**Measurement Report: important contributions of
oxygenated compounds to emissions and chemistry of VOCs
in urban air**

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1 Calculation of initial isoprene concentration

Isoprene is extremely reactive and therefore its concentration is poor to indicate direct biogenic emissions. To correct this atmospheric photochemical loss, we extrapolated the isoprene concentration back to the source using measurements of isoprene and its photo-oxidized products, methyl vinyl ketone (MVK) and methacrolein (MACR) (Karl et al., 2009). The reaction process of isoprene being oxidized by OH radicals in the atmosphere is:

$$k_1 = 1 \times 10^{-10} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

$$\frac{\text{MVK} + \text{MACR}}{\text{Isoprene}} = \frac{0.32k_1}{k_2 - k_1} (1 - \exp((k_1 - k_2)[\text{OH}]\Delta t)) + \frac{0.23k_1}{k_3 - k_1} (1 - \exp((k_1 - k_3)[\text{OH}]\Delta t)) \quad (1)$$

From the measured ratio between MVK + MACR and isoprene, the OH exposure since emission can be determined, and the observed isoprene concentration can be extrapolated back to the source (Figure S8c).

$$\text{Isoprene}_{\text{initial}} = \text{Isoprene}_{\text{meas}} \times \exp(k_1[\text{OH}]\Delta t) \quad (2)$$

Here, we used the measured concentrations from online GC-MS/FID for isoprene, as there are substantial interferences for PTR-TOF measurements of isoprene in urban air (Yuan et al., 2017). MVK+MACR was only measured by PTR-ToF-MS. We observed significant elevation of MVK+MACR concentrations in the evening when the primary emissions are highest, indicating MVK+MACR concentrations measured by PTR-ToF-MS are influenced by primary anthropogenic emissions (e.g. traffic), either due to direct emissions of MVK or MACR from vehicles, or potential interferences from other compounds that are emitted by vehicles. The data during the night time (20:00-6:00) was selected to determine the emission ratio of MVK + MACR relative to CO (Figure S8a). MVK+MACR concentrations that are solely from biogenic sources can be estimated by the following Eq. 3:

$$\text{MVK} + \text{MACR}_{\text{natural}} = \text{MVK} + \text{MACR}_{\text{meas}} - (\text{CO} - \text{CO}_{\text{BG}}) \times \text{ER}_{\text{MVK} + \text{MACR}} \quad (3)$$

Where $\text{MVK} + \text{MACR}_{\text{meas}}$ and CO are the concentration of MVK+MACR and

CO, respectively. CO_{BG} is the tropospheric background of CO (100 ppb). $ER_{MVK+MACR}$ is the emission ratio of MVK+MACR versus CO (6.0×10^{-4} ppb [ppb CO]⁻¹).

2 Calculation of photolysis rates

To estimate photolysis rates for OVOCs, we follow the method in de Gouw et al. (2018). It is assumed that the photolysis rates for all OVOCs are reduced relative to their clear-sky rates by the same factor as for j_{NO_2} and use the following equation:

$$j_{OVOC} = clear\ sky\ j_{OVOC} \times \frac{measured\ j_{NO_2}}{clear\ sky\ j_{NO_2}} \quad (4)$$

Where $clear\ sky\ j_{OVOC}$, $clear\ sky\ j_{NO_2}$ are clear-sky photolysis rates of OVOC and NO_2 , respectively. Clear-sky photolysis rates for different compounds are calculated in this study from the parameterization used in the Master Chemical Mechanism v3.3.1 (Saunders et al., 2003):

$$clear\ sky\ j = l(\cos \chi)^m \exp(-n \sec \chi) \quad (5)$$

Where χ is the solar zenith angle and l , m , and n are parameters listed for different photolysis rates. The photolysis rates of NO_2 , H_2O_2 , and $HCHO$ were measured on-site using a PFS-100 Photolysis Spectrometer (Focused Photonics Inc.) during the campaign. The above methods were used to calculate the photolysis rates of H_2O_2 and $HCHO$, and compared with the measurements. It is found that the calculated values show good agreement with the measurements for the two compounds (Figure S9). Based on this, the photolysis frequencies of other OVOCs were calculated and then the corrections to the rate constants of OH reaction for these OVOCs were estimated based on Eq. 3 in the main text.

