Apportioning the Secondary Particles in Atmospheric PM$_{10}$ in a Residential Area

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Abstract- Quality (characteristics) and quantity (concentrations) of atmospheric particles are critical in neutralizing the atmospheric acidity and aiding to formation of secondary particles. To examine the formation of secondary particles, an integrated approach involving seasonal measurements and characterization of particulate matter (PM) is adopted. 109 PM$_{10}$ samples were collected at Kidwai Nagar during 2000-2001 in a three season study. The concentration of metals and water-soluble ions in collected samples were determined for source apportionment estimations. Soil-road dust (26-36%) and inorganic secondary particles (4-11%) were two important PM$_{10}$ sources. It was found that role of ammonia was crucial in formation of secondary particles.

Keywords: apportionment analysis, particulate matter, secondary particles, residential area, seasonal variation, factor analysis, ambient air sampling

INTRODUCTION

India has set a target of 215 804 MW power generation capacity by March 2012 from the present level of 100 010 MW [1]. Thermal power generation will be the main contributor to the overall power generation (approximately 68%). The new power plants and other industries will add to the existing emissions of SO$_2$, NO$_x$ and PM significantly. The growth situation warrants a closer examination of the impacts of emission of SO$_2$, NO$_x$, PM and their interactions. SO$_2$ and NO$_x$ are not only primary pollutants but also contribute to the formation of secondary particles in the atmosphere. Indian atmospheric conditions pose certain challenges in adopting or using the information from other sources or internationally published literature on formation of secondary particles. First, significant photochemical activities at high temperature and the second, high PM$_{10}$ (particle size less than or equal to 10μm) levels around 350 μg m^{-3} make modeling and source apportionment of secondary particles difficult.

The winter levels of PM were found to be less than those in summer at each of the seven sampling locations in Delhi during the year 1990 [2]. A five-year long study (1981-85) by the Central Pollution Control Board (CPCB) at Agra concludes that PM levels were significantly less (270 μg m^{-3} 5-year average) in winter months compared to summer months (400 μg m^{-3} 5-year average). The anthropogenic emission of PM are likely to be the same throughout the year; therefore, the variation in PM levels could be due to seasonal variation in emissions from natural sources (such as soil dust) in the atmosphere caused by variable atmospheric conditions and/ or photochemistry responsible for formation of secondary particles. Seasonal variation in temperature, humidity, wind speed, mixing height, soil moisture content, emission of ammonia etc. affects the atmospheric chemistry and particle generation (from soil)/ formation. Hence, to understand the issue of secondary particle formation and source apportionment analysis, seasonal variation of PM concentration, their characterization, and their sources have to be studied together [3], [4], [5].

The objective of present study was to understand atmospheric PM sources in a residential area for which a study was designed and completed from June 2000 to December 2001 at Kidwai Nagar (KN) in Kanpur City (longitude 88°22'E and latitude 26°26'N). Finally, the sources contributing to the PM$_{10}$ levels have been quantitatively apportioned and subsequently the role of NH$_3$, SO$_2$ and NO$_x$ in formation of PM$_{10}$ has been examined. Factor analysis-multiple regression (FA-MR) technique [6], a receptor model, was employed to source apportionment.

Experimental

Description of study area

Predominant land use pattern of study area, Kidwai Nagar in Kanpur City (Fig. 1) is residential. Kanpur City experiences three dominant seasons each year: winter (November-February), summer (March–June), and monsoon (July–October). Within 1 km radius of the study area there are markets and sizeable traffic. The study area lies about 200 m away from a National Highway (connecting

New Delhi) and experiences traffic load from heavy duty diesel vehicles (such as trucks), two stroke vehicles and diesel driven three wheelers (Vikram tempos) throughout the day.

