Supplementary Information
Verification of anthropogenic VOC emission inventory through ambient measurements and satellite retrievals

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Table S1．Source classification and EFs of anthropogenic VOC sources (see the spreadsheets).

Table S2. Activity data for each source used in this study (see the spreadsheets).

Table S3. Monthly profiles used in this EF-based emission inventory (see the spreadsheets).

Table S4. Source profiles for each source used in this study (see the spreadsheets).

Table S5. VOC emission ratios (ppmv CO-1) and annual emissions (ton yr-1) for individual VOC species determined by the measurements and emission inventory for the PKU site (0.25 °×0.25 °grid).

Species	ER	Emissions		Species	ER	Emissions	
		ER	EI			ER	EI
Alkanes	--	--	--	**Halocarbon**	--	--	--
Ethane	5.93	1885.20	662.42	Chloromethane	0.51	313.83	17.08
Propane	3.15	1694.73	398.51	Chloroethylene	0.04	31.60	1.11
i-Butane	0.81	570.55	355.16	Bromomethane	0.00	5.54	0.38
n-Butane	1.19	843.33	465.99	Chloroethane	0.01	10.19	0.50
Cyclopentane	0.08	68.12	89.58	1,1-Dichloroethylene	0.00	3.05	1.11
i-Pentane	0.67	594.83	703.17	Dichloromethane	0.85	884.58	118.95
Pentane	0.44	386.99	478.85	1,1-Dichloroethane	0.05	55.37	1.11
2,2- Dimethylbutane	0.01	15.26	60.41	cis-1,2-dichloroethylene	0.02	22.43	2.90
2,3- Dimethylbutane	0.09	91.86	86.76	Chloroform	0.31	448.97	5.96
2- Methylpentane	0.18	185.45	418.12	1,1,1-Trichloroethane	0.00	2.49	0.88
3- Methylpentane	0.10	101.46	290.88	Carbon tetrachloride	0.06	118.09	17.80
n-Hexane	0.25	260.52	437.70	1,2- Dichloroethane	0.28	334.18	65.19
2,4-Dimethyl pentane	0.01	13.36	210.23	Trichloroethylene	0.04	62.77	418.53
Methylcyclopentane	0.10	104.64	182.83	1,2-Dichloropropane	0.24	330.41	41.10
2- methylhexane	0.04	51.41	226.73	tran-1,3-Dichloropropene	0.00	4.00	9.44
2,3- Dimethyl pentane	0.03	37.79	83.55	cis-1,3-Dichloropropene	0.00	1.71	13.52
3- methylhexane	0.05	60.53	186.69	1,1,2-Trichloroethane	0.02	25.19	3.75
2,2,4-Trimethylpentane	0.04	58.70	73.67	Tetrachloroethylene	0.04	72.83	604.10
n-Heptane	0.07	86.74	198.46	Chlorobenzene	0.01	16.63	4.23
Methylcyclohexane	0.04	49.54	168.08	1,3-Dichlorobenzene	0.00	3.10	4.35
2,3,4-Trimethylpentane	0.02	25.47	28.94	1,4-Dichlorobenzene	0.05	82.24	5.41
2- Methylheptane	0.02	30.22	112.59	Benzyl chloride	0.00	1.60	0.58
3- Methylheptane	0.01	13.71	172.36	1,2-Dichlorobenzene	0.00	4.27	3.85
Octane	0.04	53.59	179.01	**OVOCs**	--	--	--
Nonane	0.03	44.01	158.39	Acrolein	0.12	78.72	7.37
n-Decane	0.03	55.68	158.59	Propanal	0.12	85.76	37.96
Undecane	0.02	48.01	101.29	Isobutylene aldehyde	0.02	18.39	10.81
Alkenes	--	--	--	n-Butanal	0.05	42.57	82.25
Ethylene	5.38	1839.4	888.05	n-Pentanal	0.03	30.60	3.22

