Chemical Characterization of Summertime Dust Events at Kanpur: Insight into the Sources and Level of Mixing with Anthropogenic Emissions

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ABSTRACT

The aim of this study conducted at Kanpur (26.51°N, 80.23°E), India, was to quantify chemical properties of dust and the intensity of mixing, due to its interaction with various emissions from anthropogenic activities, during its long range transport. Aerosol mass was collected at Indian Institute of Technology, Kanpur (IIT-K) located in the Indo-Gangetic Plain from April–July 2011, a period marked by intense dust storms and onset of monsoon. The sampling days were classified as Dust, Polluted Dust$_1$ (PD$_1$), Polluted Dust$_2$ (PD$_2$) and Continental days. PM$_{10}$ (coarse mode) and PM$_{2.5}$ (fine mode) collected on filter substrates were analysed for chemical composition. Elemental concentrations were measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The results show that crustal elements like Ca, Fe, K, Na and Mg were dominant in coarse mode during dusty days, whereas, elements of anthropogenic origin like Cu, Ni, Se and V were mostly concentrated in fine mode during PD$_1$ as well as PD$_2$. Very low elemental concentrations were found during continental days. SO$_4^{2-}$, Cl$^-$ and NO$_3^-$ were found to be high during PD$_1$ and PD$_2$ days. Very good correlations of NH$_4^+$ with Cl$^-$ and SO$_4^{2-}$ ions in PD$_1$ days indicate their common sources of origin and formation of ammonium chloride and ammonium sulphate. Water Soluble Inorganic Carbon (WSIC) was found during all dust days, Water Soluble Organic Carbon (WSOC) was found to be highest during PD$_1$ and PD$_2$ days.

Keywords: Mixing; Enrichment factor; WSOC; WSIC; PM$_{2.5}$.

INTRODUCTION

The atmospheric aerosols, also known as particulate matter (PM), comprises of both solids and liquids internally mixed at various levels and suspended in air. Out of the atmospheric aerosol types (like sea salt, trace metals, carbonaceous material, secondary particles), mineral dust is a key constituent of total aerosol concentration, especially during the pre-monsoon period (April–May). Chemical composition of mineral dust is similar to the Earth's crust, as they originate due to weathering and erosion of the upper crust leading to formation of soil. Hence, chemistry of mineral dust is largely controlled by soil types that vary from place to place. Generally, coarser particles are comprised of quartz, feldspar, and carbonates whereas mica and clay minerals are dominant in finer particles. As it moves away from the source of origin, the mineral dust becomes enriched in clay and mica whereas coarser particles

get removed due to gravitational settling (Usher *et al.*, 2003).

On a local scale, especially in a polluted environment like Kanpur, dust originating from roads, and industrial and agricultural activities plays an important role in influencing the atmospheric chemistry (Usher *et al.*, 2003). Mineral dust reduces atmospheric visibility (Kim *et al.*, 2001) and disperse harmful micro-organisms that cause various pulmonary diseases and allergies (Griffin and Kellogg, 2004). Dust also affects the climate directly by influencing radiative budget (scattering and absorption of radiation) and indirectly by acting as Cloud Condensation Nuclei (CCN) (Zhang *et al.*, 2007).

Dust storms in which sand or mineral dust are carried away or entrained into the atmosphere by strong-blowing winds, occur predominantly in arid and semiarid regions e.g., Thar Desert in India (Dey *et al.*, 2004). A large number of studies on mineral dust and dust storms have been carried out in different parts of India (Kumar and Sarin, 2009; Rastogi and Sarin, 2009) but most of these studies (Dey *et al.*, 2004; Mishra *et al.*, 2012) have only discussed the optical properties of mineral dust in the Indo-Gangetic Plain. Very little investigation has been carried out on the chemical properties of crustal/mineral dust in Kanpur region

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(Chinnam *et al.*, 2006; Chakraborty and Gupta, 2010). Kanpur city, one of the most polluted cities in the World, has a variety of industries like cotton, wool, jute and tanneries. The sources of air pollution are mainly categorized into industrial, commercial, transport, domestic, institutional and fugitive (Behera and Sharma, 2010; Gupta and Mandariya, 2013).

This study mainly focuses on the chemical characterization of crustal dust, which is subsequently used to analyze intensity of mixing with anthropogenic-origin aerosols and dominant sources affecting this region. The sampling days were classified into Dust, Polluted Dust$_1$ (PD$_1$), Polluted Dust$_2$ (PD$_2$) and Continental Days. Days affected by severe dust storms were classified as dusty days. Those days where mineral dust was mixed with anthropogenic pollutants were grouped as PD$_1$ days while those dominated by Biomass burning events were PD$_2$ days. Cleaner days were called continental days composed of background concentration only. Details about classification with appropriate justification is provided in our companion paper, (Misra *et al.* (manuscript under preparation)). To get an in-depth knowledge of the dominant sources and mixing of anthropogenic pollutants with mineral dust, various methods like enrichment factor, elemental and ions signatures, NOAA back trajectory analysis etc. were used.

SAMPLING PROCEDURE

Description of Sampling Site

Sampling was carried out at 30 m above ground level, on the roof of the atmospheric monitoring tower inside the campus of Indian Institute of Technology, Kanpur (IIT-K, 26.51°N, 80.23°E) located about 15 km N-W of the central part of Kanpur city. The local climate is mainly humid subtropical, characterized by extremely hot summer and cold winters. The pre-monsoon period is very hot and dry in which temperature reaches up to a monthly mean maximum of 41.3°C and monthly mean minimum of 26.4°C (Indian Meteorological Dept., Govt. of India). Dust storms during this period bring copious amount of mineral dust from various arid regions of Western India. Wind was blowing from South–West towards North–East for most part of the sampling periods; April–May were hot and dry while June–July were relatively cooler but more humid due to onset of monsoon (Misra *et al.* (manuscript under preparation)).

Sampling Schedule

Sampling of coarse (PM$_{10}$) and fine (PM$_{2.5}$) aerosols were carried out for 8 h daily (0900 h to 1700h), every 3rd day starting from 1st April to 15th July 2011 using PM$_{10}$ (APM 541, Envirotech) and PM$_{2.5}$ (APM550, Envirotech) samplers. Flow rate of 16.7 LPM for both the samplers was controlled via a critical orifice. Additionally, eight field blanks were also collected. The sampling period covers the pre-monsoon and a part of monsoon seasons. To minimize PM mass loss, precautionary steps were taken in the preparation of filter paper, sample collection and weighing as reported earlier (Chakraborty and Gupta, 2010).

ANALYTICAL METHODS

Collection, Gravimetric and Chemical Analysis of Aerosols

PM were collected using 47 mm quartz fiber filters (Whatman QM-A) preconditioned and post conditioned to equilibrate for 24 h at 21 ± 2°C (room temperature) and (35 ± 5%) humidity. The filters were weighed gravimetrically thrice before and after sampling using a 1 µg least count micro balance (Metler 440). The mass of the sampled aerosols divided by the volume of the sampled air gives the PM mass concentration (µg/m^3).

