Measurement report: Ambient volatile organic compounds (VOCs) at an urban site in Beijing: characteristics, sources, and implications for pollution control

Lulu Cui[1], Di Wu[1], Shuxiao Wang[1,2*], Qingcheng Xu[1], Ruolan Hu[1], Jiming Hao[1,2]

[1] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

[2] State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China

----

* Corresponding author. E-mail: shxwang@tsinghua.edu.cn

Contents

Figure S1. Map of the studying location

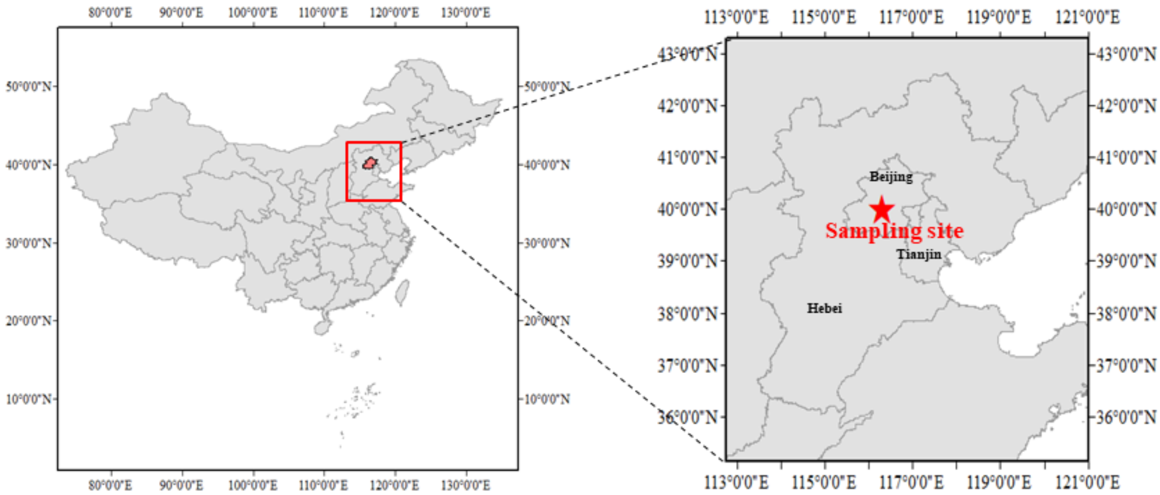

Figure S2. The performance of the random forest model in predicting the hourly concentrations of $PM_{2.5}$ and O_3. The model was constructed with 90% original data and the remained data was applied to validate the model.

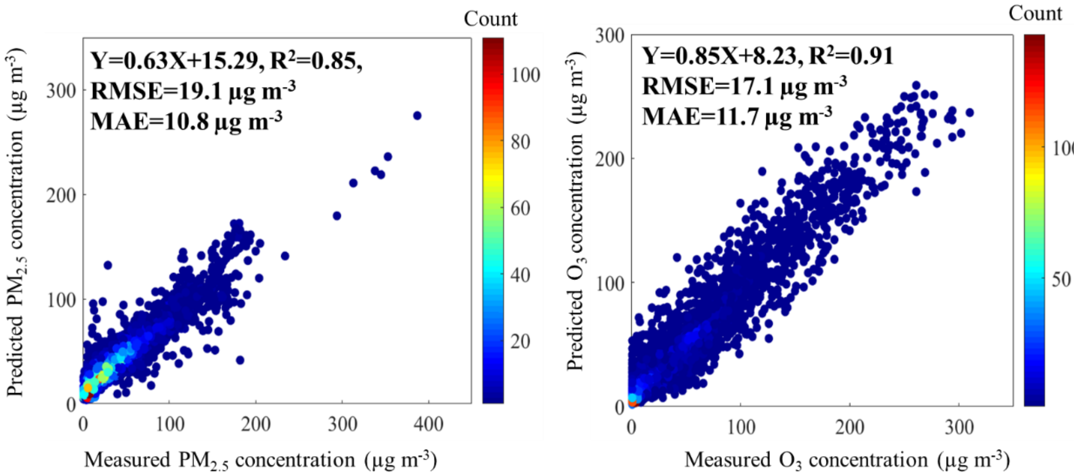

Figure S3. The values of VOCs/NO_X (ppbv $ppbv^{-1}$) during the O_3-polluted and non-O_3-polluted months.

