Supporting information for "Vertical changes in volatile organic compounds (VOCs) and impacts on photochemical ozone formation"

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Estimation of NMHC concentrations at the BMT site

In addition to the gradient measurements of trace gases on the BMT, online measurements of 56 nonmethane hydrocarbons (NMHCs) were made using a GC-MS/FID system (TH-300B, Tianhong Inc., China) with an hourly time resolution during the campaign at the Chegongzhuang site, as depicted in Fig. S1. The Chegongzhuang site is located between the Second and Third Ring Roads in downtown Beijing and is approximately 5 km southwest of the BMT site. In this study, we primarily investigated the impact of vertical variations in VOCs on atmospheric oxidation capacity and photochemical ozone formation during daytime. Therefore, the concentrations of unmeasured NMHC species at the five inlet heights were estimated only in daytime, defined as the period of 11:00-16:00 local time (UTC+8). The concentrations of NMHCs (e.g., alkanes, alkenes, and acetylene) that were not measured on the BMT could be estimated by scaling the concentrations of measured aromatic species with similar k_{OH} values. The scaling factors for a NMHC species were determined using measurements from the 56 NMHCs at the Chegongzhuang site. This approach is reasonable since vehicular exhausts and residential emissions are the predominant sources of ambient VOCs in urban Beijing. The scaling factor of a NMHC species *R*, denoted by *SF*, can be determined according to the following criteria in Eq. (S1):

$$SF_t = \begin{cases} {[R]}/{[Benzene]}, & if\ k_{OH-R} < k_{OH-Benzene} \\ 0.5 \times \left(\frac{[R]}{[Benzene]} + \frac{[R]}{[Xylene]}\right), & if\ k_{OH-Benzene} < k_{OH-R} < k_{OH-Xylene} \\ 0.5 \times \left(\frac{[R]}{[Xylene]} + \frac{[R]}{[Styrene]}\right), & if\ k_{OH-Xylene} < k_{OH-R} < k_{OH-Styrene} \\ {[R]}/{[Styrene]}, & if\ k_{OH-R} > k_{OH-Styrene} \end{cases} \quad \text{Eq. (S1)}$$

where [*R*], [Benzene], [Xylene], and [Styrene] represent concentrations of *R*, xylene, and styrene; $k_{OH\text{-}R}$, $k_{OH\text{-}Benzene}$, $k_{OH\text{-}Xylene}$, and $k_{OH\text{-}Styrene}$ represents the reaction rate coefficients between *R* and OH radicals, benzene, xylene, and styrene.

The concentrations of xylene isomers (o-xylene and m, p-xylene, *m/z*=107) and trimethylbenzene isomers (1,2,3-, 1,2,4-, 1,3,5-trimethylbenzene, *m/z*=121) were determined by scaling PTR-ToF-MS measurements using the respective concentration

ratios at the Chegongzhuang site. Similarly, the concentrations of methyl vinyl ketone (MVK) and methacrolein (MACR) were derived by scaling the PTR-ToF-MS measurements (*m/z*=121) with the respective concentration ratios determined through the PTR-ToF-MS measurements conducted in NO^+ mode during the campaign (Fig. S4). As reported in the literature *(Gkatzelis et al., 2021; Wang et al., 2022)*, anthropogenic emissions are the primary sources of monoterpenes in urban regions. Therefore, concentrations of monoterpenes measured by the PTR-ToF-MS (*m/z*=137) were allocated to α-pinene, β-pinene, and limonene with respective fractions of 25%, 25%, and 50% *(Gkatzelis et al., 2021)*.

References

Gkatzelis, G. I., Coggon, M. M., McDonald, B. C., Peischl, J., Gilman, J. B., Aikin, K. C., Robinson, M. A., Canonaco, F., Prevot, A. S. H., Trainer, M., and Warneke, C.: Observations Confirm that Volatile Chemical Products Are a Major Source of Petrochemical Emissions in U.S. Cities, Environ Sci Technol, 55, 4332-4343,10.1021/acs.est.0c05471 2021.

Wang, H., Ma, X., Tan, Z., Wang, H., Chen, X., Chen, S., Gao, Y., Liu, Y., Liu, Y., Yang, X., Yuan, B., Zeng, L., Huang, C., Lu, K., and Zhang, Y.: Anthropogenic monoterpenes aggravating ozone pollution, Natl Sci Rev, 9, nwac103,10.1093/nsr/nwac103 2022.