For elemental analyses, a punch of 16.5 mm diameter from the sampled quartz filter was taken and then shredded into smaller pieces which were then mixed with 20 mL of HNO$_3$ acid (65%, GR Merck Suprapure) in a 100 mL round bottom digestion flask. It was digested over a hot plate for 2 h at 180°C, till only a small amount of nitric acid was left. The digestion flask was cooled to room temperature and the wall of the flask was rinsed with Milli-Q water (resistivity of 18 MΩcm at 25°C). The residue was then filtered through a 0.22 µm pore size filter paper (Millipore), diluted to 100 mL with Milli-Q water and stored in 100 mL reagent bottles. The samples were subsequently analyzed for 14 elements, namely Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se, V and Zn, using ICP-OES (ICAP 6300 Thermo Inc.), following detailed procedure described by Chakraborty and Gupta, (2010). The method detection limit (MDL in ng/m^3) values for various elements analyzed are reproduced here: As = 2.12, Ca = 0.11, Cd = 1.33, Cr = 4.13, Cu = 10.42, Fe = 6.25, K = 0.11, Mg = 0.1, Mn = 2.08, Na = 0.11, Ni = 2.08, Pb = 22.93, Se = 2.08, Ti = 2.08, V = 2.08, Zn = 2.08, respectively (Chakraborty and Gupta 2010; Gupta and Mandariya, 2013).

For ionic measurements, another punch of 16.5 mm diameter was also shredded into small fragments and mixed with 20 mL of Milli Q water in a 50 mL test tube and ultrasonicated (Fast Clean Ultrasonic cleaner, 2k909008). The aliquots were then filtered using a 0.22 µm pore filter paper and analyzed for three anions (Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) and one cation (NH$_4^+$) using an Ion Chromatograph (882 Compact IC plus, Metrohm). MDL (in ng/m^3) values for various ions analyzed are reproduced here: F$^-$ = 3.0, Cl$^-$ = 3.0, NO$_3^-$ = 8.7, SO$_4^{2-}$ = 12.0, NH$_4^+$ = 17.0, respectively (Chakraborty and Gupta 2010; Gupta and Mandariya, 2013).

Total Organic Carbon TOC analysis in all filter samples was carried out by a (TOC) analyser (Model No: TOC-V CPN, Shimadzu Corporation) (Kaul *et al.*, 2012). The water soluble organic carbon (WSOC) was analysed with a TOC equipped with a highly sensitive catalyst. The non-purgeable organic carbon method (NPOC) used in the TOC analyser has been described in detail by Timonen *et al.* (2008). Briefly, the sample is extracted with deionised water, acidified and injected into an oven. In the oven, the carbon is catalytically oxidized to CO$_2$ at 680°C which is subsequently detected by a sensitive Non-Dispersive Infra-Red (NDIR) detector.

Quality Control and Quality Assurance

All the glassware used for the ionic and elemental analysis were washed with acids (chromic acid for ions and 5% nitric acid for elemental analysis) and dried in oven at

180°C. Calibrations of the instruments were carried out with the standards of known concentrations. Two commercially available standards (Multielement Standard Solution 4 and 5, Sigma Aldrich) were used for the calibration of the instrument and generation of standard calibration curves. Replicate analyses of selected samples and standards suggest reproducibility within 5%. In both the instruments, standards of known concentrations were spiked after the analysis of every 10 samples and if the elements/ions concentrations were not found within ± 5% of known concentration, the instruments were recalibrated. Blanks were also subjected to the same procedure (Chakraborty and Gupta, 2010). All the measured values reported in the manuscript were blank corrected.

RESULTS AND DISCUSSION

Temporal Variability of PM Mass Concentrations

The temporal variations in mass concentration of PM_{10} and $PM_{2.5}$ aerosols are shown in Fig. 1(a). Each data point shows the aerosol mass on a particular sampling day. PM_{10} average mass concentration for the entire sampling duration was found to be 101.91 μg/m³ which varied from 25.64 to 254.19 μg/m³. $PM_{2.5}$ mass concentration varied from 11.41 to 66.28 μg/m³ with an average value of 37.61 μg/m³. PM coarse fraction presented as the abundance of coarse mode (PM_{10}–$PM_{2.5}$) with respect to PM_{10}, is plotted in Fig. 1(b). The highest concentrations were observed on 13 May and 10 April for PM_{10} and $PM_{2.5}$, respectively. The highest PM

mass observed during the period (April–May) was due to the strong winds and presence of dry atmospheric condition which re-suspended the road dust and soil. The concentration decreased during June and July because dust particles settled down due to wet removal by rain and due to the presence of high relative humidity.

The temporal variations of PM coarse fraction shows that the highest PM coarse fraction was observed on 13 May, 10 May, 1 May and 25 April (Fig. 1) during which the coarse particles were abundant in PM_{10}. These days were classified either as Dust or Polluted Dust. The details for CO and BC measurements and complete analysis are provided in our companion paper (Misra *et al.* (manuscript under preparation)). The values for BC for two different periods were measured as: April–May (avg. = 1.249 μg/m³, std = 0.715 μg/m³), June–July (avg = 0.789 μg/m³, std = 0.2430 μg/m³). Whereas, CO ranged between 360–953 ppb for the complete sampling duration with highest values reported for PD_2 days (avg. = 789 ppb, std = 214 ppb).

Chemical Composition of Aerosols

The air masses may mix with different aerosols of natural and anthropogenic origin during their transportation. Along the air mass trajectory, contribution from different sources can vary depending on factors such as meteorological condition, chemical processes, and type of sources.

The chemical composition of aerosols in PM_{10} and $PM_{2.5}$ are summarised in Table 1. Statistically significant linear correlation coefficients ($R^2 > 0.6$) between two elements
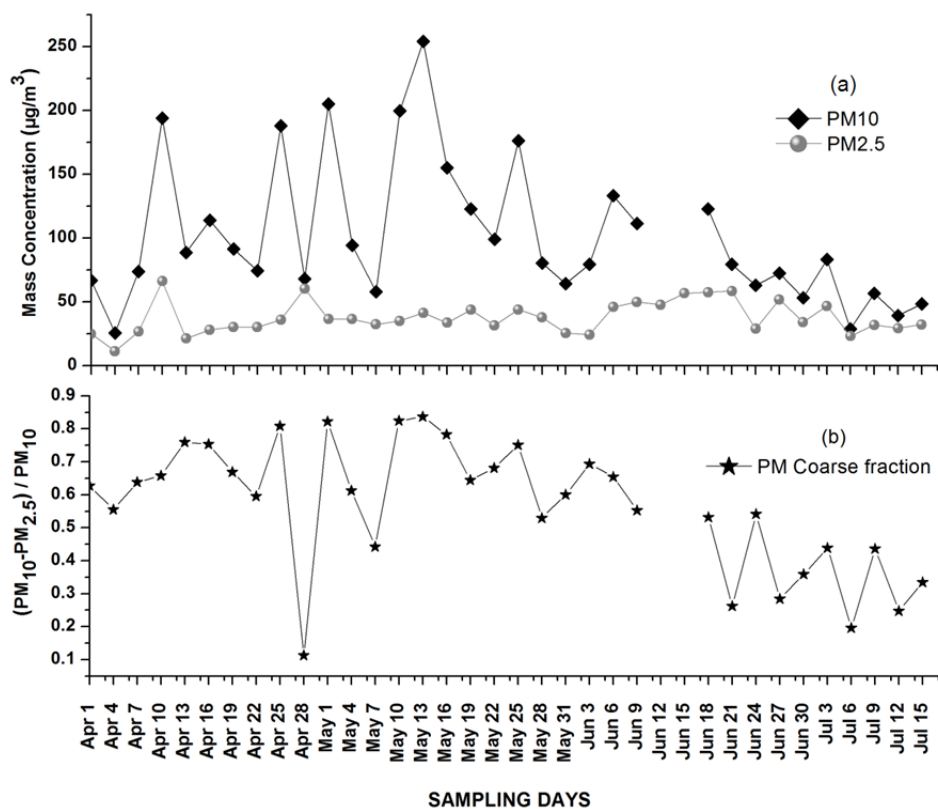
Fig. 1. Temporal variations of (a) Mass Concentration of PM_{10} and $PM_{2.5}$ and (b) PM Factor or PM Coarse Fraction ((PM_{10} – $PM_{2.5}$)/PM_{10}). The missing two data points in PM_{10} are due to the rain, when sampling had to be stopped.

