Supplementary Material for

Spatial variability of air pollutants in a megacity characterized by mobile measurements: Chemical homogeneity under haze conditions

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Table S1. The average concentrations of the 52 VOC species measured in this study compared with literature. These species are tentatively categorized into three groups including hydrocarbons (Group 1), aldehydes and ketones (Group 2), and acids and anhydrides (Group 3).

Formula		Assigned Name	*m/z*	K_{PTR}	Category /Group	Mean ± sd (non-haze)	Mean ± sd (haze)	Urban*	Suburb*
Calibrated species	$(CH_3OH)H^+$	Methanol	33.033	2.22	n/a	16.82 ±14.81	44.69 ±15.96	11.77-51.76	3.4-5.6
	$(C_2H_2O)H^+$	Ketenes	43.018	2.21	2	2.12 ±1.84	5.42 ±1.42		
	$(C_2H_4O)H^+$	Acetaldehyde	45.033	3.36	2	2.72 ±2.00	6.07 ±1.63	1.88-15.81	0.83-1.23
	$(C_2H_6O)H^+$	Ethanol	47.049	2.18	n/a	25.35 ±32.19	98.28 ±32.17		
	$(C_3H_4O)H^+$	Acrolein; MTBE	57.033	3.35	2	0.30 ±0.27	0.60 ±0.14		
	$(C_3H_6O)H^+$	Acetone + propanal	59.049	3	2	1.20 ±1.18	4.67 ±0.97	2.48-7.92	1.59-3.42
	$(C_5H_8)H^+$	Isoprene; fragmentation of 2- methyl-3-buten-2-ol (MBO); fragmentation of cyclohexanes	69.07	1.94	1	0.38 ±0.35	0.76 ±0.20		
	$(C_4H_6O)H^+$	Methyl vinyl ketone + methacrolein; crotonaldehyde; ISOPOOH	71.049	3.83	2	0.16 ±0.14	0.36 ±0.09	0.28-0.42	0.13-0.22
	$(C_4H_8O)H^+$	Methyl ethyl ketone + butanals	73.065	3.48	2	1.56 ±2.45	1.51 ±0.44	0.86-2.53	0.38-0.81
	$(C_6H_6)H^+$	Benzene	79.054	1.97	1	0. 78 ±0.59	2.90 ±0.73	1.2-4.3	0.91-1.9
	$(C_5H_{10}O)H^+$	Pentanone + pentanal; 2-methyl-3-buten-2-ol (MBO)	87.08	3.35	2	0.05 ±0.04	0.14 ±0.05		
	$(C_4H_8O_2)H^+$	Ethyl acetate; butyric acid	89.06	4.3	3	0.06 ±0.06	0.22 ±0.06		
	$(C_7H_8)H^+$	Toluene	93.07	2.12	1	1.00 ±0.94	3.09 ±0.89	1.51-6.11	0.73-3.31
	$(C_6H_{12}O)H^+$	Methyl isobutyl ketone; hexanal	101.096	2.28	2	0.04 ±0.04	0.09 ±0.06		
	$(C_8H_8)H^+$	Styrene	105.07	2.33	1	1.53 ±2.02	5.82 ±3.21	0.21-0.62	0.1-0.14

