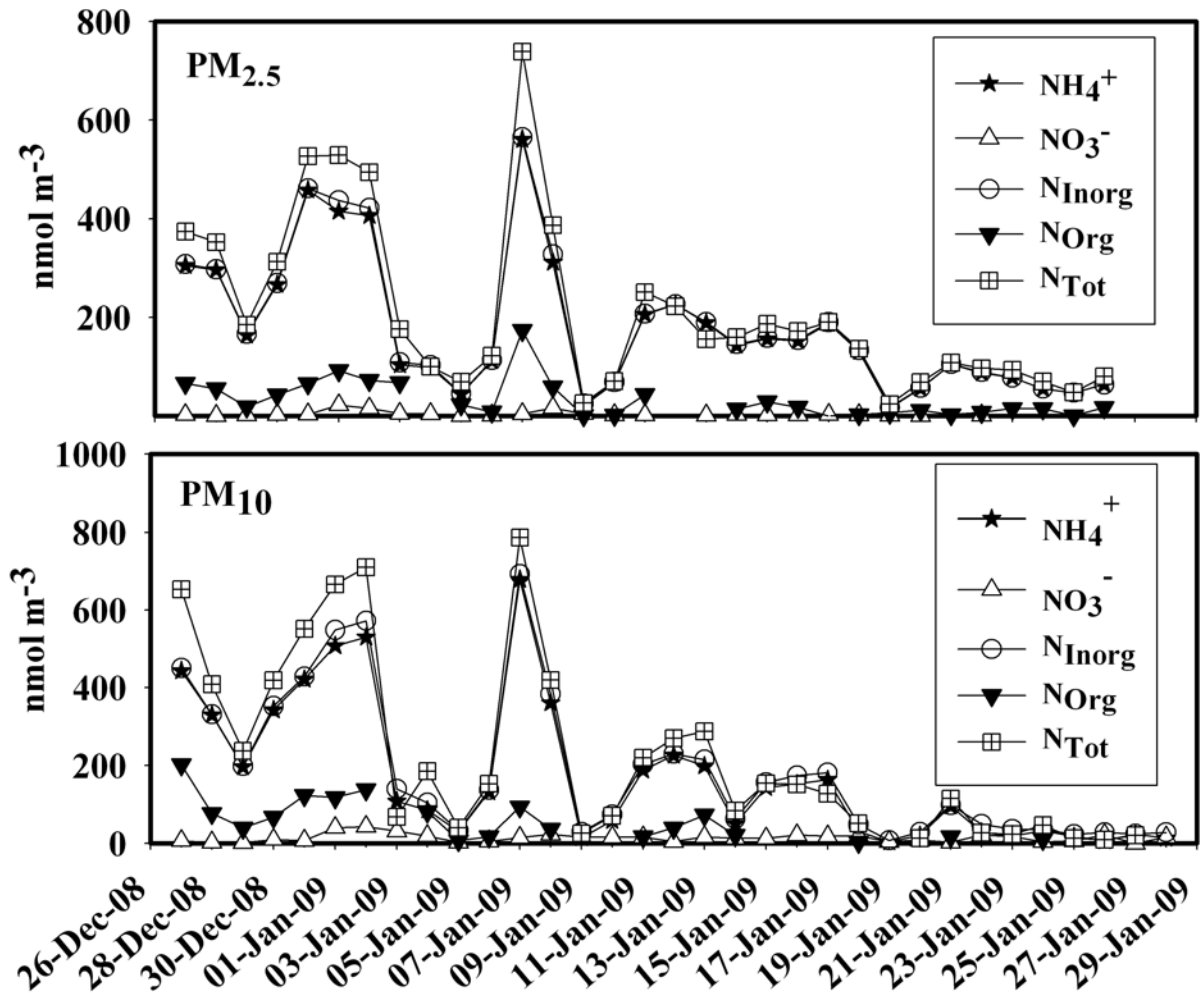


Fig. 2. Temporal variability of water soluble nitrogen species in the MABL of Bay of Bengal over a span of 30 days is associated with the temporal shift in the wind-regimes, from Indo-Gangetic Plain (during early part of the cruise) to outflow from south-east Asia.

