Dear ACP Editor,

After carefully reading the comments from both reviewers and the co-editor, we have revised our manuscript. The following are our response to the comments. In addition, we have checked the reference list and deleted all the references not cited in the text.

Anything about our paper, please feel free to contact me at wanggh@ieecas.cn

Sincerely

Gehui Wang

2016-12-29

Reviewer #1
General comments
The manuscript by Wang et al. reported the concentrations of molecular compounds and stable carbon isotopic ratio of oxalic acid before, during and after APEC. The results showed that the concentrations before APEC were much higher those during APEC, which are overall consistent with the conclusions from previous studies. The authors further investigated the differences in secondary aerosol formation among these three periods. The data presented in this study is helpful to evaluate aerosol chemistry changes during a unique period in Beijing. I have several comments which need to be addressed before its publication.
Response: We thank the reviewer for her/his helpful comments.

Comments:
My major concern is the focus of this study. The authors emphasized the focus in the abstract with "the impacts of the emissions controls on aerosol composition and formation". However, the authors failed to address how important the emission controls are in decreasing aerosol species during APEC, and how important the meteorological conditions are leading to these changes although there are several discussions. In addition, some data and analysis presented in this study need to be further validated, see my comments below.
Response: Suggestion taken. In the introduction section we have cited several papers to emphasize the effect of the emission controls on the concentrations of gaseous pollutants, and aerosols during the APEC event. Moreover, in the discussion and results section 3.1, we have made a detailed comparison for the concentration and compositions of SO_2, NO_X, and secondary inorganic ions (i.e., sulfate, nitrate and ammonium) before-, during-and after-APEC to address the impact of the emission controls on the aerosol chemistry. In the remaining part of the manuscript, we have discussed the impact of emission control on oxalic acid and related SOA. Since we have already made a lot of discussions

throughout the manuscript about "the impacts of the emissions controls on aerosol composition and formation". Thus, here we only re-wrote several sentences in the abstract section to highlight the impact of emission control measures on aerosol chemistry. See page 2, line 48-51.

Moreover, we have validated all the data and made some corrections, see detailed explanations thereinafter.

Detailed comments:
Comments:
1. Line 58: define TDOC
Response: Suggestion taken, see page 2, line 58.

Comments:
2. A mass closure analysis is needed. As indicated by Figure 1, the sum of sulfate, nitrate, ammonium, OC and EC in (d) and (e) is clearly much higher than PM$_{2.5}$ in (c). The authors need to address these differences.
Response: We are very sorry for this mistake. We uploaded an incorrect version of Figure 1 last time. Here we replaced it with the corrected one. We also updated the Table 1. Because some lines were missing from the old version, which was caused by incorrect file uploading last time. Now everything is consistent. See page 22, Table 1, and page 26, Figure 1.

Comments
3. The SO$_2$ data in Figure 1 is also suspicious. Higher SO$_2$ concentration after APEC is expected due to the influences of coal combustion. However, we didn't see such a trend in Figure 1 although Table 1 did. Please refer to Wang et al. (2015, JGR, Changes in atmospheric composition during 2014 APEC conference in Beijing).
Response: We agree with the reviewer. The problem was caused by the wrongly uploaded file. See explanation above. In the current revised version, we have corrected it. See page 26, Figure 1b

Comments
4. Line 177-178: Table 1 did not show OC/EC ratios. Also, it is a bit surprising that OC/EC has no significant differences among the three periods with largely different source emissions. The authors need to clarify this.
Response: The OC/EC ration was missing from the table due to the file loading problem above, here we have corrected it. As shown in Figure 6a, during the whole field observation period 64% of air masses are the clean type, in other words, most of the samples were collected when the northwesterly was dominant. OC/EC ratio is the abundance of OC relative to EC, which is independent of their absolute masses. Since the OC/EC ratios here are the average values of the three periods, respectively. Thus, the ratio is statistically depended by the number of the clean type of samples. We think the dominant number of the clean type samples is one of the reasons why the ratio differences among the three periods are not significant, although OC/EC ratio shows a slight increase from 3.2±0.7 before-APEC to 3.4±0.5 after-APEC (Table 1). At this

moment, we do not have enough evidence to verify this. Thus, we just mentioned this phenomenon (See page 8, line 182-183). In fact, we have been pursing an accurate source apportionment by using PMF and CMB, which is expected to solve this issue.

Comments
5. Line 242: [NO3$^-$ + SO4^{2-}] is confusing. Is it [NO3$^-$] + [SO4^{2-}] or [NO3$^-$] + 2*[SO4^{2-}]?
Response: It is [NO3$^-$] + [SO4^{2-}], which is molar ratio not equivalent ratio. We revised the statement format as [NH$_4^+$] to [NO$_3^-$] + [SO$_4^{2-}$]. See page 11, line 247-248.

Comments
6.Figure 5: I strongly suggest that the authors separate the data points into three periods, i.e., before, during, and after-APEC. The fitting can be performed for the whole data.
Response: Suggestion taken. We used different color to separate the points into three periods and performed the fitting for the whole data. See Figure 5 in page 30.

Comments
7. The definition of air mass types is not accurate. The air masses from the south are not necessarily polluted although they do for most of the time. Suggest changing the definitions.
Response: In this study, concentrations of particle mass and sulfate in the PM$_{2.5}$ samples collected during the south air mass dominated periods are 314 ± 60 and 27 ± 9.0 μg m^{-3}. These levels are 3-5 times higher than those in the clean air masses, clearly demonstrating that the south air masses during the field observation period are polluted. Thus, the definitions of the three types of air masses we classified are reasonable.

Comments
8. The back trajectory analysis was calculated at 00:00 UTC for each day, which means you have only 47-48 trajectories for cluster analysis. The statistics for each clusters could be a problem. Particularly, air masses can have significant changes in one day in Beijing. The authors need to validate this, or calculate the trajectories every 4 or 6 hours. In addition, the time of back trajectories in Figure S4 is not consistent with others.
Response: Suggestion taken. We validated this by re-calculating the trajectories every 6 hours (see Figure S1 in the supplementary section), and found that the cluster analysis result is the same as the previous version. Thus we did not make any changes for Figure 6 and related discussions. In stead, we added a new figure (Figure S1), which describes the 6-hr trajectories, into the supplementary section. In the current supplementary section, the time of back trajectories in all the figures is 6 hours.

Reviewer #2
Comments
The manuscript certainly meets the requirement of ACP and can be published as soon as one small comment is considered. In the introduction part, the authors need to emphasize the importance of dicarboxylic acids in atmospheric chemistry, e.g., its critical role in atmospheric nucleation
Response: Suggestion taken. We have added several sentences into the introduction

about the important roles of dicarboxylic acids in the atmospheric nucleation and growth processes. See page 4, line 101-105.

