

1 **Molecular and seasonal characteristics of organic vapors in**  
2 **urban Beijing: insights from Vocus-PTR measurements**

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27

28 **Abstract**

29 Understanding the composition and evolution of atmospheric organic vapors is  
30 crucial for exploring their impact on air quality. However, the molecular and  
31 seasonal characteristics of organic vapors in urban areas, with complex  
32 anthropogenic emissions and high variability, remain inadequately understood.  
33 In this study, we conducted measurements in urban Beijing during 2021-2022  
34 covering four seasons using an improved Proton Transfer Reaction-Mass  
35 Spectrometry (Vocus-PTR MS). During the measurement period, a total of 895  
36 peaks were observed, and 512 of them can be assigned to formulas. The  
37 contribution of  $C_xH_yO_z$  species is most significant, which composes up to 54%  
38 of the number and 74% of the mixing ratio of total organics. With enhanced  
39 sensitivity and mass resolution, various species with sub-ppt level or multiple  
40 oxygens ( $\geq 3$ ) were observed, with 44% of the number measured at sub-ppt  
41 level and 31% of the number containing 3-8 oxygens. Organic vapors with  
42 multiple oxygens mainly consist of intermediate/semi-volatile compounds, and  
43 many of formulae detected were reported to be the oxidation products of  
44 various volatile organic precursors. In summer, the fast photooxidation process  
45 generate organic vapors with multiple oxygens and lead to an increase in both  
46 their mixing ratio and proportion. While in other seasons, the variations of  
47 organic vapors with multiple oxygens are closely correlated with those of  
48 organic vapors with 1-2 oxygens, which could be substantially influenced by  
49 primary emissions. Organic vapors with low oxygen content ( $\leq 2$  oxygens) are  
50 comparable to the results obtained by traditional PTR-MS measurements in  
51 both urban Beijing and neighboring regions.  
52

## 53 1 Introduction

54 Volatile organic compounds (VOCs) play a crucial role in the formation of ozone  
55 and fine particulate matter (PM<sub>2.5</sub>) in the atmosphere, subsequently affecting air  
56 quality, climate, and human health (Carter, 1994; Williams and Kopppmann,  
57 2007; Jimenez et al., 2009; Hallquist et al., 2009). The sources and atmospheric  
58 evolution of VOCs in the atmosphere are complex due to the coexistence of  
59 compounds from primary emissions as well as secondary formation (Gentner  
60 et al., 2013; Gilman et al., 2015; Millet et al., 2015). Understanding their  
61 molecular characteristics is essential for studying their hydroxyl radical (OH)  
62 reactivities, ozone and secondary organic aerosol (SOA) formation potentials.  
63 However, the diverse range of species and wide distribution of oxidation  
64 products of atmospheric VOCs make it challenging to unravel their molecular  
65 properties (Goldstein and Galbally, 2007).

66 Instrumental advances have allowed for improving the understanding of the  
67 compositions and variations of VOCs at the molecular level, especially for  
68 oxygenated VOCs (OVOCs). Gas chromatography or multidimensional gas  
69 chromatography coupled with mass spectrometry is the most commonly used  
70 technology for VOC measurement, capable of detecting major non-methane  
71 hydrocarbons and select OVOCs (Lewis et al., 2000; Xu et al., 2003; Noziere  
72 et al., 2015). Proton Transfer Reaction-Mass Spectrometry (PTR-MS) enables  
73 real-time detection of VOCs without pre-concentration and separation, greatly  
74 enriching the molecular understanding of OVOCs due to its high sensitivity to  
75 oxygen-containing compounds (Hansel et al., 1995; De Gouw and Warneke,  
76 2007; Yuan et al., 2017). Hundreds of OVOCs are detected and characterized  
77 in different areas using PTR-MS, e.g. urban (Wu et al., 2020), suburban (He et  
78 al., 2022), and forest areas (Pugliese et al., 2023). Recent developments in the  
79 ion-molecule reactor (IMR) configuration have greatly increased sensitivities  
80 and concurrently lowered the limits of detection of PTR-MS by several orders  
81 of magnitude by incorporating radio frequency electric fields to focus ions  
82 (Breitenlechner et al., 2017; Krechmer et al., 2018; Reinecke et al., 2023). A  
83 consequential issue is that these advanced PTR-MS typically need to eliminate  
84 lighter ions to protect the detector from overload, and similar to traditional PTR-  
85 MS, they are incapable of obtaining molecular structure information.

86 These improvements have expanded the detection capabilities of PTR-MS,  
87 particularly for organic vapors with lower volatility and multiple oxygens ( $\geq 3$ )  
88 (Riva et al., 2019), which enables the simultaneous measurement of VOC  
89 precursors and their primary, secondary, and higher-level oxidation products  
90 using a single instrument (Li et al., 2020). Despite their low concentrations,  
91 these vapors may condense on pre-existing aerosols and make a significant  
92 contribution to secondary aerosol growth and cloud condensation nuclei  
93 (Bianchi et al., 2019; Pospisilova et al., 2020; Nie et al., 2022). Organic vapors

94 with multiple oxygens are likely to be simultaneously detected by other chemical  
95 ionization mass spectrometry (CIMS), e.g., nitrate ( $\text{NO}_3^-$ ), iodide ( $\text{I}^-$ ), bromide  
96 ( $\text{Br}^-$ ), and ammonium ( $\text{NH}_4^+$ ) (Riva et al., 2019; Huang et al., 2021), which are  
97 widely used for measuring oxygenated organic compounds in the atmosphere  
98 (Bianchi et al., 2019; Ye et al., 2021; Huang et al., 2021). Therefore, using these  
99 improved PTR-MS can supplement our understanding of oxygenated organic  
100 vapors and facilitate the study of atmospheric chemical evolution of organics  
101 (Wang et al., 2020a).

102 The improved PTR-MS systems have gradually gained traction in research  
103 applications over the past few years, including measuring organics in controlled  
104 lab studies (Zaytsev et al., 2019a; Zaytsev et al., 2019b; Riva et al., 2019; Li et  
105 al., 2022a; Li et al., 2024a), emission sources (Sreeram et al., 2022; Yu et al.,  
106 2022; Yacovitch et al., 2023; Wohl et al., 2023; Jahn et al., 2023), and ambient  
107 air. For ambient measurements, observations in forested regions have been  
108 extensively conducted to study the compositions, variations, fluxes, and  
109 emissions of organics from different plants (Li et al., 2020; Li et al., 2021; Huang  
110 et al., 2021; Fischer et al., 2021; Thomas et al., 2022; Vettikkat et al., 2023;  
111 Vermeuel et al., 2023). Terpenes and their oxidation products with oxygen  
112 number up to 6 have been detected (Li et al., 2020). Diterpenes have been  
113 directly observed in the ambient air for the first time owing to the substantial  
114 improvement in sensitivity of Vocus-PTR (Li et al., 2020). Ambient  
115 measurement has been also conducted on a mountain in China, which found  
116 that terpenes and their oxidation products dominate the detected organic  
117 compounds, while the influence of industrial emissions can also be observed  
118 (Zhang et al., 2024).

119 In urban atmospheres, the sources and evolution of VOCs are considerably  
120 complex, potentially exhibiting distinct characteristics compared to forested  
121 areas. Several studies have carried out measurements in urban air using these  
122 improved PTR-MS. Jensen et al. (2023) conducted a one-month observation to  
123 address the production of reliable measurements. Coggon et al. (2024)  
124 evaluated the fragmentation and interferences of a series of urban VOCs.  
125 Pfannerstill et al. (2023 and 2024) measured hundreds of VOCs to calculate  
126 their emission fluxes in Los Angeles. A few low-signal species including  
127 dimethylamine, icosanal, dimethyl disulfide, and siloxanes emitted from diverse  
128 emission sources have been detected as a result of the enhanced sensitivity  
129 (Wang et al., 2020b; Chang et al., 2022; Jensen et al., 2023). However, the  
130 understanding of organic vapors with multiple oxygens in urban air, including  
131 their species, mixing ratios, diurnal profiles, and seasonal variations, remains  
132 inadequate.

133 In this study, we conducted measurements of organic vapors using a Vocus-  
134 PTR in urban Beijing during 2021-2022, covering four seasons. We present  
135 general characteristics of measured organic vapors and compare them with

136 traditional PTR-MS and previous Vocus-PTR measurements. We focus on  
137 organic vapors with multiple oxygens (three or more), which have rarely been  
138 individually analyzed in previous studies due to their low mixing ratios. Their  
139 chemical compositions, atmospheric mixing ratios, diurnal and seasonal  
140 variations are reported. Cluster analysis is further conducted to resolve the  
141 main driving factors of their variations.

## 142 **2 Methods**

### 143 **2.1 Measurements**

144 The observation site is located in the central area of Tsinghua University, Beijing  
145 (40°0'N, 116°20'E). It is an urban site with no significant direct influence from  
146 industrial activities or heavy-traffic arteries ([Fig. S1](#) in the supporting information,  
147 SI). Details of this site can be found in the previous study (Cai and Jiang, 2017).  
148 Organic vapors were measured by a Vocus-2R PTR-TOF-MS (Tofwerk AG and  
149 Aerodyne Research Inc., referred to as Vocus-PTR hereinafter), which is  
150 situated on top of a fourth-floor tower building, with its sampling inlet positioned  
151 approximately 20 meters above the ground. The observation period is from May  
152 1<sup>st</sup>, 2021 to March 10<sup>th</sup>, 2022, covering four seasons. Detailed information about  
153 observation periods and their corresponding seasons is shown in [Table S1](#).