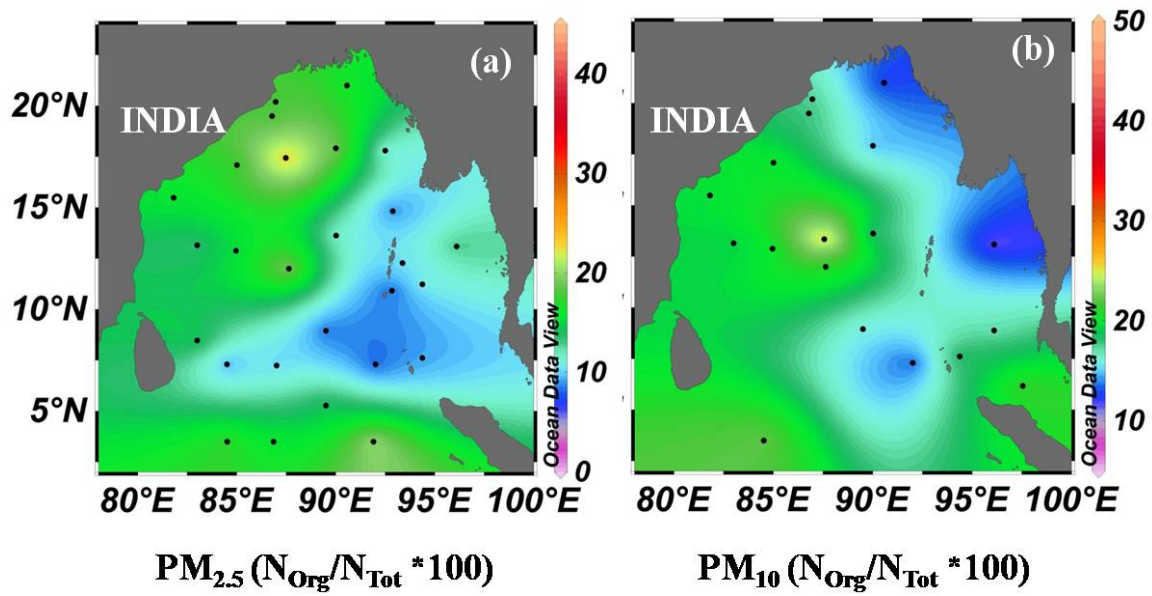


Fig. 3: Contribution (%) of water soluble organic nitrogen (N_{Org}) to total soluble nitrogen (N_{Tot}) in (a) $PM_{2.5}$ and (b) PM_{10} over Bay of Bengal during January 2009.

