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Impact of continental outflow on chemistry of atmospheric aerosols over tropical Bay of Bengal

B. Srinivas, A. Kumar, M. M. Sarin, and A. K. Sudheer

Physical Research Laboratory, Navarangapura, Ahmedabad 380 009, India

Correspondence to: M. M. Sarin (sarin@prl.res.in)

Abstract

The continental outflow from Indo-Gangetic Plain and south-east Asia dominates the widespread dispersal of pollutants over tropical Bay of Bengal (BoB) during the late NE-monsoon (January–March). It is thus pertinent to assess the impact on marine atmospheric boundary layer of BoB. The chemical data, based on analyses of size-segregated ($PM_{2.5}$ and PM_{10}) aerosols, suggest the dominance of nss-SO_4^{2-} (range: 1.3 to 28 $\mu g\,m^{-3}$) in $PM_{2.5}$. Almost all SO_4^{2-} is of anthropogenic origin and accounts for as much as 65 % of the water-soluble inorganic constituents. The impact of anthropogenic sources is further evident from the widespread depletion of chloride (range: 40 to 100 %) compared to sea-salt composition. The carbonaceous species (EC and OC) contribute nearly 25 % to $PM_{2.5}$; and significant linear relationship with K^+ suggests biomass burning as their dominant source (biofuels and agricultural waste). The enhancement in the fractional solubility of aerosol Fe, as assessed in $PM_{2.5}$, re-emphasizes the impact of combustion sources (biomass and fossil-fuel) and chemical processing (of dust) during the long-range transport. The high enrichment factors of heavy metals (Pb and Cd) further demonstrate the influence of pollution sources on the chemistry of MABL. The downwind transport of pollutants and exchange across air-sea interface can, thus, have profound impact on the ocean surface biogeochemistry.

1 Introduction

Suspended particulate matter (SPM), ubiquitous in the Earth's atmosphere, 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) (Twomey, 1977; Charlson et al., 1991; Ramanathan et al., 2001a, b). In addition, SPM provide the substrate for various chemical reactions occurring in the atmosphere which result in the change in surface properties (hydrophobic to hydrophilic) and eventually lead to the changes in the size-distribution and hence life time of the aerosols (Dentener

et al., 1996; Andreae and Crutzen, 1997). 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 et al., 2010; Rengarajan et al., 2007; Ram and Sarin, 2010; Tare et al., 2006) as well as their significant impact on the radiative forcing (Ramachandran et al., 2006; Nair et al., 2007). 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 (Martin, 1989; Jickells et al., 2005; Duce et al., 1991, 2008; Jickells, 1999; Arimoto et al., 2003; Duce, 1986; Prospero, 1981a). These nutrients may perturb the phytoplankton productivity and subsequently impact on climate (Spokes et al., 2000; Jickells et al., 2005; Mahowald et al., 2005; Doney et al., 2007).

The Bay of Bengal (BoB; situated in the eastern part of northern Indian Ocean) is one of the ideal region, 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 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 (Kaskaoutis et al., 2010; Ramanathan et al., 2001a;

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Kumar et al., 2010; Ganguly et al., 2005; Moorthy et al., 2008, 2010). One of the previous studies, during the spring inter-monsoon (March–April, 2006; (Kumar et al., 2008a) season, had shown that air flow influences both the abundance and composition of the particulate matter over the BoB using the chemical characteristics of bulk (TSP) aerosols. Till date, this is the first study undertaken, to quantify the anthropogenic impact over the marine atmospheric boundary layer (MABL) of BoB based on the chemical composition of aerosols. The abundances and atmospheric reactivity of major pollutants (nitrate, sulphate, ammonia) and their removal processes depend critically on their size 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 December–January, 2009. 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 provides evidences for continental influence over the Bay of Bengal.

2 Experimental methods

2.1 Cruise track and meteorological conditions

Aerosol samples were collected over the Bay of Bengal (BoB), onboard ORV Sagar Kanya (SK254), during December–January, 2008–2009. The cruise (cruise track shown in Fig. 1) initiated on 27 December 2008 from Chennai and terminated on

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30 January 2009 at Kochi, by making several transects between 4 to 22° N and 76 to 98° E and hence covering entire BoB. The dots along the cruise track show the position of the ship at 05:30 UTC on each day. During first half (27 December to 10 January) of SK 254, prevailing winds were north-westerlies, i.e. winds are originating from north and north-eastern part of India as well as from Bangladesh. However, during later part of cruise (11 to 28 January), a change in wind pattern is observed such that the typical air mass originated over eastern Asian region e.g. Burma, Thailand and as far as from China. This pattern is evidenced from the average wind patterns observed over the study region as shown in Fig. 2a and b. The meteorological parameters such as wind speed, relative humidity, and air temperature were measured onboard 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 measured winds were corrected for the ship's motion and found in the range of 1.2 to 6.3 m s^{-1}, whereas surface-level pressure variations were recorded between 1007 to 1017 mb.

2.2 Aerosol sampling and analysis

The ambient aerosol in PM$_{2.5}$ and PM$_{10}$ size-range were collected onboard ORV Sagar Kanya, simultaneously by operating two high-volume samplers (Thermo Andersen); with sampling inlets having 50 % cutoff size at 2.5 and 10 µm aerodynamic diameters. The samplers were set up on the upper deck, 15 m a.s.l., in front of ship's navigation room. The hi-volume samplers (HVS) were equipped with volume flow controller to maintain a constant flow rate. However, periodic calibration of samplers was performed to check on variation, if any, in the flow rate. Typically, the flow rate varied from 1.08–1.18 m^3 min^{-1} with an uncertainty of 5 %. Each sample was collected over a time period ranging from 20 to 22 h when ship was cruising at a speed ∼10 knots/hrs or above conforming to the protocol that the relative wind direction is from the bow, thus avoiding the contamination from ship's exhaust. The two size fractions of aerosols were collected on pre-combusted PALLFLEX^{TM} tissuquartz filters (20×25 cm^2).

A total of 33 (PM$_{10}$) and 31 (PM$_{2.5}$) samples were collected over a span of 35 days during the campaign over Bay of Bengal. After the sampling, filters were packed in zip-lock bags and preserved in the deep-freezer (at ca. −19 °C) during the cruise. Later, these samples were brought to the laboratory and stored in a freezer until analysis. The mass concentrations of PM$_{10}$ and PM$_{2.5}$ samples were ascertained gravimetrically by weighing the full filters (with a precision of 0.1 mg) before and after the sampling. Prior to their weighing, all filters were conditioned at a relative humidity of 40±5 % and temperature of 23±1 °C for 5–6 h.

Water soluble inorganic constituents (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$, and SO$_4^{2-}$) in the aerosols were determined using one fourth of the filter. The analytical details related to ionic components measured during this study have been described in (Kumar et al., 2010; Kumar and Sarin, 2010). In brief, the anions (Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) and cations (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, and Ca^{2+}) were analyzed on DIONEX$^®$ Ion-Chromatograph equipped with suppressed conductivity detector (ED-50) (Kumar et al., 2010).

