Low Molecular Weight Monocarboxylic Acids in PM$_{2.5}$ and PM$_{10}$: Quantification, Seasonal Variation and Source Apportionment

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ABSTRACT

PM$_{2.5}$ and PM$_{10}$ aerosols from a semi-urban site of Agra (27°10′N, 78°05′E) in North-Central India were analyzed for carbonaceous aerosols (Organic and Elemental carbon), low molecular weight monocarboxylic acids (Acetic and Formic acid) along with inorganic ions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$, K$^+$ and Ca$^{2+}$) during April 2014 to August 2015. The average PM$_{2.5}$ and PM$_{10}$ mass concentrations were 86.3 ± 71.3 and 169.7 ± 100.5 µg m$^{-3}$, respectively; about 45% of PM$_{2.5}$ and 67% of PM$_{10}$ samples were above NAAQ (National Ambient Air Quality) standards. The average organic carbon (OC) and elemental carbon (EC) concentrations were 18.2 ± 12.3 and 6.7 ± 4.5 µg m$^{-3}$, respectively in PM$_{2.5}$ and 25.2 ± 14.1 and 8.1 ± 5.9 µg m$^{-3}$ respectively in PM$_{10}$. The average concentration of acetic acid (AA) in PM$_{2.5}$ and PM$_{10}$ were 330 ± 211 and 392 ± 224 ng m$^{-3}$ respectively. The average concentration of formic acid (FA) in PM$_{2.5}$ and PM$_{10}$ were 348 ± 193 and 336 ± 175 ng m$^{-3}$ respectively. Formic acid concentration was higher in PM$_{2.5}$ than PM$_{10}$ but the difference is not statistically significant. Both AA and FA showed similar seasonal variation: winter > post-monsoon > summer > monsoon. Low temperature and high relative humidity in winter season favours gas to particle conversion resulting in high concentrations. The average FA to AA (F/A) ratio was 0.69 indicating dominance of primary sources at the study site. Correlation analysis of AA and FA with major ions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$, K$^+$ and Ca$^{2+}$), EC, secondary organic carbon and trace gases (O$_3$ and CO) was performed to identify their primary or secondary origin. The results of correlation analysis suggest that AA is mainly contributed by primary sources while FA originates from secondary sources.

Keywords: Carboxylic acid; PM$_{2.5}$; PM$_{10}$; Primary sources; Secondary sources.

INTRODUCTION

Ambient aerosol particles consist of both organic and inorganic constituents, and play an important role in global climate change, precipitation, visibility, cloud microphysical properties, and human health problems (Menon et al., 2002; Huebert et al., 2003). Carbonaceous aerosols are a major component of atmospheric particulate matter, contributing up to 10–70% of particulate mass (Tsapakis et al., 2002). A substantial fraction of carbonaceous aerosols consist of water soluble organic compounds (WSOCs) which account for up to 70% of the total aerosol mass (Sorooshian et al., 2007; Jung et al., 2010). WSOCs consist of a complex mixture of organic species and are ubiquitous in the atmosphere (Kanakidou et al., 2005). Among WSOCs, monocarboxylic acids, dicarboxylic acids and ketocarboxylic acids are group of significant interest (Saxena and Hildemann, 1996; Falkovich et al., 2004). Carboxylic acids represent major fraction of organic carbon in fog, cloud water, precipitation, vapour phase and in particulate matter because of their solubility and polar nature (Keene and Galloway, 1984; Facchini et al., 1992; Khwaja, 1995; Kumar et al., 1996; Khare et al., 1997; Loflund et al., 2002; Fornaro and Gutz, 2003; Raja et al., 2008). The monocarboxylic acids (MCA), acetic acid (AA) and formic acid (FA) constitute the most abundant part of carboxylic acids in the global troposphere with a total quantity of 1200–1400 Gmol yr$^{-1}$ (Paulot et al., 2011). Tsai et al. (2013) during their study in Chiang Mai city, Thailand estimated acetate as dominant monocarboxylate (about 27–34% of total carboxylates), followed by formate. In the forest environment of Taiwan, acetate contributes approximately 45–54% to total monocarboxylates (Tsai and Kuo, 2013).

MCA have different sources: anthropogenic sources, biogenic sources and secondary formation through chemical reactions (Chebbi and Carlier, 1996; Khare et al., 1999). Anthropogenic sources include biomass combustion (Talbot et al., 1988; Christian et al., 2003) and motor exhaust emission (Kawamura et al., 1985; Grosjean 1989) while biogenic sources are emission from soil and vegetation (Kesselmeier et al., 1998; Kesselmeier, 2001). Secondary formations include ozone-olefin reaction, peroxyacetyl radical reactions and degradation of hydrocarbons (Grosjean, 1989;
Chebbi and Carlier, 1996; Neeb, 1997). Ozone-olefins reaction results in formation of criegee biradical through electrophilic addition reaction and this criegee biradical may rearrange to form carboxylic acid (Grosjean, 1989; Neeb, 1997). Carboxylic acids are mainly removed by wet and dry depositions. Carboxylic acids are not significantly removed by gas phase reactions; the reactivity of AA and FA towards OH· and NO3· is relatively low and may lead to atmospheric lifetime of nearly 3 days (Palout et al., 2011).

Low molecular weight carboxylic acids are ubiquitous and important components in aerosols. Earlier studies (Khwaja, 1995; Khare et al., 1998; Souza et al., 1999; Veres et al., 2011) reported that AA and FA showed distinct diurnal variations; diurnal variation of AA is characterized by high concentration during morning and late afternoon hours, however, FA shows its diurnal maximum during noon-time.

Although carboxylic acids comprise a small fraction of the aerosols, but because of their hygroscopic nature they may alter microphysical properties of clouds through formation of cloud condensation nuclei (CCN) (Twomey, 1991; Yu, 2000; Kanakidou et al., 2005). Moreover, because of their water soluble nature, they can increase solubility of particulate pollutants in human respiratory tract (Latif and Brimblecombe, 2004).