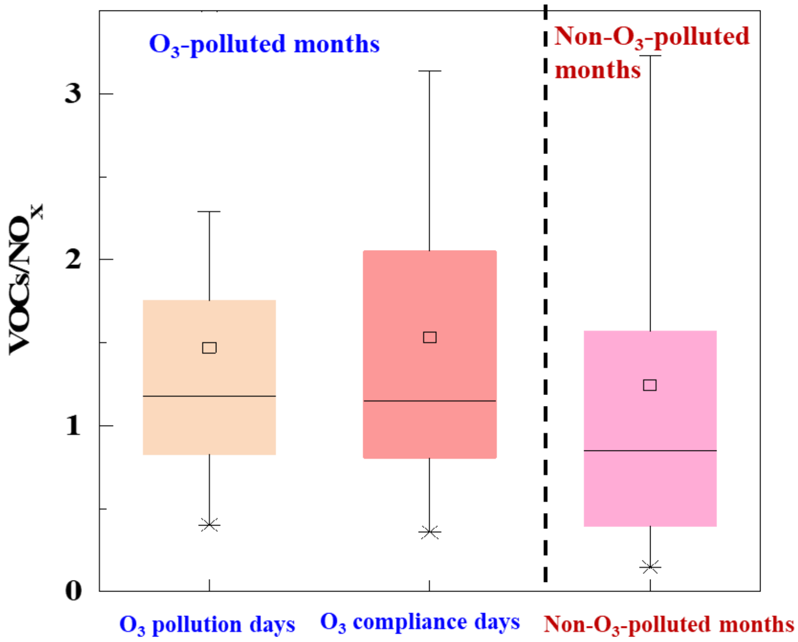

Table S2. List of VOCs and their MIR and SOA yield values used in this study.

No.	CAS	Species	MIR	SOA yield
1	75-28-5	Isobutane	1.23	0
2	106-97-8	n-Butane	1.15	0
3	78-78-4	Iso-pentane	1.45	0
4	109-66-0	n-Pentane	1.31	0
5	75-83-2	2,2-Dimethylbutane	1.17	0
6	107-83-5	2-Methylpentane	1.50	0
7	96-14-0	3-Methylpentane	1.80	0
8	110-54-3	n-Hexane	1.24	0.0028
9	108-08-7	2,4-Dimethylpentane	1.55	0
10	591-76-4	2-Methylhexane	1.19	0
11	589-34-4	3-Methylhexane	1.61	0
12	142-82-5	n-Heptane	1.07	0.0066
13	540-84-1	2,2,4-Trimethylpentane	1.26	0.0073
14	565-75-3	2,3,4-Trimethylpentane	1.03	0.0073
15	592-27-8	2-Methylheptane	1.07	0.003
16	589-81-1	3-Methylheptane	1.24	0.005
17	111-65-9	n-Octane	0.90	0.013
18	111-84-2	n-Nonane	0.78	0.021
19	124-18-5	n-Decane	0.68	0.033
20	1120-21-4	n-Undecane	0.61	0.05
21	112-40-3	n-Dodecane	0.55	0.069
22	287-92-3	Cyclopentane	2.39	0.012
23	96-37-7	Methyl cyclopentane	2.19	0.022
24	110-82-7	Cyclohexane	1.25	0.022
25	108-87-2	Methyl cyclohexane	1.70	0.035
26	106-98-9	1-Butene	9.73	0
27	624-64-6	Trans-2-butene	15.16	0
28	590-18-1	Cis-2-butene	14.24	0
29	106-99-0	1,3-Butadiene	12.61	0
30	109-67-1	1-Pentene	7.21	0.026
31	109-68-2	2-Pentene	10.38	0.026
32	78-79-5	Isoprene	10.61	0.026
33	592-41-6	1-Hexene	5.49	0.077
34	71-43-2	Benzene	0.72	0
35	108-88-3	Toluene	4.00	0.09
36	100-41-4	Ethylbenzene	3.04	0.049
37	108-38-3/106-42-3	m/p-Xylene	7.80	0.049
38	95-47-6	o-Xylene	7.64	0.049
39	100-42-5	Styrene	1.73	0.049
40	98-82-8	Iso-propylbenzene	2.52	0.073
41	103-65-1	n-Propylbenzene	2.03	0.073

