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Supplement of

Measurement report: Intra- and interannual variability and source apportionment of volatile organic compounds during 2018–2020 in Zhengzhou, central China

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Text S1 Relative reactivity of VOCs

To better understand the role of VOCs in the formation of troposphere O_3, reactive substances should be firstly determined. In this paper, OFP and the PE concentration are investigated to analyze the chemical reactivity of VOC species.

OFP is based on the concentration and MIR of each VOC species, as given in the following equation:

$$OFP_{(i)} = concentration_{(i)} \times MIR(i) \times \frac{M_{(i)}}{M_{(Ozone)}} \qquad (1)$$

Where M(ozone) and M(i) are the molar mass of O_3 and individual VOC species, respectively. $OFP_{(i)}$ is the O_3 formation potential of VOC species i and concentration $_{(VOCs)}$ is the mass concentration of each VOC (μg m^{-3}). And the MIR value of each VOC species was given by Carter (1994).

The PE concentration is defined as Eq. (2)

$$\mathrm{PE}_{(i)} = \mathrm{concentration}_{(i)} \times \frac{\mathrm{k_{OH}(i)}}{\mathrm{k_{OH}(propene)}} \qquad (2)$$

Where $k_{OH(i)}$ and $k_{OH\ (propene)}$ represent a rate constant for the reactivity of each VOC with an OH radical and the reaction of C_3H_6 with OH radicals. The k_{OH} rate constants were from Atkinson and Arey (2003).

Table S1. Results of monitored 57 VOCs species monitored: MDLs, concentrations with statistical analysis (unit: μg/m^3) (during 2018-2020).

	MDL	Mean	SD
Ethane	0.11	11.8	6.7
Propane	0.08	8.3	4.9
Toluene	0.12	6.6	4.5
i-Pentane	0.06	6.1	6.4
m p-Xylene	0.12	6	6
n-Butane	0.08	6	4.4
Ethene	0.09	5.9	5
n-Pentane	0.06	3.9	3.5
Benzene	0.1	3.8	2.1
i-Butane	0.08	3.4	2.6
Acetylene	0.05	3	3.8
Ethylbenzene	0.09	2.4	1.9
Cyclopentane	0.06	2.2	3.4
1-Isoprene	0.06	1.8	2.7
3-Methylpentane	0.18	1.8	1.8
n-Hexane	0.15	1.5	1.9
o-Xylene	0.09	1.4	1.4
Styrene	0.09	1.4	1.4
Propene	0.06	1.3	2.1
p-Diethylbenzene	0.12	1.2	1.2
m-Ethyltoluene	0.19	0.9	0.9
n-Heptane	0.13	0.9	1.3
2-Methylpentane	0.13	0.9	1.3
n-Dodecane	0.23	0.8	1.5
n-Undecane	0.14	0.7	2.1
n-Decane	0.38	0.6	0.6
n-Nonane	0.11	0.6	1.1
1,2,3-Trimethylbenzene	0.11	0.5	0.5
Methylcyclopentane	0.21	0.5	1.1
o-Ethyltoluene	0.11	0.5	0.5
p-Ethyltoluene	0.21	0.5	0.5
1,2,4-Trimethylbenzene	0.64	0.5	0.5
1,3,5-Trimethylbenzene	0.16	0.5	0.5
i-Propylbenzene	0.11	0.5	0.5
n-Propylbenzene	0.11	0.5	1.1
n-Octane	0.1	0.5	1
2,2,4-Trimethylpentane	0.15	0.5	0.5
2-Methylheptane	0.1	0.5	1
1-Butene	0.05	0.5	0.8
cis-2-Butene	0.08	0.5	1
trans-2-Butene	0.05	0.5	1.5

2,4-Dimethylpentane	0.13	0.4	0.4
2-Methylhexane	0.13	0.4	0.4
3-Methylhexane	0.13	0.4	0.4
2,3-Dimethylbutane	0.12	0.4	0.4
2,2-Dimethylbutane	0.15	0.4	0.4
1-Hexene	0.15	0.4	0.8
Methylcyclohexane	0.11	0.4	0.4
Cyclohexane	0.15	0.4	0.4
1-Pentene	0.09	0.3	0.3
cis-2-Pentene	0.09	0.3	0.6
trans-2-Pentene	0.09	0.3	0.6
2,3,4-Trimethylpentane	0.02	BDL	
2,3-Dimethylpentane	0.03	BDL	
3-Methylheptane	0.02	BDL	
m-Diethylbenzene	0.02	BDL	

Table S2 Average ambient VOCs concentrations and chemical species during 2018 to 2020 (unit: μg/m^3).

