



*Supplement of*

## **Seasonal variation in oxygenated organic molecules in urban Beijing and their contribution to secondary organic aerosol**

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8      **Section S1. Determination of Original OOM Molecule**

9      In the measurement of nitrate CIMS, one OOM molecule (X) could be detected as deprotonated ion ( $X^-$ ), adduct with  
10      $\text{NO}_3^-$  ( $X \bullet \text{NO}_3^-$ ) or adduct with  $\text{HNO}_3 \bullet \text{NO}_3^-$  ( $X \bullet \text{HNO}_3\text{NO}_3^-$ ). The acidity of OOM molecules is not very strong so that  
11     they hardly exist in de-protonated ions. In Ehn et al., by using isotopically labeled nitric acid ( $\text{H}^{15}\text{NO}_3$ ) as the reagent, it  
12     was found that OOMs mainly existed as adducts with  $\text{NO}_3^-$ , and to a lesser extent with  $\text{HNO}_3\text{NO}_3^-$  (Ehn et al., 2014).  
13     This is because the binding energy of OOMs with  $\text{NO}_3^-$  is smaller than with  $\text{HNO}_3\text{NO}_3^-$  (Hyttinen et al., 2015).

14     Besides, the evidence that most OOMs cluster with  $\text{NO}_3^-$  could also be found from the time variations of corresponding  
15     OOMs. As shown in Fig. S1, the time variations of  $\text{C}_7\text{H}_{10}\text{O}_5\text{NO}_3^-$  and  $\text{C}_7\text{H}_{11}\text{O}_8\text{NNO}_3^-$  are not consistent, indicating that  
16     they are different OOMs charged both by  $\text{NO}_3^-$ , instead of the same OOM charged by  $\text{NO}_3^-$  and  $\text{HNO}_3\text{NO}_3^-$ , respectively.  
17     This is also the same for other OOMs, such as  $\text{C}_8\text{H}_{12}\text{O}_5\text{NO}_3^-$  and  $\text{C}_8\text{H}_{13}\text{O}_8\text{NNO}_3^-$ .

18     From the above discussion, we know that OOM molecules are primarily detected as clusters with  $\text{NO}_3^-$ . ( $X \bullet \text{NO}_3^-$ ).  
19     Therefore, the original formula of a detected ion Y could be obtained based on the following criteria:  
20     a. If there is no nitrogen atom in Y, it is treated as a deprotonated species.  
21     b. If there is at least one nitrogen atom in Y, it is treated as an adduct with  $\text{NO}_3^-$ .

22      **Section S2. Definition of Oxygenated Organic Molecules (OOMs)**

23      The terminology OOMs comes from the term HOMs (Highly Oxygenated Organic Molecules), which is defined based  
24      on three criteria (Bianchi et al., 2019): a. HOMs are formed via autoxidation involving peroxy radicals, b. HOMs are  
25      formed in the gas phase under atmospherically relevant conditions, and c. HOMs typically contain six or more oxygen  
26      atoms. However, when looking into the oxygenated organic molecules measured at urban Beijing, the criteria of a. and  
27      c. are not always met. For example, in the oxidation processes, precursor VOCs may undergo multi-generation oxidation  
28      (Zaytsev et al., 2019; Garmash et al., 2020) and the autoxidation is sometimes suppressed by high  $\text{NO}_x$  level. This leads  
29      to the fact that not all organic molecules measured by nitrate CIMS contain six or more oxygen atoms (see Fig. S7). This  
30      is the reason why we didn't use the term HOMs.

31      OOMs is a more general terminology that refers to the gas phase organic compounds which are formed via oxidation  
32      process under atmospheric conditions. Thus, the guidelines for the classification of OOMs should be:

- 33      a. OOMs are the gas-phase oxygen-containing organic molecules detected under atmospherically relevant conditions.  
34      b. OOMs can be formed via oxidations in the gas phase, heterogeneous reactions on aerosol surface, or evaporated  
35      processes from aerosols.

36      **Section S3. Estimation of OOM Volatility**

37      Detailed structure information of OOMs in real atmosphere is still unknown, therefore, the volatility of each OOM  
38      molecule was estimated based on a parameterization using numbers of different atoms (Donahue et al., 2011). For the  
39      oxidation products from monoterpenes, previous studies show that except from hydroxyl (-OH), carbonyl (=O) and  
40      carboxyl (-O=O) groups, hydroperoxide (-OOH) also takes a large portion (Tröstl et al., 2016; Stolzenburg et al.,  
41      2018). Then by assuming that all nitrogen atoms exist as organonitrate groups (-ONO<sub>2</sub>), the saturation mass  
42      concentration of OOM molecule at 300 K can be given as follows (Mohr et al., 2019):

43            $\log_{10}C^*(300K) = (25 - nC) \cdot bC - (nO - 3nN) \cdot bO - 2 * \left[ \frac{(nO - 3nN) \cdot nC}{nC + nO - 3nN} \right] \cdot bCO - nN \cdot bN$  (1)

44 where  $nC$ ,  $nO$  and  $nN$  are the numbers of carbon, oxygen, and nitrogen in each molecule respectively, and  $bC=0.475$ ,  
 45  $bO=0.2$ ,  $bCO=0.9$ , and  $bN=2.5$ . For oxidation products from aromatics, the work of Wang et al. shows that they possess  
 46 more hydroxyl and carbonyl groups as well as less hydroperoxides, and that their estimated saturation concentrations  
 47 suggested by Donahue et al. (Donahue et al., 2011) match well with the experiment ones (Wang et al., 2020). Therefore,  
 48 for those non-monoterpene OOMs, the estimation from Donahue et al. was applied:

49            $\log_{10}C^*(300K) = (25 - nC) \cdot bC - nO_{eff} \cdot bO - 2 * \left( \frac{nC \cdot nO_{eff}}{nC + nO_{eff}} \right) \cdot bCO$  (2)

50 where  $nC$ ,  $nO_{eff}$  and  $nN$  are the numbers of carbon, effective oxygen and nitrogen in each molecule separately, and  
 51  $bC=0.475$ ,  $bO=2.3$ , and  $bCO=-0.3$ .

52 The temperature dependence of  $C^*$  is given by the Clausius-Clapeyron equation (Epstein et al., 2010;Donahue et al.,  
 53 2012), which we can be approximated as:

54            $\log_{10}C^*(T) = \log_{10}C^*(300K) + \frac{\Delta H_{vap}}{R \ln(10)} \left( \frac{1}{300} - \frac{1}{T} \right)$  (3)

55 where the evaporation enthalpy  $\Delta H_{vap}$  can be linked with  $\log_{10}C^*(300K)$  according to the following equation:

56            $\Delta H_{vap} [\text{kJ mol}^{-1}] = -5.7 \cdot \log_{10}C^*(300K) + 129$  (4)

57 After the temperature related saturation concentrations were calculated, OOMs were then grouped into different bins  
 58 based on the volatility basis set (VBS) (Donahue et al., 2006), and further classified as ELVOCs (extremely low volatility  
 59 organic compounds), LVOCs (low volatility organic compounds), SVOCs (semi-volatile organic compounds), IVOCs  
 60 (intermediate volatility organic compounds) and VOCs (volatile organic compounds) according to their volatilities  
 61 (Donahue et al., 2012).

## 62 Section S4. Uncertainty Discussion on OOM Volatility Estimation

63 The derived OOM volatility may vary among different methods. Volatility parameterization based on numbers of  
 64 different atoms originated from the work of Donahue (Donahue et al., 2011). This study gave a good volatility estimation  
 65 for OOMs which only contain carbon, hydrogen and nitrogen atoms, and meet the requirements of containing mostly  
 66 hydroxyl, carbonyl and carboxyl groups and possessing equal fraction of hydroxyl and carbonyl.

67 With deeper understanding of monoterpene oxidation mechanism during the past decade, many studies have found  
 68 that hydroperoxide is also a key functional group of monoterpene oxidation products (Ehn et al., 2014;Jokinen et al.,  
 69 2014;Praplan et al., 2015;Berndt et al., 2016). Based on the proposed structures of those products, the group-contribution  
 70 method SIMPOL could be applied to calculate the volatilities of monoterpene-derived OOMs. And the results were  
 71 further used for revising the original volatility parameterization (Tröstl et al., 2016;Stolzenburg et al., 2018;Mohr et al.,  
 72 2019;Bianchi et al., 2019). And therefore, the volatility estimation of monoterpene OOMs based on Eq. 1 should be  
 73 pretty robust and has the least uncertainty compared with other types of OOMs.

74 For aromatic OOMs, the volatility estimation according to Eq. 2 was also evaluated by Wang et al. (Wang et al.,  
 75 2020). In this work, the oxidation experiments of toluene and naphthalene by OH radical were performed under

76 conditions similar to typical urban environments. Results showed that this equation works well for toluene dimers,  
77 naphthalene monomers and naphthalene dimers, while overestimates the volatility a little bit for toluene monomers. In  
78 our study, it is likely that most aromatic OOMs are in the form of monomers. And thus, the values of  $\log_{10}C^*$  for aromatic  
79 OOMs derived from Eq. 2 might be overestimated slightly.

80 The chemical pathways of atmospheric isoprene oxidation have been investigated for years. Early studies showed  
81 that carbonyl, hydroxyl and organonitrate groups are the main functional groups of isoprene OOMs (Lee et al.,  
82 2014; Schwantes et al., 2015). In recent years, some studies found that hydroperoxide could also be formed through the  
83 process of intramolecular H-shift (Wang et al., 2018b; Zhao et al., 2021; Wu et al., 2021). However, different from the  
84 stable hydroperoxides on monoterpene OOMs, some hydroperoxides on isoprene OOMs are unstable and may undergo  
85 fragmentation (Teng et al., 2017). Besides, this formation of hydroperoxides tend to occur under low- $\text{NO}_x$  or  
86 experimentally design conditions (D'Ambro et al., 2017; Zhao et al., 2021; Wu et al., 2021). Therefore, the fraction of  
87 hydroperoxide groups on isoprene OOMs could not be taken directly from experimental results. Fortunately, the work  
88 of Xu et al. (Xu et al., 2021) provided us valuable information of observed isoprene OOMs in Nanjing, one of the Chinese  
89 megacities. Results showed that there is large fraction of organonitrate groups and probably small fraction of  
90 hydroperoxide groups for isoprene OOMs formed under megacity atmosphere. And this is reason why we didn't apply  
91 the volatility parameterization from monoterpene OOMs, which contain large fraction of hydroperoxides, to isoprene  
92 OOMs. In addition, the work of Wu et al. (Wu et al., 2021) estimated the volatility of isoprene nitrates by comparing the  
93 difference between two sets of experiments with and without seed aerosol addition. But as seed aerosols inevitably  
94 brought in heterogeneous reactions on the surface and liquid phase reactions in the particle phase, this method seems not  
95 suitable for volatility acquisition. Future thermal desorption experiments like the one conducted by Wang et al. (Wang  
96 et al., 2020) may give better estimation.

97 For aliphatic OOMs, direct volatility parameterization has been lacking, and only few studies proposed its formation  
98 pathways. Conventional knowledge suggests that the oxidation products from alkanes as well as alkenes mainly contain  
99 carbonyl, hydroxyl and organonitrate groups (Ziemann, 2011), while possibilities still remain for the formation of  
100 hydroperoxides (Rissanen et al., 2014; Rissanen, 2018; Wang et al., 2021). Yet, the lack of mechanism on aliphatic OOM  
101 formation under urban-related atmospheric conditions hampers the understanding of aliphatic OOM structures. Thus we  
102 are not able to decide whether Eq. 1 or Eq. 2 is more suitable for them.

103 To solve this problem, we calculated aliphatic OOM volatility with both methods the results were summarized in Fig.  
104 S2. Although some difference appears for detailed volatility distribution, the concentrations of condensable aliphatic  
105 OOMs (ELVOCs and LVOCs) based on Eq. 1 and Eq. 2 are very consistent. And therefore, the contribution of aliphatic  
106 OOMs to SOA condensation growth will not be influenced too much by the method chosen. In this study, we finally use  
107 Eq. 2 to calculate the volatility of aliphatic OOMs.

108 **Section S5. Simulation of OOM Net Condensation Flux**

109 An aerosol growth model was used to calculate the OOM net condensation flux onto particles (Tröstl et al.,  
 110 Stolzenburg et al., 2018). This model is based on the VBS distribution mentioned above, and each VBS bin is  
 111 regarded as a single surrogate species with the averaged mass and concentration.

112 The condensation flux,  $\dot{\varrho}_{i,p}$ , of low volatile OOMs at each moment can be simulated as:

113 
$$\dot{\varrho}_{i,p} = N_p \cdot \sigma_{i,p} \cdot k_{i,p} \cdot F_{i,p}$$

114 where  $N_p$ ,  $\sigma_{i,p}$ ,  $k_{i,p}$  and  $F_{i,p}$  are the particle number concentration at a given size ( $p$ ), the particle-vapor collision cross-  
 115 section between each VBS bin ( $i$ ) and a given particle size ( $p$ ), the deposition rate of OOM vapor at the particle surface,  
 116 and the driving force of condensation respectively.  $\sigma_{i,p}$  is derived from the particle diameter  $d_p$  and vapor diameter  $d_i$   
 117 as:

118 
$$\sigma_{i,p} = \pi/4(d_p + d_i)^2$$

119 The deposition rate of OOMs,  $k_{i,p}$ , depends on the center mass velocity of particle and vapor  $v_{i,p}$ , the mass  
 120 accommodation coefficient  $\alpha_{i,p}$ , and the non-continuum dynamic factor  $\beta_{i,p}$ :

121 
$$k_{i,p} = \alpha_{i,p} v_{i,p} \beta_{i,p}$$

122 where  $v_{i,p} = \sqrt{\frac{8RT}{\pi\mu_{i,p}}}$ , is the average velocity for Maxwell's velocity distribution law.  $\mu_{i,p}$  is the reduced mass and is  
 123 defined as  $\frac{M_i M_p}{M_i + M_p}$ .

