Responses to Reviewer #1

We appreciate the reviewer for his/her thorough reading and thoughtful comments and suggestions, which greatly improve the quality of the manuscript. We revised the MS accordingly. The point-to-point responses to all the comments are given below in blue.

This paper investigates the vertical distribution of organic acids with altitude in Beijing based on measurements from a tower. The results show slightly higher concentrations of oxidized species aloft, not too surprising if the source are mainly from surface emissions which would mean less aged and less oxygenated. The data analysis is very detailed, but overall the results are only mildly interesting despite the measurements being very unique. This is because really no definite results are presented. The analysis is largely based on looking at ratios of species to infer processes or sources, and the interpretation of the results are always highly qualified with words such as, might, and especially may. I wonder why there are not plots of altitude vs concentration in this paper, since that is fundamentally what the measurements were all about. It is not clear what the main contribution of the PMF source apportionment analyses is to the overall results of this paper on species vertical distributions; why was source apportionment not done at each altitude, was it because of insufficient data? The paper needs to be edited to improve the grammar. Overall, the data in this paper are interesting, but the analysis is very weak.

Response: We thank the reviewer's careful reading and important comments, based on which we tried our best to improve the quality of our manuscript.

The ratios of organic compounds can be effectively applied to assessing the photochemical aging level and relative importance of primary emissions, because the ratio values vary with different sources and photochemical aging level of aerosols. Saxena and Hildemann (1996) and Seinfeld and Pandis (2006) reported that the fresh anthropogenic organic aerosols are mainly comprised by organic compounds with low oxidation level and hydrophobicity, such as alkanes, whereas aged particles and secondary organic aerosols have more hygroscopic compounds with oxygenated polar functional groups. The proportion of hydrophobic compounds in atmospheric particles decreases progressively when moving from the urban background to continental and to remote marine locations. Simultaneously, a population of more hygroscopic particles is always present (Kanakidou et al., 2005; Seinfeld and Pandis, 2006). For instance, the relative contents of total dicarboxylic acids in aerosol organic carbon (total diacids-C/OC) in remote marine and polar areas (≥ 10%) is higher than those in urban atmospheres (1 − 3%) (Kawamura and Sakaguchi, 1999; Wang et al., 2006; Bikkina et al., 2015; Zhang et al., 2016).

Figure S3 has been redrawn for concentration variations and vertical properties of organic acids in the supporting information. Owing to the insufficient data, the PMF analysis run at each altitude existed high uncertainties, thus the PMF source apportionment analysis is to the overall results in this paper. The sample numbers will be considered to increase at each altitude. Simultaneously, more analyses will be employed to the aerosol samples to better estimate the relative contribution of sources and secondary process at different height.

This paper firstly shows the vertical distribution of organic compounds at the molecular level in megacity in China, investigates the sources and possible formation routes in clean and polluted days, and demonstrates the feedback of diacids and related compounds on the reduction of anthropogenic emissions. Such measurements in the troposphere are also critical for estimating the regional transport to air quality in Beijing and improving the simulation of aerosols in chemical transport models, which needs to be investigated in the future to give more precise conclusions. Moreover, the synchronous measurements, like Chemical Ionization Mass Spectrometer, is considered to use in combination with the sampling of diacids, oxoacids and α-dicarbonyls in gas and particle phase to better understand the gas-particle transformation of these acids at different heights.

Pg 3 lines 12-13. Needs to be edited.

Response: we have rephrased these sentences. Please see lines 12 − 15 in page 3 in the revised manuscript.

Please make clear that the high volume samplers were located at the elevation stated. That is, long sampling lines were not used in this study.

Response: The samplers were located directly at the three layers, that is, the ground surface (8 m), 120 m, and 260 m at the 325-m meteorological tower. We have rephrased the sentences in the revised manuscript. Please see lines 18 − 19 in page 4.

What type of filter was used, quartz, Teflon? Were the samples gas denuded (apparently not). There should be a discussion on possible artifacts associated with this sampling system, such as loss of the small acids due to evaporation, etc. Maybe this is why no light organic acids (eg, formate, acetate) are reported?

Response: We thank for the reviewer's suggestion. $PM_{2.5}$ samples were collected on quartz-fiber filters (Pallflex). Please see lines 17 − 18 in page 4, where contains the filter information. Aerosol sampling onto quartz-fiber filters is accompanied by positive (e.g., adsorption of organic vapors) and/or negative (e.g., volatilization of organic aerosols after sample collection) artifacts. The collected particulate matter may chemically react with vapor components that pass through the filter during sampling to change the chemical composition of the deposit. This can result in positive or negative artifacts, especially if individual chemical compounds or chemical functionalities are being measured (Bennett and Stockburger, 1994). These sampling artifacts complicate the organic aerosol measurements, and it is difficult to separate the different competing artifact processes although this has been the object of many studies.

The positive artifact, as indicated by field blanks and backup filters, is believed to exceed the negative artifact for most samples (ten Brink et al., 2004; Watson et al., 2009). Without blank or backup filter subtraction, the artifact inflates organic carbon concentrations (Chow et al., 2010). Composition of the adsorbed/desorbed material, its exchange between gas and particle phases, the degree to which filters become saturated, and how the sign and amount of artifact differ among filter media and sampling environments have been studied, but these issues are not well understood (ten Brink et al., 2004; Watson et al., 2009; Vecchi et al., 2009; Arp et al., 2007; Zhu et al., 2012). In studies where the investigators attempted to measure the sampling error, the magnitudes of the determined positive or negative artifacts have varied considerably (Zhu et al., 2012; Liu et al., 2014a; Cheng et al., 2010a; Cheng et al., 2010b). This is probably due, in part, to differences in the organic molecular composition (hence in the relative volatilities and sorptivities) and in the concentrations that occurred at the different sampling locations. Multiple component sampling systems employing vapor phase separation devices such as denuders require a thorough evaluation to demonstrate efficient removal of the vapor at the operating conditions. This has been done for specific PAH compounds (Liu et al., 2014b; Schauer et al., 2003; Tsapakis and Stephanou, 2003; Liu et al., 2006). However, the application of their multiple component system to the determination of total OC aerosol for mixtures of atmospheric organic compounds presents a formidable challenge. The use of paired, parallel samplers (denuder difference method) is subject to the propagation of errors through subtraction, which degrades the precision. More development work with control experiments needs to be done on a wide range of organic compounds and concentrations before the sampling approach becomes credible for extended field studies.

Based on PM_{10} aerosols collected using a high-volume sampler with two quartz fiber filters, Ray and McDow (2005) found that dicarboxylic acids are affected by significant sampling artifact errors at concentrations below thresholds ($0.5\ \mathrm{ng\ m^{-3}} \leq$ artifact thresholds $\leq 12\ \mathrm{ng\ m^{-3}}$), but sampling artifacts are considerably lower at high concentrations expected when their primary emission sources and/or secondary formation are most important. Sihabut et al. (2005) also reported that the amount of dicarboxylic acids ($C_3 - C_9$) collected on the backup filter was consistently a small fraction of the amount collected on the front filter.

Due to the large contribution of primary emissions and secondary formation pathways to organic aerosols in Beijing, the concentrations of dicarboxylic acids detected in our study were larger than the artifact thresholds determined by Ray and McDow (2005). So far, most studies use single filter to collect organic and inorganic compounds in particulate aerosols (Wang et al., 2012; Zhang et al., 2015; Huang et al., 2014; Shi et al., 2018; Lyu et al., 2019; Mikhailov et al., 2017; Cheng et al., 2014; Ding et al., 2016; Cheng et al., 2016; Andreae et al., 2012; Saturno et al., 2018; Hsieh et al., 2008; Sanderson and Farant, 2005; Yue et al., 2019; Wang et al., 2016; Wang et al., 2017; An et al., 2019; Elser et al., 2016; Li et al., 2018; Kang et al., 2018; Liang et al., 2020; Zhang et al., 2016; Zhang et al., 2017; Wu et al., 2019; Zotter et al., 2014).

As for monocarboxylic acids, formic ($HCOOH$) and acetic (CH_3COOH) acids are among the most abundant and ubiquitous trace gases in the atmosphere (Khare et al., 1999; Talbot et al., 1988), and they have also been detected in remote, rural, polar, marine and urban aerosols, clouds and rain water (Chang et al., 2019; Andreae et al., 1988; Stavrakou et al., 2012; Paulot et al., 2011; Chattopadhyay et al., 2015; Chameides and Davis, 1983; Herndon et al., 2007; Zhang et al., 2011; Trentmann et al., 2005; Liu et al., 2012; Liang et al., 2020; Kesselmeier et al., 1998; Wang et al., 2007; Willey and Wilson, 1993; Avery et al., 2001; Xu et al., 2009; Kumar et al., 1996).

Our further work will focus on calculating the concentration thresholds of organic compounds in different locations and conditions and will try to find out more suitable sampling techniques to better understand the relationship between observed thresholds to adsorptive vapor concentrations and filter adsorption capacity for better evaluating the contribution of water-soluble organic acids to organic aerosol.

Page 7 lines 13 to 14. Stating that there is no direct analytical route to measure SOC may be strictly true, but there are ways that get pretty close, such as AMS measurements with PMF analysis. The statements and method to determine SOC in this paper are like reading a paper about 10 to 15 years old. Note the dates for the references for the method are 1995 and 1999.

The reason this method is rarely used is that it is highly inaccurate. Limitations with the method need to be discussed.

Response: Several indirect methods are widely employed to estimate the concentrations of primary and secondary organic aerosols, which can be categorized as the EC tracer method (Turpin and Huntzicker, 1995; Castro et al., 1999; Lim and Turpin, 2002; Chu, 2005; Yu et al., 2009), receptor modeling (Zheng et al., 2002; Na et al., 2004; Schauer et al., 2007) and chemical transport modeling (Pandis et al., 1992; Johnson et al., 2006b; Johnson et al., 2006a). Among these, the EC tracer method has received the widest application due to its simplicity and reliance on ambient measurements (Chu, 2005; Yu et al., 2009; Sun et al., 2011; Ji et al., 2016; Amato et al., 2011; Bougiatioti et al., 2013; Day et al., 2015; Grivas et al., 2012; Harrison and Yin, 2008; Kim et al., 2012; Kumar et al., 2012; Lin et al., 2009; Lonati et al., 2007; Samara et al., 2014; Saylor et al., 2006; Seguel A et al., 2009; Takegawa et al., 2006; Weber et al., 2007; Wu and Yu, 2016; Zhang et al., 2005; Zhang et al., 2014; Zhao et al., 2013; Zhou et al., 2012; Pio et al., 2011).

The EC tracer method is used here to derive POC and SOC empirically. The assumptions and methodology of EC tracer method are described in detail elsewhere (Castro et al., 1999; Turpin and Huntzicker, 1991, 1995; Yu et al., 2007). Briefly, total OC is defined as the sum of POC and SOC. By this method, the POC concentration can be defined as

$$\mathrm{POC} = (\mathrm{OC/EC})_{\mathrm{pri}} \times \mathrm{EC} + c, \qquad (1)$$

where $(\mathrm{OC/EC})_{\mathrm{pri}}$ is the estimated primary OC/EC ratio and c is to account for non-combustion sources contributing to POC (Turpin and Huntzicker, 1995; Castro et al., 1999). The SOC concentration can be estimated as

$$\mathrm{SOC} = \mathrm{OC} - \mathrm{POC} \qquad (2)$$

Previous studies often summarized the linear least-squares fit results of OC vs. EC from the lowest 5% and 10% OC/EC values to estimate $(\mathrm{OC/EC})_{\mathrm{pri}}$ (Sun et al., 2011; Miyazaki et al., 2006; Chu, 2005; Day et al., 2015; Ji et al., 2016), which is seasonally-dependent (Yuan et al., 2006). Therefore, the $(\mathrm{OC/EC})_{\mathrm{pri}}$ should be calculated at each sampling height (8 m, 120 m and 260 m) in our study due to the different influence strength of primary sources and secondary formation pathways. But it is worth mentioning that the number of $PM_{2.5}$ samples collected at each sampling height were less than 30 in our study, which means that there is no statistical significance for the $(\mathrm{OC/EC})_{\mathrm{pri}}$ estimation from the lowest 5% and 10% OC/EC values. The $(\mathrm{OC/EC})_{\mathrm{pri}}$ is 0.21, 0.14 and 0.24 calculated from the lowest 20% OC/EC values at the ground surface, 120 m and 260 m, respectively (Fig. 1). Based on these $(\mathrm{OC/EC})_{\mathrm{pri}}$ values, the possible uncertainties (±138% − ±207%) largely vary for the estimated SOC. Meanwhile, these $(OC/EC)_{pri}$ ratios are not comparable to those (1.9 − 2.8) based on the lowest 5% OC/EC values in four seasons in Beijing, China (Ho et al., 2007; Ji et al., 2016).

The direct emission from vegetation, the major non-combustion source, contributed 3.8% to OC in total suspended particles in summer in Beijing (Li et al., 2018), so OC emitted from non-combustion sources is assumed to be negligible in the approach used here. Using the minimum OC to EC ratio, $(OC/EC)_{min}$, to substitute for $(OC/EC)_{pri}$, the SOC and POC can therefore be estimated (Yu et al., 2009; Cabada et al., 2004; Castro et al., 1999),. The $(OC/EC)_{min}$ ratios were 5.0, 2.6 and 2.5 at the ground level, 120 m and 260 m in summer in Beijing, respectively. The sampling site is a typical urban location largely influenced by traffic and cooking emissions in Beijing, especially at the ground surface (Zhou et al., 2018b; Zhou et al., 2018a). Additionally, cooking emission also correspond to high OC/EC ratios (Samara et al., 2014). Thus, the $(OC/EC)_{min}$ ratio at the ground surface (5.0) was larger than those at 120 m (2.6) and 260 m (2.5) in our study and those (1.9 − 2.8) detected in other sampling sites in Beijing (Ho et al., 2007; Ji et al., 2016). It is rational to use the minimum OC/EC ratio to estimate the SOC and POC concentrations in this paper.