	$(C_8H_{10})H^+$	Xylenes; C_8 aromatics	107.086	2.29	1	0.84 ±1.03	2.59 ±1.14	1.1-7.35	0.71-1.17
	$(C_9H_{12})H^+$	Trimethylbenzenes; C_9 aromatics	121.1	2.47	1	0.27 ±0.24	0.59 ±0.25	0.31-1.35	0.21-1.02
	$(C_{10}H_{16})H^+$	Monoterpenes	137.132	2.44	1	0.07 ±0.09	0.18 ±0.10	0.06-0.39	0.04-0.27
Uncalibration species with known K_{PTR}	$(C_3H_4)H^+$	Fragmentation from isoprene or other hydrocarbons	41.039	1.58	1	1.02 ±0.47	5.31 ±2.04		
	$(C_3H_6)H^+$	Propene; fragmentation from hydrocarbons and propanols	43.054	1.58	1	0.15 ±0.05	0.71 ±0.21		
	$(CH_2O_2)H^+$	Formic acid	47.013	2.02	3	0.74 ±1.11	3.15 ±2.26	2.39-4.39	2.73-3.02
	$(C_4H_8)H^+$	Butenes; fragments from butanol or other hydrocarbons	57.06	1.76	1	0.70 ±1.02	2.55 ±1.03		
	$(C_2H_4O_2)H^+$	Acetic acid; glycolaldehyde; fragmentation of ethyl acetate	61.028	2.27	3	2.02 ±1.67	5.76 ±1.23	4.0-4.5	2.31-4.06
	$(C_2H_6S)H^+$	Dimethyl sulfide	63.023	2	n/a	0.04 ±0.03	0.20 ±0.11		
	$(C_4H_4O)H^+$	Furan	69.033	1.78	2	0.06 ±0.06	0.13 ±0.05		
	$(C_3H_4O_2)H^+$	Methylglyoxal; acrylic acid	73.028	2.67	2	0.12 ±0.11	0.21 ±0.06		
	$(C_3H_6O_2)H^+$	Hydroxyacetone; propanoic acid	75.044	2.41	2	0.30 ±0.31	1.06 ±0.25		
	$(C_6H_{10})H^+$	Hexyne; methylcyclopentane	83.085	2.16	1	0.13 ±0.14	0.33 ±0.10		
	$(C_4H_6O_2)H^+$	Butanedione; methacrylic acid	87.044	4.51	3	0.06 ±0.06	0.15 ±0.05		
	$(C_6H_6O)H^+$	Phenol	95.049	2.52	2	0.01 ±0.02	0.12 ±0.09		
	$(C_5H_4O_2)H^+$	Furfural	97.028	4.83	2	0.10 ±0.10	0.11 ±0.04		
	$(C_7H_{12})H^+$	Cycloheptene; methylcyclohexane	97.1	2.09	1	0.07 ±0.07	0.16 ±0.06		
	$(C_5H_8O_2)H^+$	Glutaraldehyde; pentanediones, pentenoic acid	101.061	3.9	3	0.05 ±0.04	0.12 ±0.04		
	$(C_7H_6O)H^+$	Benzaldehyde	107.049	4.12	2	0.02 ±0.04	0.17 ±0.06		
	$(C_7H_{14}O)H^+$	Heptanal; heptanone; methyl hexanone	115.11	3.14	2	0.01 ±0.01	0.02 ±0.01		
	$(C_8H_8O)H^+$	Tolualdehyde; methylbenzaldehyde	121.063	3.84	2	0.01 ±0.01	0.06 ±0.03		

	$(C_7H_6O_2)H^+$	Benzoic acid; hydroxybenzaldehyde	123.044	3.02	3	0.02±0.04	0.04±0.03
	$(C_{10}H_8)H^+$	Naphthalene	129.07	2.59	1	0.06±0.06	0.13±0.08
Uncalibration species with unknown K_{PTR}	$(C_2H_4O_3)H^+$	PAN; glycolic acid; peracetic acid	77.023	2	3	0.03±0.04	0.07±0.09
	$(C_5H_6O)H^+$	Methyl furan	83.049	2	2	0.06±0.05	0.14±0.05
	$(C_3H_4O_3)H^+$	Pyruvic acid; ethylene carbonate	89.024	2	3	0.05±0.09	0.13±0.08
	$(C_6H_8O)H^+$	Dimethyl furans; cyclohexenone; methyl cyclopentenone	97.064	2	2	0.03±0.03	0.10±0.04
	$(C_4H_4O_3)H^+$	Succinic anhydride; hydroxyfuranone; fumaraldehydic acid	101.023	2	3	0.07±0.12	0.16±0.10
	$(C_5H_4O_3)H^+$	Furoic acid; citraconic anhydride	113.024	2	3	0.11±0.14	0.12±0.10
	$(C_6H_8O_2)H^+$	Sorbic acid; hexadienic acid	113.056	2	3	0.04±0.05	0.12±0.06
	$(C_7H_{12}O)H^+$	Methylcyclohexanones; heptenone; heptenal; dimethylpentenone	113.096	2	2	0.01±0.01	0.04±0.02
	$(C_5H_6O_3)H^+$	Glutaric anhydride; pentenoic acid	115.038	2	3	0.02±0.03	0.04±0.03
	$(C_6H_{10}O_2)H^+$	Hexenoic acid; ethyl butenoate; hexanedione	115.075	2	3	0.02±0.02	0.05±0.05
	$(C_4H_4O_4)H^+$	Fumaric acid; formyl pyruvate	117.018	2	3	0.01±0.01	0.04±0.07
	$(C_5H_8O_3)H^+$	Levulinic acid; methyloxobutanoic acid;	117.057	2	3	0.01±0.01	0.01±0.02
	$(C_6H_{12}O_2)H^+$	C_6 acids (acetate)	117.09	2	3	below detection limit	0.02±0.03
	$(C_8H_{10}O)H^+$	C_2 phenols	123.08	2	2	below detection limit	0.01±0.01

