Atmospheric ionic species in PM$_{2.5}$ and PM$_1$ aerosols in the ambient air of eastern central India

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Abstract This study elucidates the characteristics of ambient PM$_{2.5}$ (fine) and PM$_1$ (submicron) samples collected between July 2009 and June 2010 in Raipur, India, in terms of water soluble ions, i.e. Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$. The total number of PM$_{2.5}$ and PM$_1$ samples collected with eight stage cascade impactor was 120. Annual mean concentrations of PM$_{2.5}$ and PM$_1$ were 150.9±78.6 μg/m^3 and 72.5±39.0 μg/m^3, respectively. The higher particulate matter (PM) mass concentrations during the winter season are essentially due to the increase of biomass burning and temperature inversion. Out of above 8 ions, the most abundant ions were SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ for both PM$_{2.5}$ and PM$_1$ aerosols; their average concentrations were 7.86±5.86 μg/m^3, 3.12±2.63 μg/m^3 and 1.94±1.28 μg/m^3 for PM$_{2.5}$, and 5.61±3.79 μg/m^3, 1.81±1.21 μg/m^3 and 1.26±0.88 μg/m^3 for PM$_1$, respectively. The major secondary species SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ accounted for 5.81%, 1.88% and 1.40% of the total mass of PM$_{2.5}$ and 11.10%, 2.68%, and 2.48% of the total mass of PM$_1$, respectively. The source identification was conducted for the ionic species in PM$_{2.5}$ and PM$_1$ aerosols. The results are discussed by the way of correlations and principal component analysis. Spearman correlation indicated that Cl$^-$ and K$^+$ in PM$_{2.5}$ and PM$_1$ can be originated from similar type of sources. Principal component analysis reveals that there are two major sources (anthropogenic and natural such as soil derived particles) for PM$_{2.5}$ and PM$_1$ fractions.

Keywords PM$_{2.5}$ · PM$_1$ · Water soluble ions · Secondary species · Biomass burning · Eastern central India

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1 Introduction

Over the past two decades there has been a rapid increase in urbanization and industrialization in many cities of India. With this has come a dramatic increase in the number and density of motor vehicles (Taneja et al. 2008). With rapid urbanization and corresponding increase in traffic, there has been growing evidence that ambient concentration level of particulate matter (PM) is also rising up (He et al. 2001; Wang et al. 2005). Airborne PM is a mixture of solid and liquid particles suspended in the air. These particles are important in terms of their impact on the environment and public health. Hence, international policy on air quality, protection of human health and the protection of the environment requires research on ambient air particulate pollution (Hellebust et al. 2010). The various possible impacts caused by PM depend on their size, chemical composition, concentrations, accumulation time and exposure time (Mkoma et al. 2009). In recent years in Asian countries, such as India and China, the aerosol problem has become increasingly acute due to elevated loadings of atmospheric pollutants from increasing vehicular and industrial emissions as well as from increasing energy for domestic uses (Srivastava et al. 2008; Tsang et al. 2008; Zhang et al. 2008). Recently, many Indian studies have focused on PM measurement and their characterization for health and local air quality assessment covering urban areas (Katiyar et al. 2002; Sastry et al. 2004; Gadgil and Jadhav 2004; Ramachandran 2005; Ganguly et al. 2006; Karar and Gupta 2006; Chowdhury et al. 2007; Badrinath et al. 2007; Srivastava and Jain 2007; Bhaskar et al. 2008: Kulshrestha et al. 2009; Bhaskar and Mehta 2010; Deshmukh et al. 2010). However, more measurements and detailed chemical characterization of aerosols are needed for highly industrialized and densely populated metropolitan city of eastern central India.

The source characteristics and health hazards of the PM_{10}, coarse ($PM_{2.5-10}$; $2.5 < d_p < 10 \ \mu m$), fine ($PM_{2.5}$; $d_p < 2.5 \ \mu m$) and submicron (PM_1; $d_p < 1 \ \mu m$) particulate matter are distinct. It is admitted that the impact of $PM_{2.5}$ and PM_1 particles is larger than the impact of $PM_{2.5-10}$ because these particles go deeper in the respiratory tract and become trapped on it, which affects the lung function (Fang et al. 2007).

In many urban and rural areas water soluble ionic species (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) accounts for large fractions of atmospheric particle mass and are associated with adverse effects on human health and acidification of the environment (Grantz et al. 2003; Jung and Kim 2006). Determining their composition is essential to understand their properties and reactivity and hence their environmental effects (Singh et al. 2010). The major components of PM are sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonia (NH_4^+), organic carbon (OC), and elemental carbon (EC) (Lee et al. 2001). Sufficient data on PM_{10} (Kyotani and Iwatsuki 2002; Shi et al. 2003; Dan et al. 2004; Samburova et al. 2005; Johnson et al. 2006; Nicolas et al. 2009; Khan et al. 2010; Pateraki et al. 2010) and $PM_{2.5}$ (Niemi et al. 2005; Wang et al. 2006; Chen et al. 2008; Raman et al. 2008; Mkoma et al. 2009; Mena et al. 2010; Tai et al. 2010) are now available worldwide that emphasize on characteristics and sources. Nowadays, in developed countries, attention has been paid for $PM_{2.5}$ and PM_1 particles. However, much less is known, and even less has been done about PM_1. Although some literature (Cabada et al. 2004; Shen et al. 2009) reported that the major components of PM_1 and $PM_{2.5}$ originate from the same sources and they concluded the investigation of PM_1 did not yield significant new information in with that obtained from the $PM_{2.5}$, it is clear that the PM_1 was a better indicator for anthropogenic sources than $PM_{2.5}$, because compared with $PM_{2.5}$ and PM_{10}, it minimized interference from natural sources (Lee et al. 2006).

Therefore, this study was carried out to characterize $PM_{2.5}$ and PM_1 and water soluble ions associated with these size fractions in the eastern central India.

