



Characterization of Dicarboxylates and Inorganic Ions in Urban PM₁₀ Aerosols in the Eastern Central India

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ABSTRACT

Size-segregated aerosol samples were collected continuously from July 2009 to June 2010 at urban area of Raipur, the eastern central India. The collected samples were analyzed for PM₁₀ mass and its water-soluble dicarboxylate species and major inorganic ions. Results showed that the annual mean PM₁₀ concentration was 270.5 μg/m³, which varied from 109.8 to 455.6 μg/m³. The higher concentration of PM₁₀ mass was found during winter season followed by spring and summer, and lower during monsoon season. High PM₁₀ mass concentration in Raipur could be attributed to the anthropogenic activities which may include high rate of construction activities, biomass combustion and mechanical erosion from road dusts. The concentrations of total dicarboxylates (TDCs) ranged from 325.3 to 1537.7 ng/m³ with an average of 904.0 ng/m³ constituting only 0.3% of PM₁₀ mass. The oxalate (C₂) and malonate (C₃) were the dominant DCs followed by succinate (C₄) and phthalate (Ph). The water-soluble major inorganic ions constituted 10.0% of PM₁₀ mass with SO₄²⁻ and NO₃⁻ being the dominant species followed by Cl⁻ and Ca²⁺. The concentrations of dicarboxylates and major inorganic ions also showed maxima in winter and spring than summer and monsoon seasons. The ratio of malonate to succinate was used to distinguish primary sources from secondary sources of these dicarboxylates. The average C₃/C₄ ratio in spring and summer was 1.6 and 2.1, respectively, which suggested a large contribution of secondary sources to particulate dicarboxylates formation. Correlation analysis of DCs with SO₄²⁻ and K⁺ was investigated to interpret their possible secondary formation pathways. Source identification study by principal component analysis (PCA) revealed that photochemical, secondary sources and vehicular emissions were the main sources contributing to overall PM₁₀ mass with minor contribution from paved road dust and explained almost 95.5% variance of total aerosol data set.

Keywords: Particulate matter; Meteorological variables; Water-soluble ions; Seasonal variation; Source identification.

INTRODUCTION

In recent years many Asian countries have experienced significant economic growth leading to increased urbanization, motorization and energy use (Colbeck *et al.*, 2010). The Clean Air Initiative for Asian Cities (http://www.cleanairnet.org/caiasia/1412/articles-59689_Asia_AQ.pdf) has reported, in 64 cities, that ambient PM₁₀ concentration remains above the World Health Organization (WHO) guidelines. Worldwide urban air pollution is estimated to be responsible for 865,000 premature deaths every year and about 60% of

these deaths occur in Asia (WHO, 2007). Particulate matter in the lower atmosphere is composed of highly water-soluble inorganic and organic species, which can influence the hygroscopicity of aerosols and further the atmospheric visibility (Hopke *et al.*, 2008; Huang *et al.*, 2011). It is known that aerosol and their associated ions play an important role in the content of chemical species in atmospheric ecosystem interfaces (Chakraborty and Gupta, 2010; Wang *et al.*, 2012). PM pollution is a serious environmental issue mainly due to the presence of organic and inorganic components in the atmosphere (Jung *et al.*, 2010). Organic aerosols play an important role in climate forcing, directly and indirectly (Ho *et al.*, 2007). Of these, dicarboxylic acids comprise significant fractions of organic aerosols (Pavuluri *et al.*, 2010; Yang and Yu, 2008). Although, dicarboxylic acids can be generated from primary sources including fossil fuel combustion (Schauer *et al.*, 2002) and biomass burning (Pio *et al.*, 2005), they are mainly formed by secondary processes

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in the atmosphere (Wang *et al.*, 2006). Photochemical oxidation and breakdown of relatively higher diacids and other precursors are important source of lower diacids in the atmosphere (Kawamura *et al.*, 2010). Oxalic acid, generally the most abundant dicarboxylic acids in the atmosphere is formed from oxidation of volatile organic compounds (VOCs) as well as from primary emissions from fossil fuel combustion and biomass burning (Warneck *et al.*, 2003). In the atmosphere of many urban and heavily industrialized areas, water-soluble inorganic components also constitute a major proportion of PM (Kothai *et al.*, 2008). SO_4^{2-} , NO_3^- and NH_4^+ are the most common components of secondary inorganic aerosol in the atmosphere that are formed from direct emissions of sulfur dioxides (SO_2), oxides of nitrogen (NO_x), and ammonia (NH_3) gases, respectively (Karar and Gupta, 2006; Tsai *et al.*, 2012). It was reported that water-soluble ions such as sulfate, nitrate and other acid rain related pollutants have severe effects on human health (Wang *et al.*, 2006). The continued use of wood and coal for cooking are unavoidable issues in developing countries and India is no exception to it. Several studies have been conducted in the world in various environments for characterization of water-soluble organic (Ho *et al.*, 2007; Pavuluri *et al.*, 2010) and inorganic components (Nicolas *et al.*, 2009; Mena *et al.*, 2010; Parmar *et al.*, 2001). However, the information on air quality in terms of water-soluble dicarboxylates (DCs) associated with inorganic species in PM_{10} aerosols is inadequate for a rapidly growing industrial city Raipur, Chhattisgarh, situated at the eastern central region of India.

Raipur is the largest industrial city in state Chhattisgarh, thus its air quality is an important environmental issue. Industrial and vehicular emissions, rapidly increasing constructions and fast growing population have led to a significant rise in PM levels in Raipur (Deshmukh *et al.*, 2011a). PM from these sources may contain hazardous

pollutants that can have carcinogenic and mutagenic effects. Under such complicated pollution conditions, it is of interest to examine the detailed characteristics and sources of chemical species in ambient air in the industrial city Raipur. To improve our knowledge on the PM pollution in Raipur, we systematically studied, for the first time, concentrations of dicarboxylates (DCs) and inorganic ions in PM_{10} aerosols. The main objectives of the present paper are to report the mass concentration and seasonal distributions of PM_{10} aerosols collected in Raipur, India under a variety of meteorological conditions, to determine the detailed chemical composition in terms of water-soluble DCs and inorganic ions and to find the likely sources of analyzed DCs and inorganic ions through the application of correlation and principal component analysis.

EXPERIMENTAL

Study Area

Raipur, the capital and the largest industrial city of a newly formed state Chhattisgarh, was selected for continuous sampling of size-segregated aerosols. It lies between $21^\circ 14'N$ and $81^\circ 38'E$ at an elevation of 297 m above sea level with a total area of 160 km^2 . The location of sampling site at Raipur is shown in Fig. 1. According to the Census of India 2001, the estimated population of Raipur is 1.2 million with a huge vehicular growth rate especially after it became the capital of a new state Chhattisgarh (http://www.censusindia.gov.in/towns/chh_towns.pdf). There is a National Highway, namely, Great Eastern road that adjoins Kolkata and Mumbai, approximately 400 m away from the sampling point with frequent heavy vehicular traffic volume of nearly 25,000 vehicles per day (Deshmukh *et al.*, 2012). The study area is literally sandwiched between two industrial complexes on its eastern and western outskirts extended at distances of about 20–30 km, and comprised of some big

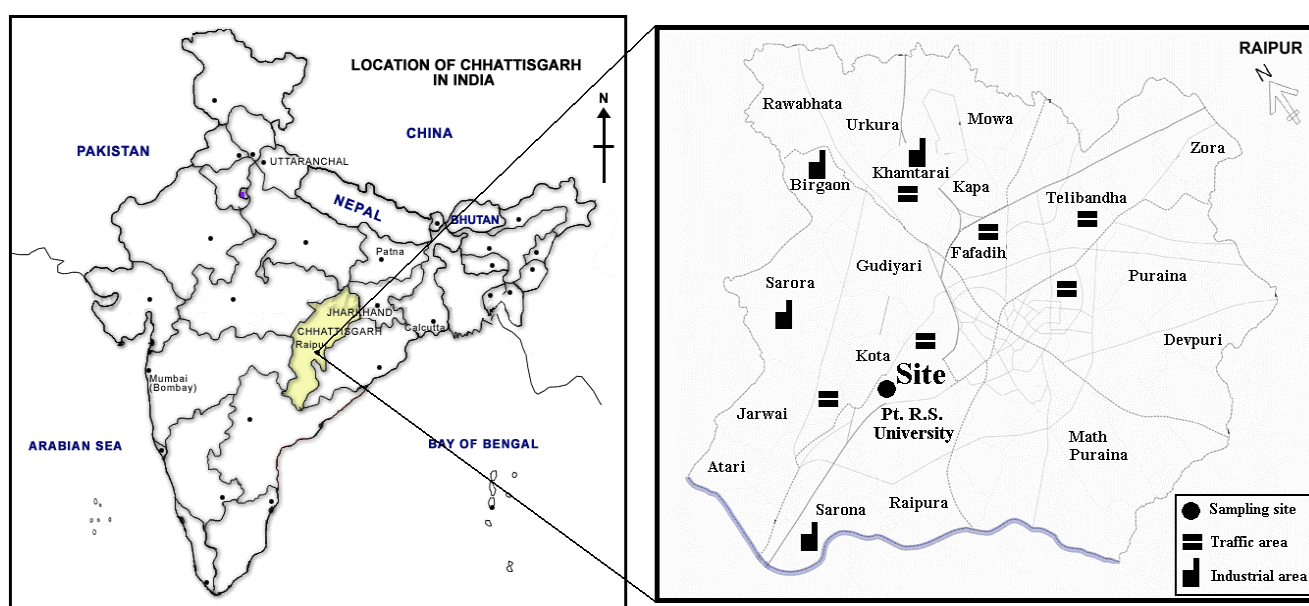


Fig. 1. Map of Raipur city showing the location of sampling site.

industries such as Bhilai Steel Plant, Jamul Cement Factory, Century Cement, Larson & Toubro Cement, Monnet Sponge Iron and Power Plant, Woolworth Textile Plant, etc. These huge coal burning industries produce a large amount of fly ash and PM, which affect the local environment as well as surroundings by the aerial dispersion processes.