[*](Li et al., 2019; Li et al., 2017a; Li et al., 2015; Li et al., 2016a; Li et al., 2017b; Yang et al., 2019; Li et al., 2016b)

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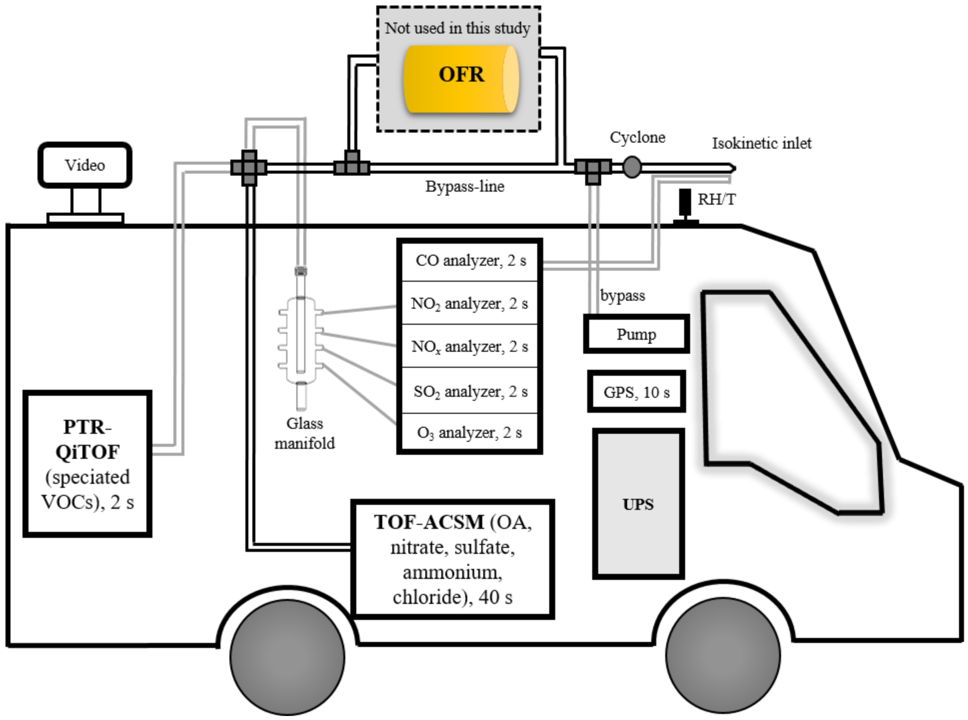

Figure S1. Schematic of the PKU mobile laboratory. The black and grey lines represent stainless steel and Teflon tubes, respectively. Temporal resolution for each instrument is shown with a unit of second.

