

Measurement report: High Contributions of Halohydrocarbon and Aromatic Compounds to Emissions and Chemistry of Atmospheric VOCs in Industrial Area

Ahsan Mozaffar^{1,2,3}, Yan-Lin Zhang^{1,2,3*}, Yu-Chi Lin^{1,2,3}, Feng Xie^{1,2,3}, Mei-Yi Fan^{1,2,3}, and Fang Cao^{1,2,3}

5 ¹Yale-NUIST Center on Atmospheric Environment, International Joint Laboratory on Climate and Environment Change, Nanjing University of Information Science and Technology, Nanjing, 210044, China.

10 ²Key Laboratory Meteorological Disaster; Ministry of Education & Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disaster, Nanjing University of Information Science and Technology, Nanjing, 210044, China.

³Jiangsu Provincial Key Laboratory of Agricultural Meteorology, College of Applied Meteorology, Nanjing University of Information Science & Technology, Nanjing 210044, China.

Correspondence to: Yan-Lin Zhang (dryanlinzhang@outlook.com)

15 **Table S1: OH reaction rate constant (K^{OH}), maximum incremental reactivity (MIR), and SOA formation potential (SOAP^P) of VOCs**

Compounds	K^{OH} (Carter, 2010)	MIR (Carter, 2010)	SOAP ^P (Derwent et al., 2010)
ethane	2.54E-13	0.28	0.1
propane	1.11E-12	0.49	0
isobutane	2.14E-12	1.23	0
n-butane	2.38E-12	1.15	0.3
isopentane	3.60E-12	1.45	0.2
n-pentane	3.84E-12	1.31	0.3
2,2 dimethylbutane	2.27E-12	1.17	0
2,3 dimethyl butane	5.79E-12	0.97	0.4
2-methyl pentane	5.20E-12	1.5	0
cyclopentane	5.02E-12	2.39	0
3-methylpentane	5.20E-12	1.8	0.2
n-hexane	5.25E-12	1.24	0.1
2,4-dimethylpentane	4.77E-12	1.55	0
methylcyclopentane	5.68E-12	2.19	0
isoheptane	6.81E-12	1.07	0

cyclohexane	7.02E-12	1.25	0
2,3-dimethylpentane	7.15E-12	1.34	0
3-methylhexane	7.17E-12	1.61	0
2,2,4-trimethylpentane	3.38E-12	1.26	0
heptane	6.81E-12	1.07	0.1
methylcyclohexane	9.64E-12	1.7	0
2-methylheptane	8.31E-12	1.07	0
n-octane	8.16E-12	0.9	0.8
n-nonane	9.75E-12	0.78	1.9
decane	1.10E-11	0.68	7
n-hendecane	1.23E-11	0.61	16.2
dodecane	1.32E-11	0.55	34.5
ethylene	8.15E-12	9	1.3
Propylene	2.60E-11	11.66	1.6
trans-2-butene	6.32E-11	15.16	4
cis-2-butene	5.58E-11	14.24	3.6
1-butene	3.11E-11	9.73	1.2
1,3- butadiene	6.59E-11	12.61	1.8
1-pentene	3.14E-11	7.21	0
trans-2-pentene	6.70E-11	10.56	3.1
isoprene	9.96E-11	10.61	1.9
cis-2-pentene	6.50E-11	10.38	3.1
1-hexene	3.70E-11	5.49	0
acetylene	7.56E-13	0.95	0.1
benzene	1.22E-12	0.72	92.9
toulene	5.58E-12	4	100
ethylbenzene	7.00E-12	3.04	111.6
m,p-xylene	2.31E-11	9.75	84.5
o-xylene	1.36E-11	7.64	95.5
styrene	5.80E-11	1.73	212.3
cumene	6.30E-12	2.52	95.5
n-propylbenzene	5.80E-12	2.03	109.7
3-ethyltoulene	1.86E-11	7.39	100.6
4-ethyltoulene	1.18E-11	4.44	69.7
mesitylene	5.67E-11	11.76	13.5
2-ethyltoulene	1.19E-11	5.59	94.8
1,2,4-trimethylbenzene	3.25E-11	8.87	20.6
1,2,3-trimethylbenzene	3.27E-11	11.97	43.9
1,3-diethylbenzene	2.55E-11	7.1	0
1,4-diethylbenzene	1.64E-11	4.43	0
naphthalene	2.30E-11	3.34	0

chloromethane	4.48E-14	0.038	0
vinyl chloride	6.90E-12	2.83	0
methyl bromide	4.12E-14	0.0187	0
chloroethene	0	0	0
trichlorofloromethane	0	0	0
Vinylidene chloride	0	0	0
1,1,2-Trichlor-1,2,2-trifluorethan	0	0	0
dichloromethane	1.45E-13	0.041	0
trans-1,2-dichloroethylene	0	0	0
1,1-dichloroethane	2.60E-13	0.069	0
cis-1,2-dichloroethylene	0	0	0
chloroform	1.06E-13	0.022	0
carbon tetrachloride	0	0	0
1,2-dichloroethane	2.53E-13	0.21	0
trichloroethylene	2.34E-12	0.64	0
1,2-dichloropropane	4.50E-13	0.29	0
bromodichloromethane	0	0	0
trans-1,3-dichloropropene	1.44E-11	5.03	0
cis-1,3-dichloropropene	8.45E-12	3.7	0
1,1,2-trichloroethane	2.00E-13	0.086	0
tetrachloroethylene	0	0	0
1,2-dibromoethane	2.27E-13	0.102	0
chlorobenzene	7.70E-13	0.32	0
bromoform	0	0	0
1,1,2,2-tetrachloroethane	0	0	0
1,3-dichlorobenzene	5.55E-13	0.178	0
1,4 dichlorobebezne	5.55E-13	0.178	0
benzyl chloride	0	0	0
1,2-dichlorobenzene	5.55E-13	0.178	0
1,2,4-trichlorobenzene	0	0	0
hexachloro-1,3-butadiene	0	0	0
carbon disulfide	2.76E-12	0.25	0
Acrolein	1.99E-11	7.45	0
acetone	1.91E-13	0.36	0.1
isopropanol	5.09E-12	0.61	0.4
MTBE	0	0	0
vinyl acetate	3.16E-11	3.2	0
MEK	1.20E-12	1.48	0.6
ethyl acetate	1.60E-12	0.63	0.1
tetrahydrofuran	1.61E-11	4.31	0

methyl methacrylate	5.25E-11	15.61	0
1,4-dioxane	3.83E-11	2.62	0
4-methyl-2-pentanone	1.27E-11	3.88	0.6
2-hexanone	9.10E-12	0	0

18
19

Table S2: VOC concentrations measured in the industrial area in Nanjing. VOC concentrations observed in previous studies in Nanjing are also listed.

