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Fine mode aerosol chemistry over a tropical urban atmosphere: characterization of ionic and carbonaceous species

A. Chatterjee · C. Dutta · T. K. Jana · S. Sen

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Abstract An extensive aerosol sampling program was conducted during January-December 2006 over Kolkata (22º33′ N and 88º20′ E), a mega-city in eastern India in order to understand the sources, distributions and properties of atmospheric fine mode aerosol ($PM_{2.5}$). The primary focus of this study is to determine the relative contribution of natural and anthropogenic as well as local and transported components to the total fine mode aerosol loading and their seasonal distributions over the metropolis. The average concentrations of fine mode aerosol was found to be 71.2±25.2 μgm^{-3} varying between 34.5 μgm^{-3} in monsoon and 112.6 μgm^{-3} in winter. The formation pathways of major secondary aerosol components like nitrate and sulphate in different seasons are discussed. A long range transport of dust aerosol from arid and semi-arid regions of western India and beyond was observed during pre-monsoon which significantly enriched the total aerosol concentration. Vehicular emissions, biomass burning and transported dust particles were the major sources of $PM_{2.5}$ from local and continental regions whereas sea-salt aerosol was the major source of $PM_{2.5}$ from marine source regions.

Keywords Fine mode aerosol · Ionic and carbonaceous species · Secondary aerosol · Kolkata

1 Introduction

Atmospheric aerosols particularly in fine mode (aerodynamic diameter less than 2.5 μm) play an important role in changing radiative balance of the earth-atmosphere system (IPCC 2007). It has been observed that the global radiative forcing due to aerosol is roughly −1.67±

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A. Chatterjee (✉) · C. Dutta · S. Sen
Department of Chemistry, University of Calcutta, Kolkata, India
e-mail: abhijit_atm@yahoo.com

T. K. Jana
Department of Marine Science, University of Calcutta, Kolkata, India

Present Address:
A. Chatterjee
Environmental Sciences Section, Bose Institute, Kolkata, India

1.3 Wm^{-2}, which nearly compensates the mean global radiative forcing of $+2.47\pm0.3$ Wm^{-2} due to greenhouse gases warming (IPCC 2007). One of the largest source of uncertainties in predicting climate change is the uncertainty in the knowledge about the aerosol radiative forcing which in turn needs a comprehensive database on aerosol chemical characterization along with their sources and temporal variations to fit into the climate models.

India is one of the developing nations that suffer severe air pollution. It has been observed that Asian megacities which cover<2 % of the land area emit~16 % of the total anthropogenic emission of Asia (Gautam et al. 2007). While most of the developed countries in the world are now targeting fine mode aerosol ($PM_{2.5}$) for monitoring and imposed legislative standard for control strategy, unfortunately, there was no systematic monitoring protocol in Indian cities and Central Pollution Control Board of India could not set any guideline for $PM_{2.5}$ standard till November 2009. Kolkata, situated in the eastern part of India amidst world's largest Ganges delta is one of the important Indian megacities. With rapid pace of industrialization and urbanization, air quality over this region is severely affected resulting heavy fine particulate loading in Kolkata. Amongst all the sources, vehicular emission plays a major and significant role in deteriorating air quality of Kolkata. The total number of registered vehicles in Kolkata city is 841,530 (as on March, 2003) of which~85 % is light vehicles (2 and 3 wheelers, cars, taxis etc) and the rest is medium and heavy vehicles (small and large buses, trucks, trailers etc) according to a report (Air quality status of West Bengal—a state of environment report 2004, http://www.wbpcb.gov.in/html/downloads/report_soe_air.pdf) published from West Bengal Pollution Control Board (WBPCB), Kolkata. The number of total registered vehicles has been found to be raised by~4 times since 1983 according to this report. The average number of vehicles per hour over residential cum commercial regions (our study site is a well representative of such a residential cum commercial area) in Kolkata is 14,529 as observed by WBPCB. The average age of small cars is 15–20 years and most of the large vehicles are over 20 years old suggesting that there is very little turnover in the vehicle fleet which in turn minimizes the air quality over Kolkata.

Kolkata has remained a virgin field of research for physical and chemical characterization of aerosols. Several source apportionment studies were made in India including Kolkata (Karar and Gupta 2007) but they are mainly based on the chemical composition of the total suspended particulate matter (TSPM) and PM_{10} fractions but not on fine mode aerosol ($PM_{2.5}$).

Other than the large scale local emissions, because of its unique geographic location, Kolkata acts as a receptor of the huge anthropogenic and dust emission by long and medium range transport under the influence of different monsoon system. Easterly and northeasterly wind during winter brings anthropogenic aerosols from continental source regions like China. Enhanced convection and the steep pressure gradient across the Indo-Gangetic region during pre-monsoon/summer months favor the transport of dust aerosols from arid regions like Thar Desert in western India. Southwesterly / southeasterly wind brings sea-salt aerosols from marine source regions like the Arabian Sea / Bay of Bengal during monsoon. A strong seasonal variation in aerosol chemistry is thus expected over this region. To understand the formation and distribution of atmospheric fine mode aerosols over Kolkata with distinctly different seasonal behaviors, a year-long (January-December 2006) study was undertaken.

Plausible formation mechanisms of secondary ionic species in different seasons, distribution of primary and secondary ionic and carbonaceous species, long range transport of dust aerosol and the interaction between transported marine aerosol and locally generated anthropogenic aerosol are highlighted. An attempt was made to explore the possible sources of fine mode aerosol components from different source regions.

2 Site description

Kolkata formerly known as Calcutta (22º33′ N and 88º20′ E) is the second most populous city of India after Mumbai. According to 2011 census report, the city population is 4,486,679 (~ 4.5 million) and the urban agglomeration (spread over 1750 km^2) had a population of about 13.5 million. The city is bounded to the west and north-west by Hooghly river spread along 80 km. The core area is flat with elevation ranging from 6 m above the mean sea level. Sundarban mangroves forest, the world's largest mangrove eco-region at the land-ocean boundary of the Ganges delta is situated at about 100 km from Kolkata.

The city has a tropical Savannah climate with a marked monsoon season. The seasonal variations of micrometeorological parameters is discussed later and shown in Fig. 1.

University Colleges of Science and Technology premises situated in the northern part of Kolkata was chosen as the study site. The site is a combination of commercial and residential area with several small-scale industries scattered intermittently. The sampling was done at the terrace of the university building which is at the height of about 15 m from the ground level. The sampler was mounted on a wooden platform at a height of 1.5 m from the roof level.

