Concentrations and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before, during and after the 2014 APEC

Jiayuan Wang¹,³, Gehui Wang¹,²,³,⁴,*, Jian Gao⁵,⁶,*, Han Wang⁵,⁶, Yanqin Ren¹,³,
Jianjun Li¹, Bianhong Zhou¹, Can Wu¹,³, Lu Zhang¹,³, Shulan Wang⁵,⁶, Fahe Chai⁵,⁶

¹State Key Laboratory of Loess and Quaternary Geology, Key Lab of Aerosol Chemistry and
Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an 710061, China
²School of Human Settlements and Civil Engineering, Xi’an Jiaotong University, Xi’an 710079,
China
³University of Chinese Academy of Sciences, Beijing 100049, China
⁴Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment,
Chinese Academy of Sciences, Xiamen 361021, China
⁵State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research
Academy of Environmental Sciences, Beijing 100084, China
⁶Collaborative Innovation Center of Atmospheric Environment and Equipment Technology,
Nanjing 210000, China

Correspondence to: Gehui Wang (wanggh@ieecas.cn) and Jian Gao (gaojian@craes.org.cn)
Abstract: To ensure the good air quality for the 2014 APEC, stringent emission controls were implemented in Beijing and its surrounding regions, leading to a significant reduction in PM$_{2.5}$ loadings. To investigate the impact of the emission controls on aerosol chemistry, high-volume PM$_{2.5}$ samples were collected in Beijing from 8$^{th}$ October to 24$^{th}$ November, 2014 and determined for secondary inorganic ions (SIA, i.e., SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$), dicarboxylic acids, keto-carboxylic acid and $\alpha$-dicarbonyls, as well as stable carbon isotope composition of oxalic acid (C$_2$). Our results showed that SIA, C$_2$ and related SOA in PM$_{2.5}$ during-APEC were 2–4 times lower than those before-APEC, which is firstly ascribed to the strict emission control measures and secondly attributed to the relatively colder and drier conditions during the event that are unfavorable for secondary aerosol production.

C$_2$ in the polluted air masses, which mostly occurred before-APEC, are abundant and enriched in $^{13}$C. On the contrary, C$_2$ in the clean air masses, which mostly occurred during-APEC, is much less abundant but still enriched in $^{13}$C. In the mixed type of clean and polluted air masses, which mostly occurred after-APEC, C$_2$ is lower than that before-APEC but higher than that during-APEC and enriched in lighter $^{12}$C. A comparison on chemical composition of fine particles and $\delta^{13}$C values of C$_2$ in two events that are characterized by high loadings of PM$_{2.5}$ further showed that after-APEC SIA and the total detected organic compounds (TDOC) are much less abundant and fine aerosols are enriched with primary organics and relatively fresh, compared with those before-APEC.

Key words: Secondary organic aerosols; Emission controls; Sources and formation mechanisms; Aqueous-phase oxidation; Aerosol acidity and water content.
1. Introduction

Atmospheric aerosols profoundly impact the global climate directly by scattering and absorbing solar radiation and indirectly by affecting cloud formation and distribution via acting as cloud condensation nuclei (CCN) and ice nuclei (IN). Moreover, atmospheric aerosols exert negative effects on human health because of their toxicity. Due to fast urbanization and industrialization, high level of atmospheric fine particle (PM$_{2.5}$) pollution has been a persistent problem in many cities of China since the nineties of last century (van Donkelaar et al., 2010). As the capital of China and one of the largest megacities in the world, Beijing has suffered from frequent severe haze pollution especially in winter, affecting more than 21 million people by the end of 2014 (Beijing Municipal Bureau of Statistics, 2015) and causing billions of economic loses (Mu and Zhang, 2013). To improve the air quality Beijing government has put many efforts to reduce the pollutant emissions (i.e., SO$_2$, NOx, dust, and volatile organic compounds (VOCs)) from a variety of sources.

The 2014 Asia-Pacific Economic Cooperation (APEC) summit was hosted in Beijing from the 5th to 11th November. To ensure good air quality for the summit, a joint strict emission control program was conducted from 3rd November 2014 in Beijing and its neighboring provinces including Inner Mongolia, Shanxi, Hebei and Shandong provinces. During this period thousands of factories and power plants with high emissions were shut down and/or halted, all the construction activities were stopped and the numbers of on-road vehicles were reduced. These strict emission controls resulted in the air quality of Beijing during the APEC period being significantly improved, leading to a decrease in PM$_{2.5}$ concentration by 59.2% and an increase in visibility by 70.2% in Beijing during the summit compared with those before the APEC (Tang et
and a term of “APEC-Blue” being created to refer to the good air quality. Such strong artificial intervening not only reduced PM$_{2.5}$ and its precursors’ loadings in Beijing and its surrounding areas but also affected the composition and formation mechanisms of the fine particles (Sun et al., 2016).

A number of field measurements have showed that particle compositions in Beijing during wintertime haze periods are dominated by secondary aerosols (Guo et al., 2014; Huang et al., 2014; Xu et al., 2015). Rapid accumulation of particle mass in Beijing during haze formation process is often accompanied by continuous particle size growth (Guo et al., 2014; Zhang et al., 2015), which is in part due to the coating of secondary organic aerosols (SOA) on pre-existing particles (Li et al., 2010). Several studies have found that SOA production during the 2014 Beijing APEC periods significantly reduced and ascribed this reduction to the efficient regional emission control (Sun et al., 2016; Xu et al., 2015). However, up to now information of the SOA decrease on a molecular level has not been reported.

Dicarboxylic acids are the major class of SOA species in the atmosphere and ubiquitously found from the ground surface to the free troposphere (Fu et al., 2008; Myriokefalitakis et al., 2011; Sorooshian et al., 2007; Sullivan et al., 2007). Previous studies have suggested that organic acids including dicarboxylic acids could take part in atmospheric particle nucleation (Zhang et al., 2004; Zhao et al., 2009) and growth processes (Zhang et al., 2012). Furthermore, organic acids may play a central role in aging of black carbon particles (Xue et al., 2009; Ma et al., 2013), enhancing their roles in air pollution accumulation and direct radiative forcing (Peng et al., 2016).

