Supplement of

Origin and Transformation of Ambient VOCs during a Dust-to-Haze Episode in Northwest China

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S1 Sampling procedures

Volatile organic compound (VOC) samples were collected using ¼" o.d. stainless steel multi-bed adsorbent tubes filled with Tenax-TA, Carbograph I TD and Carboxen 1003 (C3-DXXX-5266, ~380 mg in adsorbent weight per tube, Markes International Ltd., Llantrisant, U.K.). A low-flow module pump (ACTI-VOC, Markes International Ltd.) was used for these collections, and it operated at a flow rate of 50 mL min^{-1}. Ambient VOC samples were collected every hour for 60 min (i.e., total sampling volume = 3 L). Insignificant breakthrough (<5%) was observed in the field and in laboratory tests for these flow and volume conditions (Ho et al., 2017). The sampling inlet was 1.5 m above ground level. Prior to the sampling, all sorbent tubes were cleaned in a thermal conditioner (TC20, Markes International Ltd.) at 330℃ for 20 min. All pre-conditioned and sampled tubes were sealed with Difflok caps (Markes International Ltd.) and stored in desiccators at 0℃ for a maximum of two weeks. The desiccators were filled with silica gel and activated carbon to avoid passive adsorption of water vapor and VOCs. The pump was calibrated with a mass flow calibrator (Defender 510, Bios, Torrance, CA, USA) before each sampling event. A Teflon™ filter assembly (47mm, Whatman, Clifton, NJ, USA) and a custom-made ozone scrubber, made of a 1 m long and ¼" o.d. copper tube coated on the inside with saturated potassium iodide, was installed upstream of the sample tube to remove any influences from particulate matter (PM) and O_3, respectively. The O_3 removal efficiency was > 99% at a concentration of 100 ppbv for 60 min as determined in a laboratory test. One field blank was collected on each sampling day. The sorbent samples were promptly transported to the laboratory for chemical analysis.

Real-time concentrations of trace gases were monitored continuously during the study. NO_2/NOx was measured with a chemiluminescence detector (Model 42i, Thermo Electron, Waltham, MA, USA), The time resolution for these instruments was 5 min, and the minimum detection limits (MDL) for NO_2/NOx 0.5 ppbv.

S2 Chemical Analysis

A total of 72 valid adsorbent tube samples were collected. The samples were analyzed using a thermal desorption (TD) unit (Series 2 UNITY-xr system, Markes International Ltd.) coupled to a gas chromatograph/mass spectrometric detector (GC/MSD, Models 7890A/5977B, Agilent, Santa Clara, CA, USA) within one week of collection. A description of the chemical analysis procedures may be found in a previous paper[52]. Briefly, a sample tube was connected to the TD unit at room temperature (~25℃) and purged with ultra-high purity (UHP) helium (He) gas at a flow rate of 40 mL min^{-1} for 60 s to eliminate air and prevent oxygen intrusion. For the first desorption step, the analytes were desorbed at 330℃ for 5 min and refocused onto a cryogenic-trap (U-T1703P-2S, Markes International Ltd.) at -15℃ to capture high-volatility target compounds. For the second desorption step, the trap was dry-purged for 6 s and

56   rapidly heated from −15℃ to 320℃ and maintained at that temperature for 5 min. The analytes were passed

57   through a heated transfer line at 160∘C and re-refocused onto a cold GC capillary column head (Rtx®-1,

58   105 m × 0.25 mm with 1 μm film thickness, Restek Corporation, Bellefonte, PA, USA) at −45℃ with an

59   aid of liquid nitrogen (N_2) in the GC oven. Once the second desorption step was completed, the oven

60   temperature program started at an initial temperature of −45℃ for 4 min, ramped to 230℃ at a rate of 6℃

61   min^{-1}, and maintained at 230℃ for 5 min. The He carrier gas was delivered at constant flow rate of 1.0 mL

62   min^{-1} throughout the GC analysis. The MSD was operated in selective ion monitoring mode at 230℃ and

63   70 eV for electron ionization.

