Atmospheric
Chemistry
and Physics
Discussions

Open Access

EGU

1 Impact of anthropogenic emissions on biogenic secondary

2 organic aerosol: Observation in the Pearl River Delta,

3 South China

4 Yu-Qing Zhang[1, *], Duo-Hong Chen[2, *], Xiang Ding[1, †], Jun Li[1], Tao Zhang[2], Jun-Qi
5 Wang[1], Qian Cheng[1], Hao Jiang[1], Wei Song[1], Yu-Bo Ou[2], Peng-Lin Ye[3], Gan Zhang[1],
6 Xin-Ming Wang[1, 4]

7 1 State Key Laboratory of Organic Geochemistry and Guangdong Provincial Key Laboratory of
8 Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese
9 Academy of Sciences, Guangzhou, 510640, China
10 2 State Environmental Protection Key Laboratory of Regional Air Quality Monitoring, Environmental
11 Monitoring Center of Guangdong Province, Guangzhou, 510308, China
12 3 Aerodyne Research Inc., Billerica, Massachusetts 01821, United States
13 4 Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese
14 Academy of Sciences, Xiamen, 361021, China

15 * These authors contributed equally to this work.
16 † *Correspondence to*: Xiang Ding (xiangd@gig.ac.cn)

17

Atmospheric
Chemistry
and Physics
Discussions

18   **Abstract.** Secondary organic aerosol (SOA) formation from biogenic precursors is affected by

19   anthropogenic emissions, which is not well understood in polluted areas. In the study, we accomplished

20   a year-round campaign at nine sites in the polluted areas located in Pearl River Delta (PRD) region during

21   2015. We measured typical biogenic SOA (BSOA) tracers from isoprene, monoterpenes, and β-

22   caryophyllene as well as major gaseous and particulate pollutants and investigated the impact of

23   anthropogenic pollutants on BSOA formation. The concentrations of BSOA tracers were in the range of

24   45.4 to 109 ng m^{-3} with the majority composed of products from monoterpenes (SOA$_M$, 47.2 ± 9.29 ng

25   m^{-3}), followed by isoprene (SOA$_I$, 23.1 ± 10.8 ng m^{-3}), and β-caryophyllene (SOA$_C$, 3.85 ± 1.75 ng m^{-3}).

26   We found that atmospheric oxidants, O$_x$ (O$_3$ plus NO$_2$), and sulfate correlated well with high-generation

27   SOA$_M$ tracers, but not so for first-generation SOA$_M$ products. This suggested that high O$_x$ and sulfate

28   could promote the formation of high-generation SOA$_M$ products, which probably led to relatively aged

29   SOA$_M$ we observed in the PRD. For the SOA$_I$ tracers, not only 2-methylglyceric acid (NO/NO$_2$-channel

30   product), but also the ratio of 2-methylglyceric acid to 2-methyltetrols (HO$_2$-channel products) exhibit

31   NO$_x$ dependence, indicating the significant impact of NO$_x$ on SOA$_I$ formation pathways. The SOA$_C$ tracer

32   elevated in winter at all sites and positively correlated with levoglucosan, O$_x$, and sulfate. Thus, the

33   unexpected increase of SOA$_C$ in wintertime might be highly associated with the enhancement of biomass

34   burning, atmospheric oxidation capacity and sulfate components in the PRD. The BSOAs that were

35   estimated by the SOA tracer approach showed the highest concentration in fall and the lowest

36   concentration in spring with an annual average concentration of 1.68 ± 0.40 μg m^{-3}. SOA$_M$ dominated

37   the BSOA mass all year round. We also found that BSOA correlated well with sulfate and O$_x$. This

38   implicated the significant effects of anthropogenic pollutants on BSOA formation and highlighted that

39   we could reduce the BSOA through controlling on the anthropogenic emissions of sulfate and O$_x$

40   precursors in polluted regions.

41   **1 Introduction**

42   Secondary organic aerosols (SOA) that are produced through homogenous and heterogeneous processes

43   of volatile organic compounds (VOCs) have significant effects on global climate change and regional air

44   quality (von Schneidemesser et al., 2015). Globally, the emissions of biogenic VOCs (BVOCs) are

45   dominant over anthropogenic VOCs. Thus, biogenic SOA (BSOA) is predominant over anthropogenic

46 SOA. In the past decade, laboratorial, field, and modeling studies have demonstrated that BSOA

47 formation is highly affected by anthropogenic emissions (Zhang et al., 2015; Hoyle et al., 2011; Carlton

48 et al., 2010). Increasing NO_x shifts isoprene oxidation from the low-NO_x conditions to the high-NO_x

49 conditions (Surratt et al., 2010) and enhances nighttime SOA formation via nitrate radical oxidation of

50 monoterpenes (Xu et al., 2015). High SO_2 emission leads to abundant sulfate and acidic particles, which

51 accelerates the BSOA production by the salting-in effect and acid-catalyzed reactions (Offenberg et al.,

52 2009; Xu et al., 2016). In polluted regions, the increase of O_3 levels due to high emissions of NO_x and

53 VOCs, likely results in significant SOA formation through the ozonolysis of BVOCs (Sipilä et al., 2014;

54 Riva et al., 2017). In addition, large emission and formation of anthropogenic organic matter (OM) in

55 urban areas enhance the incorporation of BVOCs' oxidation products into the condensed phase (Donahue

56 et al., 2006). Recently, Carlton et al. (2018) found that the removal of anthropogenic emissions of NO_x,

57 SO_2, and primary OA in the CMAQ simulations could reduce BSOA by 23, 14, and 8% in summertime,

58 respectively.

59   The Pearl River Delta region (PRD) (Figure 1a) is the most developed region in China. Rapid

60 economic growth during the past three decades has resulted in large amounts of anthropogenic emissions

61 in the PRD (Lu et al., 2013). Our observation during fall-winter season in 2008 at a regional site of the

62 PRD showed that daily $PM_{2.5}$ was as high as 150 μg m^{-3} (Ding et al., 2012). Fortunately, due to more and

63 more strict and effective pollution controls in the PRD, $PM_{2.5}$ concentrations have significantly shrunk

64 during the last decade and met the national ambient air quality standard (NAAQS) for annual-mean $PM_{2.5}$

65 (35 μg m^{-3}) since the year of 2015 (Figure 1b). However, O_3 and oxidant (O_x, $O_x = O_3 + NO_2$) are still in

66 high levels and do not decrease apparently (Figure 1b), indicating that atmospheric oxidative capacity in

67 the PRD is still high (Hofzumahaus et al., 2009). On the other hand, BVOCs emissions in the PRD are

68 expected to be high all the year in such a subtropical area (Zheng et al., 2010). In the process of such a

69 dramatic change in air pollution characteristics (e.g. $PM_{2.5}$ and O_3), BSOA origins and formation

70 mechanisms in the PRD should be profoundly affected in the last decade. In this study, year-round $PM_{2.5}$

71 samples were collected at nine sites in the PRD during 2015. We investigated SOA tracers from typical

72 BVOCs (isoprene, monoterpenes, and β-caryophyllene) across the PRD for the first time. We checked

73 seasonal variations in concentrations and compositions of these BSOA tracers and evaluated the impact

74 of anthropogenic pollutants on BSOAs formation in the PRD. We also accessed the SOA origins and

75 discussed the implication in further reducing BSOA through controlling on the anthropogenic emissions.

