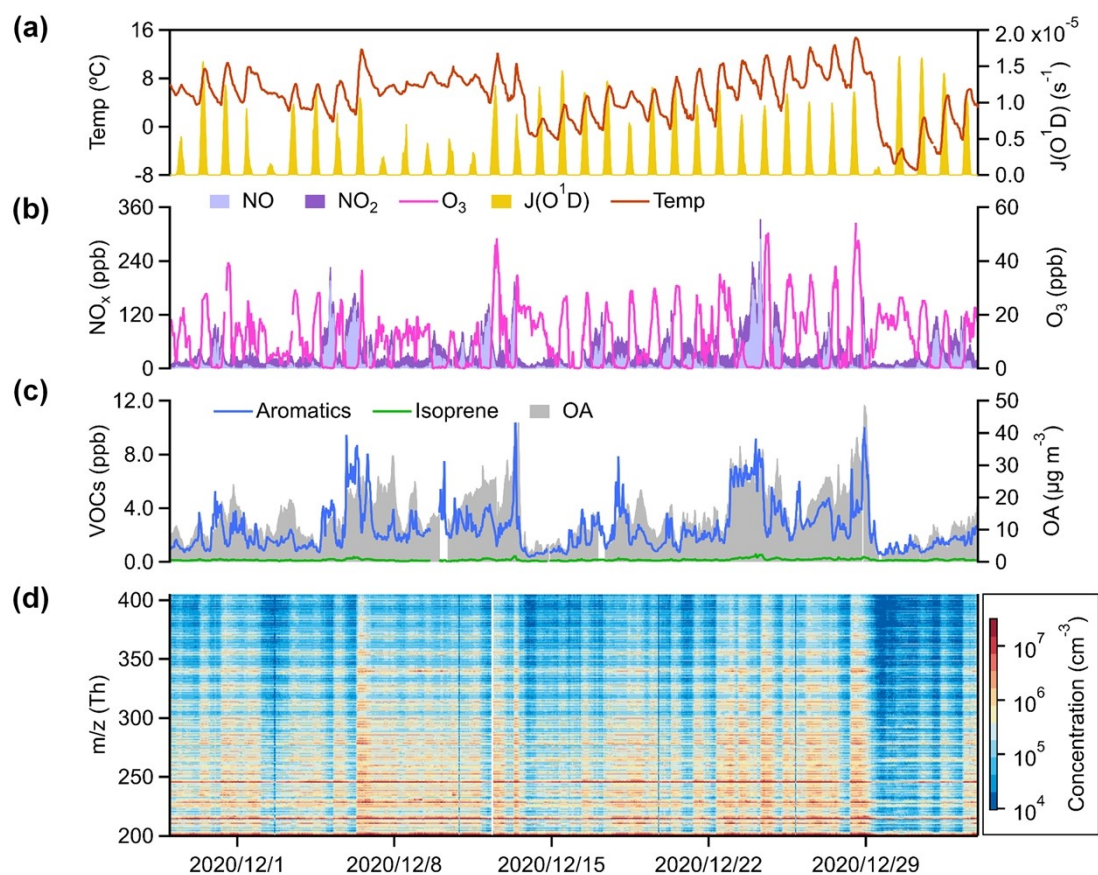


1

2 Table of contents

3	S1 Overview of measurements	1
4	S2 binPMF analysis	2
5	S3 Calculation of molecular properties of OOMs	8
6	S4 Main peaks of 7 discussed non-nitrated-phenols factors	9
7	S5 The additional information of the Arom-OOM factor.....	13
8	S6 The additional information of two Aliph-OOM factors	14
9	S7 The additional information of two O ₃ -related factors.....	16
10	S8 The additional information of the Mixed-OOM and the MT-mixed-OOM factors ...	17
11	S9 The additional information of NP factors	19
12	S10 The molecular information of the high-quality OOMs dataset	20
13	S11 Relationship of OOMs with O ₃ , PM _{2.5}	21
14	S12 Relationship of PM _{2.5} with O _x and PAN.....	21
15	S13 The calculation of OH proxy	22
16		

17 S1 Overview of measurements



18

19 Fig. S1 Overview of measurements during the campaign. Time series of (a) temperature
20 (Temp) and the photolysis frequency of O₃ (J(O¹D)); (b) O₃ and NO_x (NO + NO₂); (c)
21 total aromatics (benzene + toluene + C₈ aromatics + C₉ aromatics + C₁₀ aromatics +
22 styrene), isoprene, and OAs; and (d) mass spectra of the nitrate CI-API-TOF with m/z

23 in the range of 203–404 Th.

24 S2 binPMF analysis

25 S2.1 binPMF inputs

26

27 Data matrix

28

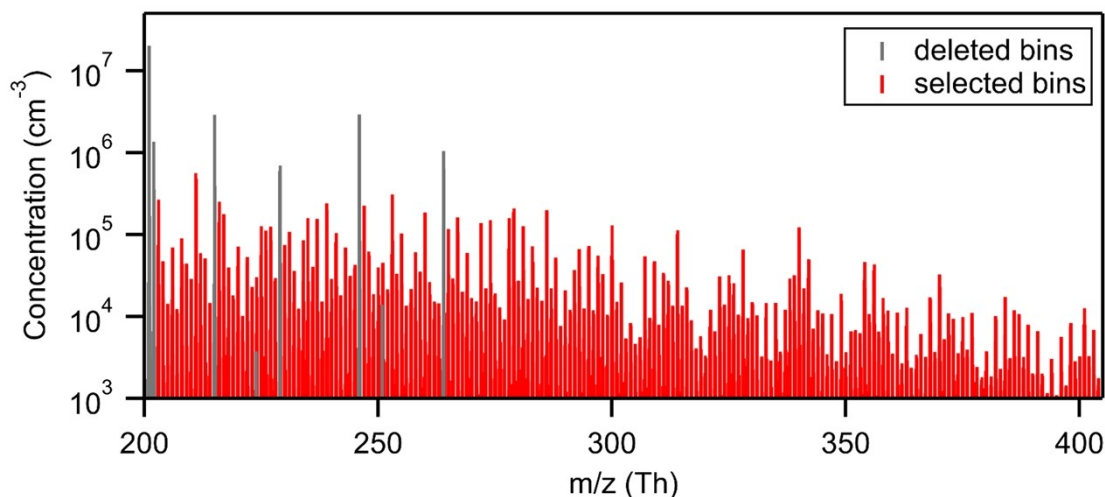
29 As described in Zhang et al.¹, we divided the mass spectra measured by nitrate CI-APi-
30 TOF into small bins of 0.006 Th width and performed the baseline subtraction and mass
31 axis calibration. Figure S2 shows the averaged binned spectrum with marked deleted
32 bins that nitrated phenol and some fluorinated contaminations (Table S1) that are not
33 our main focus. Besides, we selected the mass bins in the range of 203-404 Th with an
34 appropriate signal-to-noise ratio (SNR > 0.9) as data matrix for binPMF input,
35 neglecting quite weak signals to reduce unnecessary computation.

36

37 Table S1. Peak list of deleted bins

Mass-to-charge (Th)	Formulas
201.0153	$C_6H_5NO_3(NO_3^-)$
215.0310	$C_7H_7NO_3(NO_3^-)$
223.8617	$ICl(NO_3^-)$
229.0466	$C_8H_9NO_3(NO_3^-)$
246.0004	$C_6H_4N_2O_5c$
250.8807	$IONO_2(NO_3^-)$
264.0110	$C_6H_5NO_3(HNO_3NO_3^-)$

38



39

40 Fig. S2 The averaged binned spectrum. The delete bins (gray) listed in Table S1, other
41 bins (red) with unit m/z in the range of 203-404 Th were adopted as data matrix for
42 PMF inputs.

43

44 Error matrix

45

46 The error matrix was calculated by Eq. (1)²

47

48
$$S_{ij} = \sigma_{ij} + \sigma_{noise} \quad (1)$$

49

50 where S_{ij} is estimated the measurement uncertainty of m/z j at time i , σ_{ij} represents the
51 analytical uncertainty from counting statistics and σ_{noise} is the standard deviation of
52 instrument noise. σ_{ij} is estimated as follows:

53

$$\sigma_{ij} = a \times \frac{\sqrt{I_{ij}}}{\sqrt{t}} \quad (2)$$

54

55

56 where I is the signal intensity term, in unit of ions per second; t stands for length of
57 averaging in seconds, and a is an empirical coefficient to compensate for unaccounted
58 uncertainties^{3, 4} and is 1.28 in this study as previously estimated from laboratory
59 experiments⁴. The σ term was estimated as the median of the standard deviations from
60 signals in the bins in the region between nominal masses, where no physically
61 meaningful signals are expected.

62

63 **S2.2 Diagnostics**

64

65 It is the most critical to select a proper number of factors towards interpreting the PMF
66 results. The Q/Q_{exp} value is one of the main mathematical diagnoses to PMF results⁴⁻⁶.
67 For our PMF result, when the number of factor solution exceeds 8, the rate of decline
68 in Q/Q_{exp} value slowed down (Fig. S3(a)). The unexplained fraction decreased from
69 20% to 10% from 1- to 8-factor solution and then decreased slowly in subsequent
70 solutions (Fig. S3(b)). Based on the mathematical diagnostics, we should select an
71 appropriate solution from 9-20 factors. The evolution of PMF solutions should been
72 noticed carefully, since solutions with more factors can interpret subtler processes, but
73 too many factors will split a significant factor into unrealistic ones. The main factors
74 with first occurrences are marked in the corresponding solutions (Fig. S3 (a)). As we
75 can see, the O_3 -related-I factor is separated first in the 3-factor solution, while the O_3 -
76 related-II factor first appear purely in the 12-factor solution and the MT-mixed-OOM
77 factor is separated first in the 13-factor solution. For more than 14-factor solutions, this
78 is more difficult to interpret because they do not provide new physically meaningful
79 factor and will make the main factor split and uncorrelated with external tracers.