77 **Table S1.** Sensitivities of PTR-ToF-MS for various VOC species calibrated with
78 standard gas and Liquid Calibration Unit (LCU).

VOC species	Ion formula	Sensitivity, cps/ppb
Species calibrated with gas standard		
Formaldehyde	CH_2OH^+	1042
Methanol	CH_4OH^+	629.3
Acetonitrile	$\text{C}_2\text{H}_3\text{NH}^+$	3374
Acetaldehyde	$\text{C}_2\text{H}_4\text{OH}^+$	2767
Ethanol	$\text{C}_2\text{H}_6\text{OH}^+$	99.23
Acrolein	$\text{C}_3\text{H}_4\text{OH}^+$	4107
Acetone	$\text{C}_3\text{H}_6\text{OH}^+$	4299
Furan	$\text{C}_4\text{H}_4\text{OH}^+$	2544
Isoprene	$\text{C}_5\text{H}_8\text{H}^+$	1888
MVK	$\text{C}_4\text{H}_6\text{OH}^+$	3868
MEK	$\text{C}_4\text{H}_8\text{OH}^+$	4467
Benzene	$\text{C}_6\text{H}_6\text{H}^+$	3151
2-Pentanone	$\text{C}_5\text{H}_{10}\text{OH}^+$	4510
Toluene	$\text{C}_7\text{H}_8\text{H}^+$	3978
Phenol	$\text{C}_6\text{H}_6\text{OH}^+$	4076
Furfural	$\text{C}_5\text{H}_4\text{O}_2\text{H}^+$	7460
Methyl Isobutyl Ketone	$\text{C}_6\text{H}_{12}\text{OH}^+$	3988
Styrene	$\text{C}_8\text{H}_8\text{H}^+$	4289
O-xylene	$\text{C}_8\text{H}_{10}\text{H}^+$	4241
m-Cresol	$\text{C}_7\text{H}_8\text{OH}^+$	4299
1,2,4-Trimethylbenzene	$\text{C}_9\text{H}_{12}\text{H}^+$	4413
Naphthalene	$\text{C}_{10}\text{H}_8\text{H}^+$	5117
α -Pinene	$\text{C}_{10}\text{H}_{16}\text{H}^+$	2332
Species calibrated with the Liquid Calibration Unit (LCU).		
Formic acid	$\text{CH}_2\text{O}_2\text{H}^+$	856.6

Acetic acid	$\text{C}_2\text{H}_4\text{O}_2\text{H}^+$	1711
Propionic acid	$\text{C}_3\text{H}_6\text{O}_2\text{H}^+$	2072
Butyric acid	$\text{C}_4\text{H}_8\text{O}_2\text{H}^+$	2358
Pyrrole	$\text{C}_4\text{H}_5\text{NH}^+$	2842
Formamide	CH_3NOH^+	2871
Acetamide	$\text{C}_2\text{H}_5\text{NOH}^+$	3992

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Table S2. Rate constants of OVOCs representing the combined loss to OH oxidation and photolysis.

Species	k_{ovoc}	$j_{ovoc}/[OH]$	k_{ovoc}^*	f
	$10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
Formaldehyde	9.4	7.86±0.120	17.26	1.84
Acetaldehyde	15	0.426±0.006	15.42	1.03
Propionaldehyde	20	1.89±0.026	21.89	1.09
n-butyraldehyde	24	3.26±0.046	27.26	1.14
i-butyraldehyde	24	5.64±0.080	29.64	1.24
MACR	29	1.99±0.030	30.99	1.07
Acetone	0.17	0.051±0.0007	0.22	1.29
MEK	1.22	0.368±0.005	1.59	1.30
MVK	20	3.22±0.049	23.22	1.16
Glyoxal	11	3.02±0.044	14.02	1.27
Methyl peroxide	5.5	0.628±0.009	6.13	1.11
Methyl nitrate	0.023	0.107±0.001	0.13	5.65
Ethyl nitrate	0.18	0.122±0.002	0.30	1.67
n-Propyl nitrate	0.58	0.163±0.002	0.74	1.28
i-Propyl nitrate	0.29	0.28±0.004	0.57	1.97
t-butyl nitrate	1.6	0.818±0.011	2.42	1.51