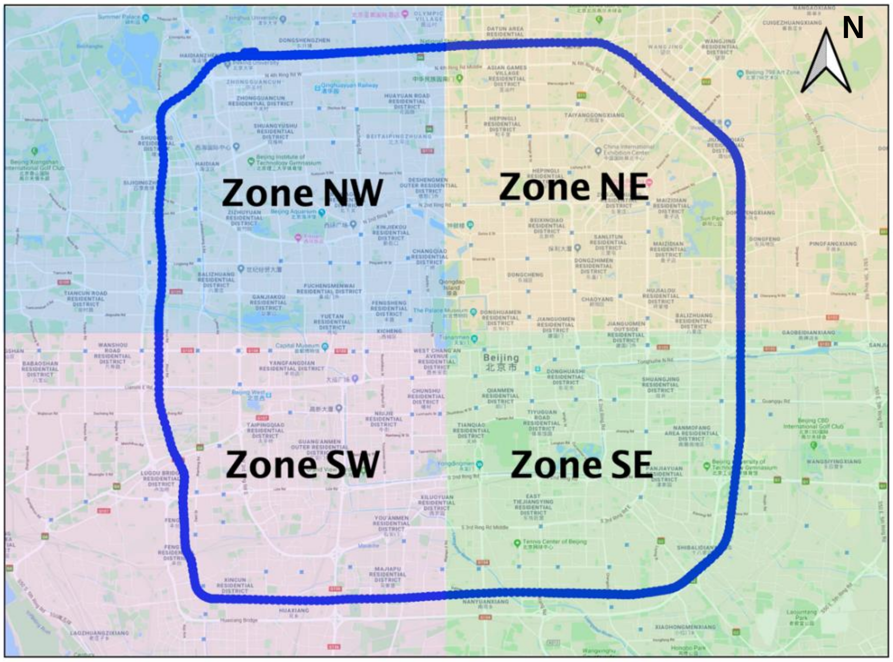

Figure S2. The map of the 4th Ring Road in Beijing (source: © Google Maps 2020) and the 4 zones named by Zone NE, Zone NW, Zone SE, and Zone SW in this study.

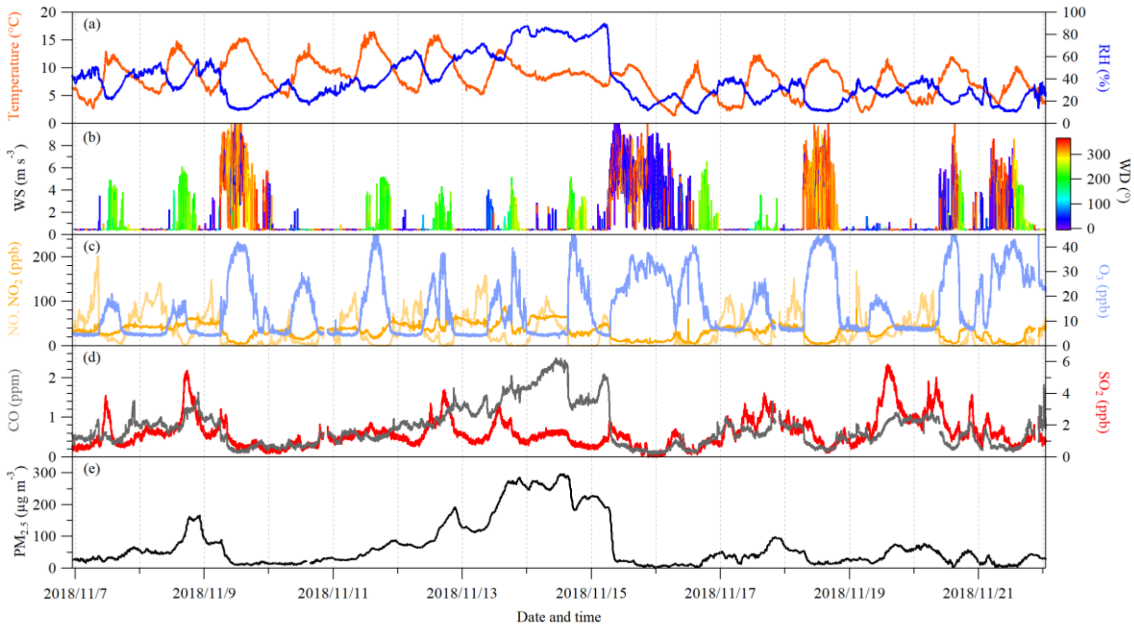

Figure S3. Time series of (a) temperature and relative humidity (RH), (b) wind speed (WS) and wind direction (WD), (c) NO, NO_2, and O_3, (d) CO and SO_2, (e) $PM_{2.5}$ mass concentration the PKU campus roof site during the entire mobile campaign.