64   Identification was achieved by comparing the mass spectra and retention times of the chromatographic

65   peaks with those authentic standards. Certified PAMS (57 non-methane hydrocarbon) standard mixtures

66   (Restek Corp.) were used in calibrations. A multi-point calibration curve with linearity > 0.999 was

67   established to quantify each of the target compounds. The minimum detection limits (MDLs) were in the

68   range of 0.003–0.808 ppbv for a sampling volume of 3 L. The measurement precisions determined from the

69   analyses of eight replicates of standard samples at 2 ppbv were ≤ 5%(Ho et al., 2017;Ho et al., 2018;Li et

70   al., 2017).

71   **S3 Source characterization**

72   **Source assessment by Positive Matrix Factorization (PMF)**

73   PMF was used to identify the major pollution sources: the data input to the model were the mixing ratios

74   and uncertainties in the VOCs mixing ratios for all valid samples collected during the study. Calibrations

75   were run for 3-7 factors with random seeds. The five factor solution produced object function Q values

76   (both robust and true) close to the theoretical Q value (Figure S2), and because these factors are reasonably

77   explained, we chose these results for the following discussion.

78   Factor 1 had high loadings of ethylene, ethane, toluene, ethylbenzene, chloromethane. The first two of

79   these compounds contributed more than 30% of the total measured loadings of VOCs. Liu et al. (2008)

80   found that ethylene and ethane are among the most important markers in biomass burning emissions

81   (Abeleira and Farmer, 2017). Together with high contributions of benzene, toluene, ethylbenzene, xylene

82   (BTEX), and 1,3-butadiene, factor 1 can be ascribed to biomass burning emissions. Factor 2 had high

83   loadings of iso-pentane, n-butane, n-pentane, 2-methylpentane, 3-methypentane, toluene, xylene,

84   ethylbenzene, chloromethane and 1,3-butadiene (in descending order). In addition, the contributions of

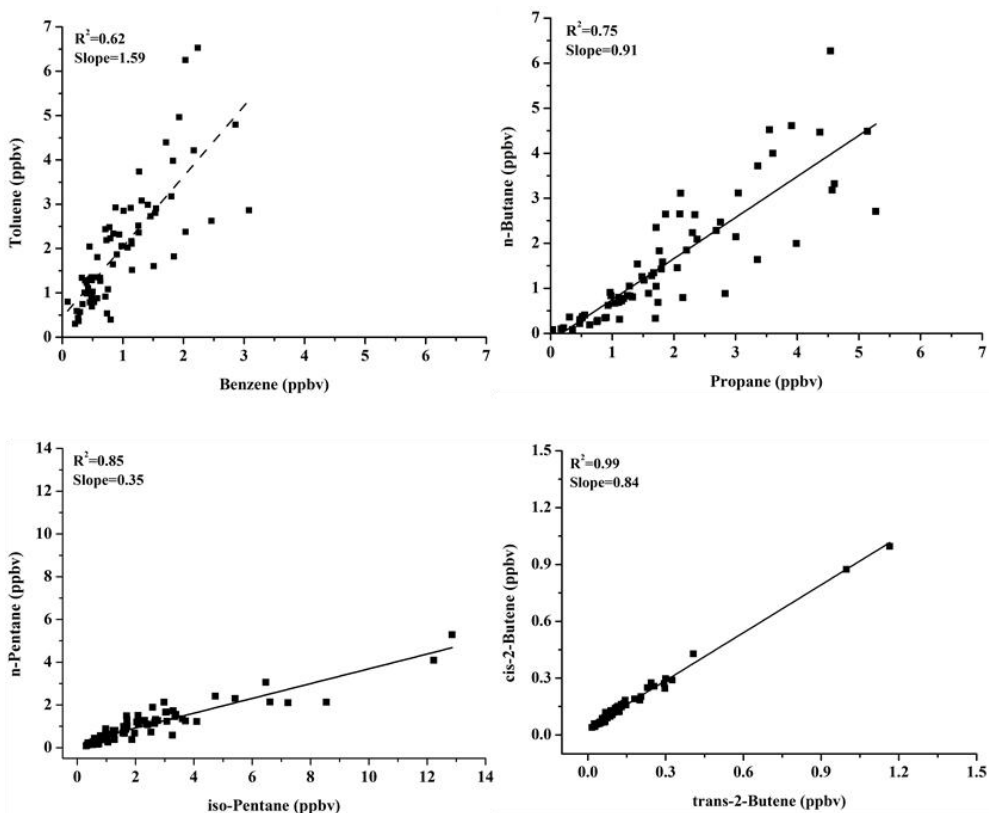
85   propylene, 1-butene, trans/cis-butene were relatively high compared with those in other factors. C_4-C_5