	Alkanes	Alkenes	Alkynes	Aromatics	TVOC
2018	63.1±55	16.6±8.9	4.8±4.9	28.6±12.8	113.2±65.2
2019	55.8±34.2	9.5±8.3	3.3±4.8	22±13.2	90.7±52.5
2020	45.2±24.6	11.1±8	0.9±1	21.9±14.1	79.1±41.7
Average	54.7±37.9	12.4±8.4	3±3.6	24.2±13.3	94.3±53.1

Table S3. Comparison of VOCs (ppbv) between this study and other studies.

City	TVOC	alkanes	alkenes	aromatics	alkynes	Reference
Zhengzhou	38.2±15.6	23.0±19.5	7.1±3.3	5.5±1.3	2.6±2.6	This study
Nanjing	34.40 ±25.20	14.98±12.72	7.35 ± 5.93	9.06 ± 6.64	3.02 ± 2.01	Shao, et al. 2016
Guangzhou	44.56	26.2	7.33	11.03	--	Zou, et al. 2015
Chengdu	41.8 ± 20.8	23.6 ± 13.0	8.2 ± 6.4	7.2 ± 6.1	2.7 ± 2.3	Song et al. 2019b
Langfang	33.38 ± 26.03	22.93 ± 19.15	3.7 ± 2.72	4.91 ± 5.7	2.56 ± 1.85	Song, et al. 2019a
Tianjin	28.7 ± 11.4	18.3 ± 6.0	5.2 ± 2.0	5.3 ± 5.9	--	Liu et al. 2016

Table S4 Variations in the monthly average of meteorological parameters (T, RH, UV, and WS) and pollutant gases (O_3, NO_2, CO, and TVOC).

Month	RH (%)	Pr (mm)	T (°C)	WS (m/s)	UV (W/m^2)	TVOC ($\mu g/m^3$)	NO_2 ($\mu g/m^3$)	O_3 ($\mu g/m^3$)	CO (mg/m^3)
1	46.4±22	7±0.1	3.1±3.3	1.3±0.8	85±33.8	145±80.7	65.4±29.4	22.6±19.5	1.4±0.7
2	55.9±16.1	3.9±0	4.3±5	1.2±1	114.5±45.3	99.8±62.4	45.3±29.5	50.4±35.5	1.2±0.6
3	38.1±16.7	3.3±0.1	13.9±4.8	1.6±0.8	206.5±55	91.6±44.7	48.4±29.3	65.2±42.8	0.5±0.3
4	52.2±19.7	20.2±0.2	16.7±5.3	1.9±1.1	238.5±86.6	95.4±37.8	41.4±23.6	76.7±49.1	0.8±0.4
5	40.9±17.6	0.2±0	24.8±5.5	1.5±0.9	315.2±62.6	72.2±35.8	39±29.4	100.1±62.1	0.7±0.3
6	48.4±22.3	20.6±0.2	30±7.6	0.6±0.4	291.6±112	76.1±32.6	32.9±23.1	114±63.9	0.6±0.3
7	60±15.3	18.2±0.3	30.6±4.6	0.4±0.2	305.6±70.3	81.3±38.3	36.4±27.8	110.4±66.9	0.7±0.3
8	70±18	60.5±0.6	27.8±3.7	0.4±0.2	265±80.1	65.3±25.1	32.6±20.6	95.5±58.5	0.8±0.3
9	65±19.2	1.9±0	23.8±4.3	1.2±0.8	208.3±85.9	80.6±39.3	45.7±35.8	95±73.3	0.9±0.4
10	63±21.5	81.8±0.5	16.8±4.8	1.5±1.3	160±61.8	86.5±56	49.3±30	54.6±49.7	0.9±0.5
11	54.9±22.4	4±0.1	11.3±5.3	1.6±1.3	118.7±42.3	91.2±51.6	55.4±30	35±31.6	1±0.5
12	58.5±23.8	3.4±0	5.6±3.9	1.4±0.8	102.9±41.7	104.5±55.2	49.8±24.5	28.2±25	1.2±0.6

Table S5 The OH reactivity towards the total VOCs and the comparison with other studies (unit: s^{-1}).