The chemical characterization of organic fraction of particulate matter is highly essential to understand their effects on visibility, climate change and human health (Kanakidou et al., 2005) but because of their highly complex nature, these organic species are the least studied and analyzed fraction. Studies in India on PM2.5 and PM10 have been mainly focused on carbonaceous aerosols (organic and elemental carbon), inorganic constituents and metals (Rengarajan et al., 2007; Ram and Sarin, 2010; Pavuluri et al., 2011; Dubey et al., 2012; Pachauri et al., 2013a, b; Satsangi et al., 2013). However, studies of carboxylic acids in PM2.5 and PM10 in India are scanty (Khare et al., 1998; Khare et al., 2011). This is the first comprehensive study on water soluble carboxylic acids in aerosols reported from India.

Present study includes identification of AA and FA in PM2.5 and PM10 at a semi-urban site in Agra during April 2014 to August 2015. The major objectives of this study are: (1) distribution and seasonal variations of AA and FA in particulate matter; (2) to identify the possible sources of organic acids.

**METHODOLOGY**

**Sampling Site**

Agra (27°10′N, 78°05′E), is situated in North-central India, south of Delhi. Agra has semi-arid climate as it is surrounded by the Thar Desert of Rajasthan. Sampling for this study was carried out on the Institute campus (semi-urban site) located in the northern part of the city (Fig. 1). The institute is connected to the rest of the city through one major road on which about 10⁴ vehicles pass in a day. The National Highway NH-2 is about 2 km south to the site which has high vehicular density (10⁵ vehicles per day). Industrial area of the city is about 6 km away from the site. The major industrial activities of the city are metal casting and rubber processing. The weather of Agra can be divided into four seasons; summer (March–June), monsoon (July–September), post-monsoon (October and November) and winter (December–February). Summer season is associated with strong, hot, and dry westerly winds and high temperature ranging between 25 and 47°C. Relative humidity (RH) in the summer ranges between 14 and 50%. The monsoon
season is hot and humid; temperature ranges from 22 to 35°C and the relative humidity ranges from 70 to 95%. During post-monsoon, temperature ranges from 17 to 34°C and relative humidity is around 50%. In winter temperature drops below 3°C and relative humidity ranges from 23 to 90%.

Sample Collection
Airborne particulate samples (N = 80), both fine (PM\textsubscript{2.5}) and coarse (PM\textsubscript{10}) fractions were collected using Fine Particulate Sampler (Envirotech APM 550) operated at a constant flow of 16.6 L min\textsuperscript{-1} on preweighed 47 mm quartz fiber filters (Pallflex, Tissuquartz). Each filter paper was desiccated for 24 h both before and after the sampling. The particulate mass concentration was calculated from the difference in weight of filters before and after sampling.

Analysis of Water Soluble Ions
For analysis of carboxylic acids (Acetic and formic acid) and major anions (Cl\textsuperscript{–}, NO\textsubscript{3}\textsuperscript{–}, SO\textsubscript{4}\textsuperscript{2–}), one-fourth of sample filter paper was cut and extracted ultrasonically for 30 min in 15 mL deionized water (resistivity of 18 MΩ cm). For analysis of cations (K\textsuperscript{+} and Ca\textsuperscript{2+}), half of the sample filter paper was cut and extracted ultrasonically for 30 min in 10 mL deionized water. After ultrasonication, the extracts were filtered through microporous membrane filter paper (Sartorius 393). All reagents and standards were of analytical grade. For carboxylate analysis, sodium acetate and sodium formate (> 99.0% purity) were procured from Sigma Aldrich (St. Louis, MO, USA) and other reagents were procured from Merck (Darmstadt, Germany). The stock solutions of 1000 mg L\textsuperscript{–1} were prepared and stored at –18°C from which working standards were prepared when required.

The carboxylic acids, anions and cations were analyzed by ion chromatography (IC), Dionex ICS 1100 (isocratic system) controlled by Chromeleon software. For analysis of carboxylic acids and anions, IC was equipped with an ASRS-Ultra anion self-regenerating suppressor, a conductivity detector in combination with an analytical column (AS11, 4 mm) and a guard column (AG11). For determination of major anions (Cl\textsuperscript{–}, NO\textsubscript{3}\textsuperscript{–} and SO\textsubscript{4}\textsubscript{2–}) an eluent of 6.0 mM NaOH was used, while for acetic and formic acid determination 0.03 mM NaOH was used at a flow rate of 1.0 mL min\textsuperscript{-1}.

Cations (K\textsuperscript{+}, Ca\textsuperscript{2+}) were analyzed using a guard column (CG12A), analytical column (CS12A), cation self-regenerating suppressor (CSRS) and 20.0 mM MSA (Methane Sulphonic Acid) as eluent at a flow rate of 1.0 mL min\textsuperscript{-1}.

Quality Control and Assurance
Acetic and formic acid measurement may be associated with evaporation loss (negative artifact) due to their high vapor pressure. The aerosol acidity and the relative humidity (RH) can significantly affect amount of artifacts (Pathak and Chan, 2005). Earlier study by Wang \textit{et al.} (2007) in Beijing has suggested that high RH (~60%) and decrease in aerosol acidity may bring more carboxylic acids to the particulate phase and reduce the sampling artifact. They reported that aerosols in Beijing are alkaline in nature and high concentration of NH\textsubscript{3} could absorb and neutralize acidic gases such as NO\textsubscript{3} and SO\textsubscript{2}; and decrease the acidity of aerosols. Similarly earlier studies (Parmar \textit{et al.}, 2001; Kumar \textit{et al.}, 2007) at the present site reported alkaline nature of aerosols due to high concentration of NH\textsubscript{3} and the average RH during study period was 62%. These conditions suggest that there might be minimal evaporation loss of carboxylic acids during sampling. To prevent evaporation loss after sampling, filters were kept in refrigerator and analyzed within a month of sampling. The extraction was done on the same day of analysis. To minimize the carbon content, filters were kept in a muffle furnace at 800°C for 4 h before sampling.