Atmospheric
Chemistry
and Physics
Discussions

2 Experimental Section

2.1 Field Sampling

Concurrent sampling was performed at 9 out of 23 sites in the Guangdong-Hong Kong-Macao regional air quality monitoring network (http://www.gdep.gov.cn/hjjce/, Figure 1a), including three urban sites in Zhaoqing (ZQ), Guangzhou (GZ) and Dongguan (DG), two suburban sites in Nansha (NS) and Zhuhai (ZH), and four rural sites in Tianhu (TH), Boluo (BL), Heshan (HS) and Taishan (TS).

At each site, 24-hr sampling was conducted every six days from January to December in 2015 using a $PM_{2.5}$ sampler equipped with quartz filters (8 × 10 inches) at a flow rate of 1.1 m^3 min^{-1}. Additionally, field blanks were collected monthly at all sites. Blank filters were covered with aluminum foil and baked at 500 ºC for 12 hrs and stored in a container with silica gel. After sampling, the filter samples were stored at −20 ºC.

In this study, the filters collected in January, April, July and October 2015 were selected to represent winter, spring, summer, and fall samples, respectively. A total of 170 field samples (4-5 samples for each season at each site) were analyzed in the current study.

2.2 Chemical Analysis

For each filter, organic carbon (OC) and elemental carbon (EC) were measured by an OC-EC aerosol analyzer (Sunset Laboratory Inc.). Water-soluble ions were analyzed by ion chromatography (Metrohm). All these species are major components in $PM_{2.5}$ (see Figure 2). Meteorological parameters (temperature and relative humidity) and gaseous pollutants (SO_2, CO, NO_2, NO, and O_3) at each site were recorded hourly. We further calculated the daily averages to probe the potential influence of air pollutants on BSOA formation.

For BSOA tracer analysis, detailed information of the processes is described in the previous literatures (Shen et al., 2015; Ding et al., 2012). Isotope-labeled standard mixtures, including dodecanoic acid-d_{23}, hexadecanoic acid-d_{31}, docosanoic acid-d_{43} and levoglucosan-$^{13}C_6$ were added into each sample as internal standards. Then, samples were extracted by sonication with the mixed solvents of dichloride methane (DCM)/hexane (1:1, v/v) and DCM/methanol (1:1, v/v), sequentially. The extraction solutions of each sample were combined, filtered, and concentrated to ~2 mL. Each concentrated sample was split into two parts for silylation and methylation, respectively.

We analyzed fourteen BSOA tracers in the derivatized samples using GC/MSD (Agilent

105   7890/5975C). The isoprene-derived SOA (SOA_I) tracers were composed of 2-methylglyceric acid (2-

106   MGA), 2-methyltetrols (2-MTLs, 2-methylthreitol and 2-methylerythritol), 3-MeTHF-3,4-diols (*cis*-3-

107   methyltetrahydrofuran-3,4-diol and *trans*-3-methyltetrahydrofuran-3,4-diol) and C_5-alkene triols (*cis*-2-

108   methyl-1,3,4-trihydroxy-1-butene,   *trans*-2-methyl-1,3,4-trihydroxy-1-butene   and   3-methyl-2,3,4-

109   trihydroxy-1-butene). The monoterpenes-derived SOA (SOA_M) tracers included 3-hydroxy-4,4-

110   dimethylglutaric acid (HDMGA), 3-hydroxyglutaric acid (HGA), pinic acid (PA), *cis*-pinonic acid

111   (PNA), and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). The β-caryophyllene-derived SOA

112   (SOA_C) tracer was β-caryophyllenic acid (CA). Due to the lack of authentic standards, surrogate

113   standards were used to quantify BSOA tracers except PNA. Specifically, erythritol, PNA and

114   octadecanoic acid were used for the quantification of SOA_I tracers (Ding et al., 2008), other SOA_M tracers

115   (Ding et al., 2014) and CA (Ding et al., 2011), respectively. The method detection limits (MDLs) for

116   erythritol, PNA and octadecanoic acid were 0.01, 0.02, and 0.02 ng m^{-3}, respectively. Table S1

117   summarizes BSOA data at each site in the PRD.

118   **2.3 Quality Assurance / Quality Control**

119   These target BSOA tracers were not detected or lower than MDLs in the field blanks. The results of

120   spiked samples (erythritol, PNA and octadecanoic acid spiked in pre-baked quartz filters) indicated that

121   the recoveries were 65 ± 14 % for erythritol, 101 ± 3 % for PNA, and 83 ± 7 % for octadecanoic acid.

122   The results of paired duplicate samples indicated that all the relative differences for target BSOA tracers

123   were lower than 15%.

124   It should be noted that the application of surrogate quantification introduces additional errors to the

125   results. Based on the empirical approach to calculate uncertainties from surrogate quantification (Stone

126   et al., 2012), we estimated the errors in analyte measurement which were propagated from the

127   uncertainties in field blanks, spike recoveries, repeatability and surrogate quantification. As Table S2

128   showed, the estimated uncertainties in the tracers' measurement ranged from 15% (PNA) to 157% (CA).

129   **3 Results and Discussion**

130   **3.1 PM$_{2.5}$ and gaseous pollutants**

131   Figure 2 presents spatial and seasonal variations of PM$_{2.5}$ and its major components. Although annual-

132   mean PM$_{2.5}$ (34.8 ± 6.1 μg m^{-3}) in the PRD met the NAAQS value of 35 μg m^{-3}, PM$_{2.5}$ at the urban sites

Atmospheric
Chemistry
and Physics
Discussions

133   (ZQ, GZ and DG) all exceeded the NAAQS value. The rural TH site in the northern part of PRD

134   witnessed the lowest concentration of $PM_{2.5}$ (25.0 μg m^{-3}) among the nine sites. $PM_{2.5}$ levels were highest

135   in winter (on average 60.1 ± 21.6 μg m^{-3}) and lowest in summer (on average 22.8 ± 3.3 μg m^{-3}).

136   Carbonaceous aerosols and water-soluble ions together explained 98 ± 11 % of $PM_{2.5}$ masses. OM

137   (OC×1.6) was the most abundant component in $PM_{2.5}$, followed by sulfate, ammonium, nitrate and EC.

138   Similar to $PM_{2.5}$, the five major components all increased in winter and fall (Figure S1), suggesting severe

139    $PM_{2.5}$ pollution during fall-winter season in the PRD.

140   In the gas phase, SO_2, CO, NO_2 and NO_x presented similar seasonal trends as $PM_{2.5}$, i.e. higher

141   levels occurred during fall and winter and lower concentrations during spring and summer (Figure 3 a-

142   d). Annual-mean SO_2 and NO_2 in the PRD both met the NAAQS values of 60 μg m^{-3} and 40 μg m^{-3},

143   respectively (Figure 3a and 3c). As a typical secondary pollutant, O_3 was highest in summer (Figure 3e),

144   probably because of the strong photo-chemistry. Due to the compromise of opposite seasonal trends of

145   O_3 and NO_2, O_x showed less seasonal variation (Figure 3f) compared with other gaseous pollutants. And

146   annual-mean O_x reached 96.1 ± 14.9 μg m^{-3}. These imply that atmospheric oxidative capacity is high all

147   the year in the PRD.

