

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

Response to the reviewer's comments

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

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

Reviewer #1

This manuscript presents the annual variations of SOA tracers from biogenic VOCs at nine sites in PRD region. The measured biogenic SOA tracers are found to be correlated with O_x and anthropogenic sulfate, indicating the impacts of anthropogenic emissions on biogenic SOA formation. This is an extensive study by analyzing 170 filters. Overall, the data analysis is solid and the manuscript is well-written. I recommend publication after major revisions.

We thank the reviewer for the helpful comments and suggestions for this manuscript. We respond to the reviewer point by point below and modified the manuscript according to the comments.

Major Comments

1. Recent studies¹⁻² demonstrated that C_5 -alkene triols and 3-methyltetrahydrofuran-3,4-diols are largely GC/EI-MS artifacts from the degradation of methyltetrol sulfates and dimers. The authors used figure 7 (ternary plots) to argue that these tracers are indeed formed from different pathways rather than thermal decomposition. However, I beg to differ. The lack of correlation between IEPOX-derived SOA tracers and be explained by that the three tracers in figure 7 arise from the thermal decomposition of different dimers/OS and the parent dimers/OS concentration varies with sites and season. To fully prove that the three tracers are not decomposition products, the authors need to sample authentic methyltetrol sulfate standard with GC-MS.

Reply: We agree that thermal degradation of methyltetrol sulfates and dimers could produce C_5 -alkene triols, 3-methyltetrahydrofuran-3,4-diols and 2-methyltetrols during the GC/MS analysis (Watanabe et al., 2018). Using a hydrophilic interaction liquid chromatography (HILIC) method developed by Jason

26 Surratt group, Cui et al (2018) estimated that 30.0%, 42.8%, and 14.7% of C₅-alkene triols measured by
27 GC/MS were attributed to the potential thermal degradation of the 2-methyltetrol sulfates in the SOA
28 from β -IEPOX, and the PM_{2.5} samples from Look Rock and Manaus sites, respectively. The fractions of
29 2-methyltetrols attributed to thermal degradation were 11.1%. And approximately all
30 3-MeTHF-3,4-diols were produced from thermal degradation. Recently, we also measured
31 2-methyltetrol sulfates in two samples at HS and TS sites, respectively (see Table R1-1 below).
32 Assuming that all the 2-methyltetrol sulfates decomposed to these tracers, the thermal decomposition of
33 2-methyltetrol sulfates would account for 15.1-31.6% of C₅-alkene triols, 6.0-10.0% of 2-methyltetrols
34 and all 3-methyltetrahydrofuran-3,4-diols measured by GC/ MS. Thus, C₅-alkene triols and
35 2-methyltetrols are major from isoprene oxidation rather than thermal decomposition of 2-methyltetrol
36 sulfates, while 3-methyltetrahydrofuran-3,4-diols are only in trace amount in the air and might be
37 produced largely from thermal degradation. Coupled with significant variations in tracer compositions
38 observed in the PRD, we believe that these SOA₁ tracers are mainly formed through different pathways
39 in the ambient atmosphere, although part of them might arise from the thermal decomposition of
40 different dimers/OSs and the parent dimers/OSs varies with sites and seasons.

41 All these discussion (see below) are added in the revised manuscript in line 250-271.

42 “Previous studies found that thermal decomposition of low volatility organics in IEPOX-derived
43 SOA could produce SOA₁ tracers, e.g. 2-MTLs, C₅-alkene triols and 3-MeTHF-3,4-diols
44 (Lopez-Hilfiker et al., 2016, Watanabe et al., 2018). This means that these tracers detected by GC-MSD
45 might be generated from thermal decomposition of IEPOX-derived SOA. As estimated by Cui et al.
46 (2018), 14.7-42.8% of C₅-alkene triols, 11.1% of 2-MTLs and approximately all
47 3-MeTHF-3,4-diols measured by GC/ MSD could be attributed to the thermal degradation of
48 2-MTLs-derived organosulfates (MTL-OSs). We also measured MTL-OSs in two samples at HS and
49 TS sites, respectively (Table S6) using the widely used LC-MS approach (He et al., 2014, 2018).
50 Assuming that all MTL-OSs decomposed to these tracers, the thermal decomposition of MTL-OSs
51 would account for 15.1-31.6% of C₅-alkene triols, 6.0-10.0% of 2-MTLs and all 3-MeTHF-3,4-diols
52 measured by GC/ MSD. Thus, C₅-alkene triols and 2-MTLs are major from isoprene oxidation rather
53 than thermal decomposition of MTL-OSs, while 3-MeTHF-3,4-diols are only in trace amount in the air
54 and might be produced largely from thermal degradation.