124 The driving force of condensation is defined as:

125 
$$F_{i,p} = C_i^0 (S_i - a'_{i,p})$$

126 where  $C_i^0$ ,  $S_i$  and  $a'_{i,p}$  are the saturation vapor concentration, saturation ratio and particle phase activity of each VBS bin,  
 127 respectively. The excess saturation ratio  $S_i^{XS} = S_i - a'_{i,p}$  is the key diagnostic for condensation.  $a'_{i,p}$  accounts for particle  
 128 mixture effect with Raoult term  $X_{i,p} \gamma_{i,p}$  and curvature effect with Kelvin term  $K_{i,p}$  as:

129 
$$a'_{i,p} = X_{i,p} \gamma_{i,p} K_{i,p}$$

130 where  $X_{i,p}$  is the mass fraction of organic compounds of each VBS bin ( $i$ ) in the condensed phase at given particle size  
 131 ( $p$ ), and  $\gamma_{i,p}$  is the mass based activity coefficient in the condensed phase. In this study,  $\gamma_{i,p} = 1$  was used with the  
 132 assumption of ideal solution. The Kelvin term,  $K_{i,p} = \exp\left(\frac{4\sigma_p M_i}{RT\rho_p D_p}\right)$ , is related to surface tension  $\sigma_p$ , molar weight  $M_i$   
 133 and density  $\rho_p$ .

134 For OOMs with relatively higher volatility (i.e.,  $C_i^* > 0.1 \text{ } \mu\text{g m}^{-3}$ ), their partitioning between the gas and condensed  
 135 phase will likely reach equilibrium when the condensation and evaporation of OOMs are approximately equal. Then the  
 136 fraction of species  $i$  in condensed phase,  $f_i^{\text{aer}}$ , can be described by the aerosol partition theory (Seinfeld and Pandis, 2016)  
 137 as:

138 
$$f_i^{\text{aer}} = \frac{1}{1 + C_i^*/C_{OA}^{\text{aer}}} = \frac{C_i^{\text{aer}}}{C_i}$$

139 where  $C_i^*$ ,  $C_i$ ,  $C_{OA}^{aer}$ , and  $C_i^{aer}$  are the effective saturation concentration of the OOMs vapor in each VBS bin, total mass  
140 concentration of species i in the gas and condensed phase, total mass concentration of organic aerosol, and mass  
141 concentration of species i in the condensed phase.

142 The seasonal variations of OOM condensation fluxes for low volatility OOMs (ELVOCs and LVOCs) and high  
143 volatility OOMs (SVOCs, IVOCs and VOCs) are shown in Fig. S3 (A) and (B) respectively. It can be found that,  
144 compared with low volatility OOMs, the condensation flux of high volatility OOMs is minor, and the net flux of them  
145 onto particles are zero over a period of time. Consequently, the rate of OOMs condensing onto particles could be  
146 approximately estimated based on the condensation of ELVOCs and LVOCs.

147 According to the above model, the condensation flux is mainly influenced by the oversaturation of OOMs and the  
148 surface area of aerosols ( $Area_{aero}$ ). Since ELVOCs and LVOCs undergo almost irreversible condensation (Ehn et al.,  
149 2014), their gas phase concentration is nearly the same as their oversaturated concentration. Therefore, we further looked  
150 into the relationship between condensation flux and ELVOC and LVOC concentration ( $[ELVOCs+LVOCs]$ ) times  
151  $Area_{aero}$ . Results in Fig. S4 show that they have perfect linear correlation in all four seasons. The slope in the figure  
152 represents the ability of ELVOCs and LVOCs forming SOA through condensation, to be more specific, the amount of  
153 SOA produced through condensation by unit concentration of ELVOCs and LVOCs ( $1 \mu\text{g}/\text{m}^3$ ) under unit aerosol surface  
154 concentration ( $1 \text{ m}^2/\text{m}^3$ ) in an hour. This condensation ability of ELVOCs and LVOCs is quite stable during the year  
155 ( $6.3\text{--}8.4 \text{ m}^2 \cdot \text{m}^{-3} \cdot \text{h}$ ). And its influencing factors are possibly particle composition, concentration of gaseous vapors and  
156 the interaction between vapors and particle surface.

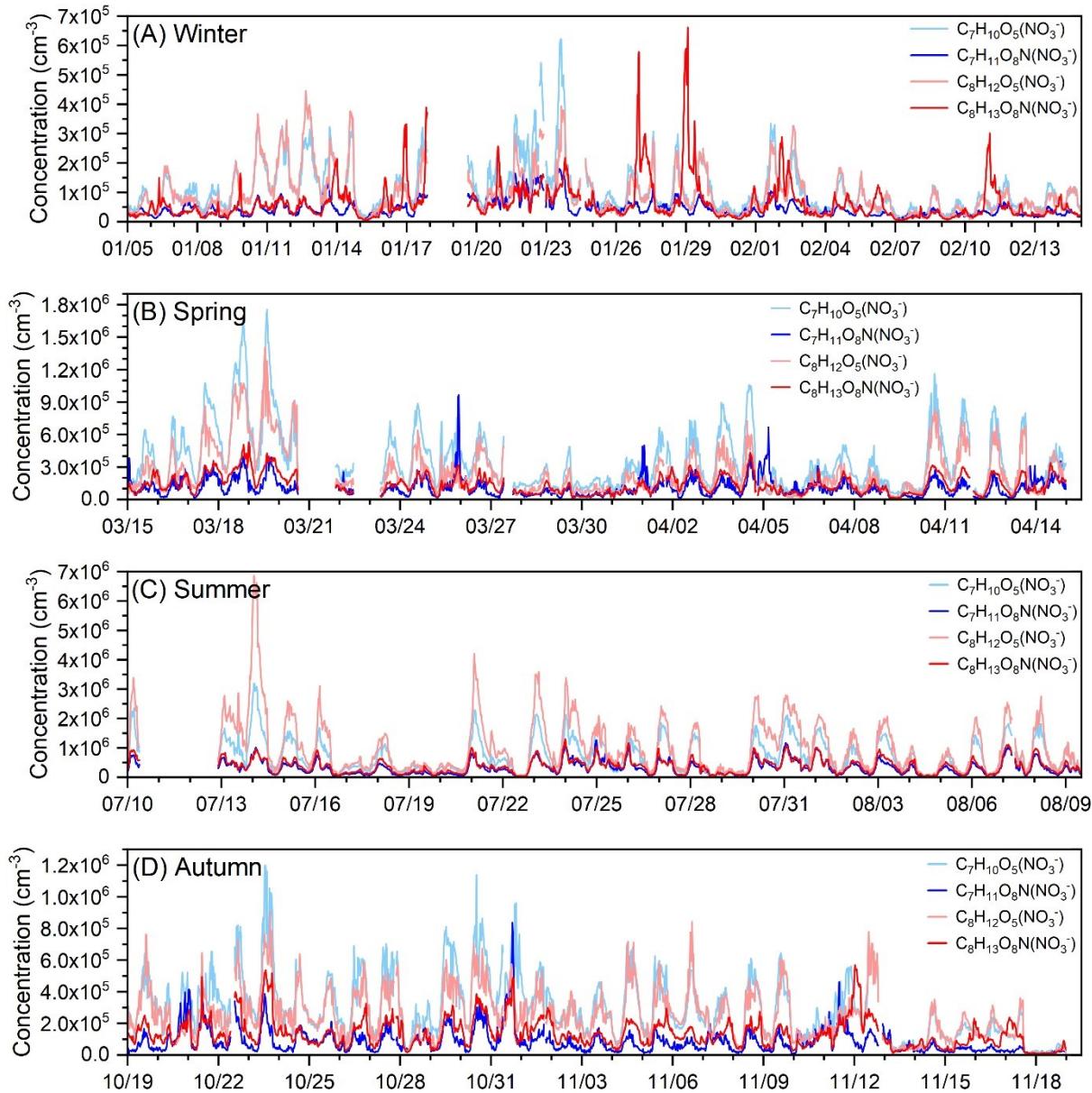
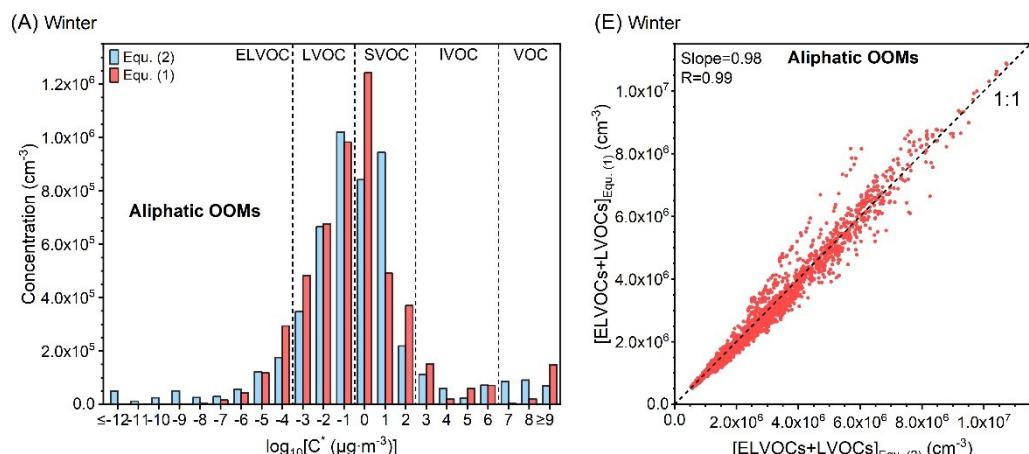
## 157 **Section S6. Definition of Characteristic Accumulation Time**

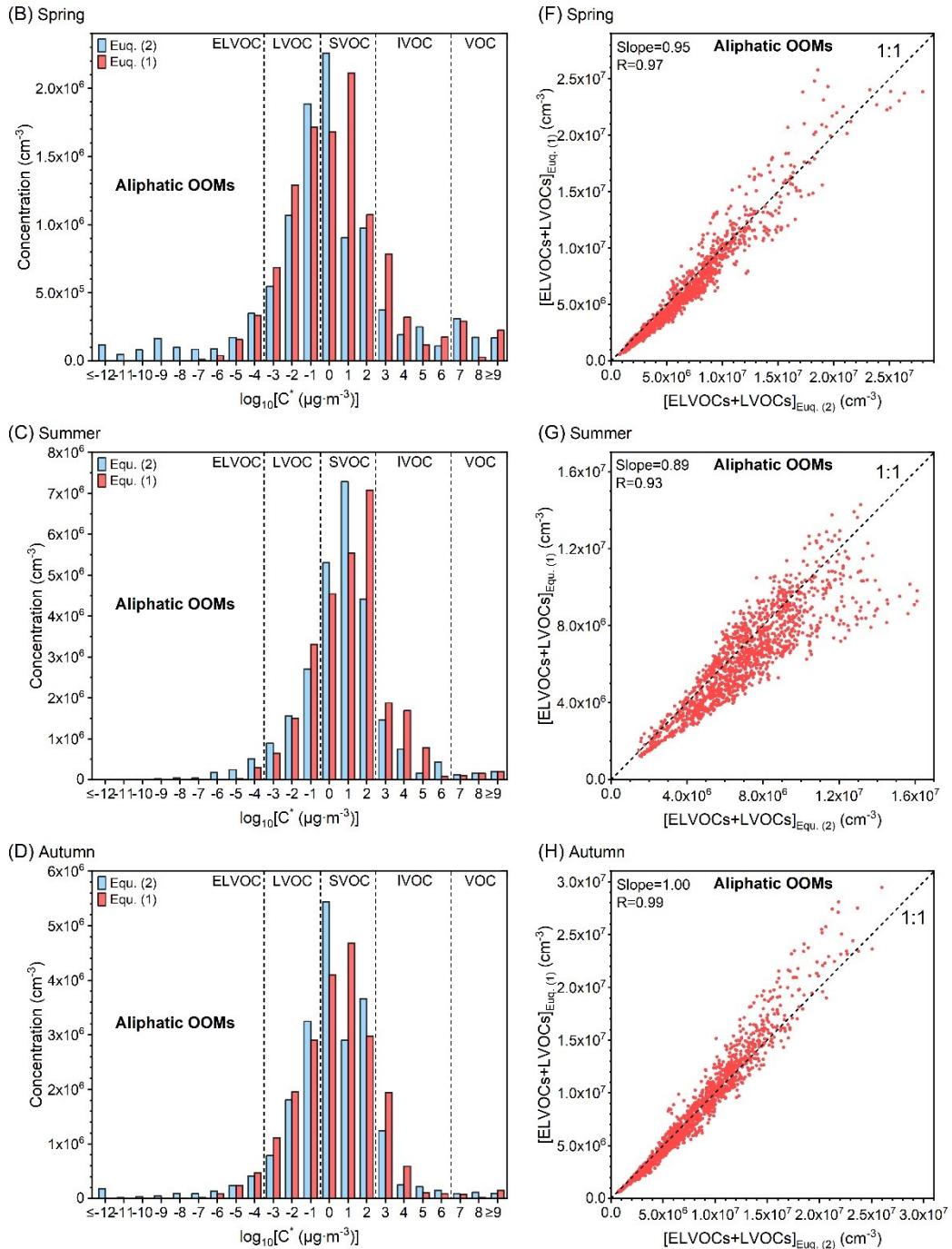
158 The characteristic accumulation time (AccTime), which is introduced for roughly comparison of SOA formation rates  
159 from OOM condensation among different seasons, is defined as:

$$160 \quad AccTime = \frac{[SOA]}{[CondenFlux]_{ELVOC+LVOC}}$$

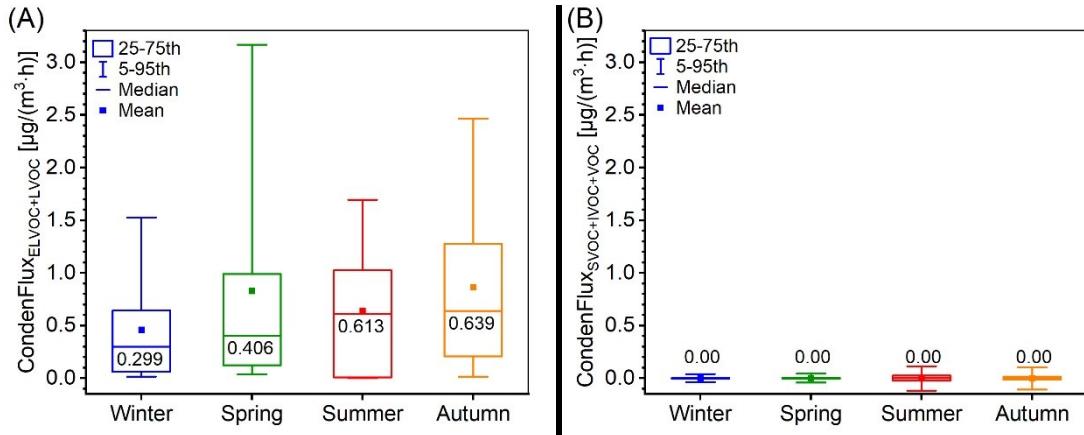
161 where [SOA] is the mass concentration of SOA in  $\mu\text{g}\cdot\text{m}^{-3}$ , and  $[CondenFlux]_{ELVOC+LVOC}$  is the mass condensation flux of  
162 OOMs in  $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ , and therefore, AccTime is in the unit of hour.

