

Study of temporal variability and mass closure of PM_{2.5} and its chemical constituents during weak south-west monsoon

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ABSTRACT

Ambient PM_{2.5} (n = 42) samples have been collected during a weak South-west (SW) monsoon (July–September, 2015) from central part of the Indo-Gangetic Plain (IGP; at Kanpur). Organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), water-soluble inorganic species (WSIS) and metals have been measured in this study. Air-mass back trajectory (AMBT) analysis reveals atmospheric transport from three major pathways indicated as Type-1 (n = 24; traversing through western region), Type-2 (n = 8; traversing eastern region) and Type-3 (n = 10; terrestrial air-masses). Total carbonaceous aerosols (TCA), mineral dust (MD) and WSIS in Type-1 air-mass contributed $18.7 \pm 8\%$, $40.3 \pm 14.5\%$ and $35.2 \pm 13.4\%$, respectively to the PM_{2.5} mass. TCA, MD and WSIS mass fractions constituted $27.1 \pm 13.2\%$, $29.1 \pm 7.9\%$ and $34.9 \pm 10.7\%$ in Type-2 air-mass and $25.2 \pm 14.1\%$, $34.6 \pm 14\%$ and $33.3 \pm 9.8\%$ in Type-3 air-mass, respectively. Mineral dust percentage fraction and composition (based on Fe/Al ratio) suggests significant differences between Type-1 and Type-2 air-masses. Based on statistical two-tailed *t*-test, the mineral dust composition of Type-1 versus Type-3 and Type-2 versus Type-3 air-masses look near similar. However, average mass ratios of OC/EC (6.2–6.4), WSOC/OC (≈ 0.50 ; exception being difference in Type-2 versus Type-3) and K_{BB}^+/OC (0.05–0.07; K_{BB}^+ : biomass burning derived potassium) look near similar in PM_{2.5} associated with all the three air-masses; indicating carbonaceous aerosols from well-mixed sources with dominant contribution from biomass burning emission. A significant abundance of organic aerosols and mineral dust in presence of high moisture content and their mixing over IGP has implications to perturbation in regional scale radiative forcing.

1. Introduction

Indo-Gangetic Plain (IGP) stretches from northern to eastern part in India and has a unique topography: Himalayan range in its north and Deccan plateau in the south. Seasonal and annual practices of large-scale biomass burning emission and fossil-fuel combustion in conjunction with mineral dust largely influence the variability in chemical composition and optical properties of atmospheric aerosols over the IGP (Reddy and Venkataraman, 2002; Ramanathan and Ramana, 2005; Nair et al., 2007; Dey et al., 2012; Rajput et al., 2014a; Rai et al., 2016). Biomass burning and secondary aerosol formation are the major sources of organic aerosols over northern India with large seasonal variation (Ram et al., 2010; Kaul et al., 2011; Rajput et al., 2014a; Rai et al., 2016; Singh and Gupta, 2016). Furthermore, the crustal dust also plays a crucial role in influencing the atmospheric composition, chemistry and radiative forcing besides acting as cloud condensation nuclei (CCN) (Usher et al., 2003). Previous studies have suggested that over this region there is a significant contribution of mineral dust which is

transported from western region including dust from Thar Desert (Dey et al., 2004; Chakraborty and Gupta, 2010; Ghosh et al., 2014). Long-range transport of mineral dust over the region is very conspicuous during summer months resulting into high variability in aerosol chemical composition and optical properties. Thus, assessing seasonal composition of particulate matter is of utmost importance for identification of emission sources and health risk evaluation (Voutsas et al., 2002; Pipal et al., 2014; Singh and Gupta, 2016).

Indian summer monsoon, during the months from June–September, is usually marked with more than 80% of the total annual rainfall over the region. During this period, South-westerly wind system favors the transport of air-masses from oceanic region (Bay of Bengal or Arabian Sea) to the Indian sub-continent (Goswami and Mohan, 2001; Wang and LinHo, 2002). Particles concentration is generally low due to high convective mixing and frequent wet precipitation events during this period. However in 2015, less rainfall events have been recorded due to El-Niño and positive phase of PDO (Pacific Decadal Oscillations). These phenomena have caused a weak Summer Monsoon (also referred to as

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SW-monsoon) which facilitated us to assess the aerosol composition during this period. A priori information of these phenomena, based on long-term meteorological records, has motivated us to carry out a study focussing on composition of fine aerosols ($PM_{2.5}$) under expected high content of mineral dust resulting due to high wind speed and low moisture content in top soil layer owing to less precipitation during the weak monsoon (Zhang et al., 1997; Krishnamurthy and Krishnamurthy, 2014; Rajeev et al., 2016).

In this study, chemical composition and characteristics of fine aerosols ($PM_{2.5}$) have been assessed from central IGP during SW-monsoon. Our study provides hitherto unknown data set on chemical composition of $PM_{2.5}$ and highlights the significance of interaction of organic aerosols and mineral dust over this region. To understand the sources and chemical characteristics of $PM_{2.5}$ and interactions among various chemical constituents, organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), metals (Fe, Al, Ca and Mg) and water-soluble inorganic species (WSIS) have been measured. These chemical constituents of $PM_{2.5}$ and their characteristic ratios have been studied in detail by categorizing and segregating the dataset on the basis of distinct air-mass back trajectories (AMBTs).

