Chemical Characterization and Source Apportionment of Submicron (PM$_1$) Aerosol in Kanpur Region, India

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ABSTRACT

PM$_1$ (particles having aerodynamic diameter < 1.0 µm) concentrations were measured at a sampling site inside the Indian Institute of Technology (IIT) Kanpur campus for 11 months from July, 2008–May, 2009. The sampling was carried out for all the major seasons of India and a total of 90 samples were collected. The chemical speciation data in terms of element and anion concentrations of all the collected samples were closely studied for any seasonal phenomena and different source contributions to PM$_1$ mass. Average PM$_1$ concentration was found to be highest (199 µg/m^3) during winter and lowest (31 µg/m^3) during monsoon season. Concentrations of different elements and anions also followed similar trend as PM$_1$ concentration. Nitrate and sulfate were the two most predominant anionic species contributing to almost 80%–90% of total anionic concentrations. Crustal elements (Ca, Mg, and Fe) were the main contributors within the total elemental concentrations. Overall, it was found that anions contributed up to 35% of the total PM$_1$ mass. Factor Analysis of chemical speciation data and UNMIX (Version 6) revealed that secondary sources and vehicular emissions were the two main sources contributing to PM$_1$ mass with minor contributions from paved road dust and coal combustion sources.

Keywords: PM$_1$; Source apportionment; PCA; UNMIX; Anions; Elements.

INTRODUCTION

Several epidemiological studies (Schwartz *et al.*, 1996; Pope, 2000) have suggested a statistical association between health effects and ambient fine particle concentrations, especially the submicron fraction (PM$_1$) that can penetrate deep into the alveolar region of the lungs. There is an abundance of mass concentration, distribution, and chemical component measurements for ambient PM$_{2.5}$ and PM$_{10}$ in many urban and heavily industrialized areas around the World. However, very little is known, and even less has been done specifically about PM$_1$. Fine particles (PM$_{2.5}$, particles having aerodynamic diameter less than 2.5 µm) in urban areas arise predominantly from the gas-to-particle conversion processes within the atmosphere, or they consist of secondary anthropogenic combustion products originating mainly from vehicular traffic and activities related to electricity production (Hildemann *et al.*, 1991; Schauer *et al.*, 1996; Kleeman and Cass, 1998). Typically, the major components of urban ambient PM$_{2.5}$ have been extensively measured and reported as sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), organic carbon (OC), and elemental carbon (EC)

(Brook *et al.*, 1997; Chan *et al.*, 1997; Kyotani and Iwatsuki, 2002; Hopke *et al.*, 2008).

Kanpur is one of the most polluted cities in India today. Kanpur's climate can be characterized by a very hot and dry summer and very cold winter, the temperature during summer can go up to 48°C and winter goes below 4°C. The city's population is around 6 million at present and it is dangerously congested and overcrowded and due to the onset of leather industries air pollution has risen to dangerously high levels. Alarming vehicular and population growth rate, frequent traffic jams and overall poor infrastructure has lead to a significant rise in the RSPM (Respirable Suspended Particulate Matter, PM$_{10}$) level of Kanpur. Although vehicles and industries are the two most important contributors to the Kanpur's ambient RSPM level but contributions from other pollution sources, such as roadside dust, trans-boundary migrations, power plants, solid waste and local sources can't be ruled out. Particulate matter from these sources may contain hazardous pollutants that can have carcinogenic and mutagenic effects. Thus, identification of the sources is important. Very few studies have been conducted in this part of the world on characterization of fine particulate matter (PM$_{2.5}$ or less), but their characterization and source identification is very much important as these particles can remain suspended in the air for long time and can be transported to a long distance with wind and can easily penetrate deep into our respirable tract. In the past, several methods have been

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used to estimate the major sources for air pollutants including principle component analysis (PCA or Factor Analysis), multiple linear regression analysis (MLR) and the chemical mass balance (CMB) receptor model, positive matrix factorization (PMF), UNMIX, molecular marker method etc.

The present research study was carried out primarily to find out the seasonal trend of PM_1 mass and its chemical constituents and finally the identification of different unknown sources contributing to the PM_1 mass. In the present investigation, PCA and UNMIX models have been applied for the source identification and apportionment of PM_1 in the ambient air of Kanpur.

MATERIALS AND METHOD

Sampling Site

Sampling was carried out on the roof of a 12 m high building (Western Lab Extension, WLE) inside the IIT Kanpur campus. IIT Kanpur is an educational institute having residential campus with no commercial and industrial activities. The campus lies about 15 km north of Kanpur city in the upwind direction with minimum emissions in its near vicinity. Within the campus, the vehicular population mainly comprises of two wheelers and cars. Fig. 1 depicts the land-use pattern for the city of Kanpur as well as shows the exact location of the sampling site for the current study.

Sampling Procedure

Sampling was carried out for 8 h each day spread over all the major seasons; Monsoon (July–August, n = 15),

Post Monsoon (September–October, n = 15), winter (December–January, n = 23), Pre-Summer (March, n = 19), summer (April–May, n = 18). Total 90 samples ($\sum n = 90$) were collected (Table 1). In addition, 10 field blanks were collected.

Sampling was carried out using a single stage round nozzle, grease impaction substrate based impactor type PM_1 sampler previously developed in our lab at IITK itself (Gupta *et al.*, 2009). This sampler (d_{50} = 1.05 μm and GSD = 1.24) has been validated with polydisperse artificial aerosol generated in the lab and measured using an APS (Aerodynamic Particle Sizer, model 3021, TSI Inc., USA) following well established methods for impactor characterization (Demokritou *et al.*, 2002; Gupta *et al.*, 2004). Flow rate of the sampler was 10 LPM (measured by rotameter, calibrated using mass flow meter, Dakota Inc., USA) and a backup PTFE or Teflon filter with 46.2 mm collection diameter was used for PM_1 collection. The overall pressure drop through the sampler, including the Teflon backup filter, was 18.5 cm of water. Teflon filters were used for following reasons: (a) they are chemically very inert and contain very little impurities which made them especially suitable for trace element analysis; (b) very less moisture absorption capacity and high PM collection efficiency; (c) can endure a very wide range of weather conditions without any deformation.

Quality Control

(i) Clear forceps were used to handle the filters and each time the forceps were cleaned with ethanol and then with Milli-Q water to avoid any contamination.
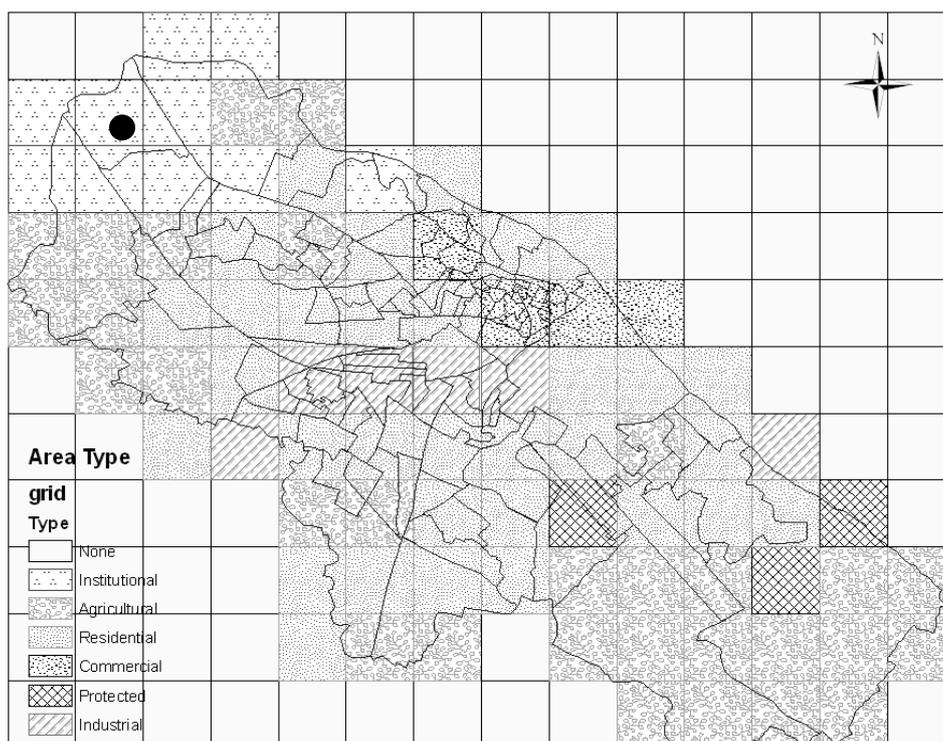(ii) Filters were kept in sealed plastic containers in the refrigerator until the analysis was done.

