Vertical distribution of particle-phase dicarboxylic acids, oxoacids and \(\alpha\)-dicarbonyls in the urban boundary layer based on the 325 m tower in Beijing

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Abstract. Vertical distributions of dicarboxylic acids, oxoacids, \(\alpha\)-dicarbonyls and other organic tracer compounds in fine aerosols (PM\(_{2.5}\)) were investigated at three heights (8, 120 and 260 m) based on a 325 m meteorological tower in urban Beijing in the summer of 2015. Results showed that the concentrations of oxalic acid (C\(_2\)), the predominant diacid, were more abundant at 120 m (210 \(\pm\) 154 ng m\(^{-3}\)) and 260 m (220 \(\pm\) 140 ng m\(^{-3}\)) than those at the ground surface (160 \(\pm\) 90 ng m\(^{-3}\)). Concentrations of phthalic acid (Ph) decreased with the increase in height, indicating that local vehicular exhausts were the main contributor. Positive correlations were noteworthy for C\(_2\)/total diacids with mass ratios of C\(_2\) to main oxoacids (Pyr and \(\omega\)C\(_2\)) and \(\alpha\)-dicarbonyls (Gly and MeGly) in polluted days (0.42 \(\leq\) \(r^2\) \(\leq\) 0.65), especially at the ground level. In clean days, the ratios of carbon content in oxalic acid to water-soluble organic carbon (C\(_2\)−C/WSOC) showed larger values at 120 and 260 m than those at the ground surface. However, in polluted days, the C\(_2\)−C/WSOC ratio mainly reached its maximum at ground level. These phenomena may indicate the enhanced contribution of aqueous-phase oxidation to oxalic acid in polluted days. Combined with the wind field, total diacids, oxoacids and \(\alpha\)-dicarbonyls decreased by 22\%–58\% under the control on anthropogenic activities during the 2015 Victory Parade period. Furthermore, the positive matrix factorisation (PMF) results showed that the secondary formation routes (secondary sulfate formation and secondary nitrate formation) were the dominant contributors (37\%–44\%) to organic acids, followed by biomass burning (25\%–30\%) and motor vehicles (18\%–24\%). In this study, the organic acids at ground level were largely associated with local traffic emissions, while the long-range atmospheric transport followed by photochemical ageing contributed more to diacids and related compounds in the urban boundary layer than the ground surface in Beijing.

1 Introduction

Organic aerosols typically make up 20\%–50\% of the mass concentrations of atmospheric fine aerosols (PM\(_{2.5}\)) at continental mid-latitudes. A large portion of organic aerosol is water soluble, contributing 20\%–75\% to the carbon mass of aerosols emitted from uncompleted combustion sources (Falkovich et al., 2005; Pathak et al., 2011; Graham et al., 2002). Low molecular weight (LMW) dicarboxylic acids and
related compounds are water soluble and are found abundantly in urban (Wang et al., 2012; Zhao et al., 2018), mountainous (Kawamura et al., 2013; Cong et al., 2015), remote marine (Mochida et al., 2007; H. Wang et al., 2006; Fu et al., 2013a; Yang et al., 2020), and Arctic (Kawamura et al., 2010, 1996) aerosols and also in snow, rain, and fog waters (Sempére and Kawamura, 1994; Kawamura et al., 2001; Zhao et al., 2019a, b).

Owing to high water solubility and hygroscopicity, dicarboxylic acids play an important role in aerosol chemistry via atmospheric processing (e.g. iron-catalysed photolysis and secondary component formation) (Laskin et al., 2012; Drozd et al., 2014; Pavuluri and Kawamura, 2012) and in the Earth’s climate by enhancing hygroscopic behaviour of aerosols to act as cloud condensation nuclei (Andreae and Rosenfeld, 2008; Bilde et al., 2015; Kanakidou et al., 2005). Dicarboxylic acids and related compounds are largely produced by secondary oxidation pathways, including photochemical (Kawamura and Gagosian, 1987; Pavuluri et al., 2015) and aqueous oxidation (Carlton et al., 2007; Ervens and Volkamer, 2010) in the atmosphere. In addition, they are directly emitted from natural emissions such as marine plankton activities (Rinaldi et al., 2011; Tedetti et al., 2006) and anthropogenic sources including biomass burning (Legrand and Angelis, 1996; Narukawa et al., 1999), vehicular exhausts and fossil fuel combustion (Rogge et al., 1993; Kawamura and Kaplan, 1987).

Previous field measurements mostly focused on organic aerosols at the ground surface. Vertical measurements have been conducted at a global scale since the early 2010s (Han et al., 2015; Hu et al., 2011; Andreae et al., 2012; Chi et al., 2013). The Amazon Tall Tower Observatory (ATTO) was established ~150 km northeast of the city of Manaus, Brazil for comprehensive studies of meteorology (Morton et al., 2014; Quesada et al., 2012; Sun et al., 2011), trace gases (Andreae et al., 2012; Trebs et al., 2012), aerosol compositions (Andreae et al., 2012; Yáñez-Serrano et al., 2015; Yáñez-Serrano et al., 2018; Rizzo et al., 2013; Saturno et al., 2018), and ecology (Pühlker et al., 2019; Quesada et al., 2012) to investigate long-term trends of the Amazonian hydrological and biogeochemical cycling linked with the human perturbation (Andreae et al., 2015). The 304 m tower of the Zotino Tall Tower Observatory (ZOTTO) in central Siberia serves as a basis for monitoring biogeochemical gases (Chi et al., 2013; Mikhailov et al., 2017; Winderlich et al., 2010), aerosol characteristics (Chi et al., 2013; Heintzenberg et al., 2011; Mikhailov et al., 2017) and atmospheric transport (Mikhailov et al., 2017) at a wide range of spatial and temporal scales.

