Supporting Information for:

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

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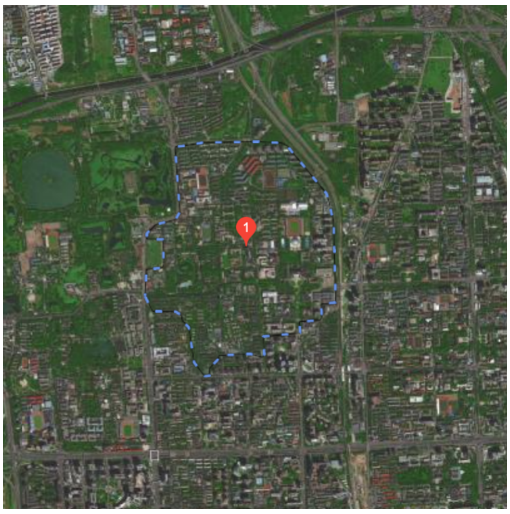

Figure S1. The map of the observation site (© Baidu Maps). The boundary of the campus of Tsinghua University is labeled as the dashed blue line, part of which overlaps with traffic roads. The site is approximately 1 kilometer away from the nearby traffic roads.

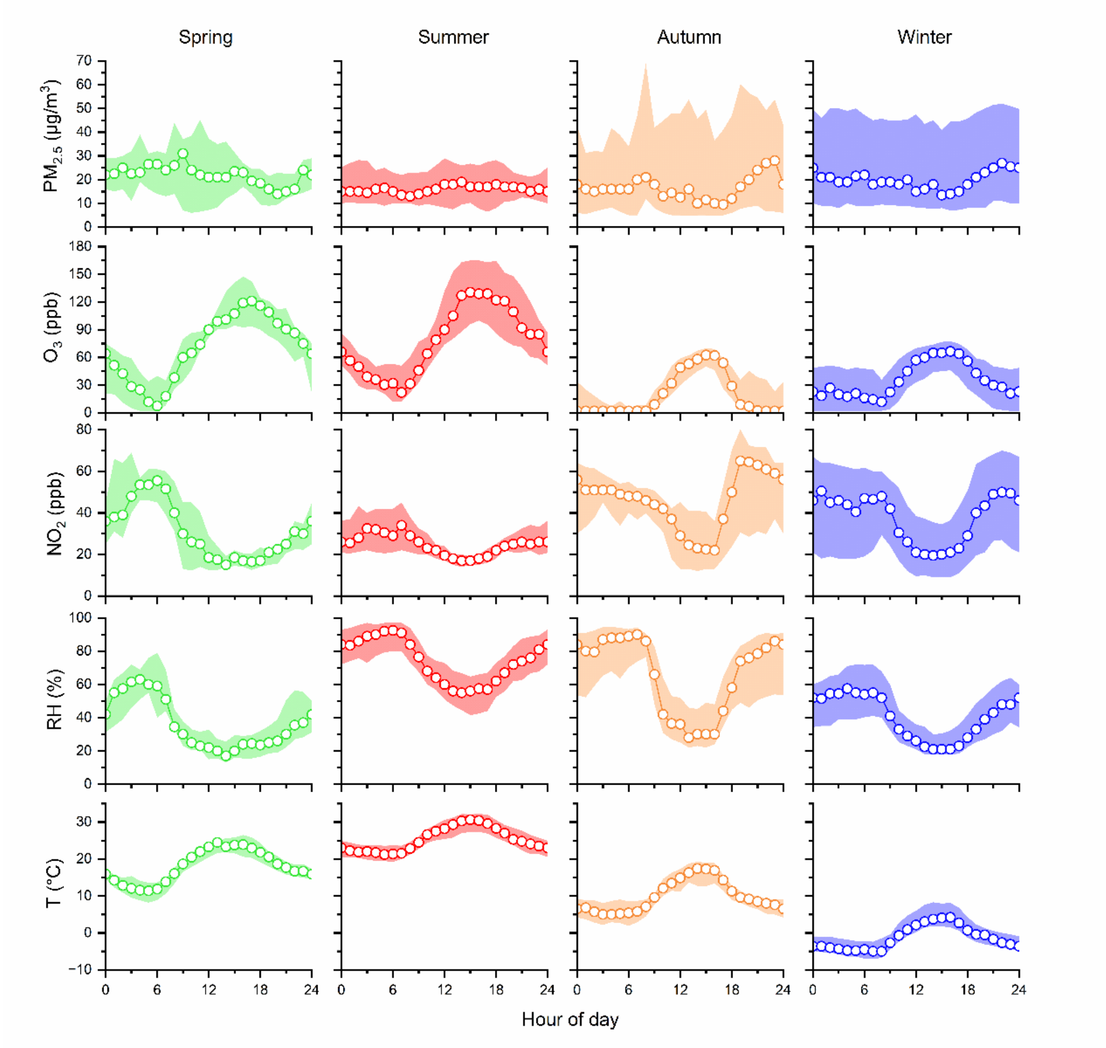

Figure S2. Median diurnal variations of $PM_{2.5}$, O_3, NO_x ($NO+NO_2$), relative humidity (RH), and temperature (T) in four seasons. The shaded areas in the graph represent the 25th and 75th percentiles.