2. Methodology

2.1. Site description and ambient meteorology

$PM_{2.5}$ (particulate matter with aerodynamic diameter $\leq 2.5 \mu m$) sampling was carried out at Kanpur (26.30 °N; 80.14 °E, 142 m above mean sea level), situated in the states of Uttar Pradesh (central part of IGP). Samples have been collected on the roof-top of Centre for Environmental Science and Engineering (CESE) building in the premises of Indian Institute of Technology Kanpur. This region experiences extreme weather conditions with very hot and dry summer (April–May; temperature as high as 48 °C) and cold winters (December–February; temperature < 5 °C). Generally, IGP receives an annual rainfall of 800–1000 mm, of which over 90% of the wet-precipitation occurs during the SW-monsoon (June–September). In 2015, this region received only 375 mm of annual wet precipitation, of which only 45% occurred during SW-monsoon season due to El-Niño and PDO phenomena. Ambient temperature and relative humidity recorded during sampling period exhibited variability from 22.1 to 37.4 °C and 53–97%, respectively. The south-westerly winds (~ 8 m/s) were prevalent during the study period (July–September 2015; SW-monsoon) (Fig. 1).

2.2. Aerosol sampling and chemical analyses

$PM_{2.5}$ samples ($n = 42$) were collected for 8 h (from 08:00 a.m. to 04:00 p.m.) onto pre-combusted quartz fiber filters (Whatman™: 20.3×25.4 sq. cm) by filtering $\sim 480 m^3$ of ambient air using a high volume sampler (calibrated flow-rate: $0.97 m^3/min$) from 15th July, 2015–30th September, 2015 (Kumar and Gupta, 2015). The collected samples were stored in deep freezer at -19 °C until further chemical analysis. Mass concentrations of $PM_{2.5}$ have been measured gravimetrically after equilibrating filters at 25 ± 2 °C temperature and $40 \pm 5\%$ RH for 8–10 h. A portion (1/4th) of each aerosol sample (pre-soaked) was extracted with 60 mL of Milli-Q water (resistivity: $18.2 M\Omega cm$) in pre-cleaned Teflon vials utilizing the sonication technique (Rajeev et al., 2016). Subsequently, each extract was filtered through a $0.22 \mu m$ filter in polypropylene vial. These filtered extracts have been used to measure water-soluble ionic species (WSIS) and water-soluble organic carbon (WSOC). The quantification of WSIS (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-}) has been achieved on a dual channel ion-chromatograph (Metrohm, Swiss) equipped with an anion column (Metrosep: A Supp 5-250/4.0) and a cation column (Metrosep: C 4-250/4.0). The dipicolinic acid (0.7 mM) has been used as an eluent for cation separation whereas a mixture of Na_2CO_3 (3.2 mM) and $NaHCO_3$ (1.0 mM) was used as an eluent for

anion separation. The calibration standards and individual samples were passed through a $100 \mu L$ loop (Rajeev et al., 2016; Rajput et al., 2016b). The measurement of HCO_3^- has been performed independently in all samples by titration with a 5 mM HCl solution using Methyl orange solution (Thomas Baker) as a pH indicator. Quantification of WSOC in aqueous extracts was carried out on a total organic carbon analyzer (TOC Shimadzu) using a non-dispersive infrared detection (NDIR) technique. Linear calibrations for TC and IC were achieved ($R^2 > 0.999$) on a TOC analyzer with standard solutions of potassium hydrogen phthalate (KHP) and sodium carbonate-bicarbonate mixture ($Na_2CO_3 + NaHCO_3$), respectively.

For metal analysis, aerosol samples were treated with high purity HF (0.5 mL), HNO_3 (2 mL) and H_2O_2 (0.5 mL) along with 5 mL Milli-Q water in Teflon vials and digested at 150 °C (Rajput and Gupta, 2016). After ensuring complete digestion, samples were evaporated at 100 °C till near dryness. Subsequently, 1 mL of 8N HNO_3 was added and the final solution was made to 31 mL with Milli-Q water. Using ICP-OES (Inductively Coupled Plasma-Atomic Emission Spectrometry; Thermo Scientific; iCAP 6300), metals (Fe, Al, Ca and Mg) concentrations have been measured (Rajput et al., 2016a). The OC and EC concentrations were determined on a Sunset Lab EC-OC analyzer using thermo-optical transmittance protocol (NIOSH: National Institute for Occupational Safety and Health) (Rajput et al., 2017). Analytical accuracy in the measurement of total carbon ($TC = OC + EC$), was achieved by analyzing known amounts of potassium hydrogen phthalate (KHP). Analytical uncertainty of less than 7% has been estimated through replicate analyses of the samples ($n = 6$) for each measured species. Quality control of the data has been assessed routinely by analyzing signal-to-noise ratio from filter analysis-to-procedural blanks ($S/N > 10$).

3. Results and discussion

3.1. Temporal variability of $PM_{2.5}$ and major constituents

In this study, $PM_{2.5}$ concentration varied from 15.9 to $119.6 (42.2 \pm 22.4) \mu g/m^3$. Due to inefficient wet scavenging of atmospheric particles during SW-monsoon in 2015 (due to El-Niño and positive phase of PDO: Pacific Decadal Oscillation), $PM_{2.5}$ concentration during the study period is quite comparable to that reported in a previous study from this region ($37.6 \mu g/m^3$) during pre-monsoon season (Ghosh et al., 2014). The concentrations (minimum, maximum, average and standard deviation) of measured chemical species during SW-monsoon are provided in supplementary material (Table S1). Overall, $PM_{2.5}$ concentration constitutes of 36.8% mineral dust (MD), 34.7% water soluble inorganic species (WSIS), 21.8% total carbonaceous aerosols (TCA) and 6.7% unidentified matter (UM). This unidentified matter mainly represents the moisture present in ambient aerosols. The OC, EC and WSOC varied from 0.7 to $11.9 (4.7 \pm 2.4) \mu g/m^3$, $0.1\text{--}1.8 (0.7 \pm 0.4) \mu g/m^3$ and $0.4\text{--}5.6 (2.3 \pm 1.1) \mu g/m^3$, respectively. High correlation of OC with EC ($R^2 = 0.9$) in this study plausibly indicates that they are mainly produced from the anthropogenic combustion sources. Besides this, 49% of the total OC is water-soluble (WSOC/OC ratio = 0.49 ± 0.05). The WSIS contribute 35% (WSIS/ $PM_{2.5} = 0.35 \pm 0.12$) in the total $PM_{2.5}$ mass followed by 21.8% contribution of total carbonaceous species (TCA; $TCA = OM + EC$, where $OM = 1.6 \times OC$) (Turpin and Lim, 2001; Rajput and Sarin, 2014).

