

## Radical formation by fine particulate matter associated with highly oxygenated molecules

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1 **Radical Formation by Fine Particulate Matter Associated with Highly**  
2 **Oxygenated Molecules**

3 Haijie Tong,<sup>\*1</sup> Yun Zhang,<sup>2</sup> Alexander Filippi,<sup>1</sup> Ting Wang,<sup>1,3</sup> Chenpei Li,<sup>1,3</sup> Fobang Liu,<sup>1,4</sup>  
4 Denis Leppla,<sup>2</sup> Ivan Kourtchev,<sup>5</sup> Kai Wang,<sup>2,a</sup> Helmi-Marja Keskinen,<sup>6</sup> Janne T. Levula,<sup>6</sup>  
5 Andrea M. Arangio,<sup>1,7</sup> Fangxia Shen,<sup>8</sup> Florian Ditas,<sup>1</sup> Scot T. Martin,<sup>9,10</sup> Paulo Artaxo,<sup>11</sup>  
6 Ricardo H. M. Godoi,<sup>12</sup> Carlos I. Yamamoto,<sup>13</sup> Rodrigo A. F. de Souza,<sup>14</sup> Ru-Jin Huang,<sup>15</sup>  
7 Thomas Berkemeier,<sup>1</sup> Yueshe Wang,<sup>3</sup> Hang Su,<sup>1</sup> Yafang Cheng,<sup>1</sup> Francis D. Pope,<sup>16</sup>  
8 Pingqing Fu,<sup>17</sup> Maosheng Yao,<sup>18</sup> Christopher Pöhlker,<sup>1</sup> Tuukka Petäjä,<sup>6</sup> Markku Kulmala,<sup>6</sup>  
9 Meinrat O. Andreae,<sup>1,19</sup> Manabu Shiraiwa,<sup>20</sup> Ulrich Pöschl,<sup>1</sup> Thorsten Hoffmann,<sup>\*2</sup> and  
10 Markus Kalberer<sup>\*5,21</sup>

11 <sup>1</sup> Multiphase Chemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany.

12 <sup>2</sup> Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University, 55128 Mainz,  
13 Germany.

14 <sup>3</sup> State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an,  
15 710049, China.

16 <sup>4</sup> School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta,  
17 Georgia 30332, United States.

18 <sup>5</sup> Centre for Atmospheric Science, Department of Chemistry, University of Cambridge, Cambridge  
19 CB2 1EW, United Kingdom.

20 <sup>6</sup> Institute for Atmospheric and Earth System Research / Physics Faculty of Science, University of  
21 Helsinki FI-00014, Finland.

22 <sup>7</sup> École polytechnique fédérale de Lausanne, Lausanne 1015, Switzerland.

23 <sup>8</sup> School of Space and Environment, Beihang University, Beijing, 100191, China.

24 <sup>9</sup> School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts  
25 02138, United State.

26 <sup>10</sup> Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts  
27 02138, United State.

28 <sup>11</sup> Physics Institute, University of Sao Paulo, Sao Paulo, Brazil.

29 <sup>12</sup> Environmental Engineering Department, Federal University of Parana, Curitiba, Brazil.

30 <sup>13</sup> Chemical Engineering Department, Federal University of Parana, Curitiba, PR, Brazil.

31 <sup>14</sup> State University of Amazonas, Av. Darcy Vargas, 1200, 69065-020, Manaus-AM, Brazil.

- 32 <sup>15</sup> Key Laboratory of Aerosol Chemistry and Physics, State Key Laboratory of Loess and Quater-  
33 nary Geology, Institute of Earth and Environment, Chinese Academy of Sciences, Xi'an, 710061,  
34 China.
- 35 <sup>16</sup> School of Geography, Earth and Environmental Sciences, University of Birmingham, Birming-  
36 ham, B15 2TT, United Kingdom.
- 37 <sup>17</sup> Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China.
- 38 <sup>18</sup> College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China.
- 39 <sup>19</sup> Scripps Institution of Oceanography, University of California San Diego, CA 92093, United  
40 States.
- 41 <sup>20</sup> Department of Chemistry, University of California, Irvine, California 92697-2025, United States.
- 42 <sup>21</sup> Department of Environmental Sciences, University of Basel, Klingelbergstrasse 27, 4056 Basel,  
43 Switzerland.
- 44 <sup>a</sup> now at: Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C,  
45 Denmark.

46 **ABSTRACT**

47 Highly oxygenated molecules (HOMs) play an important role in the formation and evolu-  
48 tion of secondary organic aerosols (SOA). However, the abundance of HOMs in different  
49 environments and their relation to the oxidative potential of fine particulate matter (PM)  
50 are largely unknown. Here, we investigated the relative HOM abundance and radical yield  
51 of laboratory-generated SOA and fine PM in ambient air ranging from remote forest areas  
52 to highly polluted megacities. By electron paramagnetic resonance and mass spectrometric  
53 investigations, we found that the relative abundance of HOMs especially the dimer and low  
54 volatile types in ambient fine PM was positively correlated with the formation of radicals  
55 in aqueous PM extracts. SOA from photooxidation of isoprene, ozonolysis of  $\alpha$ - and  $\beta$ -  
56 pinene as well as fine PM from tropical (central Amazon) and boreal (Hyytiälä, Finland)  
57 forests exhibited a higher HOM abundance and radical yield than SOA from photooxida-  
58 tion of naphthalene and fine PM from urban sites (Beijing, Guangzhou, Mainz, Shanghai,  
59 and Xi'an), confirming that HOMs are important constituents of biogenic SOA to generate  
60 radicals. Our study provides new insights into the chemical relationship of HOM abun-  
61 dance, composition, and sources with the yield of radicals by laboratory and ambient aer-  
62 osols, enabling better quantification of component-specific contribution of source- or site-  
63 specific fine PM to its climate and health effects.

## 64 1. INTRODUCTION

65 Secondary organic aerosols (SOA) account for a major fraction of fine particulate matter  
66 (PM<sub>2.5</sub>),<sup>1</sup> which plays a key role in climate change and public health.<sup>2-7</sup> Insights into the  
67 chemical and redox characteristics of SOA are important for properly understanding the  
68 role of fine PM at the atmosphere-biosphere interface.<sup>8</sup> SOA particles contain a large frac-  
69 tion of reactive substances such as peroxides and highly oxygenated molecules (HOMs).<sup>9-</sup>  
70 <sup>12</sup> The HOMs exist in the gas<sup>12-15</sup> and particle phases<sup>16-21</sup> and they increase the oxidation  
71 state and initial growth of organic aerosols, as well as influencing the stability and reactiv-  
72 ity of fine PM upon redox chemistry including radical reactions.<sup>12, 20, 22-24</sup> Therefore, a  
73 comprehensive understanding of the physicochemical properties of HOMs and their rela-  
74 tionship with the oxidative potential of fine PM is challenging but vital to unravel the cli-  
75 mate and health effect of SOA.<sup>24</sup>

76 To date, a few studies have explored the formation mechanism, structure, and chemical  
77 aging processes of particle phase HOMs. For instance, gas phase oxidation of organic com-  
78 pounds including Criegee intermediates has been found as efficient formation pathway of  
79 HOMs.<sup>13, 16, 20, 25-27</sup> Therein, SOA-bound HOMs were suggested to contain multiple func-  
80 tional groups including hydroperoxides and to have molecular formulae with high atom  
81 ratio of oxygen-to-carbon (>0.6 or 0.7).<sup>11-13, 16, 28-30</sup> To subdivide HOMs into different  
82 types, HOMs with carbon oxidation state<sup>31</sup> ( $\overline{OS}_C \approx 2 \cdot \frac{O}{C} - \frac{H}{C}$ )  $\geq 0$  were assigned to be both  
83 highly oxygenated and highly oxidized compounds, while HOMs with  $\overline{OS}_C < 0$  were at-  
84 tributed to be highly oxygenated but less oxidized.<sup>16</sup> Furthermore, HOMs in fresh biogenic  
85 SOA were found to have formulae more closely resembling low-volatile oxygenated or-  
86 ganic aerosols (LV-OOA) than HOMs in aged SOA.<sup>16</sup> Tröstl et al.<sup>11</sup> and Ehn et al.<sup>12</sup> found