163 In real atmosphere, there are various SOA sources. So this AccTime should not be interpreted as that SOA is entirely  
164 formed from OOM condensation within this characteristic time, but only a straightforward estimation of how fast SOA  
165 is formed if its source only comes from OOM condensation.

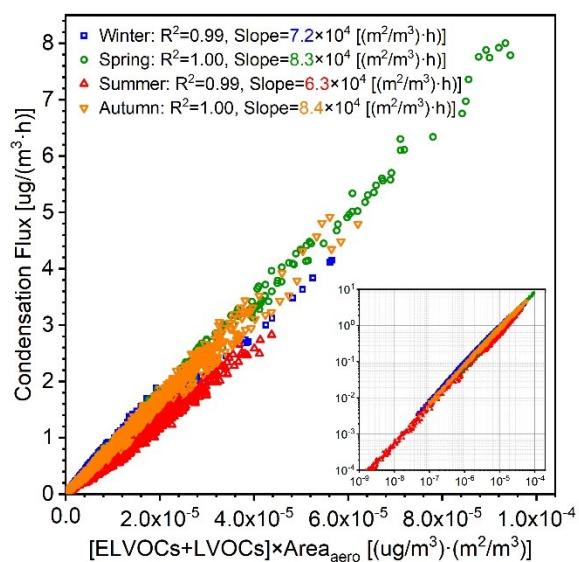
**FIGURES****Figure S1.** The time variations of  $C_7H_{10}O_5(NO_3^-)$ ,  $C_7H_{11}O_8N(NO_3^-)$ ,  $C_8H_{12}O_5(NO_3^-)$  and  $C_8H_{13}O_8N(NO_3^-)$  during four seasons.



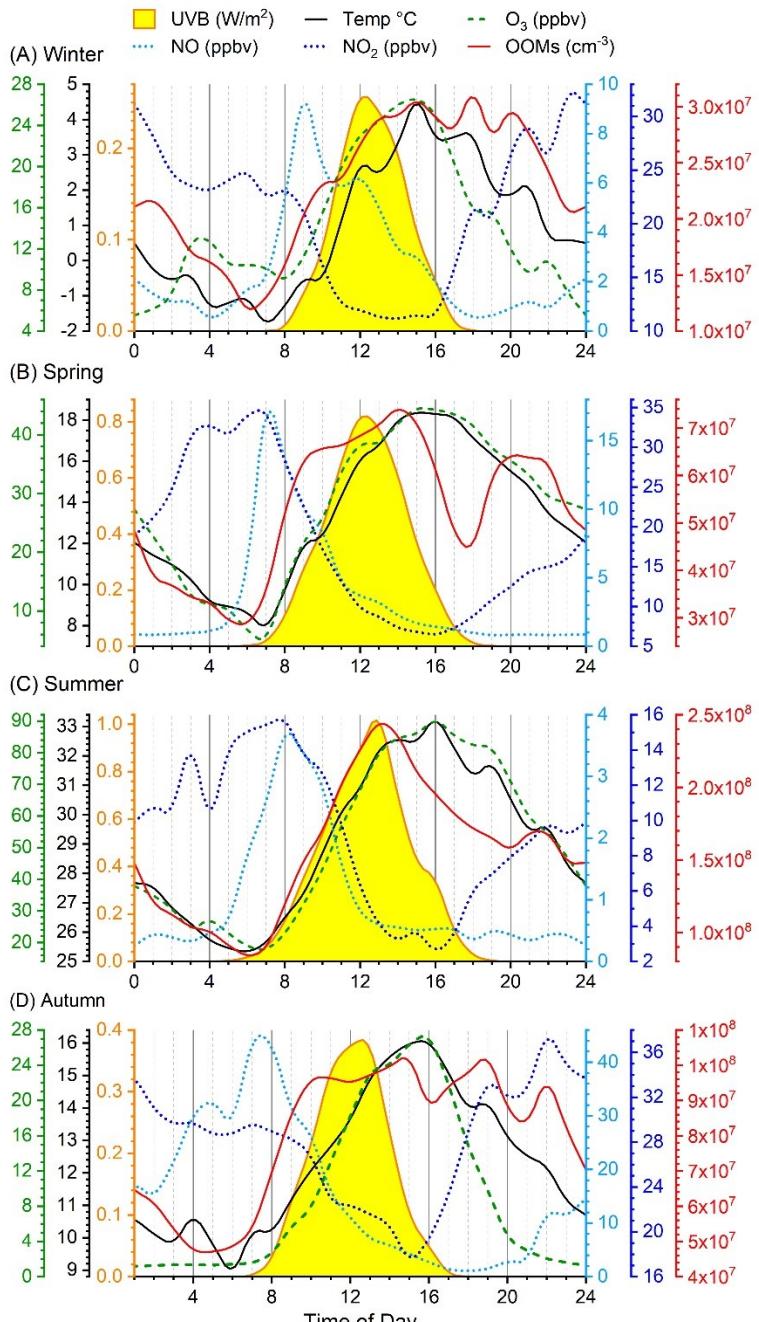
**Figure S2.** (A) - (D) Estimated aliphatic OOM volatility distribution derived from two parameterization methods for four seasons. (E) - (F) Comparison of aliphatic OOM concentrations belonging to ELVOCs and LVOCs between two parameterization methods for four seasons. In Fig. (E) to (F), the slopes of least-square linear fit and Pearson coefficients are also listed.



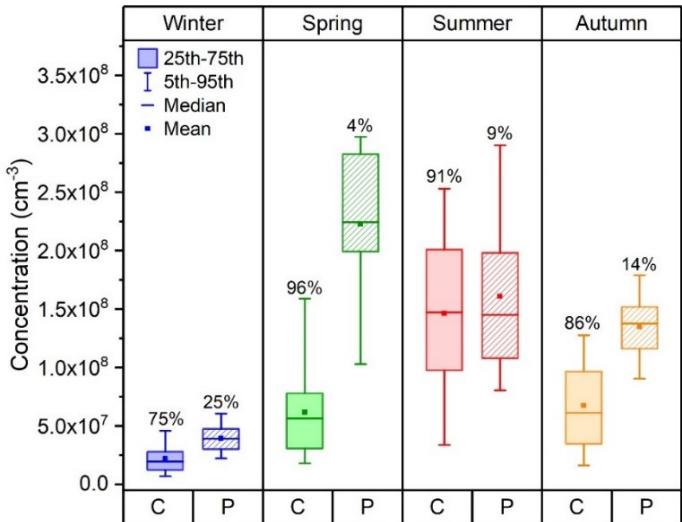
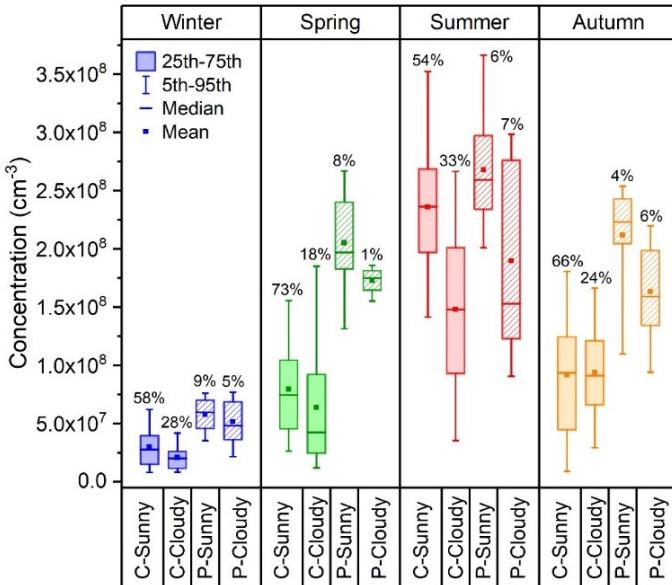
**Figure S3.** Condensation fluxes of (A) low volatility OOMs (ELVOCs and LVOCs) estimated by the particle dynamic model (Tröstl et al., 2016), and (B) high volatility OOMs (SVOCs, IVOCs and VOCs) calculated based on the aerosol partition theory (Seinfeld and Pandis, 2016) in four seasons. The values in each box are the median values.



**Figure S4.** Relationship between OOM condensation flux and concentration of ELVOCs and LVOCs ( $[\text{ELVOCs} + \text{LVOCs}]$ ) times aerosol surface area ( $\text{Area}_{\text{aero}}$ ). The figure inserted is in log scale.



191  
192 **Figure S5.** Diurnals variations of UVB, temperature (Temp), mixing ratio of O<sub>3</sub>, NO and NO<sub>2</sub>, and OOM concentration in four  
193 seasons.  
194



195

**Figure S6.** Left panel: Concentration of total OOMs in four seasons under different atmospheric conditions during daytime (08:00-16:00). The abbreviations “C” and “P” represent clean and polluted condition respectively. Clean and polluted conditions are divided by PM<sub>2.5</sub> with a value of 75 µg/m<sup>3</sup>. Sunny and cloudy day are distinguished by brightness parameter (Dada et al., 2017) with a value of 0.5. The percentages are fractions taken up by each condition in each season. Right panel: Concentration of total OOMs in four seasons under different atmospheric conditions during nighttime (20:00-04:00 next day). The abbreviations “C” and “P” represent clean and polluted respectively. Those two conditions are divided by PM<sub>2.5</sub> with a value of 75 µg/m<sup>3</sup>. The percentages are fractions taken up by each condition in each season.