The temporal variability of $PM_{2.5}$ and its constituent fractions i.e. OC/ $PM_{2.5}$, EC/ $PM_{2.5}$, WSIS/ $PM_{2.5}$ and MD/ $PM_{2.5}$ are shown in Fig. 2. $PM_{2.5}$ concentration showed a decrease on the sampling days having wet precipitation (Fig. 2a). Furthermore, there was an increase in $PM_{2.5}$ loading after mid of August due to less amount of rainfall received at the site. Mineral dust has been estimated using Al as a proxy (Al = 8% of upper continental mineral dust) (McLennan, 2001). The percentage contribution of mineral dust to $PM_{2.5}$ [$\sim 37\%$; MD/ $PM_{2.5} = 0.37 \pm 0.14 (0.16\text{--}0.78)$] was predominant among all species, which can be attributed to relatively high wind speed (~ 8 m/s)

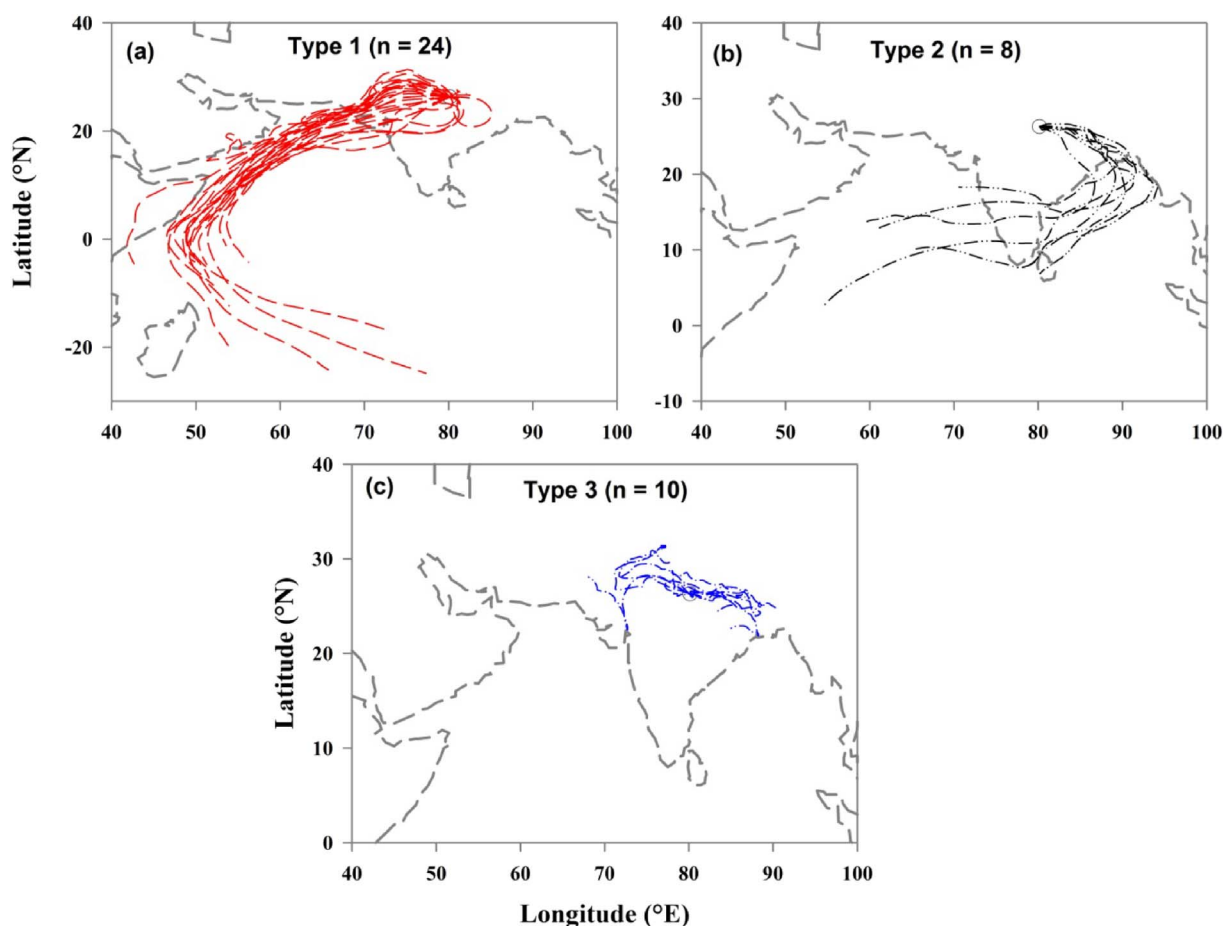


Fig. 1. Air mass back trajectories during study period. Type 1: long-range air mass from Indian Ocean and traversing through Arabian Sea (marine); Type 2: traverses through Bay of Bengal (long-range; marine); Type 3: local air masses (terrestrial).

