Supplementary Information

Scattered coal is the largest source of ambient volatile organic compounds during the heating season in Beijing

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Text S1. Description of analyses and calibrations.

Ambient VOCs were sampled and plumed into an electronic refrigeration and pre-concentration system. To prevent particulate matter from entering the system, a Teflon filter was placed inside the sample inlet. A soda asbestos tube and water removal trap were used to remove CO2 and moisture. Prior to VOC analyses, the air sample and internal calibrating gas were dried, frozen, and captured by two-way adsorption columns at -160°C. For resolving and analyses, adsorption columns were heated instantaneously to 100°C and captured compounds were transferred to a gas chromatograph. Programmed temperature increases were used to separate each VOC species. Ambient C2–C12 VOC species were analyzed by dual detectors. C2–C5 hydrocarbons were separated on a PLOT-Al2O3 column (15 m × 0.32 mm ID × 3 μm, J&W Scientific, USA) and measured with a flame ionization detector (FID) channel, while other compounds were separated on a semi-polar column (DB-624,60 m × 0.25 mm ID × 1.4 μm, J&W Scientific, USA) and quantified using a quadrupole mass spectrograph detector. Heating and back flushing of the adsorption columns was necessary to remove residual compounds after detection. Calibration curves were performed at six concentrations from 0.2 to 8 ppbv for each compound before and after sample analyses by bubbling a series of external calibrating gases. Two types of gas were used: a Photochemical Assessment Monitoring Stations (PAMS) ozone precursor series (mixture of 57 NMHCs), and a gas series customized by the PKU National Key Laboratory (a mixture of 55 oxygenated VOCs and halocarbons). In addition, internal calibrating gas (4 ppbv) was pumped into the system to reduce instrumental error. All three calibrating gases were obtained from Linde Electronics and Specialty Gases, USA. R2 values of calibration curves for all species were >0.99. Variation in target species responses was within 10% of the calibration curve in daily calibrations.

Text S2. Identification of eight VOC sources.

The first factor was rich in ethylene, acetylene and propylene as the products of incomplete combustion of fossil fuel, such as coal (Liu et al., 2008;Borbon et al., 2003), and contributed more than 30% of ambient short-chain olefins and acetylene. The source profiles of resident coal combustion measured in China contained significant alkenes (Wang et al., 2013). As associated with coal burning stoves, benzene and toluene are adequate in profile of factor 1 (Chattopadhyay et al., 1997). Moreover, aromatics and aliphatic hydrocarbons (heptane and octane) are the most abundant compounds in solid coal (Fernandez-Martinez et al., 2000), and contributing a large part of ambient components. Therefore, the first factor was defined as coal burning. Ascending trend in morning reflects the beginning of daily livelihood like cooking.

The second factor was characterized by a significant amount of ethane, propane and iso-/n-butane, which are mainly emitted from the usage of LPG, LNG and fuel oil in China (Blake and Rowland, 1995;Ling et al., 2011;Liu et al., 2016;Lu et al., 2006). Therefore, this source likely represented emissions from residential fuel oil and gas consumption, and was identified as fuel oil and gas usage.

The ambient contribution of third factor has significant vehicle exhaust emission characteristics, and this factor excludes the part of unburned gasoline vaporization from motor vehicles (reckoned in factor 4). Factor 3 markedly contributed more than 40% of total measured ambient MTBE content. As mentioned above, MTBE is regarded as the fingerprint of gasoline vehicle tailpipe exhaust (Song et al., 2007;McCarthy et al., 2013). High contribution of various benzene derivatives, OVOCs, and heavy alkanes reveal factor 3 mainly come from gasoline and diesel vehicle exhaust (Liu et al., 2008). The diurnal variation of this source is characterized by a double wave profile with an initial increase at 07:00–11:00 and a second increase at the end of the afternoon between 16:00 and 20:00. These increases correspond to morning and evening rush-hour traffic periods.