154 The operating parameters of the Vocus-PTR used in this study are briefly  
155 described here. In PTR-MS, VOCs are ionized via proton transfer by hydronium  
156 ions ( $\text{H}_3\text{O}^+$ ) in the IMR (Hansel et al., 1995; Yuan et al., 2016). The sensitivity  
157 can be quantified based on the proton transfer reaction rate while  
158 simultaneously considering ion transmission, detector efficiency, etc. (Cappellin  
159 et al., 2012; Jensen et al., 2023). The ion source was supplied with a water  
160 vapor flow of 20 sccm. The IMR was operated at 100°C and 2 mbar with axial  
161 voltage of 600 V and quadrupole amplitude voltage of 450 V. The IMR operating  
162 parameters were optimized to minimize the formation of water clusters. Mass  
163 spectra were collected from  $m/z$  11 to  $m/z$  398 with a time resolution of 5 s,  
164 achieving a mass resolution  $\sim 10,000$  for  $\text{C}_7\text{H}_9^+$  throughout the measurement  
165 period. Ambient air was sampled via a tetrafluoroethylene (PTFE) tube (1.35 m  
166 long, 1/4-inch OD) at a flow rate of 3 LPM to reduce wall losses, with only 150  
167 sccm flow entering the Vocus-PTR. The sampling tube was heated to  $50 \pm 5^\circ\text{C}$   
168 during the measurement. A regularly replaced Teflon filter (every 7 days) was  
169 used in front of the sampling line to prevent the orifice from clogging. The data  
170 within 30 minutes after membrane replacement was excluded. Measurements  
171 were made on a 2-hour cycle with 110 min for ambient air, 5 min for zero gas,  
172 and 5 min for fast calibration. The fast calibrations involved the use of mixed  
173 calibration gases, with detailed information available in [Table S2](#).

174 The ambient  $\text{PM}_{2.5}$ ,  $\text{NO}_2$ , and  $\text{O}_3$  data are from a state-operated air quality

175 station (Wanliu station), located approximately 3.6 km away from our  
176 observation site. The meteorological parameters, including temperature (T),  
177 relative humidity (RH), wind speed, and wind direction are also from Wanliu  
178 station. The diurnal variations of PM<sub>2.5</sub>, O<sub>3</sub>, NO<sub>x</sub>, RH, and T in four seasons are  
179 shown in [Figure S2](#).

## 180 **2.2 Data processing**

181 Data analysis of Vocus-PTR mass spectra, including mass calibration, baseline  
182 subtraction, and high-resolution peak fitting was conducted using Tofware  
183 (v3.2.3, Tofwerk AG and Aerodyne Research Inc.) within the Igor Pro 8 platform  
184 (WaveMetrics, OR, USA). The ambient mass spectra were averaged over 1 min  
185 for subsequent processing in Tofware. The peaklist used for high-resolution  
186 peak fitting was manually made based on mass spectra of both clean days  
187 (PM<sub>2.5</sub> < 75 µg/m<sup>3</sup>) and polluted days (PM<sub>2.5</sub> ≥ 75 µg/m<sup>3</sup>). The maximum mass  
188 error allowed for identifying peaks is 5-10 ppm, which is consistent of the error  
189 of mass calibration. When there are multiple options of formulas meeting the  
190 error limit under, especially at high molecular weights, a peak with oxygen  
191 numbers ≤ 8 and carbon numbers ≤ 20, and lower degree of unsaturation were  
192 selected; otherwise, the peak would be classified as unknown peak. The  
193 maximum peak area residual for each unit mass resolution is 5%. Subsequent  
194 analysis was performed in MATLAB R2022a (The MathWorks Inc., USA).

195 In PTR-MS, the sensitivities of organic vapors are typically determined through  
196 their direct linear correlation with their PTR rate constant ( $k_{\text{PTR}}$ ). Vocus-PTR  
197 utilizes a big segmented quadrupole with a high-pass band filter, which detects  
198 ions < 35 m/z with reduced transmission efficiency (Krechmer et al., 2018).  
199 Consequently, determining sensitivities in Vocus-PTR involves consideration of  
200 both reaction efficiency and transmission efficiency. [Figure S3a](#) shows the  
201 measured sensitivities of mixed calibration gases and their corresponding  $k_{\text{PTR}}$   
202 values. The linear regression between  $k_{\text{PTR}}$  and sensitivities was obtained  
203 based on sensitivities of C<sub>7</sub>H<sub>9</sub><sup>+</sup>, C<sub>8</sub>H<sub>11</sub><sup>+</sup>, C<sub>9</sub>H<sub>13</sub><sup>+</sup>, C<sub>10</sub>H<sub>9</sub><sup>+</sup>, and C<sub>5</sub>H<sub>9</sub>O<sub>2</sub><sup>+</sup> with an R<sup>2</sup>  
204 of 0.87. Sensitivities of other ions in mixed calibration gases may be influenced  
205 by transmission (ions labeled as gray) and fragmentation (C<sub>5</sub>H<sub>9</sub><sup>+</sup>, C<sub>10</sub>H<sub>17</sub><sup>+</sup> and  
206 C<sub>11</sub>H<sub>11</sub><sup>+</sup>). The transmission efficiency of mixed calibration gases was calculated  
207 using sensitivities of mixed calibration gases, as shown in [Figure S3b](#). The  
208 transmission efficiency of mixed calibration gases aligns well with the fitted  
209 transmission efficiency curve, except for C<sub>5</sub>H<sub>9</sub><sup>+</sup>, C<sub>10</sub>H<sub>17</sub><sup>+</sup> and C<sub>11</sub>H<sub>11</sub><sup>+</sup>, which  
210 potentially experience fragmentation (fragmentation of measured ions are  
211 discussed below). For organic vapors without standards, their theoretical  $k_{\text{PTR}}$   
212 were used to constrain sensitivities, while for organic vapors with no theoretical  
213  $k_{\text{PTR}}$ , an average  $k_{\text{PTR}}$  of known species,  $2.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was used  
214 to constrain their sensitivities. The theoretical  $k_{\text{PTR}}$  of organic vapors are from  
215 previous studies (Zhao and Zhang, 2004; Cappellin et al., 2012; Sekimoto et

216 al., 2017). Average limits of detection (LODs, 1 min) of the measured  
217 compounds were determined using zero-gas background measurements taken  
218 every 2 hours during the observation periods, as shown in [Figure S4](#). The LODs  
219 were calculated as 3 times the standard deviation of the zero-gas background  
220 divided by the obtained sensitivity. The LODs show a correlation with masses;  
221 as masses increase, instrument backgrounds decrease, leading to lower LODs.  
222 This trend was observed for species with different oxygen content, with LODs  
223 around  $0.03 \pm 0.03$  pptv at  $m/z$  200. Note that LODs in this study are one-minute  
224 averages, with raw 1-second data averaged to 1 minute before ToFware  
225 analysis as mentioned before, which may account for the lower LODs  
226 compared to those in Jensen et al. (2023). Data below the LODs were excluded  
227 from further analysis.

228 The fragmentation, water cluster, and interferences for calibrated and  
229 uncalibrated species were corrected. The ratio of the electric field strength (E)  
230 to the buffer gas number density (N) used in our study was 146.9 Td, and the  
231 gradient between BSQ skimmer 1 and skimmer 2 was 9.8 V, which in case  
232 limited the formation of water clusters, promoted the simple reaction kinetics,  
233 and improved the sensitivity, but may lead to stronger fragmentation. For  $\alpha$ -  
234 pinene, we identified its fragments based on GC chromatograms. The Vocus-  
235 PTR was calibrated in GC mode before atmospheric measurement. A total of 4  
236 species were tested in GC mode, including severely fragmented  $\alpha$ -pinene. The  
237 spectrum of  $\alpha$ -pinene showed that the main fragment was  $C_6H_9^+$ . Several long-  
238 chain aldehydes and cycloalkanes may fragment on  $C_5H_8H^+$ , the ion typically  
239 attributed to isoprene in PTR-MS (Gueneron et al., 2015; Pfannerstill et al.,  
240 2023a; Coggon et al., 2024). We corrected isoprene signals following an  
241 approach by Coggon et al. (2024). The correction was calculated as follows:

$$242 \quad m/z \ 69.07_{\text{Corrected}} = S_{69.07} - S_{111.12+125.13} \cdot f_{69.07/(111.12+125.13)} \quad (1)$$

243  $S_{69.07}$  is the signal measured at  $C_5H_9^+$ .  $S_{111.12+125.13}$  is the signal of the isoprene  
244 interferences, referring to  $C_8H_{15}^+$  ( $m/z$  111.12) and  $C_9H_{17}^+$  ( $m/z$  125.13), which  
245 are dehydrated products from octanal and nonanal, respectively.  
246  $f_{69.07/(111.12+125.13)}$  was determined from nighttime data (0:00-4:00) of each period.  
247 Similarly, acetaldehyde was corrected for ethanol fragments. We also checked  
248 the fragments and water cluster list in Pfannerstill et al. (2023a) and Jensen et  
249 al. (2023). When the Pearson correlation coefficient  $r$  is greater than 0.95, the  
250 ions were considered as fragments or water clusters of the parent ion. We also  
251 tried to exclude the effects of unknown fragments and water clusters based on  
252 correlations of times series. Similar to Pfannerstill et al. (2023a), any ion  
253 showing a correlation with another ion with  $r^2 > 0.97$  (if chemical reasonable)  
254 was analyzed for possible water clustering or fragmentation effects and added  
255 up with its parent ion. The ions corrected are listed as follows:  $C_2H_4N^+$  with  
256 water cluster  $C_2H_6NO^+$ ,  $C_3H_7O^+$  with water cluster  $C_3H_9O_2^+$ ,  $C_5H_9^+$  with fragment  
257  $C_5H_7^+$ ,  $C_7H_9^+$  with fragment  $C_7H_7^+$ ,  $CH_4NO^+$  with water cluster  $CH_6NO_2^+$ ,