55 Moreover, we see significant variations in SOA₁ tracer compositions in the PRD. For instant,

56 C₅-alkene triols have three isomers. If these tracers were mainly generated from a thermal process, their
 57 compositions should be similar in different samples. In fact, the relative abundances of three C₅-alkene
 58 triol isomers significantly changed from site to site (Figure 7) and season to season (Figure S8), and
 59 their compositions in the PRD were different from those measured in the chamber samples (Lin et al.,
 60 2012). In addition, the slopes of linear correlations among these IEPOX-derived SOA tracers also
 61 varied from site to site (Figure S9). Coupled with the seasonal trend of 2-MGA/2-MTLs ratios, the
 62 apparent variations in SOA_I tracer compositions demonstrate that these SOA_I tracers are mainly formed
 63 through different pathways in the ambient atmosphere, although part of them might arise from the
 64 thermal decomposition of different dimers/OSs and the parent dimers/OSs varies with sites and
 65 seasons.”

66 Table R1-1 Concentrations of isoprene SOA products at HS and TS sites

	HS 20150701	TS 20150701
2-Methyltetrol sulfates (ng m ⁻³)	6.65	2.99
C ₅ -alkene triols (ng m ⁻³)	11.5	10.8
2-Methyltetrols (ng m ⁻³)	41.8	31.2
3-MeTHF-3,4-diols (ng m ⁻³)	0.482	0.227

67 Reference

- 68 1. Cui, T., Zeng, Z., dos Santos, E. O., Zhang, Z., Chen, Y., Zhang, Y., Rose, C. A., Budisulistiorini, S.
 69 H., Collins, L. B., Bodnar, W. M., de Souza, R. A. F., Martin, S. T., Machado, C. M. D., Turpin, B. J.,
 70 Gold, A., Ault, A. P., and Surratt, J. D.: Development of a hydrophilic interaction liquid
 71 chromatography (HILIC) method for the chemical characterization of water-soluble isoprene epoxydiol
 72 (IEPOX)-derived secondary organic aerosol, *Environ. Sci.: Processes Impacts*, 20, 1524-1536,
 73 10.1039/C8EM00308D, 2018.
 74 2. Watanabe, A. C., Stropoli, S. J., and Elrod, M. J.: Assessing the potential mechanisms of
 75 isomerization reactions of isoprene epoxydiols on secondary organic aerosol, *Environ. Sci. Technol.*, 52,
 76 8346-8354, 10.1021/acs.est.8b01780, 2018.

77 2. The authors use the BSOA vs sulfate slope to infer the magnitude of sulfate control on BSOA. As the
 78 authors have performed the same measurements in the same region for a long time, I encourage the
 79 authors to look at their historic measurements, based on which to estimate the sulfate-control
 80 magnitude. As shown in figure 1, the O₃ concentration has been relatively flat in the past 13 years, but
 81 SO₂ concentration has largely declined. This provides a nice opportunity to deconvolve the effect of
 82 sulfate vs O₃ on BSOA formation.

83 Reply: Thanks for the suggestion. Since 2007, we have carried out one-month campaign during

84 fall-winter season every year at a regional site, Wanqingsha (WQS) in the PRD. At present, we have
85 long-term data of sulfate from 2007 to 2016. Similar to SO₂, sulfate keeps decreasing in the past decade
86 (see Figure R1-1 below). Unfortunately, we have not completed the time-consuming measurements of
87 BSOA tracers yet. Currently, we cannot deconvolve the effect of sulfate vs O₃ on BSOA formation
88 based on long-term data. We will write another manuscript focusing on these long-term measurements
89 and discussing the changing effects of sulfate and O₃ on BSOA formation.