Sampling and quality control

PM_{10} measurements were carried at a height of about 10 m (above the ground), at the roof of a house in Kidwai Nagar during the study period. The frequency of sampling was two 24-h (6 am - 6 am) samples per week in accordance with National Air Quality Monitoring Program in the country. The collected PM_{10} was analyzed quantitatively as well as qualitatively (details in Table 1). Weighing of filter papers was done in humidity-controlled room using 440 Mettler Balance with sensitivity 0.00001 g and filters were conditioned in desiccators for 24 hours before and after the sampling. High volume sampler (model: APM 450, Envirotech, New Delhi) was used for sampling PM_{10} on Whatman GF/A 8″×10″ size filter paper at a flow rate of 1 $m^3 min^{-1}$ [7]. During the sampling period, meteorological parameters were recorded using wind monitor (model: WM251, Envirotech, New Delhi).
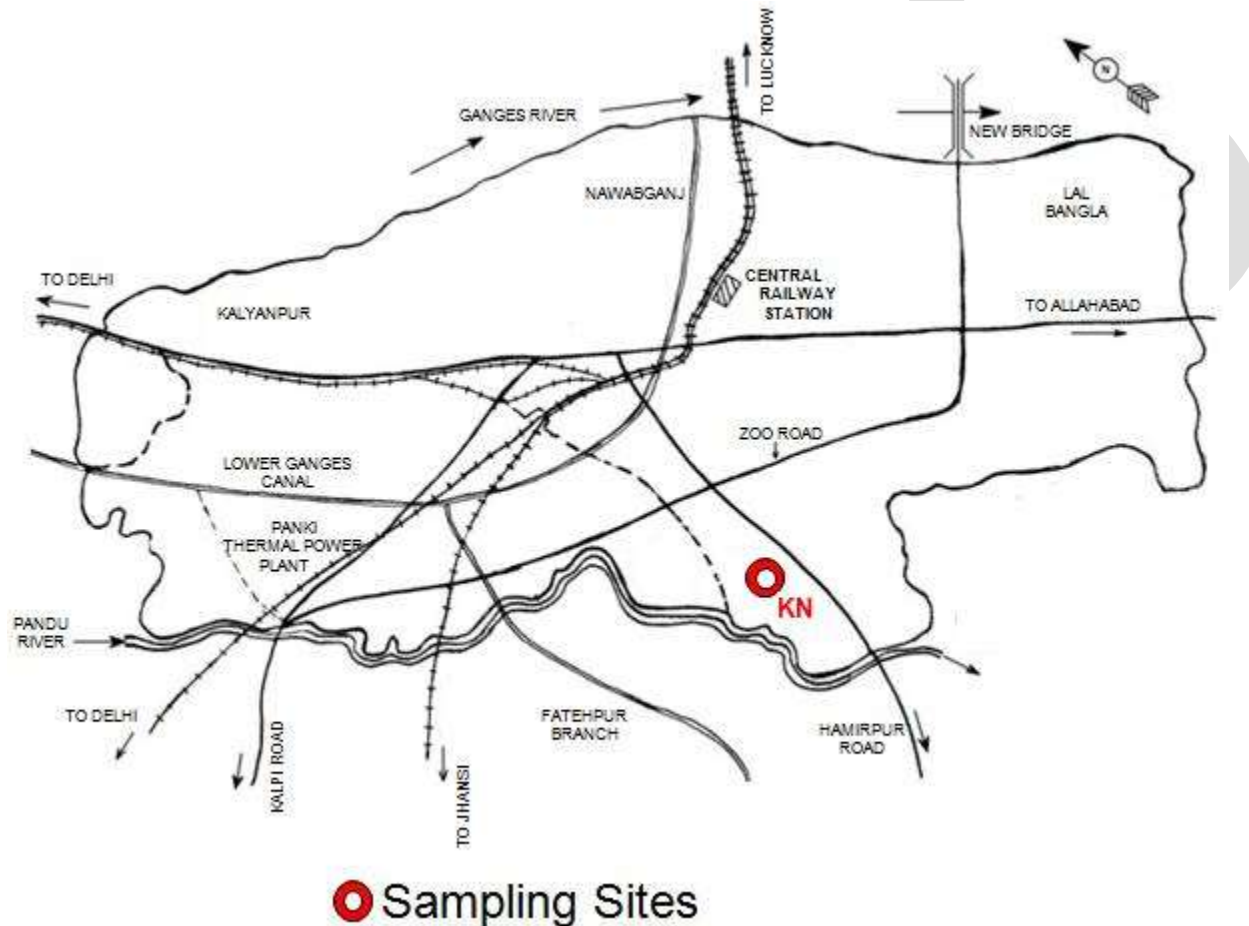
Fig. 1. Map showing location of sampling site