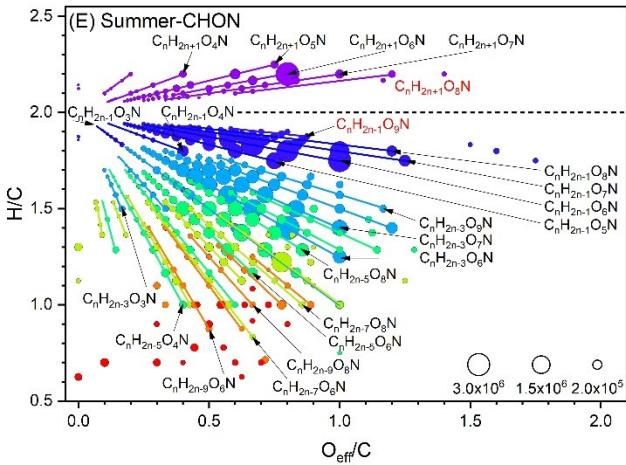
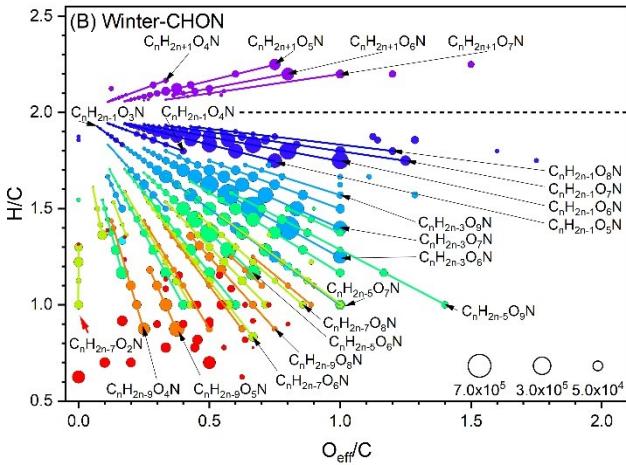
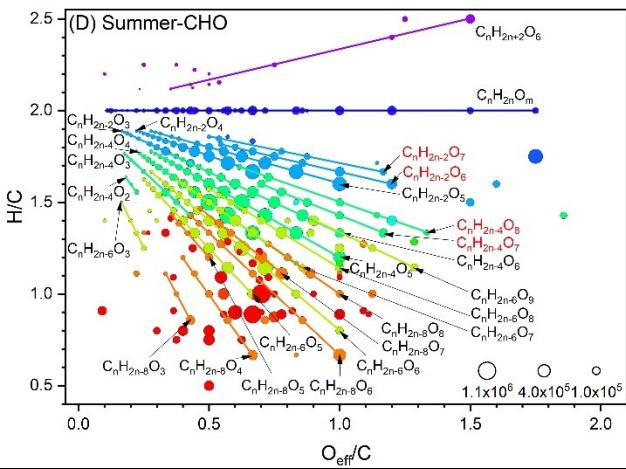
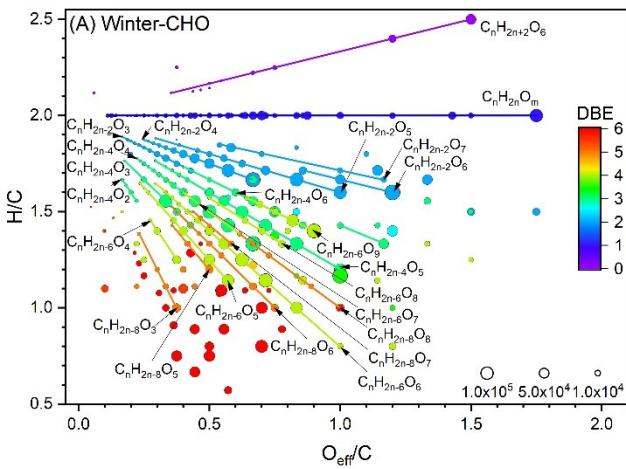
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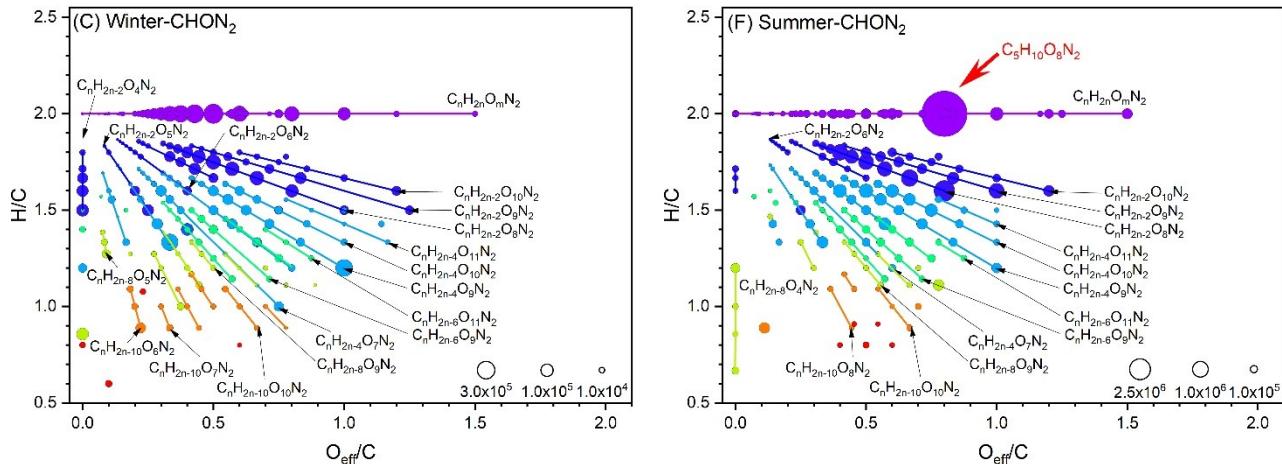
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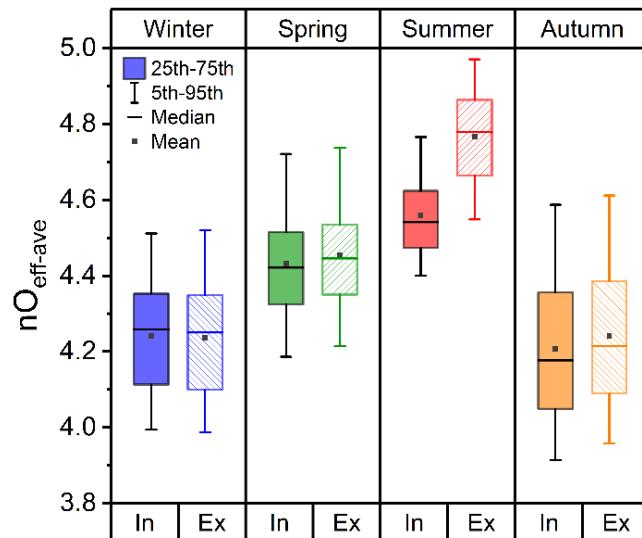
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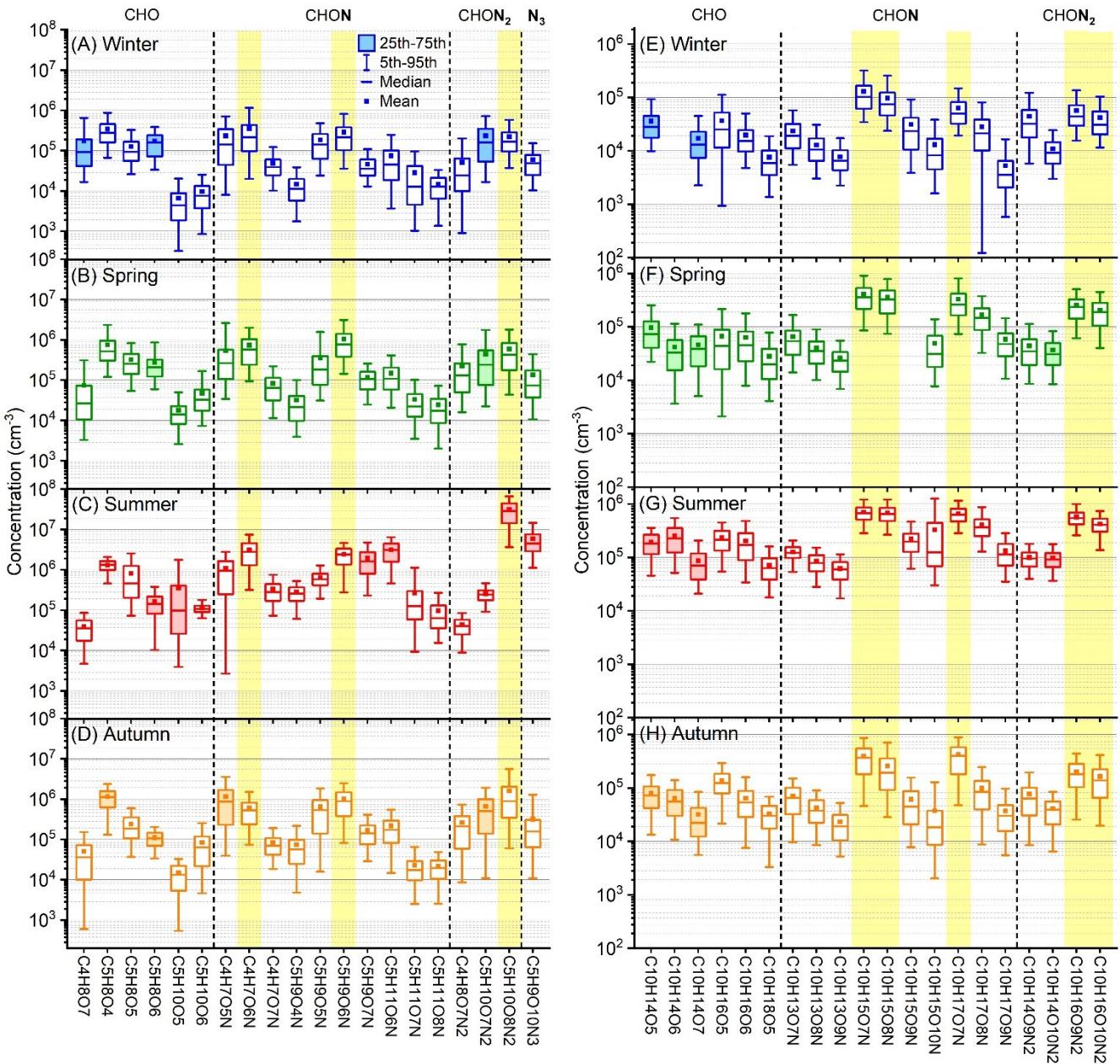




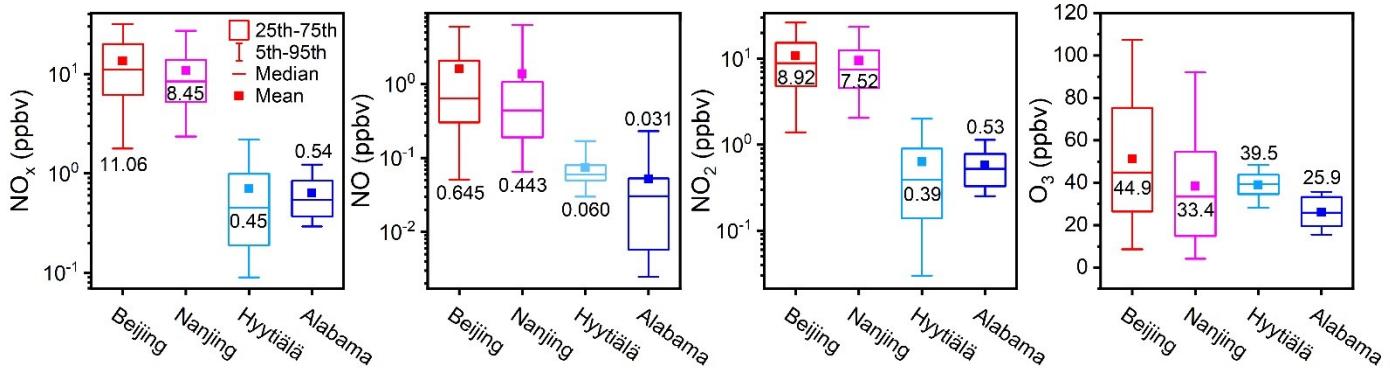
**Figure S7.** The ratio of hydrogen number to carbon number (H/C) against the corresponding ratio of effective oxygen number to carbon number ( $O_{eff}/C$ ) for (A) winter CHO OOMs, (B) winter CHON OOMs, (C) winter  $CHON_2$  OOMs, (D) summer CHO OOMs, (E) summer CHON OOMs, and (F) summer  $CHON_2$  OOMs. The size relates to the concentration of each OOMs molecules. CHO OOMs are those only contain carbon, hydrogen and oxygen atoms. CHON OOMs and  $CHON_2$  OOMs are those contain additional one and two nitrogen atoms respectively.



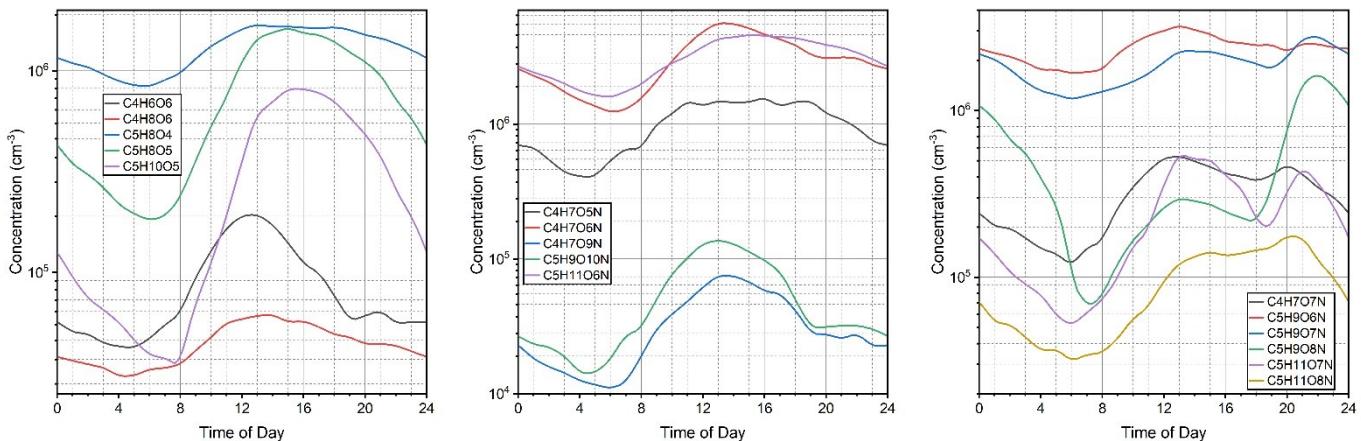
**Figure S8.** Concentration weighted average number of effective oxygen ( $nO_{eff-ave}$ ) in four seasons. The abbreviations “In” and “Ex” represent the averaged values for OOMs with and without IP-derived OOMs respectively.



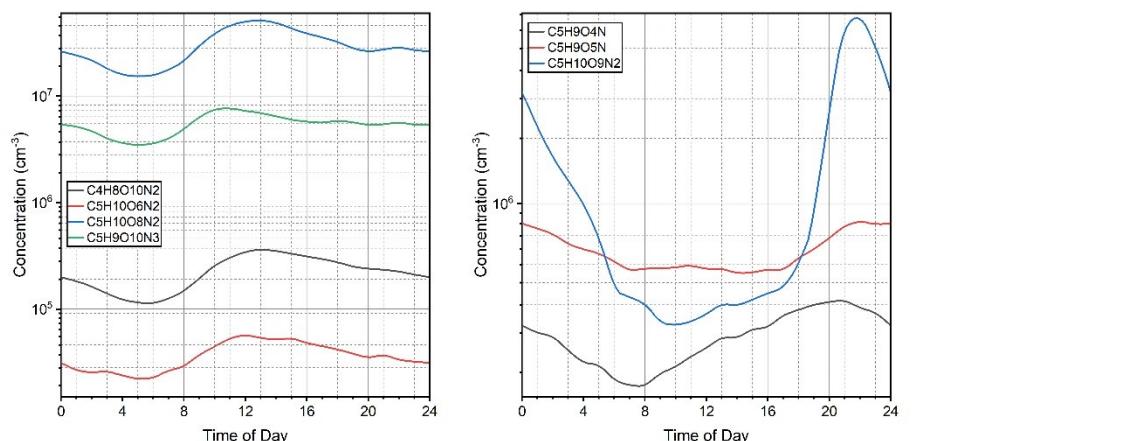
218  
219 **Figure S9.** Concentration of typical IP OOMs in (A) winter, (B) spring, (C) summer and (D) autumn, and typical MT OOMs in (E)  
220 winter, (F) spring, (G) summer and (H) autumn. Species in grey background are distinct ones in different seasons. Compounds in  
221 yellow background are primary ones during the year. The filled boxes are special compounds in each season.



222  
223 **Figure S10.** NO<sub>x</sub>, NO, NO<sub>2</sub> and O<sub>3</sub> mixing ratios in summer Beijing, summer Nanjing (Liu et al., 2021), spring Hyytiälä (Yan et  
224 al., 2016) and summer Alabama (Massoli et al., 2018).