258  $C_2H_7O^+$  with water cluster  $C_2H_9O_2^+$ ,  $C_3H_3O_2^+$  with water cluster  $C_3H_5O_3^+$ ,  
259  $C_4H_5O_2^+$  with water cluster  $C_4H_7O_3^+$ ,  $C_3H_5^+$  with fragment  $C_3H_3^+$ ,  $C_2H_5O^+$  with  
260 water cluster  $C_2H_7O_2^+$ ,  $C_2H_4NO^+$  with water cluster  $C_2H_6NO_2^+$ ,  $C_4H_5O_2^+$  with  
261 water cluster  $C_4H_7O_3^+$ ,  $C_3H_3O_3^+$  with water cluster  $C_3H_5O_4^+$ ,  $C_6H_6NO^+$  with  
262 water cluster  $C_6H_8NO_2^+$ ,  $C_8H_8NO_2^+$  with water cluster  $C_8H_{10}NO_3^+$ ,  $C_{10}H_{21}O^+$  with  
263 water cluster  $C_{10}H_{23}O_2^+$ ,  $C_9H_{13}O_3^+$  with water cluster  $C_9H_{15}O_4^+$ ,  $C_{10}H_{13}O_3^+$  with  
264 water cluster  $C_{10}H_{15}O_4^+$ , and  $C_{14}H_{13}^+$  with water cluster  $C_{14}H_{15}O^+$ .

265 Here, we discuss the uncertainties of quantification for calibrated and  
266 uncalibrated compounds. The uncertainty of calibrated ions ranges from 2% to  
267 16% determined from the standard deviations of the fast calibrations during the  
268 measurement periods. The semi-quantification was conducted for uncalibrated  
269 compounds with their sensitivities constrained by  $k_{PTR}$  linear relationship and  
270 transmission efficiency. The uncertainty of these uncalibrated compounds  
271 arising from linear fitting and transmission efficiency fitting is 20% using Monte  
272 Carlo simulation. Additionally, undetermined fragmentations and water clusters  
273 also contribute to the uncertainty, though we identified some potential  
274 fragments and water clusters through the strength of correlations as previously  
275 indicated. We acknowledge that this method cannot identify all fragments and  
276 clusters, and fragments and clusters may still be present in the measured VOCs  
277 and OVOCs. Further research is needed to explore the impact of fragments  
278 and clusters on the measurements, particularly concerning OVOCs with  
279 multiple oxygens.

280 Double bond equivalent (DBE), carbon oxidation state ( $\overline{OS}_C$ ), and volatility of  
281 organic vapors were calculated to address the chemical and physical properties  
282 of detected organic vapors (see Text S1). The condensational growth rates  
283 contributed by detected organic vapors were simulated using a kinetic  
284 partitioning method, as detailed in Li et al. (2024b). For comparison, the  
285 condensational growth rates of low volatile and extremely low volatile organic  
286 compounds measured by nitrate-CIMS were also simulated (Li et al., 2024b).  
287 The OH reactivities of detected organic vapors were calculated, and the rate  
288 constants are from Data S1 in Pfannerstill et al. (2024) and Table S4 in Wu et  
289 al. (2020). For species with unreported rate constants, we calculated the OH  
290 reactivities for hydrocarbons and OVOCs using the reported median rate  
291 constants of hydrocarbons and OVOCs, respectively.

292 Quantified or semi-quantified mixing ratios were further processed by cluster  
293 analysis to investigate their characteristics. Intra-class correlation coefficient  
294 (ICC) is a suitable method for assessing the consistency of trends in  
295 unbalanced data. It quantifies the stability of differences between two sets of  
296 measurement results, enabling evaluation of their consistency. ICC combined  
297 with k-means cluster analysis were used. ICC(C, 1) was selected among  
298 several typical consistency evaluation parameters for its evaluation results  
299 exhibit the highest level of differentiation based on factual evidence (Qiao et al.,



300 2021). ICC(C, 1) was calculated as follows:

$$301 \quad ICC(C, 1) = (D(X + Y) - D(X - Y)) / (D(X + Y) + D(X - Y)) \quad (1)$$

302 where  $D(\cdot)$  is the arithmetic operators of variance.  $X$  and  $Y$  are two sets of  
303 measurement data, in this case referring to the mixing ratios of any organic  
304 vapors we are concerned about. The ICC matrices of various organic vapors  
305 were subsequently utilized as input for k-means analysis. Square Euclidean  
306 distance was selected to calculate the distances between different organic  
307 vapors.

## 308 **3 Results and discussion**

### 309 **3.1 General characteristics of organic vapors**

310 During the measurement period, a total of 895 peaks were observed, and 512  
311 of them can be assigned to formulae, divided into  $C_xH_y$ ,  $C_xH_yO_z$ ,  $C_xH_yN_i$ , and  
312  $C_xH_yO_zN_i$  categories based on their elemental compositions (Fig. 1a).  $C_xH_yO_z$   
313 composes up to 54% of the total number of formulae followed by  $C_xH_yO_zN_i$ ,  
314  $C_xH_y$ , and  $C_xH_yN_i$ , with proportions of 26%, 14%, and 6%, respectively (Fig. 1b).  
315  $C_xH_yO_z$  dominates contributing 74% of the annual median mixing ratios of total  
316 organics, followed by  $C_xH_y$ ,  $C_xH_yO_zN_i$ , and  $C_xH_yN_i$ , with proportions of 22%, 2%,  
317 and 2%, respectively (Fig. 1c). In addition to these resolved formulae, we also  
318 detect 18 peaks containing other elements such as S, Cl, Si, etc., and 79  
319 CH(O)(N) peaks that do not comply with nitrogen rules, which we consider as  
320 fragments or free radicals. Others are unknown peaks for which formulae  
321 cannot be assigned or water clusters/fragments excluded from analysis. The  
322 mixing ratios of organic vapors vary substantially in urban Beijing, ranging from  
323 0.01 parts per trillion (ppt) to 10 parts per billion (ppb) in volume under a time  
324 resolution of 1 min, with many species detected at sub-ppt levels notably (Fig.  
325 1d). The units of the mixing ratio in the following text are all volume fractions.  
326 As the molecular masses of organics increase, their annual median mixing  
327 ratios decrease. The mixing ratios of  $C_xH_yO_z$  and  $C_xH_yO_zN_i$  categories start to  
328 decrease below the ppt level above molecular weights of 160 and 125,  
329 respectively.

330 With enhanced sensitivity and mass resolution, an increased number of  
331 formulae have been identified compared to traditional PTR-MS measurements  
332 in urban Beijing, especially formulae with lower mixing ratios and higher oxygen  
333 contents. Note that most organics with low mixing ratios have high oxygen  
334 content. 44% number of formulae measured in this study are at sub-ppt level  
335 while 31% number of formulae are between 1 and 10 ppt (Fig. 1e). Only  
336 compounds detected above ppt levels were previously reported in urban sites  
337 within Beijing (Sheng et al., 2018; Li et al., 2019), as well as at a suburban site  
338 located 100 km southwest of Beijing (He et al., 2022). Simultaneously, organic

339 vapors with multiple oxygens ( $C_xH_yO_{\geq 3}$  and  $C_xH_yO_{\geq 3}N_i$  species) have been  
340 successfully detected in this study in the urban atmosphere. Traditionally, they  
341 have been often recognized as total  $C_xH_yO_{\geq 3}$  species, with no individual  
342 analysis in traditional PTR-MS (Yuan et al., 2023; Li et al., 2022b; He et al.,  
343 2022). Many other studies only focus on reporting OVOCs containing up to 2-3  
344 oxygens or omit to address the presence of nitrogen containing OVOCs (Wang  
345 et al., 2021a; Liu et al., 2022). The low mixing ratios and high wall losses of  
346 organic vapors with multiple oxygens impact the detection in traditional PTR-  
347 MS (Breitenlechner et al., 2017). [Figure 2a](#) reinterprets the mass defect plot of  
348 measured organics with a focus on oxygen numbers, ranging from 0 to 8. The  
349 analysis of mixing ratio levels and variations of organic vapors with multiple  
350 oxygens ( $\geq 3$ ) are shown in [Section 3.2](#). Organic vapors with low oxygen content  
351 ( $\leq 2$ ) are reported in [Section 3.3](#). Subsequent comparison of Vocus-PTR and  
352 traditional PTR in urban Beijing and both Vocus-PTR measurements in urban  
353 Beijing and European forests are also shown in [Section 3.3](#).

### 354 **3.2 Organic vapors with high oxygen content**

355 195 observed organics with multiple oxygen atoms account for 38% in number  
356 of the total organics, including 136 species of  $C_xH_yO_{\geq 3}$  and 59 species of  
357  $C_xH_yO_{\geq 3}N_i$ . Organics with oxygen numbers 3 and 4 dominates within the  
358  $C_xH_yO_{\geq 3}$  and  $C_xH_yO_{\geq 3}N_i$  species ([Fig. 2b](#) and [Fig. 2c](#)). Organics with oxygen  
359 number of 3, 4, 5, and  $\geq 6$  comprise 15%, 11%, 7%, and 6% of the total species  
360 number of  $C_xH_yO_z$  compounds, respectively. While compounds with oxygen  
361 number of 3, 4, 5, and  $\geq 6$  comprise 15%, 12%, 7%, and 2% of the total species  
362 number of  $C_xH_yO_zN_i$  compounds, respectively.