during the study period. The high wind speed and less rainfall (influence of El-Niño) during the study period have led to the upliftment of mineral dust, as evident from high loading of mineral dust in $PM_{2.5}$. It is important to mention here that mineral dust concentration represented a quite similar temporal variability with that of $PM_{2.5}$ (Fig. 2a and d). This observation is attributable to predominant contribution of mineral aerosols to $PM_{2.5}$ mass during the study period. The mineral dust fraction in different months of July, August and September was 34.1%, 44.7% and 30.9% respectively to total $PM_{2.5}$ mass, while OC fraction was 10.5%, 8.7% and 16.6% respectively. The OC and EC fractions in $PM_{2.5}$ were observed to be increasing during September due to lower fractional contribution of mineral dust in that period.

3.2. $PM_{2.5}$ characteristics for distinct AMBTs

Air mass back trajectory (AMBT) analysis for all sampling days was carried out to understand about the origin of air parcels arriving at the receptor site. AMBTs (7 days) were constructed using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model at 500 m above mean sea level during the SW-monsoon (Stein et al., 2015). The air mass trajectories were categorized into three major types: Type 1: originating over Indian Ocean and traversing through western region; Type 2: originating over Indian Ocean and traversing through Bay of Bengal and eastern region; Type 3: originating over terrestrial region within the Indian subcontinent (Fig. 1).

Based on above classified AMBTs, the $PM_{2.5}$ mass concentration and fractions of OC, EC, $\Sigma WSIS$ and MD in $PM_{2.5}$ have been documented in Table 1. Average mass concentration of $PM_{2.5}$ associated with Type-1 ($PM_{2.5} = 46.1 \mu g/m^3$) air-mass shows no significant difference with

those associated with Type-2 ($PM_{2.5} = 30.3 \mu g/m^3$) and Type-3 ($PM_{2.5} = 42.4 \mu g/m^3$) air-masses ($p > 0.05$ for each case; Table S2). Both OC and EC mass fractions in $PM_{2.5}$ corresponding to Type-1 air-mass are significantly different (OC/ $PM_{2.5}$: $p = 0.04$; EC/ $PM_{2.5}$: $p = 0.02$) as compared to that of Type-2 (Table 1). There is a significant difference in mineral dust fraction of $PM_{2.5}$ in Type-1 and Type-2 ($p = 0.04$) air-masses as well as in their characteristic Fe/Al ratio ($p = 0.003$; Table 1). The significant difference in mineral dust fraction (MD/ $PM_{2.5}$) of Type-1 with respect to that of Type-2 air-mass (Table S1) is attributable to the transport of mineral dust from western region including long-range transport from Thar Desert as observed from the AMBTs (Fig. 1a). Therefore, assessing the air-mass characteristics of Type-1 and Type-2 separately was important during this study. The WSOC/OC ratio in Type-3 air-mass is significantly different as compared to that in Type-2 air-mass. No other significant difference has been observed between the air-masses arriving from different directions (reference made to supplementary file). This observation is in good agreement with a previous study reporting nearly similar ionic composition of aerosol species in air-masses arriving from different directions during the SW-monsoon (Rajeev et al., 2016). In Table 1, several characteristic mass ratios (OC/EC, WSOC/OC, K_{BB}^+/OC , Fe/Al, Ca/Al, Mg/Al) in $PM_{2.5}$ associated with different types of air-masses during the SW-monsoon (this study) have been documented.

3.3. Carbonaceous aerosols composition and characteristics

OC/ $PM_{2.5}$ and EC/ $PM_{2.5}$ ratios in Type-2 air-mass are significantly higher than that in Type-1 air-mass (Table S2). However, the OC/EC ratio in both Type-1 (6.4 ± 1.3) and Type-2 (6.2 ± 1.1) air-masses