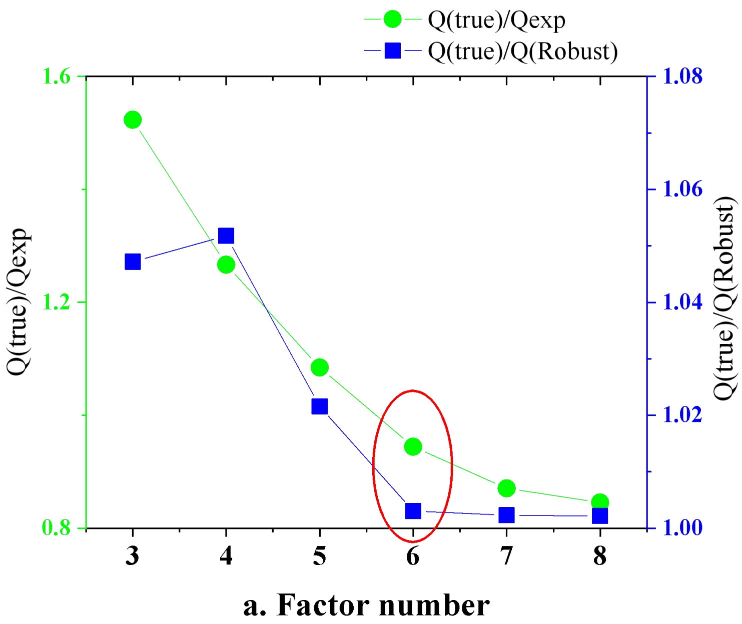
	The OH reactivity of the total VOCs	The OH reactivity of the total OVOCs	The OH reactivity after deducting OVOCs	References
Zhengzhou	6.7	-	6.7	This study
Xianghe	7.9	2.4	5.5	Yang et al., 2020
Beijing	15.5	7.2	8.3	Yang et al., 2021
Heshan	18.3	4.7	13.6	Yang et al., 2017
Shanghai	6.21	2.97	3.24	Tan et al., 2019
Guangzhou	10.9	4.6	6.4	Tan et al., 2019
Chongqing	8.9	2.136	6.8	Tan et al., 2019

Table S6 The detailed contribution of each VOC group to the total OH reactivity during the sampling periods (unit: s^{-1}).

Species	2018	Species	2019	Species	2020	Species	Average
Isoprene	1.7	Isoprene	1.1	Isoprene	1.1	Isoprene	1.8
Ethene	1.4	Ethene	0.8	Ethene	0.9	Ethene	1.1
cis-2-Butene	0.6	Propene	0.6	m/p-Xylene	0.5	Propene	0.5
m/p-Xylene	0.6	m/p-Xylene	0.5	Propene	0.4	m/p-Xylene	0.5
Propene	0.6	Styrene	0.3	Styrene	0.4	Styrene	0.4
Styrene	0.6	trans-2-Butene	0.3	Toluene	0.2	cis-2-Butene	0.3
trans-2-Butene	0.4	cis-2-Butene	0.2	trans-2-Butene	0.2	trans-2-Butene	0.3
Toluene	0.3	Toluene	0.2	cis-2-Butene	0.2	Toluene	0.3
i-Pentane	0.2	i-Pentane	0.2	1-Butene	0.1	i-Pentane	0.2
n-Pentane	0.2	1-Butene	0.2	i-Pentane	0.1	1-Butene	0.2
Cyclopentane	0.2	trans-2-Pentene	0.2	n-Butane	0.1	n-Butane	0.1
1-Hexene	0.2	n-Butane	0.2	Propane	0.1	trans-2-Pentene	0.1
1,3,5-Trimethylbenzene	0.2	Propane	0.1	trans-2-Pentene	0.1	Propane	0.1
cis-2-Pentene	0.2	n-Pentane	0.1	o-Xylene	0.1	n-Pentane	0.1
trans-2-Pentene	0.2	o-Xylene	0.1	1,2,4-Trimethylbenzene	0.1	o-Xylene	0.1
n-Butane	0.2	i-Butane	0.1	Ethylbenzene	0.1	1,3,5-Trimethylbenzene	0.1
1-Butene	0.1	Ethylbenzene	0.1	i-Butane	0.1	cis-2-Pentene	0.1
o-Xylene	0.1	3-Methylpentane	0.1	1,3,5-Trimethylbenzene	0.1	Ethylbenzene	0.1
Propane	0.1	n-Hexane	0.1	n-Pentane	0.1	1-Hexene	0.1
Ethylbenzene	0.1	cis-2-Pentene	0.1	1,2,3-Trimethylbenzene	0.1	Cyclopentane	0.1

Table S7 The detailed contribution of each VOC group to the total OH reactivity in different seasons (unit: s^{-1}).