363 The measured organic vapors with multiple oxygens are mainly intermediate  
364 volatile organic compounds (IVOCs) and semi-volatile organic compounds  
365 (SVOCs). The dominant carbon numbers range from 5 to 9 and DBE between  
366 1-5, accounting for over three-quarters of the total species number of organic  
367 vapors with multiple oxygens ([Fig. 3a](#) and [Fig. 3b](#)). The maximum occurrence  
368 of organic vapors with 3 or 4 oxygen atoms is observed within the carbon range  
369 of 7-8 and a DBE value of 2. For organic species with 5 or more oxygens, they  
370 reach their peak at a smaller carbon number of 4-5 and a higher DBE value of  
371 3. Aromatic VOCs have DBE values no smaller than 4, while aliphatic VOCs  
372 usually have DBE values smaller than 2. For organic vapors with DBE between  
373 2-3, they are likely oxidation products of aliphatic and aromatic VOCs (Wang et  
374 al., 2021b; Nie et al., 2022). For the same number of carbon atoms, organic  
375 vapors with a higher number of oxygen atoms exhibit a higher carbon oxidation  
376 state (as shown in [Figure S5](#)). Compared to organic vapors with 3 or 4 oxygen  
377 atoms, organic vapors with 5 or more oxygens have undergone more extensive  
378 atmospheric oxidation and functionalization processes (Kroll et al., 2011;  
379 Isaacman-Vanwertz et al., 2018). Based on calculated volatility, 81% of the

380 species are IVOCs, and the remaining 19% are SVOCs (Fig. 3c). With the  
381 increase in oxygen number, the volatility of the compounds gradually decreases,  
382 while the potential partitioning to aerosols increases, manifested by a gradual  
383 reduction in the peak values of the  $\log_{10}C_0$ . Compounds containing nitrogen,  
384 referred to shaded bars with white stripes in Figure 3c, have a lower volatility  
385 compared to non-nitrogen species.

386 The annual median mixing ratio of measured organic vapors with multiple  
387 oxygens in median  $\pm$  standard deviation is 2.0 ppb  $\pm$  1.0 ppb, accounting for 4%  
388 of the total  $C_xH_yO_z$  and  $C_xH_yO_zN_i$  mixing ratios. For  $C_xH_yO_z$  category, the annual  
389 median mixing ratios of species with 3, 4, 5, and  $\geq 6$  oxygens are 1.4 ppb, 186.4  
390 ppt, 18.1 ppt, and 6.4 ppt, respectively. For  $C_xH_yO_zN_i$  category, the annual  
391 median mixing ratios of species with 3, 4, 5, and  $\geq 6$  oxygens are 49.9, 24.5, 2.6,  
392 and 0.5 ppt, respectively (Fig. 2d and 2e). Organic vapors with 3 oxygens  
393 constitute the overwhelming majority of the mixing ratio of measured organic  
394 vapors with more than three oxygens. As a result, the mixing ratio-weighted  
395 carbon number and DBE distributions (Fig. 3d and Fig. 3e) are significantly  
396 different from that of species number distributions for organic vapors with  
397 multiple oxygens. The mixing ratios of species with carbon numbers ranging  
398 from 2 to 6 are significantly higher, with those containing four carbons exhibiting  
399 the highest mixing ratios. Similarly, the mixing ratios of species with DBE  
400 ranging from 0-4 are notably higher than that of other DBE values. As  
401 compounds containing 3 oxygens dominate the mixing ratio, IVOCs nearly  
402 entirely contribute to the mixing ratio-weighted volatility of organic vapors with  
403 multiple oxygens (Fig. 3f). The mixing ratios of organic vapors with multiple  
404 oxygens measured in this study are higher than other studies, which will be  
405 detailed in Section 3.3.

406 Though the contribution of the measured IVOCs and SVOCs to the overall VOC  
407 mixing ratio is low, their contribution to the condensational growth rates is non-  
408 negligible, which may influence the growth of new particles (Ehn et al., 2014),  
409 SOA formation (Jimenez et al., 2009), and haze (Nie et al., 2022). The  
410 condensational growth rates of total organic vapors are calculated, including  
411 extremely low, low, and semi volatile organic compounds detected by nitrate-  
412 CIMS and I/SVOCs detected by Vocus-PTR. The contribution to the  
413 condensational growth rate from I/SVOCs detected by Vocus-PTR increases  
414 with particle size and decreases with temperature. For 8 nm particles, the  
415 contribution of SVOCs detected by Vocus-PTR is 9%, while IVOCs contribute  
416 1%. For 40 nm particles, the contribution of SVOCs increases to 13%, and  
417 IVOCs rise to 4%. At sub-zero temperatures for 8 nm particles, the SVOC  
418 contribution detected by Vocus-PTR can reach up to 21%, with IVOCs  
419 contributing 10%.

420 The molecular formulae of the measured organic vapors with multiple oxygens  
421 are displayed in the mass spectra, categorized by carbon numbers ranging from

422 2-11 (Fig. 4 and Table S3). Many of the formulae are reported as oxidation  
423 products of various VOC precursors in previous studies. Take isoprene as an  
424 example, detected formulae are reported as various oxidation products of  
425 isoprene, including  $C_5H_{10}O_3$  and subsequent oxidation products in C5 species,  
426 e.g.,  $C_5H_8O_6$ ,  $C_5H_9NO_4$ , etc. (Wennberg et al., 2018). For several C4 species,  
427 such as  $C_4H_7NO_4$ ,  $C_4H_4O_3$ , etc., they are reported as oxidation products of two  
428 additional important oxidation products of isoprene, methacrolein (MACR) and  
429 methyl vinyl ketone (MVK). We also see formulae reported as oxidation  
430 products of precursors such as benzene (C6) (Priestley et al., 2021), alkyl-  
431 substituted benzenes (C7-C9) (Pan and Wang, 2014; Wang et al., 2020c;  
432 Cheng et al., 2021), and monoterpenes (C10) (Rolletter et al., 2019). Besides,  
433 we can also detect some organic vapors with relatively low DBE ( $\leq 3$ ), which  
434 may originate from the oxidation of aliphatic precursors. For example,  $C_5H_8O_4$   
435 observed are reported as one of the oxidation products of C5 aldehyde, the  
436 photolysis of which release OH radicals. This mechanism may explain the  
437 source gap of OH radicals between simulations and observations in low  
438 nitrogen oxide and high VOCs regimes (Yang et al., 2024). Note that these  
439 species may be oxidation products as reported by previous studies; however,  
440 confirming this would require additional techniques such as GC.

441 Measured molecular formulae may react with OH radicals, contributing to OH  
442 reactivity. The calculated OH reactivity of organic vapors with multiple oxygens  
443 account for 6% of the total detected VOCs, with an average annual value of 1.2  
444  $s^{-1}$ . Previous studies show differences between measured and calculated or  
445 modeled OH reactivity (Hansen et al., 2014), and unmeasured species from  
446 photochemical oxidation likely explain this gap (Ferracci et al., 2018). Therefore,  
447 the OH reactivity contributed by detected organic vapors with multiple oxygens  
448 in this study may potentially reduce this gap, thereby improve the accuracy of  
449 diagnosis of sensitivity regimes for ozone formation (Wang et al., 2024). Using  
450 Vocus-PTR has the potential to simultaneously measure both precursors and  
451 multi-generational oxygenated products, which is beneficial for studying the  
452 evolution process of organic compounds in the atmosphere.

453 As for the seasonal variations, the overall mixing ratio of organic vapors with  
454 multiple oxygens is the highest in winter, followed by summer, spring and the  
455 lowest in autumn (Fig. 5a). The mixing ratios expressed in median  $\pm$  standard  
456 deviation (ppb  $\pm$  ppb) are  $1.9 \pm 0.5$ ,  $1.9 \pm 0.9$ ,  $1.4 \pm 1.2$ , and  $2.2 \pm 0.8$  for spring,  
457 summer, autumn, and winter, respectively. Compounds with different oxygens  
458 exhibit different seasonal variations, shown in Figure 5b and 5c and Table S4.  
459 For  $C_xH_yO_z$  with 3 or 4 oxygens, the mixing ratios are higher in winter than in  
460 other seasons, while for compounds containing 5 or more oxygens, the mixing  
461 ratios are highest in summer. For  $C_xH_yO_zN_i$  with 3 or 4 oxygens, the mixing  
462 ratios are high in both summer and winter, while for compounds containing 5 or  
463 more oxygens, the mixing ratios are high in summer and spring. As the oxygen

464 number increases, the contribution from secondary sources becomes greater,  
465 and the high mixing ratio of oxidants in summer intensifies this process. Thus,  
466 the fraction of the mixing ratio of compounds with multiple oxygens increases  
467 with the oxygen number in summer (Fig. 5d). In winter, the mixing ratios of  
468 compounds containing five or more oxygens are substantially suppressed,  
469 which may be due to reduced generation. Alternatively, it could be that these  
470 compounds belong to SVOCs, with a majority being partitioned onto particulate  
471 matter at low temperatures.