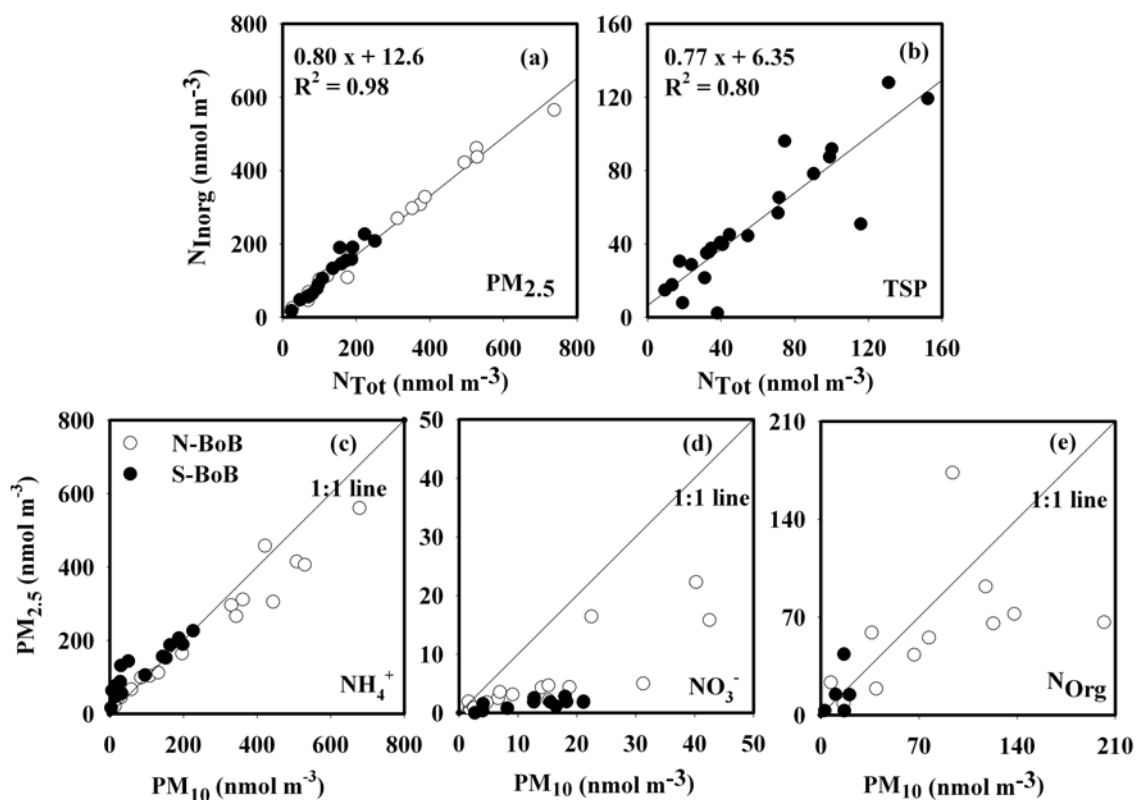


Fig.4. Scatter plot (a) N_{Inorg} versus N_{Tot} in $PM_{2.5}$, (b) N_{Inorg} and N_{Tot} for TSP (Mar-April 2006); NH_4^+ , NO_3^- and N_{Org} in $PM_{2.5}$ versus PM_{10} (c, d & e), suggesting dominance of NH_4^+ , organic nitrogen (N_{Org}) in the fine mode and coarse mode NO_3^- . Dominant contribution of N_{Inorg} to total nitrogen (N_{Tot}) is very evident from the plot shown in (a) & (b). The data presented here refer to Jan-2009 cruise when both $PM_{2.5}$ and PM_{10} sampling was carried out.

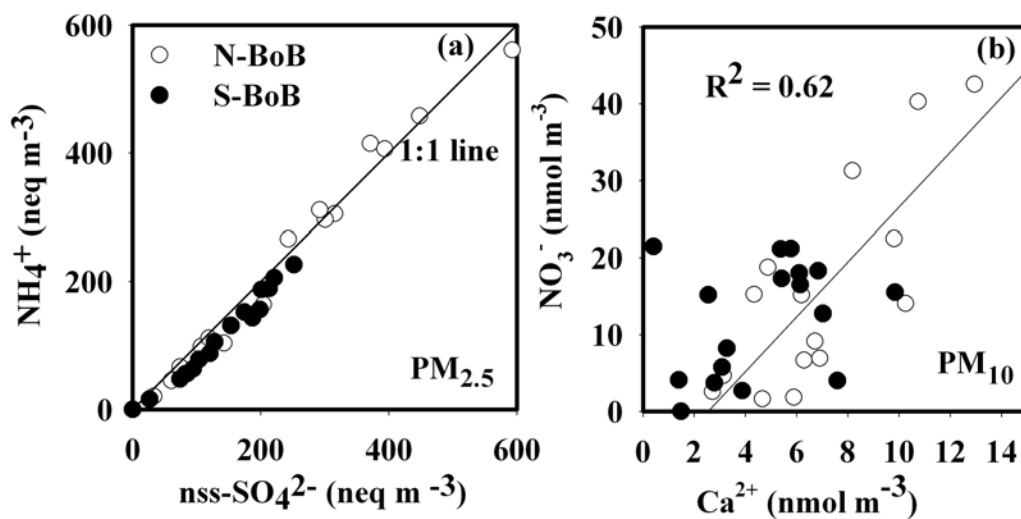


Fig. 5. Scatter plot between (a) NH_4^+ and nss-SO_4^{2-} (equivalent units); (b) Ca^{2+} and NO_3^- over Bay of Bengal during Jan-2009.