Compounds	Current study										(An et al., 2017), Nanjing		(Wu et al., 2020), Nanjing
	Summer		Autumn		Winter		Spring		Yearly		Summer	Winter	Yearly
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Mean	Mean
ethane	2.81	0.58	8.06	1.77	7.66	1.39	4.76	1.25	5.82	2.49	2.76	7.66	2.89
propane	3.12	0.63	6.09	1.21	4.92	0.91	2.73	0.92	4.22	1.57	1.70	4.51	3.29
isobutane	0.75	0.16	1.25	0.26	1.16	0.15	0.48	0.14	0.91	0.36	1.04	2.25	0.9
n-butane	1.75	0.39	2.61	0.63	2.32	0.26	0.87	0.29	1.89	0.76	1.09	2.35	1.53
isopentane	1.59	0.29	1.56	0.47	1.63	0.31	0.42	0.19	1.30	0.59	0.86	1.13	1.26
n-pentane	0.66	0.17	1.06	0.29	1.36	0.25	0.31	0.10	0.85	0.46	0.50	0.86	0.78
2,2 dimethylbutane	0.08	0.01	0.06	0.01	0.06	0.01	0.06	0.01	0.06	0.01	0.28	0.03	0.04
2,3 dimethyl butane	0.13	0.03	0.18	0.03	0.11	0.00	0.20	0.02	0.16	0.04	0.12	0.35	0.04
2-methyl pentane	0.26	0.08	0.32	0.10	0.44	0.11	0.29	0.06	0.33	0.08	0.25	0.41	0.16
cyclopentane	0.15	0.03	0.10	0.02	0.08	0.01	0.22	0.03	0.14	0.06	0.08	0.12	0.08
3-methylpentane	0.25	0.06	0.38	0.09	0.37	0.12	0.25	0.08	0.31	0.07	0.22	0.31	0.26
n-hexane	0.17	0.04	0.33	0.09	0.41	0.17	0.21	0.06	0.28	0.11	0.41	0.48	0.47
2,4- dimethylpentane	0.06	0.00	0.06	0.01	0.06	0.00	0.13	0.01	0.08	0.03	0.05	0.08	0.01

methylcyclopentane	0.12	0.03	0.16	0.04	0.14	0.04	0.13	0.03	0.14	0.02	0.08	0.13	0.26
isoheptane	0.13	0.04	0.12	0.04	0.11	0.04	0.16	0.03	0.13	0.02			
cyclohexane	0.44	0.29	0.37	0.15	0.43	0.31	0.21	0.13	0.36	0.10	0.41	0.60	0.15
2,3-dimethylpentane	0.86	0.59	0.73	0.30	0.85	0.63	0.42	0.25	0.72	0.21	0.11	0.20	0.02
3-methylhexane	0.10	0.02	0.12	0.03	0.09	0.02	0.14	0.02	0.11	0.02	0.04	0.05	0.08
2,2,4-trimethylpentane	1.59	0.37	2.81	0.82	3.26	0.78	1.16	0.74	2.21	0.99	0.03	0.02	0.03
heptane	0.10	0.01	0.12	0.02	0.12	0.01	0.10	0.01	0.11	0.01	1.92	0.2	0.11
methylcyclohexane	0.18	0.02	0.18	0.04	0.19	0.03	0.16	0.03	0.18	0.01	0.08	0.12	0.08
2-methylheptane	0.08	0.00	0.08	0.01	0.08	0.00	0.17	0.01	0.10	0.04	0.01	0.05	0.02
n-octane	0.09	0.01	0.08	0.01	0.09	0.01	0.20	0.01	0.11	0.06	0.19	0.21	0.05
n-noane	0.06	0.00	0.08	0.02	0.08	0.02	0.07	0.00	0.07	0.01	0.03	0.05	0.03
decane	0.05	0.00	0.06	0.01	0.06	0.01	0.05	0.00	0.06	0.01	0.05	0.06	0.04
n-hendecane	0.04	0.01	0.16	0.01	0.22	0.01	0.17	0.01	0.15	0.07	0.06	0.09	0.02
dodecane	0.08	0.00	0.36	0.02	0.50	0.01	0.22	0.02	0.29	0.18	0.07	0.13	0.03
ethylene	2.02	0.58	3.80	0.89	4.71	1.09	1.25	0.71	2.95	1.59	3.08	6.62	1.21
Propylene	0.41	0.34	0.91	0.46	0.97	0.31	0.44	0.58	0.68	0.30	0.98	2.09	0.70
trans-2-butene	0.02	0.00	0.06	0.02	0.23	0.01	0.03	0.01	0.09	0.10	0.07	0.14	0.07
cis-2-butene	0.07	0.00	0.16	0.03	0.33	0.03	0.09	0.01	0.16	0.12	0.06	0.10	0.05
1-butene	0.07	0.00	0.10	0.02	0.43	0.02	0.31	0.13	0.22	0.17	0.18	0.23	0.15

1,3- butadiene	0.31	0.07	0.34	0.05	0.30	0.03	0.28	0.00	0.31	0.02			
1-pentene	0.16	0.03	0.14	0.03	0.08	0.03	0.10	0.03	0.12	0.04	0.04	0.05	0.04
tran-2-pentene	0.09	0.03	0.06	0.02	0.05	0.01	0.09	0.02	0.07	0.02	0.03	0.04	0.03
isoprene	0.51	0.37	0.15	0.06	0.09	0.02	0.19	0.02	0.23	0.19	0.58	0.07	0.18
cis-pentene	0.07	0.02	0.06	0.01	0.07	0.01	0.17	0.02	0.09	0.05	0.03	0.02	0.02
1-hexene	0.05	0.03	0.06	0.02	0.06	0.03	0.24	0.01	0.10	0.09	0.03	0.02	0.01
acetylene	1.02	0.15	1.77	0.24	1.59	0.15	1.20	0.13	1.40	0.35	2.63	6.46	
benzene	0.80	0.19	1.41	0.41	1.63	0.39	0.58	0.37	1.10	0.50	1.86	3.21	0.82
toulene	0.84	0.40	1.88	0.51	1.67	0.31	0.49	0.12	1.22	0.66	1.47	3.20	1.07
ethylbenzene	0.22	0.05	0.83	0.21	0.65	0.15	0.20	0.10	0.48	0.32	1.27	1.79	0.43
m,p-xylene	0.24	0.07	0.86	0.24	0.80	0.17	0.19	0.07	0.52	0.36	0.46	0.59	0.67
o-xylene	0.43	0.09	1.67	0.42	1.30	0.29	0.40	0.21	0.95	0.63	0.28	0.39	0.21
styrene	0.47	0.15	1.71	0.49	1.58	0.35	0.36	0.15	1.03	0.71	0.17	0.30	0.12
cumene	0.87	0.19	3.34	0.84	2.60	0.59	0.80	0.41	1.90	1.27			
n-propylbenzene	0.04	0.01	0.13	0.02	0.14	0.01	0.08	0.11	0.10	0.05	0.09	0.08	0.03
3-ethyltoulene	0.10	0.02	0.29	0.06	0.26	0.05	0.18	0.21	0.21	0.09	0.05	0.05	0.03
4-ethyltoulene	0.07	0.00	0.08	0.01	0.08	0.01	0.10	0.06	0.08	0.01	0.19	0.29	0.03
mesitylene	0.03	0.00	0.06	0.02	0.08	0.03	0.04	0.00	0.05	0.02			
2-ethyltoulene	0.04	0.01	0.07	0.02	0.07	0.02	0.06	0.07	0.06	0.02	0.51	0.08	
1,2,4-trimethylbenzene											0.33	0.42	0.09
	0.06	0.01	0.06	0.02	0.08	0.03	0.13	0.11	0.08	0.03			