In the current work we measured molecular distributions of dicarboxylic acids, keto-carboxylic acids and α-dicarbonyls and stable carbon isotope composition of oxalic acid in PM$_{2.5}$ aerosols.
collected in Beijing before, during and after the APEC event in order to explore the impact of the APEC emission control on SOA in Beijing. We first investigated the changes in concentration and composition of dicarboxylic acids and related compounds during the three periods, then recognized the difference in stable carbon isotope composition of oxalic acid in different air masses in Beijing during the APEC campaign. Finally we compared the differences in chemical compositions of PM$_{2.5}$ during two heaviest pollution episodes.

2. Experimental section

2.1 Sample collection

PM$_{2.5}$ samples were collected by using a high-volume sampler (TISCH, USA) from 8$^{th}$ October to 24$^{th}$ November 2014 on the rooftop of a three-storey building located on the campus of China Research Academy of Environmental Sciences, which is situated in the north part of Beijing and close to the 5$^{th}$-ring road. All the PM$_{2.5}$ samples were collected onto pre-baked (450 $^\circ$C for 8 h) quartz fiber filters (Whatman 41, USA). The duration of each sample collection is 23 hr from 08:00 am of the previous day to 07:00 am of the next day. Field blanks were also collected before and after the campaign by mounting a pre-baked filter onto the sampler for 15 min without pumping air. After collection, all the filter samplers were individually sealed in aluminum foil bags and stored in a freezer (-18 $^\circ$C) prior to analysis. Daily values of SO$_2$, NOx and meteorological parameters were cited from the website of Beijing Environmental Protection Agency.

2.2 Sample analysis

2.2.1 Elemental carbon (EC), organic carbon (OC), water-soluble organic (WSOC), inorganic ions, aerosol liquid water content (ALWC) and aerosol acidity
Detailed methods for the analysis of EC, OC, WSOC and inorganic ions in aerosols were reported elsewhere (Wang et al. 2010). Briefly, EC and OC in the PM$_{2.5}$ samples were determined by using DRI Model 2001 Carbon analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al., 2007). WSOC and inorganic ions in the samples were extracted with Milli-Q pure water and measured by using Shimadzu TOC-L CPH analyzer and Dionex-600 ion chromatography, respectively (Wang et al. 2010). In the current work, aerosol liquid water content (ALWC) and acidity (i.e., liquid H$^+$ concentrations, [H$^+$]) of the samples were calculated by using ISORROPIA-II model, which treated the Na$^+$−NH$_4^+$−K$^+$−Ca$^{2+}$−Mg$^{2+}$−Cl$^-$−NO$_3^-$−SO$_4^{2-}$ system and was performed in a “metastable” mode (Hennigan et al., 2015; Weber et al., 2016).

2.2.2 Dicarboxylic acids, keto-carboxylic acids and $\alpha$-dicarbonyls

The method of analyzing PM$_{2.5}$ samples for dicarboxylic acids, ketocarboxylic acids and $\alpha$-dicarbonyl has been reported elsewhere (Wang et al., 2002, 2012; Meng et al., 2014; Cheng et al., 2015). Briefly, one eighth of the filter was extracted with Milli-Q water, concentrated to near dryness, and reacted with 14% BF$_3$/butanol at 100 °C for 1 h to convert aldehyde group into dibutoxy acetal and carboxyl group into butyl ester. Target compounds in the derivatized samples were identified by GC/MS and quantified by GC-FID (Agilent GC7890A).

2.3. Stable carbon isotope composition of oxalic acid (C$_2$)

Stable carbon isotope composition ($\delta^{13}$C) of C$_2$ was measured using the method developed by Kawamura and Watanabe (2004). Briefly, $\delta^{13}$C values of the derivatized samples above were determined by gas chromatography-isotope ratio-mass spectrometry (GC-IR-MS) (Thermo Fisher, Delta V Advantage). The $\delta^{13}$C value of C$_2$ was then calculated from an isotopic mass
balance equation based on the measured $\delta^{13}$C of the derivatizations and the derivatizing reagent (1-butanol) (Kawamura and Watanabe, 2004). Each sample was measured for three times to ensure the difference of the $\delta^{13}$C values less than 0.2‰, and the isotope data reported here is the averaged value of the triplicate measurements.

3. Results and discussion

3.1 Variations in meteorological conditions, gaseous pollutants and major components of PM$_{2.5}$ during the Beijing 2014 APEC campaign

Based on the emission control implementation for the APEC, we divided the whole study period into three phases: before-APEC (08/10 to 02/11), during-APEC (03/11 to 12/11) and after-APEC (13/11 to 24/11). Temporal variations in meteorological parameters and concentrations of gaseous pollutants and major components of PM$_{2.5}$ during the three phases are shown in Fig. 1 and summarized in Table 1.

Temperature during the sampling campaign showed a continuous decreasing trend with averages of 13 ± 2.6 °C, 7.0 ± 1.7 °C and 4.3 ± 1.3 °C before-, during- and after-APEC periods, respectively, while relative humidity (RH) did not show a clear trend with mean values of 62 ± 19%, 47 ± 14% and 51 ± 16% during the three periods (Fig.1a and Table 1). SO$_2$ showed a similar level before- and during-APEC periods (8.8 ± 4.6 μg m$^{-3}$ versus 7.6 ± 3.9 μg m$^{-3}$) (Table 1 and Fig.1b), but increased dramatically to 23 ± 8.8 μg m$^{-3}$ after-APEC due to domestic coal burning for house heating. NO$_2$ concentration (45 ± 18 μg m$^{-3}$) during the APEC reduced by about 30% compared to that in the before- and after-APEC phases (71 ± 27 μg m$^{-3}$ versus 78 ± 29 μg m$^{-3}$) (Table 1), mainly because of the reduction of the on-road vehicle numbers, as well as the reduced productivities of power plant and industry. O$_3$ displayed a decreasing trend similar to
that of temperature (Fig. 1c). PM$_{2.5}$ pollution episodes in Beijing showed a periodic cycle of 4–5 days, which is caused by the local weather cycles. Secondary inorganic ions (SIA, i.e., SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) are major components of PM$_{2.5}$ and present a temporal variation pattern similar to that of the fine particles (Fig. 1d). In the current work mass ratio of NO$_3^-$/SO$_4^{2-}$ in PM$_{2.5}$ during the whole study time is 1.8 ± 1.9 (Table 1), which is in agreement with the ratio (1.6–2.4) for PM$_1$ observed during the same time by using aerosol mass spectrometry (AMS) (Sun et al., 2016). OC and EC of PM$_{2.5}$ linearly correlated each other ($R^2=0.91$) and varied periodically in a cycle similar to SIA (Fig. 1e). OC/EC ratio during the whole sampling period is 3.3 ± 0.6 (range: 2.2–4.7) with no significant differences among the three APEC phases (Table 1), although the source emissions could be largely different.