148   **3.2 Spatial distribution and seasonal variation of SOA tracers**

149   The total concentrations of BSOA tracers ranged from 45.4 to 109 ng m^{-3} among the nine sites. SOA_M

150   tracers (47.2 ± 9.29 ng m^{-3}) represented predominance, followed by SOA_I tracers (23.1 ± 10.8 ng m^{-3}),

151   and SOA_C tracer (3.85 ± 1.75 ng m^{-3}).

152   **3.2.1 Monoterpenes-derived SOA tracers**

153   Annual averages of total SOA_M tracers at the nine sites were in the range of 26.5 to 57.4 ng m^{-3} (Table

154   S1). Figure 4 and Figure S2a show the spatial distribution of SOA_M tracers and monoterpene emissions

155   in the PRD (Zheng et al., 2010). The highest concentration of SOA_M tracers was observed at the rural

156   TH site where monoterpene emissions were high. Figure 4 also presents seasonal variations of SOA_M

157   tracers. At most sites, high levels occurred in summer and fall. Monoterpene emission rates are

158   influenced by temperature and solar radiation (Guenther et al., 2012). Thus, high temperature and

159   intensive solar radiation during summer and fall in the PRD (Zheng et al., 2010) could stimulate

160   monoterpene emissions and then the SOA_M formation.

Atmospheric
Chemistry
and Physics
Discussions

161   Among the five SOA_M tracers, HGA (20.1 ± 4.28 ng m^{-3}) showed the highest concentration,

162   followed by HDMGA (14.7 ± 2.93 ng m^{-3}), MBTCA (7.63 ± 1.49 ng m^{-3}), PNA (3.75 ± 2.72 ng m^{-3}) and

163   PA (1.01 ± 0.48 ng m^{-3}). SOA_M formation undergoes multi-generation reactions. The first-generation

164   SOA_M (SOA_{M_F}) products, PNA and PA, can be further oxidized and form the high-generation (SOA_{M_H})

165   products, e.g. MBTCA (Müller et al., 2012). Thus, the (PNA+PA) / MBTCA ratio has been used to probe

166   SOA_M aging (Haque et al., 2016; Ding et al., 2014). The (PNA+PA) / MBTCA ratios in chamber-

167   generated α-pinene SOA samples were reported in the range of 1.51 to 5.91 depending on different

168   oxidation conditions (Offenberg et al., 2007; Eddingsaas et al., 2012). In this study, the median values of

169   (PNA+PA) / MBTCA varied from 0.27 at ZH to 1.67 at TH. The ratios observed in this study were

170   consistent with our previous observations at the regional site, Wangqingsha (WQS) in the PRD (Ding et

171   al., 2012), but lower than those in the fresh α-pinene SOA samples from chamber experiments (Figure

172   S3), indicating relatively aged SOA_M in the air of PRD.

173   Moreover, the levels of SOA_{M_H} tracers (HGA + HDMGA + MBTCA) were much higher than those

174   of SOA_{M_F} tracers (PNA + PA), with mean mass fractions of SOA_{M_H} tracers reaching 86% (Figure 4).

175   Mass fractions of SOA_{M_F} tracers decreased in the summer samples (Figure 4), probably resulting from

176   strong photo-chemistry and more intensive further oxidation during summer. High abundances of

177   SOA_{M_H} tracers in the PRD were different from our year-round observations at 12 sites across China

178   (Ding et al., 2016b). In that study, the (PNA+PA) / MBTCA ratio suggested generally fresh SOA_M (Figure

179   S3) and SOA_{M_F} tracers were the majority. Thus, we see more aged SOA_M in the PRD.

180   As Figure 5 a-b showed, the SOA_{M_F} tracers did not show good correlations with O_x at most sites,

181   while the SOA_{M_H} tracers exhibited significant O_x dependence. When atmospheric oxidation capacity is

182   high, strong photo-oxidation of PNA and PA could reduce their concentrations and promote the formation

183   of SOA_{M_H} tracers (Müller et al., 2012). Thus, the levels of SOA_{M_H} tracers would increase with

184   increasing O_x but not so for SOA_{M_F} tracers. On the other hand, sulfate is a key species in particles that

185   determines aerosol acidity and promotes SOA formation through the salting-in effect and heterogeneous

186   reactions (Offenberg et al., 2009; Xu et al., 2016). The SOA_{M_F} tracers poorly correlated with sulfate

187   (Figure 5c), while the SOA_{M_H} tracers presented significant sulfate dependence at all the 9 sites (Figure

188   5d). This suggested that sulfate also played a critical role in forming SOA_{M_H} tracers through particle

189   phase reactions. Here, we conclude that high concentrations of O_x and sulfate could stimulate SOA_{M_H}

190   tracers' production and thereby lead to aged SOA_M in the PRD.

Atmospheric
Chemistry
and Physics
Discussions

3.2.2 Isoprene-derived SOA tracers

Annual averages of total SOA_I tracers at the nine sites were in the range of 10.8 to 49.3 ng m^{-3} (Table S1). Figure 6 and Figure S2b show the spatial distribution of SOA_I tracers and isoprene emissions in the PRD (Zheng et al., 2010), respectively. The highest concentration occurred at ZQ where the emissions were high. Figure 6 also presents seasonal variations of SOA_I tracers at the nine sites. High levels occurred in summer and fall. Similar to monoterpenes, the emission rate of isoprene is influenced by temperature and solar radiation (Guenther et al., 2012), which are expected to be higher in summer and fall in the PRD (Zheng et al., 2010). Among these SOA_I tracers, 2-MTLs (14.2 ± 5.61 ng m^{-3}) were the most abundant products, followed by C_5-alkene triols (6.81 ± 5.05 ng m^{-3}), 2-MGA (1.99 ± 0.72 ng m^{-3}) and 3-MeTHF-3,4-diols (0.19 ± 0.08 ng m^{-3}).

SOA_I formation is highly affected by NO_x (Surratt et al., 2010). Under the low-NO_x or NO_x free conditions, isoprene is oxidized by the OH and HO_2 radicals through the HO_2-channel which generates a hydroxy hydroperoxide (ISOPOOH) and then forms epoxydiols (IEPOX) (Paulot et al., 2009). Reactive uptake of IEPOX on acidic particles eventually produces 2-MTLs, C_5-alkene triols, 3-MeTHF-3,4-diols, 2-MTLs-organosulfates and oligomers (Lin et al., 2012). Under the high-NO_x conditions, isoprene undergoes oxidation by NO_x through the NO/NO_2-channel and generates methacrolein (MACR) and then forms peroxymethylacrylic nitric anhydride (MPAN). Further oxidation of MPAN by the OH radical produces hydroxymethel-methyl-α-lactone (HMML) and/or methacrylic acid epoxide (MAE). HMML and MAE are the direct precursors to 2-MGA, 2-MGA-organosulfate and its corresponding oligomers (Nguyen et al., 2015). As Figure 6 showed, the concentrations of HO_2-channel tracers (2-MTLs + C_5-alkene triols + 3-MeTHF-3,4-diols) were much higher than those of the NO/NO_2-channel product (2-MGA) at all the nine sites. The dominance of HO_2-channel products was also observed at another regional site in the PRD (WQS), largely due to strong heterogeneous reactions of IEPOXs on the acidic particles in the polluted air (He et al., 2018).

