Speciation and temporal characterization of dicarboxylic acids in PM$_{2.5}$ during a PM episode and a period of non-episodic pollution

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ABSTRACT

PM$_{2.5}$ aerosol was collected during a PM episode and a non-episodic pollution period between September and November 2004 in suburban southern Taiwan and dicarboxylic acid and inorganic species content and provenance were investigated. Oxalic acid was the dominant dicarboxylic acid species, followed by succinic acid and malonic acid. Tartaric acid concentrations were the lowest. There was 49.3% more dicarboxylic acid in PM episode aerosol than in non-episodic aerosol. However, daily oxalic acid concentration increased 72.7% in PM episode aerosol, while succinic acid fell 20.9% and malonic acid fell 21.6%, indicating higher conversion of these acids into oxalic acid in PM episode aerosol. Dicarboxylic acid concentrations, particularly oxalic acid, peaked at night during the PM episode, due to accumulation of daytime oxalic acid combined with low wind velocity and low mixing layer height at this time. SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were the dominant ionic species in both PM episode and non-episodic aerosols. NO$_3^-$ concentration increased 106% during the PM episode, while HNO$_3$, a gaseous precursor of NO$_3^-$, fell 57%, indicating a large conversion of HNO$_3$ to aerosol phase NO$_3^-$ in PM episode aerosol. Backward trajectory data indicate that burning of paddy fields may also contribute to oxalic acid content in PM episode aerosol in the study area, especially during nighttime. Principal component analyses showed that succinic acid, malonic acid and oxalic acid were important factors in both pollution periods and also that there was high correlation between tartaric acid and NO$_x$ or HNO$_2$, indicative of vehicle emissions. The mass ratio of oxalic acid to sulfate in this aerosol was as high as 60.3\%\%, 35.5\% higher than in non-episodic aerosol. Principal component analyses showed that photochemical aerosols contributed by succinic acid, malonic acid and oxalic acid were important factors in both periods. There was high correlation between tartaric acid and NO$_x$ or HNO$_2$, indicative of vehicle emissions.

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1. Introduction

DICARBOXYLIC ACIDS, UBQUITOUS IN THE TROPOSPHERE AND A SIGNIFICANT FRACTION OF ATMOSPHERIC ORGANIC PARTICULATE MATTER (OPM), ARE IMPORTANT ORGANICS RESULTING FROM THE MARINE PATHWAY, FOSSIL FUEL AND BIOMASS BURNING, COOKING, FOREST BIOSOURCES AND ANTHROPOGENIC EMISSIONS (Stephanou et al., 1993; Chebbi and Carlier, 1996; Schauer et al., 2001, 2002; Mayol-Bracero et al., 2002; Pio et al., 2005). LOW
molecular weight dicarboxylic acids (low-M$_w$ DCAs) have vapor pressures $10^2$–$10^4$ lower than low molecular weight monocarboxylic acids, and as a result dominate in aerosol. They are end products in the photochemistry of hydrocarbons, e.g. aromatic hydrocarbons, alkanes, alkene and alkyl (Rogge et al., 1993; Chebbi and Carlier, 1996; Kalberer et al., 2000).

Non-methane volatile organic compounds that originate from traffic exhaust are converted through photochemical reactions in the atmosphere to dicarboxylic acids such as succinic acid, malonic acid, and oxalic acid (Hatakeyama et al., 1987), while non-saturated fatty acids from sea sprays may react with O$_3$ to form monocarboxylic and dicarboxylic acids (Kawamura et al., 1996). Although constituting only a small fraction of the total aerosol mass, these acids are important in cloud condensation nuclei (CCN), ice nuclei (IN), hygroscopic properties, acid precipitation, and optical properties and thereby affect the earth’s radiation budget, global climate, and human health (Chebbi and Carlier, 1996; Facchini et al., 1999; Yu, 2000; Charlson et al., 2001; Sattler et al., 2001; Acker et al., 2002).