Beijing, the capital of China, is surrounded by highly industrialised and urbanised areas (Xia et al., 2007) and has encountered severe haze events, especially in winter (Huang et al., 2014; Wang et al., 2016; Xie et al., 2020). The haze pollution in Beijing is characterised by regional transport (Zhao et al., 2013) followed by the accumulation of local emissions and is mainly driven by secondary aerosol formation, which accounts for 30%–77% of total aerosol mass and 44%–71% of organic aerosol mass in the fine mode (Huang et al., 2014). Field measurements in urban regions at ground level are heavily influenced by local sources, which bring uncertainties to quantify the relative contribution of regional transport to air quality. However, the vertical analysis can largely make up for the deficiency of surface observation and provide more physical and chemical information about the atmospheric process and structure. Guo et al. (2016) found that the thermal stratification was clearly observed for the urban boundary layer in severe haze events, and the vertical distributions of air pollutants were largely affected by the structure of the atmospheric boundary layer. Guinot et al. (2006) reported that the urban canopy layer (60–90 m) in Beijing is associated with the height of buildings and the mean width of the street, both factors that direct influence local turbulence and pollutant dispersion. Furthermore, vertical measurements of the extinction coefficient, gas precursors and aerosol compositions (e.g. organic compounds, sulfate and nitrate) (Wang et al., 2018; Zhang et al., 2017) have also been conducted in detail at the 325 m meteorological tower in Beijing to better understand the formation and evolution mechanisms of haze events. High loadings of dicarboxylic acids in the atmosphere are closely linked to substantial anthropogenic activities (Kawamura et al., 2013; G. Wang et al., 2012, 2006b; Zhao et al., 2018). Understanding of the vertical characteristics of organic components in aerosols is important to elaborate the oxidation mechanism and their interactions with the lower boundary layer in haze events. The vertical investigation of organic aerosols at a molecular level is far from complete, especially for diacids and related compounds.

This study investigates, for the first time, the vertical distributions of LMW dicarboxylic acids, oxoacids and α-dicarboxyls in PM$_{2.5}$ collected at Beijing during August to September 2015, along with analyses of ions, water-soluble organic carbon (WSOC), organic carbon (OC), elemental carbon (EC), and tracer compounds like levoglucosan (biomass burning tracer) and isoprene-oxidation products. The sources, aerosol chemistry, atmospheric long-range transport and the effects of emission control on anthropogenic activities are discussed.

2 Experimental methods

2.1 Aerosol sampling

The three-layer sampling was performed at the rooftop of a two-storey building (ground level, 8 m a.g.l.) and two platforms (120 and 260 m a.g.l.) on the 325 m meteorological tower in the campus of the Institute of Atmospheric Physics, Chinese Academy of Sciences (39°58′28″N, 116°22′16″E) (Fig. 1), a typical urban location influenced by traffic.
and cooking emissions in Beijing (Sun et al., 2012; Yue et al., 2017). PM$_{2.5}$ samples were collected onto pre-heated (450°C, 6 h) quartz-fibre filters ( Pallflex) by using three high-volume air samplers (TISCH, USA), which were deployed directly at the ground surface (8 m), 120 m, and 260 m on the tower. All of the samplers were run at an airflow rate of 1.0 m$^3$ min$^{-1}$ for 23 h during the 2015 Victory Parade period (from 15 August to 10 September, n = 77). The sampling time was divided into the first non-restriction period, the restriction period and the second non-restriction period. Field blanks were collected in each period at three sampling layers by placing filters on the samplers for half a minute without pumping. After the campaign, all filters were stored at -20°C until analysis.

2.2 Analyses of diacids and related compounds

The quantitative determinations of diacids, oxoacids and α-dicarboxyls in PM$_{2.5}$ samples followed the analytical measurements as described elsewhere (Kawamura and Ikushima, 1993; Kawamura and Bikkina, 2016). Briefly, 3.14 cm$^2$ of each filter sample was extracted with Milli-Q water under ultrasonication for water-soluble organic acids. Next, these extracts were concentrated to dryness using a rotary evaporator under vacuum and reacted with 14% BF$_3$/n-butanol at 100°C for 1 h. Finally, the derivatives were dissolved in n-hexane and were analysed by using a gas chromatograph (GC, Agilent 6980) equipped with an HP-5 column (0.2 mm × 25 m, 0.5 µm film thickness) and an flame ionization detector (FID) detector. The same analytical method was also used for field blank filters. The concentrations of targeted organic acids in this study were corrected for the field blanks, and their recoveries were > 85%.

2.3 Determinations of organic tracers

Small discs of filters were extracted with dichloromethane / methanol (2 : 1, v/v). The extracts were filtered through quartz wool, concentrated under vacuum and blown to dryness. Derivatisation was the reaction with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) containing pyridine (5 : 1) and 1% trimethylsilyl chloride at 70°C for 3 h. Finally, the derivatives were added with n-hexane containing the internal standard of C$_{13}$ n-alkane (1.43 ng µL$^{-1}$) before the gas chromatography / mass spectroscopy (GC / MS). The GC / MS analysis was performed using a Hewlett-Packard model 7890A GC coupled to an Agilent model 5975C mass-selective detector (MSD). The recoveries of levoglucosan and isoprene secondary organic aerosol (SOA) tracers were better than 80%, and both concentrations were corrected for the field blanks. Detailed analytical methods can be found in previous studies (Fan et al., 2020; Fu et al., 2013b).

2.4 Inorganic ions, WSOC, OC and EC measurements

For the analysis of ions, a filter aliquot of each sample was extracted by ultrapure Milli-Q water under ultrasonication. Then the extracts were determined for cations (Na$^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}$) and anions (F$^-, Cl^-, NO_3^-, SO_4^{2-}, NO_3^-$) via ion chromatography ( Dionex Aquion, Thermo Scientific, America). Data of cations and anions were determined simultaneously. The extraction step of WSOC is similar to that of ions, but the material of the extraction bottle is glass. Next, the extracts were measured for WSOC by a Shimadzu TOC-V CPH total carbon analyzer with the limit of detection of 0.1 µg C m$^{-3}$ (Kawamura et al., 2013). OC and EC were determined using thermal optical reflectance (TOR) following the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol on a DRI Model 2001 Thermal/Optical Carbon Analyzer (Chow et al., 2005). The limit of detection for the carbon analysis is 0.8 and 0.4 µg C cm$^{-2}$ for OC and EC, respectively, with a precision better than 10% for total carbon (TC). Mass concentrations of ions, WSOC, OC and EC reported in the present study were all corrected for the field blanks.

2.5 FLEXPART-WRF modelling

The Lagrangian particle dispersion model FLEXPART-WRF can be used to quantify the impact of potential source regions (Brioude et al., 2013). Atmospheric particles were released at the height of 8 m at the sampling site every 3 h for a day. Backward simulation was run for 3 d and the residence time of aerosols was calculated.

2.6 Meteorological parameters

The meteorological data, such as temperature (T), relative humidity (RH) and wind (wind speed and direction), were also obtained at same locations, except for the highest sampling site (280 m a.g.l.). The wind speed and direction at ground level were almost same in the field campaign (Fig. S1a in the Supplement). During the restriction period in Beijing, the organic compounds at 120 m were largely influenced by clean northern wind, while the aerosol particles at 280 m were mainly affected by the northwestern wind and accompanied by the influence of polluted southern and southeastern winds. In contrast with the second non-restriction period, the air quality at 120 and 280 m were largely associated with southwestern wind from industrialisations in the first non-restriction episode.

