



# Ion chemistry and source identification of coarse and fine aerosols in an urban area of eastern central India

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## ABSTRACT

This work focuses on size segregated atmospheric aerosol mass concentrations and water soluble inorganic components in Chhattisgarh, the eastern central India. Investigation on the monitoring of ambient air levels of atmospheric particulates were done around a large source of primary anthropogenic particulate emissions: the industrial area and coal based power plants. Chemical characterization was carried out for aerosol samples collected in urban area, Raipur, (21°14'N, 81°38'E) of Chhattisgarh region over a period of one year, using cascade impactor. Annual mean of mass concentration for coarse (PM<sub>2.5-10</sub>) and fine (PM<sub>2.5</sub>) aerosols were monitored to be 238.1 ± 89.9 and 167.0 ± 75.3 μg m<sup>-3</sup> respectively. This work deals with the seasonal variation and meteorological influences of inorganic components of the aerosols viz. NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>. The annual mean concentration of the inorganic components were monitored to be 3.8 ± 2.5, 8.9 ± 2.7, 10.2 ± 1.5, 2.6 ± 0.6, 8.7 ± 7.2, 4.6 ± 1.8, 16.4 ± 6.9 and 0.4 ± 0.5 μg m<sup>-3</sup> respectively in coarse particles and 8.2 ± 7.1, 6.8 ± 3.6, 46.5 ± 32.8, 1.7 ± 0.6, 7.4 ± 3.6, 5.9 ± 3.4, 10.2 ± 2.9, and 8.8 ± 7.7 μg m<sup>-3</sup> respectively in fine particles, for the above ions. The average distribution of nitrate and sulphate in PM<sub>2.5-10</sub> were found to be 1.6 and 4.2% and in PM<sub>2.5</sub> were 4.9 and 27.9% respectively indicating the dominance of sulphate in both PM<sub>2.5-10</sub> and PM<sub>2.5</sub> particles. Here, industrial emission plays important role for contribution of PM<sub>2.5</sub> particle loading in the atmosphere. The cation–anion ratio analysis indicated that the PM<sub>2.5-10</sub> particles were mostly neutralized and PM<sub>2.5</sub> particle were acidic. The major ions were mainly in the form of NaCl > CaSO<sub>4</sub> > K<sub>2</sub>SO<sub>4</sub> > MgSO<sub>4</sub> > KCl > NH<sub>4</sub>Cl > Ca(NO<sub>3</sub>)<sub>2</sub> > KNO<sub>3</sub> > MgCl<sub>2</sub> > Mg(NO<sub>3</sub>)<sub>2</sub> > NH<sub>4</sub>NO<sub>3</sub> > (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in coarse aerosol particles and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> > K<sub>2</sub>SO<sub>4</sub> > CaSO<sub>4</sub> > NaCl > NH<sub>4</sub>NO<sub>3</sub> > CaCl<sub>2</sub> > KNO<sub>3</sub> > MgCl<sub>2</sub> > Ca(NO<sub>3</sub>)<sub>2</sub> > KCl > NH<sub>4</sub>Cl in fine particles.

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## 1. Introduction

Atmospheric aerosols vary markedly in size, chemical composition, amount and distribution in atmosphere (Andreae, 1995; Mouli et al., 2003). Aerosol particles have been widely studied in the last ten years due to its potential health impact and demand for its control. The various studies indicate that the fine aerosol particles have the strongest health effects (Schwartz et al., 1996; Borja-Aburto et al.,

1998). The sources, characteristics and potential health effects of PM<sub>10</sub> (particles having diameter <10 μm) and PM<sub>2.5</sub> (particles having diameter <2.5 μm) are different (Sharma and Maloo, 2005). Aerosol concentrations are influenced by meteorological factors, geographic conditions and particle emissions such as industrial emissions, traffic, agriculture activities and natural sources. The aerosol particles are of great importance in affecting atmospheric radiation, cloud formation as well as atmospheric photochemical reactions and the light extinction effect that influence global weather changes (Seinfeld and Pandis, 1998; Tsai et al., 2003). The above characteristics of the aerosol particles are due to their water

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soluble components, e.g. magnesium, sodium, potassium, calcium, ammonium, nitrate, sulphate, chloride, etc. (Tang et al., 1995; Tsai and Kuo, 2005).

The present trends for particulate monitoring strategies tend to monitor  $PM_{2.5}$  and  $PM_{10}$  because it fits more direct relationship with health effect, and to avoid natural particulate interferences (Gomiscek et al., 2004). Industrial activities with high primary particulate emissions, such as coal, cement, concrete or the mining sectors, have a great impact on the air quality due to their intensive particulate emissions in 2.5–10  $\mu m$  range.

The continued use of wood and coal for home heating and cooking are unavoidable issues in developing countries (He et al., 2001; Streets et al., 2001; Schauer et al., 1996, 2001; Rogge et al., 1998; McDonald et al., 2000) and India is no exception to it. Several investigators have studied the chemical composition, mass and size distribution of atmospheric aerosols both in India (Khemani et al., 1985; Mahadevan, 1986; Safai et al., 1993; Tripathi et al., 1996; Kumar et al., 2002, 2003, 2006; Rastogi and Sarin, 2005) and abroad (Whitby, 1978; Hubert and Lazrus, 1980; Shrestha et al., 2000). A bimodal distribution of ambient aerosol has been reported for many urban sites (Lioy and Daisey, 1987; Aceves and Grimalt, 1993; Lin et al., 1999). The coarse fraction is mainly due to crustal material, paved road dust, non-catalyst equipped gasoline engines and background sea salts. The fine fraction is a mixture of primary and secondary aerosol emitted from anthropogenic, rather than natural sources, or formed by vapor nucleation/condensation mechanisms (Hildemann et al., 1991; Kleeman and Cass, 1998). In Agra a few sporadic measurements have been made (Kulshrestha et al., 1998; Parmar et al., 2001) in which chemical compositions of particulate matter have been reported. The chemical composition of aerosols, their mass and size distribution and seasonal variations at Dayalbagh, a suburban site in the Agra region of tropical India were reported by Kumar et al. (2007).

There is scarce availability of aerosol data ( $PM_{10}$  and  $PM_{2.5}$ ) for the central India. The systematic study of aerosol particles concentration in any air shed, their characteristic diameter, distribution in fine and coarse mode, as well as their seasonal variations is still needed.

Therefore, the main aim of this study was to present the data on the distribution of water soluble inorganic aerosols between coarse and fine aerosols and to delineate their sources of origin during the different seasons based on one year of continuous measurements at a residential area of an industrial city situated at the eastern central part of India. This paper introduces physico-chemical patterns of ambient air particulate matter in coal combustion industrial city. In this area, the largest source contribution in high particulate event is due to primary emissions of mineral matter from power plants. In this study, monthly coarse and fine aerosol samples were collected during a whole year in Raipur city for the characterization of water soluble inorganic components in aerosol and their distribution in coarse and fine aerosols with source identification.

## 2. Methods

### 2.1. Description of study area

Raipur, an industrially important city with population of 1.2 million, of Chhattisgarh state situated in the eastern

central India, was selected for the present study. Fig. 1 shows the geographical map of Raipur in Chhattisgarh. Raipur ( $21^{\circ}14'N$ ,  $81^{\circ}38'E$ ), the premiere city of Chhattisgarh region, is literally sandwiched between two industrial complexes on its eastern and western outskirts. The western complex has its nucleus at the colossal Bhilai Steel Plant at a distance of about 30 km, and also the Jamul Cement Factory as well as allied industries producing fertilizers and merchandise out of iron and steel. The eastern complex has a mixed nature, including plants that extract oil from forest and farm products, or those who manufacture electrical goods, iron, steel, aluminum and copper. There are also a few cement factories at Siltara, at a distance of about 15 km, and at Mandhar, at a distance of about 30 km. Siltara comprises of numerous big and small-scale agro-forest, iron, oil and paint, etc. basic factories. Besides, there are houses for the factory workers and other people who surround this site. The study area is the municipal corporation area encircling about 160  $km^2$ .

These huge coal burning industries produce a large amount of fly ash and particulate matter, these particulate matters contain huge amount of trace elements along with the secondary particulates which affect the local environment as well as surroundings by the aerial dispersion processes.

The whole year can be divided into four distinctive seasons, i.e. spring (mid January–mid March), summer (mid March–mid June), fall (mid June–September) and winter (October–mid January) due to distinct variation in the temperature and rainfall. Raipur city lies in the extreme climatic zone. Since equator is not too far, this place is usually very hot and dry in summer (up to  $46^{\circ}C$ ). Mostly, the whole area experiences extreme heat and hot dust storms blow during summer. This region receives heavy rainfall from the south-west monsoon during fall (annual rainfall of 1624 mm). The south-west monsoon carries rain clouds and passes from the Bay of Bengal and crosses the East Coast, resulting in heavy falls in the region. Also, stormy winds blow in this area. During January and February, sometimes dense fog covers the area.

During the study period, the minimum and maximum temperatures were  $10^{\circ}C$  in winter and  $46^{\circ}C$  in summer, respectively. The relative humidity varied between 10% (May) to 98% (August) and annual average relative humidity was 53.8% during the investigation period. The mean monthly temperature ranged from  $25^{\circ}C$  to  $41.6^{\circ}C$ . Fall season accounted for almost 88.8% of the annual rainfall during which relative humidity ranged from 60% to 98%. In dry months the relative humidity ranged from 48% to 72% and 10% to 40% in winter and summer, respectively. Winter was characterized by  $10^{\circ}C$  to  $33.5^{\circ}C$  day temperature.