Dicarboxylic acids contribute 1–10% to total aerosol carbon (Khwaja, 1995; Kawamura and Sakaguchi, 1999; Wang et al., 2002). Oxalic acid is the dominant species, and malonic acid and succinic acid are major species (Kawamura et al., 1996; Kerminen et al., 2000). In rural environments, oxalic acid concentration is between 10 ng m$^{-3}$ and 50 ng m$^{-3}$ while in urban areas it may reach 900 ng m$^{-3}$ (Kawamura and Sakaguchi, 1999). Hsieh et al. (2007) reported an average oxalic acid concentration of 449.3 ng m$^{-3}$ in suburban southern Taiwan in autumn 2002 and in summer 2003, followed by malic acid (53.0 ng m$^{-3}$), maleic acid (45.5 ng m$^{-3}$), succinic acid (29.6 ng m$^{-3}$), malonic acid (20.8 ng m$^{-3}$) and tartaric acid (11.6 ng m$^{-3}$).

Yao et al. (2004) studied oxalic, malonic, and succinic acid during an August PM episode in Hong Kong and reported concentrations about 2.5 times their average and a mass concentration ratio of malonic acid/succinic acid of 0.5 in PM$_{2.5}$, indicating that primary traffic exhaust was the principal source of dicarboxylic acids during this episode. Mixing layer height was only 740 m, much lower than the summer average of 1110 m, leading to the accumulation of air pollutants. Tsai and Cheng (2004) studied inorganic salts during a PM episode in a metropolitan area in central Taiwan and noted that nitrate concentration and its percentage in PM mass increased significantly from 2.5 µg m$^{-3}$ and 4.6% during non-episodic pollution to 17.3 µg m$^{-3}$ and 8.6% during the PM episode. NO$_3$ is correlated with CO concentrations and is considered as a pollution indicator often significantly exceeds the concentration of other pollutants. PM$_{2.5}$ was collected in a non-episodic pollution period (19 September–20 October 2004) and a PM episode (24–30 November 2004). During the non-episodic pollution period, the hourly average PM$_{10}$ concentration (1-h PM$_{10}$) of 85 µg m$^{-3}$ represents moderate air quality, while during the PM episode the average PM$_{10}$ concentration was 113 µg m$^{-3}$. Significant differences ($p$ value <0.01) of PM$_{10}$ concentration were found between the two periods.

There were a total of 64 gaseous compounds/PM$_{2.5}$ sample sets collected during the non-episodic period and 12 gaseous compounds/PM$_{2.5}$ sample sets collected during the PM episode.

2. Methodology

2.1. Sites and aerosol sampling

PM$_{2.5}$ samples were collected at a suburban location in southern Taiwan during a moderate pollution loading (non-episodic) period and a high pollution loading (PM episode) period using a VAPS (Versatile Air Pollutant Sampler; URG-3000K, URG, USA) with a total flow rate of 32 L min$^{-1}$, three filter packs and two denuders designed to avoid sampling errors and artifacts (Cheng and Tsai, 1997; Matsumoto and Okita, 1998; Tsai and Perng, 1998). The VAPS consists of two fine particle (PM$_{2.5}$) samplers operated simultaneously at a sampling flow rate of 15.0 ± 0.2 L min$^{-1}$, and one coarse particle (PM$_{10}$) sampler operated at 1.9 ± 0.1 L min$^{-1}$. PM$_{2.5}$ particles were collected on a 47-mm Teflon filter (Zefluor, Pall) (1st stage filter). Untrapped particulates pass on to a 47-mm nylon filter (Nylasorb, Pall) (2nd stage filter) and a 47-mm pre-combusted quartz filter (2500 QAT-UP, Pall) (3rd stage filter), on which coarse particles were collected. Two sets of atmospheric PM$_{2.5}$ samples were collected daily, one from 8 am to 7 pm (11 h: ‘daytime’) and the other from 7 pm to 8 am (13 h: ‘nighttime’). The URG-VAPS was placed on a rooftop 15 m above ground in a suburban site, with medium traffic, 2 km NW of a petrochemical industrial zone. The nearest major conurbation was Tainan City, located about 8 km to the north, with a population of approximately 750,000 people. The nearest main road was approximately 100 m to the west, and two busy highways were about 200 m to the north and 3 km to the east, respectively.