For trace metals (Cd and Pb) and crustal constituents (Al, Fe, Ca and Mg), ca. 1.0 cm diameter filter punches were digested using 0.5 mL distilled HF, 5.0 mL distilled 8 N HNO$_3$ and 3.0 mL Milli-Q water (>18.2M-cm specific resistivity) in Teflon digestion vessels using a high pressure Microwave digestion system (Milestone). After digestion these solutions were made to suitable volume (25 mL) with Milli-Q water and stored in pre cleaned polypropylene bottles. These solutions were subsequently analyzed for Al, Fe, Ca and Mg on Inductively Coupled Atomic Emission Spectrometer (ICP-AES, HORIBA, JobinYvon–ULTIMA model), as well as Cd and Pb on Graphite Furnace-Atomic Absorption Spectrophotometer (GF-AAS). Based on the repeat measurements of procedural blanks and repeat samples, the overall uncertainty in the measurement of these metals is found to be less than ±10%.

Elemental Carbon (EC) and Organic Carbon (OC) were measured on sunset EC-OC analyzer using NIOSH (National Institute for Occupational Safety and Health, Birch and Cary, 1996) protocol. For detailed analytical procedures reference is made to

(Rengarajan et al., 2007; Sudheer and Sarin, 2008a; Ram et al., 2008). For water soluble iron (Fe_{ws}), ca. 2.0 cm dia filter punches were extracted with 10.0 mL of Milli-Q water (18.2 MΩ-cm specific resistivity). This water extract is filtered using 0.45 µm PTFE syringe filter cartridge and acidified to pH ~2 with double distilled HNO_3, subsequently measured on GF-AAS for soluble Fe. The details of the extraction procedure are given in (Kumar et al., 2010).

3 Results and discussion

3.1 Air mass back trajectory analysis and mass concentrations of PM_{10} and $PM_{2.5}$

To identify the potential sources contributing to aerosol chemical composition over the Bay of Bengal, 7-days air-mass back trajectories (AMBT) were computed by using NOAA Air Resource Laboratory HYSPLIT-Model (Draxler, 2002) (GADS data set) at different arrival heights (100 m, 500 m and 1000 m). The back-trajectory analyses suggest the dominance of air-masses transported from Indo-Gangetic Plains (IGP) during initial period (27 December 2008 to 10 January 2009). However, in the later part of the cruise (i.e. in south Bay of Bengal), most of the air-masses were originating from south-east Asia. The air-masses observed in the Bay of Bengal during campaign period have been classified into three different categories as IGP (air masses originating from Indo Gangetic Plain) and SEA (air masses originating from South East Asian Countries) and MAP (air masses which are also originated from south east Asian countries but spent more time in the Marine atmospheric boundary layer) (Kumar et al., 2010). Albeit, distinctions were made based on the air-mass back trajectories, it was observed that samples collected in the northern part of Bay of Bengal are mainly affected by the IGP and southern bay witnesses SEA and MAP. Based on the wind patterns (shown in Fig. 2), we have divided our data set into two groups, N-BoB (Samples collected during 27 December–10 January) and S-BoB (Samples collected between

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11 January–28 January) for documenting the spatial distribution of different aerosol components.

Table 1 gives the average mass concentration of PM_{10} and $PM_{2.5}$ along with their maximum and minimum value during transects in N-BoB and S-BoB. The mass concentrations of $PM_{2.5}$ and PM_{10} exhibit a strong temporal variability, with higher value in N-BoB (range: 13.2 to 76.7 and 16.2 to 108 µg m^{-3} respectively) compared to that in S-BoB (range: 2.0 to 35.3 and 6.0 to 60.7 µg m^{-3} respectively). High mass loading of PM_{10} and $PM_{2.5}$ in N-BoB is mainly attributed to the proximity of sampling locations near to continents associated with favourable continental outflow from Indian subcontinent during initial part of the cruise. 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., 2008b). The average wind patterns observed during the campaign (Fig. 2a, b) were originating from continents compared to the mixed wind-pattern found (land to sea vis-à-vis sea to land) during ICARB-2006 (Kumar et al., 2008b). A very significant correlation is observed between $PM_{2.5}$ and PM_{10} in N-BoB ($r^2 = 0.93$; Fig. 3) as well as in S-BoB ($r^2 = 0.84$; Fig. 3) indicating the similar sources (i.e. continental outflow) for fine and coarse mode aerosols. During the study period, the percent contribution of $PM_{2.5}$ mass to PM_{10} 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, $PM_{2.5}$ contributes significantly (~65 % of PM_{10}) to ambient aerosol over Bay of Bengal. The studies based on optical properties of atmospheric aerosols, during ICARB-2006, have shown higher Ångström exponent values (1.12) over the Bay of Bengal and indicated the predominance of fine mode aerosols (Kedia and Ramachandran, 2008; Moorthy et al., 2008).

3.2 Chemical composition of PM_{10} and $PM_{2.5}$

The various components of ambient aerosol (PM_{10} and $PM_{2.5}$) in Bay of Bengal, calculated based on chemical proxies have been discussed in this section. These constituents include water-soluble inorganic component (Sea-salts and anthropogenic

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species), mineral dust and carbonaceous species. An attempt has been made to achieve chemical mass closure by summing up the measured chemical species and comparing it with gravimetrically measured mass loading in PM_{10} and $PM_{2.5}$ at the end of this section.

3.2.1 Water-soluble ionic composition

The sum of cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and anions (Cl^-, NO_3^-, and SO_4^{2-}) constitute the water-soluble ionic composition (WSIC expressed in $\mu g\,m^{-3}$) which varied from 3.0 to 40.2 (Av. = 17.5±11.1) $\mu g\,m^{-3}$ in the fine ($PM_{2.5}$) and 6.6 to 50.3 (Av. = 23.6±13.3) $\mu g\,m^{-3}$ in PM_{10} over northern Bay of Bengal. The WSIC shows a decreasing trend as cruise proceeded to the southern region (Table-1). The contribution of WSIC to total mass loading of $PM_{2.5}$ and PM_{10} was more or less consistent (~45 %) throughout Bay of Bengal (Table-1). The percentage contribution of an individual ionic component to the WSIC is shown as the pie-charts (Fig. 4) for $PM_{2.5}$ and PM_{10} in N-BoB and S-BoB. SO_4^{2-} and NH_4^+ are the major contributors to WSIC in PM_{10} and $PM_{2.5}$ over N-BoB with minor contributions from K^+ in $PM_{2.5}$ and that of NO_3^- and Na^+ in PM_{10}. In S-BoB, the contribution of SO_4^{2-} and NH_4^+ remained consistent in $PM_{2.5}$, however, there is an increase in the contribution from Na^+ and NO_3^- in PM_{10}. Overall, SO_4^{2-} is the dominant contributor to the ionic budget of aerosols over Bay of Bengal during winter monsoon.