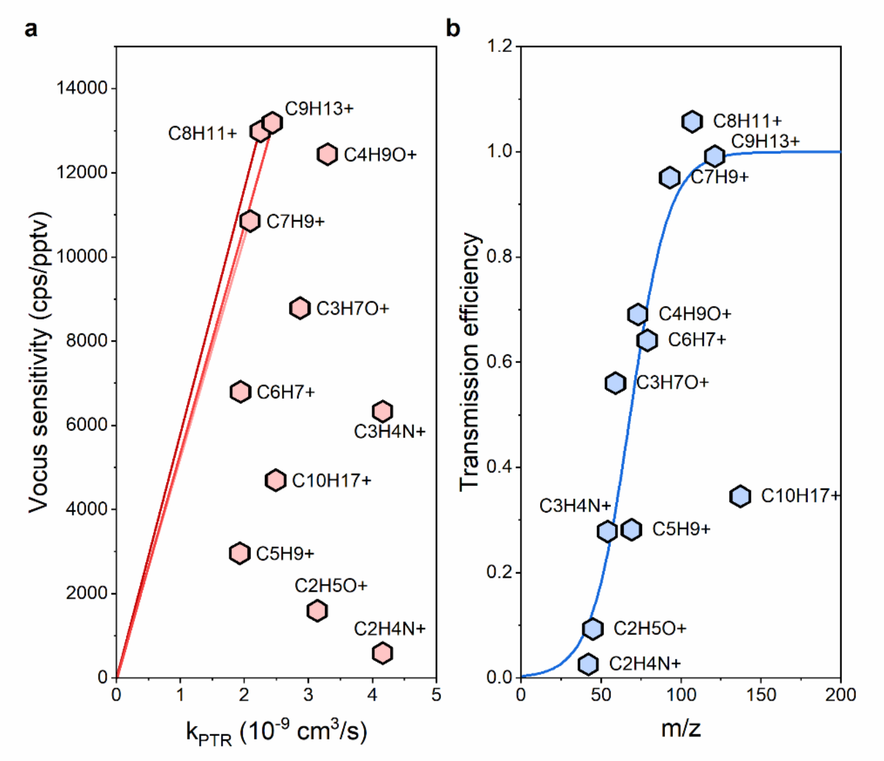

Figure S3. Calibration results of mixed calibration gases. (a) The scatter plot of the sensitivities of mixed calibration gases and their k_{PTR}. The red lines are linear fitting of $C_7H_9^+$, $C_8H_{11}^+$, and $C_9H_{13}^+$, respectively. (b) The transmission efficiency of mixed calibration gases. The blue line is the fitted transmission efficiency curve based on that of mixed calibration gases.

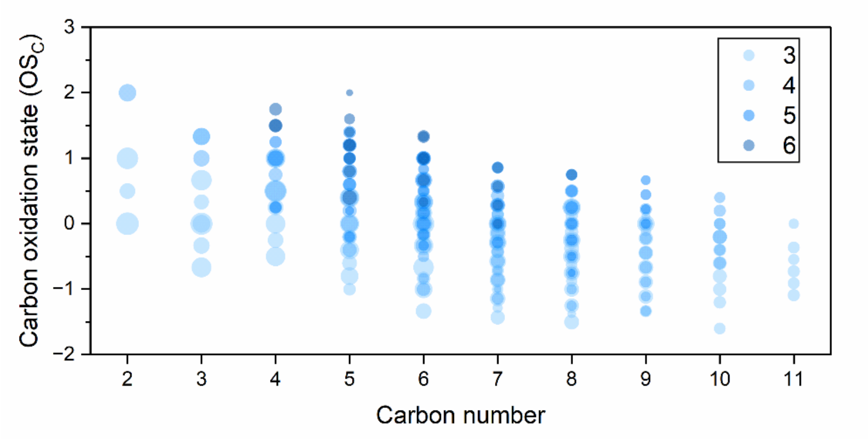

Figure S4. Carbon oxidation state of organic vapors with different oxygens. The sizes of the bubbles are determined by the annual median concentrations. The bubbles are colored by different oxygen numbers as labeled in the legend. Bars labeled as 6 refers to organic vapors with oxygen number equal or larger than 6.

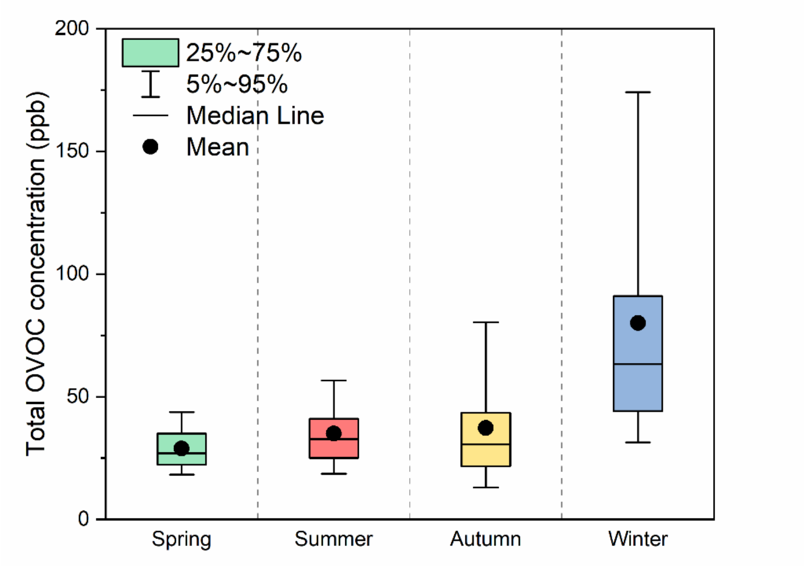

Figure S5. Boxplot of total OVOC concentrations in four seasons.