Analytical errors in measurements of acetic acid, formic acid, major anions (Cl\textsuperscript{–}, NO\textsubscript{3}\textsuperscript{–} and SO\textsubscript{4}\textsubscript{2–}) and cations (Ca\textsuperscript{2+} and K\textsuperscript{+}) were determined in terms of accuracy and precision. Accuracy and precision of method are expressed in terms of relative error and relative standard deviation (RSD) given in Table 1.

The values of relative error and RSD suggest that accuracy and precision of method are satisfactory. Experimental errors were determined using blank measurements and concentrations of all determined ions were corrected for blanks. To determine the limit of detections (LODs), blank filters were analyzed together with the samples, following the same procedures. LODs were calculated for each ion as three times the standard deviation of the blank values (Table 1). Recovery experiment was conducted by spiking the small amount (0.1 mL) of standards onto a blank quartz fiber filter, then extracted and analyzed using the same method (as mentioned above). The recoveries of ions were in the range of 90–100%.

Carbonaceous Aerosols (Organic and Elemental Carbon)
The Organic carbon (OC) and Elemental carbon (EC) concentrations were determined using thermal/optical Carbon analyzer, Sunset Laboratory which is based on thermal-optical transmittance (TOT) (Birch and Cary, 1996; Birch, 1998). For analysis a punch of 1.5 cm\textsuperscript{2} was taken from loaded filter paper and placed in the carbon analyzer. A detailed procedure for the analysis of OC-EC has been described by Satsangi \textit{et al.} (2012). LODs for OC and EC were 1.34 and 0.01 µg m\textsuperscript{–3} respectively. The RSD of this method for OC and EC were 2.7% and 8.5% respectively. For quality control carbon analyzer was calibrated using blank punch of prebaked quartz filter paper and standard sucrose solution (3.2 µg µL\textsuperscript{–1}) before analysis.

Table 1. Table showing limit of detection (LOD), relative error and relative standard deviation (RSD) of various species.

<table>
<thead>
<tr>
<th></th>
<th>Acetic acid</th>
<th>Formic acid</th>
<th>Cl\textsuperscript{–}</th>
<th>NO\textsubscript{3}\textsuperscript{–}</th>
<th>SO\textsubscript{4}\textsubscript{2–}</th>
<th>Ca\textsuperscript{2+}</th>
<th>K\textsuperscript{+}</th>
</tr>
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<tbody>
<tr>
<td>LOD (ng m\textsuperscript{–3})</td>
<td>3.3</td>
<td>6.0</td>
<td>17.2</td>
<td>5.9</td>
<td>12.8</td>
<td>7.5</td>
<td>16.9</td>
</tr>
<tr>
<td>Relative error (%)</td>
<td>2.4</td>
<td>2.3</td>
<td>3.7</td>
<td>1.4</td>
<td>3.6</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>2.1</td>
<td>0.9</td>
<td>2.0</td>
<td>0.7</td>
<td>2.8</td>
<td>1.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Ozone and Carbon Monoxide

Surface O₃ (ozone) concentrations were recorded using continuously operating O₃ analyzer (Thermo Fischer Model 49i). The principle of ozone concentration determination is based on Beer-Lambert law. A detailed principle, procedure of data collection and calibration of O₃ analyzer has been described by Singla et al. (2011). Surface CO (carbon monoxide) concentrations were recorded using continuously operating CO analyzer (Teledyne Model T300). CO analyzer works on the principle of infrared (IR) absorption at 4.67 µm. In T300 a broad beam of IR radiation is generated through a high energy heated element. The sample cell consists of a large number of mirrors (32 reflective mirrors) to increase the sensitivity of the analyzer. The analyzers were regularly calibrated using multipoint calibrator (Teledyne Model T700). For trace gas measurements, detection limits of O₃ and CO analyzer were 1.0 ppb and < 0.04 ppm respectively. Analyzers were regularly calibrated to give best results.

Meteorological parameters viz. solar radiation, temperature, relative humidity, rainfall, wind speed and wind direction were recorded using Automatic Weather Station WM271 Data Logger at every 1-hr interval.

RESULTS AND DISCUSSION

Mass Concentration of PM₂.₅ and PM₁₀ Aerosols

The average mass concentrations of PM₂.₅ and PM₁₀ were 86.3 ± 71.3 and 169.7 ± 100.5 µg m⁻³, respectively during the study period. The National Ambient Air Quality Standards (NAAQS, 2009) for PM₂.₅ is 60 µg m⁻³ while for PM₁₀; it is 100 µg m⁻³ for 24 hours. Almost 45% PM₂.₅ and 67% PM₁₀ mass concentrations were higher than NAAQS values, showing high particulate loading (especially the coarse part). Earlier studies at other sites in Indo-Gangetic plain in Kanpur, Allahabad and Lucknow have also reported PM₂.₅ and PM₁₀ concentration in the same range (Sharma et al., 2004; Dey et al., 2012; Pandey et al., 2012).