Aerosol Sampling and Mass Measurement

The collection of size-segregated aerosols was performed at the terrace of a double-storied building, i.e., Department of Chemistry, Pandit Ravishankar Shukla University, at an altitude of approximately 15 m above the ground level. Ambient aerosol samples were collected with eight-stage cascade impactor sampler (TE 20–800, Tisch Air Pollution Monitoring Equipment, USA) for one year from July 2009 to June 2010 spread over all the major seasons, monsoon (July to September), winter (October to January), spring (February to March) and summer (April to June). The sampling frequency was nearly two samplings per week starting at 06:00 hrs (local time) for 24 hrs. The flow rate of the eight-stage cascade impactor was 28.3 L/min. The filters used in this study were quartz fiber filters. Before use, the quartz fiber filters were pre-backed at 550°C for about 15 hours to remove residual impurities. It may be noted that quartz filters may render positive artifacts by absorbing volatile compounds, resulting in overestimated gravimetric data, and concentrations of organics (e.g. oxalate) and ionic species (Yu *et al.*, 2006). The samplings were performed at a rate of 1.7 m³/h and in total 40.8 m³/day of air passed through each filter. The sampler was operated in a location free of any obstructing units. Eight-stage cascade impactor separated particles into eight-size fractions between 0.4 µm and 10.0 µm, according to the following equivalent aerodynamic cutoff diameter, 10.0–9.0 µm (stage 0), 9.0–5.8 µm (stage 1), 5.8–4.4 µm (stage 2), 4.4–2.5 µm (stage 3), 2.5–2.1 µm (stage 4), 2.1–1.0 µm (stage 5); 1.0–0.7 µm (stage 6) and 0.7–0.4 µm (stage 7). Particulate matter of diameter less than 0.4 µm was collected in backup filter installed in the final stage of cascade impactor. During the period of study 120 samplings (120 × 8 size fractions = 960 samples of eight different size fractions) were carried out. PM₁₀ particles presented the sum up of particles of stage 0 to stage 7 of the eight-stage cascade impactor. After the collection of aerosol samples, the eight-stage cascade impactor loaded with sampled filters was transported from the sampling site to the laboratory. The filters were unloaded in a dust free room and subsequently stored in Petri dishes and transported to the weighing room for gravimetric analysis.

The mass concentration of size-segregated aerosols was determined by the gravimetric analysis. The filters were placed in desiccators for ~24 hrs before and after the sampling to remove the absorbed water and weighed in a controlled environment chamber, after taking the filters out of the desiccators, using an analytical balance (Sartorius, Model CP225D) with a reading precision of 10 µg. In this study, PM₁₀ concentration was calculated by summing the concentration of particulate matter in all eight-size ranges (0.4 µm to 10.0 µm) and backup filter, therefore, each of the filters was analyzed gravimetrically by taking proper care in

order to prevent minute deviation in weight measurements. Two of the most important factors to consider mass concentration measurement are variation of weight with temperature (T) and relative humidity (RH). Thus, the filters were first conditioned for ~24 hrs at 20°C and 40% RH. All weight measurements were repeated three times to ensure reliability. To ensure the quality of weighing, field blanks ($n = 24$), i.e., filters brought to the field and installed in the sampler but through which no air was pumped, were also collected. The gravimetric mass (µg) was calculated by subtracting the weight of the filter after sampling from that of the prior sampling and the concentration (µg/m³) was determined by dividing the aerosol mass by total volume of air sampled (m³). After the gravimetric analysis, the loaded filters and field blanks were placed in clean polyethylene (PE) bottles and stored in a refrigerator at about 4°C to prevent the loss of volatile or semi-volatile species from the sample filters. The mass of the sampled filters obtained were corrected for field blank values.

Chemical Analysis

For chemical analysis, eight-size ranges of sample filters were extracted and analyzed separately. One-fourth of the each size range of sampled filter was placed in PE bottle, 10.0 mL of deionized water (resistivity > 18.0 MΩ/cm at 25°C, Barnstead) was added to it and the content was shaken (Yihder TS-500 Shaker) in an unlit refrigerator at 4°C for 90 min to prevent the decomposition of extracted dicarboxylate species. The liquid was then filtered through a 0.2 µm ester acetate filter and the aqueous filtrate was characterized using ion chromatography (IC, Dionex, DX-600, USA). The IC was equipped with a gradient pump (Model GP50), ASRS-Ultra anion self-regenerating suppressor, conductivity detector (CD25), Spectrasystem automated sampler (AS1000) with 2 mL vials, Teflon injection valve with 1000 µL sample loop, AS11 analytical column (250 mm × 4 mm I.D.) with AG11 guard column (50 mm × 4 mm I.D.), anion trap column (ATC-3), 5–100 mM NaOH (gradient) and 100% methanol (eluent). The flow rate was maintained at 2.0 mL/min during the analysis of water-soluble DCs.

Another one-fourth of the each size ranges of sampled filters was soaked in 10 mL Milli-Q water (18.2 MΩ resistivity) for ~45 min and ultrasonicated (UT-105 S, Sharp, Japan) for 20 min for the analysis of water-soluble inorganic ions. The extracted solutions were filtered through a microporous membrane (pore size, 0.45 µm; diameter, 25 mm) and were made up to known volume (100 mL) using Milli-Q water. The solutions were then kept in PE bottles and stored at ~4°C until analysis. The major ions, namely anions (Cl⁻, NO₃⁻ and SO₄²⁻) and cations (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) were quantitatively determined by ion chromatography (Dionex, DX-120, USA). Anions were analyzed using analytical column IonPac AS 12A with micro-membrane suppressor ASRS ultra II 2mm, 2.7 mM Na₂CO₃ and 0.3 mM NaHCO₃ (Wako, Japan) as eluent and triple distilled water as regenerator for anions with a pump flow rate of 1.5 mL/min. Similarly, the IonPac CS 16A column with micro-membrane suppressor CSRS ultra II 2 mm, 2.6 mM methanesulfonic acid (CH₃SO₃H) (Wako, Japan) as

eluent and triple distilled water as regenerator was used for cations analysis with a pump flow rate of 1.0 mL/min.

Quality Control (QC) and Quality Assurance (QA)

Method Detection Limits (MDLs)

The MDLs were calculated as three times of SD, where SD is the standard deviation of the replicate analyses for dicarboxylates and major inorganic ions to determine the lowest concentration level that can be detected and to be statistically different from a blank. 1 ppm of the laboratory prepared calibration standards were used to calculate MDL. The obtained MDLs were found to be in the range of 1.49 to 7.06 $\mu\text{g/L}$ for dicarboxylates and 4.21 to 18.40 $\mu\text{g/L}$ for inorganic ions. Table 1 shows the method detection limits, % spike recovery, relative standard deviation and field blank concentrations of individual dicarboxylate species and inorganic ions for the quality control and assurance of the analyzed aerosol parameters.

Spike Recovery and Duplicate Analysis

Spike recovery was tested for water-soluble DCs and inorganic ions using ion chromatograph. For the recovery of diacids, a free mixed standard (C_2 – C_6 , M, F, hC₄, Ta, Ph) was prepared and used. 1 ppm of laboratory prepared concentration of DCs and inorganic ions was added separately to blank samples. Thereafter, a complete extraction procedure was followed and analyzed for water-soluble DCs and inorganic ions. The recovery results (Table 1) were found to be in the range of 92.8% to 106.1% for all dicarboxylates tested. The recovery results were found to be in the range of 96.9% to 103.3% for inorganic ions. The precision (Table 1, % of relative standard deviation) estimated from the standard deviation of repeated measurements of standards and samples were found to be in the range of 0.86% to

2.35% and 1.36% to 4.89% for dicarboxylates and inorganic ions, respectively, demonstrating good repeatability for our analytical method (Tsai *et al.*, 2008).

Blank Concentration

Blank concentration was measured using field blank samples. Blank filters were extracted and carried through similar procedures as followed for the extraction and preparation of the sampled filters to analyze with the IC. The overall mean concentrations of field blank samples collected over one year were found to be in the range of 0.81 to 12.70 ng/m^3 for dicarboxylates and 0.00 to 0.15 $\mu\text{g/m}^3$ for inorganic ions. The concentrations of all the reported PM mass, water-soluble DCs and inorganic ions concentration have been corrected for field blanks.

Meteorology of the Study Area

Meteorological data (temperature, relative humidity, rainfall, atmospheric pressure, wind speed, mixing height and wind direction) were obtained from Department of Agrometeorology, Indira Gandhi Agricultural University, Raipur (Chhattisgarh). The annual and seasonal mean and ranges of above meteorological variables are given in Table 2. The daily highest temperature was recorded as 44.6°C on May 24, 2010 and lowest was 8.6°C on January 3, 2010. April 5, 2010 was recognized as the driest day (RH: 10%) and September 1, 2009 was the most humid (RH: 95%). Moreover, the daily highest wind speed was recorded as 13.0 m/s on July 13, 2009 and the lowest was 1.3 m/s on January 11, 2010. The daily highest rainfall was recorded as 334.0 mm on July 10, 2009. The daily highest atmospheric pressure was observed as 3.6 kPa on July 20, 2009 and lowest was 0.9 kPa on January 18, 2010. The prevalent wind direction during winter was mainly northeasterly (NE) and

Table 1. Method detection limits, recovery ratio, relative standard deviation and field blank concentrations of water-soluble dicarboxylates and inorganic ions analyzed by ion chromatography.