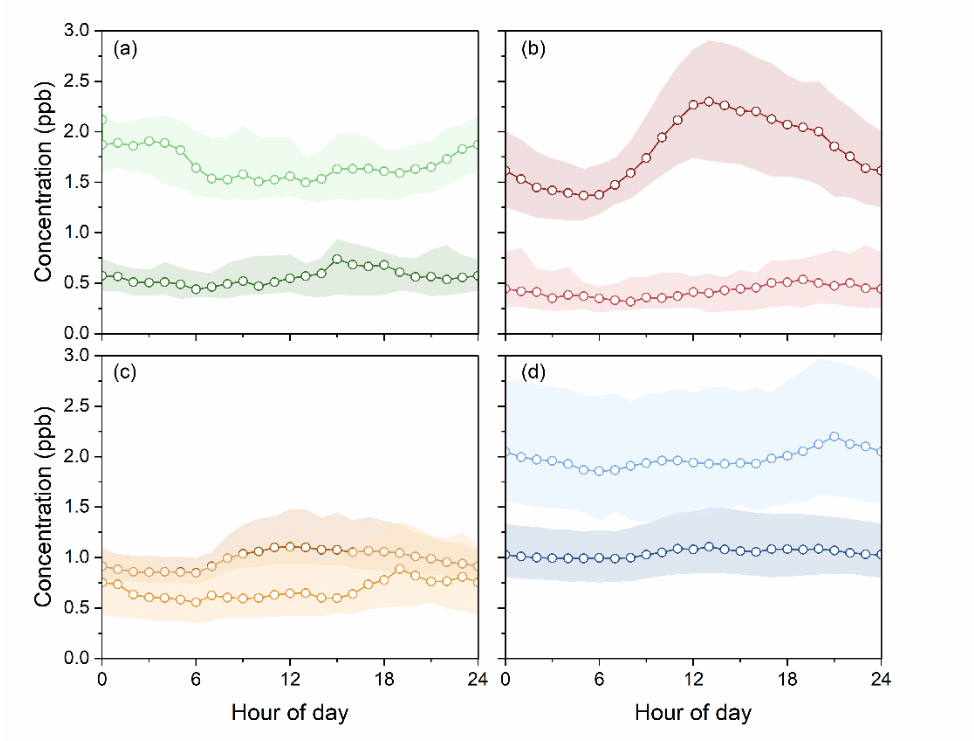

Figure S6. Diurnal variation cluster results of organic vapors with multiple oxygens. Median concentrations are presented. The shaded areas in the graph are 25th and 75th percentiles. The colors of the clusters are consistent with Figure 5. (a) Spring. (b) Summer. (c) Autumn. (d) Winter.