Table 1. Details of PM_{10} sampling

Sampling Seasons	Sampling Months	Number of Samples
Summer	June, 2000

March-June, 2001 | 32 |

Monsoon	July-October, 2000	38
	July-October, 2001	
Winter	November, 2000-February, 2001	39
	November-December, 2001	

Estimation of heavy metals and water soluble ions

Half of the filter paper was used for metal (Al, As, Ba, Ca, Fe, K, Mg, Mn and Pb) analysis and remaining half of the filter paper was used for analysis of water-soluble ions. The extraction and analysis of metals was carried out as per the USEPA method [8] using atomic absorption spectrophotometer (AAS) (Model Varian SpectrAA 220FS and GBC Avanta, Australia). The water-soluble cation NH_4^+ and anions F^-, Cl^-, NO_3^- and SO_4^{2-} were analyzed by ion chromatograph (IC) (model: Metrohm 761 compact) following the prescribed extraction procedure [9].

Source apportionment analysis

A multivariate analysis technique, FA-MR which does not require a priori information on source composition [10] is used in this study. [6] have also used one such technique of FA, principal component analysis (PCA), successfully for source apportionment of PM at traffic junctions in Mumbai and the same has been used in this study. A detailed description of the FA-MR can be seen in [11]. Varimax rotated PCA, to apportion sources of PM_{10}, has been conducted using a conventional R analysis of elemental correlations about their means using a statistical software package, SYSTAT. On the basis of measured variables of data set for each season, PC loadings and scores are determined. However, the 'absolute zero' PC scores (APCS) have subsequently been estimated for each PC by subtracting the PC score of an extra 'observation' (wherein concentrations of all the variables are assumed as zero) from PC scores of each observation [11]. Regressing observed PM_{10} concentration on APCS gave regression coefficients, which convert the APCS into PM_{10} source mass contributions for each observation. Mathematically for j^{th} observation,

$$[PM]_j = C_0 + \sum_{i=1}^{n} C_i [APCS]_j$$

where, n = number of PCs

j = 1, 2,....., m.

m = number of observations

C_0 = constant

C_i = regression coefficient

Product of corresponding $APCS_i$ for observation j and estimated regression coefficient (C_i) will give the contribution of ith source in PM_{10}.