Fig. 1. Map of Kanpur city showing the land-use pattern and the IIT Kanpur sampling site (black dot).

Table 1. Seasonal average PM_1 mass concentration ($\mu g/m^3$).

Study locaton	Secson	Concentraton (±Std)
IITK	Monsoon	30.1 ± 13.7
IITK	Post Monsoon	63.8 ± 23.7
IITK	Winter	199.0 ± 66.0
IITK	Pre Summer	77.1 ± 31.0
IITK	Summer	142.3 ± 45.0

Std = Standard Deviation

(iii) Flow rate was monitored at every 30 min interval during the 8 h sampling duration.

(iv) All the glass wares were acid (chromic acid) washed and oven dried before use.

(v) An additional 10% of the total number of exposed filters in each season were kept as blank and subjected to exactly the same analytical procedure as the exposed filters.

(vi) Both the gravimetric mass (using a microbalance, Mettler Toledo) and chemical composition data obtained were corrected subsequently using the blank values.

Gravimetric and Chemical Analysis of Collected Samples

Since the collected mass of PM_1 was of very low quantity, utmost care was taken for filter preparation, sample collection and weighing of the filter papers. Each filter paper used for the sampling was pre-conditioned and post-conditioned in a controlled environment at 25°C and 40% RH for 24 h before and after the sampling and difference in weight of filters before and after sampling gave the collected PM_1 mass and hence concentration after dividing PM_1 mass by the sampled volume of air (in this study it was a constant = 4.8 m^3).

Each exposed filter was cut into two equal half portions. One half was divided into several small fragments and kept in a digestion vessel (a 100 mL round bottom flask). Then 20 mL of conc. nitric acid (Suprapure, 70% GR grade, Merck) was poured into the digestion vessel and then placed over a hot plate and kept for around 2 h at 180°C until most of the nitric acid got almost completely evaporated. The residual was then filtered through a 0.22 μm Teflon filter and diluted to 100 mL with Milli-Q water (resistivity 18.2 MΩ) for subsequent elemental analysis. Each blank filter was digested in the same way as the sample filters. The elemental analysis was performed using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry, ICAP 6300 Thermo Inc.). This instrument uses superheated Argon plasma of 7000–10000 K to breakdown and excite the atoms of the different elements and then identifies the elements from the characteristic wavelength emitted during the excitation process, it's a fairly rapid process and can identify up to 60 elements simultaneously. 13 elements were selected for our analysis: As, Ca, Co, Cr, Cd, Mg, Fe, Ni, Pb, Cu, Zn, V, Se, out of these 12 were found be present at detectable levels in the samples and Co was found to be mostly below the detection limit of the instrument. The other half of the filter samples were analyzed for 5 anions: F^-, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} by Ion Chromatography

(Compact IC 761, Metrohm) after aqueous extraction followed by ultrasonication for 20 minutes (Haobo and Shooter, 2001).

Factor Analysis for Source Identification

Factor analysis is a method for investigating whether a number of variables of interest Y_1, Y_2,…, Y_N, are linearly related to a smaller number of unobservable factors F_1, F_2,…, F_k .

It is assumed that each Y variable is linearly related to the two factors, as follows:

$$Y_1 = \beta_{10} + \beta_{11}F_1 + \beta_{12}F_2 + e_1 \qquad (1)$$
$$Y_2 = \beta_{20} + \beta_{21}F_1 + \beta_{22}F_2 + e_2 \qquad (2)$$
$$Y_3 = \beta_{30} + \beta_{31}F_1 + \beta_{32}F_2 + e_3 \qquad (3)$$

The error terms e_1, e_2, and e_3, serve to indicate that the hypothesized relationships are not exact. In the special vocabulary of factor analysis, the parameters β_{ij} are referred to as loadings. For example, β_{12} is called the loading of variable Y_1 on factor F_2.

Source Quantification

UNMIX (Version 6) model of US EPA was used for source quantification that means to find out contribution of different sources to the overall PM_1 mass. It has been used in several studies (Henry, 2000; Lee *et al.*, 2002; Larsen and Baker, 2003; Lewis *et al.*, 2003; Maykut *et al.*, 2003; Mukerjee *et al.*, 2004) in the past and has produced satisfactory results comparable with other source apportionment methodology like- CMB, PCA/APCS, PMF etc. (Henry, 2000; Larsen and Baker, 2003; Lewis *et al.*, 2003; Maykut *et al.*, 2003; Mukerjee *et al.*, 2004). In fact, in some of the studies it has been reported that UNMIX provided estimates which were even better and more closer to the observed data as compared to other methods (Song *et al.*, 2006)

UNMIX uses the singular value decomposition (SVD) method to estimate the source number by reducing the dimensionality of data space m to p (Henry, 2003). The UNMIX model can be expressed as

$$C = U_N D_N V_N^T + \varepsilon \qquad (4)$$

where U, D, and V are n × N, N × N diagonal, and m × N matrices, respectively; and ε is the error term consisting of all the variability in C not accounted for by the first N principal components. Geometrical concepts of self modeling curve resolution are used to ensure that the

results obey (to within error) the nonnegative constraints on source compositions and contributions. Additional constraints are also used to help determine the results. UNMIX normalizes the data matrix such that all the species are on the same scale with a mean of 1. The data are then projected to a plane perpendicular to the first axis of N-dimensional space. The edges represent the samples that characterize the source. Such edges in point sets are then used to calculate the vertices, which are used with the matrices decomposed by SVD to obtain the source profiles and contributions.

RESULTS AND DISCUSSION

In the current study, PM_1 concentrations (Table 1, Fig. 2) vary significantly in different seasons of the year, with lowest average concentration (30.1 $\mu g/m^3$) observed during monsoon season and highest average concentration during winter (199 $\mu g/m^3$) season which is close to the value (203 $\mu g/m^3$, $PM_{0.95}$) reported in a study carried out during winter, December 2004 in IIT Kanpur (Tare *et al.*, 2006). The lowest concentration observed during monsoon season can be attributed to washout by rainfall and higher relative humidity which lead to reduced resuspension of crustal dust. Higher concentration during winter can be attributed to low temperature and wind speed which lead to lower mixing height and poor dispersion conditions coupled with increase in anthropogenic activities such as biomass burning, space heating etc. During summer season the PM_1 concentration was found to be higher likely due to the enhanced resuspension of crustal dust caused by the higher wind speed. Also, a few incidents of minor dust storms were observed during the sampling period in summer.

Seasonal Variation in Elemental Concentrations

Like PM_1 mass concentrations, concentrations of different elements varied significantly in different seasons (Table 2, Figs. 3, 4). Among the 13 elements analyzed, Co (Cobalt)

was found to be always below detection limit in all the samples and As (Arsenic) was only detected during the winter season. Table 2 also shows the method detection limit (MDL, ng/m^3) and percentage of sample values below detection limit (BDL) (ICP-OES Instrument manual, Kim *et al.*, 2005; Kim and Hopke, 2007). Elements like – Ca, Mg, Fe which are mainly originated from crustal sources (Wang *et al.*, 2006a; Srivastava *et al.*, 2008; Balakrishna and Pervez, 2009) were found to be present in higher concentrations even in the submicron fraction. The same trend was also reported in a study carried out at Delhi, winter 2006 (Srivastava *et al.*, 2008). The concentrations of these elements were found to be higher in summer season due to higher wind speed which resulted in enhanced resuspension of crustal dust and were lowest during monsoon season when high humidity and rainfall minimized the resuspension of crustal dust. However, during winter season when the atmosphere was most stable with almost no turbulence and lower mixing heights, concentrations of these elements were still higher indicating that in submicron fraction some portion of these elements may also be contributed by anthropogenic sources. It has been reported in several studies that vehicular exhaust also contains significant amount of Ca, Fe (Schroeder *et al.*, 1987; Hare, 1977) and it was also reported that almost 80% of the vehicular PM emission was within ultrafine to fine (0.1–2.8 μm) (Junker *et al.*, 2000) range.

