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Response to the reviewer's comments

2 **“Impact of anthropogenic emissions on biogenic secondary organic aerosol:**
3 **Observation in the Pearl River Delta, South China” by Yu-Qing Zhang et al.**

4 In the following, the comments made by the referees appear in black, while our replies are in blue, and
5 the revised texts in the manuscript are in red.

6 **Reviewer #2**

7 This manuscript by Zhang et al. represent a detailed analysis on tracer organic compounds quantified in
8 PM_{2.5} samples collected at 23 sites in the Pearl River Delta (PRD) region. Based on the tracer
9 concentrations, the authors performed correlation analyses and source apportionment to understand the
10 source of secondary organic aerosol (SOA), as well as the impact of anthropogenic emissions to
11 biogenic SOA (BSOA). The topic of the study is timely and is within the scope of ACP. Especially, the
12 interaction of anthropogenic and biogenic emissions in relatively polluted regions, such as the PRD, is
13 not well understood, and the results from this study is highly valuable. The manuscript is of high
14 quality in terms of chemical analysis, discussion, implication, and literary presentation. I recommend
15 publication of this work in ACP and I have a number of minor and technical suggestions.

16 We thank the referee for the positive evaluation of our manuscript and the useful comments and
17 suggestions. A point-by-point response is included below and we have revised the manuscript
18 according to the comments.

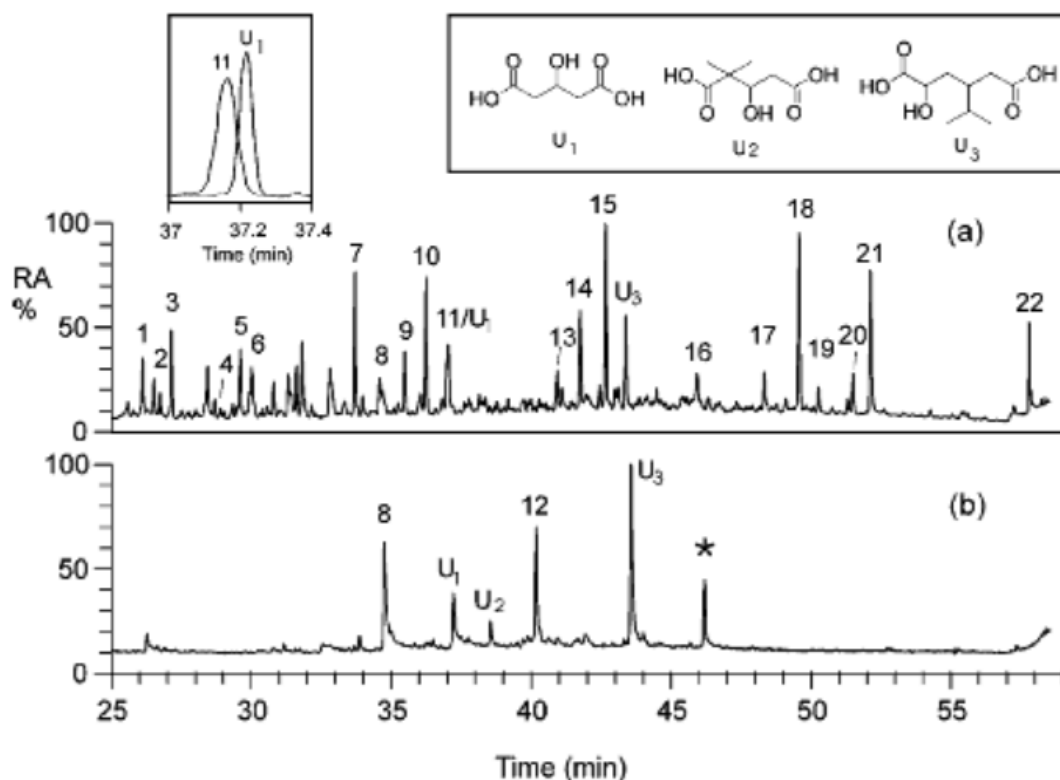
19 1. - Section 2.2: The authors quantified quite a number of organic tracers. The authors should justify
20 how representative are these tracers for SOA_I, SOA_M, and SOA_C. In particular, I am not familiar with
21 HDMGA and HGA as tracers for monoterpenes. Citation is needed to justify the specificity and
22 selectivity of these tracers.