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

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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 8th October to 24th 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 α-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.

64   **1. Introduction**

65   Atmospheric aerosols profoundly impact the global climate directly by scattering and

66   absorbing solar radiation and indirectly by affecting cloud formation and distribution via acting

67   as cloud condensation nuclei (CCN) and ice nuclei (IN). Moreover, atmospheric aerosols exert

68   negative effects on human health because of their toxicity. Due to fast urbanization and

69   industrialization, high level of atmospheric fine particle ($PM_{2.5}$) pollution has been a persistent

70   problem in many cities of China since the nineties of last century (van Donkelaar et al., 2010).

71   As the capital of China and one of the largest megacities in the world, Beijing has suffered from

72   frequent severe haze pollution especially in winter, affecting more than 21 million people by the

73   end of 2014 (Beijing Municipal Bureau of Statistics, 2015) and causing billions of economic

74   loses (Mu and Zhang, 2013). To improve the air quality Beijing government has put many efforts

75   to reduce the pollutant emissions (i.e., SO_2, NOx, dust, and volatile organic compounds (VOCs))

76   from a variety of sources.

77   The 2014 Asia-Pacific Economic Cooperation (APEC) summit was hosted in Beijing from

78   the 5th to 11th November. To ensure good air quality for the summit, a joint strict emission control

79   program was conducted from 3rd November 2014 in Beijing and its neighboring provinces

80   including Inner Mongolia, Shanxi, Hebei and Shandong provinces. During this period thousands

81   of factories and power plants with high emissions were shut down and/or halted, all the

82   construction activities were stopped and the numbers of on-road vehicles were reduced. These

83   strict emission controls resulted in the air quality of Beijing during the APEC period being

84   significantly improved, leading to a decrease in $PM_{2.5}$ concentration by 59.2% and an increase in

85   visibility by 70.2% in Beijing during the summit compared with those before the APEC (Tang et

86   al., 2015; Wang et al., 2015b) and a term of "APEC-Blue" being created to refer to the good air

87   quality. Such strong artificial intervening not only reduced $PM_{2.5}$ and its precursors' loadings in

88   Beijing and its surrounding areas but also affected the composition and formation mechanisms of

89   the fine particles (Sun et al., 2016).

90   A number of field measurements have showed that particle compositions in Beijing during

91   wintertime haze periods are dominated by secondary aerosols (Guo et al., 2014; Huang et al,

92   2014; Xu et al., 2015). Rapid accumulation of particle mass in Beijing during haze formation

93   process is often accompanied by continuous particle size growth (Guo et al, 2014; Zhang et al.,

94   2015), which is in part due to the coating of secondary organic aerosols (SOA) on pre-existing

95   particles (Li et al., 2010). Several studies have found that SOA production during the 2014

96   Beijing APEC periods significantly reduced and ascribed this reduction to the efficient regional

97   emission control (Sun et al., 2016; Xu et al, 2015). However, up to now information of the SOA

98   decrease on a molecular level has not been reported.

99   Dicarboxylic acids are the major class of SOA species in the atmosphere and ubiquitously

100 found from the ground surface to the free troposphere (Fu et al., 2008; Myriokefalitakis et al.,

101 2011; Sorooshian et al., 2007; Sullivan et al., 2007). Previous studies have suggested that organic

102 acids including dicarboxylic acids could take part in atmospheric particle nucleation (Zhang et

103 al., 2004; Zhao et al., 2009) and growth processes (Zhang et al., 2012). Furthermore, organic

104 acids may play a central role in aging of black carbon particles (Xue et al., 2009; Ma et al., 2013),

105 enhancing their roles in air pollution accumulation and direct radiative forcing (Peng et al., 2016).

106 In the current work we measured molecular distributions of dicarboxylic acids, keto-carboxylic

107 acids and α-dicarbonyls and stable carbon isotope composition of oxalic acid in $PM_{2.5}$ aerosols

108   collected in Beijing before, during and after the APEC event in order to explore the impact of the

109   APEC emission control on SOA in Beijing. We first investigated the changes in concentration

110   and composition of dicarboxylic acids and related compounds during the three periods, then

111   recognized the difference in stable carbon isotope composition of oxalic acid in different air

112   masses in Beijing during the APEC campaign. Finally we compared the differences in chemical

113   compositions of $PM_{2.5}$ during two heaviest pollution episodes.

114   **2. Experimental section**

115   **2.1 Sample collection**

116    $PM_{2.5}$ samples were collected by using a high-volume sampler (TISCH, USA) from 8th

117   October to 24th November 2014 on the rooftop of a three-storey building located on the campus

118   of China Research Academy of Environmental Sciences, which is situated in the north part of

119   Beijing and close to the 5th-ring road. All the $PM_{2.5}$ samples were collected onto pre-baked (450

120   ^{o}C for 8 h) quartz fiber filters (Whatman 41, USA). The duration of each sample collection is 23

121   hr from 08:00 am of the previous day to 07:00 am of the next day. Field blanks were also

122   collected before and after the campaign by mounting a pre-baked filter onto the sampler for 15

123   min without pumping air. After collection, all the filter samplers were individually sealed in

124   aluminum foil bags and stored in a freezer (-18 ^{o}C) prior to analysis. Daily values of SO_2, NOx

125   and meteorological parameters were cited from the website of Beijing Environmental Protection

126   Agency.

127   **2.2 Sample analysis**

128   **2.2.1 Elemental carbon (EC), organic carbon (OC), water-soluble organic (WSOC),**

129   **inorganic ions, aerosol liquid water content (ALWC) and aerosol acidity**

130   Detailed methods for the analysis of EC, OC, WSOC and inorganic ions in aerosols were

131   reported elsewhere (Wang et al 2010). Briefly, EC and OC in the $PM_{2.5}$ samples were determined

132   by using DRI Model 2001 Carbon analyzer following the Interagency Monitoring of Protected

133   Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al.,

134   2007). WSOC and inorganic ions in the samples were extracted with Milli-Q pure water and

135   measured by using Shimadzu TOC-L CPH analyzer and Dionex-600 ion chromatography,

136   respectively (Wang et al 2010). In the current work, aerosol liquid water content (ALWC) and

137   acidity (i.e., liquid H^+ concentrations, $[H^+]$) of the samples were calculated by using

138   ISORROPIA-II model, which treated the $Na^+-NH_4^+-K^+-Ca^{2+}-Mg^{2+}-Cl^--NO_3^--SO_4^{2-}$ system

139   and was performed in a "metastable" mode (Hennigan et al, 2015; Weber et al., 2016).