Dicarboxylates and Inorganic ions	Method detection limit ($\mu\text{g/L}$)	Recovery ratio (% , $n = 3$)	Relative standard deviation (RSD, %)	Field blank concentrations ^a (^b ng/m^3 , $n = 24$; ^c $\mu\text{g/m}^3$, $n = 24$)
Oxalate (C_2)	7.06	99.8	2.35	12.70
Malonate (C_3)	1.49	106.1	0.86	1.10
Succinate (C_4)	4.20	103.7	1.48	0.92
Glutarate (C_5)	2.43	101.1	1.27	0.86
Adipate (C_6)	2.28	92.8	1.68	0.86
Maleate (M)	1.58	99.2	0.93	1.11
Fumarate (F)	2.45	104.3	1.34	1.00
Phthalate (Ph)	5.28	103.2	1.83	0.95
Malate (hC ₄)	2.41	97.0	1.39	1.02
Tartarate (Ta)	4.89	92.8	1.68	0.81
Na ⁺	10.3	103.3	3.28	0.04
K ⁺	4.21	99.7	2.64	0.07
NH ₄ ⁺	7.91	96.9	1.36	0.01
Mg ²⁺	18.40	100.1	4.89	0.01
Ca ²⁺	7.37	102.6	2.44	0.07
Cl ⁻	6.98	101.4	2.04	0.15
NO ₃ ⁻	7.81	98.5	2.58	0.00
SO ₄ ²⁻	4.79	100.3	1.54	0.14

^a Average value; ^b Dicarboxylates; ^c Inorganic ions.

Table 2. Descriptive statistics of meteorological variables and PM₁₀ concentration in the eastern central India.

Seasons	Statistics	Meteorological variables						PM ₁₀ ($\mu\text{g}/\text{m}^3$)
		T ^a (°C)	RH ^b (%)	RF ^c (mm)	AP ^d (kPa)	WS ^e (m/s)	MH ^f (m)	
Annual (n = 120)	Mean \pm Stdev ^h (Range)	27.3 \pm 5.5 (8.6–44.6)	60.0 \pm 19.0 (10–95)	20.6 \pm 54.5 (0.0–334.0)	2.0 \pm 0.8 (0.9–3.6)	5.1 \pm 3.1 (1.3–13.0)	720.2 \pm 187.4 (467.2–1128.2)	270.5 \pm 105.5 (109.8–455.6)
Monsoon (n = 30)	Mean \pm Stdev ^h (Range)	28.3 \pm 0.9 (24.4–33.0)	82.0 \pm 6.0 (57–95)	65.4 \pm 95.2 (4.0–334.0)	3.1 \pm 0.2 (2.9–3.6)	7.1 \pm 3.2 (3.3–13.0)	718.4 \pm 79.9 (619.2–892.0)	173.5 \pm 75.0 (109.8–375.3)
Winter (n = 40)	Mean \pm Stdev ^h (Range)	21.5 \pm 3.4 (8.6–32.7)	66.0 \pm 8.0 (21–94)	4.5 \pm 12.1 (0.0–50.8)	1.6 \pm 0.6 (0.9–3.1)	2.4 \pm 1.3 (1.3–6.5)	518.0 \pm 39.6 (467.2–610.0)	368.2 \pm 46.9 (226.4–455.5)
Spring (n = 20)	Mean \pm Stdev ^h (Range)	27.1 \pm 3.8 (13.2–40.4)	46.0 \pm 9.0 (14–88)	0.8 \pm 1.8 (0.0–5.6)	1.4 \pm 0.2 (1.2–1.8)	3.7 \pm 1.8 (1.7–6.9)	761.8 \pm 90.7 (583.0–900.0)	306.1 \pm 94.6 (153.4–419.6)
Summer (n = 30)	Mean \pm Stdev ^h (Range)	34.0 \pm 2.5 (22.5–44.6)	41.0 \pm 18.0 (10–85)	10.5 \pm 18.7 (0.0–61.4)	2.0 \pm 0.6 (1.2–3.0)	7.8 \pm 1.8 (4.4–10.5)	963.9 \pm 104.7 (768.9–1128.6)	213.3 \pm 66.7 (127.7–330.1)

^a Temperature; ^b Relative humidity; ^c Rainfall; ^d Atmospheric pressure; ^e Wind speed; ^f Mixing height; ^g Prevalent wind direction; ^h Standard deviation.

northwesterly (NW), and it was mainly southwesterly (SW) during monsoon and summer. Wind rose (WR) plots (Fig. 2) were generated by using a WRPLOT View (Lakes Environmental, Canada) indicated that the winter and spring were relatively calm (74.2% and 68.4%) than summer (18.6%) and monsoon (14.2%).

RESULTS AND DISCUSSION

Concentration of PM₁₀ Aerosols

A total of 120 samples of PM₁₀ aerosols were collected between the periods July 2009 and June 2010 at Raipur, India. Table 2 shows the annual mean and concentration ranges of PM₁₀ aerosols collected during the study period. The data on PM mass concentrations of eight different size fractions separated by cascade impactor have been reported elsewhere in our recent publication (Deshmukh *et al.*, 2012). The concentration of PM₁₀ aerosols ranged from 109.8 to 455.6 $\mu\text{g}/\text{m}^3$ with an average of 270.5 $\mu\text{g}/\text{m}^3$. The observed annual mean PM₁₀ concentration at Raipur was significantly high compared to prescribed limit of 60 $\mu\text{g}/\text{m}^3$ as set by the National Ambient Air quality Standards of India (<http://www.scorecard.org/env-release/def/capnaaqs.html>) and the air quality standard (20 $\mu\text{g}/\text{m}^3$) of the World Health Organization (WHO, 2005). In Raipur, the major PM emission sources include industries using heavy oil and coal, vehicles, disorderly mixed traffic causing congestion, use of soft coal for domestic cooking and construction activities (Deshmukh *et al.*, 2010). High PM₁₀ concentration in Raipur could be attributed to the anthropogenic activities which may include high rate of construction activity refuse dusts, biomass combustion and mechanical erosion from road dusts. The sampling site at Raipur is encompassed with educational institutions surrounded by areas exclusively devoted to residential and industrial activities. The existence of a National Highway, 400 m away from the sampling point, has favored industrial development in this region. The huge coal burning industries such as Bhilai Steel Plant, Thermal Power Plant, large number of cement plants and sponge iron industries produce huge amount of fly ash and affect the local environment as well as surroundings by the aerial dispersion process. Road dust resuspension may in fact have a great influence on PM₁₀ levels in Raipur 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 25,000 vehicles per day at a nearby highway (Deshmukh *et al.*, 2012). The alarming population and vehicular growth rate has resulted in a significant rise in the particulate matter levels over Raipur.

In order to establish the seasonal distribution trend for concentration of PM₁₀ aerosols, the PM₁₀ concentrations were calculated separately for monsoon, winter, spring and summer seasons. Table 2 summarizes the statistics of PM₁₀ concentrations for above four seasons. The monitored data from the above study period at Raipur reveals a general trend of maximum concentration during winter as well as in spring and minimum concentrations during summer and monsoon. During winter and spring, the PM₁₀ concentration

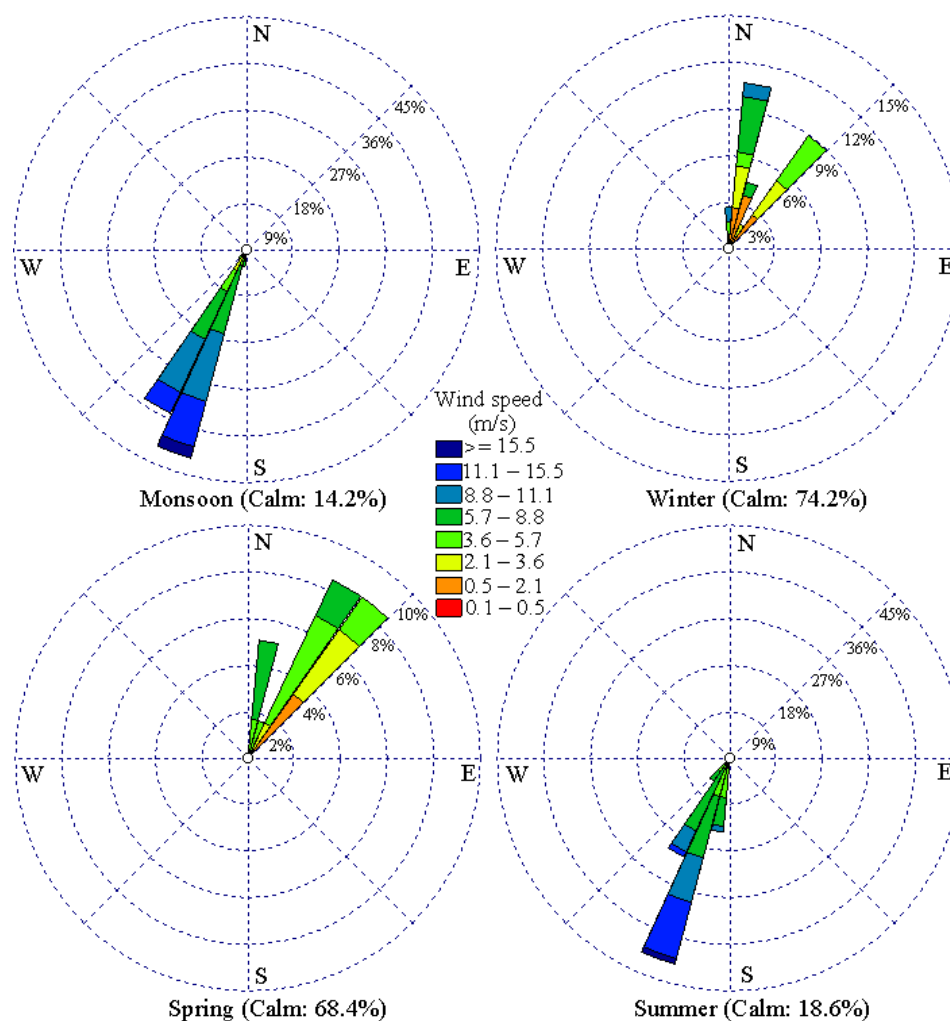


Fig. 2. Wind rose plots for all four seasons between the period July 2009 and June 2010.