### 2.2. Aerosol sampling

Aerosol particles were continuously collected on quartz fiber filters (81 mm diameter) with eight stage cascade impactor with flow rate of 28.3 actual litre per minute (Tisch Environment Pvt. Ltd., USA) with a maximum possible change from initial to final sampling by 2% at Raipur for over a one year period from April 2005 to March 2006. For collection of the samples, the sampler was operated continuously for 24 h. The mass collection of aerosol was done once in a month but

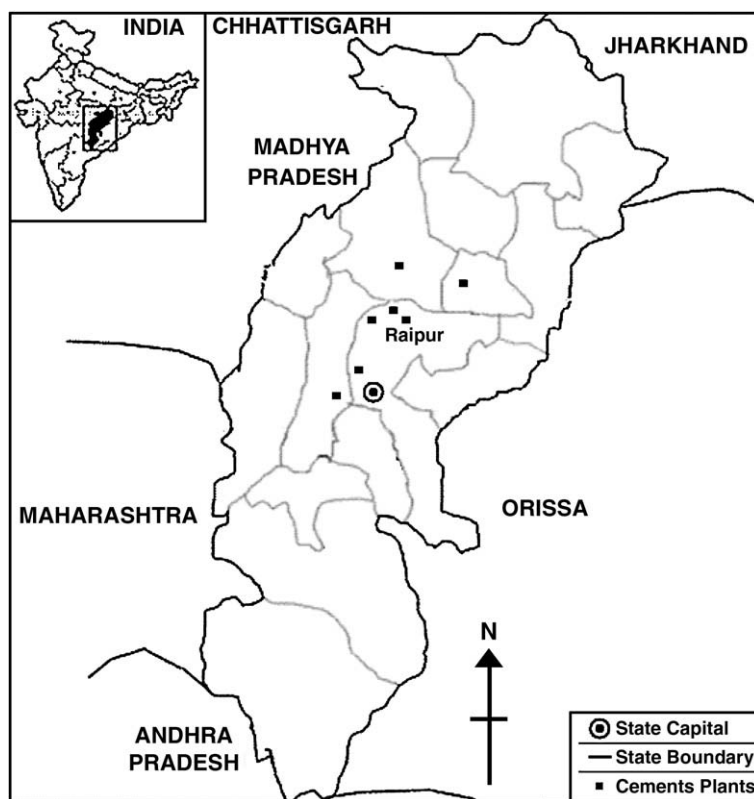


Fig. 1. Geographical location of the study area in India.

the chemical analysis was performed for four seasonally representative months. The particular sampling events were, April 16–17, 2005; May 21–22, 2005; June 16–17, 2005; July 18–19, 2005; August 19–20, 2005; September 15–16, 2005; October 16–17, 2005; November 21–22, 2005; December 17–18, 2005; January 20–21, 2006; February 20–21, 2006 and March 17–18, 2006. The above sampler is able to collect particles separately on eight stages of particulate dimensions i.e. 10–9.0, 9.0–5.8, 5.8–4.4, 4.4–3.3, 3.3–2.1, 2.1–1.1, 1.1–0.7, 0.7–0.4  $\mu\text{m}$ . The filters were baked at 500 °C for 2 h in order to eliminate organic species, conditioned in a desiccator for 24 h and then weighed in Sartorius electronic balance, AG (Göttingen, Germany) Model CP225D. Soon after the sampling was done, the samples were put in zipped polyethylene packets and brought to the laboratory. Samples were weighed after sampling with an analytical balance (Sartorius, reading precision 10  $\mu\text{g}$ ) after stabilizing under constant temperature ( $20 \pm 5$  °C) and humidity ( $40 \pm 5\%$ ). A sample blank was always taken by carrying away a sampler to the field and all data reported were against the blank value obtained.

### 2.3. Chemical analysis

One-fourth of sample filter and blank filter was extracted ultrasonically with 10 ml water which was deionized to resistibility of  $18 \text{ M}\Omega \text{ cm}^{-1}$ . After passing through microporous membranes (pore size, 0.45  $\mu\text{m}$ ; diameter, 25 mm) each filter was stored at 4 °C in clean tube for analysis. The samples were then shipped under cryogenic conditions by fast courier to Public Health and Research Institute of Kobe City, Kobe,

Japan for Analysis. This, being a cumbersome and expensive process, restricted to the analysis of limited number of samples only. A total of 8 ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) were analyzed in each sample by Ion Chromatography (IC, Model, Dionex DX-120 for anion; and Dionex 120 for cation). The instrumental specifications used were as follows: separation column—Ionpac AS-12A for anions and CS16A for cations; column temperature—room temperature for anions and 40 °C for cations; solvent—2.7 mM  $\text{Na}_2\text{CO}_3$  + 0.3 mM  $\text{NaHCO}_3$  for anions and 30 mM methane sulfonic acid for cations; flow rate—1.5 mL/min and 1.0 mL/min respectively for anions and cations; suppressor—ASRA-1 and CSRS-1 respectively for anions and cations; detector—electrical conductivity detector ED50 for both anions and cations; sample volume—25  $\mu\text{L}$  sample was used for both anion and cation analyses.

### 2.4. Analytical protocols

The analytical protocols viz., resolution, accuracy, and detection limits of the above IC used and species analyzed were determined to be as follows. The resolution ( $R_s$ ), defined as  $(t_1 - t_2)/(W_1 + W_2)$ , where  $W$  is the width of the peak at half height for  $\text{Na}^+$ – $\text{NH}_4^+$ ,  $\text{NH}_4^+$ – $\text{K}^+$ ,  $\text{K}^+$ – $\text{Mg}^{2+}$ ,  $\text{Mg}^{2+}$ – $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ – $\text{NO}_3^-$  and  $\text{NO}_3^-$ – $\text{SO}_4^{2-}$  were 6.1, 11.2, 6.0, 7.1, 13.8 and 9.6, respectively. The coefficients of variance (CV) values were calculated to check the accuracy in this analysis. For  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , the CV values were found to be 1.9%, 1.6%, 3.1%, 2.2%, 1.6%, 4.5%, 12.5%, 11.0%, respectively. The detection limits (DL) were obtained

from  $3\sigma$  in 5 repeated analysis of a 0.1 ppm standard solution. Further, the linearity of the calibration curve in low concentrations was also confirmed. The DL of the 5 cations was 0.01 ppm. For  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , those were 0.02, 0.05, and 0.1 ppm, respectively.

### 2.5. Air mass trajectory

To identify the potential importance of different source regions on aerosol composition at the sampling sites the air mass trajectories were calculated using the HYSPLIT 4 model of the air resources laboratory of NOAA (Draxler and Rolph, 2003). Fig. 2 shows the trajectories of the air mass over Raipur when actual samplings were conducted in May, 2005; August, 2005; November, 2005 and February, 2006. Under normal meteorological conditions, the transported aerosol mass loading occurs due to prevailing airflow directions such as NW in summer carrying hot winds, SW carrying monsoonal rain in fall and N carrying cold waves in winter in the study area. Normally, spring is calm in this region.

## 3. Results and discussion

### 3.1. Mass concentration and distribution of coarse and fine aerosols

Table 1 shows the mass concentrations of  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  aerosols during the study period. The concentrations of

$\text{PM}_{2.5-10}$  aerosols ( $n = 12$ ) and  $\text{PM}_{2.5}$  aerosols ( $n = 12$ ) at the study area were found to be in the range 105.4 (August) to 301.8 (May)  $\mu\text{g m}^{-3}$  and 25.8 (January) to 297.2 (April)  $\mu\text{g m}^{-3}$ , respectively during the whole study period. The seasonal average of mass concentrations were observed to be in the range 111.0–245.3  $\mu\text{g m}^{-3}$  and 74.1–239.0  $\mu\text{g m}^{-3}$ , respectively for  $\text{PM}_{2.5-10}$  (summer>spring>winter>fall) and for  $\text{PM}_{2.5}$  (summer>winter>spring>fall).

Frequencies of  $\text{PM}_{10}$  ( $\text{PM}_{2.5-10} + \text{PM}_{2.5}$ ) concentrations exceeding 150  $\mu\text{g m}^{-3}$  (National Ambient Air Quality Standards, India, NAAQS; [http://www.scorecard.org/env-releases/def/cap\\_naaqs.html](http://www.scorecard.org/env-releases/def/cap_naaqs.html)) at Raipur were 100% in all cases, i.e. in all seasons, during the study period. Similarly, the frequencies of  $\text{PM}_{2.5}$  concentrations exceeding 65  $\mu\text{g m}^{-3}$  (NAAQS) in the same seasons were also 100%. However, due to small data set ( $n = 4$ ), the frequency distribution calculated from the seasonal mean involve a great deal of uncertainty with standard deviation ranging 7.4–78.9  $\mu\text{g m}^{-3}$  for  $\text{PM}_{2.5-10}$  and 23.0–74.8  $\mu\text{g m}^{-3}$  for  $\text{PM}_{2.5}$ , Table 1.

The high concentration in summer was most likely due to the high wind speed, which brought large quantities of particles both from outside and local areas. The low concentration in fall was likely related to large precipitation in this season. Backward trajectories indicate that the sandstorms in summer bring heavy amount of sandy particles at the study area from the northwest directions, probably from deserts of Rajasthan, India and also from Pakistan and Afghanistan (Fig. 2).  $\text{SO}_x$  showed good correlations with  $\text{PM}_{2.5}$

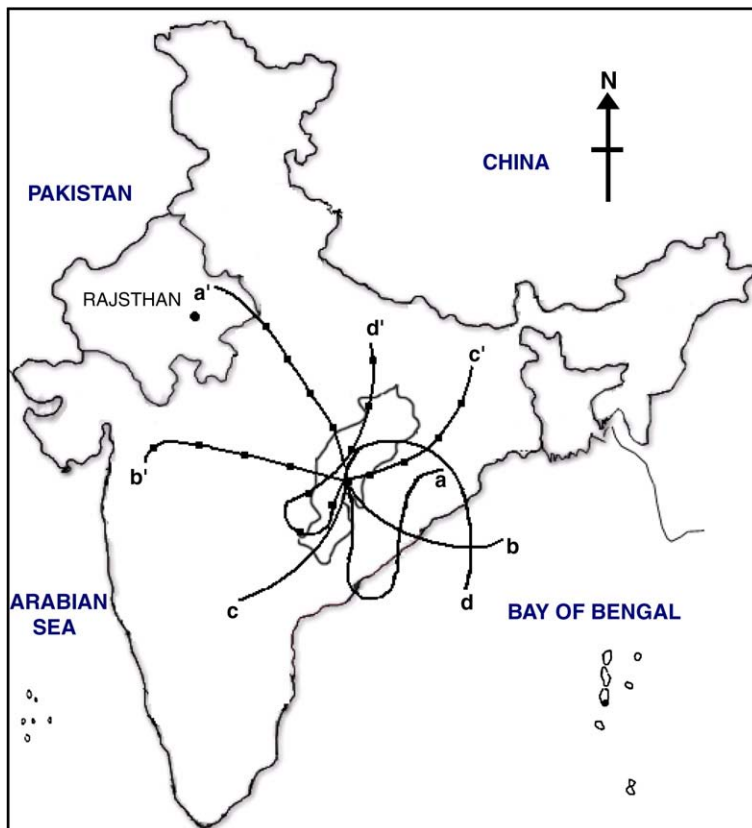


Fig. 2. Forward and backward air mass trajectory, responding air mass arriving in Raipur on sampling days (NOAA HYSPLIT MODEL forward (a,b,c,d) and backward (a',b',c',d') trajectories starting at 16 UTC GDAS meteorological data). a,a' = May 21, 2005; b,b' = August 20, 2005; c,c' = November 21, 2005; d,d' = February 20, 2006.