Fig. 2 shows seasonal variation of PM₂.₅ and PM₁₀. Seasonal variation of both PM₂.₅ and PM₁₀ were characterized by high levels in winter followed by post-monsoon, summer and monsoon. The back trajectories were simulated in each season using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model based on the GDAS Meteorological Data (Draxler and Rolph, 2003) (Fig. S1, supplementary information). In winter season, trajectories were dominantly localized in nature and the increase in local emission sources like burning of coal or wood to combat cold (in absence of any other domestic heating source) may result in high levels of both PM₂.₅ and PM₁₀. In addition, stagnant weather conditions in winter (like low temperature, wind speed and mixing layer height) also limit the dilution and dispersion of particulate matter. In summer season, trajectories mainly passed over Thar Desert which may lead to high concentration of particulate matter on the days of dust storm (2–3 times higher than normal days). Lowest levels of particulate mass were observed in monsoon season due to wet scavenging of particulate matter. In addition, trajectories showed transport of cleaner air masses from Arabian Sea during southwest monsoon also results in lower concentrations. Post monsoon is a transition period from monsoon to winter and trajectories originate from northwest region as well as local emissions resulting in moderate concentration. Similar seasonal variations of PM were reported in earlier studies at the site (Pachauri et al., 2013b).

Carbonaceous Aerosols

Carbonaceous aerosols include organic carbon (OC) and elemental carbon (EC). The average concentrations of OC
POC = EC × (OC/EC)_{min} (1)

using the following equation: organic carbon (POC) from total organic carbon (TOC)
SOC concentration can be estimated by subtracting primary ratio are from primary organic carbon (POC) exclusively. This method indicates that samples having low OC/EC ratio is expected to contain exclusively primary OC, small proportion of SOC may still exist. Therefore, the results of this method provide a lower limit of SOC content. The average concentrations of estimated SOC were 13.4 ± 9.7 µg m^{-3} and 18.5 ± 17.9 µg m^{-3} in PM2.5 and PM10 respectively.

Total carbonaceous aerosol (TCA) was calculated by the sum of EC and organic matter (OM) which is a product of OC and 1.6 (TCA = 1.6 × OC + EC) (Turpin and Lim 2001; Rengarajan et al., 2007). The concentrations of TCA ranged from 16.4 to 56.3 µg m^{-3} in PM2.5 while 24.9 to 78.4 µg m^{-3} in PM10. However, the average concentration of TCA was found to be 33.3 ± 21.3 and 44.3 ± 24.0 µg m^{-3} in PM2.5 and PM10 respectively.

To interpret emission and transformation processes of carbonaceous aerosols, OC/EC ratio can be used as EC is a tracer of primary sources while OC may be primary or secondary in origin (Pankow, 1994; Duan et al., 2004; Kumar and Yadav, 2016). In the present study, OC/EC ratio ranged from 1.7 to 6.4 with a mean value of 3.7 ± 1.2 for PM10 while it ranged from 1.0 to 3.9 with an average value of 2.8 ± 0.7 for PM2.5. When OC/EC ratio is more than 2.0 it indicates the contribution of both secondary and primary organic emissions (Chow et al., 1996); and at this site average OC/EC ratio was greater than 2.0.

**Estimation of Secondary Organic Carbon (SOC)**

Secondary organic carbon (SOC) was determined by (OC/EC)_{min} ratio method (Turpin and Huntzicker, 1995). This method indicates that samples having low OC/EC ratio are from primary organic carbon (POC) exclusively. SOC concentration can be estimated by subtracting primary organic carbon (POC) from total organic carbon (TOC) using the following equation:

POC = EC × (OC/EC)_{min} (1)

SOC = TOC – POC (2)

The observed values of (OC/EC)_{min} were 1.0 and 1.7 for PM2.5 and PM10 respectively. The lowest values of OC/EC ratio in PM2.5 was used as (OC/EC)_{min} for PM2.5 similarly the lowest value of OC/EC ratio in PM10 was used as (OC/EC)_{min} for PM10. As there was no distinct seasonal variation in (OC/EC)_{min} for PM2.5 and PM10 and seasonal minima were very close to the annual minimum, therefore annual minimum was selected for calculation of SOC. Similar method was also adopted in earlier studies (Cao et al., 2004; Ye et al., 2007; Pavuluri et al., 2011; Satsangi et al., 2012). Although carbonaceous sample with minimum OC/EC ratio is expected to contain exclusively primary OC, small proportion of SOC may still exist. Therefore, the results of this method provide a lower limit of SOC content. The average concentrations of estimated SOC were 13.4 ± 9.7 µg m^{-3} and 18.5 ± 17.9 µg m^{-3} in PM2.5 and PM10 respectively.

**Characteristics of Carboxylic Acids in Aerosols**

The average concentration of acetic acid (AA) in PM2.5 and PM10 were 330 ± 211 and 392 ± 224 (ng m^{-3} ± SD) respectively. The average concentration of formic acid (FA) in PM2.5 and PM10 were 348 ± 193 and 336 ± 175 (ng m^{-3} ± SD) respectively. Formic acid concentration was higher in PM2.5 than PM10 but the difference is not statistically significant. However, high concentration of formic acid in PM2.5 may be due to its dominant production from secondary sources at the study site. PM2.5 contains large fraction of secondary particles in comparison to PM10; and these secondary particles originate through nucleation process of low vapor pressure gases and gas to particle conversion (Koziel et al., 2006). In most of the aerosol samples AA concentration was higher than FA. Although the Henry’s law coefficient for FA is higher than AA (Limon-Sanchez et al., 2002), higher partitioning of AA into aerosol phase may be related to its low vapour pressure compared to FA (Saxena and Hildemann, 1996).

The sum of both the carboxylic acids may be considered as total monocarboxylic acids (MCA). The total MCA varied from 0.18% to 0.95% of aerosol mass concentration. The percentage contribution of AA and FA to PM mass concentration showed variation in summer and winter seasons. The average percentage contribution is slightly greater in winter (0.7%) than summer (0.45%; Fig. 3(a)). The contribution of total MCA to OC ranged 0.9–8.5%, with an average value of 4.0%.

Fig. 3(b) shows regression analysis between AA and FA. Regression analysis (r = 0.5) suggests that AA and FA may probably have only some common sources. Table 3 shows comparison of AA and FA concentrations with other sites around the world. The concentrations of FA and AA acid at present site were higher than urban sites in South America (Vasconcellos et al., 2011), rural site in Tanzania (Mkoma et al., 2012), urban site in Nanjing, China (Yang et al., 2005).