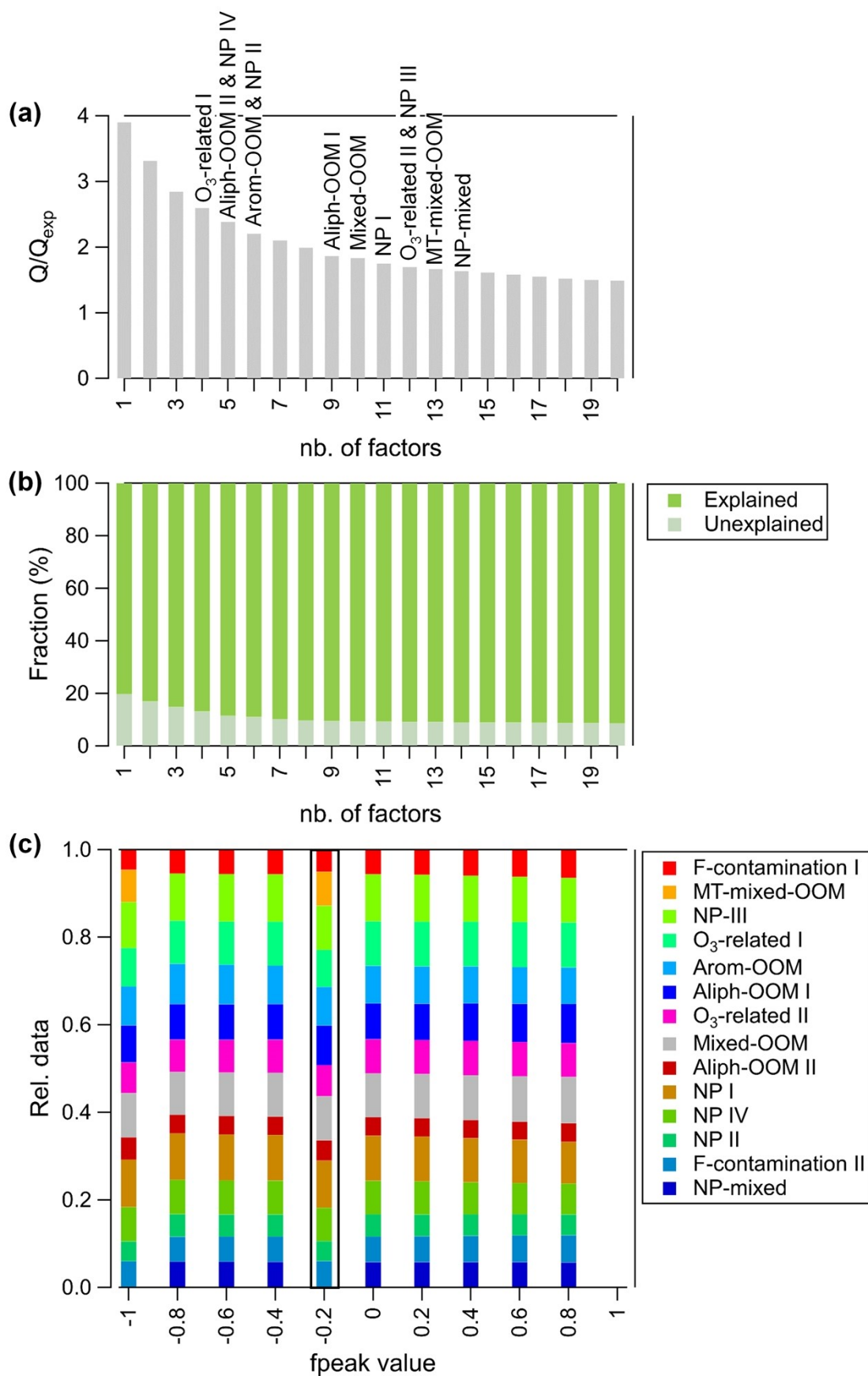
80

81 We used the rotational ambiguity with setting the f_{peak} to increase from -1.0 to 1.0
82 with a difference of 0.2 to check the 13-factor solution (Fig. S3(c)). All solutions are
83 divided into two type solutions, one containing 12 + 'MT-mixed-OOM' factors and the
84 other containing 12 + 'NP-mixed' factors. The 'MT-mixed-OOM' factor contains
85 potential monoterpene-derived OOMs mixing other anthropogenic OOMs. The 'NP-
86 mixed' factor consists of mainly by nitrated phenol which are not our main concern.
87 Finally, the solution with a f_{peak} value of -0.2 is selected to analysis data. It is currently
88 difficult to prove that the PMF solution we chose is optimal, but it is certain that this
89 solution separates enough information for understanding OOMs.

90

91 Meanwhile, it is should be point out that when naming these factors, we prioritize the
92 description of dominated species or their precursors, but if the precursors are complex

93 mixtures, our naming highlights the characteristics of the chemical processes that
 94 drive certain factors.

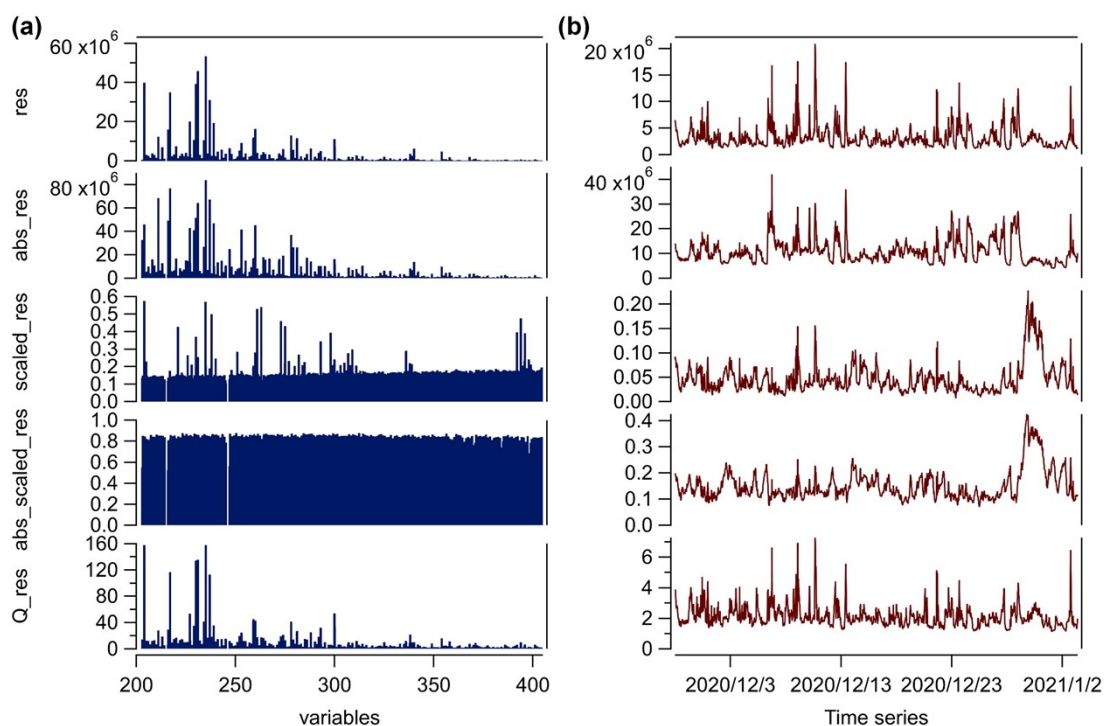


96 Fig. S3 The diagnostics of PMF solution. (a) Q/Q_{exp} , (b) the explained and unexplained
97 fraction in PMF results, (c) the relative contribution ratio of factors in each solution
98 with different values $([-1,1])$ of f_{peak} .

99

100 The residual histograms are a simple and fast method for checking whether the PMF
101 result contains several systematic under- or overestimation. As showed in Fig. S4, the
102 variables of residual appear some compounds with high signal, but we found the most
103 of them are the nitrated phenols like $C_6H_3ClNO_5^-$ ($m/z = 203.9705$ Th), $C_6H_5NO_4$
104 (NO_3^-) ($m/z = 217.102$ Th), $C_7H_7NO_4$ (NO_3^-) ($m/z = 231.0259$ Th) and
105 $C_6H_4ClNO_3(NO_3^-)$ ($m/z = 234.9763$ Th), etc. It is over-split for other physically
106 significant factors if we separate out these compounds. Therefore, it is appropriate to
107 choose the 14-factor solution since the factors about nitrated phenols are not our main
108 concern.

109



110

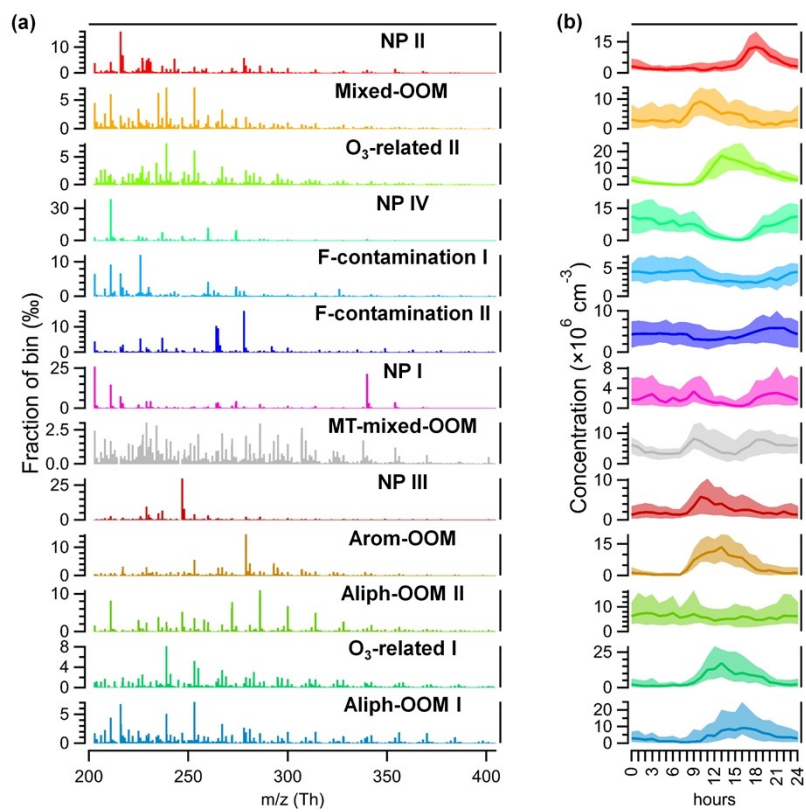
111 Fig. S4 (a) Mass spectra and (b) time series plots showing the residual histograms of
112 the 13-factor solution.