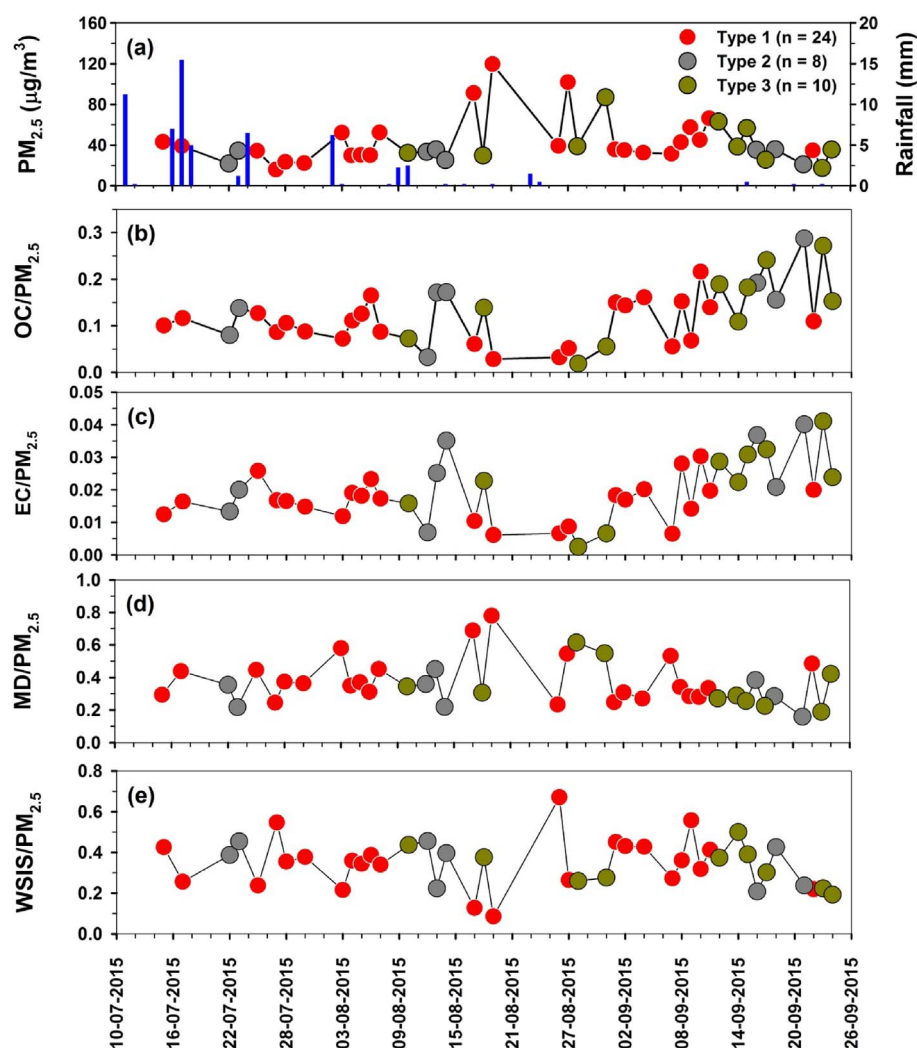


Fig. 2. Temporal variability of $PM_{2.5}$, $OC/PM_{2.5}$, $EC/PM_{2.5}$, $MD/PM_{2.5}$ and $\Sigma WSIS/PM_{2.5}$ for different air-masses at the receptor site (Kanpur; central IGP). In (a) vertical blue bars represent the rainfall events and their amount (in mm).

Table 1

Chemical composition and characteristics of $PM_{2.5}$ associated with different types of air-masses arriving at Kanpur in northern India during the SW-monsoon period (this study).

Parameters	Type-1 (N = 24)	Type-2 (N = 8)	Type-3 (N = 10)
$PM_{2.5}$ ($\mu g/m^3$)	46.1 ± 25.5	30.3 ± 6.5	42.4 ± 20.7
$OC/PM_{2.5}$ (%) ^a	10.7 ± 4.6	15.4 ± 7.6	14.3 ± 8.1
$EC/PM_{2.5}$ (%) ^a	1.7 ± 0.6	2.5 ± 1.2	2.3 ± 1.2
$\Sigma WSIS/PM_{2.5}$ (%)	35.2 ± 13.4	34.9 ± 10.7	33.3 ± 9.8
$MD/PM_{2.5}$ (%) ^a	40.3 ± 14.5	29.1 ± 7.9	34.6 ± 14.0
OC/EC	6.4 ± 1.3	6.2 ± 1.1	6.4 ± 1.2
$WSOC/OC$ ^a	0.49 ± 0.05	0.52 ± 0.05	0.47 ± 0.04
K_{BB}^+/OC	0.048 ± 0.023	0.074 ± 0.067	0.049 ± 0.033
Fe/Al ^a	0.71 ± 0.06	0.82 ± 0.14	0.74 ± 0.03
Ca/Al	1.03 ± 0.07	0.99 ± 0.2	1.05 ± 0.00
Mg/Al	0.53 ± 0.09	0.61 ± 0.19	0.51 ± 0.01

^a Significant differences have been found on the basis of two-tailed *t*-test (For details reference is made to Table S2). Based on two-tailed *t*-test, significant differences have been observed in $WSOC/OC$ ratio (Type-2 and Type-3 air-masses) and Fe/Al ratio (Type-1 and Type-2 air-masses) in $PM_{2.5}$.

looks quite similar. The OC/EC average ratio of 6.4 ± 1.2 in this study is quite similar to that reported in a previous study from the same site during the month of June ($OC/EC = 7.7 \pm 4.1$) (Ram et al., 2010). Earlier studies have reported that aerosols with high contribution from biomass burning emission and secondary organic aerosol (SOA) exhibit

higher OC/EC ratio (> 6) (Maenhaut et al., 1996; Ferek et al., 1998; Saarikoski et al., 2008; Ram et al., 2010; Rajput et al., 2014b). In order to assess overall value of OC/EC , $WSOC/OC$ and K_{BB}^+/OC , these ratios have been constrained through linear regression analysis with total data set. The $WSOC/OC$ ratio averaged at 0.49 ($R = 0.98$) in this study (Fig. 3b). There is a significant difference in $WSOC/OC$ ratio for Type-2 and Type-3 air-masses ($p < 0.05$, Table S2). Relatively high $WSOC/OC$ ratio in Type-2 air mass (traversing through Bay of Bengal and eastern part of India) than in Type-3 air mass (terrestrial origin) is attributable to aged Type-2 air-mass (Fig. 1). This observation of higher $WSOC/OC$ ratio associated with long-range transported air-masses has been previously observed from foothills of NE-Himalaya (Rajput et al., 2013). This indicates that the water-soluble fraction of OC in Type-2 air-mass is significantly different than that in Type-3. However, no significant difference has been observed in OC/EC and K_{BB}^+/OC ratios in different types of air-masses arriving at the receptor site in this study (Table S2).