42	620-14-4	m-Ethyl toluene	7.39	0.073
43	622-96-8	p-Ethyl toluene	4.44	0.073
44	611-14-3	o-Ethyl toluene	5.59	0.073
45	108-67-8	1,3,5-Trimethylbenzene	11.76	0.073
46	526-73-8	1,2,3-Trimethylbenzene	11.97	0.073
47	95-63-6	1,2,4-Trimethylbenzene	8.87	0.073
48	141-93-5	1,3-Diethylbenzene	7.10	0.1
49	105-05-5	1,4-Diethylbenzene	4.43	0.1
50	75-72-9	Trichlorofluoromethane	0.00	0
51	26523-64-8	Trichlorotrifluoroethane	0.00	0
52	1320-37-2	Dichlorotetrafluoroethane	0.00	0
53	74-87-3	Methyl chloride	0.04	0
54	75-09-2	Dichloromethane	0.04	0
55	67-66-3	Chloroform	0.02	0
56	56-23-5	Carbon tetrachloride	0.00	0
57	75-27-4	Bromodichloromethane	0.00	0
58	124-48-1	Dibromochloromethane	0.00	0
59	74-83-9	Methyl bromide	0.02	0
60	75-25-2	Tribromomethane	0.00	0
61	557-91-5	1,1-Dibromoethane	0.10	0
62	75-00-3	Chloroethane	0.29	0
63	75-34-3	1,1-Dichloroethane	0.07	0
64	107-06-2	1,2-Dichloroethane	0.21	0
65	71-55-6	1,1,1-Trichloroethane	0.00	0
66	79-00-5	1,1,2-Trichloroethane	0.09	0
67	79-34-5	1,1,2,2-Tetrachloroethane	0.00	0
68	78-87-5	1,2-Dichloro-propane	0.29	0
69	75-01-4	Vinyl chloride	2.83	0
70	75-35-4	1,1-Dichloroethene	1.79	0
71	156-60-5	Trans-1,2-dichloroethene	1.70	0
72	156-59-2	Cis-1,2-dichloroethene	1.70	0
73	79-01-6	Trichloroethylene	0.64	0
74	10061-01-5	Cis-1,3-dichloropropene	3.70	0
75	10061-02-6	Trans-1,3-dichloropropene	5.03	0
76	127-18-4	Tetrachloroethylene	0.03	0
77	87-68-3	Hexachloro-1,3-butadiene	0.00	0
78	108-90-7	Chlorobenzene	0.32	0
79	95-50-1	1,2-Dichlorobenzene	0.18	0
80	541-73-1	1,3-Dichlorobenzene	0.18	0
81	106-46-7	1,4-Dichlorobenzene	0.18	0
82	120-82-1	1,2,4-Trichlorobenzene	0.09	0
83	100-44-7	Benzyl chloride	2.92	0
84	1634-04-4	Methyl tert butyl ether	0.73	0
85	109-99-9	Tetrahydrofuran	4.31	0

86	123-91-1	1,4-Dioxane	2.62	0
87	67-63-0	Isopropyl alcohol	0.61	0
88	107-02-8	Acrolein	7.45	0
89	67-64-1	Acetone	0.36	0
90	78-93-3	2-Butanone	1.48	0
91	591-78-6	2-Hexanone	3.14	0
92	108-10-1	4-Methyl-2-pentanone	3.88	0
93	108-05-4	Vinyl acetate	3.20	0
94	141-78-6	Ethyl acetate	0.63	0
95	80-62-6	Methyl methacrylate	15.61	0

Text S1. Source appointment by PMF

Factor 1 was characterized with high loadings of SO_2 (72%), carbon tetrachloride (30%), methylchloride (27%), trichloromethane (20%), and benzene (20%). It was well known that SO_2 and trichloromethane were typical tracers of coal combustion and biomass burning, respectively(Ren et al., 2021; Zhang et al., 2018). Moreira dos Santos et al. (2004) also found that coal combustion could release significant amounts of benzene into the atmosphere(dos Santos et al., 2004). Especially in summer, open biomass burning in the rural regions of Beijing could release a large amount of Cl-containing VOC and aromatics to the atmosphere(Li et al., 2007). Therefore, this factor could be attributed to combustion source.

The predominant species found in factor 2 were O-ethyltoluene (65%), and styrene (58%). It is well documented that many aromatics such as benzene, ethyltoluene could be released from either vehicle emission or solvent use(Borbon et al., 2002; Shao et al., 2016). The poor correlation among these aromatics and other combustion tracers (e.g., SO_2) in this source further revealed that these species might be sourced from solvent usage. O-ethyltoluene was often used in the production of other chemical products(Shao et al., 2016), and thus the factor could be identified as the solvent use.