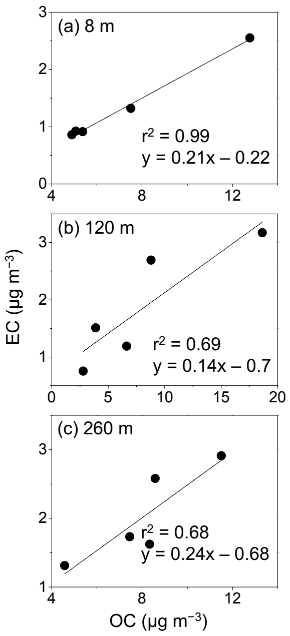

Figure 1. The linear least-squares analysis fitting results grouped by the lowest 20% of OC/EC ratios at the ground level, 120 m and 260 m

Based on AMS online data, the PMF result does get closer to the true SOC value, but this method is not widely used and is beyond the scope of our study. Because our group focus on the offline analyses of aerosol chemistry at the molecular level.

The 1995 and 1999 references cited for the EC tracer method in our study are the most classic literatures, which have been widely cited. Please see the lines 18 − 19 in page 7, where we have updated the references.

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Responses to Reviewer #2

We appreciate this reviewer for the useful comments and suggestions, which greatly improve the quality of the manuscript. We revised the MS accordingly. The point-to-point responses to all the comments are given below in blue.

The manuscript studied the vertical distribution of particle-phase dicarboxylic acids, oxoacids, and α-dicarbonyls in urban Beijing during the 2015 Victory Parade period based on the 325-meter tower by using GC/MS, Ion Chromatography, and OC/EC analyzer. This study showed that concentrations of oxalic acid at 120 m and 260 m were more abundant than that at 8 m during the sampling period because of higher oxidation at high altitude. Vehicular exhausts were demonstrated as the main contributor for phthalic acid. Although this study did many correlation analyses in section 3, simple correlation analyses didn't effectively evidence the sources and formation of species such as oxalic acid. In addition, many results and conclusions in section 3 were concluded with indefinite words such as may, causing that the conclusions were too speculative. Therefore, the authors should provide some stronger evidences in this section. This study further indicated the sources of organic acids based on meteorological parameters and FLEXPART-WRF model analyses. However, the source analysis at each sampling altitude was not showed. Is there any difference in the source of organic acids at each altitude? Because the study conducted on the vertical measurement, the data is valuable compared to the ground base. I might ask the author to make significant improvement on this paper before they can be accepted in the ACP.

Response: The real atmospheric environment is complex, where diverse formation mechanisms of organic aerosols exist. Field campaign estimates the dominant mechanism of aerosol components based on the atmospheric variables, which can not reveal the detailed mechanisms of organic compounds like smog chamber study. Owing to the insufficient data, the PMF analysis run at each altitude existed high uncertainties, thus the PMF source apportionment analysis is to the overall results in our study.

The sample numbers will be considered to increase at each altitude. Simultaneously, more analyses will be employed to the aerosol samples to better estimate the relative contribution of sources and secondary process at different height.

This paper firstly investigates the vertical distribution of diacids, oxoacids and α-dicarbonyls in Beijing, analyzes the primary sources and secondary processes in clean and polluted days, and demonstrates the feedback of organic acids under the control of anthropogenic emissions. Such measurements in the troposphere are also critical for estimating the regional transport to air quality in Beijing, which are favorable for chemical transport models to better evaluate the vertical contributions of local emissions, regional transport, aqueous and photochemical oxidation processes. Furthermore, the synchronous measurements, like Chemical Ionization Mass Spectrometer, is considered to use in combination with the sampling of diacids, oxoacids and α-dicarbonyls in gas and particle phase to better understand the gas-particle transformation of these acids at different heights.

P13 L21: How to exclude the contribution of accumulation of local emissions? Other evidences of aqueous-phase oxidation also should be provided.

Response: The local emissions also contributed to diacids and related compounds in polluted days. Owing to the increase of relative humidity in the low troposphere, the aqueous formation of oxalic acid enhanced in the polluted days, which was more important than local primary emissions.

Hydrated glyoxal (Gly) and methyglyoxal (MeGly) can ultimately produce oxalic acid (C_2) via the formation of glyoxylic (ωC_2) and pyruvic (Pyr) acids as intermediates (Carlton et al., 2007;Carlton et al., 2009;Tan et al., 2010). The concentration ratio of relative abundance of C_2 in total diacids (C_2/total diacids) is known as a useful marker to assess the aerosol oxidation level, because C_2 is the end product mostly formed via the oxidation of longer carbon-chain diacids and other precursors in the atmosphere (Kawamura and Bikkina, 2016). Therefore, the relationships for $C_2/\omega C_2$, C_2/Pyr, C_2/Gly and C_2/MeGly with C_2/total diacids were applied to better understand the aqueous formation of C_2. Compared to clean days, good coefficients were obtained for $C_2/\omega C_2$, C_2/Pyr, C_2/Gly and C_2/MeGly with C_2/total diacids in polluted days, which generally decreased with the sampling height. This phenomenon suggested that the vertical transformations of ωC_2, Pyr, Gly and MeGly to form C_2 were more clearly observed at the ground surface due to the higher relative humidity. It's worth noting that the value order of relative humidity was 8 m > 120 m > 260 m (Fig. S1).

Furthermore, the relative content of C_2 in water-soluble organic carbon (C_2-C/WSOC) showed different vertical distributions and variations in clean and polluted days. Aged organic aerosols are usually characterized by the larger contribution of oxalic acid to WSOC (C_2-C/WSOC). For example, C_2-C/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 with 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 wastes plastic burning, coal power plants and vehicular emissions in Ulaanbaatar (Jung et al., 2010). Generally, in clean days, the C2-C/WSOC ratio showed relatively large values at upper heights in this study (Fig. 9a). Moreover, in the transition from clean to polluted days, the C2-C/WSOC ratio values at the ground level, 120 m and 260 m slightly increased. However, in the more polluted days, C_2-C/WSOC ratios at the ground level were obviously higher than those at 120 m and 260 m owing to the accumulation of pollutants and moisture in ground surface atmosphere, which also supported the conclusion that the increased aqueous-phase oxidation may be a major source of oxalic acid in polluted days.

P4 L21: why were the blank samples only collected for half a minute? I saw that $PM_{2.5}$ samples were collected for 23 h.

Response: The field blank is sampled to see whether the aerosol samples have been polluted during the operation process, including the placing and collecting processes of the filter, which takes a few seconds. This sampling procedure doesn't aim to see the environmental impact during sampling time. Please see the definition of field blank at website (https://www.lcslaboratory.com/field-blank/).

P5 L6: Grammatically something wrong.

Response: Corrected.

P8 L4: How to exclude other sources (e.g., long-range transport, aqueous or heterogeneous reactions) for SOC?

Response: We have modified the sentence to avoid contradiction. "The SOC/POC ratios at 120 m (1.8 ± 0.79) and 260 m (1.9 ± 0.92) were higher than those at the ground level (0.51 ± 0.3) (Table. S1), demonstrating that more aged aerosols accumulated at upper layers (Fig. 2f)."

P8 L10: other sources should be discussed. Please see the above comment.

Response: We have modified the sentence in the revised manuscript. "These vertical phenomena were also observed for total oxoacids and α-dicarbonyls, suggesting that the aging level of diacids and related compounds slightly increased at 260 m of the atmosphere."

P12 L16: C_3/C_4 should be C_2/C_3?

Response: Corrected.

P13 L9: What is the definition criteria of polluted episodes?

Response: The pollution level is defined by air quality index (AQI), and is classified as light (101 − 150), moderate (151 − 200), heavy (201 − 300) and extremely heavy (301 − 500) pollution by Chinese Environmental Protection Ministry. Zhao et al. (2017) has also investigated chemical composition and diurnal variations of submicron aerosol species at ground level and 260 m during same polluted episodes in overlapped sampling time.

P14 L15-16: Definition of pollution level should be provided.

Response: The pollution level is defined by air quality index (AQI) according to local report from environmental monitor station. AQI is calculated from the following equation:

$$\mathrm{AQI} = \frac{AQI_h - AQI_l}{C_h - C_l}(C - C_l) + AQI_l$$

C is the pollutant concentration. AQI_l and AQI_h are AQI values corresponding to C_l and C_h, respectively. C_l and C_h are lower and upper limits near the pollutant concentration. AQI_l, AQI_h, C_l and C_h are constants, which can be obtained from the document of Technical Regulation on Ambient Air Quality Index (HJ 633 − 2012) issued by Chinese Environmental Protection Ministry. AQI is classified as light (101 − 150), moderate (151 − 200), heavy (201 − 300) and extremely heavy (301 − 500) pollution by Chinese Environmental Protection Ministry. We have added the definition of pollution level in the manuscript. Please see lines 9 – 10 in page 13.

P17 L8: Was the coal combustion included in the anthropogenic emissions? Maybe need related literature?

Response: Zhang et al. (2008) found that the saturated *n*-diacids ($C_3 - C_{10}$), unsaturated diacids (fumaric, maleic, phthalic, isophthalic and terephthalic acids) and related organic precursors, such as n-alkanes, PAHs and unsaturated fatty acids, can be directly emitted by industrial and residential coal combustion in China. Guo et al. (2013) reported that the contribution of coal combustion was associated with cooking in urban outskirts and rural areas during Beijing 2008 Olympics. Coal combustion accounted for 5.8 ± 5.5% and 7.8 ± 4.6% of the measured OC under the control on anthropogenic emissions (Guo et al., 2013), which was similar to the result in our study. The uncontrolled coal combustion in the rural areas was an important source to hopanes and PAHs in Beijing (Yu et al., 2018; Ren et al., 2018; Guo et al., 2013).

Coal combustion is an important anthropogenic source (Zhu et al., 2018), which largely influence the mass concentrations of organic compounds in China, especially in winter (Wang et al., 2012; Wang et al., 2006; Yu et al., 2018; Ren et al., 2018; Sun et al., 2016; Sun et al., 2013; Wang et al., 2019). We have added the reference and corrected the mistake in the revised manuscript. Please see lines 7 − 9 in page 17.

P17 L22: Same question as above.

Response: We have added the reference and corrected the mistake in the revised manuscript. "In this paper, PMF analysis showed that 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 larger than that of secondary formation pathways (37 − 44%)." Please see lines 21 − 23 in page 17.

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A list of all relevant changes made in the manuscript

1. Detailed information on the sampling site and sample collection is added and presented in the main text.
2. Extra description on the EC-tracer method and related references are provided in Section 3.1 in the revised manuscript.
3. Definition of the pollution levels are added in Page 13.
4. Evidences of aqueous-phase oxidation and related discussions are added in the revision.

Vertical distribution of particle-phase dicarboxylic acids, oxoacids and α-dicarbonyls in the urban boundary layer based on the 325-meter tower in Beijing

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Abstract. Vertical distributions of dicarboxylic acids, oxoacids, α-dicarbonyls and other organic tracer compounds in fine aerosols (PM$_{2.5}$) were investigated at three heights (8 m, 120 m and 260 m) based on a 325-meter 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 ± 154 ng m^{-3}) and 260 m (220 ± 140 ng m^{-3}) than those at the ground level (160 ± 90 ng m^{-3}). Concentrations of phthalic acid (Ph) decreased with the increase of 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 ωC$_2$) and α-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 m and 260 m than those at the ground surface. However, in polluted days, the C$_2$-C/WSOC ratio mainly reached its maximum at the ground level. These phenomena may indicate the enhanced contribution of aqueous-phase oxidation to oxalic acid in polluted days. Combined with the influence of wind field, total diacids, oxoacids and α-dicarbonyls decreased by 22% − 58% under the control on anthropogenic activities during the 2015 Victory Parade period. Furthermore, the 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 the ground level were largely associated with local traffic emissions, while the long-range atmospheric transport followed by photochemical aging 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 midlatitudes. A large portion of organic aerosols 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), mountainous (Kawamura et al., 2013; Cong et al., 2015), remote marine (Mochida et al., 2007; Wang et al., 2006c), and the Arctic (Kawamura et al., 2010; Kawamura et al., 1996) aerosols, and also in snow, rain and fog waters (Sempére and Kawamura, 1994; Kawamura et al., 2001).

Owing to high water-solubility and hygroscopicity, dicarboxylic acids play an important role in aerosol chemistry via atmospheric processing (e.g., iron catalyzed photolysis and secondary component formation) (Laskin et al., 2012; Drozd et al., 2014; Pavuluri and Kawamura, 2012) and in Earth's climate by enhancing hygroscopic behavior 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 extensively 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 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 (Pöhlker 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 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 industrialized and urbanized areas (Xia et al., 2007) and has encountered severe haze events, especially in winter (Wang et al., 2016). The haze pollution in Beijing is characterized 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 the ground level are heavily influenced by local sources (Huang et al., 2014), 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 street, both factors directly influencing local turbulence and pollutants dispersion. Furthermore, vertical measurements of 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; Wang et al., 2012; Wang et al., 2006b). 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-dicarbonyls in $PM_{2.5}$ collected at Beijing during August to September 2015, along with the 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 were discussed.