RESULTS AND DISCUSSION

24-h average PM_{10} concentrations in ambient air measured at the sampling site are presented in Fig. 2. PM_{10} levels show significant seasonal variations, lowest concentration in monsoon and higher variability in summer. Seasonal variability in chemical composition of PM_{10} from one season to another can be observed from Table 2. Similar observations have been reported by [12] for other parts of Kanpur city. Levels of soil-derived elements (Ca, Al and Mg) are highest in summer due to dry soil, which gets airborne due to high speed winds. Indicators of secondary particles (SO_4^{2-} and NO_3^{-}) have shown marked variation in winter as compared to other seasons. The variation in quantity and chemical species concentration of PM_{10} will impact the neutralization of acid (gas phase) present in atmosphere to form secondary particles.
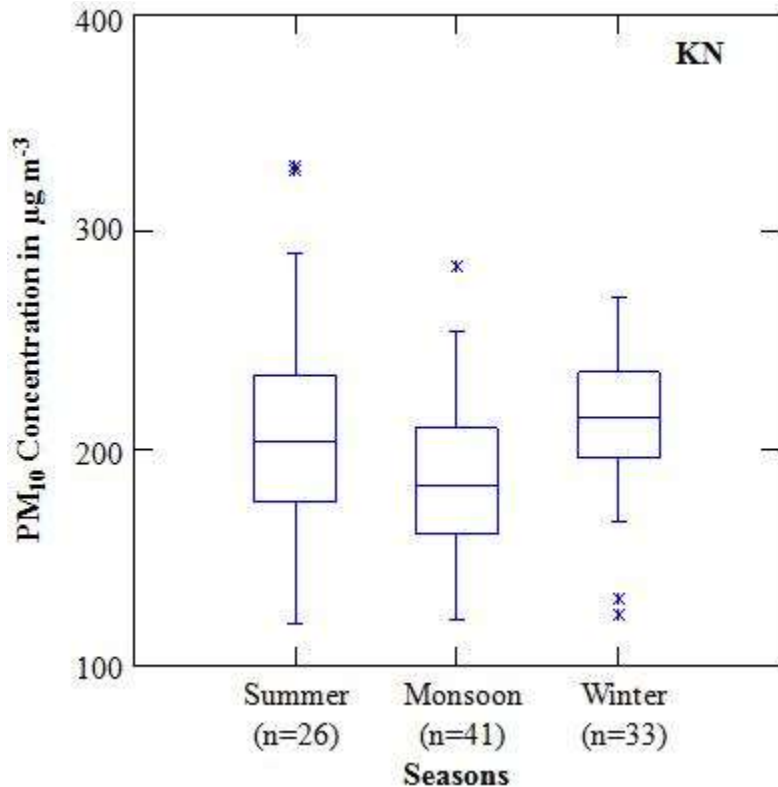

Fig. 2. 24-h average ambient air PM_{10} concentrations

Table 2. Mean ambient air (24-h) PM_{10} concentrations of various species

Species	Summer (n=32)	Monsoon (n=38)	Winter (n=39)
	($\mu g\ m^{-3}$)		
Al	26.65±16.17	10.92±4.11	8.74±2.16
As	0.16±0.13	0.04±0.02	0.12±0.07
Ba	7.40±6.62	2.03±1.17	10.67±6.33
Ca	35.76±18.84	11.80±6.11	17.12±3.61
Fe	0.46±0.26	2.19±0.85	0.88±0.24

K	5.97±7.79	2.16±2.03	4.79±2.24
Mg	4.36±2.13	6.65±3.63	2.58±0.56
Mn	0.11±0.07	0.07±0.04	0.07±0.03
Pb	0.23±0.16	0.16±0.08	0.25±0.15
NH_4^+	1.62±2.46	5.40±3.49	4.29±2.83
F^-	0.22±0.15	0.17±0.12	0.16±0.08
Cl^-	1.88±2.03	1.50±1.53	2.20±1.29
NO_3^-	7.11±9.45	18.12±10.62	14.72±8.61
SO_4^{2-}	11.24±7.21	10.74±5.01	8.97±4.11

Identification of sources contributing towards PM_{10}

Seasonal PM_{10} data were analyzed to get information of seasonal dominant contributing sources. Results of PCA along with corresponding sources are presented in Tables 3, 4 and 5 for summer, monsoon and winter seasons respectively. Based on strong loadings of various variables in factors, the sources have been identified. [13] classified the factor (PC) loadings as 'strong', 'moderate', and 'weak' corresponding to absolute loading values of >0.75, 0.75–0.50 and 0.50–0.30. Strong loading of crustal elements in all seasons can be identified as originating from crustal contribution which can be identified to soil dust emission.

Table 3. Varimax rotated PC matrix for PM_{10} during summer

| Species | Identified Emission Sources | | |
	Soil & Road Dust	Secondary Particles	Vehicular Emission and Biomass Burning
Al	**0.83**	0.16	0.40
As	**0.89**	-0.04	-0.17
Ba	0.09	-0.01	**0.95**
Ca	**0.90**	0.32	0.16
Fe	**0.80**	0.48	0.01
K	0.11	-0.03	**0.74**
Mg	**0.72**	0.54	0.21
Mn	0.30	**0.79**	0.05
Pb	0.13	**0.79**	0.13
NH_4^+	0.34	**0.74**	-0.22