**Table 1**Concentration of aerosols and ratio of PM<sub>2.5</sub>/PM<sub>2.5–10</sub>.

Season	Size fraction	Max <sup>a</sup>	Min <sup>b</sup>	Mean	SD <sup>c</sup>	PM <sub>2.5</sub> /PM <sub>2.5–10</sub>
		μg m <sup>–3</sup>	μg m <sup>–3</sup>	μg m <sup>–3</sup>		%
Summer	PM <sub>2.5–10</sub>	301.8	159.4	245.3	75.6	97.4
	PM <sub>2.5</sub>	297.2	154.6	239.0	74.8	
Fall	PM <sub>2.5–10</sub>	120.0	105.4	111.0	7.4	66.7
	PM <sub>2.5</sub>	93.5	48.6	74.1	23.0	
Winter	PM <sub>2.5–10</sub>	282.3	145.0	191.1	78.9	57.7
	PM <sub>2.5</sub>	182.6	73.2	110.3	62.6	
Spring	PM <sub>2.5–10</sub>	263.2	173.0	209.0	47.7	36.8
	PM <sub>2.5</sub>	125.8	25.8	77.1	50.0	

<sup>a</sup> Maximum.<sup>b</sup> Minimum.<sup>c</sup> Standard deviation.

than with PM<sub>2.5–10</sub>. Meteorological parameters (temperature and wind velocity) also showed higher correlations with PM<sub>2.5</sub> than with PM<sub>2.5–10</sub>. However, the effect of the meteorological factors on particles could be very complicated. For example, high temperature might favor the evaporation of volatile or semi-volatile components from the particles; meanwhile it can favor the formation of secondary species, such as sulphate and organic components, for the strong solar radiation. High relative humidity means high water content in the atmosphere, which could favor the wet deposition and the formation of the secondary particles at the same time.

### 3.2. Ionic concentration of PM<sub>2.5–10</sub> and PM<sub>2.5</sub>

Table 2 shows the statistical summary of ions of PM<sub>2.5–10</sub> and PM<sub>2.5</sub>. Of all anions, in terms of concentration, sulphate is the dominant component followed by nitrate, while concentrations of nitrate are lower than sulphate and chloride in PM<sub>2.5–10</sub> and nitrate concentrations was higher than chloride in PM<sub>2.5</sub>. Concentration of NO<sub>3</sub><sup>–</sup> varied from 1.3 to 6.8 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and from 2.3 to 16.7 μg m<sup>–3</sup> for PM<sub>2.5</sub>, with the average value of 3.8 ± 2.5 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and 8.2 ± 7.1 μg m<sup>–3</sup> for PM<sub>2.5</sub>, respectively. The concentration of SO<sub>4</sub><sup>2–</sup> varied from 8.2 to 11.8 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and from 16.6 to 92.4 μg m<sup>–3</sup> for PM<sub>2.5</sub>, with the average value of 10.2 ± 1.5 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and 46.5 ± 32.8 μg m<sup>–3</sup> for PM<sub>2.5</sub>, respectively. Average of concentrations of Cl<sup>–</sup> was about 8.9 ± 2.7 and 6.8 ± 3.6 μg m<sup>–3</sup>, respectively. The ratios of anion concentrations of PM<sub>2.5</sub> to those

of PM<sub>10</sub> were greater than 2.0, especially for SO<sub>4</sub><sup>2–</sup> (4.64) and NO<sub>3</sub><sup>–</sup> (2.13) while the chloride ratio was obtained 0.77 indicating that sulphate and nitrate are largely distributed in fine particles while chloride concentration was high in coarse particles. With respect to cations it could be found that calcium was the most prominent component, the concentration varied from 10.8 to 26.6 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and from 7.6 to 13.2 μg m<sup>–3</sup> for PM<sub>2.5</sub> with the average value of 16.4 ± 6.9 μg m<sup>–3</sup> in PM<sub>2.5–10</sub> and 10.2 ± 3.0 μg m<sup>–3</sup> in PM<sub>2.5</sub>, respectively.

The Ca<sup>2+</sup> ratio of PM<sub>2.5</sub>/PM<sub>2.5–10</sub> is 0.62. This value shows that calcium was higher in PM<sub>2.5–10</sub> than in PM<sub>2.5</sub> aerosols in the Raipur. The possible source of calcium in this region is the soil rich in lime stone and dust emitting from at least 7 cement plants that are established in the surroundings of Raipur (Fig. 1). The available lime stone belt in the earth crust is main cause of the establishment of many cement plants in this region.

Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> (sodium and ammonium) were the second most prominent cationic components for PM<sub>2.5–10</sub> and PM<sub>2.5</sub> respectively, Na<sup>+</sup> concentrations varied from 3.7 to 19.4 μg m<sup>–3</sup>, for PM<sub>2.5–10</sub> and 4.9 to 12.6 μg m<sup>–3</sup> for PM<sub>2.5</sub>. The mean value of Na<sup>+</sup> was 8.7 ± 7.2 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and 7.4 ± 3.6 μg m<sup>–3</sup> for PM<sub>2.5</sub>. NH<sub>4</sub><sup>+</sup> concentrations varied from 0.01 to 1.2 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and 0.3 to 18.3 μg m<sup>–3</sup> for PM<sub>2.5</sub>. The mean value of NH<sub>4</sub><sup>+</sup> was 0.4 ± 0.5 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and 8.7 ± 7.7 μg m<sup>–3</sup> for PM<sub>2.5</sub>. The Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ratio of PM<sub>2.5</sub>/PM<sub>2.5–10</sub> is 0.9 and 23.2 respectively, suggesting that particulate Na<sup>+</sup> was high in PM<sub>2.5–10</sub> particles and NH<sub>4</sub><sup>+</sup> largely concentrates in fine particles.

Mg<sup>2+</sup> concentrations varied from 1.9 to 3.1 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and 1.2 to 2.4 μg m<sup>–3</sup> for PM<sub>2.5</sub>. The mean value of Mg<sup>2+</sup> was 2.6 ± 0.6 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and 1.7 ± 0.6 μg m<sup>–3</sup> for PM<sub>2.5</sub>. Mg<sup>2+</sup> ratio of PM<sub>2.5</sub>/PM<sub>2.5–10</sub> is 0.65 showing that magnesium is high in PM<sub>2.5–10</sub> than in PM<sub>2.5</sub>. K<sup>+</sup> concentrations varied from 2.2 to 6.3 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and 2.5 to 10.4 μg m<sup>–3</sup> for PM<sub>2.5</sub>. The mean value of K<sup>+</sup> was 4.6 ± 1.8 μg m<sup>–3</sup> for PM<sub>2.5–10</sub> and 5.9 ± 3.4 μg m<sup>–3</sup> for PM<sub>2.5</sub>. Ratio of PM<sub>2.5</sub>/PM<sub>2.5–10</sub> for K<sup>+</sup> is 1.3 indicating that potassium is high in PM<sub>2.5</sub> than in PM<sub>2.5–10</sub>.

### 3.3. Water soluble inorganic ions in total aerosol

Water soluble inorganic ions comprise a large part of aerosol particles and play an important role in the atmosphere. The sum of water soluble ions contributed an average

**Table 2**Linear equations and ionic ratio of concentration (μg m<sup>–3</sup>) of PM<sub>2.5–10</sub> and PM<sub>2.5</sub>.

Species	PM <sub>2.5</sub>					PM <sub>2.5–10</sub>					PM <sub>2.5</sub> /PM <sub>2.5–10</sub>	r <sup>b</sup>	PM <sub>2.5</sub> = mPM <sub>10</sub> + c
	Max	Min	Mean	SD	CV <sup>a</sup>	Max	Min	Mean	SD	CV <sup>a</sup>			
NO <sub>3</sub> <sup>–</sup>	16.7	2.30	8.16	7.08	0.52	6.79	1.34	3.84	2.48	0.65	2.13	0.79	PM <sub>2.5</sub> = 2.253 × – 0.48
Cl <sup>–</sup>	9.99	3.32	6.83	3.55	0.87	12.4	6.41	8.91	2.74	0.31	0.77	– 0.12	PM <sub>2.5</sub> = – 0.156 × + 8.230
SO <sub>4</sub> <sup>2–</sup>	92.4	16.6	46.5	32.8	0.71	11.8	8.16	10.2	1.52	0.15	4.64	0.80	PM <sub>2.5</sub> = 17.29 × – 126.8
Mg <sup>2+</sup>	2.41	1.18	1.69	0.58	0.88	3.14	1.92	2.61	0.59	0.23	0.65	– 0.09	PM <sub>2.5</sub> = – 0.092 × + 1.932
Na <sup>+</sup>	12.6	4.89	7.41	3.55	0.29	19.4	3.72	8.66	7.25	0.84	0.86	0.96	PM <sub>2.5</sub> = 0.471 × + 3.329
K <sup>+</sup>	10.4	2.49	5.90	3.43	0.34	6.28	2.23	4.65	1.75	0.38	1.27	0.71	PM <sub>2.5</sub> = 1.4 × – 0.609
Ca <sup>2+</sup>	13.2	7.62	10.2	2.98	0.58	26.6	10.8	16.4	6.94	0.42	0.62	0.49	PM <sub>2.5</sub> = 0.211 × + 6.735
NH <sub>4</sub> <sup>+</sup>	18.3	0.29	8.76	7.67	0.48	1.15	0.01	0.38	0.53	1.39	23.2	0.05	PM <sub>2.5</sub> = – 36.27 × + 12.4
WSII <sup>c</sup>	95.5					55.5							

<sup>a</sup> Coefficient of variance.<sup>b</sup> Correlation coefficient.<sup>c</sup> Water soluble inorganic ions.



of  $25.6 \pm 8.4\%$  and  $63.2 \pm 29.2\%$  to  $PM_{2.5-10}$  and  $PM_{2.5}$ , respectively. In this crustal area, the contribution of water soluble inorganic ions (WSII) in  $PM_{2.5-10}$  and  $PM_{2.5}$  was observed in the order of fall>spring>winter>summer and winter>spring>fall>summer, respectively. The mass concentrations of  $PM_{10}$  and  $PM_{2.5}$  were very high in summer but the WSII were very low in total aerosol in summer than other seasons. This could possibly be due to the prevalence of sandy storm from the northwest desert of India (Rajasthan) in this period carrying a substantial amount of insoluble silicates (Fig. 2, back trajectories). The water soluble inorganic ions varied between 19.6%–38.1% and 22.9%–92.1% for  $PM_{2.5-10}$  and  $PM_{2.5}$ , respectively.