Species	Winter	Species	Spring	Species	Summer	Species	Autumn
Ethene	1.3	Isoprene	1.2	Isoprene	2	Isoprene	0.6
Propene	1	Ethene	1.1	m/p-Xylene	0.5	Propene	0.6
m/p-Xylene	0.6	Propene	0.5	Propene	0.4	m/p-Xylene	0.5
Isoprene	0.5	trans-2-Butene	0.5	Styrene	0.3	Styrene	0.4
Styrene	0.4	m/p-Xylene	0.4	Ethene	0.2	Ethene	0.4
cis-2-Butene	0.3	cis-2-Butene	0.3	cis-2-Butene	0.2	Toluene	0.3
trans-2-Butene	0.3	Styrene	0.2	Toluene	0.2	trans-2-Butene	0.2
Toluene	0.3	1-Butene	0.2	trans-2-Butene	0.2	n-Butane	0.2
1-Butene	0.3	Toluene	0.2	i-Pentane	0.2	Propane	0.2
i-Pentane	0.2	trans-2-Pentene	0.2	1-Butene	0.2	i-Pentane	0.2
trans-2-Pentene	0.2	i-Pentane	0.2	trans-2-Pentene	0.1	1-Butene	0.2
Propane	0.2	Acetylene	0.1	n-Butane	0.1	cis-2-Butene	0.1
n-Butane	0.2	n-Butane	0.1	3-Methylpentane	0.1	trans-2-Pentene	0.1
n-Pentane	0.1	Propane	0.1	Ethylbenzene	0.1	1,3,5-Trimethylbenzene	0.1
cis-2-Pentene	0.1	o-Xylene	0.1	o-Xylene	0.1	n-Pentane	0.1
i-Butane	0.1	n-Pentane	0.1	Propane	0.1	i-Butane	0.1
n-Hexane	0.1	3-Methylpentane	0.1	m-Ethyltoluene	0.1	o-Xylene	0.1
o-Xylene	0.1	cis-2-Pentene	0.1	n-Hexane	0.1	Ethylbenzene	0.1
Ethane	0.1	n-Hexane	0.1	n-Pentane	0.1	Cyclopentane	0.1
Acetylene	0.1	i-Butane	0.1	cis-2-Pentene	0.1	3-Methylpentane	0.1



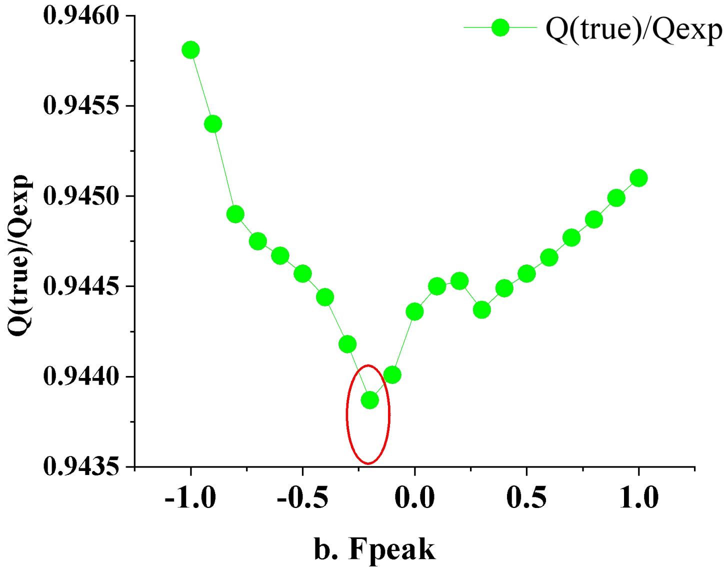


Fig. S1 The Q/Qexp and Q (ture)/Q (robust) ratios in different solutions (a); the Q/Qexp ratio for different Fpeak value solutions (b).