2. Experimental methods

2.1 Aerosol sampling

The three-layer sampling was performed at the rooftop of a two-story building (the ground level, 8 m a.g.l.) and two platforms (120 m and 260 m a.g.l.) on the 325-meter tower in 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). $PM_{2.5}$ samples were collected onto pre-heated (450°C, 6 hours) quartz-fiber filters (Pallflex) by using three high-volume air samplers (TISCH, USA), which are deployed directly at the ground surface (8 m), 120 m, and 260 m. All of them were run at an airflow rate of 1.0 m^3/min for 23 hours during the 2015 Victory Parade period (from 15th August to 10th September, n = 77). The sampling time was divided into the first non-restriction period, the restriction and the second non-restriction periods. 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-dicarbonyls 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 hour. Finally, the derivatives were dissolved in *n*-hexane and analyzed 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 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). Then the extracts were filtered through quartz wool, concentrated under vacuum and blew to dryness. Derivatization was the reaction with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) containing pyridine (5:1) and 1% trimethylsilyl chloride at 70°C for 3 hours. Finally, the derivatives were added with 30 μL of n-hexane and the internal standard of C_{13} n-alkane (1.43 ng μL^{-1}) before gas chromatography/mass spectroscopy (GC/MS) measurement. 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 SOA tracers were better than 80%, and both concentrations were corrected for the field blanks.

2.4 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_2^-, SO_4^{2-}, NO_3^-) by an 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 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 μgC 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 μgC 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 modeling

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 three hours a day. Backward simulation was run for three days 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 the ground level were almost same in field campaign (Fig. S1a). 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. Different from the second non-restriction period, the air quality at 120 m and 280 m were largely associated with southwestern wind from industrializations 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 lower value is linked to vehicular exhausts (1.1) (Sandradewi et al., 2008). And Watson et al. (2001) reported the OC/EC ratio of 4.0 attributed to fossil fuel combustion.

Figure 2 shows the daily variations of OC, EC, OC/EC, SOC and POC, SOC/POC in $PM_{2.5}$ collected at the ground level, 120 m and 260 m in summer. During the field campaign, concentration level of EC was considerably lower than OC, but their variation trends were similar (Fig. 2a & 2b). The average value of OC/EC ratios at ground surface and upper layers 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 summer harvest (Fu et al., 2012; Sun et al., 2016; Desyaterik et al., 2013). The variations of 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 ($0.59 \leq r^2 \leq 0.78$) (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):

$$POC = (OC/EC)_{min} \times EC \qquad (1)$$

$$SOC = OC_{total} - POC \qquad (2)$$

The $(OC/EC)_{min}$ ratios were the minimum OC/EC ratios calculated at each sampling height, and OC_{total} were the mass concentrations of OC. The concentration of POC calculated using the first equation means the primary carbonaceous aerosols from fossil fuel combustion (Turpin and Huntzicker, 1995). In this study, the $(OC/EC)_{min}$ ratios were 5.0, 2.6 and 2.5 at the ground level, 120 m and 260 m, respectively. POC showed the largest mass concentration at the ground level (4.7 ± 2.3 μg m^{-3}), while SOC were more abundant at 120 m (5.1 ± 2.9 μg m^{-3}) and 260 m (4.7 ± 2.2 μg m^{-3}) (Table 1). The SOC/POC ratios at 120 m (1.8 ± 0.79) and 260 m (1.9 ± 0.92) were higher than those at the ground level (0.51 ± 0.3) (Table. S1), demonstrating that more aged aerosols accumulated at upper layers (Fig. 2f).

3.2 Organic molecular characterization

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 the ground level (285 ± 143 ng m^{-3}). Meanwhile, the relative abundances of total diacids in carbonaceous fractions (organic carbon and total carbon) reached maximum values at 260 m (Table S1). These vertical phenomena were also observed for total oxoacids and α-dicarbonyls, suggesting that the aging level of diacids and related compounds slightly increased at 260 m in the troposphere.

The molecular distributions of dicarboxylic acids were characterized 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 (Figs. S3h − j) with similar diurnal trends (Figs. 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 ratio 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 (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 ($r_1^2 = 0.66$) and 260 m ($r_3^2 = 0.94$) (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 Stratigakis, 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 the ground level (Table S1), implying that C_9 may be derived from the photooxidation of corresponding hydrocarbons from local vehicular emissions. Positive linear relationship was found between C_6/C_9 and C_6/total diacids at 120 m ($r_2^2 = 0.51$) and 260 m ($r_3^2 = 0.86$) (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 oxidized from aromatic hydrocarbons like naphthalene from coal and biofuel combustions (Kautzman et al., 2010; Wang et al., 2006a). Mass concentrations of Ph decreased with the sampling heights, illustrating that vehicular exhausts at the ground level was a major source to phthalic acid. Terephthalic acid (tPh), an isomer of Ph, is a tracer of plastic burning in municipal wastes (Kawamura and Pavuluri, 2010; Simoneit et al., 2005). Contrary to the vertical distribution of Ph, the average concentration of tPh at the ground level (12 ± 10 ng m^{-3}) was slightly lower than those at 120 m (15 ± 15 ng m^{-3}) and 260 m (13 ± 11 ng m^{-3}).

Oxocarboxylic acids, the intermediates of the oxidation of mono-carboxylic acids, can further be photochemically oxidized to form diacids (Warneck, 2003; Carlton et al., 2007). The glyoxylic acid (ωC_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 ng m^{-3} to 33 ng m^{-3} with a maximum value (10 ± 7.4 ng m^{-3}) at 260 m. Glyoxal (Gly) and methyglyoxal (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., 2001) (e.g., aromatics, acetone and acetylene) volatile organic compounds (VOCs). And both are important precursors to form less-volatile organic acids such as ωC_2, Pyr (Lim et al., 2005). Concentrations of Gly and MeGly increased with the sampling heights, and their concentration variations were similar to those of ωC_2 and Pyr (Figs. S3d − g), illustrating that ωC_2, Pyr and α-dicarbonyls had similar sources and/or formation pathways.

3.3 Restriction versus 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 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 20th August to 3rd 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 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 more influence of clean northwesterly winds (Fig. S1a). The R/N ratios for OC/EC and SOC/POC were larger than or equal to unit due to the reduction of primary pollutants from incomplete burning activities under control measurements. Moreover, both R/N1 and R/N2 ratios for SOC/POC decreased with the sampling heights, demonstrating that vehicular emissions at the ground level was an important factor to dicarboxylic acids. The reduction of vehicular emissions resulted in the relatively low concentration of POC and the highest SOC/POC ratio at the ground level in restriction period. The contribution of vehicular emissions to upper sampling layers decreased during the atmospheric upward transport.

Footprint regions of atmospheric particles are shown in Fig. 5. During the non-restriction periods, Beijing was dominated by regional transport from the south and southwest industrial areas. However, the footprint area of organic aerosols in restriction period was mainly located in the northeastern direction of Beijing, where was relatively clean. Combined with the wind field, the wind speeds and directions at the ground level showed little difference in the whole sampling time (Fig. S1a). The wind direction at 120 m was similar to that at 260 m in each non-restriction period, but wind speeds at 260 m were larger than those at 120 m. In comparison to the second non-restriction period, the organic aerosols at 120 m and 260 m were mainly affected by southwesterly wind in the first non-restriction episode. As for the restriction period in Beijing, more clean air masses from the northern areas arrived at 120 m, 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 ωC_2, Pyr, tPh and α-dicarbonyls. Owing to the influence of wind, the decreased level of main diacids, oxoacids and α-dicabonyls (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 the ground level < 120 m < 260 m in restriction period compared to the non-restriction periods (Table S2). This also supported the conclusion that a upward transport of vehicular emissions was 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 defined as the sum of six oxidation products of isoprene, including 2-methylglyceric acid, C_5-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-methylthreitol and 2-methylerythritol (Claeys et al., 2004). Isoprene, the major biogenic volatile organic compound, is abundantly derived from plants emissions (Sharkey et al., 2007). Compared to total α-dicarbonyls, better correlations were found between isoprene SOA tracers and total diacids ($0.35 \le r^2 \le 0.46$) and oxoacids ($0.32 \le r^2 \le 0.48$), indicating that higher plants emissions contribute to diacids and related compounds to a certain extent in summer in Beijing. Levoglucosan only correlated well with total diacids ($r_2^2 = 0.51$, $r_3^2 = 0.41$), oxoacids ($r_2^2 = 0.53$, $r_3^2 = 0.43$) and α-dicarbonyls ($r_2^2 = 0.63$, $r_3^2 = 0.52$) at upper heights, demonstrating that biomass burning was a key source to organic aerosols.

The concentration ratio of relative abundance of C_2 in 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 carbon-chain diacids and other precursors in the atmosphere (Kawamura and Bikkina, 2016). The C_2/total diacids ratio enhanced with the increase of C_2-C/TC ($0.75 \le r^2 \le 0.8$), C_2/C_3 ($0.58 \le r^2 \le 0.8$) and C_2/C_4 ($0.26 \le r^2 \le 0.62$) ratios (Figs. 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 imply that the supply of longer-chain diacids may be faster than their degradation rates to produce oxalic acid in Beijing. Intermediate diacids can still be abundantly produced by oxidation of organic precursors during the atmospheric long-range transport. Meanwhile, C_4/total diacids ratio exhibited positive correlations with the C_4/C_5 ($0.28 \le r^2 \le 0.41$) and C_4/C_6 ($0.24 \le r^2 \le 0.48$) ratios (Figs. 7e − f), illustrating that glutaric and adipic acids may possibly photodegrade to form succinic acid. These results suggested that the photodegradation of longer chain diacids contributed to the formation of lower diacids homologues after primary emissions, such as biomass burning and vehicular emissions in Beijing.

The 325-m meteorological tower in Beijing is well equipped for studying the vertical structure of urban boundary layer (UBL) and the vertical mechanism of organic compounds. Guo et al. (2016) found that the urban boundary layer often has a significant thermal stratification in heavy haze periods, which shows the convective instability in daytime and the extreme convective stability in nighttime. 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 vertical structure of urban boundary layer.

Based on sampling records, 16 − 17th and 29 − 30th August and 7 − 8th September were labeled as polluted episodes. The pollution level is defined by air quality index (AQI) according to local report from 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/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 ωC_2 and Pyr (Lim et al., 2005). Thus, the ratios of $C_2/\omega C_2$, C_2/Pyr, C_2/Gly and C_2/MeGly were applied to better understand the aqueous oxidation mechanism of organic matters.

Compared to clean days, the relatively strong aqueous-phase oxidation of related precursors (ωC_2, Pyr, Gly and MeGly) contributed to the accumulation of C_2 in 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 $C_2/\omega C_2$ ($r_1^2 = 0.58$) and C_2/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 in 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 in polluted days. The aqueous formation in cloud or wet aerosol is also an important pathway to diacids and related compounds (Carlton et al., 2006; Carlton et al., 2007; Ervens and Volkamer, 2010; Tan et al., 2010).

Aged organic aerosols are usually characterized by the larger contribution of oxalic acid to WSOC (C_2-C/WSOC). For example, C_2-C/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 with 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 wastes plastic burning, coal power plants and vehicular emissions in Ulaanbaatar (Jung et al., 2010). Generally, in clean days, the C_2-C/WSOC ratio showed relatively large values at upper heights in this study (Fig. 9a). Moreover, in the transition from clean to polluted days, the C_2-C/WSOC ratio values at the ground level, 120 m and 260 m slightly increased.

However, in the more polluted days, C_2-C/WSOC ratios at the ground level were obviously higher than those at 120 m 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 17th August (P1) and 8th September (P3), C_2-C/WSOC ratio maximized at 120 m (3.2%) in lightly polluted day of 29th August (P2). According to the concentrations of OC and EC, the strongest polluted event occurred on 8th September during the field campaign in Beijing. The C_2-C/WSOC ratio at the 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 in the 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 of sampling heights. These phenomena may indicate that the moderately polluted days were favorable 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 m 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 the 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 the ground level and upper layers ($\geq$ 0.6%) in P1 and P3 also supported the stagnant meteorological condition in the moderately polluted days. But the value of Ph-C/OC ratio at the ground level in polluted days were lower than those in 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 aggravate 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 the ground level may be not as effective as clean days.

Hydrated Gly and MeGly formed via the photooxidations of biogenic and anthropogenic VOCs can subsequently produce ωC_2 and Pyr, and ultimately generate C_2 (Ervens et al., 2004; Lim et al., 2005). In P1, only ωC_2-C/WSOC ratio at the ground level remarkably increased (Fig. 9g). But all the ratios of Pyr-C/WSOC, ωC_2-C/WSOC, Gly-C/WSOC and MeGly-C/WSOC were obviously larger at the ground level than those at upper layers in P3 (Figs. 9e, i, k). These results suggested that aqueous oxidation pathway was an important factor to the formation of C_2, Pyr, ωC_2 and α-dicarbonyls in the more polluted days. The ratios of C_2-C/WSOC, Pyr-C/WSOC, ωC_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, ωC_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, ωC_2, Gly and MeGly. In addition, orders of P3/T3 ratio all values were: ground level > 120 m > 260 m. The vertical P3/T3 ratios for ωC_2-C/WSOC (the ground level: 5.2, 120 m: 1.8, 260 m: 1.4), Gly-C/WSOC (the ground level: 5.7, 120 m: 1.8, 260 m: 1.6) and MeGly-C/WSOC (the 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, ωC_2 and α-dicarbonyls 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 factorization (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 summarized in Table 3. Details of model stability of the six-factor solution was provided in Table S4. The PMF-resolved source profiles for the six factors were shown in Figs. 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 oxidized 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 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-} ($0.44 \leq r^2 \leq 0.67$) (Fig. S6), being consistent with the above conclusion. Biomass burning was identified by the dominant species of levoglucosan and EC. Contributions 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 plants emissions (Sharkey et al., 2007). Coal combustion was identified by dominant species of the 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 distribution was also observed for total diacids, oxoacids and α-dicarbonyls, but the contribution of motor vehicles 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 at Beijing based on observations is very limited. The air pollution is characterized by regional distribution in China. 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, different from the vertical distribution of Ph, the organic acids mainly showed higher values at 260 m and 120 m than those at the ground surface. The diacids and related compounds were largely influenced by vehicular emissions at the ground level, whereas the atmospheric long-range transport was an important contributor to organic compounds in the urban troposphere. Unlike clean days, the relative contribution of aqueous formation to dicarboxylic acids enhanced in polluted days, especially at the 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. In this paper, 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 dataset for this paper is available upon request from the corresponding author (fupingqing@tju.edu.cn).