140   **2.2.2 Dicarboxylic acids, keto-carboxylic acids and α-dicarbonyls**

141   The method of analyzing $PM_{2.5}$ samples for dicarboxylic acids, ketocarboxylic acids and

142   α-dicarbonyl has been reported elsewhere (Wang et al., 2002, 2012; Meng et al., 2014; Cheng et

143   al., 2015). Briefly, one eighth of the filter was extracted with Milli-Q water, concentrated to near

144   dryness, and reacted with 14% BF_3/butanol at 100 °C for 1 h to convert aldehyde group into

145   dibutoxy acetal and carboxyl group into butyl ester. Target compounds in the derivatized samples

146   were identified by GC/MS and quantified by GC-FID (Agilent GC7890A).

147   **2.3. Stable carbon isotope composition of oxalic acid (C_2)**

148   Stable carbon isotope composition ($δ^{13}C$) of C_2 was measured using the method developed

149   by Kawamura and Watanabe (2004). Briefly, $δ^{13}C$ values of the derivatized samples above were

150   determined by gas chromatography-isotope ratio-mass spectrometry (GC-IR-MS) (Thermo

151   Fisher, Delta V Advantage). The $δ^{13}C$ value of C_2 was then calculated from an isotopic mass

152   balance equation based on the measured $\delta^{13}C$ of the derivatizations and the derivatizing reagent

153   (1-butanol) (Kawamura and Watanabe, 2004). Each sample was measured for three times to

154   ensure the difference of the $\delta^{13}C$ values less than 0.2‰, and the isotope data reported here is the

155   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

159   Based on the emission control implementation for the APEC, we divided the whole study

160   period into three phases: before-APEC (08/10 to 02/11), during-APEC (03/11 to 12/11) and

161   after-APEC (13/11 to 24/11). Temporal variations in meteorological parameters and

162   concentrations of gaseous pollutants and major components of PM$_{2.5}$ during the three phases are

163   shown in Fig. 1 and summarized in Table 1.

164   Temperature during the sampling campaign showed a continuous decreasing trend with

165   averages of 13 ± 2.6 °C, 7.0 ± 1.7 °C and 4.3 ± 1.3 °C before-, during- and after-APEC periods,

166   respectively, while relative humidity (RH) did not show a clear trend with mean values of 62 ±

167   19%, 47 ± 14% and 51 ± 16% during the three periods (Fig.1a and Table 1). SO$_2$ showed a

168   similar level before- and during-APEC periods (8.8 ± 4.6 µg m^{-3} versus 7.6 ± 3.9 µg m^{-3}) (Table

169   1 and Fig.1b), but increased dramatically to 23 ± 8.8 µg m^{-3} after-APEC due to domestic coal

170   burning for house heating. NO$_2$ concentration (45 ± 18 µg m^{-3}) during the APEC reduced by

171   about 30% compared to that in the before- and after-APEC phases (71 ± 27 µg m^{-3} versus 78 ±

172   29 µg m^{-3}) (Table 1), mainly because of the reduction of the on-road vehicle numbers, as well as

173   the reduced productivities of power plant and industry. O$_3$ displayed a decreasing trend similar to

174   that of temperature (Fig. 1c). $PM_{2.5}$ pollution episodes in Beijing showed a periodic cycle of 4−5

175   days, which is caused by the local weather cycles. Secondary inorganic ions (SIA, i.e., SO_4^{2-},

176   NO_3^- and NH_4^+) are major components of $PM_{2.5}$ and present a temporal variation pattern similar

177   to that of the fine particles (Fig. 1d). In the current work mass ratio of NO_3^-/SO_4^{2-} in $PM_{2.5}$

178   during the whole study time is 1.8 ± 1.9 (Table 1), which is in agreement with the ratio (1.6−2.4)

179   for PM_1 observed during the same time by using aerosol mass spectrometry (AMS) (Sun et al.,

180   2016). OC and EC of $PM_{2.5}$ linearly correlated each other (R^2=0.91) and varied periodically in a

181   cycle similar to SIA (Fig. 1e). OC/EC ratio during the whole sampling period is 3.3 ± 0.6 (range:

182   2.2−4.7) with no significant differences among the three APEC phases (Table 1), although the

183   source emissions could be largely different.

184   Figure 2 shows the differences in chemical composition of $PM_{2.5}$ before-, during- and

185   after-APEC periods. $PM_{2.5}$ is 98 ± 46 µg m^{-3} during-APEC, about 50% lower than that before-

186   and after-APEC (178 ± 122 µg m^{-3} versus 161 ± 100 µg m^{-3}), respectively. Organic matter (OM)

187   is the most abundant component of the fine particles. Relative abundance of OM (OM, 1.6 times

188   of OC) (Xing et al., 2013) to $PM_{2.5}$ continuously increases from 24% before-APEC to 30% and

189   39% during- and after-APEC, respectively, although the mass concentration (19 ± 7.6 µg m^{-3}) of

190   OC during-APEC is the lowest compared to those before- and after-APEC (26 ± 16 µg m^{-3}

191   versus 39 ± 23 µg m^{-3}). Sulfate, nitrate and ammonium before-APEC are 15 ± 13, 28 ± 26 and

192   9.0 ± 8.0 µg m^{-3} (Table 1) and account for 8%, 16% and 5% of $PM_{2.5}$, respectively (Fig. 2). Their

193   concentrations decrease to 5.3 ± 2.8, 10 ± 8.1 and 3.1 ± 2.6 µg m^{-3} (Table 1) with the relative

194   contributions to $PM_{2.5}$ down to 5%, 10% and 3% during-APEC, respectively. While after-APEC

195   their concentrations increased to 11 ± 10, 15 ± 13 and 6.9 ± 6.4 µg m^{-3} and accounted for 7%,

196   9% and 4% of $PM_{2.5}$. Such significant decreases in concentrations of OM and SIA during-APEC

197   demonstrate the efficiency of the emission controls. OC/EC ratio is almost constant during the

198   whole period, but WSOC/OC ratio decreased by 20% from 0.42 ± 0.13 before-APEC, $0.38 \pm$

199   0.16 during-APEC to 0.35 ± 0.17 after-APEC (Table 1). Since WSOC in fine aerosols consist

200   mainly of secondary organic aerosols (SOA) (Laskin et al., 2015), the decreasing ratio of

201   WSOC/OC probably indicates a reduced SOA production during the campaign.

202   **3.2 Oxalic acid and related SOA during the Beijing 2014 APEC campaign**

203   A homogeneous series of dicarboxylic acids (C_2-C_{11}), keto-carboxylic acid and

204   α-dicarbonyls in the $PM_{2.5}$ samples were detected. As show in Table 2, total dicarboxylic acids

205   during the whole study period is 593 ± 739 ng m^{-3}, which is lower than that observed during

206   Campaign of Air Quality Research in Beijing 2006 (CAREBeijing) (average 760 ng m^{-3}) and

207   2007 (average 1010 ng m^{-3}) (Ho et al, 2010, 2015) and the averaged wintertime concentration

208   reported by a previous research for 14 Chinese cities (904 ng m^{-3}) (Ho et al, 2007). Total

209   keto-carboxylic acid is 66 ± 81 ng m^{-3}, while total dicarbonyls is 126 ± 115 ng m^{-3} (Table 2).