3 Results and discussion

3.1 OC and EC

EC is a useful tracer for incomplete combustion emissions, including vehicle exhausts, biomass burning and fossil
fuel combustion (Turpin and Huntzicker, 1991; Bond et al., 2013), while OC is either emitted from primary sources or produced by secondary oxidation pathways in the atmosphere (Clarke et al., 2004). Previous studies found that relatively large OC / EC ratio is associated with biomass burning (7.3), whereas a lower value is linked to vehicular exhausts (1.1) (Sandradewi et al., 2008). Watson et al. (2001) reported an OC / EC ratio of 4.0 attributed to fossil fuel combustion.

Figure 2 shows the daily variations in OC, EC, OC / EC, SOC, POC, and SOC / POC in PM$_{2.5}$ collected at ground level, 120 m, and 260 m in summer. During the field campaign, the concentration level of EC was considerably lower than OC, but their variation trends were similar (Fig. 2a and b). The average value of OC / EC ratios at ground surface and upper layers was nearly constant, which showed relative difference < 0.5 and a slightly higher mean value (7.5 ± 1.5) at 8 m (Table S1). Air quality in the North China Plain is considerably influenced by biomass burning after the summer harvest (Fu et al., 2012; Sun et al., 2016; Desyaterik et al., 2013). The variations in OC / EC ratios in this study covered the value known for motor exhausts, fossil fuel combustion and biomass burning sources (Fig. 2c). Good linear relationships were observed for OC with EC (0.59 ≤ r$^2$ ≤ 0.78) (Fig. 3), which indicated an important anthropogenic combustion source to OC.

Secondary organic carbon (SOC) is derived from various physical and chemical transformation processing, like gas–particle partitioning of semi-volatile compounds (Hallquist et al., 2009). Owing to the complexities of SOC formation routes, there is no valid direct analytical measurement to determine the atmospheric concentration of SOC. Primary organic carbon (POC) is directly emitted from natural and anthropogenic emissions (Blando and Turpin, 2000). Because EC only originates from primary emissions and is inert in the atmosphere, it is often used as a marker to estimate POC concentration in the atmosphere (Turpin and Huntzicker, 1991). By this approach, the concentrations of SOC and POC can be evaluated from the following equations (Turpin and Huntzicker, 1995; Strader et al., 1999; Castro et al., 1999; Chu, 2005; Yu et al., 2009; Day et al., 2015):

\[
\text{POC} = (\text{OC/EC})_{\text{min}} \times \text{EC},
\]

(1)

\[
\text{SOC} = \text{OC}_{\text{total}} - \text{POC}.
\]

(2)

The (OC / EC)$_{\text{min}}$ ratios were the minimum OC / EC ratios calculated at each sampling height, and OC$_{\text{total}}$ were the mass concentrations of OC. The concentration of POC calculated using the first equation means the primary carbonaceous
The molecular distributions of dicarboxylic acids were characterised by the dominance of oxalic acid (C$_2$), followed by malonic (C$_3$) and succinic (C$_4$) acids (Fig. 4). Their concentrations were higher at upper layers (Fig. S3h–j) with similar diurnal trends (Fig. S3a–c), illustrating C$_2$, C$_3$, and C$_4$ diacids derived from common primary sources and/or secondary oxidation pathways. C$_3$ diacid is mainly formed via hydrogen abstraction of OH radicals on C$_4$ diacid, followed by the decarboxylation reaction (Kawamura and Ikushima, 1993). The mass concentration ratio of malonic acid to succinic acid is a useful marker to estimate the relative contribution of primary production and photochemical formation to organic aerosols. The C$_3$/C$_4$ ratio shows a characteristically lower value for primary emissions (e.g. vehicular exhausts: 0.25–0.44) (Kawamura and Ikushima, 1993), whereas it has a larger value more than or equal to unity in aged aerosol (Kawamura and Sakaguchi, 1999). In this paper, the mean C$_3$/C$_4$ values at 260 m (1.2 ± 0.21) were slightly larger than those at ground surface (1.1 ± 0.2) and 120 m (1.1 ± 0.14) (Table S1), implying that organic aerosols at 260 m were influenced by photochemical formation via regional transport. Adipic acid (C$_6$), the major oxidation product of 2-methylglutaric (iC$_6$) from anthropogenic cyclic olefins, while, the relative abundances of total diacids in carbonaceous fractions (organic carbon and total carbon) reached maximum values at 260 m (Table S1). Such vertical phenomena were also observed for total oxoacids and α-dicarbonyls, suggesting that the ageing level of diacids and related compounds slightly increased at 260 m in the urban troposphere.

3.2 Organic molecular characterisation

Table 2 shows the concentration ranges of dicarboxylic acids, oxoacids and α-dicarbonyls with the mean values. Mean concentrations of total diacids at 120 m (370 ± 255 ng m$^{-3}$) and 260 m (380 ± 216 ng m$^{-3}$) were almost the same, which were larger than that at ground level (285 ± 143 ng m$^{-3}$).

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Table 1. Vertical concentrations (µg m\(^{-3}\)) of OC, EC, SOC, POC and TC in PM\(_{2.5}\) aerosols collected at Beijing.

<table>
<thead>
<tr>
<th>Species</th>
<th>Ground level (n = 27)</th>
<th>120 m (n = 25)</th>
<th>260 m (n = 25)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean/SD</td>
<td>Range</td>
</tr>
<tr>
<td>OC</td>
<td>3.1–15</td>
<td>6.6/2.5</td>
<td>2.8–18</td>
</tr>
<tr>
<td>EC</td>
<td>0.6–2.6</td>
<td>0.9/0.5</td>
<td>0.4–3.2</td>
</tr>
<tr>
<td>SOC</td>
<td>0.0–5.0</td>
<td>2.0/1.1</td>
<td>0.0–12</td>
</tr>
<tr>
<td>POC</td>
<td>2.8–13</td>
<td>4.7/2.3</td>
<td>1.1–8.2</td>
</tr>
<tr>
<td>TC</td>
<td>3.6–17</td>
<td>7.6/3.0</td>
<td>3.6–20</td>
</tr>
</tbody>
</table>

Figure 4. Molecular distributions of dicarboxylic acids and related compounds in the PM\(_{2.5}\) samples collected at the tower from 15 August to 10 September 2015 in Beijing.