Figure 6 also shows seasonal trends of the 2-MGA to 2-MTLs ratio (2-MGA/2-MTLs) which is often applied to probe the influence of NO_x on the formation of SOA_I (Ding et al., 2013; Ding et al., 2016a; Pye et al., 2013). The ratios were highest in wintertime and lowest in summertime, which were consistent with the seasonal trend of NO_x during our campaign (Figure 3d). As Table 1 showed, 2-MGA positively correlated with NO_2, probably due to the enhanced formation of MPAN from

Atmospheric
Chemistry
and Physics
Discussions

Open Access

EGU

220   peroxymethacryoyl (PMA) radical reacted with NO_2 (Worton et al., 2013; Chan et al., 2010). Previous

221   laboratory studies showed that increasing NO_2/NO ratio could promote the formation of 2-MGA and its

222   corresponding oligoesters (Chan et al., 2010; Surratt et al., 2010). However, we did not see a significant

223   correlation between 2-MGA and NO_2/NO ratio in the PRD. Instead, the 2-MGA/2-MTLs ratio correlated

224   well with NO, NO_2 and NO_2/NO ratio (Table 1). Increasing NO limits the formation of ISOPOOH but

225   prefers the production of MACR, and increasing NO_2 enhances MPAN formation. Thus, it is expected

226   that the 2-MGA/2-MTLs ratio shows stronger NO_x dependence than 2-MGA. These findings demonstrate

227   the significant impact of NO_x on SOA_I formation pathways in the atmosphere.

228   Recent studies indicated that isoprene ozonolysis might play a role in SOA_I formation in the ambient

229   air. Riva et al. (2016) found that isoprene ozonolysis with acidic particles could produce substantial 2-

230   MTLs but not so for C_5-alkene triols and 3-MeTHF-3,4-diols. Li et al. (2018) observed a positive

231   correlation between 2-MTLs and O_3 in the North China Plain. In the PRD, we also saw weak but

232   significant correlations of 2-MTLs with O_3 (Table S3). However, 3-MeTHF-3,4-diols and C_5-alkene

233   triols were detected in all samples and 2-MTLs, C_5-alkene triols and 3-MeTHF-3,4-diols correlated well

234   with each other (Table S4), which was apparently different from those reported by Riva et al. (2016).

235   Moreover, the ratios of 2-MTLs isomers in the PRD samples (2.00−2.85) were much lower than those

236   (10−22, Figure S4) reported in the SOA from isoprene ozonolysis (Riva et al., 2016). Furthermore,

237   isoprene oxidation by the OH radical is much faster than that by ozone under the polluted PRD conditions

238   (Table S5). And IEPOX yields through the ISOPOOH oxidation by the OH radical are more than 75%

239   in the atmosphere (St. Clair et al., 2016). Thus, isoprene ozonolysis might be not the major formation

240   pathway of SOA_I, even though annual-mean O_3 level reaching 67.7 μg m^{-3} in the PRD (Table S1).

241   A previous study found that thermal decomposition of low volatility organics in IEPOX-derived

242   SOA could produce SOA_I tracers, e.g. 2-MTLs, C_5-alkene triols and 3-MeTHF-3,4-diols (Lopez-Hilfiker

243   et al., 2016). This means that these tracers detected by GC-MSD might be generated from thermal

244   decomposition of IEPOX-derived SOA. If these tracers were mainly generated from such a thermal

245   process, their compositions would be similar in different samples. To verify this possibility, we presented

246   chemical compositions of three C_5-alkene triol isomers at the nine sites in ternary plots. The relative

247   abundances of three isomers significantly changed from site to site (Figure 7) and season to season

248   (Figure S5), and were different from those measured in the chamber samples (Lin et al., 2012). Moreover,

249   the slopes of linear correlations among these IEPOX-derived SOA tracers also varied from site to site

250 (Figure S6). Coupled with the seasonal trend of 2-MGA/2-MTLs ratios, the observed variations in SOA_I

251 tracers compositions demonstrated that the SOA_I tracers were mainly formed through different pathways

252 in the real atmosphere rather than thermal decomposition.

3.2.3 Sesquiterpene-derived SOA tracer

254 Annual averages of CA at the nine sites ranged from 1.82 to 7.07 ng m^{-3}. The levels of CA at the inland

255 sites (e.g. GZ, ZQ, and TH) were higher than those at the coastal sites (ZH and NS, Figure 8). Since

256 sesquiterpenes are typical BVOCs, it is unexpected that the concentrations of CA were highest during

257 winter in the PRD (Figure 8). Interestingly, seasonal trend of CA was consistent with that of the biomass

258 burning (BB) tracer, levoglucosan (Figure 8). And CA correlated well with levoglucosan at eight sites in

259 the PRD (Figure 9a). Sesquiterpenes are stored in plant tissues partly to protect the plants from insects

260 and pathogens (Keeling and Bohlmann, 2006). BB can not only stimulate sesquiterpene emissions

261 (Ciccioli et al., 2014) but also substantially alter the SOA formation and yields (Mentel et al., 2013).

262 Emissions inventories in the PRD showed that the BB emissions were enhanced during winter (He et al.,

263 2011). These suggested that the unexpected increase of SOA_C in wintertime could be highly associated

264 with BB emissions in the PRD.

265 Besides the impact of BB, we also found positive correlations of CA with O_x (Figure 9b) and sulfate

266 (Figure 9c). The oxidation of β-caryophyllene by the OH radical and O_3 is very rapid with the lifetimes

267 less than 10 min under typical conditions in the air of PRD (Table S5). The increase of sulfate could not

268 only raise aerosol acidity but also enhance the salting-in effect (Xu et al., 2015). In the PRD, both O_x

269 (Figure 3f) and sulfate (Figure S1) increased during winter, which could promote SOA_C formation. Here,

270 we conclude that the enhancement of BB emissions as well as the increase of O_x and sulfate in wintertime

271 together led to high SOA_C production during winter in the PRD.

3.3 Source apportionment and atmospheric implications

273 We further attributed BSOA by the SOA-tracer approach which was first developed by Kleindienst et al.

274 (2007). This method has applied to SOA apportionment at multiple sites across the United States

275 (Lewandowski et al., 2013) and China (Ding et al., 2016b), and over global oceans from Arctic to

276 Antarctic (Hu et al., 2013). Details of the SOA-tracer method and its application in this study as well as

277 the uncertainty of estimating procedure are described in Text S1. Table S1 lists the results of estimated

278   SOA from different BVOCs.

279   Figure 10a exhibits the spatial distribution of BSOA (SOA_M + SOA_I + SOA_C). Annual average at

280   the nine sites ranged from 0.97 µg m^{-3} (NS) to 2.19 µg m^{-3} (ZQ), accounting for 9-15% of OM. SOA_M

281   was the largest BSOA contributor with an average contribution of 64 ± 7 %, followed by SOA_C (21 ±

282   6 %), and SOA_I (14 ± 4 %). Figure 10b presents seasonal variation of BSOA. The levels were highest in

283   fall (2.35 ± 0.95 µg m^{-3}) and lowest in spring (1.06 ± 0.42 µg m^{-3}). SOA_M contributions ranged from 57%

284   in winter to 68% in spring. The shares of SOA_I were only 5% in winter and reached up to 22% in summer.

