Water Soluble Ions in PM_{2.5} and PM₁ Aerosols in Durg City, Chhattisgarh, India

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ABSTRACT

This paper reports the atmospheric concentrations of PM_{2.5} and PM₁ mass, water soluble inorganic components and their seasonal variations measured between the period of July 2009 and June 2010 in Durg city (20°23' to 22°02'N and 80°46' to 81°58'E), India. A cascade impactor sampler with Whatman 41 glass filters was used to collect aerosol samples in PM_{2.5} and PM₁ size fractions. The results showed that the annual mean concentration of PM_{2.5} and PM₁ were 135.0 µg/m³ and 64.7 µg/m³, respectively. Annual cycle shows highest concentration of PM_{2.5} and PM₁ mass and water soluble ions in winter season and the lowest during rainy season. This is attributed to the enhanced production of aerosols and prevailing meteorological conditions. The higher PM₁/PM_{2.5} ratio (0.48) during the whole campaign clearly indicates larger PM₁ particle fractions were in PM_{2.5} at this location. Out of the total aerosol mass, water soluble constituents contributed an average of 11.57% (7.48% anions, 4.09% cations) in PM_{2.5} and 16.98% (11.14% anions, 5.85% cations) in PM₁. The concentrations of SO₄²⁻ and NO₃⁻ were highest in all size fractions and accounted for 32.76% and 13.38% of the total mass of the water soluble ions in PM_{2.5} and 32.78% and 12.21% in PM₁ size fractions. Na⁺, Mg²⁺ and Ca²⁺, derived from the soil dust particles, were higher in spring and summer, as the dry weather in this season was favorable for the resuspension of soil particles. The seasonal variation of Cl⁻, K⁺ and secondary components (NH₄⁺, NO₃⁻ and SO₄²⁻) were similar with high concentrations in winter and low concentrations in fall. Two principal components explaining 76.6% and 65.9% of the variance for PM_{2.5} and PM₁ data set respectively were identified. Factor 1 has significant loading of species of anthropogenic origins and factor 2 showed partial associations with species of natural origins.

Keywords: PM_{2.5}; PM₁; Water soluble ions; Seasonal variation; Principal component analysis.

INTRODUCTION

The atmospheric particulate matter (PM) is a significant worldwide environmental issue due to several adverse impacts on human health, global climate, visibility, ecosystems and on the atmospheric chemistry (Pope, 2000; Hong *et al.*, 2002; IPCC, 2007). It is broad understanding nowadays that the PM₁₀ measurement provide very important steps towards the quality assessment; however there is equally no doubt that more accurate descriptors of the actual environment burden are still needed. There is a consensus that likely PM_{2.5} (fine) and PM₁ (submicron) particles would be the more suitable size than PM₁₀ for health related aerosol study (Kupelwieser *et al.*, 2010). There is an abundance of mass concentrations, distribution,

and chemical measurement for PM₁₀ and PM_{2.5-10} in many urban and heavily industrialized areas around the world (Karar and Gupta, 2006; Mauli *et al.*, 2006; Mkoma *et al.*, 2009; Singh *et al.*, 2010). Moreover, when these particulates are loaded with some ionic species in different forms and inhaled or ingested they impose serious health hazards. Typically, the major components of urban ambient PM_{2.5} have been reported as sulfate, nitrate, ammonium, organic carbon, and elemental carbon (Hopke *et al.*, 2008; Chakraborty and Gupta, 2010; Kim *et al.*, 2011). However, very little is known and even less has been done specially about PM₁. Hence determining their composition is essential to understanding their properties and reactivity and hence their environmental effects (Singh *et al.*, 2010). Several studies have been conducted in the world in various environment and size fractions for water soluble inorganic ions (Nicolas *et al.*, 2009; Mena *et al.*, 2010).

In year 2000, Chhattisgarh earned the status of a separate and sovereign state of India. Soon after, with the financial aid of central government, the state gained a

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boom in development in all sectors and currently has the status of fastest growing state in the country. The rapid industrialization in Chhattisgarh is due to the availability of ores and mineral resources in abundant including coal, limestone, granite, iron ore, bauxite, etc. Besides these, the alarming vehicular and population growth rate, frequent traffic jams and overall a poor infrastructure has led to a significant rise in the PM level of Durg city. Although vehicles and industries are the two most important contributors to the Durg's ambient PM level but contribution from other pollution sources, such as roadside dust, power plants and local sources can't be ruled out. Very little studies have been conducted in this part of the world on characterization of fine and submicron particulate matter ($PM_{2.5}$ and PM_{10}), but there characterization and source identification is very much important as these particles can remain suspended in air for long time and can be transported to a long distance with wind and can easily penetrate deep into our respiratory tract. In comparison to the developed countries, little attention has been given for $PM_{2.5}$ and PM_{10} particles in India. In India, ambient air quality data for water soluble ions are available for few cities like Agra (Kulshresta *et al.*, 2009), Delhi (Srivastava *et al.*, 2007), and Raipur (Deshmukh *et al.*, 2010). Durg is one of the most polluted cities in India today. Therefore, this paper present the first measurements results of water soluble inorganic ions of the $PM_{2.5}$ and PM_{10} aerosols obtained during a one year in Durg city, Chhattisgarh state, India. The main objectives were to investigate the levels, seasonal variations and sources of the ions in the city. The influence of various meteorological conditions was also examined.

EXPERIMENTAL

Study Area

The continuous aerosol samplings were carried out during one year between July 2009 and June 2010 in Durg city, located at Chhattisgarh state (Fig. 1). The city is situated between 20°23' to 22°02'N and 80°46' to 81°58'E at an elevation of about 317 m above sea level. The sampling was done at a height of 15 m above the ground level in a double storied building in front of the Government Science College. The site is a congested area with heavy traffic density mainly constituted by diesel trucks, buses, cars and double stroke automobiles. Bhilai Steel Plant (BSP) in Durg district happens to be largest integrated steel plant of the country. Durg city is also home to a number of large scale cement plants. The climate is tropical with four distinct seasons, fall (July, August, September), winter (October, November, December, January), spring (February, March) and summer (April, May, June). Generally, Durg has a typical dry weather which warms up to 42°C in summer season. The onset monsoon is usually from July and the season extends up to September, with monsoon peaking during July and August.