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

Author contributions. Pingqing Fu designed this research. $PM_{2.5}$ samples were collected by Hong Ren. Laboratory analyses were performed by Wanyu Zhao and Hong Ren. The manuscript was written by Wanyu Zhao and Pingqing Fu with consultation from all other authors.

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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.

Species (Abbr.)	The ground level (n = 27)		120 m (n = 25)		260 m (n = 25)	
	Range	Mean/SD	Range	Mean/SD	Range	Mean/SD
OC	3.1–15	6.6/2.5	2.8–18	8.2/4.4	2.5–16	7.7/3.5
EC	0.6–2.6	0.9/0.5	0.4–3.2	1.3/0.7	0.3–3.3	1.3/0.8
SOC	0.0–5.0	2.0/1.1	0.0–12	5.1/2.9	0.0–10	4.7/2.2
POC	2.8–13	4.7/2.3	1.1–8.2	3.2/1.9	0.77–8.2	3.2/2.0
TC	3.6–17	7.6/3.0	3.6–20	9.4/5.1	2.9–21	9.0/4.1

Table 2. Vertical concentrations (ng m^{-3}) of dicarboxylic acids, oxoacids and α-dicarbonyls collected in Beijing from August 15th to September 10th, 2015.

Species (Abbr.)	The ground level (n = 27)		120 m (n = 25)		260 m (n = 25)	
	Range	Mean/SD	Range	Mean/SD	Range	Mean/SD
Dicarboxylic acids						
Oxalic, C_2	46–432	160/90	52–570	210/154	60–650	220/140
Malonic, C_3	7.1–49	22/10	8.6–82	32/25	11–75	34/17
Succinic, C_4	7.3–46	21/10	8.7–87	30/21	9.2–76	31/18
Glutaric, C_5	3.2–17	6.5/3.2	2.8–29	9.2/6.4	3.2–25	9.5/5.2
Adipic, C_6	2.5–14	5.3/2.5	3.7–21	8.2/4.2	4.8–21	13/5.0
Pimeric, C_7	0.7–4.7	1.6/1.1	0.2–7.5	2.5/2.1	0.4–9.4	2.5/2.0
Suberic, C_8	BDL–0.3	BDL/0.1	BDL–0.8	0.1/0.2	BDL–1.2	0.2/0.4
Azelaic, C_9	12–34	18/4.8	4.9–53	21/10	5.6–38	17/7.6
Decanedioic, C_{10}	0.4–3.1	1.3/0.7	0.2–4.2	1.6/1.0	BDL–3.7	1.5/0.8
Undecanedioic, C_{11}	BDL–2.9	1.2/0.6	0.4–6.7	1.5/1.4	0.4–5.3	1.4/1.0
Dodecanedioc, C_{12}	BDL–0.2	BDL	BDL–0.7	0.1/0.2	BDL–0.7	0.2/0.2
Methylmalonic, iC_4	0.4–2.8	0.9/0.5	0.2–4.1	1.2/0.8	0.5–2.3	1.1/0.5
Methylsuccinic, iC_5	0.5–3.8	1.6/0.8	0.6–7.9	2.2/1.8	0.7–6.3	2.2/1.4
2-methylglutaric, iC_6	BDL–1.7	0.5/0.4	0.3–4.8	1.0/0.9	0.3–3.9	1.0/0.8
Maleic, M	0.7–2.6	1.3/0.5	0.5–6.0	1.8/1.2	0.9–4.3	2.0/0.9
Fumaric, F	0.2–3.0	1.4/0.7	0.2–6.3	1.5/1.5	0.5–5.8	1.6/1.3
Methylmaleic, mM	0.7–3.0	1.3/0.5	0.5–7.4	1.9/1.6	0.6–4.2	1.9/1.0
Phthalic, Ph	8.3–61	26/11	8.6–51	23/11	8.2–40	21/7.9
Isophthalic, iPh	0.3–1.3	0.6/0.3	0.2–3.0	1.2/1.0	BDL–8.4	1.0/1.7
Terephthalic, tPh	1.8–49	12/10	3.4–64	15/15	2.8–49	13/11
Malic, hC_4	BDL−1.7	0.3/0.3	0.2–2.4	0.6/0.5	0.1–2.4	0.7/0.5
Oxomalonic, kC_3	0.5–9.6	2.7/2.2	0.6–13	4.0/3.4	0.6–12	4.1/2.5
4-oxopimelic, kC_7	0.5–9.7	3.0/2.2	0.4–13	4.4/3.6	1.1–12	5.0/2.6
Total diacids	99–733	285/143	110–945	370/255	126–1001	380/216
Oxocarboxylic acids						
Pyruvic, Pyr	0.6–17	5.6/3.8	0.8–30	10/9.1	0.7–30	8.5/6.8
Glyoxylic, ωC_2	0.5–44	15/11	2.6–80	21/19	2.5–65	20/17
3-oxopropanoic, ωC_3	0.9–8.2	2.9/1.8	1.3–11	4.1/3.1	1.0–12	3.7/2.4
4-oxobutanoic, ωC_4	1.0–11	4.5/2.5	2.7–21	7.3/4.4	1.9–17	6.9/3.8
5-oxopentanoic, ωC_5	0.3–3.4	1.5/0.7	0.6–4.7	2.0/1.1	0.7–3.9	1.9/0.9
7-oxoheptanoic, ωC_7	1.1–5.4	3.2/1.2	1.3–8.6	4.2/2.2	1.8–8.0	4.0/1.5
8-oxooctanoic, ωC_8	0.7–8.7	4.0/1.9	0.8–15	5.0/3.3	0.1–15	5.0/3.4
9-oxononanoic, ωC_9	0.2–2.4	1.2/0.6	0.3–4.9	1.2/1.0	BDL–4.8	1.4/1.2
Total oxoacids	7.3–95	38/22	1.8–170	56/41	11–150	52/34
α-dicarbonyls						
Glyoxal, Gly	0.5–6.1	2.2/1.2	1.0–13	3.3/2.7	0.8–9.8	3.4/2.3
Methylglyoxal, MeGly	1.4–12	4.1/2.6	1.0–20	5.2/4.0	1.3–22	6.7/5.2
Total dicarbonyls	1.8–17	6.3/3.7	2.2–33	8.5/6.6	2.0–31	10/7.4

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

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

Tracers	Grouping	Sources	Mean/SD		
			The ground level	120 m	260 m
PAHs276	indeno[1,2,3-cd]pyrene, benzo[ghi]perylene	Combustion sources (mainly coal combustion)	0.41/0.23	0.24/0.18	0.08/0.06
Levoglucosan		Biomass burning	19/16	21/14	23/15
Hopanes	*αβ*-hopane, *αβS&R*-homohopane, *αβS&R*-bishomohopane	Fossil fuel combustion (e.g. vehicle exhaust, coal combustion)	1.5/0.5	2.0/1.0	1.0/0.6
Isoprene SOA tracers	2-methylglyceric acid, 2-methylthreitol, 2-methylerythritol, C_5-alkene triols	Isoprene derived SOA, plants emissions	31/20	41/38	48/37
SO_4^{2-}		Secondary sulfate formation	36/34	43/46	51/46
NO_3^-		Secondary nitrate formation	20/19	29/30	36/43

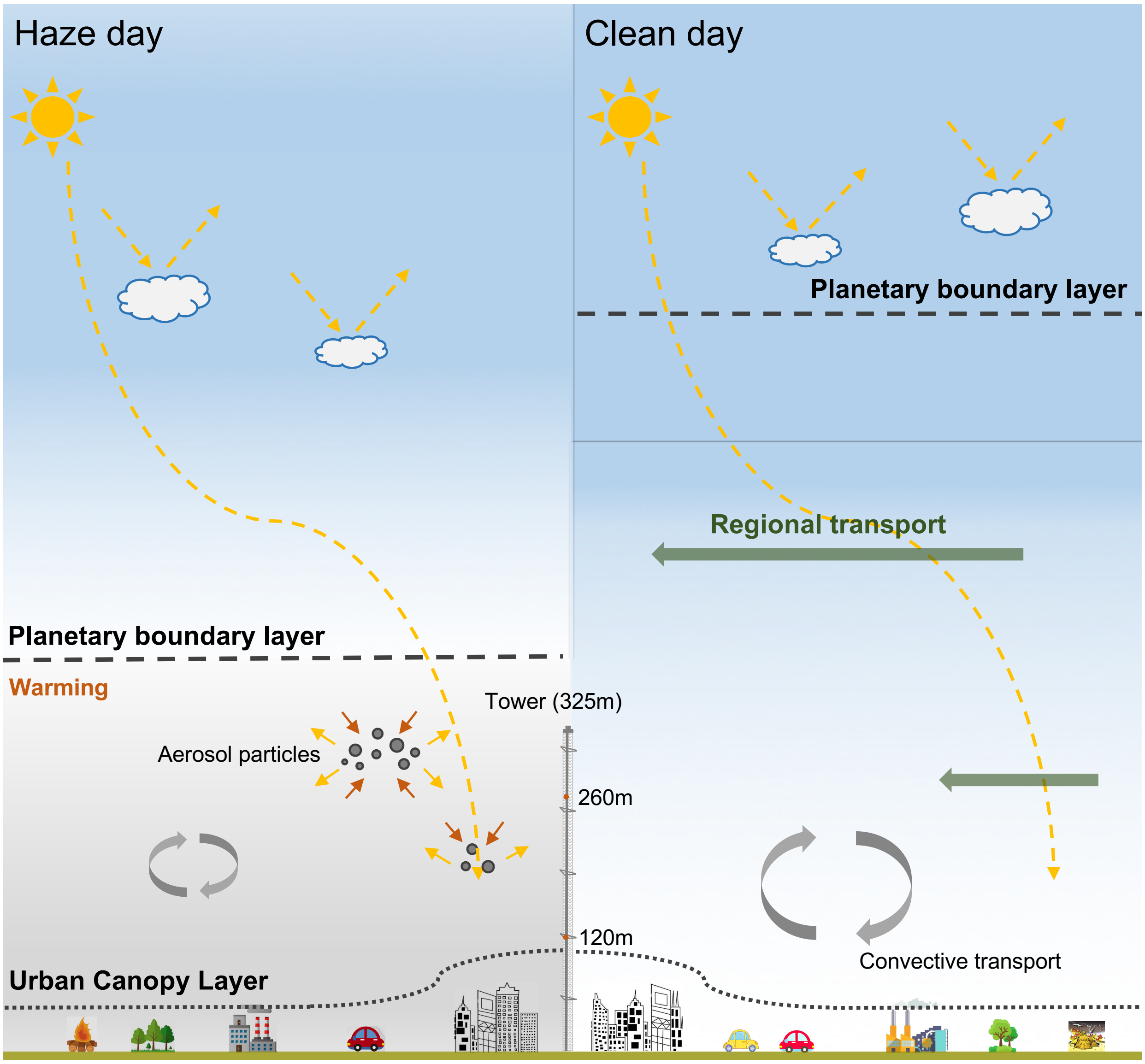

Figure 1. A schematic cartoon showing the atmospheric vertical structure over Beijing in polluted and clean days.

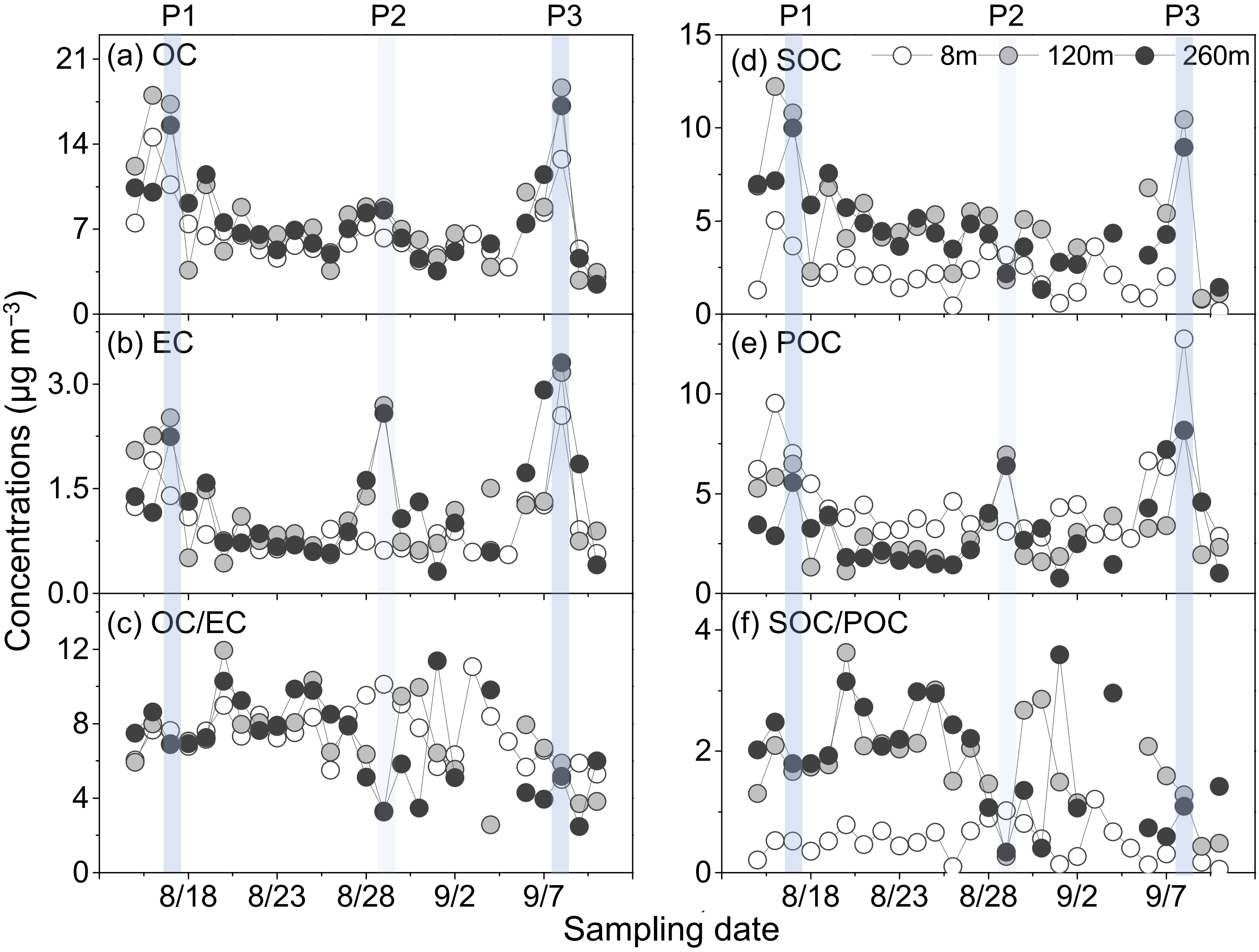

Figure 2. Daily variations in the concentrations of (a) OC, (b) EC, (c) OC/EC, (d) SOC, (e) POC and (f) SOC/POC at three sampling heights in Beijing. Two moderately polluted days (P1 and P3) and one lightly polluted day (P2) are marked for further discussions.