87 that HOMs in laboratory-generated  $\alpha$ -pinene SOA fell into the following chemical compo-  
88 sition range of  $C_xH_yO_z$ : monomers with  $x = 8-10$ ,  $y = 12-16$  and  $z = 6-12$ , and dimers with  
89  $x = 17-20$ ,  $y = 26-32$  and  $z = 8-18$ .<sup>12, 32</sup> Beyond this, it has been assumed that organic  
90 peroxides in  $\alpha$ - and  $\beta$ -pinene SOA have molecular weights of  $< 300 \text{ g mol}^{-1}$ ,<sup>33</sup> falling in the  
91 typical molecular weight range of HOM monomers.<sup>12</sup> These peroxides are redox active<sup>11</sup>  
92 and can generate reactive species such as radicals through Fenton-like reactions,<sup>23, 34</sup> and  
93 photolytic or hydrolytic decomposition in water.<sup>23, 35-37</sup> The reactive species are ubiquitous  
94 in atmospheric, environmental, and biological processes exerting strong impacts on climate  
95 change and public health.<sup>38, 39</sup> In addition to organic peroxides, high-molecular weight di-  
96 mer esters have been found as major products in aerosols from cyclohexene and  $\alpha$ -pinene  
97 ozonolysis and boreal forest.<sup>40-42</sup> Therefore, HOMs have different sources, complicated  
98 composition, and various redox activities. Beyond these findings, the volatility, reactivity,  
99 and fate of different source HOMs remain unclear.<sup>24</sup> Insights into these uncertainties will  
100 enable a better assessment of aerosol climate and health effects.

101 In this study, HOMs from all laboratory and ambient samples were defined by molecular  
102 formula matching the criteria from Tröstl et al.<sup>11</sup> filtering out HOM monomers with  $O/C$   
103 ratio  $< 0.7$ .<sup>16</sup> Based on this criterium, we investigated the relative HOM abundance and  
104 radical yield of laboratory SOA formed in a chamber and ambient fine PM in the air rang-  
105 ing from remote forests to highly polluted megacities. The correlation of radical yield of  
106 fine PM in water with relative fraction of HOMs ( $RF_{\text{HOM}}$ ) among organic constituents was  
107 investigated. The  $RF_{\text{HOM}}$  was defined as the ratio of the number of HOMs ions to all for-  
108 mulas identified in a spectrum. The molecular composition of organic aerosol components  
109 was determined using an ultra-high-resolution mass spectrometer,<sup>43, 44</sup> and the radicals in

110 water were identified and quantified using continuous wave electron paramagnetic reso-  
111 nance spectrometry in combination with a spin trapping technique.<sup>36</sup>

## 112 **2. MATERIALS AND METHODS**

113 **2.1 Ambient Particle Sampling.** Ambient particles were collected at seven different loca-  
114 tions: central Amazon, Hyytiälä, Mainz, Beijing, Shanghai, Guangzhou, and Xi'an. De-  
115 tailed information on sampling time and instrumentation can be found in Table S1.

116 The central Amazon fine PM was collected at two different stations. One set of samples  
117 was collected from the site 'T3' of GoAmazon2014/5 located in a pasture area that was 70  
118 km west and downwind of Manaus, Amazonas State, Brazil.<sup>45</sup> These samples were used  
119 for analyzing the  $RF_{HOM}$ . The other set of samples was collected at the Amazon Tall Tower  
120 Observatory (ATTO) station, which is located in a remote area of the central Amazon Ba-  
121 sin, about 150 km northeast (upwind) of the city of Manaus.<sup>46</sup> At the T3 site, a Harvard  
122 impactor (Air Diagnostics, Harrison, ME, USA) and polycarbonate filters ( $\varnothing$  47 mm, Nu-  
123 clepore) and were used for PM collection at an air flow of  $\sim 10$  L  $\text{min}^{-1}$ . Particles were  
124 collected in the dry and wet seasons in 2014 (Table S1). The collected particle samples  
125 were stored in a  $-20$  or  $-80$  °C freezer until analysis. At the ATTO site, a micro-orifice  
126 uniform deposition impactor (MOUDI, model 125R, MSP corporation, USA) collected  
127 sample air from 60 m high inlet at a 80-m tall tower with an air flow rate of  $\sim 10$  L  $\text{min}^{-1}$ .  
128 Afterwards, the filters were transported from ATTO to Mainz in an ice box and then stored  
129 in a  $-80$  °C freezer before analysis. Dry season ATTO PM samples were collected from 20  
130 to 21 October 2017 and 25 to 31 October 2018. These samples were used for analyzing the  
131 relationship between ion number and chromatographic peak area indicated relative abun-  
132 dance of HOMs. Wet season samples were collected from 27 March to 25 April 2017.

133 These samples were used for analyzing the radical yield of PM. More information about  
134 the ATTO tower and the typical characteristics of aerosol particles in the upper troposphere  
135 over the Amazon Basin can be found in previous studies.<sup>46, 47</sup>

136 The Hyytiälä fine PM samples were collected from the boreal forest site SMEAR II in  
137 Finland from 7 July to 4 August 2014 and from 31 May to 19 July 2017. Scots pine and  
138 Norway spruce are the dominant type of trees surrounding the station.<sup>48</sup> A three-stage Dek-  
139 ati PM<sub>10</sub> impactor together with 47 mm diameter quartz fiber (Pallflex Tissuquartz  
140 2500QAT-UP) and Teflon filters (PALL, Teflon) were used for particle sampling. The  
141 quartz filters were pre-baked at 600 °C for half a day to remove organics. The air flow rate  
142 through the sampler was ~35 L min<sup>-1</sup>. After collection, all filter samples were stored at -  
143 20 °C before analysis.

144 The Mainz PM<sub>2.5</sub> samples were collected onto borosilicate glass fiber filters (Ø 70 mm,  
145 Pallflex T60A20, Pall Life Science, USA) using a PM<sub>2.5</sub> low volume air sampler in January  
146 2015 at the campus site of Johannes Gutenberg University of Mainz. Additional fine MP  
147 samples were collected onto 47 mm diameter Teflon filters (100 nm pore size, Merck  
148 Chemicals GmbH) on the roof of the Max Planck Institute for Chemistry with a micro-  
149 orifice uniform deposition impactor (MOUDI, 110-R, MSP Corporation). The samplings  
150 were conducted from August to November 2017 and from March to April 2018. The air  
151 flow rate through both samplers was ~30 L min<sup>-1</sup>. The collected filter samples were stored  
152 in -20 °C (samples collected in 2015) or -80 °C (samples collected in 2017 and 2018)  
153 freezers before analysis. More information about the aerosol sampling and chemical char-  
154 acterization can be found in our recent studies.<sup>49, 50</sup>



155 PM<sub>2.5</sub> samples in urban site of Beijing,<sup>49</sup> Shanghai, and Guangzhou were collected onto  
156 prebaked quartz-fiber filters (8 × 10 inch) in the period between 1 and 23 January 2014  
157 using a high volume air sampler (Tisch, Cleveland, OH, USA) at a flow rate of ~1050 L  
158 min<sup>-1</sup>. Additional PM<sub>2.5</sub> samples were collected at Peking University campus, central urban  
159 region of Beijing, onto 47 mm diameter Teflon filters (100 nm pore size, Merck Chemicals  
160 GmbH) in 2016 and 2017 with a TH-16 sampler (Tianhong company, China) at an air flow  
161 of ~30 L min<sup>-1</sup>. The samples collected in 2014 and 2018 were stored in -20 or -80 °C  
162 freezers before analysis.

163 The Xi'an fine PM samples were collected using a low-pressure cascade impactor  
164 (Tisch TE-20-800, USA) on the roof of Xi'an Jiaotong University in China. The cut-off  
165 aerodynamic diameters of the sampler are 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8, and 9 μm.  
166 Particles were collected onto 90 mm diameter Teflon filters (100 nm pore size, Omnipore  
167 JWVP09025, Millipore). Each particle filter sample was collected for 48 h in the period  
168 between 14 and 22 September 2017. Before sampling, each filter was cleaned, dried, and  
169 weighed.<sup>50</sup> After sampling, filters were stored in a -80 °C freezer before analysis.