Elements like – As, Cd, Cr, Cu, Zn, Ni, Se which are mainly originated from anthropogenic sources (vehicular exhaust, coal burning, industrial processes etc.) (Wang *et al.*, 2006b) were found to be higher during winter season and lowest during summer period. In winter, increased anthropogenic activities (biomass burning, space heating etc.), lower mixing height, low wind speed and temperature lead to poor dispersion conditions which increased the concentration of these anthropogenic elements. An interesting trend can be observed for Pb (Fig. 3) which is highest during summer season, although CNG driven vehicles were introduced in
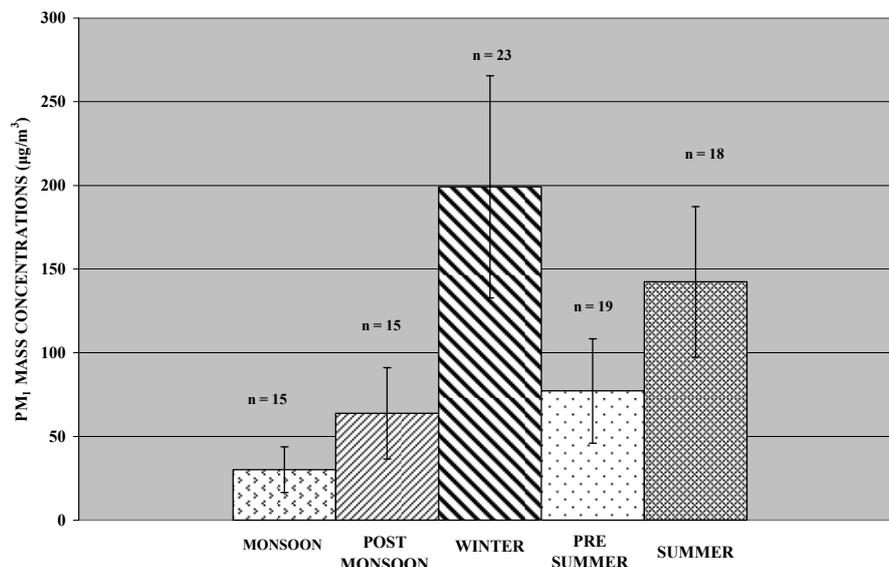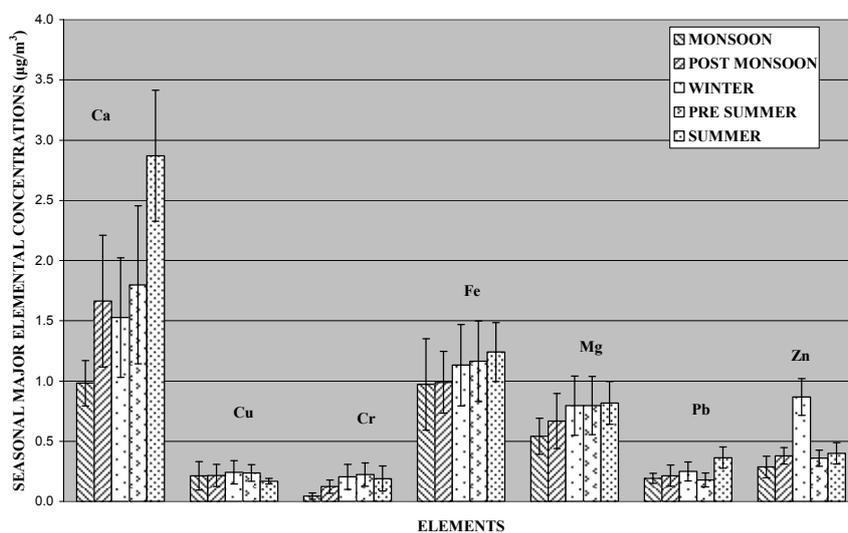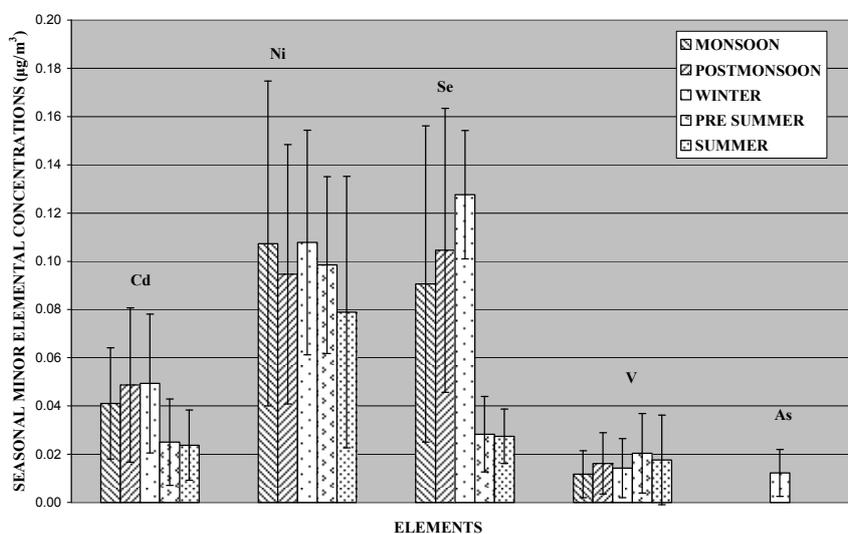

Fig. 2. Seasonal average PM_1 mass concentrations. (n = number of collected samples).

Table 2. Seasonal average elemental concentrations (± Std).

Element	Season						
	M (µg/m³)	PM (µg/m³)	W (µg/m³)	PS (µg/m³)	S (µg/m³)	MDL (ng/m³)	BDL (%)
As	ND	ND	0.012 ± 0.01	ND	ND	40.8	98.9
Ca	0.98 ± 0.18	1.66 ± 0.54	1.52 ± 0.49	1.69 ± 0.65	2.87 ± 0.54	0.1	1.1
Cd	0.04 ± 0.02	0.05 ± 0.03	0.05 ± 0.02	0.01 ± 0.01	0.02 ± 0.01	1.3	11.1
Cr	0.04 ± 0.02	0.12 ± 0.05	0.02 ± 0.1	0.2 ± 0.09	0.19 ± 0.1	4.1	5.6s
Cu	0.21 ± 0.11	0.21 ± 0.09	0.24 ± 0.09	0.23 ± 0.06	0.16 ± 0.02	10.4	2.2
Fe	0.97 ± 0.37	0.98 ± 0.25	1.03 ± 0.33	1.06 ± 0.33	1.24 ± 0.24	6.3	2.2
Mg	0.54 ± 0.14	0.66 ± 0.22	0.79 ± 0.24	0.79 ± 0.34	0.82 ± 0.14	0.1	1.1
Ni	0.10 ± 0.06	0.09 ± 0.05	0.10 ± 0.04	0.09 ± 0.03	0.08 ± 0.05	7.1	15.6
Pb	0.19 ± 0.04	0.21 ± 0.08	0.24 ± 0.07	0.17 ± 0.05	0.36 ± 0.08	22.9	1.1
Se	0.09 ± 0.06	0.10 ± 0.08	0.12 ± 0.02	0.03 ± 0.02	0.03 ± 0.01	32.1	30.0
V	0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.02	0.02 ± 0.02	6.3	22.2
Zn	0.28 ± 0.09	0.37 ± 0.07	0.86 ± 0.15	0.35 ± 0.06	0.39 ± 0.08	2.1	0.0

ND = Not Detected, M = Monsoon, PM = Post-monsoon, W = Winter, PS = Pre-summer, S = summer, MDL = method detection limit, BDL = below detection limit.

