Measurement report: Intra-, inter-annual variability and source apportionment of VOCs during 2018-2020 in Zhengzhou, Central China

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Text S1 Positive Matrix Factorization model

The source of VOCs was performed with the EPA PMF 5.0 model, which is a widely receptor model for source apportionment (Gao et al., 2018; Yadav et al., 2019). Detailed information about this method was described in the user manual (Norris et al., 2014) and related literatures (Song et al., 2019a, 2019b). It should be noted that not all of the VOC species were used in the PMF analysis. In this study, the principles for the selection of VOC species are established based on previous studies and listed as follows. (1) species with more than 25% data lacking or that fell below the MDLs were rejected, which follows the methodology of previous studies (Zhou et al., 2019); (2) species with short atmospheric lifetimes were excluded because they rapidly react away in the atmosphere; and (3) species with represented source tracers of emission sources were retained (For example, in the case of isoprene). Eventually, a total of 38 VOC species were selected for source apportionment analysis. In this study, seven-factors are extracted by PMF model based on: (1) principal component analysis of the VOC data; (2) VOC emission inventory of research region based on field investigation; and (3) Q/Qexp ratio for different factor numbers in the PMF (Fig. S1).

Text S2 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:

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

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)

$$PE_{(i)} = concentration_{(i)} \times \frac{k_{OH}(i)}{k_{OH}(propene)} \quad (2)$$

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: ppbv) (during 2018-2020).

	MDL	Mean	SD
Ethane	0.08	8.8	5
Ethene	0.07	4.7	4
Propane	0.04	4.2	2.5
Acetylene	0.04	2.6	3.3
n-Butane	0.03	2.3	1.7
i-Pentane	0.02	1.9	2
Toluene	0.03	1.6	1.1
i-Butane	0.03	1.3	1
n-Pentane	0.02	1.2	1.1
Benzene	0.03	1.1	0.6
m p-Xylene	0.02	1	1
Cyclopentane	0.02	0.7	1.1
Propene	0.03	0.7	1.1
1-Isoprene	0.02	0.6	0.9
Ethylbenzene	0.02	0.5	0.4
3-Methylpentane	0.04	0.4	0.4
n-Hexane	0.04	0.4	0.5
o-Xylene	0.02	0.3	0.3
Styrene	0.02	0.3	0.3
1-Butene	0.02	0.2	0.3
2-Methylpentane	0.03	0.2	0.3
cis-2-Butene	0.03	0.2	0.4
m-Ethyltoluene	0.04	0.2	0.2
n-Heptane	0.03	0.2	0.3
p-Diethylbenzene	0.02	0.2	0.2
trans-2-Butene	0.02	0.2	0.6
1,2,3-Trimethylbenzene	0.02	0.1	0.1
1,2,4-Trimethylbenzene	0.12	0.1	0.1
1,3,5-Trimethylbenzene	0.03	0.1	0.1
1-Hexene	0.04	0.1	0.2
1-Pentene	0.03	0.1	0.1
2,2,4-Trimethylpentane	0.03	0.1	0.1
2,2-Dimethylbutane	0.04	0.1	0.1
2,3-Dimethylbutane	0.03	0.1	0.1
2,4-Dimethylpentane	0.03	0.1	0.1
2-Methylheptane	0.02	0.1	0.2
2-Methylhexane	0.03	0.1	0.1
3-Methylhexane	0.03	0.1	0.1
cis-2-Pentene	0.03	0.1	0.2
Cyclohexane	0.04	0.1	0.1
i-Propylbenzene	0.02	0.1	0.1

Methylcyclohexane	0.03	0.1	0.1
Methylcyclopentane	0.04	0.1	0.2
n-Decane	0.06	0.1	0.1
n-Dodecane	0.03	0.1	0.2
n-Nonane	0.02	0.1	0.2
n-Octane	0.02	0.1	0.2
n-Propylbenzene	0.02	0.1	0.2
n-Undecane	0.02	0.1	0.3
o-Ethyltoluene	0.02	0.1	0.1
p-Ethyltoluene	0.04	0.1	0.1
trans-2-Pentene	0.03	0.1	0.2
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.