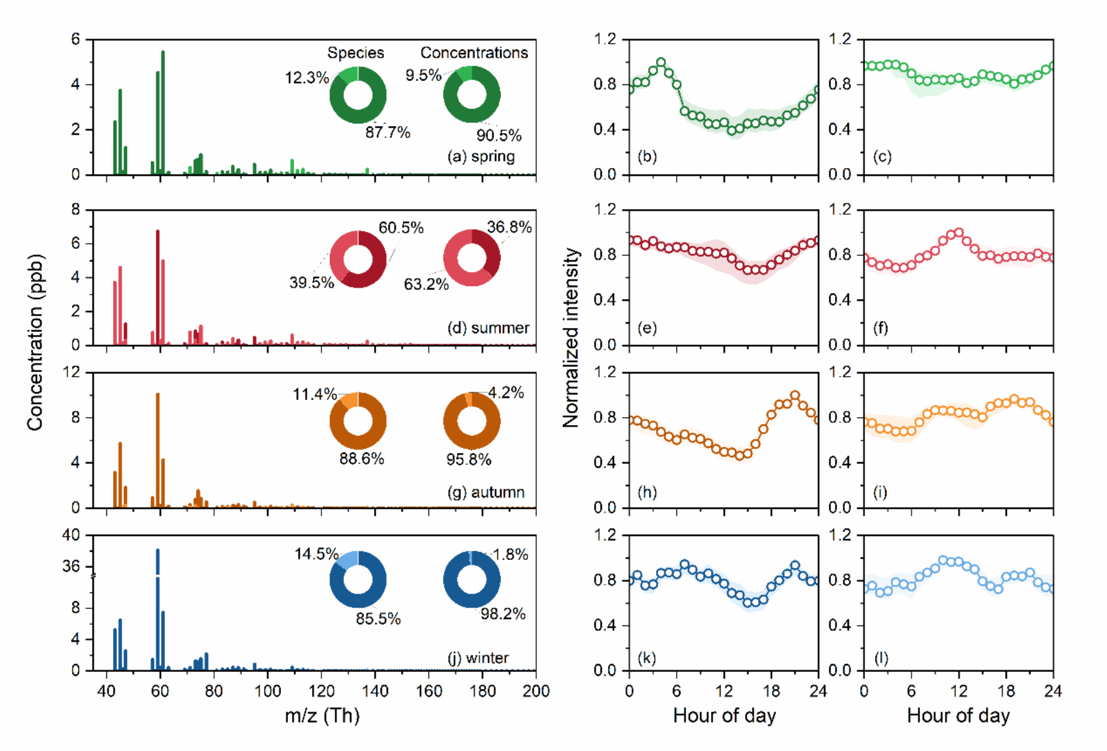

Figure S7. Cluster results of organic vapors with one or two oxygens. (a) – (c) Cluster results for spring. (a) Mass spectra of organic vapors with one or two oxygens in spring. Y axis is the mean concentration of each compound. Two different shades of colors are used to distinguish between two clusters. Two pie charts represent the distribution of species numbers and concentrations of for two clusters. (b) Normalized median diurnal variation of cluster 1. (c) Normalized median diurnal variation of cluster 2. The shaded areas in the graph (b) and (c) represent the 25th and 75th percentiles. (d) – (f) Cluster results for summer. (g) to (i) Cluster results for autumn. (j) – (l) Cluster results for winter.

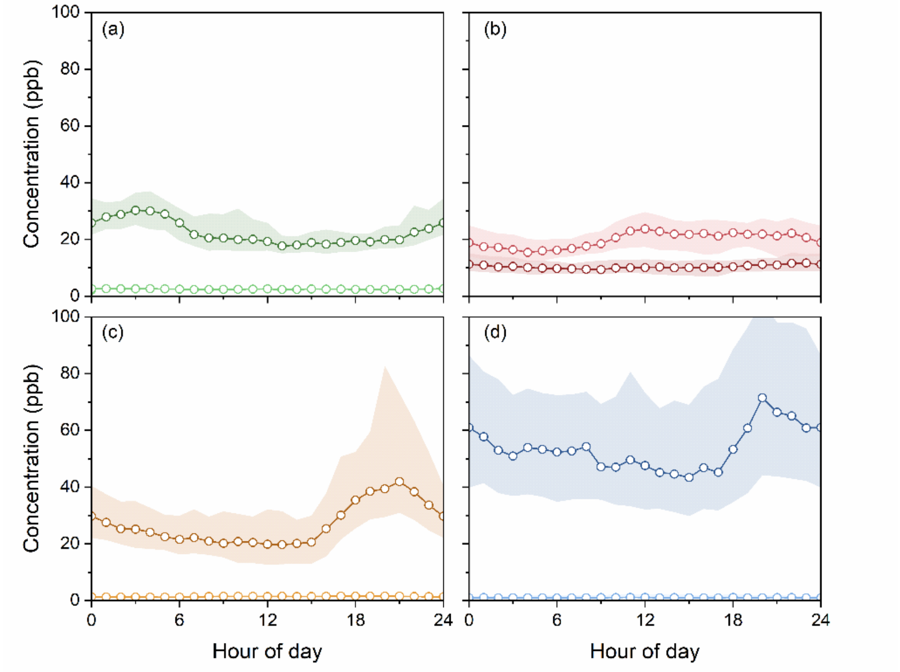

Figure S8. Diurnal variation cluster results of organic vapors with one or two oxygens. Median concentrations are presented. The shaded areas in the graph are 25th and 75th percentiles. The colors of the clusters are consistent with Figure S8. (a) Spring. (b) Summer. (c) Autumn. (d) Winter.

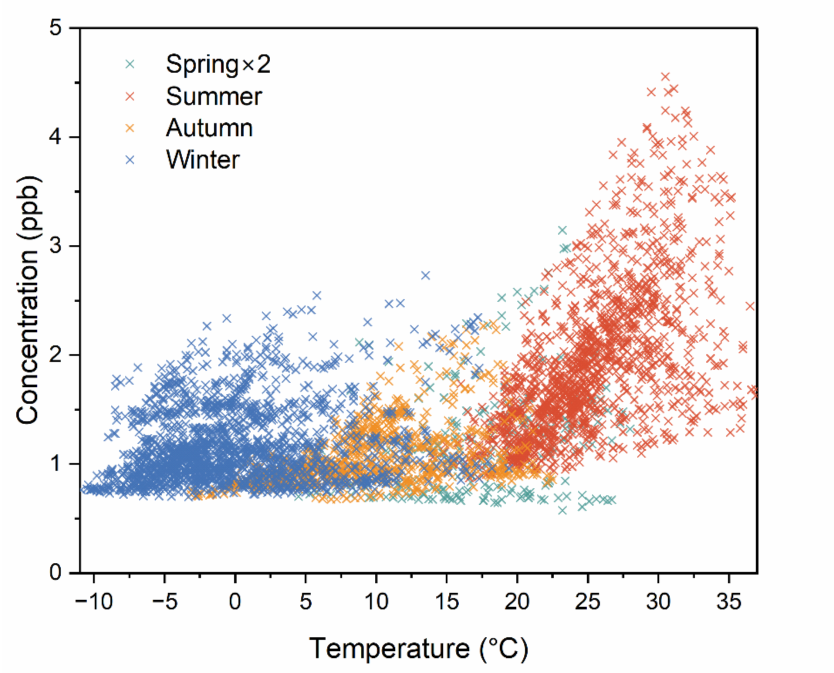

Figure S9. Dependence of daytime clusters on temperature.