f represents the ratio of the rate constant representing the combined losses of reaction with OH radical and photolysis (k_{OVOC}^*) and the OH rate constant (k_{OVOC}).

86 **Table S3.** The average concentrations of NMHCs measured by GC-MS/FID and their OH rate constants, which were used for calculating OH
87 reactivity.

Compound	Average concentration (ppb)	OH rate constant ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Source of OH rate constants
Cyclohexane	0.075±0.081	6.97	Atkinson 2003
Cyclopentane	0.096±0.060	4.97	Atkinson 2003
Ethane	3.402±1.344	0.248	Atkinson 2003
i-Butane	1.759±1.398	2.12	Atkinson 1997
i-Pentane	1.387±1.234	3.6	Atkinson 1997
Methylcyclohexane	0.089±0.116	4.97	Atkinson 2003
Methylcyclopentane	0.121±0.125	5.2	Atkinson 2003
n-Nonane	0.043±0.032	9.7	Atkinson 2003
n-Butane	3.155±2.615	2.36	Atkinson 2003
n-Decane	0.029±0.028	11	Atkinson 2003
n-Dodecane	0.062±0.032	13.9	Atkinson 2003
n-Heptane	0.130±0.212	6.76	Atkinson 2003
n-Hexane	0.637±0.795	5.2	Atkinson 2003
n-Octane	0.050±0.049	8.11	Atkinson 2003
n-Pentane	0.774±0.789	3.8	Atkinson 2003
n-Undecane	0.021±0.017	12.3	Atkinson 2003
Propane	6.520±5.175	1.09	Atkinson 2003
2-Methylheptane	0.023±0.031	7	Atkinson 2003

2-Methylhexane	0.121±0.189	5.65	Atkinson 2003
2-Methylpentane	0.342±0.333	5.4	Atkinson 2003
2,2-Dimethylbutane	0.042±0.034	2.23	Atkinson 2003
2,2,4-Trimethylpentane	0.038±0.035	3.34	Atkinson 2003
2,3-Dimethylbutane	0.063±0.057	5.78	Atkinson 2003
2,3-Dimethylpentane	0.048±0.066	1.5	Atkinson 2003
2,3,4-Trimethylpentane	0.016±0.013	6.6	Atkinson 2003
2,4-Dimethylpentane	0.044±0.038	4.77	Atkinson 2003
3-Methylheptane	0.023±0.030	7	Yang 2017
3-Methylhexane	0.144±0.224	5.6	Yang 2017
3-Methylpentane	0.335±0.344	5.2	Atkinson 2003
cis-2-Butene	0.028±0.028	56.4	Atkinson 2003
cis-2-Pentene	0.007±0.012	65	Atkinson 2003
Ethene	1.856±1.220	8.52	Atkinson 2003
Isoprene	0.203±0.304	100	Atkinson 2003
Propene	0.458±0.492	26.3	Atkinson 2003
Styrene	0.126±0.188	58	Atkinson 2003
trans-2-Butene	0.038±0.038	56.4	Atkinson 2003
trans-2-Pentene	0.016±0.031	67	Atkinson 2003
1-Butene	0.089±0.066	31.4	Atkinson 2003
1-Hexene	0.025±0.022	37	Atkinson 2003
1-Pentene	0.030±0.020	31.4	Atkinson 2003