86   alkanes often originate from the incomplete combustion of gasoline while propylene, 1-butene and

87   trans/cis-butene are key markers of gasoline combustion. As a result, the source type for factor 2 is

88   identified as emissions from gasoline and exhaust from gasoline powered vehicles (Huang et al., 2015;Li et

89   al., 2017;Liu et al., 2008). Factor 3 is in highly loaded with ethylene, propylene, ethane, 2-methylpentane,

90 n-hexane, C_{10}-C_{12} alkanes, benzene, toluene, chloromethane (descending order). Propylene is a typical
91 marker of engine combustion emission, and heavy alkanes and BTEX are connected with diesel exhaust.
92 The levels of 1,3-butadiene, 1-butene, cis/trans-2-butene were lower in compared with gasoline exhaust
93 (factor 2). Thus, we conclude that the source type for factor 3 is diesel exhaust (Liu et al., 2008). Factor 4
94 had high loadings of propane, n-butane, iso-pentane, n-pentane, benzene and toluene. Propane is a major
95 component in liquefied petroleum gas (LPG), and the C_2-C_5 n-alkanes, benzene and toluene are often
96 detected in incomplete combustion products of natural gas (Hesterberg et al., 2008;Turrio-Baldassarri et al.,
97 2006). Considering that a large numbers of vehicles (i.e., public buses and taxis) are fueled by concentrated
98 natural gas (CNG) in Xi'an, factor 4 is identified as emissions from combustions of LPG and CNG. Factor
99 5 had high loadings of ethylene, ethane, n-heptane and BTEX, which is similar to a profile of coal
100 combustion[10], and this factor is thus concluded to be a product of coal combustion.

102 **Figure S1: Correlations between selected volatile organic compounds. All correlations are significant at p < 0.05.**

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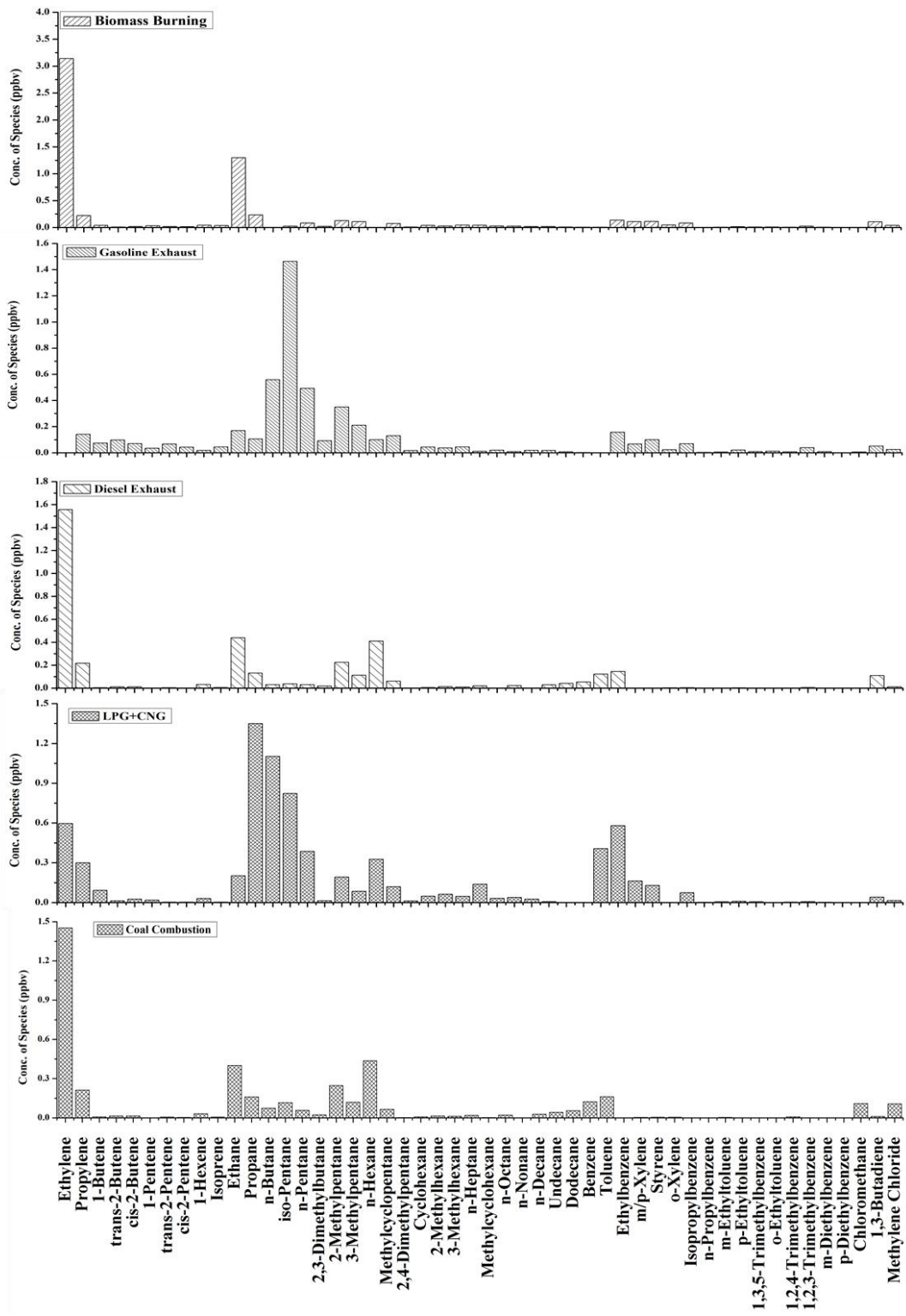
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105   **Figure S2: Source profiles of volatile organic compounds calculated with the positive matrix factorization model.**