170 **2.2 Laboratory SOA Formation and Collection.** To compare the relative HOM abun-  
171 dance in anthropogenic and biogenic SOA, we measured the RF<sub>HOM</sub> in SOA formed from  
172 the oxidation of naphthalene, isoprene, and α-pinene, which were used as SOA precursors  
173 representative for Beijing,<sup>51</sup> Amazon,<sup>52</sup> and Hyytiälä,<sup>53</sup> respectively. Laboratory SOA was  
174 generated in a 7 L quartz flow tube and a laboratory-scale reaction chamber (33 L).<sup>23</sup> α-  
175 pinene SOA particles were generated through gas-phase ozonolysis. The isoprene and  
176 naphthalene SOA were generated through gas-phase photooxidation by •OH radicals. For  
177 the generation of SOA, the O<sub>3</sub> concentration was adjusted in the range of 600-1100 ppb to

178 generate  $\alpha$ -pinene SOA. The \*OH concentrations were estimated to be  $\sim 5.0 \times 10^{11} \text{ cm}^{-3}$  for  
179 the formation of isoprene and naphthalene SOA.<sup>36</sup> Based on a calibration function meas-  
180 ured by gas chromatography-mass spectrometry, the precursor concentration was estimated  
181 to be in the range of 1-2 ppm for  $\alpha$ -pinene and 0.5-1 ppm for isoprene and naphthalene. A  
182 scanning mobility particle sizer (SMPS, GRIMM Aerosol Technik GmbH & Co. KG) was  
183 used to characterize the number and size distribution of SOA particles, which were col-  
184 lected onto 47 mm diameter Teflon filters (JVWP04700, Omnipore membrane filter) and  
185 extracted into water immediately after sampling. More information about the SOA for-  
186 mation, characterization, and collection are described in previous studies.<sup>23, 34, 36</sup>

### 187 **2.3 Ultra-High-Resolution Mass Spectrometer Measurements and Data Processing.**

188 The chemical composition of organics in the Amazon and Hyytiälä 2014 fine PM samples  
189 were identified using a negative ion mode electrospray ionization (ESI) LTQ Orbitrap mass  
190 spectrometer (Thermo Fisher Scientific, MA, USA) at the University of Cambridge. All  
191 other filter samples were analyzed at the Johannes Gutenberg University of Mainz, using  
192 a Q-Exactive Orbitrap MS (Thermo Fisher Scientific, MA, USA) operated in both negative  
193 and positive ion mode ESI and coupled with an ultra-high performance liquid chromatog-  
194 raphy (UHPLC) system (Dionex UltiMate 3000, Thermo Scientific, Germany). A Hypersil  
195 Gold column (C18,  $50 \times 2.0 \text{ mm}$ ,  $1.9 \mu\text{m}$  particle size, Thermo Fisher Scientific, MA,  
196 USA) was used for analyte separation. Eluent A (ultrapure water with 2% acetonitrile and  
197 0.04% formic acid) and eluent B (acetonitrile with 2% ultrapure water) were used in gra-  
198 dient mode with a flow rate of  $500 \mu\text{L min}^{-1}$ . Detailed information on the optimized gradi-  
199 ent can be found in our recent study.<sup>49</sup> Both mass spectrometers were optimized, calibrated

200 and tuned using chemical standard kits. The filter extraction and data processing methods  
201 are the same as we used for organic aerosol composition analysis in previous studies.<sup>49, 54</sup>

202 After obtaining the MS spectrum and UHPLC chromatogram of one sample, we pro-  
203 cessed the data through a non-target screening approach by using the commercially avail-  
204 able software SIEVE® (Thermo Fisher Scientific, MA, USA).<sup>49</sup> Briefly, we searched the  
205 ions with peak abundance  $> 1 \times 10^5$  first, then subtracted the background signals and as-  
206 signed molecular formulae. The number of C, H, O, N, S, and Cl atoms was constrained to  
207 be: 1-39, 1-72, 0-20, 0-7, 0-4, and 0-2 with a tolerance of  $\pm 2$  ppm. Furthermore, the atom  
208 limits of H/C (0.3-3), O/C (0-3), N/C (0-1.3), S/C (0-0.8), and Cl/C (0-0.8) were used to  
209 eliminate chemically unreasonable formulae.

210 **2.4 Continuous Wave Electron Paramagnetic Resonance Measurements.** Continuous  
211 wave electron paramagnetic resonance (EMXplus-10/12, Bruker, Germany) spectrometry  
212 in combination with spin trapping techniques was used to detect radicals. 5-*tert*-Butoxycar-  
213 bonyl-5-methyl-1-pyrroline-N-oxide (BMPO, high purity, Enzo Life Sciences GmbH) was  
214 used as spin trapping agent.<sup>55</sup> The concentration of BMPO in all extracts was 10 mM. The  
215 aqueous PM mass concentration in the extracts of ambient fine PM and laboratory SOA  
216 was in the range of 250-6300  $\mu\text{g mL}^{-1}$ , with higher concentration for ambient fine PM and  
217 lower concentration for laboratory SOA. The aqueous PM mass concentration is defined  
218 here as the total PM mass on the filter cut divided by the volume of extraction solvent. The  
219 EPR parameters used in this study were the same as in our previous studies.<sup>23, 34, 50</sup> A mod-  
220 ulation frequency of 100 kHz, a modulation amplitude of 1, microwave power of 2.1 mW  
221 (20 dB), a receiver gain of 40 dB, a time constant of 0.01 ms, a scan number of 50, and a

222 magnetic field scan of 100 G. The spin fitting and counting methods embedded in the  
223 Bruker software, Xenon, were applied for quantification of radicals.<sup>56</sup>

### 224 **3. RESULTS AND DISCUSSION**

225 **3.1 Spectral Fingerprint of HOMs.** We distinguished HOMs from other organic compo-  
226 nents in ambient fine PM from Beijing, Amazon, Hyytiälä, and laboratory SOA from oxi-  
227 dation of  $\alpha$ -pinene, isoprene, and naphthalene. We found that ion number fraction of HOMs  
228 is in linear positive correlation with the fraction of chromatographic peak area of HOMs  
229 averaged from measured samples (Figure S1a,  $y=2.37 + 0.70 \times x$ ,  $R^2=0.88$ ), with the latter  
230 one showing positive exponential correlation with radical yield of PM (Figure S1b,  $y=0.10$   
231  $+ 0.016 \times \exp(0.37 \times x)$ ,  $R^2=0.99$ ), indicating that  $RF_{HOM}$  may be an indicator of the relative  
232 abundance of particle-phase HOMs. Therefore, we showed the mass spectra as well  $RF$  of  
233 HOMs in Figures 1 and S2.

234 In ambient samples, most HOMs have been found in remote samples dominated by bi-  
235 ogenic SOA, while almost no HOMs found in fine PM in polluted urban sites. The lack of  
236 peaks meeting the HOM criteria in Figure 1a indicates that HOMs account for only a little  
237 fraction of organic components in Beijing fine PM, with a relative fraction of  $\sim 1\%$ . In  
238 contrast to Beijing fine PM, fine particles in remote forest air of the Amazon and Hyytiälä  
239 have much higher  $RF_{HOM}$  of  $\sim 4\%$  (Figure 1b) and  $\sim 13\%$  (Figure 1c), respectively. This  
240 finding agrees well with previous studies, reporting that HOMs and high-molecular weight  
241 dimer esters are major components of fine PM from a measurement site in an agricultural  
242 pasture area in Germany (Melpitz, Leibniz Institute for Tropospheric Research (TROPOS))  
243 and Hyytiälä, respectively.<sup>20,41</sup> Thus, ambient particle-phase HOMs are enriched in organic  
244 aerosols related to biogenic sources.