472 The seasonal variations of organic vapors with multiple oxygens differ from  
473 those of total OVOCs (Fig. S6), with the latter's mixing ratio being primarily  
474 influenced by organic vapors containing 1-2 oxygen atoms. The mixing ratio of  
475 total OVOCs in winter is substantially higher than in the other three seasons,  
476 followed by autumn and summer, with the lowest mixing ratio observed in spring.  
477 The seasonal variations of OVOCs are partly caused by the variation of mixing  
478 layer height (Li et al., 2023), which is lowest in winter. Cluster analysis is  
479 performed to further explore the dominated driving factors of the seasonal  
480 variations of organic vapors with multiple oxygens. Three clusters are identified  
481 in each season based on the diurnal profiles of each compound. To increase  
482 the interpretability of the clusters, two of them are merged. Figure 6 and Figure  
483 S7 shows the cluster results for organic vapors with multiple oxygens. For  
484 comparison, cluster analysis is performed on organic vapors with 1-2 oxygens  
485 as well (Fig. S8 and Fig. S9).

486 Daytime clusters, where the peak occurs during the daytime, were identified  
487 across the four seasons for organic vapors with multiple oxygens (shown as  
488 cluster 1 in Fig. 6). Daytime clusters start to rise at 6:00-7:00 (6:00 for summer  
489 and 7:00 for other seasons), peak at 11:00-14:00 and then slowly decrease,  
490 following the diurnal variation of solar radiation (Li et al., 2023), ozone and  
491 temperature (Fig. S2). Figure S10 further demonstrates the dependence of  
492 daytime clusters on temperature. The mixing ratio of daytime clusters show an  
493 apparent increase in summer (when temperature is higher than 15 °C), which  
494 indicates that higher temperatures accompanied by an increase in solar  
495 radiation and ozone favors the formation of daytime clusters. The number and  
496 corresponding mixing ratios of species allocated to the daytime clusters vary in  
497 four seasons. In summer, the vast majority of species (77%) exhibit daytime  
498 characteristics, with a mixing ratio percentage as high as 85%, which may be  
499 related to the strongest solar radiation (Li et al., 2023) and lowest NO<sub>x</sub>  
500 concentrations (Fig. S2). The contribution of daytime clusters in autumn is also  
501 significant, with 67% and 58% of the species and mixing ratios being accounted  
502 for. The noon peaks of daytime clusters in winter and spring are relatively less  
503 pronounced, with the species and mixing ratio day/night ratios also being  
504 comparatively lower. The afternoon peak of daytime clusters in autumn and  
505 winter are accompanied by a decrease in mixing layer height (Li et al., 2023).



506 For organic vapors with 1 or 2 oxygens, a significant daytime cluster was  
507 observed only in summer (Fig. S8 d-f).

508 Another cluster type is considered to be nighttime clusters, as the  
509 corresponding species have their highest mixing ratios at night. Unlike the  
510 daytime cluster, the diurnal variations of nighttime clusters are different in four  
511 seasons (Fig. 6). In spring, the nighttime cluster comprises over 86% of  
512 nighttime species and 77% of mixing ratios, and it peaks at 4:00 with low  
513 daytime values. The nighttime clusters in winter and autumn show bimodal  
514 diurnal variations, with the highest peak occurring during the night from 19:00  
515 to 23:00, and the second peak appearing during the day from 8:00 to 12:00. 47%  
516 and 33% of species exhibit the characteristics of the nighttime cluster in winter  
517 and autumn, constituting 58% and 42% of the mixing ratio, respectively. The  
518 contribution of the nighttime cluster is minimal in summer, reaching its peak at  
519 midnight. We found that each nighttime cluster of organic vapors with multiple  
520 oxygens shows good consistency with the corresponding major clusters of  
521 organic vapors containing 1-2 oxygens (Fig. S8 and Fig. S11), while the mixing  
522 ratios during midday differ. Nighttime clusters also show better consistency with  
523 PM<sub>2.5</sub> compared to daytime clusters (Fig. S2), which may be related to mixed  
524 sources.

525 Most organic vapors with multiple oxygens could be assigned to different  
526 clusters in different seasons (Fig. S12). Only a small number of species can be  
527 categorized into the same cluster in four seasons. Figure S13 shows the  
528 average C, H, O, and N number of species assigned to daytime cluster 0-4  
529 times during the four seasons. As compounds exhibit more characteristics  
530 associated with daytime cluster, there is no significant change in the carbon  
531 number, but there is an increase in hydrogen and oxygen number, and a  
532 decrease in nitrogen number. This may be due to multi-step oxidation reactions  
533 in the atmosphere, causing an increase in oxygen number and DBE of species  
534 (Kroll et al., 2011; Isaacman-Vanwertz et al., 2018), with diurnal variations  
535 peaking at noon as a result of the strongest photochemistry. The decreasing  
536 trend of the number of nitrogen atoms in Figure S13 indicates that nitrogen  
537 containing compounds measured in this study are more likely to come from  
538 nocturnal production or emissions. Regarding the average elemental  
539 composition (C, H, O, and N) of species assigned to two clusters (see Fig. S14),  
540 daytime clusters typically exhibit higher oxygen content and lower H/C  
541 compared to nighttime clusters, providing further evidence supporting the  
542 atmospheric photochemical origin of daytime clusters. The nighttime clusters  
543 have higher nitrogen contents than daytime clusters, indicating more of the  
544 impacts of nocturnal sources.

### 545 **3.3 Organic vapors with low oxygen content**

546 In addition to multiple oxygens, organic vapors with low oxygen content were

547 also measured in urban Beijing in this study. Here we primarily discuss  
548 comparisons between the results of this study and those of previous studies.  
549 The mixing ratios and variations of typical VOCs measured in this study are  
550 comparable to the results obtained by traditional PTR-MS measurements in  
551 both urban Beijing and neighboring regions. [Figure S15](#) shows the diurnal  
552 profiles of 12 representative VOCs in four seasons. OVOCs of  $C_2H_4O$ ,  $C_3H_6O$ ,  
553 and  $C_4H_4O$ , usually identified as acetaldehyde, acetone, and furan, are mainly  
554 from anthropogenic sources as reported by previous studies (Qian et al., 2019).  
555 Their diurnal variations exhibit a characteristic of being higher at night and lower  
556 during the day, similar to other studies reported in Beijing during the winter  
557 (Sheng et al., 2018; He et al., 2022). The mixing ratios of acetaldehyde, methyl  
558 ethyl ketone (MEK), and furan in winter are slightly lower than those observed  
559 in winter Beijing in 2016 and 2018 (Sheng et al., 2018; He et al., 2022). The  
560 winter mixing ratios of acetone are higher than other seasons and observed in  
561 other studies, indicating an unknown emission source during winter. The mixing  
562 ratios of benzene ( $C_6H_6$ ), toluene ( $C_7H_8$ ), and naphthalene ( $C_{10}H_8$ ) in winter are  
563 slightly lower than reported in winter in Beijing during the past few years (Sheng  
564 et al., 2018; Li et al., 2019; He et al., 2022), possibly due to improvements in  
565 air pollution policies, especially those targeting emissions from residential  
566 combustion and motor vehicles (Liu et al., 2023). As for phenols, the mixing  
567 ratios of  $C_6H_6O$  are similar to measurement at a background site in the North  
568 China Plain in winter, while the mixing ratios of  $C_7H_8O$  are much lower than that  
569 (He et al., 2022). High mixing ratios of biogenic emissions in summer are  
570 observed, for example isoprene ( $C_5H_8$ ) and the sum of its oxidation products  
571 MACR and MVK (Apel et al., 2002) have peak mixing ratios of 2.6 ppb and 0.6  
572 ppb, respectively. Their mixing ratios in winter are lower and consistent with  
573 other studies (Sheng et al., 2018; He et al., 2022).

574 The mixing ratio fractions of organic categories in urban Beijing using Vocus-  
575 PTR differ from the results obtained using traditional PTR-MS. Previous studies  
576 in Beijing have only reported a few selected VOCs up to around 100 species,  
577 resulting in limited results on systematic characterizations of VOCs using PTR-  
578 MS in Beijing (Sheng et al., 2018; Li et al., 2019; Wang et al., 2021a; Liu et al.,  
579 2022). Therefore, we compare with a suburban site, Gucheng, which is located  
580 100 km southwest from our site. The two sites (urban Beijing and Gucheng) are  
581 both located in the North China Plain and are subject to regional air pollutions  
582 simultaneously. [Figure S16](#) shows the comparison results of five categories,  
583 including  $C_xH_y$ ,  $C_xH_yO$ ,  $C_xH_yO_2$ ,  $C_xH_yO_{\geq 3}$ , and N/S containing compounds. The  
584 first difference is that the mixing ratio fraction of species containing two or more  
585 oxygens measured by Vocus-PTR is higher than those measured by traditional  
586 PTR-MS. The mixing ratio fractions of  $C_xH_yO_2$  and  $C_xH_yO_{\geq 3}$  in Vocus-PTR are  
587 12% and 4%, respectively, whereas they are 6% and 1% for traditional PTR-  
588 MS. In terms of mixing ratios, the mixing ratio of  $C_xH_yO_{\geq 3}$  is approximately  
589 double in Vocus-PTR compared to traditional PTR-MS, while the mixing ratio of

590  $C_xH_yO$  is half compared to traditional PTR-MS measurement. The mixing ratio  
591 of  $C_xH_yO_2$  remains similar. This is because Vocus-PTR can detect more OVOCs  
592 with multiple oxygens due to its high sensitivity and mass resolution, whereas  
593 due to its low transmission efficiency for low masses, it is difficult to detect high  
594 mixing ratio OVOCs such as methanol and formaldehyde. The other difference  
595 is that the mixing ratio and the corresponding fraction of  $C_xH_y$  species measured  
596 by Vocus-PTR are much lower than those measured by traditional PTR. For  
597 several major  $C_xH_y$  compounds such as benzene, C7, C8, and C9 aromatics,  
598 their mixing ratios are comparable between the two methods. The main  
599 difference between the two methods lies in the mixing ratio of low-mass  
600 hydrocarbons. Overall, when applied to the urban atmosphere, Vocus-PTR has  
601 advantages in measuring oxygenated VOCs, especially with multiple oxygens.  
602 However, it has limitations in measuring low molecular weight VOCs due to the  
603 low-mass cutoff in the transmission efficiency.