285   The contributions of SOA_C increased to 40% in wintertime.

286   It is interesting to note that SOA_M, SOA_I and SOA_C all positively correlated with sulfate and O_x in

287   the PRD (Table 2). Anthropogenic emissions significantly influence BSOA formation (Carlton et al.,

288   2018). The observed sulfate and O_x dependence of BSOA in the air of PRD indicates that the reduction

289   of 1 µg m^{-3} in sulfate and O_x could lower BSOA levels by 0.17 and 0.02 µg m^{-3}, respectively. If both

290   concentrations decline by 50%, the reduction of O_x is more efficient than sulfate in reducing BSOA in

291   the PRD (Table 2). Due to strict control of SO_2 emissions (Wang et al., 2013), ambient SO_2 significantly

292   shrank over the PRD (Figure 1b). However, O_x levels did not decrease during the past decade (Figure 1b)

293   and O_x concentrations were much higher than sulfate in the PRD (96.1 ± 14.9 µg m^{-3} vs. 8.44 ± 1.09 µg

294   m^{-3} on average). At present, short-term despiking and long-term attainment of O_3 concentrations are

295   challenges for air pollution control in the PRD (Ou et al., 2016). Thus, lowering O_x is critical to improve

296   air quality in the PRD. Our results highlight the importance of future reduction in anthropogenic pollutant

297   emissions (e.g. SO_2 and O_x precursors) for considerably reducing the BSOA burden in polluted regions.

298   **Code/Data availability**

299   The experimental data in this study are available upon request to the corresponding author by email.

300   **Author Contribution**

301   Xiang Ding, Duo-Hong Chen and Jun Li conceived the project and designed the study. Yu-Qing Zhang

302   and Duo-Hong Chen performed the data analysis and wrote the manuscript. Duo-Hong Chen, Tao Zhang

303   and Yu-Bo Ou arranged the sample collection and assisted with the data analysis. Jun-Qi Wang, Qian

304   Cheng and Hao Jiang analyzed the samples. Xiang Ding, Peng-Lin Ye, Wei Song, Gan Zhang and Xin-

305 Ming Wang performed data interpretation and edited the manuscript. All authors contributed to the final

306 manuscript development.

307 **Competing interests**

308 The authors declare that they have no conflict of interest.

309 **Acknowledgments**

315 **References**

316 Carlton, A. G., Pinder, R. W., Bhave, P. V., and Pouliot, G. A.: To what extent can biogenic SOA be

317 controlled?, Environ. Sci. Technol., 44, 3376-3380, 10.1021/es903506b, 2010.

318 Carlton, A. G., Pye, H. O. T., Baker, K. R., and Hennigan, C. J.: Additional benefits of federal air-quality

319 rules: Model estimates of controllable biogenic secondary organic aerosol, Environ. Sci. Technol., 52,

320 9254-9265, 10.1021/acs.est.8b01869, 2018.

321 Chan, A. W. H., Chan, M. N., Surratt, J. D., Chhabra, P. S., Loza, C. L., Crounse, J. D., Yee, L. D., Flagan,

322 R. C., Wennberg, P. O., and Seinfeld, J. H.: Role of aldehyde chemistry and NO_x concentrations in

323 secondary organic aerosol formation, Atmos. Chem. Phys., 10, 7169-7188, 10.5194/acp-10-7169-

324 2010, 2010.

325 Ciccioli, P., Centritto, M., and Loreto, F.: Biogenic volatile organic compound emissions from vegetation

326 fires, Plant. Cell. Environ., 37, 1810-1825, 10.1111/pce.12336, 2014.

327 Ding, X., Zheng, M., Yu, L., Zhang, X., Weber, R. J., Yan, B., Russell, A. G., Edgerton, E. S., and Wang,

328 X.: Spatial and seasonal trends in biogenic secondary organic aerosol tracers and water-soluble organic

329 carbon in the southeastern United States, Environ. Sci. Technol., 42, 5171-5176, 10.1021/es7032636,

330 2008.

Atmospheric
Chemistry
and Physics
Discussions

331   Ding, X., Wang, X., and Zheng, M.: The influence of temperature and aerosol acidity on biogenic

332   secondary organic aerosol tracers: Observations at a rural site in the central Pearl River Delta region,

333   South China, Atmos. Environ., 45, 1303-1311, 10.1016/j.atmosenv.2010.11.057, 2011.

334   Ding, X., Wang, X., Gao, B., Fu, X., He, Q., Zhao, X., Yu, J., and Zheng, M.: Tracer based estimation of

335   secondary organic carbon in the Pearl River Delta, South China, J. Geophys. Res-Atmos., 117, D05313,

336   10.1029/2011JD016596, 2012.

337   Ding, X., Wang, X., Xie, Z., Zhang, Z., and Sun, L.: Impacts of Siberian biomass burning on organic

338   aerosols over the North Pacific Ocean and the Arctic: Primary and secondary organic tracers, Environ.

339   Sci. Technol., 47, 3149-3157, 10.1021/es3037093, 2013.

340   Ding, X., He, Q. F., Shen, R. Q., Yu, Q. Q., and Wang, X. M.: Spatial distributions of secondary organic

341   aerosols from isoprene, monoterpenes, β-caryophyllene, and aromatics over China during summer, J.

342   Geophys. Res-Atmos., 119, 11877-11891, 10.1002/2014JD021748, 2014.

343   Ding, X., He, Q. F., Shen, R. Q., Yu, Q. Q., Zhang, Y. Q., Xin, J. Y., Wen, T. X., and Wang, X. M.: Spatial

344   and seasonal variations of isoprene secondary organic aerosol in China: Significant impact of biomass

345   burning during winter, Sci. Rep., 6, 20411, 10.1038/srep20411, 2016a.

346   Ding, X., Zhang, Y. Q., He, Q. F., Yu, Q. Q., Shen, R. Q., Zhang, Y., Zhang, Z., Lyu, S. J., Hu, Q. H.,

347   Wang, Y. S., Li, L. F., Song, W., and Wang, X. M.: Spatial and seasonal variations of secondary organic

348   aerosol   from   terpenoids   over   China,   J.   Geophys.   Res-Atmos.,   121,   14661–14678,

349   10.1002/2016JD025467, 2016b.

350   Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and

351   chemical aging of semivolatile organics, Environ. Sci. Technol., 40, 2635-2643, 10.1021/es052297c,

352   2006.

353   Eddingsaas, N. C., Loza, C. L., Yee, L. D., Chan, M., Schilling, K. A., Chhabra, P. S., Seinfeld, J. H., and

354   Wennberg, P. O.: α-pinene photooxidation under controlled chemical conditions – Part 2: SOA yield

355   and composition in low- and high-NO_x environments, Atmos. Chem. Phys., 12, 7413-7427,

356   10.5194/acp-12-7413-2012, 2012.

357   Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.:

358   The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): an extended and

359   updated framework for modeling biogenic emissions, Geosci. Model. Dev., 5, 1471-1492,

360   10.5194/gmd-5-1471-2012, 2012.

Atmospheric
Chemistry
and Physics
Discussions

361   Haque, M. M., Kawamura, K., and Kim, Y.: Seasonal variations of biogenic secondary organic aerosol

362   tracers   in   ambient   aerosols   from   Alaska,   Atmos.   Environ.,   130,   95-104,

363   10.1016/j.atmosenv.2015.09.075, 2016.