1,2,3-trimethylbenzene	0.08	0.01	0.20	0.03	0.22	0.01	0.10	0.01	0.15	0.07	0.05	0.05	0.05
1,3-diethylbenzene	0.09	0.00	0.18	0.02	0.17	0.01	0.16	0.01	0.15	0.04	0.03	0.05	0.01
1,4-diethylbenzene	0.09	0.00	0.17	0.02	0.20	0.01	0.17	0.01	0.16	0.05	0.04	0.10	0.04
naphthalene	0.13	0.02	3.09	0.98	2.14	0.22	1.35	0.29	1.68	1.25			
chloromethane	0.16	0.02	0.56	0.08	1.21	0.33	0.15	0.01	0.52	0.50			
vinyl chloride	0.05	0.00	0.07	0.02	0.09	0.02	0.16	0.01	0.09	0.05			
methyl bromide	0.04	0.00	0.05	0.01	0.04	0.01	0.03	0.00	0.04	0.01			
chloroethene	0.08	0.01	0.08	0.02	0.10	0.03	0.05	0.01	0.08	0.02			
trichlorofluoromethane	0.23	0.01	0.18	0.01	0.30	0.02	0.21	0.04	0.23	0.05			
Vinylidene chloride	0.05	0.01	0.05	0.01	0.04	0.00	0.05	0.01	0.05	0.00			
1,1,2-Trichloro-1,2,2-trifluoroethane	0.08	0.00	0.08	0.01	0.10	0.00	0.08	0.01	0.08	0.01			
dichloromethane	1.26	0.09	3.09	0.54	2.62	0.47	1.97	0.53	2.23	0.80			
trans-1,2-dichloroethylene	0.05	0.00	0.05	0.01	0.05	0.01	0.14	0.01	0.07	0.05			
1,1-dichloroethane	0.33	0.08	0.65	0.18	0.82	0.34	0.41	0.13	0.55	0.22			
cis-1,2-dichloroethylene	0.07	0.00	0.07	0.01	0.03	0.00	0.20	0.01	0.09	0.07			

chloroform	0.17	0.02	0.57	0.16	0.53	0.18	0.18	0.04	0.36	0.22
carbon tetrachloride	0.12	0.01	0.18	0.02	0.17	0.03	0.18	0.02	0.16	0.03
1,2- dichloroethane	0.95	0.14	3.19	0.40	2.95	0.43	1.15	0.31	2.06	1.17
trichloroethylene	0.13	0.02	0.14	0.02	0.10	0.02	0.06	0.00	0.11	0.04
1,2- dichloropropane	0.57	0.21	1.48	0.53	0.96	0.23	0.14	0.05	0.79	0.57
bromodichlorom ethane	0.06	0.00	0.03	0.01	0.03	0.00	0.06	0.00	0.04	0.01
trans-1,3- dichloropropene	0.10	0.00	0.08	0.01	0.13	0.00	0.17	0.01	0.12	0.04
cis-1,3- dichloropropene	1.68	0.79	3.76	1.02	3.35	0.62	0.98	0.23	2.44	1.33
1,1,2- trichloroethane	0.06	0.01	0.12	0.04	0.11	0.07	0.05	0.05	0.09	0.03
tetrachloroethyle ne	0.06	0.00	0.09	0.02	0.08	0.02	0.06	0.01	0.07	0.01
1,2- dibromoethane	0.03	0.00	0.02	0.01	0.02	0.00	0.02	0.00	0.02	0.01
chlorobenzene	0.31	0.18	1.89	0.91	1.73	1.14	0.20	0.16	1.03	0.90
bromoform	0.02	0.00	0.02	0.01	0.02	0.00	0.02	0.00	0.02	0.00
1,1,2,2- tetrachloroethan e	0.94	0.30	3.43	0.97	3.16	0.70	0.73	0.30	2.06	1.43
1,3-	0.02	0.00	0.09	0.03	0.14	0.05	0.04	0.01	0.07	0.05

dichlorobenzene										
1,4 dichlorobenzene	0.11	0.01	0.65	0.20	0.40	0.05	0.09	0.01	0.31	0.27
benzyl chloride	0.12	0.02	0.10	0.05	0.13	0.07	0.24	0.23	0.15	0.06
1,2- dichlorobenzene	0.03	0.01	0.25	0.11	0.15	0.04	0.08	0.01	0.13	0.10
1,2,4- trichlorobenzene	0.04	0.00	0.17	0.04	0.25	0.01	0.14	0.02	0.15	0.09
hexachloro-1,3- butadiene	0.02	0.00	0.17	0.04	0.15	0.04	0.02	0.00	0.09	0.08
carbon disulfide	0.42	0.11	0.59	0.13	0.66	0.15	0.21	0.07	0.47	0.20
Acrolein	0.09	0.02	0.07	0.02	0.05	0.01	0.07	0.02	0.07	0.01
acetone	1.60	0.29	2.98	0.25	1.94	0.22	2.61	0.61	2.28	0.63
isopropanol	0.46	0.07	2.34	0.60	1.28	0.34	0.44	0.10	1.13	0.90
MTBE	0.37	0.11	0.66	0.23	0.35	0.11	0.35	0.13	0.43	0.15
vinyl acetate	0.17	0.04	0.33	0.09	0.42	0.18	0.26	0.08	0.30	0.11
MEK	0.69	0.06	1.14	0.10	0.73	0.09	0.77	0.43	0.84	0.21
ethyl acetate	1.06	0.17	1.56	0.25	1.43	0.18	1.34	0.95	1.35	0.21
tetrahydrofuran	0.41	0.56	0.08	0.11	0.43	0.45	0.24	0.03	0.29	0.16
methyl methacrylate	0.11	0.01	0.21	0.01	0.20	0.01	0.32	0.00	0.21	0.09
1,4-dioxane	0.05	0.00	0.07	0.01	0.09	0.00	0.26	0.01	0.12	0.10
4-methyl-2- pentanone	0.23	0.08	0.31	0.07	0.28	0.06	0.30	0.03	0.28	0.03

2-hexanone	0.15	0.00	0.23	0.01	0.28	0.01	0.29	0.02	0.23	0.07
TVOC	38.81	10.21	83.05	20.07	77.51	16.77	39.62	13.12	59.75	28.57