Table 1. Chemical composition of aerosols in PM_{10} and $PM_{2.5}$ for n no. of samples.

Element	PM_{10} ($\mu g/m^3$)		$PM_{2.5}$ ($\mu g/m^3$)	
	Mean (n = 36)	SD (1 σ)	Mean (n = 36)	SD (1 σ)
Ca	3.70	4.23	1.14	1.25
Cd	0.05	0.08	0.03	0.03
Cr	0.71	0.50	0.33	0.30
Cu	0.35	0.31	0.23	0.23
Fe	3.38	2.66	1.31	1.07
K	1.63	1.36	1.20	1.08
Mg	2.48	2.15	0.55	0.56
Mn	0.39	0.62	0.18	0.46
Na	2.19	2.38	0.9	1.18
Ni	0.39	0.30	0.25	0.24
Pb	0.49	0.34	0.32	0.26
Se	0.32	0.37	0.26	0.36
V	0.40	0.26	0.30	0.21
Zn	1.39	1.46	0.58	0.65

indicate that they may have been emitted from similar sources. Good correlations were found among the crustal elements in PM_{10}: Fe and Ca ($R^2 = 0.79$), Mg and Ca ($R^2 = 0.77$), and Na and Ca ($R^2 = 0.80$). Similarly, in $PM_{2.5}$, statistically significant relationships between anthropogenic elements like Ni and Cu ($R^2 = 0.85$), Cr and Cu ($R^2 = 0.71$), Ni and Cr ($R^2 = 0.63$), and Zn and Pb ($R^2 = 0.61$) were obtained. Even though Mn is usually emitted from mineral dust it shows good correlation with Zn ($R^2 = 0.66$) in $PM_{2.5}$, suggesting substantial contributions from anthropogenic sources like mining/metallurgy and vehicular exhaust (Rastogi and Sarin, 2009; Gangwar *et al.*, 2012).

Table 2 presents statistical summary of the ionic concentrations measured in PM_{10} and $PM_{2.5}$, clearly showing highest average concentration of SO_4^{2-} followed by NO_3^-. The concentration of NH_4^+ varied between 0.90 $\mu g/m^3$ to 19.33 $\mu g/m^3$ and 0.49 $\mu g/m^3$ to 9.56 $\mu g/m^3$ in PM_{10} and $PM_{2.5}$, respectively.

Enrichment Factor analysis was carried out to differentiate anthropogenic sources from natural ones. It shows degree of enrichment of a particular element compared to the relative abundance of that element in Earth's crust (Behera and Sharma, 2010; Chakraborty and Gupta, 2010). Here, Ca has been used as a reference element assuming that Ca is of crustal origin only. Enrichment factor (EF) is defined as follows:

$$EF_x = \frac{C_{x_s} / C_{Ca_s}}{C_{x_c} / C_{Ca_c}} \qquad (1)$$

where C_{x_s} and C_{ca_s} are concentrations of the element x and Ca in samples, C_{x_s} and C_{ca_s} are average concentration in the Earth's upper crust (Taylor *et al.*, 1981; Rudnick and Gao, 2003). By convention (Zhang *et al.*, 2010), if EF ≤ 10 it is considered that element in aerosols has a significant crustal contribution, and hence termed as the non-enriched element. Whereas, EF > 10 indicates that element has an important proportion derived from non-crustal sources and hence termed as an enriched element.

Elemental concentration (Fig. 2) and EF's (Fig. 3) on dusty days as well as on days just before and after dusty days were calculated and compared to see how dust storms affected aerosol composition. The variations in the elemental concentrations for different sampling days of this study have been depicted by the error bars. It can be seen that major crustal elements like Ca, Na, Mg, K and Fe were about twice the concentration on dusty days when compared to non-dusty days. Their crustal nature was well explained by their EF's close to 1 on all days. In contrast, anthropogenic elements showed only a little increase in concentration and their EF's were lower on dusty days when compared to normal days implying that most of them were re-suspended in air due to erosion of native soil caused by heavy winds. Since crustal elements are coarser particles, they settled out quickly and their concentration decreased immediately after the dust event, while anthropogenic elements, which are majorly finer particles and have longer residence times, continued to stay in the atmosphere for longer durations even after the storm subsided.

The data (Tables 3 and 4) suggests that Ca and Mg originated from crustal sources during all the days as their EF values are close to unity in both PM_{10} and $PM_{2.5}$. However, elements like Cr, Cu, Cd, Pb, Se, and Zn have very high EF values in both PM_{10} and $PM_{2.5}$, suggesting contribution from various anthropogenic sources like fossil fuel combustion and industrial emissions etc. (Kang *et al.*, 2011; Gangwar *et al.*, 2012). Highest EF values of Cu, Ni, and Pb during PD_1 days indicate their contributions from emissions of non-crustal origin. The highest EF values for Cd, Cr, Se, V and Zn in Continental days suggest that their sources were mostly localized which formed background aerosol. Se had the highest EF among all the elements, which may have originated from sources like thermal power plant situated near sampling site (Chakraborty and Gupta, 2010; Kang *et al.*, 2011). Similar results were reported in a study conducted in Xiamen, China (Zhao *et al.*, 2011).

Table 2. Summary table depicting ionic concentration in PM_{10} and $PM_{2.5}$ for n no. of samples.