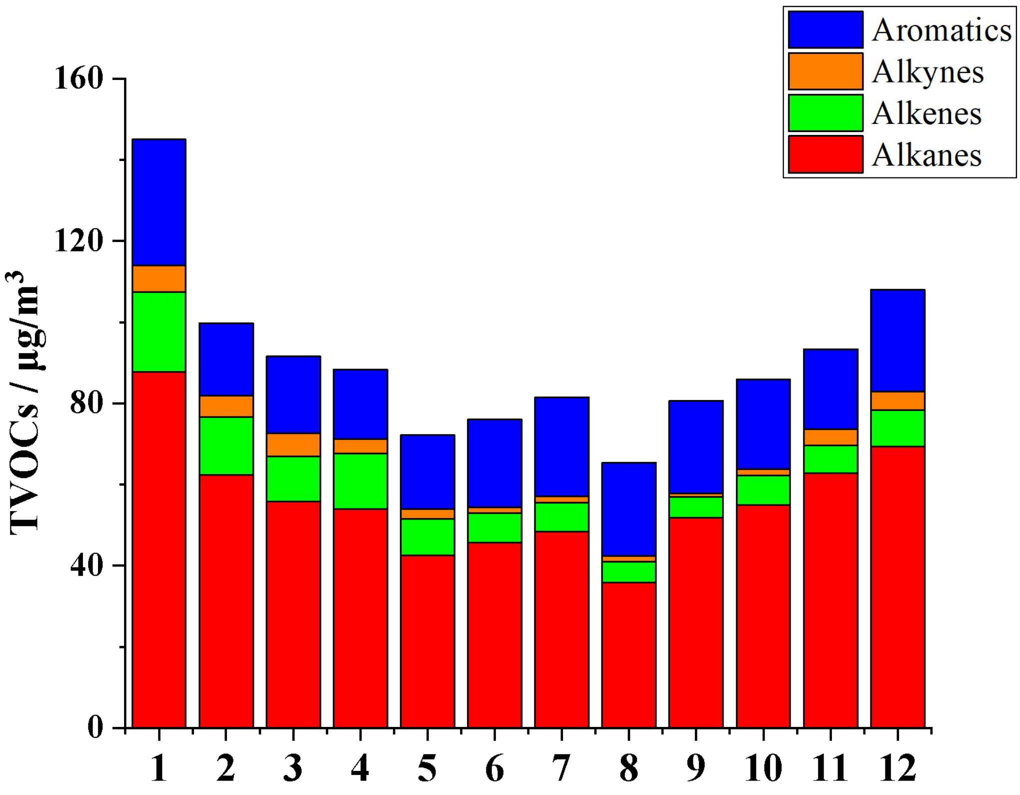


Fig. S2 Monthly changes in the concentrations of VOCs in Zhengzhou.

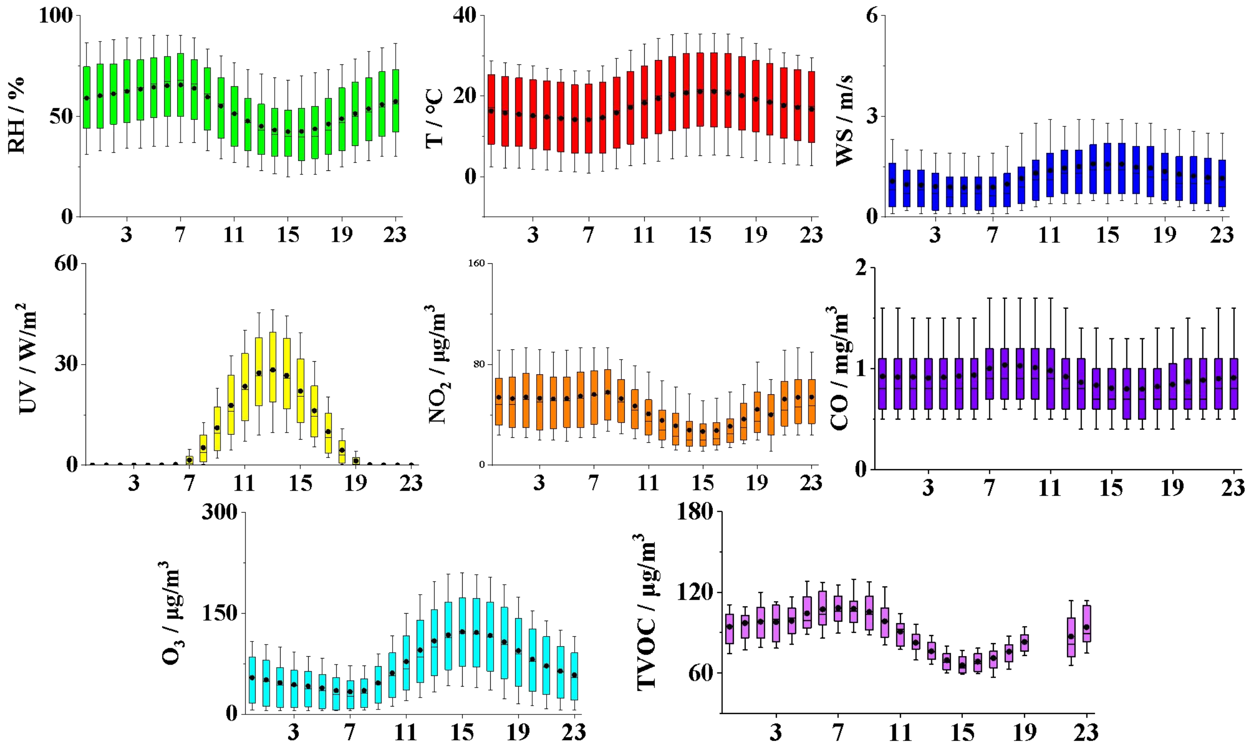


Fig. S3 Diurnal variations of VOCs meteorological conditions during the measurements.