210   These values are higher than those during CAREBeijing 2006 and 2007 (Ho et al, 2010, 2015),

211   but close to the value observed for the 14 Chinese megacities (Ho et al, 2007). Being similar to

212   those previous observations, oxalic acid (C_2) is the most abundant diacid in the 2014 APEC

213   samples with an average of 334 ± 461 ng m^{-3} (range: $10-2127$ ng m^{-3}, Table 2) during the whole

214   campaign, followed by methylglyoxal (mGly), succinin acid (C_4), terephthalic acid (tPh), and

215   glyoxal (Gly). These five species account for 43%, 10%, 9%, 6% and 6% of total detected

216   organic compounds (TDOC), respectively (Fig. 3).

217   As see in Fig. 4, TDOC in $PM_{2.5}$ are 1099 ± 1104, 325 ± 220 and 487 ± 387 ng m^{-3} before-,

218   during- and after-APEC, respectively. In comparison with those before-APEC, TDOC

219   during-APEC decreased by 71%. Oxalic acid (C_2) is the leading species among the detected

220   organic compounds and accounted for 46%, 31% and 34% of TDOC during the three phases,

221   respectively (Fig. 4). C_2 is an end product of precursors that are photochemically oxidized in

222   aerosol aqueous phase via either oxidation of small compounds containing two carbon atoms or

223   decomposition of larger compounds containing three or more carbon atoms. Thus mass ratio of

224   C_2 to TDOC is indicative of aerosol aging (Wang et al., 2012; Ho et al., 2015). As shown in Fig.

225   4, the highest proportion of C_2 before- APEC suggests that organic aerosols during this period are

226   more oxidized, compared to those during- and after-APEC. Glyoxal (Gly) and methylglyoxal

227   (mGly) are the precursors of C_2. Mass ratios of both compounds to TDOC are lowest

228   before-APEC (Fig. 4), further indicating an enhanced SOA production during this period.

229   **3.3 Formation mechanism of oxalic acid**

230   **3.3.1 Correlation of oxalic acid with temperature, relative humidity (RH), aerosol liquid**

231   **water content (ALWC) and acidity and sulfate**

232   A few studies have pointed out that aerosol aqueous phase oxidation is a major formation

233   pathway for oxalic acid (Yu et al., 2005; van Pinxteren, et al., 2014; Bikkina et al., 2015; Tilgner

234   et al, 2010). To explore the formation mechanism of oxalic acid, we calculated ALWC and

235   acidity (i.e., proton concentration, $[H^+]$) of $PM_{2.5}$ aerosols by using ISOROPPIA-II model

236   (Weber et al., 2016). As shown in Fig. 5, during the entire period C_2 showed a strong linear

237   correlation with sulfate (R^2=0.70 Fig. 5b), which is consistent with those observed in Xi'an

238   (Wang et al., 2012) and other Chinese cities (Yu et al, 2005). Previous studies on particle

239   morphology showed that sulfate particles internally mixes with SOA in Beijing especially on

240   humid haze days (Li et al., 2010, 2011), which probably indicates that they are formed via

241   similar aqueous phase pathways (Wang et al., 2016). In addition, a robust correlation was also

242   found for C_2 with RH (R^2=0.64, Fig. 5b) and aerosol liquid water content (ALWC) (R^2=0.61, Fig.

243   5c), indicating that humid conditions are favorable for the aqueous phase formation of C_2, which

244   is most likely due to an enhanced gas-to-aerosol aqueous phase partitioning of the precursors

245   (e.g., Gly and mGly) (Fu et al., 2008; Wang et al., 2015a).

246   NH_4^+, NO_3^- and SO_4^{2-} are the dominant cation and anions of fine particles in Beijing,

247   respectively (Guo et al., 2014; Zhang et al., 2015) and the molar ratio of $[NH_4^+]$ to $[NO_3^-]$ +

248     $[SO_4^{2-}]$ in this study is 1.1. Thus it is plausible that SO_4^{2-} during the APEC campaign largely

249   existed as ammonium bisulfate, resulting in a strong linear correlation between $[H^+]$ and SO_4^{2-}

250   with a molar slope of 1.03 (Fig. 5d) (Zhang et al., 2007). In addition, $[H^+]$ shows a significant

251   positive correlation with C_2 ($R^2 = 0.84$) (Fig. 5e), possibly due to the fact that acidic conditions

252   are favorable for the formation of C_2 precursors. For example, Surratt et al (2007; 2010) found

253   that aerosol acidity can promote the formation of biogenic SOA (BSOA) derived from isoprene

254   oxidation such as 2-methylglyceric acid, Gly and mGly. These BSOA precursors can be further

255   oxidized into C_2 (Meng et al., 2014; Wang et al., 2009).

256   There is a significant positive correlation ($R^2 = 0.58$, $p<0.001$) between the mass ratios of

257   C_2/TDOC and ambient temperatures (Fig. 5f), which is similar to the results found by previous

258   researchers (Ho et al., 2007; Strader et al., 1999), indicating that organic aerosols are more aged

259   under a higher temperature condition (Erven et al, 2011; Carlton et al., 2009). Thus, compared

260   with those before-APEC the lower C_2/TDOC ratios (31% and 34%, respectively) (Fig. 4) during-

261   and after-APEC can be ascribed in part to the relatively lower temperature conditions that are not

262   favorable for oxidation of the precursors to produce oxalic acid (13 ± 2.6 °C, 7.0 ± 1.7 °C and

263   4.3 ± 1.3 °C before-, during- and after-APEC periods, respectively) (Table1).

264   **3.3.2 Temporal variation in stable carbon isotopic composition of oxalic acid**

265   To further discuss the formation mechanism of C_2, we investigated the temporal variations

266   of concentration and stable carbon isotopic composition of C_2 in the $PM_{2.5}$ samples (Fig. 6).

267   Previous studies have demonstrated that Gly, mGly, glyoxylic acid (ωC_2) and pyruvic acid (Pyr)

268   are the precursors of C_2 (Carlton et al., 2006, 2007; Ervens and Barbara, 2004; Wang et al., 2012).