Ions	PM_{10} ($\mu g/m^3$)		$PM_{2.5}$ ($\mu g/m^3$)	
	Mean (n = 36)	SD (1 σ)	Mean (n = 36)	SD (1 σ)
NH_4^+	4.11	3.76	2.54	1.87
Cl^-	2.68	2.86	2.06	1.82
NO_3^-	4.97	3.86	3.10	2.83
SO_4^{2-}	6.54	3.61	5.38	2.51
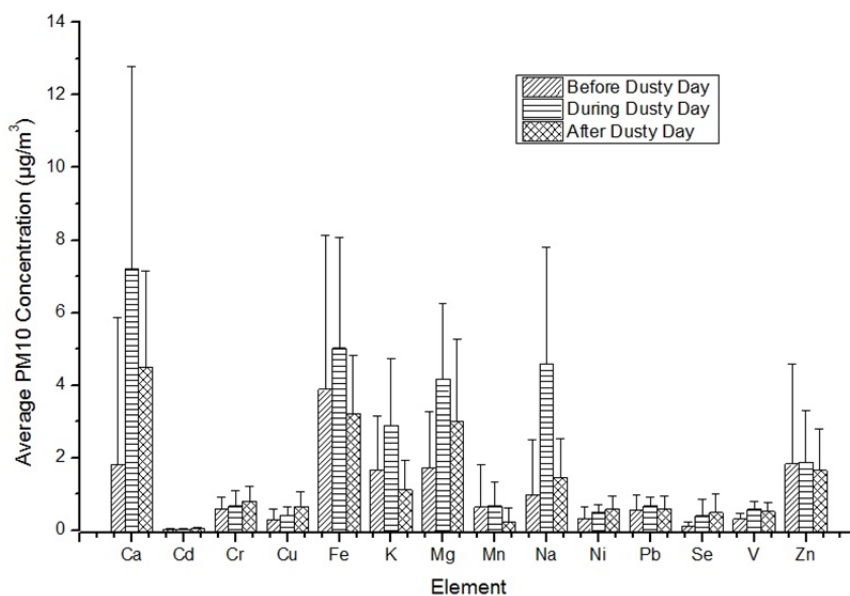
Fig. 2. Elemental concentration comparison between dusty and non dusty days in PM_{10}. Error bars shown represent one standard deviation.
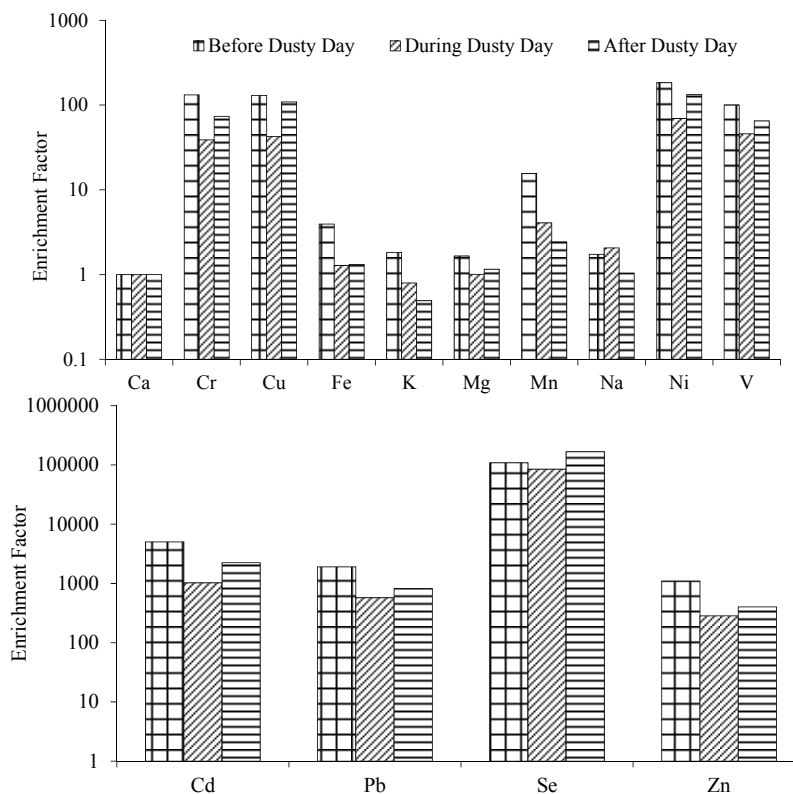
Fig. 3. Enrichment Factor comparison between dusty and non-dusty days in PM_{10}.

Table 3. Average Enrichment Factor in crust ($EF_{Crust} \pm 1\ \sigma$) of each category for PM_{10}.

Element	Dust	PD_1	PD_2	Continental
Ca	1 ± 0	1 ± 0	1 ± 0	1 ± 0
Cd	540.04 ± 837.7	3778.14 ± 3389.57	5876.36 ± 6179.06	93582.72 ± 225451.51
Cr	27.78 ± 11.62	93.65 ± 112.04	39.46 ± 43.81	1083.2 ± 2388.32
Cu	18.28 ± 14.62	139.75 ± 192.81	66.18 ± 5.19	2445.01 ± 7302.88
Fe	0.52 ± 0.24	0.58 ± 0.42	2.06 ± 2.05	10.95 ± 29.76
K	0.5 ± 0.26	0.8 ± 0.76	9.34 ± 11.51	12.09 ± 31.83
Mg	0.76 ± 0.14	1.03 ± 0.74	4.88 ± 5.65	18.11 ± 51.05
Mn	5.14 ± 4.9	4.07 ± 5.75	17.66 ± 23.54	40.6 ± 123.19
Na	1.07 ± 0.34	0.92 ± 0.67	2.6 ± 3.1	14.91 ± 35.6
Ni	16.97 ± 12.32	97.36 ± 117.68	43.57 ± 34.98	2073.95 ± 6112.3
Pb	206.19 ± 53.83	496.69 ± 475.55	640.38 ± 557.24	7740.11 ± 22450.01
Se	4174.47 ± 5181.2	122183.17 ± 99101.62	58763.55 ± 61790.65	931125.3 ± 1937198.91
V	13.29 ± 5.17	38.13 ± 33.71	134.42 ± 165.43	349.33 ± 652.45
Zn	121.43 ± 155.7	192.47 ± 112.07	797.45 ± 748.11	1049.73 ± 2223.91

Table 4. Average Enrichment Factor in crust ($EF_{Crust} \pm 1\ \sigma$) of each category for $PM_{2.5}$.

Element	Dust	PD_1	PD_2	Continental
Ca	1 ± 0	1 ± 0	0 ± 0	1 ± 0
Cd	1101.89 ± 2203.77	7381.13 ± 7259.83	0 ± 0	26663.13 ± 26332.61
Cr	16.44 ± 12.83	185.02 ± 238.53	0 ± 0	315.61 ± 349.41
Cu	37.21 ± 31.5	295.22 ± 400.5	0 ± 0	219.65 ± 217.78
Fe	0.86 ± 0.56	0.79 ± 0.66	0 ± 0	1.68 ± 1.84
K	1.26 ± 0.54	1.7 ± 1.72	0 ± 0	5.65 ± 7.92
Mg	0.66 ± 0.13	0.84 ± 1.31	0 ± 0	2.51 ± 5.32
Mn	8.36 ± 6.9	4.74 ± 9.61	0 ± 0	2.49 ± 4.31
Na	1.63 ± 1.06	1.8 ± 1.73	0 ± 0	2.1 ± 4.31
Ni	15.4 ± 27.08	228.6 ± 290.73	0 ± 0	186.01 ± 235.14
Pb	412.26 ± 164.2	1035.71 ± 786.68	0 ± 0	942.92 ± 1126.05
Se	9537.84 ± 14328.72	465699.62 ± 738998.45	0 ± 0	708399.02 ± 1725662.88
V	35.4 ± 25.21	103.69 ± 137.79	0 ± 0	614.72 ± 1860.96
Zn	72.89 ± 84.71	318.13 ± 272.65	0 ± 0	377.74 ± 525.5

* No Calcium was detected in $PM_{2.5}$ samples from PD_2.

*Elemental and Ionic Mass Concentration on Different Days*
Dust Events

During Dust events, the average concentration of Ca was 11.50 ± 3.22 μg/m³ (3.70 ± 4.23 μg/m³ on other days) in PM_{10} and 2.27 ± 1.73 μg/m³ (1.14 ± 1.25 μg/m³ on other days) in $PM_{2.5}$. Ca, Mg, and Fe are indicators of crustal weathering and mineral dust (Cheng *et al.*, 2005) and therefore high concentration of these elements should be observed for dusty events, which is also reflected in our data (Fig. 4). Trace amounts of Zn, Mn and Cr were also found in both PM_{10} and $PM_{2.5}$. The source of Zn could be tire wear (Councell *et al.*, 2004) or the lubricant (Gulyaeva *et al.*, 1972) and fuel additives which get suspended in the air due to vehicular activity (Lowenthal *et al.*, 1988). Cr can originate from brake dust (Kulshrestha *et al.*, 2009; Gangwar *et al.*, 2012), apart from other anthropogenic sources and also from local Cr-contaminated soil as the sampling site was near tanneries, chemical and electroplating industries which contaminate the soil with Cr (Sanghi and Sasi, 2001) as well as dumping of Cr-rich industrial waste. Considerable amount of Pb was found even after the ban of leaded petrol in Kanpur in 2006. Pb discharged by vehicles driven in earlier days, in due course of time, has become a part of road dust. During dust days, Na mass concentration was found to be 7.03 ± 2.50 μg/m³ in PM_{10} and 2.40 ± 2.16 μg/m³ in $PM_{2.5}$. As the sampling site is far from coastal region, sea salt contibution is insignificant. The salt affected soil map of India shows that Na is distributed evenly in the Indo-Gangetic plain (Kumar and Sarin, 2010). It is inferred that sodic soil from the locality may have been a significant source of Na in the aerosols.