20 S1. Source apportionment of VOCs

Figure S1 shows the source profile of summertime VOCs obtained from the PMF model. The resolved factors were identified as industrial source-1, vehicle emission-1, industrial process and combustion, vehicle emission-2, solvent usage, vehicle emission-3, gasoline evaporation, and biogenic source. Factor 1 was characterized by high concentrations of 2,3-dimethylpentane, chlorobenzene, and benzene. These compounds are emitted from industries (Liu et al., 2008; Wu et al., 2016) and chlorobenzene is used as a solvent in industries (Dörter et al., 2020). Therefore, factor 1 was identified as industrial source-1. Factor 2 was distinguished by a significant presence of vehicle emission VOCs 1-butene, trans-2-butene, cis-2-butene, 1,3-butadiene, and n-nonane (Liu et al., 2008; Zhang et al., 2017). So, factor 2 was identified as vehicle emission-1. Factor 3 was dominated by high concentrations of industrial solvent dichloromethane, acetone, 1,2-dichloroethane, MEK (Yu et al., 2014; Pallavi et al., 2019; Saeaw & Thepanondh, 2015) and also combustion markers like acetylene and chloromethane (An et al., 2014; McCulloch et al., 1999). Therefore, factor 3 was identified as an industrial process and combustion. Factor 4 possessed high concentrations of vehicle exhaust VOCs benzene, toluene, and acetylene (Song et al., 2018). Although these VOCs are also emitted by industrial processes, the contribution of benzene was twice of toluene in this factor. Therefore, factor 4 was assigned to vehicle emission-2. Factor 5 was attributed to solvent usage as it was characterized by high concentrations of m,p-xylene, o-xylene, styrene, ethylbenzene, 3-ethyltoluene (Li et al., 2018). Factor 6 was dominated by vehicle exhaust markers propylene, ethylene, ethane, propane, and n-hexane (An et al., 2014). SO, we identified this factor as vehicle emission-3. Factor 7 was distinguished by high concentrations of MTBE, isopentane, n-pentane, 2-methylpentane, and 3-methylpentane. These compounds are typical traces of gasoline evaporation and combustion (Song et al., 2018; Wang et al., 2016). However, the contributions of combustion markers (e.g. acetylene, ethylene) were low in this factor. Therefore, factor 7 was assigned to gasoline evaporation. Factor 8 was attributed to the biogenic source, which was mainly distinguished by a high concentration of isoprene (Song et al., 2018).

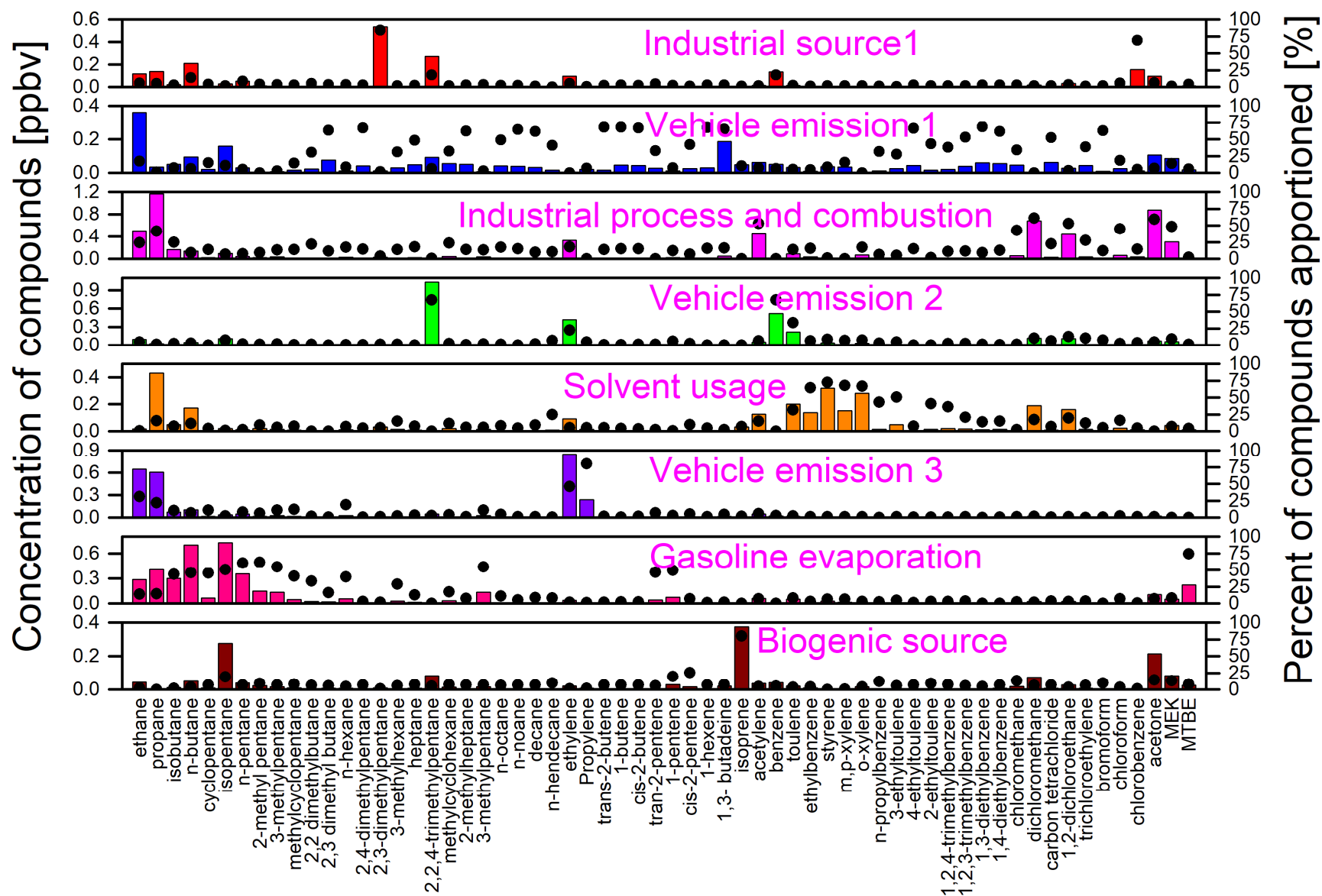
During autumn, the possible VOC sources were solvent usage, vehicle emission-1, industrial process and combustion, vehicle emission-2, gasoline evaporation, biomass burning, industrial source-1, and industrial source-2 (Fig.S2). Factor 1 was represented by a high concentration of

50 m,p-xylene, o-xylene, styrene, ethylbenzene, 3-ethyltoluene, which are typical markers of solvent usage (Li et al., 2018). Factor 2 was dominated by vehicle exhaust markers propylene, ethylene, ethane, propane, and n-hexane (An et al., 2014). Factor 3 was identified as an industrial process and combustion source as it was characterized by high concentrations of industry-emitted halohydrocarbons (e.g. chloroform, 1,2-dichloroethane) and combustion-related VOCs
55 (e.g. acetylene and propane) (Zhang et al., 2018; Song et al., 2020). The 4th factor was identified as vehicle emission-2, it was mainly composed of 2-methylheptane, n-nonane, and 1-butene (Song et al., 2018). Factor 5 was assigned to gasoline evaporation as isopentane, MTBE, and 2-methylpentane were the main contributor to it (Song et al., 2018; Wang et al., 2016). Factor 6 was characterized by a high concentration of chloromethane, which is a typical tracer of biomass
60 burning (Song et al., 2018; Hui et al., 2018, 2019). Factor 7 was identified as industrial source-1, it was dominated by high concentrations of 2-ethyltoluene and cyclopentane (Song et al., 2018). Factor 8 was assigned to industrial source-2, which was characterized by high concentrations of chlorobenzene, 2,3-dimethylpentane, and benzene (Liu et al., 2008; Wu et al., 2016; Dörter et al., 2020).