113

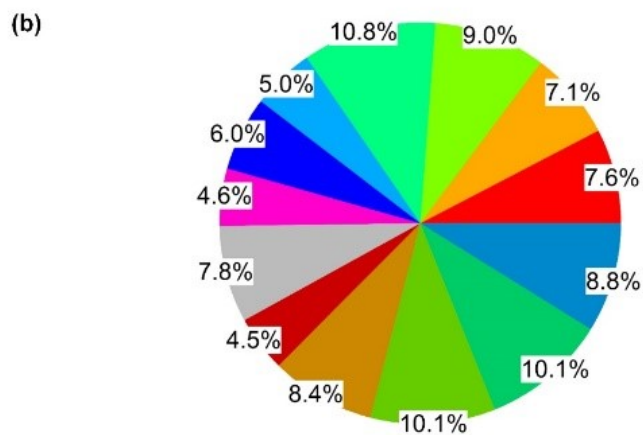
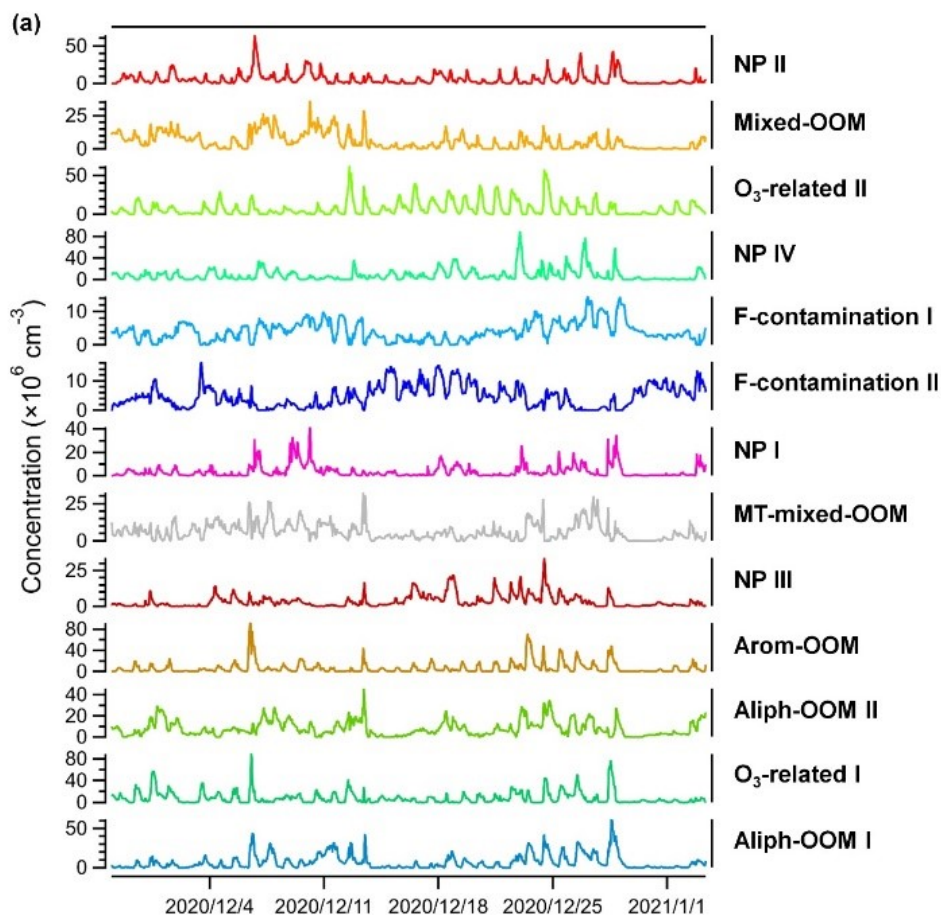
114 S2.3 The binPMF result

115

116 In summary, we selected 13-factor solution to analysis our dataset.

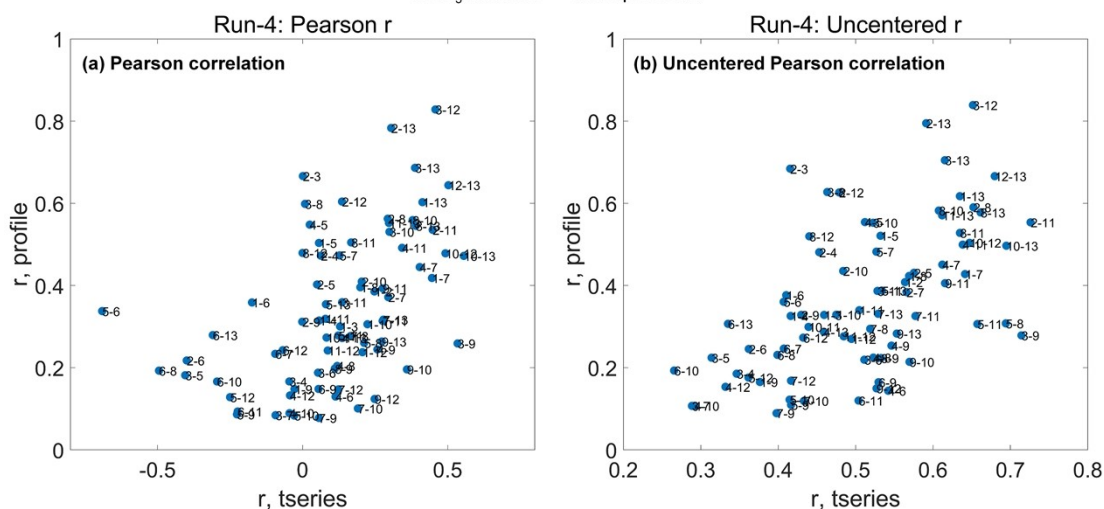


117
 118 Fig. S5. The binPMF analysis with 13-factor solution. (a) the mass profile, (b) the
 119 diurnal pattern.
 120



121
 122 Fig. S6 The binPMF result. (a) the time series, (b) the contribution of each factor to the
 123 total signal.
 124

1: NP II 2: Mixed-OOM 3: O₃-related II 4: NP IV 5: F-contamination I 6: F-contamination II
 7: NP I 8: MT-mixed-OOM 9: NP III 10: Arom-OOM 11: Aliph-OOM II
 12: O₃-related II 13: Aliph-OOM I



125
 126 Fig. S7 Comparison among the factors through (a) Pearson correlation and (b)
 127 Uncentered Pearson correlation. The x-axis shows the correlation of the time series
 128 between the factors, and the y-axis shows the correlation of the spectra between the
 129 factors.

130

131 S3 Calculation of molecular properties of OOMs

132 Carbon oxidation state (OS_c)

133

134 The OS_c of each **non-nitro** OOM was calculated based on Eq. (3) modified from that
 135 in Kroll et al.⁷ include organic nitrate contributions:

136

$$137 \quad OS_{c=2} = (n_O - 3n_N)/n_C - n_H/n_C + n_N/n_C \quad (3)$$

138

139 Where n_C , n_H , n_O , and n_N denote the number of carbons, hydrogen, oxygen, and nitrogen
 140 in the molecule, respectively.

141

142 Double bond equivalent (DBE)

143

144 The DBE of each OOM was calculated using Eq. (4), by assuming that all nitrogen
 145 come from the nitrate group (-ONO₂) or nitro group (-NO₂). Here DBE represents the
 146 combined effect of double or triple bonds, as well as the ring structure, in the molecule.

147

$$148 \quad DBE = n_C + 1 - (n_H + n_N)/2 \quad (4)$$

149

150 Volatility Basis Set (VBS)

151

152 The saturation concentration (volatility) of selected OOMs was estimated based on the
 153 group-contribution method proposed by Donahue et al.⁸:
 154

$$155 \log_{10} C^*(300K) = (25 - n_C) \times b_C - (n_O - 2n_N) \times b_O - 2 \left[\frac{(n_O - 2n_N) \times n_C}{n_C + n_O - 2n_N} \right] \times b_{CO}$$

156 (5)

157
 158 Where $b_C = 0.475$, $b_O = 2.3$, $b_{CO} = -0.3$. The effect of nitrate group (-ONO₂) on volatility
 159 is similar to hydroxyl group (-OH).

160
 161 The temperature dependence of volatilities is described by Eq. (6), according to
 162 Stolzenburg et al.⁹:

$$163 \log_{10} C_i^*(T) = \log_{10} C_i^*(300K) + \frac{\Delta H_{vap}}{R \times \ln(10)} \left(\frac{1}{300} - \frac{1}{T} \right)$$

164 (6)

165
 166 The evaporation enthalpy (ΔH_{vap}) can be linked to the saturation mass concentration at
 167 300 K, $\log_{10} C^*(300K)$, according to Donahue et al.⁸ and combined with Epstein et al.¹⁰:

$$168 \Delta H_{vap} [kJ mol^{-1}] = 129 - 5.7 \cdot \log_{10}(C^*(300K))$$

169 (7)

171 Effective Oxygen Number ($n_{O_{eff}}$)

172
 173 The effective oxygen number which represents effective oxidation was calculated by
 174 Eq. (8), by assuming that all nitrogen of **non-nitro** OOM come from the nitrate group
 175 (-ONO₂):

$$176 n_{O_{eff}} = n_O - 2 \times n_N$$

177 (8)

179 S4 Main peaks of 7 discussed non-nitrated-phenols factors

180 S4.1 Arom-OOM factor

181
 182 Table S2. Molecular characteristics of the Arom-OOM factor. Presented as several sets
 183 of compounds, and the members of each set differ in the addition of a -CH₂ moiety.
 184 Only the signals that account for more than one thousandth of the factor are selected to
 185 reduce uncertainties. The clustering reagent ion NO₃⁻ or HNO₃NO₃⁻ has been omitted
 186 from the formulas.

187

No.	Formulas	Contribution to the factor (%)	DBE	n_O	n_N
1	C _x H _{2x-5} O ₆ N, x= [6, 12]	15.0	3	6	1
2	C _x H _{2x-3} O ₆ N, x= [6, 12]	8.8	2	6	1
3	C _x H _{2x} O ₇ N ₂ , x= [4, 14]	5.5	0	7	2

4	$C_xH_{2x-5}O_7N$, $x = [7, 11]$	3.9	3	7	1
5	$C_xH_{2x-1}O_5N$, $x = [4, 14]$	3.9	1	5	1
6	$C_xH_{2x+1}O_5N$, $x = [4, 13]$	3.4	0	5	1
7	$C_xH_{2x-1}O_6N$, $x = [4, 12]$	3.1	1	6	1
8	$C_xH_{2x-5}O_8N$, $x = [7, 11]$	2.5	3	8	1
9	$C_xH_{2x-3}O_7N$, $x = [6, 10]$	2.2	2	7	1
10	$C_xH_{2x-3}O_5N$, $x = [7, 13]$	1.9	2	5	1

188

189 S4.2 Aliph-OOM-I factor

190

191 Table S3. Molecular characteristics of the Aliph-OOM I factor. Presented as several
 192 sets of compounds, and the members of each set differ in the addition of a $-CH_2$ moiety.
 193 Only the signals that account for more than one thousandth of the factor are selected to
 194 reduce uncertainties. The clustering reagent ion NO_3^- or $HNO_3NO_3^-$ has been omitted
 195 from the formulas.

196

No.	Formulas	Contribution to the factor (%)	DBE	n_O	n_N
1	$C_xH_{2x-3}O_6N$, $x = [5, 13]$	12.6	2	6	1
2	$C_xH_{2x}O_7N_2$, $x = [4, 14]$	9.9	0	7	2
3	$C_xH_{2x-1}O_5N$, $x = [4, 14]$	6.8	1	5	1
4	$C_xH_{2x-2}O_8N_2$, $x = [5, 13]$	5.0	1	8	2
5	$C_xH_{2x-1}O_6N$, $x = [5, 12]$	3.8	1	6	1
6	$C_xH_{2x-4}O_4$, $x = [6, 11]$	2.8	3	4	0
7	$C_xH_{2x-2}O_7N_2$, $x = [6, 14]$	2.1	1	7	2
8	$C_xH_{2x-5}O_6N$, $x = [6, 12]$	2.1	3	6	1
9	$C_xH_{2x-2}O_4$, $x = [6, 10]$	2.1	2	4	0
10	$C_xH_{2x-3}O_7N$, $x = [6, 12]$	1.7	2	7	1

197

198 S4.3 Aliph-OOM-II factor

199

200 Table S4. Molecular characteristics of the Aliph-OOM II factor. Presented as several
 201 sets of compounds, and the members of each set differ in the addition of a $-CH_2$ moiety.
 202 Only the signals that account for more than one thousandth of the factor are selected to
 203 reduce uncertainties. The clustering reagent ion NO_3^- or $HNO_3NO_3^-$ has been omitted
 204 from the formulas.