Figure 2 shows the differences in chemical composition of PM$_{2.5}$ before-, during- and after-APEC periods. PM$_{2.5}$ is 98 ± 46 μg m$^{-3}$ during-APEC, about 50% lower than that before- and after-APEC (178 ± 122 μg m$^{-3}$ versus 161 ± 100 μg m$^{-3}$), respectively. Organic matter (OM) is the most abundant component of the fine particles. Relative abundance of OM (OM, 1.6 times of OC) (Xing et al., 2013) to PM$_{2.5}$ continuously increases from 24% before-APEC to 30% and 39% during- and after-APEC, respectively, although the mass concentration (19 ± 7.6 μg m$^{-3}$) of OC during-APEC is the lowest compared to those before- and after-APEC (26 ± 16 μg m$^{-3}$ versus 39 ± 23 μg m$^{-3}$). Sulfate, nitrate and ammonium before-APEC are 15 ± 13, 28 ± 26 and 9.0 ± 8.0 μg m$^{-3}$ (Table 1) and account for 8%, 16% and 5% of PM$_{2.5}$, respectively (Fig. 2). Their concentrations decrease to 5.3 ± 2.8, 10 ± 8.1 and 3.1 ± 2.6 μg m$^{-3}$ (Table 1) with the relative contributions to PM$_{2.5}$ down to 5%, 10% and 3% during-APEC, respectively. While after-APEC their concentrations increased to 11 ± 10, 15 ± 13 and 6.9 ± 6.4 μg m$^{-3}$ and accounted for 7%,
9% and 4% of PM$_{2.5}$. Such significant decreases in concentrations of OM and SIA during-APEC demonstrate the efficiency of the emission controls. OC/EC ratio is almost constant during the whole period, but WSOC/OC ratio decreased by 20% from 0.42 ± 0.13 before-APEC, 0.38 ± 0.16 during-APEC to 0.35 ± 0.17 after-APEC (Table 1). Since WSOC in fine aerosols consist mainly of secondary organic aerosols (SOA) (Laskin et al., 2015), the decreasing ratio of WSOC/OC probably indicates a reduced SOA production during the campaign.

3.2 Oxalic acid and related SOA during the Beijing 2014 APEC campaign

A homogeneous series of dicarboxylic acids (C$_2$−C$_{11}$), keto-carboxylic acid and $\alpha$-dicarbonyls in the PM$_{2.5}$ samples were detected. As show in Table 2, total dicarboxylic acids during the whole study period is 593 ± 739 ng m$^{-3}$, which is lower than that observed during Campaign of Air Quality Research in Beijing 2006 (CAREBeijing) (average 760 ng m$^{-3}$) and 2007 (average 1010 ng m$^{-3}$) (Ho et al, 2010, 2015) and the averaged wintertime concentration reported by a previous research for 14 Chinese cities (904 ng m$^{-3}$) (Ho et al, 2007). Total keto-carboxylic acid is 66 ± 81 ng m$^{-3}$, while total dicarbonyls is 126 ± 115 ng m$^{-3}$ (Table 2). These values are higher than those during CAREBeijing 2006 and 2007 (Ho et al, 2010, 2015), but close to the value observed for the 14 Chinese megacities (Ho et al, 2007). Being similar to those previous observations, oxalic acid (C$_2$) is the most abundant diacid in the 2014 APEC samples with an average of 334 ± 461 ng m$^{-3}$ (range: 10−2127 ng m$^{-3}$, Table 2) during the whole campaign, followed by methylglyoxal (mGly), succinin acid (C$_4$), terephthalic acid (tPh), and glyoxal (Gly). These five species account for 43%, 10%, 9%, 6% and 6% of total detected organic compounds (TDOC), respectively (Fig. 3).

As see in Fig. 4, TDOC in PM$_{2.5}$ are 1099 ± 1104, 325 ± 220 and 487 ± 387 ng m$^{-3}$ before-,
during- and after-APEC, respectively. In comparison with those before-APEC, TDOC during-APEC decreased by 71%. Oxalic acid (C₂) is the leading species among the detected organic compounds and accounted for 46%, 31% and 34% of TDOC during the three phases, respectively (Fig. 4). C₂ is an end product of precursors that are photochemically oxidized in aerosol aqueous phase via either oxidation of small compounds containing two carbon atoms or decomposition of larger compounds containing three or more carbon atoms. Thus mass ratio of C₂ to TDOC is indicative of aerosol aging (Wang et al., 2012; Ho et al., 2015). As shown in Fig. 4, the highest proportion of C₂ before-APEC suggests that organic aerosols during this period are more oxidized, compared to those during- and after-APEC. Glyoxal (Gly) and methylglyoxal (mGly) are the precursors of C₂. Mass ratios of both compounds to TDOC are lowest before-APEC (Fig. 4), further indicating an enhanced SOA production during this period.

3.3 Formation mechanism of oxalic acid

3.3.1 Correlation of oxalic acid with temperature, relative humidity (RH), aerosol liquid water content (ALWC) and acidity and sulfate

A few studies have pointed out that aerosol aqueous phase oxidation is a major formation pathway for oxalic acid (Yu et al., 2005; van Pinxteren, et al., 2014; Bikkina et al., 2015; Tilgner et al, 2010). To explore the formation mechanism of oxalic acid, we calculated ALWC and acidity (i.e., proton concentration, [H⁺]) of PM₂.₅ aerosols by using ISOROPPIA-II model (Weber et al., 2016). As shown in Fig. 5, during the entire period C₂ showed a strong linear correlation with sulfate (R²=0.70 Fig. 5a), which is consistent with those observed in Xi’an (Wang et al., 2012) and other Chinese cities (Yu et al, 2005). Previous studies on particle morphology showed that sulfate particles internally mixes with SOA in Beijing especially on
humid haze days (Li et al., 2010, 2011), which probably indicates that they are formed via similar aqueous phase pathways (Wang et al., 2016). In addition, a robust correlation was also found for C$_2$ with RH ($R^2=0.64$, Fig. 5b) and aerosol liquid water content (ALWC) ($R^2=0.61$, Fig. 5c), indicating that humid conditions are favorable for the aqueous phase formation of C$_2$, which is most likely due to an enhanced gas-to-aerosol aqueous phase partitioning of the precursors (e.g., Gly and mGly) (Fu et al., 2008; Wang et al., 2015a).

NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ are the dominant cation and anions of fine particles in Beijing, respectively (Guo et al., 2014; Zhang et al., 2015) and the molar ratio of [NH$_4^+$] to [NO$_3^-$] + [SO$_4^{2-}$] in this study is 1.1. Thus it is plausible that SO$_4^{2-}$ during the APEC campaign largely existed as ammonium bisulfate, resulting in a strong linear correlation between [H$^+$] and SO$_4^{2-}$ with a molar slope of 1.03 (Fig. 5d) (Zhang et al., 2007). In addition, [H$^+$] shows a significant positive correlation with C$_2$ ($R^2 = 0.84$) (Fig. 5e), possibly due to the fact that acidic conditions are favorable for the formation of C$_2$ precursors. For example, Surratt et al (2007; 2010) found that aerosol acidity can promote the formation of biogenic SOA (BSOA) derived from isoprene oxidation such as 2-methylglyceric acid, Gly and mGly. These BSOA precursors can be further oxidized into C$_2$ (Meng et al., 2014; Wang et al., 2009).

There is a significant positive correlation ($R^2 = 0.58$, $p<0.001$) between the mass ratios of C$_2$/TDOC and ambient temperatures (Fig. 5f), which is similar to the results found by previous researchers (Ho et al., 2007; Strader et al., 1999), indicating that organic aerosols are more aged under a higher temperature condition (Erven et al, 2011; Carlton et al., 2009). Thus, compared with those before-APEC the lower C$_2$/TDOC ratios (31% and 34%, respectively) (Fig. 4) during- and after-APEC can be ascribed in part to the relatively lower temperature conditions that are not
favorable for oxidation of the precursors to produce oxalic acid (13 ± 2.6 °C, 7.0 ± 1.7 °C and 4.3 ± 1.3 °C before-, during- and after-APEC periods, respectively) (Table 1).

3.3.2 Temporal variation in stable carbon isotopic composition of oxalic acid

To further discuss the formation mechanism of C2, we investigated the temporal variations of concentration and stable carbon isotopic composition of C2 in the PM2.5 samples (Fig. 6). Previous studies have demonstrated that Gly, mGly, glyoxylic acid (ωC2) and pyruvic acid (Pyr) are the precursors of C2 (Carlton et al., 2006, 2007; Ervens and Barbara, 2004; Wang et al., 2012). Thus, higher mass ratios of C2 to its precursors indicate that organic aerosols are more oxidized (Wang et al., 2010). As shown in Table 3, δ13C of C2 in this work positively correlated with the mass ratios of C2/ωC2, C2/mGly and TDOC/WSOC, demonstrating an enrichment of 13C during the aerosol oxidation process. Because decomposition (or breakdown) of larger molecular weight precursors in aerosol aqueous phase is the dominant formation pathway for C2 in aerosol ageing process (Kawamura et al., 2016; Gensch et al., 2014; Kirillova et al., 2013), during which organic compounds release CO2/CO by reaction with OH radical and other oxidants, resulting in the evolved species enriched with lighter isotope (12C) and the remaining substrate enriched in 13C due to kinetic isotope effects (KIE) (Hoefs, 1997; Rudolph et al., 2002).

72-h backward trajectory analysis showed that air masses moved to Beijing during the whole sampling period can roughly be categorized into three types (Fig. 6a) (all trajectories during the entire study period can be found in the supplementary materials). (1) Polluted type, by which air masses originated from inland and east coastal China and moved slowly into Beijing within 72-h from its south regions, i.e., Henan, Shandong and Jiangsu provinces. This type of air masses mostly occurred before-APEC with high PM2.5 concentrations. Air pollution has widely
distributed in the three provinces (Wei et al., 2016); thus aerosols transported by this type of air masses are of regional characteristics. (2) Mixed type, by which air masses originated from Mongolia and North China, and moved quickly into Hebei province and then turned back to Beijing. Air in Mongolia and North China was clean but polluted in Hebei province, which is adjacent to Beijing. This type of air masses is a mixture of clean and polluted air and thus named as mixed type. Since the resident time of the mixed type of air masses within Hebei province is very short, thus aerosols transported by this type of air masses is of local characteristics and relatively fresh. (3) Clean type, by which air masses originated from Siberia and moved rapidly into Beijing directly via a long-range transport. Aerosols from the clean type of air masses are much more aged, while those from the mixed type of air masses are fresh. Since severe air pollution is widespread in the south regions, gas-to-aerosol phase partitioning of precursors and subsequent aerosol-phase oxidation to produce SOA including C₂ continuously proceed during the air mass movement. However, such a partition for producing SOA is not significant when air mass move from Siberia, Mongolia and North China because of the much less abundant VOCs. In stead, aerosols in the clean air masses are continuously oxidized, during which C₂ is produced by photochemical decomposition of larger molecular weight precursors. Therefore, C₂ in PM₉₅ transported by the mixed type air masses are not only fresh and abundant but also enriched in ¹²C, whereas C₂ in PM₂₅ transported by the clean type air masses are aged, less abundant and enriched in ¹³C due to KIE effects, as illustrated by the pink and light blue columns in Fig. 6b, respectively. C₂ in PM₂₅ transported by the polluted type of air masses are most abundant compared with that in other two types of air masses, which is not only due to the severe air pollution in the Henan, Shandong and Jiangsu provinces but also due to the enhanced
photochemical oxidation under the humid, higher temperature and stagnant conditions that occurred mostly before-APEC, as discussed previously. Therefore, C₂ in the polluted type of air masses is not only abundant but also enriched in \(^{13}\text{C}\) (see black columns in Fig. 6b).