245 As shown in Figure 1d-1f, naphthalene SOA has the lowest  $RF_{\text{HOM}}$  of ~3% (Figure 1d).  
246 In contrast, relative more HOM molecules were observed in isoprene (~7%, Figure 1e) and  
247  $\alpha$ -pinene SOA (~14%, Figure 1f). The higher  $RF_{\text{HOM}}$  of  $\alpha$ -pinene SOA than naphthalene  
248 SOA agrees with previous studies,<sup>57, 58</sup> and the lower  $RF_{\text{HOM}}$  of naphthalene SOA may  
249 relate to the lower molar yield of extremely low volatile organic compounds (ELVOC) or  
250 HOMs from oxidation of naphthalene (~1.8%) compared with  $\alpha$ -pinene SOA (~3.4%).<sup>19</sup>  
251 In addition, it has been estimated that organic peroxides contributed up to 49%, 85%, 61%,  
252 and 28% of  $\alpha$ -pinene,  $\beta$ -pinene, isoprene, and naphthalene SOA mass, respectively.<sup>33, 36, 59,</sup>  
253 <sup>60</sup> The consistent lower abundance of organic peroxides and HOMs in naphthalene SOA  
254 than in isoprene,  $\alpha$ - and  $\beta$ -pinene SOA may reflect that organic peroxides are one type of  
255 HOMs. Finally, the order of  $RF_{\text{HOM}}$  in the laboratory experiments with naphthalene, iso-  
256 prene, and  $\alpha$ -pinene SOA (Figure 1d-1f) is consistent with ambient fine PM from Beijing,  
257 Amazon, and Hyytiälä (Figure 1a-1c), confirming that oxidation of biogenic volatile or-  
258 ganic compounds including their autoxidation chemistry, is an efficient formation pathway  
259 of ambient particle-phase HOMs.<sup>27</sup> To demonstrate the source dependence of  $RF_{\text{HOM}}$ , it is  
260 useful to clarify the chemical composition and volatility of fine PM-bound HOMs in air  
261 ranging from clean background to heavily polluted areas.

262 **3.2 Chemical Composition of Particle Phase HOMs.** As shown in Figure 2a, HOM prod-  
263 ucts only composed of carbon, hydrogen, and oxygen (CHO) were preferentially found in  
264 laboratory SOA, which was due to the extremely low concentration of  $\text{NO}_x$  during the  
265 experiments. In contrast, ambient fine PM contained relatively little pure CHO compounds  
266 as HOMs, however, increasing with the decrease of air pollution levels from Beijing

267 (~0.4%) to Hyytiälä (~5.1%). In addition to CHO, ambient fine PM also contained sub-  
268 stantial fractions of CHON, CHOS, and CHONS forms of HOMs, with higher RF in  
269 cleaner air. The RF of CHOS and CHONS forms of HOMs in Amazon and Hyytiälä fine  
270 PM accounted for ~2% of total assigned formula, which is comparable to previous findings  
271 of organosulfates contributing 4-30% of aerosol mass in central Amazonia,<sup>61</sup> Hungary, and  
272 the southeastern U.S.<sup>47, 62, 63</sup> Furthermore, we have observed a synchronous increase of the  
273 concentration of NO<sub>x</sub> and nitrogen containing organic compounds at Hyytiälä,<sup>64</sup> which  
274 might reflect the important role of NO<sub>3</sub>-related multigenerational chemistry in organoni-  
275 trate aerosol formation.<sup>65, 66</sup> Beyond this, Table S2 shows that the RF of the total CHOS  
276 subgroup in Shanghai fine PM was ~23%, while the HOMs only account for ~0.4% (Figure  
277 2a). Such a result is in line with previous findings that the major CHOS compounds in  
278 Shanghai organic aerosols were organosulfates, which possess distinctive characteristics  
279 of long aliphatic carbon chains and a low degree of oxidation.<sup>67, 68</sup>

280 In this study, all HOMs were assumed to have the same signal response when we com-  
281 pared their peak areas among different samples. However, different organic compounds  
282 might have different sensitivity in the mass spectrometer in different ionization modes.  
283 Thus, uncertainties exist when comparing the peak areas of HOMs in PM from different  
284 sources. To investigate the impact of ion mode on the RF<sub>HOM</sub>, we compared the RF<sub>HOM</sub> of  
285 different type of PM measured in positive and negative ion modes in Table S3. It was found  
286 that 63-93% of particle-phase HOMs were detected in negative mode. This finding is in  
287 agreement with the study by Tu et al., which found much more HOMs in laboratory-gen-  
288 erated limonene,  $\alpha$ - and  $\beta$ -pinene SOA using a quadrupole-orbitrap mass spectrometer cou-  
289 pled with a negative ion mode ESI probe.<sup>16</sup> Thus, the HOMs detected in negative ESI mode

290 dominate the total HOMs in PM. Furthermore, due to the complexity of the elemental com-  
291 position of HOMs, more insights into their structural characteristics will enable a better  
292 understanding of the connection of different type of HOMs to the oxidative potential of  
293 organic aerosols.

294 **3.3 Volatility of Particle-Phase HOMs.** The volatility of HOMs in fine PM from different  
295 sources was estimated using recently developed parameterization procedure for the vola-  
296 tility of organic compounds.<sup>69</sup> As shown by Figure 2b, laboratory biogenic SOA contained  
297 higher RF of highly oxygenated low volatile and extremely low volatile organic com-  
298 pounds (LVOC and ELVOC types of HOMs) compared to ambient fine PM, which con-  
299 tained less LVOC and ELVOC types of HOMs. In addition, the ELVOC type of HOMs  
300 were not found in isoprene SOA, which may correlate with the low SOA yield of isoprene  
301 and the remarkably low molar yield of gas-phase ELVOC.<sup>57</sup> Furthermore, both LVOC and  
302 ELVOC were not found in Shanghai particulate HOMs, an observation that agrees with a  
303 previous finding of semi-volatile organic compounds and LVOC as dominant component  
304 of CHO subgroup in Shanghai winter fine PM.<sup>68</sup> The RF trend in the ambient samples of  
305 LVOC and ELVOC types of HOMs in Figure 2b resembles CHO form of HOMs in Figure  
306 2a, likely reflecting that particle phase HOMs are mainly low volatile CHO species. The  
307 generally higher RF of LVOC and ELVOC types of HOMs in the CHOS and CHONS  
308 subgroups (Figure S3) indicates that atmospheric nitrogen or sulfur chemistry of particulate  
309 HOMs may decrease the volatility and change the oxidative characteristics of organic aer-  
310 osols.

311 **3.4 HOM Monomers and Dimers in fine PM.** Figure 2c showed the RF of HOM mono-  
312 mers and dimers in ambient fine PM and laboratory SOA. The HOM monomers were found

313 in all analysed particle samples, whereas HOM dimers were only found in fine PM from  
314 lightly polluted urban air (Mainz), remote forest air (Amazon and Hyytiälä), and laboratory  
315 SOA from  $\alpha$ - and  $\beta$ -pinene. The absence of HOM dimers in isoprene-derived SOA may be  
316 due to the high volatility of products during the photochemical oxidation of isoprene pre-  
317 cursor in the chamber.<sup>57</sup> The relative fraction of dimers in all PM samples increased in the  
318 order of polluted urban fine PM < remote forest fine PM < monoterpene SOA, which resem-  
319 bles the trend of  $RF_{HOM}$ . The  $\alpha$ - and  $\beta$ -pinene SOA were mainly composed of HOM dimers,  
320 with RF of ~12% and ~9%, supporting previous findings of high-molecular weight dimer  
321 esters as major products in aerosols from  $\alpha$ -pinene ozonolysis and boreal forest.<sup>40, 41</sup> Krapf  
322 et al. found that peroxide-containing HOMs have half-lives shorter than 1 hr under dark  
323 conditions and are thermodynamically unstable.<sup>11</sup> Thus, the extremely low relative fraction  
324 of particle phase HOM dimers in urban air may relate to the chemical aging and decompo-  
325 sition of HOMs in ambient fine PM. Furthermore, chemical aging of HOMs via redox  
326 chemistry of  $NO_x$  or sulfur oxides may change the composition and physicochemical prop-  
327 erties of particle phase HOMs in urban fine PM. For example, recent studies have shown  
328 that atmospheric sulfur chemistry of HOMs<sup>70</sup> and reactive nitrogen chemistry in aerosol  
329 water<sup>71</sup> can be sources of organic and inorganic sulfates, respectively. Finally, it has been  
330 found that  $NO_x$  chemistry could alter the abundance of organic peroxides in laboratory  
331 SOA.<sup>59, 60</sup> This might be a reason for the low abundance of HOM dimers in urban PM,  
332 because the HOMs always contain multiple peroxide functionalities.<sup>17</sup>