205

No.	Formulas	Contribution to the factor (%)	DBE	n_O	n_N
1	$C_xH_{2x}O_7N_2$, $x = [4, 13]$	25.3	0	7	2
2	$C_xH_{2x-1}O_5N$, $x = [4, 10]$	6.7	1	6	1
3	$C_xH_{2x-2}O_8N_2$, $x = [5, 13]$	6.2	1	8	2
4	$C_xH_{2x-3}O_6N$, $x = [5, 10]$	5.0	2	6	1

5	$C_xH_{2x-2}O_7N_2$, x= [5, 13]	4.3	1	7	2
6	$C_xH_{2x-1}O_9N_3$, x= [5, 11]	2.0	0	9	3
7	$C_xH_{2x-4}O_8N_2$, x= [7, 12]	1.9	2	8	2
8	$C_xH_{2x-1}O_{10}N_3$, x= [5, 10]	1.2	0	10	3
9	$C_xH_{2x+1}O_5N$, x= [4, 8]	1.2	0	5	1
10	$C_xH_{2x-1}O_6N$, x= [5, 9]	1.2	1	6	1

206

207 **S4.4 O₃-related-I factor**

208

209 Table S5. Molecular characteristics of the O₃-related I factor. Presented as several sets
 210 of compounds, and the members of each set differ in the addition of a -CH₂ moiety.
 211 Only the signals that account for more than one thousandth of the factor are selected to
 212 reduce uncertainties. The clustering reagent ion NO₃⁻ or HNO₃NO₃⁻ has been omitted
 213 from the formulas.

214

No.	Formulas	Contribution to the factor (%)	DBE	n_O	n_N
1	$C_xH_{2x-3}O_6N$, x= [4, 12]	12.1	2	6	1
2	$C_xH_{2x-1}O_6N$, x= [4, 11]	7.2	1	6	1
3	$C_xH_{2x-3}O_7N$, x= [4, 11]	6.0	2	7	1
4	$C_xH_{2x-2}O_8N_2$, x= [4, 13]	5.9	1	8	2
5	$C_xH_{2x-5}O_7N$, x= [6, 11]	3.3	3	7	1
6	$C_xH_{2x-5}O_8N$, x= [7, 11]	3.1	3	8	1
7	$C_xH_{2x-5}O_6N$, x= [6, 10]	2.7	3	6	1
8	$C_xH_{2x}O_8N_2$, x= [4, 11]	2.5	0	8	2
9	$C_xH_{2x-2}O_9N_2$, x= [4, 11]	2.0	1	9	2
10	$C_xH_{2x-4}O_8N_2$, x= [6, 13]	1.9	2	8	2

215

216 **S4.5 O₃-related-II factor**

217

218 Table S6. Molecular characteristics of the O₃-related II factor. Presented as several sets
 219 of compounds, and the members of each set differ in the addition of a -CH₂ moiety.
 220 Only the signals that account for more than one thousandth of the factor are selected to
 221 reduce uncertainties. The clustering reagent ion NO₃⁻ or HNO₃NO₃⁻ has been omitted
 222 from the formulas.

223

No.	Formulas	Contribution to the factor (%)	DBE	n_O	n_N
1	$C_xH_{2x-3}O_6N$, x= [4, 10]	11.3	2	6	1
2	$C_xH_{2x-1}O_6N$, x= [4, 9]	4.9	1	6	1
3	$C_xH_{2x-4}O_4$, x= [6, 10]	4.7	3	4	0
4	$C_xH_{2x-3}O_7N$, x= [4, 10]	4.1	2	7	1
5	$C_xH_{2x-4}O_5$, x= [5, 10]	3.8	3	5	0

6	$C_xH_{2x}O_7N_2$, $x = [4, 10]$	3.5	0	7	2
7	$C_xH_{2x-5}O_6N$, $x = [5, 10]$	3.1	3	6	1
8	$C_xH_{2x-5}O_7N$, $x = [5, 10]$	2.8	3	7	1
9	$C_xH_{2x-6}O_5$, $x = [6, 10]$	2.8	4	5	0
10	$C_xH_{2x-2}O_4$, $x = [6, 9]$	2.4	2	4	0

224

225 S4.6 MT-mixed-OOM factor

226

227 Table S7. Molecular characteristics of the MT-mixed-OOM factor. Presented as several
 228 sets of compounds, and the members of each set differ in the addition of a $-CH_2$ moiety.
 229 Only the signals that account for more than one thousandth of the factor are selected to
 230 reduce uncertainties. The clustering reagent ion NO_3^- or $HNO_3NO_3^-$ has been omitted
 231 from the formulas.

232

No.	Formulas	Contribution to the factor (%)	DBE	n_O	n_N
1	$C_xH_{2x-3}O_6N$, $x = [5, 12]$	5.0	2	6	1
2	$C_xH_{2x-1}O_5N$, $x = [4, 13]$	4.8	1	5	1
3	$C_xH_{2x}O_7N_2$, $x = [5, 10]$	4.7	0	7	2
4	$C_xH_{2x-5}O_6N$, $x = [6, 12]$	4.6	3	6	1
5	$C_xH_{2x-4}O_4$, $x = [6, 11]$	3.5	3	4	0
6	$C_xH_{2x-1}O_6N$, $x = [4, 11]$	3.4	1	6	1
7	$C_xH_{2x+1}O_5N$, $x = [4, 10]$	3.2	0	5	1
8	$C_xH_{2x-3}O_5N$, $x = [4, 12]$	2.9	2	5	1
9	$C_xH_{2x-2}O_4$, $x = [6, 9]$	2.0	2	4	0
10	$C_xH_{2x-4}O_7N_2$, $x = [9, 10]$	1.5	2	7	2

233

234 S4.7 Mixed-OOM factor

235

236 Table S8. Molecular characteristics of the Mixed-OOM factor. Presented as several sets
 237 of compounds, and the members of each set differ in the addition of a $-CH_2$ moiety.
 238 Only the signals that account for more than one thousandth of the factor are selected to
 239 reduce uncertainties. The clustering reagent ion NO_3^- or $HNO_3NO_3^-$ has been omitted
 240 from the formulas.

241

No.	Formulas	Contribution to the factor (%)	DBE	n_O	n_N
1	$C_xH_{2x-3}O_6N$, $x = [4, 11]$	11.1	2	6	1
2	$C_xH_{2x-1}O_5N$, $x = [4, 12]$	8.2	1	5	1
3	$C_xH_{2x-5}O_6N$, $x = [6, 11]$	3.3	3	6	1
4	$C_xH_{2x-2}O_8N_2$, $x = [5, 10]$	2.5	1	8	2
5	$C_xH_{2x}O_7N_2$, $x = [5, 12]$	2.5	0	7	2
6	$C_xH_{2x-1}O_6N$, $x = [4, 8]$	2.1	1	6	1

7	$C_xH_{2x-2}O_4$, x= [6, 9]	2.1	2	4	0
8	$C_xH_{2x-3}O_5N$, x= [4, 12]	1.8	2	5	1
9	$C_xH_{2x-4}O_4$, x= [6, 10]	1.7	3	4	0
10	$C_xH_{2x-6}O_4$, x= [6, 8]	1.3	4	4	0

242 **S5 The additional information of the Arom-OOM factor**

243 The aromatic oxidation proxy represents the aromatic photo-oxidation and can calculate
 244 by Eq. (9):

245

$$246 \quad \text{Aromatic oxidation proxy} = k_{OH} \times \text{Aromatics} \times J(O^1D) \quad (9)$$

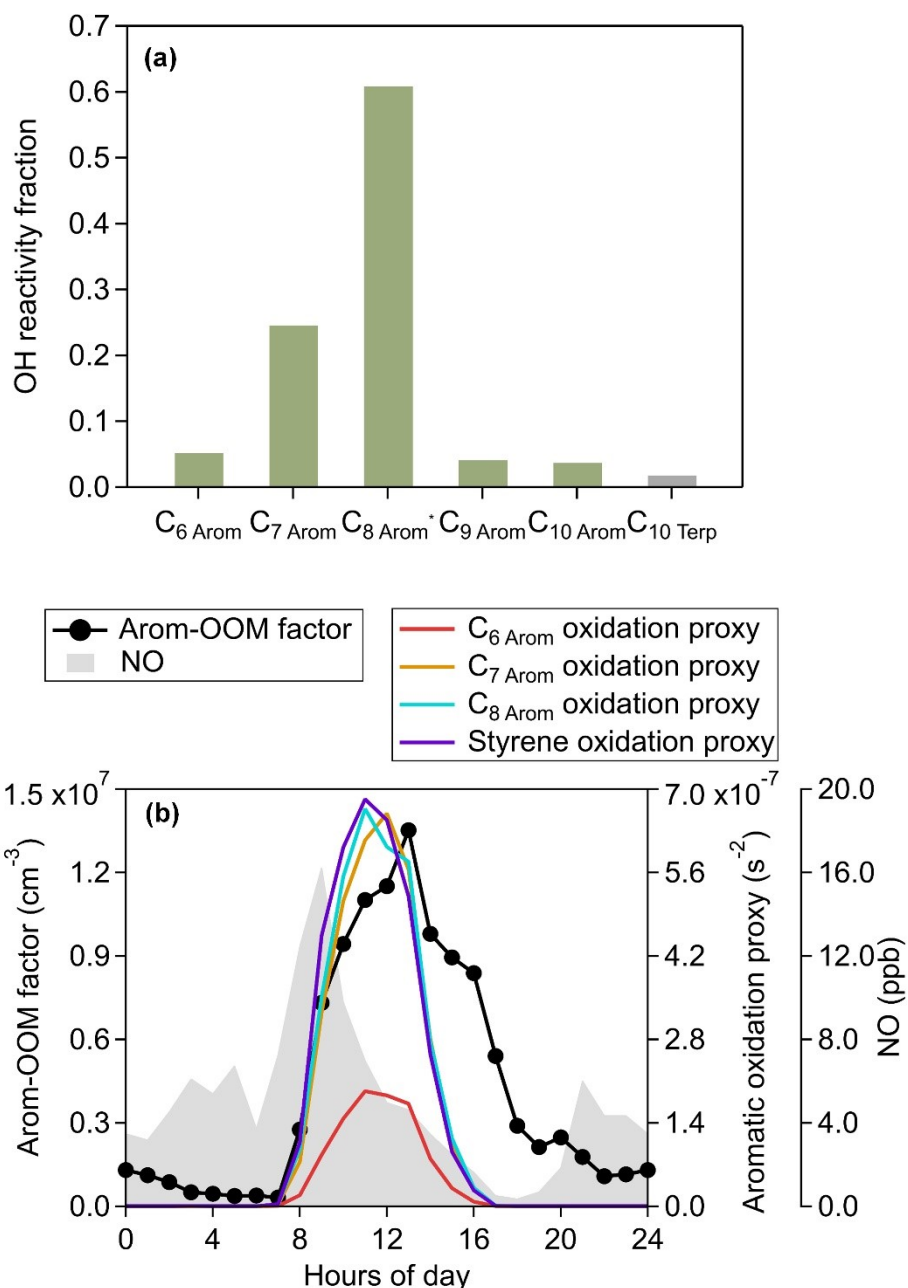
247

248 Where k_{OH} is a reaction constant for the photo-oxidation of aromatics.

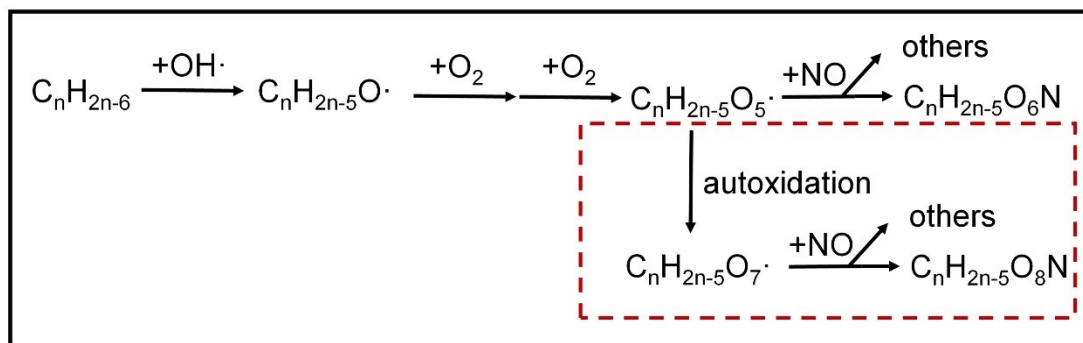
249

250 Here, we add the OH reactivity of monoterpenes to analysis.

251



252
 253 Fig. S8 The analysis of the Arom-OOM factor. (a) The OH reactivity distribution of C₆
 254 Arom, C₇ Arom, C₈ Arom*, C₉ Arom, C₁₀ Arom and C₁₀ Terp (Note: C₈ Arom* = C₈ Arom + Styrene),
 255 (b) the median diurnal patterns of Arom-OOM factor and C₆ Arom, C₇ Arom, C₈ Arom,
 256 Styrene oxidation proxy.