(Hamilton et al., 2006; Müller et al., 2007) and intermediate of relatively long-chain diacids, was more abundant at upper heights, especially at 260 m (Fig. 4). Good correlations were observed for C\(_6\)/iC\(_6\) with C\(_6\)/total diacids at the ground level \((r^2 = 0.66)\) and 260 m \((r^2 = 0.94)\) (Fig. S4a), which indicated that the photooxidation of cyclic olefins from anthropogenic sources is an important contributor to adipic acid in Beijing. Azelaic acid (C\(_9\)) is a major oxidation product of unsaturated fatty acids (Matsunaga et al., 1999) from meal cooking (Rogge et al., 1991) (Stephanou and Strati-gakis, 1993), biomass burning (Ballentine et al., 1998), marine plankton activities (Mochida et al., 2007) and terrestrial higher plants emissions (Ballentine et al., 1998). Meanwhile, Kawamura and Kaplan (1987) reported that vehicular emission is also an important source to azelaic acid. The relative abundance of C\(_9\) in total diacids (C\(_9\)/total diacids) showed the largest value \((0.07 ± 0.02)\) at ground level (Table S1), implying that C\(_9\) may be derived from the photooxidation of corresponding hydrocarbons from local vehicular emissions.

Positive linear correlations were found between C\(_6\)/C\(_9\) and C\(_6\)/total diacids at 120 m \((r^2 = 0.51)\) and 260 m \((r^2 = 0.86)\) (Fig. S4b), suggesting that the breakdown of C\(_9\) carbon chain to form C\(_6\) may enhance during its upward transport.

Phthalic acid (Ph) was the fourth abundant diacid in this study (Fig. 4), which can be emitted from motor vehicles and fossil fuel combustion or secondarily oxidised from aromatic hydrocarbons like naphthalene from coal and biofuel combustions (Kautzman et al., 2010; G. Wang et al., 2006a). Mass concentrations of Ph decreased with the sampling heights, illustrating that vehicular exhausts at the ground level were a major source to phthalic acid. Terephthalic acid (tPh), an isomer of Ph, is a tracer of plastic burning in municipal wastes (Fu et al., 2010; Kawamura and Pavuluri, 2010; Simoneit et al., 2005). Contrary to the vertical distribution of Ph, the average concentration of tPh at ground level \((12 ± 10 \text{ ng m}^{-3})\) was slightly lower than those at 120 m \((15 ± 15 \text{ ng m}^{-3})\) and 260 m \((13 ± 11 \text{ ng m}^{-3})\).
Table 2. Vertical concentrations (ng m\textsuperscript{-3}) of dicarboxylic acids, oxoacids and α-dicarbonyls collected in Beijing from 15 August to 10 September 2015.

<table>
<thead>
<tr>
<th>Species</th>
<th>Ground level (n = 27)</th>
<th>120 m (n = 25)</th>
<th>260 m (n = 25)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range Mean/SD</td>
<td>Range Mean/SD</td>
<td>Range Mean/SD</td>
</tr>
<tr>
<td><strong>Dicarboxylic acids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxalic, C\textsubscript{2}</td>
<td>46–432 160/90</td>
<td>52–570 210/154</td>
<td>60–650 220/140</td>
</tr>
<tr>
<td>Malonic, C\textsubscript{3}</td>
<td>7.1–49 22/10</td>
<td>8.6–82 32/25</td>
<td>11–75 34/17</td>
</tr>
<tr>
<td>Succinic, C\textsubscript{4}</td>
<td>7.3–46 21/10</td>
<td>8.7–87 30/21</td>
<td>9.2–76 31/18</td>
</tr>
<tr>
<td>Glutaric, C\textsubscript{5}</td>
<td>3.2–17 6.5/3.2</td>
<td>2.8–29 9.2/6.4</td>
<td>3.2–25 9.5/5.2</td>
</tr>
<tr>
<td>Adipic, C\textsubscript{6}</td>
<td>2.5–14 5.3/2.5</td>
<td>3.7–21 8.2/4.2</td>
<td>4.8–21 13/5.0</td>
</tr>
<tr>
<td>Pimeric, C\textsubscript{7}</td>
<td>0.7–4.7 1.6/1.1</td>
<td>0.2–7.5 2.5/2.1</td>
<td>0.4–9.4 2.5/2.0</td>
</tr>
<tr>
<td>Suberic, C\textsubscript{8}</td>
<td>BDL–0.3 BDL/0.1</td>
<td>BDL–0.8 0.1/0.2</td>
<td>BDL–1.2 0.2/0.4</td>
</tr>
<tr>
<td>Azelaic, C\textsubscript{9}</td>
<td>12–34 18/4.8</td>
<td>4.9–53 21/10</td>
<td>5.6–38 17/7.6</td>
</tr>
<tr>
<td>Decanedioic, C\textsubscript{10}</td>
<td>0.4–3.1 1.3/0.7</td>
<td>0.2–4.2 1.6/1.0</td>
<td>BDL–3.7 1.5/0.8</td>
</tr>
<tr>
<td>Undecanedioic, C\textsubscript{11}</td>
<td>1.2/0.6</td>
<td>0.4–6.7 1.5/1.4</td>
<td>0.4–5.3 1.4/1.0</td>
</tr>
<tr>
<td>Dodecanedioic, C\textsubscript{12}</td>
<td>BDL–0.2 BDL</td>
<td>BDL–0.7 0.1/0.2</td>
<td>BDL–0.7 0.2/0.2</td>
</tr>
<tr>
<td>Methylmalonic, iC\textsubscript{4}</td>
<td>0.4–2.8 0.9/0.5</td>
<td>0.2–4.1 1.2/0.8</td>
<td>0.5–2.3 1.1/0.5</td>
</tr>
<tr>
<td>Methylsuccinic, iC\textsubscript{5}</td>
<td>0.5–3.8 1.6/0.8</td>
<td>0.6–7.9 2.2/1.8</td>
<td>0.7–6.3 2.2/1.4</td>
</tr>
<tr>
<td>2-methylglutaric, iC\textsubscript{6}</td>
<td>BDL–1.7 0.5/0.4</td>
<td>0.3–4.8 1.0/0.9</td>
<td>0.3–3.9 1.0/0.8</td>
</tr>
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<td>Maleic, M</td>
<td>0.7–2.6 1.3/0.5</td>
<td>0.5–6.0 1.8/1.2</td>
<td>0.9–4.3 2.0/0.9</td>
</tr>
<tr>
<td>Fumaric, F</td>
<td>0.2–3.0 1.4/0.7</td>
<td>0.2–6.3 1.5/1.5</td>
<td>0.5–5.8 1.6/1.3</td>
</tr>
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<td>Methylmaleic, mM</td>
<td>0.7–3.0 1.3/0.5</td>
<td>0.5–7.4 1.9/1.6</td>
<td>0.6–4.2 1.9/1.0</td>
</tr>
<tr>
<td>Phthalic, Ph</td>
<td>8.3–61 26/11</td>
<td>8.6–51 23/11</td>
<td>8.2–40 21/10</td>
</tr>
<tr>
<td>Isophthalic, iPh</td>
<td>0.3–1.3 0.6/0.3</td>
<td>0.2–3.0 1.2/1.0</td>
<td>BDL–8.4 1.0/1.7</td>
</tr>
<tr>
<td>Terephthalic, iPh</td>
<td>1.8–49 6/10</td>
<td>3.4–64 15/15</td>
<td>2.8–49 13/11</td>
</tr>
<tr>
<td>Malic, hC</td>
<td>0.5–9.6 2.7/2.2</td>
<td>0.6–13 4.0/3.4</td>
<td>0.6–12 4.1/2.5</td>
</tr>
<tr>
<td>Oxalonic, kC\textsubscript{3}</td>
<td>0.5–9.7 3.0/2.2</td>
<td>0.4–13 4.4/3.6</td>
<td>1.1–12 5.0/2.6</td>
</tr>
<tr>
<td><strong>Oxocarboxylic acids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyruvic, Pyr</td>
<td>0.6–17 5.6/3.8</td>
<td>0.8–30 10/9.1</td>
<td>0.7–30 8.5/6.8</td>
</tr>
<tr>
<td>Glyoxyl, ωC\textsubscript{2}</td>
<td>0.5–44 15/11</td>
<td>2.6–80 21/19</td>
<td>2.5–65 20/17</td>
</tr>
<tr>
<td>3-oxopropanoic, ωC\textsubscript{3}</td>
<td>0.9–82 2.9/1.8</td>
<td>1.3–11 4.1/3.1</td>
<td>1.0–12 3.7/2.4</td>
</tr>
<tr>
<td>4-oxobutyric, ωC\textsubscript{4}</td>
<td>1.0–11 4.5/2.5</td>
<td>2.7–21 7.3/4.4</td>
<td>1.9–17 6.9/3.8</td>
</tr>
<tr>
<td>5-oxopentanoic, ωC\textsubscript{5}</td>
<td>0.3–3.4 1.5/0.7</td>
<td>0.6–4.7 2.0/1.1</td>
<td>0.7–3.9 1.9/0.9</td>
</tr>
<tr>
<td>7-oxooctanoic, ωC\textsubscript{7}</td>
<td>1.5–5.4 3.2/1.2</td>
<td>1.3–8.6 4.2/2.2</td>
<td>1.8–8.0 4.0/1.5</td>
</tr>
<tr>
<td>8-oxooctanoic, ωC\textsubscript{8}</td>
<td>0.7–8.7 4.0/1.9</td>
<td>0.8–15 5.0/3.3</td>
<td>0.1–15 5.0/3.4</td>
</tr>
<tr>
<td>9-oxononanoic, ωC\textsubscript{9}</td>
<td>0.2–2.4 1.2/0.6</td>
<td>0.3–4.9 1.2/1.0</td>
<td>BDL–4.8 1.4/1.2</td>
</tr>
<tr>
<td>Total oxacids 7.3–95 38/22</td>
<td>110–945 370/255</td>
<td>126–1001 380/216</td>
<td></td>
</tr>
<tr>
<td><strong>α-dicarbonyls</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyoxal, Gly</td>
<td>0.5–6.1 2.2/1.2</td>
<td>1.0–13 3.3/2.7</td>
<td>0.8–9.8 3.4/2.3</td>
</tr>
<tr>
<td>Methylglyoxal, MeGly</td>
<td>1.4–12 4.1/2.6</td>
<td>1.0–20 5.2/4.0</td>
<td>1.3–22 6.7/5.2</td>
</tr>
<tr>
<td>Total dicarbonyls 1.8–17 6.3/3.7</td>
<td>2.2–33 8.5/6.6</td>
<td>2.0–31 10/7.4</td>
<td></td>
</tr>
</tbody>
</table>