was found to be in the range of 226.4 to 455.5 $\mu\text{g}/\text{m}^3$ and 153.4 to 419.6 $\mu\text{g}/\text{m}^3$ with an average of 368.2 and 306.1 $\mu\text{g}/\text{m}^3$, respectively. Whereas, in summer it ranged from 127.7 to 330.1 $\mu\text{g}/\text{m}^3$ and during monsoon season it ranged from 109.8 to 375.3 $\mu\text{g}/\text{m}^3$ with an average of 213.3 and 173.5 $\mu\text{g}/\text{m}^3$, respectively. The variation of PM_{10} concentration is influenced by the seasonal anthropogenic activities during the study period. The reason for higher PM_{10} concentration in winter is due to the massive biomass burning especially during night time in winter days. People use combustible material, such as fire wood and cow dung, in open fires for heat generation in winter, resulting in the release of significant quantities of airborne smoke particles. The high PM_{10} mass in winter is also due to the operation of a number of brick kilns, which utilize low quality coal, paddy husk and other combustible materials available at low cost. The concentration of PM_{10} also depends on the prevailing meteorological conditions at the study area. The highest concentration of PM_{10} aerosols observed during winter season can be attributed to low wind speed (1.3 to 6.5 m/s, October to January) and low temperature (8.6 to 32.7°C, October to January) which led to lower mixing height (467.2 to 610.0 m, October to January) and poor dispersion conditions coupled with increase

in anthropogenic activities such as biomass burning, industrial processes and space heating etc. Therefore, the meteorological conditions that prevailed in winter resulted in higher PM_{10} levels at Raipur. In summer, the increase in wind speed (4.4 to 10.5 m/s, April to June) and temperature (22.5 to 44.6°C, April to June) brought down PM concentrations remarkably. The lowest PM_{10} concentration during monsoon can be attributed to washout by rainfall and higher humidity, which led to the reduced resuspension of crustal dust.

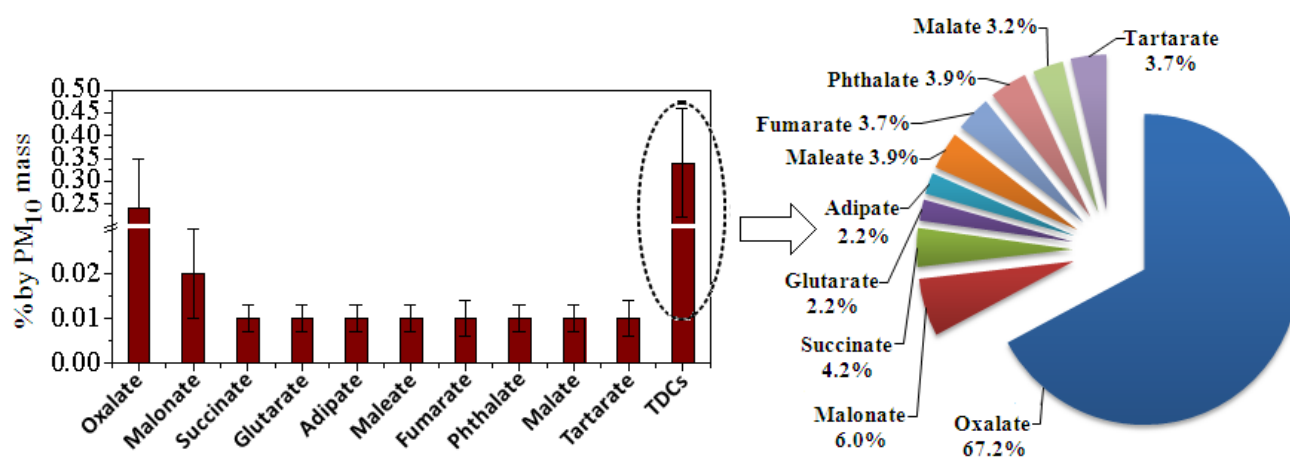
Molecular Composition of Dicarboxylic Acids

The average and concentration ranges of water-soluble dicarboxylates in PM_{10} aerosols in Raipur, India are given in Table 3. The relative abundance of individual dicarboxylates to the PM_{10} mass and total dicarboxylates (TDCs) are shown in Fig. 3. The concentration of total dicarboxylates ranged from 325.3 to 1537 ng/m^3 with an average of 904.0 ng/m^3 . The relative abundance of TDCs was found to be in the range of 0.2% to 0.8% with an average of 0.3% of the PM_{10} mass. The concentration of TDCs observed in Raipur, India were similar to those reported in Chinese cities (904.0 ng/m^3 , Ho *et al.*, 2007) and East China Sea (850.0 ng/m^3 , Mochida *et al.*, 2003a). Concentrations of TDCs observed

Table 3. Descriptive statistics on concentrations of dicarboxylate species (ng/m^3) in PM_{10} aerosols in the eastern central India.

Dicarboxylate Species (DCs)	Annual ($n = 120$)	Monsoon ($n = 30$)	Winter ($n = 40$)	Spring ($n = 20$)	Summer ($n = 30$)
	Mean \pm Stdev ^a (Range)	Mean \pm Stdev ^a (Range)	Mean \pm Stdev ^a (Range)	Mean \pm Stdev ^a (Range)	Mean \pm Stdev ^a (Range)
Oxalate (C_2)	618.9 \pm 303.4 (201.7–998.0)	401.1 \pm 221.8 (201.7–906.2)	836.5 \pm 268.5 (292.3–997.7)	680.4 \pm 331.9 (300.1–998.0)	502.7 \pm 189.4 (278.2–848.3)
Malonate (C_3)	51.8 \pm 29.7 (11.2–123.2)	17.5 \pm 7.0 (11.2–37.6)	69.2 \pm 33.3 (24.0–123.2)	67.6 \pm 18.9 (45.4–106.4)	52.4 \pm 7.7 (43.4–71.0)
Succinate (C_4)	36.0 \pm 23.7 (9.5–157.4)	16.6 \pm 6.5 (9.5–32.2)	54.1 \pm 26.4 (23.9–157.4)	47.5 \pm 20.8 (25.4–74.3)	26.1 \pm 4.9 (18.8–33.8)
Glutarate (C_5)	19.2 \pm 12.1 (5.4–65.1)	10.7 \pm 4.2 (5.4–18.3)	30.1 \pm 8.6 (14.7–43.6)	12.1 \pm 16.0 (8.5–65.1)	11.9 \pm 5.5 (5.7–23.0)
Adipate (C_6)	19.0 \pm 11.0 (5.0–78.8)	10.4 \pm 4.2 (5.0–17.4)	28.0 \pm 13.5 (13.5–78.8)	17.8 \pm 6.8 (7.7–30.9)	16.5 \pm 3.6 (8.5–21.3)
Maleate (M)	33.8 \pm 16.3 (12.1–65.5)	18.0 \pm 4.5 (12.1–30.9)	51.7 \pm 7.6 (35.6–65.5)	36.8 \pm 11.7 (20.3–51.3)	23.6 \pm 9.4 (14.6–51.6)
Fumarate (F)	30.2 \pm 18.4 (9.9–101.6)	18.3 \pm 4.7 (12.0–28.2)	51.4 \pm 17.8 (26.6–101.6)	31.7 \pm 7.6 (15.8–47.4)	20.8 \pm 8.3 (9.9–33.7)
Phthalate (Ph)	33.9 \pm 17.1 (6.7–79.5)	13.1 \pm 5.1 (6.7–22.7)	44.1 \pm 12.9 (6.9–79.5)	47.8 \pm 13.3 (28.9–71.7)	32.1 \pm 10.6 (16.7–53.0)
Malate (hC_4)	26.8 \pm 13.4 (11.0–81.4)	16.6 \pm 4.3 (11.0–27.0)	37.3 \pm 15.6 (16.8–81.4)	27.9 \pm 12.5 (15.2–18.3)	22.2 \pm 4.3 (15.3–31.4)
Tartarate (Ta)	31.8 \pm 14.3 (8.6–64.6)	14.9 \pm 5.8 (8.6–29.0)	41.9 \pm 11.2 (23.9–64.6)	37.6 \pm 10.5 (30.0–63.0)	31.2 \pm 10.7 (16.8–52.7)
TDCs ^b	904.0 \pm 386.5 (325.3–1537.7)	540.3 \pm 256.3 (325.3–1081.1)	1244.3 \pm 264.0 (684.7–1537.7)	1016.0 \pm 379.9 (579.6–1413.4)	739.4 \pm 176.8 (534.3–1060.7)

^a Standard deviation; ^b Total dicarboxylates.