90 Instead, we compared the data in 2015 with those during fall-winter season in 2008 at WQS (Ding
91 et al., 2012), since BSOA tracers, sulfate and O_x were all measured in both studies. As the below Table
92 R1-2 showed, all BSOA species positively correlated with sulfate but exhibited no O_x dependence.
93 Thus, BSOA formation in 2008 was largely influenced by sulfate, probably due to high sulfate levels
94 then (as high as 46.8 μg m⁻³). Coupled with the decrease trend of sulfate and the relatively flat trend of
95 O_x, such a difference in sulfate and O_x dependence between 2015 and 2008 highlights the critical role
96 of O_x in BSOA formation currently in the PRD.

97 In the revised manuscript, we add these discussion in line 324-332 “We further compared the
98 results in 2015 with those during fall-winter season in 2008 at WQS (Ding et al., 2012). We found that
99 all BSOA species positively correlated with sulfate but exhibited no O_x dependence (Table S7). Thus,
100 in 2008 BSOA formation was largely influenced by sulfate, probably due to high sulfate levels then (as
101 high as 46.8 μg m⁻³). Owing to strict control of SO₂ emissions (Wang et al., 2013), ambient SO₂
102 significantly shrank over the PRD (Figure 1b). Our long-term observation during fall-winter season at
103 WQS also witnessed a decreasing trend of sulfate from 2007 to 2016 (Figure S10). However, O_x levels
104 did not decrease during the past decade (Figure 1b) and O_x concentrations were much higher than
105 sulfate in 2015 in the PRD (96.1 ± 14.9 μg m⁻³ vs. 8.44 ± 1.09 μg m⁻³ on average). All these underline
106 the importance of O_x in BSOA formation currently in the PRD.”

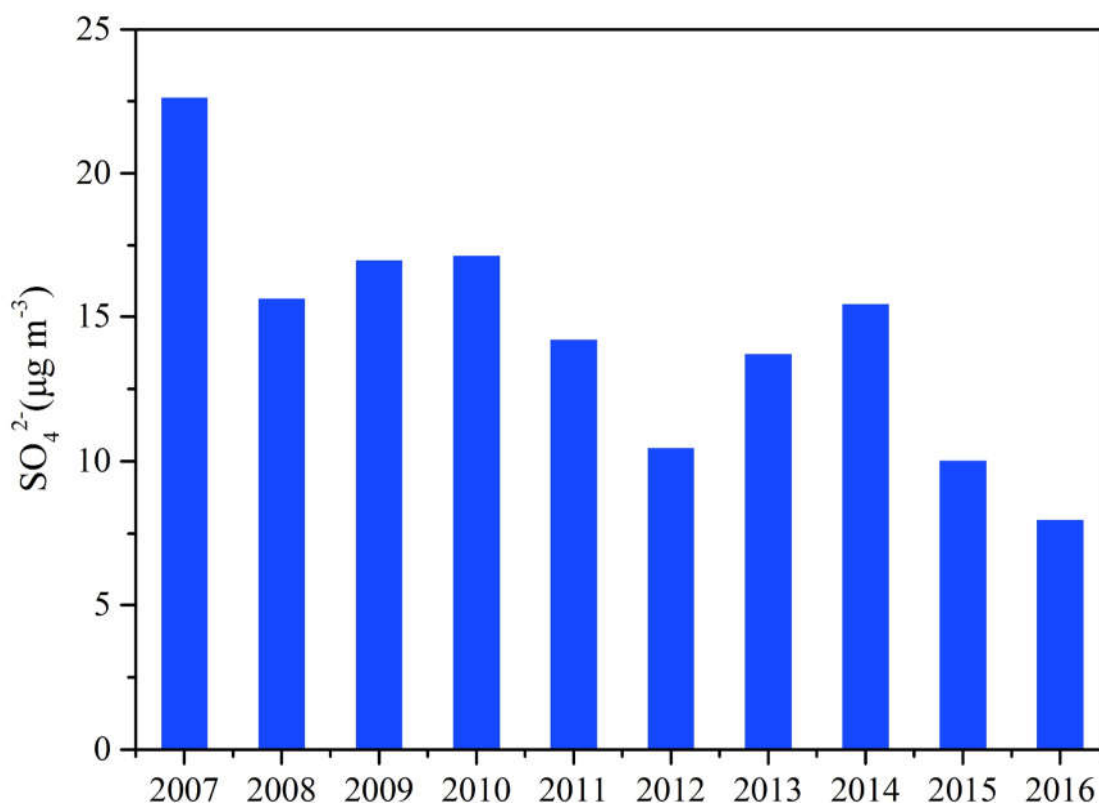


Figure R1-1 Long-term variation of sulfate in fall at WQS from 2007-2016.