BDL stands for below detection limit, which is ca. 0.005 ng m\textsuperscript{-3} for the target compounds.

Oxocarboxylic acids, the intermediates of the oxidation of mono-carboxylic acids, can further be photochemically oxidised to form diacids (Warneck, 2003; Carlton et al., 2007). The glyoxylic acid (ωC\textsubscript{2}) is the dominant oxoacid, followed by pyruvic acid (Pyr) (Fig. 4). Both acids were more abundant at upper layers. Concentrations of total dicarbonyls varied from 1.8 to 33 ng m\textsuperscript{-3} with a maximum value (10 ± 7.4 ng m\textsuperscript{-3}) at 260 m. Glyoxal (Gly) and methylglyoxal (MeGly), the two smallest α-dicarbonyls, are mainly produced by the photooxidation of biogenic (Zimmermann and Poppe, 1996; Fick et al., 2004; Ervens et al., 2004) (e.g. isoprene and monoterpenes) and anthropogenic (Volkamer et al., 2003; Carlton et al., 2007).
et al., 2001) (e.g. aromatics, acetone and acetylene) volatile organic compounds (VOCs), and both are important precursors to form less volatile organic acids, such as \( \omega C_2 \), Pyr (Lim et al., 2005). Concentrations of Gly and McGly increased with the sampling heights, and their concentration variations were similar to those of \( \omega C_2 \) and Pyr (Fig. S3d–g), illustrating that \( \omega C_2 \), Pyr and \( \alpha \)-dicarbonyls had similar sources and/or formation pathways.

3.3 Restriction vs. non-restriction periods

Owing to the regional scale of haze events in China, the Chinese government took measures to cut down anthropogenic emissions in Beijing and surrounding areas to ensure good air quality during the 2015 Victory Parade period. These strict restrictions included the stopping of construction and demolition activities, banning vehicles with odd and even plate numbers on alternate days, forbidding open burnings, and shutting down factories and power plants in Tianjin City, Inner Mongolia Autonomous Region, Hebei, Shandong, Shanxi, and Henan provinces. The restriction time (R) started from 20 August to 3 September 2015. Before and after this period were defined as the first (N1) and second (N2) non-restriction periods, respectively. The concentration ratios of selected organic compounds during the restriction to non-restriction periods (R/N) were calculated (Fig. S5). The ratio of less than unity indicates that the control on the air quality effectively improves in Beijing. Both the primary incomplete combustion sources and the wind are two key influential factors (Liang et al., 2017; Xu et al., 2017). In this study, the R/N ratios of OC, EC, POC, total diacids, total oxoacids and dicarbonyls were lower than unity, but their R/N2 ratios were larger than corresponding R/N1 values (Fig. S5). These results showed that the improvement of air quality in Beijing was mainly influenced by the control on anthropogenic emissions, followed by the wind (Liang et al., 2017; Xu et al., 2017). The lower concentrations of organic compounds in the second non-restriction period than those in the first non-restriction period were attributed to the increased influence of clean northwesterly winds (Fig. S1a). The wind direction at 120 m was similar to that at 260 m in the restriction period compared to 120 m in the first non-restriction period, while organic aerosols at 260 m were largely influenced by the northwesterly wind and accompanied by the influence of polluted southerly and southeasterly winds. Photochemical production of diacids and related compounds can occur in the atmospheric long-range transport.