364   He, M., Zheng, J., Yin, S., and Zhang, Y.: Trends, temporal and spatial characteristics, and uncertainties

365   in biomass burning emissions in the Pearl River Delta, China, Atmos. Environ., 45, 4051-4059,

366   10.1016/j.atmosenv.2011.04.016, 2011.

367   He, Q. F., Ding, X., Fu, X. X., Zhang, Y. Q., Wang, J. Q., Liu, Y. X., Tang, M. J., Wang, X. M., and

368   Rudich, Y.: Secondary organic aerosol formation from isoprene epoxides in the Pearl River Delta,

369   South China: IEPOX‑ and HMML‑derived tracers, J. Geophys. Res-Atmos., 123, 6999-7012,

370   10.1029/2017JD028242, 2018.

371   Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Holland, F., Kita,

372   K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner, A., and Zhang, Y.: Amplified trace gas

373   removal in the troposphere, Science, 324, 1702-1704, 10.1126/science.1164566, 2009.

374   Hoyle, C. R., Boy, M., Donahue, N. M., Fry, J. L., Glasius, M., Guenther, A., Hallar, A. G., Huff Hartz,

375   K., Petters, M. D., Petäjä, T., Rosenoern, T., and Sullivan, A. P.: A review of the anthropogenic

376   influence on biogenic secondary organic aerosol, Atmos. Chem. Phys., 11, 321-343, 10.5194/acp-11-

377   321-2011, 2011.

378   Hu, Q. H., Xie, Z. Q., Wang, X. M., Kang, H., He, Q. F., and Zhang, P.: Secondary organic aerosols over

379   oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic, Sci. Rep., 3, 2280,

380   10.1038/srep02280, 2013.

381   Keeling, C. I., and Bohlmann, J.: Genes, enzymes and chemicals of terpenoid diversity in the constitutive

382   and induced defence of conifers against insects and pathogens, New. Phytol., 170, 657-675,

383   10.1111/j.1469-8137.2006.01716.x, 2006.

384   Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhave, P. V., and Edney,

385   E. O.: Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic

386   aerosol   at   a   southeastern   US   location,   Atmos.   Environ.,   41,   8288-8300,

387   10.1016/j.atmosenv.2007.06.045, 2007.

388   Lewandowski, M., Piletic, I. R., Kleindienst, T. E., Offenberg, J. H., Beaver, M. R., Jaoui, M., Docherty,

389   K. S., and Edney, E. O.: Secondary organic aerosol characterisation at field sites across the United

390   States   during   the   spring–summer   period,   Int.   J.   Environ.   An.   Ch.,   93,   1084-1103,

391   10.1080/03067319.2013.803545, 2013.

392   Li, J., Wang, G., Wu, C., Cao, C., Ren, Y., Wang, J., Li, J., Cao, J., Zeng, L., and Zhu, T.: Characterization

393   of isoprene-derived secondary organic aerosols at a rural site in North China Plain with implications

394   for anthropogenic pollution effects, Sci. Rep., 8, 535, 10.1038/s41598-017-18983-7, 2018.

395   Lin, Y.-H., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S.,

396   Knipping, E., Edgerton, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.: Isoprene epoxydiols as

397   precursors to secondary organic aerosol formation: Acid-catalyzed reactive uptake studies with

398   authentic standards, Environ. Sci. Technol., 46, 189-195, 10.1021/es202554c, 2012.

399   Lopez-Hilfiker, F. D., Mohr, C., D'Ambro, E. L., Lutz, A., Riedel, T. P., Gaston, C. J., Iyer, S., Zhang,

400   Z., Gold, A., Surratt, J. D., Lee, B. H., Kurten, T., Hu, W. W., Jimenez, J., Hallquist, M., and Thornton,

401   J. A.: Molecular composition and volatility of organic aerosol in the southeastern U.S.: Implications

402   for IEPOX derived SOA, Environ. Sci. Technol., 50, 2200-2209, 10.1021/acs.est.5b04769, 2016.

403   Lu, Q., Zheng, J., Ye, S., Shen, X., Yuan, Z., and Yin, S.: Emission trends and source characteristics of

404   SO_2, NO_x, PM_{10} and VOCs in the Pearl River Delta region from 2000 to 2009, Atmos. Environ., 76,

405   11-20, 10.1016/j.atmosenv.2012.10.062, 2013.

406   Müller, L., Reinnig, M. C., Naumann, K. H., Saathoff, H., Mentel, T. F., Donahue, N. M., and Hoffmann,

407   T.: Formation of 3-methyl-1,2,3-butanetricarboxylic acid via gas phase oxidation of pinonic acid – a

408   mass spectrometric study of SOA aging, Atmos. Chem. Phys., 12, 1483-1496, 10.5194/acp-12-1483-

409   2012, 2012.

410   Mentel, T. F., Kleist, E., Andres, S., Maso, M. D., Hohaus, T., Kiendler-Scharr, A., Rudich, Y., Springer,

411   M., Tillmann, R., Uerlings, R., Wahner, A., and Wildt, J.: Secondary aerosol formation from stress-

412   induced biogenic emissions and possible climate feedbacks, Atmos. Chem. Phys., 13, 8755-8770,

413   10.5194/acp-13-8755-2013, 2013.

414   Nguyen, T. B., Bates, K. H., Crounse, J. D., Schwantes, R. H., Zhang, X., Kjaergaard, H. G., Surratt, J.

415   D., Lin, P., Laskin, A., Seinfeld, J. H., and Wennberg, P. O.: Mechanism of the hydroxyl radical

416   oxidation of methacryloyl peroxynitrate (MPAN) and its pathway toward secondary organic aerosol

417   formation in the atmosphere, Phys. Chem. Chem. Phys., 17, 17914-17926, 10.1039/C5CP02001H,

418   2015.

419   Offenberg, J. H., Lewis, C. W., Lewandowski, M., Jaoui, M., Kleindienst, T. E., and Edney, E. O.:

420   Contributions of toluene and α-pinene to SOA formed in an irradiated toluene/α-pinene/NO$_x$/ air

Atmospheric
Chemistry
and Physics
Discussions

421 mixture: Comparison of results using ^{14}C content and SOA organic tracer methods, Environ. Sci.

422 Technol., 41, 3972-3976, 10.1021/es070089+, 2007.

423 Offenberg, J. H., Lewandowski, M., Edney, E. O., Kleindienst, T. E., and Jaoui, M.: Influence of aerosol

424 acidity on the formation of secondary organic aerosol from biogenic precursor hydrocarbons, Environ.

425 Sci. Technol., 43, 7742–7747, 10.1021/es901538e, 2009.

426 Ou, J., Yuan, Z., Zheng, J., Huang, Z., Shao, M., Li, Z., Huang, X., Guo, H., and Louie, P. K. K.: Ambient

427 ozone control in a photochemically active region: Short-term despiking or long-term attainment?,

428 Environ. Sci. Technol., 50, 5720–5728, 10.1021/acs.est.6b00345, 2016.

429 Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kürten, A., St. Clair, J. M., Seinfeld, J. H., and Wennberg,

430 P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene, Science, 325, 730-

431 733, 10.1126/science.1172910, 2009.