**Fig. 3.** Percentage contribution of dicarboxylate species in overall PM_{10} mass.

in the PM_{10} aerosols at Raipur, India were lower than those reported in Sea of Japan ($1200 \text{ ng}/\text{m}^3$, Mochida *et al.*, 2003b) but higher than those reported in Gosan Jeju Island ($660.0 \text{ ng}/\text{m}^3$, Kawamura *et al.*, 2004), Tokyo Japan ($355.0 \text{ ng}/\text{m}^3$, Kawamura and Yasui, 2005) and Sapporo Japan ($406.0 \text{ ng}/\text{m}^3$, Aggarwal and Kawamura, 2008). Oxalate (C_2) was found to be the most abundant dicarboxylate species in PM_{10} aerosols in Raipur, India. The concentration of C_2 was found to be in the range of 201.7 to $998.0 \text{ ng}/\text{m}^3$ with an average of $618.9 \text{ ng}/\text{m}^3$. Relative abundance of C_2 to the TDCs ranged from 39.3% to 89.8% with an average of 67.2%. The predominance of C_2 has been also observed in the aerosol samples collected from different regions

including Chinese megacities (Ho *et al.*, 2007), Hong Kong (Yao *et al.*, 2004), Southern India (Pavuluri *et al.*, 2010) and New Zealand (Wang and Shooter, 2004) because C_2 diacid is the end product of the photooxidation of aromatic hydrocarbons, isoprene, ethylene and acetylene. The C_2 diacid is also emitted from fossil fuel combustion and biomass burning (Warneck *et al.*, 2003). The second and third most abundant dicarboxylates were malonate (C_3) and succinate (C_4) followed by phthalate (Ph) and maleate (M). The concentrations of C_3 and C_4 dicarboxylates ranged from 11.2 to $123.2 \text{ ng}/\text{m}^3$ and from 9.5 to $157.4 \text{ ng}/\text{m}^3$ with an average of $51.8 \text{ ng}/\text{m}^3$ and $36.0 \text{ ng}/\text{m}^3$, respectively. Relative abundance of C_3 and C_4 dicarboxylates to the TDCs analyzed

in PM₁₀ aerosols were found to be in the range of 1.9% to 16.4% and 1.9% to 10.7% with an average of 6.0% and 4.2%, respectively. The high abundance of C₄ in TDCs were also reported in urban aerosols in Sapporo, Japan (Aggarwal and Kawamura, 2008), Chinese megacities (Ho *et al.*, 2007) and Hong Kong (Ho *et al.*, 2006). Phthalate (range: 6.7 to 79.5 ng/m³; average: 33.9 ng/m³) and maleate (range: 12.1 to 65.5 ng/m³; average: 33.8 ng/m³) diacids were the next most abundant dicarboxylate species detected in PM₁₀ aerosols, accounting for 3.9% (0.5% to 7.5%) and 3.9% (1.4% to 7.2%) of the TDCs, respectively. Phthalic acid is directly emitted from combustion sources and/or generated by atmospheric degradation of aromatic hydrocarbons such as naphthalene (Legrand *et al.*, 2007). As shown in Tables 6 and 7, phthalate did not correlate with NO₃⁻ that is expected to be contributed from vehicular sources. Therefore, the burning of fossil fuels like coal for heating purpose might be the major source of phthalates in Raipur city. The average concentrations of fumarate, malate and tartarate were 30.2 ng/m³, 26.8 ng/m³ and 31.8 ng/m³ and contributed 3.7%, 3.2% and 3.7% of the TDCs, respectively. The C₅ (glutarate) and C₆ (adipate) dicarboxylates are less abundant than C₂–C₄ dicarboxylates. The mean concentrations of C₅ and C₆ dicarboxylates were found to be 19.2 ng/m³ and 19.0 ng/m³, accounting for 2.2% and 2.2% of the TDCs, respectively.

The statistics on seasonal concentrations of DCs are also given in Table 3. The TDCs and the individual dicarboxylates showed highest concentrations during winter followed by spring and summer and lowest during the monsoon season. The formation of inversion layers due to the low mixing height and low wet deposition are believed to be the major factors for the high concentrations of dicarboxylate species in winter. High wind speed, low emission strength and the washout effect by rainfall are the major factors for the low concentrations of DCs in summer and monsoon seasons. Large variations were found among the four seasons on the concentrations of DCs. The TDCs concentrations ranged from 684.7 to 1537 ng/m³ in winter, 579.6 to 1413 ng/m³ in spring, 534.3 to 1060 ng/m³ in summer and 325.3 to 1081 ng/m³ in monsoon with an average of 1244 ng/m³, 1016 ng/m³, 739.4 ng/m³, 540.3 ng/m³ in the respective seasons. The relative abundances of TDCs in PM₁₀ mass were found to be in the range of 0.2% to 0.4% (average: 0.3%), 0.2% to 0.5% (average: 0.3%), 0.2% to 0.8% (average: 0.4%) and 0.2% to 0.4% (average: 0.3%) in winter, spring, summer and monsoon, respectively. The TDCs concentration observed in this study in winter is also higher than those reported in cities of China (904.0 ng/m³, Ho *et al.*, 2007), Gosan, Jeju Island (499.1 ng/m³, Kundu *et al.*, 2010) and Chennai, India (694.5 ng/m³, Pavuluri *et al.*, 2010). The TDCs concentration observed in spring is also higher than those reported at Gosan, Jeju Island (735.4 ng/m³, Kundu *et al.*, 2010). The concentration of TDCs in summer is lower than those reported at the cities of China (892.0 ng/m³, Ho *et al.*, 2007) and Gosan, Jeju Island (784.0 ng/m³, Kundu *et al.*, 2010) but higher than those reported at Chennai, India (502.9 ng/m³, Pavuluri *et al.*, 2010). The most abundant dicarboxylate, C₂ showed highest concentration in winter followed by spring and lowest during summer and monsoon

seasons. It is reported that the C₂ may be produced by the photo-oxidation of cyclo-olefins and aliphatic diolefins emitted from motor vehicles (Nolte *et al.*, 2001). As the traffic emissions could be constant all the year round, this seasonal cycle of C₂ might be more related to the other emission sources and the prevailing meteorological conditions during winter. The high concentration of oxalate in winter might be due to the enhanced emissions from heating sources. During winter period (October–January), the minimum temperature ranges between 8.6°C and 15.3°C in Raipur city. The coals/biomasses, combustion efficiency of which is very low, are commonly used in central India for heating and cooking purposes. The low level of oxalate in summer and monsoon seasons may be explained either by a weak source of burning or the rainfall that allows efficient scavenging of water-soluble species in aerosols (Wang *et al.*, 2007). The second and third most abundant diacids C₃ and C₄ also showed maximum concentrations in winter and spring than in summer and monsoon seasons. In this study, phthalate, which is a tracer of anthropogenic emissions (Kawamura and Yasui, 2005) showed higher concentrations in spring and winter and lower in summer and monsoon. The high value in spring and winter seasons indicated that primary emissions from coal burning, which is only significant in spring and winter seasons for domestic heating is the possible source of phthalate in Raipur city. The different seasonal variation of phthalate indicated its different sources and behavior in the atmosphere. The lower dicarboxylates, C₅ and C₆ also showed higher concentrations in winter and spring than summer and monsoon seasons.

Concentration Ratios of Selected Dicarboxylic Acids

The statistical summary on concentration ratios of selected dicarboxylates in PM₁₀ aerosols in Raipur, India is given in Table 4. Previous studies suggested that water-soluble DCs are produced in the atmosphere by photochemical chain reactions of unsaturated hydrocarbons of fatty acids as well as from their oxidation products. Some saturated diacids such as C₆ diacid may be generated from cyclic olefin via O₃ and OH radical reactions in gas phase (Carlton *et al.*, 2006). In contrast, unsaturated dicarboxylic acids have been considered to be generated via photochemical oxidation of the other precursors such as aromatic hydrocarbons and methylcycloalkenes (Legrand *et al.*, 2007). The C₂/C₄ and C₃/C₄ ratios were used in many previous studies to evaluate photochemical aging and tracking the possible sources of diacids (Sorooshian *et al.*, 2007). The ratios of C₂/C₄ were found to be in the range of 5.1 to 41.7 with an average of 19.3. The C₂/C₄ ratios in monsoon, winter, spring and summer seasons were 24.1, 18.2, 14.4 and 19.2, respectively. However, much lower C₂/C₄ ratio (3.5) reported in Brazil from biomass burning suggested that diacids were likely emitted not only from biomass burning but also from incomplete combustion of fossil fuels (Kundu *et al.*, 2010). Higher C₂/C₄ ratios in this study were also attributed to photochemical production of C₂ from C₄ within biomass burning plumes. In this study, C₃/C₄ ratios ranged between 0.5 and 3.0 with an average of 1.5, which are slightly higher than those reported from vehicular emissions (0.74,

Table 4. Descriptive statistics on concentration ratios of dicarboxylate species in PM₁₀ aerosols in the eastern central India.