Propylene	1.24	635.64	517.20	Hexanal	0.10	122.55	25.96
tran-2-Butene	0.07	44.95	99.02	Acetone	1.61	1139.32	356.46
1-Butene	0.20	135.26	198.21	Methyl vinyl ketone	0.11	91.81	6.47
cis-2-Butene	0.04	26.43	91.90	2-Butanone	0.62	543.43	103.36
1,3-Butadiene	0.15	101.44	102.92	2-Pentanone	0.02	22.88	2.24
1-Pentene	0.03	23.48	82.68	3-Pentanone	0.03	33.78	0.38
tran-2-Pentene	0.02	13.65	82.26	Methyl acetate	0.24	216.87	1.52
Isoprene	0.03	24.70	24.22	MTBE	0.15	163.95	27.07
cis-2-Pentene	0.01	6.88	91.90	Vinyl acetate	0.01	6.24	11.21
1-Hexene	0.02	18.72	43.35	Ethyl acetate	0.65	697.92	531.73
Aromatics	--	--	--	Methyl methacrylate	0.58	704.38	0.12
Benzene	0.78	741.09	940.01	Butyl acetate	0.32	452.31	3.04
Toluene	0.86	968.52	1506.05	**Nitriles**	--	--	--
Ethylbenzene	0.22	289.34	1441.41	Acetonitrile	0.21	106.7	16.52
m/p-Xylene	0.25	318.34	2289.14	**Alkyne**	--	--	--
o-Xylene	0.19	241.11	887.66	Acetylene	3.62	1326.39	390.19
Styrene	0.08	99.30	313.55				
i-Propylbenzene	0.01	17.47	93.46				
n-Propylbenzene	0.02	27.69	110.55				
3-Ethyl toluene	0.05	75.91	140.27				
4-Ethyl toluene	0.03	40.44	176.27				
1,3,5-Trimethylbenzene	0.02	33.82	8.45				
2-Ethyl toluene	0.02	33.91	140.27				
1,2,4-Trimethylbenzene	0.07	95.59	520.92				
1,2,3-trimethylbenzene	0.02	35.52	185.99				
1,3-Diethyl benzene	0.00	8.07	40.78				
1,4-Diethyl benzene	0.02	25.15	69.66				

Table S6. Source contributions derived by PMF analysis.

Source	January	April	July	October
Fuel combustion	54.94%	11.92%	3.69%	5.88%
Transportation	19.46%	22.47%	50.37%	32.52%
Industrial processes	14.24%	20.69%	5.92%	15.89%
Solvent utilization	2.86%	6.56%	12.40%	22.78%
Aged air mass	7.30%	33.42%	10.09%	17.55%
Biogenic	1.19%	4.94%	17.54%	5.39%

Table S7. Comparison of the relative contributions of sources of VOC emissions in Beijing calculated by the PMF model in this study and results from the other studies.

Reference	Sampling period			Site type	Source categories					
	Year	Period	Season		Vehicle	Industrial	Solvent	Fuel	Biogenic	Others [a]
This study	2015	April	Spring	Urban	22%	21%	7%	12%	5%	33%
This study	2015	July	Summer	Urban	50%	6%	12%	4%	18%	10%
Song et al.,2007	2005	1–26 August	Summer	Urban	55%	20%	5%	5%	2%	11%
Li et al.,2016	2015	11–19 August	Summer	Urban	57%	4%	14%	10%	1%	14%
Yuan et al., 2009	2006	15 August to 10 September	Summer to Autumn	Urban	62%		16%	6%	3%	13%
Yuan et al., 2009	2006	15 August to 10 September	Summer to Autumn	Rural	39%		14%	3%	8%	37%
This study	2015	October	Autumn	Urban	33%	16%	23%	6%	5%	18%
Wu et al., 2016	2014	1–15 October	Autumn	Urban	49%	11%	9%	22%		9%
Li et al.,2015	2014	18–31 October	Autumn	Urban	43%	22%	12%	9%		14%
Yang et al.,2018	2014	25 October–2 November	Autumn	suburban	42%	14%	22%	22%		0%
This study	2015	January	Winter	Urban	19%	14%	3%	55%	1%	7%
Li et al.,2015	2014	13–22 November	Winter	Urban	20%	14%	11%	45%		10%
Yang et al.,2018	2014	13 November–13 December	Winter	suburban	17%	25%	13%	45%		0%

[a] The source categories of different PMF studies are different. Except for some comment categories (vehicle, industrial processes, solvent utilization, fuel combustion, and biogenic), there are some other categories such as aged air mass, long-lived species, biomass burning, background, secondary formation, LPG, NG, which were defined as others in Table S7.

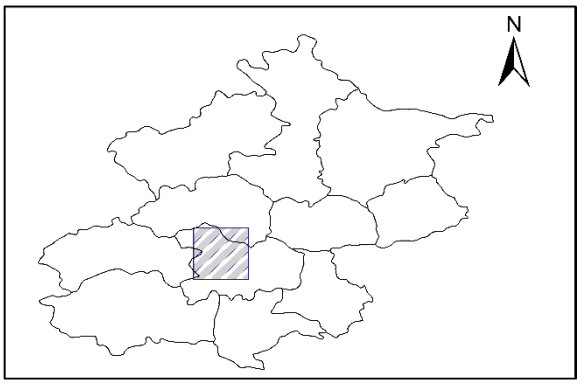

Figure S1. The emission grid PKU site loacted in (Black square).