Table R1-2 Correlations of BSOA with sulfate and O_x during fall-winter in 2008 at WQS

	Sulfate (2008-PRD)			O _x (2008-PRD)	
	Slope	<i>p</i> -value	% ^a	Slope	<i>p</i> -value
SOA _M	0.023	0.005	50	-	0.551
SOA _I	0.032	<0.001	76	-	0.509
SOA _C	0.032	<0.001	87	-	0.139
BSOA	0.087	<0.001	69	-	0.563

^a Percentages of SOA reduction at 50% decline of sulfate or O_x

Reference

Ding, X., Wang, X., Gao, B., Fu, X., He, Q., Zhao, X., Yu, J., and Zheng, M.: Tracer based estimation of secondary organic carbon in the Pearl River Delta, South China, *J. Geophys. Res-Atmos.*, 117, D05313, 10.1029/2011JD016596, 2012.

Minor Comments

1. Line 34. Replace “high-generation” with “later-generation” throughout the manuscript including acronyms.

Reply: We have replaced it as suggested. We also replace “SOA_{M_H}” with “SOA_{M_L}” throughout the

120 manuscript.

121 2. Line 231-232. The correlation between SOA_{M_H} and sulfate is intriguing. The formation of SOA_{M_H}
122 tracers, like MBTCA, does not involve sulfate. Thus, how to explain the correlation?

123 Reply: Müller et al. (2012) reported that MBTCA could be formed through the gas-phase OH oxidation
124 of pinonic acid. The triacid nature of MBTCA makes it highly water-soluble and able to partition into
125 cloud water and aerosol liquid water (Aljawhary et al 2016). Besides the gas-phase OH oxidation, the
126 heterogeneous OH oxidation of pinonic acid could also produce MBTCA (Lai et al. 2015). Aljawhary
127 et al. (2016) reported the kinetics and mechanism of pinonic acid oxidation in acidic solutions and
128 found that the molar yields of MBTCA through the aqueous-phase reactions were similar to those in
129 the gas-phase oxidation. Sulfate is a key species in particles that determines aerosol liquid water
130 amount, aerosol acidity, and particle surface area (Xu et al., 2015, 2016). Thus, the increase of sulfate
131 could promote aqueous and heterogeneous reactions and produce substantial MBTCA in particles.

132 In the revised manuscript, we add these discussion in line 187-197 “On the other hand, sulfate is a
133 key species in particles that determines aerosol liquid water amount, aerosol acidity, and particle
134 surface area (Xu et al., 2015, 2016). Thus, the increase of sulfate could promote aqueous and
135 heterogeneous reactions. In this study, the SOA_{M_F} tracers poorly correlated with sulfate (Figure 5c),
136 while the SOA_{M_L} tracers positively correlated with sulfate at all the 9 sites (Figure 5d). At each site the
137 SOA_{M_L} tracers exhibited more sulfate dependence than SOA_{M_F} tracers (Figure S5). This suggested
138 that sulfate also played a critical role in forming SOA_{M_L} tracers through the particle-phase reactions.
139 Besides the gas-phase OH oxidation (Müller et al., 2012), the heterogeneous OH oxidation of pinonic
140 acid could also produce SOA_{M_L} tracers (Lai et al. 2015). Aljawhary et al., (2016) reported the kinetics
141 and mechanism of pinonic acid oxidation in acidic solutions and found that the molar yields of
142 MBTCA through the aqueous-phase reactions were similar to those in the gas-phase oxidation.”