432 Pye, H. O. T., Pinder, R. W., Piletic, I. R., Xie, Y., Capps, S. L., Lin, Y.-H., Surratt, J. D., Zhang, Z., Gold,

433 A., Luecken, D. J., Hutzell, W. T., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Lewandowski, M.,

434 and Edney, E. O.: Epoxide pathways improve model predictions of isoprene markers and reveal key

435 role of acidity in aerosol formation, Environ. Sci. Technol., 47, 11056-11064, 10.1021/es402106h,

436 2013.

437 Riva, M., Budisulistiorini, S. H., Zhang, Z., Gold, A., and Surratt, J. D.: Chemical characterization of

438 secondary organic aerosol constituents from isoprene ozonolysis in the presence of acidic aerosol,

439 Atmos. Environ., 130, 5-13, 10.1016/j.atmosenv.2015.06.027, 2016.

440 Riva, M., Budisulistiorini, S. H., Zhang, Z., Gold, A., Thornton, J. A., Turpin, B. J., and Surratt, J. D.:

441 Multiphase reactivity of gaseous hydroperoxide oligomers produced from isoprene ozonolysis in the

442 presence of acidified aerosols, Atmos. Environ., 152, 314-322, 10.1016/j.atmosenv.2016.12.040, 2017.

443 Shen, R. Q., Ding, X., He, Q. F., Cong, Z. Y., Yu, Q. Q., and Wang, X. M.: Seasonal variation of secondary

444 organic aerosol tracers in Central Tibetan Plateau, Atmos. Chem. Phys., 15, 8781-8793, 10.5194/acp-

445 15-8781-2015, 2015.

446 Sipilä, M., Jokinen, T., Berndt, T., Richters, S., Makkonen, R., Donahue, N. M., Mauldin Iii, R. L., Kurtén,

447 T., Paasonen, P., Sarnela, N., Ehn, M., Junninen, H., Rissanen, M. P., Thornton, J., Stratmann, F.,

448 Herrmann, H., Worsnop, D. R., Kulmala, M., Kerminen, V. M., and Petäjä, T.: Reactivity of stabilized

449 Criegee intermediates (sCIs) from isoprene and monoterpene ozonolysis toward SO_2 and organic acids,

450 Atmos. Chem. Phys., 14, 12143-12153, 10.5194/acp-14-12143-2014, 2014.

451   St. Clair, J. M., Rivera-Rios, J. C., Crounse, J. D., Knap, H. C., Bates, K. H., Teng, A. P., Jørgensen, S.,

452   Kjaergaard, H. G., Keutsch, F. N., and Wennberg, P. O.: Kinetics and products of the reaction of the

453   first-generation isoprene hydroxy hydroperoxide (ISOPOOH) with OH, J. Phys. Chem. A., 120, 1441-

454   1451, 10.1021/acs.jpca.5b06532, 2016.

455   Stone, E. A., Nguyen, T. T., Pradhan, B. B., and Man Dangol, P.: Assessment of biogenic secondary

456   organic aerosol in the Himalayas, Environ. Chem., 9, 263-272, 10.1071/EN12002, 2012.

457   Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P.,

458   Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary

459   organic aerosol formation from isoprene, P. Natl. Acad. Sci. USA., 107, 6640-6645,

460   10.1073/P.Natl.Acad.Sci.USA.0911114107, 2010.

461   Von Schneidemesser, E., Monks, P. S., Allan, J. D., Bruhwiler, L., Forster, P., Fowler, D., Lauer, A.,

462   Morgan, W. T., Paasonen, P., Righi, M., Sindelarova, K., and Sutton, M. A.: Chemistry and the linkages

463   between air quality and climate change, Chem. Rev., 115, 3856-3897, 10.1021/acs.chemrev.5b00089,

464   2015.

465   Wang, X., Liu, H., Pang, J., Carmichael, G., He, K., Fan, Q., Zhong, L., Wu, Z., and Zhang, J.: Reductions

466   in sulfur pollution in the Pearl River Delta region, China: Assessing the effectiveness of emission

467   controls, Atmos. Environ., 76, 113-124, 10.1016/j.atmosenv.2013.04.074, 2013.

468   Worton, D. R., Surratt, J. D., LaFranchi, B. W., Chan, A. W. H., Zhao, Y., Weber, R. J., Park, J.-H.,

469   Gilman, J. B., de Gouw, J., Park, C., Schade, G., Beaver, M., Clair, J. M. S., Crounse, J., Wennberg,

470   P., Wolfe, G. M., Harrold, S., Thornton, J. A., Farmer, D. K., Docherty, K. S., Cubison, M. J., Jimenez,

471   J.-L., Frossard, A. A., Russell, L. M., Kristensen, K., Glasius, M., Mao, J., Ren, X., Brune, W., Browne,

472   E. C., Pusede, S. E., Cohen, R. C., Seinfeld, J. H., and Goldstein, A. H.: Observational insights into

473   aerosol formation from isoprene, Environ. Sci. Technol., 47, 11396–11402, 10.1021/es4011064, 2013.

474   Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz,

475   G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J.,

476   Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions

477   on aerosol formation from isoprene and monoterpenes in the southeastern United States, P. Natl. Acad.

478   Sci. USA., 112, 37-42, 10.1073/ P.Natl.Acad.Sci.USA.1417609112, 2015.

479   Xu, L., Middlebrook, A. M., Liao, J., de Gouw, J. A., Guo, H., Weber, R. J., Nenes, A., Lopez-Hilfiker,

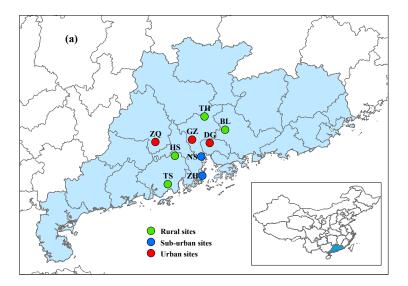480   F. D., Lee, B. H., Thornton, J. A., Brock, C. A., Neuman, J. A., Nowak, J. B., Pollack, I. B., Welti, A.,
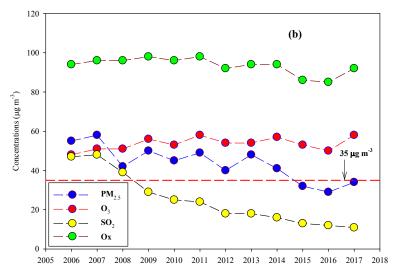
481   Graus, M., Warneke, C., and Ng, N. L.: Enhanced formation of isoprene-derived organic aerosol in

482   sulfur-rich power plant plumes during Southeast Nexus, J. Geophys. Res-Atmos., 121, 11137-11153,

483   10.1002/2016JD025156, 2016.

484   Zhang, R. Y., Wang, G. H., Guo, S., Zarnora, M. L., Ying, Q., Lin, Y., Wang, W. G., Hu, M., and Wang,

485   Y.: Formation of urban fine particulate matter, Chem. Rev., 115, 3803-3855,

486   10.1021/acs.chemrev.5b00067, 2015.

487   Zheng, J., Zheng, Z., Yu, Y., and Zhong, L.: Temporal, spatial characteristics and uncertainty of biogenic

488   VOC emissions in the Pearl River Delta region, China, Atmos. Environ., 44, 1960-1969,

489   10.1016/j.atmosenv.2010.03.001, 2010.