Benzene	0.454±0.207	1.22	Atkinson 2003
Ethylbenzene	0.344±0.345	7	Atkinson 2003
i-Isopropylbenzene	0.013±0.011	6.3	Atkinson 2003
m-Ethyltoluene	0.039±0.038	11.8	Atkinson 2003
m+p-Xylene	0.927±0.932	18.9	Atkinson 2003
n-Propylbenzene	0.017±0.013	5.8	Atkinson 2003
o-Ethyltoluene	0.020±0.018	11.9	Atkinson 2003
o-Xylene	0.357±0.369	13.6	Atkinson 2003
1,4-Diethylbenzene	0.016±0.014	10	Gilman 2015
p-Ethyltoluene	0.025±0.023	18.6	Atkinson 2003
Toluene	2.056±1.917	5.63	Atkinson 2003
1,2,3-Trimethylbenzene	0.020±0.018	32.7	Atkinson 2003
1,2,4-Trimethylbenzene	0.079±0.088	32.5	Atkinson 2003
1,3,5-Trimethylbenzene	0.020±0.020	56.7	Atkinson 2003

89 **Table S4.** The average concentrations of VOCs measured by PTR-ToF-MS and their OH rate constants, which were used for calculating OH
90 reactivity.

Ion exact mass (Th)	Ion formula	Compound	Average concentration (ppb)	OH rate constant ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Source of OH rate constants
Common OVOCs					
30.0178	CH ₂ O	Formaldehyde	2.991±2.059	9.4	Atkinson 2003
32.0335	CH ₄ O	Methanol	11.43±7.612	0.8	Atkinson 2003
44.0335	C ₂ H ₄ O	Acetaldehyde	2.027±1.292	15.0	Atkinson 2003
56.0335	C ₃ H ₄ O	Acrolein	0.173±0.102	20.0	Gilman 2015
58.0491	C ₃ H ₆ O	Acetone	3.798±2.508	0.2	Atkinson 2003
70.0491	C ₄ H ₆ O	MVK+MACR	0.362±0.249	24.8	Koss 2018
72.0648	C ₄ H ₈ O	MEK	1.420±1.309	5.5	Koss 2018
86.0804	C ₅ H ₁₀ O	Pentanones	0.085±0.049	7.9	Atkinson 2003
100.096	C ₆ H ₁₂ O	Hexanones	0.101±0.091	18.6	Koss 2018
NMHCs					
184.36	C ₁₃ H ₂₈	Tridecane [#]	0.066±0.060	15.3	Atkinson 2003
198.39	C ₁₄ H ₃₀	Tetradecane [#]	0.050±0.047	16.7	Atkinson 2003
212.41	C ₁₅ H ₃₂	Pentadecane [#]	0.045±0.042	18.1	Atkinson 2003
226.44	C ₁₆ H ₃₄	Hexadecane [#]	0.036±0.033	19.4	Atkinson 2003
240.46	C ₁₇ H ₃₆	Heptadecane [#]	0.021±0.020	20.7	Atkinson 2003
254.49	C ₁₈ H ₃₈	Octadecane [#]	0.013±0.014	21.9	Atkinson 2003
268.52	C ₁₉ H ₄₀	Nonadecane [#]	0.005±0.009	23	Atkinson 2003