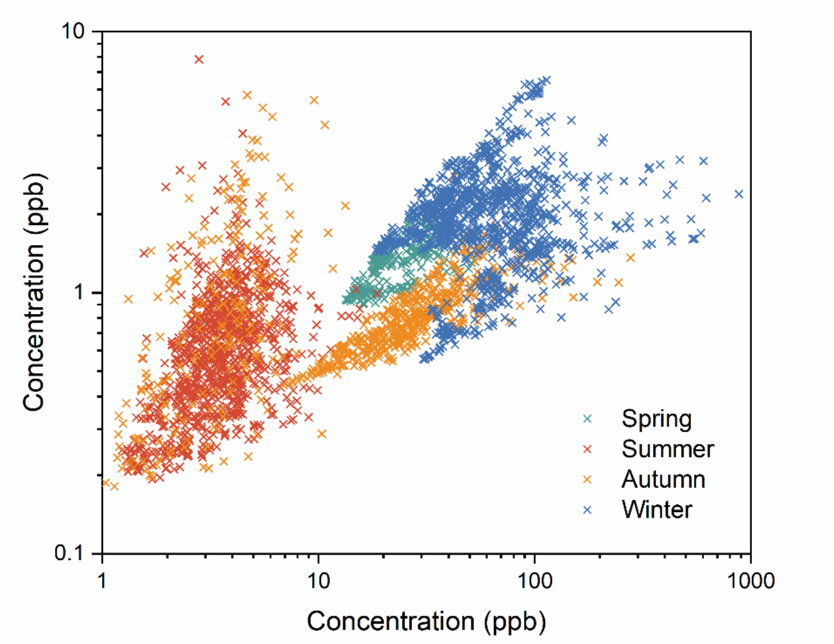

Figure S10. Dependence of nighttime clusters on major clusters of organic vapors with 1-2 oxygens.

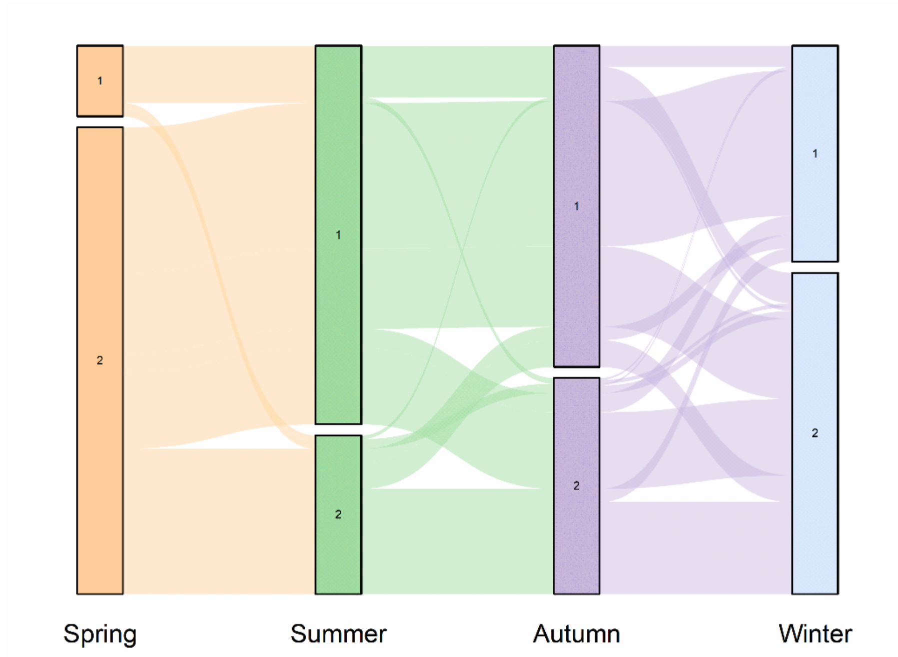

Figure S11. The distribution of organic vapors with multiple oxygens across different clusters.

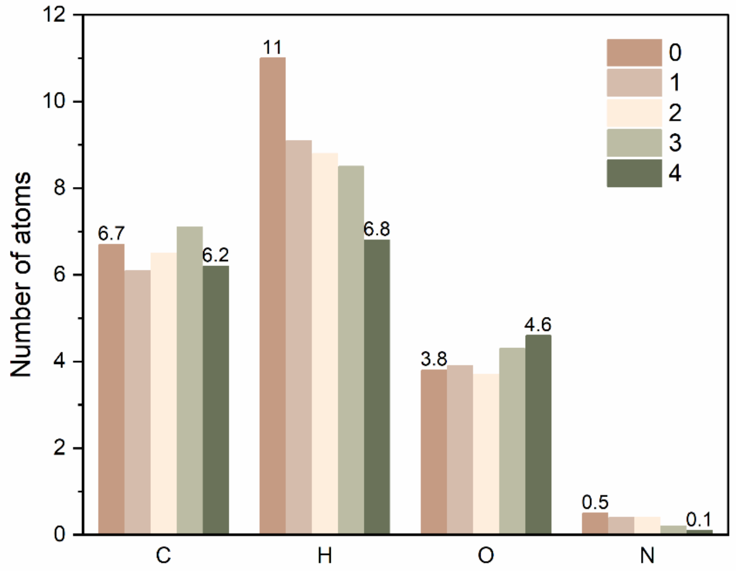

Figure S12. Average C, H, O, and N number of organic vapors containing multiple oxygens with different diurnal patterns. For each compound, different colors labeled as 0 to 4 are used to represent the number of seasons belonging to daytime cluster.