<table>
<thead>
<tr>
<th>Season</th>
<th>Type</th>
<th>PM Mass (µg m^{-3})</th>
<th>OC (µg m^{-3})</th>
<th>EC (µg m^{-3})</th>
<th>TCA (µg m^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>PM_{2.5}</td>
<td>56.1 ± 25.2</td>
<td>17.5 ± 10.0</td>
<td>5.7 ± 2.8</td>
<td>34.6 ± 18.4</td>
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<tr>
<td></td>
<td>PM_{10}</td>
<td>174.8 ± 56.6</td>
<td>20.9 ± 5.1</td>
<td>6.3 ± 3.4</td>
<td>38.7 ± 10.9</td>
</tr>
<tr>
<td>Monsoon</td>
<td>PM_{2.5}</td>
<td>33.8 ± 13.0</td>
<td>8.6 ± 2.5</td>
<td>2.7 ± 0.7</td>
<td>16.4 ± 4.5</td>
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<tr>
<td></td>
<td>PM_{10}</td>
<td>59.4 ± 37.4</td>
<td>13.2 ± 4.1</td>
<td>3.7 ± 1.3</td>
<td>24.9 ± 7.5</td>
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<tr>
<td>Post-monsoon</td>
<td>PM_{2.5}</td>
<td>120.6 ± 55.9</td>
<td>20.3 ± 11.6</td>
<td>6.9 ± 5.2</td>
<td>39.4 ± 22.9</td>
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<tr>
<td></td>
<td>PM_{10}</td>
<td>228.5 ± 34.6</td>
<td>27.0 ± 18.2</td>
<td>8.0 ± 5.5</td>
<td>40.1 ± 10.0</td>
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<tr>
<td>Winter</td>
<td>PM_{2.5}</td>
<td>162.9 ± 89.7</td>
<td>32.1 ± 14.9</td>
<td>11.3 ± 2.9</td>
<td>56.3 ± 27.2</td>
</tr>
<tr>
<td></td>
<td>PM_{10}</td>
<td>264.1 ± 95.2</td>
<td>42.3 ± 12.7</td>
<td>12.3 ± 3.4</td>
<td>78.4 ± 23.2</td>
</tr>
</tbody>
</table>
Fig. 3. (a) Percentage contribution of monocarboxylic acids to particulate mass in summer and winter season. (b) Linear regression analysis between acetic and formic acid.

and campus site in Singapore (Karthikeyan and Balasubramanian, 2005) but comparable with those in subtropical site in Jorhat, India (Khare et al., 2011), and urban site in Zurich (Fisseha et al., 2006). The levels of FA and AA in PM_{2.5} were lower than urban site of Sao Paulo (Souza et al., 1999). Few studies have reported FA and AA in PM_{10} and levels in present study were higher than other sites. Although the level of AA is comparable to the levels at an urban site of Thailand (Tsai et al., 2013) but FA concentration was much higher.

Seasonality of Acetic and Formic Acid Concentration

Fig. 4 shows seasonal variations of FA and AA in PM_{2.5} and PM_{10}. Seasonal variation in the atmospheric concentration of carboxylic acids is influenced by variations in the sources, atmospheric reactions and meteorology. The concentrations of FA and AA displayed similar seasonal variations with concentration following the order: winter > post-monsoon > summer > monsoon.

According to Henry’s law, partitioning of a gas to aerosol phase is favourable under low temperature conditions; this may result in higher levels of AA and FA in particulate phase in winter season. Both AA and FA showed a significant negative correlation (r = −0.65, p < 0.01 and r = −0.56, p < 0.01 respectively) with temperature (Figs. 5(a) and 5(b)). In addition, high RH also favours gas to particle conversion because liquid water content (LWC) of aerosols increases with increase in RH (Volkamer et al., 2009; Engelhart et al., 2011; Bian et al., 2014). LWC is a major component of aerosol particles which serves as a medium for aqueous-phase reactions and an increase in LWC results in increased organic acids concentration in aerosol phase (Lim et al., 2005). LWC of a particle can significantly influence gas-to-particle partitioning of organic precursors and subsequent heterogeneous reactions on aerosol aqueous phase (Pathak et al., 2003). LWC cannot be directly measured and is usually calculated through models. In the present study, it was calculated by Aerosol Inorganic Model II (AIM-II) (online version) (Clegg et al., 1998). The concentrations of SO_4^{2−}, NO_3^{−}, NH_4^{+}, ambient temperature (T), relative humidity (RH), and the calculated H^+_\text{strong} [For acidic aerosols with neutralization factor < 1, strong acidity (H^+_\text{strong}) was estimated from the difference between mole concentrations of (2 × SO_4^{2−} + NO_3^{−}) and NH_4^{+}] were entered into the model as inputs. During the study period LWC ranged from 2.8–317 µg m^{−3} with a mean of 88.0 µg m^{−3}. LWC showed a significant positive correlation with AA and FA (r = 0.55, p < 0.01 and r = 0.52, p < 0.01 respectively) suggesting that higher LWC can enhance the partitioning of the gaseous carboxylic acids into the aerosol aqueous phase (Figs. 5(c) and 5(d)).