282.54	C ₂₀ H ₄₂	Eicosane [#]	0.0007±0.004	24	Atkinson 2003
40.038	C ₃ H ₄		0.391±0.501	0.695	Pfannerstill 2019
66.054	C ₅ H ₆		0.026±0.020	92.0	Gilman 2015
82.085	C ₆ H ₁₀		0.176±0.124	86.9	Pfannerstill 2019
84.101	C ₆ H ₁₂		0.078±0.062	66.3	Pfannerstill 2019
94.085	C ₇ H ₁₀		0.039±0.034	46.8	Pfannerstill 2019
96.101	C ₇ H ₁₂		0.087±0.062	79.8	Pfannerstill 2019
102.054	C ₈ H ₆		0.004±0.004	1.0	Gilman 2015
108.101	C ₈ H ₁₂		0.034±0.038	107	Pfannerstill 2019
110.116	C ₈ H ₁₄		0.067±0.049	120	Pfannerstill 2019
116.07	C ₉ H ₈		0.003±0.008	78.0	Atkinson 2003
118.086	C ₉ H ₁₀		0.029±0.028	50.4	Atkinson 2003
128.07	C ₁₀ H ₈		0.052±0.061	23.0	Atkinson 2003
130.086	C ₁₀ H ₁₀		0.004±0.004	28.5	Koss 2018
132.101	C ₁₀ H ₁₂		0.027±0.024	33.0	Koss 2018
134.117	C ₁₀ H ₁₄		0.127±0.135	9.5	Koss 2018
136.132	C ₁₀ H ₁₆		0.161±0.245	162.8	Koss 2018
142.086	C ₁₁ H ₁₀		0.014±0.017	50.0	Koss 2018
144.101	C ₁₁ H ₁₂		0.001±0.003	78.0	Koss 2018
146.116	C ₁₁ H ₁₄		0.011±0.015	58	Pfannerstill 2019
148.132	C ₁₁ H ₁₆		0.029±0.030	50.0	Koss 2018
152.07	C ₁₂ H ₈		0.001±0.003	15.1	Koss 2018

156.101	C ₁₂ H ₁₂		0.008±0.009	60.0	Koss 2018
160.132	C ₁₂ H ₁₆		0.009±0.013	58	Pfannerstill 2019
162.148	C ₁₂ H ₁₈		0.010±0.010	113.0	Koss 2018
174.148	C ₁₃ H ₁₈		0.005±0.008	38.5	Pfannerstill 2019
176.164	C ₁₃ H ₂₀		0.009±0.011	113.0	Koss 2018
Novel OVOCs					
46.0128	CH ₂ O ₂		1.880±3.155	0.4	Koss 2018
46.0491	C ₂ H ₆ O		5.634±5.192	3.2	Atkinson 2003
48.0284	CH ₄ O ₂		0.004±0.003	7.0	Koss 2018
54.0178	C ₃ H ₂ O		0.004±0.048	20.0	Koss 2018
58.0128	C ₂ H ₂ O ₂		0.002±0.003	11.0	Atkinson 2003
60.0284	C ₂ H ₄ O ₂		4.618±4.681	3.7	Koss 2018
62.044	C ₂ H ₆ O ₂		0.059±0.057	14.5	Pfannerstill 2019
64.023	CH ₄ O ₃		0.041±0.050	7.1	Pfannerstill 2019
68.0335	C ₄ H ₄ O		0.055±0.036	40.0	Gilman 2015
70.0128	C ₃ H ₂ O ₂		0.006±0.007	26.0	Koss 2018
72.0284	C ₃ H ₄ O ₂		0.135±0.088	21.1	Koss 2018
74.0441	C ₃ H ₆ O ₂		1.438±2.188	2.2	Koss 2018
76.059	C ₃ H ₈ O ₂		0.050±0.044	16.2	Pfannerstill 2019
80.0335	C ₅ H ₄ O		0.008±0.007	20.0	Gilman 2015 2-methylfuran
82.0491	C ₅ H ₆ O		0.062±0.048	37.1	Gilman 2015 cyclopentenone
84.0284	C ₄ H ₄ O ₂		0.038±0.026	44.5	Gilman 2015

