

Journal: ACP

Title: Molecular characteristics and diurnal variations of organic aerosols at a rural site in the North China Plain with implications for the influence of regional biomass burning

Author(s): Jianjun Li et al.

MS No.: acp-2019-75

Dear Editor,

After reading the comments from the two referees, we have carefully revised our manuscript. Our response to the comments and related revisions are attached with this letter.

Anything about our paper, please feel free to contact me at ghwang@geo.ecnu.edu.cn.

Best regards,

Sincerely yours

Gehui Wang

Jul. 18, 2019

Anonymous Referee #1:

The manuscript by Li et al. had a comprehensive characterization of molecular composition of organic aerosol at a rural site in North China Plain, and investigated the impacts of biomass burning, and the sources of organic aerosol. One advantage of this study is the high time resolution of filter sampling (3 h) compared with previous studies. The authors chose two different periods to discuss the differences between local and regional sources. Overall, this study presents a huge dataset containing rich chemical information, and it is worth for publication in ACP.

My major concern is the selection of period 2 (P2). The time series of species showed that P2 was characterized by a clean period (winds dominantly from the north, see supplementary) followed by a strong local event (very likely). This indicated a mixed event rather than a pure local. In fact, the chosen of P2 can affect the conclusion substantially. I suggest the authors reevaluating the event of P2.

Biomass burning typically showed much higher OC/EC ratios than those reported in this study, could the authors give more explanation?

Response: We thank the referee's comments.

For the selection of the period 2 (P2). We agree that it's not easy to select a period that is representative of a pure local emission in field study. However, in this study, the 72 h backward trajectories clearly show that air masses came predominantly from the surrounding areas of the sampling site during P2 (Figure 1). Although the winds in sometimes from the north, the wind speed in most time of P2 are $<2 \text{ m s}^{-1}$ (Figure S2). In addition, all the chemical compositions present very low concentrations during P2 except 2 samples affected by a near-site biomass burning emission. These results confirm that local fresh emissions dominated the chemical compositions of aerosols during P2.

For the OC/EC ratios, as suggested by the referee, we compared the OC/EC ratios in this study with those reported by some chamber or filed studies. We concluded that the relatively low OC/EC ratio in our study is related to more complex source contributions and different combustion conditions of open biomass burning. More explanation can be found in Line 225-237.

Anonymous Referee #3:

This manuscript presents measurement results from a field study conducted in the North-China Plain, which is notorious for high aerosol pollution. While suffering slightly from a relatively short measurement period, this study presents an impressive suite of organic aerosol component concentrations at a rather high time resolution. Two specific periods were singled out, including one episode with high biomass smoke impact. The results presented in this paper are helpful for a better understanding of the sources and characteristics of organic aerosols in this highly polluted part of China. Prior to publication of the manuscript in ACP, the authors should address the comments and suggestions below.

Response: We thank the referee's comments, which are very helpful for us to improve our work. Detailed revision and response to the comments are list below.

Specific comments:

1. Line 136: The total sampling period is rather short, especially when dividing it into 2 special periods, requiring caution in the discussion of the measurement results. The authors may want to add a statement regarding how representative the data are.

Response: Suggestion taken. We revised related description, please see Line 134-140.

2. Lines 161-163: The authors corrected the data for the field blanks, although the blank values were relatively low, in contrast to the recoveries which introduced larger errors for certain species. Why were the recoveries not taken into account as well?

Response: In our study, averaged recoveries of the target compounds were better than 70%. Recovery experiment is a method for QA and QC. However, compounds used in a recovery experiment are usually pure agent while those in real samples are a mixture with other organic and inorganic components, which means that the recovery experiment could not entirely reflect the conditions of target compounds in the atmosphere. Thus, many documents report the data without a correction by recovery. For example, US ASTM method D 6209-98 for atmospheric PAH, the section 16.4.2

at page 12 notes that “Typically, measured PAH analyte concentrations are not corrected for surrogate recovery”. Therefore, in this paper the data reported were not corrected by the recoveries.

3. Lines 220-223: Do the authors have a possible explanation for the rather low OC/EC ratios measured during the biomass burning period? Previous studies, especially those investigating burns which were dominated by smoldering combustion, were characterized by emissions with significantly higher OC/EC ratios. Is it possible that the wheat straw combustion during the study period occurred to some extent in the flaming phase?

Response: By comparing the OC/EC ratios in this study with those reported in some chamber or field studies, we do agree with the referee’s comment that wheat straw combustion during the study period occurred to some extent in the flaming phase. On the other hand, we think the contribution of fossil fuel combustion in NCP is also a reason for lower OC/EC ratio in this study. Thus, we added more explanation at Line 225-237 in the manuscript.

4. Lines 241-245: Indeed, the regional biomass burning activities contributed to the elevated WSOC/OC fractions, but it may also be worthwhile mentioning here (as the authors do later on in the paper) that SOA was likely produced in the biomass burning plumes (especially considering the transport distance/time to the sampling site), and thus contributed to the higher degree of oxygenation of the organic aerosol as well.

Response: We do agree with the referee’s comment, and revised the related description as “many SOA could be produced in the biomass burning plumes during the long-range transport (detailed discussions are given in Section 3.3), these results indicate that particulate WSOC in the region is mostly contributed from biomass burning activities including direct emission and secondary oxidation” (Line 256-260).

5. Lines 287-288: It would be helpful for the readers who are not familiar with these diagnostic ratios to at least briefly explain how the high L/M ratios indicate straw burning.

Response: Suggestion taken. We gave an explanation at Line 302-307.

6. Lines 288-289: How are the anhydrosugar emission ratios of lignites relevant to this study? Wouldn't it be more useful to mention results from some of the previous studies which specifically investigated anhydrosugar emissions from burning of straw or similar types of biomass?

Response: We thank the referee's comment. We clarified the statement as " Fabbri et al. (2009) compared the concentrations of the three anhydrosaccharides in the smokes from different fuel types, and proposed that levoglucan/(galactosan+mannosan) (L/G+M) and levoglucan/mannosan (L/M) values range in 0.2-18 and 0.23-33 for various source tests for biomass burning as compared to the average of 54 and 54 for lignites" (Line 303-307).

7. Lines 290-294: It would be helpful if the authors showed more quantitative results, e.g., state what is considered "higher". And how specifically do these results confirm the contribution of wheat straw burning?

Response: Suggestion taken. We added quantitative results of L/G+M and L/M ratios in the statement, and reevaluated results as "average ratios of L/G+M and L/M during P1 (10.1 ± 3.41 and 6.77 ± 1.97 , respectively) and P2 (29.7 ± 12.2 and 18.0 ± 4.28) suggest that biomass burning is always the dominated contributor for these compounds in NCP" (Line 307-310).

8. Lines 503-505: Why do the authors mention measurements from this area, as there seems to be no relation to this study region? Why not show data from other areas in Asia?

Response: Suggestion taken. We revised the related discussion, and cited a new data measured in the PM_{2.5} samples emitted from burning of three main kinds of cereal straws (wheat, maize, and rice) in China. Please see Line 517-519.

Technical corrections:

1. Lines 61, 199, 491: A better expression for "access" might be "estimate".

Response: Suggestion taken. Please see Line 60, 201, 504.

2. Lines 106, 107, 295, 296: Use correct singular vs. plural forms of words throughout the manuscript, such as "straw" instead of "straws", "amounts" instead of "amount", "composition" instead of "compositions" and "concentration" instead of

"concentrations", respectively.

Response: Suggestion taken. We have carefully checked the grammar mistakes thorough the whole manuscript, such as Line 106, 107, 311, 312.

3. Lines 137: Please specify if a size-selective inlet was used on the Hi-vol or if total suspended particles (TSP) were collected.

Response: Suggestion taken. Please see Line 138-139.

4. Lines 190 and 196: The definite article "the" before "North China" and "wheat" is not needed.

Response: Suggestion taken. Please see Line 192 and 198.

5. Lines 239-240: Shouldn't the favorable conditions for photo-chemical oxidation result in higher WSOC/OC values?

Response: Indeed, the favorable conditions during afternoon for photo-chemical oxidation should result in higher WSOC/OC values. However, in this study, we found that WSOC/OC value presents lower value in the afternoon. On the other hand, we found diurnal variation pattern of WSOC/OC is similar to that of levoglucosan/OC. Thus, we concluded that WSOC/OC value in the study area is mainly affected by the transportation of biomass burning. Related discussion please see Line 252-260.

6. Line 265: Change "ranged" to "ranging".

Response: Suggestion taken. Please see Line 280.

7. Lines 333-337: This sentence is not easy to understand and therefore needs to be reworded.

Response: We revised the sentence, please see Line 348-352.

8. Lines 350-352: Another study by Yang et al (STOTEN, 2012) specifically addresses this phenomenon.

Response: We thank the referee's comment, and cited the reference at Line 368.

9. Lines 385-386: These correlations are not weak but there is no correlation.

Response: We revised the sentence, please see Line 401-402.

10. Lines 392-395: Revise the sentence as follows: "..., consistent with the favorable dispersion conditions caused by high temperatures and planetary boundary layer (PBL) height.

Response: Suggestion taken. Please see Line 410-411.

11. Line 451: Change "aerosol" to "particle".

Response: Suggestion taken. Please see Line 465.

12. Lines 503-505: Are these % values?

Response: They are absolute values, not % values.

1 **Molecular characteristics and diurnal variations of organic aerosols**
2 **at a rural site in the North China Plain with implications for the**
3 **influence of regional biomass burning**

4
5
6 Jianjun Li^{1,4}, Gehui Wang^{1,2,3 *}, Qi Zhang^{4*}, Jin Li¹, Can Wu², Wenqing Jiang⁴, Tong
7 Zhu⁵, and Limin Zeng⁵

8
9
10 ¹Key Lab of Aerosol Chemistry & Physics, SKLLQG, Institute of Earth Environment,
11 Chinese Academy of Sciences, Xi'an 710061, China

12 ²Key Laboratory of Geographic Information Science of the Ministry of Education,
13 School of Geographic Sciences, East China Normal University, Shanghai 200241,
14 China

15 ³Institute of Eco-Chongming, 3663 N. Zhongshan Rd., Shanghai 200062, China

16 ⁴Department of Environmental Toxicology, University of California, Davis, CA
17 95616, USA

18 ⁵BIC-ESAT and SKL-ESPC, College of Environmental Sciences and Engineering,
19 Peking University, Beijing, China

20
21
22
23
24 *Corresponding authors:

25 Prof. Gehui Wang, E-mail: ghwang@geo.ecnu.edu.cn;

26 Prof. Qi Zhang, E-mail: dkwzhang@ucdavis.edu

29 **Abstract**

30 Field burning of crop residue in early summer releases into the atmosphere a
31 large amount of pollutants with significant impacts on the air quality and aerosol
32 properties in the North China Plain (NCP). In order to investigate the influence of this
33 regional anthropogenic activity on molecular characteristics of organic aerosol, we
34 collected PM_{2.5} filter samples every 3 hours at a rural site of NCP during June 10th to
35 25th, 2013, and analyzed them for more than 100 organic tracer compounds, including
36 both primary (*n*-alkanes, fatty acids/alcohols, sugar compounds, polycyclic aromatic
37 hydrocarbons, hopanes, and phthalate esters) and secondary (phthalic acids, isoprene-,
38 α -/ β -pinene, β -caryophyllene, and toluene-derived products) organic aerosol tracers,
39 as well as for organic carbon (OC), elemental carbon (EC), and water-soluble organic
40 carbon (WSOC). Total concentrations of the measured organics ranged from 177 to
41 6248 ng m⁻³ (mean 1806 \pm 1308 ng m⁻³) during the study period, most of which were
42 contributed by sugar compounds, followed by fatty acids and fatty alcohols.
43 Levoglucosan (240 \pm 288 ng m⁻³) was the most abundant single compound and
44 strongly correlated with OC and WSOC, suggesting that biomass burning (BB) is an
45 important source of summertime organic aerosols in this rural region. Based on
46 analysis of fire spots and backward trajectories of air masses, two representative
47 periods were classified, which are (1) Period 1 (P1), Jun 13th 21:00-16th 15:00, when
48 air masses were uniformly from the southeast part of NCP, where intensive open-field
49 biomass burning (BB) occurred and (2) Period 2 (P2), Jun 22nd 12:00-24th 06:00,
50 which is representative of local emission. Nearly all the measured PM components
51 showed much higher concentrations in P1 than in P2. Although *n*-alkanes, fatty acids,

52 and fatty alcohols presented similar temporal/diurnal variations as those of
53 levoglucosan throughout the entire period, their molecular distributions were more
54 dominated by high molecular weight (HMW) compounds in P1, demonstrating an
55 enhanced contribution from BB emissions. In contrast, intensive BB emission in P1
56 seems to have limited influences on the concentrations of polycyclic aromatic
57 hydrocarbons (PAHs), hopanes and phthalate esters. Both 3-hydroxyglutaric acid and
58 β -caryophyllinic acid showed strong linearly correlations with levoglucosan ($R^2=0.72$
59 and 0.80, respectively), indicating that BB is also an important source for terpene-
60 derived SOA formation. A tracer-based method was used to estimate the distribution
61 of biomass-burning OC, fungal-spore OC and secondary organic carbon (SOC)
62 derived from isoprene, α -/ β -pinene, β -caryophyllene, and toluene in the different
63 periods. The results showed that the contribution of biomass-burning OC to total OC
64 in P1 (27.6%) was 1.7 times of that in P2 (17.1%). However, the contribution of SOC
65 from oxidation of the four kinds of VOCs increased slightly from 16.3% in P1 to
66 21.1% in P2.

67 **Key words:** Organic aerosols; Molecular composition; North China Plain; Biomass
68 Burning

69

70 **1. Introduction**

71 Organic aerosols (OA, i.e., the organic fraction of particles) constitute a substantial
72 fraction (~10-90%) (Jimenez et al., 2009;Zhang et al., 2007a;Hallquist et al., 2009) of
73 atmospheric particles, and have significant effects on global and regional climate
74 (Venkataraman et al., 2005;Kanakidou et al., 2005), air quality (Aggarwal et al.,
75 2013;Wang et al., 2006b), human health (Lelieveld et al., 2015), and ecosystems (Tie
76 et al., 2016). Organic aerosols in the atmosphere can be emitted directly from various
77 sources, such as combustion of fossil fuels, biomass burning, plant emission, and so on,
78 which is defined as primary organic aerosols (POA). On the other hand, atmospheric
79 secondary OA (SOA) are produced from photochemical oxidation products of volatile
80 organic compounds (VOCs) via gas-particle conversion processes such as nucleation,
81 condensation and heterogeneous chemical reactions (Hallquist et al., 2009). These
82 organic species could modify physicochemical characteristics of atmospheric aerosols
83 such as hygroscopicity, albedo, and oxidation state (Dinar et al., 2008;Chan et al.,
84 2005;Fu et al., 2010). Thus, a thorough understanding of molecular composition and
85 source of organic aerosols is necessary in order to address aerosol related environmental
86 issues and to improve the accuracy of modelling studies.