	Alkanes	Alkenes	Alkynes	Aromatics	TVOC
2018	25.2±17.2	9.2±5.7	4.2±4.3	6.4±2.9	45.0±25.2
2019	23.5±13.9	5.2±5.1	2.9±4.1	5.1±3	36.7±22
2020	19.4±9.9	5.5±4.0	0.7±0.8	4.9±3.1	30.5±15.4
Average	23±19.5	7.1±3.3	2.6±2.6	5.5±1.3	38.2±15.6

Table S3 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	T	WS	UV	TVOC	NO_2	O_3	CO
1	46.4±22	7±0.1	3.1±3.3	1.3±0.8	85±33.8	62.6±32.2	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	45.5±26	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	40±18.1	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	47.5±20.6	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	26.7±12.5	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	26.3±10.9	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	27.6±13.1	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	21.5±8	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	28.2±13.3	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	33±21.2	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	36.3±19.2	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	42±20.9	49.8±24.5	28.2±25	1.2±0.6

Table S4 The detailed contribution of each VOC group to the total OH reactivity during the sampling periods.

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 S5 The detailed contribution of each VOC group to the total OH reactivity in different seasons.

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

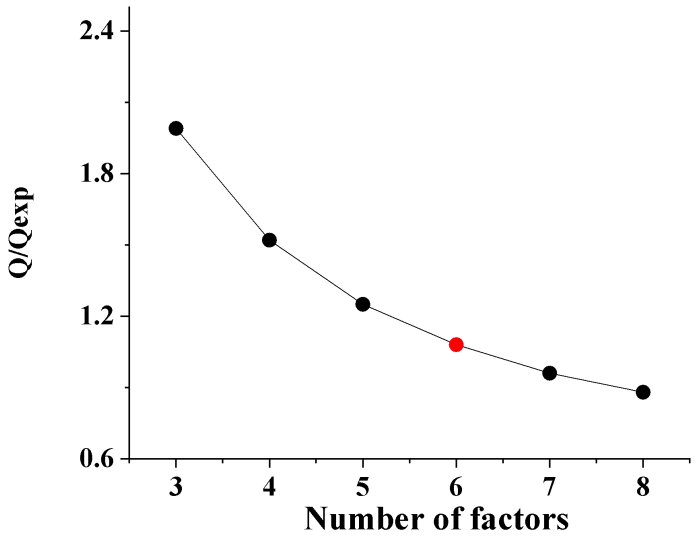

Fig. S1 The ratios of Q/Qexp at factor size ranged from 2–8.