84.0648	C ₅ H ₈ O		0.078±0.055	11.5	Atkinson 2003, NIST Database
86.0441	C ₄ H ₆ O ₂		0.218±0.137	0.8	Gilman 2015, NIST Database
88.0233	C ₃ H ₄ O ₃		0.010±0.029	0.1	Gilman 2015
88.0597	C ₄ H ₈ O ₂		2.273±2.367	0.9	Koss 2018
94.0491	C ₆ H ₆ O		0.041±0.034	28.0	Gilman 2015
96.0284	C ₅ H ₄ O ₂		0.023±0.020	35.6	Gilman 2015
96.0648	C ₆ H ₈ O		0.031±0.021	132.0	Gilman 2015 25dimethylfuran
98.0441	C ₅ H ₆ O ₂		0.081±0.054	13.6	Koss 2018
98.0804	C ₆ H ₁₀ O		0.345±0.366	6.4	Atkinson 2003 cyclohexanone
100.023	C ₄ H ₄ O ₃		0.045±0.070	20.0	Koss 2018
100.06	C ₅ H ₈ O ₂		0.229±0.151	30.3	Gilman 2015
102.039	C ₄ H ₆ O ₃		0.032±0.025	43.0	Koss 2018
102.0753	C ₅ H ₁₀ O ₂		0.053±0.050	8.71	Pfannerstill 2019
106.049	C ₇ H ₆ O		0.143±0.136	12.0	Atkinson 2003
108.028	C ₆ H ₄ O ₂		0.017±0.016	4.6	NIST Database
108.065	C ₇ H ₈ O		0.030±0.029	26.2	NIST Database
110.044	C ₆ H ₆ O ₂		0.022±0.017	80.1	Koss 2018
110.08	C ₇ H ₁₀ O		0.022±0.014	23.3	Koss 2018
112.023	C ₅ H ₄ O ₃		0.059±0.055	49.0	Koss 2018
112.06	C ₆ H ₈ O ₂		0.049±0.035	57.0	Koss 2018
112.096	C ₇ H ₁₂ O		0.039±0.036	10.0	NIST Database cycloheptanone
114.039	C ₅ H ₆ O ₃		0.033±0.027	100.0	Koss 2018

114.075	C ₆ H ₁₀ O ₂		0.076±0.058	20.0	Koss 2018
114.112	C ₇ H ₁₄ O		0.025±0.018	21.4	Atkinson 2003
116.055	C ₅ H ₈ O ₃		0.025±0.020	5.0	Koss 2018
116.091	C ₆ H ₁₂ O ₂		0.134±0.136	6.0	NIST Database
118.049	C ₈ H ₆ O		0.006±0.007	37.0	NIST Database
120.065	C ₈ H ₈ O		0.074±0.058	16.0	Atkinson 2003 average tolualdehydes
122.044	C ₇ H ₆ O ₂		0.029±0.030	38.0	Koss 2018
122.08	C ₈ H ₁₀ O		0.012±0.012	46.6	Koss 2018
124.023	C ₆ H ₄ O ₃		0.002±0.003	4.6	Koss 2018
124.06	C ₇ H ₈ O ₂		0.015±0.011	75.0	NIST Database
124.096	C ₈ H ₁₂ O		0.016±0.009	40.4	Pfannerstill 2019
126.039	C ₆ H ₆ O ₃		0.013±0.010	100.0	Koss 2018
126.111	C ₈ H ₁₄ O		0.032±0.035	98.8	Pfannerstill 2019
128.055	C ₆ H ₈ O ₃		0.026±0.021	132.0	Koss 2018
128.127	C ₈ H ₁₆ O		0.028±0.020	11	Pfannerstill 2019
132.065	C ₉ H ₈ O		0.003±0.005	37.0	Gilman 2015
134.08	C ₉ H ₁₀ O		0.016±0.013	4.5	NIST Database
136.06	C ₈ H ₈ O ₂		0.020±0.018	12.0	Koss 2018
138.075	C ₈ H ₁₀ O ₂		0.009±0.007	100.0	NIST Database
140.127	C ₉ H ₁₆ O		0.018±0.013	43.5	Pfannerstill 2019
144.05	C ₆ H ₈ O ₄		0.004±0.004	4.6	Koss 2018
144.065	C ₁₀ H ₈ O		0.001±0.002	37.0	Koss 2018