Aerosol Collection

Size-segregated aerosol samples were collected using eight stage cascade impactor type aerosol sampler (Model

TE 20-800 Tisch Air Pollution Monitoring Equipment, USA) for eight size ranges 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: 2.5–2.1 μm , stage 6: 2.1–1.0 μm ; stage 7: 1.0–0.7 μm and stage 8: 0.7–0.4 μm . $PM_{2.5}$ 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_{10} particles presented the sum total of particles of size ranges 1.0–0.7 and 0.7–0.4 μm . The average flow rate of suction pump was maintained at 28.3 L/min. The samples were collected twice in a week for a period of 24 h at a rate of 1.7 m^3/h . The samples were collected on pre-weighed 80 mm Whatman 41 glass filters. Total 120 samples (fall, $n = 30$; winter, $n = 40$; spring, $n = 20$; summer, $n = 30$) were collected during the monitoring period. The blank filters were stored and carried to the field to simulate the same environment as the actual samples used in the measurements.

PM Mass Measurement

Particulate mass concentrations were determined gravimetrically. Before weighing, the filters for the samples and field blanks were conditioned at a temperature of 20°C and a relative humidity of 40% for 24 h and the weighing were done at these conditions. The conditioned sample filters were weighed before and after sampling with an electronic balance (reading precision 10 μg). The actual samples and blank filters were placed into polyethylene bottles and kept frozen at –20°C during storage and transported cool to the Public Health and Research Institute of Kobe City, Japan for analysis.

Water Soluble Ion Analysis

One-fourth of the filter samples were extracted into 10 mL ultrapure water (specific resistance: 18 $\text{M}\Omega\text{ cm}$) 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. 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 water soluble ions was performed using separation columns Ionpac AS 12A and CS 16A, respectively for anion and cations. Eluents of 2.7 mM Na_2CO_3 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. A 2.6 mM methane sulphonic acid ($\text{CH}_3\text{SO}_3\text{H}$) solution was used as an eluent for cation analysis with a pump flow rate of 1 mL/min. Ions were identified based on their retention time. The method detection limit (DL) was calculated for the Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} ions from 1 ppm of the laboratory prepared calibration standards. The obtained DL were 0.01, 0.03, 0.02, 0.01, 0.01, 0.01, 0.01 and 0.02 $\mu\text{g}/\text{m}^3$ for Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} , respectively. The overall mean concentrations for field blank samples collected over a year were

Fig. 1. A map of the study area showing location of the sampling site.

observed to be 0.03, 0.06, 0.01, 0.01, 0.08, 0.04, 0.00 and $0.14 \mu\text{g}/\text{m}^3$ for Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} , respectively. Blank filters were treated in similar way as the actual aerosol samples and all the reported ionic concentrations and PM mass were corrected using field blanks.

Meteorology

Meteorological data for the period of aerosol sampling from July 2009 to June 2010 was obtained from Department

of Agrometeorology, Indira Gandhi Agricultural University, Raipur, India. Table 1, shows monthly mean and range for the meteorological parameters temperature (T, °C), relative humidity (RH, %), rainfall (RF, mm), vapour pressure (VP, kPa), wind speed (WS, m/s) and wind direction (WD, degree) during the study period. January was a cold winter month with a mean temperature of 16.2°C , and May attained the maximum mean summer temperature of 33.6°C . It is clearly seen from Table 1 that the monthly mean temperature was almost consistent in summer and monsoon months and

Table 1. Mean and ranges for meteorological parameters at sampling site Durg, India during July 2009 to June 2010.

Month	Temperature (°C)	Rainfall (mm)	Relative humidity (%)	Vapor pressure (kPa)	Wind speed (m/s)	PWD ^a
July 2009	25.6 (22.0–30.8)	132.1 (21.2–335.2)	80 (58–92)	2.9 (2.8–3.4)	10.5 (7.7–12.7)	SW, W
August 2009	25.5 (21.6–29.6)	57.9 (18.4–100.8)	87 (75–96)	3.0 (2.9–3.0)	5.8 (4.5–8.2)	SW
September 2009	26.3 (21.9–30.8)	9.7 (5.2–18.4)	81 (63–96)	2.9 (2.8–3.0)	4.0 (3.0–4.7)	NW, NE
October 2009	23.1 (12.5–30.5)	10.8 (0.0–52.0)	71 (26–95)	2.0 (1.3–3.0)	2.5 (1.4–6.2)	N, NE
November 2009	19.3 (8.0–28.2)	0.8 (0.0–4.2)	70 (33–94)	1.6 (1.3–2.3)	2.8 (1.3–4.5)	NE
December 2009	17.6 (8.8–27.3)	4.3 (0.0–20.4)	67 (37–95)	1.3 (1.1–1.4)	1.5 (1.2–1.7)	NE
January 2010	16.2 (5.8–26.3)	3.3 (0.0–16.6)	61 (22–95)	1.0 (0.8–1.4)	1.6 (1.0–2.2)	N
February 2010	21.5 (10.4–32.2)	1.9 (0.0–6.8)	54 (22–89)	1.2 (1.2–1.7)	2.2 (1.4–2.7)	NW
March 2010	27.7 (16.5–38.2)	0.4 (0.0–2.0)	40 (18–65)	1.3 (1.0–1.4)	4.6 (3.0–6.6)	SW
April 2010	31.1 (19.7–41.2)	1.2 (0.0–6.0)	30 (11–58)	1.2 (1.0–1.6)	6.2 (4.1–8.1)	SW, W
May 2010	33.6 (23.3–42.4)	4.7 (0.0–12.5)	35 (17–58)	1.7 (1.5–2.1)	7.2 (6.0–8.8)	SW, W
June 2010	29.9 (22.7–41.5)	27.3 (0.0–62.6)	61 (21–86)	2.5 (1.6–2.8)	9.1 (8.1–10.2)	SW
Annual	26.4 (5.8–42.4)	22.5 (0.0–335.2)	64 (11–96)	1.9 (0.8–3.4)	4.8 (1.0–12.7)	SW, W

^a Prevalent wind direction.

commences decreasing thereafter. The relative humidity varied from a minimum of 11% in April to a maximum of 96% in August and September. The prevailing winds were south-west during the study period with wind speed varying from 1.0 m/s (January) to 12.7 m/s (July). The annual mean wind speed was found to be 4.8 m/s during the study period.