In addition to ozone, PM$_{10}$ is the pollutant most responsible for air quality variation in southern Taiwan (Tsai, 2005; Tsai et al., 2007). In this study, air quality determination was based on PM$_{10}$ because its concentration often significantly exceeds the concentration of other pollutants. PM$_{2.5}$ was collected in a non-episodic pollution period (19 September–20 October 2004) and a PM episode (24–30 November 2004). During the non-episodic pollution period, the hourly average PM$_{10}$ concentration (1-h PM$_{10}$) of 85 µg m$^{-3}$ represents moderate air quality, while during the PM episode the average PM$_{10}$ concentration was 113 µg m$^{-3}$. Significant differences ($p$ value <0.01) of PM$_{10}$ concentration were found between the two periods.

Before and after sample collection, filters were conditioned at 35 ± 1% RH for 24 h and subsequently weighed at
50 ± 3% RH using a Mettler Toledo AT26i analytical balance with a sensitivity of 10 μg and a Sartorius CP2P analytical balance with a sensitivity of 1 μg. All weight measurements were repeated three or more times and the Shewart control procedures were followed to ensure reliability. Additionally, blank filters were prepared by purging in 99.995% pure nitrogen for 30 s and then processed as for sample-containing filters.

Determinations of semi-volatile species are complicated by sampling artifacts resulting from gas/particle and particle/particle interactions (Sickles et al., 1999). Denuders and back filters are widely accepted as effective tools to minimize sampling artifacts (Chow and Watson, 1998). In order to circumvent artifacts, therefore, two annular automated sampler (AS1000) with 2 mL vials, and a Teflon pump (Model GP50), an ASRS-Ultra anion self-regenerating suppressor, a CD25, an AS1000 with 2 mL vials, and a Teflon injection valve. A CS12A analytical column (250 mm × 4 mm I.D.) with a CG12A guard column (50 mm × 4 mm I.D.) and an isotropic 20 mM MSA (CH₃CO₂S) eluent at a flow rate of 1.0 mL min⁻¹ was used for determination of cations, including Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺.

All reagents were of analytical grade, obtained from Merck and were used without further purification. The solutions were prepared using deionized water from which organic carbon had been removed and the detection limits corresponded to 10–50 ng for the dicarboxylic acids investigated. The method detection limit (MDL) was defined as a signal-to-noise ratio from multiple injections of a lowest-concentration standard of 3:1. MDLs were 0.009 μg m⁻³ for F⁻, 0.037 μg m⁻³ for Cl⁻, 0.046 μg m⁻³ for NO₂⁻, 0.019 μg m⁻³ for Br⁻, 0.046 μg m⁻³ for NO₃⁻, 0.028 μg m⁻³ for SO₄²⁻, 0.046 μg m⁻³ for Na⁺, 0.060 μg m⁻³ for NH₄⁺, 0.056 μg m⁻³ for K⁺, 0.045 μg m⁻³ for Mg²⁺, and 0.033 μg m⁻³ for Ca²⁺, 2.54 ng m⁻³ for succinic acid, 1.96 ng m⁻³ for malonic acid, 3.58 ng m⁻³ for maleic acid, 2.81 ng m⁻³ for tartaric acid, 0.33 ng m⁻³ for malic acid, and 1.42 ng m⁻³ for oxalic acid at a nominal volume of 10.8 m³ for a typical 12-h PM₂.₅ gaseous sample. Average recoveries of inorganic ions ranged from 91.3% for K⁺ to 105.1% for NH₄⁺. In particular, average recoveries of Cl⁻ and SO₄²⁻ were near 100% with <3.3% relative standard deviations (RSDs). About 92.8–106.1% of dicarboxylic acid was recovered with <2% RSDs representing a high degree of accuracy and reproducibility. Also, as pretreatment does not use any organic solvent, possible analyte losses and contamination in extraction steps are minimized.