Ratios of dicarboxylates	Annual (<i>n</i> = 120)	Monsoon (<i>n</i> = 30)	Winter (<i>n</i> = 40)	Spring (<i>n</i> = 20)	Summer (<i>n</i> = 30)
	Mean ± Stdev ^a (Range)	Mean ± Stdev ^a (Range)	Mean ± Stdev ^a (Range)	Mean ± Stdev ^a (Range)	Mean ± Stdev ^a (Range)
C ₂ /C ₄	19.3 ± 7.9 (5.1–41.7)	24.1 ± 6.9 (13.3–39.1)	18.2 ± 9.5 (5.1–41.7)	14.4 ± 5.5 (8.9–27.9)	19.2 ± 5.3 (8.3–27.3)
C ₃ /C ₄	1.5 ± 0.6 (0.5–3.0)	1.1 ± 0.1 (1.0–1.2)	1.3 ± 0.6 (0.5–2.5)	1.6 ± 0.6 (1.0–2.7)	2.1 ± 0.5 (1.5–3.0)
hC ₄ /C ₄	0.9 ± 0.3 (0.2–2.0)	1.0 ± 0.2 (0.6–1.2)	0.8 ± 0.3 (0.4–1.6)	0.7 ± 0.5 (0.2–2.0)	1.9 ± 0.3 (0.6–2.5)
F/M	1.0 ± 0.3 (0.6–1.9)	0.8 ± 0.1 (0.9–1.3)	0.9 ± 0.3 (0.6–1.9)	0.9 ± 0.4 (0.7–1.6)	1.2 ± 0.2 (0.7–1.4)
Ph/C ₆	2.0 ± 1.2 (0.3–7.5)	1.3 ± 0.1 (1.1–1.6)	1.9 ± 1.0 (0.3–4.0)	3.2 ± 1.8 (0.9–7.5)	2.1 ± 0.9 (0.8–4.1)

See Table 2 for abbreviation; ^a Standard deviation.

Ho *et al.*, 2007). The C₃/C₄ ratios in monsoon, winter, spring and summer seasons were found to be 1.1, 1.3, 1.6 and 2.1. This result may suggest that a significant fraction of C₃ is formed as secondary product in the atmosphere by photochemical degradation of C₄. The malic acid (hC₄) can be photochemically generated from succinic acid (C₄) via hydroxylation reaction (Miyazaki *et al.*, 2009). The hC₄/C₄ ratio was two times (1.88) higher in summer than monsoon, winter and spring, supporting this hypothesis. Maleic acid (M) can be isomerized to fumaric acid (F) in the presence of sunlight (Miyazaki *et al.*, 2009) in summer. The F/M ratio was higher during summer (1.2) and lower during winter season (0.9). This trend is probably related with an enhanced isomerization reaction in summer under intensified solar radiation. Adipic (C₆) and phthalic (Ph) acids may be produced by the oxidation of anthropogenic cyclohexene and aromatic hydrocarbons such as naphthalene (Schauer *et al.*, 2002). The Ph/C₆ ratio obtained to be 2.0 in this study is lower than that observed in the other urban areas in India (Pavuluri *et al.*, 2010).

Concentrations of Major Inorganic Ions

The mass concentrations of major inorganic ions analyzed in PM₁₀ aerosols in Raipur, India are reported in Table 5. The percentage contribution of each inorganic ion to PM₁₀ mass and total water-soluble inorganic ions (TWSII) are shown in Fig. 4. The TWSII ranged from 1.4% to 22.6% with an average of 10.0% to the PM₁₀ mass. The unusually low fraction of inorganic ions may be presumed to be due to, besides high carbonaceous matters such as water-soluble organic carbon (WSOC), organic carbon (OC) and elemental carbon (EC), in PM₁₀, the contribution from unanalyzed water soluble ions like carbonate, bicarbonate, fluoride, phosphate, etc. along with the insoluble metals and refractory metal oxides which emit as off-gas components from industries during material handling and storage, grinding, drying, sintering, roasting and smelting like mechanical processes (IPPC, 2001). The study area encompasses with large number of big steel and sponge iron industries, cement plants and thermal power plants which do not always practice stringently the emission norms. Low percentage contributions of TWSII have been also reported in previous

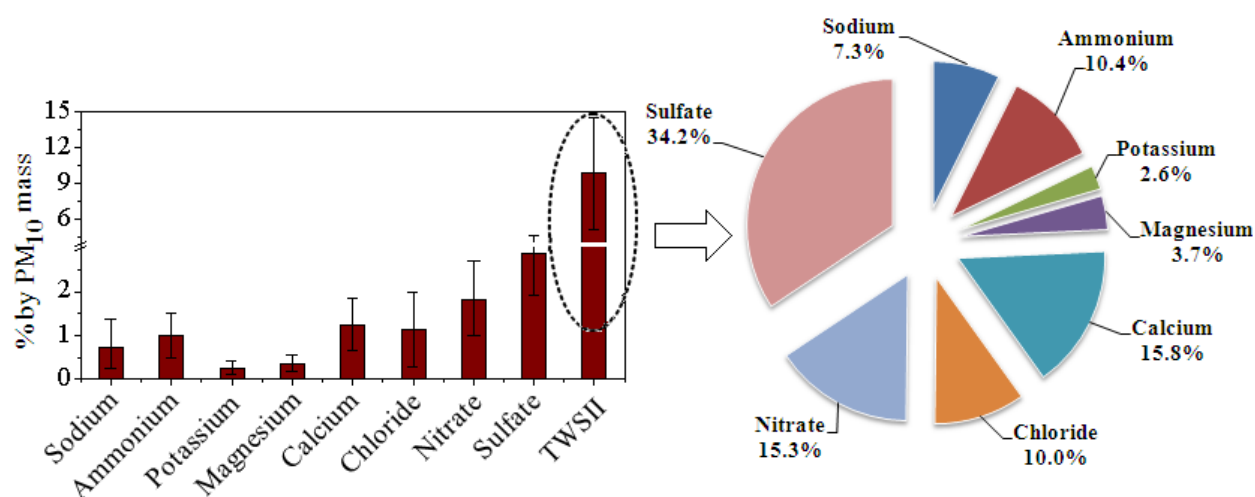
studies conducted in the cities of eastern central India (Deshmukh *et al.*, 2010; Deshmukh *et al.*, 2011b). In analyzed TWSII, the maximum contribution is of anions that ranged from 31.3% to 86.5% with an average of 59.5%. The cations ranged from 13.5% to 68.7% with an average of 40.5%. Among all major ions, SO₄²⁻ has the highest concentration, which varied between 1.3 to 29.2 µg/m³ with an average of 9.9 µg/m³. The abundance of SO₄²⁻ to the TWSII varied from 9.2% to 48.9% with a mean of 34.2%. The second and third dominant species were NO₃⁻ and Cl⁻ and their concentrations ranged from 0.02 to 21.1 µg/m³ and 0.02 to 10.9 µg/m³ with an average concentration of 5.5 µg/m³ and 3.4 µg/m³, respectively. The abundance of NO₃⁻ and Cl⁻ to the TWSII varied from 0.1 to 34.2% and 0.1 to 22.1% with an average of 15.3% and 10.0%, respectively. The concentration of NH₄⁺ ranged from 0.4 to 8.5 µg/m³ with an average of 2.9 µg/m³ and contributed 1.0% and 10.4% to the PM₁₀ mass and TWSII, respectively. The higher levels of NH₄⁺ in Raipur is due to the extensive agricultural activities around the region and perhaps also due to the larger impact from biomass burning. Among all ions analyzed, the annual average concentration of potassium was found to be lowest. Biomass burning is one of the major sources of PM in central India, however, small amount of K⁺ was found in this study (Table 5; Fig. 4). Previous studies conducted in the cities of central India and other Indian sites also reported lower concentration of K⁺ in PM fractions (Deshmukh *et al.*, 2010; Deshmukh *et al.*, 2011b; Rengarajan *et al.*, 2011). The concentration of potassium ranged from 0.11 to 2.2 µg/m³ with a mean concentration of 0.7 µg/m³ and accounted for 0.2% and 2.6% to the PM₁₀ mass and TWSII.

The statistics on seasonal variation on water-soluble inorganic ions analyzed in PM₁₀ aerosols are also given in Table 5. The mass concentration of TWSII was higher in winter and spring followed by summer. The lowest concentration of TWSII was observed in monsoon. In winter, the high concentration of TWSII at Raipur might be related to the massive biomass burning and industrial emissions. The low concentration in monsoon is due to the more precipitation that washed-out water-soluble ions. The crustal ions, Na⁺, Ca²⁺ and Mg²⁺, were frequently observed

Table 5. Descriptive statistics on concentrations of major inorganic ions ($\mu\text{g}/\text{m}^3$) in PM_{10} aerosols in the eastern central India.

Species	Annual ($n = 120$)	Monsoon ($n = 30$)	Winter ($n = 40$)	Spring ($n = 20$)	Summer ($n = 30$)
	Mean \pm Stdev ^a (Range)	Mean \pm Stdev ^a (Range)	Mean \pm Stdev ^a (Range)	Mean \pm Stdev ^a (Range)	Mean \pm Stdev ^a (Range)
Na^+	1.7 ± 1.4 (0.2–6.8)	0.5 ± 0.2 (0.3–0.8)	1.2 ± 0.5 (0.2–2.0)	3.4 ± 1.6 (1.4–6.8)	2.6 ± 1.0 (1.1–4.0)
NH_4^+	2.9 ± 2.0 (0.4–8.5)	1.0 ± 0.5 (0.4–1.9)	4.8 ± 1.8 (2.9–8.5)	3.4 ± 1.2 (1.8–5.3)	1.8 ± 1.3 (0.5–4.5)
K^+	0.7 ± 0.5 (0.1–2.2)	0.3 ± 0.3 (0.1–1.0)	1.1 ± 0.6 (0.3–2.2)	0.6 ± 0.3 (0.2–0.9)	0.5 ± 0.3 (0.1–1.0)
Mg^{2+}	0.8 ± 0.7 (0.04–4.0)	0.2 ± 0.1 (0.1–0.3)	0.2 ± 0.1 (0.04–0.4)	2.4 ± 1.0 (1.1–4.0)	1.3 ± 0.5 (0.4–2.0)
Ca^{2+}	3.0 ± 1.1 (1.3–6.3)	2.0 ± 0.7 (1.3–3.6)	2.9 ± 0.8 (2.0–5.3)	4.1 ± 1.4 (2.3–6.3)	3.1 ± 0.9 (2.1–5.0)
Cl^-	3.4 ± 2.9 (0.02–10.9)	0.5 ± 0.8 (0.02–1.8)	6.8 ± 2.0 (2.1–10.9)	3.1 ± 0.9 (2.1–4.7)	1.9 ± 1.5 (0.02–4.2)
NO_3^-	5.5 ± 4.4 (0.02–21.1)	0.8 ± 1.1 (0.03–2.6)	11.4 ± 5.0 (3.1–21.1)	4.5 ± 1.6 (2.7–7.9)	2.8 ± 2.2 (0.02–5.9)
SO_4^{2-}	9.9 ± 4.4 (1.3–29.2)	2.8 ± 1.8 (1.3–6.0)	17.9 ± 6.4 (6.4–29.2)	10.2 ± 2.8 (6.1–15.0)	6.3 ± 3.8 (1.3–12.5)
TWSII ^b	27.8 ± 17.8 (4.1–77.2)	8.2 ± 4.9 (4.1–16.8)	46.2 ± 14.0 (18.1–77.2)	31.6 ± 7.6 (21.8–43.0)	20.3 ± 6.9 (11.0–34.4)

^a Standard deviation; ^b Total water-soluble inorganic ions.