In this study, a significant fraction ($\sim 26\%$) of the organic carbon is of secondary origin ($SOC/OC = 0.26 \pm 0.14$). Secondary organic carbon (SOC) formation takes place by the oxidation of volatile organic species (VOCs; either anthropogenic or biogenic) in presence of oxidants such as ozone, OH radicals or oxides of nitrogen. SOC fraction has been estimated in this study using the EC tracer method (Castro et al., 1999). The concentration of secondary organic carbon (SOC) has been determined using the minimum OC/EC ratio method (Castro et al., 1999; Rajput et al., 2018).

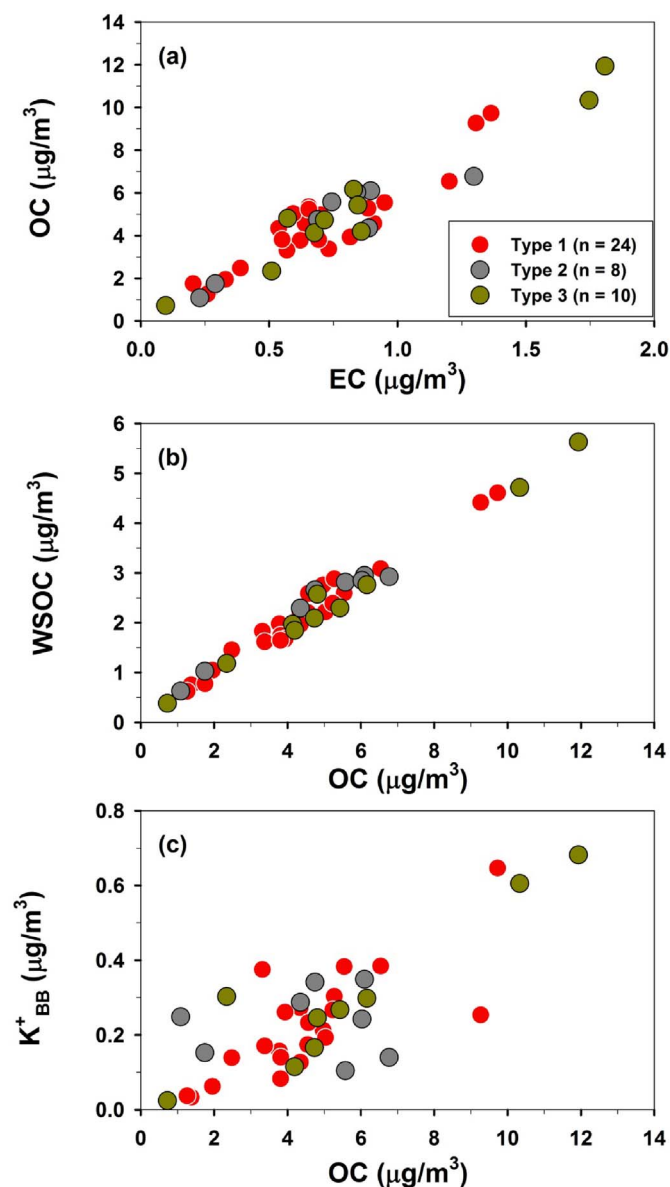


Fig. 3. Scatter plots of: (a) OC and EC, (b) WSOC and OC and (c) K^+ and OC at Kanpur during SW-monsoon period.

$$OC_{total} = OC_{prim} + SOC \quad (1)$$

$$OC_{prim} = EC \cdot (OC/EC)_{min} \quad (2)$$

$$SOC = OC_{total} - OC_{prim} \quad (3)$$

here, OC_{prim} refers to primary organic carbon whereas $(OC/EC)_{min}$ indicates the minimum ratio of OC/EC. A strong correlation between WSOC and SOC ($R = 0.81$; Figure S1) indicates that major fraction of water-soluble component of organic aerosol is of secondary nature. In general, WSOC in fine fraction aerosols over heavily polluted site (high emission from anthropogenic sources) can mainly be the SOC (Weber et al., 2007). High fraction of water-soluble component in total organic carbon ($WSOC/OC \sim 50\%$) could be attributed to predominant contribution from biomass burning emission and/or SOA formation during the study period.

3.4. Inorganic aerosol composition

Water-soluble inorganic species (WSIS) constitutes $\sim 35\%$ ($WSIS/PM_{2.5} = 0.35 \pm 0.12$) to the total $PM_{2.5}$ mass. WSIS concentration

varies from 3.9 to 32.1 (13.7 ± 6.7) $\mu g/m^3$ with major contribution from SO_4^{2-} (34.1%) > NH_4^+ (22.8%) > HCO_3^- (13.4%) > PO_4^{3-} (12.3%) > NO_3^- (8.2%) > Ca^{2+} (3.9%). The other ions K^+ , Na^+ , Mg^{2+} , Cl^- , F^- contributes $\sim 5\%$ to the total WSIS. In a previous study (Rajeev et al., 2016), we have discussed about the chemical characteristics of $PM_{2.5}$ based on WSIS in detail. In that study, no significant difference was observed in the characteristics ratios among ionic species in $PM_{2.5}$ for different air-masses (Type-1, Type-2 and Type-3 air-mass).