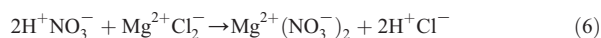
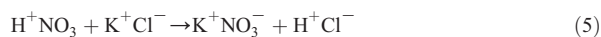
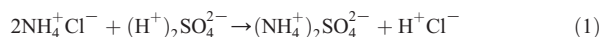
When considering the amount of water soluble inorganic ions in aerosols it shows the lower % contents in summer in both coarse and fine modes, which is mainly due to the insoluble sand contributed by storm from desert area from northwest directions to the Raipur city. The data shows that the water soluble inorganic ions are main content in fine particles than coarse particles. In fine particle it comes 92.0% in winter which shows the water soluble inorganic ions were large part of the fine aerosols. Thus, it must be noted that the air pollution in Raipur could be under the influence of both the local emissions and the long-range transport from outside areas.

Most of fine particles are secondary aerosols largely formed through the reactions of gas in the atmosphere and in the submicrometer size range. While most of coarse particles are primary aerosols directly emitted into the atmosphere and generally in the supermicrometer size range.

Compared with other metropolitan areas located in different parts of the world, the  $PM_{2.5-10}$  concentration observed in Raipur city was higher than other cities except Yamaguchi, Japan and Nanjing, China. Table 3 shows the comparison of concentrations of particulate matter and water soluble inorganic ions at different sites over the world.

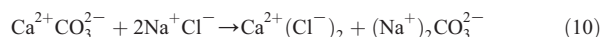
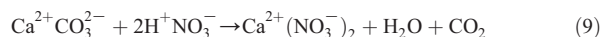
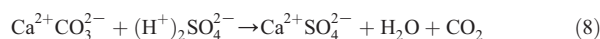
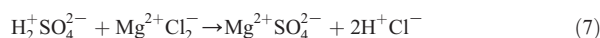
### 3.4. Molecular composition of major ionic species

The chemical forms of ions in both  $PM_{2.5-10}$  and  $PM_{2.5}$  in Raipur were identified by bivariate correlations. The concentrations of these species have been calculated based on the individual ion concentrations and their mutual relationships. The following are the possible reaction mechanism for formation of aerosol particles at the study area.



**Table 3**  
Concentrations of particulate matter and water soluble inorganic ions at different sites over the world.

Coarse particles ( $PM_{2.5-10}$ ), $\mu g m^{-3}$										Fine particles ( $PM_{2.5}$ ), $\mu g m^{-3}$										Site	Reference
Mass	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>		Mass	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>			
189.2	2.61	8.66	4.65	16.4	0.38	3.84	8.91	10.0		125.1	1.69	7.41	5.90	10.2	8.76	8.16	6.83	46.5		Raipur, India	This Study
–	–	–	–	–	–	–	–	–		217.8	0.28	0.57	0.63	1.25	3.78	6.23	3.00	10.4		Shanghai China	Wang et al. (2006)
44.5	0.14	0.91	0.07	2.98	0.18	1.74	8.50	1.72		26.2	0.03	0.34	0.08	0.52	0.77	0.18	0.55	4.27		Beirut, Lebanon	Kouyoumdjian and Saliba (2005)
–	–	–	–	–	–	–	–	–		62.6	0.34	0.54	0.72	0.93	8.14	7.83	0.92	9.75		Taiwan	Tsai and Kuo (2005)
195	2.03	–	–	5.72	–	6.06	–	4.43		109	–	–	–	–	2.69	0.95	–	8.93		Yamaguchi, Japan	Mori et al. (2003)
–	–	–	–	–	–	–	–	–		154.3	0.55	0.17	1.55	1.63	8.72	11.5	3.07	17.07		Beijing China	Wang et al. (2005b)
42.5	0.20	1.71	0.37	0.24	0.31	0.73	3.09	1.08		–	–	–	–	–	–	–	–	–		Christchurch, New Zealand	Wang et al. (2005a)
24.1	0.35	0.04	0.18	0.23	0.04	0.48	4.94	1.18		–	–	–	–	–	–	–	–	–		Auckland, New Zealand	
17.7	0.14	0.54	ND	0.99	0.88	1.10	0.36	3.85		12.80	0.04	0.17	ND	0.27	1.10	0.20	0.12	3.61		Monagrega Ebro Basin, Spain	Alastuey et al. (2004)
49.6	0.28	0.94	0.42	2.26	2.67	5.78	1.05	6.66		33.4	0.07	0.23	0.23	0.52	3.20	4.21	0.49	5.57		Eastern Spain	Rodriguez et al. (2001)
316	0.38	3.77	3.81	4.58	10.8	9.19	1.51	18.1		225	6.14	2.36	3.29	1.72	9.49	7.46	1.08	16.3		Nanjing, China	Wang et al. (2003)
–	–	–	–	–	–	–	–	–		18.7	0.03	0.31	0.26	0.09	1.68	0.99	0.39	5.42		Tokchok island, South Korea	Lee et al. (2002)
37.2	0.70	0.88	0.7	1.6	2.14	2.18	0.64	7.33		–	–	–	–	–	–	–	–	–		Spain	Querol et al. (2001)



In  $\text{PM}_{2.5-10}$ , the correlation coefficients decreased from 0.96 for  $\text{Mg}^{2+}-\text{NO}_3^-$ , 0.94 for  $\text{NH}_4^+-\text{Cl}^-$ , 0.90 for  $\text{K}^+-\text{NO}_3^-$ , 0.90 for  $\text{Mg}^{2+}-\text{SO}_4^{2-}$ , 0.84 for  $\text{K}^+-\text{SO}_4^{2-}$ , 0.78 for  $\text{NH}_4^+-\text{NO}_3^-$ , 0.72 for  $\text{K}^+-\text{Cl}^-$ , 0.68 for  $\text{Ca}^{2+}-\text{SO}_4^{2-}$ , 0.50 for  $\text{Mg}^{2+}-\text{Cl}^-$ , 0.32 for  $\text{Na}^+-\text{Cl}^-$ , 0.28 for  $\text{Ca}^{2+}-\text{NO}_3^-$  and 0.23 for  $\text{NH}_4^+-\text{SO}_4^{2-}$  in  $\text{PM}_{2.5-10}$ . The concentration of molecular species in  $\text{PM}_{2.5-10}$  was found in the following order,  $\text{NaCl} > \text{CaSO}_4 > \text{K}_2\text{SO}_4 > \text{MgSO}_4 > \text{KCl} > \text{NH}_4\text{Cl} > \text{Ca}(\text{NO}_3)_2 > \text{KNO}_3 > \text{MgCl}_2 > \text{Mg}(\text{NO}_3)_2 > \text{NH}_4\text{NO}_3 > (\text{NH}_4)_2\text{SO}_4$ . The correlation studies show that the  $\text{Mg}^{2+}$  was highly correlated to  $\text{NO}_3^-$ . Because the concentrations of molecular species were depended according to concentration of individual ions, the concentrations of the succeeding species were calculated based on the concentrations of the formed ions and the foregoing species (Wang et al., 2005a,b; 2006), concentration of NaCl was high than other molecular species. In the  $\text{PM}_{2.5-10}$  sodium chloride was in high concentration  $9.80 \mu\text{g m}^{-3}$  and ammonium sulphate was in low concentration  $0.91 \mu\text{g m}^{-3}$ .

The correlation values for ionic species in  $\text{PM}_{2.5}$  was calculated in the following order 0.99 for  $\text{Ca}^{2+}-\text{Cl}^-$ , 0.98 for  $\text{NH}_4^+-\text{SO}_4^{2-}$ , 0.97  $\text{K}^+-\text{NO}_3^-$ , 0.95 for  $\text{NH}_4^+-\text{NO}_3^-$ , 0.92 for  $\text{K}^+-\text{SO}_4^{2-}$ , 0.91 for  $\text{Mg}^{2+}-\text{Cl}^-$ , 0.57 for  $\text{Na}^+-\text{Cl}^-$ , 0.54 for  $\text{K}^+-\text{Cl}^-$ , 0.40 for  $\text{Ca}^{2+}-\text{SO}_4^{2-}$ , 0.34 for  $\text{Ca}^{2+}-\text{NO}_3^-$  and 0.13 for  $\text{NH}_4^+-\text{Cl}^-$ . The molecular composition of ionic species in  $\text{PM}_{2.5}$  are found in order of,  $(\text{NH}_4)_2\text{SO}_4 > \text{K}_2\text{SO}_4 > \text{CaSO}_4 > \text{NaCl} > \text{NH}_4\text{NO}_3 > \text{CaCl}_2 > \text{KNO}_3 > \text{MgCl}_2 > \text{Ca}(\text{NO}_3)_2 > \text{KCl} > \text{NH}_4\text{Cl}$ .

Based on the average ( $n=4$ ) concentrations of major chemical species, a comparison was made on some molecular composition of the ions in  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  at Raipur, India, Table 4. The data showed that NaCl and  $\text{CaSO}_4$  in  $\text{PM}_{2.5-10}$ ,

contributing 4.1 and 3.6%, and  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  in  $\text{PM}_{2.5}$ , contributing 14.3 and 12.4%, respectively, to the analyzed total WSII components, were the major molecular species found at Raipur. The results were also compared with similar work for  $\text{PM}_{2.5}$  ion components in China. It was noticed that the order of magnitude of a calculated secondary aerosol  $(\text{NH}_4)_2\text{SO}_4$  were almost similar with percent contribution to the total WSII components analyzed, i.e., 14.3% at Raipur, India and 7.5–14.1% in China.