RESULTS AND DISCUSSION

Concentrations of PM_{2.5} and PM₁

The concentrations of PM_{2.5} and PM₁ aerosols during the whole study period ranged from 26.7 to 263.0 µg/m³ and from 8.6 to 134.7 µg/m³, respectively. The mean annual concentrations of PM_{2.5} and PM₁ mass were 135.0 ± 76.2 and 64.7 ± 36.9 µg/m³, respectively (Table 2 and 3). The observed annual mean PM_{2.5} concentration was significantly high compared to the prescribed limit of 65 µg/m³ of the National Ambient Air Quality Standards (NAAQS) of India (<http://www.scorecard.org/envreleases/def/capnaaq.html>).

The results also showed that the daily PM_{2.5} concentrations exceeded the air quality guidelines of the World Health Organization (WHO) of 20 µg/m³ for PM_{2.5} (WHO, 2005). In Chhattisgarh, the major particulate emission sources include industries (using heavy oil and coal), vehicles, disorderly mixed traffic causing congestion, construction activities, use of soft coal for domestic cooking (Deshmukh *et al.*, 2010). The sampling site is encompassed with educational institutions surrounded by areas exclusively devoted to residential, agricultural and industrial activities. The presence of the National Highway and railroads has favored industrial development of the region. The huge coal burning industries such as Bhilai Steel Plant, Bhilai, Thermal Power Plant, Durg, large number of big cement plants and sponge iron industries are located in a radius of only about 10–40 km which produce huge amount of fly ash and affect the local environment as well as surrounding by the aerial dispersion (Verma *et al.*, 2010). Road dust resuspension may in fact have a great influence on PM_{2.5}.

Table 2. Mean mass (and ranges) concentration and associated standard deviation (µg/m³) of PM_{2.5} and water soluble ions and percentage contribution of water soluble constituents in PM_{2.5} at Durg, India.

Species	Concentration				Percentage contribution of PM mass (%)			
	Mean	Stdev ^b	Min ^c	Max ^d	Mean	Stdev ^b	Min ^c	Max ^d
PM _{2.5}	135.0	76.2	26.7	263.0	-	-	-	-
Na ⁺	1.08	1.19	0.15	3.86	1.04	1.27	0.15	3.76
NH ₄ ⁺	2.13	1.04	0.31	3.87	1.66	0.80	0.41	3.81
K ⁺	0.87	0.70	0.05	1.93	0.55	0.30	0.07	0.88
Mg ²⁺	0.18	0.20	0.03	0.60	0.18	0.22	0.01	0.59
Ca ²⁺	0.70	0.52	0.28	1.82	0.66	0.59	0.14	1.78
Cl ⁻	2.06	2.10	0.03	6.39	1.26	0.97	0.05	3.05
NO ₃ ⁻	3.16	3.62	0.05	11.16	1.85	1.64	0.07	5.33
SO ₄ ²⁻	6.75	6.04	0.17	19.51	4.37	3.00	0.23	9.31
TWSII ^a	16.93	12.67	1.11	41.88	11.57	6.46	1.48	21.03
Total anions	11.97	11.65	0.26	37.06	7.48	5.41	0.35	17.69
Total cations	4.96	2.58	0.85	9.56	4.09	2.73	1.13	9.56
Ionic ratio	4.85	8.25	0.28	28.97	-	-	-	-

^a Total water soluble inorganic ions; ^b Standard deviation; ^c Minimum; ^d Maximum; Ionic ratio is $\Sigma \text{cations (equivalent mass)} / \Sigma \text{anions (equivalent mass)}$

Table 3. Mean mass (and ranges) concentration and associated standard deviation ($\mu\text{g}/\text{m}^3$) of PM_{10} and water soluble ions and percentage contribution of water soluble constituents in PM_{10} at Durg, India.

Species	Concentration				Percentage contribution of PM mass (%)			
	Mean	Stdev ^b	Min ^c	Max ^d	Mean	Stdev ^b	Min ^c	Max ^d
PM_{10}	64.7	36.9	8.6	134.7	-	-	-	-
Na^+	0.81	1.00	0.09	3.15	1.64	2.16	0.14	6.01
NH_4^+	1.43	0.65	0.21	2.39	2.38	1.11	0.59	4.68
K^+	0.78	0.66	0.02	1.75	1.00	0.61	0.06	1.64
Mg^{2+}	0.06	0.04	0.03	0.15	0.12	0.10	0.03	0.33
Ca^{2+}	0.36	0.39	0.06	1.24	0.72	0.85	0.06	2.45
Cl^-	1.51	1.63	0.03	4.88	1.93	1.66	0.09	5.10
NO_3^-	2.11	2.64	0.03	8.03	2.56	2.65	0.08	8.38
SO_4^{2-}	4.91	4.62	0.05	15.02	6.65	5.01	0.16	15.68
TWSII ^a	11.96	9.50	0.56	31.44	16.98	10.29	1.60	32.82
Total anions	8.53	8.75	0.12	27.93	11.14	8.82	0.35	29.15
Total cations	3.44	1.90	0.44	6.91	5.85	4.00	1.25	14.57
Ionic ratio	5.29	9.09	0.26	31.46	-	-	-	-