87 Tremendous amounts of air pollutants including both particulate matters (PM) and
88 their gaseous precursors (e.g., SO₂, NO_x, NH₃, and VOCs) are emitted into the
89 atmosphere from power plants, industries and vehicles due to rapid economy
90 development in China, leading to serious air conditions in the recent decades (Zhang et
91 al., 2009;Guo et al., 2014;Wang et al., 2016;Huang et al., 2014;Li et al., 2017). The

92 North China Plain (NCP) has been recognized as one of the most polluted regions in
93 the world, with very high concentrations of PM_{2.5} on the ground surface (van Donkelaar
94 et al., 2010). The NCP is also one of the most significant aerosol sources in the world,
95 which has a significant impact on the East China Sea and Western North Pacific
96 (Andreae and Rosenfeld, 2008). Thus, extensive efforts have been made in recent years
97 to characterize the sources, properties, and processes of PM in the NCP. Most of these
98 results concluded that the severe air pollution in the region is related to the source
99 strength and frequently happens under stagnant weather conditions. Recently, it has
100 been shown that the rapid growth of secondary aerosols could lead to an severe haze
101 event in China under certain meteorological conditions (Wang et al., 2016;Sun et al.,
102 2014;Quan et al., 2013).

103 In the rural area of NCP, biomass burning for domestic cooking and heating and
104 agricultural waste disposal is an important source of atmospheric PM (Wang et al.,
105 2009b;Li et al., 2010;Zhang et al., 2016). Particularly, the open-field burning is still a
106 common way for disposal of crop residues (mainly wheat straw) in early summer (Li
107 et al., 2007). This traditional activity could release huge amounts of pollutants into the
108 atmosphere and significantly affect air quality and aerosol properties in the region.
109 Zhu et al. (2016) examined the amounts of VOCs in the air at a rural site of Yucheng
110 (Shandong Province, East China), and found that their concentrations during the
111 wheat straw burning period are approximately twice of those in normal periods.
112 Model results also revealed a significant influence of open burning of crop residual on
113 ozone, CO, black carbon (BC) and organic carbon (OC) concentrations in NCP.

114 Moreover, both off-line (Fu et al., 2012; Wang et al., 2009b; Wang et al., 2011) and
115 on-line (Sun et al., 2016) observations indicated that the intensive emission from
116 wheat straw burning in the region could change the molecular distribution of organic
117 aerosols of the downwind urban or mountain areas.

118 During June 10th to 25th of 2013, we conducted a continuous sampling campaign
119 at a rural site in the northern part of NCP. PM_{2.5} filter samples were collected with a
120 3-hour time resolution and determined for more than 100 organic compounds
121 including aliphatic lipids, sugar compounds, hopanes, polycyclic aromatic
122 hydrocarbons (PAHs), phthalate esters, and secondary oxidation products. The first
123 objective of this study was to get an overall understanding of temporal/diurnal
124 variation and molecular distribution of summertime OA in the rural region. The
125 second objective was to compare the results in two representative periods to
126 investigate the influence of regional field burning of wheat straw on the molecular
127 characteristics of organic aerosols.

128 **2. Experimental section**

129 **2.1 Sample collection**

130 The sampling was performed at the Integrated Ecological-Meteorological
131 Observation and Experiment Station of Chinese Academy of Meteorological Sciences
132 (39°08' N, 115°40' E, 15.2 m asl), which is located in a rural area of Gucheng, Hebei
133 Province. Detailed information of the station and sampling campaign was described in
134 Li et al. (2018). Briefly, time-resolved (06:00–09:00, 09:00–12:00, 12:00–15:00,
135 15:00–18:00, 18:00–21:00, 21:00–24:00, 00:00–03:00, and 03:00–06:00, Beijing

136 time) PM_{2.5} samples were collected on the rooftop (about 10 m above the ground) of a
137 three-story building on the campus of the Gucheng station. The sampling was
138 conducted by using a high volume (1.13 m³ min⁻¹) sampler (Anderson) with a PM_{2.5}
139 inlet from June 10th to 25th, 2013. This period was chosen, because open-field burning
140 of wheat straw in NCP mainly occur in the mid of June. All samples were collected
141 onto pre-baked (450 °C, 6-8 hr) quartz fiber filters. Field blank samples were also
142 collected by mounting blank filters onto the sampler for about 15 min without
143 pumping any air. After sampling, the sample filter was individually sealed in
144 aluminum foil bags and stored in a freezer (-20 °C) prior to analysis.

145 2.2 Organic compounds determination

146 A size of 12.5-25 cm² of the filter sample was cut and extracted with a mixture of
147 dichloromethane and methanol (2:1, v/v) under ultrasonication. The extracts were
148 concentrated using a rotary evaporator under vacuum conditions and then blow down
149 to dryness using pure nitrogen. After reaction with N,O-bis-(trimethylsilyl)
150 trifluoroacetamide (BSTFA) at 70 °C for 3 hrs., the derivatives were determined
151 using gas chromatography/electron ionization mass spectrometry (GC/EI-MS) (Li et
152 al., 2013b).

153 GC/EI-MS analysis of the derivatized fraction was performed using an Agilent
154 7890A GC coupled with an Agilent 5975C MSD. The GC separation was carried out
155 on a DB-5MS fused silica capillary column with the GC oven temperature
156 programmed from 50 °C (2 min) to 120 °C at 15 °C min⁻¹ and then to 300 °C at 5 °C
157 min⁻¹ with a final isothermal hold at 300 °C for 16 min. The sample was injected in a

158 splitless mode at an injector temperature of 280 °C, and scanned from 50 to 650

159 Daltons using electron impact (EI) mode at 70 eV.

160 GC/EI-MS response factors of all the target compounds were determined using
161 authentic standards except several isoprene-derived SOA tracers. Response factors of
162 isoprene-derived SOA tracers were substituted by those of related surrogated
163 standards, which were described in Li et al. (2018). No significant contamination
164 (<5% of those in the samples) was found in the blanks. Recoveries of all the target
165 compounds ranged from 80% to 120%. Data presented were corrected for the field
166 blanks but not corrected for the recoveries.

167 **2.3 OC, EC, and WSOC analysis**

168 OC (organic carbon) and EC (elemental carbon) were analyzed using DRI Model
169 2001 Carbon Analyzer following the Interagency Monitoring of Protected Visual
170 Environments (IMPROVE) thermal/optical reflectance (TOR) protocol. A size of
171 0.526 cm² sample filter was placed in a quartz boat inside the analyzer and stepwise
172 heated to temperatures of 140 °C (OC1), 280 °C (OC2), 480 °C (OC3), and
173 580 °C (OC4) in a non-oxidizing helium (He) atmosphere, and 580 °C (EC1),
174 740 °C (EC2), and 840 °C (EC3) in an oxidizing atmosphere of 2% oxygen in
175 helium. Pyrolyzed carbon (PC) is determined by reflectance and transmittance of 633
176 nm light. One sample was randomly selected from every 10 samples and re-analyzed.
177 Differences determined from the replicate analyses were <5% for TC, and <10% for
178 OC and EC.

179 Another aliquot of filter sample was extracted with organic-free Milli-Q water

180 under ultrasonication (15 min each, repeated 3 times) and filtered through a PTFE
181 filter to remove any particles and filter debris. Then the water-extract was analyzed
182 for water-soluble organic carbon (WSOC) using a TOC analyzer (TOC-L CPH,
183 Shimadzu, Japan). The difference between OC and WSOC was considered as water-
184 insoluble OC (WIOC). All carbonaceous components data reported here were
185 corrected by the field blanks.

186 **3. Results and discussion**

187 **3.1 Fire spots and air masses**

188 At present, open-field burning is still a common activity for disposal of crop
189 residue in the rural area of the North China Plain, especially during wheat harvest period
190 from the end of May to the middle of June (Fu et al., 2012). These extensive emissions
191 from regional biomass burning in the provinces of Anhui, Jiangsu, Shandong, Henan
192 and Hebei **in NCP** can cause severe air pollution on a local and regional scale. In our
193 previous study, the fire spots in NCP during the sampling period were provided based
194 on the NASA satellite observation (<https://firms.modaps.eosdis.nasa.gov/firemap/>).
195 Combining with information on air mass back-trajectories
196 (<http://ready.arl.noaa.gov/HYSPLIT.php>), the sampling period was divided into two
197 sections: (1) June 10-18, when air masses were mainly transported via long distances
198 from the southeast part of NCP, where intensive emissions **from wheat straw** burning
199 occurred; (2) June 19-25, when air masses were mostly influenced by local emissions
200 and regional emission from biomass burning decreased dramatically (Li et al., 2018).
201 In this study, we further selected two representative periods to **estimate** the contribution

202 of regional biomass burning. Period 1 (P1) designates 13th Jun 21:00 pm to 16th Jun
203 15:00 pm, during which air masses were influenced by intensive biomass burning and
204 transported uniformly from the southeast part of NCP (Figure 1 a and b, and Figure S1).
205 Period 2 (P2) designates 22nd Jun 12:00 pm to 24th Jun 06:00 am, during which fire
206 spots in the regions were relatively scarce and air masses came predominantly from the
207 surrounding areas of the sampling site (Figure 1 c and d). In addition, there were several
208 intermittent rainfalls during June 20-22, which are favorable for wet deposition of
209 atmospheric pollutants. Thus, aerosols collected in P2 are well representative of local
210 fresh emission. It is worthwhile to note that the two samples collected during 21st June
211 18:00-24:00 pm were excluded from P2, because they were highly affected by near-site
212 biomass burning emission (detailed information is provided in Section 3.3).

213 **3.2 Concentrations of PM_{2.5}, OC, EC, WSOC and WIOC**

214 Concentrations of PM_{2.5} and carbonaceous components are presented in Table 1.
215 PM_{2.5} concentrations ranged from 21 to 395 $\mu\text{g m}^{-3}$ with a mean value at $159 \pm 89 \mu\text{g}$
216 m^{-3} during the whole sampling period. As shown in Figure 2, PM_{2.5} concentrations in
217 P1 (average $\pm 1\sigma = 231 \pm 89 \mu\text{g m}^{-3}$) increased continuously from around 150 μg
218 m^{-3} to higher than 300 $\mu\text{g m}^{-3}$, indicating the occurrence of a severe air pollution
219 episode. In contrast, PM_{2.5} concentration during P2 is as low as $43 \pm 14 \mu\text{g m}^{-3}$.
220 Similarly, the average concentration of OC is $29.4 \pm 7.8 \mu\text{g m}^{-3}$ in P1, which is more
221 than 5 time higher than that in P2 ($5.5 \pm 1.7 \mu\text{g m}^{-3}$). EC concentrations also
222 decreased dramatically from P1 ($12.1 \pm 4.0 \mu\text{g m}^{-3}$) to P2 ($1.5 \pm 1.5 \mu\text{g m}^{-3}$). The
223 average OC/EC ratio is 3.0 ± 0.9 for the whole sampling period, but the ratio was

224 higher in P2 (3.8 ± 1.0) than in P1 (2.5 ± 0.4), mainly due to the high SOA formation
225 activities in the rural areas of NCP in summer. It's worthwhile to note that the average
226 OC/EC ratio during the BB-influenced P1 is much lower than the results reported for
227 wheat straw burning in combustion chamber (12.9 ± 2.1) (Tian et al., 2017) or
228 residential stove (6.3-11.1) (Li et al., 2009). The first reason is that fossil fuel burning
229 (such as coal burning and vehicle exhaust) with lower OC/EC ratio (Tian et al., 2017)
230 are still important sources in the region, which are also discussed in Section 3.4. On
231 the other hand, this phenomenon may also be related to different combustion
232 conditions of agricultural residuals in the open field. Li et al. (2009) found that the
233 flaming fire from biomass burning would result in more EC emission and lower
234 OC/EC ratio compared to smoldering fire. Actually, Hays et al. (2005) obtained
235 similar low OC/EC ratio of 2.4 for open wheat straw burning smoke from
236 Washington, US. Thus, the lower ratio of OC/EC observed in this work may indicate
237 that wheat straw combustion in NCP during P1 occurred mainly in the flaming phase.

238 As shown in Figure 2 and 3, the concentrations of WSOC show a consistent
239 temporal variation as those of OC ($R^2=0.82$), highlighting the fact that WSOC is an
240 important fraction of OC in this region. In addition, the average ratio of WSOC/OC is
241 higher during P1 (0.62 ± 0.16) than during P2 (0.48 ± 0.12), mainly due to enhanced
242 emissions of water-soluble organic compounds (such as sugars, fatty alcohols/acids)
243 from biomass burning during P1. Due to the removal effect of the intermittent raining,
244 concentrations of water-insoluble OC in P2 ($3.0 \pm 1.3 \mu\text{g m}^{-3}$) are also much lower
245 than those in P1 ($10.3 \pm 4.4 \mu\text{g m}^{-3}$).

246 The diurnal variation profiles of EC/OC and WSOC/OC are shown in Figure 4.
247 EC/OC is generally lower in daytime and the lowest value occurred during 12:00-
248 15:00 pm, mainly due to enhanced daytime formation of SOC. Previous studies have
249 shown that secondary organic aerosols are mainly composed of water-soluble
250 compounds, e.g., polyacids/polyalcohols and phenols (Kondo et al., 2007; Wang et al.,
251 2009a). However, these compounds can come from primary emissions as well,
252 especially from biomass burning (Shen et al., 2017; Fu et al., 2012). In this study, the
253 WSOC/OC presents lower value during daytime, especially in the afternoon when
254 photo-chemical oxidation is favorable. In addition, the diurnal variation pattern of
255 WSOC/OC is similar to that of levoglucosan/OC. Given that levoglucosan is a marker
256 of biomass burning emissions (Simoneit et al., 1999; Simoneit et al., 2004a), and many
257 SOA could be produced in the biomass burning plumes during the long-range
258 transport (detailed discussions are given in Section 3.3), these results indicate that
259 particulate WSOC in the region is mostly derived from biomass burning activities
260 including direct emission and secondary oxidation.

261 3.3 Organic molecular composition

262 More than 100 organic species were detected in the aerosol samples, and their
263 concentrations are shown in Table 2 and S1. In this study, these organic compositions
264 are grouped into 10 compound classes based on functional groups and sources. Total
265 concentrations of the measured organics ranged from 177 to 6248 ng m⁻³ (average =
266 1806 ± 1308 ng m⁻³) during the whole sampling period with the predominance of
267 sugar compounds, followed by fatty acids and fatty alcohols. The temporal variation

268 profiles of the determined organic groups are shown in Figure 5. Nearly all the
269 measured organic species, especially *n*-alkanes, fatty acids, fatty alcohols, sugar
270 compounds, and PAHs, show much higher concentrations in P1 than in P2 (Figure
271 S2), indicating an important influence of regional biomass burning on airborne
272 organic aerosols in NCP.

273 3.3.1 Biomass-burning tracers

274 As described in Section 3.1, intensive emissions of open biomass burning were
275 observed in the southern part of NCP during June 13-16 (P1), which is an important
276 reason for the severe regional air pollution during this period. Levoglucosan, which is
277 produced in large quantities during pyrolysis of cellulose, is a key tracer for biomass
278 burning emissions (Simoneit, 2002; Simoneit et al., 1999). As shown in Table 2,
279 levoglucosan is the most abundant single compound in the whole sampling period,
280 ranged from 5.6 to 1447 ng m⁻³ with a mean concentration of 240 ± 288 ng m⁻³.