490

491

492

Figure 1 Sampling sites in the PRD (a) and long-term trends of annual-mean $PM_{2.5}$, O_3, SO_2 and O_x recorded by the Guangdong-Hong Kong-Macao regional air quality monitoring network (http://www.gdep.gov.cn/hjjce/) (b). The red dash line indicates the NAAQS for annual-mean $PM_{2.5}$ concentrations (35 µg m^{-3}).
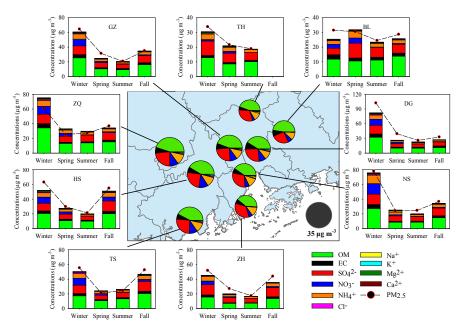
496

Figure 2 Major components in PM$_{2.5}$ and their seasonal variation at 9 sites. The pie charts in the central figure represent the annual average of major components. High levels of PM$_{2.5}$ and major components were observed in wintertime.

502

Figure 3 Seasonal variation of gaseous pollutants in the PRD. Box with error bars represent 10th, 25th, 75th, 90th

percentiles for each pollutant. The line in each box represents the median value. Blue dash lines indicate annual

average concentrations of SO_2 (14.9 µg m^{-3}), CO (0.74 mg m^{-3}), NO_2 (28.5 µg m^{-3}), NO_x (39.0µg m^{-3}), O_3 (67.7 µg

m[-3]) and O_x (96.1 µg m^{-3}).

507

508

509 Figure 4 Spatial and seasonal variations of SOA_M tracers at 9 sites in the PRD. The bars in the central figure represent

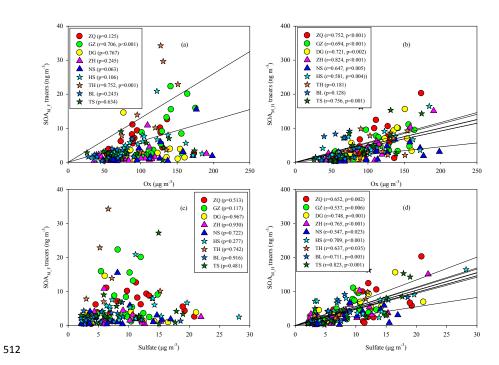510 the annual average concentrations of the SOA_M tracers.

511

512

513   Figure 5 Correlations of SOA_{M_F} and SOA_{M_H} tracers with O_x (a, b) and sulfate (c, d)
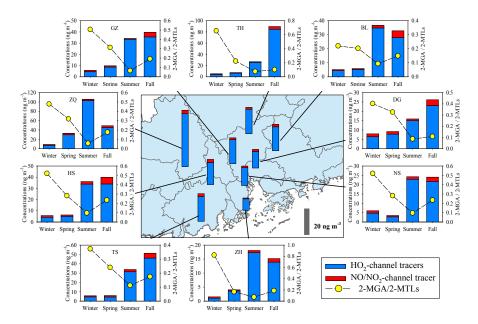
514

515

516   Figure 6 Spatial and seasonal variations of SOA$_I$ tracers at 9 sites in the PRD. The bars in the central figure represent

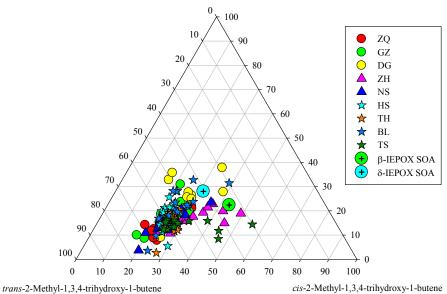517   the annual average concentrations of the SOA$_I$ tracers.

518

Figure 7 Ternary plot of C_5-alkene triol isomers in the PRD samples and in the β-IEPOX and δ-IEPOX derived SOA (Lin et al., 2012).
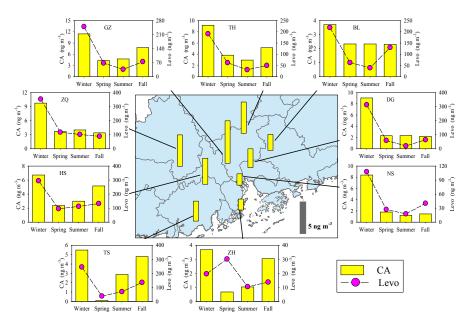
519

520

521

522

Figure 8 Spatial and seasonal variations of SOA$_c$ tracer (CA) at 9 sites in the PRD. The bars in the central figure represent the annual average concentration of the SOA$_c$ tracers. The pink circle indicates the BB tracer, levoglucosan (Levo).

Atmospheric
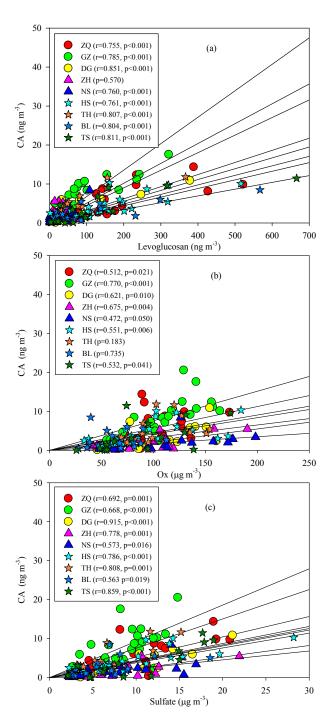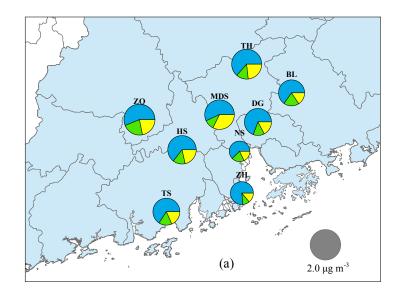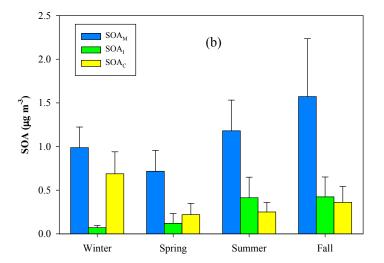Chemistry
and Physics
Discussions

528

529   Figure 9 Significant correlations of CA with levoglucosan (a), O$_x$ (b) and sulfate (c).

530

531

532

533
534   Figure 10 Spatial (a) and seasonal variations (b) of BSOA

535

536   Table 1 Correlations between SOA_I tracers and NO_x

	2-MGA		2-MGA/2-MTLs	
	Coefficient (r)	p-value	Coefficient (r)	p-value
NO	0.028	0.733	0.166	0.043
NO_2	0.205	0.008	0.352	<0.001
NO_x	0.132	0.102	0.286	<0.001
NO_2/NO	0.001	0.986	0.162	0.048

537

538

539   Table 2 Correlations of BSOA with sulfate and O_x

	Sulfate			O_x		
	Slope	p-value	% [a]	Slope	p-value	% [a]
SOA_M	0.112	<0.001	45	0.013	<0.001	57
SOA_I	0.020	<0.001	34	0.003	<0.001	50
SOA_C	0.041	<0.001	46	0.004	<0.001	55
BSOA	0.172	<0.001	44	0.019	<0.001	55

540   [a] Percentages of SOA reduction at 50% decline of sulfate or O_x

541