The non sea salt (nss) components of K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} have been calculated by using the following equations: nss-K^+ = $K^+ - 0.037 \cdot Na^+$; nss-Ca^{2+} = $Ca^{2+} - 0.038 \cdot Ca^{2+}$; nss-$Mg^{2+}$ = $Mg^{2+} - 0.12 \cdot Na^+$; nss-$SO_4^{2-}$ = $SO_4^{2-} - 0.25 \cdot Na^+$; where 0.037, 0.038, 0.12, 0.25 are weight ratios of K^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} to Na^+ in seawater (Keene et al., 1986) and considering Na^+ as a reference element for the correction of sea-salt contribution. On an average, nss-sulphate constitutes 99 and 94 % of total sulphate in $PM_{2.5}$ and PM_{10} respectively, suggesting anthropogenic dominance

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in the MABL of Bay of Bengal. Comparison of the winter-ICARB (ICARB-W) data with earlier data from Bay of Bengal (Sarin et al., 2011), suggests the strong anthropogenic impact over the MABL during the north-east monsoon. This is evident from the scatter plots between (a) SO_4^{2-} versus nss-SO_4^{2-} (b) K^+ versus nss-K^+ and (c) Ca^{2+} versus nss-Ca^{2+} (Fig. 5). The spatio-temporal distribution of major ions for $PM_{2.5}$ and PM_{10} are shown in Fig. 6. In general, lower values were observed for the concentration of each ion during S-BoB transects closely resembling the feature observed for $PM_{2.5}$ and PM_{10} mass, except a higher values for Na^+ is found over S-BoB in PM_{10}. The spatio-temporal variability further reflects to the dominance of NH_4^+, nss-K^+ and nss-SO_4^{2-} in $PM_{2.5}$ than in PM_{10}, emphasizing their abundance in fine mode. However, Na^+, NO_3^-, and nss-Ca^{2+} are abundant in PM_{10} suggest their association with coarser particle viz sea-salt and dust (Fig. 6). 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}. The spatial variation of nss-Ca^{2+} in PM_{10} exhibits the higher concentrations in the northern Bay where the continental influence is more pronounced, however, its contribution is almost negligible in $PM_{2.5}$. Another major constituent in water soluble species is nss-K^+ which can be used as a tracer for bio-mass burning emissions. The mass concentration of nss-K^+ shows a similar spatial distribution to that of anthropogenic components SO_4^{2-} and NH_4^+ (Fig. 6).

The relationship between the concentrations of nss-SO_4^{2-} and NH_4^+ in $PM_{2.5}$ and PM_{10} over N-BoB and S-BoB is shown in Fig. 7. Both species showed excellent correlation in $PM_{2.5}$ ($r^2 = 0.98$) for entire BoB. However, relatively large scatter ($r^2 = 0.75$) is observed in PM_{10}, during the S-BoB transect compared to N-BoB ($r^2 = 0.92$). Such significant correlation suggests that nss-SO_4^{2-} exist as ammonium salt in fine mode ($PM_{2.5}$), similar to the observation reported from coastal (Zhuang et al., 1999b) as well as marine locations (Matsumoto et al., 2004; Hsu et al., 2007). An increased scatter in PM_{10} is resulted due to the association of nss-SO_4^{2-} with sea-salt and/or mineral particles in the absence of NH_4^+ over S-BoB. The mean equivalence ratio of NH_4^+ to

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nss–SO_4^{2-} in $PM_{2.5}$ is found close to 1 in N-BoB and S-BoB (Fig. 7) suggesting the complete neutralization of acidic sulphate by NH_4^+. However, lower ratios were seen in PM_{10} (0.56±0.34) suggests that particulate nss-SO_4^{2-} is not completely neutralized by NH_4^+ (due to lower contribution of NH_4^+ in PM_{10} over N-BoB and S-BoB); and hence near absence of particulate ammonium nitrate (Matsumoto and Tanaka, 1996). As a result, neutralization of nitrate is favoured by its uptake on the coarser sea-salt particles, thus leading to relatively higher concentration of NO_3^- in PM_{10} (Fig. 5).

The mass ratio of NO_3^- and nss-SO_4^{2-} in aerosol samples has been used to assess the relative importance of emissions from stationary versus mobile sources (Wang et al., 2006; Arimoto et al., 1996; Yao et al., 2002). In the present study, the ratio varied from 0.01 to 0.18 with an average of 0.03 in $PM_{2.5}$ samples, whereas the same for PM_{10} samples varied from 0.01 to 0.43 with an average of 0.10. Over the marine region, due to the reaction of sea salt and dust with HNO_3, nitrate exists in coarse mode, however, sulfate exists in both fine and coarse mode due to the formation of $(NH_4)_2SO_4$, $CaSO_4$, Na_2SO_4. The mass ratio of NO_3^-/nss-SO_4^{2-}, during long range transport, will be low in $PM_{2.5}$ because of the various processes such as evaporative loss of NH_4NO_3 and the complete neutralization reaction of NH_3 with H_2SO_4, as a result of which sulfate concentrations are far more higher compared to nitrate mass concentrations in fine mode aerosols.

3.2.2 Carbonaceous species

The spatio-temporal variability of EC and OC is shown in Fig. 8 and mean concentrations along with maximum and minimum value in N-BoB and S-BoB have been reported in Table-1. The average EC concentrations in $PM_{2.5}$ and PM_{10} are 2.0±1.3 (range: 0.8–5.0) $\mu g\,m^{-3}$ and 2.7±1.7 (range: 1.0–6.7) $\mu g\,m^{-3}$ respectively over N-BoB. The spatial variability is found to be similar to that of mass loading, showing a decreasing trend in the mass concentration of EC towards S-BoB with average concentration of 1.2±0.4 (range: 0.2–1.8) $\mu g\,m^{-3}$ and 1.1±0.5 (range: 0.2–2.3) $\mu g\,m^{-3}$ in $PM_{2.5}$ and

PM_{10} respectively. It is interesting to note that EC concentration is more or less similar in PM_{10} and $PM_{2.5}$ over S-BoB (Fig. 8), suggesting its existence in sub-micron size particles leading to longer lifetime in the atmosphere. In a previous study over Bay of Bengal by (Kumar et al., 2008b), in the bulk aerosol samples, the mean concentration (0.4 $\mu g\,m^{-3}$) was order of magnitude lower than that found in the present study. However, spatial distribution was similar (decreasing trend from north to south) to the present study. The relative contribution of EC towards $PM_{2.5}$ ranged from 2.7 to 9.6 % with an average contribution remaining similar (∼6%) over N-BoB and S-BoB. However, the contribution of EC to PM_{10} was averaged around 4 %, almost twice the contribution observed during background condition within the MABL of Bay of Bengal (Kumar et al., 2008b; Sudheer and Sarin, 2008).

The OC concentrations show similar kind of spatial distribution as that of EC, over the N-BoB and S-BoB as illustrated in Fig. 8. The OC concentration varied from 1.6–11.6 $\mu g\,m^{-3}$ (Av = 5.9±3.7 $\mu g\,m^{-3}$) and 1.9–19.7 $\mu g\,m^{-3}$ (Av = 9.1±6.0 $\mu g\,m^{-3}$) in $PM_{2.5}$ and PM_{10} respectively, over N-BoB. In contrast to the predominance of EC in fine mode ($PM_{2.5}$), OC is abundant in both $PM_{2.5}$ and PM_{10} (Fig. 8), exhibiting a bimodal distribution over Bay of Bengal. 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.