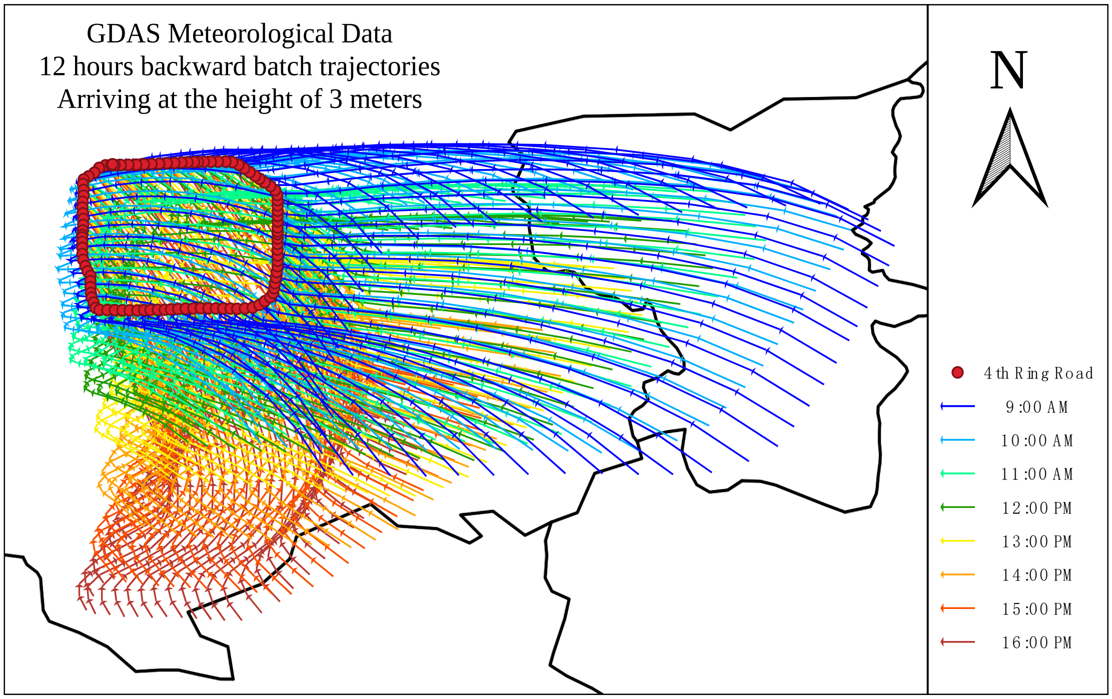

Figure S4. The 12-hour backward trajectories arriving at the height of 3 m of the 4th Ring Road in Beijing during the haze day on 14 November 2018. The start time was 9:00 a.m. and repeated every 1 hours until 4:00 p.m. local time.