5

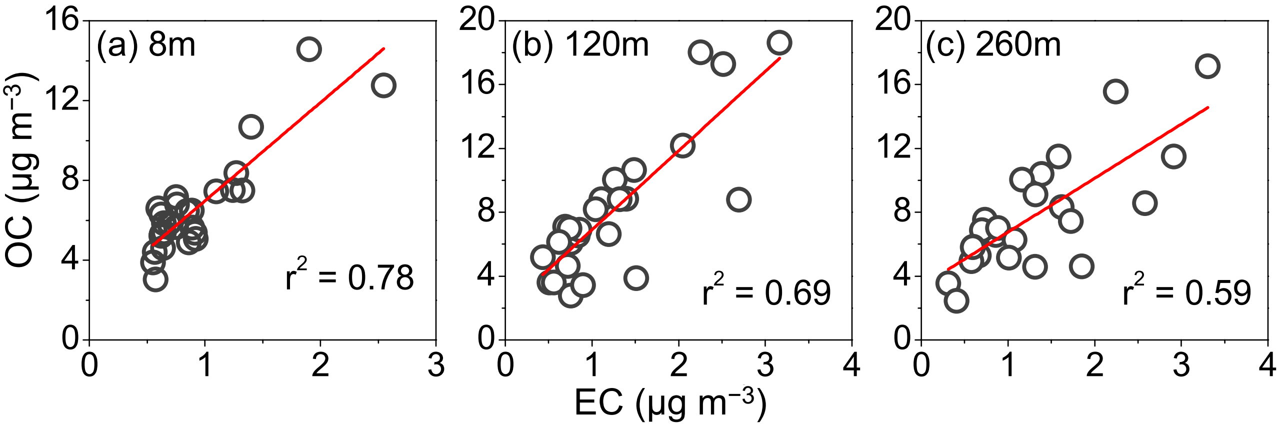

Figure 3. Correlations between OC and EC at the ground level, 120 m and 260 m.

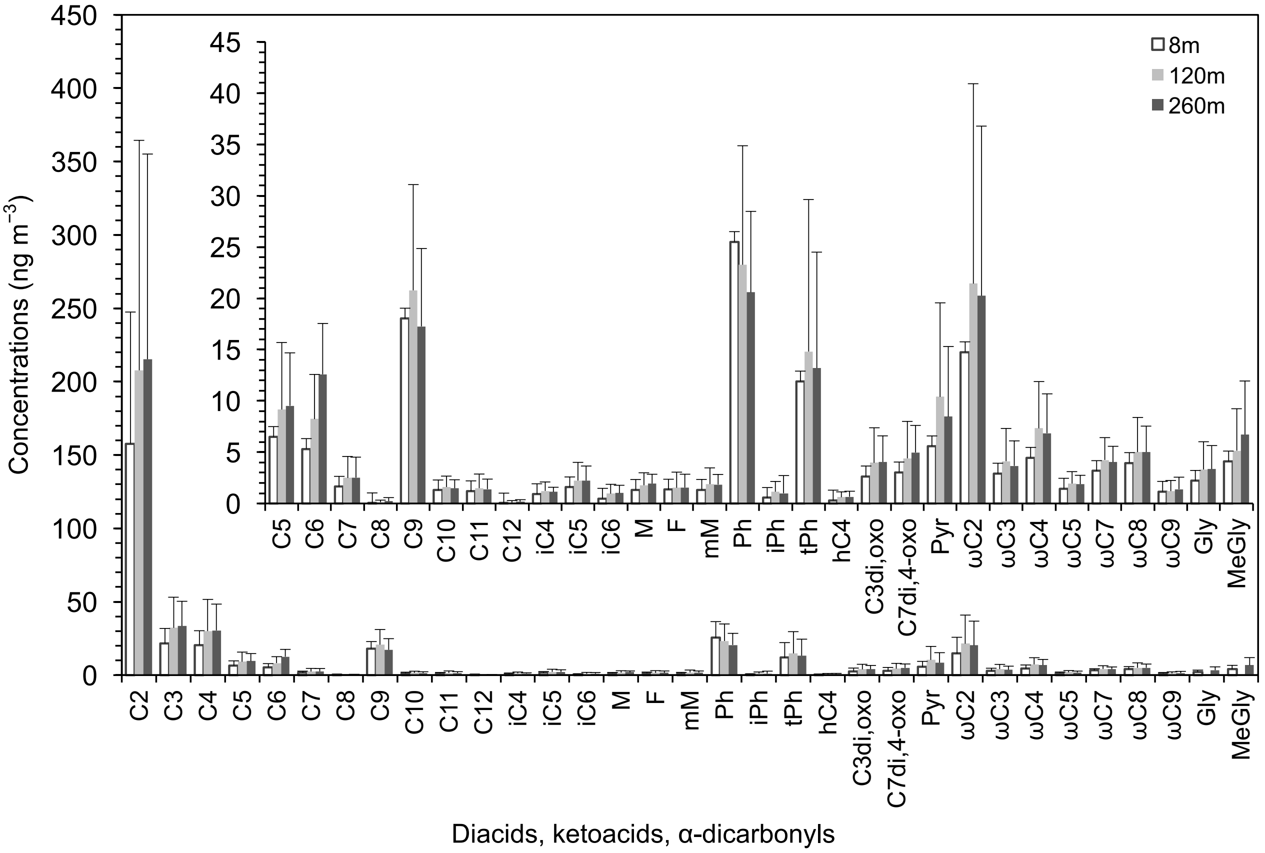

Figure 4. Molecular distributions of dicarboxylic acids and related compounds in the $PM_{2.5}$ samples collected at the tower from 15th August to 10th September 2015 in Beijing.

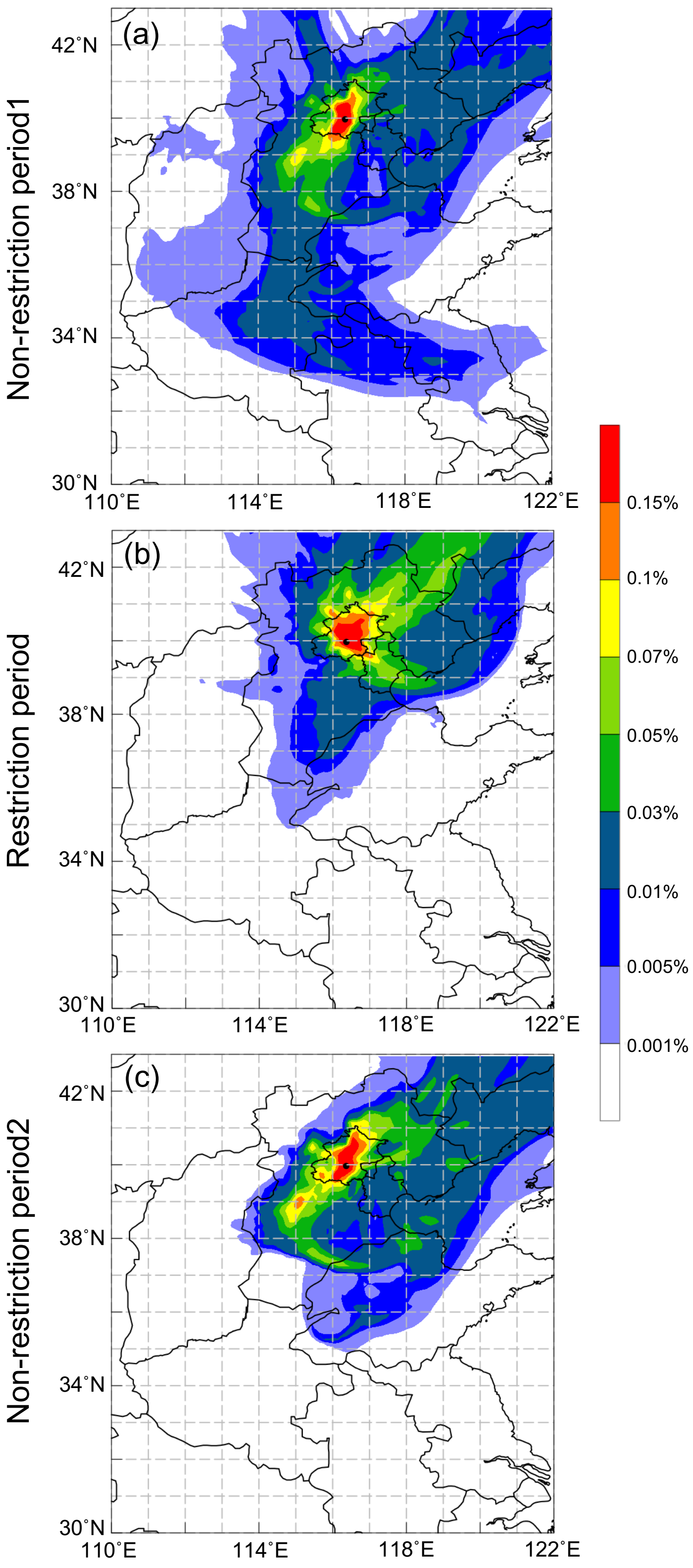

Figure 5. Aerosols footprint regions of non-restriction and restriction periods. The color bar indicates the relative residence time of tracer particles. And the black dot represents the sampling site.

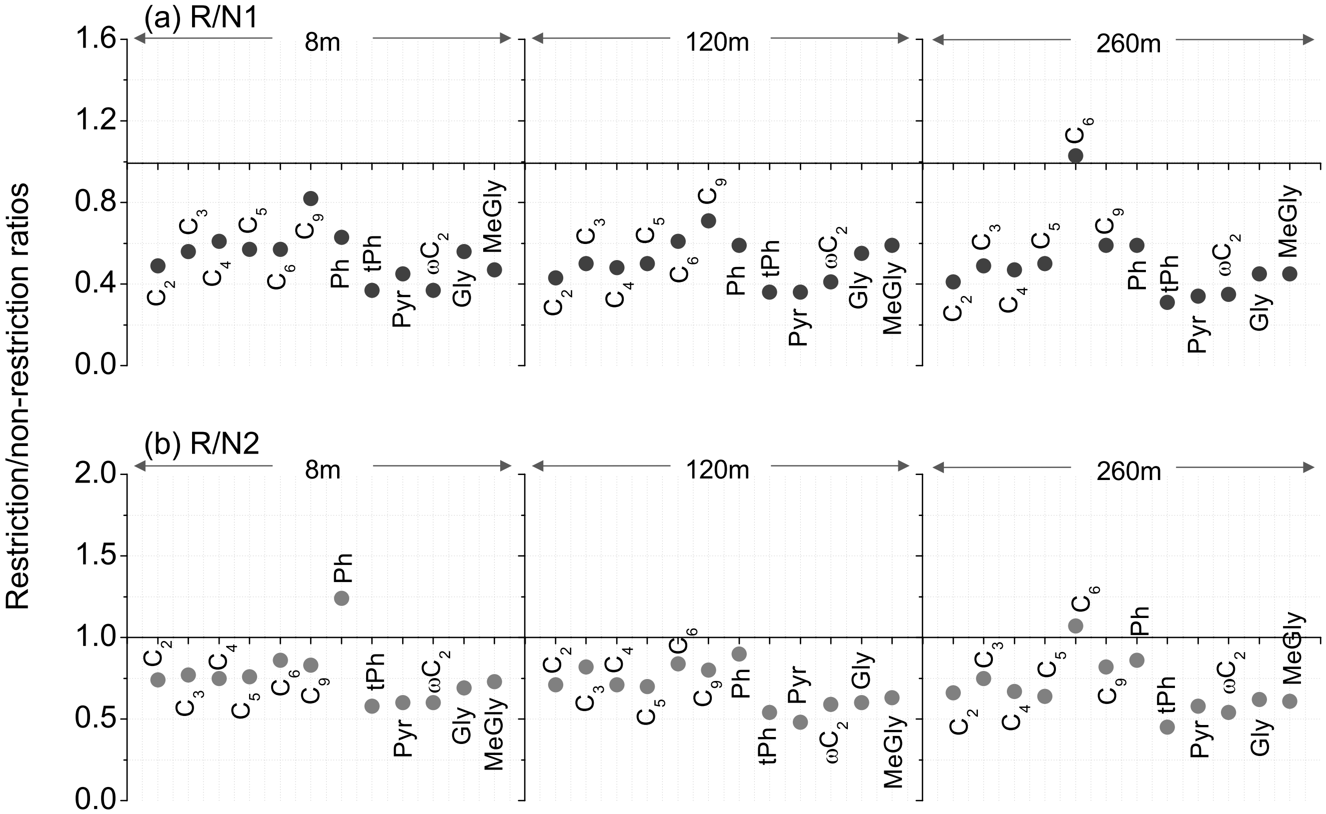

Figure 6. The R/N ratios of diacids and related compounds observed at the tower in Beijing in summer 2015.