The linear regression analysis performed between EC and OC, for N-BoB and S-BoB in $PM_{2.5}$ and PM_{10} is shown in Fig. 9. A significant correlation between EC and OC has been observed for $PM_{2.5}$ ($r^2 = 0.87$) and PM_{10} ($r^2 = 0.80$) for samples collected in the northern region suggesting the co-genetic sources as well as primary nature of OC in N-BoB. However, relatively poor correlation is found for both (PM_{10} and $PM_{2.5}$; Fig. 9) in S-BoB. Similar kind of feature was observed in previous study by (Sudheer

and Sarin, 2008), and several plausible reasons including preferential removal of one component over the other during long-range transport and additional sources of OC has been discussed. As evident from the spatial distribution of carbonaceous species (Fig. 8), a decrease in OC and EC concentration is observed as cruise moved to S-BoB. However, the spatial distribution of OC/EC (Fig. 8c), show an increase in the ratio (11 to 17 January), suggesting the relatively higher contribution of OC caused by biomass burning during S-BoB transects when winds were from south-east Asia. The evidence for biomass burning as a dominant source for OC is further illustrated from the significant linear relationship between OC and nss-K^+ (Fig. 10) for the IGP and SEA outflow in $PM_{2.5}$ and PM_{10}.

During the campaign, in most of the samples OC/EC ratio lies in the range of 2.0–4.0 (Fig. 8). Earlier studies suggest that (OC/EC) ratio more than 2.0 can have contribution from biomass burning and any value less than this can be explained by their origin derived from fossil fuel combustion (Turpin et al., 1991; Turpin and Huntzicker, 1991; Chow et al., 1996). In the N-BoB, OC/EC ratio for $PM_{2.5}$ varied from 1.9 to 4.9 with a mean and standard deviation of 2.9±0.8 where as for S-BoB, it varied from 0.9 to 4.0 with mean (± stdev) = 2.4±1.3. Surprisingly, in the Southern Bay, 4 samples having their EC values higher compared to their OC values and hence their OC/EC values are less than one. These four samples were collected during the MAP wind regime. The spatio-temporal variability observed in the OC/EC ratio can be explained owing to the differences in chemical reactivity, volatile nature and scavenging rates of OC and EC. Due to the non-volatile nature and thermal stability, residence time of EC is more compared to OC (Lim et al., 2003). This particulate organic carbon may contain semi-volatile organic compounds which can evaporate during their long range transport from the source regions and may partition themselves between gas-particle phases. Hence the measured OC/EC ratio, away from the source regions can vary significantly as they get transported away from the source (Lim et al., 2003). This kind of lower OC/EC ratio is reported elsewhere in the marine and other regions by several researchers (Louie et al., 2005; Wang et al., 2005; Novakov et al., 2000, 2005; Lonati et al., 2007; Neusüß

et al., 2002; Castro et al., 1999; Turpin and Huntzicker, 1995).

In this study, a suite of diagnostic ratios 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 measured in aerosol) have 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, we adopted the mixing model approach, 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 as representative value of two end members (viz. 2.0 for fossil fuel and 9.1 for biomass burning), the TC/EC averaging around 4.3 over entire BoB for PM_{10} indicates ∼35 and 65 % contribution from biomass and fossil fuel combustion respectively. Similarly for $PM_{2.5}$, this value averages around 3.5, suggesting that the carbonaceous species in fine mode have 20 % and 80 % contribution from biomass and fossil fuel combustion sources respectively. Such observation point towards mixed contribution from both sources contrary to the previous study by (Sudheer and Sarin, 2008b), reporting the dominant (more than 80 %) contribution from biomass burning over Bay of Bengal during spring inter-monsoon.

According to (Andreae and Merlet, 2001), the K^+/EC ratio in the bio mass burning emission lies in between 0.1 to 0.63 and the observed ratio over Bay of Bengal for $PM_{2.5}$ and PM_{10} averaged around 0.35±0.10 and 0.39±0.15 respectively, which signifies the source of K^+ and carbonaceous aerosol from biomass burning as fossil fuel combustion produces insignificant amount of K^+. In order to quantify the relative contribution of carbonaceous species from two sources we assumed that K^+/EC ratio from fossil-fuel combustion sources is zero and that from biomass burning sources as 0.63. Based on the average K^+/EC value, the estimated contribution towards EC

from biomass burning is more than 50% in $PM_{2.5}$ and PM_{10}. This further supports our inference of mixed contribution from both (fossil fuel and biomass burning) sources towards carbonaceous aerosols over Bay of Bengal. It is also interesting to note that the nss-K^+/EC ratio are relatively higher in S-BoB (0.39 ± 0.09 for $PM_{2.5}$ and 0.47 ± 0.15 for PM_{10}) as compared to N-BoB (0.29 ± 0.09 for $PM_{2.5}$ and 0.29 ± 0.08 for PM_{10}). This suggests the dominant contribution of biomass burning emissions during SEA outflow over S-BoB. Except one study by (Sudheer and Sarin, 2008a), previous studies (INDOEX) attributed the carbonaceous mass concentration over the northern Indian Ocean is mainly from fossil-fuel combustion sources. Our study, together with high concentrations of nss-K^+ and EC in $PM_{2.5}$ aerosols further suggests the significant contribution of carbonaceous aerosol mass concentration is from bio-mass burning during the ICARB-2009 campaign.

3.2.3 Mineral dust

In the $PM_{2.5}$ and PM_{10} Fe and Al are well correlated (Fig. 11) and the average ratio of Fe/Al in $PM_{2.5}$ is about 0.51 (±0.30), whereas in PM_{10} it is about 0.40 (±0.09). In PM_{10}, 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 $PM_{2.5}$, which contains fine mode aerosols, can be attributed to the anthropogenic combustion sources (Kumar et al., 2010). Similarly Ca/Al and Mg/Al in PM_{10} aerosols are close to the UCC values (Ca/Al = 0.37, Mg/Al = 0.17) reported by (Taylor and McLennan, 1985), where as the relative enrichment in $PM_{2.5}$ can have contributions from anthropogenic sources. The average values of Fe/Al, Ca/Al and Mg/Al along with the standard deviations are given in the Table-2 for both $PM_{2.5}$ and PM_{10} aerosols collected from the MABL of Bay of Bengal during the campaign. Surprisingly in some samples, depleted values of Fe/Al, Ca/Al, Mg/Al ratios (lower than the upper continental crustal value reported by (Taylor and McLennan, 1985) were observed. Such lower Fe/Al ratios are reported elsewhere by several researchers (Gomes and Gillette, 1993; Zhang et al., 1997). The air-mass back trajectories computed at arrival heights 1500, 2500 and

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4000 m indicates the transport of air-parcels from African and central Asian regions rich in dust content. In some regions of these deserts, the transport of mineral dust from Puerto Rico, African desert (Reid et al., 2003) and from Chinese desert regions (Zhang et al., 1997; Arimoto et al., 2006; Buck et al., 2010a), are reported with low Fe/Al ratio. Some back trajectories are showing localized pattern within the marine boundary layer for which Fe/Al ratio is also low (MAP type). The variability of Ca/Al, Fe/Al and Mg/Al is quite larger in $PM_{2.5}$ because of low dust concentrations. Table-3 presents the comparison of these crustal derived elemental ratios with other studies reported elsewhere.