Fig. 3. Seasonal average major elemental concentrations.

Fig. 4. Seasonal average minor elemental concentrations.

Kanpur in 2006 and leaded gasoline is banned at majority of urban areas but over the years Pb emitted by the vehicles driven by leaded fuel has eventually become a part of the road dust (Artaxo *et al.*, 1999) and during summer season it gets resuspended resulting in higher Pb concentration in the ambient air. The other possibility of still higher Pb concentration is that Pb is originating from tailpipes of the vehicles still using leaded gasoline and running in rural and semi-urban areas where strict compliance has not been enforced yet. Another source for Pb is from the wearing of vehicular tires (Aatmeeyata *et al.*, 2009). This can very well support the measured higher concentrations for Pb during the summertime. Vanadium (V) (Fig. 4) also shows similar kinds of trend as Pb. In a study carried out in Japan, it was reported that V had a trimodal distribution (Wang *et al.*, 2006b) with peak concentrations at one submicron fraction (0.65–0.43 μm) and two supermicron fractions (2.1–1.1 μm and 4.7–7 μm) indicating diverse emission sources. It was also reported that most of the fine fraction V (almost 65% of total fine V concentration) was contributed by oil combustion. Since this type of source is absent in the near vicinity of IIT Kanpur, so it can be suggested that the measured V at this sampling site is either coming from any far off emission source or originating from other sources like paved road dusts (US EPA, Speciate, Version 3.2) etc. which may explain it's higher concentrations during Pre-Summer and Summer seasons. Arsenic (As) was detected only in winter season, since As is a very volatile element (Jerome and Cliff, 1987) so may be during other seasons it remains in gaseous form and only during the winter season it condenses onto the PM surface. Another reason could be that during winter season there were lots of wood/biomass burning activities which also contribute to As emission (Jerome and Cliff, 1987). Co was not detected in any of the samples and this is likely due to the fact that it is mostly associated with coarser size fractions with peak concentrations observed for 3.3–7 μm (Wang *et al.*, 2006b).

Enrichment Factor of Elements in Different Seasons

Enrichment factor (EF) of elements in different particle fractions was determined by comparing the concentration of each element against the concentration of a reference (crustal) element to obtain a preliminary idea about possible sources of different elements – crustal or anthropogenic. Usually Si, Al or Fe is used as the reference element, but there is no universally accepted rule for its choice. In this present study, Fe was used as a reference element as done previously by other investigators (Bilos *et al.*, 2001; Manoli *et al.*, 2002). The appropriateness can be found from its more significant distribution in coarse particles (83%) than other metals, with very low contribution from non-crustal inputs (Wang *et al.*, 2006a). The abundance ([E/R] $_{Crust}$ values) of elements in the earth crust was taken from Wang *et al.* (2006a).

The EF$_{Crust}$ of element E in aerosols is defined as below:

$$EF_{Crust} = [E/R]_{Air}/[E/R]_{Crust} \qquad (5)$$

where R is a reference element (R = Fe for this present study) of crustal material and $[E/R]_{Air}$ is the concentration ratio of E to R in collected aerosol sample, and $[E/R]_{Crust}$ is the concentration ratio of E to R in the Earth's crust. If EF$_{Crust}$ approaches unity, crustal soils are most likely the predominant source of element E. Operationally, if EF$_{Crust}$ value is over 10, the element would have a significant contribution from non-crustal sources (Wang *et al.*, 2006a). The EF$_{Crust}$ values of individual elements in PM$_1$ size fractions for the current study are presented in Table 3.

From the above table it can be said that Ca, Mg, Fe are mainly of crustal origin as their EF$_{Crust}$ values are much below 10. EF$_{Crust}$ values of V is also lower than 10 which indicates that V detected in the samples may have originated from road/crustal dusts, similar values were obtained for V in a study carried out in Korea (Lee *et al.*, 2002). EF$_{Crust}$ values of elements – Cd, Cr, Ni, Pb, Zn, As, Se, Cu are very high indicating their possible anthropogenic origin. Especially, the EF$_{Crust}$ values of anthropogenic elements like – Cd, Cr, Ni, Pb, Cu, Se are much higher than the values reported for PM$_{2.5}$ (Lee *et al.*, 2002; Zhang and Sun, 2006), PM$_{1.6}$ (Srivastava *et al.*, 2008)

Table 3. Seasonal EF$_{Crust}$ values for different elements.

Element	Season				
	M	PM	W	PS	S
As	ND	ND	301	ND	ND
Ca	1.38	2.3	1.84	2.11	2.16
Cd	16500	19200	21679	8366	7419
Cr	23	62	190	173	76
Cu	198	197	294	169	127
Fe	1	1	1	1	1
Mg	1.32	2.32	1.67	2.34	1.57
Ni	64	63	74	57	46
Pb	760	780	790	592	1125
Se	93000	125600	115780	24000	14000
V	2.2	6	4.05	6.24	5.3
Zn	210	273	546	220	229

which indicates that there is a significant enrichment of these toxic anthropogenic elements taking place in PM_1 in this part of the world. Again this analysis suggests non-tailpipe sources for Pb (Aatmeeyata *et al.*, 2009). For most of the anthropogenic elements, EF_{crust} values decreases from winter to summer which indicates that during summer due to the huge resuspension of crustal dust, the contributions from anthropogenic sources are kind of overshadowed.

Anion Concentrations

In submicron fraction, water soluble anions contribute a significant portion to the overall PM_1 mass (Pérez *et al.*, 2008). Like PM_1 mass and elemental concentrations, anions too have shown significant variability in different seasons (Table 4, Figs. 5, 6) with highest overall concentrations in winter and lowest during monsoon, the same trend was reported in previous studies (Wang *et al.*, 2006a). The main reason for highest concentrations of anions during winter can be attributed to lower temperature which favored the transformation of anions from gas phase to particle phase and also due to lower mixing height and increased anthropogenic activities. Lowest concentrations measured during monsoon period can be attributed to the washout of PM containing water soluble anions by rainfall (Sanhueza *et al.*, 1988; Wang *et al.*, 2006a; Budhavant *et al.*, 2009). Among the water

soluble anions, sulfate (SO_4^{2-}) and nitrate (NO_3^-) were the predominant anion species contributing about 80%–90% of total anion concentration, which is in agreement with previous studies (Wang *et al.*, 2006a; Sanhueza and Rondon, 1988).

NO_3^- and SO_4^{2-} both show highest concentrations during winter season (Fig. 5). NO_3^- is generally formed from the oxidation of NO_x (Wang *et al.*, 2006a) and its subsequent reaction with ammonia (Seinfeld and Pandis, 1998) leads to ammonium nitrate particle formation. From previous studies (Han *et al.*, 2008), it can also be said that most of the fine particulate NO_3^- and SO_4^{2-} exists as ammonium nitrate (NH_4NO_3) and ammonium sulfate [$(NH_4)_2SO_4$]. The lower temperature in winter would also favor the shift from the gas phase of nitric acid to the particle phase of nitrate, which could lead to the high concentration of NO_3^- in winter (Wang *et al.*, 2006a). In summer season, lower concentrations can be attributed to volatilization of NH_4NO_3 as volatilization of NH_4NO_3 increases as temperature increases and relative humidity (RH) decreases (Mariani and Mello, 2007; Seinfeld and Pandis, 1998). In addition, water soluble nitrate (NO_3^-) is subjected to higher sampling losses at higher temperatures (> 35ºC).

The high SO_4^{2-} concentrations in winter would indicate that SO_4^{2-} in this season was mostly originating from the local emission sources like – vehicular emission, paved road dust, biomass burning etc. (US EPA, Speciate, Version 3.2),

Table 4. Seasonal anion concentrations (±Std).