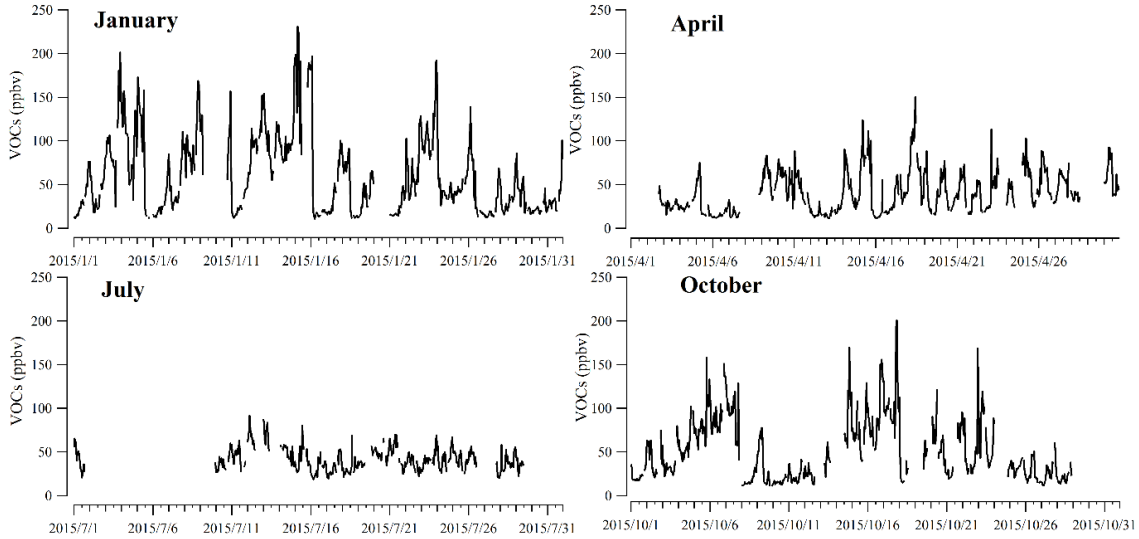

Figure S2. Time series of mixing ratios of VOCs in January, April, July, and October 2015.

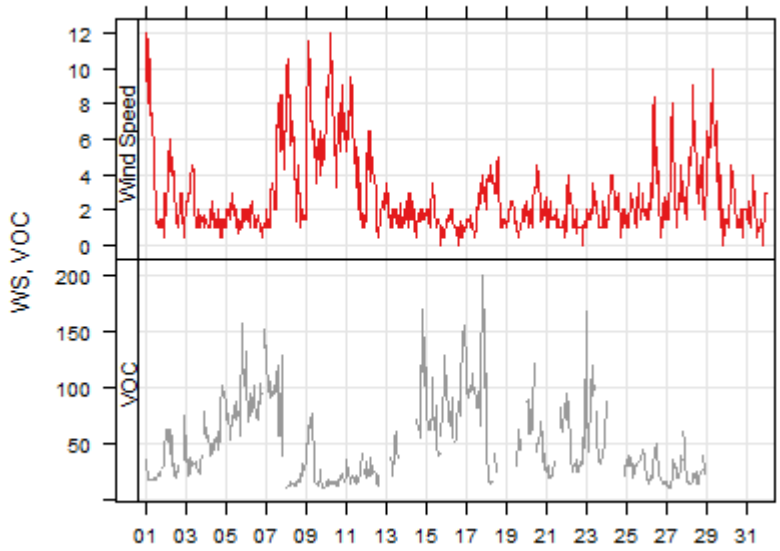

Figure S3. Time series of wind speed and VOC mixing ratios in October 2015.

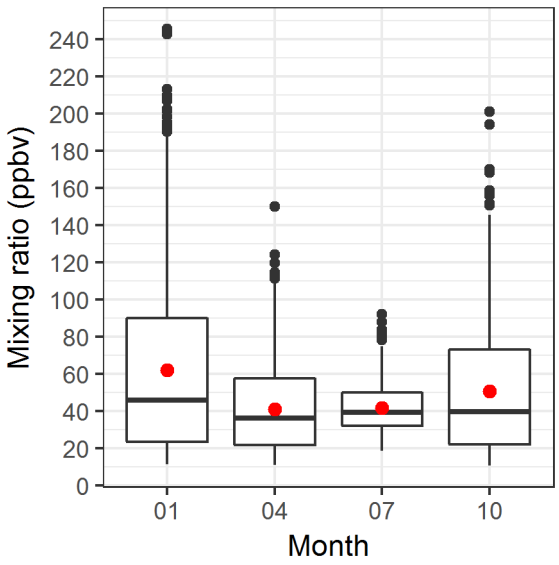

Figure S4. Box-plot of VOC mixing ratios in in January, April, July, and October 2015.