In the present study, Al concentration has been used to calculate the mineral dust mass by assuming that on average, the upper continental crust contains 8.04% of Al (Taylor and McLennan, 1985). Mineral dust contributes to about 11% to the $PM_{2.5}$ mass, suggests the presence of fine dust. Though, total Ca concentration is low in $PM_{2.5}$, the mass ratio of soluble Ca^{2+} to total aerosol Ca is ~100%, indicates that atmospheric processing of dust by anthropogenic acids such as nss-SO_4^{2-} and NO_3^- and hence leads to its enhanced solubility in $PM_{2.5}$ aerosols. Similarly in the PM_{10} aerosols, percentage contribution of water soluble Ca^{2+} towards total Ca is about 76%, where the mineral dust contribution to average PM_{10} mass is about 33%. In the N-BoB, significant correlation (r^2 = 0.53; p-value <0.01) observed between Ca and NO_3^- further confirms the acid uptake by mineral aerosol. No such significant linear relationship is observed over the south Bay, where the dust levels significantly low in compared to that over N-BoB.

3.2.4 Mass closure

Mass concentrations of $PM_{2.5}$ and PM_{10} aerosols were estimated from the measured constituents in aerosol samples and compared with the gravimetrically obtained $PM_{2.5}$ and PM_{10} mass concentrations. In the present study, particulate mass concentration (PM_x) in aerosols is calculated as follows.

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PM_x = Mineral dust + Sea Salt + Anthropogenic + Organic Matter + EC = (Al·12.5) + (Cl^- + 1.47·Na^+) + (NH_4^+ + NO_3^- + nss-SO_4^{2-}) + (1.6·OC) + EC Here X = 2.5 or 10 respectively.

Sea-Salt concentrations were estimated by the following relation (Quinn et al 2007):

Sea Salt = Cl^- ($\mu g\,m^{-3}$) + 1.47·Na^+ ($\mu g\,m^{-3}$)

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^+ and Cl^- are mainly derived from sea water and hence excluding the contribution from non sea salt (nss) -components such as K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, HCO_3^- there by allowing for the Cl^- 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. Estimated concentration of $PM_{2.5}$ and PM_{10} in N-BoB and S-BoB are in well agreement with the gravimetrically obtained mass concentrations (Fig. 12).

The relative contributions of chemical species to average $PM_{2.5}$ and PM_{10} mass in north and south BoB were also shown as pie diagrams (Fig. 13). The anthropogenic components constitute the major fraction in both sizes throughout Bay of Bengal whereas mineral dust is next major contributor in PM_{10} with significantly lower contribution in $PM_{2.5}$. The contribution of sea-salts is insignificant in $PM_{2.5}$, however, significant contribution is observed in PM_{10} over S-BoB. The carbonaceous components (POM+EC) also constitute the significant fraction in $PM_{2.5}$ and PM_{10} over entire Bay of Bengal. Our work presents the quantitative chemical composition of size-segregated aerosols ($PM_{2.5}$ and PM_{10}) in the MABL of Bay of Bengal during winter period (27 December 2008–30 January 2009). This study also emphasize the impact of biomass burning over the north Indian ocean and also as a significant source of carbonaceous species over Bay of Bengal during NE-monsoon (winter season).

3.3 Impact of continental outflow

3.3.1 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 (Yao et al., 2003; Hsu et al., 2007; Zhuang et al., 1999a). 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 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^-/Na^+ ratio can be much lower in marine aerosols than their actual mass ratio from seawater (Cl^-/Na^+ sea-water ratio is 1.8) (Pakkanen, 1996; Zhuang et al., 1999a, b; Yao et al., 2003). 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_{meas}^+ and Cl_{meas}^- 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 (Yao et al., 2003; Zhuang et al., 1999a; Pakkanen et al., 1996). The calculation is based on the assumption that Na^+ in aerosol samples is solely derived from seawater and does not have significant anthropogenic source. In the present study over Bay of Bengal large chloride deficit have been observed ranging from 39–100 and 13–100 % with a mean value of 86±20 and 89±20 % in $PM_{2.5}$ and PM_{10} 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_2SO_4 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_2 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.

3.3.2 Dry-deposition of mineral dust

In the present study, the mineral dust mass concentrations in PM_{10} aerosols varied from 2.6–43.4 $\mu g\,m^{-3}$ with an average value of 13.8±11.9 $\mu g\,m^{-3}$. Average mass concentration of mineral dust contributes almost 11 % in $PM_{2.5}$ and 33 % to PM_{10} aerosols respectively. Further, mineral aerosol mass concentrations were converted into dry-deposition fluxes ($f_{\mathrm{mineral\ dust}}$ = mineral dust ($\mu g\,m^{-3}$) · (0.02 $m\,s^{-1}$); Here 0.02 $m\,s^{-1}$ is the dry-deposition velocity of mineral dust, adopted from (Duce et al., 1991). The average dry-deposition flux of mineral dust for PM_{10} is ~1.0×10^{13} $g\,yr^{-1}$, is compared with earlier estimates over the northern Indian Ocean (2.0×10^{13} $g\,yr^{-1}$) by Goldberg and Griffin, (1979). Further, we also compared the mineral dust input to the Bay of Bengal from the present study with the dust estimates (2.9×10^{13} $g\,yr^{-1}$) of (Duce et al., 1991). It is noteworthy that on a decadal scale, there were no substantial changes in the amount of dust flux to the northern Indian Ocean.

3.3.3 Anthropogenic sources and aerosol iron solubility

Aeolian supply of soluble iron has significant impact on the ocean surface biogeochemistry. In the present-day scenario of growing anthropogenic activities from south and south-east Asia, it is expected to have substantial changes in the abundance of soluble Fe in aerosols (mineral dust vis-à-vis anthropogenic combustion sources). In the present study, the water-soluble aerosol Fe (Fe_{WS}) and total aerosol Fe (Fe_{Tot}) have been measured in both sizes (Kumar et al, 2010). The transport of alluvial dust from the Indo-Gangetic Plain is a dominant source of mineral dust to the Bay of Bengal. During the study period, Fe_{ws} (%) varied from 3.5–49.7 % and 1.4–23.9 % for $PM_{2.5}$ and PM_{10} respectively (Kumar et al., 2010). The high Fe_{WS} (%) over the Bay of Bengal has been attributed to relatively large impact of continental outflow from Indo-Gangetic

Plain and south-east Asia. Our study has revealed that atmospheric processing of mineral dust by acidic species contribute significantly towards the soluble aerosol Fe, as evident from the linear relationship between Fe_{ws} (%) and nss-SO_4^{2-} in $PM_{2.5}$ over north Bay of Bengal (Kumar et al., 2010). Furthermore, the aerosol Fe from combustion sources (biomass burning vis-à-vis fossil-fuel combustion) were found to contribute towards aerosol soluble Fe over the Bay. The significant linear correlation observed among nss-K^+, EC, OC and WS-Fe suggest their common source of bio-mass burning (Kumar et al., 2010). Several studies highlighted the importance of bio-mass burning as a potential source for the supply of soluble Fe (Guieu et al., 2005; Paris et al., 2010). During the study period, the high mass concentration of nss-K^+ further confirms the bio-mass burning as the significant source of aerosol Fe over the Bay.