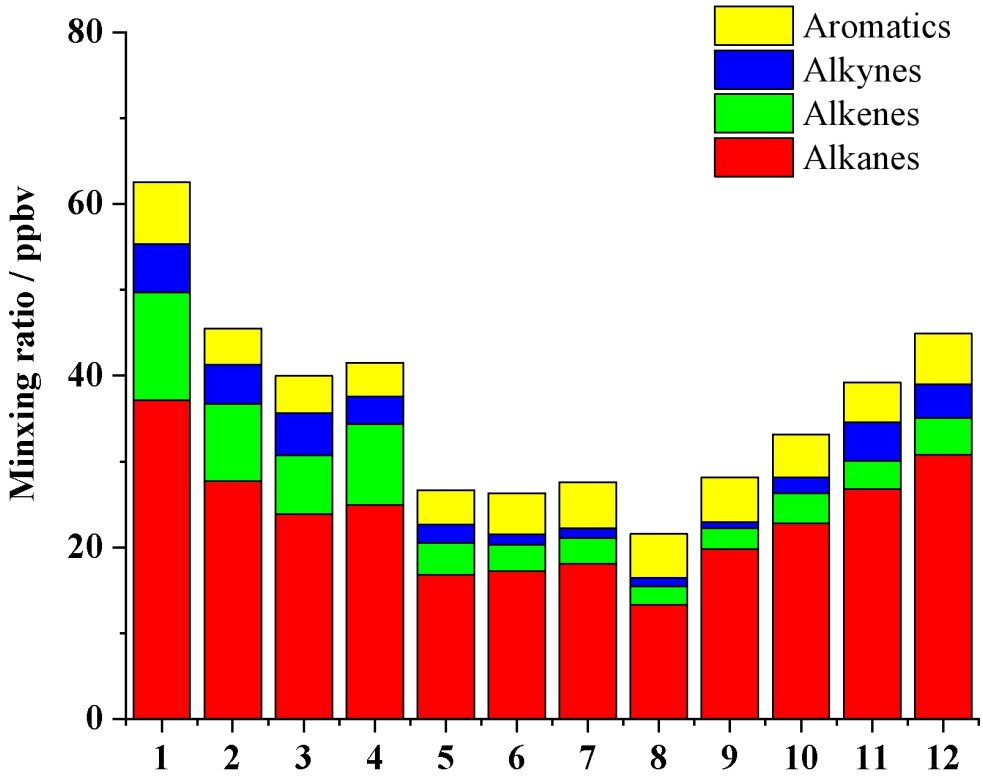

Fig. S2 Monthly changes in the concentrations of VOCs in Zhengzhou.

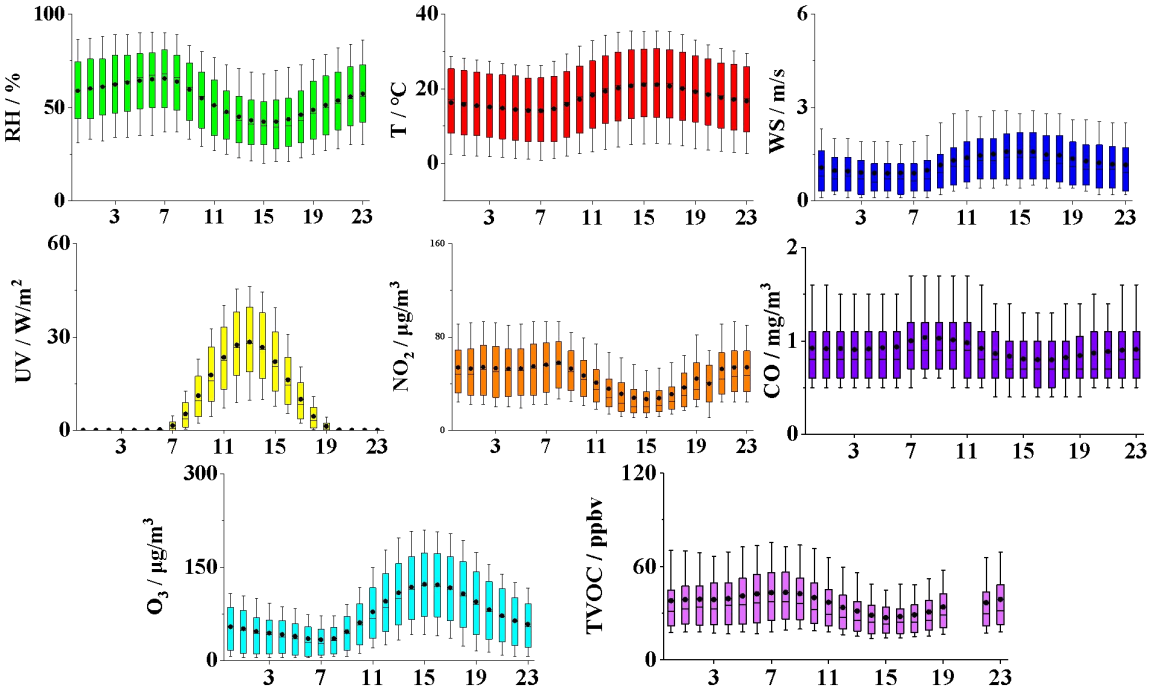

Fig. S3 Diurnal variations of VOCs meteorological conditions during the measurements.