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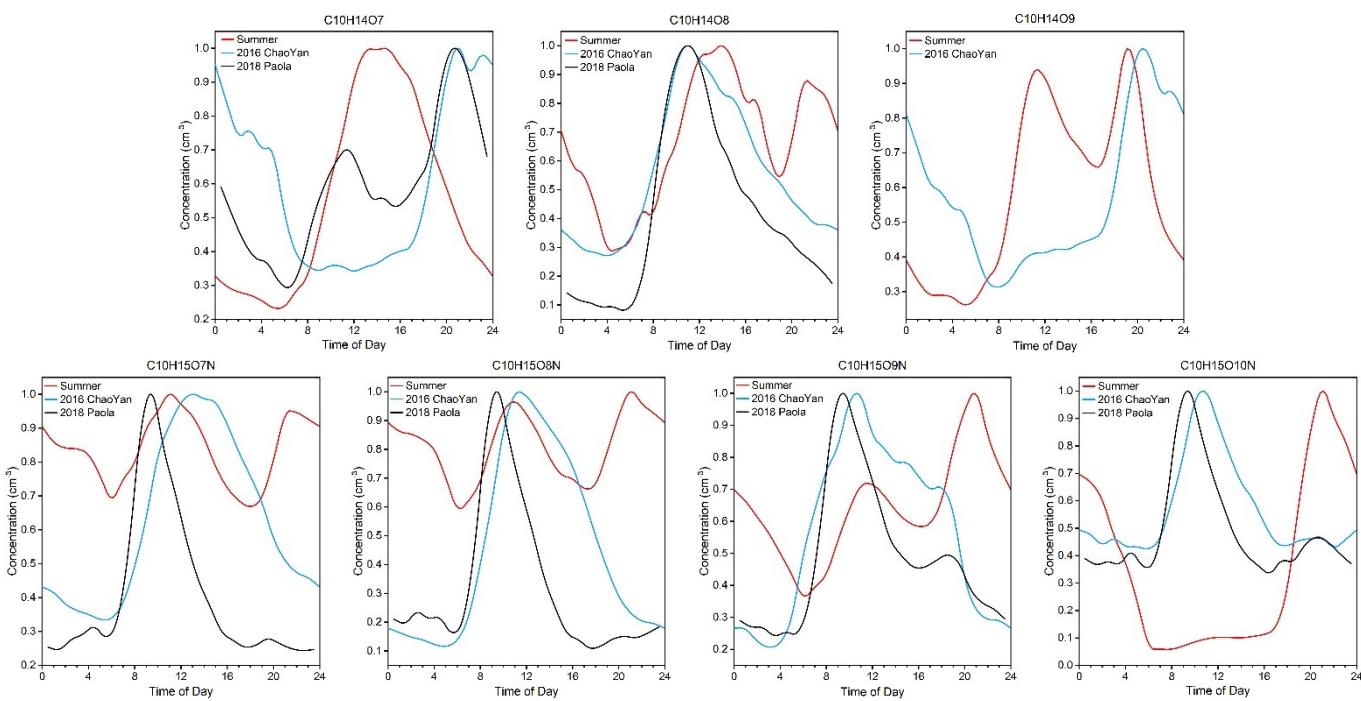


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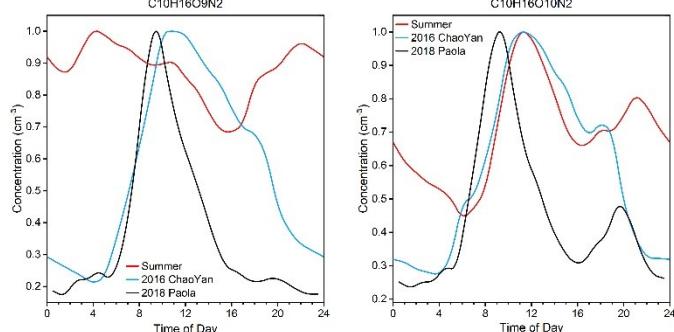
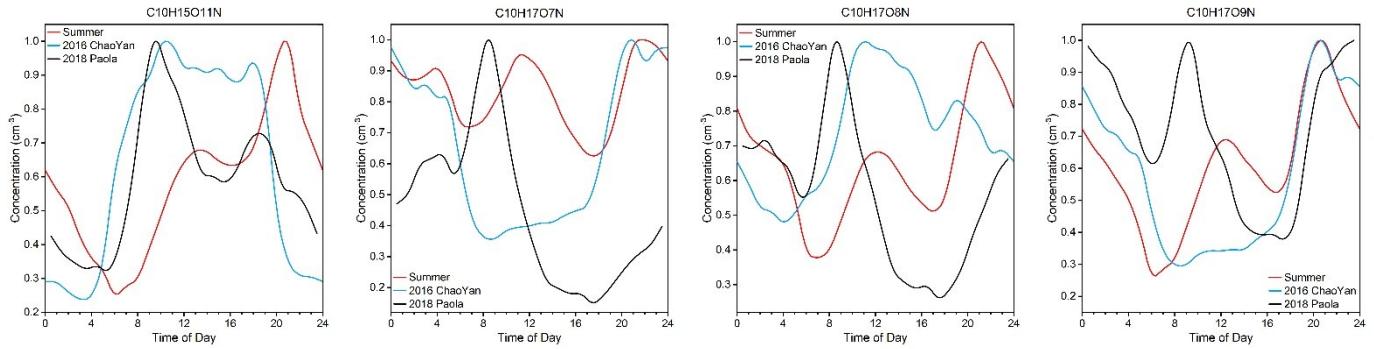
**Figure S11.** Diurnal variations of representative isoprene OOMs during summertime in this study.

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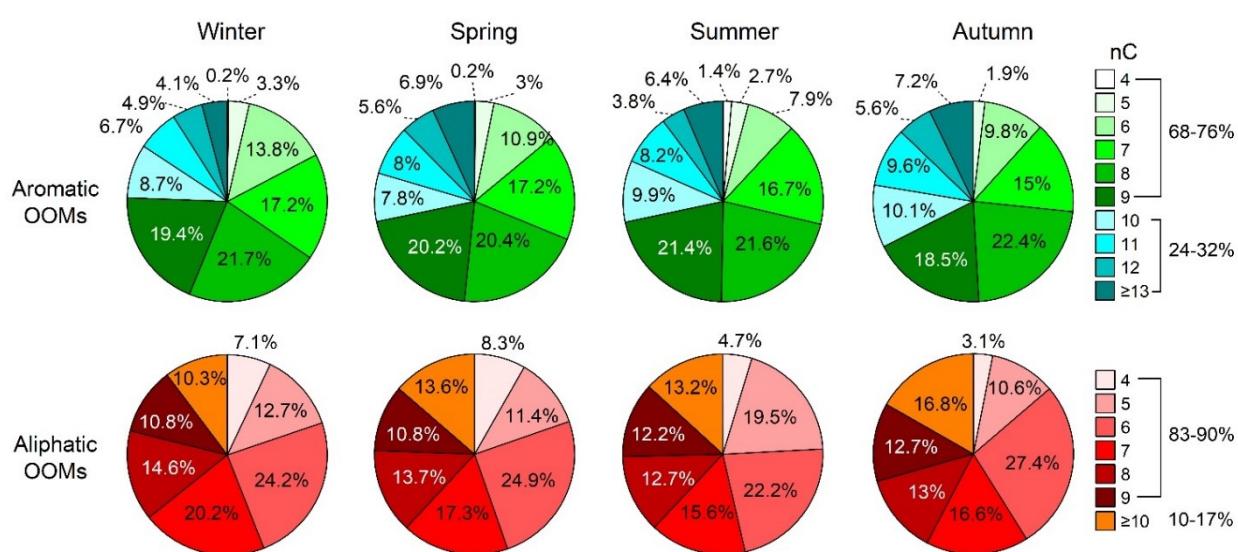


229

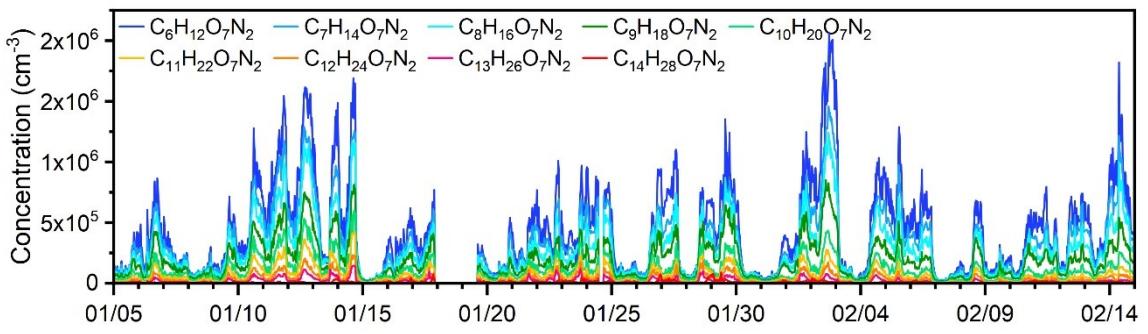
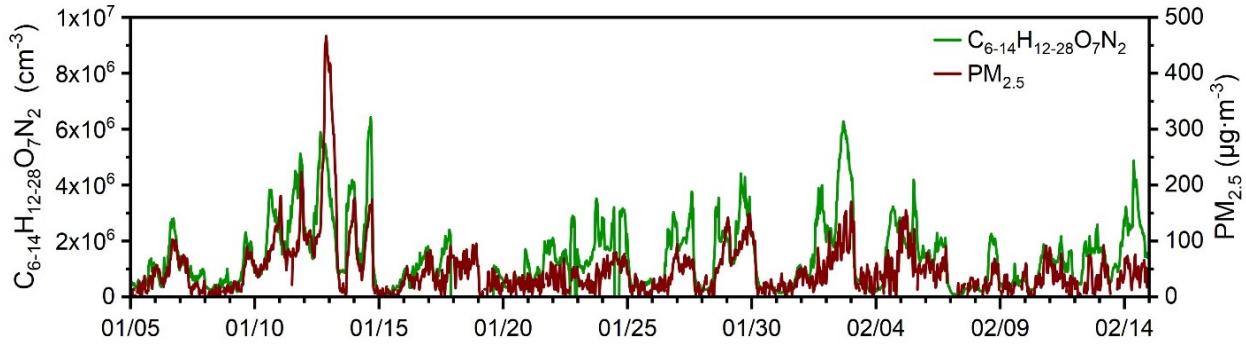
230



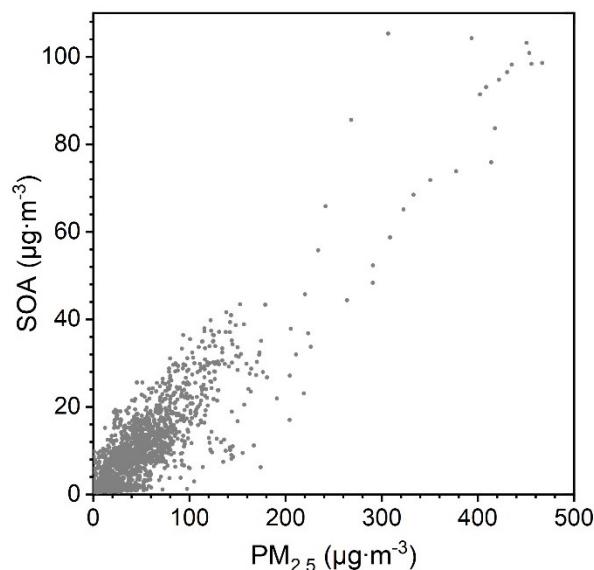
233 **Figure S12.** Diurnal variation of representative monoterpene OOMs during summertime in our study and from other two reported  
234 forest sites (Yan et al., 2016; Massoli et al., 2018).  
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236 **Figure S13.** Fractions of aromatic (first row) and aliphatic (second row) OOMs with different number of carbon atoms (nC) in winter  
237 (first column), spring (second column), summer (third column) and autumn (forth column). Colors in green, blue, red and orange  
238 series are for monocyclic aromatic OOMs ( $nC \leq 9$ ), polycyclic aromatic OOMs ( $nC \geq 10$ ), short-chain aliphatic OOMs ( $nC \leq 9$ ) and  
239 long-chain aliphatic OOMs ( $nC \geq 10$ ) respectively.  
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**Figure S14.** Time variation of  $C_{6-14}H_{12-28}O_7N_2$  OOMs and  $PM_{2.5}$  in winter.



**Figure S15.** Correlation of SOA with  $PM_{2.5}$  in winter.

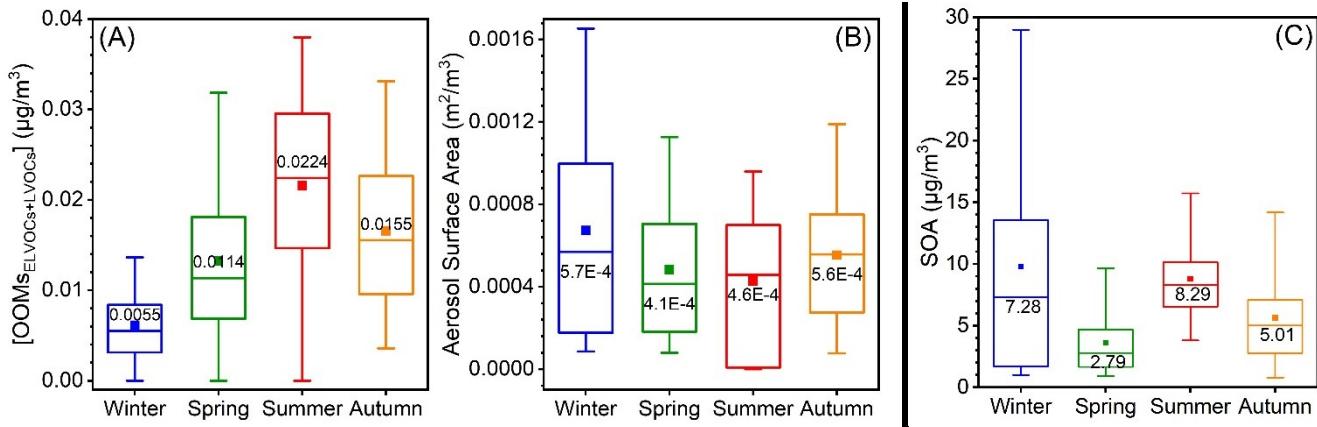


Figure S16. (A) Mass concentration of ELVOCs and LVOCs, (B) aerosol surface area in four seasons and (C) mass concentration of secondary organic aerosol (SOA) in four seasons. The values in each box are the median values of corresponding parameters.