2 Experimental

2.1 The study area

Continuous sampling of aerosols was conducted in Raipur (22° 33′ to 21°14′N Latitude and 82° 6′ to 81°38′E Longtitude). Figure 1 shows the geographical location of the sampling
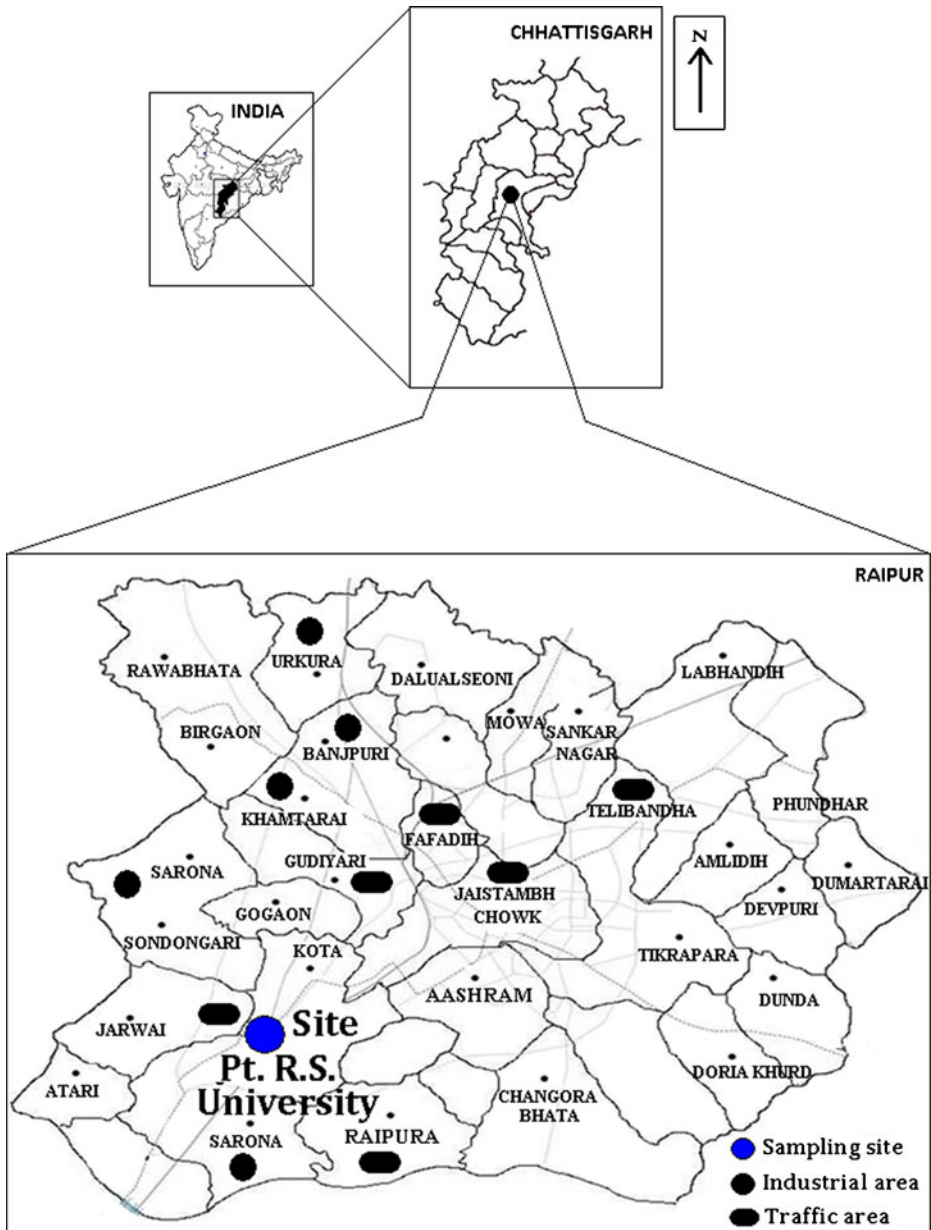
Fig. 1 A map of study area showing location of the sampling site

site. The atmospheric air collections were performed at the terrace, i.e. at an altitude of approximately 15 m from the ground level, of the building School of Studies in Chemistry, Pt. Ravishankar Shukla University Raipur, India. It is the largest institution for higher education in this region of eastern central India. The national highway connecting to the University has heterogeneous and heavy traffic flow. It is a congested area with heavy traffic density. The climate is tropical with four distinct seasons, viz., fall (July–Sept), winter (October–January), spring (February–March), and summer (April–June).

2.2 Sample collection

Size-segregated aerosol samples were collected between July 2009 and June 2010 by 8-Stage cascade impactor type aerosol sampler (TE 20–800 Tisch Air Pollution Monitoring Equipment, USA, flow rate 28.3 ALPM) at sampling site Raipur, India in four different seasons (fall, winter, spring and summer). During each season, the $PM_{2.5}$, and PM_1 samples were collected twice in a week for the period of 24 h. Table 1 gives an overview of the sampling period. Power failure during sampling hours was added for additional sampling time period. The sampling were performed at a rate of 1.7 m^3 h^{-1} and in total 40.8 m^3 day^{-1} of air passed through each filter. Total 120 samples were collected at sampling site. The samples were collected on Whatmann 41 glass filters. Each set of samples consist of eight different filters for various size ranges. These size ranges are as follows—stage 1: 10.0–9.0 μm, stage 2: 9.0–5.8 μm, stage 3: 5.8–4.4 μm, stage 4: 4.4–2.5 μm, stage 5: 2.5–2.0 μm, stage 6: 2.0–1.0 μm; stage 7: 1.0–0.7 μm and stage 8: 0.7–0.4 μm. Subsequently, these eight size ranges particles were divided into two broad categories, viz. $PM_{2.5}$, and PM_1. $PM_{2.5}$ particles presented the sum total of particles of size ranges 2.5–2.0, 2.0–1.0, 1.0–0.7 and 0.7–0.4 μm and PM_1 particles presented the sum total of particles of size ranges 1.0–0.7 and 0.7–0.4 μm.

The filters were kept in vacuum desiccators for 24 h to remove moisture content before mounting them on the air sampler. After sampling the filters were immediately transferred to vacuum desiccators to again de-moisture in the same manner. Before and after sampling, the filters were weighed using an analytical balance (Sartorius CP225D) with a reading precision of 10 μg after stabilizing under a constant temperature (20±5°C) and humidity (40±2%). All weight measurements were repeated three or more times to ensure reliability. To ensure the

Table 1 Overview of the sampling periods and meteorological data at sampling site Raipur, India during July 2009 to June 2010

Sampling period	Date	Seasons	Samples (n)	T (°C)	RF (mm)	RH (%)	VP (kPa)	WS (m/s)	PWD
SP 1	1 July 2009 to 30 September 2009	Fall	30	28.3	65.4	82	3.1	7.1	SW, W
SP 2	1 October 2009 to 30 January 2010	Winter	40	21.5	4.5	66	1.6	2.4	NE, N
SP 3	1 February 2010 to 30 March 2010	Spring	20	27.1	0.8	46	1.4	3.7	NW
SP 4	1 April 2010 to 30 June 2010	Summer	30	34.0	10.5	41	2.0	7.8	SW, W
Annual	1 July 2009 to 30 June 2010		120	27.3	20.6	60	2.0	5.1	SW, W

T Temperature; *RF* Rainfall; *RH* Relative humidity; *VP* Vapour pressure; *WS* Wind speed; *PWD* Prevalent wind direction

quality of weighing, another blank filter was dealt with simultaneous using the same method as the samples. The exposed filters and field blanks were placed into polyethylene bottles and kept frozen at −20°C during storage and transported cool for analysis. All the procedures were strictly quality-controlled to avoid possible contaminations of the samples.

2.3 Chemical analysis

One-fourth of the filter samples were extracted into 10 ml ultrapure water (specific resistance: 18 MΩ cm) by using an ultrasonic bath (UT-105 S, Sharp, Japan) and a shaker (EYELA Multi Shaker, Rikakikoi Co., Tokyo, Japan) to measure various water soluble inorganic ions. The ultrasonic and mechanical agitations were operated for 45 min each. The extracted solution was filtered through a microporous membranes (pore size, 0.45 μm, diameter, 25 mm), and filtrate was stored in a refrigerator at 4°C until chemical analysis. An ion chromatograph (Dionex, DX-120, USA) was used to measure Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} ions in the aqueous extract.

The determination of ions Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} was performed using the following setup: Separation columns, Ionpac AS 12A and CS 16A were used, respectively for anion and cations. Eluents of 2.7 mM Na_2CO_3 (Wako, Japan) and 0.3 mM $NaHCO_3$ (Wako, Japan) were prepared and used for the detection of anions with a pump flow rate of 1.5 ml min^{-1}. A 2.6 mM methane sulphonic acid (CH_3SO_3H) (Wako, Japan) solution was used as an eluent for cation analysis with a pump flow rate of 1 ml min^{-1}. Ions were identified based on their retention time. The analytical uncertainties, generating from the non-ideal chemical or physical behavior of analytical systems, were checked for working standard solutions prepared freshly by proper dilutions of the stock standard solutions of all ions analyzed. The variation in calculated area under the peaks obtained for these ions ($n=6$, for each ion analysis) were between 2–5%. The field blanks, as a measure for the experimental uncertainties, were determined to be less than the method detection limits only for ions, namely, NH_4^+, Mg^{2+} and NO_3^-. Blank concentration was measured using field blank samples. Blanks filters were extracted and passed through similar procedures as followed for the extraction and preparation of the regular particulate sample to analyze with the ion chromatography. The description on the method detection limit (DL) calculated using 1 ppm laboratory prepared calibration standards, analytical accuracy in terms of relative error and precision in terms of relative standard deviation are listed in Table 2 for all cations and

Table 2 Method detection limits, accuracy, precision and field blank concentrations of water soluble ionic species analyzed by ion chromatography

Species	Method detection limit (μg/m³)	Accuracy (%, Relative error)	Precision (% , Relative standard deviation)	Field blank concentrations[a] (μg/m³, $n=30$)
Na^+	0.01	4.8	3.28	0.04
K^+	0.03	4.6	2.64	0.07
NH_4^+	0.02	5.0	1.36	0.01
Mg^{2+}	0.01	6.0	4.89	0.01
Ca^{2+}	0.01	6.2	2.44	0.07
Cl^-	0.01	4.3	2.04	0.15
NO_3^-	0.01	4.2	2.58	0.00
SO_4^{2-}	0.02	6.3	1.54	0.14

[a] Average value

anions analyzed. The overall mean concentrations for field blank samples (n=30), collected over a year, are also shown in Table 2. All the reported water-soluble ion concentrations and PM mass have been corrected using field blanks.