**Fig. 4.** Percentage contribution of major inorganic ions in overall PM_{10} mass.

of higher concentrations in spring and summer due to the re-suspension of airborne dust particles. The concentrations of these crustal ions were low in monsoon which could be due to more precipitation. The concentration of K^+ and Cl^- in Raipur was higher in winter followed by spring and summer, and lower in monsoon, indicating that K^+ and Cl^- were primarily related to the burning activities, which is very common in winter season. The major source of Cl^- in Raipur might be coal burning (Deshmukh *et al.*, 2011b), which could reasonably explain the higher Cl^- concentration in winter. The seasonal variations of secondary components such as SO_4^{2-} , NO_3^- and NH_4^+ were also found to be in high concentrations in winter and spring than in summer and monsoon. The high SO_4^{2-} concentration in winter indicated that SO_4^{2-} in this season was mostly from the local

industrial emissions due to the poor dispersion and the lower rate of removal via wet deposition. The higher concentration of SO_4^{2-} in winter is also due to the higher consumption of domestic coal for heating purpose. The higher concentration of NO_3^- in winter could be associated with the lower temperature, which favor the shift from the gas phase of nitric acid to the particle phase of ammonium nitrate. However, the meteorological variations could also be the factors affecting the degree of air pollution. The low wind speed and temperature in winter favor the accumulation of pollutants, while the high temperature in summer favors the air convection and the dispersion of pollutants. The seasonal variation of NH_4^+ basically coincided with those of SO_4^{2-} and NO_3^- , indicating that NH_4^+ is largely originated from the neutralization between ammonia and the acidic species.

Relationship between PM Pollutants and Meteorology

We conducted correlation analysis in order to gain some preliminary understandings as to how closely the mass levels of PM₁₀, water-soluble dicarboxylate species and inorganic ions are related to the influence of meteorological factors and thus estimating their emission sources. The results of correlation analysis are given in Table 6. The correlation coefficients are marked in the table to indicate the significant levels ($p < 0.01$ or $p < 0.05$). Analysis of the highly correlated species suggests their identical source regions. However, those species, which are not significantly correlated with each other, suggest their diverse source regions. As shown in Table 6, PM₁₀ was well correlated with dicarboxylate species (C₂, C₃, C₄, M, F, hC₄ and Ta; $p < 0.01$) and major ions (NH₄⁺, K⁺, NO₃⁻, SO₄²⁻ and Cl⁻; $p < 0.01$), which indicated the similar nature of origin. A good correlation between C₂ and the precursor compounds, such as C₃ and C₄ as well as hC₄, implied secondary production of C₂ through photochemical degradation of the precursor compounds (Gao et al., 2003). Most of the dicarboxylate species (C₂–C₆, M, and F) showed significant positive correlation ($p < 0.01$) with SO₄²⁻ concentrations. This significantly good correlation could be attributed to the increased formation of secondary aerosols via oxidation of gaseous volatile organic compounds (Kawamura et al., 2010). To investigate the effects of biomass burning on dicarboxylates species, K⁺ can be used as a tracer of wood burning (Nair et al., 2006). A strong correlation coefficients ($p < 0.01$) obtained from most of the dicarboxylate species, except tartarate versus K⁺ concentration, supports the hypothesis that the dicarboxylate species in Raipur city were influenced by the biomass burning emissions during the study period. Among the water-soluble major ions, Na⁺ correlated well with NH₄⁺, Mg²⁺ and Ca²⁺ ($p < 0.01$). The close relationships between Na⁺, Mg²⁺ and Ca²⁺ showed their origin mainly from crustal resuspension. The significant and high correlation between K⁺ and Cl⁻ ($p < 0.01$) indicated the similar anthropogenic origin, of these species, which is normally related to coal/wood burning. NH₄⁺ had a strong correlation with K⁺, NO₃⁻ and SO₄²⁻ ($p < 0.01$). The high correlation coefficient between NO₃⁻ and SO₄²⁻ ($p < 0.01$) is due to the formation of secondary inorganic aerosols in the atmosphere. Chloride in this region may be originated from neutralization of atmospheric NH₃ by HCl that is originated from wood/coal burning and some other combustion processes (Tiwari et al., 2009). Sodium in this region is present in sufficient amount in soil in the form of Na₂SO₄ and may be originated from natural sources (Deshmukh et al., 2010).

Meteorological factors such as temperature, relative humidity, rainfall, mixing height and wind speed all play important role in determining the air pollution level in the atmosphere (Bhaskar and Mehta, 2010). The pollutant residence in the atmosphere and the formation of secondary species is controlled not only by the rate of emission of the reactants into the air from the sources, but also by temperature, precipitation and wind speed. The annual and seasonal mean and ranges of the above meteorological variables are given in Table 2 and also

summarized earlier, elsewhere. The relationship of PM₁₀, water-soluble dicarboxylate species and inorganic ions with meteorological variables was also investigated by correlation analysis and results are given in Table 6. PM₁₀ mass showed significant negative correlation with temperature ($p < 0.05$). As shown in Table 2, PM₁₀ concentration was found higher at low temperatures during winter and lower at high temperature during summer season. Higher temperature increases the boundary layer height, which increase the ventilation effect and further leads to faster dispersion of PM. Thus, the increase in ventilation effect resulted in the decrease in concentrations of PM. Low temperature causes decrease in boundary layer height and results a slower dispersion and increase in the concentrations of PM. Similar results were also found in previous studies conducted in other Indian cities (Deshmukh et al., 2011b; Bhaskar et al., 2010; Tiwari et al., 2009). The correlation of water-soluble dicarboxylate species and inorganic ions with meteorological variables is also shown in Table 6. Photochemical processes play an important role in controlling the atmospheric concentrations of dicarboxylic acids (Ho et al., 2006). As shown in Table 6, dicarboxylate species (C₂, C₃, C₄, F, hC₄) were well correlated with temperature during the study period indicated that the dicarboxylates are produced in the atmosphere by photochemical chain reactions of unsaturated hydrocarbons or fatty acids as well as their oxidation products (Kawamura and Sakaguchi, 1999). Water-soluble inorganic ions (NH₄⁺, K⁺, Ca²⁺, and Cl⁻) were negatively correlated but not in significant levels with temperature during the study period. The high relative humidity helped high PM mass to occur due to the lower inversion layer caused by low mixing height that limits dispersion of PM in the atmosphere. Therefore, most of the dicarboxylate species (C₂, C₃, C₄, C₅, F, and hC₅) and major inorganic ions (SO₄²⁻, NO₃⁻, and NH₄⁺) were well correlated with relative humidity ($p < 0.01$, $p < 0.05$) during the study period. The strong positive relationship of NO₃⁻ with relative humidity (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 explains the particularly strong nitrate-RH correlation here. The effect of rainfall on PM₁₀, water-soluble dicarboxylate species and inorganic ion concentration was investigated. As can be seen from Table 2, the scavenging of PM from the atmosphere due to precipitation is an important removal mechanism (Sahu et al., 2004). Therefore, water-soluble dicarboxylate species and inorganic ions analyzed in this study were negatively correlated with rainfall. The correlation of PM₁₀, water-soluble dicarboxylates species and inorganic ions with wind speed was also investigated. Strong winds flush pollutants out of the system and low winds allow pollution level to increase (Chaloulakou et al., 2003). As shown in Tables 2, maximum levels of PM₁₀ concentrations were observed at low wind speed during the winter and spring seasons, and minimum levels were seen at high wind speed during summer and monsoon. The increase in wind speed causes an increase in the ventilation effects, thereby dispersing the

Table 6. Correlation analysis between PM₁₀, dicarboxylate species, major inorganic ions and meteorological variables in the eastern central India.