2.1 Prevailing meteorology

The monthly variations of surface meteorological parameters like temperature (°C), relative humidity (%), wind speed (cm s^{-1}) along with total rainfall (mm) over the entire study period (Jan–Dec 2006) are shown in Fig. 1. The surface wind directions are presented seasonally namely winter (Dec–Feb), pre-monsoon (Mar–May), monsoon (June–Sept) and post-monsoon (Oct–Nov) in Fig. 2. The average temperature during the study period was found to be 29±4°C with minimum of 21.3°C during December and maximum of 34.6°C during June. The average relative humidity was 74±5 %. The dry season (Jan–May, Oct–Dec) remained moderately dry with an average relative humidity of 71 % compared to the wet season with an average relative humidity of 81 %. The total rainfall during the entire study period (Jan–Dec) was found to be 1586 mm, 80 % of which (1271 mm) was during monsoon (June–Sept) with no rainfall during winter and scanty rainfall during pre-monsoon (210 mm) and post-monsoon (105 mm). The surface wind pattern during winter was mainly easterly and north-easterly with average speed of 0.62 m s^{-1} and during monsoon it was mainly south-

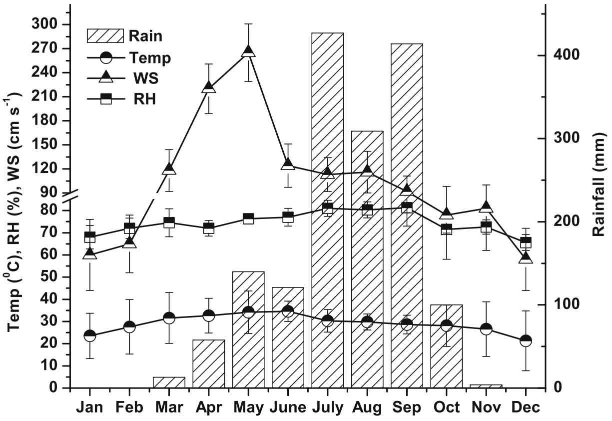

Fig. 1 Seasonal variations of micro-meteorological parameters including rainfall

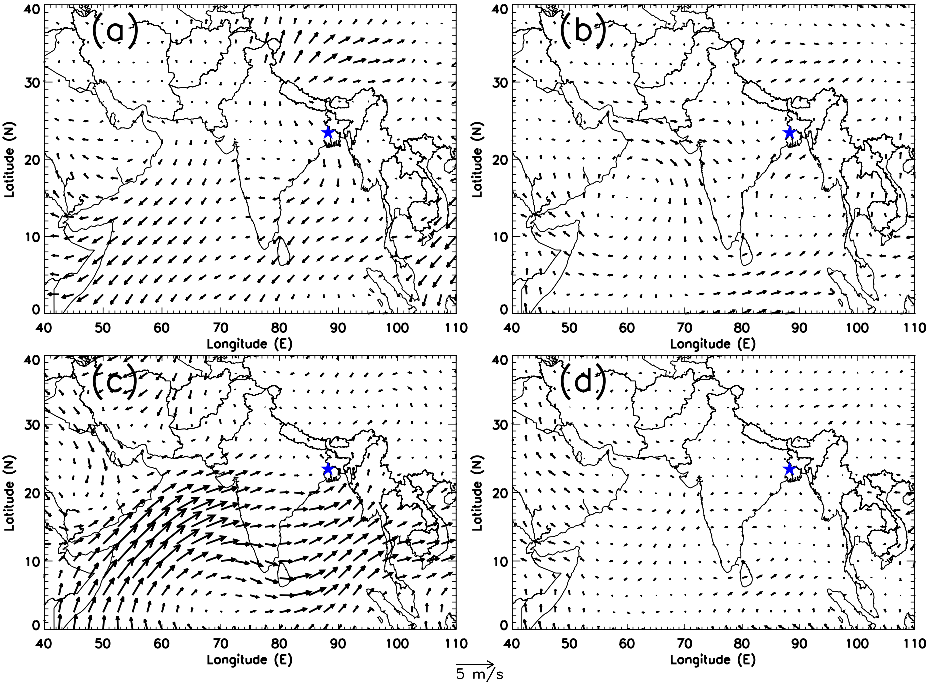

Fig. 2 Mean wind at 950 mb level obtained from NCEP/NCAR analysis during **a** winter **b** pre-monsoon **c** monsoon and **d** post-monsoon over Kolkata

westerly and south-easterly with an average speed of 1.14 ms^{-1}. During pre-monsoon, it was westerly and south-westerly with an average speed of 2.4 ms^{-1}. In order to know the wind pattern variations in different seasons, the monthly mean wind vectors (at 950 mb level) for four different seasons; winter (Dec-Feb), pre-monsoon (Mar–May), monsoon (June–Sept) and post-monsoon (Oct–Nov) were analyzed, for the region covering equator to 40 ^{0}N and 40–130 ^{0}E. The NCEP reanalysis data clearly shows the contrasting wind pattern between winter and monsoon whereas pre-monsoon and post-monsoon represents the transition phase in the circulation patterns. Winter shows weak northeasterly wind from the continental area whereas pre-monsoon shows strong westerly wind from semi arid regions passing over densely populated cities whereas monsoon shows strong south-westerly and south-easterly wind originating from Arabian Sea and Bay of Bengal respectively. These distinctly different wind fields impart extreme temporal variability in aerosol characteristics.

3 Experimental methods

3.1 Collection of aerosol samples and determination of mass concentration

For the collection of $PM_{2.5}$ in ambient air, a fine particulate sampler (Envirotech Instrument Pvt Ltd, India, model APM 550) was used. The sampler is based on the impactor design standardized by USEPA for ambient air quality monitoring. The samples were collected with a flow rate of 1 m^3 hr^{-1}. After entering through the inlet of the sampler, the coarse particulate matter (aerodynamic diameter more than 2.5 μm) was removed using a GF/A (Glass Fiber) filter paper of 37 mm diameter immersed in silicone oil, used as an impaction surface. The impaction surface was placed above the main aerosol collection filter. The fine particles were collected on a quartz substrate (Whatman QM-A) of 47 mm diameter.

On an average, one aerosol sample was collected on every 5th day during the study period. Thus a total of 69 samples were collected (41 during winter, premonsoon and postmonsoon and 28 during monsoon). Each sampling was started at 1000 h (local time) and run for ~24 h.