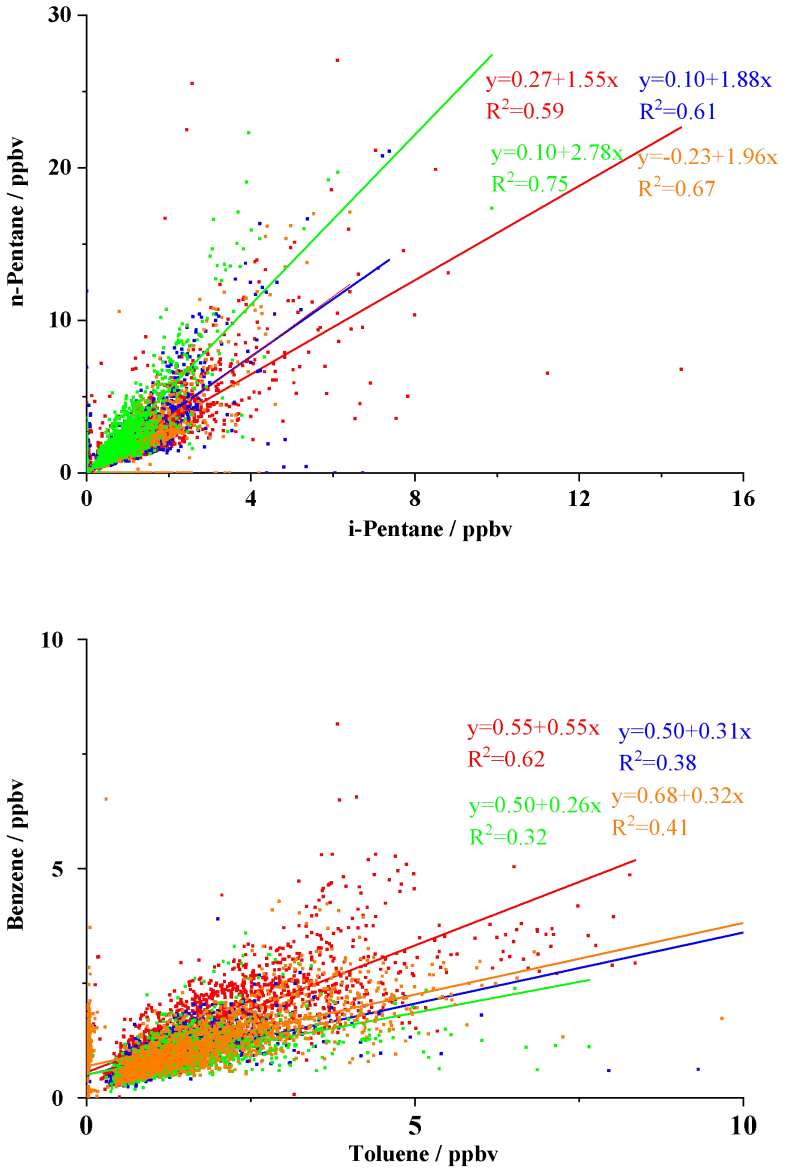

Fig. S4 Seasonal variation in B/T and i-/n-Pentane in Zhengzhou.