281 Levoglucosan shows good positive correlations with both OC (R²=0.61) and WSOC
282 (R²=0.65) (Figure 3), confirming that biomass burning is an important source of both
283 aerosol OC and WSOC in the rural region of NCP during the sampling period. As
284 clearly shown in Figure 6, the concentrations of levoglucosan present a continual
285 increasing trend during P1 with a mean value of 404 ± 344 ng m⁻³. However, the tracer
286 presents very low concentrations (11-123 ng m⁻³) for the most of time during Jun 20-
287 22. Interestingly, the concentration of levoglucosan suddenly increased by more than
288 10 times at 21st Jun 18:00 pm to approximately 1200 ng m⁻³ within less than 3 hours
289 and decreased to its beginning concentration (less than 100 ng m⁻³) within 6 hours (2

290 samples) afterwards. The concentrations of OC, WSOC and EC also showed obvious
291 peaks during this event. However, based on analyses of back-trajectories (Figure 1c)
292 and wind conditions (Figure S1), we didn't find significant change of air mass origins.
293 Also, not all organic markers showed similar variation as levoglucosan. For example,
294 the concentrations of PAHs, hopanes, and phthalate esters changed little during this
295 event. Thus, it is plausible to conclude that this variation was caused by emissions
296 from biomass burning activities nearby the sampling site. For this reason, the data of
297 the 2 samples were excluded from P2.

298 The two isomers of levoglucosan, galactosan and mannosan, are also produced
299 by the pyrolysis of cellulose/hemicelluloses (Simoneit, 2002), and thus also
300 considered as important markers of biomass burning. Similar to levoglucosan, the
301 concentrations of these two anhydrosugars in P1 are 5-6 times higher than those in P2.

302 The isomeric ratios of levoglucosan to other anhydrosugars are considered as good
303 indicators of biomass burning. Fabbri et al. (2009) compared the concentrations of the
304 three anhydrosaccharides in the smokes from different fuel types, and proposed that
305 levoglucan/(galactosan+mannosan) (L/G+M) and levoglucan/mannosan (L/M) values
306 range in 0.2-18 and 0.23-33 for various source tests for biomass burning as compared
307 to the average of 54 and 54 for lignites. As shown in Table 2, average ratios of L/G+M
308 and L/M during P1 (10.1 ± 3.41 and 6.77 ± 1.97 , respectively) and P2 (29.7 ± 12.2 and
309 18.0 ± 4.28) suggest that biomass burning is always the dominated contributor for
310 these compounds in the rural area of NCP in summer.

311 3.3.2 Aliphatic lipid composition

312 The average concentration of all the *n*-alkanes (C₁₈–C₃₆) measured in this study
313 is 207 ± 149 ng m⁻³ with the most abundant individual compound being nonacosane
314 (C_{max}=C₂₉H₆₀) (Table S1). *n*-Alkanes derived from terrestrial plants are dominated by
315 high molecular weight species (HMW, carbon number >25) with an odd number
316 preference. In contrast, fossil fuel derived *n*-alkanes do not have odd/even number
317 preference (Rogge et al., 1993a; Simoneit et al., 2004b). In general, *n*-alkanes with a
318 carbon preference index (CPI, odd/even) more than 5 are considered as plant wax,
319 while those with a CPI nearly unity are mostly derived from fossil fuel combustion
320 (Rogge et al., 1993a, b). In this study, the mean value of CPI is 2.47 ± 1.12 , indicating
321 that both fossil fuel and plant wax contributed to *n*-alkanes in the rural areas of NCP
322 in summer. However, *n*-alkanes showed a stronger odd/even carbon number
323 predominance in P1 (CPI=2.85) than in P2 (CPI=1.64). In addition, all the low
324 molecular weight *n*-alkanes (LMW, carbon number <25) presented a higher
325 contribution to total *n*-alkanes in P2 than in P1 (Figure 7 a and d). These results
326 demonstrate that plant waxes from biomass burning emissions made a bigger
327 contribution to organic aerosols in the sampling region during P1.

328 A homologous series of 19 saturated fatty acids (C_{12:0}–C_{32:0}) and 3 unsaturated
329 fatty acids (C_{16:1}, C_{18:1}, and C_{18:2}) were detected in the samples (Table S1), and their
330 total concentration was 514 ± 384 ng m⁻³ during the whole period. A strong even
331 carbon number predominance was observed with C_{max} at C_{28:0} and C_{16:0} (Table S1).
332 Higher molecular weight (HMW) fatty acids (\geq C₂₀) are derived from terrestrial plant
333 waxes, while LMW fatty acids (\leq C₁₉) have multiple sources such as vascular plants,

334 microbes and marine phytoplankton as well as kitchen emissions (Rogge et al.,
335 1993b; Kawamura et al., 2003). The total concentrations of fatty acids presented
336 similar temporal variation to levoglucosan with a robust linear correlation ($R^2=0.72$)
337 (Figure 8a), indicating that fatty acids are mostly affected by biomass burning
338 emission during the whole sampling period. Still, there are some evidences that
339 regional emission from wheat straw burning significantly affected the distribution of
340 fatty acids in the aerosols of Gucheng during P1. Firstly, the total concentrations of
341 fatty acids in P1 ($900 \pm 358 \text{ ng m}^{-3}$) are more than 6 times higher than those in P2
342 ($145 \pm 48 \text{ ng m}^{-3}$). Secondly, the concentrations and relative contributions of HMW
343 fatty acids ($C_{20:0}$ – $C_{32:0}$) are much higher in P1 than in P2, similar to the results of *n*-
344 alkanes. In addition, the mean value of CPI of HMW fatty acids in P1 (4.21 ± 1.14) is
345 also higher than that in P2 (3.50 ± 1.64).

346 Fatty alcohols in the range of C_{22} – C_{30} were detected for the $PM_{2.5}$ samples with a
347 mean concentration of $193 \pm 187 \text{ ng m}^{-3}$ (Table 2 and S1) during the whole sampling
348 period. Their distributions are characterized by even carbon number predominance
349 with a maximum at C_{28} (Figure 7c and f). The total concentration of fatty alcohols
350 strongly correlated with levoglucosan ($R^2=0.73$) (Figure 8b), suggesting that they can
351 also emitted from biomass burning. It is reasonable since HMW fatty alcohols ($\geq C_{20}$)
352 abundantly present in higher plants and loess deposits (Wang and Kawamura, 2005).
353 Similar to fatty acids, nearly 10 times higher concentration of fatty alcohols was
354 observed in P1 ($322 \pm 151 \text{ ng m}^{-3}$) compared with those in P2 ($34 \pm 23 \text{ ng m}^{-3}$).

355 3.3.3 Primary saccharides

356 In addition to the three anhydrosugars, 4 primary sugars (fructose, glucose, sucrose
357 and trehalose) and 3 sugar alcohols (arabitol, mannitol and inositol) were detected in
358 the samples. Primary saccharides have been used as biomarkers for primary biota
359 emissions (Wang et al., 2011). Their mean concentrations ranged from 3.6 to 49 ng m⁻³
360 during the whole sampling period. In this study, concentrations of fructose, sucrose
361 and trehalose in P1 were 7-10 times higher than those in P2 (Table S1). They well
362 correlated with levoglucosan ($R^2=0.47-0.62$, Figure S3) during P1, in contrast to P2,
363 during which no relationships were found between them. These results indicated that
364 these primary sugars were also affected by open-field emissions of biomass burning
365 during P1. Sugar alcohols, mainly arabitol and mannitol, are abundant in airborne
366 fungal spores (Graham et al., 2002). Some studies suggested that biomass burning
367 activities can enhance the emission of sugar alcohols at a certain level (Engling et al.,
368 2009;Fu et al., 2012;Yang et al., 2012). However, no significant relationship ($R^2<0.10$)
369 can be found between these sugar alcohols and levoglucosan even in P1, indicating the
370 negligible contribution of biomass burning to the tracers in this study.

371 **3.3.4 PAHs, Hopanes and Phthalates**

372 As shown in Figure 5, the temporal variation of PAHs, hopanes, and phthalate
373 esters were clearly different from those of the molecular tracers for biomass burning,
374 especially in P1. In contrast to the continuous increase of sugars, fatty acids, fatty
375 alcohols, and n-alkanes during P1, the concentration of PAHs, hopanes, and phthalate
376 esters showed obvious day-night variations, indicating that biomass burning activities
377 contributed little on these species. Phthalates are widely used as plasticizers in synthetic

378 polymers or softeners in polyvinylchlorides (PVC) (Simoneit et al., 2004b) and can be
379 directly emitted from the matrix into the air as they are not chemically bonded with the
380 matrix. Six phthalate esters were detected in the sampling aerosols, i.e., dimethyl
381 (DMP), diethyl (DEP), diisobutyl (DiBP), butyl isobutyl (BiBP), di-n-butyl (DnBP),
382 and bis(2-ethylhexyl) (BEHP) phthalates (Table S1). The concentrations of total
383 detected phthalate esters in P1 ($112 \pm 33 \text{ ng m}^{-3}$) are around 2 times only higher than
384 those in P2 ($51 \pm 18 \text{ ng m}^{-3}$). Hopanes are abundant in coal and crude oils and enriched
385 in lubricant oil fraction (Oros and Simoneit, 2000; Kawamura et al., 1995). They can be
386 emitted to the atmosphere from coal burning and/or internal combustion of fuel in
387 engines. Only two dominant hopanes, $17\alpha(\text{H}),21\beta(\text{H})$ -30-norhopane($\text{C}_{29\alpha\beta}$) and
388 $17\alpha(\text{H}),21\beta(\text{H})$ -hopane($\text{C}_{30\alpha\beta}$), were detected in all of the samples in this study. Their
389 average concentration in P1 ($4.40 \pm 2.48 \text{ ng m}^{-3}$) is ~ 2.5 times of that in P2 ($1.81 \pm$
390 0.31 ng m^{-3}). Considering the much higher concentrations of levoglucosan in P1 (on
391 average ~ 8 times higher than P2), these results again confirmed a limited influence of
392 biomass burning on concentrations of phthalate esters and hopanes in the aerosols in
393 the rural region. Thus, there were no significant concentration changes of the two
394 species at 21st Jun 18:00-24:00 pm, when the air masses were highly affected by nearby
395 biomass burning activities.

396 PAHs are the products of incomplete combustion of carbon-containing materials
397 and are of high toxicity and carcinogenicity (Halek et al., 2008; Sultan et al., 2001).
398 Previous studies indicated that PAHs are mainly emitted from coal burning and vehicle
399 exhaust in most areas of China (Wang et al., 2006a). However, it has been reported that

400 combustion of biomass materials can also contribute to the PAHs in the atmosphere
401 (Simoneit, 2002;Ge et al., 2012;Young et al., 2016). In this study, PAH has no
402 significant correlation with levoglucosan during the whole sampling period. Yet the
403 concentrations of total PAHs in P1 ($18.6 \pm 11 \text{ ng m}^{-3}$) are nearly 8 times higher than
404 those in P2 ($2.3 \pm 1.0 \text{ ng m}^{-3}$). These results mean that although the emission of biomass
405 burning is not the most important source for PAHs during the entire period, the intensive
406 regional burning of wheat straw in P1 can also enhance the PAHs concentration in the
407 atmosphere of Gucheng.

408 As shown in Figure 9, all the primary aerosol markers mentioned above showed
409 lower concentrations in daytime with lowest concentrations at afternoon (12:00-18:00
410 pm), in consistent with the favorable dispersion conditions caused by high temperature
411 and planetary boundary layer (PBL) height. However, the day-night variation of PAHs,
412 hopanes, and phthalate esters are more obvious than other species, again confirming the
413 lower contribution of biomass burning to these organic compositions.

414 **3.3.5 Secondary organic aerosols (SOA) tracers**

415 Eight compounds were identified as isoprene oxidation products in the $\text{PM}_{2.5}$
416 samples, including two methyltetrahydrofuran diols, three C_5 -alkene triols, two 2-
417 methyltetrols, and 2-methylglyceric acid (Table S1). Detailed information about
418 formation and contribution of these compositions were discussed in our previous paper
419 (Li et al., 2018). The concentrations of total detected isoprene-derived products are
420 $\pm 86 \text{ ng m}^{-3}$, with much higher concentration in P1 ($209 \pm 105 \text{ ng m}^{-3}$) than in P2 (57
421 $\pm 29 \text{ ng m}^{-3}$).

422 *cis*-Pinonic acid (PNA), pinic acid (PA), 3-hydroxyglutaric acid (HGA) and 3-
423 methyl-1,2,3-butanetricarboxylic acid (MBTCA) were detected as tracers for α -/ β -
424 pinene oxidation in this study, and their concentration are shown in Table S1. The
425 concentration of total detected α -/ β -pinene oxidation tracers is $66 \pm 31 \text{ ng m}^{-3}$, with
426 MBTCA ($31 \pm 14 \text{ ng m}^{-3}$) being the major compound during the whole sampling period.
427 PNA and PA are considered as first-generation products of α -/ β -pinene oxidation. They
428 can be produced by further oxidation of carbonyl-substituted Criegee intermediates
429 formed by α -pinene ozonolysis (Jenkin et al., 2000;Ma et al., 2008), or by OH oxidation
430 of α -pinene under NO_x free conditions (Eddingsaas et al., 2012;Xuan et al., 2015). The
431 formation of 3-HGA is supposed to be based on a ring opening mechanism and may be
432 related to a heterogeneous reaction of these monoterpenes with irradiation in the
433 presence of NO_x (Jaoui et al., 2005;Claeys et al., 2007). As shown in Figure 6b-d, PNA,
434 PA and HGA present similar temporal variations and correlated well each other
435 ($R^2=0.48-0.76$, Figure S4). The formation of MBTCA is explained by further
436 photodegradation of *cis*-pinonic acid and pinic acid with OH radical (Müller et al.,
437 2012;Szmigielski et al., 2007). As a later-generation oxidation products, MBTCA
438 showed an obviously different temporal variation profile than those of PNA and PA,
439 and had no significant increase during P1. In addition, the concentration of PNA, PA and
440 HGA in P1 are 2-8 times higher than those in P2. However, the concentrations of
441 MBTCA in the two periods are comparable. These results are consistent with the longer
442 time scales of formation pathway, lower volatility and longer lifetime of MBTCA in the
443 atmosphere compared to the first-generation products of α -/ β -pinene oxidation. β -

444 Caryophyllinic acid, formed either by ozonolysis or photo-oxidation of β -caryophyllene
445 (a sesquiterpene) (Jaoui et al., 2007), was also determined in this study, and its
446 concentration ranged from 0.49 to 78 ng m⁻³ (Ave. 17±17 ng m⁻³). The mean
447 concentration of β -caryophyllinic acid in P1 is 35±21 ng m⁻³, being 5 times higher than
448 that in P2 (4.1±1.2 ng m⁻³).