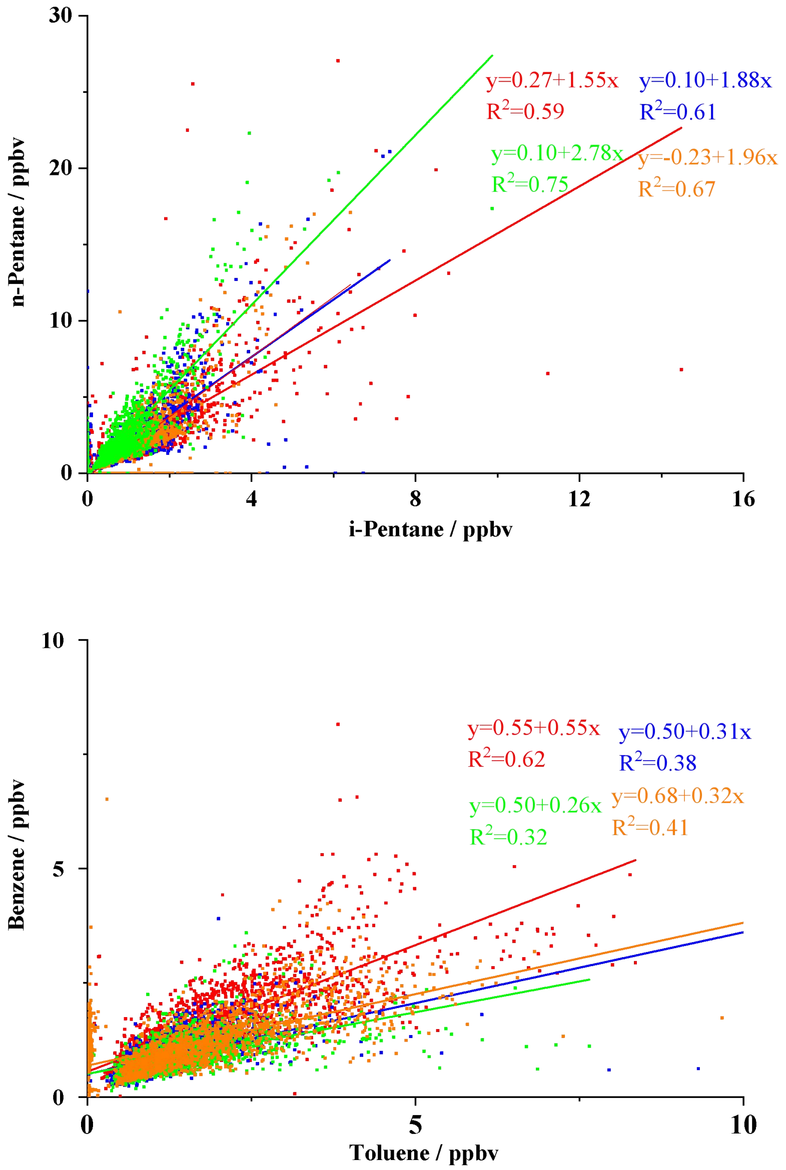


Fig. S4 Seasonal variation in B/T and i-/n-Pentane in Zhengzhou.

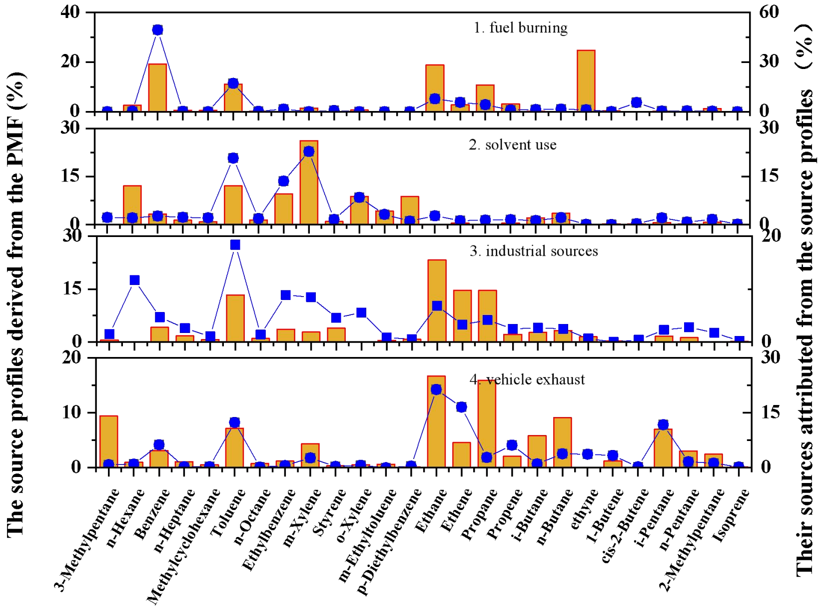


Fig.S5 The comparison between source profiles derived from the PMF against their attributed sources from the source profiles (bar is associated with PMF and dot is associated with source profiles).