333 **3.5 Oxidation State of HOMs.** Both  $O/C$  ratio and oxidation state of carbon ( $\overline{OS}_C$ ) were  
334 used to describe the oxidation degree of HOMs,<sup>31</sup> where the  $\overline{OS}_C = -\sum_i OS_i \frac{n_i}{n_C}$  and the  $OS_i$   
335 is the oxidation state associated with element  $i$ , and the  $n_i/n_C$  is the molar ratio of element



336 *i* to carbon. We found that Beijing HOM monomers (Figure 3a) had an *O/C* ratio of 0.89,  
337 which is lower than Amazon HOM monomers (0.95) but higher than Hyytiälä monomers  
338 (0.88). Such a trend is inconsistent with the RF of HOMs and may not reflect the oxidation  
339 state of organic aerosols properly. Therefore, we plotted the *O/C* and *H/C* ratios of HOMs  
340 as well as  $\overline{OS}_C$  for different values in Figure 3. To obtain  $\overline{OS}_C$ , we assumed the oxidation  
341 state of *N* and *S* to be +5 and +6 respectively. We found that the oxidation state of carbon  
342 in HOM monomers in fine PM from Beijing (-0.11, Figure 3a) is on average lower than in  
343 the Amazon (-0.06, black circles in Figure 3b) and Hyytiälä (0.21, black circles in Figure  
344 3c). This may relate to the stronger contribution of alkane derivatives from gasoline and  
345 lubrication oil vapors from anthropogenic emissions in Beijing.<sup>72</sup> Furthermore, Beijing fine  
346 PM contained amounts of HOM dimers below the detection limit (Figure 2c), whereas  
347 Amazon and Hyytiälä fine PM contained a large fraction of HOM dimers (pink circles in  
348 Figure 3b and 3c) exhibiting typical  $\overline{OS}_C$  between -1.0 (red dotted line) and 0.0 (blue dot-  
349 ted line), with average values of -0.64 and -0.59, respectively. Therefore, the oxidation  
350 state and RF of HOMs (Figure 2c) in Beijing, Amazon, and Hyytiälä were observed in the  
351 same range, however, with higher values for the cleaner sites.

352 To compare the oxidation state characteristics of HOMs in anthropogenic and biogenic  
353 SOA, Figure 3d-3f show the *O/C* and *H/C* ratios of laboratory-generated naphthalene, iso-  
354 prene, and  $\alpha$ -pinene SOA as well as the  $\overline{OS}_C$  lines. We found that the HOM monomers in  
355 naphthalene SOA had a larger *O/C* ratio (1.06) than biogenic SOA (isoprene: 0.90, and  $\alpha$ -  
356 pinene: 0.78), and the  $\overline{OS}_C$  of HOM monomers in naphthalene SOA (0.73) is also higher  
357 than in isoprene (0.14) and  $\alpha$ -pinene SOA (-0.65), which is different from the lower  $\overline{OS}_C$   
358 of HOM monomers in Beijing fine PM than in Amazon and Hyytiälä fine PM. This may

359 be due to the different chemical aging processes of ambient fine PM from laboratory SOA,  
360 e.g., the absence of NO<sub>x</sub>- and SO<sub>2</sub>-related chemistry in our chamber experiments. Finally,  
361 ~20%, ~43%, and ~62% of the HOMs in Beijing (Figure 3a), Amazon (Figure 3b), and  
362 Hyytiälä (Figure 3c) fine PM had an oxidation state between -1.0 and 0.0. Similarly, none,  
363 ~19%, and ~91% of the HOMs in naphthalene (Figure 3d), isoprene (Figure 3e), and  $\alpha$ -  
364 pinene SOA (Figure 3f) had the same range of oxidation states. This consistency indicates  
365 that highly oxygenated but less oxidized HOMs should determine the oxidative potential  
366 of ambient fine PM and laboratory SOA.<sup>16</sup>

367 **3.6 Yield and Formation Potential of Radicals by Ambient fine PM.** To characterize  
368 the reactive species formation potential of ambient fine PM, we measured the radical yield  
369 and radical formation potential of fine PM from different sources in water. The results are  
370 shown in Figures 4, 5, and S4. Figure 4a displays the EPR spectra of BMPO-radical adducts  
371 formed in fine PM water extracts with BMPO. The multiple peaks in the spectra indicate  
372 the formation of different radicals. Individual peaks were assigned to adducts of  $\cdot\text{OH}$ ,  $\text{O}_2\cdot^-$ ,  
373 C- and O-centered radicals, respectively. Figure 4b shows the relative fraction of formed  
374 radicals ( $\text{RF}_{\text{radical}}$ ), and the amount of individual radicals quantified based on spin-fitting  
375 and -counting techniques.<sup>36</sup> The fine PM from highly polluted megacities such as Shanghai,  
376 Guangzhou, and Beijing mainly generated  $\cdot\text{OH}$  and  $\text{O}_2\cdot^-$  radicals, whereas the fine PM from  
377 less polluted urban and remote forest sites of Mainz, Amazon, and Hyytiälä dominantly  
378 yielded organic radicals. The higher yield of  $\cdot\text{OH}$  and  $\text{O}_2\cdot^-$  by fine PM from highly polluted  
379 megacities may be related to the enhanced Fenton-like reactions associated with higher  
380 abundance of water-soluble transition metals.<sup>73</sup> The lower  $\cdot\text{OH}$  but higher organic radical

381 yield of fine PM from the Amazon and Hyytiälä may be due to Fenton-like reactions initi-  
382 ated by transition metals and relatively stable organic hydroperoxides,<sup>23, 35, 36</sup> and also the  
383 interaction of  $\cdot\text{OH}$  with SOA material.<sup>74</sup>

384 Beyond the  $\text{RF}_{\text{radical}}$ , the radical yield from a given mass of particles or the formation  
385 potential in a given volume of air can also reflect radical formation of fine PM. Figure 5a  
386 shows that the sample-volume-normalized radical formation potential of ambient fine PM  
387 has a positive linear correlation with  $\text{PM}_{2.5}$  concentration ( $R^2 = 0.85$ ):  $y = 1.47 + 0.11 \times x$ .  
388 Shanghai fine PM exhibited the highest formation potential of  $\sim 15 \text{ pmol m}^{-3}$  radicals in  
389  $\sim 96 \mu\text{g m}^{-3}$   $\text{PM}_{2.5}$ , whereas  $\sim 3.5 \mu\text{g m}^{-3}$  Amazon  $\text{PM}_{2.5}$  generated only  $\sim 3 \text{ pmol m}^{-3}$  radicals.  
390 Thus, the radical formation potential of fine PM may become a metric reflecting the relative  
391 health risk of different concentrations of fine PM in air ranging from clean background to  
392 heavily polluted areas. As indicated in Figure 3, the oxidation state of HOMs in fine PM  
393 from remote forests (Amazon and Hyytiälä) and laboratory  $\alpha$ -pinene SOA was mainly in  
394 the range of -1.0-1.0. Thus, we assume that radical formation by organic aerosols in water  
395 was mainly driven by highly oxygenated but less oxidized HOMs,<sup>16</sup> which had molecular  
396 formulae similar to low-volatile oxygenated organic aerosols.<sup>16, 75</sup> Figure 5b shows the aer-  
397 osol-sample-mass-normalized total radical yield of ambient fine PM, which shows a neg-  
398 ative power-law correlation with  $\text{PM}_{2.5}$  concentrations ( $R^2 = 0.90$ ):  $y = x^{-0.43}$ . Specifically,  
399 the Hyytiälä fine PM had the highest radical yield of  $\sim 0.7 \text{ pmol } \mu\text{g}^{-1}$ , while the fine PM  
400 from Xi'an, Beijing, Guangzhou, and Shanghai generated only 0.1-0.2  $\text{pmol } \mu\text{g}^{-1}$  radicals.  
401 The trend of higher radical yield from fine PM at remote forest sites compared to urban  
402 sites resembles the organic radical yield in Figure 4b and Figure S4 as well as the  $\text{RF}_{\text{HOM}}$

403 in Figure 2, supporting the conclusion that HOMs represent important source for radicals,  
404 especially organic radicals in water.