^a Total water soluble inorganic ions; ^b Standard deviation; ^c Minimum; ^d Maximum; Ionic ratio is Σ cations (equivalent mass) / Σ anions (equivalent mass)

and PM_{10} levels in the Durg city since there are more than 200,000 registered motor vehicles. Due to the high degree of commercial activities and services within the city the average daily traffic volume was about 2050–2120 per hour at a nearby highway (Sharma *et al.*, 2003). Traffic includes animal-driven carts, diesel-powered buses and trucks, 2-stroke motorcycles, and three-wheelers (auto rickshaws) running on a mixture of petroleum gasoline and motor oil, and motor vehicle that use petroleum gasoline or compressed natural gas. The municipal corporation area of Durg city extends over 137 km^2 with a present population of about 0.6 million (Census of India, 2011). Durg is the second largest city with an average population and vehicular growth rates of 3.24% and 4.42% per year, respectively. This alarming population and vehicular growth rate has resulted in a significant rise in the particulate matter levels over Durg. However, emission from small scale industries and workshops and soil derived aerosols are considered as other important contributing sources (Sharma *et al.*, 2003). Over the last decades, Indian cities have undergone a substantial growth in development and urbanization coupled with motorization and increase in energy use (Kumar *et al.*, 2001; Gupta and Kumar, 2006; Kulshrestha *et al.*, 2009). When comparing our results with those for urban sites in India, as reported in the literature (Kothai *et al.*, 2008; Tiwari *et al.*, 2009; Deshmukh *et al.*, 2010; Verma *et al.*, 2010), the levels of the $\text{PM}_{2.5}$ and PM_{10} mass in Durg are slightly higher than at the other Indian sites.

In order to establish the seasonal trends in the aerosol load, the PM mass concentrations for the two size fractions as well as the PM ratios, were discussed separately for fall, winter, spring and summer. Fig. 2 shows variation of mean $\text{PM}_{2.5}$ and PM_{10} mass concentrations and $\text{PM}_{10}/\text{PM}_{2.5}$ ratio during the monitoring period. $\text{PM}_{2.5}$ and PM_{10} mass concentrations showed pronounced seasonality with high levels in winter season ($\text{PM}_{2.5}$: 215.0 $\mu\text{g}/\text{m}^3$ and PM_{10} : 101.3 $\mu\text{g}/\text{m}^3$) followed by spring ($\text{PM}_{2.5}$: 144.0 $\mu\text{g}/\text{m}^3$ and PM_{10} : 76.1 $\mu\text{g}/\text{m}^3$), summer ($\text{PM}_{2.5}$: 83.5 $\mu\text{g}/\text{m}^3$ and PM_{10} : 37.5

$\mu\text{g}/\text{m}^3$) and fall season with the lowest levels ($\text{PM}_{2.5}$: 73.9 $\mu\text{g}/\text{m}^3$ and PM_{10} : 35.4 $\mu\text{g}/\text{m}^3$). The seasonal variability of $\text{PM}_{2.5}$ and PM_{10} concentrations are influenced by the seasonal anthropogenic activities and by meteorological factors during the study period. The large level of $\text{PM}_{2.5}$ and PM_{10} in Durg are due to the huge agricultural practices and brick kiln emissions in winter (Deshmukh *et al.*, 2010). During the winter season, heaps of solid waste comprising mostly of fallen leaves, garden cuttings, plastic bags and paper are set alight along road sides. Chhattisgarh with more than 600 rice mills is known as rice bowl of central India. There is an intense agricultural work in and around Durg, with the main crop being rice and wheat. After crop harvesting the biomass residues are set on fire on the field to fertilize the land for the coming year. The reason for higher PM concentrations in winter is also due to the massive biomass burning especially during night time in winter season. The only plausible reason for this can be attributed to the close proximity of a large open field where hundreds of slums are present. Besides, slums in and around the city use biomass as a cooking fuel. Peoples also use combustible goods like, wooden blocks, fire wood, and cow dung cake as bonfire in the open space to keep themselves warm in winter season, resulting in significant quantities of ashes in the atmosphere. Moreover, the release height of the emissions is low and the air mixing can be poor during the winter season, which both amplifies the local air quality impact. The high particulate mass in winter is also due to the operation of a number of brick kilns approximately 10 km northeast to the sampling site, which utilize low quality coal, paddy husk and other combustible materials available at low cost. Additionally, the higher concentration of $\text{PM}_{2.5}$ and PM_{10} aerosols in winter at Durg is also attributed to a high concentration of anthropogenic aerosols which is injected into the atmosphere due to burning of crackers and fire-works during the Diwali festival period (18 October to 2 November) and other ceremonial occasions like marriages in this region (November–January) (Tiwari *et al.*, 2009).

Fig. 2. Seasonal variation of $PM_{2.5}$ and PM_1 mass concentrations and PM_1 to $PM_{2.5}$ ratio during the period of July 2009 to June 2010.

In addition to the above local sources, the meteorological conditions prevailing at the study area also had the influence on the higher concentrations of $PM_{2.5}$ and PM_1 during the winter and lower concentrations in summer and fall. The meteorological data on temperature, rainfall, relative humidity, vapor pressure, wind speed and prevalent wind direction are shown in Table 1 for the entire period of study. Low concentrations during the fall months (July–September) could be due to wash out effect of rainfall (5.2–335.2 mm, July–September) which leads to reduction in suspension of crustal dust. The high relative humidity (95%, October–January), low temperature (5.8°C, January) and relatively calm wind speed (~1.0 m/s, October–January) helped high particulate mass loading in winter (October–January) and spring (February–March) months due to the lower inversion layer caused by low mixing height that limits dispersion of fine and submicron particulates (Salve *et al.*, 2006). High temperature (~42°C, April–June), low relative humidity (11%, April), frequent changes in wind speed (4.1–10.2 m/s, April–June) and direction increased the atmospheric turbulence during summer months (April, May and June), thereby increasing the dispersion of PM emission. Many other studies also indicate similar trend in these seasons (Ravindra *et al.*, 2003; Gupta and Kumar, 2006).

Since different sizes of atmospheric particles probably originate from different sources, the mean $PM_1/PM_{2.5}$ ratios have been used to understand the contribution of PM_1 in

$PM_{2.5}$ and identify the sources of $PM_{2.5}$ and PM_1 (Sun *et al.*, 2004; Charron *et al.*, 2005). It could be seen that PM_1 accounted for 48, 47, 54 and 44% of $PM_{2.5}$ in fall, winter, spring and summer, respectively. However, the $PM_1/PM_{2.5}$ for the whole period of monitoring was 0.48 which clearly indicates larger submicron particle fractions in $PM_{2.5}$ at this location. The regression relationship between PM_1 and $PM_{2.5}$ is displayed in Fig. 3, which shows a good correlation (0.965) between the two size fractions indicating possible similar sources (Parmar *et al.*, 2001).

