



Supplement of

Origin and transformation of ambient volatile organic compounds during a dust-to-haze episode in northwest China

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23 S1 Sampling procedures

24 Volatile organic compound (VOC) samples were collected using 1/4" o.d. stainless steel multi-bed adsorbent 25 tubes filled with Tenax-TA, Carbograph I TD and Carboxen 1003 (C3-DXXX-5266, ~380 mg in adsorbent 26 weight per tube, Markes International Ltd., Llantrisant, U.K.). A low-flow module pump (ACTI-VOC, 27 Markes International Ltd.) was used for these collections, and it operated at a flow rate of 50 mL min⁻¹. 28 Ambient VOC samples were collected every hour for 60 min (i.e., total sampling volume = 3 L). 29 Insignificant breakthrough (<5%) was observed in the field and in laboratory tests for these flow and 30 volume conditions (Ho et al., 2017). The sampling inlet was 1.5 m above ground level. Prior to the 31 sampling, all sorbent tubes were cleaned in a thermal conditioner (TC20, Markes International Ltd.) at 32 330°C for 20 min. All pre-conditioned and sampled tubes were sealed with Difflok caps (Markes 33 International Ltd.) and stored in desiccators at 0°C for a maximum of two weeks. The desiccators were 34 filled with silica gel and activated carbon to avoid passive adsorption of water vapor and VOCs. The pump 35 was calibrated with a mass flow calibrator (Defender 510, Bios, Torrance, CA, USA) before each sampling 36 event. A Teflon[™] filter assembly (47mm, Whatman, Clifton, NJ, USA) and a custom-made ozone scrubber, 37 made of a 1 m long and $\frac{1}{4}$ " o.d. copper tube coated on the inside with saturated potassium iodide, was 38 installed upstream of the sample tube to remove any influences from particulate matter (PM) and O_3 , 39 respectively. The O_3 removal efficiency was > 99% at a concentration of 100 ppbv for 60 min as 40 determined in a laboratory test. One field blank was collected on each sampling day. The sorbent samples 41 were promptly transported to the laboratory for chemical analysis.

42 Real-time concentrations of trace gases were monitored continuously during the study. NO₂/NOx was 43 measured with a chemiluminescence detector (Model 42i, Thermo Electron, Waltham, MA, USA), The 44 time resolution for these instruments was 5 min, and the minimum detection limits (MDL) for NO₂/NOx 45 0.5 ppbv.

46 S2 Chemical Analysis

47 A total of 72 valid adsorbent tube samples were collected. The samples were analyzed using a thermal 48 desorption (TD) unit (Series 2 UNITY-xr system, Markes International Ltd.) coupled to a gas 49 chromatograph/mass spectrometric detector (GC/MSD, Models 7890A/5977B, Agilent, Santa Clara, CA, 50 USA) within one week of collection. A description of the chemical analysis procedures may be found in a 51 previous paper⁵². Briefly, a sample tube was connected to the TD unit at room temperature ($\sim 25^{\circ}$ C) and 52 purged with ultra-high purity (UHP) helium (He) gas at a flow rate of 40 mL min⁻¹ for 60 s to eliminate air 53 and prevent oxygen intrusion. For the first desorption step, the analytes were desorbed at 330°C for 5 min 54 and refocused onto a cryogenic-trap (U-T1703P-2S, Markes International Ltd.) at -15°C to capture 55 high-volatility target compounds. For the second desorption step, the trap was dry-purged for 6 s and 56 rapidly heated from -15° C to 320° C 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 \times 0.25 mm with 1 µm film thickness, Restek Corporation, Bellefonte, PA, USA) at -45°C 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°C for 4 min, ramped to 230°C at a rate of 6°C 61 min⁻¹, and maintained at 230°C 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°C and 63 70 eV for electron ionization.

Identification was achieved by comparing the mass spectra and retention times of the chromatographic peaks with those authentic standards. Certified PAMS (57 non-methane hydrocarbon) standard mixtures (Restek Corp.) were used in calibrations. A multi-point calibration curve with linearity > 0.999 was established to quantify each of the target compounds. The minimum detection limits (MDLs) were in the range of 0.003–0.808 ppbv for a sampling volume of 3 L. The measurement precisions determined from the analyses of eight replicates of standard samples at 2 ppbv were \leq 5%(Ho et al., 2017;Ho et al., 2018;Li et al., 2017).

71 S3 Source characterization

72 Source assessment by Positive Matrix Factorization (PMF)

PMF was used to identify the major pollution sources: the data input to the model were the mixing ratios and uncertainties in the VOCs mixing ratios for all valid samples collected during the study. Calibrations were run for 3-7 factors with random seeds. The five factor solution produced object function Q values (both robust and true) close to the theoretical Q value (Figure S2), and because these factors are reasonably 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, C₁₀-C₁₂ 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 C2-C5 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 combustion¹⁰, 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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105 Figure S2: Source profiles of volatile organic compounds calculated with the positive matrix factorization model.

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111 Figure S3: Source apportionment of volatile organic compounds in ambient air from Xi'an in winter (LPG,

112 Liquefied Petroleum Gas; CNG, Concentrated Natural Gas).





114 Figure S4: Map of the sampling site (39.90°N, 116.40°E) and 24-h air mass back-trajectories determined by the

- 115 National Oceanic and Atmospheric Administration Hybrid Single Particle Lagrangian Integrated Trajectory
- 116 (HYSPLIT) model (Stein et al., 2015; Rolph et al., 2017). The trajectories represent the synoptic flow patterns
- 117 during the observation period, and they are used to illustrate the air masses that influenced the measurements at
- 118 Xi'an. The upper figure (a) represents back-trajectories for the dust event while the lower figure (b) represents
- 119 back-trajectories in fine-particle pollution period.

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

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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				

¹SD standard deviation

City	Statistic	Concentration (ppbv)				Compositi	on (%)	Deference	
		Total	Alkanes	Alkenes	Aromatics	Alkanes	Alkenes	Aromatics	Kelefence
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)

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

¹SD 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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