3. Results and discussion

3.1. Evaluation of the partitioning of dicarboxylic acids on three different collection media

Partitioning data (Fig. 1(a)) show that the majority of all acids in non-episodic aerosol bar succinic was collected on the first-stage Teflon filter. For example, 85.6 ± 4.9% of oxalic acid was collected on the Teflon. However, 4.3 ± 3.3% evaporated and diffused to the second-stage nylon filter. Indeed, all six aerosol dicarboxylic acids were also detected on the third-stage quartz filter (10.1% of succinic acid, 14.4% of malic acid, 14.6% of malonic acid, 13.1% of tartaric acid, 21.4% of maleic acid and 10.1% of oxalic acid). The results for succinic acid, malonic acid and oxalic acid are close to those reported elsewhere, of 10–15% (Limbeck et al., 2001; Yao et al., 2002a). Quartz is clearly effective for the collection of maleic acid and important for the collection of all of these acids during non-episodic pollution. During the PM episode
(Fig. 1(b)), malic acid on the Teflon filter increased to 81.0 ± 12.3%, slightly lower than the 87.2 ± 11.6% for oxalic acid, while percentages of succinic acid, malonic acid and tartaric acid were close to those collected from non-episodic aerosol. All efficiencies were <60%, demonstrating that using only a Teflon filter for collection of these acids is inadequate. The nylon filter contributed notably to the collection of succinic acid, malonic acid and tartaric acid during the PM episode, trapping 62.1 ± 9.3%, 34.7 ± 14.4%, and 29.5 ± 19.3% of these acids, respectively. The quartz filter collected 4.8–22.9% of dicarboxylic acids during the PM episode. Maleic acid collection was 22.9%, similar to the 21.4% collection during non-episodic pollution. Additionally, the 13.3–14.9% collection for malonic acid and tartaric acid on quartz indicate that this filter contributed significantly to the collection of these acids also during the PM episode.

Clearly, Teflon and nylon filters suffer various degrees of sample loss when collecting aerosol dicarboxylic acids. The losses were 10.1–21.4% during non-episodic pollution and 4.8–22.9% during the PM episode, with the highest loss for maleic acid. A third-stage quartz filter must therefore be added to the Teflon and nylon filters to collect complete aerosol dicarboxylic acid samples and avoid artifacts associated with loss of aerosol components.

### 3.2. Chemical species and compositions of daily PM$_{2.5}$ during non-episodic pollution period and PM episode

PM$_{2.5}$ mass concentration was 55.9 ± 15.9 µg m$^{-3}$ during non-episodic pollution and 74.1 ± 12.3 µg m$^{-3}$ during the PM episode. Table 1 shows that SO$_4^{2-}$ was the dominant ionic species during both periods, followed by NO$_3^-$ and NH$_4^+$, respectively and, in insignificant percentages of the total PM mass, Cl$^-$, Na$^+$ and K$^+$. F$^-$, Br$^-$ and NO$_2$. The sulfate concentration in PM$_{2.5}$ during the PM episode was 15.4 ± 5.8 µg m$^{-3}$, higher than the 11.3 ± 5.3 µg m$^{-3}$ during non-episodic pollution. Further, during the PM episode sulfate concentration alone exceeded the US NAAQS annual PM$_{2.5}$ mass standard of 15 µg m$^{-3}$. The concentration of NH$_4^+$ in PM$_{2.5}$ increased from 6.08 µg m$^{-3}$ during non-episodic pollution to 8.06 µg m$^{-3}$ during the PM episode. Nevertheless, sulfate and ammonium levels during the PM episode, at 20.77% and 10.88% of the PM$_{2.5}$ mass, were only slightly higher than the 20.17% and 10.87% during non-episodic pollution, indicating the consistent impact of non-local photochemical reactions during both periods. NOx, the predominant emitting species of traffic sources, is converted into HNO$_3$ through photochemical transformation. The average HNO$_3$ concentration decreased about 57% from 1.52 µg m$^{-3}$ during non-episodic pollution to 0.65 µg m$^{-3}$ during the PM episode. Thus, a large quantity of HNO$_3$ was clearly converted from gaseous phase into aerosol NO$_3$ to raise the concentration of nitrate in PM$_{2.5}$, from 6.14 µg m$^{-3}$ (11.0% by PM$_{2.5}$ mass) during non-episodic pollution to 12.62 µg m$^{-3}$ (17.0% by PM$_{2.5}$ mass) during the PM episode. During the PM episode photochemical reactions were stronger and this accelerated aerosol nitrate formation. Low wind speed, 1.32 m s$^{-1}$ on average, resulted in less atmospheric mixing, allowing the trapping of locally transformed NO$_3$ during the PM episode. This observation equates closely to that of the conversion of traffic emissions into nitrate during a PM episode in central Taiwan (Tsai and Cheng, 2004).