405 A previous study showed that at -20 °C, the concentration of peroxides in  $\alpha$ -pinene SOA  
406 decreased < 20% in one week.<sup>35</sup> In this study, the laboratory SOA were collected immedi-  
407 ately after their formation and analyzed within 4 hours. Thus, the influence of aging effects  
408 on the relative HOM abundance and radical yield of laboratory SOA is negligible. Regard-  
409 ing the ambient PM samples, their  $RF_{HOM}$  and radical yield were measured within a few  
410 days. Therefore, particle aging should not influence the relationship of  $RF_{HOM}$  and radical  
411 yield in Figure 6 significantly.

412 **3.7 Association of  $RF_{HOM}$  with Radical Yield.** As shown in Figure 6 and S1b, both radical  
413 yields of ambient fine PM ( $y=0.071 + 0.015 \times \exp(0.44 \times x)$ ,  $R^2 = 0.74$ ) and laboratory  
414 SOA ( $y=1.8 + 0.011 \times \exp(0.52 \times x)$ ,  $R^2 = 0.92$ ) showed positive exponential correlations  
415 with the  $RF_{HOM}$  and chromatographic peak area fraction of HOMs, with the laboratory  
416 SOA showing a higher radical yield. This may reflect the different redox activity of HOMs  
417 in ambient fine PM and laboratory SOA. The larger deviations of radical yield and  $RF_{HOM}$   
418 of Amazon and Hyytiälä fine PM than urban fine PM may be due to the seasonal or year-  
419 to-year aerosol composition variations due to changing meteorological conditions.<sup>43, 64, 76</sup>  
420 In contrast to ambient fine PM, laboratory SOA had much higher radical yield. Among  
421 laboratory SOA,  $\beta$ -pinene SOA had the highest  $RF_{HOM}$  of ~11.5% and radical yield of ~5.9  
422  $\text{pmol } \mu\text{g}^{-1}$ , whereas naphthalene SOA had the lowest  $RF_{HOM}$  of ~3.3% and radical yield of  
423 ~1.8  $\text{pmol } \mu\text{g}^{-1}$ . Isoprene and  $\alpha$ -pinene SOA exhibited similar  $RF_{HOM}$  of ~10.4% and  
424 ~10.0%, and radical yields of ~4.5 and ~3.4  $\text{pmol } \mu\text{g}^{-1}$ . The higher radical yield of labora-  
425 tory SOA may mainly be due to the higher relative fraction of CHO forms of HOMs in

426 fresh laboratory SOA (Figure 3b). The consistent positive exponential correlations of  
427  $RF_{HOM}$  and radical yield of ambient fine PM and laboratory SOA strongly indicate that  
428 HOMs are closely associated with the radical formation by PM in water.

429 To explore the influence of ionization mode during mass spectrometry analysis on the  
430 association of radical yield by PM with  $RF_{HOM}$ , we show the Spearman correlation coeffi-  
431 cients ( $r$ ) of radical yields ( $\text{pmol } \mu\text{g}^{-1}$ ) with chemical groups analyzed in negative mode,  
432 positive mode, and their sum in Table S4. It can be seen that radical yield has close corre-  
433 lation with RF of total HOMs, HOM dimer, and LVOC type of HOMs identified in the  
434 different modes. Therefore, Tables S3 and S4 indicate that  $RF_{HOM}$  measured in negative  
435 mode resembles the distribution of total HOMs in fine PM.

436 To explore the association of different types of HOMs with the radical yield, we calcu-  
437 lated the Spearman correlation matrix<sup>77</sup> of total HOMs and individual chemical subgroups  
438 with the aerosol-sample-mass-normalized radical yield (Figure 7 and Table S4, method see  
439 SI). As shown in Figure 7, blue colors and negative values indicate negative correlations,  
440 and red colors and positive values indicate positive correlations. When Spearman  $r$  is  $\geq 0$ ,  
441 lighter color represents weaker correlation, vice versa for negative Spearman  $r$ . The relative  
442 fraction of total HOMs showed one of the strongest correlations with the yield of total  
443 radicals (Spearman  $r = 0.92$ ), confirming the important role of HOMs in generating radi-  
444 cals. Moreover, the CHO forms of HOMs showed close positive correlation with the total  
445 radical yield (Spearman  $r = 0.91$ ). In contrast, the CHON form of HOMs showed much  
446 weaker correlation with total radical yield (Spearman  $r = 0.13$ ). Furthermore, both CHOS  
447 and CHONS forms of HOMs had negative correlations with the radical yield (Spearman  $r$   
448 = -0.30 and -0.35). Therefore, the CHO forms of HOMs may play stronger roles than

449 CHON, CHOS, and CHONS forms of HOMs in radical formation, and atmospheric chem-  
450 istry of nitrogen or sulfur should decrease the radical yield of organic aerosols in water.  
451 This can be explained by the decreased abundance of organic hydroperoxides upon for-  
452 mation of organic nitrates.<sup>66, 78, 79</sup> In addition to the CHO form of HOMs, the highly oxy-  
453 genated SVOC and LVOC subgroups also showed close correlation with total radical yield  
454 (Spearman  $r = 0.56$  and  $0.95$ ), which is in line with the lower RF of ELVOCs in the CHO  
455 form of HOMs (Figure S3). Furthermore, the HOM dimers showed a closer correlation  
456 with the total radical yield of fine PM (Spearman  $r=0.94$ ), reflecting an important role of  
457 HOM dimers in generating radicals. This is consistent with previous findings of higher  
458 oxidation potential of oligomer-rich fractions of SOA from polycyclic aromatic hydrocar-  
459 bons.<sup>80</sup> In contrast, the HOM monomers had weak correlation with the radical yield (Spear-  
460 man  $r=0.23$ ), indicating that HOM monomers may decompose and lost more efficiently  
461 during particle aging. This hypothesis is supported by the finding of Krapf et al., which  
462 demonstrated that organic peroxides in  $\alpha$ -pinene SOA are thermodynamically unstable  
463 with half-lives shorter than 1 hr under dark conditions.<sup>11</sup> In addition, other studies also  
464 found that organic peroxides including organic hydroperoxides might be involved in the  
465 formation of organosulfates,<sup>20</sup> oligomers,<sup>81</sup> and radicals in water.<sup>23, 34-36</sup> Therefore, organic  
466 peroxides may undergo heterogeneous chemical reactions during atmospheric aging pro-  
467 cesses. Given the presence of peroxide functional groups in HOMs, we speculate that the  
468 weak correlation of HOM monomers with the radical yield of fine PM from different  
469 sources may be due to aging processes of particle-phase HOMs. Furthermore, organic-  
470 metal interactions have shown synergistic effects in producing reactive oxygen species.<sup>80</sup>  
471 <sup>82</sup> Thus, we suggest that the close correlation of  $RF_{HOM}$  with radical formation may also

472 relate to redox chemistry involving metal ions. Finally, Table S4 and Figure S5 indicate  
473 that radical yields of ambient fine PM and laboratory SOA have a weak negative correla-  
474 tion with the *O/C* ratio (Spearman  $r=-0.42$ ) and oxidation state ( $\overline{OS_C}$ ) (Spearman  $r = -0.3$ )  
475 of totally assigned compounds, supporting the conclusion of highly oxygenated but less  
476 oxidized HOMs as important radical precursor of fine PM in water.