269   Thus, higher mass ratios of C_2 to its precursors indicate that organic aerosols are more oxidized

270   (Wang et al., 2010). As shown in Table 3, $\delta^{13}C$ of C_2 in this work positively correlated with the

271   mass ratios of $C_2/\omega C_2$, $C_2/mGly$ and TDOC/WSOC, demonstrating an enrichment of ^{13}C during

272   the aerosol oxidation process. Because decomposition (or breakdown) of larger molecular weight

273   precursors in aerosol aqueous phase is the dominant formation pathway for C_2 in aerosol ageing

274   process (Kawamura et al., 2016; Gensch et al., 2014; Kirillova et al., 2013), during which

275   organic compounds release CO_2/CO by reaction with OH radical and other oxidants, resulting in

276   the evolved species enriched with lighter isotope (^{12}C) and the remaining substrate enriched in

277   ^{13}C due to kinetic isotope effects (KIE) (Hoefs, 1997; Rudolph et al., 2002).

278   72-h backward trajectory analysis showed that air masses moved to Beijing during the

279   whole sampling period can roughly be categorized into three types (Fig. 6a) (all trajectories

280   during the entire study period can be found in the supplementary materials). (1) Polluted type, by

281   which air masses originated from inland and east coastal China and moved slowly into Beijing

282   within 72-h from its south regions, i.e., Henan, Shandong and Jiangsu provinces. This type of air

283   masses mostly occurred before-APEC with high $PM_{2.5}$ concentrations. Air pollution has widely

284   distributed in the three provinces (Wei et al., 2016); thus aerosols transported by this type of air

285   masses are of regional characteristics. (2) Mixed type, by which air masses originated from

286   Mongolia and North China, and moved quickly into Hebei province and then turned back to

287   Beijing. Air in Mongolia and North China was clean but polluted in Hebei province, which is

288   adjacent to Beijing. This type of air masses is a mixture of clean and polluted air and thus named

289   as mixed type. Since the resident time of the mixed type of air masses within Hebei province is

290   very short, thus aerosols transported by this type of air masses is of local characteristics and

291   relatively fresh. (3) Clean type, by which air masses originated from Siberia and moved rapidly

292   into Beijing directly via a long-range transport. Aerosols from the clean type of air masses are

293   much more aged, while those from the mixed type of air masses are fresh. Since severe air

294   pollution is widespread in the south regions, gas-to-aerosol phase partitioning of precursors and

295   subsequent aerosol-phase oxidation to produce SOA including C_2 continuously proceed during

296   the air mass movement. However, such a partition for producing SOA is not significant when air

297   mass move from Siberia, Mongolia and North China because of the much less abundant VOCs.

298   In stead, aerosols in the clean air masses are continuously oxidized, during which C_2 is produced

299   by photochemical decomposition of larger molecular weight precursors. Therefore, C_2 in $PM_{2.5}$

300   transported by the mixed type air masses are not only fresh and abundant but also enriched in ^{12}C,

301   whereas C_2 in $PM_{2.5}$ transported by the clean type air masses are aged, less abundant and

302   enriched in ^{13}C due to KIE effects, as illustrated by the pink and light blue columns in Fig. 6b,

303   respectively. C_2 in $PM_{2.5}$ transported by the polluted type of air masses are most abundant

304   compared with that in other two types of air masses, which is not only due to the severe air

305   pollution in the Henan, Shandong and Jiangsu provinces but also due to the enhanced

306   photochemical oxidation under the humid, higher temperature and stagnant conditions that

307   occurred mostly before-APEC, as discussed previously. Therefore, C_2 in the polluted type of air

308   masses is not only abundant but also enriched in ^{13}C (see black columns in Fig. 6b).

309   **3.4 Different chemical characteristics of PM$_{2.5}$ between two severe haze events**

310   From Fig. 1 and Table 4, it can be found that PM$_{2.5}$ showed two equivalent maxima on 9th

311   October and 20th November during the whole study period. However, the chemical compositions

312   of PM$_{2.5}$ during these two pollution events are significantly different. As shown in Fig. 7a,

313   relative abundances of SIA (sum of SO_4^{2-}, NO_3^- and NH_4^+) to PM$_{2.5}$ are 30% during the event I

314   and 23% during the event II, respectively. The relative abundance of OM (21%, Fig. 7a) during

315   the event I is lower than that (37%) during the event II (Fig. 7b). In contrast, the ratios of

316   WSOC/OC and TDOC/OC are higher in the event I than in the event II, which is consistent with

317   lower levels of O_3 after-APEC (Table 1), suggesting a weaker photochemical oxidation capacity

318   during the event II. Organic biomarkers in the PM$_{2.5}$ samples have been measured for the source

319   apportionment (Wang et al., 2016) and citied here to further identify the difference in chemical

320   composition of PM$_{2.5}$ between the two events. Levoglucosan is a key tracer for biomass burning

321   smoke. Mass ratio of levoglucosan to OC in PM$_{2.5}$ (Lev/OC) is comparable between the two

322   events, suggesting a similar level of contributions of biomass burning emission to PM$_{2.5}$ before-

323   and after-APEC. However, the mass ratios of PAHs and hopanes to OC are lower in event I than

324   those in event II (Fig. 7c), which again demonstrates the enhanced emissions from coal burning

325   for house heating, because these compounds are key tracers of coal burning smokes (Wang et al.,

326   2006). As seen in Fig. 7d, C_2 in the event I was enriched in ^{13}C. Such relatively more abundant

327   SIA, WSOC and TDOC and heavier C_2 in PM$_{2.5}$ clearly demonstrate that PM$_{2.5}$ during the event

328   I are enriched with secondary products while the fine particles during the event II are enriched

329   with primary compounds. After-APEC house heating activities including residential coal burning

330   were activated, which emitted huge amounts of SO_2, NOx, and VOCs as well as primary

331   particles, resulting in both absolute concentrations and relative abundances of CO and EC

332   30−40% higher after-APEC than before-APEC (see Table 1). Li et al (2015) reported that VOCs

333   in Beijing was 86 ppbv before-APEC, 48 ppbv during-APEC and 73 ppbv after-APEC. As

334   shown in Table 4, temperature (16.7±0.8 ^{o}C for event I and 4.5±1.7 ^{o}C for event II) and relative

335   humidity (RH) (82±4% for event I and 62±13% for event II) are lower during the event II than

336   during the event I. Moreover, air masses arriving in Beijing during the event II are the mix type,

337   of which the resident time in Hebei province is short. Compared with those in the event I, such

338   colder and drier conditions and short reaction time during the event II are unfavorable for

339   photochemical oxidation, resulting in SOA not only less abundant but also enriched with lighter

340   ^{12}C during the event II, although VOCs levels are comparable before- and after-APEC.