The fourth factor is identified as a mixture of petroleum-related evaporation, including the emissions from usage, storage and transportation of petroleum production, gasoline, diesel, etc. High factor loadings of C4-C6 alkanes, such as cyclopentane, 3-methylpentane, 2-methypentane, etc. were found (Liu et al., 2005;Liu et al., 2016;Srivastava et al., 2005;Gaimoz et al., 2011;Chang et al., 2006;Lu et al., 2006), with more than 30% of their variabilities explained by this factor. Factor 4 also includes a significant proportion of MACR (70%) and MVK (50%), the oxidation products of isoprene, in

agreement with the finding of isoprene associated with traffic activities (Borbon et al., 2001;Hellen et al., 2006). Oxygenated compounds of factor 4 were observed during the highway tunnel experiment (Baudic et al., 2016). 40% of the total measured MTBE exists in factor 4 as gasoline additive. The diurnal variation of this second factor contribution is characterized by a nighttime maximum and daytime decrease. This factor therefore represents the emissions of less reactive species, for which concentrations cannot be expected to be consumed photochemically in short transport times.

VOC-related industry represents the fifth factor. It was characterized by relatively large ambient contribution of 1-butene, trans-/cis-2-butene, 1,3-Butadiene, 1,4-Dichlorobenzene, some aromatics and OVOCs, which are tracers of industries (Ras-Mallorqui et al., 2007;Scheff and Wadden, 1993;Jiun-Horng et al., 2008). Aromatics and halocarbons are used as industrial solvents or adhesives found in car printing, furniture manufacturing and architectural coating (Cai et al., 2010); alkenes have higher ambient level in the coating industry developed areas (Chiang et al., 2007). The increasing concentration of this factor in the morning can be explained by the daily schedule of industrial manufacture.

The profile of sixth factor consists mostly of alkenes, aromatics, and halocarbons. Many proofs manifest factor 6 to be solvent utilization: many aromatic species are the major components of organic paints (Watson et al., 2001;Seila et al., 2001;Yuan et al., 2010). There were significant tracers present in the sixth factor, accounting for 20% of toluene, 20% of ethylbenzene, 35% of xylene, 50% of the acrolein, 35% of chloroethane, 40% of dichloroethane and 35% of 1,2-dichloropropane measured in this campaign, respectively. This factor contributions decreased from 09:00 and reached their minimum in 14:00 (the strongest light of the whole day). Due to the rich of high photochemical activity species (alkenes, aromatics and OVOCs), the drastic decline of this factor is mainly influenced by greater photochemical reactions under stronger midday illumination.

The seventh factor is distinguished by a significant presence of acetonitrile, an indicator of biomass burning emissions (Wang et al., 2014). About 65% of the total acetonitrile mixing ratios is apportioned to this factor. Very small quantities of other compounds add to the total factor mass. This factor was identified as biomass burning.

The profile for the last factor was characterized by abundant long lifetime species, including 60% of Freon113, 100% of Freon114 and 80% of Freon11. These chemicals have a long lifespan in the atmosphere and depend on background levels (McCarthy et al., 2007). Besides, the profile of this factor also consists of: a portion of carbonyls, the secondary formation products probably transferred from

surroundings (Mo et al., 2016). Thus, the factor 8 was identified as transmitted/long-lived species. this factor has inconspicuous diurnal variation and reaches maximum value at noon, which is the characteristic of secondary products from photochemical reaction (Li et al., 2016). These secondary products are mostly transmitted from surrounding area. Long-lived species also scarcely change with time.

Text S3. Explanation of scattered coal application.

Detailed explanation of different SC application sectors is shown below.

SC for residential sector: household heating and cooking in urban and rural areas; SC for rural production sector: heating for greenhouses, breeding, flue-cured tobacco and tea making in rural areas; SC for commercial and public sector: heating, cooking and steaming supplies for restaurants, hotels, baths, institutions, schools, hospitals, etc.; SC for industrial sector: small-scale boilers and furnaces of industrial field.

Temperature is a direct indicator of heating demand and is found to affect residential fuel consumption. Fuel choice is also impacted by various socioeconomic factors including household income, energy prices, fuel access, electrification, and level of education (Peng et al., 2019).