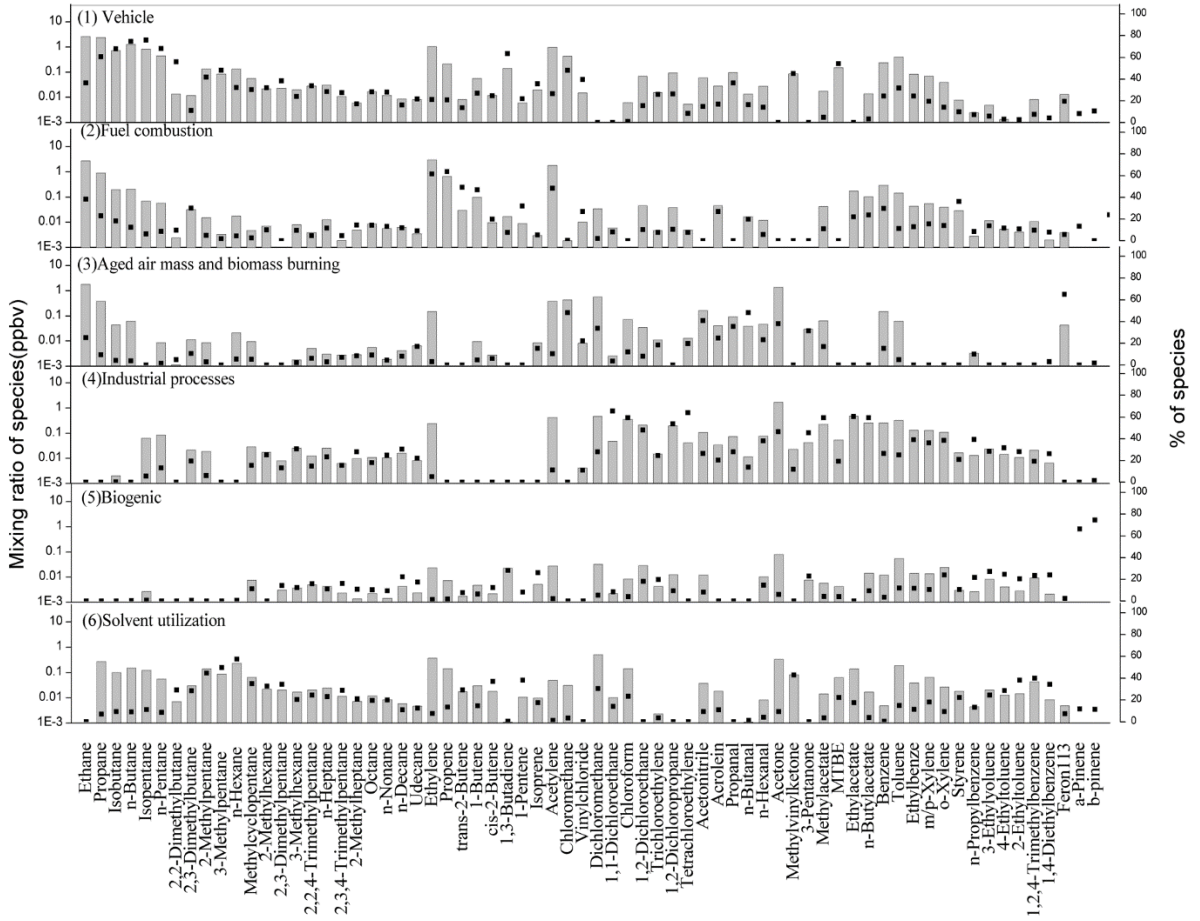

Figure S5. Source profiles for VOCs in the PKU site calculated by PMF (bars: mixing ratio of species; dots: % of species).