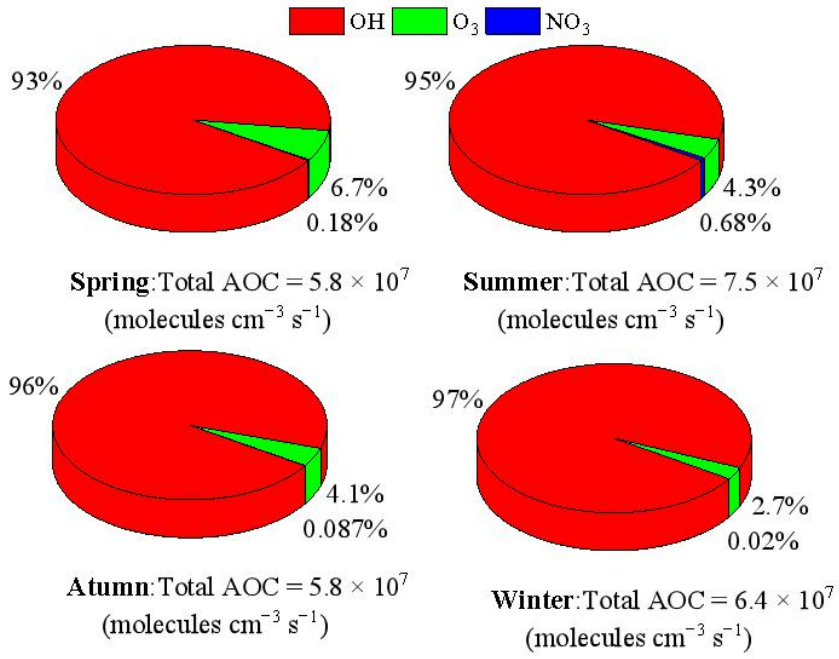

Fig. S5 Comparison of the relative contributions of OH, O_3 and NO_3 of the AOC in Zhengzhou in different seasons.

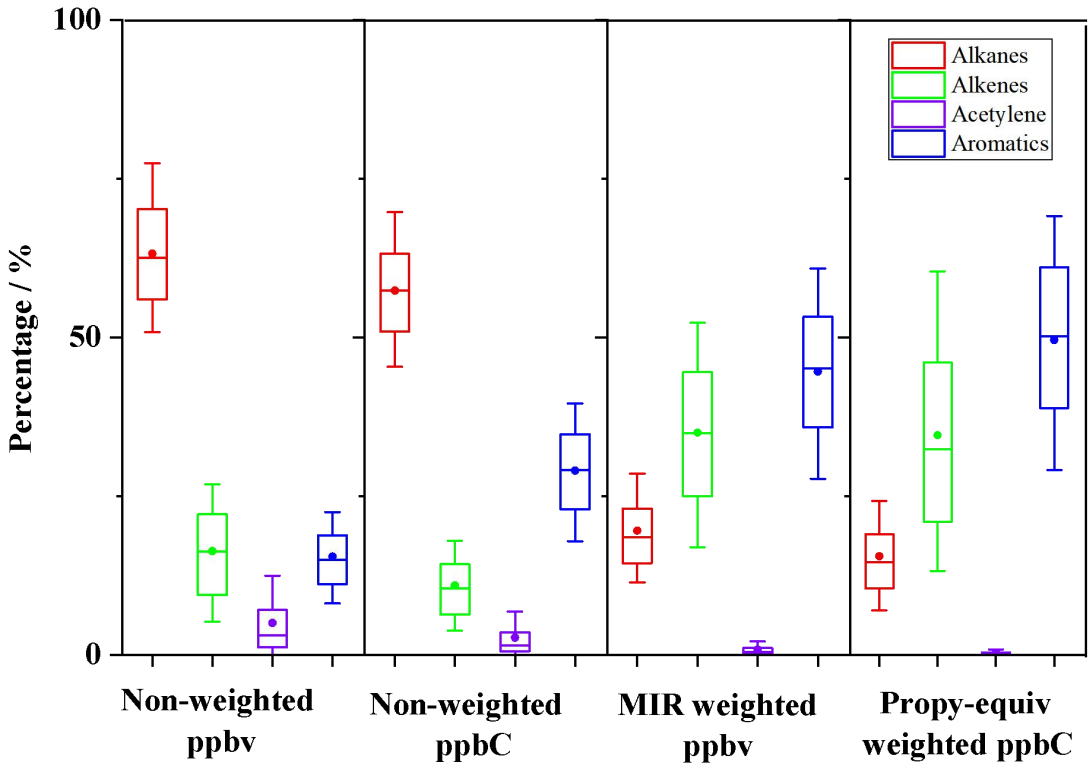

Fig. S6 Box and whisker plots of VOC profiles based on different scales during the entire sampling period.