449 Undoubtedly, the combustion of biomass materials can release a large amount of
450 volatile organic compounds, including isoprene and terpenoids (Andreae and Merlet,
451 2001). As shown in Figure 5 and 6, the total biogenic SOA tracers, the sum of detected
452 tracers of isoprene, α -/ β -pinene, and β -caryophyllene derived SOA, showed a similar
453 temporal variation pattern as levoglucosan with a moderate correlation ($R^2=0.56$,
454 Figure S5a). Specifically, levoglucosan showed strong linearly correlations with 3-
455 hydroxyglutaric acid ($R^2=0.72$) (Figure 8c) and β -caryophyllinic acid ($R^2=0.80$) (Figure
456 8d), indicating a significant contribution of biomass burning emissions to the formation
457 of SOA derived from mono- and sesqui- terpene oxidation. In our previous paper (Li et
458 al., 2018), we discussed the different diurnal variations of isoprene-derived SOA tracers.
459 In this study, the diurnal variations of other SOA tracers are shown in Figure 10. All the
460 SOA tracers presented weaker day-night variations compared to primary organic
461 aerosol markers, because of the competition between the enhanced daytime formation
462 by photooxidation and the nighttime accumulation associated with a low PBL. Yet, there
463 are some differences between these SOA tracers. For example, PNA and PA presented
464 lowest concentrations in the afternoon (12:00-18:00 pm) due to their relatively high
465 volatilities, which is unfavorable for **gas-to-particle** phase partitioning. However, the

466 later-generation product of PNA and PA, i.e., the less volatile MBTCA, continuously
467 increased during the daytime.

468 Two classes of aromatic SOA markers, phthalic acids and 2,3-dihydroxy-4-oxopentanoic acid (DHOPA), were detected in the samples as well. Phthalic acids are
469 believed to be produced by the oxidation of naphthalene and other PAHs (Kawamura
470 et al., 2005; Kawamura and Ikushima, 1993; Kanakidou et al., 2005). The mean
471 concentrations of total phthalic acids in the whole sampling period ranged from 17 to
472 487 ng m⁻³ with a mean value of 155±94 ng m⁻³. Their different temporal variation
473 patterns than levoglucosan suggest that biomass burning emission contributes little to
474 phthalic acids formation in the region. The DHOPA was considered to be a tracer
475 compound for toluene-derived SOA (Kleindienst et al., 2004). DHOPA presented a
476 similar temporal variation and moderate correlation to levoglucosan ($R^2=0.51$, Figure
477 S5b), indicating a certain contribution of biomass burning. Similar to MBTCA, the
478 volatility of DHOPA is quite low, and thus mainly exists in the particle phase at field
479 temperature (Ding et al., 2017). Thus, DHOPA showed a similar diurnal variation to
480 MBTCA, with higher concentrations during daytime.

482 **3.4 Assessment of source contributions**

483 In order to investigate the differences in organic aerosol sources between the two
484 representative periods, we classified all the measured organic compounds into seven
485 different sources: (a) “plant emission” represented by higher plant wax n-alkanes,
486 HMW fatty acids and fatty alcohols ($\geq C_{20}$); (b) “fossil fuel combustion” mainly
487 represented by fossil fuel derived n-alkanes, hopanes, and PAHs; (c) “biomass burning”

488 represented by levoglucosan and its isomers; (d) “marine/microbial source” represented
489 by LMW fatty acids (<C₂₀); (e) “soil/fungal spore/pollen” represented by primary
490 saccharides and sugar alcohols; (f) “plastic emission” represented by phthalate esters;
491 and (g) “secondary oxidation” represented by biogenic SOA tracers, DHOPA, and
492 phthalic acids. The concentrations of individual classes and their contributions to OC
493 content during P1 and P2 are summarized in Figure 11. Plant emission-derived
494 compounds accounted for a larger fraction of PM_{2.5} OC during P1 than during P2 (mean
495 fractions of 28.7 ± 9.3‰ in P1 vs. 16.5 ± 7.2‰ in P2). The average fraction of biomass
496 burning-derived organics in P1 was also higher in P1 than in P2 (6.0 ± 3.9‰ vs. 4.6 ±
497 2.1 ‰), so do organics derived from soil/fungal spore/pollen. However, organic
498 molecules from the other 4 sources presented a higher contribution to OC in P2 than in
499 P1.

500 Since organic compounds in the PM_{2.5} samples cannot be completely determined
501 and some of them are of different sources, thus the above classification based on the
502 measured compounds could result in certain uncertainty in assessing source
503 contributions (Simoneit et al., 2004b). Here, we further used a tracer-based source
504 apportionment method to quantitatively estimate the contributions of primary and
505 secondary sources to the fine particulate OC at the rural site. As described above, two
506 samples collected at 21st Jun 18:00-24:00 pm were considered to be highly affected by
507 the direct emission from biomass burning nearby the sampling site. Thus, the average
508 OC/levoglucosan ratio in the smoke of biomass burning $\left(\left(\frac{OC}{Levo}\right)_{BB}\right)$ can be estimated
509 by using the following equation:

$$510 \quad \left(\frac{OC}{Levo}\right)_{BB} = \frac{OC_n - \frac{1}{2}(OC_{before} + OC_{after})}{Levo_n - \frac{1}{2}(Levo_{before} + Levo_{Levo})} \quad (E1)$$

511 where OC_n and $Levo_n$ are the average concentrations of OC and levoglucosan in
 512 the two $PM_{2.5}$ samples affected by the nearby sources. OC_{before} and $Levo_{before}$ are the
 513 concentrations of OC and levoglucosan in the samples collected before the event, while
 514 OC_{after} and $Levo_{after}$ are the concentrations of OC and levoglucosan in the samples
 515 collected after the event. The mean values in the “before” and the “after” samples were
 516 subtracted to minimize the influence of local background contribution. The calculated
 517 $\left(\frac{OC}{Levo}\right)_{BB}$ in this study is 18.7, which is somewhat higher than the average value of 12.1
 518 measured in $PM_{2.5}$ aerosols emitted from the burning of three types of cereal straws
 519 (i.e., wheat, maize, and rice) in China (Zhang et al., 2007b). This difference can be
 520 attributed to the differences of burning conditions. For other sources, the measured
 521 concentrations of mannitol were used to calculate the contributions of fungal spores to
 522 OC (Bauer et al., 2008), and SOA tracers were used to estimate the SOC formed from
 523 the oxidation of isoprene, α -/ β -pinene, β -caryophyllene, and toluene (Kleindienst et al.,
 524 2007). Also, these tracer-based approaches tend to have large uncertainties, especially
 525 for SOC estimation (Li et al., 2013a). However, our results are still meaningful to
 526 understand the relative abundances of organic aerosols from these sources in different
 527 periods.

528 As shown in Figure 12, biomass-burning derived OC, ranging from 0.11-27.5 μgC
 529 m^{-3} , is the dominant source, which accounts for 1.16-74.8% (ave. 22.6%) of OC in the
 530 aerosols of the rural region during the whole sampling period. Fungal-spore derived OC
 531 (0.003-5.12 $\mu\text{gC m}^{-3}$) is a minor source, only accounting for 0.43% (0.003-5.12%) of

532 OC. The contribution of total SOC derived from oxidation of isoprene, α -/ β -pinene, β -
533 caryophyllene, and toluene to OC ranged from 5.90-34.1% with an average at 16.7%.
534 Among the four SOC precursors, toluene-derived products accounted for 7.78% (2.06-
535 21.7%) of OC, being the most important SOC contributor. The relative abundances of
536 these sources showed clear temporal variations during the whole sampling period
537 (Figure 12). The contribution of biomass burning derived OC to total OC in P1 (27.6%)
538 was 1.7 times of that in P2 (17.1%) (Figure 13), further indicating the strong regional
539 impact of open-field wheat straw burning on the molecular compositions of organic
540 aerosols in the rural area of NCP. The contribution of SOC from oxidation of the four
541 VOCs increased slightly from P1 (16.3%) to P2 (21.1%). It should be noted that
542 biomass burning can also release a large amount of VOCs, which may produce more
543 secondary organic aerosols during the long-range transport. Thus, the impact of
544 intensive biomass burning in the southern region of NCP on organic aerosols in the
545 Gucheng area is likely even stronger than the estimation presented above with
546 implications for regional climate.

547 **4. Summary and Conclusion**

548 During the entire sampling period, OC and WSOC showed strong positive
549 correlations with levoglucosan, and the diurnal variation of WSOC/OC was similar to
550 that of levoglucosan/OC, suggesting that summertime organic aerosols in the rural
551 area of NCP are highly affected by direct emission of BB. Higher relative abundances
552 and CPI values of HMW n-alkanes, fatty acids and fatty alcohols in P1 indicated an
553 enhancing effect of open-field biomass burning on molecular composition of organic

554 aerosols. PAHs, hopanes, and phthalate esters presented different temporal and diurnal
555 variations from levoglucosan because of the lower contribution of BB to these organic
556 compositions. The total biogenic SOA tracers showed a similar temporal variation and
557 a moderate correlation with levoglucosan, demonstrating the enhancing effect of BB
558 emission on BSOA formation. Later-generation SOA products, e.g., MBTCA in this
559 study, are unlikely affected directly by BB emission, and thus show little changes in
560 concentrations between the two periods. The source distribution results derived using
561 a tracer-based method demonstrated that the contribution of BB to organic aerosols
562 increased by more than 50% during the period influenced by regional open-field
563 biomass burning (P1) compared to the period when local emissions were more
564 dominant (P2). However, this contribution may even be underestimated since BB can
565 also release a large amount of VOCs enhancing the formation of SOA in the
566 atmosphere. Our results confirmed that intensive field burning of biomass fuels can
567 significantly influence the concentration and composition of aerosols, and thus affect
568 atmospheric chemistry and climate on a regional scale.

569

570 **Author Contributions**

571 G.H. Wang designed the experiment. G.H. Wang, T. Zhu and L.M. Zeng arranged the
572 sample collection. J.J. Li. and G.H. Wang collected the samples. J.J. Li, G.H. Wang, J.
573 Li, C. Wu and W.Q. Jiang analyzed the samples. J.J. Li, and G.H. Wang performed the
574 data interpretation. J.J. Li, G.H. Wang and Q. Zhang wrote the paper.

575

576

577 **Acknowledgements**

578 This work was financially supported by the program from National Nature Science
579 Foundation of China (No. 41773117, 91543116, 41405122). The authors gratefully
580 acknowledge the use of fire spots data products from the Land, Atmosphere Near real-
581 time Capability for EOS (LANCE) system operated by the NASA/GSFC/Earth

582 Science Data and Information System (ESDIS) with funding provided by NASA/HQ
583 (<https://firms.modaps.eosdis.nasa.gov/firemap/>), and the NOAA Air Resources
584 Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model
585 and/or READY website (<http://www.ready.noaa.gov>) used in this publication.
586
587
588

589 Reference

- 590 Aggarwal, S. G., Kawamura, K., Umarji, G. S., Tachibana, E., Patil, R. S., and Gupta, P. K.: Organic and
591 inorganic markers and stable C-, N-isotopic compositions of tropical coastal aerosols from megacity
592 Mumbai: sources of organic aerosols and atmospheric processing, *Atmos. Chem. Phys.*, 13, 4667-
593 4680, 10.5194/acp-13-4667-2013, 2013.
- 594 Andreae, M. O., and Merlet, P.: Emission of trace gases and aerosols from biomass burning, *Global*
595 *Biogeochemical Cycles*, 15, 955-966, 10.1029/2000gb001382, 2001.
- 596 Andreae, M. O., and Rosenfeld, D.: Aerosol–cloud–precipitation interactions. Part 1. The nature and
597 sources of cloud-active aerosols, *Earth-Science Reviews*, 89, 13-41,
598 10.1016/j.earscirev.2008.03.001, 2008.
- 599 Chan, M. N., Choi, M. Y., Ng, N. L., and Chan, C. K.: Hygroscopicity of water-soluble organic
600 compounds in atmospheric aerosols: Amino acids and biomass burning derived organic species,
601 *Environ. Sci. Technol.*, 39, 1555-1562, 10.1021/es049584l, 2005.
- 602 Claeys, M., Szmigielski, R., Kourtshev, I., Van der Veken, P., Vermeylen, R., Maenhaut, W., Jaoui, M.,
603 Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., and Edney, E. O.: Hydroxycarboxylic
604 Acids: Markers for Secondary Organic Aerosol from the Photooxidation of α -Pinene, *Environ. Sci.*
605 *Technol.*, 41, 1628-1634, 10.1021/es0620181, 2007.
- 606 Dinar, E., Anttila, T., and Rudich, Y.: CCN activity and hygroscopic growth of organic aerosols following
607 reactive uptake of ammonia, *Environ. Sci. Technol.*, 42, 793-799, 10.1021/es071874p, 2008.
- 608 Ding, X., Zhang, Y. Q., He, Q. F., Yu, Q. Q., Wang, J. Q., Shen, R. Q., Song, W., Wang, Y. S., and Wang,
609 X. M.: Significant Increase of Aromatics-Derived Secondary Organic Aerosol during Fall to Winter
610 in China, *Environ. Sci. Technol.*, 51, 7432-7441, 10.1021/acs.est.6b06408, 2017.
- 611 Eddingsaas, N. C., Loza, C. L., Yee, L. D., Chan, M., Schilling, K. A., Chhabra, P. S., Seinfeld, J. H., and
612 Wennberg, P. O.: alpha-pinene photooxidation under controlled chemical conditions - Part 2: SOA
613 yield and composition in low- and high-NOx environments, *Atmos. Chem. Phys.*, 12, 7413-7427,
614 10.5194/acp-12-7413-2012, 2012.
- 615 Engling, G., Lee, J. J., Tsai, Y. W., Lung, S. C. C., Chou, C. C. K., and Chan, C. Y.: Size-Resolved
616 Anhydrosugar Composition in Smoke Aerosol from Controlled Field Burning of Rice Straw,
617 *Aerosol Science and Technology*, 43, 662-672, 10.1080/02786820902825113, 2009.
- 618 Fabbri, D., Torri, C., Simoneit, B. R. T., Marynowski, L., Rushdi, A. I., and Fabiańska, M. J.:
619 Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites,
620 *Atmos. Environ.*, 43, 2286-2295, 2009.
- 621 Fu, P. Q., Kawamura, K., Pavuluri, C. M., Swaminathan, T., and Chen, J.: Molecular characterization of
622 urban organic aerosol in tropical India: contributions of primary emissions and secondary
623 photooxidation, *Atmos. Chem. Phys.*, 10, 2663-2689, 2010.
- 624 Fu, P. Q., Kawamura, K., Chen, J., Li, J., Sun, Y. L., Liu, Y., Tachibana, E., Aggarwal, S. G., Okuzawa,
625 K., Tanimoto, H., Kanaya, Y., and Wang, Z. F.: Diurnal variations of organic molecular tracers and
626 stable carbon isotopic composition in atmospheric aerosols over Mt. Tai in the North China Plain:
627 an influence of biomass burning, *Atmos. Chem. Phys.*, 12, 8359-8375, 10.5194/acp-12-8359-2012,
628 2012.
- 629 Ge, X., Setyan, A., Sun, Y., and Zhang, Q.: Primary and secondary organic aerosols in Fresno, California
630 during wintertime: Results from high resolution aerosol mass spectrometry, *Journal of Geophysical*
631 *Research: Atmospheres*, 117, n/a-n/a, 10.1029/2012jd018026, 2012.
- 632 Graham, B., Mayol-Bracero, O. L., Guyon, P., Roberts, G. C., Decesari, S., Facchini, M. C., Artaxo, P.,
633 Maenhaut, W., Koll, P., and Andreae, M. O.: Water-soluble organic compounds in biomass burning
634 aerosols over Amazonia - 1. Characterization by NMR and GC-MS, *J. Geophys. Res.-Atmos.*, 107,
635 DOI:804710.801029/802001jd000336, 2002.
- 636 Guo, S., Hu, M., Zamora, M. L., Peng, J., Shang, D., Zheng, J., Du, Z., Wu, Z., Shao, M., Zeng, L.,
637 Molina, M. J., and Zhang, R.: Elucidating severe urban haze formation in China, *Proceedings of the*
638 *National Academy of Sciences of the United States of America*, 111, 17373-17378,

639 10.1073/pnas.1419604111, 2014.