The quartz substrates were baked for 12 h at 700°C to reduce their carbon blank level. The mass concentration of aerosol was determined by gravimetric measurement. The filters were placed in desiccators for ~24 h before and after the sampling to remove the absorbed water and were weighed in a controlled environment chamber (with the temperature of 25°C and RH of 35–40 %) using an analytical balance (Mettler, model: AE 240) with readability of 0.01 mg and reproducibility of 0.02 mg. The aerosol mass (μg) was determined by the differences between initial and final weight of the filter and the concentration ($\mu g\ m^{-3}$) was obtained dividing the aerosol mass by total volume of air (m^3). After taking the final weight, the substrates were put in Petri dishes sealed with the Teflon tape. The samples were kept in 4°C until further analysis.

3.2 Meteorological parameters

Portable weather monitor with computerized weather station (Model No. Davis 7440) with temperature probe and cup anemometer were installed for collecting micrometeorological data. Wind speed and its direction, temperature, pressure, relative humidity were monitored at 30 mins intervals. The rainfall data was obtained from Indian Meteorological Department, India.

3.3 Chemical analysis

3.3.1 Water soluble ionic species

For the analysis of water soluble ions, one-half of the filter was soaked in 20 ml Milli-Q water (18.2 MΩ resistivity) for ~30 min followed by ultrasonication for 20 min. The solutions were made up to known volume (100 ml) using Milli-Q water and kept in polypropylene bottles at~4°C until analysis. Prior to storage, the bottles were cleaned repeatedly using distilled water and soaked for ~72 h. The major ions, namely anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+ and Ca^{2+}) were determined by Ion Chromatograph (Metrohm 792 basic IC) equipped with separator columns (Metrosep cation 1–2, 6.1010.000 for cation and Metrosep A Supp 3, 6.1005.320 for anion), fitted with a guard column (PRP-1 IC guard column cartridge, 6.1005.050). The eluents were a mixture of 1.8 mmol L^{-1} Na_2CO_3 and 1.7 mmol L^{-1} $NaHCO_3$ for anion and a mixture of 0.75 mmol L^{-1} pyridine dicarboxylic acid and 4 mmol L^{-1} L (+) tartaric acid for cation analysis and were passed at a flow rate of 1 ml min^{-1}. Detection limit of the ionic species (concentrations corresponding to three times the standard deviation of five replicate blank level measurements) namely Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, NO_3^- and SO_4^{2-} were 9.0, 1.3, 3.0, 1.5, 2.4, 9.0, 5.0 and 8.0 ng m^{-3}, respectively. The precision estimated from the standard deviation of repeat measurements of standard and samples was 2 % for Na^+, K^+ and Ca^{2+}; 3 % for Mg^{2+}; 5 % for NH_4^+; 2 % for Cl^-, SO_4^{2-} and 4 % for NO_3^-. For calibration purpose, multi-element ion chromatographic standard solutions (procured from Dionex) were used. To ensure the quality of the trace analysis, a standard reference rain water sample (NIST 2694-A) was analyzed by similar procedure.

3.3.2 Carbonaceous species

A circular punch of diameter 1.5 cm was cut from the loaded quartz fiber substrates and analyzed for elemental and organic carbon content using the thermal-optical carbon analysis method of Huntzicker et al. (1982) as modified by Birch and Cary (1996) using a thermal/optical aerosol carbon analyzer (Sunset Laboratory, Forest Grove, USA). Correction for pyrolytic formation of elemental carbon during organic carbon determination from the samples was accomplished using the methodology described by Kleeman et al. (1999). The analyses of carbonaceous fraction of $PM_{2.5}$ were done at Central Pollution Control Board (CPCB), New Delhi, India.

4 Results and discussion

4.1 Seasonal variation of particulate matter

The average concentration of fine mode aerosol over Kolkata during the entire study period was found to be 71.2±25.2 μgm^{-3} varying between 34.5 μgm^{-3} and 112.6 μgm^{-3}. The seasonal variation of $PM_{2.5}$ concentration (Fig. 3) shows higher concentrations during winter (Dec–Feb) and pre-monsoon (Apr–May) and minimum during monsoon. In winter, very frequent and persistent thermal inversion and fog situations at ground level caused a considerable amount of aerosol to accumulate in the lower layers of the atmosphere. During winter, aerosol transported from the continental source regions driven by north-east monsoon could also enhance the concentration of $PM_{2.5}$ over Kolkata. On the other hand, the higher loading of $PM_{2.5}$ during pre-monsoon could be attributed to the enhanced dust loading (in addition to the locally generated aerosol) transported from the arid and semi-arid region of western India and beyond (*vide supra*). The sharp fall in $PM_{2.5}$ aerosol concentrations and high precipitation amount (1271 mm) during monsoon indicates the significant below-cloud scavenging (wash out) of aerosol and its components.

The National Ambient Air Quality Standard (NAAQS) of annual average concentration of $PM_{2.5}$ is 40 μgm^{-3} as set by Central Pollution Control Board (CPCB) in India in the year

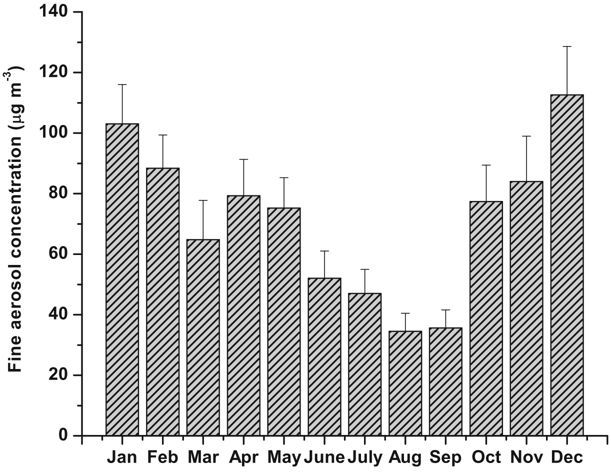

Fig. 3 Seasonal variations of fine particulate matter ($PM_{2.5}$)

2009 (http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php). Thus, it can clearly be seen from Fig. 3, that, the $PM_{2.5}$ concentrations over Kolkata were found to be much higher than the NAAQS mainly during winter which shows 2.3–2.8 times higher and premonsoon and postmonsoon which show 1.6–2.2 times higher $PM_{2.5}$ concentrations. This clearly indicates the severe fine particulate loading in the atmosphere of Kolkata during those seasons. However, monsoon shows much lower $PM_{2.5}$ concentrations (with slightly higher in June and July) than NAAQS. The significant wash-out of fine mode aerosol by heavy rainfall was found to bring $PM_{2.5}$ concentration well below NAAQS mainly during late monsoon (August and September).