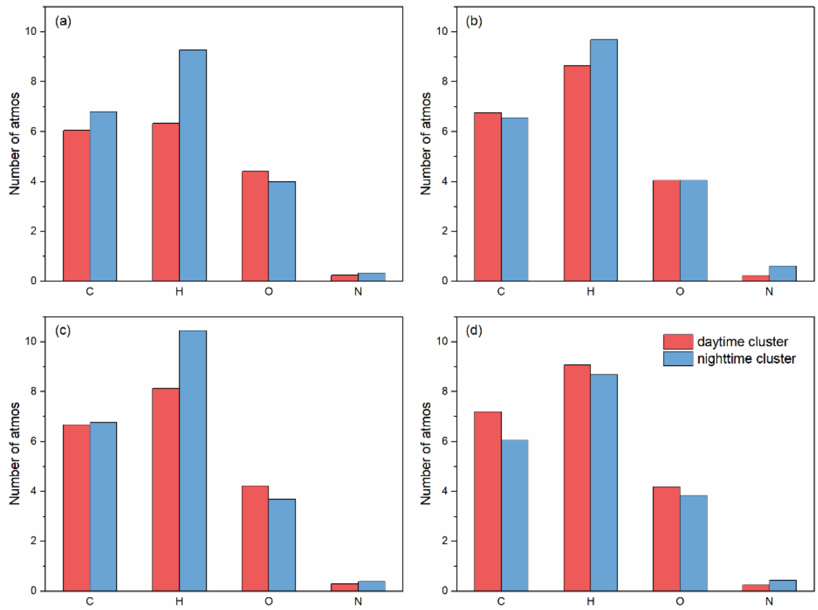

Figure S13. Average C, H, O, and N number of organic vapors containing multiple oxygens in two clusters. (a) Spring. (b) Summer. (c) Autumn. (d) Winter.

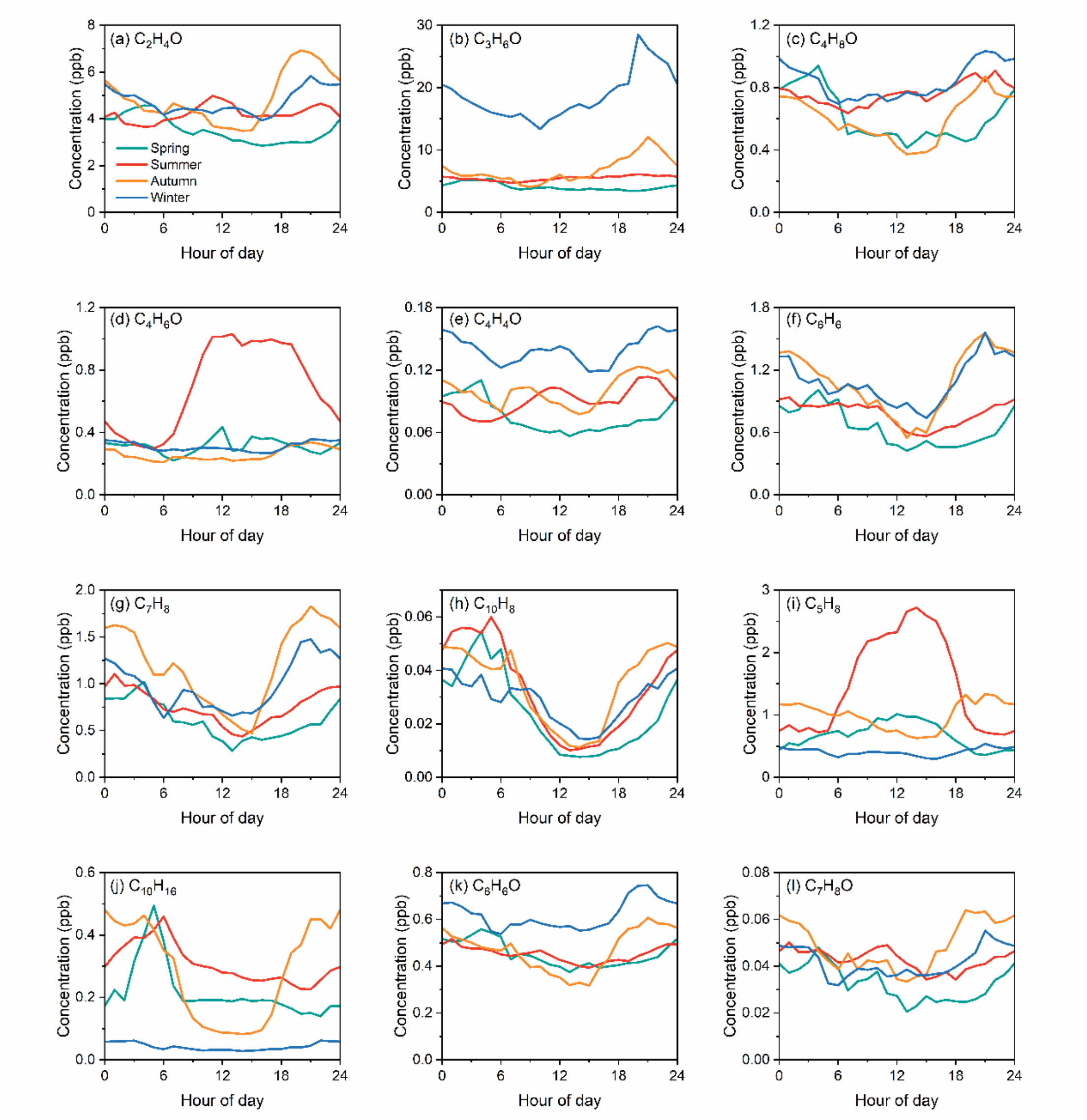

Figure S14. Diurnal profiles of representative VOCs in four seasons. Median concentrations are used.