146.08	C ₁₀ H ₁₀ O		0.003±0.004	37.0	Koss 2018
148.096	C ₁₀ H ₁₂ O		0.008±0.007	50.0	NIST Database: 1-methoxy-4-(2-propenyl) benzene
150.075	C ₉ H ₁₀ O ₂		0.005±0.004	100.0	Koss 2018
152.055	C ₈ H ₈ O ₃		0.017±0.011	85.0	Koss 2018
152.127	C ₁₀ H ₁₆ O		0.031±0.019	4.3	Atkinson 2003
154.07	C ₈ H ₁₀ O ₃		0.005±0.004	100.0	Koss 2018
154.143	C ₁₀ H ₁₈ O		0.012±0.010	25.0	NIST Database Fenchol, Borneol
156.159	C ₁₀ H ₂₀ O		0.053±0.068	13.0	Atkinson 2003 2-decanone
164.091	C ₁₀ H ₁₂ O ₂		0.003±0.003	100.0	Koss 2018
N/S-containing species					
27.0182	HCN		0.003±0.003	0.0	Cicerone 1983
33.995	H ₂ S		0.002±0.002	4.6	NIST database
41.0338	C ₂ H ₃ N		0.412±2.258	0.02	Gilman 2015
43.0495	C ₂ H ₅ N		0.007±0.008	0.2	Koss 2018
45.0287	CH ₃ NO		0.060±0.121	1.5	NIST database: CH ₂ =NOH
45.0651	C ₂ H ₇ N		0.003±0.005	45.5	Koss 2018
48.0106	CH ₄ S		0.009±0.011	33.0	NIST database
53.0338	C ₃ H ₃ N		0.016±0.011	4.0	Gilman 2015
55.0495	C ₃ H ₅ N		0.004±0.006	0.3	Gilman 2015
57.0287	C ₂ H ₃ NO		0.012±0.008	0.1	Koss 2018
57.0651	C ₃ H ₇ N		0.003±0.004	15.0	Koss 2018

59.0444	C ₂ H ₅ NO		0.039±0.076	8.6	NIST database
61.0237	CH ₃ NO ₂		0.008±0.008	0.3	Gilman 2015
62.0263	C ₂ H ₆ S		0.008±0.010	6.0	NIST database
65.0338	C ₄ H ₃ N		0.001±0.010	4.0	Koss 2018
67.0495	C ₄ H ₅ N		0.006±0.006	111.4	Gilman 2015
69.0651	C ₄ H ₇ N		0.012±0.007	7.7	Koss 2018
71.0808	C ₄ H ₉ N		0.001±0.001	25.0	Koss 2018
73.0237	C ₂ H ₃ NO ₂		0.002±0.009	1.2	NIST Database
73.06	C ₃ H ₇ NO		0.523±0.919	12.5	Pfannerstill 2019
75.0393	C ₂ H ₅ NO ₂		0.006±0.006	0.1	NIST Database
77.0008	CH ₃ NOS		0.001±0.001	0.2	Koss 2018
79.0495	C ₅ H ₅ N		0.010±0.007	5.6	Koss 2018
81.0651	C ₅ H ₇ N		0.005±0.006	62.7	Gilman 2015
83.0808	C ₅ H ₉ N		0.011±0.005	0.5	Koss 2018
89.055	C ₃ H ₇ NO ₂		0.002±0.002	1.2	NIST Database
93.0287	C ₅ H ₃ NO		0.000±0.001	40.0	Koss 2018
93.0651	C ₆ H ₇ N		0.005±0.005	2.6	NIST Database methylpyridines average
93.9984	C ₂ H ₆ S ₂		0.003±0.004	230.0	NIST Database
95.0444	C ₅ H ₅ NO		0.002±0.002	0.5	Koss 2018
95.0808	C ₆ H ₉ N		0.002±0.002	145.0	Koss 2018
97.0964	C ₆ H ₁₁ N		0.003±0.002	5.0	Koss 2018
103.049	C ₇ H ₅ N		0.014±0.011	1.0	Gilman 2015