4.2 Water-soluble ionic species in $PM_{2.5}$

4.2.1 Primary ionic species

It was observed that Na^+ and Cl^- constituted 7.7±4.1 % of $PM_{2.5}$. Na^+ shows highest concentrations during monsoon whereas Cl^- concentration was found to be higher in dry season (winter, premonsoon and postmonsoon) compared to monsoon (Fig. 4a). The higher Na^+ concentration during monsoon is due to the higher loading of sea-salt aerosol driven by monsoon air masses which mostly originate in the Bay of Bengal. Higher Cl^- concentration during the entire dry season could be attributed to biomass and coal burning (domestic and industrial) (Shapiro et al. 2007). We observed a strong correlation between black carbon and Cl^- ($R^2=0.76$, n=41) during dry seasons indicating their common burning source. On the other hand, comparatively lower concentration of Cl^- during monsoon is due to the chloride depletion from sea-salt aerosols through the interaction between marine aerosols and polluted urban anthropogenic aerosols. Chloride depletion results when the acidic species, mainly nitrate, sulphate and some organic acids react with the sea-salt particles replacing Cl^- in the form of HCl gas.

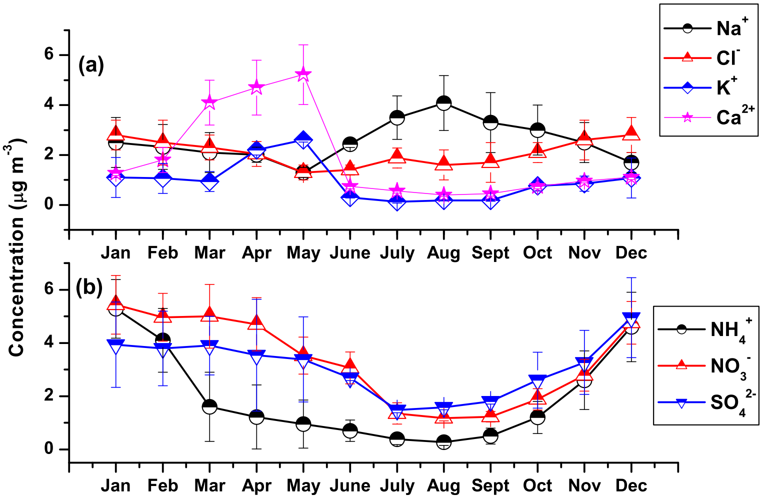

Fig. 4 Seasonal variations of water soluble **a** primary and **b** secondary ionic species

The percentage of Cl⁻ depletion is calculated as (Zhuang et al. 1999):

$$\begin{aligned}\mathrm{Cl}^{-}_{dep}(\%) &= \left[\left([\mathrm{Cl}^{-}]_{seawater,\,estimated} - [\mathrm{Cl}^{-}]_{aerosol,\,measured}\right)/[\mathrm{Cl}^{-}]_{seawater,\,estimated}\right] \times 100\% \\ &= \left[\left(1.17[\mathrm{Na}^{+}]_{aerosol,\,measured} - [\mathrm{Cl}^{-}]_{aerosol,\,measured}\right)/1.17[\mathrm{Na}^{+}]_{aerosol,\,measured}\right] \times 100\%\end{aligned}$$

Here, the source of measured Na^+ concentration in aerosol is assumed to be sea water. The average Cl^- depletion during monsoon was 54.5±7.5 %. The surface reaction mechanism is the principal cause for higher depletion from the fine aerosol with smaller particle size (McInnes et al. 1994; Pakkanen 1996). The dynamics of the chloride depletion reactions favor smaller particles because of their larger surface area distribution and longer atmospheric residence time.

The average concentrations of K^+ and Ca^{2+} in $PM_{2.5}$ were 0.95±0.63 μgm^{-3} and 1.84±1.56 μgm^{-3}, respectively. The seasonal variation of K^+ (Fig. 4a) shows higher concentrations during winter and pre-monsoon. On the other hand, Ca^{2+} shows gradual increase from winter with maximum concentration during pre-monsoon. During winter, non-sea-K^+ shows strong correlations with non-sea-SO_4^{2-} ($R^2=0.71$, n=17) and black carbon ($R^2=0.68$, n=17) pointing to their common source (biomass burning). K^+ can be treated as the tracer or reference element for biomass burning (Li et al. 2010). The higher concentrations of K^+ and Ca^{2+} during pre-monsoon could be related to the long-range transport of dust aerosol. Strong correlation ($R^2=0.85$, n=11) was also observed between non-sea-Ca^{2+} and non-sea-K^+ during pre-monsoon indicating their enrichment in aerosol mainly as dust aerosol. While the annual average contribution of K^+ and Ca^{2+} to $PM_{2.5}$ was 3.5 %, it increased to 10.5 % during pre-monsoon.

Several studies using satellite and surface observations (Husar et al. 1997; Prospero et al. 2002) showed that the arid and semiarid desert regions are the global source of the atmospheric dusts contributing to the long-range transport of dust particles lifted by strong surface winds. The Thar Desert centered in western India and eastern Pakistan is the primary potential source of dusts in the Indian subcontinent (Dey et al. 2004 and references therein). During the pre-monsoon period, dust storms are often experienced in different parts of the Indo-Gangetic basin, dominated by the urban/industrial aerosols (Monkkonen et al. 2004). During this time, due to enhanced convection and steep pressure gradient across the Indo-Gangetic region along with a considerable heat wave running across the region, the dust aerosols are transported from the arid and semi-arid regions of western India driven by the pre-monsoon westerlies and mixed up with the natural and anthropogenic aerosols over the Indo-Gangetic basin.

4.2.2 Secondary ionic species

NH_4^+, NO_3^- and SO_4^{2-}, the secondary components of aerosol, constituted 11.3±2.8 % of $PM_{2.5}$ with their higher concentrations during winter and pre-monsoon. The secondary aerosol components constituted half of the total water soluble ionic species (50.5±11.8 %).

Gaseous NH_3 participates in a temperature-and humidity-dependent equilibrium reaction with gaseous HNO_3 to produce NH_4NO_3 in aerosols under ambient conditions. The formation of particulate NH_4NO_3 is given by the following equilibrium,

$$\mathrm{NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(s).}$$

The dissociation constant for the equilibrium between gas-phase NH_3 and HNO_3 and solid-phase NH_4NO_3 is defined as,

$$\mathrm{Keq} = (\mathrm{pNH_3} * \mathrm{pHNO_3})/[\mathrm{NH_4NO_3}].$$

Where pNH_3 and $pHNO_3$ are partial pressures at equilibrium in ppbv, and the activity of solid-phase NH_4NO_3 is assumed to be unity. The partial pressure product, Pr, for the gas-phase species must be greater than the equilibrium reaction constant, Keq, for there to be a net production of an aerosol NH_4NO_3 phase, i.e., if $Pr<Keq$, any ammonium nitrate will evaporate back into its gaseous components. Pryor et al. (2001) suggested that evaporation occurs when $Pr<Keq/2$ for dry NH_4NO_3 particles. The extent of evaporation would be hindered if the ambient RH were above the deliquescence RH (RHD) of NH_4NO_3. Stelson and Seinfeld (1982) found that the RHD of NH_4NO_3 varies with temperature with a lower RHD at higher temperatures. However the measurements of gas phase NH_3 and HNO_3 were beyond our scope.