Similarly, the \( R/N \) ratios for most diacids and related compounds were lower than unity (Fig. 6), especially for \( \omega C_2 \), Pyr, tPh and \( \alpha \)-dicarbonyls. Owing to the influence of wind, the decreased level of main diacids, oxoacids and \( \alpha \)-dicarbonyls (20%–69%) were stronger during the first non-restriction period than that (10%–55%) in the second non-restriction period. These phenomena indicated that anthropogenic emissions largely contributed to diacids and related organic precursors in Beijing. Furthermore, the decreased orders of most diacids and related compounds were ground level < 120 < 260 m in the restriction period compared to the non-restriction periods (Table S2). This also supported the conclusion that a upward transport of vehicular emissions existed, and organic aerosols at upper layers were more attributed to regional transport.

3.4 Possible formation pathways of organic acids

To better estimate the relative contribution of primary sources and photochemical transformation to diacids and related compounds, linear regression analyses for selected marker compounds (Fig. S2) and diagnostic ratios (Fig. 7) were employed in this study. Levoglucosan is an important tracer of biomass burning (Simoneit, 2002). The isoprene SOA tracers are the sum of six oxidation products of isoprene, including 2-methylglyceric acid, C5-alkene triols (cis-2-methyl-1,3,4-trihydroxy-1-butane, trans-2-methyl-1,3,4-trihydroxy-1-butene and 3-methyl-2,3,4-trihydroxy-1-butane), 2-methylfurfural and 2-methylfurfuril (Claeys et al., 2004; Fan et al., 2020). Isoprene, the major biogenic volatile organic compound, is abundantly derived from plants emissions (Sharkey et al., 2007). Compared to total \( \alpha \)-dicarbonyls, better correlations were found between isoprene SOA tracers and total diacids \((0.35 \leq r^2 \leq 0.46)\) and oxoacids \((0.32 \leq r^2 \leq 0.48)\), indicating that higher plant emissions contribute to diacids and related compounds to a certain extent in summer in Beijing. Levoglucosan only correlated well with total diacids.
The end product mostly formed via the oxidation of longer carbon-chain diacids and other precursors in the atmosphere (Kawamura and Bikkina, 2016). The $C_2$/total diacid ratio enhanced with the increase in $C_2$–C/TC ($0.75 \leq r^2 \leq 0.8$), $C_2$/C$_3$ (0.58 $\leq r^2 \leq 0.8$) and $C_2$/C$_4$ (0.26 $\leq r^2 \leq 0.62$) ratios (Fig. 7a, c–d), suggesting a possible formation of oxalic acid from higher carbon number homologues and related compounds. However, there was no relationship between $(C_3$–$C_{12})$–C/TC and $C_2$/total diacids, which implies that the supply of longer chain diacids may be faster than their degradation rates for producing oxalic acid in Beijing. Intermediate diacids can still be abundantly produced by oxidation of organic precursors during atmospheric long-range transport. Meanwhile, $C_4$/total diacid ratio exhibited positive correlations with the $C_4$/C$_5$ (0.28 $\leq r^2 \leq 0.41$) and $C_4$/C$_6$ (0.24 $\leq r^2 \leq 0.48$) ratios (Fig. 7e–f), illustrating that glutaric and adipic acids may photodegrade to form succinic acid. These results suggested that the photodegradation of longer chain diacids contributed to the formation of lower diacid homologues after primary emissions, such as biomass burning and vehicular emissions in Beijing.

The 325 m meteorological tower in Beijing is well equipped for the investigation of the vertical structure of the urban boundary layer (UBL) and the mixing mechanism of organic aerosols among the UBL. Guo et al. (2016) found that the UBL often has a significant thermal stratification in heavy haze periods, which shows the convective instability in daytime and the extreme convective stability at night-time. Meanwhile, the geometric parameters of wind speed vector and the efficiency of turbulent transport also show more obvious diurnal variations. Concentrations of organic compounds are significantly affected by the combined effect of source intensity, meteorological condition and the vertical structure of the UBL.

Based on the sampling records, 16–17 August, 29–30 August and 7–8 September were labelled as polluted episodes. The pollution level was defined by the air quality index (AQI) according to local reports from the environmental monitor station. Previous studies reported that the photochemical oxidation of biogenic and anthropogenic VOCs results in semi-volatile gaseous Gly and MeGly, which can partition into the aerosol phase enriched with liquid water content or cloud and/or fog droplets (Volkamer et al., 2001; Zimmermann and Poppe, 1996; Fick et al., 2004; Ervens et al., 2004). In these transformations, $C_2$ is an end product formed via photochemical oxidation of the key intermediates such as $\omega$C$_2$ and Pyr (Lim et al., 2005). Thus, the ratios of $C_2$/Gly and $C_2$/MeGly were applied to better understand the aqueous oxidation mechanism of organic matter.

Compared to clean days, the relatively strong aqueous-phase oxidation of related precursors (Gly, Pyr and MeGly) contributed to the accumulation of $C_2$ on polluted days. Positive correlations were noteworthy for $C_2$/total diacids with $C_2$/Gly (0.42 $\leq r^2 \leq 0.58$) and $C_2$/MeGly (0.53 $\leq r^2 \leq 0.65$) at three sampling heights, while good linear relationships for $C_2$/total diacids with $C_2$/Gly ($r^2 = 0.51$, $r^2 = 0.41$), oxoacids ($r^2 = 0.53$, $r^2 = 0.43$) and $\alpha$-dicarboxyls ($r^2 = 0.63$, $r^2 = 0.52$) at upper heights, demonstrating that biomass burning was a key source to organic aerosols.

The concentration ratio of relative abundance of $C_2$ to total diacids ($C_2$/total diacids) is known as a useful marker to assess the photochemical processing level, because $C_2$ is the end product mostly formed via the oxidation of longer
Figure 6. The \( R/N \) ratios of diacids and related compounds observed at the tower in Beijing in summer 2015.