341   **4. Summary and conclusion**

342   Temporal variations in molecular distribution of SIA, dicarboxylic acids, ketoacids and

343   α-dicarbonyl and stable carbon isotopic composition (δ^{13}C) of C_2 in $PM_{2.5}$ collected in Beijing

344   before-, during- and after- the 2014 APEC were investigated. Absolute concentrations and

345   relative abundances of SIA and C_2 in $PM_{2.5}$ are highest before-APEC, followed by those after-

346   and during-APEC, suggesting that the fine aerosols before-APEC are enriched with secondary

347   products, mainly due to an enhanced photochemical oxidation under the warm, humid and

348   stagnant conditions. Concentrations of SIA, oxalic acid and related SOA in $PM_{2.5}$ during-APEC

349   are 2−4 times lower than those before-APEC, which can be ascribed to the effective emission

350   controls and the favorable meteorological conditions that brought clean air from Siberia and

351   Mongolia into Beijing.

352   Positive correlations of C_2 with sulfate mass, RH, ALWC and aerosol acidity indicate that

353   C_2 formation pathway is involved an acid-catalyzed aerosol aqueous phase oxidation. SIA, C_2

354   and related SOA in the polluted type of air masses are abundant with C_2 enriched in ^{13}C. On the

355   contrary, those in the clean type of air masses are much less abundant, although C_2 is also

356   enriched in ^{13}C. By comparing the chemical composition of $PM_{2.5}$ and $\delta^{13}C$ values of C_2 in two

357   events that are characterized by the highest loadings of $PM_{2.5}$ before- and after-APEC, we further

358   found that compared with those before- APEC fine aerosols after-APEC are enriched with

359   primary species and C_2 is depleted in heavier ^{13}C, although SO_2, NOx and VOCs are abundant

360   during the heating season, again demonstrating the important role of meteorological conditions

361   in the secondary aerosol formation process, which are warmer, humid and stagnant before-APEC

362   and result in secondary species much more abundant than those during- and after-APEC.

363

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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)).

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Table 1. Meteorological parameters and concentrations of gaseous pollutants and chemical components of PM$_{2.5}$ in Beijing during the 2014 APEC campaign

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

[a]Organic (OC) and elemental carbon (EC); [b]Water-soluble organic carbon (WSOC); [c]Aerosol liquid water content (ALWC); [d]Hydrogen ion concentration ([H$^+$])

Table 2. Concentrations of dicarboxylic acids and related compounds in PM$_{2.5}$ in Beijing during the 2014 APEC campaign (ng m^{-3})

	Whole period (N=48)	Before-APEC (08/10−02/11) (N=26)	During-APE (03/11−12/11) (N=10)	After-APEC (13/11−14/11) (N=12)
		I. Dicarboxylic acids		
Oxalic, C$_2$	334 ± 461 (10−2127)	502 ± 564 (10.5−2127)	101 ± 69 (35−251)	166 ± 157 (22−554)
Malonic, C$_3$	31 ± 42 (ND−247)	45.7 ± 52.1 (1.44−247)	12 ± 8.0 (3.4−22.8)	16± 10.9 (ND−36)
Succinic, C$_4$	74 ± 118 (3.0−722)	111 ± 150 (3.0−722)	24 ± 14 (7.1−42)	36 ± 26 (4.9−90)
Glutaric, C$_5$	8.7 ± 12 (ND−68)	13± 15 (ND−68.1)	2.9 ± 2.24 (0.9−5.8)	4.9 ± 4.2 (ND−13)
Adipic, C$_6$	13± 14 (0.9−83)	17 ± 18 (1.9−83)	5.9 ±3.8 (2.1−14)	9.9 ± 7.1 (2.0−23)
Pimelic, C$_7$	2.1 ± 3.8 (ND−27)	2.6 ± 5.1(ND−27)	1.1 ± 0.7(0.2−2.3)	2.0 ± 1.1 (0.9−4.4)
Suberic, C$_8$	10 ± 11 (ND−66)	12± 13 (ND−66)	7.6 ± 5.0 (1.3−16)	8.7 ± 6.0(2.0−21)
Azelaic, C$_9$	5.0 ± 4.9(0.5−21)	6.4 ± 5.7 (0.6−21)	1.7± 0.9 (0.5−3.2)	4.6 ± 3.3 (1.3−13)
Sebacic, C$_{10}$	7.7 ± 7.4 (ND−34)	9.4 ± 8.8 (ND−34)	4.2± 3.6 (0.5−11)	6.8 ± 4.9 (1.4−16)
Undecanedioic, C$_{11}$	11 ± 13 (ND−77)	14 ± 16 (ND−77)	3.3 ± 2.5 (ND−7.5)	9.4 ± 6.4 (0.8−23)
Methylsuccinic, iC$_5$	13 ± 16 (0.6−79)	18 ± 19 (0.6−79)	4.8 ± 3.0 (1.0−9.2)	8.4 ± 6.0(2.3−19)
Methyglutaric, iC$_6$	7.5 ± 10 (ND−36)	11± 12 (ND−36)	0.9 ± 09 (ND−2.6)	4.6± 5.1 (ND−14)
Maleic, M	3.4 ± 3.9 (ND−15)	4.6± 4.7 (ND−15)	1.4 ± 0.8 (ND−2.9)	2.4 ± 2.0 (ND−6.3)
Fumaric, F	7.2 ± 8.8 (ND−64)	10 ± 11 (ND−64)	2.2 ± 1.5 (ND−5.4)	4.7 ± 3.2 (1.4−10)
Phthalic, Ph	17 ± 14 (1.5−64)	20 ± 16 (1.5−64)	10 ± 6.8 (2.3−20)	17 ± 9.0 (6.4−31)
Isophthalic, iPh	2.1 ± 2.5 (ND−10)	2.9 ± 2.8 (ND−10)	2.0 ± 2.1 (0.2−5.9)	0.5 ± 0.3 (ND−3.2)
Terephthalic, tPh	46 ± 35 (2.6−133)	50 ± 35 (2.6−123)	28 ± 19(4.7−59)	53± 40 (7.4−133)
Subtotal	593 ± 739 (25−3788)	849 ± 905 (25−3788)	214 ± 135 (72−447)	354 ± 279 (85−965)
		II. Keto-carboxylic acids		
Pyruvic, Pyr	24 ± 20 (1.3−84)	31± 23 (2.4−84)	15 ± 12 (1.3−36)	15 ± 9.3 (3.2−33)
Glyoxylic, ωC$_2$	33 ± 51 (1.2−300)	48± 64 (1.2−300)	10 ± 7.7 (2.6−21)	20 ± 23 (2.8−80)
7-Oxoheptanoic, ωC$_7$	8.8 ± 14 (ND−90)	13 ± 17 (ND−90)	4.2 ± 3.6 (ND−13)	4.5 ± 5.1 (ND−17)
Subtotal	66 ± 81 (3.6−474)	92 ± 99 (3.6−474)	30 ± 22 (5.9−66)	40 ± 35 (13−128)
		III α-Dicarbonyls		
Glyoxal, Gly	44 ± 47 (4.2−270)	57 ± 56 (4.2−270)	22 ± 19 (4.9−47)	35 ± 30 (7.3−101)
Methylglyoxal, mGly	82 ± 82 (ND−406)	102 ± 96 (ND−406)	60 ± 52 (15−139)	58 ± 51 (5.8−144)
Subtotal	126 ± 115 (5.3−466)	158 ± 132 (5.3−466)	81.6 ± 67.4 (22−186)	93 ± 80 (14−225)
TDOC[b]	785 ± 872 (36−4636)	1099 ± 1104 (36−4636)	325 ± 220 (107−664)	487 ± 387 (117-1318)

[a]ND: not detectable; [b]TDOC: total detected organic compounds.