Figure 4(b) shows the month wise variations of secondary species. The higher concentration of particulate ammonium and nitrate in winter was due to the shifting from the gas phase nitric acid to the particulate phase nitrate at lower temperature. NH_4^+ and NO_3^- show higher concentrations during winter with a strong correlation ($R^2=0.81$, n=17). Due to volatilization of NH_4NO_3, the equilibrium shifts towards the left with rise in temperature (Wang et al. 2005). Olszyna et al. 2005 observed that partial pressure products (Pr) of gas phase NH_3 and HNO_3 were 2–20 times below the threshold value for NH_4NO_3 formation in $PM_{2.5}$ and 2–3 folds increase in NH_3 levels or 2°C drop in temperature was sufficient to produce NH_4NO_3 aerosol. The present study shows that the concentrations of NH_4^+ and NO_3^- gradually decreased from winter till monsoon. Production of sulphate by the reaction of OH radical and SO_2 also acts as a sink for ammonia. Once ammonia forms either ammonium bisulphate or ammonium sulphate, it becomes unavailable for nitrate formation. High production of sulphate in fine mode aerosol through SO_2 oxidation by OH radical (*vide supra*) is observed during pre-monsoon. In addition to the local emission sources, the higher NH_4^+ concentrations during winter is under the influence of northeastern wind flow transporting the large scale pollutants from continental sources whereas the lower concentration of NH_4^+ in monsoon suggests either the dominant occurrence of NH_4^+ as gas phase NH_3 or the significant wash-out particulate NH_4^+.

The seasonal variation in SO_4^{2-} concentration shows a slow decrease from January till monsoon and a gradual increase till winter. The sulfur oxidation ratio defined as SOR=non-sea-SO_4^{2-}/(non-sea-SO_4^{2-}+SO_2) was used as an indicator of the secondary transformation process and the formation route and source of sulphate in the atmosphere (Ohta and Okita 1990). Figure 5 shows the month wise variation of SOR with temperature. The ratio varied between 0.04 and 0.26 with an average of 0.11±0.06. SOR was found to increase gradually with temperature from January reaching maxima during pre-monsoon. Photochemical oxidation of SO_2 in the atmosphere is proposed (Ohta and Okita 1990) when the ratio value is greater than 0.10. Gas phase photochemical oxidation of SO_2 followed by the condensation and absorption into the particle phase seems to be the most important pathway for the production of fine mode SO_4^{2-} over Kolkata during pre-monsoon (SOR>0.1). The gas phase oxidation of SO_2 to SO_4^{2-} by OH radical is a strong function of temperature (Seinfeld et al. 1986). The comparatively lower SOR during the winter months indicate some aqueous phase transformation processes such as metal catalyzed oxidation of SO_2, aqueous phase H_2O_2/O_3 oxidation of SO_2 etc. Similar observation was also reported by Xiu et al. (2004).

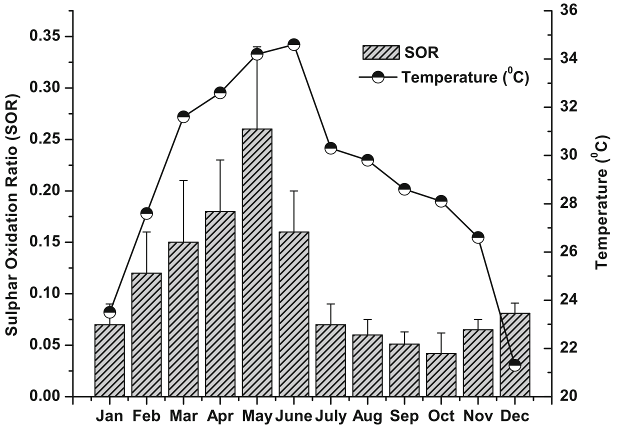

Fig. 5 Seasonal variation of sulphar oxidation ratio (SOR) with ambient temperature

4.3 Seasonal variation of carbonaceous species

The annual average concentrations of black carbon (BC) and organic carbon (OC) in $PM_{2.5}$ during the entire study period were found to be 5.8±2.7 μgm^{-3} and 12.2±5.5 μgm^{-3}, respectively. On an average, total carbonaceous aerosol (BC+OC) constituted 24 % of the total $PM_{2.5}$ where the contribution of OC was found to be almost doubles that of BC.

The seasonal variations of BC, OC and OC/BC ratio are shown in Fig. 6. They show higher concentrations in January followed by gradual decrease till March, small peaks were observed during pre-monsoon, minimum concentrations during monsoon followed by gradual increase till December. During winter, the continental air masses driven by north-eastern wind flow enhance the loading of carbonaceous species along with other anthropogenic aerosol components. In addition to the transported carbonaceous species, frequent burning activities during nighttimes in winter also increase the concentration of carbonaceous species. During pre-monsoon, the long range transport of dust aerosol driven by westerly wind flow has already been discussed. The air mass picks up anthropogenic

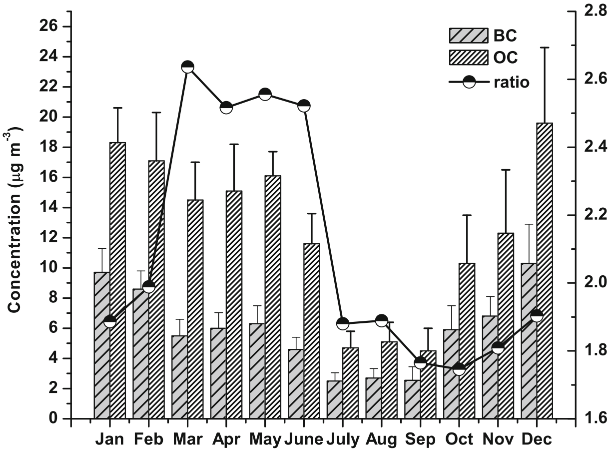

Fig. 6 Seasonal variations of black carbon, organic carbon and their ratio

particles containing carbonaceous species during their travel over Indo-Gangetic regions before reaching eastern part of India (Gautam et al. 2011). The minimum concentration of BC and OC during monsoon is due to significant wash-out by the precipitation.