Figure S1. The location of Beijing in China (red area) and the sampling site at Peking University, Beijing (red point).

1.Coal burning
2.Fuel oil and gas usage
3.Traffic exhanst
4.Petroleum-related evaporation
source profile (ppbv/ppbv)
contribution (%)
1
0.1
0.01
100
50
0
Ethane
Propane
Isobutane
n-Butane
Isopentane
n-Pentane
2-Methylpentane
3-Methylpentane
Cyclopentane
n-Hexane
Methylcyclopentane
2-Methylhexane
3-Methylhexane
Cyclohexane
n-Heptane
Methylcyclohexane
n-Octane
Ethylene
Propene
1-Butene
trans-2-Butene
cis-2-Butene
Isoprene
1,3-Butadiene
Acetylene
Benzene
Toluene
Ethylbenzene
m/p-Xylene
o-Xylene
Styrene
3-ethyltoluene
4-ethyltoluene
acrolein
Propanal
Methacrolein
Acetone
Methylvinylketone
Methylethylketone
MTBE
Freon11(CFCl3)
Freon114(C2F4Cl2)
Freon113(C2F3Cl3)
Chloromethane
Chloroethane
1,1-Dichloroethane
1,2-Dichloroethane
1,2-Dichloropropane
Tetrachloroethylene
Chloroform
Chlorobenzene
1,4-Dichlorobenzene
Acetonitrile

Figure S2. Modelled source profiles (ppbv ppbv−1) together with the relative contributions of individual sources to each parsed species derived from PMF result.

Figure S3. Diurnal variations in mixing ratios of eight sources in Beijing during the non-control and control periods.

Figure S4. Full-time variations in mixing ratios of eight sources in Beijing during the non-control and control periods.

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					
	Period	Season		Vehicle	Industrial	Solvent	Fuel	Biogenic	Others [a]
Li et al. (2019)	Apr, 2015	Spring	Urban	22%	21%	7%	12%	5%	33%
Li et al. (2019)	Jul, 2015	Summer	Urban	50%	6%	12%	4%	18%	10%
Song et al. (2007)	1–26 Aug, 2005	Summer	Urban	55%	20%	5%	5%	2%	11%
Li et al. (2016)	11–19 Aug, 2015	Summer	Urban	57%	4%	14%	10%	1%	14%
Yuan et al. (2009)	15 Aug to 10 Sep, 2006	Summer to Autumn	Urban	62%		16%	6%	3%	13%
Yuan et al. (2009)	15 Aug to 10 Sep, 2006	Summer to Autumn	Rural	39%		14%	3%	8%	37%
Li et al. (2019)	Oct, 2015	Autumn	Urban	33%	16%	23%	6%	5%	18%
Wu et al. (2016)	1–15 Oct, 2014	Autumn	Urban	49%	11%	9%	22%		9%
Li et al. (2015)	18–31 Oct, 2014	Autumn	Urban	43%	22%	12%	9%		14%
Yang et al. (2018)	25 Oct–2 Nov, 2014	Autumn	suburban	42%	14%	22%	22%		0%
Li et al. (2019)	Jan, 2015	Winter	Urban	19%	14%	3%	55%	1%	7%
Li et al. (2015)	13–22 Nov, 2014	Winter	Urban	20%	14%	11%	45%		10%
Yang et al. (2018)	13 Nov–13 Dec, 2014	Winter	suburban	17%	25%	13%	45%		0%
This study	Dec, 2016–Jan, 2017	Winter	Urban	33% [b]	14% [b]	4%	37%		12%
This study	Dec, 2017	Winter	Urban	28% [b]	11% [b]	15%	19%		27%
This study	Jan, 2018	Winter	Urban	32% [b]	13% [b]	5%	21%		29%

[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.

[b] the source categories of the PMF results of this study is different from other studies, “vehicle” includes traffic exhaust, traffic evaporation and petrochemical evaporation; industrial does not include petrochemical evaporation.

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