Figure 7. Contributions of (a) \( C_2^-/TC \) (%), (b) \( (C_3^-C_{12})^-/TC \) (%), (c) \( C_2/C_3 \) and (d) \( C_2/C_4 \) ratios as a function of relative abundance of \( C_2 \) in total diacids, as well as correlations for \( C_4 \) / total diacids with (e) \( C_4/C_3 \) and (f) \( C_4/C_6 \). The \( r_1^2 \), \( r_2^2 \) and \( r_3^2 \) values are the correlation coefficients for those samples collected at 8, 120 and 260 m, respectively.

0.58) and \( C_2^- / \text{Pyr} \) (\( r_1^2 = 0.5 \)) only existed at the ground level in polluted episodes (Fig. 8). In contrast, no significant connections were found between relative abundance of \( C_2 \) in total diacids and its mass ratios with four precursors on clean days. Therefore, the increased aqueous-phase oxidation may be a major source of oxalic acid. It is worth noting that OH radical-initiated aqueous oxidation may dominate the production of secondary organic aerosol on polluted days. The aqueous formation in cloud or wet aerosol is also an important pathway to diacids and related compounds (Carlton et al., 2006, 2007; Ervens and Volkamer, 2010; Tan et al., 2010).

Aged organic aerosols are usually characterised by the larger contribution of oxalic acid to WSOC (\( C_2^-/\text{WSOC} \)). For example, the \( C_2^-/\text{WSOC} \) ratio was higher in the photochemically aged aerosols collected at Hong Kong (6.8 %) (Ho et al., 2011) and Mount Hua (6.3 %) (Meng et al., 2014) compared to the ratio (0.17 %) in Ulaanbaatar aerosols that are significantly affected by substantial anthropogenic emissions (Jung et al., 2010). Due to the high temperature and relative humidity, the photochemical reaction is active in Hong Kong (Ho et al., 2011). Mount Hua is the highest mountain in central China and is a typically isolated site to investigate the atmospheric long-range transport of organic compounds (Meng et al., 2014). In contrast, diacids and related compounds in winter were mainly associated with uncontrolled waste plastic burning, coal power plants and vehicular emissions in Ulaanbaatar (Jung et al., 2010). Generally, on clean days, the \( C_2^-/\text{WSOC} \) ratio values at the ground level, 120 m and 260 m slightly increased.
However, on the more polluted days, C$_2$−C / WSOC ratios at ground level were obviously higher than those at 120 and 260 m owing to the accumulation of pollutants and moisture in ground surface atmosphere (Guinot et al., 2006). In comparison to the moderately polluted events of 17 August (P1) and 8 September (P3), C$_2$−C / WSOC ratio maximised at 120 m (3.2 %) on the lightly polluted day of 29 August (P2). According to the concentrations of OC and EC, the strongest polluted event occurred on 8 September during the field campaign in Beijing. The C$_2$−C / WSOC ratio at ground level in P3 (5.3 %) was higher than that in P1 (4.7 %), which may increase with an enhancement of the pollution. Furthermore, C$_2$−C / WSOC ratio was larger at ground level (5.3 %) followed by 120 m (2.4 %) and 260 m (2.2 %) in P3, demonstrating that C$_2$−C / WSOC ratio may decrease with an increase in sampling heights. These phenomena may indicate that the moderately polluted days were favourable for aqueous formation of C$_2$ in the lower troposphere, especially at the ground level. Similarly, the C$_2$−C / OC ratios at three sampling layers were higher in polluted days than clean days in general (Fig. 9b). We observed largest values of C$_2$−C / OC at higher levels of 120 and 260 m, which may be caused by more accumulation of POC from local anthropogenic emissions at the ground level (Fig. 2).

Different from the vertical distribution of C$_2$−C / WSOC ratios, the largest value of Ph−C / WSOC was mostly observed at ground level (0.70 %), followed by 120 m (0.53 %) and 260 m (0.45 %) (Fig. 9c). In comparison to the ratio value in P2, the large differences between Ph−C / WSOC ratio at ground level and in the upper layers (≥ 0.6 %) in P1 and P3 also supported the stagnant meteorological condition on the moderately polluted days. But the value of Ph−C / OC ratio at the ground level on polluted days was lower than that on clean days (Fig. 9d), which may be caused by the accumulation of organic precursors, like naphthalene. Unlike gas pollutants, high loadings of fine aerosol interact strongly with meteorological variables in the planetary boundary layer (PBL). Both aerosol scattering and absorption reduce the amount of solar radiation reaching the ground and thus reduce the sensible heat fluxes, which suppresses the development of PBL and further aggravates the pollution level (Li et al., 2017). Such positive feedback is especially
strong in heavy pollution events (Li et al., 2017), hence the photochemical formation of Ph at ground level may be not as effective as on clean days.

Hydrated Gly and MeGly formed via the photooxidation of biogenic and anthropogenic VOCs can subsequently produce $\omega$C$_2$ and Pyr, and ultimately generate C$_2$ (Ervens et al., 2004; Lim et al., 2005). In P1, only $\omega$C$_2$−C / WSOC ratio at the ground level remarkably increased (Fig. 9g), but all the ratios of Pyr−C / WSOC, $\omega$C$_2$−C / WSOC, Gly−C / WSOC and MeGly−C / WSOC were obviously larger at ground level than those at upper layers in P3 (Fig. 9e, i, k). These results suggested that aqueous oxidation pathway was an important factor to the formation of C$_2$, Pyr, $\omega$C$_2$ and $\alpha$-dicarboxyls on the more polluted days. The ratios of C$_2$−C / WSOC, Pyr−C / WSOC, $\omega$C$_2$−C / WSOC, Gly−C / WSOC and MeGly−C / WSOC at three sampling levels in transformation periods were divided by those in the moderately polluted days ($P/T$) to evaluate the importance of aqueous formation. The transformation periods were defined as the day before haze days. The P1/T1 ratios of C$_2$−C / WSOC, Pyr−C / WSOC, $\omega$C$_2$−C / WSOC, Gly−C / WSOC and MeGly−C / WSOC were lower than corresponding P3/T3 ratios (Table S3), implying that during the strongest polluted event in this study, aqueous formation may contribute more to the concentrations of C$_2$, Pyr, $\omega$C$_2$, Gly and MeGly. In addition, orders of P3/T3 ratio all values were ground level > 120 > 260 m. The vertical P3/T3 ratios for $\omega$C$_2$−C / WSOC (ground level: 5.2; 120 m: 1.8; 260 m: 1.4), Gly−C / WSOC (ground level: 5.7; 120 m: 1.8; 260 m: 1.6) and MeGly−C / WSOC (ground level: 5.8; 120 m: 2.0; 260 m: 1.5) were higher than those of C$_2$−C / WSOC and Pyr−C / WSOC. These phenomena implied that the aqueous formation of C$_2$, Pyr, $\omega$C$_2$ and $\alpha$-dicarboxyls may decrease with the sampling heights in the most polluted events, and the increasing level of aqueous formation of C$_2$ and related precursors may be associated with the pollution strength in Beijing.