2.4 Meteorological data

Daily meteorological data, including temperature (T, °C), rainfall (RF, mm), relative humidity (RH, %), vapour pressure (VP, kPa), wind speed (WS, m/s) and wind direction (WD, degree) etc. were obtained from Department of Agrometeorology, Indira Gandhi Agricultural University, Raipur, India. The meteorological data during the study period are presented in Table 1.

3 Results and discussion

3.1 $PM_{2.5}$ and PM_1 mass concentrations and seasonal variation

A total of 120 samples of $PM_{2.5}$ and PM_1 aerosols were collected from July 2009 to June 2010 at sampling site School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, India. The concentrations of $PM_{2.5}$ and PM_1 ranged from 24.0 to 269.7 μg/m^3 and from 4.4 to 135.3 μg/m^3, respectively. Respective annual mean concentration of 150.9± 78.6 and 72.5±39.0 μg/m^3 were recorded for $PM_{2.5}$ and PM_1. Table 3 shows mean concentration with standard deviation values for each fraction of the particulate matter ($PM_{2.5}$ and PM_1) collected during the sampling period. The results indicated that the observed annual mean $PM_{2.5}$ concentration exceeded 65 μg/m^3 of the annual National

Table 3 Annual mean concentrations of $PM_{2.5}$ and PM_1, ratio of $PM_1/PM_{2.5}$ and concentration of water soluble ionic species in $PM_{2.5}$ and PM_1 size fractions at sampling site Raipur, India during the period of July 2009 to June 2010

| Species	$PM_{2.5}$ (μg/m^3) (n=120)					PM_1 (μg/m^3) (n=120)				
	Mean	SD[a]	Min[b]	Max[c]	CV[d]	Mean	SD[a]	Min[b]	Max[c]	CV[d]
PM mass	150.9	78.6	24.0	269.7	0.52	72.1	39.0	4.4	135.3	0.54
Na^+	0.92	0.67	0.06	5.65	0.73	0.61	0.42	0.06	2.60	0.69
NH_4^+	1.94	1.28	0.22	6.83	0.66	1.26	0.88	0.11	3.33	0.70
K^+	0.52	0.35	0.02	1.95	0.67	0.37	0.32	0.02	1.22	0.86
Mg^{2+}	0.26	0.17	0.03	1.92	0.64	0.08	0.04	0.02	0.33	0.53
Ca^{2+}	0.91	0.74	0.02	3.56	0.81	0.40	0.30	0.05	1.39	0.77
Cl^-	2.10	1.82	0.02	7.82	0.87	1.19	0.39	0.02	4.89	0.33
NO_3^-	3.12	2.63	0.03	16.14	0.84	1.81	1.21	0.02	8.42	0.67
SO_4^{2-}	7.86	5,86	1.14	23.75	0.75	5.61	3.79	0.48	12.79	0.68
Mass ratio of PM_1 to $PM_{2.5}$										
	Mean	SD[a]	Min[b]	Max[c]	CV[d]					
$PM_1/PM_{2.5}$	0.47	0.08	0.18	0.69	0.18					

[a] Standard deviation

[b] Minimum

[c] Maximum

[d] Coefficient of variation

Ambient Air Quality Standards (NAAQS) of India (http://www.scorecard.org/env-releases/def/capnaaqs.html).

The seasonal variation of $PM_{2.5}$ and PM_1 aerosols was shown in Fig. 2, where the error bars show the standard deviation of seasonal mean. Figure 2 showed numerous high concentration as well as low concentration of $PM_{2.5}$ and PM_1. Several months of rainfall might be responsible for low concentration months. As shown in Fig. 2, the concentration of $PM_{2.5}$ and PM_1 were higher in winter compared to those in spring, summer and fall. The high concentration in winter was likely due to the high burning of fossil fuels for heating purpose. The low concentration in fall was likely related to more precipitation in this season. The high concentrations of $PM_{2.5}$ in the present study may be due to the contribution from heavy traffic and other human particle-generating activities in near by areas. The highest concentrations of $PM_{2.5}$ were experienced during December 2009, whereas the highest concentrations of PM_1 were found in October 2009 compared with other sampling period of the year. Temperature was found to be at the lowest level (21.5°C) on winter as shown in Table 1. Figure 3 shows the weekly variation of $PM_{2.5}$ and PM_1 concentrations versus corresponding temperature, wind speed and mixing height during the study period. The temperature, wind speed and mixing height were found to be low during the winter weeks and gradually increased during summer weeks. Frequent changes in temperature and wind speed increased the atmospheric turbulence during summer weeks, thereby increasing the dispersion of PM emission. Further, in winter weeks winds were relatively calm (~ 1.3 m/s, October to January). These prevailing calm conditions favored more stable atmospheric condition, consequently reducing the dispersion of particulate matter. Thus stable and cold meteorology in most of the days in winter weeks favored the prolonged life of $PM_{2.5}$ in ambient air. In summer weeks increased wind speed and
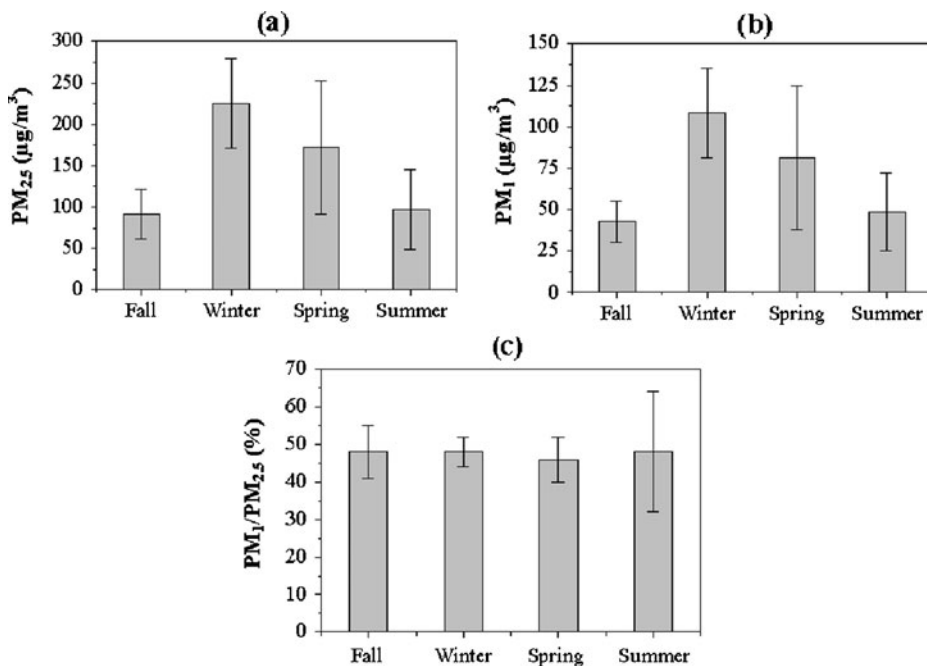
Fig. 2 Seasonal variation of PM ($PM_{2.5}$ and PM_1) and ratio of $PM_1/PM_{2.5}$ at sampling site Raipur, India during the period of July 2009 to June 2010
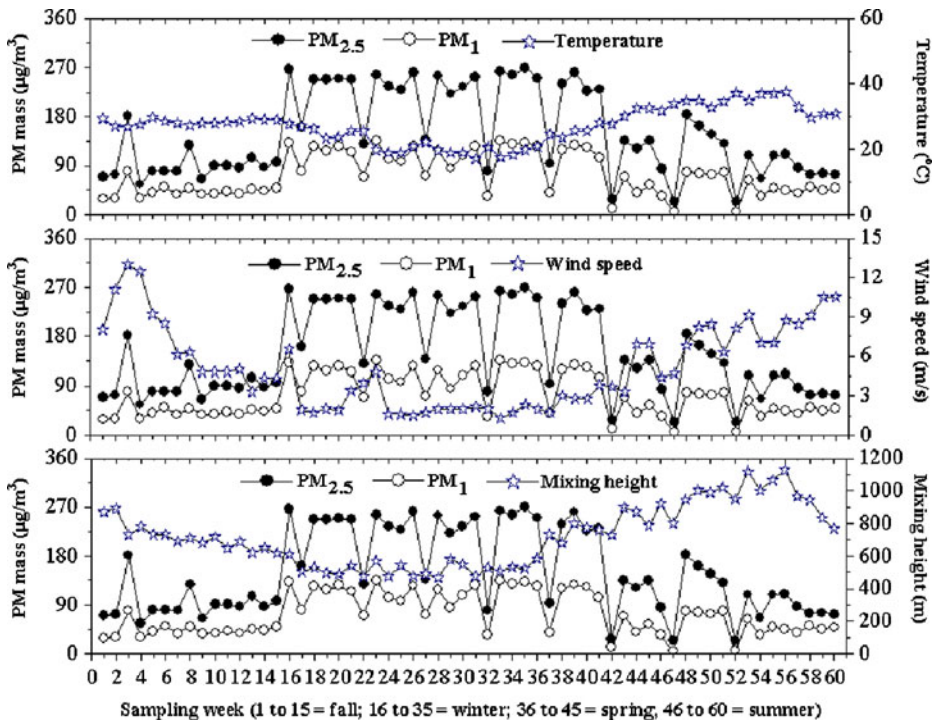
Fig. 3 Variation of $PM_{2.5}$ and PM_1 mass concentrations versus temperature, wind speed and mixing height during the study period of July 2009 to June 2010