Fig. 3. Relationship between $PM_{2.5}$ and PM_1 mass concentrations.

Water Soluble Ionic Content of PM_{2.5} and PM₁

Water soluble ions are chemical species which are easily soluble in water in the lower troposphere under certain conditions and they are usually significant components by mass of atmospheric aerosols. Mean concentration and concentration ranges ($\mu\text{g}/\text{m}^3$) of water soluble ions and percentage contribution of water soluble constituents in PM_{2.5} aerosols collected during the study period in Durg city are presented in Table 2. The trend for the mean water soluble ionic concentrations in PM_{2.5} was $\text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ > \text{Cl}^- > \text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$. The concentration of total water soluble inorganic ions ranged from 1.11 $\mu\text{g}/\text{m}^3$ to 41.88 $\mu\text{g}/\text{m}^3$ with mean concentration of 16.93 $\mu\text{g}/\text{m}^3$. The total water soluble inorganic ions accounted for 11.57% of the total mass of PM_{2.5}. Out of the total PM_{2.5} fractions 88.43% are unanalyzed. The unanalyzed residue likely includes silicates, phosphate, trace metals, carbon and organics (Kumar et al., 2007). The contribution of cations and anions ranged from 1.13% to 9.56% and 0.35% to 17.69% with mean value of 4.09% and 7.48%, respectively. The major ions species in PM_{2.5} were SO_4^{2-} , NO_3^- and NH_4^+ and their concentrations varied from 0.05 to 19.51 $\mu\text{g}/\text{m}^3$, with annual mean concentrations of 6.75 $\mu\text{g}/\text{m}^3$, 3.16 $\mu\text{g}/\text{m}^3$ and 2.13 $\mu\text{g}/\text{m}^3$ for SO_4^{2-} , NO_3^- and NH_4^+ respectively. The SO_4^{2-} , NO_3^- and NH_4^+ accounted 32.76%, 13.83% and 19.58% of the total mass of water soluble inorganic ions analyzed in PM_{2.5}, respectively. The highest sulfate ion concentrations suggest a large component of secondary inorganic aerosols resulting from emissions of SO_2 by a variety of combustion sources using sulfurous fuels, such as coal and oil. The annual average concentration of Cl^- and K^+ in PM_{2.5} aerosols were 2.06 $\mu\text{g}/\text{m}^3$ and 0.87 $\mu\text{g}/\text{m}^3$, respectively. The annual average concentrations of Na^+ , Ca^{2+} and Mg^{2+} in PM_{2.5} aerosols were 1.08 $\mu\text{g}/\text{m}^3$, 0.70 $\mu\text{g}/\text{m}^3$ and 0.18 $\mu\text{g}/\text{m}^3$, respectively. Cl^- , K^+ , Na^+ , Ca^{2+} and Mg^{2+} accounted for 9.23, 5.25, 9.82, 8.30 and 1.68% respectively of the total PM_{2.5} mass of the water soluble inorganic ions.

Table 3 shows the mass concentrations and percentage contribution of the water soluble ionic species in PM₁. The trend of the mean water soluble ionic concentrations in PM₁ was $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$. The concentrations of total water soluble inorganic ions in PM₁ accounted for 16.98% of the total PM₁ mass and varied from 1.60% to 32.82%. The concentrations of SO_4^{2-} , NO_3^- , Cl^- and NH_4^+ were highest among all ions in PM₁. Among all the chemical species SO_4^{2-} has the highest concentration in PM₁ aerosols, which varied from 0.05 $\mu\text{g}/\text{m}^3$ to 15.02 $\mu\text{g}/\text{m}^3$, with mean concentrations of 4.91 $\mu\text{g}/\text{m}^3$. The annual average concentrations of NO_3^- , Cl^- , K^+ and NH_4^+ in PM₁ aerosols were 2.11 $\mu\text{g}/\text{m}^3$, 1.51 $\mu\text{g}/\text{m}^3$, 0.78 $\mu\text{g}/\text{m}^3$ and 1.43 $\mu\text{g}/\text{m}^3$, respectively. NO_3^- , Cl^- , K^+ and NH_4^+ were reported as 12.21%, 21.58%, 6.32% and 10.63% of the total mass of the ionic species in PM₁ particles, respectively. The annual average concentrations of Na^+ , Ca^{2+} and Mg^{2+} in PM₁ aerosols were 0.81 $\mu\text{g}/\text{m}^3$, 0.36 $\mu\text{g}/\text{m}^3$ and 0.06 $\mu\text{g}/\text{m}^3$, respectively. Na^+ , Ca^{2+} and Mg^{2+} accounted for 10.63%, 5.57% and 1.22% of the total mass of the ionic species analyzed in PM₁ aerosols. In case of

PM_{2.5} and PM₁ the ionic ratios $\{\Sigma(\text{sum of cations in } \mu \text{ equivalents})/\Sigma(\text{sum of anions in } \mu \text{ equivalents})\}$ ratio reported in Table 2 and 3 varied from 0.28 to 28.97 $\mu\text{g}/\text{m}^3$ with a mean and standard deviation of 4.85 ± 8.25 for PM_{2.5} and from 0.26 to 31.46 $\mu\text{g}/\text{m}^3$ with mean and standard deviation of 5.29 ± 9.09 for PM₁. It is clear from the Table 2 and 3 that there is a large difference between concentrations of anions and cations in PM_{2.5}, while the difference in PM₁ is less indicating that cations which mainly comprise of Mg^{2+} , Ca^{2+} and Na^+ are abundant in PM_{2.5} than PM₁. Other studies in India (Parmar et al., 2001; Kumar et al., 2007) also reported excess cation in the ion balance. It is also known that the aerosols of the region are alkaline and Ca^{2+} , Mg^{2+} are derived from soil while SO_4^{2-} , NO_3^- , NH_4^+ , K^+ and Cl^- are anthropogenic sources.