Although concentrations of Cl$^-$, Na$^+$ and K$^+$ during the PM episode were higher than non-episodic pollution period, percentages of these water-soluble inorganic species in PM$_{2.5}$ mass did not show much variation. Ca$^{2+}$ and Mg$^{2+}$ concentrations during the PM episode were 0.48 µg m$^{-3}$ (0.64% of the mass) and 0.15 µg m$^{-3}$ (0.21% of the mass), respectively, lower than the 0.71 µg m$^{-3}$ (1.28% of the mass) and 0.17 µg m$^{-3}$ (0.31% of the mass) observed during non-episodic pollution. The low wind speed during the PM episode (1.32 ± 0.33 m s$^{-1}$ versus 1.87 ± 0.46 m s$^{-1}$ during non-episodic pollution) reduces the re-entrainment of road dust that contains Ca$^{2+}$ and Mg$^{2+}$ thus causing lower concentrations and percentages of PM mass of Ca$^{2+}$ and Mg$^{2+}$ than during non-episodic pollution. Concentrations of HCl, SO$_2$ and NH$_3$ were also lower during the PM episode and this was due to increased levels of...
Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>During non-episodic pollution period</th>
<th>During PM episode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean (n = 64)</td>
<td>SD</td>
</tr>
<tr>
<td>PM2.5 mass (µg m⁻³)</td>
<td>55.91</td>
<td>15.87</td>
</tr>
<tr>
<td>Sodium (µg m⁻³)</td>
<td>1.42 (2.54%)</td>
<td>0.87</td>
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<tr>
<td>Ammonium (µg m⁻³)</td>
<td>6.08 (10.87%)</td>
<td>1.99</td>
</tr>
<tr>
<td>Potassium (µg m⁻³)</td>
<td>1.51 (2.70%)</td>
<td>0.94</td>
</tr>
<tr>
<td>Magnesium (µg m⁻³)</td>
<td>0.17 (0.31%)</td>
<td>0.06</td>
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<tr>
<td>Calcium (µg m⁻³)</td>
<td>0.71 (1.28%)</td>
<td>0.19</td>
</tr>
<tr>
<td>Fluoride (µg m⁻³)</td>
<td>0.05 (0.10%)</td>
<td>0.07</td>
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<td>Chloride (µg m⁻³)</td>
<td>1.84 (3.29%)</td>
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<td>Nitrite (µg m⁻³)</td>
<td>1.00 (1.79%)</td>
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<tr>
<td>Bromide (µg m⁻³)</td>
<td>0.09 (0.17%)</td>
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<tr>
<td>Nitrate (µg m⁻³)</td>
<td>6.14 (10.98%)</td>
<td>3.39</td>
</tr>
<tr>
<td>Sulfate (µg m⁻³)</td>
<td>11.28 (20.17%)</td>
<td>5.30</td>
</tr>
<tr>
<td>Dicarboxylic acid</td>
<td>656.0 (1.17%)</td>
<td>277.4</td>
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<tr>
<td>Succinic acid</td>
<td>77.4 (11.80%)</td>
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<td>Malic acid</td>
<td>36.3 (5.53%)</td>
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<tr>
<td>Malonic acid</td>
<td>64.7 (9.86%)</td>
<td>30.7</td>
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<tr>
<td>Tartaric acid</td>
<td>4.00 (0.61%)</td>
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<tr>
<td>Maleic acid</td>
<td>13.2 (2.02%)</td>
<td>12.5</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>460.4 (70.19%)</td>
<td>203.7</td>
</tr>
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</table>