Figure 7 shows the seasonal variations in BC concentrations, along with ΔT (°C) (the differences between monthly mean maximum and minimum temperature) and wind speed (m s^{-1}). ΔT was found to be higher (11–15°C) during October–March than that in April–May (8–10°C) while it was minimum during monsoon (4–6°C). Clearly, the variation in BC concentration was similar to that of ΔT. Babu and Moorthy (2002) showed higher correlation coefficient between BC mass concentration and ΔT over Trivandrum, a coastal station in southwest India. Ramachandran et al. (2007) also observed the high BC mass concentration with high ΔT. Chen et al. (2001) observed that the BC emissions, in particular, from heavy duty diesel engines, increase with increase in ambient temperatures at Maryland, a suburban site in USA. They suggested that the BC emission increases once it exceeds a threshold value. This would become important during the dry months when the ambient temperature becomes higher. The present study shows that the BC concentration varied inversely to the wind speed. The vehicular emission which is one of the major sources of BC remained relatively constant throughout the entire study period. In such a case, lower wind speed during winter would lead to much less dispersion of BC and the emitted BC particles remain concentrated around the emission site. During pre-monsoon, BC was found to increase with the increase in wind speed instead of expected rapid dispersion. This indicates that other than the local emission sources, long-range transport of BC from distant source regions was the major factor in enhancing BC concentration during this season. During monsoon, the role of high precipitation amount dominated over the role of ΔT and wind speed when much lower BC concentration was observed. Other than the various source emissions, surface boundary layer also plays significant role in the variations of carbonaceous species concentrations. The shallower surface boundary layer over Kolkata during winter and post-monsoon traps and inhibits the ventilation of the fine mode carbonaceous species leading to higher concentrations. With increase in surface temperature and convective activity in summer, the pollutants are easily dispersed into a larger volume as the boundary layer height increase leading to lower concentrations.

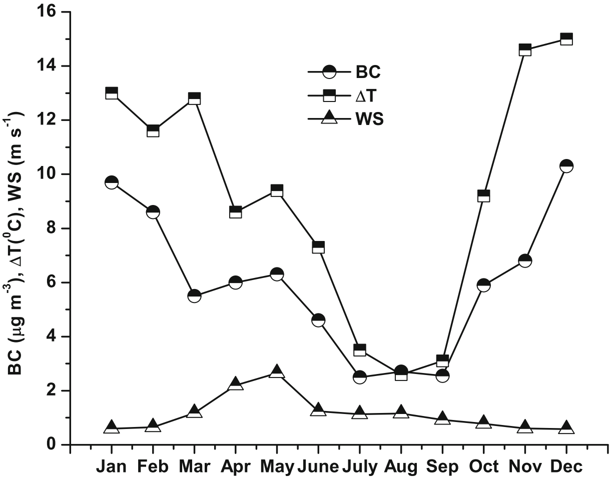

Fig. 7 Variations of black carbon with the differences between maximum and minimum temperature (ΔT) and wind speed

The OC/BC ratio has been used to identify the presence of secondary organic aerosols when the ratio exceeds 2.0 (chow et al. 1996). The average ratio was 2.1±0.4 ranging between 1.7 and 2.6. The ratio was found to exceed 2.0 during March–June. The higher temperature and higher solar radiative fluxes during this period could enhance the photo-oxidation of hydrocarbons leading to the formation of secondary organic species. Strong correlations were observed between BC and OC ($R^2=0.92$ in winter, 0.86 in pre-monsoon, 0.78 in monsoon and 0.91 in post-monsoon) in all seasons indicating their common primary sources. Thus, during Mar–June, both the primary emission sources and the secondary formation pathway are important for the production of carbonaceous species over Kolkata while primary source emission is the only dominant source of carbonaceous species during Jan–Feb and July–Dec. Secondary organic carbon (SOC) was estimated using the following relation (Castro et al. 1999).

$SOC=OC-BC\ (OC/BC)_{min}$, where $(OC/BC)_{min}$ is the observed minimum ratio of OC to BC. The average SOC concentration was found to be 2.1±1.9 μgm^{-3} ranging between 0.05 and 5.1 μgm^{-3}. It was found that the primary carbonaceous species [BC+(OC−SOC)] constituted more than 90 % of the total carbonaceous aerosol in all seasons except during Mar–June (75 %) which has been discussed earlier based on higher OC/BC ratio leading to the formation of secondary species during those period.

Thus, we have seen that ionic and carbonaceous matter contributed nearly 50 % mass of $PM_{2.5}$ over Kolkata. The rest mass could be constituted by several heavy metals (as observed by Karar and Gupta 2007 and Kar et al. 2010 over Kolkata) of which Al, Si, Ca could have large contribution rich in soil-dust (local and transported) along with other heavy metals from several anthropogenic sources. Ionic species (other than those analyzed in this study) and carbonate carbon could also contribute to $PM_{2.5}$ mass in a significant portion. We have found that the contribution of OC in $PM_{2.5}$ is 17 %. If we consider the contribution of total organic matter (OM), it would be 27 % as total OM is considered as 1.6 times of OC (Turpin and Lim 2001; Bates et al. 2004).

4.4 Sources of aerosol

4.4.1 Source identification by air mass parcels using HYSPLIT back trajectory

In order to find out the possibility of atmospheric transport of different species away from Kolkata, backward trajectories for air parcels arriving at the sampling site during the sampling period were calculated with the HYSPLIT_4 (Hybrid Single Particle Lagrangian Integrated Trajectory, www.arl.noaa.gov/ready/hysplit4.html) model developed by NOAA/ARL. Back trajectories were computed (for 72 h) for all sampling events at 0500 UTC at three levels (100, 500 and 1000 m agl). The Final Run (FNL) meteorological data was used for the trajectory calculation.