Seasonal Variations of Water Soluble Ions

Fig. 4 shows the seasonal variation of major water soluble components in PM_{2.5} and PM₁ during the one year monitoring period from July 2009 to June 2010. Similar seasonal trends are observed for all water soluble ionic species in PM_{2.5} and PM₁ aerosols. Like PM_{2.5} and PM₁ mass total water soluble ionic species were higher in winter (31.32 $\mu\text{g}/\text{m}^3$ and 22.73 $\mu\text{g}/\text{m}^3$ in PM_{2.5} and PM₁, respectively) and spring (17.24 $\mu\text{g}/\text{m}^3$ and 12.01 $\mu\text{g}/\text{m}^3$ in PM_{2.5} and PM₁, respectively) and lowest during summer (11.18 $\mu\text{g}/\text{m}^3$ and 7.46 $\mu\text{g}/\text{m}^3$ in PM_{2.5} and PM₁, respectively) and fall (3.30 $\mu\text{g}/\text{m}^3$ and 2.10 $\mu\text{g}/\text{m}^3$ in PM_{2.5} and PM₁, respectively). The same trend was reported in previous studies (Wang et al., 2006; Kumar et al., 2007). The main reason for highest concentrations of water soluble ions during winter can be attributed to lower temperature which favored the transformation of ions from gas phase to particle phase and also due to lower mixing height and increased anthropogenic activities (Wang et al., 2006). Lower concentrations measured during fall period can be attributed to the washout of PM containing water soluble ions by rainfall while for summer months (April, May and June) ventilation effect of high wind movements could be the possible reason (Bhaskar et al., 2010).

SO_4^{2-} and NO_3^- both show highest concentrations during winter season (Fig. 4). NO_3^- is generally formed from the oxidation of NO_x (Wang et al., 2006) and its subsequent reaction with ammonia (Utsunomiya and Shinji, 1996) leads to ammonium nitrate particle formation. From previous studies (Han et al., 2008), it can also be said that most of the fine particulate SO_4^{2-} and NO_3^- exist as ammonium nitrate (NH_4NO_3) and ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$]. 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 be due to the high concentration of NO_3^- in winter (Wang et al., 2006). The lower concentrations in summer season can be attributed to volatilization of NH_4NO_3 with increased temperature and decreased relative humidity (RH) (Seinfeld and Pandis, 1998). A similar observation has been reported in other studies in India on the seasonal variation of NO_3^- (Kumar et al., 2007). The high SO_4^{2-} concentrations in winter would indicate that SO_4^{2-} in this season was mostly originated from the local

Fig. 4. Seasonal variation of water soluble ionic species in PM_{2.5} and PM₁ in Durg city during the period of July 2009 to June 2010.

emission sources like – industrial emissions, coal combustion, diesel combustion etc., and it can also be related to the poor dispersion and lower rate of removal via wet deposition. Also, ammonium sulfate is much less volatile than NH_4NO_3 (Utsunomiya and Shinji, 1996) and remain in particulate phase which may explain the observed moderately higher SO_4^{2-} concentrations found in this study. Ammonium seasonal cycles, in the PM_{2.5} and PM₁ particles, followed a

pattern similar to those observed for sulfate and nitrate ions with a maximum in winter and a minimum in summer and fall, indicating that NH_4^+ is largely originated from the neutralization between ammonia and acidic species (Wang et al., 2006). As to the somewhat higher levels of NH_4^+ in winter, this is likely due to the much more extensive agricultural activities around the sampling site and perhaps also to the larger impact from biomass burning there. It is

well known that agricultural activities is an important source of ammonia (IPCC, 2007) and that ammonia is emitted by biomass burning, generally during smoldering combustion.

As the tracers of crustal dust, Na^+ , Ca^{2+} and Mg^{2+} were found to be higher in spring and summer due to the higher wind speed (1.4–6.1 and 4.1–10.4 m/s, respectively in spring and summer) which resulted in enhanced resuspension of crustal dust and lowest during winter and fall seasons when high humidity and rainfall minimized the resuspension of crustal dust. Because of rainfall, the soil become damp restricting the possibility of soil derived particles being released (Bhaskar et al., 2010).

Concentrations of chloride (Cl^-) and potassium (K^+) ions also followed a similar trend as that of NO_3^- and SO_4^{2-} with highest values in winter and lowest values during summer and fall seasons (Fig. 4). The seasonal variation of potassium ion (K^+) was similar to chloride ion (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). As stated earlier, the major fuel used for cooking in this region is biomass. In addition to this, as part of agricultural activity, significant amount of biomass burning (slash burning) take place in the region especially during winter season. Potassium is tracer of biomass burning (Nair et al., 2006) that is measured in both $\text{PM}_{2.5}$ and PM_1 size fractions (Table 2 and 3). Also K^+ showed a substantially correlation coefficient especially in the PM_1 ($r = 0.64$, Table 4) with PM mass. This suggests that the PM mass had a contribution from biomass burning in the study site. The fine and submicron mode potassium could also be released in the atmosphere by burning of vegetative scrap (Kundu et al., 2010). The higher concentration of K^+ in winter is due to the enormous biomass burning around Durg especially during night times in winter as discussed earlier. During summer season, volatilization of NH_4Cl also leads to the lower concentration of Cl^- (Kulshrestha et al., 2009).

Spearman Correlation Analysis and Influence of Meteorology

The aim of performing non-parametric Spearman correlation analysis was to gain some preliminary understanding as to how closely the mass levels of PM and its ions are related to the influence of meteorology and their emission sources (Singh et al., 2010). Meteorology plays a crucial role in ambient distribution of air pollution. The pollutants 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 (Bhaskar et al., 2010).