Source Identification

Formic to Acetic Acid Ratio

FA and AA are emitted from both primary and secondary sources; primary sources include emissions from biomass burning, vegetations, industrial and motor vehicle exhaust; while secondary sources include oxidation of hydrocarbons (biogenic or anthropogenic in origin) (Neeb et al., 1997; Guenther et al., 2006; Lee et al., 2006; Guo et al., 2015). Since AA is mainly released from primary sources while FA is largely from secondary sources (Kawamura et al., 2000; Wang et al., 2007; Mkoma et al., 2012; Millet et al., 2015), FA to AA ratio (F/A) may be used as an indicator of secondary sources; F/A > 1 suggests dominance of secondary sources, while, F/A < 1 indicates dominance of primary sources (Talbot et al., 1988). Fig. S2 (supplementary information) shows the monthly variation of F/A ratio, which was maximum in May (1.4) and minimum in February (0.21). The high ratio observed in May (summer) may be due to generation of FA from secondary sources as a result of increase in rate of photochemical reactions and decrease
<table>
<thead>
<tr>
<th>Site</th>
<th>Sampling Period</th>
<th>Size</th>
<th>Formic Acid (ng m$^{-3}$)</th>
<th>Acetic Acid (ng m$^{-3}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sao Paulo, Brazil (Urban)</td>
<td>Winter, 1996</td>
<td>PM$_{10}$</td>
<td>480 ± 340</td>
<td>430 ± 240</td>
<td>Souza et al., 1999</td>
</tr>
<tr>
<td>Singapore (Campus)</td>
<td>2000</td>
<td>PM$_{2.5}$</td>
<td>80 ± 50</td>
<td>60 ± 90</td>
<td>Karthikeyan and Balasubramanian, 2005</td>
</tr>
<tr>
<td>Nanjing, China (Urban)</td>
<td>2001</td>
<td>PM$_{2.5}$</td>
<td>17.3–107</td>
<td>4.5–32.8</td>
<td>Yang et al., 2005</td>
</tr>
<tr>
<td>Zurich City, Switzerland (Urban)</td>
<td>2002–2003 August</td>
<td>PM$_{2.5}$</td>
<td>170</td>
<td>90</td>
<td>Fisseha et al., 2006</td>
</tr>
<tr>
<td></td>
<td>September</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>March</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beijing, China</td>
<td>2002–2003</td>
<td>PM$_{2.5}$</td>
<td>110 ± 81</td>
<td>78 ± 221</td>
<td>Wang et al., 2007</td>
</tr>
<tr>
<td>New York, USA (Rural)</td>
<td>August, 2002</td>
<td>PM$_{2.5}$</td>
<td>10–180</td>
<td>120–400</td>
<td>Hussain et al., 2009</td>
</tr>
<tr>
<td>Jorhat City, India (subtropical)</td>
<td>Summer, 2007–2008</td>
<td>PM$_{2.5}$</td>
<td>110 ± 100</td>
<td>250 ± 220</td>
<td>Khare et al., 2011</td>
</tr>
<tr>
<td></td>
<td>Winter, 2007–2008</td>
<td>PM$_{2.5}$</td>
<td>330 ± 430</td>
<td>240 ± 280</td>
<td></td>
</tr>
<tr>
<td>South America</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sao Paulo (Urban)</td>
<td>August, 2008</td>
<td>PM$_{10}$</td>
<td>78 ± 39</td>
<td>40 ± 11</td>
<td></td>
</tr>
<tr>
<td>Buenos Aires (Urban)</td>
<td>Aug–Sept, 2008</td>
<td>PM$_{10}$</td>
<td>71 ± 84</td>
<td>39 ± 48</td>
<td></td>
</tr>
<tr>
<td>Bogota (Urban)</td>
<td>Nov–Dec, 2008</td>
<td>PM$_{10}$</td>
<td>95 ± 52</td>
<td>24 ± 26</td>
<td></td>
</tr>
<tr>
<td>Morogoro, Tanzania (Rural)</td>
<td>Apr–May, 2011</td>
<td>PM$_{2.5}$</td>
<td>5.4 ± 2.2</td>
<td>0.71 ± 0.3</td>
<td>Mkoma et al., 2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PM$_{10}$</td>
<td>22.7 ± 3.3</td>
<td>1.2 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>Puli, Taiwan, (Forest)</td>
<td>Nov, 2009</td>
<td>PM$_{2.5}$</td>
<td>22.3 ± 9.5</td>
<td>261.8 ± 108.2</td>
<td>Tsai and Kuo, 2013</td>
</tr>
<tr>
<td>Chaing Mai, Thailand (Urban)</td>
<td>Feb–Apr, 2010</td>
<td>PM$_{10}$</td>
<td>58.2 ± 37.6</td>
<td>335 ± 266</td>
<td>Tsai et al., 2013</td>
</tr>
<tr>
<td>Dayalbagh, Agra, India (Campus)</td>
<td>2014–2015</td>
<td>PM$_{2.5}$</td>
<td>348 ± 193</td>
<td>330 ± 211</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PM$_{10}$</td>
<td>336 ± 175</td>
<td>392 ± 224</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4. Box plots for the seasonal variation of (a) acetic acid and (b) formic acid in PM$_{2.5}$ and PM$_{10}$. Solid line represents median, square box represents mean, box lower (25%) and upper (75%) quartiles, whiskers represent 99% and 1% ranges.

Figs. 5. Regression analysis between temperature and (a) acetic acid, (b) formic acid; regression analysis between liquid water content (LWC) and (c) acetic acid, (d) formic acid.
in emissions from heating sources (coal and wood burning) resulting in low concentration of AA. The lowest ratio observed in February (winter) may be because of increase in primary emissions from heating sources. Table 4 shows F/A ratios for different emission sources as reported in literature. The average F/A was 0.69 indicating primary emissions are dominant sources of carboxylic acids at the study site.

FA and AA together with tracers of other sources (NO$_3^-$, SO$_4^{2-}$, Cl$, K^+$, Ca$^{2+}$, EC, SOC, CO and O$_3$) were subjected to correlation analysis in order to understand their possible sources and mechanism of formation. The selected source indicators include Ca$^{2+}$ for dust aerosols, K$^+$ for biomass burning, Cl$^-$ for coal burning, NO$_3^-$ for traffic emissions, EC for primary emissions, SO$_4^{2-}$ for heterogeneous reactions and SOC for secondary formation. Table 5 shows results of correlation analysis.