640 Halek, F., Nabi, G., and Kavousi, A.: Polycyclic aromatic hydrocarbons study and toxic equivalency
641 factor (TEFs) in Tehran, IRAN, *Environmental Monitoring and Assessment*, 143, 303-311,
642 10.1007/s10661-007-9983-9, 2008.

643 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J.,
644 Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma,
645 Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G.,
646 Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt,
647 J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues,
648 *Atmos. Chem. Phys.*, 9, 5155-5236, 2009.

649 Hays, M. D., Fine, P. M., Geron, C. D., Kleeman, M. J., and Gullett, B. K.: Open burning of agricultural
650 biomass: Physical and chemical properties of particle-phase emissions, *Atmos. Environ.*, 39, 6747-
651 6764, <https://doi.org/10.1016/j.atmosenv.2005.07.072>, 2005.

652 Huang, R. J., Zhang, Y. L., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., Daellenbach, K. R., Slowik, J.
653 G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Brun, E. A., Crippa, M., Ciarelli,
654 G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z.
655 S., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S. H.: High secondary aerosol
656 contribution to particulate pollution during haze events in China, *Nature*, 514, 218-222,
657 10.1038/nature13774, 2014.

658 Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., and Edney, E. O.: Identification and
659 quantification of aerosol polar oxygenated compounds bearing carboxylic or hydroxyl groups. 2.
660 Organic tracer compounds from monoterpenes, *Environ. Sci. Technol.*, 39, 5661-5673,
661 10.1021/es048111b, 2005.

662 Jaoui, M., Lewandowski, M., Kleindienst, T. E., Offenberg, J. H., and Edney, E. O.: β -caryophyllinic
663 acid: An atmospheric tracer for β -caryophyllene secondary organic aerosol, *Geophysical Research*
664 *Letters*, 34, doi:10.1029/2006GL028827, 2007.

665 Jenkin, M. E., Shallcross, D. E., and Harvey, J. N.: Development and application of a possible mechanism
666 for the generation of cis-pinonic acid from the ozonolysis of α - and β -pinene, *Atmos. Environ.*, 34,
667 2837-2850, 2000.

668 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., , Kroll, J. H., Decarlo,
669 P. F., Allan, J. D., Coe, H., , and Ng, N. L.: Evolution of organic aerosols in the atmosphere, *Science*,
670 326, 1525-1529, 2009.

671 Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen,
672 R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth,
673 J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G.,
674 and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5,
675 1053-1123, 2005.

676 Kawamura, K., and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban
677 atmosphere, *Environ. Sci. Technol.*, 27, 2227-2235, 1993.

678 Kawamura, K., Kosaka, M., and Sempere, R.: Distributions and seasonal changes in hydrocarbons in
679 urban aerosols and rain waters, *Chikyū Kagaku (Geochemistry)*, 29, 1-15 (In Japanese), 1995.

680 Kawamura, K., Ishimura, Y., and Yamazaki, K.: Four years' observations of terrestrial lipid class
681 compounds in marine aerosols from the western North Pacific, *Global Biogeochemical Cycles*, 17,
682 10.1029/2001gb001810, 2003.

683 Kawamura, K., Imai, Y., and Barrie, L. A.: Photochemical production and loss of organic acids in high
684 Arctic aerosols during long-range transport and polar sunrise ozone depletion events, *Atmos.*
685 *Environ.*, 39, 599-614, 10.1016/j.atmosenv.2004.10.020, 2005.

686 Kleindienst, T. E., Conner, T. S., McIver, C. D., and Edney, E. O.: Determination of secondary organic
687 aerosol products from the photooxidation of toluene and their implications in ambient PM_{2.5}, *J.*
688 *Atmos. Chem.*, 47, 79-100, 2004.

689 Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhavsar, P. V., and Edney,
690 E. O.: Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary
691 organic aerosol at a southeastern US location, *Atmos. Environ.*, 41, 8288-8300,
692 10.1016/j.atmosenv.2007.06.045, 2007.

693 Kondo, Y., Miyazaki, Y., Takegawa, N., Miyakawa, T., Weber, R. J., Jimenez, J. L., Zhang, Q., and
694 Worsnop, D. R.: Oxygenated and water-soluble organic aerosols in Tokyo, *Journal of Geophysical*
695 *Research*, 112, doi: 10.1029/2006jd007056, 10.1029/2006jd007056, 2007.

696 Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., and Pozzer, A.: The contribution of outdoor air
697 pollution sources to premature mortality on a global scale, *Nature*, 525, 367-371,
698 10.1038/nature15371, 2015.

699 Li, J. J., Wang, G. H., Cao, J. J., Wang, X. M., and Zhang, R. J.: Observation of biogenic secondary
700 organic aerosols in the atmosphere of a mountain site in central China: temperature and relative
701 humidity effects, *Atmos. Chem. Phys.*, 13, 11535-11549, 10.5194/acp-13-11535-2013, 2013a.

702 Li, J. J., Wang, G. H., Wang, X. M., Cao, J. J., Sun, T., Cheng, C. L., Meng, J. J., Hu, T. F., and Liu, S.
703 X.: Abundance, composition and source of atmospheric PM 2.5 at a remote site in the Tibetan
704 Plateau, China, *Tellus B*, 65, doi:10.3402/tellusb.v3465i3400.20281, 2013b.

705 Li, J. J., Wang, G. H., Wu, C., Cao, C., Ren, Y. Q., Wang, J. Y., Li, J., Cao, J. J., Zeng, L. M., and Zhu,
706 T.: Characterization of isoprene-derived secondary organic aerosols at a rural site in North China
707 Plain with implications for anthropogenic pollution effects, *Scientific reports*, 8, DOI:
708 10.1038/s41598-41017-18983-41597, 10.1038/s41598-017-18983-7, 2018.

709 Li, W. J., Shao, L. Y., and Buseck, P. R.: Haze types in Beijing and the influence of agricultural biomass
710 burning, *Atmos. Chem. Phys.*, 10, 8119-8130, 10.5194/acp-10-8119-2010, 2010.

711 Li, X., Wang, S., Duan, L., Hao, J., and Nie, Y.: Carbonaceous Aerosol Emissions from Household
712 Biofuel Combustion in China, *Environ. Sci. Technol.*, 43, 6076-6081, 10.1021/es803330j, 2009.

713 Li, Y. J., Sun, Y., Zhang, Q., Li, X., Li, M., Zhou, Z., and Chan, C. K.: Real-time chemical
714 characterization of atmospheric particulate matter in China: A review, *Atmos. Environ.*, 158, 270-
715 304, 10.1016/j.atmosenv.2017.02.027, 2017.

716 Li, Z. Q., Xia, X. G., Cribb, M., Mi, W., Holben, B., Wang, P. C., Chen, H. B., Tsay, S. C., Eck, T. F.,
717 Zhao, F. S., Dutton, E. G., and Dickerson, R. R.: Aerosol optical properties and their radiative effects
718 in northern China, *J. Geophys. Res.-Atmos.*, 112, 10.1029/2006jd007382, 2007.

719 Müller, L., Reinnig, M. C., Naumann, K. H., Saathoff, H., Mentel, T. F., Donahue, N. M., and Hoffmann,
720 T.: Formation of 3-methyl-1,2,3-butanetricarboxylic acid via gas phase oxidation of pinonic acid –
721 a mass spectrometric study of SOA aging, *Atmos. Chem. Phys.*, 12, 1483-1496, 10.5194/acp-12-
722 1483-2012, 2012.

723 Ma, Y., Russell, A. T., and Marston, G.: Mechanisms for the formation of secondary organic aerosol
724 components from the gas-phase ozonolysis of alpha-pinene, *Physical Chemistry Chemical Physics*,
725 10, 4294-4312, 10.1039/b803283a, 2008.

726 Oros, D. R., and Simoneit, B. R. T.: Identification and emission rates of molecular tracers in coal smoke
727 particulate matter, *Fuel*, 79, 515-536, [http://dx.doi.org/10.1016/S0016-2361\(99\)00153-2](http://dx.doi.org/10.1016/S0016-2361(99)00153-2), 2000.

728 Quan, J. N., Gao, Y., Zhang, Q., Tie, X. X., Cao, J. J., Han, S. Q., Meng, J. W., Chen, P. F., and Zhao, D.
729 L.: Evolution of planetary boundary layer under different weather conditions, and its impact on
730 aerosol concentrations, *Particuology*, 11, 34-40, 10.1016/j.partic.2012.04.005, 2013.

731 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.: Sources of Fine
732 Organic Aerosols. 2. Noncatalyst and Catalyst-equipped Automobile and Heavy-duty Diesel Trucks,
733 *Environ. Sci. Technol.*, 27, 636-651, 1993a.

734 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.: Sources of Fine
735 Organic Aerosols .4. Particulate Abrasion Products from Leaf Surfaces of Urban Plants, *Environ.*
736 *Sci. Technol.*, 27, 2700-2711, 1993b.

737 Shen, Z., Zhang, Q., Cao, J., Zhang, L., Lei, Y., Huang, Y., Huang, R. J., Gao, J., Zhao, Z., Zhu, C., Yin,
738 X., Zheng, C., Xu, H., and Liu, S.: Optical properties and possible sources of brown carbon in PM
739 2.5 over Xi'an, China, *Atmos. Environ.*, 150, 322-330, 10.1016/j.atmosenv.2016.11.024, 2017.

740 Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and
741 Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles,
742 *Atmos. Environ.*, 33, 173-182, 1999.

743 Simoneit, B. R. T.: Biomass burning - A review of organic tracers for smoke from incomplete combustion,
744 *Applied Geochemistry*, 17, 129-162, 2002.

745 Simoneit, B. R. T., Elias, V. O., Kobayashi, M., Kawamura, K., Rushdi, A. I., Medeiros, P. M., Rogge,
746 W. F., and Didyk, B. M.: Sugars - Dominant water-soluble organic compounds in soils and
747 characterization as tracers in atmospheric particulate matter, *Environ. Sci. Technol.*, 38, 5939-5949,
748 10.1021/es0403099, 2004a.

749 Simoneit, B. R. T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H. J., Turpin, B. J., and
750 Komazaki, Y.: Composition and major sources of organic compounds of aerosol particulate matter
751 sampled during the ACE-Asia campaign, *J. Geophys. Res.-Atmos.*, 109, D19S10,
752 10.1029/2004jd004598, 2004b.

753 Sultan, C., Balaguer, P., Terouanne, B., Georget, V., Paris, F., Jeandel, C., Lumbroso, S., and Nicolas, J.
754 C.: Environmental xenoestrogens, antiandrogens and disorders of male sexual differentiation,
755 *Molecular and Cellular Endocrinology*, 178, 99-105, 10.1016/s0303-7207(01)00430-0, 2001.

756 Sun, Y. L., Jiang, Q., Wang, Z. F., Fu, P. Q., Li, J., Yang, T., and Yin, Y.: Investigation of the sources and
757 evolution processes of severe haze pollution in Beijing in January 2013, *J. Geophys. Res.-Atmos.*,
758 119, 4380-4398, 10.1002/2014jd021641, 2014.

759 Sun, Y. L., Jiang, Q., Xu, Y. S., Ma, Y., Zhang, Y. J., Liu, X. G., Li, W. J., Wang, F., Li, J., Wang, P. C.,
760 and Li, Z. Q.: Aerosol characterization over the North China Plain: Haze life cycle and biomass
761 burning impacts in summer, *J. Geophys. Res.-Atmos.*, 121, 2508-2521, 10.1002/2015jd024261,
762 2016.

763 Szmigielski, R., Surratt, J. D., Gomez-Gonzalez, Y., Van der Veken, P., Kourtchev, I., Vermeylen, R.,
764 Blockhuys, F., Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Edney, E. O.,
765 Seinfeld, J. H., Maenhaut, W., and Claeys, M.: 3-methyl-1,2,3-butanetricarboxylic acid: An
766 atmospheric tracer for terpene secondary organic aerosol, *Geophysical Research Letters*, 34, L24811,
767 10.1029/2007gl031338, 2007.

768 Tian, J., Ni, H. Y., Cao, J. J., Han, Y. M., Wang, Q. Y., Wang, X. L., Chen, L. W. A., Chow, J. C., Watson,
769 J. G., Wei, C., Sun, J., Zhang, T., and Huang, R. J.: Characteristics of carbonaceous particles from
770 residential coal combustion and agricultural biomass burning in China, *Atmospheric Pollution*
771 *Research*, 8, 521-527, 10.1016/j.apr.2016.12.006, 2017.

772 Tie, X. X., Huang, R. J., Dai, W. T., Cao, J. J., Long, X., Su, X. L., Zhao, S. Y., Wang, Q. Y., and Li, G.
773 H.: Effect of heavy haze and aerosol pollution on rice and wheat productions in China, *Scientific*
774 *reports*, 6, 10.1038/srep29612, 2016.

775 van Donkelaar, A., Martin, R. V., Brauer, M., Kahn, R., Levy, R., Verduzco, C., and Villeneuve, P. J.:
776 Global Estimates of Ambient Fine Particulate Matter Concentrations from Satellite-Based Aerosol
777 Optical Depth: Development and Application, *Environmental Health Perspectives*, 118, 847-855,
778 10.1289/ehp.0901623, 2010.

779 Venkataraman, C., Habib, G., Eiguren-Fernandez, A., Miguel, A. H., and Friedlander, S. K.: Residential
780 biofuels in south Asia: Carbonaceous aerosol emissions and climate impacts, *Science*, 307, 1454-
781 1456, 10.1126/science.1104359, 2005.

782 Wang, G. H., and Kawamura, K.: Molecular characteristics of urban organic aerosols from Nanjing: A
783 case study of a mega-city in China, *Environ. Sci. Technol.*, 39, 7430-7438, 10.1021/es051055+,
784 2005.

785 Wang, G. H., Kawamura, K., Lee, S., Ho, K. F., and Cao, J. J.: Molecular, seasonal, and spatial
786 distributions of organic aerosols from fourteen Chinese cities, *Environ. Sci. Technol.*, 40, 4619-
787 4625, 10.1021/es060291x, 2006a.

788 Wang, G. H., Kawamura, K., Watanabe, T., Lee, S. C., Ho, K. F., and Cao, J. J.: High loadings and source
789 strengths of organic aerosols in China, *Geophysical Research Letters*, 33,
790 L2280110.1029/2006gl027624, 2006b.

791 Wang, G. H., Kawamura, K., Umemoto, N., Xie, M. J., Hu, S. Y., and Wang, Z. F.: Water-soluble organic
792 compounds in PM_{2.5} and size-segregated aerosols over Mount Tai in North China Plain, *J. Geophys.*
793 *Res.-Atmos.*, 114, doi: 10.1029/2008jd011390, D1920810.1029/2008jd011390, 2009a.

794 Wang, G. H., Kawamura, K., Xie, M. J., Hu, S. Y., Cao, J. J., An, Z. S., Weston, J. G., and Chow, J. C.:
795 Organic Molecular Compositions and Size Distributions of Chinese Summer and Autumn Aerosols
796 from Nanjing: Characteristic Haze Event Caused by Wheat Straw Burning, *Environ. Sci. Technol.*,
797 43, 6493-6499, 10.1021/es803086g, 2009b.