105.065	C ₇ H ₇ N		0.002±0.003	57.0	NIST Database
107.044	C ₆ H ₅ NO		0.003±0.003	12.0	Koss 2018
107.081	C ₇ H ₉ N		0.003±0.005	3.2	NIST Database
109.096	C ₇ H ₁₁ N		0.001±0.001	89.4	Koss 2018
111.039	C ₅ H ₅ NO ₂		0.003±0.002	10.3	Koss 2018
113.019	C ₄ H ₃ NO ₃		0.005±0.004	40.0	Koss 2018
117.05	C ₄ H ₇ NO ₃		0.004±0.004	50.8	Koss 2018
117.065	C ₈ H ₇ N		0.004±0.003	1.2	Koss 2018
119.081	C ₈ H ₉ N		0.000±0.001	0.5	Koss 2018
123.039	C ₆ H ₅ NO ₂		0.004±0.008	0.1	NIST Database
125.128	C ₈ H ₁₅ N		0.001±0.001	8.0	Koss 2018
131.081	C ₉ H ₉ N		0.002±0.002	5.6	Koss 2018
137.055	C ₇ H ₇ NO ₂		0.003±0.003	0.1	Koss 2018
149.127	C ₁₀ H ₁₅ N		0.000±0.001	148	Pfannerstill 2019

91 # # The concentrations of these higher alkanes were measured by NO⁺ PTR-ToF-MS.

Figure S1. The sampling site at Guangzhou Geochemistry Institute, Chinese Academy of Sciences and its surrounding environment in Guangzhou, China. Note that the map is extracted from © Google Maps by the authors.

Figure S2. Schematic drawing of the inlet system for PTR-ToF-MS during the campaign.

Figure S3. Calibration results of PTR-ToF-MS for different species during the campaign. From October 27 to 31, the sensitivity reduction is due to the unstable current of the ion source.

Figure S4. The humidity dependence of benzene, toluene, o-xylene, formaldehyde, acetone and acetaldehyde from laboratory experiments.

Figure S5. Scatter plots of the PTR-ToF-MS and online GC-MS/FID measurements for (a) toluene, (b) styrene, (c) C8 aromatics, (d) C9 aromatics, (e) Scatter plots of formaldehyde between PTR-ToF-MS and the Hantzsch formaldehyde analyzer. The blue and black lines correspond to the linear regression fits for all data points and the 1:1 relationship, respectively.

Figure S6. Sensitivities of PTR-ToF-MS as a function of the kinetic rate constants for proton-transfer reactions for 20 different VOCs. The red markers indicate the species used for the calculation of average sensitivity in this study. The green line represents the average sensitivity of red markers.

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120 **Figure S7.** The average fractions of different OVOCs species in the total concentrations
 121 of OVOCs with one oxygen atom measured by PTR-ToF-MS during the campaign.

Figure S8 (a) Correlations of MVK+MACR with isoprene. (b) Time series of the measured MVK+MACR concentrations and MVK+MACR concentrations after deducting anthropogenic sources emissions. (c) Time series of ambient concentrations of MVK+MACR and isoprene and isoprene concentrations converted back to the source (isoprene_{initial}).

Figure S9. Comparisons of measured and calculated photolysis rates of H_2O_2 and HCHO .

Figure S10. Scatter plot of the concentrations of acetylene versus CO during the campaign. The blue line is the linear fit to the data points in the plot.

Figure S11. (a) Diurnal variations of m+p-xylene/ethylbenzene concentration ratios. Red dots are measured ratios during the campaign. Blue line indicates hourly geometric average, and gray areas are geometric standard deviations. (b) Correlation of m+p-xylene with ethylbenzene. The dashed lines in both graphs indicate the estimated initial emission ratio of m +p-xylene/benzene.

Figure S12. Comparisons of measured and calculated concentrations for (a) $C_xH_yO_1$, (c) $C_xH_yO_2$, and (e) $C_xH_yO_{\geq 3}$. The different colors represent the four different terms of Eq. 1. Scatterplots of the calculated and measured concentrations for (b) $C_xH_yO_1$, (d) $C_xH_yO_2$, and (f) $C_xH_yO_{\geq 3}$.

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150 **Figure S13.** Scatter plot of the measured OH reactivity and the concentrations of CO

151 during the campaign. The blue line is the linear fit to the data points in the plot.

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