257
 258 Fig.S9 The potential reaction pathway of the OH-initiated oxidation of aromatics to

259 form $C_xH_{2x-5}O_6N$ and $C_xH_{2x-5}O_8N$.

260 S6 The additional information of two Aliph-OOM factors

261 As described in Liu et al.⁶, considering a simple scenario of alkane photo-oxidation
262 under high NO_x conditions: the RO_2 generated from OH attack is completely terminated
263 by NO (Fig. S9(a)). The chain-retaining products are $C_nH_{2n}O$ (one more carbonyl group
264 than the precursor) and $C_nH_{2n+1}O_3N$ (one more nitrate group than the precursor).
265 Further re-oxidation of these products is a repetition of the same process and the 1st -
266 3rd multi-generation products of alkanes summarized in Fig. S9(b) are regarded as
267 reference compounds, which we compare OOMs with to investigate other mechanisms

268 that differ from those shown in Fig. S9(a). The number of extra oxygen ($n_{O_{extra}}$) from
269 each aliphatic OOM over its corresponding reference molecule was calculated by Eq.

270 (10). The $n_{O_{extra}}$ can represent the extra oxygenated moieties with other processes.

271

272 The $n_{O_{extra}}$ is calculated by Eq. (10):

273

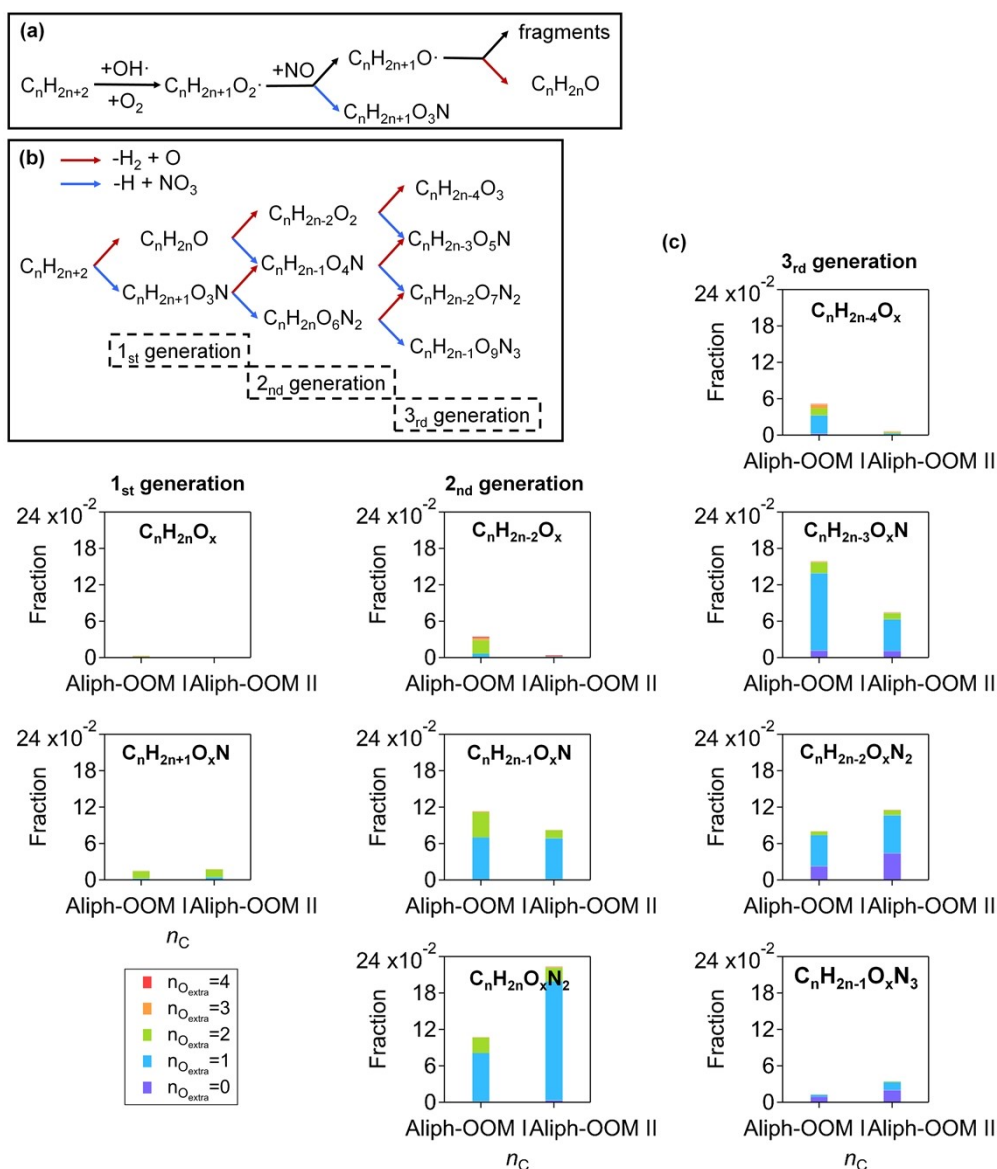
$$274 \quad n_{O_{extra}} = n_O - DBE - 3 \times n_N \quad (10)$$

275

276 Where the DBE is calculated based on Eq. (4).

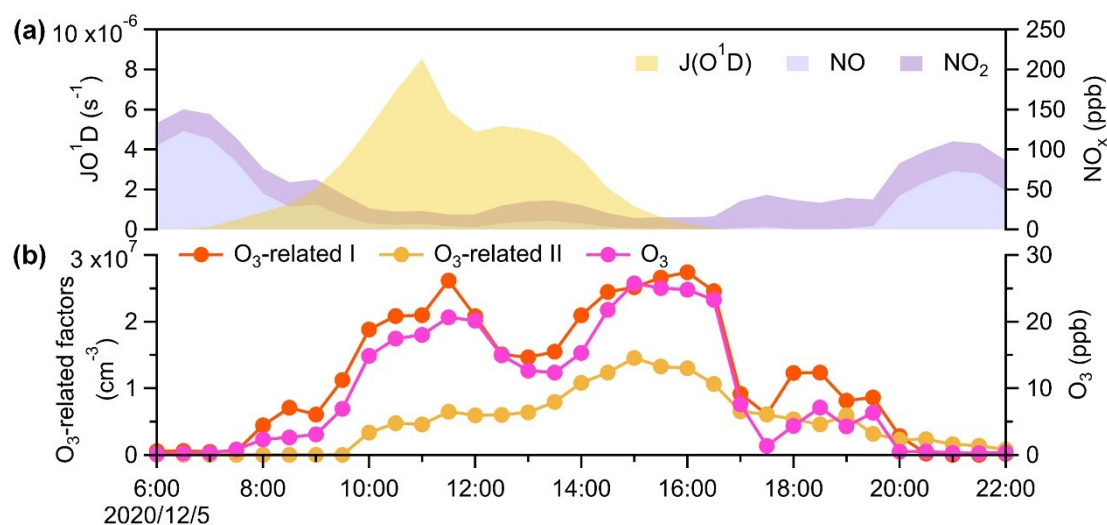
277

278 As showed in Fig. S9(c), two Aliph-OOM factors are mainly dominated by second and
279 third generation products and Aliph-OOM-I factor contains more carbonyl group while
280 Aliph-OOM-II factor prefers to contain nitrate groups.

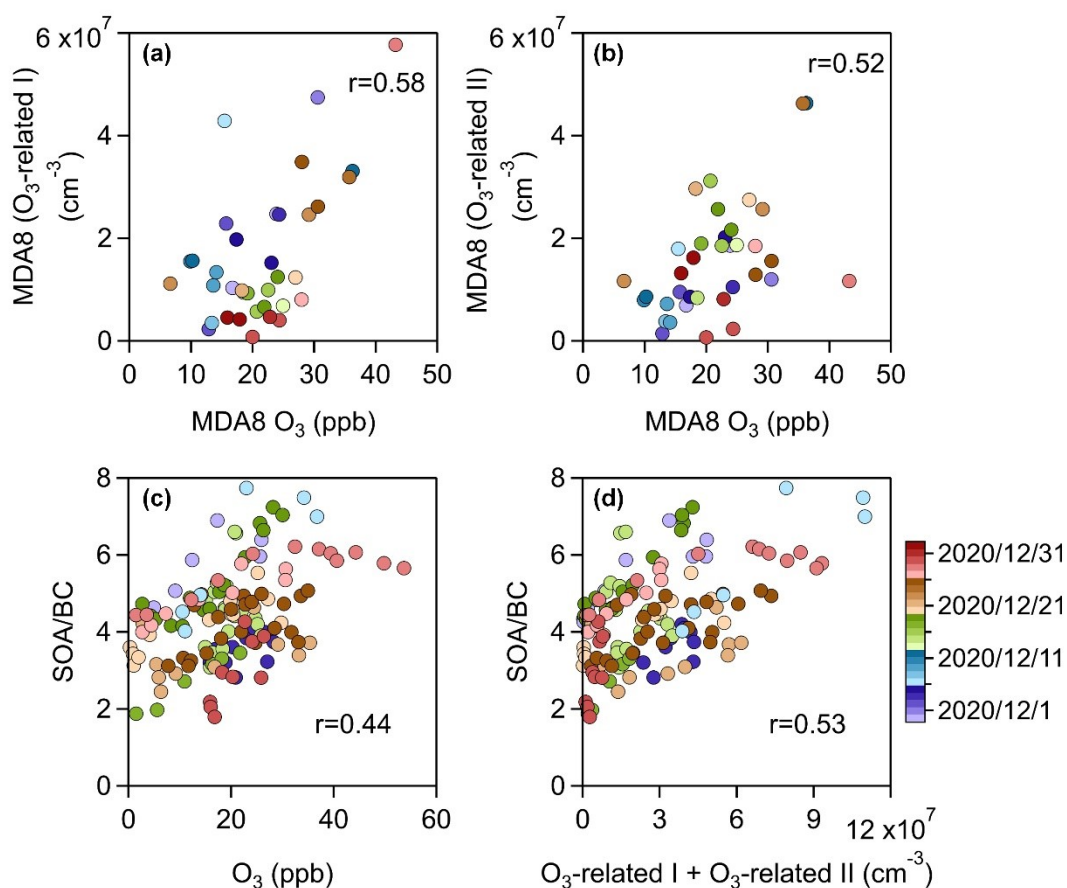


281
 282 Fig. S10 The multi-generation oxidation of two Aliph-OOM factors. (a) and (b) is
 283 adopted from Liu et al.⁶. (c) The compounds with same number of carbon, hydrogen,
 284 and nitrogen atoms but different numbers of oxygen atoms are grouped according to
 285 the molecular formulas in (b). The bars in (c) are colored with $n_{O_{extra}}$.
 286