23 Reply: For SOA_I tracers, Claeys et al (2004a) first identified 2-methyltetrols in Amazon aerosols and
24 disclosed the importance of SOA_I. They further identified 2-methylglyceric acid (Claeys et al., 2004b)
25 and C₅-alkene triols (Wang et al., 2005) as specific markers for acid-catalyzed ring opening of the

26 isoprene-derived epoxides (e.g. MAE/HMML and IEPOXs). Lin et al., (2012) identified
27 3-MeTHF-3,4-diols as the products of acid-catalyzed intermolecular rearrangement of IEPOX on
28 acidic particles.

29 For SOA_M tracers, pinic acid and pinonic acid were firstly identified in the chamber-generated
30 SOA from the ozonolysis and OH oxidation of pinenes (Christoffersen et al 1998). Further oxidation of
31 pinic acid and pinonic acid can form highly oxidized products, e.g. MBTCA whose chemical structure
32 was finally identified by Szmigielski et al. (2007). 3-Hydroxyglutaric acid (HGA) and
33 3-hydroxy-4,4-dimethylglutaric acid (HDMGA) were first reported as SOA_M tracers (U1 and U2
34 compounds in the Figure R2-1 below) by Claeys et al (2007). As a tracer for SOA_C, β-Caryophyllenic
35 acid was first identified by Jaoui et al. (2007).

36 In the revised manuscript, we add all these references to justify the specificity and selectivity of
37 these tracers in Line 107-116.



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39 Figure R2-1 GC/MS TICs obtained for the trimethylsilylated extract of PM_{2.5} aerosols and the chemical
40 structures of HGA (U1) and HDMGA (U2) from Claeys et al (2007).

41

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73 2. - Section 2.3: It seems that the recovery for erythritol is low. Why it is low and how is the result of
74 the recovery test reflected in the quantification of related tracers?

75 Reply: In our study, apart from using internal standards, we also tested “absolute” recoveries for the
76 standard compounds by analyzing spiked samples. The recovery results in QAQC showed the absolute
77 recovery of each standard compound. Compared with PNA and octadecanoic acid, erythritol has the
78 smallest carbon number and the lightest molecular weight. The loss of erythritol during chemical
79 analysis should be highest among the three target compounds. Thus, the absolute recovery of erythritol
80 is low.

81 For tracer quantification, we added internal standards to each sample before extraction and

82 quantified SOA tracers using the internal standards approach. The internal calibration procedure uses
83 the peak area ratio of target compound to internal standard to do the quantification. Since internal
84 standards have similar chemical structure and/or retention time to the target compounds, their loss
85 should be comparable to those of target compounds during sample analysis. The internal standard
86 calibration based on peak area ratios is in fact already recovery corrected with the assumption that
87 internal standards and target compounds have identical recoveries. Thus, the low absolute recovery of
88 erythritol does not affect the quantification of related tracers.

89 3. - The authors use O_x as an indicator of the atmospheric oxidative capacity. However, caution is
90 needed, as $O_x = (O_3 + NO_2)$ represents the total O_3 . While O_3 is certainly an important oxidant, the
91 contribution of OH radical (which is perhaps more important) is not considered in O_x . Is there any
92 evidence showing that OH concentration is also high when the O_x concentration is high?

93 Reply: We admit that high O_x itself cannot indicate high oxidative capacity. In fact, Hofzumahaus et al.,
94 (2009) observed extremely high OH concentrations ($15 \times 10^6 \text{ cm}^{-3}$ around noon) in the PRD and
95 proposed a recycling mechanism which increases the stability of OH in the air of polluted regions.
96 Since O_3 , NO_x and OH are intimately linked in atmospheric chemistry, we think that the atmospheric
97 oxidative capacity keeps high in the PRD. Because we did not have OH measurements in the current
98 study, in the revised manuscript we remove the statement “ O_x as an indicator of the atmospheric
99 oxidative capacity” and change the related discussion as:

100 “The SOA_C tracer elevated in winter at all sites and positively correlated with levoglucosan, O_x ,
101 and sulfate. Thus, the unexpected increase of SOA_C in wintertime might be highly associated with the
102 enhancement of biomass burning, O_3 chemistry and sulfate component in the PRD.” (Line 31-34)

103 “However, O_3 and oxidant (O_x , $O_x = O_3 + NO_2$) are still in high levels and do not decrease
104 apparently (Figure 1b). Hofzumahaus et al., (2009) observed extremely high OH concentrations in the
105 PRD and proposed a recycling mechanism which increases the stability of OH in the air of polluted
106 regions. All these indicate high atmospheric oxidative capacity in the PRD, since O_3 , NO_x and OH are
107 intimately linked in atmospheric chemistry.” (Line 64-68)

108 “Due to the compromise of opposite seasonal trends of O_3 and NO_2 , O_x showed less seasonal
109 variation (Figure 3f) compared with other gaseous pollutants. And annual-mean O_x reached 96.1 ± 14.9
110 $\mu\text{g m}^{-3}$. These indicated significant O_3 pollution all the year in the PRD.” (Line 147-150)

111 Reference

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115 4. - Section 3.2.3: It is interesting that β -caryophyllenic acid (CA) was observed to be high in the
116 winter and correlate with BB tracers. Can the authors comment on whether this observation place
117 question on the selectivity and specificity of CA as a tracer for SOAc ?

118 Reply: β -Caryophyllenic acid (CA) was identified in SOA produced through the ozonolysis and
119 photooxidation of β -caryophyllene (Jaoui et al. 2007). Previous studies have demonstrate that biomass
120 burning does emit substantial sesquiterpenes (Ciccioli et al. 2014; Mentel et al., 2013) which are
121 synthesized and stored in plant tissues to protect plants from insects and pathogens (Keeling and
122 Bohlmann, 2006). One the other hand, the oxidation of β -caryophyllene in the air is very rapid. Under
123 typical OH and O₃ levels in the air of PRD, the lifetimes of β -caryophyllene are only several minutes.
124 Once emitted from biomass burning, β -caryophyllene could react rapidly and form CA immediately.
125 Thus, it is expected to see a positive correlation between CA and levoglucosan. The unexpected high
126 levels of CA in the winter indicated that biomass burning could be an important source of SOAc in the
127 PRD, especially in wintertime.

128 In the revised manuscript, we add this discussion in Line 285-290 “The oxidation of
129 β -caryophyllene by the OH radical and O₃ is very rapid. Under typical oxidation conditions in the air of
130 PRD, the lifetimes of β -caryophyllene are only several minutes (Table S5). Once emitted from
131 vegetation or biomass burning, β -caryophyllene will react rapidly and form CA immediately. This
132 partly explains the positive correlations between CA and levoglucosan in the PRD. The unexpected
133 high levels of CA in the winter indicated that biomass burning could be an important source of SOAc
134 in the PRD, especially in wintertime.”