The average SO_4^{2-} mass concentrations during dusty days were 7.3 ± 3 μg/m³ and 4.8 ± 1.05 μg/m³ in PM_{10} and $PM_{2.5}$, respectively (Fig. 5). Coarse mode SO_4^{2-} may have originated from dispersed natural sources like biogenic decomposition processes (Alexander *et al.*, 2005) or from soils which are rich in gypsum (Yuan *et al.*, 2008). The sea-salt SO_4^{2-} is insignificant in this area which is being far away from seas.

Polluted Dust₁ Days

On an average, the anthropogenic elemental concentration during PD_1 days was found to be dominating particularly in $PM_{2.5}$. Especially, elements like Cr, Cu, Ni, Se and Zn with
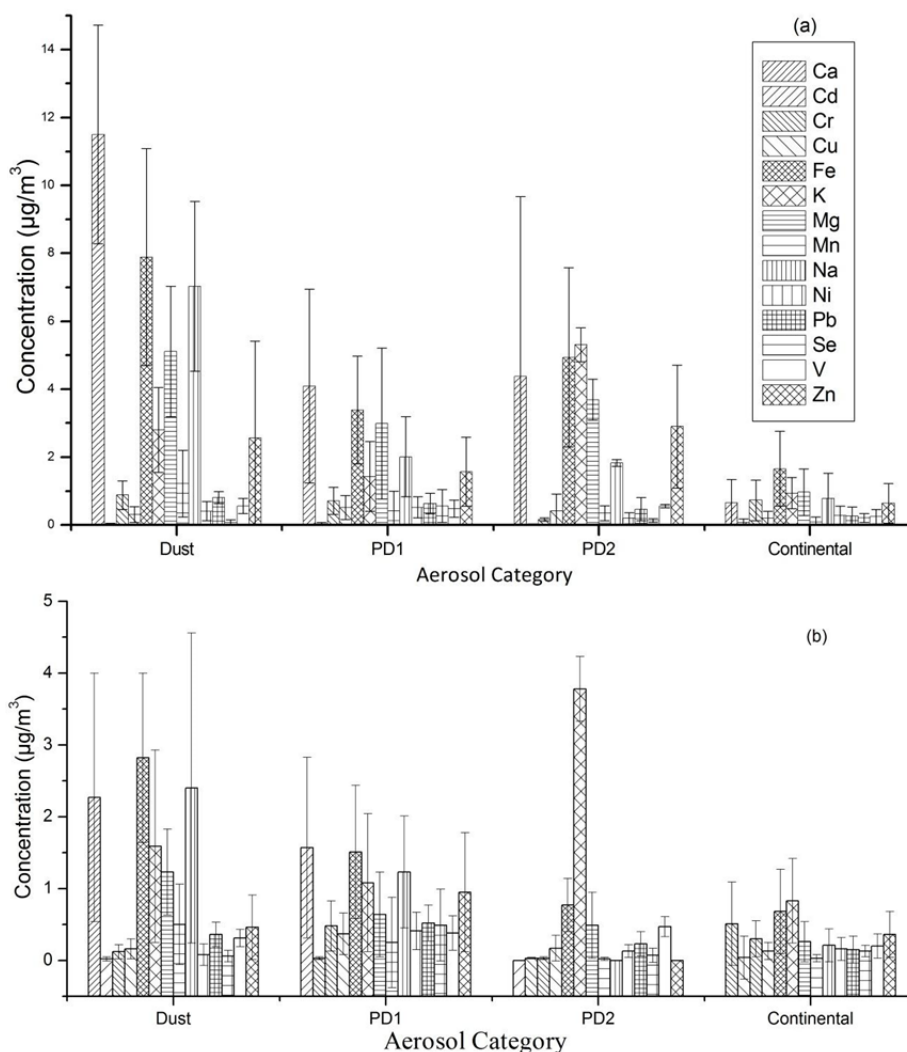
Fig. 4. Average Elemental Concentration in (a) PM_{10} and (b) $PM_{2.5}$. Error bars represent One Standard Deviation.

mean concentrations of 0.48 ± 0.35, 0.37 ± 0.29, 0.41 ± 0.26, 0.52 ± 0.25 and 0.49 ± 0.50 $\mu g/m^3$, respectively, in $PM_{2.5}$ were higher compared to other days. Cr arises in the aerosols usually from solid waste dumping, tanneries, biomedical waste incineration and power plant emission (Kulshrestha *et al.*, 2009). Kanpur has many tanneries, solid waste dumping sites and a thermal power plant nearby. High concentration of Cu could be attributed to nearby Panki Thermal Power Plant situated within 6 km of IITK sampling site (Kim and Fergusson, 1994). Kanpur has a very congested traffic is in so vehicular emissions are also very high. Ni comes from burning of lubricating oil as a part of total vehicular emissions (Kulshrestha *et al.*, 2009).The main sources of Se are fossil fuel combustion, waste incineration, copper refineries, chemical and glass industries and coal combustion (Ranville *et al.*, 2010). Zn sources are mining activities, industries, smelters, incineration, burning of fossils, fuel additives etc. (Chinnam *et al.*, 2006).

Among the ions, the concentrations of NO_3^- and SO_4^{2-} were higher than other ions with concentration of 4.69 ± 6.62 and 5.93 ± 4.13 $\mu g/m^3$ in $PM_{2.5}$ and 5.72 ± 4.06 and 6.43 ± 3.83 $\mu g/m^3$ in PM_{10}, respectively. The high SO_4^{2-}

concentration suggests mixing of dust with secondary inorganic aerosol formed from the conversion of gaseous SO_2 emitted by various combustion sources like thermal power plant, biomass burning etc. during its long range transport (Deshmukh *et al.*, 2011). NO_3^- is formed in the atmosphere by the homogeneous gas phase transformation and oxidation from NO_x to nitric acid, which then gets neutralized by ammonia to form ammonium nitrate. NO_x is emitted from various anthropogenic sources like vehicular emissions, power plant, refineries and biomass burning. Variation of NO_x emissions is strongly dependent on meteorological factors like temperature and relative humidity (Wang *et al.*, 2006a; Wang *et al.*, 2006b). Coarse mode NO_3^- can be formed by the reaction of mineral aerosols with gaseous nitric acid (Wolff, 1984; Mamane and Gottlieb, 1992). Thus, mineral aerosol surface can play an important role as a sink for nitric acid by providing an alkaline surface area for reaction of NO_2 on crustal origin particles (Tabazadeh *et al.*, 1998).