65 During winter, the source factors were identified as vehicle emission-1, solvent usage, industrial source-1, multiple sources, LPG/NG usage, vehicle emission-2, industrial source-2, and industrial process and combustion (Fig. S3). Factor 1 was assigned to vehicle emission-1, it was dominated by trans-2-butene, acetylene, cis-2-butene, 1-butene, and isobutane (Liu et al., 2008; Zhang et al., 2017). Factor 2 was represented by a high concentration of styrene, m,p-xylene, o-xylene, and ethylbenzene, which are typical tracers of solvent usage (Li et al., 2018). Factor 3
70 was identified as industrial source-1 and it was characterized by high concentrations of 2,3-dimethylpentane, chlorobenzene, and benzene (Liu et al., 2008; Wu et al., 2016; Dörter et al., 2020). Factor 4 was characterized by both the vehicle (e.g. n-hendecane, 1,3-butadiene, n-nonane) and industrial (e.g. C9-C10 aromatics) VOCs, therefore, it was identified as multiple sources
75 (Hui et al., 2019; Song et al., 2018). Factor 5 was assigned to LPG/NG usage as it was characterized by high concentrations of propylene, ethylene, and propane (Lyu et al., 2016; Hui et al., 2019; Shao et al., 2016). Factor 6 was dominated by high concentrations of n-hexane, 3-methylpentane, 2-methylpentane, and n-pentane. Therefore, it was identified as vehicle emission-2 (An et al., 2014; Song et al., 2018; Wang et al., 2016). Factor 7 was identified as industrial
80 source-2 due to the high contribution of chloroform, carbontetrachloride, 2,2,4-trimethylpentane,

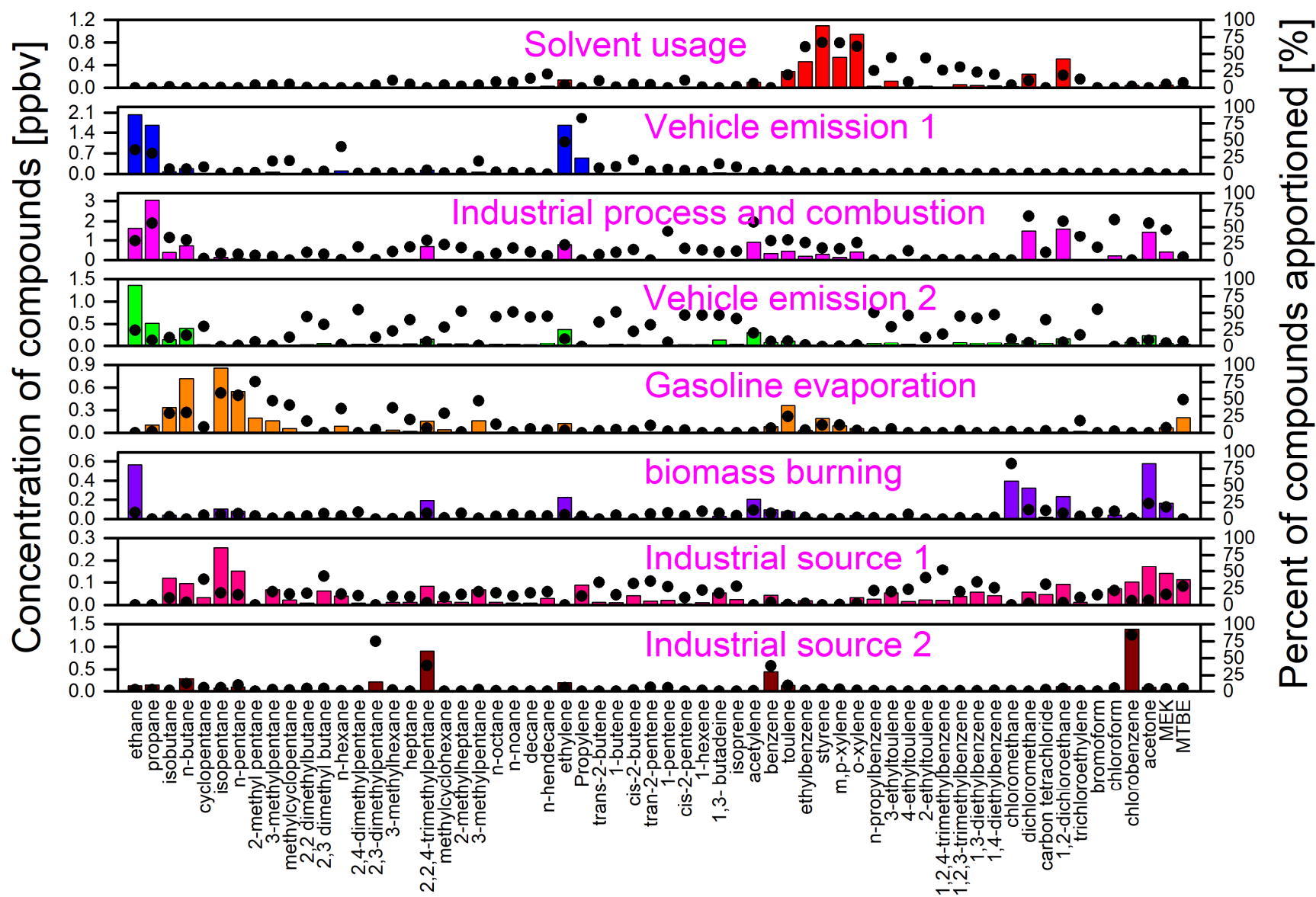
and benzene (Zhang et al., 2018; Song et al., 2020). Factor 8 was identified as an industrial process and combustion source due to the high contribution of industrial solvent acetone, dichloromethane, MEK, 1,2-dichloroethane (Yu et al., 2014; Pallavi et al., 2019; Saeaw & Thepanondh, 2015) and also combustion tracer acetylene (An et al., 2014; McCulloch et al., 85 1999).