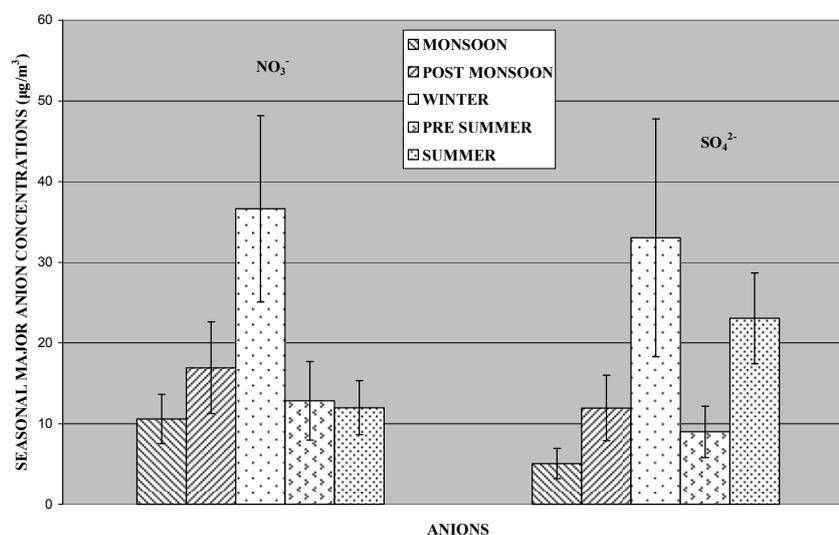| Anions	Season				
	M (µg/m³)	PM (µg/m³)	W (µg/m³)	PS (µg/m³)	S (µg/m³)
Cl^-	0.22 ± 0.11	0.61 ± 0.21	2.80 ± 0.42	0.84 ± 0.42	0.64 ± 0.25
F^-	0.05 ± 0.01	0.29 ± 0.2	0.26 ± 0.21	0.16 ± 0.1	0.16 ± 0.11
NO_3^-	10.56 ± 3.05	16.92 ± 5.67	36.61 ± 11.51	12.83 ± 4.86	11.97 ± 3.34
PO_4^{3-}	ND	0.07 ± 0.05	0.29 ± 0.12	0.09 ± 0.01	0.39 ± 0.11
SO_4^{2-}	5.05 ± 1.88	11.93 ± 4.05	33.02 ± 14.72	8.97 ± 3.19	23.04 ± 5.62

Std = Standard Deviation

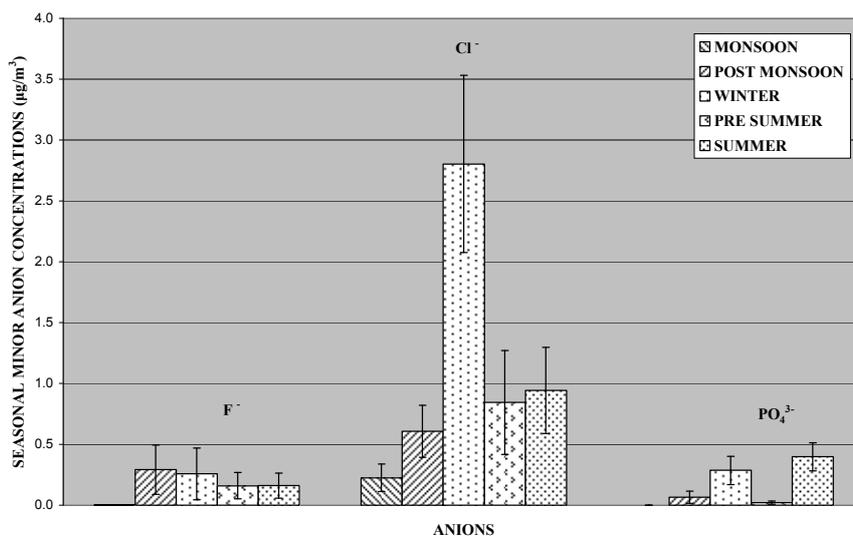**Fig.5.** Seasonal major anion concentrations.

Fig. 6. Seasonal average minor anion concentrations.

and it can be also related to the poor dispersion and the lower rate of removal via wet deposition. Also, ammonium suphate is much less volatile than NH_4NO_3 (Utsunomiya and Shinji, 1996) and remains in the particulate phase which may explain the observed moderately higher SO_4^{2-} concentrations found in this study.

Concentrations of chloride (Cl^-) and fluoride ion (F^-) also followed a similar trend (Fig. 6) as of NO_3^- and SO_4^{2-} with highest values in winter and lowest values during monsoon season. However, the Cl^- concentrations were much lower than those of NO_3^- and SO_4^{2-}; the reason can be attributed to the size distribution of Cl^- ion. In previous studies, it has been reported that Cl^- is mostly found in coarser PM fractions (> $PM_{2.5}$) (Sanhueza and Rondon, 1988; Willison *et al.*, 1984) and it is also reported that ammonium chloride (NH_4Cl) is the main Cl^- containing compound in the fine particle size fraction in inland locations (Willison *et al.*, 1984). Since, Kanpur is located in the interior part of India and away from sea, so the Cl^- in this region may be originated from neutralization of atmospheric NH_3 by HCl originated from coal burning and other combustion processes (Willison *et al.*, 1989). During summer, volatilization of NH_4Cl may lead to the lower concentration of Cl^- (Willison *et al.*, 1989).

Fluoride ions mainly originated from phosphate fertilizer generation (Hsu and Chang, 2008), marine aerosol etc. (US-EPA, Speciate, Version 3.2). Since many of these sources were not present in the near vicinity of the current study site, so F^- concentrations in all the seasons were found to be very low, and during monsoon season F^- concentration was found to be lowest. In previous studies (Hsu and Chang, 2008), it has been reported that in presence of high relative humidity F^- is mostly concentrated in 3.8–10 µm size ranges so may be due to this reason and due to washout by rainfall, F^- concentration was found to be lowest in monsoon. PO_4^{3-} (phosphate) which is mainly originating from fertilizer production, crustal phosphate rocks (US EPA, Speciate, Version 3.2) shows a somewhat different trend, PO_4^{3-} concentration is

maximum during summer followed by winter while lowest concentration is observed during monsoon period. It has been reported in previous studies (Sanhueza and Rondon, 1988), that during rainy season PO_4^{3-} is associated with coarser size fractions (> 3 µm) while during summer and winter season it is associated with finer size fractions (~0.5 µm).

Based on overall chemical analysis, it can be said that about 60% of the PM_1 mass remained unidentified (Fig. 7) in this present study which may mainly consists of organic and elemental carbon, cations (Na^+, K^+, NH_4^+, etc.), other major refractory elements like – Al, Si etc., their oxides and particle bound water. Elements contributed to about 5% of the total PM_1 mass and water soluble inorganic anions contributed to 35% of the PM_1 mass which is in good agreement with the values reported in a study carried out in Barcelona, Spain (Pérez *et al.*, 2008). On seasonal basis it can be seen (Fig. 8) that during winter and summer maximum portion of PM_1 mass remain unidentified. It has been reported in previous studies that during winter season concentrations of different organic fractions were much higher than other seasons (Pérez *et al.*, 2008), while in summer season due to increased photochemical activity secondary organic carbon production is increased and since these species were not measured in the current study therefore most of the PM_1 mass remained unidentified.