temperature brought down PM concentrations remarkably. Similar trends were also found for PM_1. PM concentration measured in winter was higher than that in the summer and spring, because many agricultural activities (burning rice straws) were carried out in winter. Many farmers burned rice straw to fertilize the land for the coming year and also due to wood and oil burning for residential heating, and condensation of semi-volatile organic species. High PM concentrations in Raipur could be attributed to the uncontrolled anthropogenic activities which may include high rate of construction activities without any preventive measures, refuse dust, biomass combustion, mechanical erosion from paved and unpaved roads and soil dusts generate particles larger than 2.5 and 1.0 μm.

The $PM_{2.5}$ and PM_1 particles are relatively different in their physical and chemical compositions. They generally originate from different sources or by different activities within the same sources (Oanh et al. 2006). Relationship between the $PM_{2.5}$ and PM_1 mass concentrations were analyzed in terms of linear regression (Fig. 4) and the results revealed that the coefficient of determination (R^2) was 0.958 during the study period. The relatively high coefficients especially imply that $PM_{2.5}$ and PM_1 have some similar sources, and they were being influenced by the same local conditions (Karaca et al. 2005). Fine particles are formed primarily by combustion and/or secondary chemical reactions in the atmosphere (Ravindra et al. 2008). In our study, the increase in $PM_{2.5}$ concentrations during the heating seasons was mainly driven by an increase in the PM_1 concentrations.

To understand the contribution of PM_1 in $PM_{2.5}$, the ratio of $PM_1/PM_{2.5}$ is calculated. Since different sizes of atmospheric particle probably originate from different sources, the mean $PM_1/PM_{2.5}$ ratios have been used for identifying the sources of $PM_{2.5}$ and PM_1 (Chan

Fig. 4 Relationship between PM$_{2.5}$ and PM$_1$
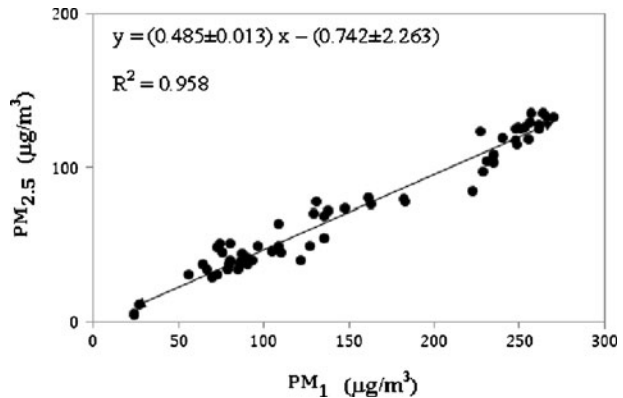
et al. 2005; Sun et al. 2004; Charron and Harrison 2005; Bogo et al. 2003; Gehrig and Buchmann 2003). Higher ratios (larger than 0.50) are generally ascribed to relatively high contribution from secondary particles and the combustion sources, while lower ratio indicate significant contributions from primary sources such as re-suspended soil/road dust and the mechanical activities (Perez et al. 2008; Querol et al. 2004). The ratios of PM$_1$/PM$_{2.5}$ were also shown in Fig. 2. The mean ratio of PM$_1$/PM$_{2.5}$ was found to be 0.47±0.08. It could be seen that PM$_1$ accounted for 48%, 48%, 46% and 48% of PM$_{2.5}$ in fall, winter, spring and summer, respectively. However, the ratio of PM$_1$/PM$_{2.5}$ is higher during the fall, winter and summer seasons (mean PM$_1$/PM$_{2.5}$=0.48), clearly indicating larger submicron particle fractions in PM$_{2.5}$ at this location. Paired t-tests for mean PM$_1$/PM$_{2.5}$ ratios were conducted to know if there is significant difference in the ratios between different seasons. The results of paired t-tests (fall-winter, $t=-0.30$, $p=0.75$; fall-spring, $t=0.70$, $p=0.48$; fall-summer, $t=-0.04$, $p=0.96$; winter-spring, $t=1.12$, $p=0.28$; winter-summer, $t=0.11$, $p=0.90$; spring-summer, $t=-0.48$, $p=0.63$) showed that there is no significant difference in the ratios of PM$_1$/PM$_{2.5}$ between the seasons.