### 3.5 Source apportionment of organic acids using PMF analysis

Based on the data of organic tracers and ions, the positive matrix factorisation (PMF, USEPA) was employed to estimate the relative contributions of primary sources and secondary formation pathways to diacids and related compounds in this study. The abundance, naming abbreviations and indicative sources of the tracer compounds were summarised in Table 3. Details of model stability of the six-factor solution were provided in Table S4. The PMF-resolved source profiles for the six factors were shown in Fig. 10a–f. Each factor was identified according to the dominant species. Secondary sulfate formation was identified by SO$_4^{2−}$ and isoprene SOA tracers, which indicated ozonolysis, OH radical-initiated oxidation and aqueous processing. Secondary nitrate formation was identified by the dominance of NO$_3^−$ and isoprene SOA tracers, mainly representing the OH radical-initiated oxidation. Owing to the existence of two double bonds, isoprene is highly reactive and is readily oxidised in the atmosphere by OH, NO$_3$ and O$_3$. Higher loading of the isoprene SOA tracers was observed in the factor of secondary sulfate formation than in secondary nitrate formation, which may indicate more overlapping of oxidation pathways.

Meanwhile, in comparison to NO$_3^−$ ($r^2 \leq 0.23$), better correlations were found between isoprene SOA tracers and SO$_4^{2−}$ (0.44 ≤ $r^2$ ≤ 0.67) (Fig. S6), being consistent with the above conclusion. Biomass burning was identified by the dominant species of levoglucosan and EC. Contribu-

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**Table 3. Abundance and naming of measured ions (µg m$^{-3}$) and organic tracers (ng m$^{-3}$) used in the PMF analysis.**

<table>
<thead>
<tr>
<th>Tracers</th>
<th>Grouping</th>
<th>Sources</th>
<th>Mean/SD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ground level</td>
<td>120 m</td>
</tr>
<tr>
<td>PAHs276</td>
<td>indeno[1,2,3-cd]pyrene, benzo[ghi]perylen list</td>
<td>Combustion sources</td>
<td>0.41/0.23</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td></td>
<td>Biomass burning</td>
<td>19/16</td>
</tr>
<tr>
<td>Hopanes</td>
<td>$\alphaβ$-hopane, $\alphaβ$S&amp;R-homohopane, $\alphaβ$S&amp;R-bishomohopane</td>
<td>Fossil fuel combustion (e.g. vehicle exhaust, coal combustion)</td>
<td>1.5/0.5</td>
</tr>
<tr>
<td>Isoprene SOA</td>
<td>2-methylglyceric acid, 2-methylthreitol, 2-methylerythritol, C$_2$-alkene triols</td>
<td>Isoprene-derived SOA, plants emissions</td>
<td>31/20</td>
</tr>
<tr>
<td>SO$_4^{2−}$</td>
<td></td>
<td>Secondary sulfate formation</td>
<td>36/34</td>
</tr>
<tr>
<td>NO$_3^−$</td>
<td></td>
<td>Secondary nitrate formation</td>
<td>20/19</td>
</tr>
</tbody>
</table>
utions of vehicle exhausts were identified by the dominance of hopanes (αβ-hopane, αβS&R-homohopane and αβS&R-bishomohopane) and EC. Plants emissions were identified by the dominance of isoprene SOA tracers. Because the isoprene SOA tracers are not only viewed as a representative of SOA tracers (Magda et al., 2004; Surratt et al., 2010) but also a marker of biogenic sources (Guenther et al., 2006), like terrestrial higher plant emissions (Sharkey et al., 2007). Coal combustion was identified by dominant species of the polycyclic aromatic hydrocarbons (PAHs) with their molecular weights of 276 (indeno-[1,2,3-cd]pyrene and benzo [ghi]perylene) and hopanes.

The PMF-resolved factor contributions to total species and total diacids, oxoacids, and α-dicarbonyls were shown in Fig. 10g–j. The secondary source (secondary sulfate formation and secondary nitrate formation) was the dominant contributor (44 %) to total species, followed by biomass burning (27 %) and motor vehicles (14 %). Similar factor distri-
bution was also observed for total diacids, oxoacids and α-dicarbonyls, but the contribution of motor vehicles was enhanced, especially in total oxoacids. The plant emission is a small contributor (5 %–8 %) to organic compounds. In this study, the contributed fraction of anthropogenic emissions (49 %–55 %), including biomass burning, motor vehicles and coal combustion (Zhu et al., 2018), to diacids and related compounds were slightly larger than that of secondary formation pathways (37 %–44 %).

4 Conclusions

Current knowledge on vertical distributions of dicarboxylic acids and related compounds in fine aerosol collected in the urban boundary layer is very limited. Compared to the ground measurements, the vertical studies can provide special insights into the photochemical mechanisms and regional transport of organic aerosols. In this study, differing from the vertical distribution of phthalic acid, the main organic acids generally showed higher values at 260 and 120 m than those at the ground surface. Thus, diacids and related compounds were influenced by both vehicular emissions at the ground level, whereas the atmospheric long-range transport was also an important contributor to organic compounds in the urban troposphere. Unlike clean days, the relative contribution of aqueous formation to dicarboxylic acids enhanced on polluted days, especially at ground level. Moreover, the increasing level of aqueous formation of C$_2$ and related precursors may be associated with the pollution strength in Beijing. Combined with the influence of wind, mass concentrations of total diacids, oxoacids and α-dicarbonyls were largely cut down (22 %–58 %) under the control on anthropogenic emissions. Here, the PMF results showed that the contributed fraction of anthropogenic emissions (49 %–55 %) to diacids and related compounds such as biomass burning, motor vehicles and coal combustion (Zhu et al., 2018) were more significant than that of secondary formation pathways (37 %–44 %).

Data availability. The data used in this manuscript are listed in the tables and figures and in the Supplement. The dataset for this paper is available upon request from the corresponding author (fupingqing@tju.edu.cn).

Supplement. A supporting description of the analysis methods, figures and tables is provided in the Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-20-10331-2020-supplement.

Author contributions. PF designed this research. PM$_{2.5}$ samples were collected by HR. Laboratory analyses were performed by WZ and HR. Data analyses were performed by WZ, HR, XZ and SY. The manuscript was written by WZ and PF with consultation from HD, XC, QX, PL and LW. The paper was reviewed by SK, YS, ZW and KK.

Competing interests. The authors declare that they have no conflict of interest.

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W. Zhao et al.: Vertical distribution of particle-phase dicarboxylic acids, oxoacids and α-dicarbonyls


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