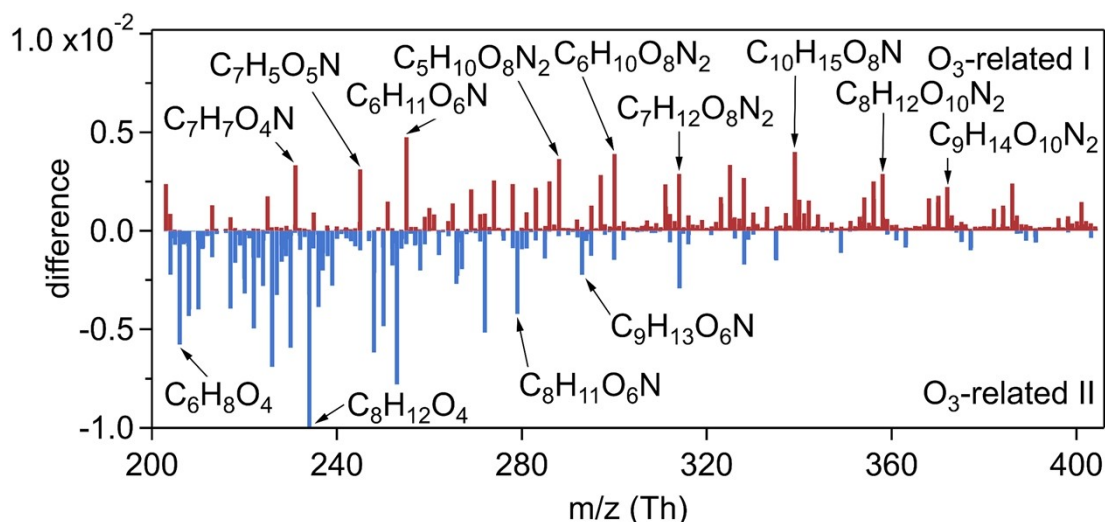
287 **S7 The additional information of two O₃-related factors**



288
 289 Fig.S11 The time series of select case that O₃-related factors follow O₃ varies, (a)
 290 J(O¹D) and NO_x, (b) O₃-related I, O₃-related II and O₃.
 291

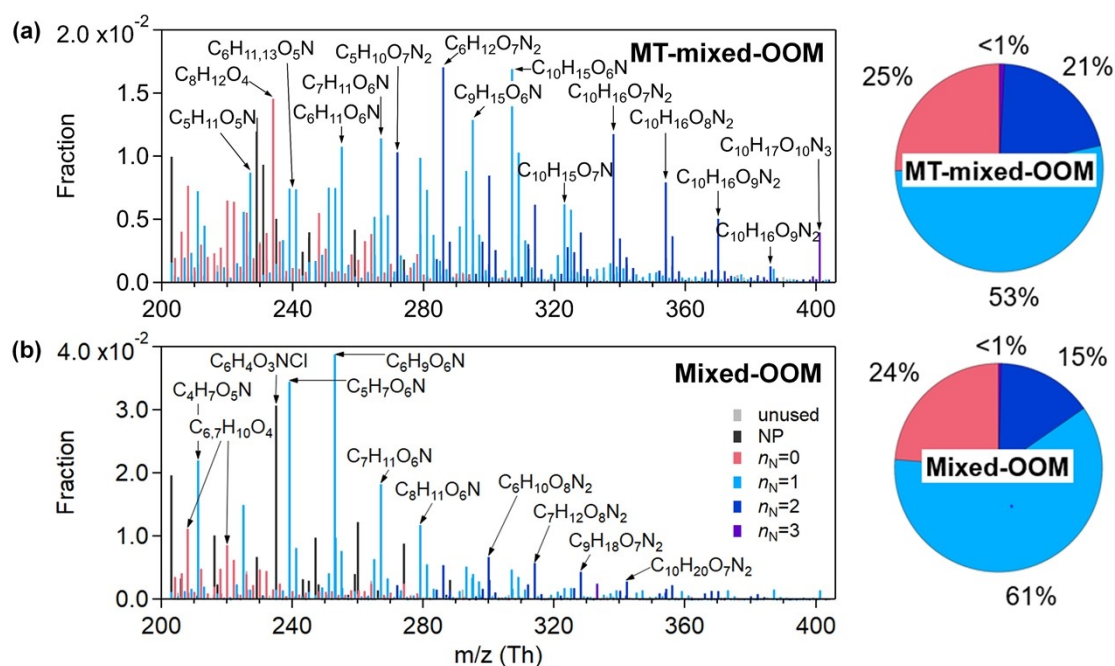


292
 293 Fig.S12 Scatter plots of (a) the maximum daily 8-h average (MDA8) O₃-related I , and
 294 (b) MDA8 O₃-related II with MDA8 O₃, secondary organic aerosol(SOA) to black
 295 carbon(BC) ratio with (c) ozone and (d) two O₃-related factors in 17 ozone production
 296 cases.
 297

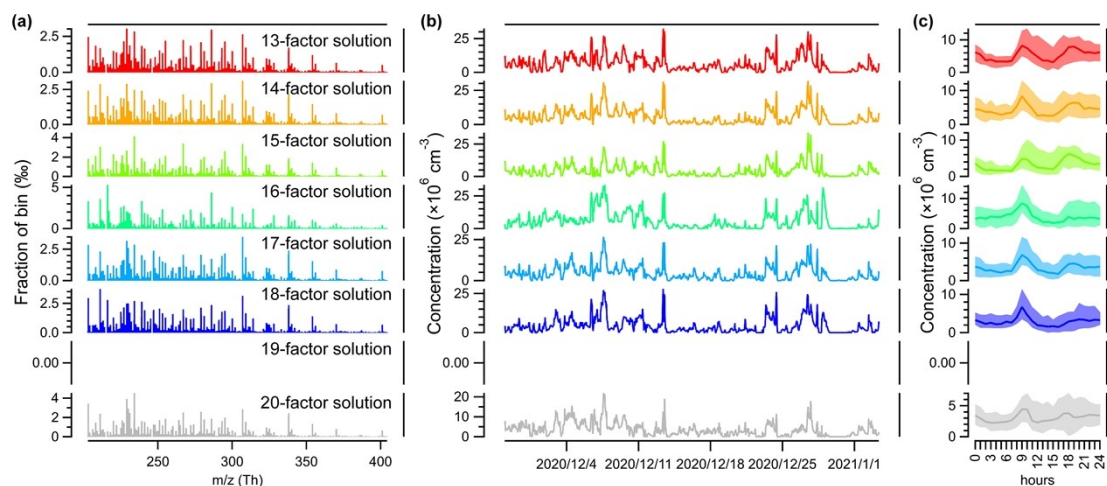


298
 299 Fig. S13 The difference in mass-to-charge of the O₃-related-I factor and O₃-related-II
 300 factor.
 301

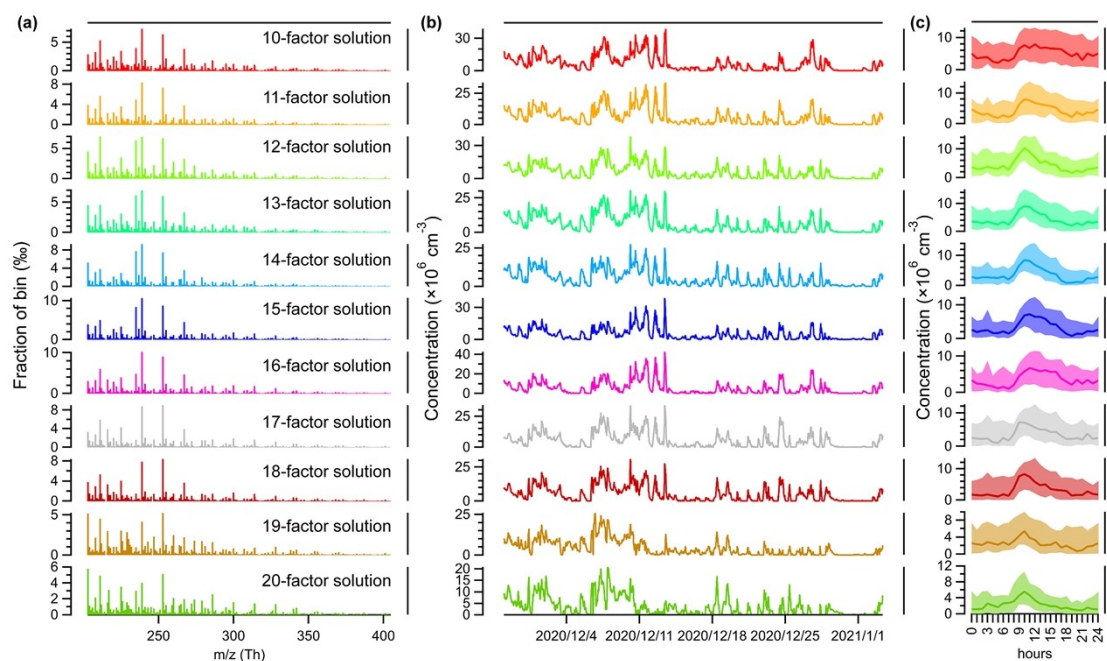
302 **S8 The additional information of the Mixed-OOM and the MT-mixed-OOM**
 303 **factors**



304
 305 Fig. S14 Profiles of 2 binPMF factors. Mass spectra and pie of (a) the MT-mixed-OOM
 306 factor, (b) the Mixed-OOM factor. The elemental formulas of major peaks are labeled
 307 above them. Peaks are color-coded by n_N , and the fractions of peaks grouped by n_N are
 308 reported in the pie chart for each factor. The gray sticks are fluorinated contaminations,
 309 or non-identified compounds. The nitrated phenols are drawn separately with black
 310 peaks. So n_N can more reliably represent the number of nitrate groups in each molecule.
 311