### 3.4.1. Ammonium species

Ammonium species were mainly present in fine particles in the form of ammonium salt. Ammonium sulphate was major species in fine particles with concentration of  $23.9 \mu\text{g m}^{-3}$  contributing 14.3% of the total aerosol mass concentration. Reaction-1 might be responsible for the ammonium sulphate species formation in the atmosphere which shows strong possibilities of combination of sulphate with ammonia to form ammonium sulphate. Concentration of ammonium sulphate in  $\text{PM}_{2.5-10}$  was  $0.9 \mu\text{g m}^{-3}$ . It was about 0.4% of the total aerosol mass concentration. This low amount of ammonium sulphate in  $\text{PM}_{2.5-10}$  aerosols indicated the low possibilities of combination of sulphate with ammonia in coarse mode. Ammonium sulphate was most prominent in  $\text{PM}_{2.5}$  and very low in  $\text{PM}_{2.5-10}$ . Ammonium chloride was calculated to be  $3.8 \mu\text{g m}^{-3}$  in  $\text{PM}_{2.5-10}$  and  $0.8 \mu\text{g m}^{-3}$  in  $\text{PM}_{2.5}$  aerosols. The formation of ammonium chloride might occur according to the reaction-2 in  $\text{PM}_{2.5-10}$  and this ammonium chloride dissociated in to ammonium sulphate in presence sulfuric acid. Ammonium and chloride showed the different sources of origin for  $\text{PM}_{2.5}$  ( $r=0.13$ ) and vice versa for the  $\text{PM}_{10}$  ( $r=0.94$ ) particles. Ammonium nitrate was found to be  $7.5 \mu\text{g m}^{-3}$  in fine particles, contributing 4.5% of the total water soluble molecular species in fine particles, while it was found to be  $1.2 \mu\text{g m}^{-3}$  in coarse particles (reaction-3).

Khemani et al. (1982) and Lewin et al. (1986) have pointed out in the coastal area that ammonium accumulates in the fine particle ranges and correlates well with sulphate, suggesting that ammonium sulphate must be the major

**Table 4**

Average ( $n=4$ ) concentrations ( $\mu\text{g m}^{-3}$ ) of major chemical species in  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  in Raipur during the study period.

Molecule	Raipur, India				China			
	$\text{PM}_{2.5-10}$		$\text{PM}_{2.5}$		$\text{PM}_{2.5}$ (Wang et al., 2006)		$\text{PM}_{2.5}$ (Wang et al., 2005b)	
	Concentration $\mu\text{g m}^{-3}$	Contribution in total WSII analyzed %	Concentration $\mu\text{g m}^{-3}$	Contribution in total WSII analyzed %	Concentration $\mu\text{g m}^{-3}$	Contribution in total WSII analyzed %	Concentration $\mu\text{g m}^{-3}$	Contribution in total WSII analyzed %
$\text{Mg}(\text{NO}_3)_2$	2.32	0.97	–	–	–	–	–	–
$\text{MgCl}_2$	2.35	0.99	3.68	2.20	–	–	–	–
$\text{MgSO}_4$	4.42	1.86	–	–	–	–	–	–
NaCl	9.80	4.12	8.65	5.18	–	–	–	–
$\text{KNO}_3$	2.89	1.22	5.86	3.51	0.52	0.32	–	–
KCl	3.94	1.65	2.48	1.48	–	–	–	–
$\text{K}_2\text{SO}_4$	4.75	2.00	20.8	12.4	–	–	–	–
$\text{Ca}(\text{NO}_3)_2$	2.90	1.22	2.67	1.60	2.15	–	–	–
$\text{CaCl}_2$	–	–	6.39	3.83	0.28	–	–	–
$\text{CaSO}_4$	8.70	3.65	9.89	5.92	0.93	–	–	–
$\text{NH}_4\text{NO}_3$	1.17	0.49	7.48	4.48	0.91	0.53	–	–
$\text{NH}_4\text{Cl}$	3.57	1.50	0.85	0.51	–	–	8.25	5.35
$(\text{NH}_4)_2\text{SO}_4$	0.91	0.38	23.9	14.3	13.1	7.46	21.7	14.1

ammonium salt. The same trend of distribution of ammonium in  $PM_{2.5-10}$  to  $PM_{2.5}$  was observed for Raipur also. But the correlation analysis of ammonium with anions yielded different results. In this crustal area, ammonium correlates highly with chloride ( $r=0.94$ ), nitrate ( $r=0.78$ ) in  $PM_{10}$  and nitrate ( $r=0.95$ ), chloride ( $r=0.13$ ) in  $PM_{2.5}$ . Ammonium was present in  $PM_{2.5-10}$  with the combination of chloride and nitrate as ammonium chloride ( $3.57 \mu\text{g m}^{-3}$ ) and ammonium nitrate ( $1.17 \mu\text{g m}^{-3}$ ). The large part of ammonium was present in the fine aerosol as ammonium sulphate ( $23.9 \mu\text{g m}^{-3}$ ) and ammonium nitrate ( $7.48 \mu\text{g m}^{-3}$ ) which are 14.3% and 4.5% of total aerosols (see in Table 4).

Ammonia ( $\text{NH}_3$ ) was the most abundant gaseous alkaline component in the atmosphere. Particulate  $\text{NH}_4^+$  found in the atmosphere originates from  $\text{NH}_3$  by the neutralization between ammonia and acidic species. The major sources for ammonia gas include animal farming, fertilizers and organic decomposition. Ammonia is not transported to very long distances as it is rapidly converted into  $\text{NH}_4^+$  aerosols at a rate  $30 \text{ h}^{-1}$  (Asman and Van-Jaarsveld, 1991).

#### 3.4.2. Sodium species

Sodium was almost equally distributed in  $PM_{2.5-10}$  and  $PM_{2.5}$  particles. In both coarse and fine aerosols the sodium ions have tendency to combine with chloride to form sodium chloride. The concentration of sea salt was found to be  $9.8 \mu\text{g m}^{-3}$  in  $PM_{2.5-10}$  and  $8.7 \mu\text{g m}^{-3}$  in  $PM_{2.5}$ . Sodium chloride contributed 4.1% of the  $PM_{2.5-10}$  mass and 5.2% of the  $PM_{2.5}$  mass.

#### 3.4.3. Potassium species

The possible molecular combinations for potassium were  $\text{K}_2\text{SO}_4$ ,  $\text{KCl}$  and  $\text{KNO}_3$ . The ratio  $PM_{2.5}/PM_{2.5-10}$  (1.0) shows the equal distribution of potassium between  $PM_{2.5-10}$  and  $PM_{2.5}$ . Concentration of potassium salt as potassium sulphate was  $4.8 \mu\text{g m}^{-3}$  and  $20.8 \mu\text{g m}^{-3}$  in  $PM_{2.5-10}$  and  $PM_{2.5}$ , respectively; as potassium chloride it was  $3.9 \mu\text{g m}^{-3}$  and  $2.5 \mu\text{g m}^{-3}$  in  $PM_{2.5-10}$  and  $PM_{2.5}$ , respectively and as a potassium nitrate  $5.9 \mu\text{g m}^{-3}$  and  $2.9 \mu\text{g m}^{-3}$  in  $PM_{2.5-10}$  and  $PM_{2.5}$ . Potassium sulphate was the second most prominent molecular species present in the fine particles; it contributed to 12.4% of total aerosol mass in fine particles. The very large difference in the concentration of potassium sulphate indicates the tendency of  $\text{KCl}$  to combine with  $\text{H}_2\text{SO}_4$  in  $PM_{2.5}$  particles than  $PM_{2.5-10}$  particles (reaction-4). The low concentration of  $\text{KCl}$  in  $PM_{2.5}$  supports the possibility of above chemical reaction. The concentration of potassium nitrate in  $PM_{2.5-10}$  and  $PM_{2.5}$  mode indicates the tendency of  $\text{HNO}_3$  to combine with  $\text{KCl}$  in  $PM_{2.5}$  particles than in  $PM_{2.5-10}$  particles (reaction-5).

#### 3.4.4. Magnesium species

Magnesium species was found in aerosols as magnesium sulphate, magnesium chloride and magnesium nitrate. The possibilities of above magnesium species were large in coarse mode than fine. The concentration of magnesium as magnesium chloride was 2.4 and  $3.7 \mu\text{g m}^{-3}$ . The magnesium chloride contributes 1.0% and 2.2% of the  $PM_{2.5-10}$  mass and  $PM_{2.5}$  mass, respectively. Magnesium nitrate and magnesium sulphate was found to be 2.3 and  $4.4 \mu\text{g m}^{-3}$  in  $PM_{2.5-10}$  aerosols, respectively. These magnesium species contribute

0.97 and 1.86% of  $PM_{2.5-10}$  mass. The formation of magnesium nitrate and magnesium sulphate might be possible by the combination reaction of magnesium chloride with nitric acid and sulfuric acid, respectively. Reactions-6 and 7 shows the possible formation mechanism of magnesium nitrate and magnesium sulphate.

#### 3.4.5. Calcium species

Calcium species shows the bimodal distribution in  $PM_{2.5-10}$  and  $PM_{2.5}$ . The concentration of calcium sulphate and calcium nitrate were observed to be  $8.7$  and  $9.9 \mu\text{g m}^{-3}$  in  $PM_{2.5-10}$  and  $2.9$  and  $2.7 \mu\text{g m}^{-3}$  in  $PM_{2.5}$ , respectively. Calcium sulphate and calcium nitrate contributed 3.6% and 5.9% of  $PM_{2.5-10}$  and 1.2% and 1.6% of the  $PM_{2.5}$  mass, respectively. Other forms of calcium, like chloride, were not found in  $PM_{2.5-10}$  but were present in  $PM_{2.5}$  in fraction of 3.8% of the total aerosols. High concentration of calcium sulphate indicates the strong possibilities of  $\text{H}_2\text{SO}_4$  to combine with  $\text{CaCO}_3$  in both  $PM_{2.5-10}$  and  $PM_{2.5}$  aerosols (reaction-8) (Wolff, 1984; Mamane and Gotlieb, 1992; Laskin et al., 2005) and the presence of calcium nitrate and calcium chloride were also an indication of the tendency of  $\text{HNO}_3$  and  $\text{NaCl}$  to react with  $\text{CaCO}_3$  (reactions-9 and 10).

The molecular species mentioned as above show the distribution of water soluble ions between coarse and fine particles. Sulphate was mostly present in fine particles in the form of ammonium sulphate (reaction-1) and potassium sulphate (reaction-4). Nitrate was mostly present as ammonium nitrate, calcium nitrate, potassium nitrate and magnesium nitrate (reactions-3, 9, 5 and 6, respectively).