3.4 Different chemical characteristics of PM₂,₅ between two severe haze events

From Fig. 1 and Table 4, it can be found that PM₂,₅ showed two equivalent maxima on 9\(^{\text{th}}\) October and 20\(^{\text{th}}\) November during the whole study period. However, the chemical compositions of PM₂,₅ during these two pollution events are significantly different. As shown in Fig. 7a, relative abundances of SIA (sum of \(\text{SO}_4^{2-}\), \(\text{NO}_3^-\) and \(\text{NH}_4^+\)) to PM₂,₅ are 30% during the event I and 23% during the event II, respectively. The relative abundance of OM (21%, Fig. 7a) during the event I is lower than that (37%) during the event II (Fig. 7b). In contrast, the ratios of WSOC/OC and TDOC/OC are higher in the event I than in the event II, which is consistent with lower levels of O₃ after-APEC (Table 1), suggesting a weaker photochemical oxidation capacity during the event II. Organic biomarkers in the PM₂,₅ samples have been measured for the source apportionment (Wang et al., 2016) and cited here to further identify the difference in chemical composition of PM₂,₅ between the two events. Levoglucosan is a key tracer for biomass burning smoke. Mass ratio of levoglucosan to OC in PM₂,₅ (Lev/OC) is comparable between the two events, suggesting a similar level of contributions of biomass burning emission to PM₂,₅ before- and after-APEC. However, the mass ratios of PAHs and hopanes to OC are lower in event I than those in event II (Fig. 7c), which again demonstrates the enhanced emissions from coal burning for house heating, because these compounds are key tracers of coal burning smokes (Wang et al., 2006). As seen in Fig. 7d, C₂ in the event I was enriched in \(^{13}\text{C}\). Such relatively more abundant SIA, WSOC and TDOC and heavier C₂ in PM₂,₅ clearly demonstrate that PM₂,₅ during the event
I are enriched with secondary products while the fine particles during the event II are enriched with primary compounds. After-APEC house heating activities including residential coal burning were activated, which emitted huge amounts of SO$_2$, NO$_x$, and VOCs as well as primary particles, resulting in both absolute concentrations and relative abundances of CO and EC 30–40% higher after-APEC than before-APEC (see Table 1). Li et al (2015) reported that VOCs in Beijing was 86 ppbv before-APEC, 48 ppbv during-APEC and 73 ppbv after-APEC. As shown in Table 4, temperature (16.7±0.8 °C for event I and 4.5±1.7 °C for event II) and relative humidity (RH) (82±4% for event I and 62±13% for event II) are lower during the event II than during the event I. Moreover, air masses arriving in Beijing during the event II are the mix type, of which the resident time in Hebei province is short. Compared with those in the event I, such colder and drier conditions and short reaction time during the event II are unfavorable for photochemical oxidation, resulting in SOA not only less abundant but also enriched with lighter $^{12}$C during the event II, although VOCs levels are comparable before- and after-APEC.

4. Summary and conclusion

Temporal variations in molecular distribution of SIA, dicarboxylic acids, ketoacids and $\alpha$-dicarbonyl and stable carbon isotopic composition ($\delta^{13}$C) of C$_2$ in PM$_{2.5}$ collected in Beijing before-, during- and after- the 2014 APEC were investigated. Absolute concentrations and relative abundances of SIA and C$_2$ in PM$_{2.5}$ are highest before-APEC, followed by those after- and during-APEC, suggesting that the fine aerosols before-APEC are enriched with secondary products, mainly due to an enhanced photochemical oxidation under the warm, humid and stagnant conditions. Concentrations of SIA, oxalic acid and related SOA in PM$_{2.5}$ during-APEC are 2–4 times lower than those before-APEC, which can be ascribed to the effective emission
controls and the favorable meteorological conditions that brought clean air from Siberia and Mongolia into Beijing.

Positive correlations of C₂ with sulfate mass, RH, ALWC and aerosol acidity indicate that C₂ formation pathway is involved an acid-catalyzed aerosol aqueous phase oxidation. SIA, C₂ and related SOA in the polluted type of air masses are abundant with C₂ enriched in $^{13}$C. On the contrary, those in the clean type of air masses are much less abundant, although C₂ is also enriched in $^{13}$C. By comparing the chemical composition of PM$_{2.5}$ and $\delta^{13}$C values of C₂ in two events that are characterized by the highest loadings of PM$_{2.5}$ before- and after-APEC, we further found that compared with those before- APEC fine aerosols after-APEC are enriched with primary species and C₂ is depleted in heavier $^{13}$C, although SO₂, NOx and VOCs are abundant during the heating season, again demonstrating the important role of meteorological conditions in the secondary aerosol formation process, which are warmer, humid and stagnant before-APEC and result in secondary species much more abundant than those during- and after-APEC.

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References


van Pinxteren, D., Neusüß, C., and Herrmann, H.: On the abundance and source contributions of dicarboxylic acids in size-resolved aerosol particles at continental sites in central Europe, Atmospheric Chemistry and Physics, 14, 3913-3928, 10.5194/acp-14-3913-2014, 2014.


**Figure Captions**

**Figure 1.** Temporal variations of meteorological conditions, gaseous pollutants and major components of PM$_{2.5}$ during the 2014 APEC campaign. (The brown shadows represent two air pollution events characterized by highest PM$_{2.5}$ levels before- and after-APEC, while the blue shadow represents the APEC event).

**Figure 2.** Chemical composition of PM$_{2.5}$ during the 2014 APEC campaign.

**Figure 3.** Molecular distributions of dicarboxylic acids and related compounds in PM$_{2.5}$ of Beijing, China during the 2014 APEC campaign. The pie chart is the average composition of total detected organic compounds (TDOC) and the top number is the average mass concentration of TDOC of the whole study period.

**Figure 4.** Compositions of total detected organic compounds (TDOC) in PM$_{2.5}$ during the 2014 APEC campaign.

**Figure 5.** Correlation analysis for oxalic acid (C$_2$) and sulfate in PM$_{2.5}$ during the whole 2014 APEC campaign. (a-c) Concentrations of C$_2$ with sulfate, relative humidity (RH), and aerosol liquid water content (ALWC); (d, e) sulfate and C$_2$ with aerosol acidity [H$^-$] and (f) temperature with mass ratio of C$_2$ to total detected organic compounds (C$_2$/TDOC).