3.3.4 Anthropogenic trace metals

In the present study, Cd and Pb have shown spatio-temporal variability within the MABL. These metals are introduced in to the atmosphere mainly from the high temperature combustion processes and exist mostly in fine mode (Lind et al., 1998). The scatter plot of Cd, Pb between $PM_{2.5}$ and PM_{10} aerosols suggest their predominant fine mode existence. Similarly, the significant linear correlations observed among Pb, Cd and nss-SO_4^{2-} confirms their anthropogenic origin. Therefore, in $PM_{2.5}$ aerosols, crustal enrichment factors of trace metals (Cd and Pb) were calculated in order to compare their abundance with upper continental crust using Al as a reference element. In comparison to N-BoB, southern Bay has shown relatively high enrichment factors (Kumar et al., 2010), further confirms their fine mode nature and indicates the long-range transport of predominate fine particles which can impact on remote marine region after depositing to surface ocean.

4 Summary and conclusions

A comprehensive study of PM$_{2.5}$ and PM$_{10}$, its mass concentration and chemical composition have been undertaken during wintertime to understand the atmospheric chemistry within the MABL of Bay of Bengal impacted by large continental outflow. The important conclusions are:

1. 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.

2. The fractional contribution of WSIC to total mass of PM$_{2.5}$ and PM$_{10}$ was more or less similar (~45 %) throughout Bay of Bengal, with dominant contribution from sulphate to the ionic budget. On average, nss-SO$_4^{2-}$ constitutes ~65 % of the total water-soluble ionic species and is primarily associated with the fine mode (PM$_{2.5}$) aerosols.

3. The spatial distribution of carbonaceous species (EC and OC) exhibit a similar pattern as that of mass loading, 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.

4. The mineral dust accounts for ~30 % of PM$_{10}$; however, insignificant contribution of dust is observed towards PM$_{2.5}$.

5. On average, anthropogenic component including carbonaceous species are the major contributor towards PM$_{2.5}$ and PM$_{10}$, however natural constituents (mineral dust and sea-salts) are insignificant in PM$_{2.5}$ with some contribution in PM$_{10}$ over Bay of Bengal during winter monsoon.

The impact of continental outflow to the atmospheric chemistry of aerosols in the MABL of Bay of Bengal is evidenced from the variety of processes discussed in this paper.

The transport of continental aerosols to the oceanic region has implication in the biogeochemistry of various elements due to atmospheric deposition as well as in the climate forcing which needs further consideration.

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Table 1. Average concentration of chemical species in $PM_{2.5}$ and PM_{10} aerosols from the MABL of Bay of Bengal along with min-max values (all units are expressed in $\mu g\,m^{-3}$) and standard deviation of the data.

	N-BoB		S-BoB			N-BoB		S-BoB	
	Range	Mean±Stdev	Range	Mean±Stdev	Parameter	Range	Mean	Range	Mean
$PM_{2.5}$	13.2–76.7	38.0±20.2	2.0–35.3	22.3±9.9	PM_{10}	16.2–108	57.8±30.6	6.0–60.7	32.2±15.1
Na^+	0.06–0.58	0.18±0.14	0.1–0.9	0.4±0.2	Na^+	0.12–3.7	0.9±0.9	0.6–4.8	2.4±1.1
NH_4^+	0.37–10.1	4.4±3.0	0.3–4.1	2.1±1.2	NH_4^+	0.25–12.2	5.1±3.8	0.06–4.1	1.4±1.4
K^+	0.21–1.1	0.6±0.3	0.1–0.7	0.5±0.2	K^+	0.33–1.3	0.7±0.3	0.15–1.0	0.6±0.3
Mg_2^+	BDL–0.1	0.03±0.02	0.01–0.11	0.05±0.03	Mg^{2+}	0.04–0.4	0.1±0.1	0.07–0.5	0.3±0.13
Ca_2^+	0.03–0.14	0.07±0.03	0.01–0.12	0.06±0.03	Ca^{2+}	0.11–0.5	0.3±0.1	0.02–0.4	0.2±0.1
Cl^-	BDL–0.1	0.06±0.02	BDL–0.4	0.2±0.1	Cl^-	BDL–1.5	0.3±0.4	0.04–1.2	0.5±0.3
NO_3^-	0.05–1.4	0.37±0.41	BDL–0.2	0.1±0.04	NO_3^-	0.1–2.6	1.0±0.8	0.17–1.3	0.8±0.4
SO_4^{2-}	1.6–28.5	11.9±7.8	1.3–12.1	7.0±3.1	SO_4^{2-}	2.6–35.1	15.2±9.3	2.3–18.1	8.9±4.2
OC	1.6–11.6	5.9±3.7	BDL–5.3	2.6±1.9	OC	1.9–19.7	9.1±6.0	0.4–8.5	3.9±2.8
EC	0.8–5.0	2.0±1.3	0.2–1.8	1.2±0.4	EC	1.0–6.7	2.7±1.7	0.2–2.3	1.1±0.5
Al	BDL–1077	349±275	28.9–446	146±107	Al	356–3468	1769±1081	205–736	555±153
Ca	BDL–176	61±35	27.8–110	57±22.9	Ca	157–732	381±182	41–433	241±101
Fe	32–612	144±140	14.8–85.0	55.7±22.9	Fe	127–1651	754±517	31–382	213±103
Mg	28–152	56±29	25.3–120	61.1±25.5	Mg	135–580	278±125	71–579	341±129
Pb	5.9–39.3	21±11	2.4–41.1	20.6±11.4	Pb	8.7–57	30.5±17.3	2.7–70	28.7±20.3
Cd	0.07–2.0	1.0±0.6	0.04–1.4	0.7±0.4	Cd	0.1–3.0	1.3±0.9	0.03–2	0.9±0.6

Table 2. Elemental ratios of Fe/Al, Ca/Al and Mg/Al in aerosol samples collected from the MABL of Bay of Bengal.

	Region	Fe/Al		Ca/Al		Mg/Al	
		Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std.Dev.
PM$_{10}$	N-BoB	0.42	0.07	0.27	0.12	0.24	0.19
	S-BoB	0.38	0.11	0.46	0.07	0.68	0.25
PM$_{2.5}$	N-BoB	0.52	0.31	0.27	0.2	0.28	0.28
	S-BoB	0.5	0.3	0.51	0.3	0.61	0.47

Table 3. Comparison of elemental ratios in mineral dust from the present study over Bay of Bengal with other regions.