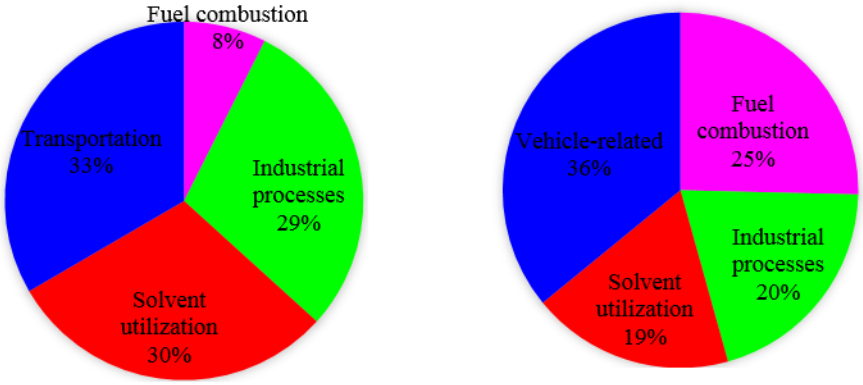

Figure S6. Comparison of anthropogenic VOC source structure in the emission inventory (left) and the PMF results (right).

Text S1. VOC time series

Figure S2 presents the time series of VOC mixing ratios. The mixing ratios of VOCs in January were variable, with maximum value of 245.54 ppbv. There were lots of periods with high VOC mixing ratios in January. In April, the average VOC mixing ratio was not as high as in January but the mixing ratios of VOCs change a lot, a maximum value of 150.24 ppbv. The mixing ratios of VOCs in July were stable, with the highest level of 92.28 ppbv. The highest VOC mixing ratio in October was 201.10 ppbv. In early October, the VOCs accumulated when the wind speed was low (Fig. S3). Then VOCs decreased sharply when the wind speed became higher. And the VOC began to accumulate again with change of the wind speed. This shows that local meteorology could affect the mixing ratios of VOCs.

Text S2. Source identification

The first factor was identified as vehicle-related source. This factor explained 54% of MTBE, which is a widely used gasoline additive, used as an oxygenate to raise the octane number. This source was also dominated by a strong presence of C3-C5 alkane and alkene (propane, 61%; isobutane, 68%; n-butane, 75; isopentane, 76%; n-pentane, 68%; 1,3-butadiene, 64%) which can release from vehicle exhaust and fuel evaporation. Tunnel studies shown the toluene/benzene ratio for vehicular exhaust was about 1.6 (Kuster et al., 2004), and the mean toluene/benzene ratio of this source profile was 1.70. Acetylene, the combustion tracer, was explained 27% by this factor.

Factor two was the only factor with a distinct maximum in winter (January) as shown in figure 7. This factor contained rather short-lived alkenes such as ethylene (contained 62% of ethylene), propene (64%), trans-2-butene (49%), 1-butene (46%), typical for incomplete combustion processes (Leuchner et al., 2015). Large parts of the acetylene (49%) were also explained in this factor, which was major species emitted from combustion process (Liu et al., 2008). This factor could be attributed to residential heating and other combustion processes, and was identified as fuel combustion source.

The third source profile contains 65% of the total Freon113, which has a long lifespan in the atmosphere. This factor was characterized by high values of unreactive species, such as ethane, acetone, and benzene. Thus, this source was concluded as VOCs in aged air masses. The ratio between benzene and toluene is a useful indicator of the age of air masses. The mean

benzene/toluene ratio of this source profile is 2.3, which is much higher than the typical values from vehicle exhaust (0.5) and solvent utilization (0.3). In aged air masses, the benzene/toluene ratios are higher than in fresh air (Wu and Xie, 2017). Moreover, the third factor contains large amount of acetonitrile (41%) and chloromethane (48%), which were regarded as the fingerprint of biomass burning. Therefore, this source was considered to represent aged air mass and biomass burning originating from air mass transport.

The fourth source was distinguished by significant amounts of chlorinated organic compounds, including 1,1-dichloroethane (65%), tetrachloroethylene (64%), chloroform (59%), 1,2-dichloropropane (54%), 1,2-dichloropropane (54%), which are tracers of industrial processes (Scheff and Wadden, 1993). This source was also characterized by significant percentage of esters (ethylacetate, 60%; n-butylacetate, 60%; methylacetate, 59%). Thus, the fourth source was identified as industrial processes source.

Factor five explained 66% and 75% of the measured α-pinene and β-pinene, respectively, which were indicators of biogenic emissions. Figure 7 reveals that the contribution of the fifth factor were presented higher levels in summer (July), and lower levels in winter (January). Biogenic emissions are strongly influenced by temperature and solar radiation (Guenther et al., 2012). Therefore, this factor was identified as biogenic emissions.

The sixth factor shown in fig.6 was rich in aromatic species and C5-C8 substituted/cyclo-alkanes, which are markers for solvent utilization sources, including painting, printing, surface coating, and solvent emissions of household and consumer products (Liao et al., 2015). We therefore concluded it is from solvent utilization source.

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