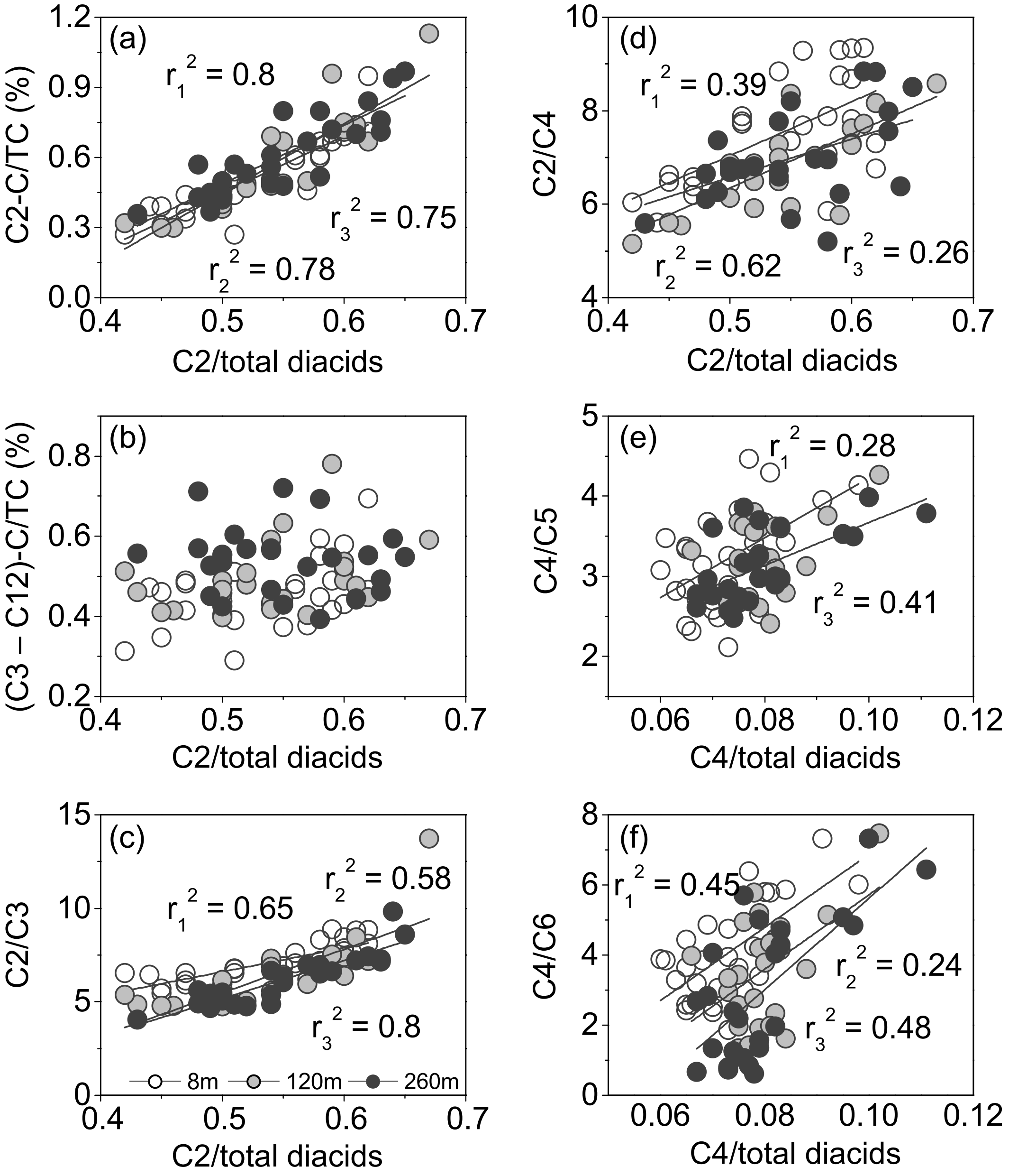

Figure 7. Contributions of (a) C_2-C/TC (%), (b) (C_3–C_{12})-C/TC (%), (c) C_2/C_3 and (d) C_2/C_4 ratios as a function of relative abundance of C_2 in total diacids, as well as correlations for C_4/total diacids with (e) C_4/C_5 and (f) C_4/C_6. The r_1^2, r_2^2, and r_3^2 values are the correlation coefficients for those samples collected at 8 m, 120 m and 260 m, respectively.

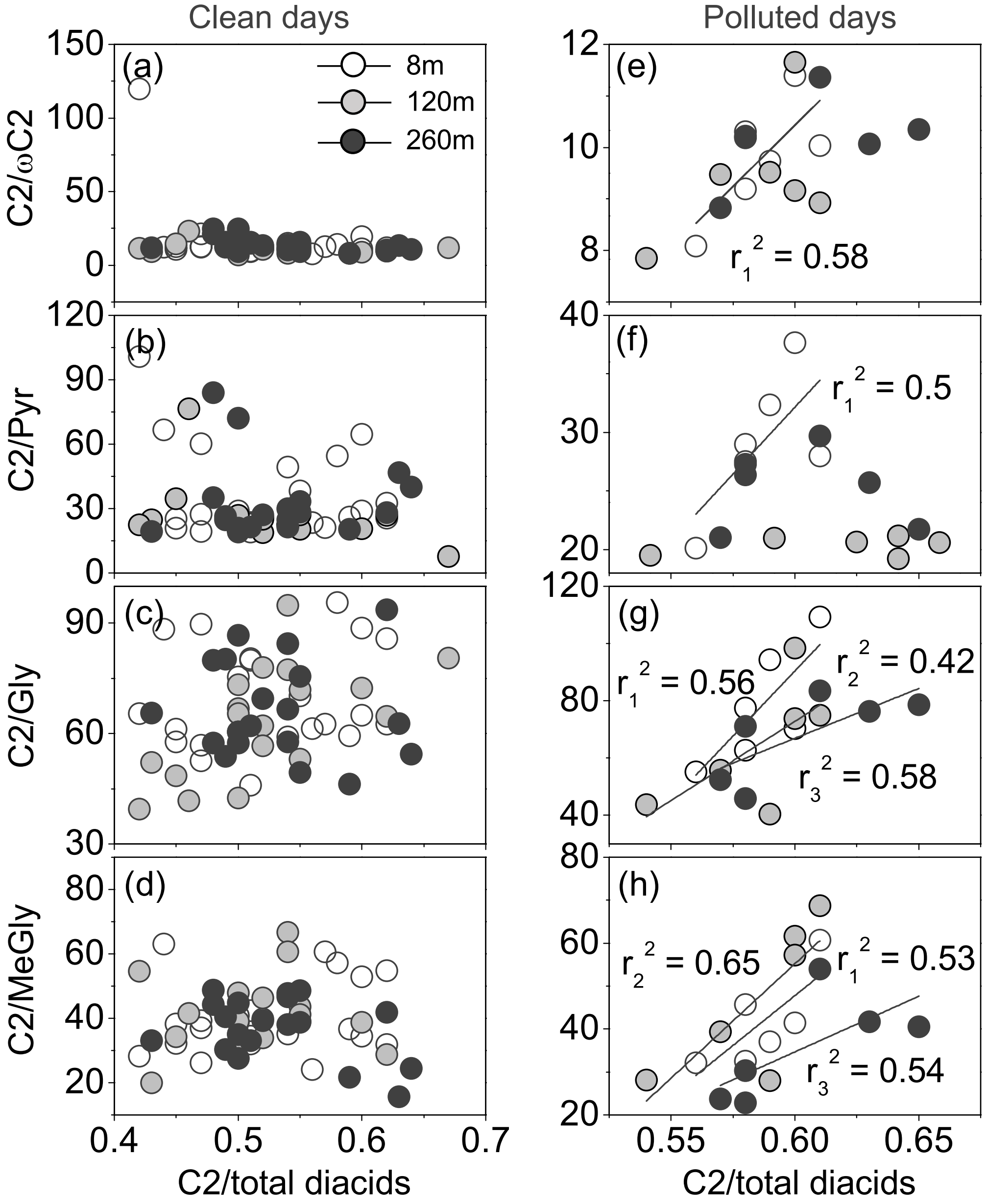

Figure 8. Correlations between concentration ratios of C_2/ωC_2, C_2/Pyr, C_2/Gly, C_2/MeGly and C_2/total diacids in clean days and polluted episodes. The r_1^2, r_2^2, and r_3^2 values represent the correlation coefficients at 8 m, 120 m and 260 m, respectively.

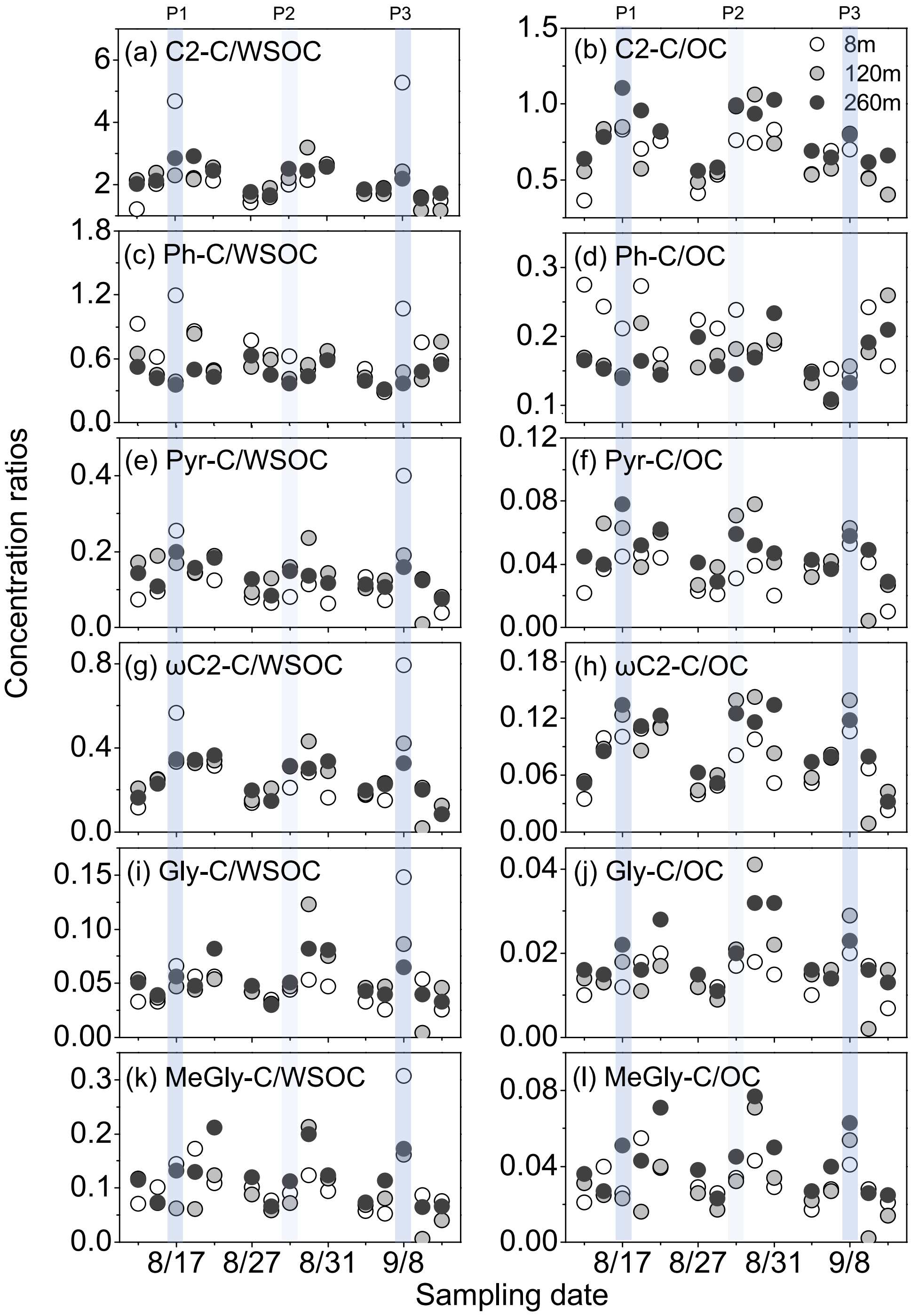

Figure 9. The relative contributions of C_2, Ph, ωC_2, Pyr, Gly and MeGly to carbonaceous fractions (WSOC and OC) in clean, transformation and polluted days. Two moderately polluted days (P1 and P3) and one lightly polluted day (P2) are marked for further discussions. 5