143 Reference

- 144 1. Aljawhary, D., Zhao, R., Lee, A. K. Y., Wang, C., and Abbatt, J. P. D.: Kinetics, mechanism, and
145 secondary organic aerosol yield of aqueous phase photo-oxidation of α -pinene oxidation products, *J.*
146 *Phys. Chem. A.*, 120, 1395-1407, 10.1021/acs.jpca.5b06237, 2016.
- 147 2. Lai, C., Liu, Y., Ma, J., Ma, Q., Chu, B., and He, H.: Heterogeneous kinetics of cis-pinonic acid with
148 hydroxyl radical under different environmental conditions, *J. Phys. Chem. A.*, 119, 6583-6593,
149 10.1021/acs.jpca.5b01321, 2015.
- 150 3. Müller, L., Reinnig, M. C., Naumann, K. H., Saathoff, H., Mentel, T. F., Donahue, N. M., and

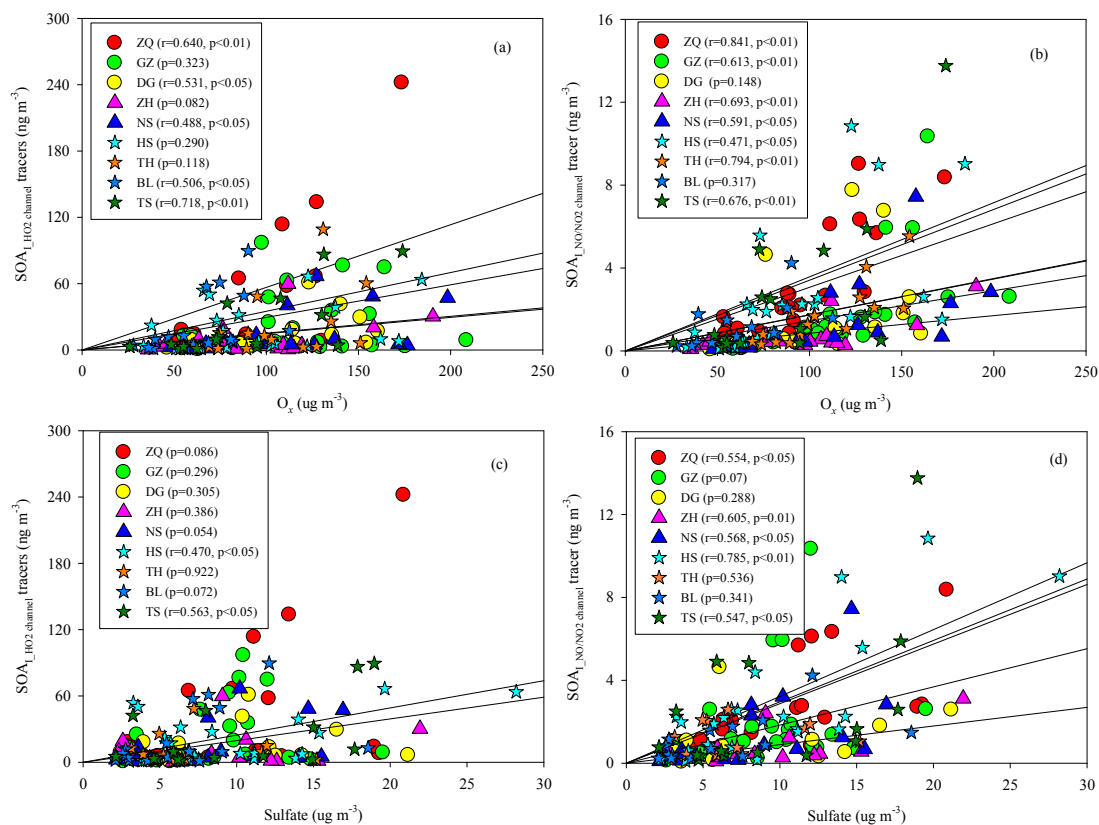
151 Hoffmann, T.: Formation of 3-methyl-1,2,3-butanetricarboxylic acid via gas phase oxidation of pinonic
152 acid – a mass spectrometric study of SOA aging, *Atmos. Chem. Phys.*, 12, 1483-1496,
153 10.5194/acp-12-1483-2012, 2012.