604 The molecular characteristics of organic vapors measured by Vocus-PTR in  
605 urban Beijing show several differences from those in forested areas (Li et al.,  
606 2020; Huang et al., 2021; Li et al., 2021). Firstly, organics up to 300 m/z can be  
607 observed in forested areas, while organics up to 230 m/z are observed (Fig.  
608 1a). Two main reasons are responsible for this. The complexity of the species  
609 introduces challenges in interpreting mass spectra, which is evidenced by the  
610 total number of species being similar to existing atmospheric measurements  
611 using Vocus-PTR, despite a narrower mass range in this study. The higher  
612 particulate matter concentrations in urban areas provide a larger sink for  
613 organic vapors (Deng et al., 2020), and this loss effect is especially pronounced  
614 for compounds with high molecular weights due to their lower volatility. The  
615 second difference is that,  $C_xH_yO_z$  and  $C_xH_yO_zN_i$  species are the dominant  
616 organics in both urban and forested areas, whilst  $C_xH_yN_i$  species are more  
617 common and abundant in urban areas, which may come from biomass burning  
618 emissions (Laskin et al., 2009). Thirdly, VOCs with low carbon and oxygen  
619 number play a more significant role in total organic mixing ratio compared to  
620 results from forested regions. As shown in Figure S17a,  $C_2$  and  $C_3$  organics  
621 contribute 79% of the total organic mixing ratio in this study, while  $C_4$ - $C_6$   
622 organics contribute approximately 75% in forested regions. In contrast to  
623 forested areas, where VOCs and IVOCs mixing ratios are comparable, the  
624 majority of the total organic mixing ratio is attributed to VOCs in this study (Fig.  
625 S17b). Typical  $C_2$  and  $C_3$  organics, such as  $C_3H_6O$ ,  $C_2H_4O$ , and  $C_2H_4O_2$ ,  
626 contribute 14%, 11%, and 5%, respectively, to the total organic mixing ratio,  
627 which are mainly originated from anthropogenic emissions including industrial  
628 and vehicular activities, solvent utilization, and other sources (Qian et al., 2019).



## 629 **4 Conclusions**

630 In this study, we explore the molecular and seasonal characteristics of organic  
631 vapors in urban Beijing using a Vocus-PTR over four seasons. A total of 895  
632 peaks are observed, and 512 of them can be assigned to formulae. The  
633 contribution of  $C_xH_yO_z$  species is most significant, which compose up to 54% of  
634 the number and 74% of the mixing ratios of total organics. With enhanced  
635 sensitivity and mass resolution, an increased number of species were observed  
636 compared to traditional PTR-MS measurements in urban Beijing, especially  
637 compounds with lower mixing ratios and higher oxygen content. 44% species  
638 in number measured in this study are at sub-ppt level and 31% species in  
639 number contain 3-8 oxygens, resulting in a higher fraction of species containing  
640 three or more oxygens compared to traditional PTR-MS measurements.  
641 Organic vapors with low oxygen content are comparable to those obtained in  
642 both urban Beijing and neighboring regions, and they exert a more substantial  
643 influence on the overall organic mixing in forested areas.

644 The mixing ratio of organic vapors with multiple oxygens accounts for 4% of the  
645 total VOC mixing ratio, with the highest levels observed in winter, followed by  
646 summer, spring, and the lowest in autumn. These vapors also make a non-  
647 negligible contribution to condensational growth and OH reactivity. In summer,  
648 the majority of species are aligned to daytime cluster (peaking at noon),  
649 primarily originating from the photooxidation process. As the oxygen number  
650 increases, the impact of the photooxidation process becomes more  
651 pronounced, leading to an increase in both mixing ratio and proportion of  
652 organic vapors with multiple oxygens during summer. In spring and winter when  
653 the nighttime cluster (peaking at night) dominated, the variations of organic  
654 vapors with multiple oxygens are strongly correlated with organic vapors with  
655 one or two oxygens. The measured compositions and seasonal variabilities of  
656 organic vapors with multiple oxygens emphasize the importance of high  
657 sensitivity and high mass resolution measurements in urban atmosphere,  
658 suggesting prospective for future research.

## 659 **Data availability**

660 Data are available upon request from the corresponding author.

## 661 **Supporting Information**

662 The content of the SI includes the map of the observation site (Fig. S1); the  
663 diurnal variations of  $PM_{2.5}$ ,  $O_3$ ,  $NO_x$ , RH, and T in four seasons (Fig. S2);  
664 calibration results of mixed calibration gases (Fig. S3); average limits of  
665 detection (1 min) for detected compounds (Fig. S4); carbon oxidation state of

666 organic vapors with different oxygens (Fig. S5); boxplot of total OVOC mixing  
667 ratios in four seasons (Fig. S6); diurnal variation cluster results of organic  
668 vapors with multiple oxygens (Fig. S7); cluster results of organic vapors with  
669 one or two oxygens (Fig. S8-S9); dependence of daytime clusters on  
670 temperature (Fig. S10); dependence of nighttime clusters on major clusters of  
671 organic vapors with 1-2 oxygens (Fig. S11); the distribution of organic vapors  
672 with multiple oxygens across different clusters (Fig. S12); average C, H, O, and  
673 N number of organic vapors containing multiple oxygens with different diurnal  
674 patterns (Fig. S13); average C, H, O, and N number of organic vapors  
675 containing multiple oxygens in two clusters (Fig. S14); diurnal profiles of  
676 representative VOCs in four seasons (Fig. S15); comparison results with  
677 Gucheng site (Fig. S16); molecular characteristics of total measured organic  
678 vapors by Vocus-PTR (Fig. S17); the observation periods of Vocus-PTR (Table  
679 S1); information about calibration gases (Table S2); main  $C_xH_yO_{\geq 3}$  and  
680  $C_xH_yO_{\geq 3}N$  species measured in this study (Table S3), and seasonal mixing  
681 ratios of OVOCs with multiple oxygens (Table S4).

## 682 **Author contributions**

683 Conceptualization: JJ and ZA. Data collection and analysis: ZA, RY, XZ, XxL,  
684 YY, JG, YuL, YZ, and XuL. Writing-original draft: ZA. Writing-review and editing:  
685 XxL, DL, YaL, DW, CY, KH, DRW, FNK, and JJ.

## 686 **Competing interests**

687 At least one of the (co-)authors is a member of the editorial board of  
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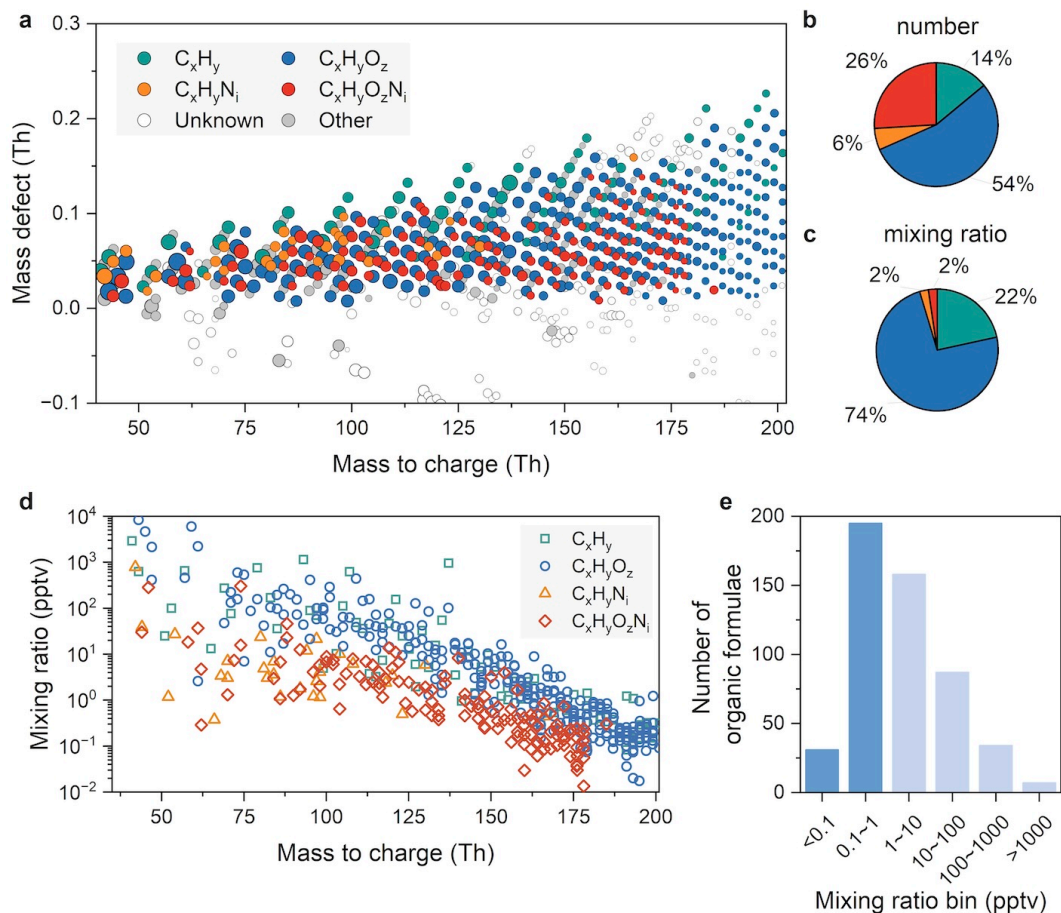
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1114 **Figures**