#### 3.5. Diffuse reflectance Fourier transform infrared spectroscopy (DRS-FTIR) analysis of sulphate in aerosols

The prevalence and dominance of  $\text{SO}_4^{2-}$  species as  $\text{CaSO}_4$  in coarse and as  $(\text{NH}_4)_2\text{SO}_4$  in fine aerosols are further clarified by DRS-FTIR spectra (Shimadzu, DRS-8000A) of most of the aerosol samples analyzed. The sulphate absorption peak variation is observed when it combines with Ca as a calcium sulphate and with ammonium as ammonium sulphate. Sulphate shows the IR absorption band at 617, 983 and  $1117 \text{ cm}^{-1}$  when formed as  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $(\text{NH}_4)_2\text{SO}_4$ . However,  $\text{CaSO}_4$  shows absorption at  $660 \text{ cm}^{-1}$  and  $597 \text{ cm}^{-1}$  (Verma and Deb, 2007). The observation of similar peak was also reported in the wave number region  $671\text{--}675 \text{ cm}^{-1}$ , instead at  $617 \text{ cm}^{-1}$  (Tsai and Kuo, 2006). In the present study  $(\text{NH}_4)_2\text{SO}_4$  was obtained to be  $23.9 \mu\text{g m}^{-3}$  in  $PM_{2.5}$  and  $0.9 \mu\text{g m}^{-3}$  in  $PM_{2.5-10}$ , respectively. The  $\text{CaSO}_4$  was observed to be  $9.9 \mu\text{g m}^{-3}$  and  $8.7 \mu\text{g m}^{-3}$  in  $PM_{2.5}$  and  $PM_{2.5-10}$ , respectively. The DRS-FTIR spectra show the absorption peak at  $660\text{--}675 \text{ cm}^{-1}$  region for sulphate in  $PM_{2.5-10}$  and  $617 \text{ cm}^{-1}$  for  $PM_{2.5}$  aerosols. The peak at  $660\text{--}675 \text{ cm}^{-1}$  region confirms the presence of calcium sulphate in the  $PM_{2.5-10}$  aerosols. This peak was weak in  $PM_{2.5}$  because the ammonium sulphate was so higher than  $\text{CaSO}_4$  in the fine mode. Table 5 shows the IR absorption peaks obtained for the tested inorganic compounds containing sulphate in their purest form. Fig. 3 shows the DRS-FTIR absorption spectra for fine and coarse aerosols.



**Table 5**

The IR absorption peaks obtained for the tested inorganic compounds containing sulphate in their purest form.

Inorganic compounds tested	Peaks obtained
Ammonium sulphate	617 cm <sup>-1</sup> , 983 cm <sup>-1</sup> , 1104 cm <sup>-1</sup>
Ammonium iron sulphate	452 cm <sup>-1</sup> , 617 cm <sup>-1</sup> , 983 cm <sup>-1</sup> , 1105 cm <sup>-1</sup> , 1400 cm <sup>-1</sup> , 3145–3130 cm <sup>-1</sup>
Ammonium hydrogen sulphate	617 cm <sup>-1</sup> , 985 cm <sup>-1</sup> , 1115 cm <sup>-1</sup> , 1404 cm <sup>-1</sup> , 3050 cm <sup>-1</sup> , 3225 cm <sup>-1</sup>
Iron sulphate	450 cm <sup>-1</sup> , 619 cm <sup>-1</sup> , 985 cm <sup>-1</sup> , 1124 cm <sup>-1</sup>
Potassium iron sulphate	619 cm <sup>-1</sup> , 984 cm <sup>-1</sup> , 1118 cm <sup>-1</sup>
Calcium sulphate	598 cm <sup>-1</sup> , 660–675 cm <sup>-1</sup> , 1005 cm <sup>-1</sup> , 1110 cm <sup>-1</sup>
Magnesium sulphate	615 cm <sup>-1</sup> , 1007 cm <sup>-1</sup> , 1120 cm <sup>-1</sup>

### 3.6. Origin and formation mechanism of molecular species

The correlation analysis was used to infer the source of major ionic species. In this area the large cationic species mostly came from the local and outside sources in the coarse and fine particles.

#### 3.6.1. Sulphate

In a coal burning area sulphate is a major anthropogenic emission product. Once SO<sub>2</sub> enters in the air, it is oxidized, and followed a binary H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O or ternary H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O–NH<sub>3</sub> nucleation. This ultimately results in the formation of new particles (sulphate) in the PM range <10 µm (Jaeger-Voirol and Mirabel, 1989; Korhonen et al., 1999). The low relative humidity and high temperature suggests that SO<sub>2</sub> is oxidized by OH radicals. Enhanced photochemical activity results in increased concentration of sulphate. It has also been reported in California (Meagher et al., 1983; Switzer et al., 1996).

Sulphate shows high correlation with magnesium ( $r=0.90$ ), potassium ( $r=0.84$ ), calcium ( $r=0.68$ ) and positive but very low correlation with ammonium ( $r=0.23$ ) in PM<sub>2.5–10</sub> while in the fine mode sulphate shows good correlation with ammonium ( $r=0.98$ ), potassium ( $r=0.90$ ) and calcium ( $r=0.40$ ). This result indicates that sulphate has tendency to combine with ammonium in PM<sub>2.5</sub> particles. The calculation of molecular ionic species indicates that in PM<sub>2.5–10</sub> sulphate was present in the order of the molecular species: CaSO<sub>4</sub> (8.7 µg m<sup>-3</sup>) > K<sub>2</sub>SO<sub>4</sub> (4.8 µg m<sup>-3</sup>) > MgSO<sub>4</sub> (4.4 µg m<sup>-3</sup>) > (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (0.9 µg m<sup>-3</sup>). In NH<sub>3</sub> and mineral rich dust environments, H<sub>2</sub>SO<sub>4</sub> may react with mineral dust and ammonia

gas resulting in the formation of CaSO<sub>4</sub> in PM<sub>2.5–10</sub> and PM<sub>2.5</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in the PM<sub>2.5</sub> mode (Pio and Lopes, 1998; Querol et al., 1998; Moreno et al., 2003). The calcium (cluster ions) originates from soil because the entire surroundings of Raipur have lime stone belt. Sulfur was main emission product of coal burning industries, this sulfur was oxidized to sulfur dioxide and then sulphate was formed by further photochemical oxidation process. The above discussion shows that the calcium in PM<sub>2.5–10</sub> mode was not long-range transported ion but regionally clustered. The absence of sodium sulphate indicates that the sulphate concentration was influenced by local anthropogenic factors.

The molecular species of sulphate in the fine mode are present in the following order: (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (23.9 µg m<sup>-3</sup>) > K<sub>2</sub>SO<sub>4</sub> (20.8 µg m<sup>-3</sup>) > CaSO<sub>4</sub> (9.9 µg m<sup>-3</sup>). SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> ions showed a good correlation ( $r=0.68$ ) for the coarse mode and ( $r=0.40$ ) for the fine mode, during the study period, indicating that SO<sub>4</sub><sup>2-</sup> is present as calcium sulphate (CaSO<sub>4</sub>) in both coarse and fine mode (Rodríguez et al., 2002). SO<sub>4</sub><sup>2-</sup> shows an excellent correlation with ammonium and potassium in the fine mode, supporting that the sulphate, ammonium and potassium were locally originated.

#### 3.6.2. Nitrate

Nitrate (NO<sub>3</sub><sup>-</sup>) was present as a salt of calcium (2.9 µg m<sup>-3</sup>), potassium (2.9 µg m<sup>-3</sup>), magnesium (2.3 µg m<sup>-3</sup>) ammonium (1.2 µg m<sup>-3</sup>) in PM<sub>2.5–10</sub> particles and as a salt of ammonium (7.5 µg m<sup>-3</sup>), potassium (5.9 µg m<sup>-3</sup>) and calcium (2.7 µg m<sup>-3</sup>) in PM<sub>2.5</sub> levels. Nitrate concentration was higher in winter and spring in PM<sub>2.5–10</sub> and PM<sub>2.5</sub>. The result suggests strongly that thermodynamic properties of nitric acid play a key

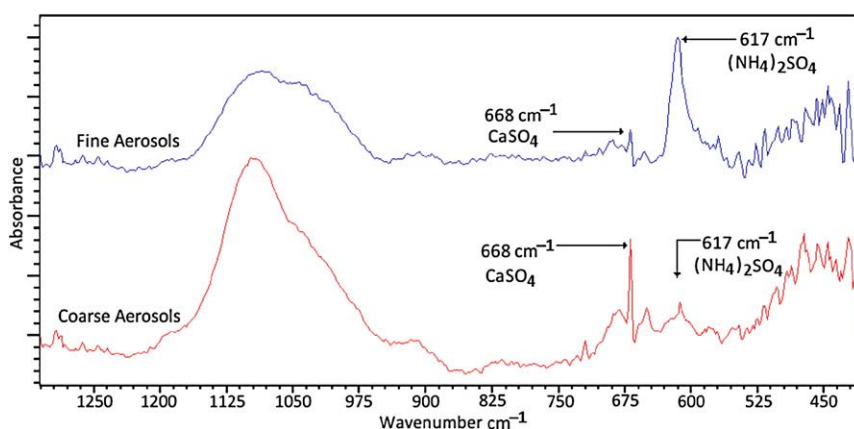


Fig. 3. DRS-FTIR absorption spectra of fine and coarse particles sampled at the study area.

role in the formation of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{NH}_4\text{NO}_3$  by means of the reactions 9 and 3, respectively. Nitric acid is mainly found in the gas phase in low troposphere and non polar latitudes given that it has a relatively high vapor pressure (Zhuang et al., 1999). Experimental and theoretical data have shown that the formation of nitrate species (calcium nitrate and ammonium nitrate) is thermodynamically favored at low temperatures, whereas in warmer environments gaseous nitric acid is more favorable (Warneck, 1987; Meszaros, 1999). Thus, in our study area the formation of enhanced amounts of calcium nitrate and ammonium nitrate in fine particles accounts for the evolution of  $\text{NO}_3^-$ . In the warm season, the occurrence of  $\text{NO}_3^-$  is attributed to the reaction of gaseous  $\text{HNO}_3$  with mineral species such as calcium carbonate magnesium chloride and potassium chloride to form  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{KNO}_3$  by the reactions 9, 6 and 5, respectively (Harrison and Sturges, 1984). The formation of nitrate aerosol in Raipur has been predicted by general circulation models, which also highlight the thermodynamic properties in the gas/particle partitioning and the seasonal evolution (Adams et al., 1999). Concentration of nitrate in  $\text{PM}_{2.5}$  was higher than that in  $\text{PM}_{2.5-10}$ . Warmer environments thermodynamically favor the prevalence of gaseous nitric acid over ammonium nitrate (reaction-3). Generally, nitric acid is found to be major acidifying component in the atmosphere. This acidic component is neutralized as sufficient amount of ammonium and other ions such as calcium are available to interact and also as the meteorological parameters favor the formation of particulate nitrate. Nitric acid is formed in the atmosphere through the oxidation of NO and  $\text{NO}_2$ . The oxidation of nitrogen oxides by OH is the main mechanism of day time formation. Nitrate in aerosol is influenced by the local vehicle emission (Pakkanen, 1996). The sources of nitrogen vary for  $\text{PM}_{2.5-10}$  to  $\text{PM}_{2.5}$  particles. Nitrate exists high with  $\text{PM}_{2.5}$  particles and low with  $\text{PM}_{2.5-10}$  particles. Nitrate was found high in both winter and spring, with concentrations  $16.7 \mu\text{g m}^{-3}$  and  $11.2 \mu\text{g m}^{-3}$  in  $\text{PM}_{2.5}$ , and  $4.9 \mu\text{g m}^{-3}$  and  $6.8 \mu\text{g m}^{-3}$  in  $\text{PM}_{2.5-10}$  particles, respectively; and low concentration in summer and fall season. Nitrate was the secondary product of nitrogen dioxide. Winter and spring with high relative humidity 72% and 68% respectively were favorable for the photochemical conversion of nitrogen dioxide to nitrate. In summer high temperature was responsible for the vaporization of nitrogen dioxide. In fall the precipitation was responsible for the lower concentration of nitrate in the atmosphere.