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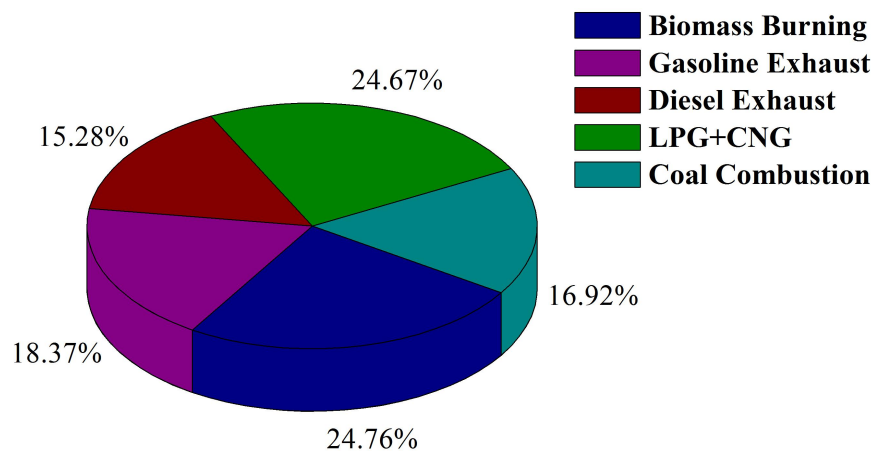
Figure S3: Source apportionment of volatile organic compounds in ambient air from Xi'an in winter (LPG, Liquefied Petroleum Gas; CNG, Concentrated Natural Gas).