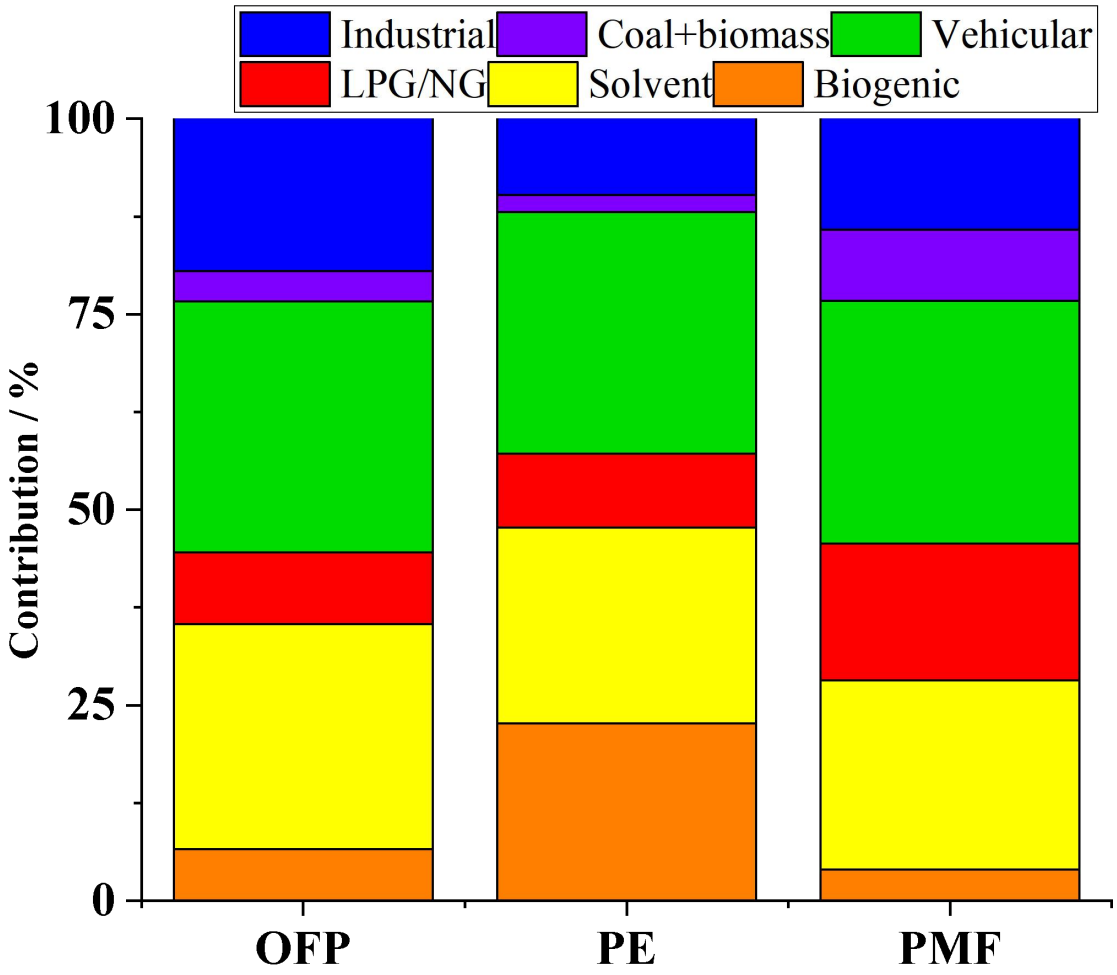

Fig.S7 Contribution of each source calculated using PMF, OFP, and PE.

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