NH_4^+ concentration was found to be 3.36 ± 3.9 $\mu g/m^3$ and 5.40 ± 5.11 $\mu g/m^3$ in $PM_{2.5}$ and PM_{10}, respectively. Its significant presence raises the pH of the droplet solution, leading to enhanced SO_2 oxidation rate, thus neutralising
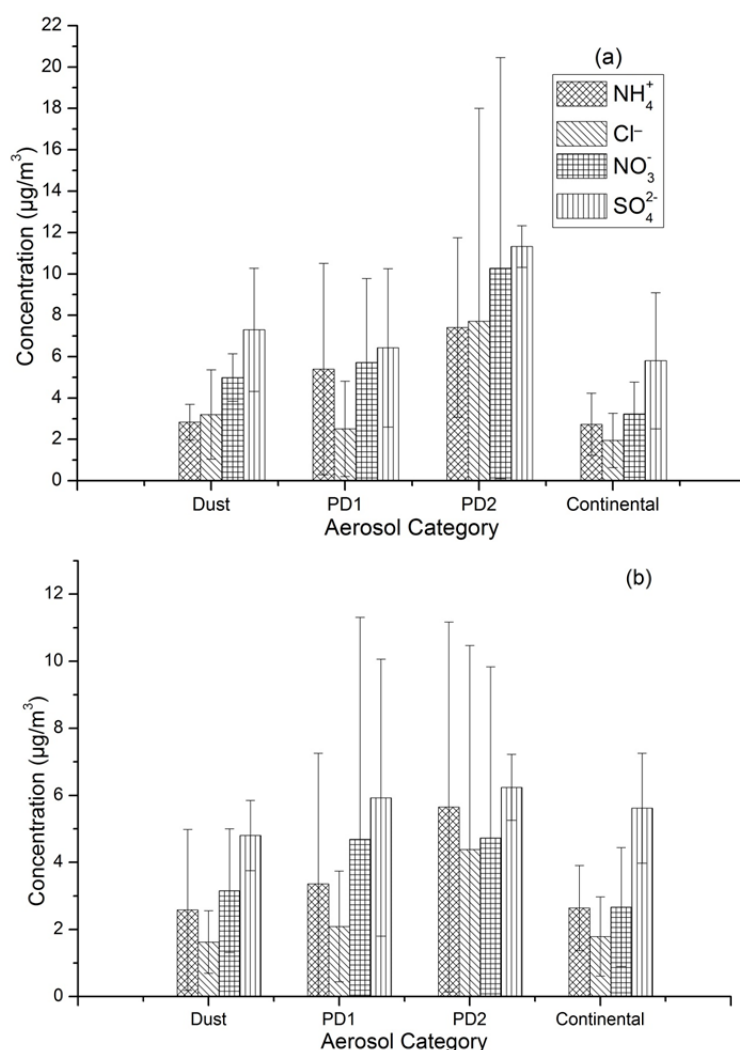
Fig. 5. Average ions concentration ($\mu g/m^3$) in (a) PM_{10} and (b) $PM_{2.5}$. Error bars represent one standard deviation.

the acidity of the aerosols (Wang *et al.*, 2006b). It comes into the aerosols by reaction of ammonia gas with acidic species such as H_2SO_4, HNO_3 and HCl or sometimes ammonia vapour may react or condense on an acidic particle/droplet surface of anthropogenic origin. The different sources of ammonia are animal waste, ammonification of humus, loss of ammonia from the fertilizers added into the soil, and emissions from industries, incineration of waste, biomass burning and also from the internal combustion engines (Seinfeld and Pandis, 2012).

Internal mixing and meteorological conditions play an important role for good correlations. High correlation was found between NH_4^+ and SO_4^{2-} ($R^2 = 0.91$ in $PM_{2.5}$), NO_3^- and SO_4^{2-} ($R^2 = 0.65$ in $PM_{2.5}$ and $R^2 = 0.77$ in PM_{10}) and NH_4^+ and NO_3^- ($R^2 = 0.6$ in $PM_{2.5}$) which shows the formation of ammonium sulphate, ammonium bisulphate (NH_4HSO_4) and ammonium nitrate (Gupta and Mandariya, 2013). Coal burning, vehicle emissions and industries are the common sources of NO_3^- and SO_4^{2-}.

Polluted Dust₂ Days

High K concentration with mean value of 3.78 ± 0.45

$\mu g/m^3$ and trace amounts of V and Pb with average concentrations of 0.47 ± 0.14 $\mu g/m^3$ and 0.23 ± 0.17 $\mu g/m^3$, respectively, in $PM_{2.5}$ were found in PD_2 type of aerosols. Whereas, PM_{10} was found to be enriched with Ca, Fe, K, Mg and Zn, with mean values of 4.38 ± 5.29, 4.94 ± 2.64, 5.31 ± 0.50, 3.69 ± 0.60 and 2.90 ± 1.81 $\mu g/m^3$, respectively. Echalar *et al.* (1995) found that K is a major cation in fine mode and that aerosols are generated during biomass burning by soil particles re-suspension, incompletely burnt plant tissues and as a result of condensation or coagulation of fine mode particles. Therefore, K can be used as a diagnostic tracer for biomass burning and thus it implies that the aerosols collected on these days got mixed with various pollutants from anthropogenic sources like burning of dry leaves, grasses and crop residue which is a common practice after crop harvesting in India. Similarly, Zn can come from biomass burning, coal and wood combustion (Rastogi and Sarin, 2009; Chakraborty and Gupta, 2010). V is present in heavy fuel oils, which is released into the atmosphere at concentrations of 10–50 mg/g as fly ashwhen oils get combusted (Mamane and Pirrone, 1998). There was no Ca found in $PM_{2.5}$ which suggests that the Ca in PD_2 were mainly associated with the

coarser particles. The crustal minerals can also come into the aerosols during burning by two ways: crustal matter can be resuspended from the ground during extreme fires creating uplift conditions and the minerals that had accumulated earlier on the flora (dry deposition) get entrained in the intense fire and are emitted as aerosols (Li *et al.*, 2003).

Overall, the mean concentration of ions was found to be highest during these days. SO_4^{2-} was the dominant ion and was found to be 11.3 ± 1.01 and 6.24 ± 0.98 µg/m³ in PM_{10} and $PM_{2.5}$, respectively. Mean NO_3^- concentration was found to be 10.27 ± 10.18 and 4.73 ± 5.10 µg/m³ in PM_{10} and $PM_{2.5}$, respectively. High concentration of Cl^- was also observed which was 7.71 ± 10.29 and 4.39 ± 6.09 µg/m³ in PM_{10} and $PM_{2.5}$, respectively. Cl^- comes from burning of fossil fuel (coal combustion), brick kilns, biomass burning, etc. It gets transformed from gas to particle phase due to the neutralization of ammonia by HCl which is released from above mentioned sources (Gupta and Mandariya, 2013).

Continental Days

Crustal elements like Fe and Mg, were found along with some other elements like Cd, Cr, Cu, K, Ni, Pb, V and Se (especially in the fine mode) from anthropogenic activities but their concentrations were quite low. These days were mainly affected by local sources. Among the ions only SO_4^{2-}, NH_4^+ and Cl^- with concentrations 5.62 ± 1.64, 2.64 ± 1.27, and 1.79 ± 1.18 µg/m³, respectively in $PM_{2.5}$ were found to be higher than dust events. However, their concentration in PM_{10} was found to be lower than all the other days. A fair correlation between Cl^- and SO_4^{2-} ($R^2 = 0.64$) in $PM_{2.5}$ was also observed.