F$^-$	0.49	0.50	0.06
Cl$^-$	-0.13	0.64	0.45
NO$_3^-$	0.16	**0.81**	-0.10
SO$_4^{2-}$	0.53	**0.75**	-0.13
Eigenvalue	4.24	4.33	2.01
% variance	30.30	30.89	14.34
Cumulative % variance	30.30	61.19	75.54

Table 4. Varimax rotated PC matrix for PM$_{10}$ during monsoon

Species	Identified Emission Sources		
	Soil & Road Dust	Secondary Particles	Vehicular Emission and Biomass Burning
Al	**0.91**	0.22	0.28
As	0.64	0.07	-0.61
Ba	0.21	0.20	**0.71**
Ca	**0.92**	0.26	0.14
Fe	**0.87**	0.28	0.29
K	0.25	-0.07	**0.74**
Mg	**0.87**	0.41	0.15
Mn	0.67	0.62	-0.02
Pb	**0.82**	0.36	0.06
NH$_4^+$	0.33	**0.83**	0.24
F$^-$	0.11	**0.75**	-0.09
Cl$^-$	0.21	0.6	-0.28
NO$_3^-$	0.33	**0.83**	0.24
SO$_4^{2-}$	0.33	**0.84**	0.23
Eigenvalue	5.22	4.03	1.87
% variance	37.30	28.78	13.38
Cumulative % variance	37.30	66.08	79.45

Table 5. Varimax rotated PC matrix for PM_{10} during winter

Species	Identified Emission Sources		
	Soil & Road Dust	Secondary Particles	Vehicular Emission and Biomass Burning
Al	**0.71**	0.30	0.49
As	0.30	0.43	0.23
Ba	0.38	-0.05	0.69
Ca	**0.86**	0.26	0.26
Fe	**0.70**	0.50	0.34
K	0.34	0.06	**0.76**
Mg	**0.77**	0.27	0.40
Mn	**0.70**	0.49	0.28
Pb	0.07	0.62	0.36
NH_4^+	0.27	**0.93**	0.01
F^-	**0.73**	0.04	-0.04
Cl^-	-0.17	0.57	0.65
NO_3^-	0.27	**0.93**	0.01
SO_4^{2-}	0.27	**0.93**	0.00
Eigenvalue	3.96	4.24	2.31
% variance	28.26	30.31	16.48
Cumulative % variance	28.26	58.57	75.05

In the receptor domain first factor having strong loading of crustal source consists of (i) natural windblown dust in ambient aerosol and (ii) dust present on the road/ road shoulders kept in suspension by vehicular movement. Hence, this source has been identified as 'soil and road dust'. Major portion of the percentage variance (28.3% to 30.3%) is explained by soil and road dust. The second factor explained 28.8% to 30.9% variance with high loading of NH_4^+, NO_3^- & SO_4^{2-} (secondary fine particles produced from gas to particle conversion of NH_3, NO_x & SO_2) and hence this source can be identified as the 'secondary particles'. The factor strongly loaded with Ba can be identified with vehicular emissions. Factor strongly loaded with K can be traced as a complex mixture of biomass burning. Total variance explained by various sources contributing towards PM_{10} concentrations is about 76% (during summer), 79% (during monsoon), and 75% (during winter). Soil and road dust and secondary particles are invariably present in all seasons as major sources contributing to PM_{10} and large chunk of the percentage variance (61%, 66%, and 59% during summer, monsoon and winter seasons respectively) is being explained by these two sources. Other sources (such as vehicular emission, biomass burning) are also contributing to PM_{10}, but in small proportions. This source identification is compatible with general land use pattern of the sampling site.