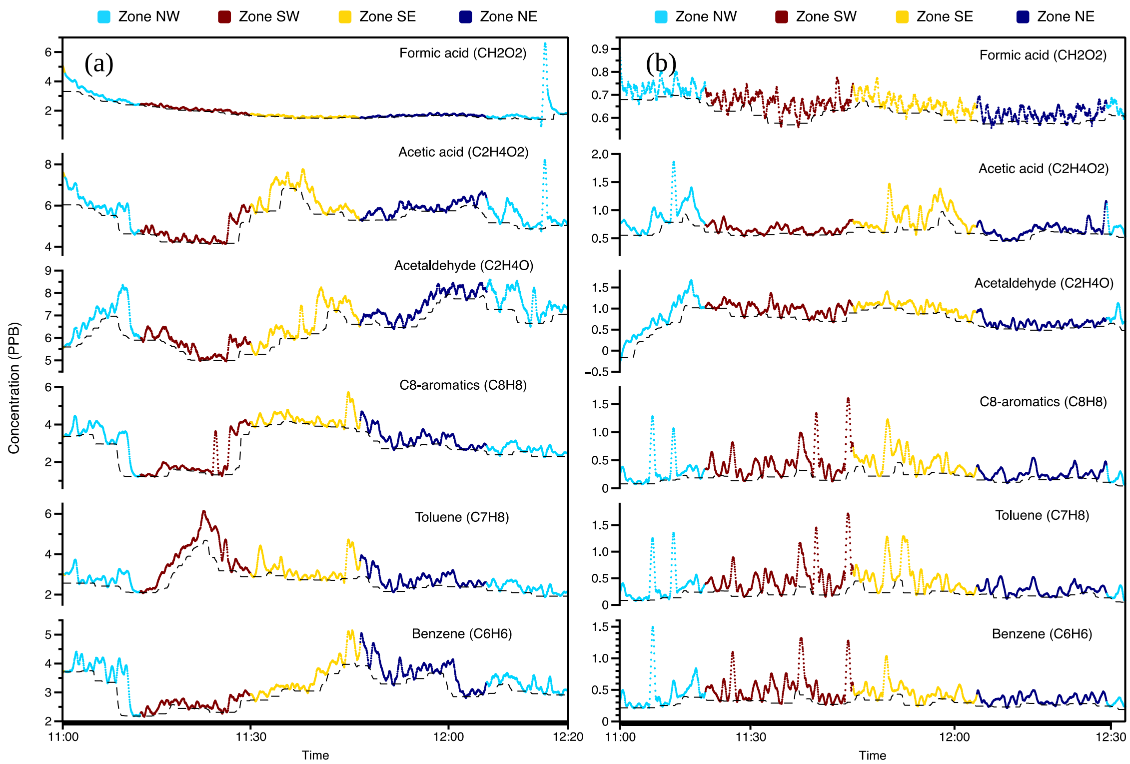

Figure S5. Time series of the mixing ratios of example VOC and OVOC species during measured during (a) the haze day on 14 November 2018 and (b) the clean day on 18 November 2018. Dashed lines are the calculated baselines. The concentrations over the baseline represent plume events.

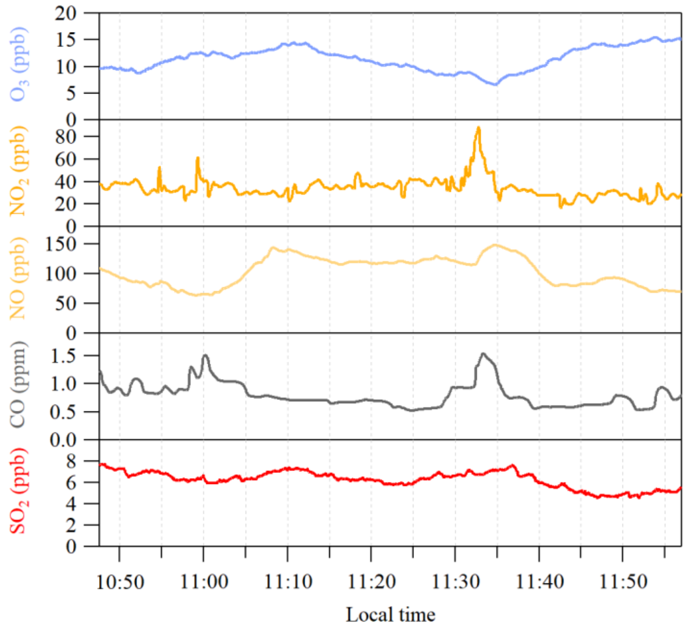

Figure S6. Example time series of the concentrations of gaseous pollutants measured during the noon cycles for the clean day on 18 November 2018.