Variations in Water Soluble Organic Carbon (WSOC) and Water Soluble Inorganic Carbon (WSIC)

WSOC is a major fraction of water soluble constituent and contributes to the CCN number density (Ram and Sarin, 2011). WSOC concentration varied from 0.70 to 24.18 µg/m³ in PM_{10} and 0.28 to 17.98 µg/m³ in $PM_{2.5}$ (Fig. 6). The ratio of WSOC in $PM_{2.5}$ to that in PM_{10} ranged between 0.05 to 0.91, indicating a wide variability in the carbonaceous aerosols in coarse and fine particle modes. WSOC mostly existed as oxygenated organic compounds like ketones, carboxylic acids, aldehydes, and peroxide emanating from biomass burning (burning of wood and agricultural waste) and emissions from vehicles and industries or through secondary heterogeneous oxidation (Pathak *et al.*, 2011). WSOC was found to be higher during PD_2 and PD_1 days especially on 10th, 16th and 25th April; 4th and 13th May; 6th and 15th June and 15th July which results from enhanced formation of biogenic and anthropogenic secondary organic aerosols (SOA). It is formed by oxidation of volatile organic compounds (VOCs) in the presence of oxidizing agents such as O_3, OH^-, peroxide and NO_3^- radicals (Ram *et al.*, 2010; Kaul *et al.*, 2011). During summertime, a strong photochemical oxidation takes place forming functional groups containing oxygen which increases hygroscopicity of the aerosol (Viana *et al.*, 2006). The WSIC ranged between 0.32 to 15.64 µg/m³ in PM_{10} (Fig. 6(a)) and 0.02 to 4.28 µg/m³ in $PM_{2.5}$ (Fig. 6(b)). The contribution of WSIC to that of total mass was only 2% in $PM_{2.5}$ and 1.7% in PM_{10}. WSIC was found during all the dusty days and on some PD_1 days which may have originated from carbonate and hydrogen bicarbonates formed mainly from crustal matter;
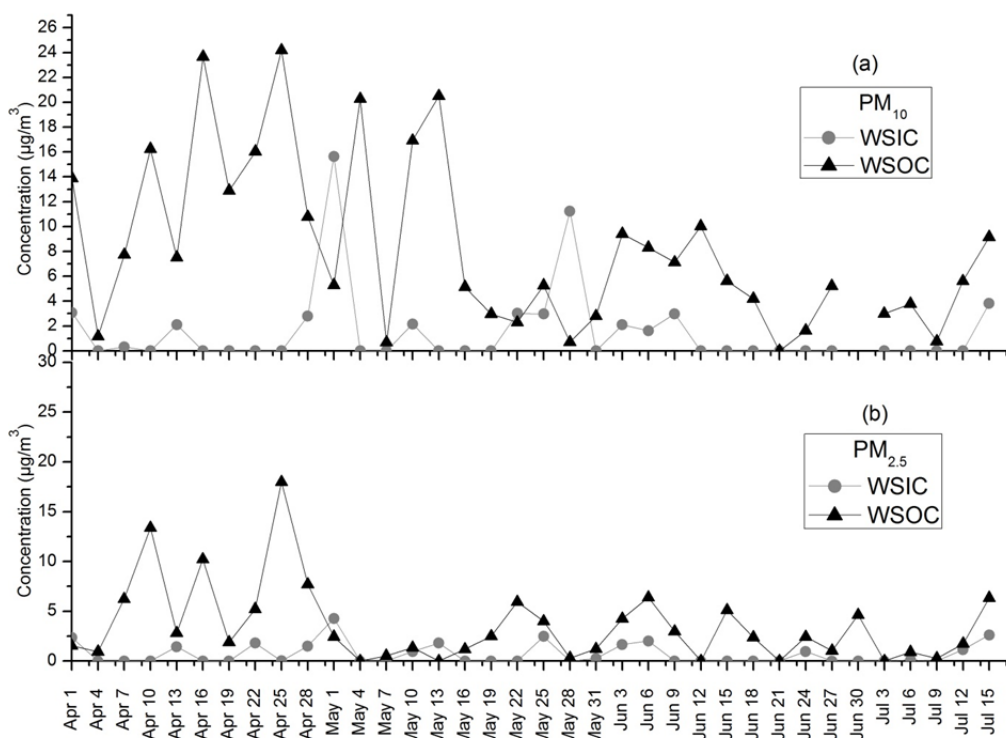
Fig. 6. Temporal variations of Water Soluble Inorganic Carbon (WSIC) and Water Soluble Organic Carbon (WSOC) in (a) PM_{10} and (b) $PM_{2.5}$.

(Khare *et al.*, 2011). It was high on 1st, 13th and 28th April 1st, 10th, 22nd, 25th and 28th May; 3rd and 6th June and 15th July. During most of the continental days the WSIC was lower suggesting lesser contribution from dust.

Case Study
25 May

25 May, classified as a dusty day, had mass concentrations of 176.16 µg/m^3 in PM$_{10}$. The concentration of elements Ca, Fe, Mg and Na was 16.81, 9.96, 7.54, and 8.34 µg/m^3, respectively in PM$_{10}$, were the highest amongst all the days. Also, the SO$_4^{2-}$ and NO$_3^-$ concentrations were 7.54 and 6.32 µg/m^3 in PM$_{10}$ and 4.81 and 3.63 µg/m^3 in PM$_{2.5}$, respectively, which show that 1.6 times of SO$_4^{2-}$ was in coarse mode. This suggests that SO$_4^{2-}$ was either coming from mineral dust like gypsum (CaSO$_4$) or formed as a result of gas to particle conversion itself on the dust particles. WSIC was found to be 2.97 µg/m^3 in PM$_{10}$. NOAA (National Oceanic and Atmospheric Administration, U.S.), Hybrid-Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model, version 4, developed by the Air Resources Laboratory (ARL) was used to calculate 120 h back trajectories (Draxler and Rolph, 2003). The arrow marks on the trajectories shown in Fig. 7 indicates 24 h movement location. The back trajectories (at 50, 500 and 1000 m above ground level) show the dust laden air masses were coming from West and South West Azimuth, i.e., originating from arid and semiarid regions of Rajasthan (Thar Desert), Gujarat and Arabian Peninsula and ending at Gulf of Aden, near Yemen.