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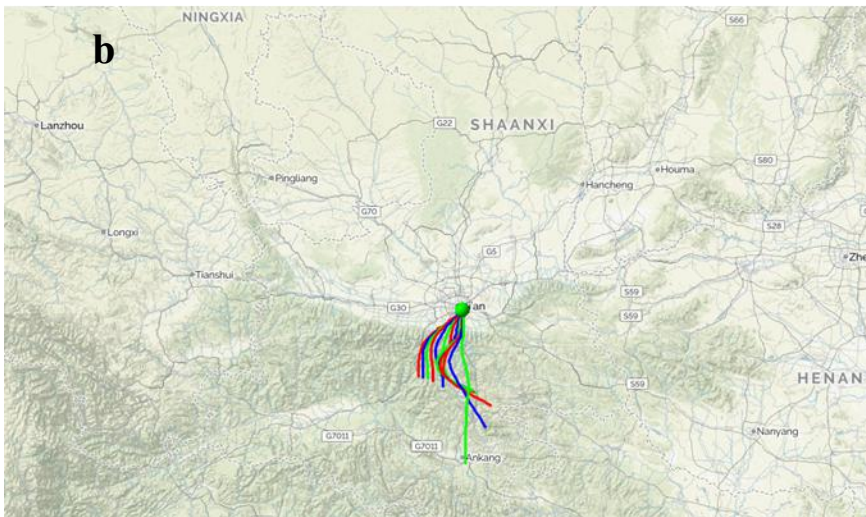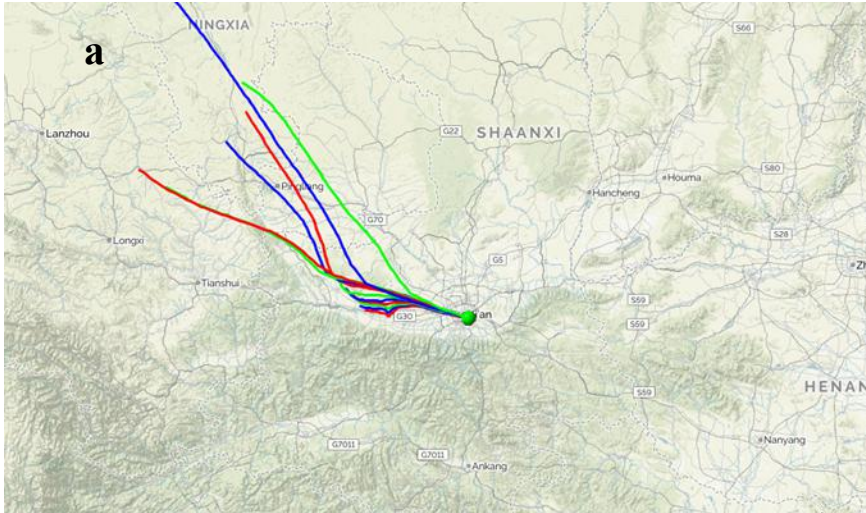
Figure S4: Map of the sampling site (39.90°N, 116.40°E) and 24-h air mass back-trajectories determined by the
National Oceanic and Atmospheric Administration Hybrid Single Particle Lagrangian Integrated Trajectory
(HYSPLIT) model. The trajectories represent the synoptic flow patterns during the observation period, and they
are used to illustrate the air masses that influenced the measurements at Xi'an. The upper figure (a) represents
back-trajectories for the dust event while the lower figure (b) represents back-trajectories in fine-particle
pollution period.

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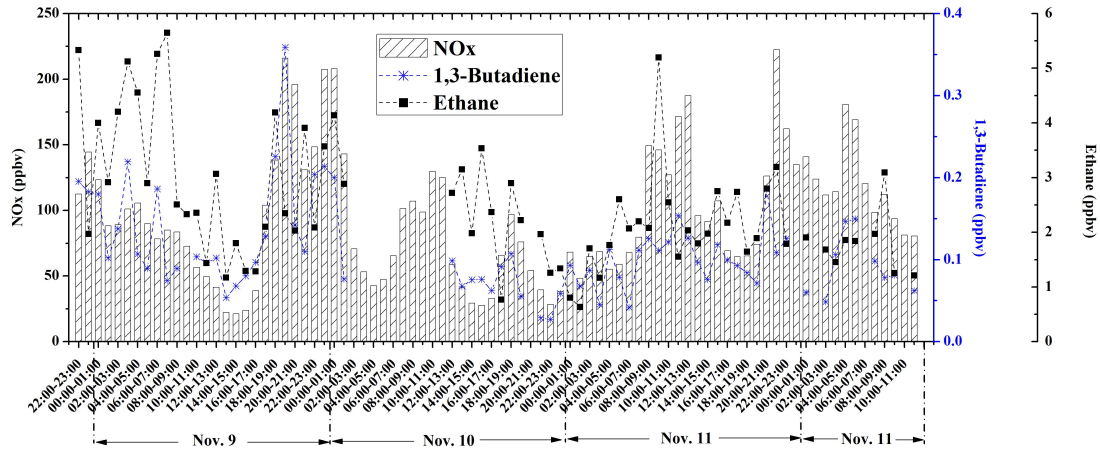
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122 **Figure S5: Temporal variations in 1,3-butadiene and ethane from November 9 to 13.**

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Table S1. Levels and minimum detection limits (MDLs) of volatile organic compounds.