**Figure 6.** (a) 72-h backward trajectories determined by the National Oceanic and Atmospheric Administration Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model arriving at the sampling site to reveal the major air mass flow types during the study period. Northwesterly wind (light blue) was most frequently (64%), followed by northerly (21%, pink) and southerly (15%, black) and is defined as clean, mixed and polluted types, respectively (see the definitions in the text and the trajectories with a 6-hr interval in the supplementary section); (b) Time series of $\delta^{13}$C values and concentration of oxalic acid during the whole study period (Colors in Fig. 6a are corresponding to those in Fig. 6b).

**Figure 7.** Comparison of chemical composition of PM$_{2.5}$ during two air pollution events. (a) Percentages of major species in PM$_{2.5}$; (b, c) mass ratios of major species and organic tracers in PM$_{2.5}$; (d) stable carbon isotope composition of oxalic acid (C$_2$) (Data about levoglucosan (Lev), PAHs and hopanes are cited from Wang et al (2016)).
### Table 1. Meteorological parameters and concentrations of gaseous pollutants and chemical components of PM$_{2.5}$ in Beijing during the 2014 APEC campaign

<table>
<thead>
<tr>
<th></th>
<th>Whole period</th>
<th>Before-APEC (08/10–02/11)</th>
<th>During-APEC (03/11–12/11)</th>
<th>After-APEC (13/11–14/11)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N=48)</td>
<td>(N=26)</td>
<td>(N=10)</td>
<td>(N=12)</td>
</tr>
<tr>
<td>I. Meteorological parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>9.5±4.3 (3.0–18)</td>
<td>13±2.6 (9.0–18)</td>
<td>7.0±1.7 (4.0–10)</td>
<td>4.3±1.3 (3.0–7.0)</td>
</tr>
<tr>
<td>Relative humidity, %RH</td>
<td>56±19 (17–88)</td>
<td>62±19 (22–88)</td>
<td>47±14 (17–65)</td>
<td>51±16 (29–80)</td>
</tr>
<tr>
<td>Visibility, km</td>
<td>8.8±6.8 (1.0–28)</td>
<td>7.3±6.6 (1.0–24)</td>
<td>13±7.7 (6.0–28)</td>
<td>7.2±4.2 (2.0–15)</td>
</tr>
<tr>
<td>Wind speed, km</td>
<td>8.0±4.9 (3.0–26)</td>
<td>7.6±4.8 (3.0–26)</td>
<td>9.4±6.6 (3.0–26)</td>
<td>7.8±2.9 (3.0–13)</td>
</tr>
<tr>
<td>II. Gaseous pollutants, μg m$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_3$</td>
<td>48±23 (6.0–115)</td>
<td>55±24 (9.0–115)</td>
<td>52±13 (25–69)</td>
<td>29±18 (6.0–60)</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>12±8.5 (2.0–43)</td>
<td>8.8±4.6 (2.0–19)</td>
<td>7.6±3.9 (2.0–15)</td>
<td>23±8.8 (13–43)</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>68±29 (10–135)</td>
<td>71±27 (22–118)</td>
<td>45±18 (10–69)</td>
<td>78±29 (45–135)</td>
</tr>
<tr>
<td>CO</td>
<td>1360±730 (220–3320)</td>
<td>1370±700 (250–2460)</td>
<td>960±410 (220–1420)</td>
<td>1720±830 (740–3320)</td>
</tr>
<tr>
<td>III. Major components of PM$_{2.5}$, μg m$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>157±110 (16–408)</td>
<td>178±122 (16–408)</td>
<td>98±46 (28–183)</td>
<td>161±100 (36–383)</td>
</tr>
<tr>
<td>SO$_{2}^{+}$</td>
<td>12±11.5 (1.2–43)</td>
<td>15±13 (1.2–43)</td>
<td>5.3±2.8 (1.8–11)</td>
<td>11±10 (2.9–34)</td>
</tr>
<tr>
<td>NO$_{3}^{-}$</td>
<td>21±22 (0.32–88)</td>
<td>28±26 (0.32–88)</td>
<td>10±8.1 (1.2–26)</td>
<td>15±13 (2.9–46)</td>
</tr>
<tr>
<td>NH$_4^{+}$</td>
<td>7.3±7.2 (0.2–28)</td>
<td>9.0±8.0 (0.2–28)</td>
<td>3.1±2.6 (0.2–8.6)</td>
<td>6.9±6.4 (1.0–22)</td>
</tr>
<tr>
<td>OC</td>
<td>28±18 (5.7–78)</td>
<td>26±16 (6.0–67)</td>
<td>19±7.6 (5.7–29)</td>
<td>39±23 (9.7–78)</td>
</tr>
<tr>
<td>EC</td>
<td>8.8±5.4 (1.4–25)</td>
<td>8.6±4.6 (1.4–18)</td>
<td>6.0±2.7 (1.5–9.6)</td>
<td>12±7.0 (2.1–25)</td>
</tr>
<tr>
<td>WSOC$^b$</td>
<td>10±6.0 (2.4–32)</td>
<td>11±4.6 (3.1–32)</td>
<td>6.4±2.6 (2.4–11)</td>
<td>11±6.1 (4.5–24)</td>
</tr>
<tr>
<td>ALWC$^c$</td>
<td>40±62 (0–299)</td>
<td>58±75 (0–299)</td>
<td>6.3±5.5 (0–19)</td>
<td>28±41 (0.4–136)</td>
</tr>
<tr>
<td>$[\text{H}^+]^d$</td>
<td>0.083±0.14 (0.0–0.56)</td>
<td>0.13±0.17 (0.0–0.56)</td>
<td>0.026±0.025 (0.0–0.072)</td>
<td>0.033±0.067 (0.0–0.20)</td>
</tr>
<tr>
<td>IV. Mass ratios of major components of PM$_{2.5}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$<em>3^{-}$/SO$</em>{2}^{+}$</td>
<td>1.6±0.8 (0.3–4.3)</td>
<td>1.7±0.9 (0.3–4.3)</td>
<td>1.6±0.7 (0.5–2.4)</td>
<td>1.4±0.4 (0.8–2.2)</td>
</tr>
<tr>
<td>OC/EC</td>
<td>3.3±0.6 (2.2–4.7)</td>
<td>3.2±0.7 (2.2–4.5)</td>
<td>3.3±0.6 (2.0–4.3)</td>
<td>3.4±0.5 (2.7–4.7)</td>
</tr>
<tr>
<td>WSOC/OC</td>
<td>0.39±0.15 (0.10–0.71)</td>
<td>0.42±0.13 (0.13–0.71)</td>
<td>0.38±0.16 (0.16–0.65)</td>
<td>0.35±0.17 (0.10–0.63)</td>
</tr>
</tbody>
</table>