798 Wang, G. H., Chen, C. L., Li, J. J., Zhou, B. H., Xie, M. J., Hu, S. Y., Kawamura, K., and Chen, Y.:
799 Molecular composition and size distribution of sugars, sugar-alcohols and carboxylic acids in
800 airborne particles during a severe urban haze event caused by wheat straw burning, *Atmos. Environ.*,
801 45, 2473-2479, 10.1016/j.atmosenv.2011.02.045, 2011.

802 Wang, G. H., Zhang, R. Y., Gomez, M. E., Yang, L. X., Zamora, M. L., Hu, M., Lin, Y., Peng, J. F., Guo,
803 S., Meng, J. J., Li, J. J., Cheng, C. L., Hu, T. F., Ren, Y. Q., Wang, Y. S., Gao, J., Cao, J. J., An, Z.
804 S., Zhou, W. J., Li, G. H., Wang, J. Y., Tian, P. F., Marrero-Ortiz, W., Secret, J., Du, Z. F., Zheng,
805 J., Shang, D. J., Zeng, L. M., Shao, M., Wang, W. G., Huang, Y., Wang, Y., Zhu, Y. J., Li, Y. X., Hu,
806 J. X., Pan, B., Cai, L., Cheng, Y. T., Ji, Y. M., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A.,
807 Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze,
808 *Proceedings of the National Academy of Sciences of the United States of America*, 113, 13630-
809 13635, 10.1073/pnas.1616540113, 2016.

810 Xuan, Z., Renee C, M., Dan D, H., Nathan F, D., Bernard, A., Richard C, F., and John H, S.: Formation
811 and evolution of molecular products in α -pinene secondary organic aerosol, *Proceedings of the*
812 *National Academy of Sciences of the United States of America*, 112, 14168-14173, 2015.

813 Yang, Y. H., Chan, C. Y., Tao, J., Lin, M., Engling, G., Zhang, Z. S., Zhang, T., and Su, L.: Observation
814 of elevated fungal tracers due to biomass burning in the Sichuan Basin at Chengdu City, China,
815 *Science of the Total Environment*, 431, 68-77, 10.1016/j.scitotenv.2012.05.033, 2012.

816 Young, D. E., Kim, H., Parworth, C., Zhou, S., Zhang, X., Cappa, C. D., Seco, R., Kim, S., and Zhang,
817 Q.: Influences of emission sources and meteorology on aerosol chemistry in a polluted urban
818 environment: results from DISCOVER-AQ California, *Atmos. Chem. Phys.*, 16, 5427-5451,

819 10.5194/acp-16-5427-2016, 2016.
820 Zhang, J. K., Cheng, M. T., Ji, D. S., Liu, Z. R., Hu, B., Sun, Y., and Wang, Y. S.: Characterization of
821 submicron particles during biomass burning and coal combustion periods in Beijing, China, *The*
822 *Science of the total environment*, 562, 812-821, 10.1016/j.scitotenv.2016.04.015, 2016.
823 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami,
824 A., Middlebrook, A. M., and Sun, Y. L.: Ubiquity and dominance of oxygenated species in organic
825 aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophysical Research*
826 *Letters*, 34, L13801, 2007a.
827 Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I. S.,
828 Reddy, S., Fu, J. S., Chen, D., Duan, L., Lei, Y., Wang, L. T., and Yao, Z. L.: Asian emissions in
829 2006 for the NASA INTEX-B mission, *Atmos. Chem. Phys.*, 9, 5131-5153, 10.5194/acp-9-5131-
830 2009, 2009.
831 Zhang, Y., Shao, M., Zhang, Y., Zeng, L., He, L., Zhu, B., Wei, Y., and Zhu, X.: Source profiles of
832 particulate organic matters emitted from cereal straw burnings, *Journal of Environmental Sciences*,
833 19, 167-175, [https://doi.org/10.1016/S1001-0742\(07\)60027-8](https://doi.org/10.1016/S1001-0742(07)60027-8), 2007b.
834 Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L., Zhang, J., Shao, M., Lu,
835 S., and Wang, W.: Characteristics of ambient volatile organic compounds and the influence of
836 biomass burning at a rural site in Northern China during summer 2013, *Atmos. Environ.*, 124, 156-
837 165, 10.1016/j.atmosenv.2015.08.097, 2016.
838
839

840 Table 1 Concentrations of carbonaceous components in the time-resolved (3-h) PM_{2.5} samples in
 841 the rural site of NCP during the whole sampling period, Period 1 (P1) and Period 2 (P2).

Component	Whole period (N=117)			Period 1 (N=28)			Period 2 (N=13)		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
PM _{2.5} (µg m ⁻³)	21~395	159	89	133~347	231	59	21~62	43	14
OC (µg m ⁻³)	1.7~45.7	17.3	11.1	13.8~44.4	29.4	7.8	3.6~8.8	5.5	1.7
EC (µg m ⁻³)	0.2~22.3	6.5	4.9	5.3~22.3	12.1	4.0	0.9~2.6	1.5	0.5
WSOC (µg m ⁻³)	0.7~33.0	11.5	8.2	5.3~33.0	19.1	8.3	1.2~4.2	2.6	0.8
WIOC (µg m ⁻³)	0.3~28.1	6.4	5.1	4.5~28.1	10.3	4.4	1.2~5.5	3.0	1.3
OC/EC	1.2~7.6	3.0	0.9	1.9~3.2	2.5	0.4	2.5~5.7	3.8	1.0
WSOC/OC	0.07~0.95	0.63	0.18	0.30~0.85	0.62	0.16	0.18~0.67	0.48	0.12
WIOC/OC	0.05~0.93	0.37	0.18	0.15~0.70	0.38	0.16	0.33~0.82	0.52	0.12

842

843

844

845 Table 2 Average concentrations of the organic compound classes (ng m⁻³) in the time-resolved (3-h)
 846 PM_{2.5} samples in the rural site of NCP during the whole study period, Period 1 (P1) and Period 2
 847 (P2).

Compounds	Whole period (N=117)			Period 1 (N=28)			Period 2 (N=13)		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
n-Alkanes	9.97~722.2	206.9	149.3	94.7~722.3	343.7	134.1	25.1~103.2	54.3	22.4
CPI (C ₁₈ -C ₃₆) ^a	1.08~8.62	2.47	1.12	1.38~4.67	2.85	0.87	1.08~3.5	1.64	0.59
Fatty acids	64.6~1777	514.4	384.3	206.7~1528	900.3	358.3	81.4~234.4	145.3	47.7
CPI (C _{21:0} -C _{30:0}) ^b	2.26~9.15	4.24	1.14	3.49~6.11	4.21	0.64	2.26~8.57	3.50	1.64
Fatty alcohols	3.18~975.9	192.6	187.4	62.4~638.2	322.0	150.7	16.6~100.2	33.9	22.6
Sugar compounds	15.9~2228	432.8	428.9	151.9~1727	718.0	403.1	39.7~241.3	93.2	52.9
galactosan (G)	1.03~97.78	18.5	20.6	2.16~97.8	29.5	27.9	1.45~13.3	4.61	3.13
mannosan (M)	0.69~54.82	9.78	10.4	1.61~54.8	15.0	13.3	0.96~6.63	2.83	1.43
levoglucosan (L)	5.56~1447	240.1	287.8	29.3~1428	404.0	344.0	11.2~123	47.8	26.2
L/M ratio	4.03~71.8	22.8	8.85	13.9~71.8	29.7	12.2	11.3~23.1	18.0	4.28
L/(G+M) ratio	1.38~19.3	8.05	2.59	5.3~19.3	10.1	3.41	4.58~10.2	6.77	1.97
PAHs	1.11~48.5	12.0	11.0	4.21~37.7	18.6	11.0	1.25~5.01	2.33	0.98
Hopanes	0.66~10.81	3.46	2.38	0.86~9.97	4.40	2.48	1.14~2.28	1.81	0.31
Phthalate esters	17.7~219.9	84.9	41.3	68.8~183.1	111.5	32.7	31.5~100.8	51.1	18.1
Phthalic acids	17.1~487.2	154.5	93.9	91.3~388.6	211.0	87.1	17.1~81	46.3	17.1
Isoprene SOA tracers	11.1~404.1	111.9	85.8	48.3~404.1	208.5	104.9	34.8~127.5	57.0	29.4
Monoterpene SOA tracers	11.1~166.2	66.1	31.2	37.3~166.2	85.3	34.9	26.7~64.5	44.6	12.6
β -Caryophyllinic acid ^c	0.49~77.7	17.4	17.1	4.6~77.8	34.7	20.8	2.44~6.28	4.08	1.21
DHOPA ^d	1.59~35.3	9.36	7.15	4.06~35.3	15.6	9.80	2.7~6.99	4.16	1.42
Total measured organics	176.9~6249	1806	1308	843.3~5499	2973	1219	334.2~913.7	537.9	151.1
Total organics C/OC ^e (%)	3.19~16.0	6.99	1.97	3.43~8.86	6.43	1.36	3.77~8.61	6.41	1.27

848 ^a CPI (C₁₈-C₃₆): carbon preference index for *n*-alkanes, (C₁₉+C₂₁+C₂₃+C₂₅+C₂₇+C₂₉+C₃₁+C₃₃+C₃₅)/

849 (C₁₈+C₂₀+C₂₂+C₂₄+C₂₆+C₂₈+C₃₀+C₃₂+C₃₄).

850 ^b CPI (C_{21:0}-C_{30:0}): carbon preference index for fatty acids, (C_{22:0}+C_{24:0}+C_{26:0}+C_{28:0}+C_{30:0})/(C_{21:0}+C_{23:0}+C_{25:0}+C_{27:0}+C_{29:0}).

851 ^c β -Caryophyllinic acid: a tracer of β -caryophyllene-derived SOA.

852 ^d DHOPA: 2,3-dihydroxy-4-oxopentanoic acid, a tracer of toluene-derived SOA.

853 ^e All the quantified organic compounds were converted to their carbon contents to calculate the OC ratios.

Figure Captions

854

855 Figure 1. Backward trajectories of air masses (a,c) (provided by NOAA HYSPLIT modeling system,
856 <http://ready.arl.noaa.gov/HYSPLIT.php>), and fire spots (b,d) (provided by Fire Information
857 for Resource Management System, FIRMS, <https://firms.modaps.eosdis.nasa.gov/firemap/>),
858 during Period 1 (P1) (Jun 13th 21:00-16th 15:00, 2013) and Period 2 (P2) (Jun 22nd 12:00-24th
859 06:00, 2013). Sampling site represented as purple star.

860 Figure 2. Temporal variations of PM_{2.5}, OC, EC, and WSOC during the whole sampling period.
861 Shadows denote the two representative periods.

862 Figure 3. Linear correlations of OC with WSOC (a), levoglucosan with OC and WSOC(b).

863 Figure 4. Diurnal variation of OC/EC (a), WSOC/OC and levoglucosan/OC (b).

864 Figure 5. Temporal variations of ten organic compound classes detected in the summertime PM_{2.5}
865 samples at the rural site of NCP.

866 Figure 6. Temporal variations of organic tracers for biomass burning (a), and secondary products
867 derived from α - β -pinene (b-d), β -caryophyllene (e), and toluene (f).

868 Figure 7. Molecular distributions of *n*-alkanes (a and d), fatty acids (b and e), and fatty alcohols (c and
869 f) in the PM_{2.5} of the rural area.

870 Figure 8. Linear correlations of fatty acids (a), fatty alcohols (b), 3-hydroxyglutaric acid (c), and β -
871 caryophyllinic acid (d) with levoglucosan.

872 Figure 9. Diurnal variation of the detected organic compound classes.

873 Figure 10. Diurnal variation of the SOA tracers derived from oxidation of α - β -pinene (a-d), β -
874 caryophyllene (e), and toluene (f).

875 Figure 11. A comparison of the average contributions of different sources-derived organics (converted
876 to carbon content) to OC during P1 and P2.

877 Figure 12. Contributions (above) of primary organic carbon from biomass burning (OC_{bb}) and fungal
878 spores (OC_{fp}), and secondary organic carbon from isoprene (SOC_i), α - β -pinene (SOC_p), β -
879 caryophyllene (SOC_p), and toluene (SOC_t) to OC in the time-resolved (3 h) rural aerosols,
880 and their relative abundances (down). All the contributions were estimated by tracer-based
881 method.

882 Figure 13. Average contributions of direct emissions from biomass burning (BB) and fungal spores
883 (OC_{fp}), secondary oxidation from isoprene (SOC_i), α - β -pinene (SOC_p), β -caryophyllene
884 (SOC_p), and toluene (SOC_t) to OC in P1 and P2. All the contributions were estimated by
885 tracer-based method.

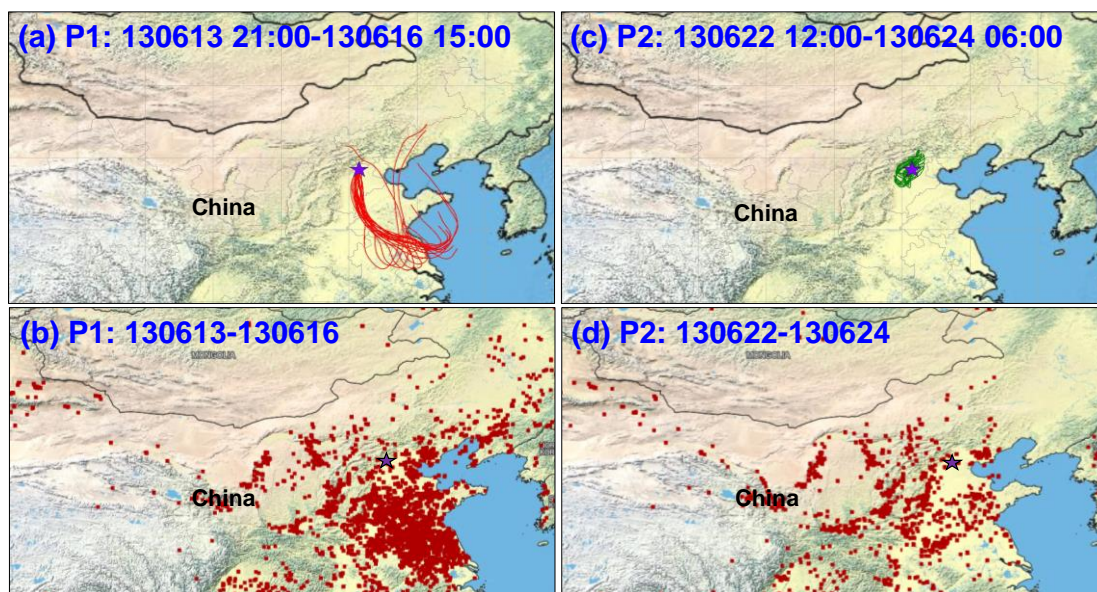
886

887

888

889

890



891

892 Figure 1. Backward trajectories of air masses (a,c) (provided by NOAA HYSPLIT modeling system,
893 <http://ready.arl.noaa.gov/HYSPLIT.php>), and fire spots (b,d) (provided by Fire Information for
894 Resource Management System, FIRMS, <https://firms.modaps.eosdis.nasa.gov/firemap/>), during Period
895 1 (P1) (Jun 13th 21:00-16th 15:00, 2013) and Period 2 (P2) (Jun 22nd 12:00-24th 06:00, 2013). Sampling
896 site represented as purple star.