Sampling site	Fe/Al	Ca/Al	Mg/Al	Reference
UCC	0.44	0.37	0.17	Taylor and Mclennan (1985)
Ahmedabad	0.59±0.06	1.04±0.13	0.26±0.05	Rastogi and Sarin (2009)
Mt.Abu	0.66±0.14	1.16±0.24	0.31± 0.05	Kumar and Sarin (2009)
Arabian sea	0.51±0.05	0.89±0.27	0.81±0.26	Kumar et al. (2008b)
Bay of Bengal	0.72±0.37	–	–	Kumar et al. (2008a)
African Dust (Puerto Rico)	0.30	0.38	0.12	Reid et al. (2003)
African Dust (eastern US)	0.47	0.15	–	Perry et al. (1997)
Chinese Desert region (Minqin)	0.35	–	0.22	Zhang et al. (1997)
Chinese Desert region (Yulin)	0.25	–	0.20	Zhang et al. (1997)
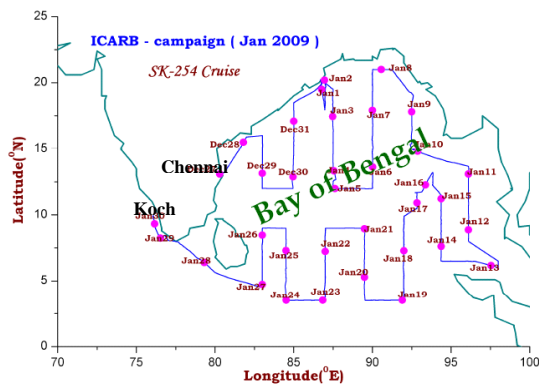
Fig. 1. Cruise track (Cruise No. SK254) undertaken onboard ORV Sagar Kanya in the Bay of Bengal during during 27 December 2008–30 January 2009.
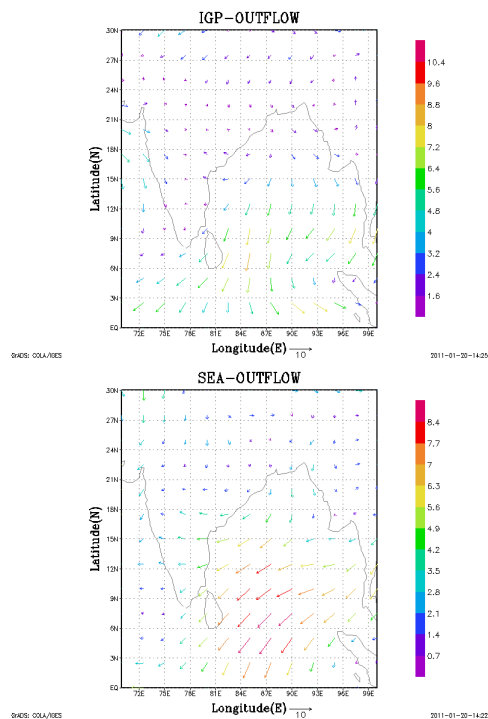
Fig. 2. Average surface wind vectors for the sampling period over Bay of Bengal. Two distinct wind patterns **(a)** outflow from the Indo-Gangetic Plain (IGP) and north/north-east of India during N-BoB transect **(b)** outflow from south-east Asia (SEA) during S-BoB transect.
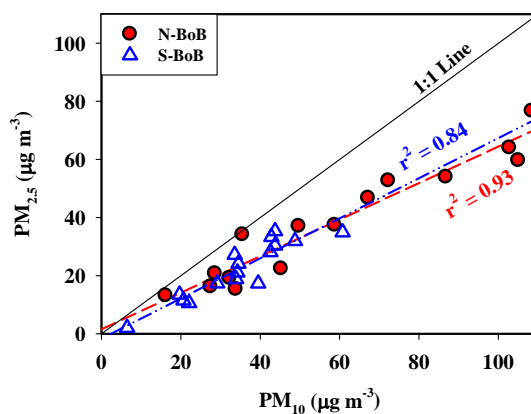
Fig. 3. Scatter plot between mass concentrations of $PM_{2.5}$ against PM_{10} over the MABL of Bay of Bengal.
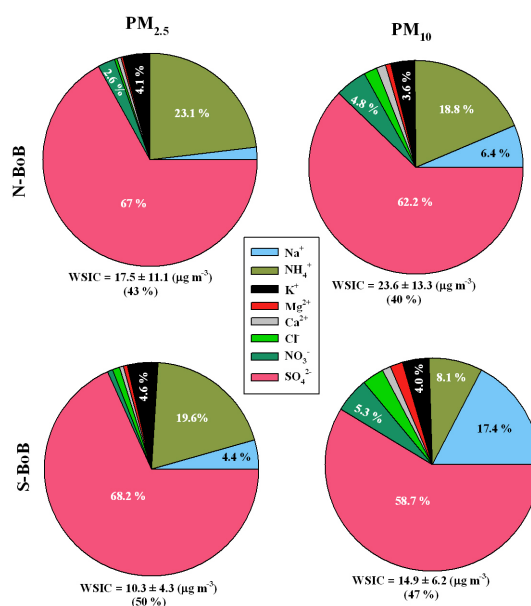
Fig. 4. Fractional contribution (%) of individual ionic species to the total WSIC for $PM_{2.5}$ and PM_{10} in N-BoB and S-BoB. The average mass concentration of WSIC and its percentage contribution in the $PM_{2.5}$ and PM_{10} is also indicated.
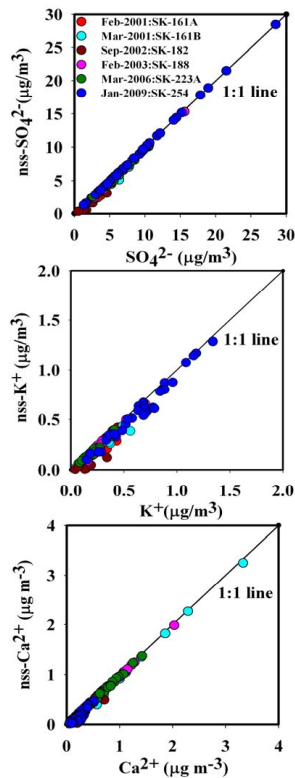
Fig. 5. Scatter plot between **(a)** SO_4^{2-} vs. nss-SO_4^{2-} **(b)** K^+ vs. nss-K^+ **(c)** Ca_2^+ vs. nss-Ca_2^+ in equivalent units, further confirms the continental impact over the Bay during NE-monsoon (January–March).
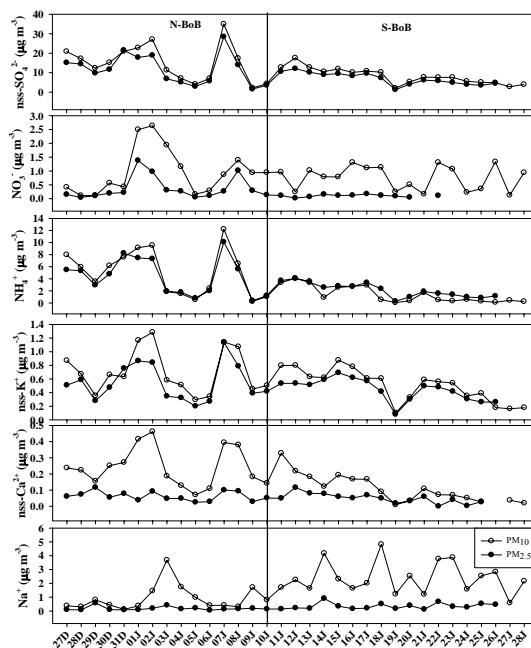
Fig. 6. Spatio-temp oral variability of water-soluble ionic species in the two size fractions (All concentrations are in $\mu g\,m^{-3}$).
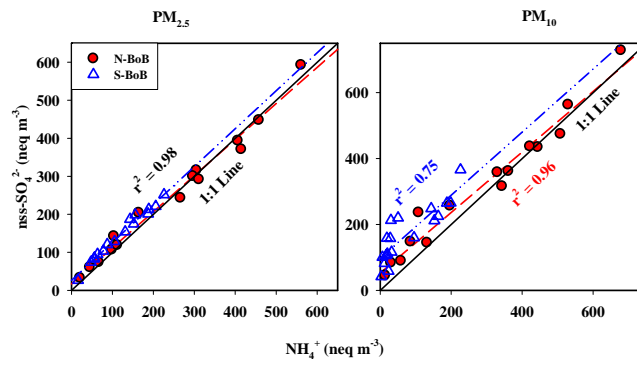
Fig. 7. A linear relationship between nss-SO$_4^{2-}$ and NH$_4^+$ (in equivalent units) in the PM$_{2.5}$ and PM$_{10}$ over Bay of Bengal suggesting their dominant contribution from anthropogenic sources.
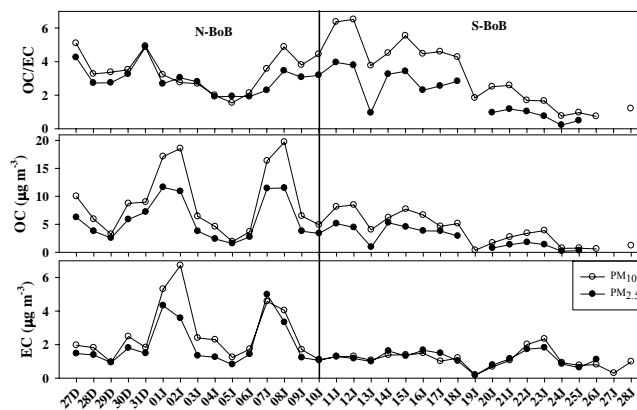
Fig. 8. Spatio-temporal variability 2 of carbonaceous species and OC/EC ratio in the two size fractions (All concentrations are in µg m^{-3}).
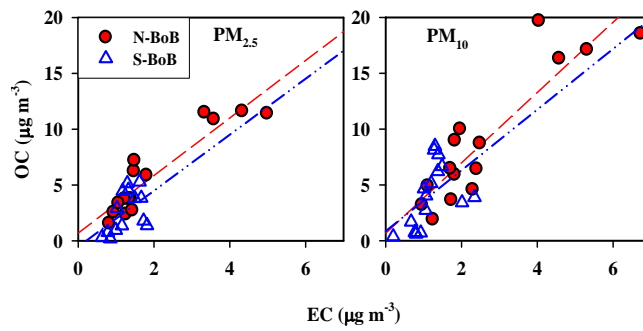
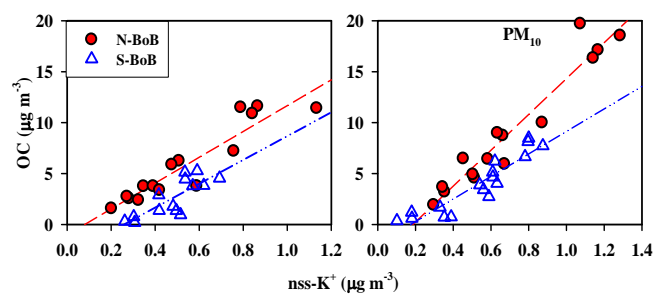**Fig. 9.** Scatter plot between EC and OC for PM$_{2.5}$ and PM$_{10}$ in Bay of Bengal.