During spring, the possible VOC sources were gasoline evaporation, solvent usage, vehicle emission-1, multiple sources, industrial source-1, LPG/NG usage, industrial source-2, and vehicle emission-2 (Fig. S4). Factor 1 was identified as a gasoline evaporation source for the high loading of isopentane (Song et al., 2018; Wang et al., 2016). Due to the high contribution of 90 o-xylene, styrene, m,p-xylene, and ethylbenzene, factor 2 was assigned to solvent usage sources (Li et al., 2018). Factor 3 had a high contribution of vehicle exhaust compounds 1,2,4-trimethylbenzene, cis-2-butene, ethane, 1,3-butadiene (Borbon et al., 2002; Liu et al., 2008). Therefore, factor 3 was identified as vehicle emission-1. Factor 4 was represented by a high concentration of 1,2,4-trimethylbenzene, isoprene, chloromethane, and n-hendecane. 1,2,4- 95 trimethylbenzene is used in furniture and coating industries (Liu et al., 2008), isoprene is emitted from trees and also from vehicles (Reimann et al., 2000), chloromethane is a tracer of biomass burning (Song et al., 2018; Hui et al., 2018, 2019), and n-hendecane is emitted from vehicles (Song et al., 2018). Therefore, factor 4 was identified as multiple sources. Factor 5 was represented by high concentrations of industrial solvent acetone, dichloromethane, MEK (Yu et 100 al., 2014; Pallavi et al., 2019; Saeaw & Thepanondh, 2015), therefore, identified as industrial source-1. Factor 6 was assigned to LPG/NG usage due to the high contribution of propane and isobutane (Shao et al., 2016). Factor 7 was identified as industrial source-2 due to the high contribution of chlorobenzene, 2,2,4-trimethylpentane, and benzene (Zhang et al., 2018; Song et al., 2020). Due to the high contribution of ethylene, propylene, and n-hexane, factor 8 was 105 identified as vehicle emission-2 (An et al., 2014).



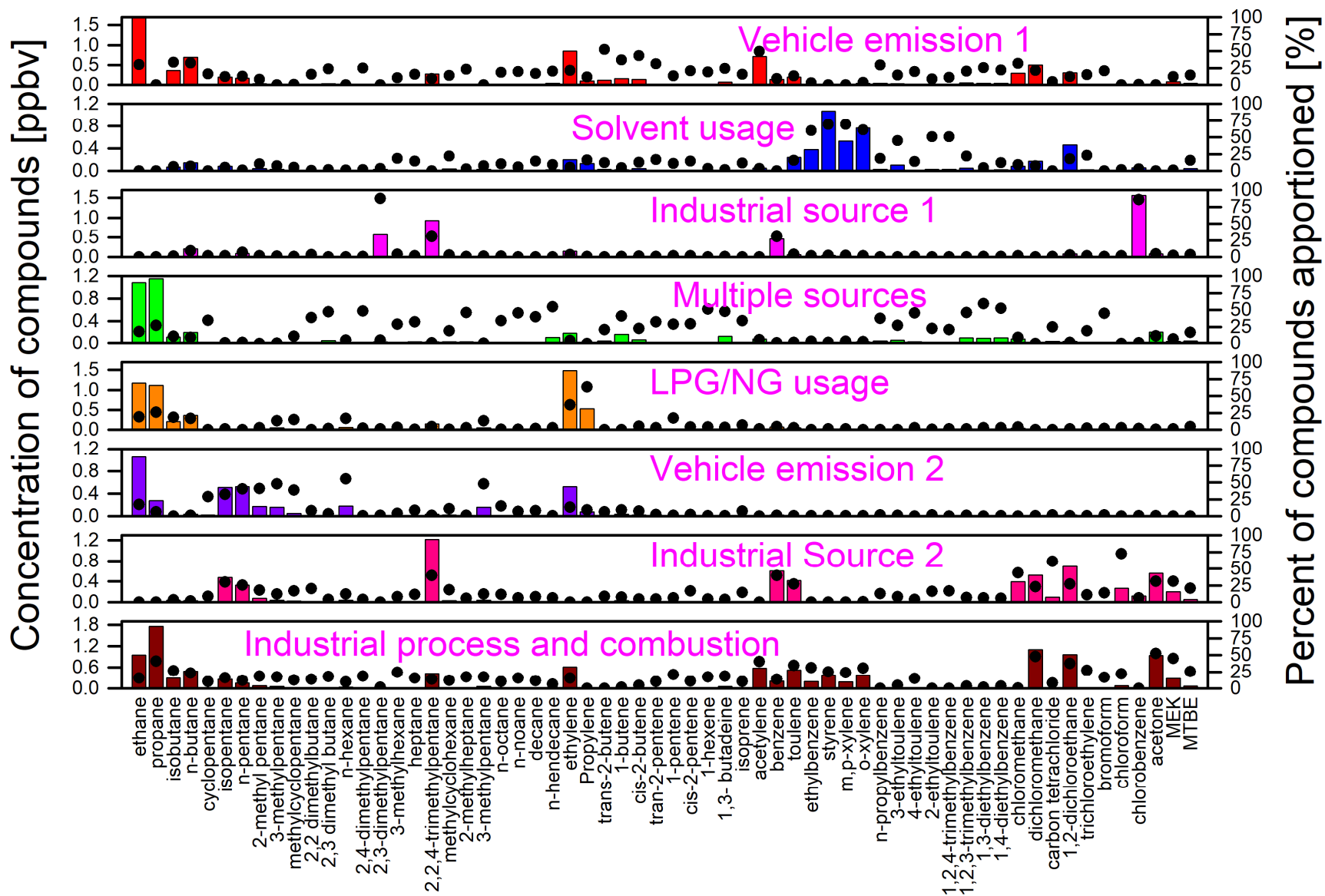
107

108 **Figure S1: Source profile of VOCs during summer in Nanjing industrial area**