### 3.7. Ratio analysis

#### 3.7.1. Anion–cation (A/C) ratio

The ion balance expressed by the sum of the concentrations of anion-to-cation is a good indicator to study the acidity of the environment. Anion–cation ratio analysis in  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  in different seasons is shown in Table 6. Anions—nitrate, chloride and sulphate; cations—magnesium, sodium, potassium calcium and ammonium were major contributors to the total PM mass. The anion–cation ratio of  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  in summer, fall, winter and spring were 0.58, 0.66, 0.61 and 0.98; 0.91, 1.59, 2.40 and 1.97, respectively. The annual mean ratio of anion to cation was obtained to be  $0.71 \pm 0.18$  and  $1.72 \pm 0.63$  for  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  respectively. The mean ratio for  $\text{PM}_{10}$  was lower than

**Table 6**

Ratio analysis.

Seasons	Aerosols	A/C <sup>a</sup>	$\text{SO}_4^{2-}/\text{NO}_3^-$	$\text{SO}_4^{2-}/\text{Na}^+$	$\text{Cl}^-/\text{Na}^+$
Summer	$\text{PM}_{2.5-10}$	0.58	4.17	0.50	0.50
Fall		0.66	6.09	1.57	1.24
Winter		0.61	2.41	3.17	1.90
Spring		0.98	1.54	1.66	1.96
	Mean	$0.7 \pm 0.2$	$3.6 \pm 2.0$	$1.7 \pm 1.1$	$1.4 \pm 0.7$
Summer	$\text{PM}_{2.5}$	0.91	6.93	1.32	0.77
Fall		1.59	13.6	5.06	0.54
Winter		2.40	5.53	15.7	1.70
Spring		1.97	4.08	9.34	9.34
	Mean	$1.7 \pm 0.6$	$7.5 \pm 4.2$	$7.9 \pm 6.2$	$3.1 \pm 4.2$

<sup>a</sup> Mass ratio of anion to cation.

unity and higher for  $\text{PM}_{2.5}$ . This value indicates that the  $\text{PM}_{2.5-10}$  particles were basic and  $\text{PM}_{2.5}$  particles were acidic.

#### 3.7.2. Sulphate–nitrate ratio ( $\text{SO}_4^{2-}/\text{NO}_3^-$ )

Sulphate–nitrate ratio indicates the contribution of sulphate and nitrate to aerosol and also indicates the possible sources of aerosol. Higher  $\text{SO}_4^{2-}/\text{NO}_3^-$  ratio indicates the more static sources and lower  $\text{SO}_4^{2-}/\text{NO}_3^-$  ratio indicates more mobile sources (Arimoto et al. 1996). In  $\text{PM}_{2.5-10}$ , the  $\text{SO}_4^{2-}/\text{NO}_3^-$  ratio was found to be 4.17, 6.09, 2.41 and 1.54 in summer, fall, winter and spring, respectively. In  $\text{PM}_{2.5}$ , the  $\text{SO}_4^{2-}/\text{NO}_3^-$  mass ratio was 6.93, 13.6, 5.53 and 4.08 in summer, fall, winter and spring, respectively. The annual mean mass ratio for  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  were found to be  $3.55 \pm 2.01$  and  $7.54 \pm 4.22$ , respectively. This signifies that the industrial emission in Raipur was high in all seasons and played an important role to contribute the  $\text{PM}_{2.5}$  particle loading in the atmosphere.

## 4. Conclusion

The analysis of aerosol samples collected in Raipur, India during the period of April 2005 and March 2006 has been presented. The annual average concentrations of  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  were  $189.2$  and  $125.1 \mu\text{g m}^{-3}$ , respectively. Especially, the fine particles pollution was quite considerable in Raipur. The sum of ions comprised 23.3% and 57.2% of  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  mass concentrations, respectively. In  $\text{PM}_{2.5}$ ,  $\text{SO}_4^{2-}$  was the highest and  $\text{Ca}^{2+}$  was the second most abundant ion. In  $\text{PM}_{2.5-10}$ ,  $\text{Ca}^{2+}$  was present in higher concentration than others. In the present study, sulphate was found higher in  $\text{PM}_{2.5}$  and lower in  $\text{PM}_{2.5-10}$ . The same trend was observed for the nitrate.  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  existed in the form of  $\text{NH}_4\text{SO}_4$ , mostly. The urban aerosols were slightly acidic in the  $\text{PM}_{2.5}$  size range, and basic in the  $\text{PM}_{2.5-10}$  size range. The acidity of  $\text{PM}_{2.5}$  particles was due to high concentration of sulphate ( $\text{SO}_4^{2-}/\text{NO}_3^- = 7.54 \pm 4.22$ ). The main species forming in both  $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$  were  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{CaSO}_4$ ,  $\text{NaCl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{CaCl}_2$  and  $\text{KNO}_3$ . Compared with the different sites of over the world, the concentrations of aerosols and water soluble inorganic ions in PM demonstrate relatively higher mass and ionic loading of aerosols in the study area.