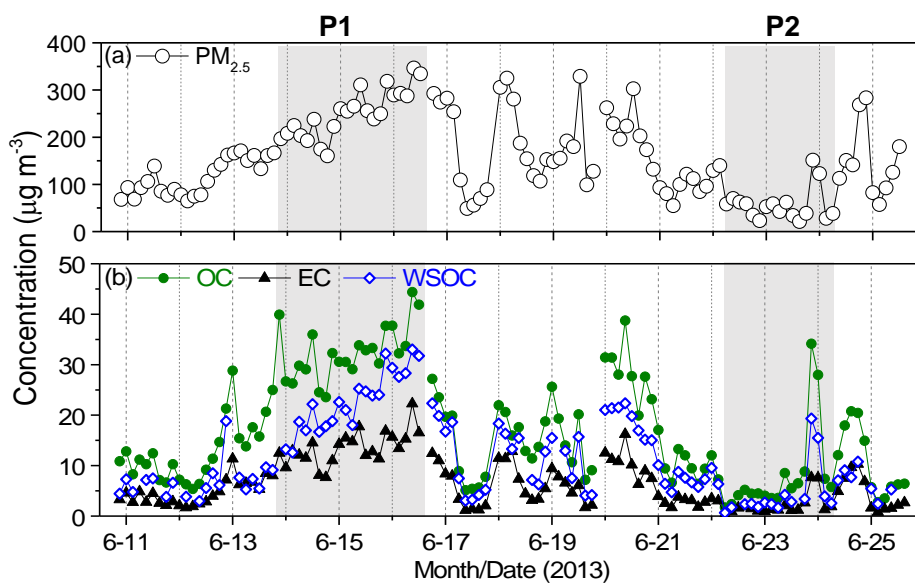
897

898

899

900

901



902

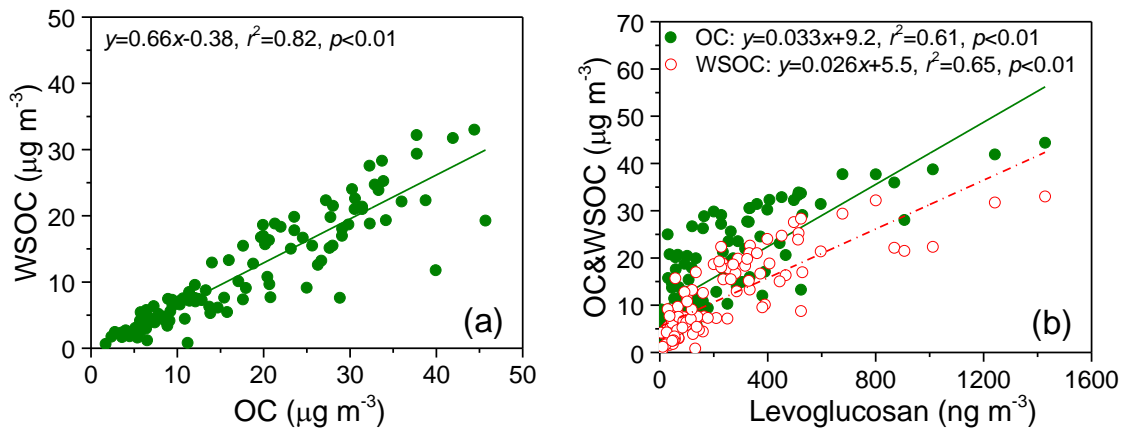
903 Figure 2. Temporal variations of PM_{2.5}, OC, EC, and WSOC during the whole sampling period.

904

Shadows denote the two representative periods.

905

906



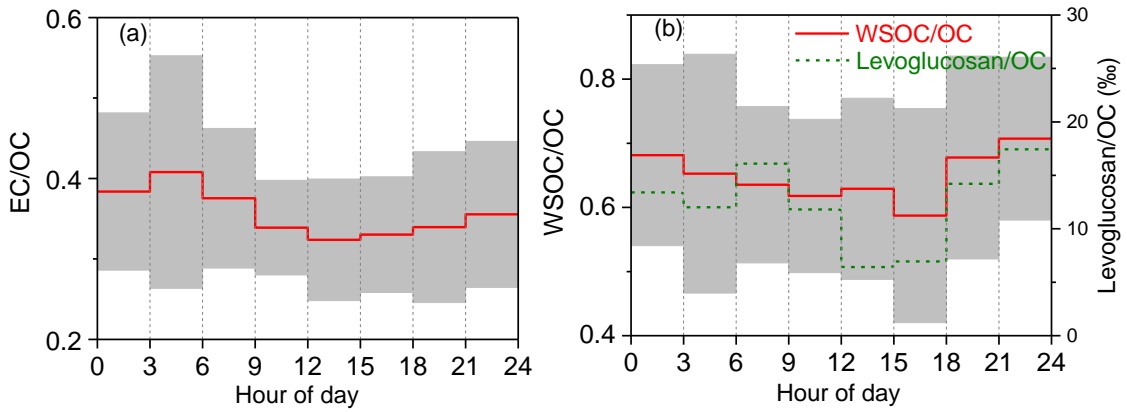
907

908 Figure 3. Linear correlations of OC with WSOC (a), levoglucosan with OC and WSOC(b).

909

910

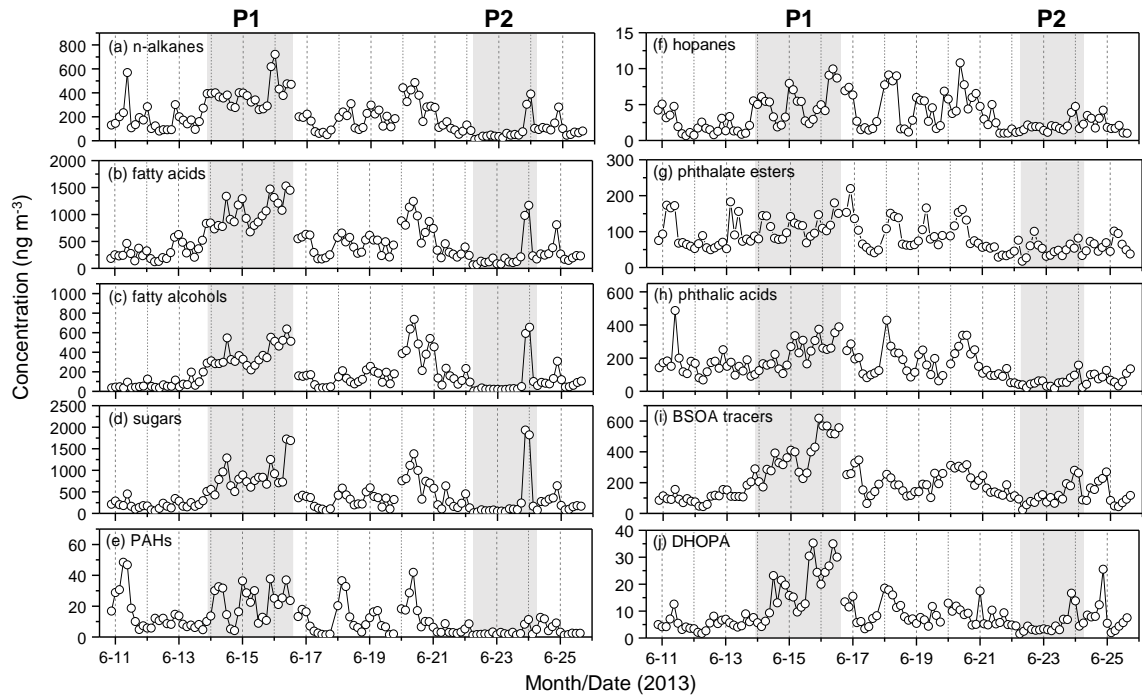
911



912

913 Figure 4. Diurnal variation of OC/EC (a), WSOC/OC and levoglucosan/OC (b).

914

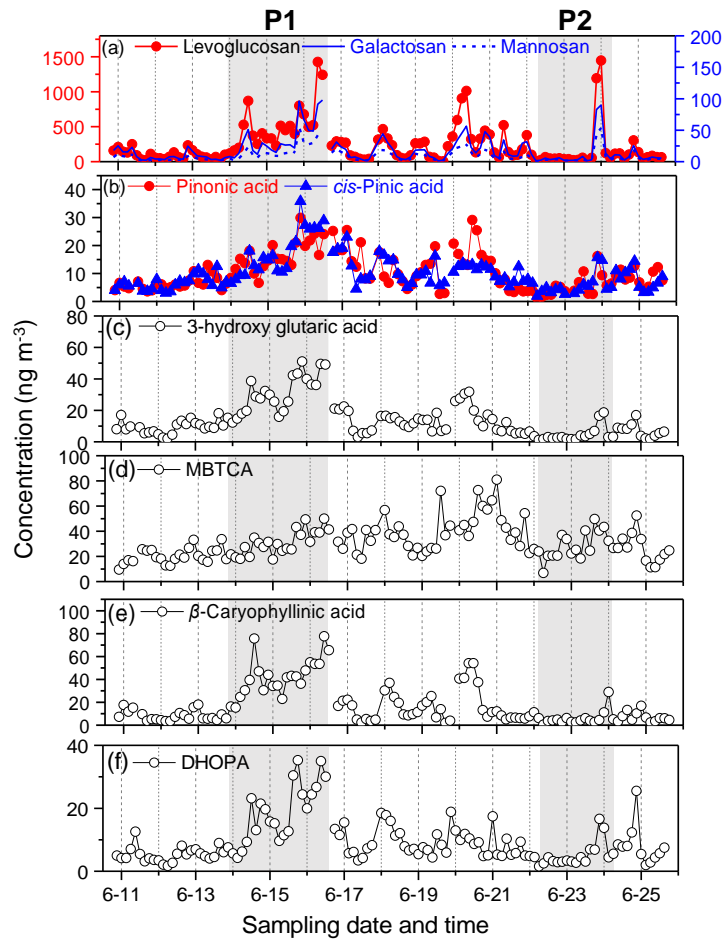


915

916 Figure 5. Temporal variations of ten organic compound classes detected in the summertime PM_{2.5}
 917 samples at the rural site of NCP.

918

919

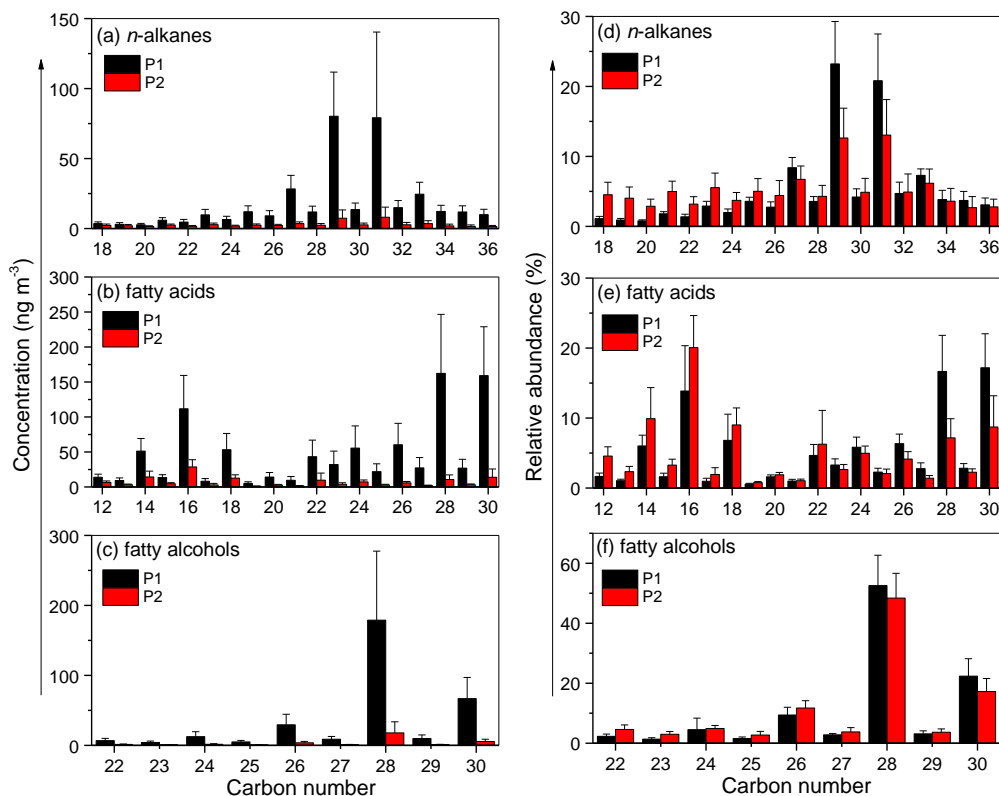


920

921 Figure 6. Temporal variations of organic tracers for biomass burning (a), and secondary products

922 derived from α - β -pinene (b-d), β -caryophyllene (e), and toluene (f).

923

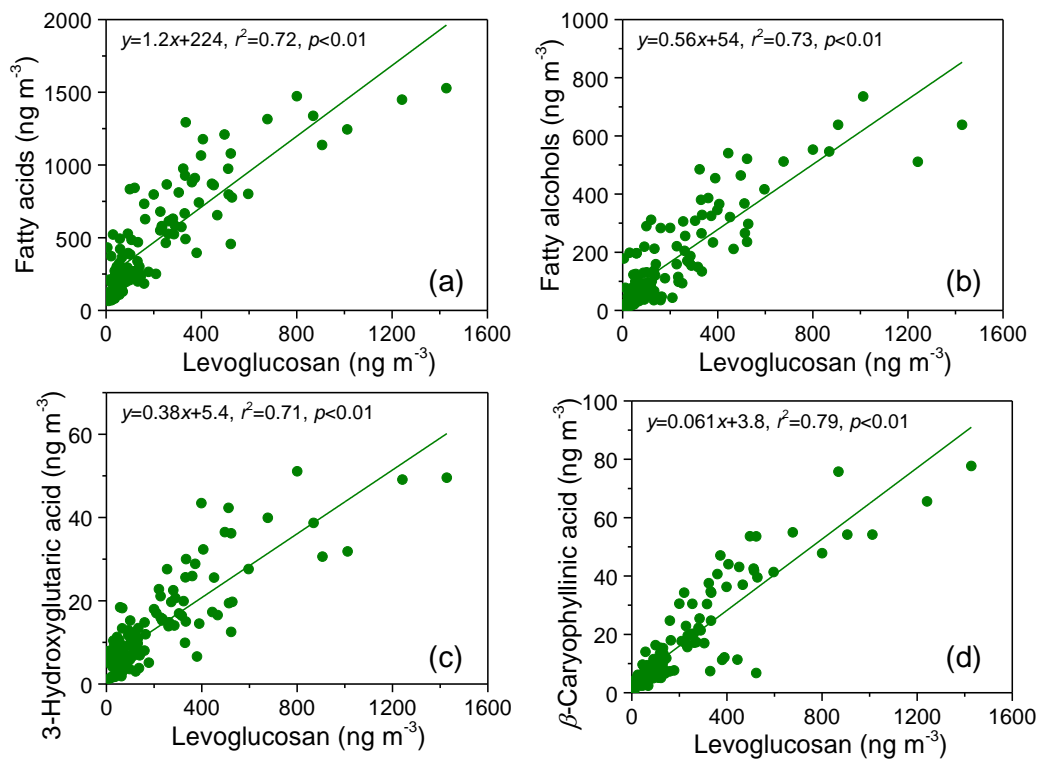


924

925 Figure 7. Molecular distributions of *n*-alkanes (a and d), fatty acids (b and e), and fatty alcohols (c and

926 f) in the PM_{2.5} of the rural area.