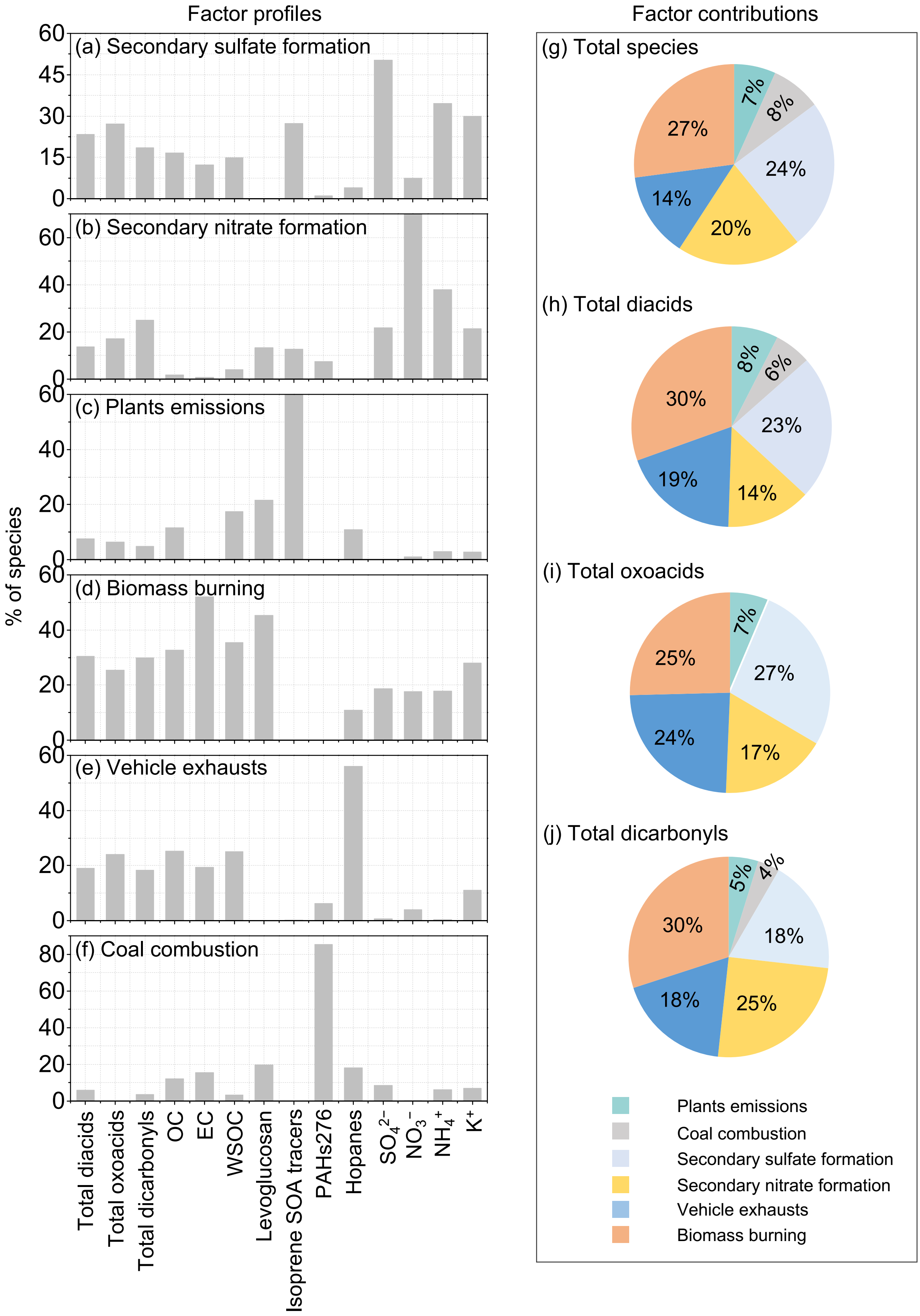

Figure 10. (a − f) Factor profiles (percentage of each species in factor) using ions and organics data for the six factors; (g − j) factor contributions to total species, diacids, oxoacids and α-dicarbonyls.

Supporting Information for

Vertical distribution of particle-phase dicarboxylic acids, oxoacids and α-dicarbonyls in the urban boundary layer based on the 325-meter tower in Beijing

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Table S1. Average vertical ratios of diacids and related organic compounds observed at the tower in Beijing in summer 2015.

Ratio	Ground level (8 m)	Mean±SD	120 m	Mean±SD	260 m	Mean±SD
OC/EC	5.0–10	7.5±1.5	2.6–12	7.0±2.2	2.5–12	7.0±2.4
SOC/POC	NA–1.2	0.5±0.3	NA–3.6	1.8±0.8	NA–3.6	1.9±0.9
C_3/C_4	0.77−1.3	1.1±0.14	0.6−1.4	1.1±0.2	0.65−1.4	1.2±0.21
C_9/total diacids	0.04−0.13	0.07±0.02	0.03−0.13	0.06±0.02	0.03−0.07	0.05±0.01
diacids-C/OC	0.9–2.2	1.5±0.3	1.1–3.0	1.6±0.4	1.2–2.5	1.7±0.3
diacids-C/TC	0.8–2.0	1.4±0.3	0.9–2.1	1.4±0.3	1.2–1.9	1.5±0.3
oxoacids-C/OC	0.75−0.35	0.23±0.06	0.03−0.66	0.27±0.11	0.14−0.4	0.27±0.06
oxoacids-C/TC	0.06−0.31	0.21±0.05	0.02−0.47	0.23±0.09	0.12−0.35	0.23±0.05
dicarbonyls-C/OC	0.03−0.09	0.04±0.02	0.0−0.11	0.05±0.03	0.03−0.1	0.06±0.03
dicarbonyls-C/TC	0.02−0.08	0.04±0.01	0.0−0.1	0.04±0.02	0.03−0.1	0.05±0.02

NA = not available.

Table S2. The decrease percent of diacids and related compound concentrations in restriction period compared to the first (DR/N1, %) and second (DR/N2, %) non-restriction period in Beijing.

	DR/N1			DR/N2		
	Ground level (8 m)	120 m	260 m	Ground level (8 m)	120 m	260 m
C_2	51	57	59	26	29	34
C_3	44	50	51	23	18	25
C_4	39	52	53	25	29	33
C_5	43	50	50	24	30	36
C_6	43	39	ND	14	16	ND
C_9	18	29	41	27	20	18
Ph	27	41	41	ND	10	14
tPh	63	67	69	42	46	55
Pyr	55	64	66	40	52	42
ωC_2	63	59	65	40	41	45
Gly	44	45	55	31	40	38
MeGly	53	41	55	27	37	39
Total diacids	47	53	55	22	27	31
Total oxoacids	52	53	58	31	32	36
Total dicarbonyls	50	43	55	29	36	39

ND = no decrease.

Table S3. The P/T ratios of C_2-C/WSOC, Pyr-C/WSOC, ωC_2-C/WSOC, Gly-C/WSOC and MeGly-C/WSOC observed at the tower in Beijing in summer 2015.

	P1/T1			P3/T3		
	Ground level (8 m)	120 m	260 m	Ground level (8 m)	120 m	260 m
C_2-C/WSOC	2.3	1.0	1.3	4.1	1.4	1.2
Pyr-C/WSOC	2.7	0.9	1.8	5.6	1.5	1.5
ωC_2-C/WSOC	2.3	1.3	1.5	5.2	1.8	1.4
Gly-C/WSOC	2.0	1.3	1.4	5.7	1.8	1.6
MeGly-C/WSOC	1.4	0.9	1.8	5.8	2.0	1.5

Table S4. Summary of error estimation diagnostics from BS and DISP for PMF.

BS Mapping (R≥0.6)		Secondary sulfate formation	Secondary nitrate formation	Plants emissions	Biomass burning	Vehicle exhausts	Coal combustion	Unmapped
Secondary sulfate formation		49	0	1	0	0	0	0
Secondary nitrate formation		0	50	1.8	0	0	0	0
Plants emissions		8	0	41	0	0	1	0
Biomass burning		0	0	0	50	0	0	0
Vehicle exhausts		0	0	0	0	50	0	0
Coal combustion		0	0	0	0	0	50	0
DISP Diagnostics		Error code: 0			Largest decrease in Q: −0.031			
Factor Swaps	dQ^{max}=4	0	0	0	0	0	0	
	dQ^{max}=8	4	0	4	0	0	4	
	dQ^{max}=15	12	0	12	0	0	9	
	dQ^{max}=25	18	0	18	1	0	11	

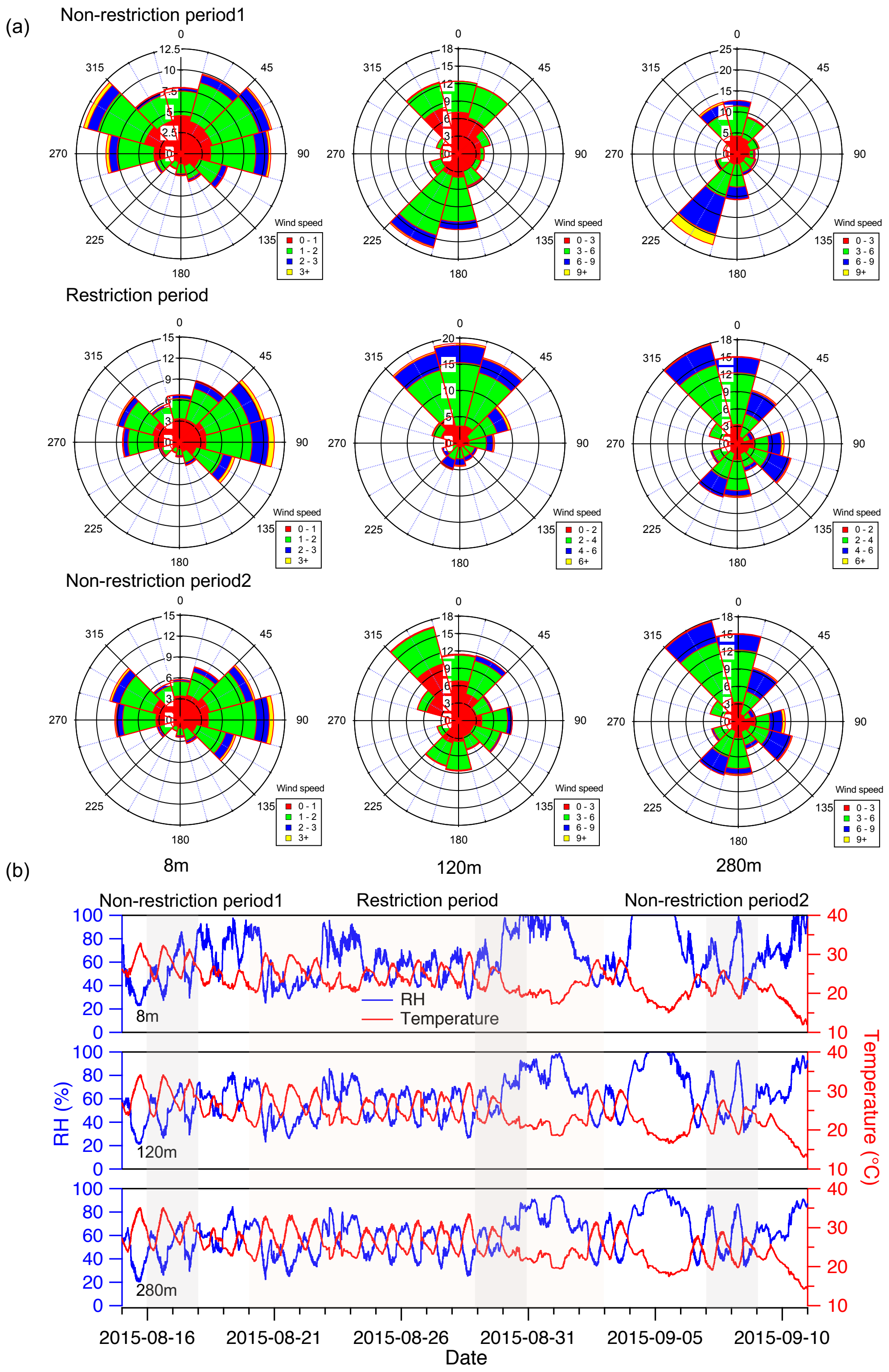

Figure S1: (a) Wind rose diagrams, (b) time series of temperature (℃) and relative humidity (%) at ground level, 120m and 280m in Beijing in summer 2015.

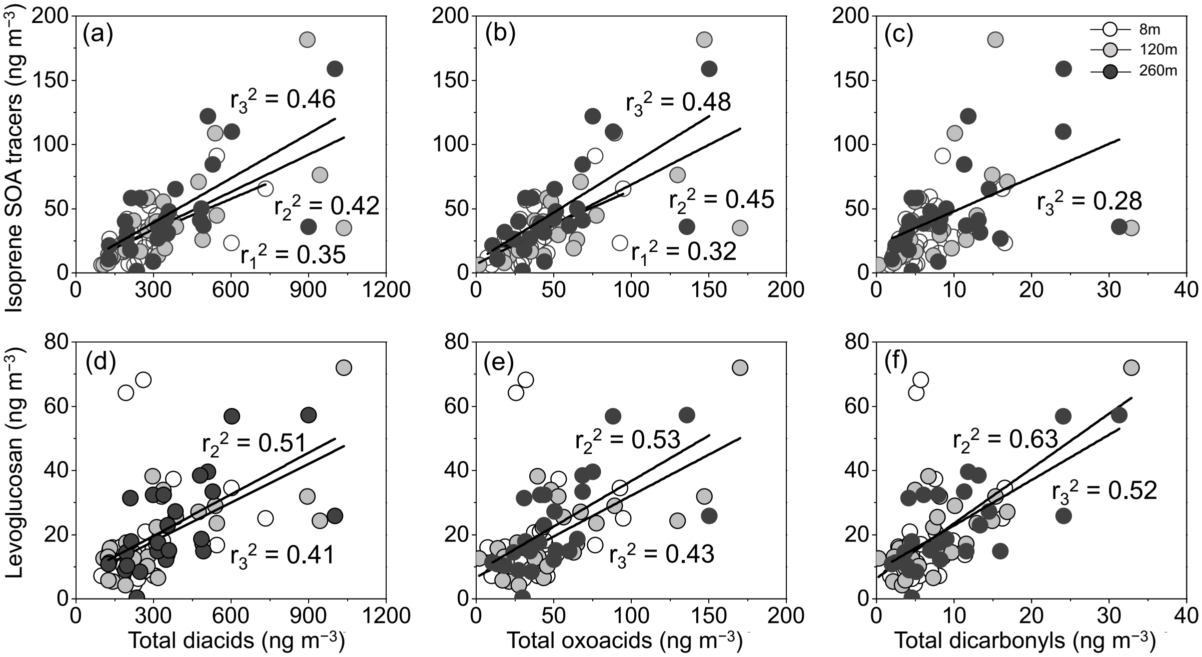

Figure S2: Linear relationships for total diacids, oxoacids and dicarbonyls with levoglucosan, isoprene SOA tracers at ground level, 120 m and 260 m in Beijing. The r_1^2, r_2^2, and r_3^2 represent the correlation coefficients at 8 m, 120 m and 260 m, respectively.