Alkanes	MDL	Mean	SD[1]	Alkenes & Aromatics	MDL	Mean	SD
Ethane	0.033	2.478	1.164	Ethylene	0.039	7.012	2.838
Propane	0.019	1.904	1.302	Propylene	0.042	1.081	0.562
Isobutane	0.024	1.468	1.392	1-Butene	0.008	0.251	0.177
n-Butane	0.017	1.726	1.730	trans-2-Butene	0.010	0.137	0.186
iso-Pentane	0.002	2.427	2.420	cis-2-Butene	0.006	0.143	0.156
n-Pentane	0.019	1.068	0.906	1-Pentene	0.013	0.133	0.087
2,2-Dimethylbutane	0.004	0.036	0.040	trans-2-Pentene	0.012	0.103	0.144
2,3-Dimethylbutane	0.004	0.155	0.156	cis-2-Pentene	0.006	0.068	0.087
2-Methylpentane	0.024	1.047	0.636	1-Hexene	0.003	0.186	0.082
3-Methylpentane	0.006	0.561	0.353	Isoprene	0.005	0.106	0.105
n-Hexane	0.018	1.320	0.800	1,3-Butadiene	0.029	0.110	0.056
Methylcyclopentane	0.008	0.399	0.233	Benzene	0.015	0.981	0.664
2,4-Dimethylpentane	0.004	0.055	0.052	Toluene	0.026	2.008	1.334
Cyclohexane	0.005	0.152	0.113	Ethylbenzene	0.004	0.704	0.436

continued

2-Methylhexane	0.007	0.249	0.172	m-Xylene	0.008	0.698	0.446
2,3-Dimethylpentane	0.007	0.055	0.053	Styrene	0.006	0.248	0.208
3-Methylhexane	0.006	0.227	0.150	o-Xylene	0.003	0.435	0.265
2,2,4-Trimethylpentane	0.010	0.067	0.060	Isopropylbenzene	0.004	0.014	0.008
n-Heptane	0.007	0.402	0.304	n-Propylbenzene	0.003	0.032	0.018
Methylcyclohexane	0.005	0.128	0.084	m-Ethyltoluene	0.002	0.082	0.049
2,3,4-Trimethylpentane	0.007	0.037	0.050	p-Ethyltoluene	0.003	0.041	0.024
2-Methylheptane	0.005	0.061	0.057	1,3,5-Trimethylbenzene	0.001	0.036	0.028
3-Methylheptane	0.006	0.043	0.052	o-Ethyltoluene	0.003	0.032	0.022
n-Octane	0.005	0.140	0.099	1,2,4-Trimethylbenzene	0.002	0.126	0.079
n-Nonane	0.004	0.110	0.101	1,2,3-Trimethylbenzene	0.002	0.029	0.021
n-Decane	0.003	0.100	0.059	m-Diethylbenzene	0.002	0.008	0.014
Undecane	0.004	0.080	0.053	p-Diethylbenzene	0.002	0.022	0.018
Dodecane	0.004	0.087	0.085				

[1]SD standard deviation

Table S2: Mixing ratios (ppbv) and composition (%) of volatile organic compounds in Xi'an and other Chinese megacities in winter.

City	Statistic	Concentration (ppbv)				Composition (%)			Reference
		Total	Alkanes	Alkenes	Aromatics	Alkanes	Alkenes	Aromatics	
Xi'an	arithmetic mean	35.965	16.331	9.181	10.324	45.6	25.6	28.8	This study
	SD[1]	15.677	9.551	3.389	6.258	26.7	9.5	17.5	
Guangzhou	arithmetic mean	47.840	32.870	8.215	6.755	69.0	17.0	14.0	(Zou et al., 2015)
Beijing	arithmetic mean	51.040	32.100	9.390	9.550	63.0	18.0	19.0	(Li et al., 2015)

[1]SD standard deviation

Data Set S1. Dataset for observed ambient VOCs, NOx and PM$_{2.5}$ reported in the accessory file (.xlsx).

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