Based on the transport pathways of air masses traveling through different regions and bringing different chemical components with the aerosol, four possible source regions were found over Kolkata. Four major air mass trajectories, representing northeastern and eastern continental, northwestern and western continental, southeastern marine and southwestern marine arriving at Kolkata are shown in Fig. 8. Southeastern marine air parcels originated from the Bay of Bengal (BOB) while southwestern marine air parcels originated from the Arabian Sea (AS) and pass over several land regions in India. Northeastern and eastern continental air masses originated mainly from China whereas southwestern and western continental air masses originated mainly from the arid and semi-arid regions of India and beyond. Thus, we segregated the different source regions based on trajectories and the

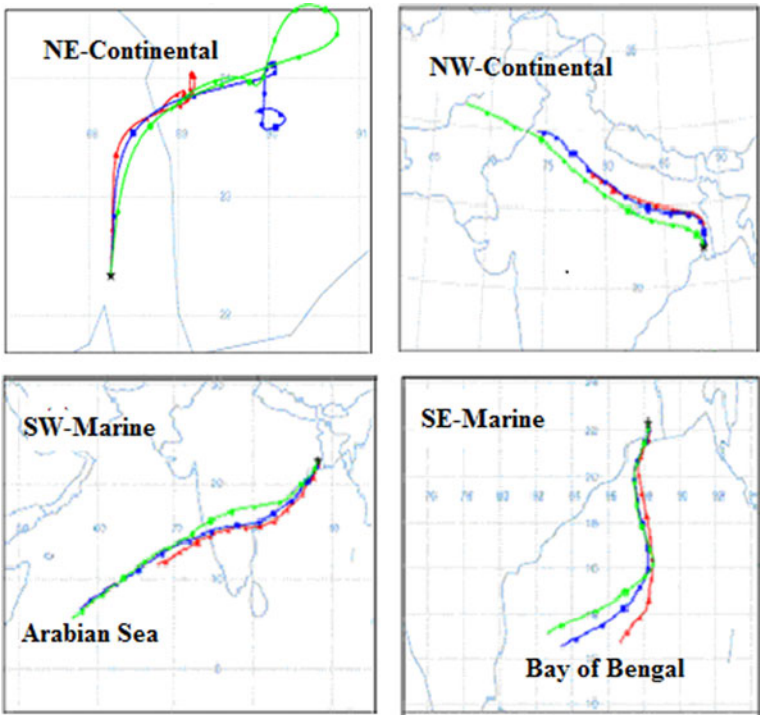

Fig. 8 HYSPLIT backward air mass trajectories from **a** northeastern continental **b** northwestern continental **c** southwestern marine and **d** southeastern marine sectors

concentrations of aerosol and its components were averaged for those source regions and presented in Table 1.

The concentrations of Na^+ was found to be maximum from southeastern sector (BOB) and about 25 % higher than that from southwestern sector (AS). On the other hand, Cl^- was not found to follow the same sequence and its concentration was maximum from northeastern continental sector and much higher than both the marine source regions (southwestern and southeastern). NH_4^+, NO_3^- and SO_4^{2-} show maximum contribution from northeastern continental source regions than others. K^+ and Ca^{2+} show maximum concentrations from southwestern (and western) sectors followed by northeastern (and eastern) sectors and southwestern sectors and with minimum contribution from southeastern sector (BOB). The concentrations of the carbonaceous species (both BC and OC) were higher for continental sources than the marine sources as expected.

The continental air masses driven by northeasterly (and easterly) wind flow during winter and northwesterly (and westerly) wind flow passing over Indo-Gangetic plain during premonsoon bring several fine mode anthropogenic species including carbonaceous aerosols and dust aerosols over Kolkata. The southwesterly wind flow originating from the Arabian Sea when passes through several urban atmospheres over southern India picks up several anthropogenic and dust aerosol before reaching Kolkata. This in turn dilutes the original air masses laden with sea-salt aerosol and enhances the concentration of anthropogenic and dust aerosol species. On the other hand, during monsoon, the air mass which originates from the Bay of Bengal and reaches over Kolkata driven by southeasterly wind flow are comparatively cleaner although they get mixed up with the anthropogenic species from the various

Table 1 Distribution of ionic and carbonaceous species between four different source regions based on HYSPLIT backward trajectories (The concentrations are in μg m^{-3})

	North-East	North-West	South-West	South-East
Na^+	1.92±0.85	1.4±0.34	2.8±1.1	3.6±2.2
NH_4^+	4.6±1.3	0.9±0.42	0.41±0.16	0.13±0.03
K^+	0.93±0.23	2.4±1.74	0.17±0.08	0.16±0.1
Non-sea-K^+	0.84±0.31	2.2±1.05	0.07±0.02	0.03±0.01
Ca^{2+}	1.4±1.1	4.8±2.06	0.73±0.33	0.56±0.24
Non-sea-Ca^{2+}	1.31±0.65	4.7±2.2	0.62±0.4	0.43±0.21
Cl^-	2.92±1.3	1.6±0.47	1.4±1.07	1.8±1.23
NO_3^-	4.86±1.65	3.6±1.6	1.84±1.21	0.85±0.41
SO_4^{2-}	3.9±2.01	3.4±2.08	1.8±1.1	1.65±1.07
Non-sea-SO_4^{2-}	3.4±2.11	3.1±1.78	1.1±0.54	0.75±0.32
BC	9.5±3.2	6.4±3.21	4.13±2.33	2.16±1.12
OC	17.6±6.5	15.4±6.5	8.1±3.07	4.4±2.33

local emissions over Kolkata. Hence in case of anthropogenic and dust aerosol species, we observed higher concentrations for continental source regions followed by the Arabian Sea (southwestern sector) and the minimum concentrations for the Bay of Bengal (southeastern sector).

4.4.2 Source apportionment by Principal Component Analysis (PCA)

In Kolkata, composite anthropogenic activities including biomass burning, vehicular emission and industrial activities play central role in loading of air pollutants in the atmosphere and identification of exact sources of the aerosol is difficult. Principal component analysis (PCA) was used to identify possible sources of aerosols in Kolkata. PCA is a multivariate analysis technique and often used as an exploratory tool to identify the major sources of air pollutant emissions (Guo et al. 2004). It allows the replacement of a large set of intercorrelated variables with a smaller number of independent variables. These new variables (principal components, PCs) are derived from the original variables, and are simply linear combinations of those variables (Thurston and Spengler 1985). The eigenvalues were used to determine the number of PCs along with the variance in each PC after rotation (Park and Kim 2005). Only those PCs that have an eigenvalue more than 1.0 were chosen to have normalized variables that carry one unit of variance. Each PC shows correlation of each variable as loadings (loading greater than 0.5 was statistically significant in this study). Since higher loading of particular variable in a PC can help in identifying the possible sources, the number of PCs selected (sources identified) represent the sources that are relevant in the receptor domain. PCA was performed using the SPSS statistical software (SPSS 2003) using the data sets separately from continental and marine sectors for fine mode aerosol over Kolkata.