AA shows high correlation with NO$_3^-$ in both PM$_{2.5}$ and PM$_{10}$ (unlike formic acid) indicating its emission from vehicles. Similarly, high correlation of AA with K$^+$ (r = 0.84, p < 0.01 and r = 0.79, p < 0.01) in PM$_{2.5}$ and PM$_{10}$ indicates biomass burning contributes significantly to its concentration while a poor correlation between FA and K$^+$ suggests that biomass burning is not a major source of FA. The moderate correlation of AA and poor correlation of FA with Ca$^{2+}$ both in PM$_{2.5}$ and PM$_{10}$ suggests that dust aerosol makes an insignificant contribution to their levels. Both AA and FA show high correlation with Cl$^-$ both in PM$_{2.5}$ and PM$_{10}$ indicating coal or waste burning as a significant source of both acids.

FA shows significant correlation with SO$_4^{2-}$ in PM$_{2.5}$ and PM$_{10}$ suggesting that in-cloud and heterogeneous reactions play an important role in the formation of FA (Mkoma et al., 2012; Laongsri and Harrison, 2013). However, AA shows moderate correlation with SO$_4^{2-}$ in PM$_{2.5}$ and weak correlation in PM$_{10}$ indicating only some fraction of AA in PM$_{2.5}$ may be formed by heterogeneous reactions. The relationships of FA and AA with SO$_4^{2-}$ are consistent with the results reported by Wang et al. (2007).

EC is a primary pollutant which is emitted from incomplete combustion of fossil fuel and agricultural waste (Park and Cho, 2011). Earlier studies at this site by Pachauri et al. (2013b) reported biomass burning, fossil fuel burning and vehicular emissions as important sources of EC. Therefore, a significant correlation of EC with MCA may be a good indicator of primary emissions. AA concentration showed a high correlation with EC in PM$_{2.5}$ and PM$_{10}$ (r = 0.74, p < 0.01 and r = 0.67, p < 0.01 respectively; Fig. 6(a)), therefore, primary emissions may significantly contribute to AA concentration. Earlier studies by Kawamura et al. (2000) further suggested that incomplete combustion of gasoline as an important source of carboxylic acids especially AA. FA showed moderate correlation (r = 0.41, p = 0.07) with EC in PM$_{2.5}$ and weak correlation (r = 0.24, p = 0.33) with EC in PM$_{10}$. SOC is the fraction of OC that transfers from the gas phase to aerosol phase as product of gas phase oxidation of parent organic species (Kanakidou et al., 2005). In order to investigate secondary sources, regression analysis of FA and AA with SOC was performed both in PM$_{2.5}$ and PM$_{10}$. Significant correlation of FA with SOC (r = 0.72, p < 0.01 and r = 0.55, p = 0.02 for PM$_{2.5}$ and PM$_{10}$ respectively; Fig. 6(b)) indicates its secondary origin while moderate correlation with AA (r = 0.49, p = 0.06 and r =

### Table 4. The ratio of formic to acetic acid (F/A) for different sources.

<table>
<thead>
<tr>
<th>F/A</th>
<th>Source</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 1</td>
<td>Primary Sources</td>
<td></td>
</tr>
<tr>
<td>0.1–0.5</td>
<td>Biomass burning</td>
<td>Talbot et al. (1988)</td>
</tr>
<tr>
<td>0.25–0.33</td>
<td></td>
<td>Hartmann et al. (1991)</td>
</tr>
<tr>
<td>0.11–0.27</td>
<td></td>
<td>Tsai et al. (2013)</td>
</tr>
<tr>
<td>0.42–0.57</td>
<td>Vehicular emissions</td>
<td>Talbot et al. (1988)</td>
</tr>
<tr>
<td>0.33–0.5</td>
<td></td>
<td>Grosjean (1989)</td>
</tr>
<tr>
<td>0.43–0.48</td>
<td></td>
<td>Grosjean (1992)</td>
</tr>
<tr>
<td>&gt; 1</td>
<td>Secondary sources</td>
<td>Talbot et al. (1988)</td>
</tr>
<tr>
<td>1.42</td>
<td></td>
<td>Wang et al. (2007)</td>
</tr>
<tr>
<td>1.13–1.93</td>
<td></td>
<td>Khare et al. (2011)</td>
</tr>
<tr>
<td>4.2–20</td>
<td></td>
<td>Mkoma et al. (2012)</td>
</tr>
<tr>
<td>0.69</td>
<td>Primary Sources</td>
<td>Present study</td>
</tr>
</tbody>
</table>

### Table 5. Correlation coefficients for acetic acid, formic acid, selected ions, EC and SOC in PM$_{2.5}$ and PM$_{10}$ fraction at study site.

<table>
<thead>
<tr>
<th></th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>Cl$^-$</th>
<th>K$^+$</th>
<th>Ca$^{2+}$</th>
<th>EC</th>
<th>SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>0.96</td>
<td>0.46</td>
<td>0.80</td>
<td>0.84</td>
<td>0.48</td>
<td>0.74</td>
<td>0.49</td>
</tr>
<tr>
<td>HCOOH</td>
<td>0.40</td>
<td>0.70</td>
<td>0.94</td>
<td>0.35</td>
<td>0.32</td>
<td>0.41</td>
<td>0.72</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>0.83</td>
<td>0.06</td>
<td>0.82</td>
<td>0.79</td>
<td>0.46</td>
<td>0.67</td>
<td>0.39</td>
</tr>
<tr>
<td>HCOOH</td>
<td>−0.25</td>
<td>0.58</td>
<td>0.66</td>
<td>0.36</td>
<td>0.26</td>
<td>0.24</td>
<td>0.55</td>
</tr>
</tbody>
</table>

*Correlation coefficients which are significant at p = 0.05 are indicated in bold.
0.39, \( p = 0.12 \) for PM\(_{2.5}\) and PM\(_{10}\) respectively) indicates a fraction of AA may also be contributed by secondary sources. Earlier, Laongsri and Harrison (2013) established secondary origin of oxalate in aerosols using SOC as source tracer for photochemical contribution.