3.2 Concentrations of water soluble ions in PM$_{2.5}$ and PM$_1$

The analytical results of water soluble ionic species in PM$_{2.5}$ and PM$_1$ size fractions collected during the period of July 2009 to June 2010 in eastern central India are presented in Table 3. Water soluble inorganic ions comprise a large part of aerosol particles and play an important role in the atmosphere. The average water soluble ionic concentrations of PM$_{2.5}$ were found in the following order: $SO_4^{2-}>NO_3^->Cl^->NH_4^+>Na^+>Ca^{2+}>K^+>Mg^{2+}$. Besides, the mean ionic concentrations of PM$_1$ were in the following order: $SO_4^{2-}>NO_3^->NH_4^+>Cl^->Na^+>Ca^{2+}>K^+>Mg^{2+}$. The concentrations of total water soluble inorganic ions (TWSII) in PM$_{2.5}$ accounted for 13.0% of the total mass. The concentrations of total water soluble inorganic ions varied from 1.7% to 76.9% for PM$_{2.5}$ and 1.5% to 95.0% for PM$_1$, respectively. The mean level of ions in PM$_1$ accounted for 18.6% with the major ions being SO_4^{2-}, NO_3^- and NH_4^+. The annual average of SO_4^{2-}, NO_3^- and NH_4^+ ions were found to be 52.7%, 11.8% and 12.6% of the total mass of the ionic species in PM$_1$. The results indicated that the average water soluble ionic species concentration in PM$_{2.5}$ were higher than those of PM$_1$. The concentrations of SO_4^{2-}, NO_3^-, NH_4^+ and Cl^- were highest among all ions in PM$_{2.5}$. The annual means of SO_4^{2-}, NO_3^-, NH_4^+ and Cl^- were observed as 45.8%, 13.1%, 11.4% and 9.8% of total mass of the ionic species in PM$_{2.5}$. Among all chemical species, SO_4^{2-} has

the highest concentration in both the aerosols, which varied from 1.14 to 23.75 $\mu g/m^3$ in $PM_{2.5}$ with a mean concentration 7.86 $\mu g/m^3$. The SO_4^{2-} concentrations in PM_1 varied between 0.48 and 14.79 $\mu g/m^3$ with a mean value of 5.61 $\mu g/m^3$. NO_3^- is the second most prominent species in both $PM_{2.5}$ and PM_1 aerosols, which varied from 0.03 to 16.14 $\mu g/m^3$ in $PM_{2.5}$ with a mean value of 3.12 $\mu g/m^3$. The NO_3^- concentrations in PM_1 varied from 0.01 to 8.42 $\mu g/m^3$ with a mean value of 1.81 $\mu g/m^3$. The high sulphate and nitrate concentrations suggest their contribution from a large component of secondary inorganic aerosols resulting from emissions of SO_2 and NO_x by a variety of combustion sources using sulfurous fuel, such as coal and oil (Seinfeld and Pandis 1998). These include power plants and heavy road transport. Ammonium (NH_4^+) concentrations varied from 0.22 to 6.83 $\mu g/m^3$ for $PM_{2.5}$ and 0.11 to 3.33 $\mu g/m^3$ for PM_1. The mean value of NH_4^+ was 1.94 $\mu g/m^3$ for $PM_{2.5}$ and 1.26 $\mu g/m^3$ for PM_1. In $PM_{2.5}$, the concentration of chloride (Cl^-) ion varied from 0.01 to 7.82 $\mu g/m^3$ with a mean concentration of 2.10 $\mu g/m^3$. However, Cl^- ion concentration in PM_1 varied between 0.01 to 4.89 $\mu g/m^3$ with a mean concentration of 1.19 $\mu g/m^3$. Calcium (Ca^{2+}) concentrations varied from 0.01 to 3.56 $\mu g/m^3$ and 0.05 to 1.39 $\mu g/m^3$, respectively for $PM_{2.5}$ and PM_1. The mean value of Ca^{2+} was 0.91 $\mu g/m^3$ and 0.40 $\mu g/m^3$ for $PM_{2.5}$ and PM_1, respectively. Similarly, Magnesium (Mg^{2+}) concentration varied between 0.03 to 1.92 $\mu g/m^3$ for $PM_{2.5}$ and from 0.01 to 0.33 $\mu g/m^3$ for PM_1 with a mean concentration of 0.26 $\mu g/m^3$ for $PM_{2.5}$ and 0.08 $\mu g/m^3$ for PM_1. The mean concentrations of potassium (K^+) and sodium (Na^+) ions were 0.52 $\mu g/m^3$ and 0.92 $\mu g/m^3$ for $PM_{2.5}$ and 0.37 $\mu g/m^3$ and 0.61 $\mu g/m^3$ for PM_1, respectively.

The percentage contribution of each ionic species in both in $PM_{2.5}$ and PM_1 was shown in Fig. 5. The measured total water soluble ionic fraction contributed to approximately 13% of the total $PM_{2.5}$ of which anions and cations account for about 9% and 4%, respectively as shown in Fig. 5. On the other hand, approximately 19% of the total PM_1 was found to contribute as total water soluble ionic fraction of which anions and cations accounted for about 16% and 6%, respectively. The unanalyzed portion of both $PM_{2.5}$ and PM_1 samples is deemed to consist of carbonaceous aerosols such as black carbon and organic carbons and other insoluble elements. The analyzed ionic species in $PM_{2.5}$ mainly consist of secondary inorganic aerosols (SO_4^{2-}, NO_3^- and NH_4^+) which on an annual basis, accounts for 12.92 $\mu g/m^3$ (9.09% of the $PM_{2.5}$ mass), salt aerosols (Na^+ and Cl^-) for 3.02 $\mu g/m^3$ (2.34%) and mineral matter (K^+, Mg^{2+} and Ca^{2+}) for 1.69 $\mu g/m^3$ (1.58%). Out of total $PM_{2.5}$ fractions, 86.99% (~133.2 $\mu g/m^3$) are unanalyzed fractions. The PM_1 are mainly made up of undetermined fractions (61.33 $\mu g/m^3$, 81.43%), secondary inorganic aerosols (8.68 $\mu g/m^3$, 16.26%), salt aerosols (1.80 $\mu g/m^3$, 3.95%) and mineral matters (0.85 $\mu g/m^3$, 1.69%).

3.3 Seasonal variation of water soluble ionic species

The seasonal variations of water soluble ionic species in $PM_{2.5}$ and PM_1 aerosols collected from July 2009 to June 2010 at eastern central India were shown in Fig 6. The period of study was divided into four seasons as shown in Table 1 in order to conduct a more detailed analysis of the behavior of the variations of the ion concentrations in $PM_{2.5}$ and PM_1. The mass concentration of the total water soluble ionic species was higher in winter (30.98 $\mu g/m^3$ and 20.01 $\mu g/m^3$, respectively for $PM_{2.5}$ and PM_1) and spring (18.82 $\mu g/m^3$ and 12.26 $\mu g/m^3$, respectively for $PM_{2.5}$ and PM_1) than summer (12.15 $\mu g/m^3$ and 7.74 $\mu g/m^3$, respectively for $PM_{2.5}$ and PM_1) and fall (4.52 $\mu g/m^3$ and 2.73 $\mu g/m^3$, respectively for $PM_{2.5}$ and PM_1). The high concentration in winter might be related to the industrial
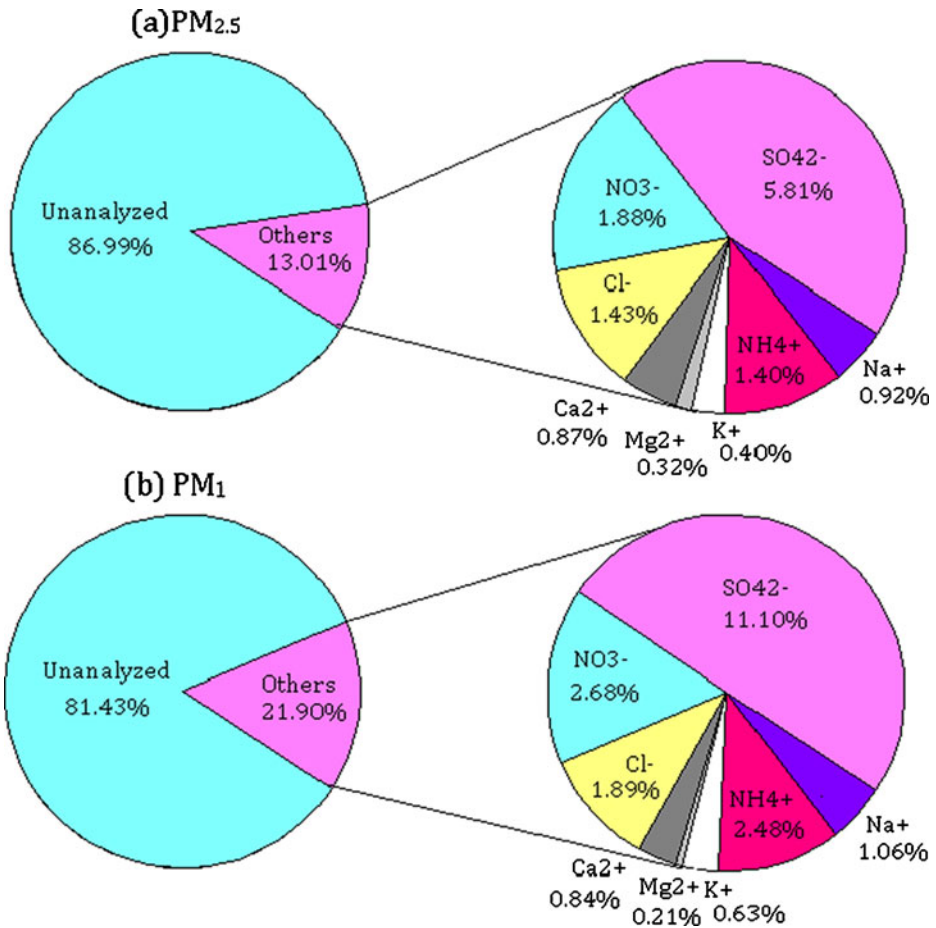
Fig. 5 Percentage contribution of water soluble ionic species in $PM_{2.5}$ and PM_1