25 April

This day, classified as dust mixed with biomass burning (PD$_2$) had mass concentration of 187.81 µg/m^3 in PM$_{10}$ and 36.09 µg/m^3 in PM$_{2.5}$, respectively. High concentration of K (3.47 µg/m^3) in PM$_{2.5}$ also confirmed biomass burning.
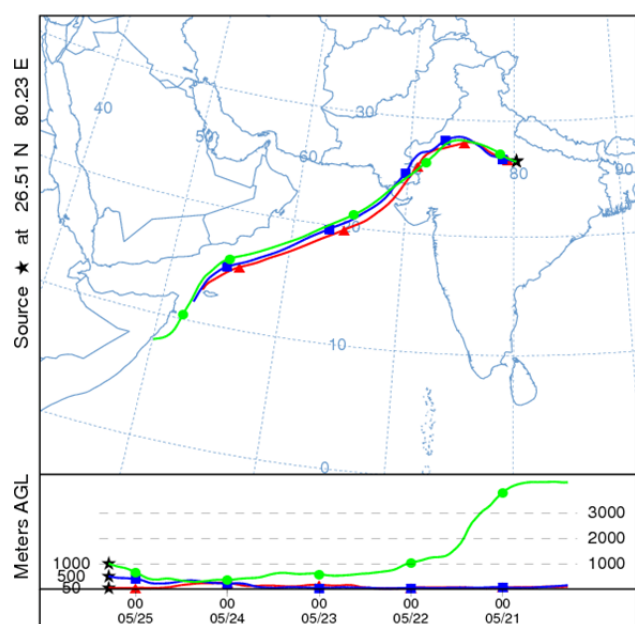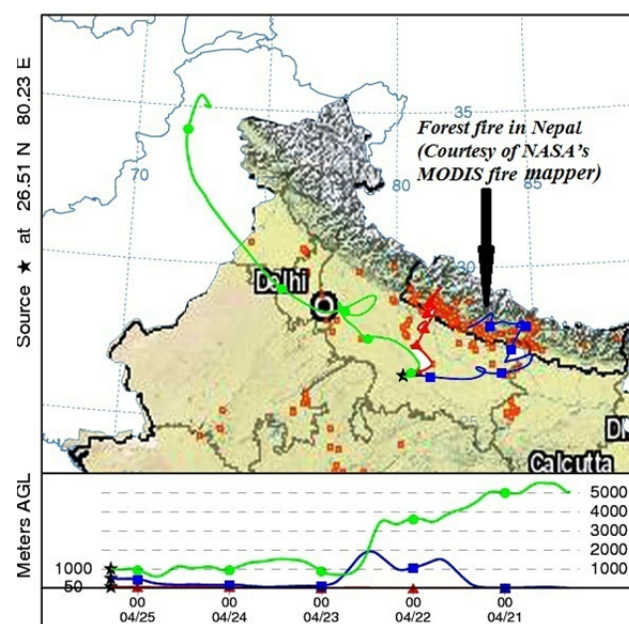
V was detected in PM$_{2.5}$ with a concentration of 0.57 µg/m^3. The ionic concentrations were highest during this day. NO$_3^-$ and Cl$^-$ with concentration of 17.47 and 14.98 µg/m^3 in PM$_{10}$ and 8.34 and 8.69 µg/m^3 in PM$_{2.5}$, respectively were dominating ions. Both these ions originated from anthropogenic sources like fossil fuel combustion and biomass burning. WSOC was mostly concentrated in the fine mode and was found to be highest on this day (24.18 µg/m^3 in PM$_{10}$ and 17.98 µg/m^3 in PM$_{2.5}$). The Back trajectory at 50 and 500 m superimposed over the Moderate Resolution Imaging Spectroradiometer (MODIS) fire count image shows that there was a series of forest fires in Nepal during this time and the air masses were coming from this region (Fig. 8) and picking up the combustion residue on its way.
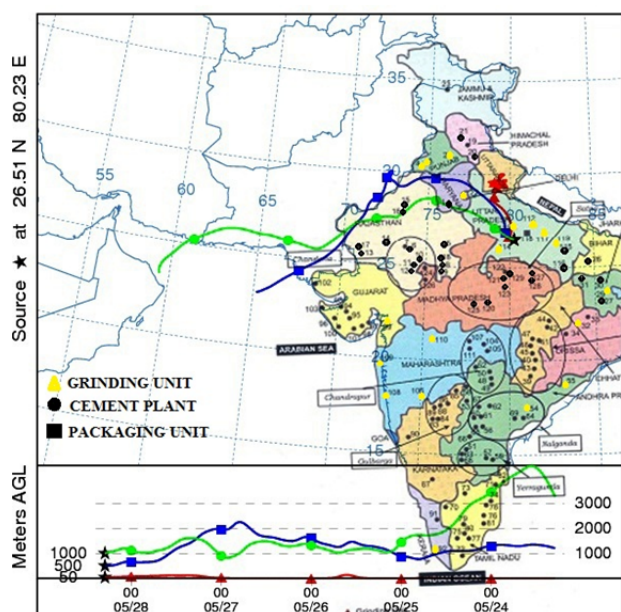
28 May

This day was classified as Continental Day and had the lowest ionic and elemental concentrations. Five days back trajectories at a height of 50 m superimposed on cement industries (Fig. 9) shows that the air masses got mixed with pollutants from this industry and these were mostly localized. Also, various industries situated nearby like iron and steel industries, rice mill, tanneries, brick kiln, thermal power plant, fertilizer, cement, refineries added various pollutants to the aerosol loading. Winds from far away regions had very little effect as they reached a significant height over the sampling location. WSOC was very low 0.70 and 0.30 µg/m^3 in PM$_{10}$ and PM$_{2.5}$, respectively, and WSIC was absent.
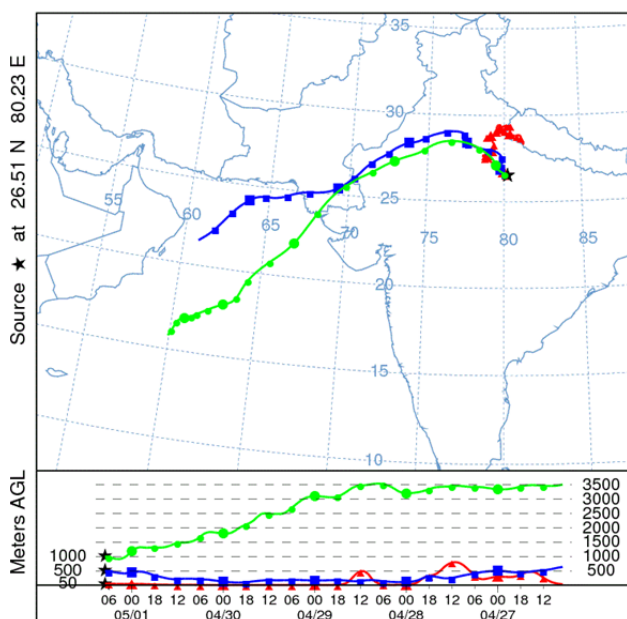
1 May

This day was classified as PD$_1$ day, with mass concentration of 204.97 and 36.49 µg/m^3 in PM$_{10}$ and PM$_{2.5}$, respectively. It was enriched with various anthropogenic elements in PM$_{2.5}$ like Cr, Cu, Ni, Pb, Se, V and Zn with corresponding mass concentration of 0.14, 0.35, 0.51, 0.39,

Fig. 7. Five days back trajectories using NOAA HYSPLIT model for 25 May at 50 m, 500 m and 1000 m.

Fig. 8. Five days back trajectories using NOAA HYSPLIT model superimposed over NASA's fire count.

Fig. 9. Five days back trajectories using NOAA HYSPLIT model superimposed over cement industries map for 28 May at 0700 UTC and 50 m, 500 m and 1000 m height above ground level.

Fig. 10. Five days back trajectories using NOAA HYSPLIT model for 1 May at 0700 UTC and 50 m, 500 m and 1000 m height above ground level.

1.02, 0.36 and 0.68 $\mu g/m^3$, respectively. WSOC was found to be 5.30 and 2.45 $\mu g/m^3$ in PM_{10} and $PM_{2.5}$,respectively. The back trajectories (Fig. 10) show that the air mass at 50 and 500 m were coming from Uttarakhand and parts of Uttar Pradesh including Lucknow, Bareilly and Meerut, and the Kathmandu region of Nepal. Various industries present in these areas contaminate the dust and caused mixing of aerosols.

CONCLUSION

This study presents chemical characterization of crustal dust sampled during pre-monsoon and monsoon period in Kanpur, India. The PM_{10} mass concentrations were higher mostly during dusty and polluted dusty days. The levels of soil derived elements (Ca, Mg and Fe) were quite high during dusty days in both size mode particles (PM_{10} and $PM_{2.5}$) as compared to other classified days, but the mass concentration of anthropogenic elements like Cu, Ni, Se, V etc. were higher in PD_1 and PD_2 days especially in $PM_{2.5}$. The fine mode K concentration, a tracer for biomass burning, was higher during PD_2 days as compared to other days. Very low elemental mass concentration was found during continental days. SO_4^{2-} and NO_3^- were higher during PD_2 days. The contribution of WSIC to total mass was only 2 % in $PM_{2.5}$ and 1.7% in PM_{10}. WSOC was high during PD_1 and PD_2 days and WSIC was high during dust and PD_1 days.

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