154 4. Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R.,
155 Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S.
156 V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of
157 anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern
158 United States, *P. Natl. Acad. Sci. USA.*, 112, 37-42, 10.1073/P.Natl.Acad.Sci.USA.1417609112, 2015.

159 5. Xu, L., Middlebrook, A. M., Liao, J., de Gouw, J. A., Guo, H., Weber, R. J., Nenes, A.,
160 Lopez-Hilfiker, F. D., Lee, B. H., Thornton, J. A., Brock, C. A., Neuman, J. A., Nowak, J. B., Pollack, I.
161 B., Welti, A., Graus, M., Warneke, C., and Ng, N. L.: Enhanced formation of isoprene-derived organic
162 aerosol in sulfur-rich power plant plumes during Southeast Nexus, *J. Geophys. Res-Atmos.*, 121,
163 11137-11153, 10.1002/2016JD025156, 2016.

164 3. Please show the correlation of isoprene SOA tracers with sulfate and O_x , like figure 5.

165 Reply: As suggested, we checked the correlations of isoprene SOA tracers with sulfate and O_x (see
166 below Figure R1-2) and added the figure into the Supporting Information as Figure S6. The
167 NO/ NO_2 -channel product exhibited more O_x and sulfate dependence than HO_2 -channel products. In the
168 revised manuscript, we add these discussion in line 234-236 “We also checked the correlations of SOA_I
169 tracers with O_x and sulfate (Figure S6). The NO/ NO_2 -channel product exhibited more O_x and sulfate
170 dependence than HO_2 -channel products.”



171

172 Figure R1-2 Correlations of SOA_{HO2-channel} tracers and SOA_{NO/NO2-channel} tracers with O_3 (a, b) and sulfate (c, d)

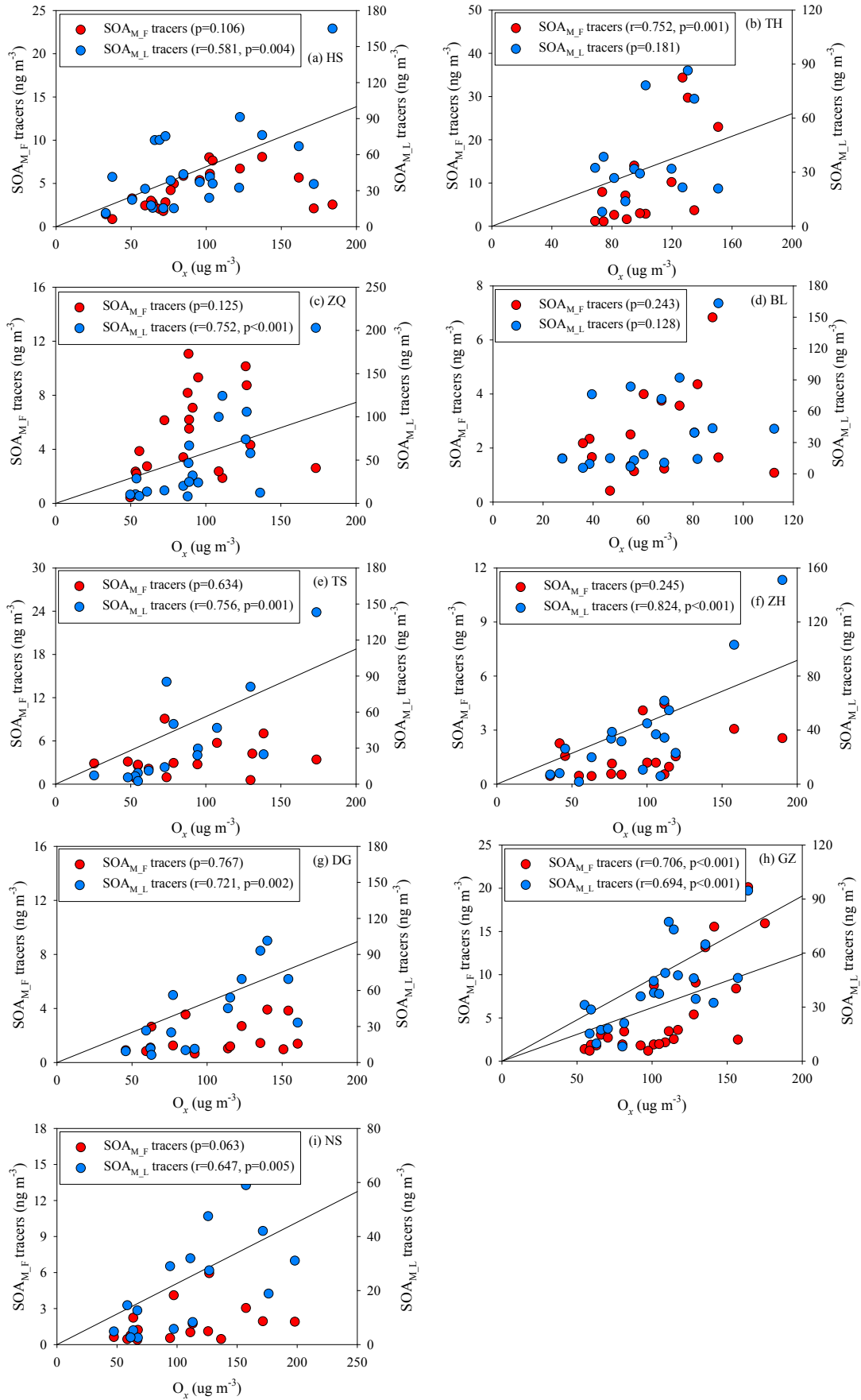
173 4. Figure 5. With so many data on the plots, it is difficult to examine the correlation at each site. I