emissions in this season and low inverse layer there. In fall, the low concentration at the study area is related to more precipitation (average rainfall, 65.4 mm) that would wash out more aerosols. The tracers of soil/dust, Ca^{2+} and Mg^{2+}, were frequently observed in lower concentrations in fall (Ca^{2+} average: 0.42 and 0.10 μg/m³ for $PM_{2.5}$ and PM_1, respectively; Mg^{2+} average: 0.06 and 0.02 μg/m³ for $PM_{2.5}$ and PM_1, respectively) and winter (Ca^{2+} average: 0.94 and 0.42 μg/m³ for $PM_{2.5}$ and PM_1, respectively; Mg^{2+} average: 0.07 and 0.03 μg/m³ for $PM_{2.5}$ and PM_1, respectively) seasons, which could be due to the more precipitation in these seasons, while in spring (Ca^{2+} average: 1.39 and 0.67 μg/m³ for $PM_{2.5}$ and PM_1, respectively; Mg^{2+} average: 0.74 and 0.26 μg/m³ for $PM_{2.5}$ and PM_1, respectively) and summer (Ca^{2+} average: 1.03 and 0.48 μg/m³ for $PM_{2.5}$ and PM_1, respectively; Mg^{2+} average: 0.39 and 0.10 μg/m³, respectively for $PM_{2.5}$ and PM_1) they were in higher concentrations, as the dry weather in these seasons was favorable for the re-suspension of soil particles.

The concentration of Cl^- in $PM_{2.5}$ and PM_1 samples was higher in winter (4.35 and 2.68 μg/m³ for $PM_{2.5}$ and PM_1, respectively) and spring (1.73 and 0.69 μg/m³ for $PM_{2.5}$ and PM_1, respectively) than those in summer (1.16 and 0.60 μg/m³ for $PM_{2.5}$ and PM_1,
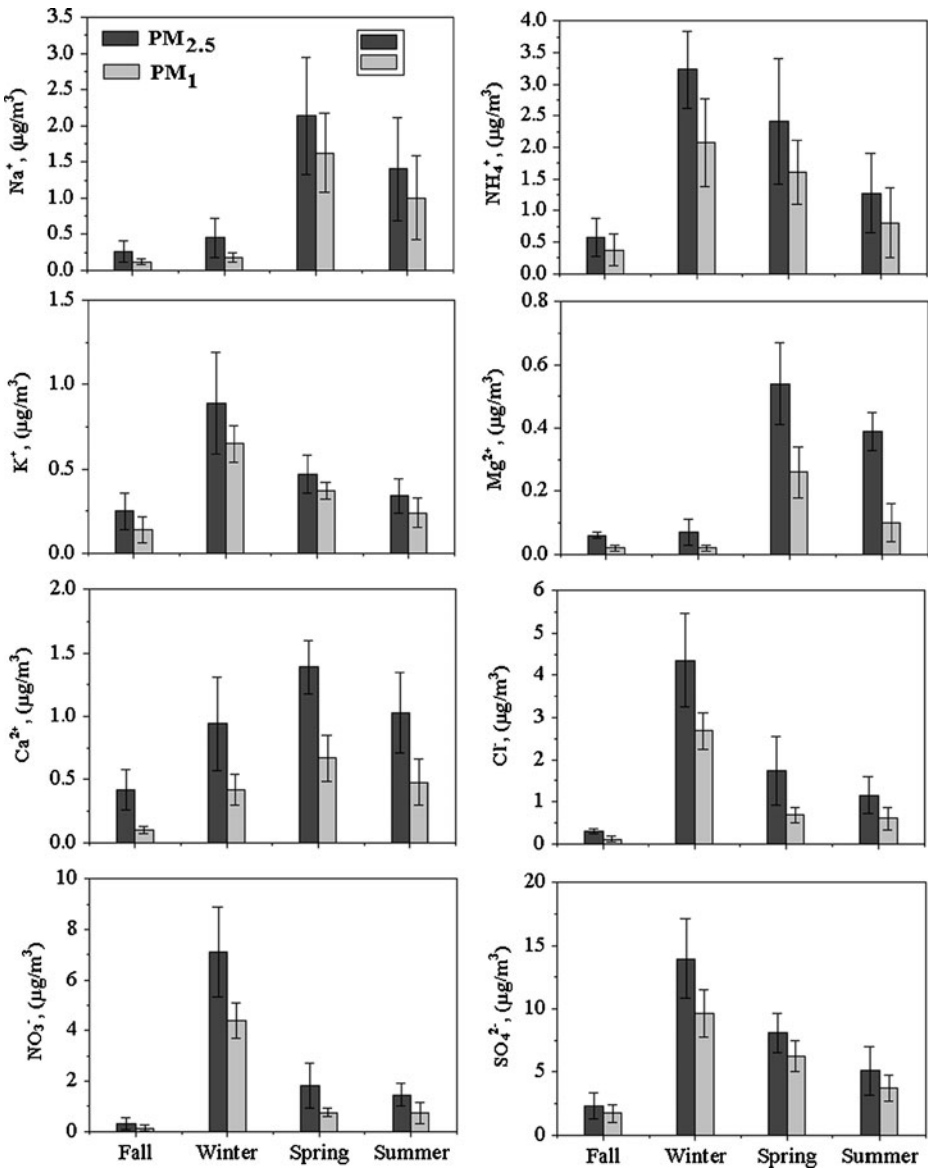
Fig. 6 Seasonal variation of water soluble ionic species in $PM_{2.5}$ and PM_1 at sampling site Raipur, India during the period of July 2009 to June 2010

respectively) and fall (0.30 and 0.12 μg/m^3 for $PM_{2.5}$ and PM_1, respectively). As the sampling site is far from the sea, it has been demonstrated that the contribution to the aerosols from the sea could be ignored here (Tiwari et al. 2009). The major source of Cl$^-$ in Raipur, India might be coal burning, which could reasonably explain the higher Cl$^-$ concentration in winter season. High K$^+$ concentrations averaged of 0.89 and 0.65 μg/m^3 for $PM_{2.5}$ and PM_1 were observed in winter, which was higher than that in fall of 0.25 and 0.14 μg/m^3 for $PM_{2.5}$ and PM_1, respectively. The seasonal variation of K$^+$ was similar to

Cl^-, indicating that both K^+ and Cl^- were primarily related to the burning activities, which were enhanced in the cold season (Wang et al. 2006).