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**TABLES**

**Table S1.** Median values of UVB, temperature (Temp), relative humidity (RH), O<sub>3</sub>, NO, NO<sub>2</sub>, condensation sink (CS), organic aerosol (OA) and secondary organic aerosol (SOA) in four seasons. Please note that note that UVB only includes daytime values from 08:00 to 16:00.

Median Values	UVB (W/m <sup>2</sup> )	Temp (°C)	RH (%)	O <sub>3</sub> (ppbv)	NO (ppbv)	NO <sub>2</sub> (ppbv)	CS (s <sup>-1</sup> )	SOA (μg/m <sup>3</sup> )	OA (μg/m <sup>3</sup> )
Winter	0.133	0.4	27	14.2	2.6	20.7	0.023	15.33	7.28
Spring	0.467	12.9	27	31.1	1.3	14.6	0.018	6.80	2.79
Summer	0.536	28.6	76	44.9	0.6	8.9	0.020	13.43	8.29
Autumn	0.176	12.1	65	7.2	10.0	28.3	0.023	11.14	5.01

**Table S2.** Mean, standard deviation (Std), median, 25 and 75 percentiles (25<sup>th</sup> and 75<sup>th</sup>) of total OOMs concentration in four seasons under different atmospheric conditions during daytime (08:00-16:00).

Season	Condition	Mean (cm <sup>-3</sup> )	Std (cm <sup>-3</sup> )	Median (cm <sup>-3</sup> )	25 <sup>th</sup> (cm <sup>-3</sup> )	75 <sup>th</sup> (cm <sup>-3</sup> )
Winter	Clean & Sunny	$3.0 \times 10^7$	$1.7 \times 10^7$	$2.8 \times 10^7$	$1.5 \times 10^7$	$4.0 \times 10^7$
	Clean & Cloudy	$2.1 \times 10^7$	$1.1 \times 10^7$	$2.0 \times 10^7$	$1.1 \times 10^7$	$2.6 \times 10^7$
	Polluted & Sunny	$5.8 \times 10^7$	$1.5 \times 10^7$	$6.0 \times 10^7$	$4.6 \times 10^7$	$7.0 \times 10^7$
	Polluted & Cloudy	$5.2 \times 10^7$	$1.9 \times 10^7$	$4.8 \times 10^7$	$3.6 \times 10^7$	$6.9 \times 10^7$
Spring	Clean & Sunny	$7.9 \times 10^7$	$4.1 \times 10^7$	$7.5 \times 10^7$	$4.5 \times 10^7$	$1.0 \times 10^8$
	Clean & Cloudy	$6.5 \times 10^7$	$5.3 \times 10^7$	$4.3 \times 10^7$	$2.6 \times 10^7$	$9.2 \times 10^7$
	Polluted & Sunny	$2.1 \times 10^8$	$4.1 \times 10^7$	$2.0 \times 10^8$	$1.8 \times 10^8$	$2.4 \times 10^8$
	Polluted & Cloudy	$1.7 \times 10^8$	$1.3 \times 10^7$	$1.8 \times 10^8$	$1.6 \times 10^8$	$1.8 \times 10^8$
Summer	Clean & Sunny	$2.4 \times 10^8$	$6.1 \times 10^7$	$2.4 \times 10^8$	$2.0 \times 10^8$	$2.7 \times 10^8$
	Clean & Cloudy	$1.5 \times 10^8$	$6.7 \times 10^7$	$1.5 \times 10^8$	$9.3 \times 10^7$	$2.0 \times 10^8$
	Polluted & Sunny	$2.7 \times 10^8$	$5.4 \times 10^7$	$2.6 \times 10^8$	$2.3 \times 10^8$	$3.0 \times 10^8$
	Polluted & Cloudy	$1.9 \times 10^8$	$8.2 \times 10^7$	$1.5 \times 10^8$	$1.2 \times 10^8$	$2.8 \times 10^8$
Autumn	Clean & Sunny	$9.2 \times 10^7$	$5.6 \times 10^7$	$9.3 \times 10^7$	$4.5 \times 10^7$	$1.2 \times 10^8$
	Clean & Cloudy	$9.4 \times 10^7$	$3.7 \times 10^7$	$9.1 \times 10^7$	$6.7 \times 10^7$	$1.2 \times 10^8$
	Polluted & Sunny	$2.1 \times 10^8$	$4.1 \times 10^7$	$2.2 \times 10^8$	$2.1 \times 10^8$	$2.4 \times 10^8$
	Polluted & Cloudy	$1.6 \times 10^8$	$4.2 \times 10^7$	$1.6 \times 10^8$	$1.3 \times 10^8$	$2.0 \times 10^8$

**Table S3.** Mean, standard deviation (Std), median, 25 and 75 percentiles (25<sup>th</sup> and 75<sup>th</sup>) of source-classified OOM concentrations in four seasons.

Season	OOMs Type	Mean (cm <sup>-3</sup> )	Std (cm <sup>-3</sup> )	Median (cm <sup>-3</sup> )	25 <sup>th</sup> (cm <sup>-3</sup> )	75 <sup>th</sup> (cm <sup>-3</sup> )
Winter	IP OOMs	$2.4 \times 10^6$	$1.8 \times 10^6$	$1.9 \times 10^6$	$9.6 \times 10^5$	$3.2 \times 10^6$
	MT OOMs	$1.4 \times 10^5$	$8.6 \times 10^5$	$1.1 \times 10^6$	$7.3 \times 10^5$	$1.8 \times 10^6$
	Aromatic OOMs	$1.0 \times 10^7$	$6.2 \times 10^6$	$8.7 \times 10^6$	$5.3 \times 10^6$	$1.4 \times 10^7$
	Aliphatic OOMs	$1.1 \times 10^7$	$7.7 \times 10^6$	$8.9 \times 10^6$	$4.6 \times 10^6$	$1.4 \times 10^7$
Spring	IP OOMs	$5.2 \times 10^6$	$4.5 \times 10^6$	$3.8 \times 10^6$	$1.9 \times 10^6$	$6.8 \times 10^6$
	MT OOMs	$4.2 \times 10^6$	$2.6 \times 10^6$	$3.5 \times 10^6$	$2.3 \times 10^6$	$5.3 \times 10^6$
	Aromatic OOMs	$2.8 \times 10^7$	$1.9 \times 10^7$	$2.4 \times 10^7$	$1.4 \times 10^7$	$3.5 \times 10^7$
	Aliphatic OOMs	$2.5 \times 10^7$	$2.2 \times 10^7$	$1.9 \times 10^7$	$9.7 \times 10^6$	$3.3 \times 10^7$
Summer	IP OOMs	$5.5 \times 10^7$	$3.3 \times 10^7$	$5.3 \times 10^7$	$2.7 \times 10^7$	$7.8 \times 10^7$
	MT OOMs	$8.5 \times 10^6$	$2.8 \times 10^6$	$8.4 \times 10^6$	$6.6 \times 10^6$	$1.0 \times 10^7$
	Aromatic OOMs	$4.7 \times 10^7$	$2.0 \times 10^7$	$4.7 \times 10^7$	$3.2 \times 10^7$	$6.2 \times 10^7$
	Aliphatic OOMs	$4.3 \times 10^7$	$1.7 \times 10^7$	$4.3 \times 10^7$	$3.2 \times 10^7$	$5.3 \times 10^7$
Autumn	IP OOMs	$8.3 \times 10^6$	$6.8 \times 10^6$	$7.4 \times 10^6$	$3.1 \times 10^6$	$1.1 \times 10^7$
	MT OOMs	$5.1 \times 10^6$	$3.1 \times 10^6$	$4.9 \times 10^6$	$2.6 \times 10^6$	$7.1 \times 10^6$
	Aromatic OOMs	$3.0 \times 10^7$	$1.7 \times 10^7$	$2.8 \times 10^7$	$1.7 \times 10^7$	$4.1 \times 10^7$
	Aliphatic OOMs	$3.4 \times 10^7$	$2.3 \times 10^7$	$3.2 \times 10^7$	$1.5 \times 10^7$	$4.9 \times 10^7$

**Table S4.** Nighttime OH radical and NO<sub>3</sub> radical concentration from previously studies in Beijing.

Measurement Site	Time Period	Radical Conc (cm <sup>-3</sup> )	Reference	Used Radical Conc (cm <sup>-3</sup> )
OH radical				
Wangdu, Beijing, rural	2014 June	5 × 10 <sup>5</sup>	(Tan et al., 2017)	
Huairou, Beijing, suburban	2016 Jan.-Mar.	2 - 4 × 10 <sup>5</sup>	(Tan et al., 2018)	3 × 10 <sup>5</sup>
Peking University, Beijing, urban	2017 Nov.-Dec.	1 - 4 × 10 <sup>5</sup>	(Ma et al., 2019)	
NO <sub>3</sub> radical				
Peking University, Beijing, urban	2016 May-June	3 - 7 × 10 <sup>8</sup> (calculated)	(Wang et al., 2018a)	5 × 10 <sup>8</sup>

**Table S5.** Estimated nighttime loss rate of precursor VOCs from OH radical or NO<sub>3</sub> radical (Loss<sub>VOC-radical</sub>). k<sub>VOC-radical</sub> is the reaction rate of VOC with OH or NO<sub>3</sub> radical.

VOC Type	k <sub>VOC-radical</sub> (cm <sup>3</sup> s <sup>-1</sup> )	Reference	Used Radical Conc (cm <sup>-3</sup> )	Loss <sub>VOC-radical</sub> (s <sup>-1</sup> )
OH radical				
Aromatics	1.2 × 10 <sup>-12</sup> - 5.7 × 10 <sup>-11</sup>	IUPAC		3.6 × 10 <sup>-7</sup> - 1.7 × 10 <sup>-5</sup>
Aliphatics	4.6 × 10 <sup>-17</sup> - 2.4 × 10 <sup>-12</sup>	MCM v3.3.1	3 × 10 <sup>5</sup>	1.4 × 10 <sup>-11</sup> - 7.2 × 10 <sup>-7</sup>
Monoterpenes	5.2 - 9.3 × 10 <sup>-11</sup>	(Atkinson and Arey, 2003)		1.6 - 2.8 × 10 <sup>-5</sup>
Isoprene	9.7 × 10 <sup>-11</sup> - 1.2 × 10 <sup>-10</sup>			2.9 - 3.7 × 10 <sup>-5</sup>
NO <sub>3</sub> radical				
Aromatics	< 3.0 × 10 <sup>-17</sup> - 1.9 × 10 <sup>-15</sup>	IUPAC		< 1.5 × 10 <sup>-8</sup> - 4.5 × 10 <sup>-7</sup>
Aliphatics	1.1 × 10 <sup>-17</sup> - 1.3 × 10 <sup>-16</sup>	MCM v3.3.1	5 × 10 <sup>8</sup>	2.5 × 10 <sup>-9</sup> - 6.5 × 10 <sup>-8</sup>
Monoterpenes	2.5 - 7.7 × 10 <sup>-12</sup>	(Atkinson and Arey, 2003)		1.3 - 3.9 × 10 <sup>-3</sup>
Isoprene	5.3 - 7.0 × 10 <sup>-13</sup>			2.7 - 3.5 × 10 <sup>-4</sup>

**Table S6.** Peak list of isoprene OOMs in this study based on the work of Xu et al. (Xu et al., 2021)

Molecular Formula	Exact Mass
<b>CHO</b>	
C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> (NO <sub>3</sub> <sup>-</sup> )	180.0150
C <sub>5</sub> H <sub>8</sub> O <sub>4</sub> (NO <sub>3</sub> <sup>-</sup> )	194.0306
C <sub>5</sub> H <sub>8</sub> O <sub>5</sub> (NO <sub>3</sub> <sup>-</sup> )	210.0255
C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> (NO <sub>3</sub> <sup>-</sup> )	212.0048
C <sub>5</sub> H <sub>10</sub> O <sub>5</sub> (NO <sub>3</sub> <sup>-</sup> )	212.0412
C <sub>4</sub> H <sub>8</sub> O <sub>6</sub> (NO <sub>3</sub> <sup>-</sup> )	214.0205
C <sub>5</sub> H <sub>12</sub> O <sub>5</sub> (NO <sub>3</sub> <sup>-</sup> )	214.0568
C <sub>5</sub> H <sub>8</sub> O <sub>6</sub> (NO <sub>3</sub> <sup>-</sup> )	226.0205
C <sub>5</sub> H <sub>10</sub> O <sub>6</sub> (NO <sub>3</sub> <sup>-</sup> )	228.0361
C <sub>4</sub> H <sub>8</sub> O <sub>7</sub> (NO <sub>3</sub> <sup>-</sup> )	230.0154
C <sub>5</sub> H <sub>12</sub> O <sub>6</sub> (NO <sub>3</sub> <sup>-</sup> )	230.0518
C <sub>5</sub> H <sub>8</sub> O <sub>7</sub> (NO <sub>3</sub> <sup>-</sup> )	242.0154
<b>CHON</b>	
C <sub>5</sub> H <sub>9</sub> O <sub>4</sub> N(NO <sub>3</sub> <sup>-</sup> )	209.0415
C <sub>4</sub> H <sub>7</sub> O <sub>5</sub> N(NO <sub>3</sub> <sup>-</sup> )	211.0208
C <sub>5</sub> H <sub>9</sub> O <sub>5</sub> N(NO <sub>3</sub> <sup>-</sup> )	225.0364
C <sub>4</sub> H <sub>7</sub> O <sub>6</sub> N(NO <sub>3</sub> <sup>-</sup> )	227.0157
C <sub>5</sub> H <sub>9</sub> O <sub>6</sub> N(NO <sub>3</sub> <sup>-</sup> )	241.0314
C <sub>4</sub> H <sub>7</sub> O <sub>7</sub> N(NO <sub>3</sub> <sup>-</sup> )	243.0106
C <sub>5</sub> H <sub>11</sub> O <sub>6</sub> N(NO <sub>3</sub> <sup>-</sup> )	243.0470
C <sub>5</sub> H <sub>9</sub> O <sub>7</sub> N(NO <sub>3</sub> <sup>-</sup> )	257.0263
C <sub>5</sub> H <sub>11</sub> O <sub>7</sub> N(NO <sub>3</sub> <sup>-</sup> )	259.0419
C <sub>5</sub> H <sub>9</sub> O <sub>8</sub> N(NO <sub>3</sub> <sup>-</sup> )	273.0212
C <sub>4</sub> H <sub>7</sub> O <sub>9</sub> N(NO <sub>3</sub> <sup>-</sup> )	275.0004
C <sub>5</sub> H <sub>11</sub> O <sub>8</sub> N(NO <sub>3</sub> <sup>-</sup> )	275.0368
C <sub>5</sub> H <sub>11</sub> O <sub>9</sub> N(NO <sub>3</sub> <sup>-</sup> )	291.0317
C <sub>5</sub> H <sub>9</sub> O <sub>10</sub> N(NO <sub>3</sub> <sup>-</sup> )	305.0110
<b>CHON<sub>2,3</sub></b>	
C <sub>5</sub> H <sub>10</sub> O <sub>6</sub> N <sub>2</sub> (NO <sub>3</sub> <sup>-</sup> )	256.0423
C <sub>4</sub> H <sub>8</sub> O <sub>7</sub> N <sub>2</sub> (NO <sub>3</sub> <sup>-</sup> )	258.0215
C <sub>5</sub> H <sub>10</sub> O <sub>7</sub> N <sub>2</sub> (NO <sub>3</sub> <sup>-</sup> )	272.0372
C <sub>5</sub> H <sub>10</sub> O <sub>8</sub> N <sub>2</sub> (NO <sub>3</sub> <sup>-</sup> )	288.0321
C <sub>5</sub> H <sub>10</sub> O <sub>9</sub> N <sub>2</sub> (NO <sub>3</sub> <sup>-</sup> )	304.0270