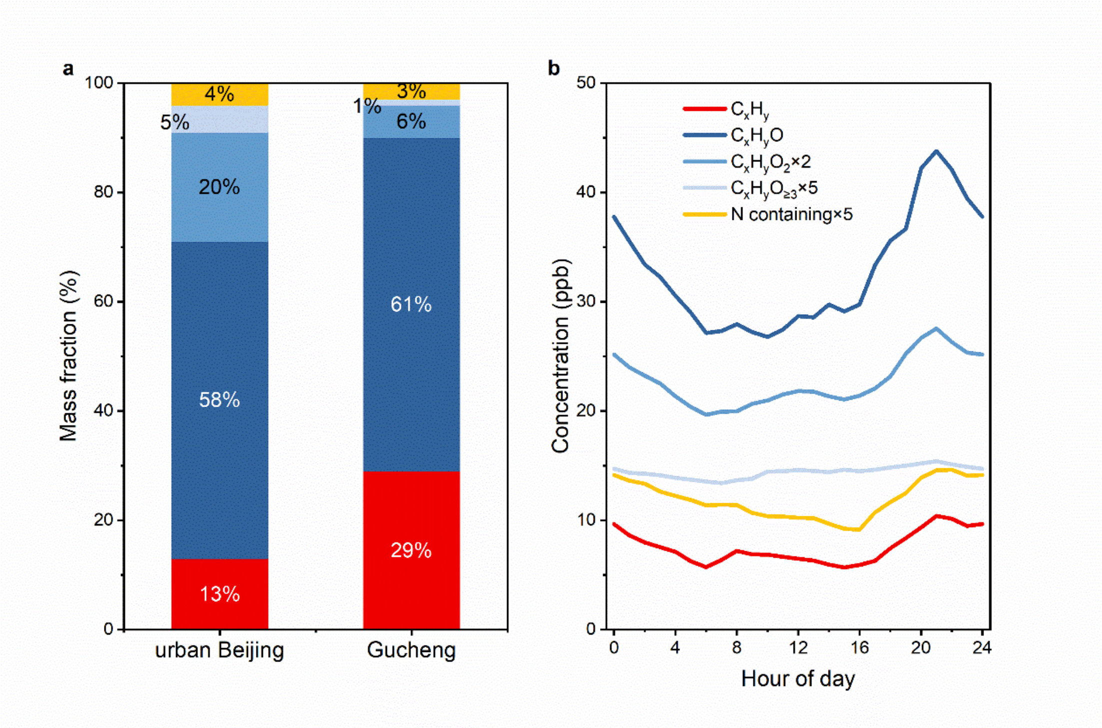

Figure S15. (a) Mass fraction of different categories. Only winter results are used here for urban Beijing. Gucheng results are measured in winter 2018 from He et al., 2022. (b) Diurnal Pattern of different categories in winter.