477 In conclusion, we found that HOMs are closely associated with the radical formation by  
478 ambient fine PM and laboratory-generated SOA in water. The formed radicals may influ-  
479 ence the formation and evolution of SOA through multigenerational chemical processes.<sup>8</sup>  
480 <sup>24, 83-86</sup> For example, aqueous-phase chemistry of HOMs has been suggested to be a major  
481 pathway for the formation of organosulfates.<sup>70, 87</sup> In addition, HOMs are suggested to con-  
482 tain at least one, and often multiple, hydroperoxide, peroxide, or peroxy acid groups.<sup>24</sup>  
483 These reactive functional groups may initiate redox chemistry including Fenton-like reac-  
484 tions,<sup>23, 28, 35, 74, 88-90</sup> which may change the reactivity and role of fine PM during atmos-  
485 pheric processing. Beyond their climate effects, HOMs may exert adverse health effects  
486 due to the enrichment of organic peroxides and their ability to generate reactive species.  
487 For instance, exposure of lung epithelial cells to photochemically aged SOA showed in-  
488 creased toxic effects, which may relate to the elevated abundance of peroxides in aged  
489 SOA.<sup>88</sup> Thus, our findings may provide new insights in quantifying the contribution of  
490 specific components to climate and health effects of fine PM from different sources.<sup>91</sup> Con-  
491 sidering that HOMs widely exist in both biogenic and anthropogenic organic aerosols, the  
492 seasonality dependence and physicochemical properties of HOMs from different sources  
493 and their exact role in environmental and biological processes need to be investigated. Fi-

494 nally, during the ESI-MS measurement, ion suppression, ion enhancement, solvent inter-  
495 action, and adduct formation etc. may influence the HOM detectability or the sensitivity of  
496 the method in distinguishing different type of HOMs, which warrants follow-up studies.



497 **ASSOCIATED CONTENT**

498 **Supporting Information**

499 Supporting material consists of three tables and four figures.

500

501 **AUTHOR INFORMATION**

502 **Corresponding Author**

503 \*E-mail: h.tong@mpic.de. Tel: +4961313057040.

504 \*E-mail: hoffmant@uni-mainz.de. Tel: +4961313925716.

505 \*E-mail: markus.kalberer@unibas.ch. Tel: +41612070701.

506

507 **ORCID**

508 Haijie Tong: 0000-0001-9887-7836

509 Maosheng Yao: 0000-0002-1442-8054

510 Christopher Pöhlker: 0000-0001-6958-425X

511 Meinrat O. Andreae: 0000-0003-1968-7925

512 Manabu Shiraiwa: 0000-0003-2532-5373

513 Ulrich Pöschl: 0000-0003-1412-3557

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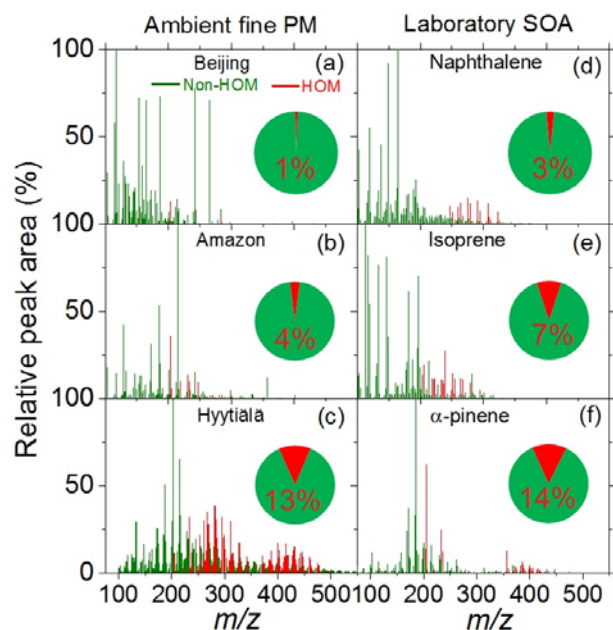
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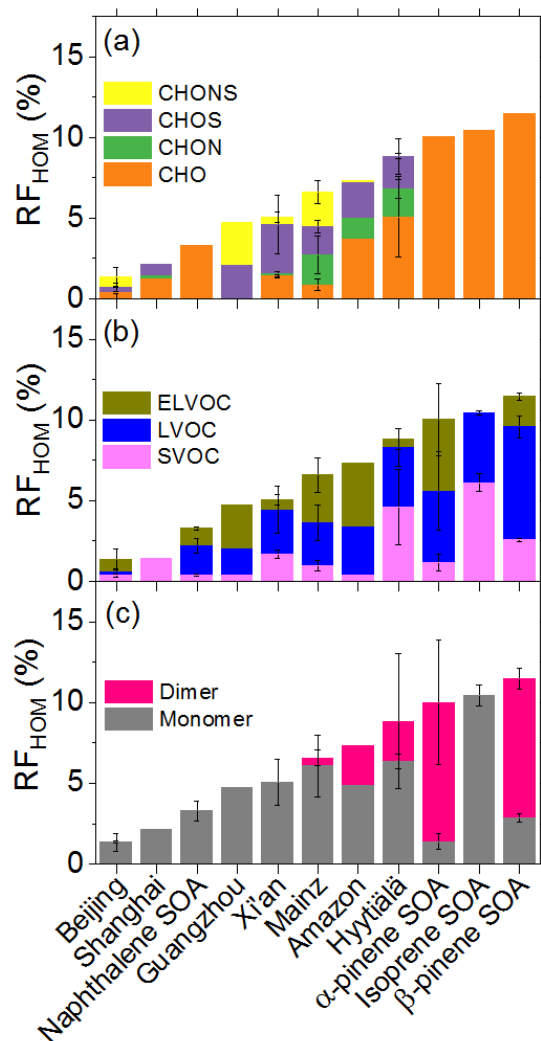
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- 906



907  
 908 **Figure 1.** The spectral fingerprint and relative fraction of HOMs (red) and non-HOMs (green) in  
 909 different type of particles. The mass spectra were measured using LC-MS technique. The chroma-  
 910 tographic peak areas were used to calculate relative fractions of HOMs for the pie charts. The rel-  
 911 ative peak area (%) of the spectra belonging to HOMs in ambient PM and laboratory SOA were  
 912 multiplied by a factor of 3 and 10, respectively. The pie charts and enclosed numbers indicate the  
 913 ion number fraction of HOMs and non-HOMs. The spectra in panel a-c are for PM samples col-  
 914 lected in January 2017, October 2018, and July-August 2014.  
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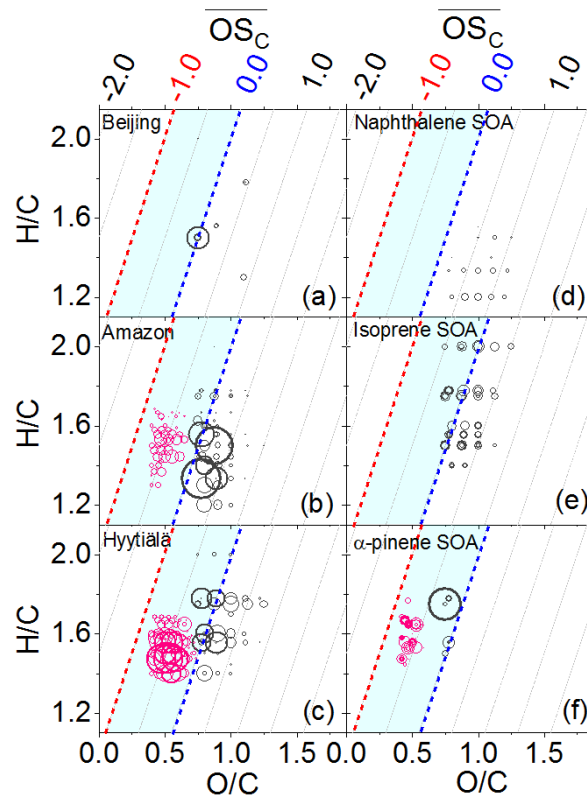
917 **Figure 2.** Chemical composition and volatility of HOMs in fine particles from different sources.

918 (a) Chemical composition of HOMs. (b) Relative fractions of HOMs with different volatility. (c)

919 Relative fractions of HOM dimers and monomers. The error bars represent the standard deviations

920 of measurements with more than three individual samples.