The seasonal variations of secondary components SO_4^{2-}, NO_3^- and NH_4^+ were similar. The concentration of SO_4^{2-} was higher in winter (13.96 and 9.59 µg/m^3 for $PM_{2.5}$ and PM_1, respectively) and spring (8.11 and 6.28 µg/m^3 for $PM_{2.5}$ and PM_1, respectively) than that in summer (5.09 and 3.74 µg/m^3 for $PM_{2.5}$ and PM_1, respectively) and fall (2.32 and 1.71 µg/m^3 for $PM_{2.5}$ and PM_1, respectively) seasons. Sulphate showed similar trend with K^+ and Cl^-. Therefore, the source of this compound can be the biomass burning as well in addition to industrial activities. The NO_3^- concentration in $PM_{2.5}$ and PM_1 was higher in winter (7.10 and 4.39 µg/m^3 for $PM_{2.5}$ and PM_1, respectively) and spring (1.83 and 0.76 µg/m^3 for $PM_{2.5}$ and PM_1, respectively) than that in other seasons. NO_3^- is generally formed from the oxidation of NO_x. Thus the variation of NO_3^- is related closely to NO_2 and meteorological factors. NO_2 is mainly from the traffic emissions in the city. Since traffic emissions are generally evenly distributed over the year round, the variation in NO_3^- might be strongly related to the meteorological factors, such as temperature and relative humidity. The lower temperature and stable meteorology favor the formation of NO_3^- aerosol reacting with NH_4^+ (Park et al. 2005; Mariani and Mello 2007). The lower temperature in winter and spring would 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 and spring. NH_4^+ concentration in $PM_{2.5}$ and PM_1 was highest in winter season in this study as 3.23 and 2.07 µg/m^3, respectively for $PM_{2.5}$ and PM_1. The magnitude of the seasonal NH_4^+ concentration in $PM_{2.5}$ and PM_1 was found to be winter>spring>summer>fall.

3.4 Relationship between PM, water soluble ionic species and meteorological parameters

Meteorology plays a crucial role in ambient distribution of air pollution. The importance of meteorological factors in the transport and diffusion stage of the air pollution cycle is well recognized. The entering of pollutants from the ground surface, their residence in the atmosphere, and the formation of secondary pollutants is controlled not only by the rate of emission of the reactants into the air from the source, but also by wind speed, air temperature and precipitation. Thus, it is often important to understand the physical process leading to an observed concentration of pollutants at a given point. Rainfall is one of the reasons for low particulate pollutants in the monsoon season as the pollutants are washed out by rain (Bhaskar and Mehta 2010).

The relationship between PM and meteorological parameters during the study periods were investigated by Spearman correlation analysis. The meteorological data, which were found to be significant in describing the variation in the 24-h averaged PM concentrations utilizing in the present work, are: temperature (°C), rainfall (mm), relative humidity (%), vapour pressure (kPa) and wind speed (m/s). The correlation coefficients (r) between weekly average (24-h) PM and meteorological parameters are shown in Table 4. The correlation coefficients were marked in the table to indicate the significant levels ($P<0.01$ or $P<0.05$). The results showed that the meteorological parameters were negatively correlated with $PM_{2.5}$ and PM_1. Correlation between PM variables and wind speed were investigated during the study period. It is obvious that the concentrations of pollutants decrease effectively with increasing wind speed. There is a significant negative relationship between particulates mass concentrations and wind speed during the study period. Correlations between PM variable and relative humidity are negative and remain weak during the study period. PM variables shows significant negative correlations with atmospheric temperature, whereas no correlation is observed between PM variable and

Table 4 Non-parametric (Spearman) correlation analysis of different particle size for pollutants and meteorology in the fine ($PM_{2.5}$) size fraction (lower diagonal triangle) and in the submicron (PM_1) size fraction (upper diagonal triangle)

	PM	Na^+	NH_4^+	K+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	Temperature	RH[a]	VP[b]	WS[c]
PM		0.01	0.60**	0.54**	−0.06	0.26	0.61**	0.62**	0.62**	−0.60**	−0.10	−0.50**	−0.53**
Na^+	0.04		0.33*	0.22	0.82**	0.14	0.07	0.14	0.23	0.19	0.01	−0.06	0.163
NH_4^+	0.68**	0.29*		0.82**	0.13	0.20	0.18	0.81**	0.86**	−0.11	0.60**	−0.04	−0.69**
K+	0.51**	0.09	0.76**		0.10	0.12	0.76**	0.16	0.75**	−0.02	−0.15	0.18	−0.08
Mg^{2+}	−0.15	0.60**	0.04	0.02		0.35*	−0.14	−0.09	−0.02	0.11	−0.02	−0.13	0.15
Ca^{2+}	0.10	0.23	0.25	0.18	0.59**		0.43**	0.39*	0.27	−0.06	−0.08	−0.05	−0.04
Cl^-	0.65**	0.08	0.06	0.65**	−0.16	0.10		0.16	0.85**	−0.18	−0.11	0.01	−0.14
NO_3^-	0.61**	0.14	0.75**	0.06	−0.08	0.08	0.10		0.88**	0.09	0.55**	0.09	−0.65**
SO_4^{2-}	0.71**	0.22	0.81**	0.64**	−0.11	0.03	0.77**	0.77**		0.14	0.45**	−0.06	−0.68**
Temperature	−0.61**	0.28	−0.19	−0.19	0.12	−0.01	−0.13	0.10	0.16		−0.32*	0.38**	0.74**
RH[a]	−0.15	0.19	0.57**	−0.23	−0.17	−0.21	−0.17	0.62**	0.53**	−0.32*		0.72**	0.07
VP[b]	−0.54**	−0.12	−0.02	0.29	−0.20	−0.01	0.04	0.12	−0.02	0.38**	0.72**		0.56**
WS[c]	−0.60**	0.10	−0.62**	−0.15	0.13	−0.03	−0.18	−0.57**	−0.68**	0.74**	0.07	0.56**	

* Correlation is significant at 0.05 level (2-tailed)

** Correlation is significant at 0.01 level (2-tailed)

[a] Relative humidity

[b] Vapour pressure

[c] Wind speed

rainfall. Particulate concentrations exhibit significant negative correlations with vapour pressure. Re-suspended soil dust under unstable atmospheric conditions (low pressure and high wind speed) during the study period might explain the cause of negative correlations observed between particulate concentrations and vapour pressure. Atmospheric pressure influences pollutant concentrations indirectly by affecting the atmospheric stability conditions. In general, high atmospheric pressure is often related to low wind speed and stable stratification, limiting dispersion of pollutants within the atmosphere (Tsai 2005; Rehwagen et al. 2005; Turalioglu et al. 2005; Chaloulakou et al. 2003). The stable atmospheric conditions with high pressure and low wind speeds are most unfavorable in terms of air pollution, whereas low pressure with high wind speed apparently leads to high coarse particle concentrations due to re-suspension processes (Harrison et al. 2001).

The correlation coefficients among major components revealed that $PM_{2.5}$ and PM_1 was well correlated with K^+, Cl^-, NO_3^- and SO_4^{2-}. Na^+ correlated well with NH_4^+ and Mg^{2+}. NH_4^+ had a strong correlation with K^+, NO_3^- and SO_4^2. In the fine and submicron fractions a higher correlation between ammonium and sulphate suggested that these two species are associated in ambient air. NO_3^- shows strong correlation with SO_4^{2-} for $PM_{2.5}$ and PM_1 aerosols. The high correlation between nitrate and sulphate is due to the formation of secondary inorganic aerosols in the atmosphere (Rastogi and Sarin 2005). A poor correlation between Na^+ and Cl^- in the $PM_{2.5}$ and PM_1 samples confirms the origin of Na^+ and Cl^- from non sea-salt substances.