From the overall results, it can be said that effect of transported aerosol is not very significant in winter. Except Zn, As (due to high rate of local biomass burning activities) all other anthropogenic elements showed very little increase in their winter concentration, whereas crustal elemental concentrations decreased due to of lack of turbulence. On the other hand, concentrations of anionic species increased due to lower temperatures and favorable humidity conditions accelerating the gas to particle conversion. In summer season, higher crustal element concentration may be contributed by long distance transported aerosol specially considering a number of dust storm events occurred in that period.
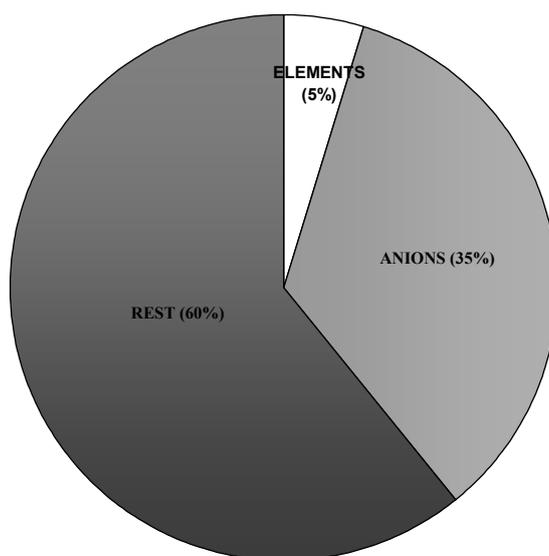
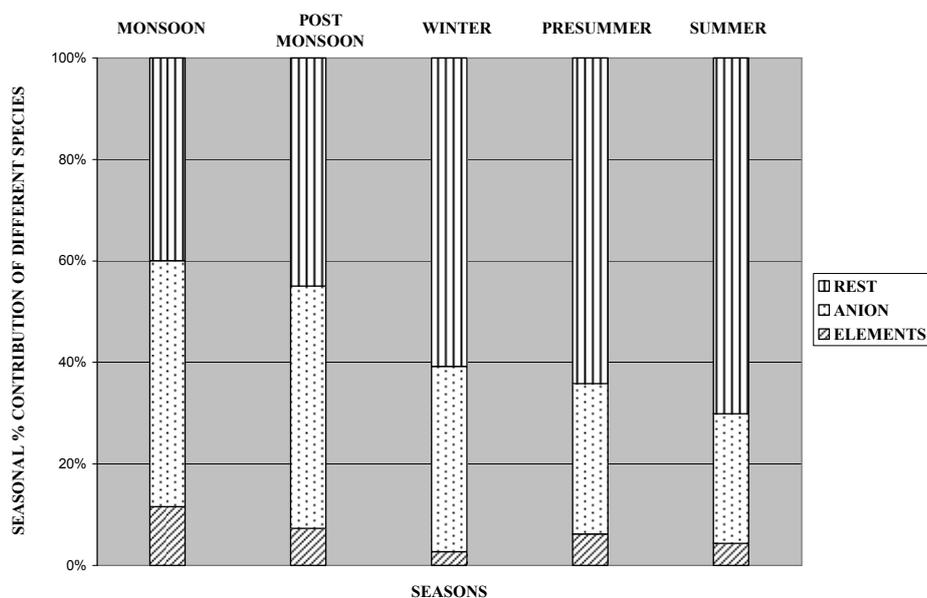**Fig. 7.** *%* contribution of different species in overall PM$_1$ mass.

Fig. 8. % contribution of different species in seasonal PM$_1$ mass.

Source Apportionment of PM$_1$
Source Identification

There are different methods of extracting the factors from a set of data like-Canonical Factor Analysis, Principal Components Analysis (PCA), Common Factor Analysis (CFA). In most of the studies PCA is used for factor extraction, so in the present study we followed PCA method of factor analysis using SPSS software package (Version 15). SPSS extracted four factors associated with eigen values > 1 which are shown in Table 5. Please note that not all the chemical species were included in the final analyses; species with large number of BDL values and higher variation were excluded-As, Co, F$^-$, and PO$_4$$^{3-}$. BDL values were also replaced with half MDL values.

Factor 1: This factor shows high loadings on Cu, Zn, Pb, these elements are very good indicators of vehicular

emission (Fung and Wong, 1995) sources, Cu can be emitted from break linings of a vehicle especially during congested traffic condition, Zn can be emitted from tire wear (US EPA Speciate, Version 3.2) and Pb can be emitted from leaded fuel. So this factor indicates vehicular emission.

Factor 2: This factor shows high loadings on Ca, Mg, Fe, Pb and moderate loadings on Zn, Cr, V, so this factor indicates paved road dust. Since Ca, Mg, Fe are predominantly of crustal origin and over the years Zn, Pb emitted from vehicular exhaust and also from tires may have become a part of road dust.

Factor 3: This factor shows high loadings on SO$_4$$^{2-}$ and NO$_3$$^-$ which are mainly originated from secondary/ photochemical reactions of different chemical species like-NO$_X$, SO$_2$ etc (Saolapurkar and Sharma, 2006). So, this factor indicates secondary fine particles sources.

Factor 4: This factor shows high loadings on Cd, Se, Pb and Cl⁻ which are very good indicator of coal combustion (Saolapurkar and Sharma, 2006). So, this source indicates coal combustion.

These 4 factors explained almost 94% variance of total data set (Table 6) that means the PCA analyses worked well for the obtained data set and extracted four factors or sources that are the major contributors to overall PM_1 mass concentrations in this part of the world.

Source Composition Obtained from UNMIX

The stand-alone EPA UNMIX version 6.0 was used in this study. In the UNMIX analysis, exactly the same four major sources were identified as with the PCA method. From the source apportionment results (Fig. 9), it is clear that secondary sources are the predominant contributor in submicron aerosol mass which is in good agreement with other source apportionment studies carried out in Beijing, China (Song *et al.*, 2006) and Gwangju, Korea (Lee *et al.*, 2002). Vehicular emission also contribute (24%) to a major portion of the PM_1 mass, similar to the trend reported for $PM_{1.6}$ in a study carried out in New Delhi,

(Srivastava and Jain, 2007). Paved road dust and coal combustion were the other two major sources identified.

The predicted Vs measured PM_1 concentrations plot (Fig. 10) shows that the UNMIX model worked well and the predicted and measured PM_1 mass concentrations are in good agreement.

In this study, number of collected samples was not large enough to do a seasonal source apportionment which could have provided us with a better idea of different sources dominating in a particular season. Also, since a large portion of PM_1 mass was chemically unidentified (OC and EC fractions) so a complete PM_1 mass closure or an ion balance (ammonium ion was not analyzed) could not be performed.

SUMMARY AND CONCLUSIONS

Although IITK is free from any industrial activity and the vehicle density inside the campus is also low, still higher concentrations of PM_1 were observed indicating its transport by wind from far off emission sources. Even after introduction of CNG replacing conventional fossil fuel, a

Table 5. Rotated Factor Component Matrix.

Species	Factors			
	1	2	3	4
Ca	.165	**.827**	.108	.110
Mg	.057	**.639**	.088	−.02
Cu	**.856**	−.015	.114	.132
Zn	**.724**	**.348**	.053	.209
NO_3^-	.204	.252	**.871**	−.003
SO_4^{2-}	.019	.097	**.727**	.027
Cl^-	−.051	.235	.12	**.403**
Se	−.038	.162	.043	**.51**
Cr	.011	**.434**	−.034	−.042
Fe	.23	**.627**	.081	.187
Cd	.074	.077	.037	**.846**
Pb	**.524**	**.649**	.08	**.476**
Ni	.112	−.187	−.012	0.56
V	.006	**.345**	.088	.036
	Vehicular Emission	Paved Road Dust	Secondary Sources	Coal Combustion

Table 6. % variance explained by extracted factors.