$^a$Organic (OC) and elemental carbon (EC); $^b$Water-soluble organic carbon (WSOC); $^c$Aerosol liquid water content (ALWC); $^d$Hydrogen ion concentration ($[\text{H}^+]$)
Table 2. Concentrations of dicarboxylic acids and related compounds in PM$_{2.5}$ in Beijing during the 2014 APEC campaign (ng m$^{-3}$)

<table>
<thead>
<tr>
<th></th>
<th>Whole period (N=48)</th>
<th>Before-APEC (08/10–02/11) (N=26)</th>
<th>During-APEC (03/11–12/11) (N=10)</th>
<th>After-APEC (13/11–14/11) (N=12)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I. Dicarboxylic acids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxalic, C$_2$</td>
<td>334 ± 461 (10–2127)</td>
<td>502 ± 564 (10.5–2127)</td>
<td>101 ± 69 (35–251)</td>
<td>166 ± 157 (22–554)</td>
</tr>
<tr>
<td>Malonic, C$_3$</td>
<td>31 ± 42 (ND–247)</td>
<td>45.7 ± 52.1 (1.44–247)</td>
<td>12 ± 8.0 (3.4–22.8)</td>
<td>16± 10.9 (ND–36)</td>
</tr>
<tr>
<td>Succinic, C$_4$</td>
<td>74 ± 118 (3.0–722)</td>
<td>111 ± 150 (3.0–722)</td>
<td>24 ± 14 (7.1–42)</td>
<td>36 ± 26 (4.9–90)</td>
</tr>
<tr>
<td>Glutaric, C$_5$</td>
<td>8.7 ± 12 (ND–68)</td>
<td>13± 15 (ND–68.1)</td>
<td>2.9 ± 2.24 (0.9–5.8)</td>
<td>4.9 ± 4.2 (ND–13)</td>
</tr>
<tr>
<td>Adipic, C$_6$</td>
<td>13± 14 (0.9–83)</td>
<td>17± 18 (1.9–83)</td>
<td>5.9 ±3.8 (2.1–14)</td>
<td>9.9 ± 7.1 (2.0–23)</td>
</tr>
<tr>
<td>Pimelic, C$_7$</td>
<td>2.1 ± 3.8 (ND–27)</td>
<td>2.6 ± 5.1 (ND–27)</td>
<td>1.1 ± 0.7 (0.2–2.3)</td>
<td>2.0 ± 1.1 (0.9–4.4)</td>
</tr>
<tr>
<td>Suberic, C$_8$</td>
<td>10 ± 11 (ND–66)</td>
<td>12± 13 (ND–66)</td>
<td>7.6 ± 5.0 (1.3–16)</td>
<td>8.7 ± 6.0(2.0–21)</td>
</tr>
<tr>
<td>Azelaic, C$_9$</td>
<td>5.0± 4.9(0.5–21)</td>
<td>6.4 ± 5.7 (0.6–21)</td>
<td>1.7± 0.9 (0.5–3.2)</td>
<td>4.6 ± 3.3 (1.3–13)</td>
</tr>
<tr>
<td>Sebacic, C$_{10}$</td>
<td>7.7 ± 7.4 (ND–34)</td>
<td>9.4 ± 8.8 (ND–34)</td>
<td>4.2± 3.6 (0.5–11)</td>
<td>6.8 ± 4.9 (1.4–16)</td>
</tr>
<tr>
<td>Undecanedioic, C$_{11}$</td>
<td>11 ± 13 (ND–77)</td>
<td>14 ± 16 (ND–77)</td>
<td>3.3 ± 2.5 (ND–7.5)</td>
<td>9.4 ± 6.4 (0.8–23)</td>
</tr>
<tr>
<td>Methylsuccinic, iC$_5$</td>
<td>13 ± 16 (0.6–79)</td>
<td>18 ± 19 (0.6–79)</td>
<td>4.8 ± 3.0 (1.0–9.2)</td>
<td>8.4 ± 6.0(2.3–19)</td>
</tr>
<tr>
<td>Methylglutaric, iC$_6$</td>
<td>7.5 ± 10 (ND–36)</td>
<td>11± 12 (ND–36)</td>
<td>0.9 ± 0.9 (ND–2.6)</td>
<td>4.6± 5.1 (ND–14)</td>
</tr>
<tr>
<td>Maleic, M</td>
<td>3.4 ± 3.9 (ND–15)</td>
<td>4.6± 4.7 (ND–15)</td>
<td>1.4 ± 0.8 (ND–2.9)</td>
<td>2.4 ± 2.0 (ND–6.3)</td>
</tr>
<tr>
<td>Fumaric, F</td>
<td>7.2 ± 8.8 (ND–64)</td>
<td>10 ± 11 (ND–64)</td>
<td>2.2± 1.5 (ND–5.4)</td>
<td>4.7 ± 3.2 (1.4–10)</td>
</tr>
<tr>
<td>Phthalic, Ph</td>
<td>17 ± 14 (1.5–64)</td>
<td>20 ± 16 (1.5–64)</td>
<td>10 ± 6.8 (2.3–20)</td>
<td>17 ± 9.0 (6.4–31)</td>
</tr>
<tr>
<td>Isophthalic, tPh</td>
<td>2.1 ± 2.5 (ND–10)</td>
<td>2.9 ± 2.8 (ND–10)</td>
<td>2.0 ± 2.1 (0.2–5.9)</td>
<td>0.5 ± 0.3 (ND–3.2)</td>
</tr>
<tr>
<td>Terephthalic, tPh</td>
<td>46 ± 35 (2.6–133)</td>
<td>50 ± 35 (2.6–123)</td>
<td>28 ± 19 (4.7–59)</td>
<td>53± 40 (7.4–133)</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td>593 ± 739 (25–3788)</td>
<td>849 ± 905 (25–3788)</td>
<td>214 ± 135 (72–447)</td>
<td>354 ± 279 (85–965)</td>
</tr>
<tr>
<td><strong>II. Keto-carboxylic acids</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pyruvic, Pyr</td>
<td>24 ± 20 (1.3–84)</td>
<td>31± 23 (2.4–84)</td>
<td>15 ± 12 (1.3–36)</td>
<td>15 ± 9.3 (3.2–33)</td>
</tr>
<tr>
<td>Glyoxylic, oC$_2$</td>
<td>33 ± 51 (1.2–300)</td>
<td>48±6 (1.2–300)</td>
<td>10 ± 7.7 (2.6–21)</td>
<td>20 ± 23 (2.8–80)</td>
</tr>
<tr>
<td>7-Oxohexanoic, oC$_7$</td>
<td>8.8 ± 14 (ND–90)</td>
<td>13± 17 (ND–90)</td>
<td>4.2 ± 3.6 (ND–13)</td>
<td>4.5 ± 5.1 (ND–17)</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td>66 ± 8 (3.6–474)</td>
<td>92 ± 99 (3.6–474)</td>
<td>30 ± 22 (5.9–66)</td>
<td>40 ± 35 (13–128)</td>
</tr>
<tr>
<td><strong>III α-Dicarbonyls</strong></td>
<td></td>
<td></td>
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<tr>
<td>Glyoxal, G</td>
<td>44 ± 47 (4.2–270)</td>
<td>57 ± 56 (4.2–270)</td>
<td>22 ± 19 (4.9–47)</td>
<td>35 ± 30 (7.3–101)</td>
</tr>
<tr>
<td>Methylglyoxal, mGly</td>
<td>82 ± 82 (ND–406)</td>
<td>102 ± 96 (ND–406)</td>
<td>60 ± 52 (15–139)</td>
<td>58 ± 51 (5.8–144)</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td>126 ± 115 (5.3–466)</td>
<td>158 ± 132 (5.3–466)</td>
<td>81.6 ± 67.4 (22–186)</td>
<td>93 ± 80 (14–225)</td>
</tr>
<tr>
<td><strong>TDOC$^b$</strong></td>
<td>785 ± 872 (36–4636)</td>
<td>1099 ± 1104 (36–4636)</td>
<td>325 ± 220 (107–664)</td>
<td>487 ± 387 (117–1318)</td>
</tr>
</tbody>
</table>