PM ₁₀	C ₂	C ₃	C ₄	C ₅	C ₆	M	F	Ph	hC ₄	Ta	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	
PM ₁₀	1.00																		
C ₂	0.81^a	1.00																	
C ₃	0.63^a	0.81^a	1.00																
C ₄	0.71^a	0.85^a	0.64^a	1.00															
C ₅	0.31	0.69^a	0.70^a	0.82^a	1.00														
C ₆	0.19	0.42^b	0.12	0.73^a	0.18	1.00													
M	0.67^a	0.68^a	0.46^b	0.60^a	0.83^a	0.08	1.00												
F	0.74^a	0.72^a	0.65^a	0.83^a	0.30	0.74^a	1.00												
Ph	0.24	0.81^a	0.06	0.11	0.24	0.08	0.04	1.00											
hC ₄	0.86^a	0.91^a	0.48^b	0.78^a	0.41^b	0.21	0.76^a	0.20	1.00										
Ta	0.64^a	0.41^b	0.43^a	0.08	0.23	0.92^a	0.28	0.07	0.13	1.00									
Na ⁺	0.21	0.08	0.25	0.78^a	0.16	0.20	0.21	0.19	0.28	0.09	1.00								
NH ₄ ⁺	0.79^a	0.92^a	0.77^a	0.87^a	0.08	0.06	0.98^a	0.16	0.87^a	0.32	0.48^b	1.00							
K ⁺	0.58^a	0.86^a	0.91^a	0.65^a	0.74^a	0.66^a	0.72^a	0.91^a	0.81^a	0.18	0.21	0.83^a	1.00						
Mg ²⁺	0.12	0.10	0.21	0.25	0.10	0.19	0.31	0.08	0.29	0.14	0.68^a	0.03	1.00						
Ca ²⁺	0.06	0.08	0.32	0.04	0.13	0.10	0.30	0.11	0.04	0.04	0.68^a	0.22	0.23	1.00					
Cl ⁻	0.62^a	0.64^a	0.44^b	0.38	0.88^a	0.46^b	0.03	0.93^a	0.67^a	0.21	0.78^a	0.72^a	0.23	0.74^a	1.00				
NO ₃ ⁻	0.69^a	0.78^a	0.69^a	0.26	0.34	0.73^a	0.22	0.06	0.14	0.94^a	0.49^b	0.61^a	0.77^a	0.39	0.74^a	1.00			
SO ₄ ²⁻	0.78^a	0.90^a	0.76^a	0.73^a	0.63^a	0.78^a	0.72^a	0.02	0.06	0.29	0.21	0.83^a	0.76^a	-0.19	0.10	0.66^a	1.00		
T	-0.51^b	0.69^a	0.51^b	0.68^a	0.22	0.18	0.50^b	0.23	0.72^a	0.17	0.23	-0.24	-0.29	0.08	-0.05	-0.09	0.12	0.20	
RH	0.35	0.66^a	0.88^a	0.62^a	0.51^b	0.28	0.86^a	0.11	0.56^b	0.18	0.19	0.64^a	-0.32	-0.11	-0.23	-0.22	0.68^a	0.78^a	
RF	0.04	0.19	-0.25	0.33	0.22	0.31	-0.12	0.19	0.20	0.08	0.12	-0.21	-0.08	0.10	0.09	0.14	0.22	0.30	
WS	-0.72^a	-0.66^a	-0.61^b	-0.52^b	0.36	0.23	-0.51^b	-0.62^a	-0.49^b	-0.48^b	0.23	-0.64^a	-0.34	0.21	-0.23	-0.20	-0.64^a	-0.70^a	

See Table 1 & 2 for abbreviation; Bold face indicate significant correlation; ^a Correlation is significant at 0.01 level (2 Tailed); ^b Correlation is significant at 0.05 level (2 Tailed).

PM₁₀ in the ambient air and consequently causing a decrease in the observed PM₁₀ mass concentrations. Therefore, PM₁₀, water-soluble dicarboxylates species and inorganic ion concentrations showed significant negative correlation ($p < 0.01$) with wind speed and indicated the predominance of local sources.

Source Identification of PM Pollutants

There are different methods of extracting the sources from a set of data. In this study, PCA procedure followed by Varimax rotation of components (PCA + Varimax) has been used in order to quantify the contribution of the main sources of analyzed dicarboxylates and inorganic ions using statistical software (Statistica 5.0) for 18 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 data set 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 diacids and inorganic ions in the present study. The results of PCA are given in Table 7. During the study period, there were four air quality PCs with eigen value exceeding 1.0 indicating that these factors have a significant influence on the air quality at Raipur, India. The variance that can be explained by the PC 1 is 50.7% and the significant component loading is mainly related to photochemical products including five dicarboxylate species namely, oxalate, malonate, succinate, fumarate and malate, and two inorganic ions, NH₄⁺ and SO₄²⁻. This indicated various photochemical sources of dicarboxylate species along with the secondary inorganic aerosol formation

process in the atmosphere. PC 2, which explained 20.2% of the variance, showed significant component loading for three dicarboxylate species, glutarate, adipate and phthalate and two inorganic species, K⁺ and Cl⁻, which suggested that their precursors are associated with anthropogenic activities including fossil fuel and biomass combustions. The high loading of C₆ and Ph dicarboxylates in the same PC shows that these are mainly derived by photooxidation of anthropogenic hydrocarbons. Significant loading of maleate and tartarate along with NO₃⁻ in PC 3 with 16.1% of the variance indicates NO_x that originate from traffic emission is converted to HNO₂ in the atmosphere. The traffic emissions related to the VOCs are converted to tartaric acid and maleic acid such that these two species can be regarded as the species to index traffic pollution (Hsieh et al., 2008). Therefore, PC 3 indicated vehicular emission as the possible sources of these species. The variance that can be explained by PC 4 is 8.4% and the significant component loadings were Na⁺, Mg²⁺ and Ca²⁺, which suggested their partial association with soil derived particles. These four PCs explained almost 96% variance of total data set and suggested that the source identification by PCA contributes to overall PM₁₀ concentration in Raipur, India.

SUMMARY AND CONCLUSIONS

This study reports, for the first time, the molecular distributions of water-soluble dicarboxylic acids in the form of dicarboxylates and major inorganic ions in PM₁₀ aerosols collected at Raipur, India between the period July 2009 and June 2010. The annual mean concentration of PM₁₀ found to be 270.5 µg/m³ is more than four times higher than NAAQS

Table 7. Rotated factor loading of dicarboxylates and major inorganic ions in PM₁₀ aerosols in the eastern central India.

Variables	PC 1	PC 2	PC 3	PC 4
Oxalate (C ₂)	0.85	0.08	-0.02	-0.08
Malonate (C ₃)	0.91	0.45	-0.20	-0.14
Succinate (C ₄)	0.78	0.37	0.08	-0.20
Glutarate (C ₅)	0.08	0.78	-0.16	0.05
Adipate (C ₆)	-0.11	0.80	-0.21	0.03
Maleate (M)	-0.20	-0.10	0.98	0.07
Fumarate (F)	0.76	0.12	-0.11	0.18
Phthalate (Ph)	0.24	0.69	0.06	0.02
Malate (hC ₄)	0.90	-0.16	0.10	0.22
Tartarate (Ta)	0.13	0.05	0.87	0.08
Na ⁺	0.17	0.13	0.21	0.80
NH ₄ ⁺	0.94	0.18	-0.04	0.31
K ⁺	-0.05	0.74	-0.13	0.16
Mg ²⁺	-0.09	0.13	0.21	0.95
Ca ²⁺	0.19	-0.09	0.34	0.87
Cl ⁻	0.14	0.79	0.06	0.26
NO ₃ ⁻	0.31	0.03	0.90	-0.11
SO ₄ ²⁻	0.98	0.41	0.04	-0.23
Eigen value	12.3	5.3	4.2	1.3
Cumulative eigen value	12.3	17.6	21.8	23.1
% Total variance	50.7%	20.2%	16.1%	8.4%
Cumulative % variance	50.7%	71.0%	87.1%	95.5%

Component loading ≥ 0.70 are in bold.

of India. The annual mean concentration of PM₁₀ is also exceeding the air quality standards of WHO. Annual cycles showed higher concentrations of PM₁₀ during winter followed by spring and summer and lowest during the monsoon season. The highest concentration observed during winter can be attributed to low wind speed and low temperature which led to lower mixing height and poor dispersion conditions coupled with the increased anthropogenic activities. The concentration of total dicarboxylates ranged from 325.3 to 1538 ng/m³ (0.2% to 0.8% of PM₁₀ mass) with an average of 904.0 ng/m³ (0.3% of the PM₁₀ mass). Molecular distributions of dicarboxylate species were characterized by the predominance of oxalate followed by malonate and succinate. The concentrations of dicarboxylates are maximized in winter and spring, which are associated with their sources and photochemical processing. A higher C₂/C₄ ratio in this study suggested photochemical production of C₂ from C₄ within biomass burning plume. The ratio of C₃/C₄ showed that a significant fraction of malonate is secondarily produced in the atmosphere by photochemical degradation of succinate. The concentration of TWSII ranged from 4.1 to 77.2 µg/m³ (1.4% to 22.6% of PM₁₀ mass) with an average of 27.8 µg/m³ (10.0% of PM₁₀ mass). Inorganic ions were characterized by a predominance of SO₄²⁻ and NO₃⁻ followed by Cl⁻ and Ca²⁺. Oxalate highly correlated with malonate and succinate, which suggested that succinic acid is an important precursor of oxalic acid in Raipur city, India. A good correlation of most of the dicarboxylates with SO₄²⁻ indicated their secondary formation pathways in the atmosphere. Most of the dicarboxylate species, except tartarate, showed strong correlation with K⁺ (biomass burning tracer). This suggests that the biomass burning activities might be its possible sources in the urban atmosphere of Raipur city, India. Principal component analysis extracted four sources namely photochemical, anthropogenic, vehicular, and soil derived particles and explains 95.5% variance of the total PM₁₀ aerosol data set. The Raipur city area is expanding rapidly and human population, vehicular traffic, industrialization are increasing. These developments are increasing particulate matter concentrations which, in turn, are increasing ambient air pollution substantially.

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