Component	Initial Eigenvalues			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.073	50.912	50.912	3.012	31.776	32.776
2	1.784	22.304	73.216	2.601	27.518	59.294
3	1.512	15.148	88.364	1.366	26.070	84.364
4	1.227	6.585	94.949	1.135	10.451	94.815
5	0.663	3.290	98.239			
6	0.580	0.999	99.238			
7	0.355	0.686	99.924			
8	0.260	0.076	100.000			
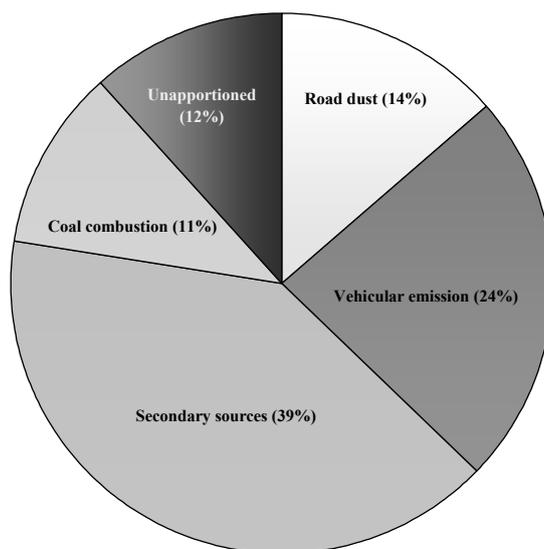
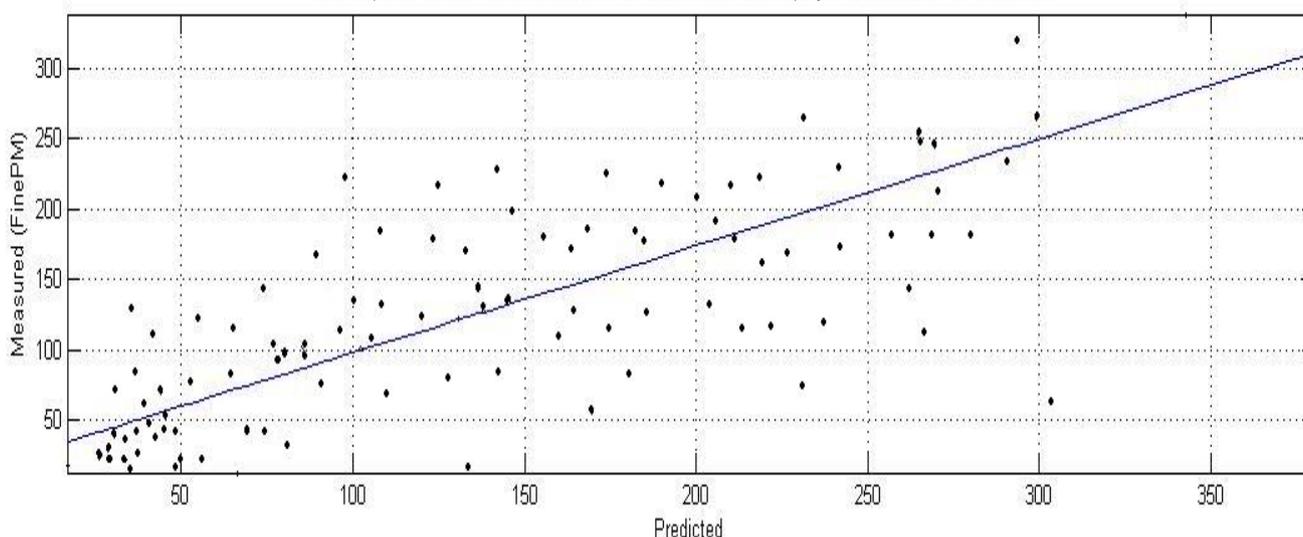**Fig. 9.** % contribution of different sources in overall PM$_1$ mass.

Fig. 10. Measured Vs predicted PM1 concentrations.

substantial amount of Pb, being emitted from various fugitive sources including tires, is present in the atmosphere of Kanpur and still pose a significant health threat. In addition, a significant enrichment of toxic anthropogenic elements is taking place in the PM$_1$ in this region and this is a matter of serious health concerns. For all the species especially originating from anthropogenic activities, concentrations were higher during winter (except Pb and crustal elements) and lower during monsoon or summer. Even within the submicron fraction, crustal elements were present in significantly higher concentrations. Water soluble inorganic anions contributed to almost 35–40% of overall PM$_1$ mass and among those anions nitrate and sulfate were the two most predominant species. Secondary sources indicating gas to particle conversion were found to be the main contributor to PM$_1$ mass.

REFERENCES

Aatmeeyata, Kaul, D.S. and Sharma, M. (2009). Traffic Generated Non-Exhaust Particulate Emissions from Concrete Pavement: A Mass and Particle Size Study for Two-Wheelers and Small Cars. *Atmos. Environ.* 43: 5691–5697.

Artaxo, P., Oyola, P. and Martinez, R. (1999). Aerosol Composition and Source Apportionment in Santiago de Chile. *Nucl. Instrum. Methods Phys. Res.* 150: 409–416.

Balakrishna, G. and Pervez, S. (2009). Source Apportionment of Atmospheric Dust Fallout in an Urban-Industrial Environment in India. *Aerosol Air Qual. Res.* 9: 359–367.

Bilos, C., Colombo, J.C., Skorupka, C.N. and Presa, M.J.R. (2001). Sources, Distribution and Variability of

Airborne Trace Metals in La Plata City Area, Argentina. *Environ. Pollut.* 111: 149–158.

Brook, J.R., Dann, T.F. and Burnett, R.T. (1997). The Relationship among TSP, PM_{10}, $PM_{2.5}$, and Inorganic Constituents of Atmospheric Particulate Matter at Multiple Canadian Locations. *J. Air Waste Manage. Assoc.* 47: 2–19.

Budhavant, K.B., Rao, P.S.P., Safai, P.D. and Ali, K. (2009). Chemistry of Monsoon and Post-Monsoon Rains at a High Altitude Location, Sinhabad, India. *Aerosol Air Qual. Res.* 9: 65-79.

Chan, Y.C., Simpson, R.W., Mctainsh, G.H., Vowles, P.D., Cohen, D.D. and Bailey, G.M. (1997). Characterization of Chemical Species in $PM_{2.5}$ and PM_{10} Aerosols in Brisbane, Australia. *Atmos. Environ.* 31: 2061–2080.

Demokritou, P., Gupta, T. and Koutrakis, P. (2002). Development and Laboratory Performance Evaluation of a Personal Cascade Impactor. *J. Air Waste Manage. Assoc.* 52: 1230–1237.

Fung, Y.S. and Wong, W.Y. (1995). Apportionment of Air Pollution Sources by Receptor Models in Hong Kong. *Atmos. Environ.* 29: 2041–2048.

Gupta, T., Demokritou, P. and Koutrakis, P. (2004). Development and Evaluation of an Ultrafine Particle Concentrator for Inhalation Toxicological Studies. *Inhalation Toxicol.* 16: 851–862.

Gupta, T., Chakraborty, A. and Ujinwal, K.K. (2009). Development and Performance Evaluation of an Indigenously Developed Air Sampler Designed to Collect Submicron Aerosol. *Annals INAE*, in press.

Han, Y.J, Tae, S.K. and Kim, H. (2008). Ionic Constituents and Source Analysis of $PM_{2.5}$ in Three Korean Cities. *Atmos. Environ.* 42: 4735–4746.

Haobo, W. and Shooter, D. (2001). Water Soluble Ions of Atmospheric Aerosols in Three New Zealand Cities: Seasonal Changes and Sources. *Atmos. Environ.* 35: 6031–6040.

Hare, C.T. (1977). *Characterization of Diesel Engine Gaseous Particulate Matter*, Final Report Prepared by South West Research Contract no. 62-02-1977.

Henry, R.C. (2000). UNMIX Version 2 Manual. p. 18–19.

Henry, R.C. (2003). Multivariate Receptor Modeling by N-Dimensional Edge Detection. *Chemom. Intell. Lab. Syst.* 65: 179–189.

Hildemann, L.M., Markowski, G.R., Jones, M.C. and Cass, G.R. (1991). Submicrometer Aerosol Mass Distributions of Emissions from Boilers, Fireplaces, Automobiles, Diesel Trucks, and Meat-Cooking Operations. *Aerosol Sci. Technol.* 14: 138–152.

Hopke, P.K., Kothai, P., Saradhi, I.V., Prathibha, P., Pandit, G.G. and Puranik, V.D. (2008). Source Apportionment of Coarse and Fine Particulate Matter at Navi Mumbai, India. *Aerosol Air Qual. Res.* 3: 18–26.