The most abundant species in factor 3 were 2,3,4-trimethylpentane, n-butane, and methyl cyclopentane with contributions of 54%, 47%, and 47%, respectively. It was reported that 2,3,4-trimethylpentane were released from petroleum products as a result of evaporation by refineries(Civan et al., 2011; Dumanoglu et al., 2014). Meanwhile, Mo et al. (2015) also verified that a high proportion of styrene was detected from petroleum refining emissions(Mo et al., 2015). Thus, the VOC species for factor 3 mainly originated from petrochemical industrial emissions.

Factor 4 was distinguished by high levels of 1-butene (84%) and trans-2-butene (78%). Guo et al. (2004) pointed out that low-carbon alkane could be considered to be the unburned fuel emissions(Guo et al., 2004). Geng et al. (2009a) also demonstrated that the C3-C5 alkenes were mainly emitted from the fuel evaporation(Geng et al., 2009). Hence, this factor represented the fuel evaporation.

Factor 5 was characterized by a large mass fraction of 1-hexene (62%), MTBE (53%), and vinyl acetate (46%). It was widely acknowledged that MTBE was a typical fingerprint of gasoline-powered vehicle emissions because it was often used as a fuel additive in motor gasoline (Liang et al., 2020). In addition, the poor correlation between the fuel evaporation factor and the MTBE are also observed ($r = 0.23$), indicating these factors shared with different origins. Hence, this factor was termed as the gasoline vehicle exhaust.

Factor 6 was dominated by N-undecanone (98%), N-dodecane (93%), and N-decane (73%). N-decane and N-undecanone were good markers of diesel exhaust emissions(Liu et al., 2008), indicating that this factor represented diesel engine emission.

References

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. Sci. Total. Environ. 292, 3, 177-191.

Civan, M.Y., Kuntasal, Ö. O., Tuncel, G., 2011. Source Apportionment of Ambient Volatile Organic Compounds in Bursa, a Heavily Industrialized City in Turkey. 12. 4.

Dumanoglu, Y., Kara, M., Altiok, H., Odabasi, M.,Elbir, T., Bayram, A., 2014. Spatial and seasonal variation and source apportionment of volatile organic compounds (VOCs) in a heavily industrialized region.

Dumanoglu, Y., Kara, M., Altiok, H., Odabasi, M., Elbir, T., Bayram, A., 2014. Spatial and seasonal variation and source apportionment of volatile organic compounds (VOCs) in a heavily industrialized region. Atmos. Environ. 98, 168-178.

Geng, F., Cai, C., Tie, X., Yu, Q., An, J., Li, P., Zhou, G.Q., Xu, J., 2009. Analysis of VOC emissions using PCA/APCS receptor model at city of Shanghai, China. J Atmos Chem. 62:229–247.

Guo, H., Wang, T., Louie, P.K.K.K., 2004. Source apportionment of ambient non-methane hydrocarbons in Hong Kong: Application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model. Environ. Pollut. 129, 3, 489-498.

Li, X., Wang, S., Duan, L., Hao, J., Li, C., Chen, Y., Yang, L., 2007. Particulate and trace gas emissions from open burning of wheat straw and corn stover in China. *Environ. Sci. Technol.* 2007, 41, 17, 6052–6058.

Liang, Y., Liu，X., Wu，F., Guo, Y., Xiao, H., 2020. The year-round variations of VOC mixing ratios and their sources in Kuytun City (northwestern China), near oilfields. Atmos. Pollut. Res. 11,9 DOI:10.1016/j.apr.2020.05.022.

Ren, Y.A., Shen, S., Shen, H., Zhong, Q., Tao, S., 2021. Contributions of biomass burning to global and regional SO_2 emissions. Atmos. Res. 260, 105709.

Shao, P., An, J.L., Xin, J.Y., Wu, F.K., Wang, J. X., Ji, D.S., Wang, Y.S., 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. Atmos. Res. 176–177, 64-74

Ying, k., Min, S., Fu, L., Lu, S., Zeng, L., Tang, D., 2008. Source profiles of volatile organic compounds (VOCs) measured in China: Part I. Atmos.Environ. 42, 25, 6247-6260.

Zhang, Y., Rui, L., Fu, H., Dong,Z., Chen, J., 2018. Observation and analysis of atmospheric volatile organic compounds in a typical petrochemical area in Yangtze River Delta, China. J. Environ. Sci. 233-248.