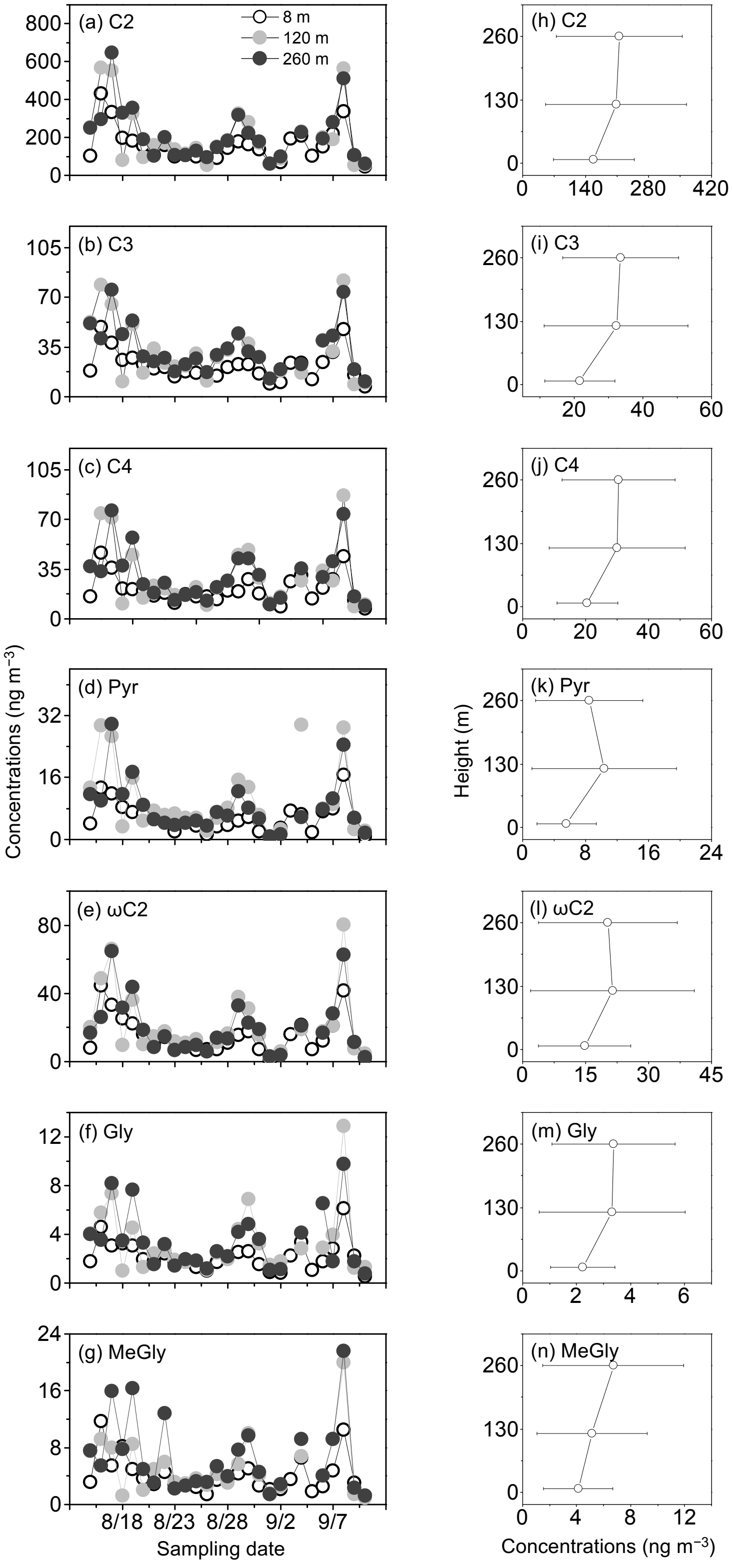

Figure S3: (a − g) Concentration variations and (h − n) vertical properties of selected organic acids at three sampling layers. The circle and bar in (h − n) represent the average concentrations and standard variations of organic acids, respectively.

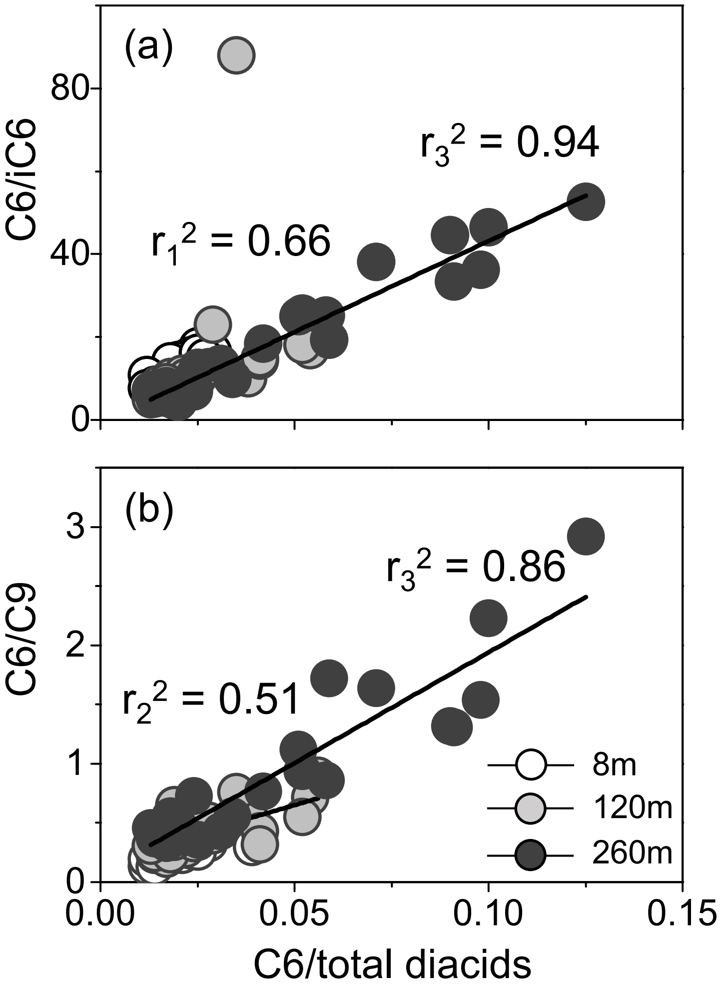

Figure S4: Relationships for C_6/total diacids with C_6/iC_6 and C_6/C_9 in Beijing in summer 2015. The r_1^2, r_2^2, and r_3^2 represent the correlation coefficients at 8 m, 120 m and 260 m, respectively.

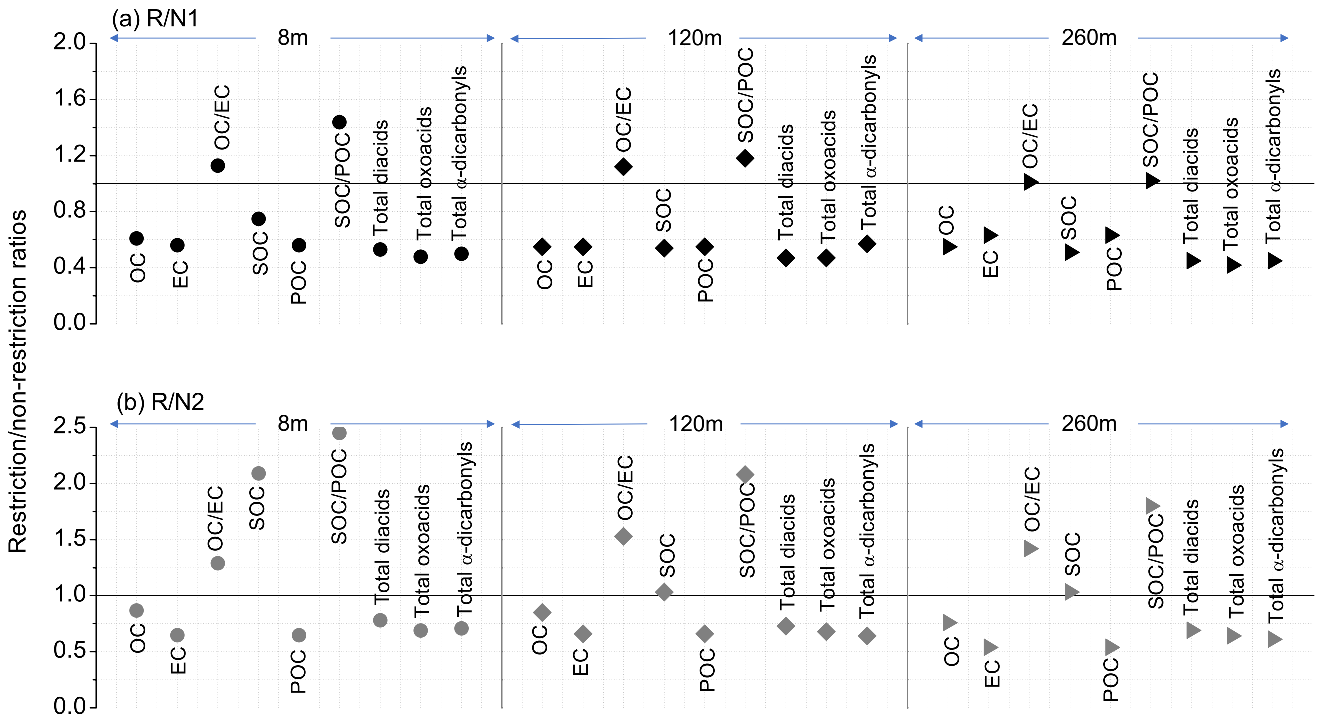

Figure S5: The R/N ratios of particulate compounds observed at the tower in Beijing in summer 2015.

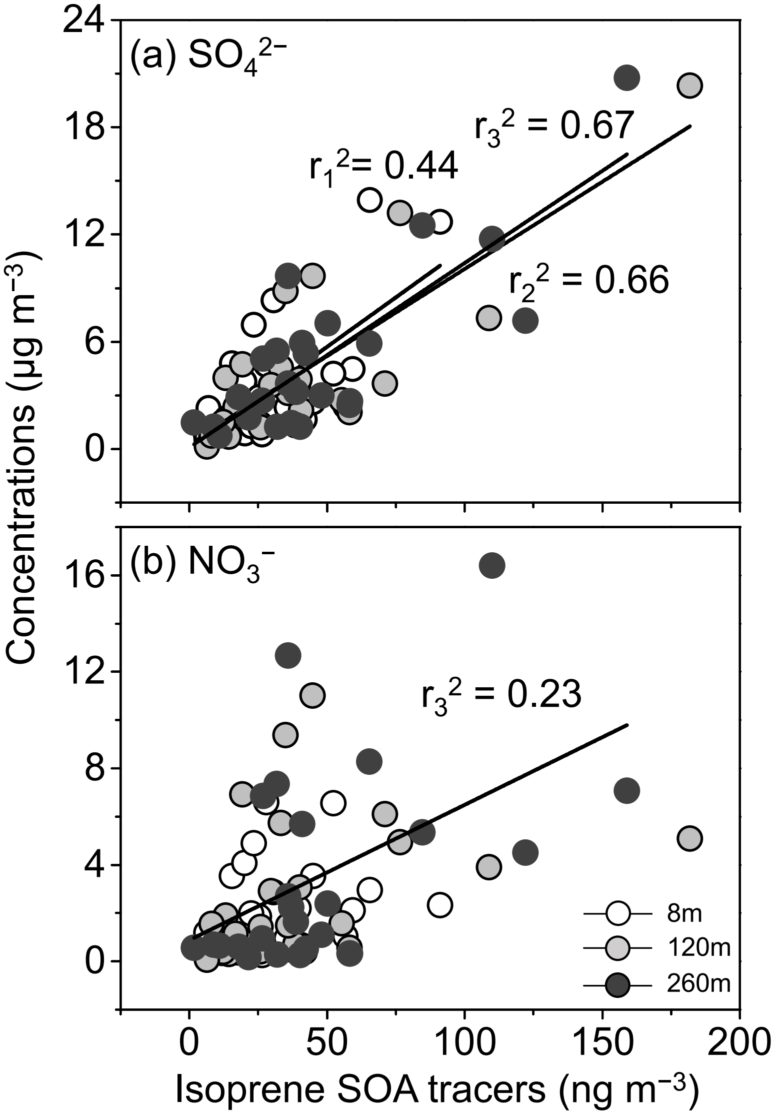

Figure S6: Relationships for isoprene SOA tracers with SO_4^{2-} and NO_3^- at ground level, 120 m and 260 m. The r_1^2, r_2^2, and r_3^2 represent the correlation coefficients at 8 m, 120 m and 260 m, respectively.