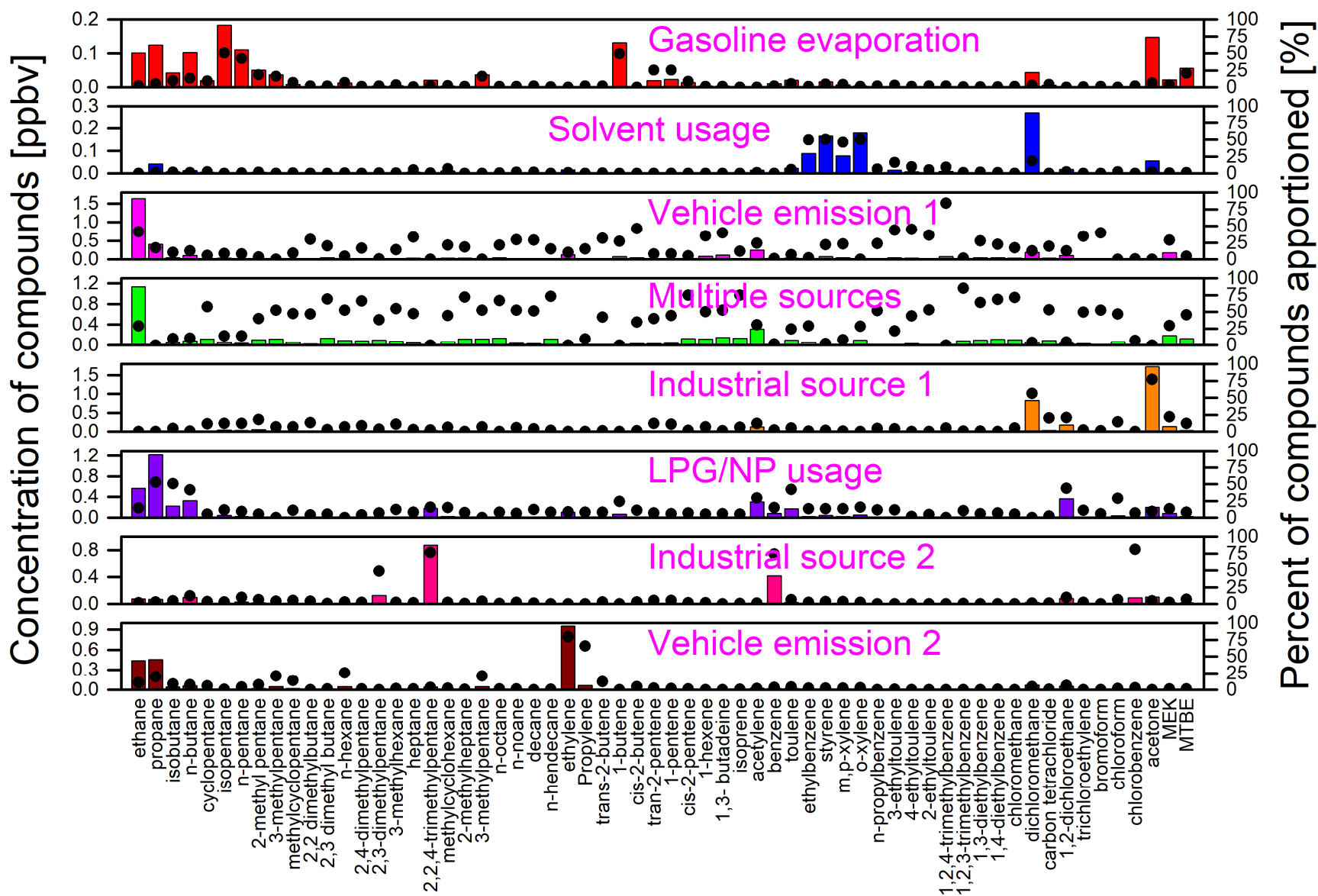
109

110 Figure S2: Source profile of VOCs during autumn in Nanjing industrial area



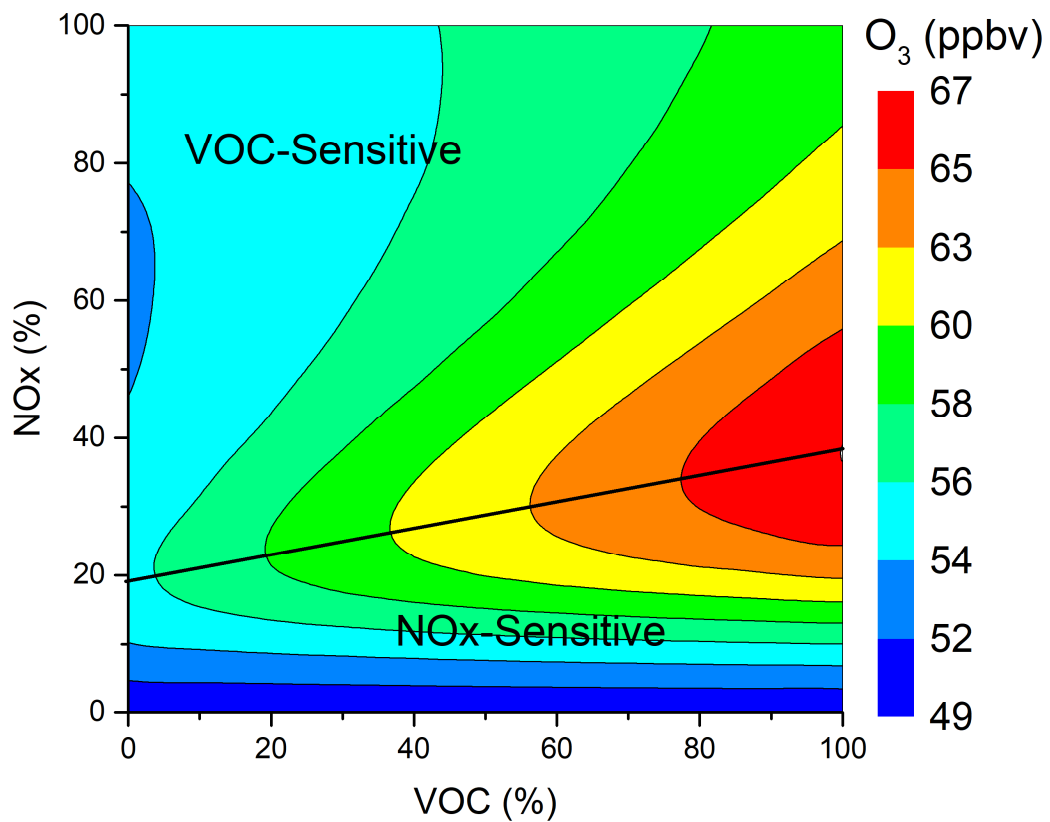
111

112 Figure S3: Source profile of VOCs during winter in Nanjing industrial area



113

114 Figure S4: Source profile of VOCs during spring in Nanjing industrial area



115

Figure S5: O₃ isopleth diagram on a high O₃ episode day (July 29 2018) in Nanjing industrial area.