For continental aerosol source regions, four PCs were extracted (Table 2). The first PC (PC1) shows high loading of NO_3^-, BC and OC with moderate loading of NH_4^+ indicating the source of vehicular emission over Kolkata. The second PC (PC2) shows high loading of K^+, Cl^-, SO_4^{2-}, BC and OC. These correspond to the massive biomass and fossil fuel burning both for domestic and industrial purpose in Kolkata. The third PC (PC3) shows high loading

Table 2 VARIMAX rotated factor loading matrix for continental and marine aerosols by Principal Component Analysis (PCA)

	PC 1		PC 2		PC3		PC 4
	Continental	Marine	Continental	Marine	Continental	Marine	Continental
Na^+	0.12	0.84	0.15	0.06	0.34	0.2	0.1
NH_4^+	0.6	0.35	0.22	0.68	0.43	0.37	0.85
K^+	0.35	0.29	0.77	0.17	0.84	0.17	0.2
Ca^{2+}	0.08	0.42	0.24	0.2	0.77	0.14	0.27
Cl^-	0.17	0.91	0.72	0.27	0.11	0.31	0.38
NO_3^-	0.78	0.28	0.22	0.81	0.3	0.79	0.91
SO_4^{2-}	0.48	0.82	0.84	0.72	0.42	0.44	0.41
BC	0.87	0.11	0.85	0.62	0.65	0.71	0.32
OC	0.83	0.14	0.9	0.55	0.7	0.62	0.38

of K^+ and Ca^{2+} and moderate loading of BC and OC. Thus PC3 is associated with the long range transport of dust along with carbonaceous aerosols mainly during pre-monsoon and winter. The fourth PC (PC4) is highly loaded with NH_4^+ and NO_3^- corresponding to the formation of secondary anthropogenic particles in the atmosphere. Activities in several solid waste disposal grounds dispersed in and around Kolkata, animal manure and human activities are the major sources for the species in PC4.

For marine aerosol source regions, three PCs were extracted (Table 2). The first PC (PC1) is found to be highly loaded with Na^+ and Cl^- and moderately loaded with SO_4^{2-}. Thus PC1 corresponds to sea-salt aerosol transported from the Bay of Bengal and the Arabian Sea. The second PC (PC2) shows high loading of NH_4^+, NO_3^- and SO_4^{2-} and moderate loading of BC and OC. These correspond to the transported (driven by southwesterly wind flow from Arabian Sea) anthropogenic aerosol species. The third PC (PC3) is highly loaded with NO_3^- and BC and moderately loaded with OC which indicates the source of vehicular emission.

The percentage distribution of various source types obtained from factor analysis by PCA is shown in Fig. 9. Vehicular emissions and biomass burning followed by the long-range transport of dust and anthropogenic species dominated for the continental aerosol source regions during dry seasons whereas sea-salt aerosols followed by local and transported anthropogenic aerosols including vehicular emissions dominated for the marine aerosol source regions during monsoon. However, anthropogenic aerosol contribution was much less effective during monsoon comparative to dry seasons.

West Bengal Pollution Control Board (WBPCB), Kolkata had made a study (Final report—air quality management (Vol—V) ADB TA 3423 IND, http://www.wbpcb.gov.in/html/downloads/adb_ta_3423_air_fin_rep.pdf) on the source apportionment of $PM_{2.5}$ aerosol over Kolkata in the year of 2003 and it has been compared with our source apportionment of $PM_{2.5}$. It shows that the percentage contributions of biomass burning, dust aerosols and secondary anthropogenic components as determined in this study (27 %, 18 % and 11 % respectively) are almost equal to those determined by WBPCB, Kolkata (23 %, 15 % and 13 % respectively). However, we found a lower contribution of the vehicular emission (38 %) compared to WBPCB (48 %).

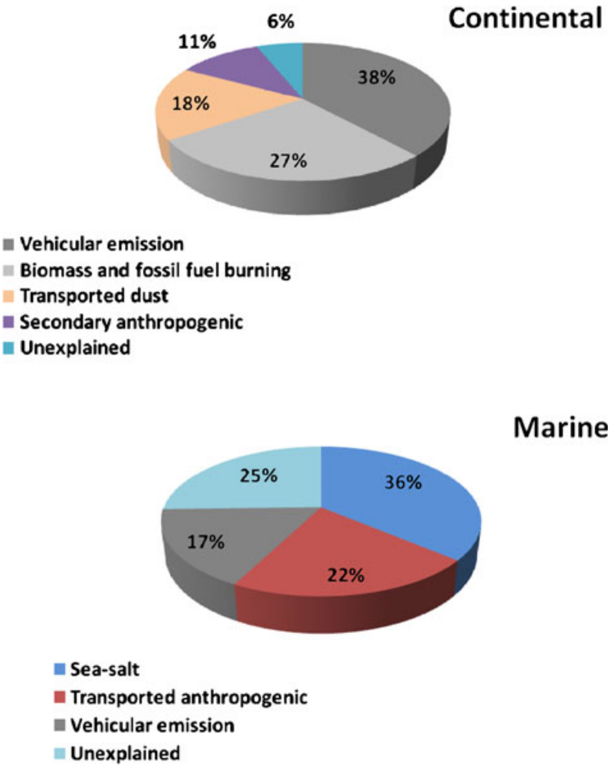

Fig. 9 Percentage source distribution of fine mode aerosols for continental and marine source regions

5 Conclusions

This study shows a large seasonal variation of $PM_{2.5}$ aerosol and its ionic and carbonaceous components over Kolkata during one calendar year. The main reason for high aerosol loading was local and transported anthropogenic species from continental sources during winter and long-range transport of dust aerosols originated over arid and semi-arid region in western India during pre-monsoon. Ambient temperature was found to play a significant role in the formation of particulate nitrate from gas phase NOx during winter whereas the formation of particulate sulphate was governed by high solar radiative flux during pre-monsoon and aqueous phase transformation processes during winter. Photochemical oxidation of hydrocarbons during pre-monsoon was found to be dominated in the formation of secondary carbonaceous species. A large scale interaction was found to be operative between marine sea-salt aerosols and anthropogenic urban aerosols resulting chloride displacement from sea-salt aerosols during monsoon. It was found that all the anthropogenic species concentrations were higher for continental sources compared to marine sources as expected. But the notable feature is that between the marine source regions, the anthropogenic aerosol species were much higher (and sea-salt species were much less) for the southwestern source (Arabian Sea) than the southeastern source (Bay of Bengal). Vehicular emissions followed by biomass burning and long-range transport of dust and anthropogenic species were the major aerosol sources for the continental aerosol source regions during dry seasons whereas sea-salt aerosols followed by local and transported anthropogenic aerosols dominated for the marine aerosol source regions during monsoon.

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