The correlation coefficients (r) between daily mean PM, ionic species 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 i.e. T, RH, VP, WS and RF were negatively correlated with $\text{PM}_{2.5}$ and PM_1 . During the study period correlation coefficient between temperature and PM variables are negative and reasonably high ($\text{PM}_{2.5} = -0.63$; $\text{PM}_1 = -0.57$,

Table 4. Non-parametric (Spearman) correlation analysis for the PM mass, water soluble ions and meteorology in the fine ($\text{PM}_{2.5}$) size fraction (lower diagonal triangle) and in the submicron (PM_1) size fraction (upper diagonal triangle) in Durg, India during July 2009 to June 2010

Species	PM	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	Temp	RH	VP	WS	RF
PM		0.02	0.63**	0.54**	-0.03	0.16	0.66**	0.62**	0.60**	-0.57**	-0.66**	-0.49**	-0.55**	-0.12
Na^+	0.01		0.38*	0.12	0.44*	0.11	0.05	0.04	0.23	0.10	0.03	-0.07	0.03	0.02
NH_4^+	0.72**	0.31*		0.75**	0.12	0.17	0.11	0.79**	0.76**	-0.11	0.59**	-0.01	-0.59**	-0.15
K^+	0.64**	0.06	0.67**		0.02	0.03	0.59**	0.14	0.65**	-0.01	-0.12	0.16	-0.07	-0.03
Mg^{2+}	-0.10	0.49*	0.04	0.01		0.65**	-0.12	-0.08	-0.02	0.12	-0.01	-0.14	0.14	0.03
Ca^{2+}	0.03	0.07	0.14	0.06	0.61**		-0.03	0.44*	0.10	-0.05	-0.04	-0.02	-0.02	0.01
Cl^-	0.68**	0.12	0.09	0.69**	-0.12	-0.05		0.11	0.76**	-0.11	-0.01	0.02	-0.13	0.07
NO_3^-	0.61**	0.13	0.72**	0.06	-0.13	-0.10	0.09		0.83**	0.06	0.52**	0.07	-0.66**	0.09
SO_4^{2-}	0.71**	0.07	0.76**	0.61**	-0.07	0.16	0.69**	0.77**		0.12	0.48**	-0.02	-0.68**	0.02
Temp	-0.63**	0.18	-0.17	-0.18	0.08	-0.02	-0.21	0.11	0.11		-0.33*	-0.39*	-0.65**	-0.10
RH	-0.52**	0.14	0.61**	-0.14	-0.13	-0.18	0.01	0.60**	0.55**	-0.33*		0.66**	0.01	-0.13
VP	-0.56**	-0.11	-0.10	0.05	-0.14	-0.09	0.04	0.13	-0.09	-0.39*	0.66**		0.41*	0.10
WS	-0.66**	0.09	-0.63**	-0.13	0.08	-0.04	-0.14	-0.56**	-0.59**	-0.65**	0.01	0.41*		-0.13
RF	-0.16	0.11	-0.19	-0.02	0.01	0.02	0.02	0.07	0.05	-0.16	-0.18	0.11	-0.17	

T: Temperature; RH: Relative humidity; VP: Vapor pressure; WS: Wind speed; RF: Rainfall.

* Correlation is significant at 0.05 level (2-tailed); ** Correlation is significant at 0.01 level (2-tailed)

$P < 0.01$), indicating that higher temperature would be against the accumulation of pollutants. Correlation between PM variables and wind speed were investigated during the study period. As expected from other studies (Pandey *et al.*, 1992; Bhaskar *et al.*, 2010), a significant negative correlation between wind speed ($PM_{2.5}$: -0.66 , PM_1 : -0.55 , $P < 0.01$) and mass concentration of $PM_{2.5}$ and PM_1 showed a dominance of local sources in which strong winds flush pollutants out of the system whereas weak wind allow the pollution levels to increase. Weak or negligible correlation indicates the more complex picture with advective bringing pollution into the region from other sources (Karar and Gupta, 2006).

$PM_{2.5}$ and PM_1 show a significant negative correlation ($P < 0.01$) with relative humidity during the study period. Hien *et al.* (2002) similarly found negative relationship between fine particulates and relative humidity and suggested that relative humidity remove atmospheric particulates and diminish the amount of re-suspended soil dust by making the soil humid. Particulate concentrations exhibit significant negative correlation with vapor pressure ($PM_{2.5}$ = -0.56 ; PM_1 : -0.49 , $P < 0.01$). Re-suspended soil dust under unstable atmospheric conditions (low pressure and high wind speed) might explain the cause of negative correlation observed between particulate concentrations and vapour pressure (Tsai *et al.*, 2005). 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 (Rehswagen *et al.*, 2005). The effects of rainfall on the concentrations of particulate matter and particle associated water soluble ionic species were also investigated. As can be seen from Table 4, the scavenging of pollutants by precipitation is an important removal mechanism from the atmosphere (Sahu *et al.*, 2004). The results showed that $PM_{2.5}$ and PM_1 mass concentrations were negatively correlated with rainfall ($PM_{2.5}$ = -0.16 , PM_1 = -0.12) but it is not in significant level during period of study.

The correlation coefficients among major components revealed that $PM_{2.5}$ and PM_1 were well correlated with K^+ , Cl^- , NO_3^- and SO_4^{2-} ($p < 0.01$) and showed that their higher association and sources of origin are same in nature. Na^+ correlated well with NH_4^+ ($p < 0.05$) and Mg^{2+} ($p < 0.01$). NH_4^+ had a strong correlation with K^+ , NO_3^- and SO_4^{2-} ($p < 0.01$). NO_3^- shows strong correlation with SO_4^{2-} ($p < 0.01$) aerosols. As inferred from other studies (Salve *et al.*, 2006; Tiwari *et al.*, 2009), a poor correlation between Na^+ and Cl^- in the $PM_{2.5}$ and PM_1 confirms the origin of Na^+ and Cl^- from the non sea-salt substances. The geographical location of Durg, in the central part of India, is at an aerial distance of more than 500 km from sea and thus the contribution to the aerosols arising from the sea could be ignored (Tiwari *et al.*, 2009). Cl^- in this region may be originated from neutralization of atmospheric NH_3 by HCl originated from wood/coal burning and other combustion processes (Kulshrestha *et al.*, 2009). Na^+ in this region is present in sufficient amount in soil in the form of Na_2SO_4

and may be originated from natural sources (Parmar *et al.*, 2001).

Table 1 shows 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. The results show that the ionic species namely Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Cl^- have lower correlation values with the temperature, relative humidity, wind speed, vapour pressure and rainfall in $PM_{2.5}$ and PM_1 particles (Table 4). Table 4 also showed that only the secondary components (SO_4^{2-} , NO_3^- and NH_4^+) have significant positive correlation with relative humidity ($P < 0.01$) and negative correlation with wind speed ($P < 0.01$). The strong positive association of nitrate with RH likely reflects the RH dependence of the ammonium nitrate formation equilibrium (Kleeman, 2008). In the agriculture fields where ammonia is in excess, production of nitrate can be largely determined by RH (Kleeman, 2008), possibly explaining the particularly strong nitrate-RH correlation here.