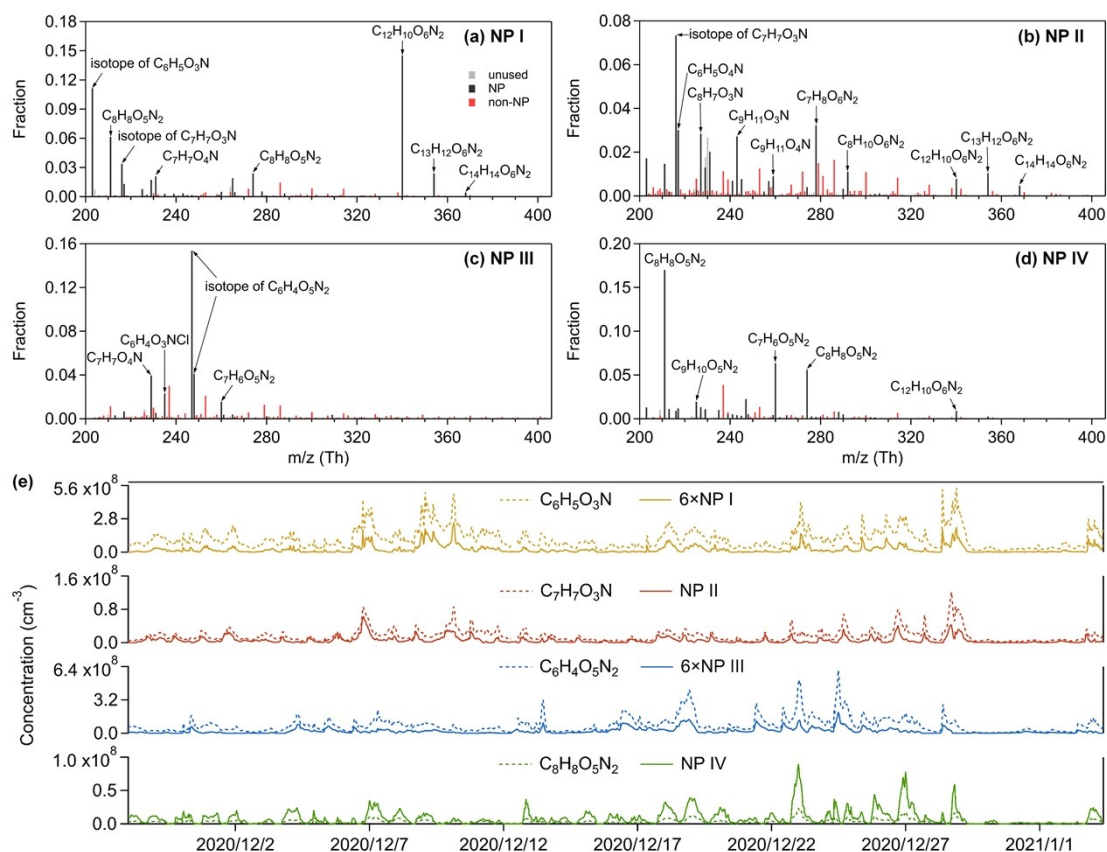


312 Fig. S15 Evolution of the MT-mixed-OOM factor. (a) profiles, (b) time series, and (c)
 313 diurnal patterns.
 314
 315

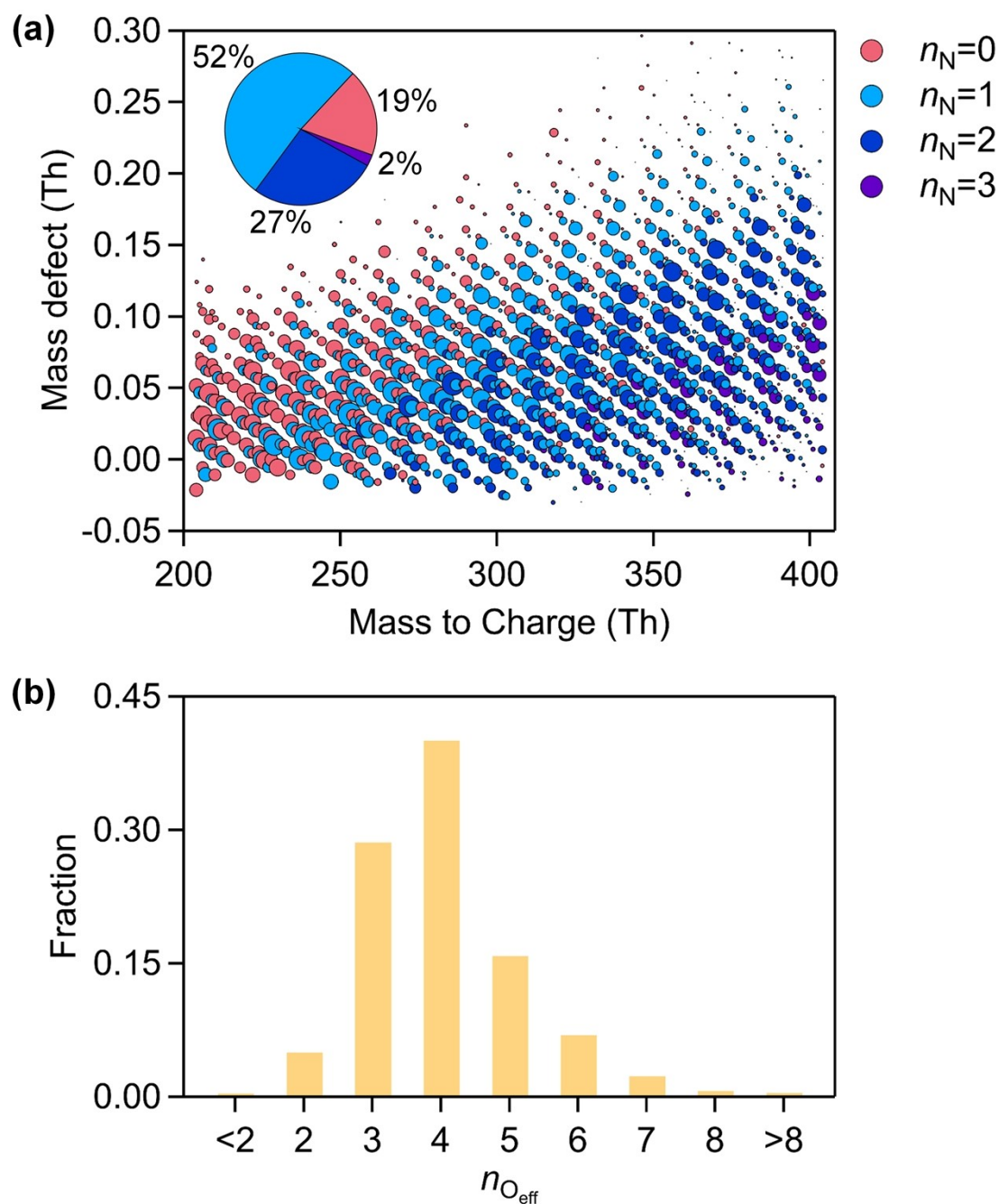


316 Fig. S16 Evolution of the Mixed-OOM factor. (a) profiles, (b) time series, and (c)
 317 diurnal patterns.
 318
 319

320 **S9 The additional information of NP factors**



321
 322 Fig. S17 Profiles of NP factors. Mass spectra and pie of (a) NP-I factor, (b) NP-II factor,
 323 (c) NP-III, (d) NP-IV. The time series of four factors and their traces was plotted in (e).
 324 The nitrated phenols are drawn separately with black peaks in (a–d), while other OOMs
 325 are plotted as red peaks.
 326

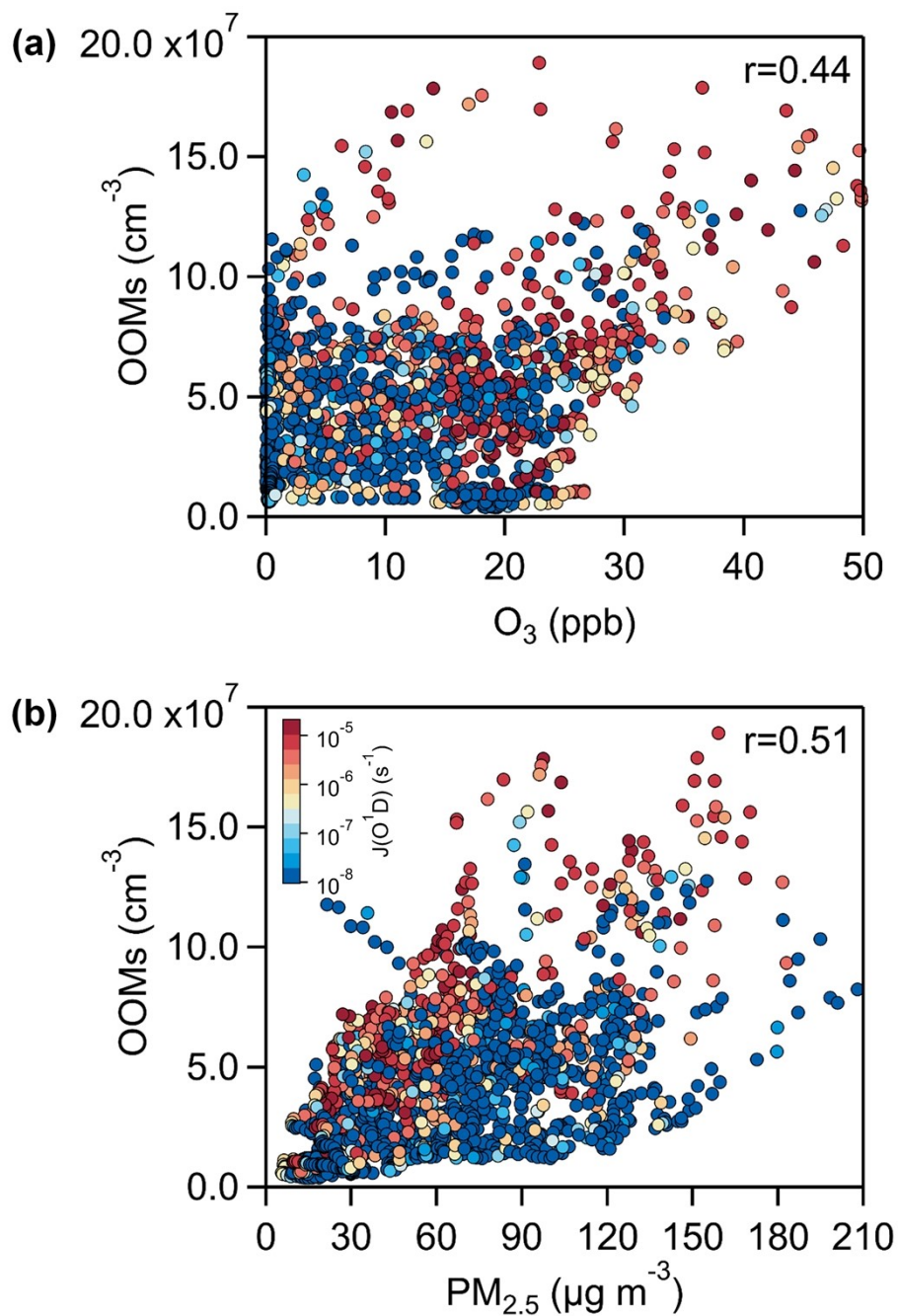


328

329 Fig. S18 The molecular information of the high-quality OOMs dataset. (a) Mass defect
 330 plot of the OOMs dataset. The x axis shows the exact mass of the OOMs and y axis
 331 shows their mass defect (exact mass subtracted by its unit mass). The color of the
 332 marker point represents n_N and the size of the marker point corresponds to the
 333 concentration of OOMs, (b) the distribution of OOMs dataset grouped by $n_{O_{eff}}$.