Table 3 Linear correlation coefficients of $\delta^{13}C$ of C_2 with $C_2/\omega C_2$, $C_2/mGly$, and TDOC/WSOC

	$C_2/\omega C_2$	$C_2/mGly$	TDOC/WSOC
$\delta^{13}C$	0.49**	0.35*	0.41*

** $p<0.01$; * $p<0.05$

Table 4. Meteorological parameters and chemical compositions ($\mu g\ m^{-3}$) of two maximum $PM_{2.5}$ between two pollution episodes in Beijing

	T (°C)	RH (%)	V^a (km)	$PM_{2.5}$	OC	EC	SIA^b	$TDOC^c$
Event I (8/10-11/10, Before-APEC)	16.7 ± 0.8	82 ± 4	1.5 ± 0.5	349 ± 57	45 ± 12	12 ± 2	106±39	2749 ± 1357
Event II (18/11-21/11, After-APEC)	4.5 ± 1.7	62 ± 13	3.5 ± 1.5	259 ± 102	60 ± 21	17 ± 6	60±32	831 ± 400

[a]V: visibility; [b]SIA: secondary inorganic ions (the sum of sulfate, nitrate and ammonium); [c]TDOC: total detected organic compounds

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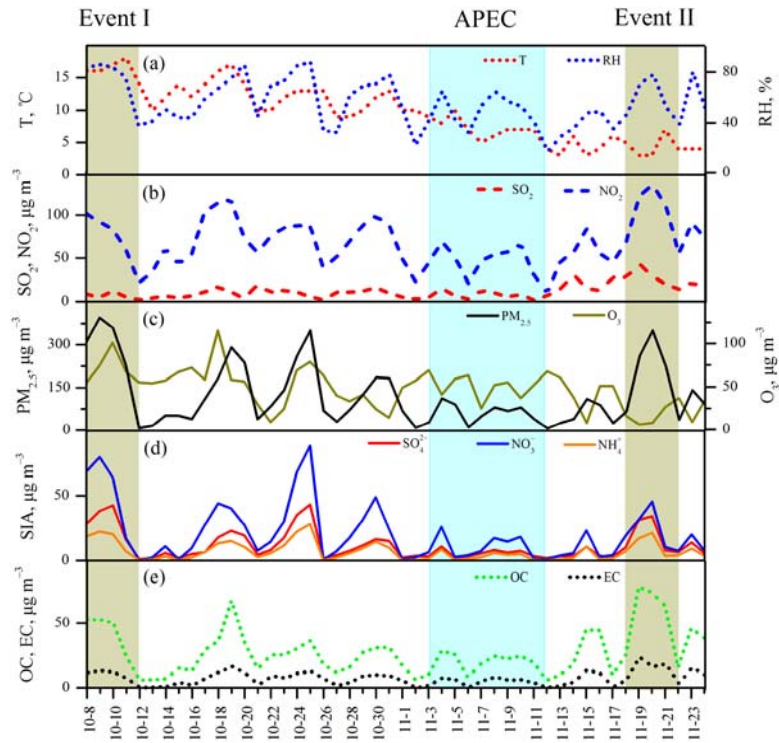
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630   by highest PM$_{2.5}$ levels before- and after-APEC, while the blue shadow represents the APEC event).

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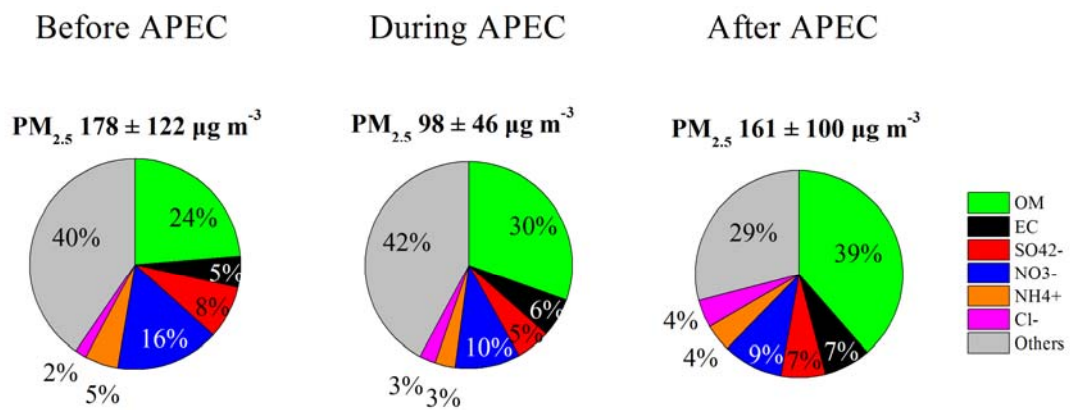
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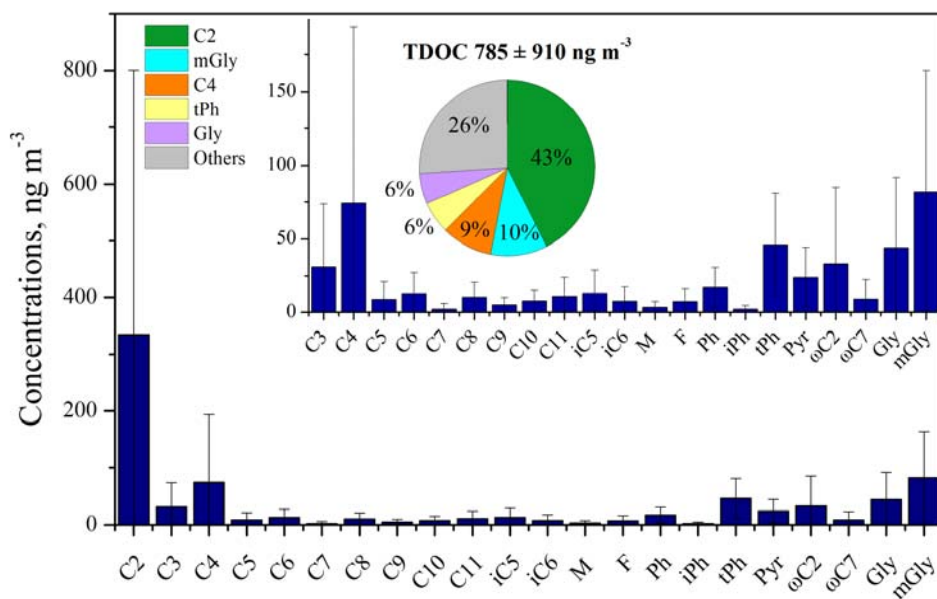
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636 **Figure 3**. Molecular distributions of dicarboxylic acids and related compounds in PM$_{2.5}$ of Beijing, China during the

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638 (TDOC) and the top number is the average mass concentration of TDOC of the whole study period.