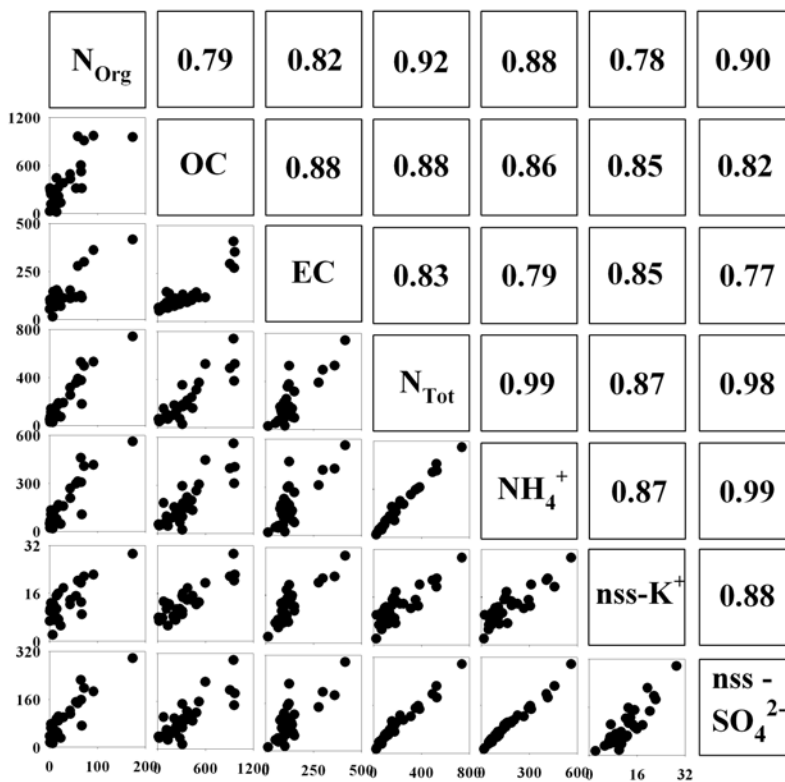


Fig. 6. Linear regression analysis of N_{Org} with N_{Tot} , EC, OC, NH_4^+ , nss-K^+ and nss-SO_4^{2-} in $\text{PM}_{2.5}$ from the Bay of Bengal during Jan-2009. All concentrations are expressed in nmol m^{-3} .

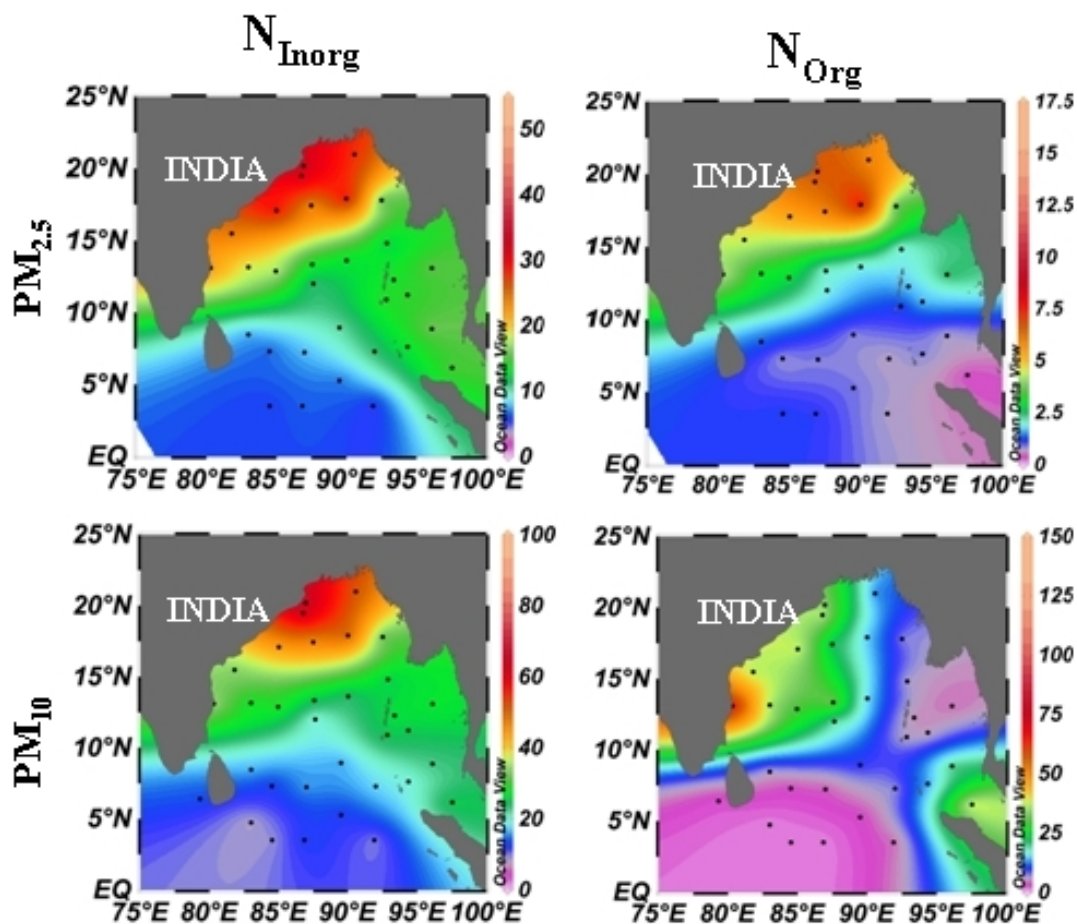


Fig.7. Dry-deposition fluxes of water-soluble inorganic nitrogen ($N_{Inorg} = \text{NH}_4^+ + \text{NO}_3^-$) and organic nitrogen (N_{Org}) in $PM_{2.5}$ and PM_{10} aerosols over the MABL of Bay of Bengal during Jan-2009 (All fluxes were expressed in $\mu\text{mol-N m}^{-2} \text{d}^{-1}$).