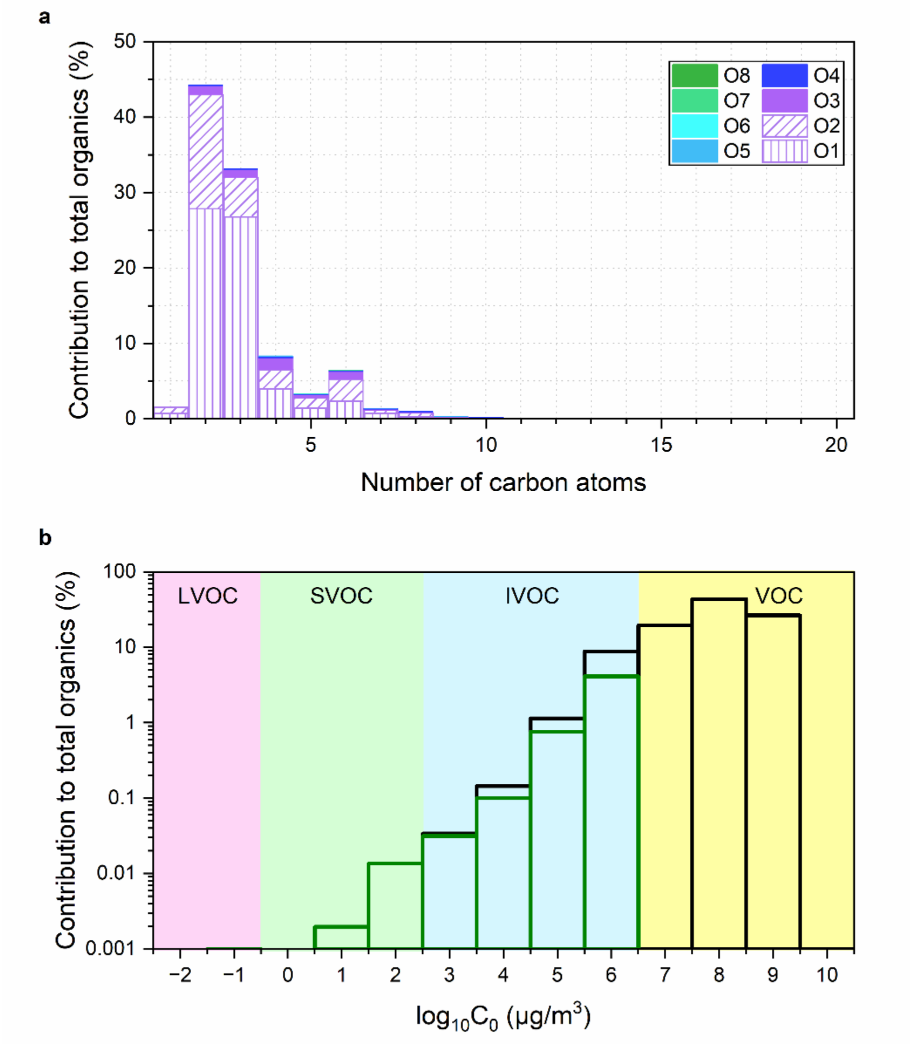

Figure S16. Molecular characteristics of total measured organic vapors by Vocus-PTR. (a) Carbon number distribution. Different colors and patterns of bars refer to compounds with different oxygens. Annual median concentrations are used to calculate the contribution to total organics. (b) Volatility distribution. Bars with black borders represent total measured organic vapors by Vocus-PTR. Bars with green borders represent organic vapors with multiple oxygens (≥3). Annual median concentrations are used to calculate the contribution to total organics.

Table S1. The observation periods of Vocus-PTR

Period NO.	Start time	End time	Season
1	5/1/2021	5/11/2021	Spring
2	6/11/2021	7/12/2021	Summer
3	7/27/2021	9/8/2021	Summer
4	10/11/2021	11/16/2021	Autumn
5	12/27/2021	3/10/2022	Winter

Table S2. Information about calibration gases

Name	Formula	Concentration (ppb)	Observation periods
Formaldehyde	CH_2O	8.16	1, 2, 3
Methanol	CH_4O		
Acetonitrile	C_2H_3N		
Acetaldehyde	C_2H_4O		
Acrylonitrile	C_3H_3N		
Acetone	C_3H_6O		
Isoprene	C_5H_8		
2-Butanone	C_4H_8O		
Benzene	C_6H_6		
Toluene	C_7H_8		
Xylene	C_8H_{10}		
1, 3, 5-Trimethylbenze	$C_9H_{1}2$		
α-Pinene	$C_{10}H_{16}$		
Methyl vinyl ketone	C_4H_6O	20	5*
Furan, 2-ethyl-	C_6H_8O		
Methyl methacrylate	$C_5H_8O_2$		
Toluene	C_7H_8		
Xylene	C_8H_{10}		
α-Pinene	$C_{10}H_{16}$		
1, 3, 5-Trimethylbenze	C_9H_{12}		
Caryophyllene	$C_{15}H_{24}$		
Naphthalene	$C_{10}H_8$		
Naphthalene, 1-methly-	$C_{11}H_{10}$		

*Ethane, 1,1-dichloro-, Benzene, 1,3-dichloro-, and decamethylsiloxane are also included the mixed calibration gases but are not used for calibration.

Table S3. Seasonal concentrations of OVOCs with multiple oxygens

Category			Spring	Summer	Autumn	Winter
O = 3	CHO	mean	1974	2165	1635	2877
		median	1889	1847	1392	2512
	CHON	mean	37	57	38	56
		median	34	52	29	46
O = 4	CHO	mean	226	185	182	385
		median	221	170	167	382
	CHON	mean	15	18	13	21
		median	13	16	11	19
O = 5	CHO	mean	21	25	16	21
		median	19	23	15	19
	CHON	mean	9.2	5.5	1.7	1.8
		median	7.4	4.8	1.4	1.4
O ≥ 6	CHO	mean	9.3	10	5.6	5.5
		median	8.4	9.3	4.6	4.7
	CHON	mean	1.0	1.8	0.4	0.3
		median	0.8	1.5	0.4	0.2

Units in ppt.

Table S4. Main $C_xH_yO_{\geqslant 3}$ and $C_xH_yO_{\geqslant 3}N$ species measured in this study

DBE	CHO	CHON
0	$C_nH_{2n+2}O_{3,4}$	
1	$C_nH_{2n}O_{3-8}$	$C_nH_{2n+1}O_{3-5}N$
2	$C_nH_{2n-2}O_{3-6}$	$C_nH_{2n-1}O_{3-5}N$
3	$C_nH_{2n-4}O_{3-8}$	$C_nH_{2n-3}O_{3-6}N$
4	$C_nH_{2n-6}O_{3-7}$	$C_nH_{2n-5}O_{3-6}N$
5	$C_nH_{2n-8}O_{3-6}$	$C_nH_{2n-7}O_{3-5}N$
6	$C_nH_{2n-10}O_{3-6}$	$C_nH_{2n-9}O_{3,4}N$
7	$C_nH_{2n-12}O_{3-5}$	$C_nH_{2n-11}O_3N$
8	$C_nH_{2n-14}O_{3-5}$	$C_nH_{2n-13}O_3N$
9	$C_nH_{2n-16}O_{3,4}$	