135 Reference

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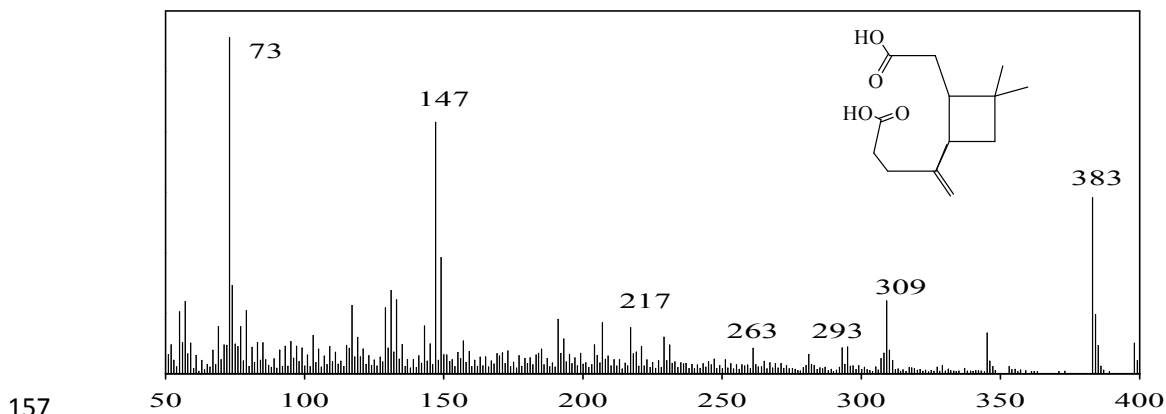
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146 stress-induced biogenic emissions and possible climate feedbacks, *Atmos. Chem. Phys.*, 13, 8755-8770,
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148 5. - Related to CA, I have come across compounds that have very similar names to β -caryophyllenic
149 acid, namely, β -caryophyllinic acid and β -caryophyllonic acid. (Jaoui et al. (2007) *Geophys. Res. Lett.*;
150 Bé et al. (2019) *ACS Earth Space Chem.*). Is β -caryophyllenic acid measured in this study a different
151 compound or this is simply a typo?

152 Reply: β -Caryophyllenic acid, β -caryophyllinic acid and β -caryophyllonic acid in different studies are
153 the same tracer of β -caryophyllene-derived SOA (see its chemical structure in the Figure R2-2 below).
154 After derivatized with BSTFA, this compound has a molecular weight of 398 with fragment ions at m/z
155 383 and m/z 309 in the EI mass spectrum. Since there is a double-bond left, β -caryophyllenic acid is
156 the accurate name.



157
158 Figure R2-2 The GC/MS EICs obtained for the trimethylsilylated extract of $PM_{2.5}$ aerosols and the
159 chemical structure of β -caryophyllenic acid.

160 6. - Section 3.3: The impact of anthropogenic emissions to BSOA is perhaps one of the most important
161 implications in this manuscript, but the current discussion appears weak. Based on the slopes obtained
162 from the correlation studies, the authors implies that reducing SO_4 and O_x in the atmosphere will lead
163 to reduction of BSOA. However, this type of correlation analysis exhibits only correlation but not
164 causation. The authors should justify why reducing anthropogenic emissions can likely reduce BSOA.

165 One way to do this, I think, is to add more discussion on the mechanisms behind the influence of
166 anthropogenic emissions to BSOA.

167 Reply: Thanks for the suggestion. In the revised manuscript, we add more discussion on the
168 mechanisms behind the influence of anthropogenic emissions to BSOA in Line 309-323 “It is
169 interesting to note that SOA_M , SOA_I and SOA_C all positively correlated with sulfate and O_x in the PRD
170 (Table 2). Since anthropogenic emissions can enhance BSOA formation (Hoyle et al., 2011), the
171 reduction of anthropogenic emissions indeed lowers BSOA production (Carlton et al., 2018). As the
172 oxidation product of SO_2 , sulfate is a key species in particles that determines aerosol acidity and
173 surface areas (Xu et al., 2015, 2016) which could promotes BSOA formation through the
174 acid-catalyzed heterogeneous reactions. Recent study found that SO_2 could directly reaction with
175 organic peroxides of monoterpene ozonolysis and form substantial organosulfates (Ye et al., 2018).
176 Thus, the decrease of SO_2 emission indeed reduces SO_2 and sulfate in the ambient air, which hereby
177 leads to less acidic particles and reduces the BSOA production. For O_x , the increase of O_3 likely results
178 in significant SOA formation through the BVOCs ozonolysis (Sipilä et al., 2014; Riva et al., 2017).
179 Hence, the decrease of O_x resulting from the control of VOCs and NO_x emissions could reduce BSOA
180 formation through O_3 chemistry. Based on the observed sulfate and O_x dependence of BSOA in this
181 study, the reduction of $1 \mu g m^{-3}$ in sulfate and O_x in the air of PRD could lower BSOA levels by 0.17
182 and $0.02 \mu g m^{-3}$, respectively. If both concentrations decline by 50%, the reduction of O_x is more
183 efficient than sulfate in reducing BSOA in the PRD (Table 2).”

184 Reference

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