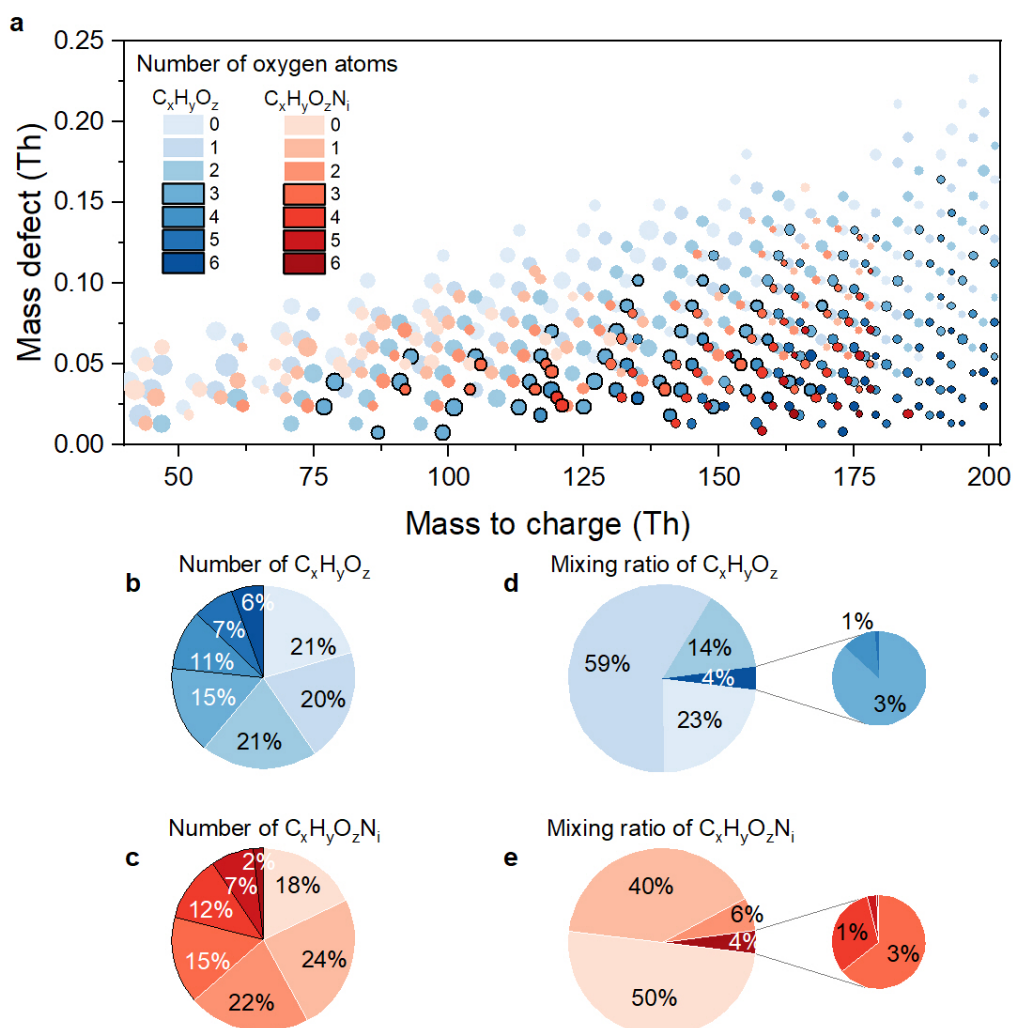


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1116 Figure 1. Identified formulae in urban Beijing using Vocus-PTR. (a) Mass defect  
 1117 plot. The sizes of the bubbles represent the annual median mixing ratios. The  
 1118 bubbles are colored by different elemental compositions as labeled in the  
 1119 legend. The “unknown” refers to fitted peaks without matched formula. The  
 1120 “other” refers to peaks containing elements other than C, H, O, and N or  
 1121 fragment peaks (or radicals). (b) Pie chart of the number of identified formulae.  
 1122 (c) Pie chart of the annual median mixing ratios of identified formulae. The color  
 1123 scheme of the pie charts is the same to that of the mass defect plot. (d) The  
 1124 annual median mixing ratios of identified formulae versus their masses. (e)  
 1125 Histogram of annual mixing ratios of identified formulae. Bins with values less  
 1126 than 1 ppt are emphasized in dark blue color.

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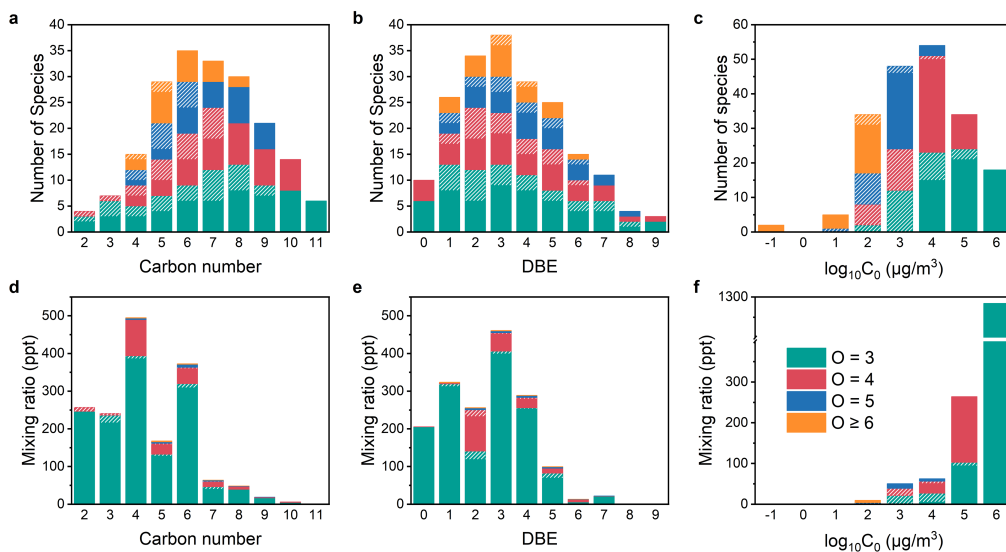
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1130 Figure 2. Organic vapors of different oxygen content. (a) Mass defect plot. The  
 1131 sizes of the bubbles represent the annual median mixing ratios. The bubbles  
 1132 are colored by different oxygen numbers as labeled in the legend. Bubbles  
 1133 representing organic vapors with 3 or more oxygens are highlighted with black  
 1134 borders. Bars labeled as 6 refers to organic vapors with oxygen number equal  
 1135 or larger than 6. (b) Pie chart of the number of  $C_xH_yO_z$  species. (c) Pie chart of  
 1136 the number of  $C_xH_yO_zN_i$  species. (d) Pie chart of the mixing ratio of  $C_xH_yO_z$   
 1137 species. (e) Pie chart of the mixing ratio of  $C_xH_yO_zN_i$  species. The color scheme  
 1138 of the pie charts is the same to that of the mass defect plot.  
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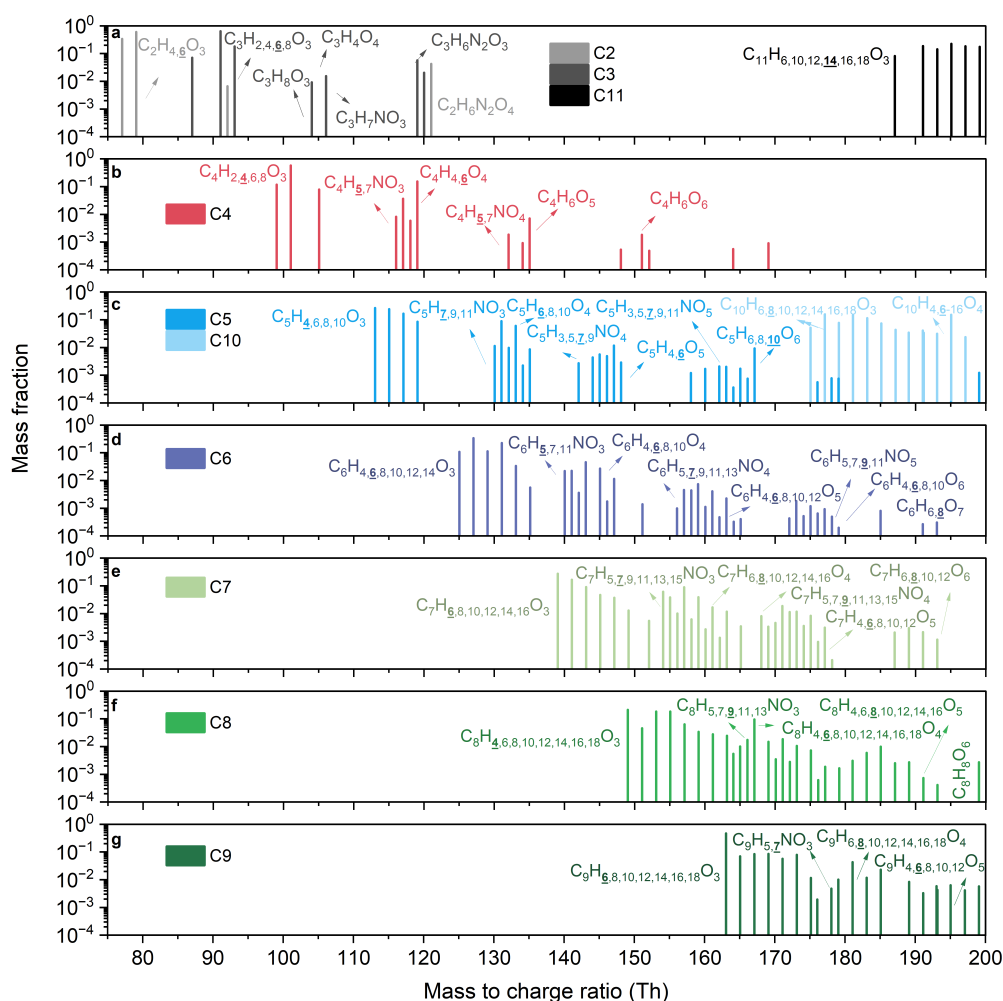
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1142 Figure 3. Distribution of carbon number, double bond equivalent (DBE), and  
 1143 volatility of organic vapors with multiple oxygens. Panels (a) - (c) represent  
 1144 species number distributions of carbon number, DBE, and volatility, respectively.  
 1145 Panels (d) - (e) represent mixing ratio distributions of carbon number, DBE, and  
 1146 volatility, respectively. Different color of bars refers to compounds with different  
 1147 oxygen content. Bars without white stripes represent  $C_xH_yO_{\geq 3}$ , while shaded  
 1148 bars with white stripes represent  $C_xH_yO_{\geq 3}N$ . Y axes refer to annual median  
 1149 mixing ratios.