The potassium ion (K^+) after correction for mineral dust and sea-salt contributions could serve as a biomass burning tracer. The K_{BB}^+ is calculated from total K^+ using the following formula (Rajput et al., 2014b):

$$K_{BB}^+ = K_{aerosol}^+ - 0.037 \times Na_{aerosol}^+ - 0.01 \times [nss - Ca^{2+} - Ca_{BB}^{2+}] \quad (4)$$

$$Ca_{BB}^{2+} = \frac{nss - K^+}{2.43} \quad (5)$$

$$nss - Ca^{2+} = (Ca^{2+})_{aerosol} - (Na^+)_{aerosol} \times \left(\frac{Ca^{2+}}{Na^+} \right)_{sea-water} \quad (6)$$

$$nss - K^+ = (K^+)_{aerosol} - (Na^+)_{aerosol} \times \left(\frac{K^+}{Na^+} \right)_{sea-water} \quad (7)$$

The estimated K_{BB}^+ constitutes 93% of total K^+ (as $K_{BB}^+/K^+ = 0.93 \pm 0.09$) which suggests that K^+ in $PM_{2.5}$ has predominant contribution from biomass burning emission in this study. The K_{BB}^+/OC ratio of 0.054 ± 0.037 (Fig. 3c) is nearly comparable with the ratios reported from biomass burning emissions from source region of agricultural waste burning in upwind IGP (0.06 ± 0.01) and Amazonian forest fires ($K^+/OC = 0.04-0.09$) (Ferek et al., 1998; Rajput et al., 2014b).

3.5. Mineral dust characteristics over IGP during SW-monsoon: abundance of major elements

During the study period, mineral dust contributes a major fraction to $PM_{2.5}$ mass, thus assessing the elemental ratios of mineral dust is quite important. In this study, Fe/Al, Ca/Al and Mg/Al ratios varied from 0.47 to 1.08 (0.73 ± 0.08), $0.72-1.06$ (1.02 ± 0.08) and $0.40-1.02$ (0.54 ± 0.10), respectively. For upper continental crust, the average Fe/Al, Ca/Al and Mg/Al ratios have been reported in a literature as 0.44, 0.37 and 0.17, respectively (McLennan, 2001). The Fe/Al average ratio of 0.73 (this study) is close to that reported in a previous study assessing soil re-suspension (~ 0.9) (Engelbrecht et al., 2016). To study the anthropogenic contribution of Fe, Ca and Mg in $PM_{2.5}$, enrichment factor (EF) for these elements has been estimated. EF provides information about excess amount of a metal present in particulate matter with respect to the upper continental crust (UCC) composition; herein Al has been used as a proxy of mineral dust. The mathematical expression for the enrichment factor of a particular element(x) is given below:

$$EF_x = \frac{x_{aerosol}/Al_{aerosol}}{x_{UCC}/Al_{UCC}} \quad (8)$$

The enrichment factors of Fe, Ca, Mg are 1.7, 2.7 and 3.2, respectively in this study. This indicates that these metals are basically of crustal origin (Chakraborty and Gupta, 2010; Gupta and Mandaria, 2013). These ratios (Fe/Al, Ca/Al and Mg/Al) can be utilized for representing mineral dust characteristic features (provided EF is quite low; < 10) even for the case of long-range transported aerosols.

Fe/Al, Ca/Al and Mg/Al ratios for different types of air-masses have been documented in Table 1. The significant difference in Fe/Al ratio of Type-1 and Type-2 air-masses suggests that elemental composition of the particulate matter in the air-masses arriving at the site from western direction and that from eastern direction is quite different. From

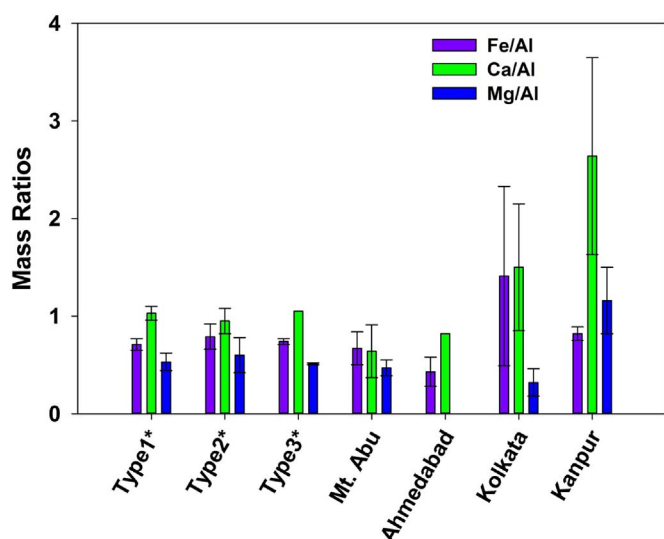


Fig. 4. Elemental ratios of atmospheric mineral dust in $PM_{2.5}$ from different sites in India. *This study; Mt. Abu (Kumar and Sarin, 2009); Ahmedabad (Sudheer and Rengarajan, 2012); Kolkata (Das et al., 2015); Kanpur (Rajput and Gupta, 2016).

AMBTs, it was noticed that the majority of air-masses during the study period are arriving from western direction. Therefore, data from a high altitude site in western Indian region (Mt. Abu; 24.6°N, 72.7°E, 1.7 km above msl) during monsoon period has been taken for comparison, which reports Fe/Al, Ca/Al and Mg/Al average ratios as 0.67 ± 0.17 , 0.64 ± 0.27 and 0.47 ± 0.08 , respectively (Kumar and Sarin, 2009). Fe/Al and Mg/Al ratios at Mt. Abu and in our study are quite similar while Ca/Al ratio at Kanpur (Central IGP; this study) is relatively high than that reported from Mt. Abu (a high-altitude site) (Fig. 4). The elemental data from Ahmedabad (semi-arid region; 23°N, 72.5°E) reports Fe/Al and Ca/Al average ratios of 0.43 and 0.82 which are significantly lower as compared to those in Type-1 air-mass (Fe/Al = 0.71 and Ca/Al = 1.03) (Sudheer and Rengarajan, 2012). While, Fe/Al ratio (1.4 ± 0.9) and Ca/Al ratio (1.5 ± 0.6) from the Kolkata site (downwind IGP; 22.5°N, 88.4°E) are higher as compared to those in Type-2 air-mass (Fe/Al = 0.82 ± 0.14 ; Ca/Al = 0.99 ± 0.2) (Das et al., 2015). This observation clearly indicates that there occurs enrichment of these metals in atmospheric aerosols from anthropogenic sources at downwind sites of the IGP.