Fig. 10. Linear regression plot between nss-K$^+$ and OC indicating the primary nature of carbonaceous species during continental outflow over Bay of Bengal.

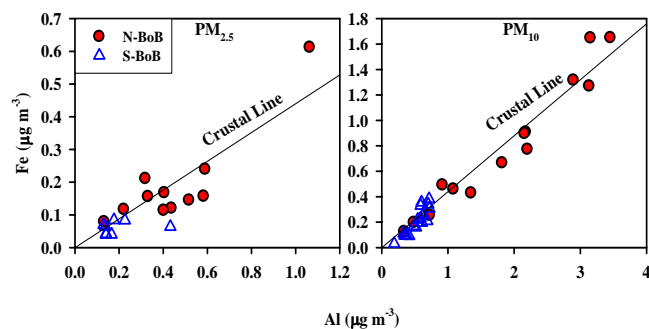**Fig. 11.** Scatter plot between Fe and Al in PM$_{2.5}$ and PM$_{10}$ aerosols, suggest their crustal origin (mineral dust).
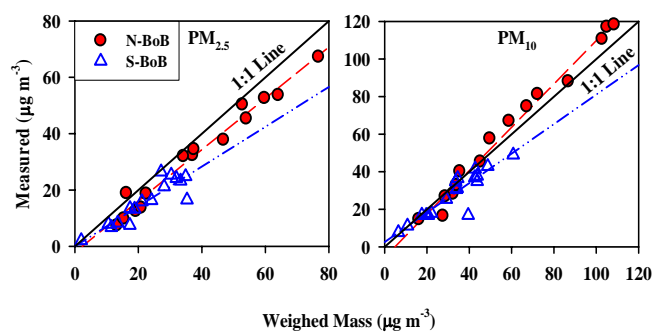
Fig. 12. Scatter plot between the measured (reconstructed) PM mass concentrations versus gravimetrically obtained PM mass concentration for both PM$_{2.5}$ and PM$_{10}$ respectively.

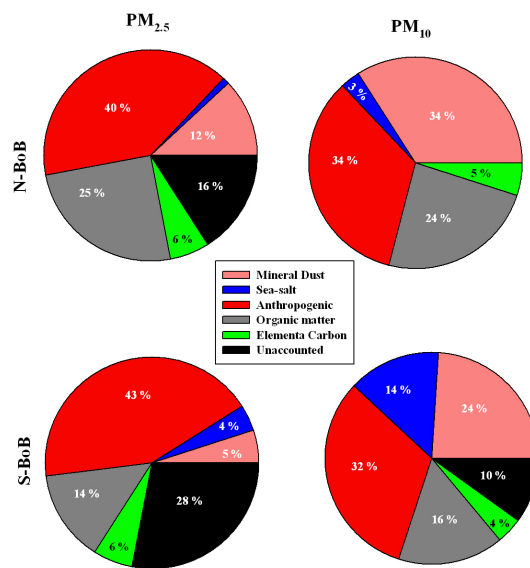**Fig. 13.** Pie chart representation of average chemical composition of PM$_{2.5}$ and PM$_{10}$ mass concentrations over north and south Bay of Bengal.