$^a$ND: not detectable; $^b$TDOC: total detected organic compounds.
Table 3 Linear correlation coefficients of $\delta^{13}C$ of C$_2$ with C$_2$/ωC$_2$, C$_2$/mGly, and TDOC/WSOC

<table>
<thead>
<tr>
<th></th>
<th>C$_2$/ωC$_2$</th>
<th>C$_2$/mGly</th>
<th>TDOC/WSOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{13}C$</td>
<td>0.49**</td>
<td>0.35*</td>
<td>0.41*</td>
</tr>
</tbody>
</table>

** $p<0.01$; * $p<0.05$
Table 4. Meteorological parameters and chemical compositions ($\mu$g m$^{-3}$) of two maximum PM$_{2.5}$ between two pollution episodes in Beijing

<table>
<thead>
<tr>
<th>Event I</th>
<th>T ($^\circ$C)</th>
<th>RH (%)</th>
<th>V (km)</th>
<th>PM$_{2.5}$</th>
<th>OC</th>
<th>EC</th>
<th>SIA $^b$</th>
<th>TDOC $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8/10-11/10, Before-APEC)</td>
<td>16.7 ± 0.8</td>
<td>82 ± 4</td>
<td>1.5 ± 0.5</td>
<td>349 ± 57</td>
<td>45 ± 12</td>
<td>12 ± 2</td>
<td>106 ± 39</td>
<td>2749 ± 1357</td>
</tr>
<tr>
<td>Event II</td>
<td>4.5 ± 1.7</td>
<td>62 ± 13</td>
<td>3.5 ± 1.5</td>
<td>259 ± 102</td>
<td>60 ± 21</td>
<td>17 ± 6</td>
<td>60 ± 32</td>
<td>831 ± 400</td>
</tr>
</tbody>
</table>

$^a$V: visibility; $^b$SIA: secondary inorganic ions (the sum of sulfate, nitrate and ammonium); $^c$TDOC: total detected organic compounds
Figure 1. Temporal variations of meteorological conditions, gaseous pollutants and major components of PM$_{2.5}$ during the 2014 APEC campaign. (The brown shadows represent two air pollution events characterized by highest PM$_{2.5}$ levels before- and after-APEC, while the blue shadow represents the APEC event).
Figure 2. Chemical composition of PM$_{2.5}$ during the 2014 APEC campaign.
Figure 3. Molecular distributions of dicarboxylic acids and related compounds in PM$_{2.5}$ of Beijing, China during the 2014 APEC campaign. The pie chart is the average composition of total detected organic compounds (TDOC) and the top number is the average mass concentration of TDOC of the whole study period.
Figure 4. Compositions of total detected organic compounds (TDOC) in PM$_{2.5}$ during the 2014 APEC campaign.
Figure 5. Correlation analysis for oxalic acid (C₂) and sulfate in PM₂.₅ during the whole 2014 APEC campaign. (a-c) Concentrations of C₂ with sulfate, relative humidity (RH), and aerosol liquid water content (ALWC); (d, e) sulfate and C₂ with aerosol acidity [H⁺] and (f) temperature with mass ratio of C₂ to total detected organic compounds (C₂/TDOC).
Figure 6. (a) 72-h backward trajectories determined by the National Oceanic and Atmospheric Administration Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model arriving at the sampling site to reveal the major air mass flow types during the study period. Northwesterly wind (light blue) was most frequently (64%), followed by northerly (21%, pink) and southerly (15%, black) and is defined as clean, mixed and polluted types, respectively (see the definitions in the text); (b) Time series of δ^{13}C values and concentration of oxalic acid during the whole study period (Colors in Fig. 6a are corresponding to those in Fig. 6b).
Figure 7. Comparison of chemical composition of PM$_{2.5}$ during two air pollution events. (a) Percentages of major species in PM$_{2.5}$; (b, c) mass ratios of major species and organic tracers in PM$_{2.5}$; (d) stable carbon isotope composition of oxalic acid (C$_2$) (Data about levoglucosan (Lev), PAHs and hopanes are cited from Wang et al (2016)).