3.6. Implications to interactions of organic species with mineral dust

Several previous studies have suggested that mineral dust surface provides highly reactive sites for various chemical transformation processes occurring in the troposphere (Usher et al., 2003; Nie et al., 2014; Laskin et al., 2016). Furthermore, it has been reported that high loading of mineral dust enhances the heterogeneous phase reactivity as well as particle formation and growth (Usher et al., 2003; Nie et al., 2014; Laskin et al., 2016). During the study period, due to the less precipitation events there was higher upliftment of mineral dust. High abundance of mineral dust has been observed in our study especially in the long range air-masses from western region including transport from Thar Desert (Type-1; MD = 40%). In Fig. 5, temporal variability of OC with Al (8% of UCC) and Fe (3.5% of UCC; major components of mineral dust) for Type-1 air-mass (McLennan, 2001) have been shown. A significant covariance is observed between OC, Al and Fe exception being on three events (17th, 19th and 27th August, 2015), on which there is very high abundance of mineral aerosols (as well as $PM_{2.5}$ concentration, Fig. 2). This can be attributed to the high wind speed and drier period during these three days, thus resulting in higher loading of mineral dust. There are emerging evidences that suggest iron (Fe) to act as a catalyst in the transformation reactions as reported in

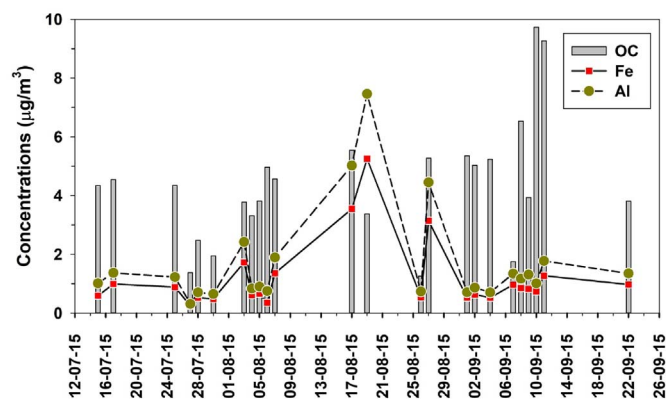


Fig. 5. Temporal variability of OC with Al and Fe in aerosols associated with Type-1 air-mass ($n = 24$).

the literature (Seinfeld and Pandis, 1999; Rajput et al., 2016a). Towards this, we have assessed the correlation of OC with Al ($R = 0.67$) and Fe ($R = 0.64$; $n = 17$) after excluding some outliers from the Type-1 air-mass cluster (Figure S3). The co-variability of OC with Al and Fe plausibly shows that high abundance of fine fraction mineral dust acts as a substrate onto which organic species formation reactions take place. Also, enhanced residence time of fine particles into the atmosphere due to less wet precipitation during the study period will augment the atmospheric chemical transformations, and thus, overall oxidation (and O/C ratio) of organic compounds. Thus, our study highlights the implications of interaction of organic compounds on the surface of mineral dust in long-range transported aerosols.

Apart from this, high RH conditions during the monsoon season would also enhance the reactivity of aerosols. There could be significant increase in the uptake of moisture due to the presence of inorganic salts and organic aerosol species in aerosols under high RH conditions, thus increasing the liquid water content of aerosols (Pilinis et al., 1989). The water uptake capacity has significance to alter the size and optical properties of aerosols during the SW-monsoon. Figure S2 shows the temporal variability of temperature and relative humidity along with the concentrations of WSOC. We urge future studies could focus on assessing influence of interactions of organic aerosol species with mineral dust under varying meteorological conditions over the IGP.

4. Conclusion

In this study, temporal variability of major chemical constituents of fine fraction aerosols and their mass closure during SW-monsoon has been reported from Kanpur location in central IGP. Carbonaceous species, mineral dust, water-soluble inorganic species constituted 22%, 37% and 35%, respectively of the $PM_{2.5}$. Characteristic ratios of OC/EC, WSOC/OC, K_{BB}^+/OC in $PM_{2.5}$ over the central IGP varied from 4.6 to 8.6 (6.4 ± 1.2), 0.42–0.59 (0.49 ± 0.05), 0.005–0.23 (0.054 ± 0.037), respectively during the entire study period. Large fraction of mineral dust in atmospheric aerosols was attributable to the El-Niño and positive phase of PDO. Elemental ratios of Fe/Al, Ca/Al and Mg/Al varied from 0.47 to 1.09 (0.73 ± 0.08), 0.72–1.06 (1.02 ± 0.08), 0.41–1.02 (0.54 ± 0.10), respectively. It has been observed that long-range transport of air-masses from western region including transport from Thar desert (Type-1) was associated with high abundance of mineral dust over the IGP. Significant differences in mineral dust composition between Type-1 and Type-2 air-masses have been inferred based on mineral dust percentage fraction and characteristic ratios of Fe/Al. However, average mass ratios of OC/EC, WSOC/OC (exception being difference in Type-2 versus Type-3 air-mass) and K_{BB}^+/OC also look near similar in all the three types of air-masses discussed herein. One of the key features of our study relates to interaction and transformation of organic aerosol species onto the surface of fine mineral dust.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apr.2018.02.008>.

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