C <sub>4</sub> H <sub>8</sub> O <sub>10</sub> N <sub>2</sub> (NO <sub>3</sub> -)	306.0063
C <sub>5</sub> H <sub>10</sub> O <sub>10</sub> N <sub>2</sub> (NO <sub>3</sub> -)	320.0219
C <sub>5</sub> H <sub>9</sub> O <sub>10</sub> N <sub>3</sub> (NO <sub>3</sub> -)	333.0172

271  
272**Table S7** Fractions of typical IP OOM molecules in total IP OOMs.

Formula	Winter	Spring	Summer	Autumn
CHO				
C <sub>4</sub> H <sub>8</sub> O <sub>7</sub>	4.58%	0.63%	0.07%	0.53%
C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	13.80%	12.42%	2.69%	16.76%
C <sub>5</sub> H <sub>8</sub> O <sub>5</sub>	4.70%	6.03%	0.94%	2.74%
C <sub>5</sub> H <sub>8</sub> O <sub>6</sub>	7.90%	5.03%	0.29%	1.54%
C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	0.22%	0.33%	0.20%	0.20%
C <sub>5</sub> H <sub>10</sub> O <sub>6</sub>	0.38%	0.79%	0.22%	0.93%
C <sub>5</sub> H <sub>12</sub> O <sub>6</sub>	0.85%	0.58%	0.03%	0.45%
CHON				
C <sub>4</sub> H <sub>7</sub> O <sub>5</sub> N	7.16%	6.27%	1.95%	12.95%
C <sub>4</sub> H <sub>7</sub> O <sub>6</sub> N	10.75%	13.68%	5.70%	7.64%
C <sub>4</sub> H <sub>7</sub> O <sub>7</sub> N	1.95%	1.54%	0.58%	1.02%
C <sub>5</sub> H <sub>9</sub> O <sub>4</sub> N	0.57%	0.51%	0.53%	0.85%
C <sub>5</sub> H <sub>9</sub> O <sub>5</sub> N	7.10%	4.43%	1.20%	7.86%
C <sub>5</sub> H <sub>9</sub> O <sub>6</sub> N	10.76%	18.24%	4.90%	13.04%
C <sub>5</sub> H <sub>9</sub> O <sub>7</sub> N	1.78%	2.57%	3.33%	2.07%
C <sub>5</sub> H <sub>11</sub> O <sub>6</sub> N	2.24%	2.59%	6.40%	2.54%
C <sub>5</sub> H <sub>11</sub> O <sub>7</sub> N	0.64%	0.52%	0.26%	0.26%
C <sub>5</sub> H <sub>11</sub> O <sub>8</sub> N	0.65%	0.41%	0.13%	0.29%
CHON <sub>2</sub>				
C <sub>4</sub> H <sub>8</sub> O <sub>7</sub> N <sub>2</sub>	1.23%	3.11%	0.08%	3.10%
C <sub>5</sub> H <sub>10</sub> O <sub>7</sub> N <sub>2</sub>	8.02%	5.75%	0.50%	7.46%
C <sub>5</sub> H <sub>10</sub> O <sub>8</sub> N <sub>2</sub>	8.41%	10.26%	58.21%	13.06%
C <sub>5</sub> H <sub>10</sub> O <sub>9</sub> N <sub>2</sub>	NaN	NaN	0.89%	0.57%
CHON <sub>3</sub>				
C <sub>5</sub> H <sub>9</sub> O <sub>10</sub> N <sub>3</sub>	2.42%	1.76%	9.26%	2.34%

273  
274**Table S8** Fractions of typical MT OOM molecules in total MT OOMs.

Formula	Winter	Spring	Summer	Autumn
CHO				
C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>	2.3%	1.2%	1.4%	1.8%
C <sub>10</sub> H <sub>14</sub> O <sub>5</sub>	2.7%	2.2%	2.3%	1.9%
C <sub>10</sub> H <sub>14</sub> O <sub>6</sub>	NaN	1.0%	2.9%	1.5%
C <sub>10</sub> H <sub>14</sub> O <sub>7</sub>	1.2%	1.3%	0.9%	0.5%
C <sub>10</sub> H <sub>16</sub> O <sub>4</sub>	2.3%	1.5%	1.7%	2.8%
C <sub>10</sub> H <sub>16</sub> O <sub>5</sub>	2.7%	1.3%	2.8%	2.6%
C <sub>10</sub> H <sub>16</sub> O <sub>6</sub>	1.5%	1.5%	2.2%	1.4%
C <sub>10</sub> H <sub>18</sub> O <sub>4</sub>	2.2%	1.5%	1.2%	2.1%
C <sub>10</sub> H <sub>18</sub> O <sub>5</sub>	0.6%	0.6%	0.9%	0.8%
CHON				
C <sub>10</sub> H <sub>13</sub> O <sub>6</sub> N	1.4%	1.0%	0.6%	1.3%
C <sub>10</sub> H <sub>13</sub> O <sub>7</sub> N	1.8%	1.7%	1.6%	1.6%
C <sub>10</sub> H <sub>13</sub> O <sub>8</sub> N	1.0%	1.1%	1.0%	0.9%
C <sub>10</sub> H <sub>13</sub> O <sub>9</sub> N	0.6%	0.7%	0.8%	0.4%
C <sub>10</sub> H <sub>15</sub> O <sub>6</sub> N	10.7%	7.7%	8.4%	12.5%
C <sub>10</sub> H <sub>15</sub> O <sub>7</sub> N	9.9%	10.6%	8.6%	9.3%
C <sub>10</sub> H <sub>15</sub> O <sub>8</sub> N	7.3%	9.6%	8.7%	5.5%
C <sub>10</sub> H <sub>15</sub> O <sub>9</sub> N	2.5%	NaN	2.5%	1.3%
C <sub>10</sub> H <sub>17</sub> O <sub>6</sub> N	8.4%	5.6%	7.0%	11.2%
C <sub>10</sub> H <sub>17</sub> O <sub>7</sub> N	5.2%	7.7%	8.1%	10.2%
C <sub>10</sub> H <sub>17</sub> O <sub>8</sub> N	2.6%	4.3%	4.7%	2.0%

C10H17O9N	0.4%	1.4%	1.5%	0.8%
CHON <sub>2</sub>				
C10H12O8N2	0.7%	0.4%	NaN	0.3%
C10H12O9N2	0.7%	0.4%	0.3%	0.3%
C10H12O10N2	0.3%	0.2%	NaN	0.2%
C10H14O8N2	0.7%	0.8%	0.9%	0.8%
C10H14O9N2	2.3%	1.1%	1.2%	1.4%
C10H14O10N2	0.9%	1.0%	1.2%	0.9%
C10H16O8N2	3.5%	8.7%	6.3%	9.7%
C10H16O9N2	4.3%	7.0%	6.9%	3.1%
C10H16O10N2	3.1%	5.7%	5.2%	3.4%

275  
276

**Table S9** Fractions of typical aromatic OOM molecules in total aromatic OOMs.

Formula	Winter	Spring	Summer	Autumn	(Garmash et al., 2020)	(Molteni et al., 2018)
CHO						
C5H4O5	0.10%	0.29%	0.17%	0.18%	×	×
C5H4O6	0.17%	0.16%	NaN	NaN	√	×
C5H6O5	0.90%	1.16%	0.72%	0.68%	×	√
C5H7O6	0.73%	0.44%	0.38%	0.17%	×	×
C6H6O4	NaN	0.76%	0.43%	0.80%	√	√
C6H6O5	0.90%	0.81%	0.26%	0.37%	√	√
C6H8O4	1.96%	1.41%	1.32%	2.18%	√	√
C6H8O5	1.29%	1.41%	0.93%	0.94%	√	√
C6H8O6	NaN	0.41%	0.31%	0.27%	√	√
C6H8O7	0.54%	0.24%	0.26%	0.11%	√	√
C7H8O4	0.98%	0.54%	0.64%	0.90%	√	√
C7H8O5	1.52%	1.33%	1.74%	0.96%	√	√
C7H8O6	0.33%	0.24%	0.12%	0.10%	√	√
C7H10O3	0.16%	0.09%	0.12%	0.38%	√	×
C7H10O4	1.47%	1.43%	2.06%	2.24%	√	√
C7H10O5	1.12%	1.48%	1.37%	1.11%	√	√
C7H10O6	0.18%	0.29%	0.66%	0.44%	√	√
C7H10O7	0.11%	0.08%	0.18%	0.27%	√	√
C7H10O8	0.08%	0.08%	0.08%	0.07%	√	√
C7H12O6	0.26%	0.20%	0.16%	0.05%	√	√
C7H12O7	0.12%	0.12%	NaN	0.07%	√	√
C8H10O3	0.30%	0.10%	NaN	0.16%		×
C8H10O4	0.72%	0.42%	0.51%	0.77%		√
C8H10O5	1.41%	1.37%	1.54%	1.35%		√
C8H12O3	0.24%	0.08%	0.08%	0.27%		×
C8H12O4	1.51%	1.91%	2.17%	2.77%		√
C8H12O5	0.97%	0.94%	1.92%	0.93%	no xylene experiment	√
C8H12O6	0.73%	0.66%	0.71%	0.56%		√
C8H12O7	NaN	0.19%	0.22%	0.11%		√
C8H12O8	NaN	0.15%	0.17%	0.15%		√
C8H14O6	NaN	0.13%	0.23%	0.01%		√
C8H14O7	NaN	0.07%	0.10%	0.11%		√
C9H12O4	NaN	0.18%	0.45%	0.51%		×
C9H12O5	0.72%	0.51%	0.70%	0.44%	no C9 aromatic hydrocarbon experiment	×
C9H12O6	NaN	0.19%	0.43%	0.45%		√
C9H12O7	0.24%	0.15%	0.67%	0.08%		×
C9H14O3	1.23%	0.28%	0.19%	0.55%		×
C9H14O4	0.85%	0.61%	0.67%	1.02%		×
C9H14O5	0.64%	0.87%	0.92%	0.77%		√
C9H14O6	0.46%	0.33%	0.65%	0.34%		√
C9H14O7	NaN	NaN	0.26%	0.11%		√

C9H16O6	NaN	0.09%	0.20%	0.10%		x	
C9H16O7	NaN	0.08%	0.10%	0.12%		✓	
C10H14O2	NaN	0.01%	0.02%	0.02%	x		no C10 aromatic hydrocarbon experiment
C10H14O3	0.16%	0.05%	0.03%	0.11%	x		
CHON							
C5H5O4N	0.41%	0.28%	0.19%	0.34%	✓		
C5H5O5N	0.32%	0.20%	0.09%	0.19%	✓		
C5H5O7N	0.48%	0.43%	0.29%	0.11%	x		
C5H7O8N	NaN	NaN	0.75%	0.21%	✓		
C6H5O6N	0.38%	0.22%	0.09%	0.14%	✓		
C6H7O3N	1.00%	0.42%	NaN	0.06%	x		
C6H7O4N	0.69%	0.48%	0.31%	0.73%	x		
C6H7O5N	0.66%	0.31%	0.13%	0.39%	✓		
C6H7O6N	1.71%	1.10%	0.47%	0.90%	x		
C6H7O7N	0.23%	0.19%	0.58%	0.35%	✓		
C6H7O8N	0.28%	0.18%	NaN	NaN	✓		
C6H9O8N	0.38%	0.27%	0.44%	0.24%	x		
C6H9O9N	NaN	NaN	0.19%	NaN	✓		
C7H7O5N	0.25%	0.14%	0.14%	0.27%			
C7H7O6N	0.47%	0.15%	0.28%	0.29%			
C7H7O7N	0.26%	0.14%	NaN	NaN			
C7H7O8N	0.17%	0.17%	0.13%	0.07%			
C7H7O9N	0.15%	0.14%	0.17%	0.06%			
C7H9O5N	0.77%	0.35%	0.21%	0.49%			
C7H9O6N	2.31%	1.93%	1.25%	1.97%			
C7H9O7N	1.13%	1.38%	1.83%	0.92%			
C7H9O8N	0.34%	1.01%	1.12%	0.27%			
C7H9O9N	0.09%	NaN	0.15%	0.05%			
C7H9O10N	NaN	NaN	0.17%	0.06%			
C7H11O8N	0.50%	0.49%	0.71%	0.27%			
C7H11O9N	0.16%	0.21%	0.22%	0.18%			
C8H9O5N	0.28%	0.26%	0.27%	0.36%			
C8H9O6N	0.30%	0.22%	0.20%	0.25%			
C8H9O7N	0.34%	0.38%	0.22%	0.14%			
C8H9O8N	0.09%	0.20%	0.09%	0.04%			
C8H9O9N	0.18%	0.15%	0.16%	0.08%			
C8H11O5N	0.41%	0.18%	0.14%	0.27%			
C8H11O6N	3.88%	2.03%	0.71%	3.38%			
C8H11O7N	1.30%	1.61%	2.87%	1.50%			
C8H11O8N	1.11%	1.58%	1.53%	0.77%			
C8H11O9N	0.25%	0.34%	0.21%	0.14%			
C8H11O10N	0.20%	0.16%	0.13%	NaN			
C8H13O8N	0.58%	0.65%	0.89%	0.51%			
C8H13O9N	NaN	NaN	0.37%	0.10%			
C8H13O10N	0.07%	0.10%	0.17%	0.06%			
C9H11O5N	0.13%	0.14%	0.11%	0.14%			
C9H11O6N	0.31%	0.23%	0.17%	0.19%			
C9H11O7N	0.35%	0.38%	0.27%	0.15%			
C9H11O8N	0.16%	0.24%	0.20%	0.08%			
C9H11O9N	0.14%	0.19%	NaN	0.12%			
C9H11O10N	0.06%	0.32%	0.13%	0.04%			
C9H13O5N	0.29%	0.13%	0.15%	0.24%			
C9H13O6N	2.71%	1.20%	0.69%	2.22%			
C9H13O7N	1.40%	1.15%	1.86%	1.28%			
C9H13O8N	1.56%	1.67%	1.61%	0.99%			
C9H13O9N	0.43%	0.49%	0.40%	0.18%			
C9H13O10N	0.12%	0.19%	0.18%	0.12%			