Quantification of sources contributing towards PM$_{10}$

To apportion the PM$_{10}$ concentrations for each observation, APCS were regressed against the observed PM$_{10}$ concentrations and the following seasonal models were obtained:

Summer season: PM$_{10}$ = 119+43*APCS1+22*APCS2+9*APCS3

Monsoon season: PM$_{10}$ = 88+40*APCS1+13*APCS2+9*APCS3

Winter season: PM$_{10}$ = 176+6*APCS1+7*APCS2+20*APCS3

Contribution of each source (factor) in individual PM$_{10}$ observations has been estimated from above models (Fig. 3). Local soil & road dust (26% to 36%) and secondary particles (4% to 11%) are the key sources in all three seasons. The study by [6] in Mumbai, India for source apportionment of PM was conducted for traffic intersection. Their study indicated major contribution of 33-41% from road dust or soil followed by contribution from vehicles and marine aerosols. The plots of estimated PM$_{10}$ concentration against observed PM$_{10}$ levels (Fig. 4) signify that estimated and observed data compare well (R^2 > 0.89).
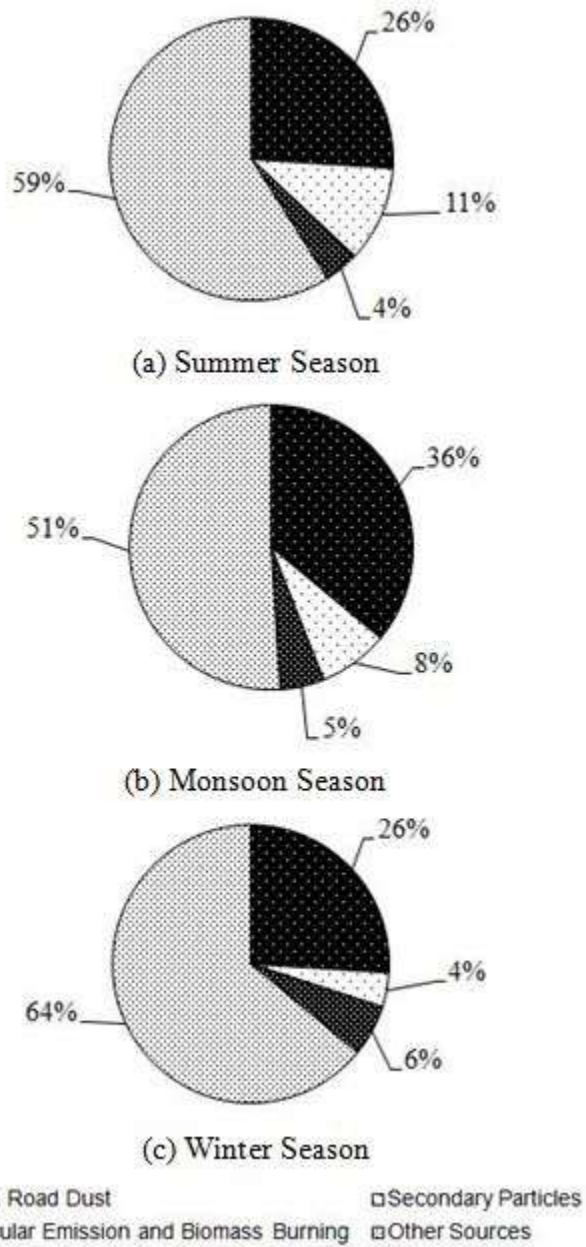
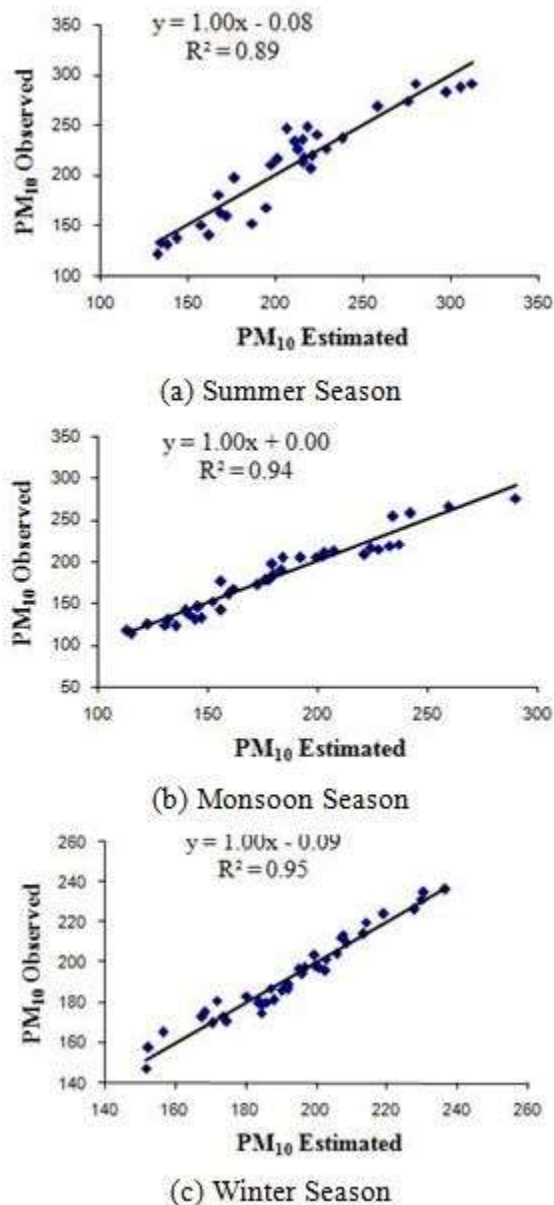**Fig. 3.** Percentage contribution of different sources towards PM_{10} levels