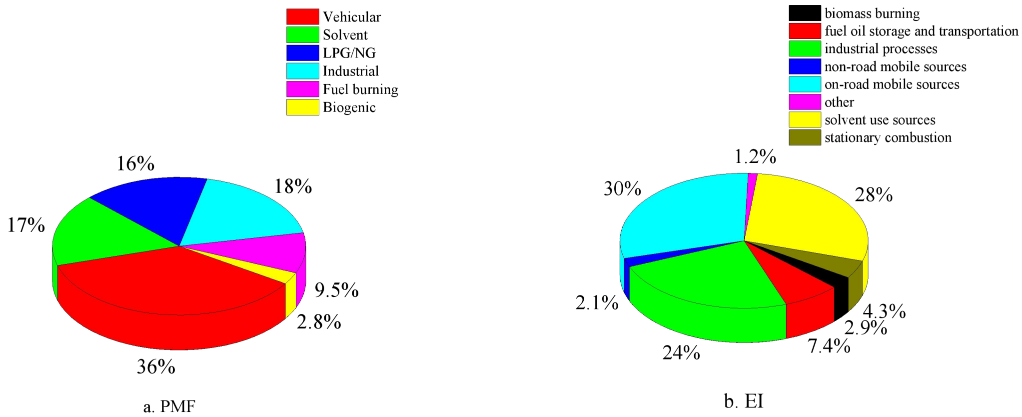


Fig.S6 Contribution of each source calculated using PMF and EI.

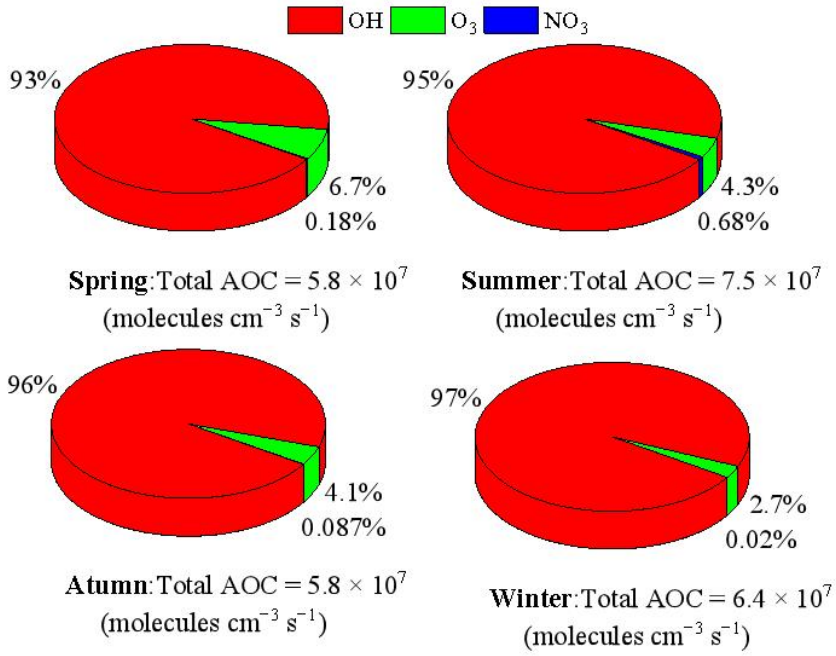


Fig. S7 Comparison of the relative contributions of OH, O_3 and NO_3 of the AOC in Zhengzhou in different seasons.