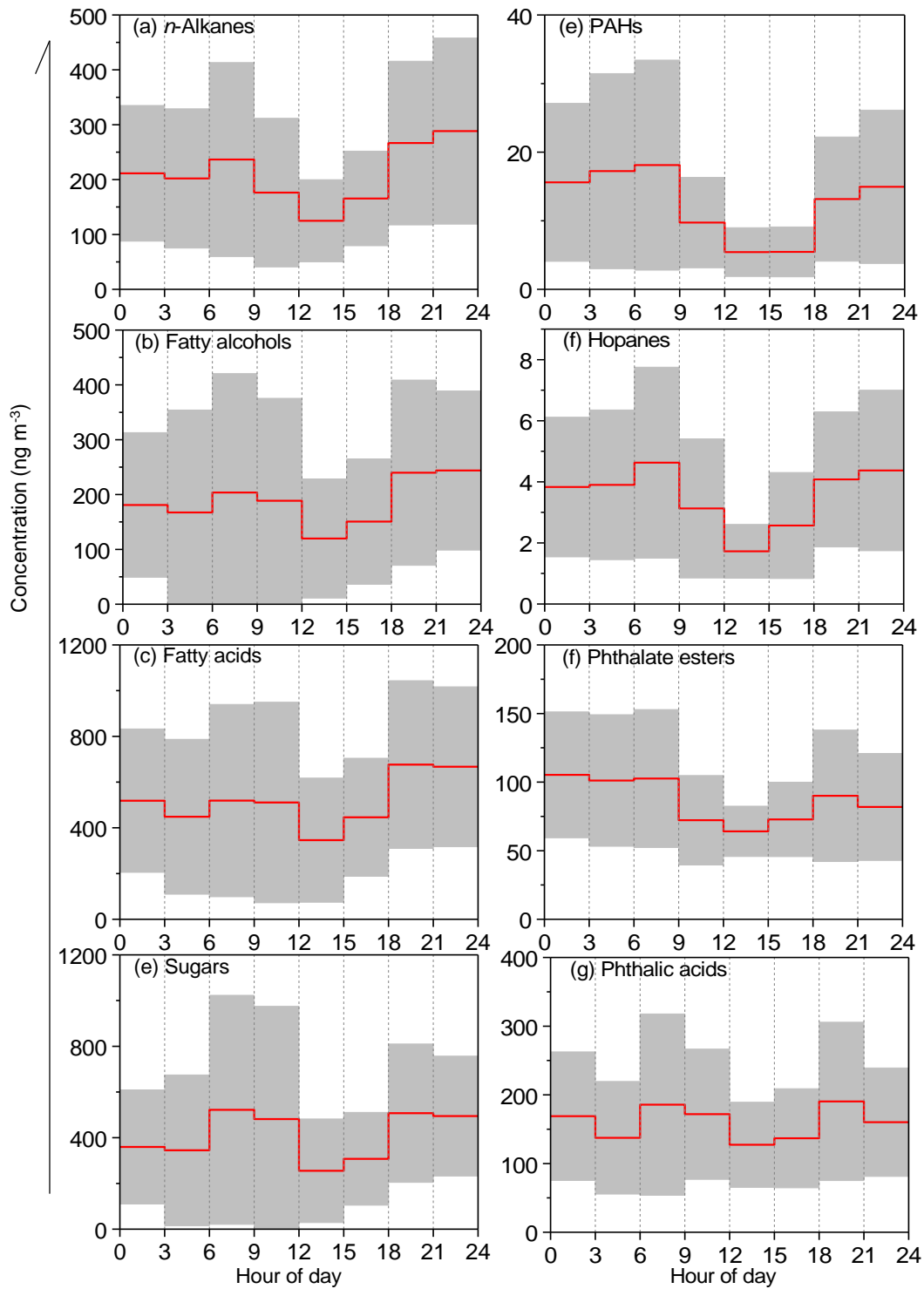
927



928

929 Figure 8. Linear correlations of fatty acids (a), fatty alcohols (b), 3-hydroxyglutaric acid (c), and β-

930 caryophyllinic acid (d) with levoglucosan.



932

933

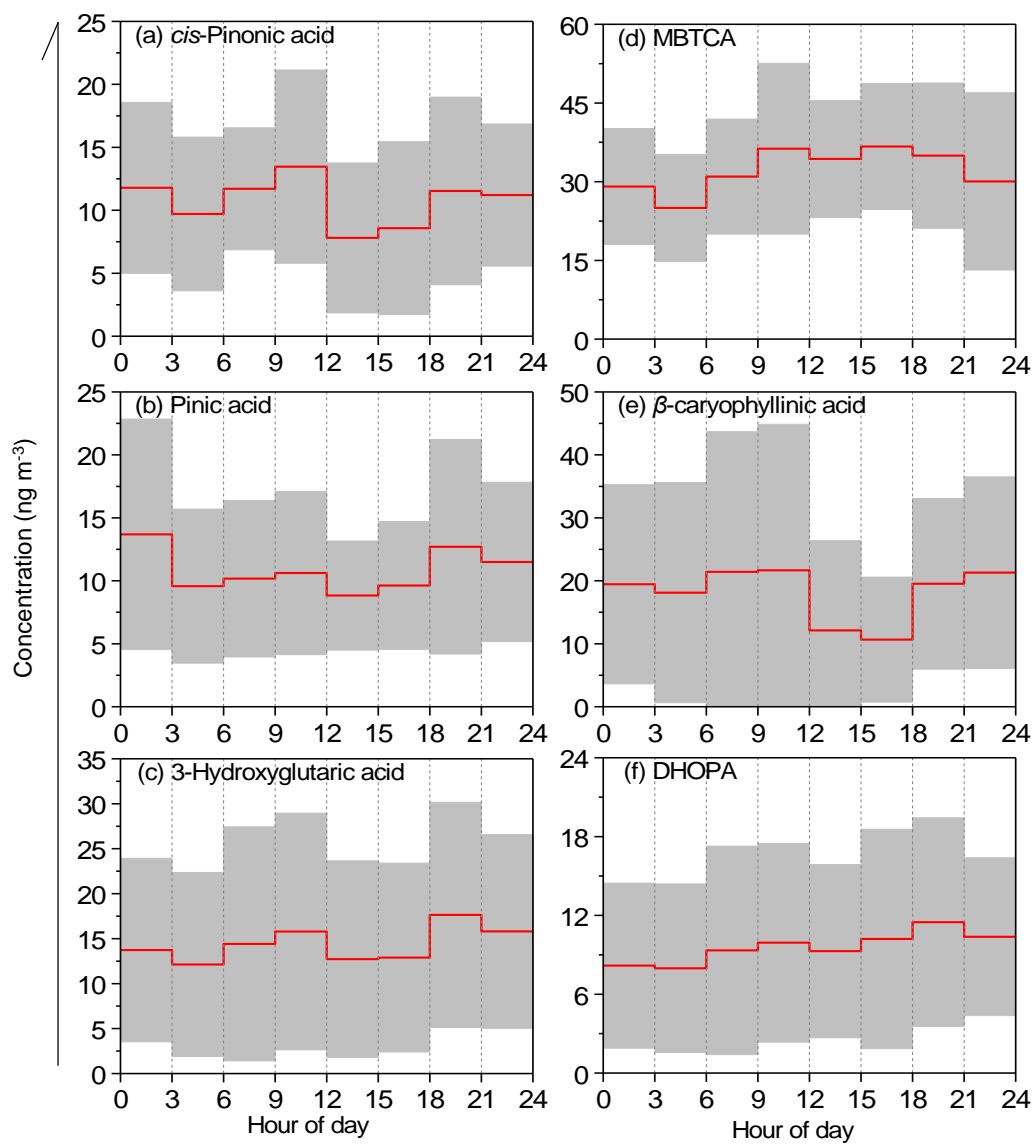
Figure 9. Diurnal variation of the detected organic compound classes.

934

935

936

937

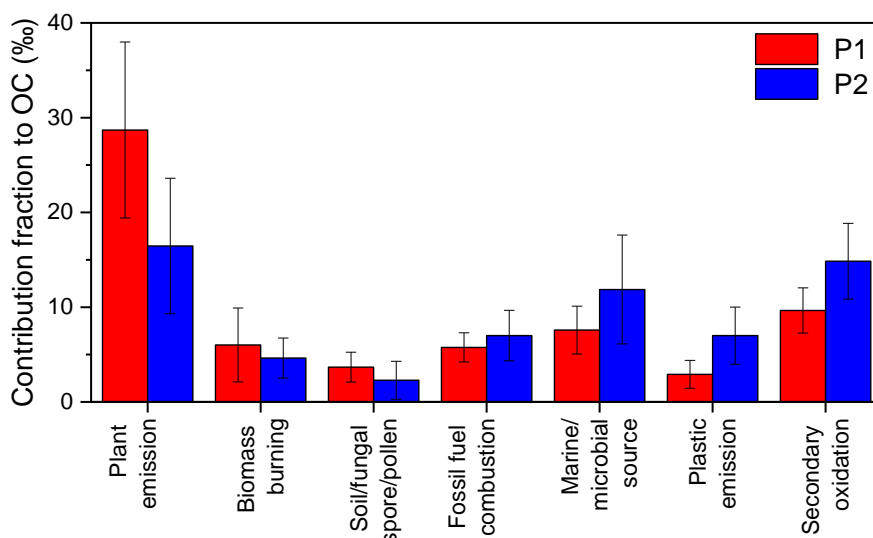


939

940 Figure 10. Diurnal variation of the SOA tracers derived from oxidation of α - β -pinene (a-d), β -
 941 caryophyllene (e), and toluene (f).

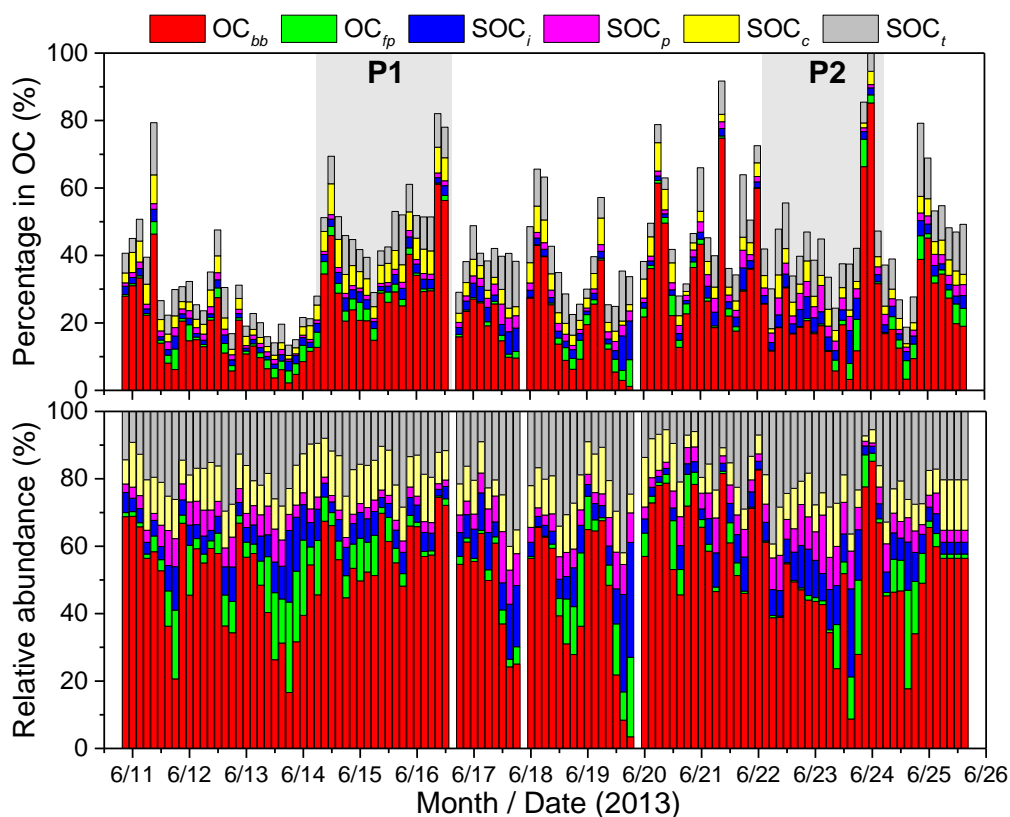
942

943



944
 945 Figure 11 A comparison of the average contributions of different sources-derived organics (converted
 946 to carbon content) to OC during P1 and P2.

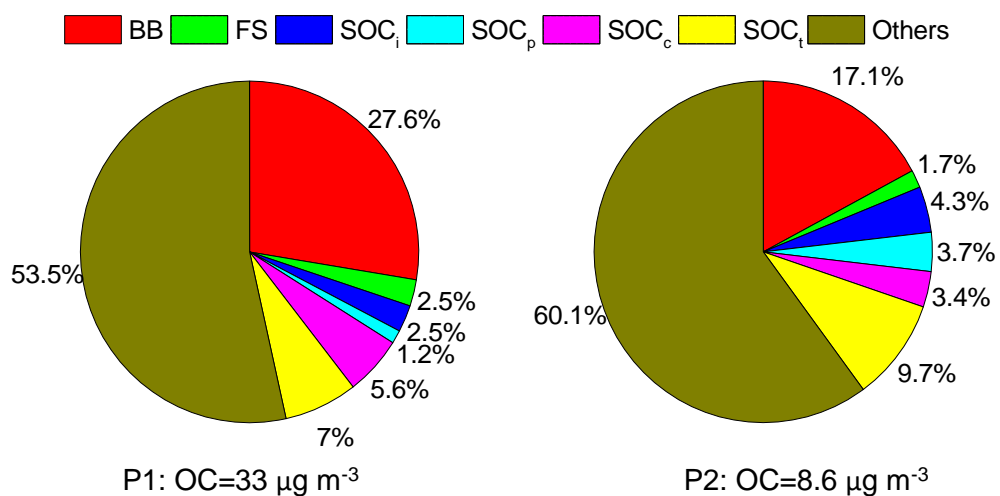
947
 948
 949
 950



951
 952 Figure 12. Contributions (above) of primary organic carbon from biomass burning (OC_{bb}) and fungal
 953 spores (OC_{fp}), and secondary organic carbon from isoprene (SOC_i), α - β -pinene (SOC_p), β -
 954 caryophyllene (SOC_c), and toluene (SOC_t) to OC in the time-resolved (3 h) rural aerosols, and their
 955 relative abundances (down). All the contributions were estimated by tracer-based method.

956

957



958

959

960

961

962

963

Figure 13. Average contributions of direct emissions from biomass burning (BB) and fungal spores (OC_{fp}), secondary oxidation from isoprene (SOC_i), α - β -pinene (SOC_p), β -caryophyllene (SOC_c), and toluene (SOC_t) to OC in P1 and P2. All the contributions were estimated by tracer-based method.