Hsu, Y.M. and Chang, Y.W. (2008). Size Distribution, Chemical Composition and Acidity of Mist Aerosols in Fertilizer Manufacturing Facilities in Florida. *J. Aerosol Sci.* 39: 127–140.

Jerome, O.N. and Cliff, I.D. (1987). *Toxic Metals in the Atmosphere*, Wiley Publication, John Wiley and Sons.

Junker, M., Kasper, M., Roosli, M., Camenzind, M., Kunzli, N., Monn, C., Theis, G. and Braun, C. (2000). Airborne Particle Number Profiles, Particle Mass Distribution and Particle Bound PAH Concentrations within the City Environment of Basle: An Assessment of the BRISKA Project. *Atmos. Environ.* 43: 3171–3181.

Kim, E., Hopke, P.K. and Qin, Y. (2005). Estimation of Organic Carbon Blank Values and Error Structures of the Speciation Trends Network Data for Source Apportionment. *J. Air Waste Manage. Assoc.* 55: 1190–1199.

Kim, E. and Hopke, P.K. (2007). Source Characterization of Ambient Fine Particles in the Los Angeles Basin. *J. Environ. Eng. Sci.* 6: 343–353.

Kleeman, M.J. and Cass, G.R. (1998). Source Contributions to the Size and Composition Distribution of Urban Particulate Air Pollution. *Atmos. Environ.* 32: 2803–2816.

Kyotani, T. and Iwatsuki, M. (2002). Characterization of Soluble and Insoluble Components in $PM_{2.5}$ and PM_{10} Fractions of Airborne Particulate Matter in Kofu City, Japan. *Atmos. Environ.* 36: 639–649.

Larsen, I.R.K. and Baker, J.E. (2003). Source Apportionment of Polycyclic Aromatic Hydrocarbons in the Urban Atmosphere: A Comparison of Three Methods. *Environ. Sci. Technol.* 37: 1873–1881.

Lee, J.H., Jang, M.S., Lim, J.M., Kim, K.H. and Chung, Y.S. (2002). *Characteristics of Trace Metals in Fine Ambient Particles in Korea*. Project Committee Meeting and Conference of Project Participants and End Users, 11-15th Nov. 2002, Beijing, China.

Lewis, C.W., Norris, G.A., Conner, T.L. and Henry, R.C. (2003). Source Apportionment of Phoenix $PM_{2.5}$ Aerosol with the UNMIX Receptor Model. *J. Air Waste Manage. Assoc.* 53: 325–338.

Manoli, E., Voutsa, D. and Samara, C. (2002). Chemical Characterization and Source Identification and Apportionment of Fine and Coarse Air Particles in Thessaloniki, Greece. *Atmos. Environ.* 36: 949–961.

Mariani, L.R. and Mello, W. (2007). $PM_{2.5-10}$, $PM_{2.5}$ and Associated Water-Soluble Inorganic Species at a Coastal Urban Site in the Metropolitan Region of Rio de Janeiro. *Atmos. Environ.* 41: 2887–2892.

Maykut, N.N., Lewtas, J., Kim, E. and Larson, T.V. (2003). Source Apportionment of $PM_{2.5}$ at an Urban IMPROVE Site in Seattle, Washington. *Environ. Sci. Technol.* 37: 5135–5142.

Mukerjee, S., Norris, G.A., Smith, L.A., Noble, C.A., Neas, L.M., Ozkaynak, A.H. and Gonzales, M. (2004). Receptor Model Comparisons and Wind Direction Analyses of Volatile Organic Compounds and Submicrometer Particles in an Arid, Binational, Urban Air Shed. *Environ. Sci. Technol.* 38: 2317–2327.

Pérez, N., Pey, J., Querol, X., Alastuey, A., López, J.M. and Viana, M. (2008). Partitioning of Major and Trace Components in PM_{10}–$PM_{2.5}$–PM_1 at an Urban Site in Southern Europe. *Atmos. Environ.* 42: 1677–1691.

Pope III, C.A. (2000). Review: Epidemiological Basis for Particulate Air Pollution Health Standards. *Aerosol Sci. Technol.* 32: 4–14.

Sanhueza, E. and Rondon, A. (1988). Particle-Size Distribution of Inorganic Water Soluble Ions in the Venezuelan Savannah Atmosphere during Burning and Nonburning Periods. *J. Atmos. Chem.* 7: 369–388.

Saolapurkar, T. and Sharma, M. (2006). *Characterization of PM₁₀ and Formation of Secondary Particles: A Source Apportionment Study*, *M.Tech thesis*, IIT Kanpur.

Schauer, J.J., Rogge, W., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T. (1996). Source Apportionment of Airborne Particulate Matter using Organic Compounds as Tracers. *Atmos. Environ.* 30: 3837–3855.

Schroeder, W.H., Dohson, M., Kane, D.M. and Johnson, N.D. (1987). Toxic Trace Elements Associated with Airborne Particulate Matter: A Review. *J. Air Waste Manage. Assoc.* 33: 1267–1285.

Schwartz, J., Dockery, D.W. and Neas, L.M. (1996). Is Daily Mortality Associated Specially with Fine Particles? *J. Air Waste Manage. Assoc.* 46: 927–939.

Seinfeld, J.H. and Pandis, S.N. (1998). *Atmospheric Chemistry and Physics*, Wiley, New York.

Song, Y., Shaodong, X., Yuanhang, Z., Limin, Z., Lynn, G. S. and Mei, Z. (2006). Source Apportionment of PM₂.₅ in Beijing Using Principal Component Analysis/ Absolute Principal Component Scores and UNMIX. *Sci. Total Environ.* 372: 278–286.

Srivastava, A. and Jain V.K. (2007). Seasonal Trends in Coarse and Fine Particle Sources in Delhi by the Chemical Mass Balance Receptor Model. *J. Hazard. Mater.* 144: 283–291.

Srivastava, A., Gupta, S. and Jain, V.K. (2008). Wintertime Size Distribution and Source Apportionment of Total Suspended Particulate Matter and Associated Metals in Delhi. *Atmos. Res.* 13: 324–330.

Tare, V., Tripathi, S.N., Chinnam, N., Srivastava, A.K., Dey, S., Manar, M., Kanawade, V.K., Agarwal, A., Kishore, S., Lal, R.B. and Sharma, M. (2006). Measurement of Atmospheric Parameters during Indian Space Research Organization Geosphere Biosphere Program Land Campaign II at a Typical Location in Ganga Basin: 2. Chemical Properties. *J. Geophys. Res.* 111: D23210, doi: 10.1029/2006JD007279.

US-EPA, SPECIATE, Version 3.2. *http://www.inchem.org*

Utsunomiya, A. and Shinji, W. (1996). Temperature and Humidity Dependence on Aerosol Composition in the Northern Kyushu, Japan. *Atmos. Environ.* 30: 2379–2386.

Wang, Y., Guoshun, Z., Xingying, Z., Kan, H., Chang, X., Aohan, Jianmin, C. and Zhisheng, A. (2006a). The Ion Chemistry, Seasonal Cycle, and Sources of PM2.5 and TSP Aerosol in Shanghai. *Atmos. Environ.* 40: 2935–2952.

Wang, X., Tsutomu, S. and Baoshan, X. (2006b). Size Distribution and Anthropogenic Source Apportionment of Airborne Trace Metals in Kanazawa, Japan. *Chemosphere* 65: 2440–2448.

Willison, M.J, Clarke, A.G. and Zeki, E.M. (1984). Seasonal Variation in Atmospheric Aerosol Concentration and Composition at Urban and Rural Sites in Northern England. *Atmos. Environ.* 19: 1081–1089.

Willison, M.J., Clarke, A.G. and Zeki, E.M. (1989). Chloride Aerosols in Central Northern England. *Atmos. Environ.* 23: 2231–2239.

Zhang, W. and Sun, Y.L. (2006). Characteristics and Seasonal Variations of PM₂.₅, PM₁₀, and TSP Aerosol in Beijing. *Biomed. Environ. Sci.* 19: 461–468.