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## References

- Aceves, M., Grimalt, J.O., 1993. Seasonally dependent size distribution of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas. *Environ. Sci. Technol.* 27, 2896–2908.
- Adams, P.J., Seinfeld, J.H., Koch, D.M., 1999. Global concentrations of tropospheric sulphate, nitrate, and ammonium aerosol simulated in a general circulation model. *J. Geophys. Res.* 104, 13791–13823.
- Alastuey, A., Querol, X., Rodríguez, S., Plana, F., Lopez-Soler, A., Ruiz, C., Mantilla, E., 2004. Monitoring of atmospheric particulate matter around sources of secondary inorganic aerosol. *Atmos. Environ.* 38, 4979–4992.
- Andreae, M.O., 1995. Climatic effects changing atmospheric aerosol level. In: Henderson-Sellers, A. (Ed.), *Future climates of the world: a modeling perspective*, world survey of climatology, vol. 16. Elsevier, Amsterdam, pp. 341–392.
- Arimoto, R., Duce, R.A., Savoie, D.L., Prospero, J.M., Talbot, R., Cullen, J.D., Tomza, U., Lewis, N.F., Ray, B.J., 1996. Relationships among aerosol constituents from Asia and the North Pacific during Pem-West A. *J. Geophys. Res.* 101, 2011–2023.
- Asman, W., Van-Jaarsveld, H., 1991. A variable-resolution transport model applied for NHx in Europe. *Atmos. Environ.* 24A (2), 445–464.
- Borja-Aburto, V.H., Castillejos, M., Gold, D.R., Bierzowski, S., Loomis, D., 1998. Mortality and ambient fine particles in southwest Mexico city, 1993–1995. *Environ. Health Perspect.* 106, 849–855.
- Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<http://www.arl.noaa.gov/ready/hysplit4.html>). NOAA Air Resources Laboratory, Silver Spring, MD.
- Gomiseck, B., Hauck, H., Stopper, S., Preining, O., 2004. Spatial and temporal variations of PM<sub>1</sub>, PM<sub>2.5</sub>, PM<sub>10</sub> and particle number concentration during the AUPHEP-project. *Atmos. Environ.* 38, 3917–3934.
- Harrison, R.M., Sturges, W.T., 1984. Physico-chemical speciation and transformation reactions of particulate atmospheric nitrogen and sulphur compounds. *Atmos. Environ.* 18, 1829–1833.
- He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C.K., Cadle, S., Chan, T., Mulawa, P., 2001. The characteristics of PM<sub>2.5</sub> in Beijing, China. *Atmos. Environ.* 35, 4959–4970.
- Hildemann, L.H., Markowski, G.R., Cass, G.R., 1991. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* 25, 744–759.
- [http://www.scorecard.org/env-releases/def/cap\\_naaqs.html](http://www.scorecard.org/env-releases/def/cap_naaqs.html).
- Hubert, B.J., Lazrus, A.L., 1980. Bulk composition of aerosols in the remote troposphere. *J. Geophys. Res.* 85, 7337–7344.
- Jaecker-Voirol, A., Mirabel, P., 1989. Heteromolecular nucleation in the sulphuric acid–water system. *Atmos. Environ.* 23, 2053–2057.
- Khemani, L.T., Momin, G.A., Naik, M.S., Vijayakumar, R., Ramana Murthy, B.V., 1982. Chemical composition and size distribution of atmospheric aerosols over the Deccan Plateau, India. *Tellus* 34, 151–158.
- Khemani, L.T., Momin, G.A., Naik, M.S., Kumar, R., Ramana Murthy, B.V., 1985. Observations of Aitkin nuclei and trace gases in different environments in India. *Water Air Soil Pollut.* 24, 131–140.
- Kleeman, M.J., Cass, G.R., 1998. Source contributions to the size and composition distribution of urban particulate air pollution. *Atmos. Environ.* 32, 2803–2816.
- Korhonen, P., Kulmala, M., Laaksonen, A., Viisanen, Y., McGraw, R., Seinfeld, J.H., 1999. Ternary nucleation of H<sub>2</sub>SO<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O in the atmosphere. *J. Geophys. Res.* 104, 26349–26353.
- Kouyoumdjian, H., Saliba, N.A., 2005. Ion concentrations of PM<sub>10</sub> and PM<sub>2.5</sub> aerosols over the eastern Mediterranean region: seasonal variation and source identification. *Atmos. Chem. Phys. Discuss.* 5, 13053–13073.
- Kulshrestha, U.C., Saxena, A., Kumar, N., Kumari, K.M., Srivastava, S.S., 1998. Chemical composition association of size differentiated aerosols at a suburban site in a semi arid tract of India. *J. Automat. Chem.* 29, 109–118.
- Kumar, R., Rani, A., Singh, S.P., Kumari, K.M., Srivastava, S.S., 2002. Measurement of dry deposition of gaseous and particulate sulphur on marble at a suburban site. *Indian J. Radio Space Phys.* 31, 80–92.
- Kumar, R., Rani, A., Kumari, K.M., Srivastava, S.S., 2003. Direct measurements of atmospheric dry deposition to natural surfaces in a semi arid region of tropical sites. *J. Geophys. Res.* 105 (D (20)), A1–12.
- Kumar, R., Kumari, K.M., Srivastava, S.S., 2006. Field measurements of aerosol particle dry deposition on tropical foliage. *Environ. Sci. Technol.* 40, 135–141.
- Kumar, R., Srivastava, S.S., Kumari, K.M., 2007. Characteristics of aerosols over suburban and urban site of semiarid region in India: seasonal and spatial variations. *Aerosol Air Qual. Res.* 7, 531–549.
- Laskin, A., Ledema, M.J., Lchkevich, A., Graber, E.R., Taraniuk, L., Rudich, Y., 2005. Direct observation of completely processed calcium carbonate dust particles. *Faraday Discuss.* 130, 450–468.
- Lee, S.B., Bae, G.N., Moon, K.C., Kim, Y.P., 2002. Characteristics of TSP and PM<sub>2.5</sub> measured at Tokchok Island in the Yellow Sea. *Atmos. Environ.* 36, 5427–5435.
- Lewin, E.E., De Pena, R.G., Shimshock, J.P., 1986. Atmospheric gas and particle measurements at a rural northeastern US site. *Atmos. Environ.* 20, 59–70.
- Lin, L.H., Harrison, R.M., Harrad, S., 1999. The contribution of traffic to atmospheric concentrations of polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 33, 3538–3542.
- Lioy, P.J., Daisey, J.M., 1987. *Toxic Air Pollution: A Comprehensive Study of Non-Criteria Air Pollutants*. Lewis Publishers Inc., Chelsea, MI.
- Mahadevan, T.N., 1986. Studies on aerosol size distribution and chemical composition in urban, rural and marine environments and their deposition through precipitation. Ph.D. Thesis, University of Bombay.
- Mamane, Y., Gottlieb, J., 1992. Nitrate formation on sea-salt and mineral particles—a single particle approach. *Atmos. Environ.* 26A, 1763–1769.
- McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., Watson, J.G., 2000. Fine particle and gaseous emission rates from residential wood combustion. *Environ. Sci. Technol.* 34, 2080–2091.
- Meagher, J.F., Bailey, E.M., Luria, M., 1983. The seasonal variations of the atmospheric SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> conversion rate. *J. Geophys. Res.* 88, 1525–1527.
- Meszaros, E., 1999. Fundamentals of atmospheric aerosol chemistry. In: Akademiai Kiado, Budapest, p. 308.
- Moreno, T., Gibbons, W., Jones, T., Richards, R., 2003. The geology of ambient aerosols: characterizing urban and rural/coastal silicate PM<sub>10</sub> and PM<sub>2.5</sub> using high-volume cascade collection and scanning electron microscopy. *Atmos. Environ.* 37, 4265–4276.
- Mori, I., Nishikawa, M., Tanimura, T., Quan, H., 2003. Change in the size distribution and chemical composition of kosa (Asian dust) aerosol during long-range transport. *Atmos. Environ.* 37, 4253–4263.
- Mouli, P.C., Venkata, M.S., Reddy, S.J., 2003. A study on major inorganic ion composition of atmospheric aerosols at Tirupati. *J. Hazard. Mater. B* 96, 217–228.
- Pakkanen, T.A., 1996. Study of formation of coarse particle nitrate. *Atmos. Environ.* 30, 2475–2482.
- Parmar, R.S., Satsangi, G.S., Kumari, K.M., Lakhani, A., Srivastava, S.S., Prakash, S., 2001. Study of size distribution of atmospheric aerosol at Agra. *Atmos. Environ.* 35, 693–702.
- Pio, C.A., Lopes, D.A., 1998. Chlorine loss from marine aerosol in a coastal atmosphere. *J. Geophys. Res.* 103, 25263–25272.
- Querol, X., Alastuey, A., Lopez-Soler, A., Plana, F., Puicercus, J.A., Ruiz, C.R., Mantilla, E., Juan, R., 1998. Seasonal evolution of atmospheric suspended particles around a coal fired power station: chemical characterization. *Atmos. Environ.* 32, 719–731.
- Querol, X., Alastuey, A., Rodríguez, S., Plana, F., Mantilla, E., Ruiz, C.R., 2001. Monitoring of PM<sub>10</sub> and PM<sub>2.5</sub> around primary particulate anthropogenic emission sources. *Atmos. Environ.* 35, 845–858.
- Rastogi, N., Sarin, M.M., 2005. Long term characterization of ionic species in aerosols from urban and high-altitude sites in western India: role of mineral dust and anthropogenic sources. *Atmos. Environ.* 39, 5541–5554.
- Rodríguez, S., Querol, X., Alastuey, A., Kallos, G., Kakaliagou, O., 2001. Saharan dust contributions to PM<sub>10</sub> and TSP levels in Southern and Eastern Spain. *Atmos. Environ.* 35, 2433–2447.
- Rodríguez, S., Querol, X., Alastuey, A., Plana, F., 2002. Sources and processes affecting levels and composition of atmospheric aerosol in the western Mediterranean. *J. Geophys. Res.* 107, 4777–4785.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1998. Sources of fine organic aerosol. 9. Pine, oak and synthetic log combustion in residential fireplaces. *Environ. Sci. Technol.* 32, 13–22.
- Safai, P.D., Khemani, L.T., Momin, G.A., Rao, P.S.P., Pillai, A.G., 1993. Mass size distribution and chemical composition of aerosols at the Silent Valley, India. *Indian J. Radio Space Phys.* 22, 56061–56069.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* 30, 3837–3855.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2001. Measurement of emissions from air pollution sources. 3. C1–C29 organic compounds from fireplace combustion of wood. *Environ. Sci. Technol.* 35, 1716–1728.
- Schwartz, J., Dockery, D.W., Neas, L.M., 1996. Is daily mortality associated specifically with the particles? *Air Waste Manage. Assoc.* 46, 927–939.
- Seinfeld, J.H., Pandis, S.N., 1998. *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*. Wiley, New York, USA.
- Sharma, M., Maloo, S., 2005. Assessment of ambient air PM<sub>10</sub> and PM<sub>2.5</sub> and characterization of PM<sub>10</sub> in the city of Kanpur, India. *Atmos. Environ.* 39, 6015–6026.
- Shrestha, A.B., Wake, C.P., Dibb, J.E., Mayewski, P.A., Whitlow, S.I., Carmichael, G.R., Ferm, M., 2000. Seasonal variations in aerosol concentrations and compositions in the Nepal Himalaya. *Atmos. Environ.* 34, 3349–3363.

- Streets, D.G., Gupta, S., Waldhoff, S.T., Wang, M.Q., Bond, T.C., Yiyun, B., 2001. Black carbon emissions in China. *Atmos. Environ.* 35, 4281–4296.
- Switzer, P., Enger, L., Hoffer, T.E., Koracin, D., White, W.H., 1996. Ambient sulphate concentrations near Grand Canyon as a function of fluctuating loads at the Mohave power project: an explanatory analysis of an atmospheric experiment. *Atmos. Environ.* 30, 2551–2564.
- Tang, I.N., Fung, K.H., Imre, D.G., Munkelwitz, H.R., 1995. Phase transformation and meta stability of hygroscopic micro particles aerosol. *Aerosol Sci. Technol.* 23, 443–453.
- Tripathi, B.D., Chaturvedi, S.S., Tripathi, R.D., 1996. Seasonal variation in ambient air concentration of nitrate and sulphate aerosols in a tropical city, Varanasi. *Atmos. Environ.* 30, 2773–2778.
- Tsai, Y.I., Kuo, S.C., 2005. PM<sub>2.5</sub> aerosol water content and chemical composition in a metropolitan and a coastal area in southern Taiwan. *Atmos. Environ.* 39, 4827–4839.
- Tsai, Y.I., Kuo, S.C., 2006. Development of diffuse reflectance infrared Fourier transform spectroscopy for the rapid characterization of aerosols. *Atmos. Environ.* 40, 1781–1793.
- Tsai, Y.I., Lin, Y.H., Lee, S.Z., 2003. Visibility variation with air qualities in the metropolitan area in southern Taiwan. *Water Air Soil Pollut.* 144, 19–40.
- Verma, S.K., Deb, M.K., 2007. Direct and rapid determination of sulphate in environmental samples with diffuse reflectance Fourier transforms infrared spectroscopy using KBr substrate. *Talanta* 71, 1546–1552.
- Wang, G., Wang, H., Yu, Y., Gao, S., Feng, J., Gao, S., Wang, L., 2003. Chemical characterization of water-soluble components of PM<sub>10</sub> and PM<sub>2.5</sub> atmospheric aerosols in five locations of Nanjing, China. *Atmos. Environ.* 37, 2893–2902.
- Wang, H., Kawamura, K., Shooter, D., 2005a. Carbonaceous and ionic components in wintertime atmospheric aerosols from two New Zealand cities: implications for solid fuel combustion. *Atmos. Environ.* 39, 5865–5875.
- Wang, Y., Zhuang, G., Tang, A., Yuan, H., Sun, Y., Chen, S., Zheng, A., 2005b. The ion chemistry and the source of PM<sub>2.5</sub> aerosol in Beijing. *Atmos. Environ.* 39, 3771–3784.
- Wang, Y., Zhuang, G., Zhang, X., Huang, K., Xu, C., Tang, A., Chen, J., An, Z., 2006. The ion chemistry, seasonal cycle, and sources of PM<sub>2.5</sub> and TSP aerosol in Shanghai. *Atmos. Environ.* 40, 2935–2952.
- Warneck P. *Chemistry of the natural atmosphere*, vol. 41, Wiley and Sons, Academy Press, 1987. p. 757 (International Geophysics Series).
- Whitby, K.T., 1978. The physical characteristics of sulfur aerosols. *Atmos. Environ.* 12, 135–159.
- Wolff, G.T., 1984. On the nature of nitrate in coarse continental aerosols. *Atmos. Environ.* 18, 977–981.
- Zhuang, H., Chan, C.K., Fang, M., Wexler, A.S., 1999. Formation of nitrate non-sea-salt sulphate on coarse particles. *Atmos. Environ.* 33, 4223–4233.