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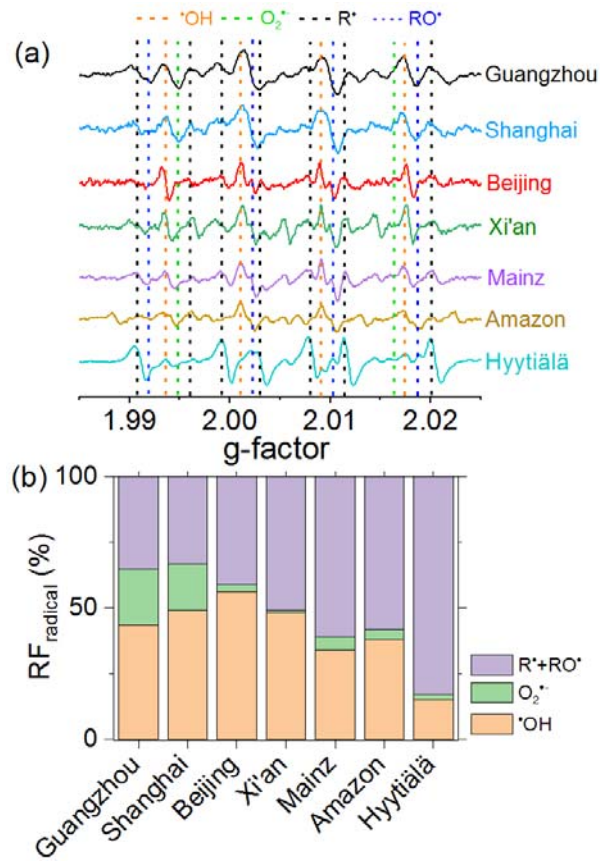


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923 **Figure 3.** Van Krevelen and oxidation state diagrams for HOMs in fine PM from Beijing (a),  
 924 Amazon (b), and Hyytiälä (c) as well as in SOA from oxidation of naphthalene (d), isoprene (e),  
 925 and  $\alpha$ -pinene (f). The red and blue dotted lines represent  $\overline{OS}_C = -1.0$  and  $0.0$ , respectively. The cyan  
 926 shaded areas represent oxidation states ranging from  $-1.0$  to  $0.0$ . Pink and dark grey data points  
 927 represent HOM dimers and monomers, respectively. The size of the symbols reflects the relative  
 928 peak intensities in the mass spectra. The scaling factor for Amazon and Hyytiälä monomers is 1  
 929 and for other data points it is 3. The results in panel a-c were based on selected fine PM samples  
 930 collected in November 2017, June 2017, and March-October 2014, respectively.

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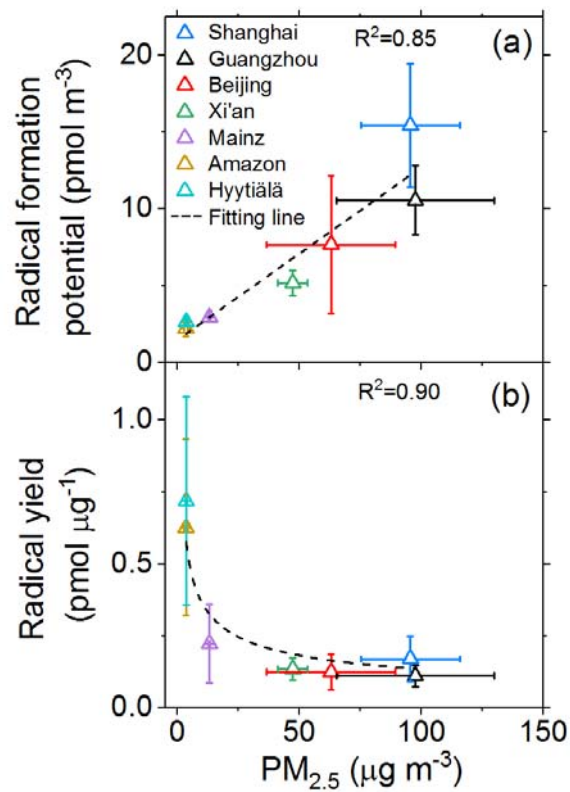
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934 **Figure 4.** (a) EPR spectra and (b) relative fraction of radicals ( $\text{RF}_{\text{radical}}$ ) formed by ambient fine

935 particles. The yellow, green, black, and blue dashed lines in panel (a) indicate the peaks assigned

936 to  $\cdot\text{OH}$ ,  $\text{O}_2^{\cdot-}$ , C- and O-centered radicals, respectively.

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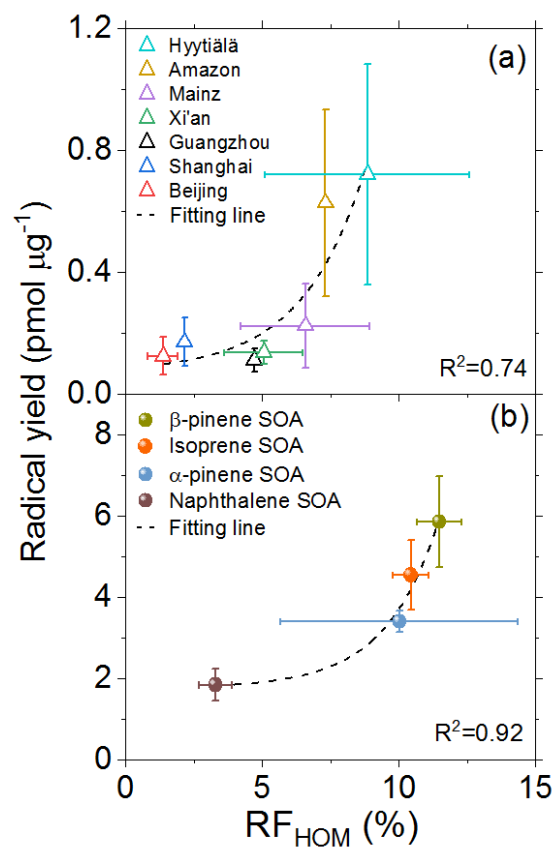
939 **Figure 5.** Correlation of air sample volume (a) and particle mass (b) normalized radical yields with

940 PM<sub>2.5</sub> concentrations. The error bars represent the standard deviation of measurements with more

941 than three individual samples.

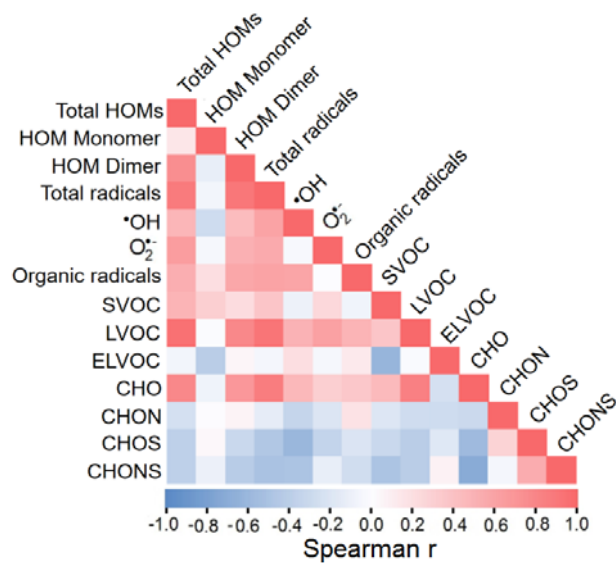
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 945 **Figure 6.** Correlation of particle mass normalized radical yield with relative ion number fraction  
 946 of HOMs associated with ambient fine PM (a) and laboratory SOA (b). The error bars represent  
 947 the standard deviation of measurement from replicates.  
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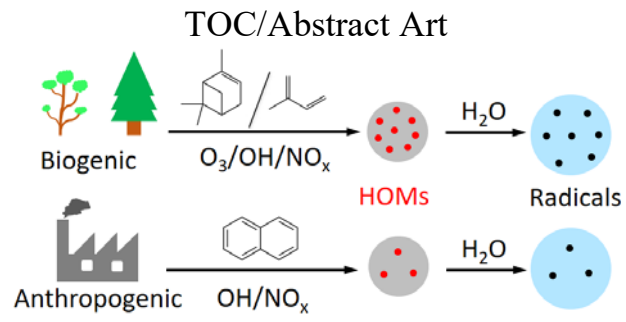


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950 **Figure 7.** Spearman correlation matrix of HOM relative abundance and aerosol mass normalized  
 951 radical yield.

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