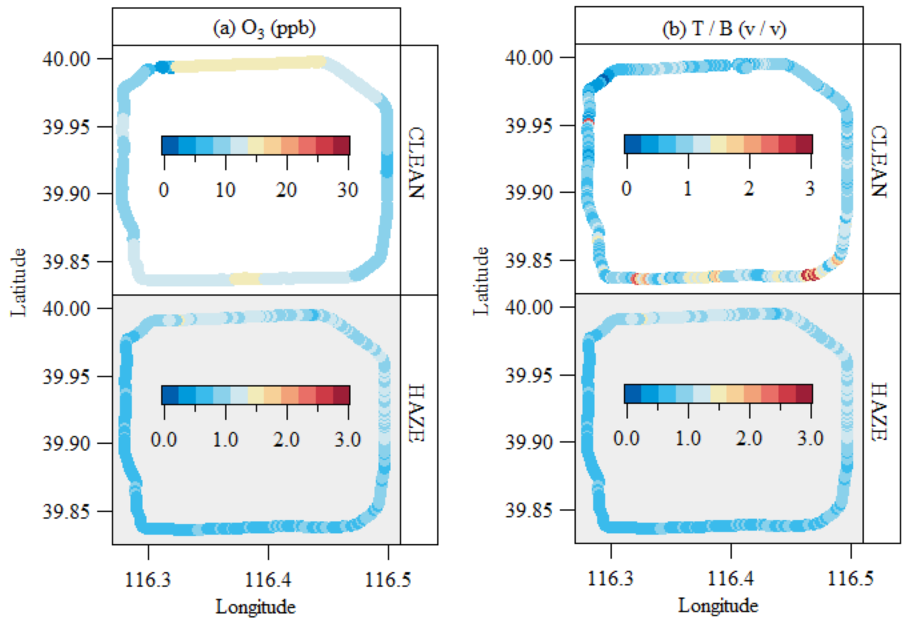

Figure S7. Spatial distributions of (a) O_3 and (b) toluene-to-benzene (T/B) ratio measured during the noontime cycles from ~11:00 AM to ~12:30 PM for the clean day on 18 November 2018 and the haze day on 14 November 2018.