Principal Component Analysis (PCA)

Ionic species in particulate matter may have their origin from a variety of sources, which includes soil and suspended road dusts, vehicular emission, industrial process, incinerator, coal combustion, oil combustion and construction sites (Kumar *et al.*, 2001). The ionic species (NH_4^+ , K^+ , Cl^- , NO_3^- , SO_4^{2-}) have been identified as markers for various anthropogenic atmosphere sources (coal combustion, traffic emission and biomass burning) while for natural sources such as soil derived particles the species Na^+ , Ca^{2+} and Mg^{2+} have been used (Yuan *et al.*, 2008).

In order to quantify the contribution of the main sources, a principal component analysis procedure followed by Varimax rotation of components (PCA + Varimax) having Eigen value > 1 (Statistica 5.0) was carried out (Viana *et al.*, 2006) for 9 selected variables. PCA defines the quantitative relationships among the variables in the form of groups within the data, which reduce the number of variables/dimensionally in a dataset using smaller number of linearly independent new variables. These new variables are principal components (PCs), each of which is a linear combination of originally correlated variables, which are ionic and particulate fractions in the present study. Table 5 shows the factor analysis on particulate ionic species during the sampling period for $PM_{2.5}$ and PM_1 . Two principal components were extracted which explain 76.6% and 65.9% of the variance respectively for $PM_{2.5}$ and PM_1 in the data set. Factor 1 has significant loading with NH_4^+ , Cl^- , NO_3^- , SO_4^{2-} , $PM_{2.5}$ and K^+ , which represents the contribution emitted from anthropogenic sources, especially coal combustion, traffic emissions and biomass burning. Factor 2 has significant loading for Na^+ , Ca^{2+} and Mg^{2+} , suggested their partial association with natural, such as soil derived particles. The source types identified in this study are similar to those reported in literatures (Tiwari *et al.*, 2009) and show that the major anthropogenic contribution of

Table 5. Principal component analysis after varimax rotation for water soluble ionic species in PM_{2.5} and PM₁ at sampling site Durg, India during July 2009 to June 2010.

PM _{2.5} (Fine particles) (n = 120)			PM ₁ (Sub-micrometer particles) (n = 120)		
Component	Factor 1	Factor 2	Component	Factor 1	Factor 2
PM _{2.5}	0.80		PM ₁	0.78	
Na ⁺		0.79	Na ⁺		0.70
NH ₄ ⁺	0.91		NH ₄ ⁺	0.90	
K ⁺	0.64		K ⁺	0.73	
Mg ²⁺		0.86	Mg ²⁺		0.83
Ca ²⁺		0.89	Ca ²⁺		0.88
Cl ⁻	0.78		Cl ⁻	0.71	
NO ₃ ⁻	0.89		NO ₃ ⁻	0.82	
SO ₄ ²⁻	0.84		SO ₄ ²⁻	0.93	
Initial Eigenvalue	3.81	1.72	Initial Eigenvalue	3.64	1.33
Variance Explained	52.1%	24.5%	Variance Explained	44.6%	21.3%
Cumulative Variance Explained	52.1%	76.6%	Cumulative Variance Explained	44.6%	65.9%

ionic species in the airborne particulate matter comes from coal combustion, biomass burning, and traffic emissions along with natural sources as proposed. It is believed that current apportionment results will be useful to the local authorities to regulate the ambient air particulate matter.

CONCLUSIONS

This study elucidates the characteristics of PM_{2.5} and PM₁ and their seasonal variation in Durg city, India. The annual mean concentrations of PM_{2.5} and PM₁ were 135.0 µg/m³ and 64.7 µg/m³, respectively. The results indicated that the observed annual mean PM_{2.5} concentrations exceeded the annual National Ambient Air Quality Standards (NAAQS) of India and the air quality guidelines of the World Health Organization (WHO). PM_{2.5} and PM₁ mass concentrations showed pronounced seasonality with high levels in winter season followed by spring, summer and fall season with the lowest levels. The high concentrations for both PM_{2.5} and PM₁ in winter season may be caused by local sources such as different kinds of agricultural practices including burning of biomass, brick kilns, fire cracker burning, high traffic volume and lower dispersion rate of pollutants, apart from the industrial emissions. The low concentrations could be due to wash out effect during the rainy season and ventilation effect of high wind movements. The ratio of PM₁/PM_{2.5} is higher during the whole campaign clearly indicating larger submicron particle fractions in PM_{2.5} at this location. The mean level of total water soluble inorganic ions in PM_{2.5} and PM₁ accounted for 11.57% and 16.98% of the total mass. The concentrations of SO₄²⁻ and NO₃⁻ were highest among all ions in PM_{2.5} and PM₁ aerosols. The concentration of SO₄²⁻ and NO₃⁻ in PM_{2.5} were 6.75 µg/m³ and 3.16 µg/m³, which accounted for 32.76% and 13.83% of the total mass of the water soluble inorganic ions analyzed. Similarly, the concentration of SO₄²⁻ and NO₃⁻ in PM₁ were 4.91 µg/m³ and 2.11 µg/m³, which accounted for 32.78% and 12.21% of the total mass of the water soluble inorganic ions analyzed. The higher concentrations of SO₄²⁻, NH₄⁺, NO₃⁻, Cl⁻ and K⁺ were observed during the winter which was due to the enhanced

burning activities and industrial emissions in this season, while Na⁺, Mg²⁺ and Ca²⁺ exhibited higher concentrations during the spring and summer as the dry weather in these seasons was favorable for the resuspension of soil particles. The secondary species (NH₄⁺, SO₄²⁻ and NO₃⁻) showed strong positive correlation with relative humidity and negative correlation with wind speed. Source identification study through PCA enabled to identify various sources of PM and water soluble ions in the atmosphere: anthropogenic sources, especially coal combustion, traffic emissions and biomass burning and natural sources, such as soil derived particles.

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