Gaseous pollutants

<table>
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<tr>
<th>Species</th>
<th>Mean (n = 64)</th>
<th>SD</th>
<th>nighttime/daytime</th>
<th>Mean (n = 12)</th>
<th>SD</th>
<th>nighttime/daytime</th>
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</thead>
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<tr>
<td>HCl (µg m⁻³)</td>
<td>1.79</td>
<td>1.82</td>
<td>0.41/0.41</td>
<td>1.12</td>
<td>0.60</td>
<td>0.75/0.83</td>
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<tr>
<td>HNO₂ (µg m⁻³)</td>
<td>4.14</td>
<td>5.86</td>
<td>3.80/2.57</td>
<td>4.74</td>
<td>3.13</td>
<td>1.28/1.21</td>
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<tr>
<td>HNO₃ (µg m⁻³)</td>
<td>1.52</td>
<td>2.76</td>
<td>0.15/0.22</td>
<td>0.65</td>
<td>0.53</td>
<td>0.83/0.79</td>
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<tr>
<td>SO₂ (µg m⁻³)</td>
<td>24.52</td>
<td>8.99</td>
<td>0.82/0.89</td>
<td>10.70</td>
<td>4.93</td>
<td>0.74/0.50</td>
</tr>
<tr>
<td>NH₃ (µg m⁻³)</td>
<td>13.28</td>
<td>5.17</td>
<td>0.96/1.12</td>
<td>7.57</td>
<td>5.49</td>
<td>0.70/0.81</td>
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<tr>
<td>NMHCs (ppm)</td>
<td>0.25</td>
<td>0.08</td>
<td>1.38/0.35</td>
<td>0.38</td>
<td>0.04</td>
<td>1.23/0.22</td>
</tr>
</tbody>
</table>

a Standard deviation.
b Estimated av.% by PM2.5 mass shown in parentheses.
c Concentrations in ng m⁻³.
d Estimated av.% by PM2.5 dicarboxylic acid concentrations shown in parentheses.
e Non-methane hydrocarbons.

transformation into aerosol chloride, sulfite and ammonium, respectively, via photochemical reactions.

Total daily dicarboxylic acid concentration was 979.1 ± 358.6 ng m⁻³ (1.32% by PM2.5 mass) during the PM episode compared to 656.0 ± 277.4 ng m⁻³ (1.17% by PM2.5 mass) during non-episodic pollution. Oxalic acid was the dominant acid, at 460.4 ± 203.7 ng m⁻³ and 70.2% of the total during non-episodic pollution and 795.1 ± 303.6 ng m⁻³ and 81.2% during the PM episode. It was found in all samples with an average concentration 2.4–4.3 times higher than other dicarboxylic acids. This observation is in agreement with those reported by Kawamura et al. (1995, 1996), Dabek-Zlotorynska et al. (2001) and Wang et al. (2002). Next was succinic acid, with an average concentration of 774 ± 45.1 ng m⁻³ (11.8% by total dicarboxylic acids in PM2.5) during non-episodic pollution and 61.2 ± 25.8 ng m⁻³ (6.3%) during the PM episode, followed by maleic acid (647 ± 30.7 ng m⁻³ and 9.9% by total dicarboxylic acids in PM2.5 during non-episodic pollution and 50.7 ± 15.7 ng m⁻³ and 5.2% during the PM period). Oxalic acid concentration increased 72.7% from non-episodic to PM episode aerosol while concentrations of succinic acid and maleic acid decreased 20.9% and 21.6%, indicating that large quantities of succinic acid and malonic acid were converted to oxalic acid in PM episode aerosol. The lowest concentrations of any dicarboxylic acid were of tartaric acid, averaging only 4.0–4.7 ng m⁻³ or 0.48–0.61% of the total dicarboxylic acid.