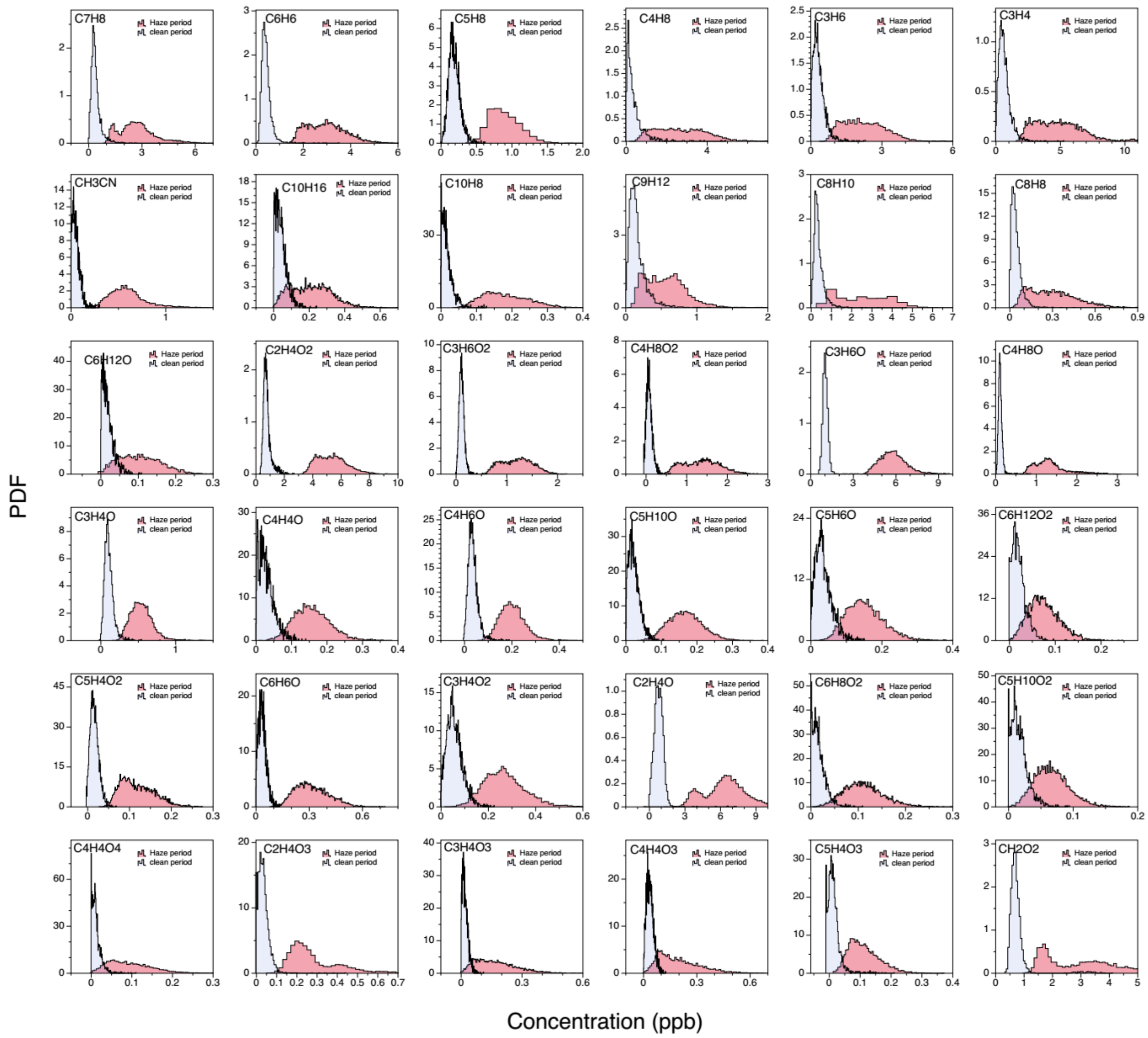

Figure S8. Probability distribution function (PDF) histograms of the mixing ratios of the main VOCs and OVOCs (36 species in total) measured during the clean day on 18 November 2018 and the haze day on 14 November 2018. All measurement cycles are included (not limited to the noon cycle).

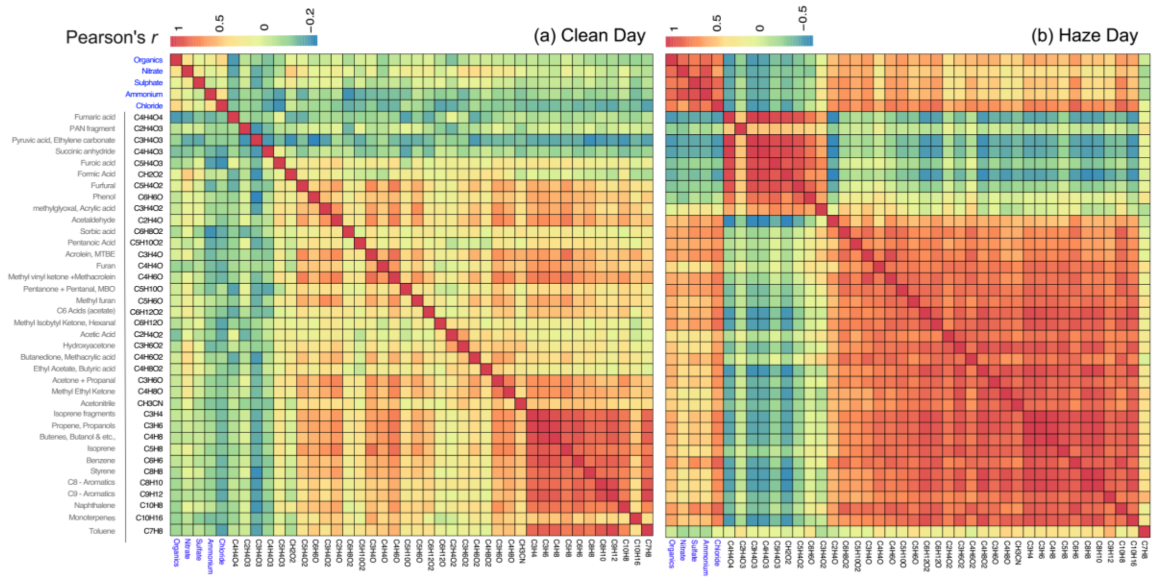

Figure S9. Correlation heatmaps for the concentrations of the main VOCs and OVOCs as well as NR-$PM_{2.5}$ components measured during (a) the clean day on 18 November 2018 and (b) the haze day on 14 November 2018.