C9H15O8N	0.51%	0.72%	1.27%	0.51%
C9H15O9N	0.14%	0.23%	0.36%	0.15%
C9H15O10N	NaN	0.20%	0.18%	NaN
CHON <sub>2</sub>				
C8H10O8N2	0.11%	0.11%	0.05%	0.10%
C8H10O9N2	NaN	NaN	0.19%	NaN
C8H10O10N2	0.24%	0.18%	0.23%	0.16%
C8H10O11N2	0.07%	0.07%	0.10%	0.03%
C8H12O10N2	0.22%	0.48%	1.01%	0.48%
C8H12O11N2	0.04%	NaN	0.15%	0.07%
C8H12O12N2	0.08%	0.04%	0.05%	0.03%
C9H12O8N2	0.14%	0.14%	0.15%	0.05%
C9H12O9N2	NaN	0.48%	0.25%	0.16%
C9H12O10N2	0.22%	0.24%	0.26%	0.14%
C9H12O11N2	0.06%	NaN	0.12%	0.04%
C9H14O10N2	0.27%	0.58%	0.90%	0.47%
C9H14O11N2	0.03%	0.10%	0.16%	0.10%
Sum	54.99%	50.31%	53.93%	48.51%
	—	—	—	—

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278 **Table S10** Fractions of DBE≤4 and DBE>4 compounds for nC≤9 and nC≥10 aromatic OOMs in four seasons.

OOM Type	Winter	Spring	Summer	Autumn
nC≤9 aromatic OOMs				
DBE≤4	83%	80%	83%	84%
DBE>4	17%	20%	17%	16%
nC≥10 aromatic OOMs				
DBE≤4	34%	32%	41%	33%
DBE>4	66%	68%	59%	67%

279  
280 **Table S11** Fractions of typical aliphatic OOM molecules in total aliphatic OOMs.

Formula	Winter	Spring	Summer	Autumn
CHO				
C6H10O4	1.68%	1.82%	1.55%	2.31%
C7H12O4	1.05%	1.23%	1.16%	1.58%
C8H14O4	0.50%	0.73%	0.55%	0.92%
C9H16O4	0.41%	0.67%	0.51%	1.04%
CHON				
C5H7O6N	7.60%	7.50%	7.52%	4.67%
C6H9O6N	8.65%	6.40%	3.63%	6.82%
C6H11O5N	1.86%	0.84%	0.97%	2.39%
C6H11O6N	2.56%	4.59%	6.96%	5.44%
C7H11O5N	1.08%	0.52%	0.34%	0.96%
C7H11O6N	5.69%	5.05%	3.53%	3.92%
C7H13O5N	1.06%	0.50%	0.51%	1.37%
C7H13O6N	1.46%	2.09%	2.37%	1.38%
C7H13O7N	0.30%	0.46%	0.47%	0.30%
C8H13O6N	3.06%	2.41%	2.01%	2.72%
C8H15O5N	0.87%	0.27%	0.40%	0.83%
C8H15O6N	1.15%	1.58%	1.68%	1.13%
C8H15O7N	0.27%	0.52%	0.68%	0.25%
C8H17O5N	0.59%	0.25%	0.17%	0.75%
C9H15O5N	1.01%	0.25%	0.17%	0.38%
C9H15O6N	1.51%	2.66%	2.76%	2.79%
C9H17O5N	0.67%	0.29%	0.36%	0.94%
C9H17O6N	0.86%	1.46%	2.21%	1.35%
C9H17O7N	0.20%	0.92%	0.47%	0.36%
C10H17O5N	0.44%	0.19%	0.18%	0.74%
C10H17O6N	1.05%	1.08%	1.28%	1.71%

C10H19O5N	0.54%	0.22%	0.25%	0.74%
C10H19O6N	0.48%	1.14%	1.04%	0.86%
C11H19O6N	0.27%	0.32%	0.42%	0.51%
CHON <sub>2</sub>				
C4H8O8N2	1.07%	NaN	0.88%	0.54%
C5H8O8N2	1.04%	NaN	4.80%	0.77%
C6H10O8N2	1.38%	1.89%	2.37%	1.38%
C6H10O9N2	0.77%	0.83%	0.81%	0.57%
C6H12O7N2	4.07%	2.54%	NaN	2.43%
C7H12O8N2	1.39%	1.55%	1.58%	1.15%
C7H12O9N2	0.37%	0.59%	0.45%	0.41%
C7H14O7N2	3.31%	1.71%	0.39%	1.98%
C7H14O8N2	0.38%	0.36%	0.35%	0.39%
C8H14O8N2	1.64%	2.43%	1.82%	1.10%
C8H16O7N2	2.60%	1.38%	0.37%	1.91%
C8H16O8N2	0.25%	0.59%	0.35%	0.32%
C9H16O8N2	1.14%	1.40%	1.28%	1.03%
C9H18O7N2	1.85%	0.65%	0.22%	1.07%
C10H18O8N2	0.76%	1.67%	1.95%	1.20%
C10H20O7N2	0.97%	0.41%	NaN	0.55%
C11H22O7N2	0.59%	0.27%	0.19%	0.69%
C12H24O7N2	0.32%	0.32%	0.14%	0.47%
C13H26O7N2	0.14%	0.20%	0.12%	0.26%
C14H28O7N2	0.07%	0.13%	0.10%	0.16%
C <sub>n</sub> H <sub>2n</sub> O <sub>7</sub> N <sub>2</sub> (n=6-14)	14.15%	7.75%	1.68%	9.74%

**Table S12.** The median volatility ( $\log_{10} [C^* (\mu\text{g}\cdot\text{cm}^{-3})]$ ) of C<sub>6-14</sub>H<sub>12-28</sub>O<sub>7</sub>N<sub>2</sub> compounds during the winter period (5<sup>th</sup> January to 14<sup>th</sup> February, 2019).

Compound	$\log_{10} [C^* (\mu\text{g}\cdot\text{cm}^{-3})]$	Volatility Type
C <sub>6</sub> H <sub>12</sub> O <sub>7</sub> N <sub>2</sub>	1.47	
C <sub>7</sub> H <sub>14</sub> O <sub>7</sub> N <sub>2</sub>	1.02	semi-volatile
C <sub>8</sub> H <sub>16</sub> O <sub>7</sub> N <sub>2</sub>	0.55	organic compounds
C <sub>9</sub> H <sub>18</sub> O <sub>7</sub> N <sub>2</sub>	0.07	
C <sub>10</sub> H <sub>20</sub> O <sub>7</sub> N <sub>2</sub>	-0.41	
C <sub>11</sub> H <sub>22</sub> O <sub>7</sub> N <sub>2</sub>	-0.90	
C <sub>12</sub> H <sub>24</sub> O <sub>7</sub> N <sub>2</sub>	-1.39	low-volatility
C <sub>13</sub> H <sub>26</sub> O <sub>7</sub> N <sub>2</sub>	-1.88	organic compounds
C <sub>14</sub> H <sub>28</sub> O <sub>7</sub> N <sub>2</sub>	-2.38	

**Table S13.** Concentrations of aromatic and aliphatic OOMs in Beijing and other Chinese megacities.

Measurement Site	Time Period	Aromatic OOMs (cm <sup>-3</sup> )	Aliphatic OOMs (cm <sup>-3</sup> )	Reference
Beijing, China	2019 Jan.-Feb.	$1.0 \times 10^7$	$1.1 \times 10^7$	This study
	2019 Mar.-Apr.	$2.8 \times 10^7$	$2.5 \times 10^7$	
	2019 July-Aug.	$4.7 \times 10^7$	$4.3 \times 10^7$	
	2019 Oct.-Nov.	$3.0 \times 10^7$	$3.4 \times 10^7$	
Hong Kong, China	2018 Nov.	$8.1 \times 10^7$	$9.7 \times 10^7$	2022, Nie et al.
Shanghai, China	2018 Nov.	$3.2 \times 10^7$	$3.0 \times 10^7$	2022, Nie et al.
Nanjing, China	2018 Nov.	$2.5 \times 10^7$	$3.7 \times 10^7$	2022, Nie et al.

**Table S14.** Common aromatic and aliphatic OOM molecules in this study and reported in Liu et al. (Liu et al., 2021).

Aromatic OOMs	Aliphatic OOMs
C <sub>6-8</sub> H <sub>8-12</sub> O <sub>4</sub>	
C <sub>8</sub> H <sub>11</sub> O <sub>6-8</sub> N	C <sub>5-7</sub> H <sub>7-11</sub> O <sub>6</sub> N
C <sub>9</sub> H <sub>17</sub> O <sub>7,8</sub> N	C <sub>6</sub> H <sub>11</sub> O <sub>6</sub> N
C <sub>10</sub> H <sub>15</sub> O <sub>8</sub> N	

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289**Table S15.** Median concentrations of ELVOCs, LVOCs and SVOCs of total OOMs in four seasons.

Season	ELVOCs ( $\text{cm}^{-3}$ )	LVOCs ( $\text{cm}^{-3}$ )	SVOCs ( $\text{cm}^{-3}$ )
Winter	$1.4 \times 10^6$	$9.4 \times 10^6$	$5.3 \times 10^6$
Spring	$8.6 \times 10^6$	$2.0 \times 10^7$	$1.5 \times 10^7$
Summer	$1.3 \times 10^7$	$4.0 \times 10^7$	$8.4 \times 10^7$
Autumn	$9.6 \times 10^6$	$2.8 \times 10^7$	$2.9 \times 10^7$

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291**Table S16.** Volatility distribution of source-classified OOMs in four seasons.

Season	OOMs Type	ELVOCs + LVOCs	SVOCs	IVOCs + VOCs
Winter	IP OOMs	42.1 %	56.3 %	1.6 %
	MT OOMs	100.0 %	0.0 %	0.0 %
	Aromatic OOMs	77.5 %	13.4 %	9.1 %
	Aliphatic OOMs	54.7 %	38.2 %	7.1 %
Spring	IP OOMs	25.2 %	56.2 %	18.5 %
	MT OOMs	95.7 %	4.3 %	0.0 %
	Aromatic OOMs	69.3 %	21.2 %	9.6 %
	Aliphatic OOMs	38.2 %	50.5 %	11.3 %
Summer	IP OOMs	3.3 %	92.2 %	4.5 %
	MT OOMs	70.9 %	29.1 %	0.0 %
	Aromatic OOMs	73.8 %	20.8 %	5.4 %
	Aliphatic OOMs	17.8 %	71.5 %	10.7 %
Autumn	IP OOMs	15.8 %	48.1 %	36.1 %
	MT OOMs	93.6 %	6.4 %	0.0 %
	Aromatic OOMs	66.7 %	21.6 %	11.7 %
	Aliphatic OOMs	30.0 %	62.0 %	8.0 %

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294**Table S17** Concentrations of NO, *n*-decane, cyclohexane and decalin as well as corresponding VOC to NO ratios in the Leipzig free-jet flow reactor experiments of Wang et al. (Wang et al., 2021)

NO (ppb)	0.17	1.15	2.27	3.42	4.46	7.0	8.93
<i>n</i> -decane (ppb)				130			
<i>n</i> -decane / NO	745	113	57	38	29	19	15
cyclohexane (ppb)				558			
cyclohexane / NO	3192	484	246	163	125	83	63
decalin (ppb)				74			
decalin / NO	426	65	33	22	17	11	8

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298**Table S18.** NO<sub>x</sub>, total hydrocarbons (HCs) and hydrocarbon to NO<sub>x</sub> ratios (HCs / NO<sub>x</sub>) for urban Beijing. The NO<sub>x</sub> concentration are the measured ones (mean values) in this study. Hydrocarbon concentrations are taken from literatures (Zhang et al., 2017; Zhang et al., 2020).

	Winter	Spring	Summer	Autumn
NO (ppb)	15.7	6.7	1.6	24.7
NO <sub>2</sub> (ppb)	23.8	18.6	10.9	27.1
NO <sub>x</sub> (ppb)	39.9	25.2	12.0	51.6
2017, Hao Zhang et al.				
Total HCs (ppb)	47.72	25.63	20.09	39.25
HCs / NO <sub>x</sub>	1.20	1.02	1.67	0.76
2020, Lihui Zhang et al.				
Total HCs (ppb)	16.37	9.0	11.61	12.95
HCs / NO <sub>x</sub>	0.41	0.36	0.97	0.25

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