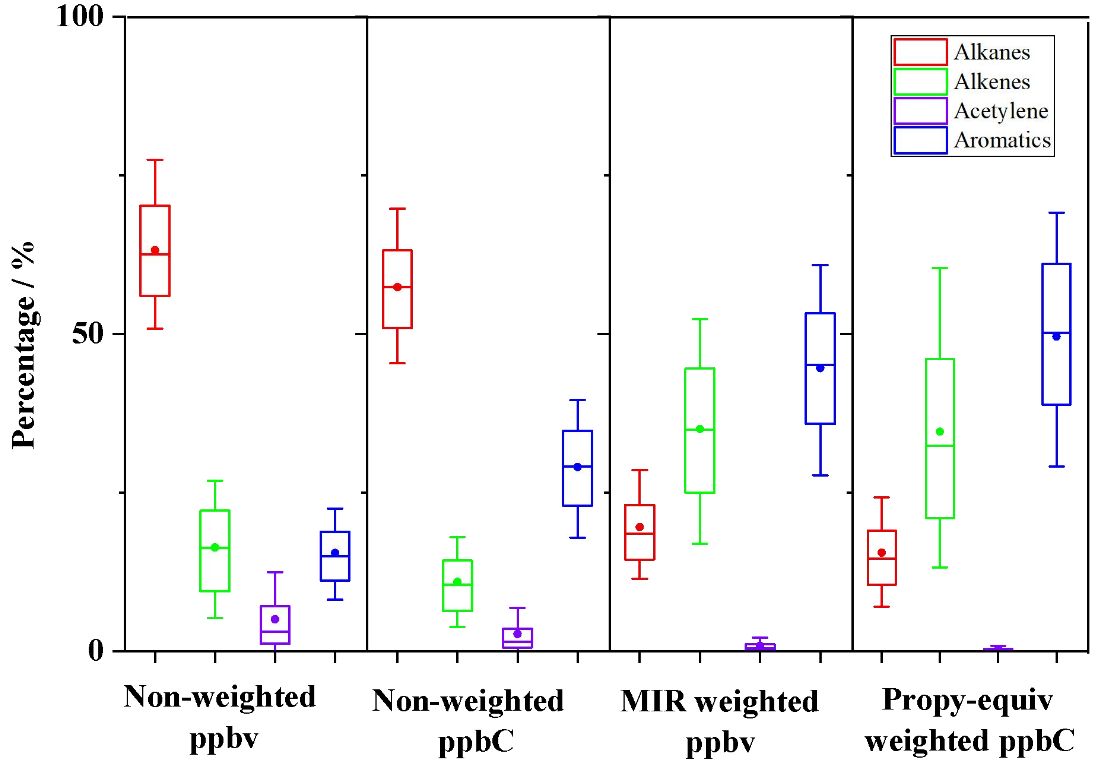


Fig. S8 Box and whisker plots of VOC profiles based on different scales during the entire sampling period.

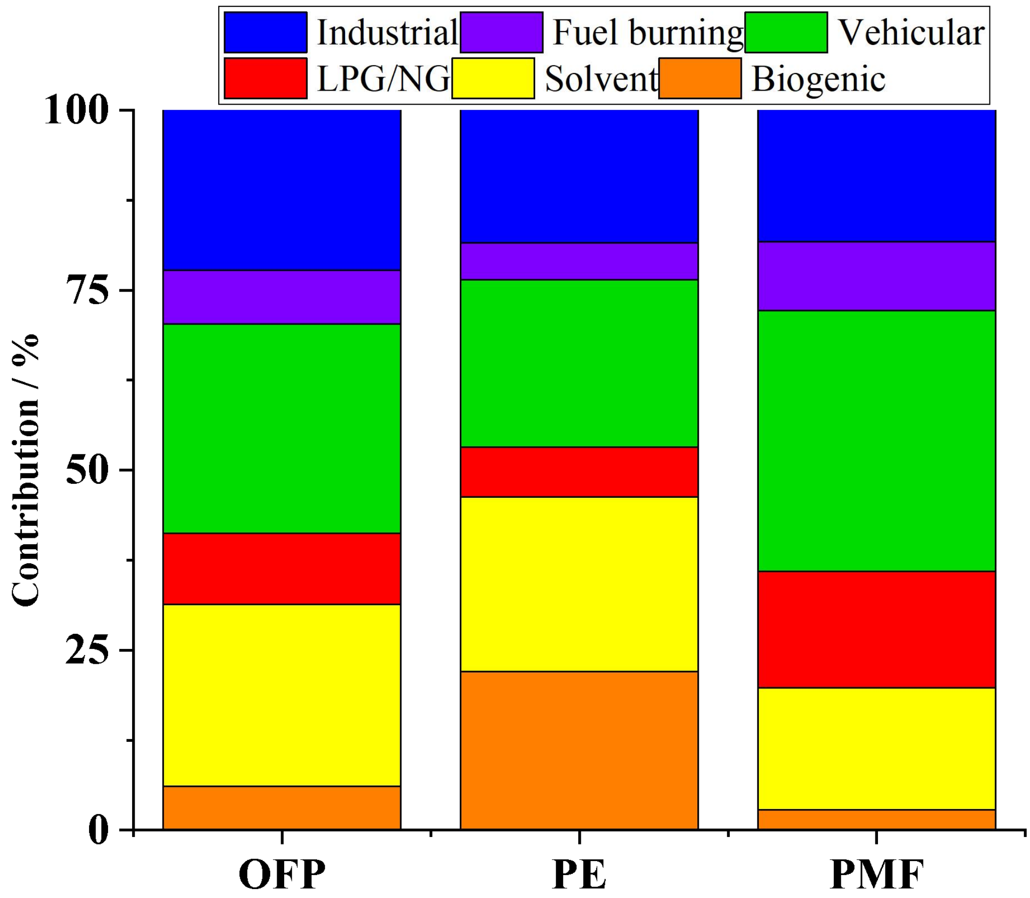


Fig.S9 Contribution of each source calculated using PMF, OFP, and PE.

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