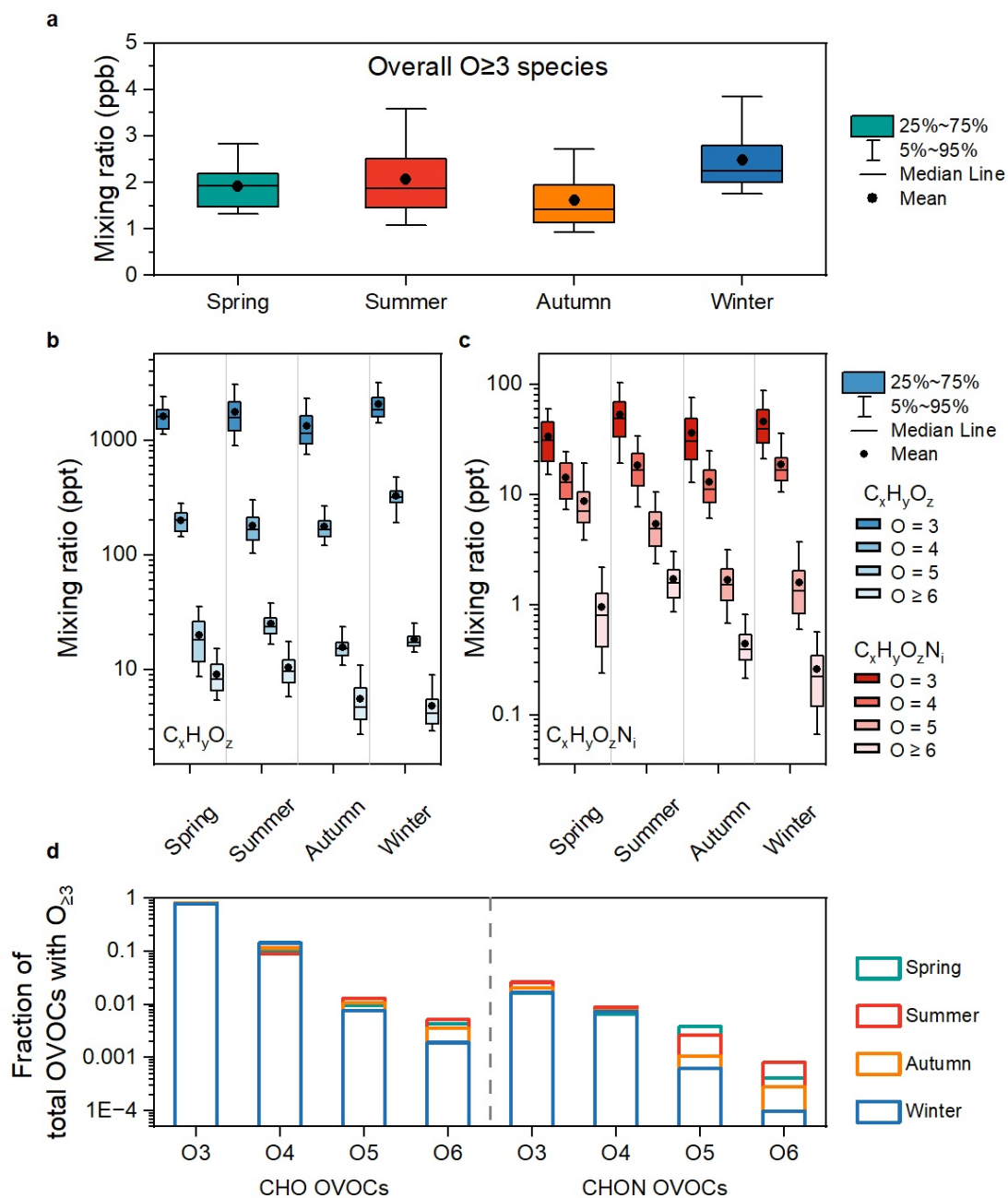
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1152 Figure 4. Mass spectra of organic vapors with multiple oxygens with different  
 1153 carbon numbers: (a) C2, C3, and C11; (b) C4; (c) C5 and C10; (d) C6; (e) C7;  
 1154 (f) C8; (g) C9. The y axis shows the annual median mixing ratio fraction of  
 1155 organic vapors for each carbon number, which means that for different organic  
 1156 vapors with the same carbon number, the sum of the mixing ratio fractions  
 1157 equals 1. The unprotonated formulae of organics vapors with multiple oxygens  
 1158 are labelled. In molecular formulas with the same number of carbons and  
 1159 oxygens, the hydrogen content in the organic vapors with the highest intensity  
 1160 is emphasized by bold and underlined formatting.



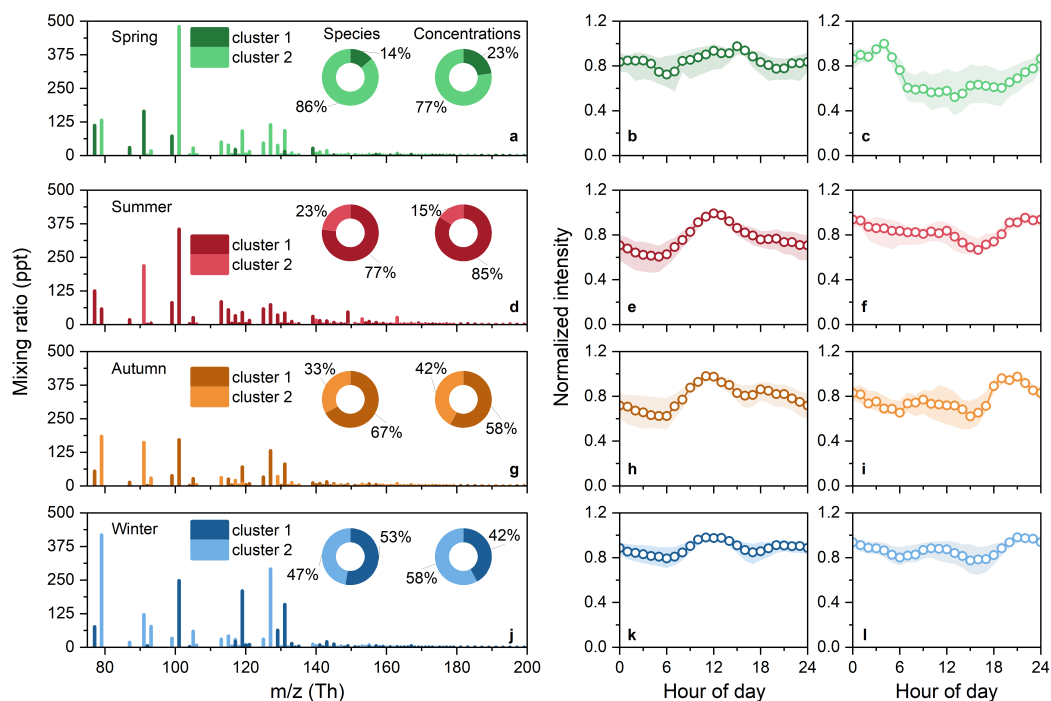


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1162 Figure 5. Seasonal variations of organic vapors with multiple oxygens in urban  
 1163 Beijing. (a) Total organic vapors with multiple oxygens. (b) C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> with different  
 1164 oxygens. (c) C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>N<sub>i</sub> with different oxygens. (d) Fractions of organic vapors  
 1165 with different oxygens of total organic vapors with multiple oxygens.

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1167

1168 Figure 6. Cluster results of organic vapors with multiple oxygens in four seasons.  
 1169 (a) – (c) Cluster results for spring. (a) Mass spectra of organic vapors with  
 1170 multiple oxygens in spring. Y axis is the median mixing ratio of each compound.  
 1171 Two different shades of colors are used to distinguish between two clusters.  
 1172 Two pie charts represent the distribution of species numbers and mixing ratios  
 1173 of organic vapors for two clusters. (b) Normalized median diurnal variation of  
 1174 cluster 1, daytime cluster. (c) Normalized median diurnal variation of cluster 2,  
 1175 nighttime cluster. The shaded areas in the graph (b) and (c) represent the 25<sup>th</sup>  
 1176 and 75<sup>th</sup> percentiles. (d) – (f) Cluster results for summer. (g) to (i) Cluster results  
 1177 for autumn. (j) – (l) Cluster results for winter.