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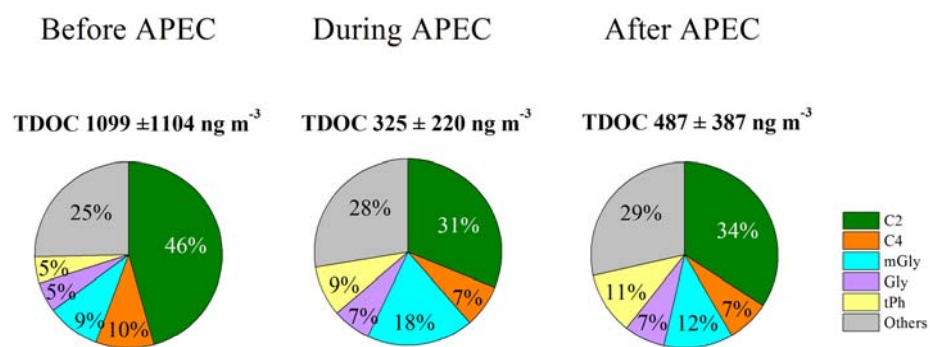
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Figure 4. Compositions of total detected organic compounds (TDOC) in $PM_{2.5}$ during the 2014 APEC campaign.

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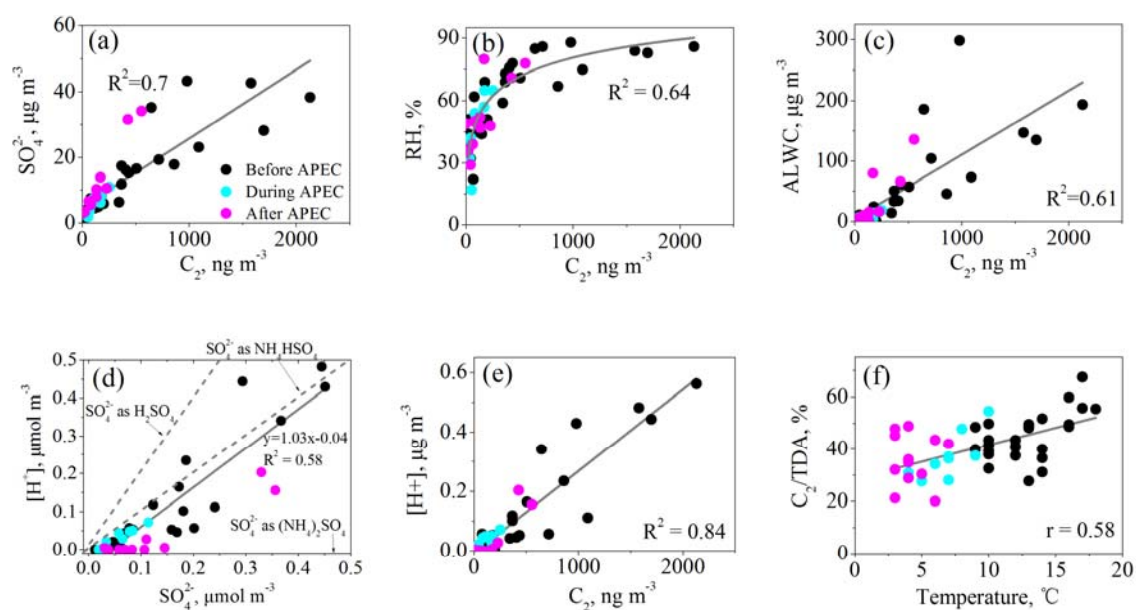
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647 Concentrations of C_2 with sulfate, relative humidity (RH), and aerosol liquid water content (ALWC); (**d, e**)
648 sulfate and C_2 with aerosol acidity [H^+] and (**f**) temperature with mass ratio of C_2 to total detected organic
649 compounds (C_2/TDOC).

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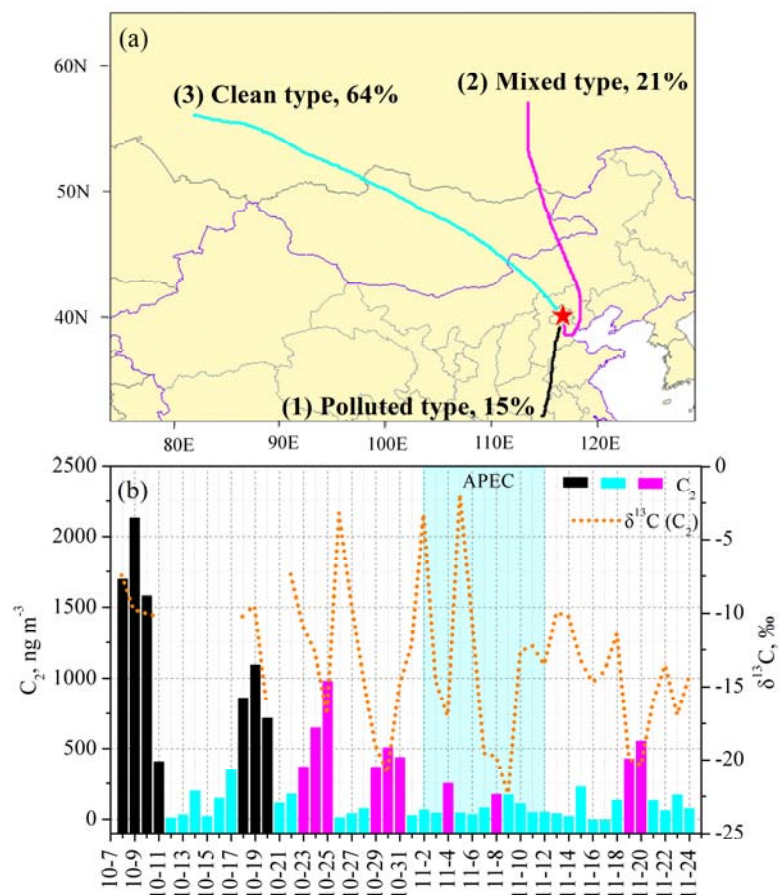
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Figure 7. Comparison of chemical composition of PM$_{2.5}$ during two air pollution events.(**a**) Percentages of major

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)).

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