To further ascertain primary and secondary sources, regression analysis of AA and FA was performed with trace gases like CO and \( O_3 \). CO may be considered as tracer for primary anthropogenic emissions since it is dominantly resulted from incomplete combustion of fossil fuel (Wang et al., 2010). Figs. 7(a) and 7(b) show regression analysis of CO with AA and FA; CO shows a high correlation (\( r = 0.57, p < 0.01 \)) with AA while a weak correlation with FA (\( r = 0.3, p = 0.25 \)), therefore, a significant correlation of AA with CO further substantiates its primary origin. Secondary formation of organic acids involves oxidation of olefins having both biogenic and anthropogenic origin, with ozone or \( \text{OH}^\cdot \) or \( \text{NO}_3^\cdot \) radicals (Chebbi and Carlier, 1996). The relative importance of these three reactions can be estimated from the relation given by Grosjean (1989).

\[
-\frac{d[\text{oilfin}]}{dt} = [\text{oilfin}][k_{\text{OH}}[\text{OH}^\cdot] + k_{\text{O}_3}[\text{O}_3] + k_{\text{NO}_3}[\text{NO}_3^\cdot]]
\]

(3)

where \([\text{OH}^\cdot], [\text{O}_3], \) and \([\text{NO}_3^\cdot] \) are their ambient concentrations and \( k_{\text{OH}}, k_{\text{O}_3} \) and \( k_{\text{NO}_3} \) are the corresponding reaction rate constants. We have tried to estimate the formation of AA and FA through oxidation of propene as:

On a particular day when, propene concentration = 1.05 ppb (from another study at the same site)

\( O_3 \) concentration = 70 ppb

Assuming \( \text{OH}^\cdot \) radical concentration = \( 10^{-5} \) ppb and \( \text{NO}_3^\cdot \) radicals = zero for daytime situation.

78% propene would be removed by reaction with ozone (reaction rate constants given by Parmar and Grosjean, 1988; \( k_{\text{O}_3} = 12.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and \( k_{\text{OH}} = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)). Using 18.5% and 9% yield of
FA and AA from propene-O<sub>3</sub> reaction as reported by Atkinson (1990), the resulting production rates of FA and AA are estimated to be 0.0152 ppb h<sup>−1</sup> and 0.0074 ppb h<sup>−1</sup> respectively. This suggests that the olefin-<em>O</em><sub>3</sub>, reaction plays a role in carboxylic acid formation.

A significant negative correlation was obtained between ozone and FA concentration (r = −0.58, p < 0.01), however, AA showed weak negative correlation with ozone (r = −0.3, p = 0.15) (Figs. 7(a) and 7(b)). These results suggest greater formation of FA in comparison to AA through the oxidation of organic precursors.

CONCLUSION

This study reflects the water-soluble carboxylic acids (acetic and formic acids) in PM<sub>2.5</sub> and PM<sub>10</sub> aerosols at a semi-urban site in Dayalbagh, Agra. The major conclusions of the study are:

1. The average mass concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> were 86.3 ± 71.3 and 169.7 ± 100.5 µg m<sup>−3</sup>, respectively. The highest concentrations of both PM<sub>2.5</sub> and PM<sub>10</sub> were observed in winter followed by post-monsoon, summer and monsoon. The seasonal variation in mass concentration is regulated by strength of emission sources and meteorological parameters. Highest concentration of particulate matter in winter was due to increase in local emissions (to combat cold) and air mass backward trajectories also support contribution of local sources. In monsoon, rainfall under the influence of southwest monsoon results in removal of particulate matter by wet scavenging.

2. OC and EC showed a distinct seasonal variation characterized by highest concentrations during winter while lowest during monsoon. The average concentrations of TCA ranged from 16.4 to 56.3 µg m<sup>−3</sup> in PM<sub>2.5</sub> while 24.9 to 78.4 µg m<sup>−3</sup> in PM<sub>10</sub>. Secondary organic carbon (SOC) was calculated by (OC/EC)<sub>min</sub> ratio method and average concentrations of SOC were 13.4 ± 9.7 µg m<sup>−3</sup> and 18.5 ± 17.9 µg m<sup>−3</sup> in PM<sub>2.5</sub> and PM<sub>10</sub> respectively.

3. The average concentrations of AA and FA were 330 ± 211 and 341 ± 193 µg m<sup>−3</sup> in PM<sub>2.5</sub> while 392 ± 224 and 336 ± 175 µg m<sup>−3</sup> respectively in PM<sub>10</sub>. The sum of total monocarboxylic acid varied from 0.18% to 0.95% of aerosol mass concentration. In most of the aerosol samples AA concentration was higher than FA.

4. The concentrations of FA and AA displayed similar seasonal variation (winter > post-monsoon > summer > monsoon). High levels were observed in winter season because gas to particle conversion is favourable under low temperature and high humidity conditions. To further ascertain, regression analysis was also performed with temperature and LWC.

5. Primary emissions were dominant source of carboxylic acids at the site suggested by F/A ratio. To understand the possible sources and mechanism of formation of FA and AA several source tracers like ions (NO<sub>3</sub><sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, Cl<sup>−</sup>, K<sup>+</sup> and Ca<sup>2+</sup>), EC, SOC and trace gases (CO and O<sub>3</sub>) were used. The results of correlation analysis suggest that FA was largely from secondary (in-cloud and heterogeneous transformations) while AA was mainly from primary (vehicular/biomass burning/coal or waste burning) emissions.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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