334

335 S11 Relationship of OOMs with O₃, PM_{2.5}

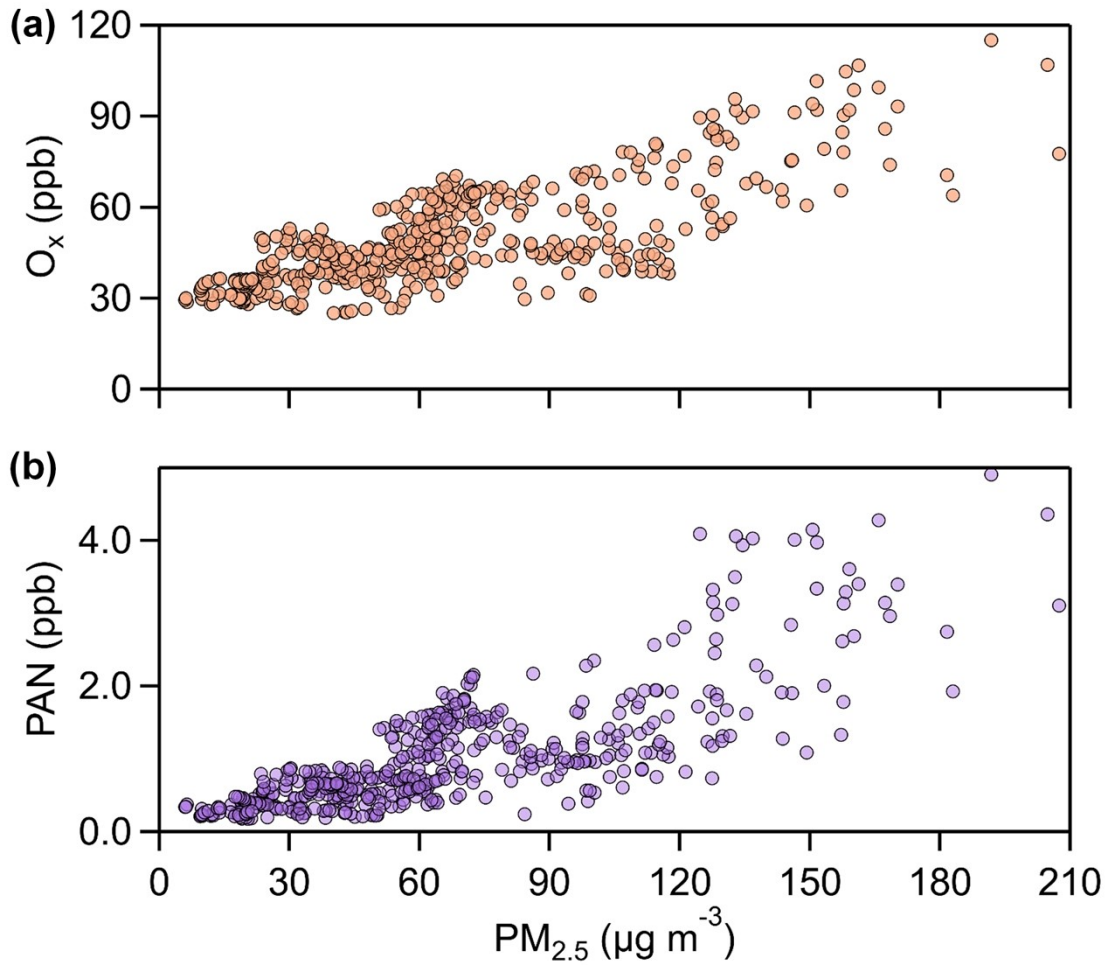


336
337 Fig. S19 The scatter plot of OOMs with (a) O₃, (b) PM_{2.5} in all time, each dot is colored
338 by J(O¹D).

339

340 S12 Relationship of PM_{2.5} with O_x and PAN

341



342
 343 Fig. S20 The scatter plot of PM_{2.5} with (a) O_x (O_x = O₃ + NO₂ + NO_z, NO_z = NO_y –
 344 NO_x), (b) PAN in the daytime.
 345

346 **S13 The calculation of OH proxy**

347 The OH proxy is calculated by applying the Eq. (11):

348

$$OH\ proxy = \frac{[H_2SO_4] \times CS}{[SO_2]} \quad (11)$$

349

350 Where the value of CS was calculated following Eq. (14)¹¹:

351

$$CS = 2\pi D \sum_i \beta_{m_i} d_{p_i} N_i \quad (12)$$

352

353

354 Where D is the diffusion coefficient of gaseous sulfuric acid, β_m is a transition-regime
 355 correction factor dependent on the Knudsen number¹², and d_{p_i} and N_i are the diameter
 356 and number concentration of particles in size bin i.

357

358

359

360

361

362

363 **Reference**

364

365 1. Y. J. Zhang, O. Perakyla, C. Yan, L. Heikkinen, M. Aijala, K. R. Daellenbach, Q. Z. Zha, M.
366 Riva, O. Garmash, H. Junninen, P. Paatero, D. Worsnop and M. Ehn, A novel approach for
367 simple statistical analysis of high-resolution mass spectra, *Atmospheric Measurement*
368 *Techniques*, 2019, **12**, 3761-3776.

369 2. A. V. Polissar, P. K. Hopke, P. Paatero, W. C. Malm and J. F. Sisler, Atmospheric aerosol over
370 Alaska: 2. Elemental composition and sources, *Journal of Geophysical Research: Atmospheres*,
371 1998, **103**, 19045-19057.

372 3. J. D. Allan, J. L. Jimenez, P. I. Williams, M. R. Alfarra, K. N. Bower, J. T. Jayne, H. Coe and D.
373 R. Worsnop, Quantitative sampling using an Aerodyne aerosol mass spectrometer 1.
374 Techniques of data interpretation and error analysis, *Journal of Geophysical Research:*
375 *Atmospheres*, 2003, **108**, 4283.

376 4. C. Yan, W. Nie, M. Äijälä, M. P. Rissanen, M. R. Canagaratna, P. Massoli, H. Junninen, T.
377 Jokinen, N. Sarnela, S. A. K. Häme, S. Schobesberger, F. Canonaco, L. Yao, A. S. H. Prévôt,
378 T. Petäjä, M. Kulmala, M. Sipilä, D. R. Worsnop and M. Ehn, Source characterization of highly
379 oxidized multifunctional compounds in a boreal forest environment using positive matrix
380 factorization, *Atmospheric Chemistry and Physics*, 2016, **16**, 12715-12731.

381 5. Q. Zhang, J. L. Jimenez, M. R. Canagaratna, I. M. Ulbrich, N. L. Ng, D. R. Worsnop and Y. Sun,
382 Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry:
383 a review, *Anal Bioanal Chem*, 2011, **401**, 3045-3067.

384 6. Y. Liu, W. Nie, Y. Li, D. Ge, C. Liu, Z. Xu, L. Chen, T. Wang, L. Wang, P. Sun, X. Qi, J. Wang,
385 Z. Xu, J. Yuan, C. Yan, Y. Zhang, D. Huang, Z. Wang, N. M. Donahue, D. Worsnop, X. Chi,
386 M. Ehn and A. Ding, Formation of condensable organic vapors from anthropogenic and
387 biogenic volatile organic compounds (VOCs) is strongly perturbed by NO_x in eastern China,
388 *ATMOSPHERIC CHEMISTRY AND PHYSICS*, 2021, **21**, 14789-14814.

389 7. J. H. Kroll, N. M. Donahue, J. L. Jimenez, S. H. Kessler, M. R. Canagaratna, K. R. Wilson, K. E.
390 Altieri, L. R. Mazzoleni, A. S. Wozniak, H. Bluhm, E. R. Mysak, J. D. Smith, C. E. Kolb and
391 D. R. Worsnop, Carbon oxidation state as a metric for describing the chemistry of atmospheric
392 organic aerosol, *Nature Chemistry*, 2011, **3**, 133-139.

393 8. N. M. Donahue, S. A. Epstein, S. N. Pandis and A. L. Robinson, A two-dimensional volatility
394 basis set: 1. organic-aerosol mixing thermodynamics, *Atmospheric Chemistry and Physics*,
395 2011, **11**, 3303-3318.

396 9. D. Stolzenburg, L. Fischer, A. L. Vogel, M. Heinritzi, M. Schervish, M. Simon, A. C. Wagner,
397 L. Dada, L. R. Ahonen, A. Amorim, A. Baccharini, P. S. Bauer, B. Baumgartner, A. Bergen, F.
398 Bianchi, M. Breitenlechner, S. Brilke, S. B. Mazon, D. Chen, A. Dias, D. C. Draper, J. Duplissy,
399 I. El Haddad, H. Finkenzeller, C. Frege, C. Fuchs, O. Garmash, H. Gordon, X. He, J. Helm, V.
400 Hofbauer, C. R. Hoyle, C. Kim, J. Kirkby, J. Kontkanen, A. Kuerten, J. Lampilahti, M. Lawler,
401 K. Lehtipalo, M. Leiminger, H. Mai, S. Mathot, B. Mentler, U. Molteni, W. Nie, T. Nieminen,
402 J. B. Nowak, A. Ojdanic, A. Onnela, M. Passananti, T. Petaja, L. L. J. Quelever, M. P. Rissanen,
403 N. Sarnela, S. Schallhart, C. Tauber, A. Tome, R. Wagner, M. Wang, L. Weitz, D. Wimmer, M.
404 Xiao, C. Yan, P. Ye, Q. Zha, U. Baltensperger, J. Curtius, J. Dommen, R. C. Flagan, M.

- 405 Kulmala, J. N. Smith, D. R. Worsnop, A. Hansel, N. M. Donahue and P. M. Winkler, Rapid
406 growth of organic aerosol nanoparticles over a wide tropospheric temperature range, *Proc. Natl.*
407 *Acad. Sci. U. S. A.*, 2018, **115**, 9122-9127.
- 408 10. S. A. Epstein, I. Riipinen and N. M. Donahue, A Semiempirical Correlation between Enthalpy
409 of Vaporization and Saturation Concentration for Organic Aerosol, *Environmental Science &*
410 *Technology*, 2010, **44**, 743-748.
- 411 11. M. Kulmala, T. Petaja, T. Nieminen, M. Sipila, H. E. Manninen, K. Lehtipalo, M. Dal Maso, P.
412 P. Aalto, H. Junninen, P. Paasonen, I. Riipinen, K. E. Lehtinen, A. Laaksonen and V. M.
413 Kerminen, Measurement of the nucleation of atmospheric aerosol particles, *Nat Protoc*, 2012,
414 **7**, 1651-1667.
- 415 12. N. A. Fuchs and A. G. Sutugin, in *Topics in Current Aerosol Research*, eds. G. M. Hidy and J. R.
416 Brock, Pergamon, 1971, p. 1.
- 417