Fig. 4. PM_{10} observed vs. PM_{10} estimated (in $\mu g\ m^{-3}$)

Formation of secondary particles like NH_4^+, SO_4^{2-} and NO_3^- depends not only on the concentration of precursor primary pollutants (NH_3, SO_2 and NO_X) but also on temperature and relative humidity. In the present study, winter-time NO_3^- is higher than summer-time levels (Table 2). [14] have also reported lower summer time concentration of NO_3^- (as compared to winter) since particulate NH_4NO_3 will be volatile at high temperatures and low relative humidity in summer. This implies that formation of inorganic secondary particulate in winter will be higher. SO_4^{2-} concentrations will be higher in summer due to increased rate of photochemical activity and high $OH\cdot$ concentration [14]. In the present study also levels of SO_4^{2-} are higher in summer (Table 2). [6] could not resolve the contribution of secondary particles as that will require measurements of water soluble ions like NH_4^+, NO_3^- and SO_4^{2-} in atmospheric particles. In the present study, focus is to understand the formation of secondary particles and their quantitative contribution to ambient levels of PM_{10}. NH_4^+ ion is correlated strongly with both SO_4^{2-} and NO_3^- in all seasons and through FA-MR analysis, group of these ions is identified as one of the main components (of PM_{10}) in all seasons. [15] emphasized the vital role of NH_3 in neutralizing acidic substances (such as H_2SO_4, HNO_3), mostly as a sole neutralizer of acidic species, leading to formation of secondary particles. It is also reported that available NH_3 will be first taken up by H_2SO_4 and then the remaining NH_3 will be available to react with HNO_3 to produce NH_4NO_3.

Although NH_3 was not measured in the present study, the concentration of NH_3 observed at Indian Institute of Technology Kanpur by [16] as 19.09 ± 5.70 μg m^{-3} during winter and 18.69 ± 6.0 μg m^{-3} during summer can be taken. The correlation between NH_4^+ and SO_4^{2-} and NH_4^+ and NO_3^- was in the range 0.56-0.79 in winter (day and night) 0.75-0.88 (summer night); no correlation was found in summer day time. This study once again signifies the formation of secondary particles and vital role played by NH_3. It may, therefore, be concluded that NH_3 is playing a significant role in formation of secondary particles that has been seen through air quality sampling, source apportionment studies and also through the atmospheric chemistry. Findings are similar to those observed by [17].

CONCLUSIONS

To apportion the sources of PM_{10} at a residential area in Kanpur City, source apportionment technique, FA–MR was applied. Two important PM_{10} sources are soil & road dust (26-36%) and inorganic secondary particles like $(NH_4)_2SO_4$ and NH_4NO_3 (4-11%). Ambient NH_3 has been found dominating primary pollutant responsible for secondary particle formation and its role is very important in overall atmospheric chemistry of particulate formation.

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