Table 1 showed the meteorological data, including temperature, relative humidity, and wind speed during the study period. The relatively low temperature and wind speed in winter season favor the formation of the permanent temperature inversion, stable atmosphere and low mixed boundary layers, which would then lead to the accumulation of pollutants. Additionally, the higher the relative humidity in winter would accelerate the formation of secondary species such as sulphate, nitrate and ammonium from their precursors, SO_2 and NO_x, and aggravate the pollution level of the atmosphere. The relative humidity and wind speed were two most important factors affecting the concentration of pollutants in the aerosols. The secondary species (NH_4^+, SO_4^{2-} and NO_3^-) showed strong positive correlation with relative humidity and negative correlation with wind speed. Besides, all pollution species showed relatively weak negative correlations with temperature, indicating that higher temperature would be against the accumulation of pollutants.

3.5 Principal component analysis

A preliminary source identification study of the water soluble ionic species was carried out by principal component analysis (PCA, Statistica 5.0 program). PCA is a widely used statistical technique for data reduction and interpretation. In our application of PCA, a small number of latent factors (principal component or PCs) were extracted from the concentration data, and they were used to interpret the relationship among the measured variables (Han et al. 2006). It is important to underline that none of the data, analysed for ionic species, was an outlier that could have caused overlapping of data points in PC analysis. The correlation matrix was used for the present study because the communality of these eight water soluble ionic species was rather reasonable. Furthermore, in this study all factors extracted with eigenvalues>1.0, were retained for interpretation as suggested by the Kaiser criterion (Kaiser 1960). When the VARIMAX normalized rotation is used in PCA, as was the case in our study, each PC score contains information on correlations among all of

the variables combined into a single number. The individual loadings for each ion indicate its relative contribution each of the PC scores. Table 5 shows factor loading for ionic species in $PM_{2.5}$ and PM_1 aerosols. Only factor loading >0.25 were included in Table 5, smaller loading (<0.25) were considered to be insignificant (Karakas and Semra 2008). The PCA model gives two factors for the water soluble ionic species in $PM_{2.5}$ and PM_1 aerosol samples, which accounted for 74.5% and 69.2% of the total variance in the concentration data, respectively. Factor 1 accounts for 49.2% and 45.7% of the total variance, respectively for $PM_{2.5}$ and PM_1 aerosol samples, and it was strongly loaded with NH_4^+, K^+, Cl^-, NO_3^- and SO_4^{2-}, suggesting likely origins from anthropogenic sources, especially coal combustion, traffic emissions and biomass burning. Factor 2 accounts for the 25.3% and 23.5% of the total variance for $PM_{2.5}$ and PM_1 aerosol samples, respectively, which shows significant higher loadings of Na^+, Mg^{2+} and Ca^{2+}, suggesting their partial association with natural, such as soil derived particles.

4 Conclusion

To better understand the causes of the air pollution problem in eastern central India, atmospheric aerosols $PM_{2.5}$ and PM_1 size fractions were collected between July 2009 and June 2010. This study elucidate the characteristics of $PM_{2.5}$ and PM_1 in capital city Raipur, India and their annual mean concentrations were found as 150.9 and 72.5 $\mu g/m^3$, respectively. The annual mean concentrations of $PM_{2.5}$ exceeded annual National Ambient Air Quality Standards (NAAQS) guidelines of India. Very high elevated levels of $PM_{2.5}$ and PM_1 were observed in winter ($PM_{2.5}$: 225.1 $\mu g/m^3$; PM_1: 108.4 $\mu g/m^3$) and spring ($PM_{2.5}$: 172.1 $\mu g/m^3$; PM_1: 81.4 $\mu g/m^3$) seasons indicating critical pollution situation, whereas low levels in rainy season ($PM_{2.5}$: 91.3 $\mu g/m^3$; PM_1: 42.7 $\mu g/m^3$) indicates the influence of monsoon precipitation washing down the pollutants. The ratios of $PM_1/PM_{2.5}$ were calculated to understand the contribution of PM_1 in $PM_{2.5}$. It could be seen that PM_1 accounted for 48, 48, 46 and 48% of the $PM_{2.5}$ in fall, winter, spring and summer, respectively, clearly indicating larger PM_1 fractions in $PM_{2.5}$ at this area of eastern central state of India.

Table 5 Rotated component matrix for water soluble ionic species in $PM_{2.5}$ and PM_1 aerosols

PM₂.₅ (Fine particles)			PM₁ (Submicron particles)		
Component	Factor 1	Factor 2	Component	Factor 1	Factor 2
Na^+	0.36	0.76	Na^+		0.76
NH_4^+	0.94		NH_4^+	0.89	
K+	0.69	0.41	K+	0.77	
Mg^{2+}		0.80	Mg^{2+}		0.92
Ca^{2+}		0.87	Ca^{2+}	0.36	0.94
Cl^-	0.74	0.49	Cl^-	0.70	0.34
NO_3^-	0.91		NO_3^-	0.76	0.49
SO_4^{2-}	0.94		SO_4^{2-}	0.93	0.36
Initial Eigenvalue	3.97	1.84	Initial Eigenvalue	3.71	1.44
Variance Explained	49.2%	25.3%	Variance Explained	45.7%	23.5%
Cumulative Variance Explained	49.2%	74.5%	Cumulative Variance Explained	45.7%	69.2%

The concentrations of total water soluble inorganic ions varied from 13.7% to 76.9% with an average of 11.8% for $PM_{2.5}$ and from 1.5% to 85.0% with an average of 21.9% for PM_1, respectively. The concentrations of SO_4^{2-}, NO_3^- and NH_4^+ were significantly high in the total water soluble inorganic fraction in $PM_{2.5}$ and PM_1. Among the detected ions SO_4^{2-} was the major chemical component of $PM_{2.5}$ (7.68 μg/m^3, 45.8% of the TWSII) and PM_1 (5.61 μg/m$_3$, 52.7% of the TWSII), while NO_3^- (3.12 μg/m^3, 13.0% of the TWSII for $PM_{2.5}$ and 1.81 μg/m^3, 11.8% of the TWSII for PM_1) was second higher water soluble component followed by NH_4^+ (1.94 μg/m^3, 11.4% of the TWSII for $PM_{2.5}$ and 1.26 μg/m^3, 12.6% of the TWSII for PM_1). The higher concentrations of SO_4^{2-}, NH_4^+, NO_3^-, Cl^- and K^+ were observed during the winter due to the enhanced burning activities and industrial emissions in this season, while Na^+, Mg^{2+} and Ca^{2+} exhibited higher concentrations during the spring and summer as the dry weather in these seasons was favorable for the resuspension of soil particles.

The correlation study revealed a number of strong correlations between PM and different ionic pairs, pointing towards the probable common origin in the atmosphere. $PM_{2.5}$ and PM_1 were negatively correlated with temperature and wind speed, indicating that the higher temperature and wind speed would be against the accumulation of pollutants. Among the ionic species, NH_4^+, NO_3^- and SO_4^{2-} were found to be positively correlated with the relative humidity and negatively with the wind speed. $PM_{2.5}$ and PM_1 were positively correlated with K^+, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+. NH_4^+ had strong correlation with K^+, NO_3^- and SO_4^{2-}. A poor correlation between Na^+ and Cl^- in PM confirms that the origin of Na^+ and Cl^- is from non-sea salt substances.

The source identification by Principal Component Analysis demonstrated the major contribution of ionic species from anthropogenic and natural sources. SO_4^{2-}, NH_4^+, NO_3^-, Cl^- and K^+ are attributed to an origin from anthropogenic sources. Furthermore, Na^+, Mg^{2+} and Ca^{2+} are originated mainly from natural sources.

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