174 suggest to make a scatter plot for each site and then synthesize a figure like figure 4.

175 Reply: As suggested, we add the scatter plots of SOA_{M_F} tracers and SOA_{M_L} tracers with O_3 and

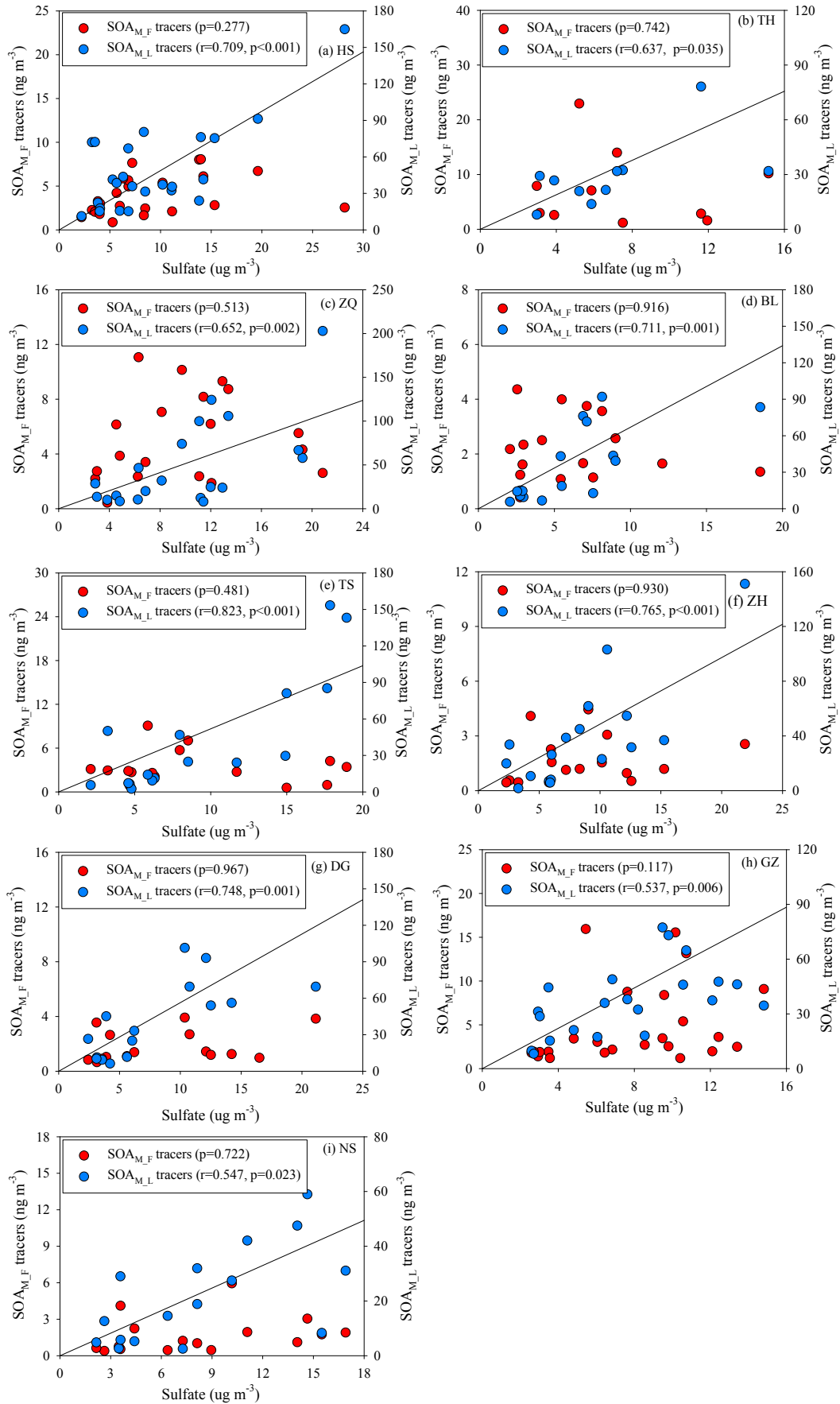
176 sulfate at each site in Supporting Information of the revised manuscript (Figure S4 and S5, see the