In addition to succinic acid, the most abundant C₄ diacid was malic acid with average concentrations of 36.3 ± 20.6 ng m⁻³ in non-episodic aerosol and 41.7 ± 23.5 ng m⁻³ during the PM episode. Maleic acid, a cis-unsaturated C₄ diacid, was abundant in both aerosols and this is attributed to the photochemical oxidation of aromatic hydrocarbons (Kawamura et al., 1996). During PM episode and associated with an increase in primary pollutants from traffic emissions, maleic acid concentrations increased significantly from an average non-episodic concentration of 13.2 ng m⁻³ to 25.8 ng m⁻³, demonstrating that traffic-related aromatic hydrocarbons in the atmosphere are subject to photochemical reactions that produce and increase the concentration of maleic acid.

During non-episodic pollution nighttime/daytime concentration ratios were <1.0 for all gaseous pollutants and aerosol species other than HNO₂ and non-methane hydrocarbons (NMHCs), as a result of increased anthropogenic activity and photochemical reactions of daytime. HNO₂ and NMHCs can only be converted into secondary products such as HNO₃ and O₃ in the presence of sunlight and therefore accumulated at nighttime leading to higher concentrations. Due to photo lytic reactions HNO₂ and NMHCs show higher nighttime concentrations during PM episode (Lin et al., 2006; Harrison et al., 1996), while other gaseous pollutants have higher concentrations during daytime. Ren et al. (2003) suggested that higher HNO₃ level...
former is converted into aerosol NO$_3$ in PM episode aerosol.

PCA revealed that non-episodic pollution aerosol contained three dicarboxylic acids (succinic, malonic, and oxalic) and three inorganic salts (NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$), whereas PM episode aerosol contained four dicarboxylic acids (succinic, malic, malonic, and oxalic) and two inorganic (NH$_4^+$ and SO$_4^{2-}$).

Total dicarboxylic acid concentration in PM episode aerosol, at 979.1 ± 358.6 ng m$^{-3}$ (1.32% by PM$_{2.5}$ mass), was 49.3% higher than in non-episodic aerosol, at 656.0 ± 277.4 ng m$^{-3}$ (1.17% by PM$_{2.5}$ mass). Oxalic acid was the dominant species, followed by succinic acid and malonic acid. Tartaric acid was present in the smallest amounts, averaging only 4.0–4.7 ng m$^{-3}$. Further, the daily concentration of oxalic acid in PM episode aerosol was 72.7% higher than in non-episodic aerosol, while concentrations of succinic acid and malonic acid were 20.9% and 21.6% lower, respectively, revealing that the majority of succinic acid and malonic acid was converted to oxalic acid.

Dicarboxylic acid concentrations peaked at night in PM episode aerosol, due to accumulation of daytime oxalic acid combined with low wind velocity and low mixing layer height at this time, 1.09 ± 0.25 m s$^{-1}$ and 376 ± 244 m, respectively, compared with daytime equivalents of 1.58 ± 0.17 m s$^{-1}$ and 1156 ± 399 m. Oxalic acid concentrations rose particularly strongly, up 71.9% from daytime levels to 1005.3 ± 302.9 ng m$^{-3}$ and to 81.3% of the total dicarboxylic acid. SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ were also major contributors to nighttime PM episode aerosol. The mass ratio of oxalic acid to sulfate at this time was as high as 60.3%$_{\text{ox}}$ substantially higher than the 44.5%$_{\text{ox}}$ in non-episodic aerosol. High correlations between Cl$^-$, K$^+$, and Na$^+$ and oxalic acid plus backward trajectory data indicate that biomass burning in paddy fields may contribute to oxalic acid content in PM episode aerosol in the study area, especially during nighttime.

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