120

125

130 **References**

- An, J., Wang, J., Zhang, Y., & Zhu, B. (2017). Source Apportionment of Volatile Organic Compounds in an Urban Environment at the Yangtze River Delta, China. *Archives of Environmental Contamination and Toxicology*, 72(3), 335–348. <https://doi.org/10.1007/s00244-017-0371-3>
- 135 An, J., Zhu, B., Wang, H., Li, Y., Lin, X., & Yang, H. (2014). Characteristics and source apportionment of VOCs measured in an industrial area of Nanjing, Yangtze River Delta, China. *Atmospheric Environment*, 97, 206–214. <https://doi.org/10.1016/j.atmosenv.2014.08.021>
- 140 Borbon, A., Locoge, N., Veillerot, M., Galloo, J. C., & Guillermo, R. (2002). Characterisation of NMHCs in a French urban atmosphere: overview of the main sources. *Science of The Total Environment*, 292(3), 177–191. [https://doi.org/10.1016/S0048-9697\(01\)01106-8](https://doi.org/10.1016/S0048-9697(01)01106-8)
- Carter, W. P. L. (2010). Development of the SAPRC-07 chemical mechanism. *Atmospheric Environment*, 44(40), 5324–5335. <https://doi.org/10.1016/j.atmosenv.2010.01.026>
- 145 Derwent, R. G., Jenkin, M. E., Utembe, S. R., Shallcross, D. E., Murrells, T. P., & Passant, N. R. (2010). Secondary organic aerosol formation from a large number of reactive man-made organic compounds. *Science of the Total Environment*, 408(16), 3374–3381. <https://doi.org/10.1016/j.scitotenv.2010.04.013>
- 150 Dörter, M., Odabasi, M., & Yenisoy-Karakaş, S. (2020). Source apportionment of biogenic and anthropogenic VOCs in Bolu plateau. *Science of the Total Environment*, 731, 1–18. <https://doi.org/10.1016/j.scitotenv.2020.139201>
- Hui, L., Liu, X., Tan, Q., Feng, M., An, J., Qu, Y., ... Cheng, N. (2019). VOC characteristics, sources and contributions to SOA formation during haze events in Wuhan, Central China. *Science of the Total Environment*, 650, 2624–2639. <https://doi.org/10.1016/j.scitotenv.2018.10.029>
- 155 Hui, L., Liu, X., Tan, Q., Feng, M., An, J., Qu, Y., ... Jiang, M. (2018). Characteristics, source apportionment and contribution of VOCs to ozone formation in Wuhan, Central China. *Atmospheric Environment*, 192(August), 55–71. <https://doi.org/10.1016/j.atmosenv.2018.08.042>
- 160 Li, J., Zhai, C., Yu, J., Liu, R., Li, Y., Zeng, L., & Xie, S. (2018). Spatiotemporal variations of ambient volatile organic compounds and their sources in Chongqing, a mountainous megacity in China. *Science of the Total Environment*, 627, 1442–1452. <https://doi.org/10.1016/j.scitotenv.2018.02.010>
- 165 Liu, P. W. G., Yao, Y. C., Tsai, J. H., Hsu, Y. C., Chang, L. P., & Chang, K. H. (2008). Source impacts by volatile organic compounds in an industrial city of southern Taiwan. *Science of the Total Environment*, 398(1–3), 154–163. <https://doi.org/10.1016/j.scitotenv.2008.02.053>
- Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., & Tang, D. (2008). Source profiles of volatile organic

- compounds (VOCs) measured in China: Part I. *Atmospheric Environment*, 42(25), 6247–6260. <https://doi.org/https://doi.org/10.1016/j.atmosenv.2008.01.070>
- 170 Lyu, X., Guo, H., Simpson, I. J., Meinardi, S., Louie, P. K. K., Ling, Z., ... Blake, D. R. (2016). Effectiveness of replacing catalytic converters in LPG-fueled vehicles in Hong Kong. *Atmospheric Chemistry and Physics*, 16(10), 6609–6626. <https://doi.org/10.5194/acp-16-6609-2016>
- 175 McCulloch, A., Aucott, M. L., Benkovitz, C. M., Graedel, T. E., Kleiman, G., Midgley, P. M., & Li, Y.-F. (1999). Global emissions of hydrogen chloride and chloromethane from coal combustion, incineration and industrial activities: Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research: Atmospheres*, 104(D7), 8391–8403. <https://doi.org/https://doi.org/10.1029/1999JD900025>
- 180 Pallavi, Sinha, B., & Sinha, V. (2019). Source apportionment of volatile organic compounds in the northwest Indo-Gangetic Plain using a positive matrix factorization model. *Atmospheric Chemistry and Physics*, 19(24), 15467–15482. <https://doi.org/10.5194/acp-19-15467-2019>
- Reimann, S., Calanca, P., & Hofer, P. (2000). The anthropogenic contribution to isoprene concentrations in a rural atmosphere. *Atmospheric Environment*, 34(1), 109–115. [https://doi.org/https://doi.org/10.1016/S1352-2310\(99\)00285-X](https://doi.org/https://doi.org/10.1016/S1352-2310(99)00285-X)
- 185 Saeaw, N., & Thepanondh, S. (2015). Source apportionment analysis of airborne VOCs using positive matrix factorization in industrial and urban areas in Thailand. *Atmospheric Pollution Research*, 6(4), 644–650. <https://doi.org/https://doi.org/10.5094/APR.2015.073>
- 190 Shao, P., An, J., Xin, J., Wu, F., Wang, J., Ji, D., & Wang, Y. (2016). Source apportionment of VOCs and the contribution to photochemical ozone formation during summer in the typical industrial area in the Yangtze River Delta, China. *Atmospheric Research*, 176–177, 64–74. <https://doi.org/10.1016/j.atmosres.2016.02.015>
- Song, M., Li, X., Yang, S., Yu, X., Zhou, S., Yang, Y., ... Zhang, Y. (2020). Spatiotemporal Variation, Sources, and Secondary Transformation Potential of VOCs in Xi'an, China, 30(August). Retrieved from <https://doi.org/10.5194/acp-2020-704>
- 195 Song, M., Tan, Q., Feng, M., Qu, Y., Liu, X., An, J., & Zhang, Y. (2018). Source Apportionment and Secondary Transformation of Atmospheric Nonmethane Hydrocarbons in Chengdu, Southwest China. *Journal of Geophysical Research: Atmospheres*, 123(17), 9741–9763. <https://doi.org/10.1029/2018JD028479>
- 200 Wang, G., Cheng, S., Wei, W., Zhou, Y., Yao, S., & Zhang, H. (2016). Characteristics and source apportionment of VOCs in the suburban area of Beijing, China. *Atmospheric Pollution Research*, 7(4), 711–724. <https://doi.org/10.1016/j.apr.2016.03.006>
- 205 Wu, F., Yu, Y., Sun, J., Zhang, J., Wang, J., Tang, G., & Wang, Y. (2016). Characteristics, source apportionment and reactivity of ambient volatile organic compounds at Dinghu Mountain in Guangdong Province, China. *Science of the Total Environment*, 548–549, 347–359. <https://doi.org/10.1016/j.scitotenv.2015.11.069>

- Wu, R., Zhao, Y., Zhang, J., & Zhang, L. (2020). Variability and sources of ambient volatile organic compounds based on online measurements in a suburban region of nanjing, eastern China. *Aerosol and Air Quality Research*, 20(3), 606–619. <https://doi.org/10.4209/aaqr.2019.10.0517>
- 210 Yu, C. H., Zhu, X., & Fan, Z. (2014). Spatial/temporal variations and source apportionment of VOCs monitored at community scale in an urban area. *PloS One*, 9(4), e95734–e95734. <https://doi.org/10.1371/journal.pone.0095734>
- Zhang, H., Li, H., Zhang, Q., Zhang, Y., Zhang, W., Wang, X., ... Xia, F. (2017). Atmospheric volatile organic compounds in a typical urban area of beijing: Pollution characterization, health risk assessment and source apportionment. *Atmosphere*, 8(3). <https://doi.org/10.3390/atmos8030061>
- 215
- Zhang, Y., Li, R., Fu, H., Zhou, D., & Chen, J. (2018). Observation and analysis of atmospheric volatile organic compounds in a typical petrochemical area in Yangtze River Delta, China. *Journal of Environmental Sciences (China)*, 71, 233–248. <https://doi.org/10.1016/j.jes.2018.05.027>
- 220