177 Figure R1-3, R1-4 below).



178

179 Figure R1-3 Correlations of SOA_{M,F} tracers and SOA_{M,L} tracers with O_x



180

181 Figure R1-4 Correlations of SOA_{M,F} tracers and SOA_{M,L} tracers with sulfate

182 5. The correlation between β -caryophyllenic acid (CA) and levoglucosan is interesting. Does biomass
183 burning emit CA?

184 Reply: To the best of our knowledge, biomass burning does not emit CA but its precursor.
185 Sesquiterpenes, including β -caryophyllene are synthesized and stored in plant tissues partly to protect
186 plants from insects and pathogens (Keeling and Bohlmann, 2006). When biomass burning events
187 happen, high temperature could release substantial sesquiterpenes into the air (Ciccioli et al. 2014).
188 On the other hand, the oxidation of β -caryophyllene by the OH radical and O₃ is very rapid. Under
189 typical oxidation conditions in the air of PRD, the lifetimes of β -caryophyllene are only several
190 minutes. This means that once emitted from biomass burning, β -caryophyllene could react rapidly and
191 form CA immediately. Thus, it is expected to see a positive correlation between CA and levoglucosan.

192 In the revised manuscript, we add this discussion in Line 285-288 “The oxidation of
193 β -caryophyllene by the OH radical and O₃ is very rapid. Under typical oxidation conditions in the air of
194 PRD, the lifetimes of β -caryophyllene are only several minutes (Table S5). Once emitted from
195 vegetation or biomass burning, β -caryophyllene will react rapidly and form CA immediately. This
196 partly explains the positive correlations between CA and levoglucosan in the PRD.”

197 Reference

- 198 1. Keeling, C. I., and Bohlmann, J.: Genes, enzymes and chemicals of terpenoid diversity in the
199 constitutive and induced defence of conifers against insects and pathogens, *New Phytol.*, 170, 657-675,
200 10.1111/j.1469-8137.2006.01716.x, 2006.
- 201 2. Ciccioli, P., Centritto, M., and Loreto, F.: Biogenic volatile organic compound emissions from
202 vegetation fires, *Plant Cell Environ.*, 37, 1810-1825, 10.1111/pce.12336, 2014.

203 6. Line 331. The authors need to be careful about the salting-in effect, because it is highly
204 compound-specific. Xu et al. 2015 proposed that sulfate introduces salting-in effect on IEPOX, but this
205 is just a hypothesis. It would be overreaching to argue that sulfate has salting-in effect on
206 β -caryophyllene SOA.

207 Reply: We agree. In the revised manuscript, we change the statement as “In addition, the increase of
208 sulfate could raise aerosol acidity and thereby promote aqueous and heterogeneous reactions to form
209 SOA_c.” in line 290-291.