Table S1 Summary of the VOC species and related parameters used in this study

Type	VOC Species	Mean*	Median*	5th percentile*	95th percentile*	k_{OH} ($\times 10^{-12}$)**
NMHC	Ethane	2.083	1.797	0.658	4.467	0.24
	Propane	2.046	1.617	0.480	4.779	1.10
	Iso-butane	1.375	1.035	0.300	3.500	2.12
	n-Butane	2.123	1.600	0.453	5.794	2.35
	i-pentane	1.295	0.975	0.281	3.566	3.60
	n-Pentane	0.528	0.382	0.101	1.648	3.80
	2,2-Dimethylbutane	0.044	0.030	0.010	0.123	2.23
	Cyclopentane	0.333	0.228	0.074	0.897	4.97
	2,3-Dimethylbutane	0.088	0.061	0.022	0.250	5.78
	2-Methylpentane	0.265	0.204	0.057	0.705	5.20
	3-Methylpentane	0.194	0.151	0.048	0.488	5.20
	n-Hexane	0.492	0.309	0.095	1.541	5.20
	Methylcyclopentane	0.162	0.122	0.042	0.426	7.65
	2,4-Dimethylpentane	0.036	0.027	0.009	0.078	4.77
	Cyclohexane	0.102	0.074	0.024	0.321	6.97
	2-Methylhexane	0.081	0.064	0.023	0.190	5.65
	2,3-Dimethylpentane	0.035	0.027	0.007	0.085	6.89
	3-Methylhexane	0.077	0.058	0.019	0.197	6.54
	2,2,4-Trimethylpentane	0.051	0.043	0.014	0.115	3.34
	n-Heptane	0.105	0.078	0.027	0.277	6.76
	Methylcyclohexane	0.070	0.052	0.015	0.223	9.64
	2,3,4-Trimethylpentane	0.022	0.017	0.004	0.058	6.60
	2-Methylheptane	0.026	0.020	0.006	0.071	12.20
	3-Methylheptane	0.022	0.018	0.005	0.060	14.00
	n-Octane	0.059	0.040	0.013	0.143	8.11
	Nonane	0.045	0.026	0.008	0.086	9.70
	n-Decane	0.057	0.036	0.010	0.175	11.00
	n-Undecane	0.024	0.019	0.007	0.053	12.30
	n-Dodecane	0.023	0.018	0.006	0.051	13.20
	1-Hexene	0.058	0.037	0.009	0.149	37.00
	ethene	1.700	1.330	0.451	3.885	7.80
	propene	0.597	0.430	0.112	1.530	29.00
	trans-2-Butene	0.060	0.040	0.008	0.151	64.00
	1-Butene	0.168	0.131	0.033	0.435	31.00

	cis-2-Butene	0.060	0.038	0.008	0.149	56.00
	trans-2-Pentene	0.029	0.019	0.005	0.079	67.00
	1-Pentene	0.061	0.043	0.012	0.163	31.40
	cis-2-Pentene	0.045	0.031	0.010	0.116	65.00
	Isoprene	0.749	0.492	0.111	1.940	100.00
	Acetylene	0.888	0.771	0.245	1.976	0.75
	Benzene	0.280	0.241	0.082	0.647	1.20
	Toluene	0.746	0.590	0.183	1.709	5.60
	Ethylbenzene	0.197	0.169	0.048	0.403	7.00
	m,p-Xylene	0.705	0.528	0.151	1.612	23.10
	Styrene	0.057	0.047	0.020	0.119	58.00
	o-Xylene	0.329	0.247	0.072	0.767	13.60
	Isopropylbenzene	0.009	0.008	0.002	0.022	6.30
	n-Propylbenzene	0.030	0.022	0.007	0.066	5.80
	m-Ethyltoluene	0.069	0.053	0.016	0.154	18.60
	p-Ethyltoluene	0.029	0.022	0.006	0.060	11.80
	1,3,5-Trimethylbenzene	0.042	0.032	0.007	0.104	56.70
	1,2,4-Trimethylbenzene	0.147	0.113	0.035	0.328	32.50
	1,2,3-Trimethylbenzene	0.057	0.042	0.013	0.132	32.70
	o-Ethyltoluene	0.029	0.022	0.007	0.061	11.90
	m-Diethylbenzene	0.031	0.018	0.005	0.091	22.00
	p-Diethylbenzene	0.035	0.021	0.005	0.097	16.00
	α-piene	0.088	0.069	0.021	0.221	54.00
	β-piene	0.088	0.069	0.021	0.221	76.00
	Limonene	0.176	0.137	0.043	0.441	165.00
OVOC	Formaldehyde	0.703	0.385	0.004	2.203	9.40
	Methanol	8.349	7.511	3.378	15.324	0.94
	Acetaldehyde	1.917	1.762	0.742	3.558	15.00
	Acetone	3.775	3.561	1.908	6.322	0.17
	MEK	0.763	0.715	0.309	1.365	1.10
	Hydroxyacetone	0.738	0.617	0.170	1.763	5.90
	Phenol	0.008	0.007	0.001	0.015	27.00
	MVK	0.603	0.518	0.102	1.377	20.00
	MACR	0.314	0.289	0.075	0.661	29.00

* The unit is ppb.

** The unit is cm^3 $molecule^{-1}$ s^{-1}.

Figure S1. (A) Map showing locations of the Beijing Meteorological Tower (BMT) and the Chegongzhuang sites. (B) Picture showing the BMT. Note that the map in panel (A) was extracted from © Google Maps by the authors and the photo in panel (B) was taken by the authors.

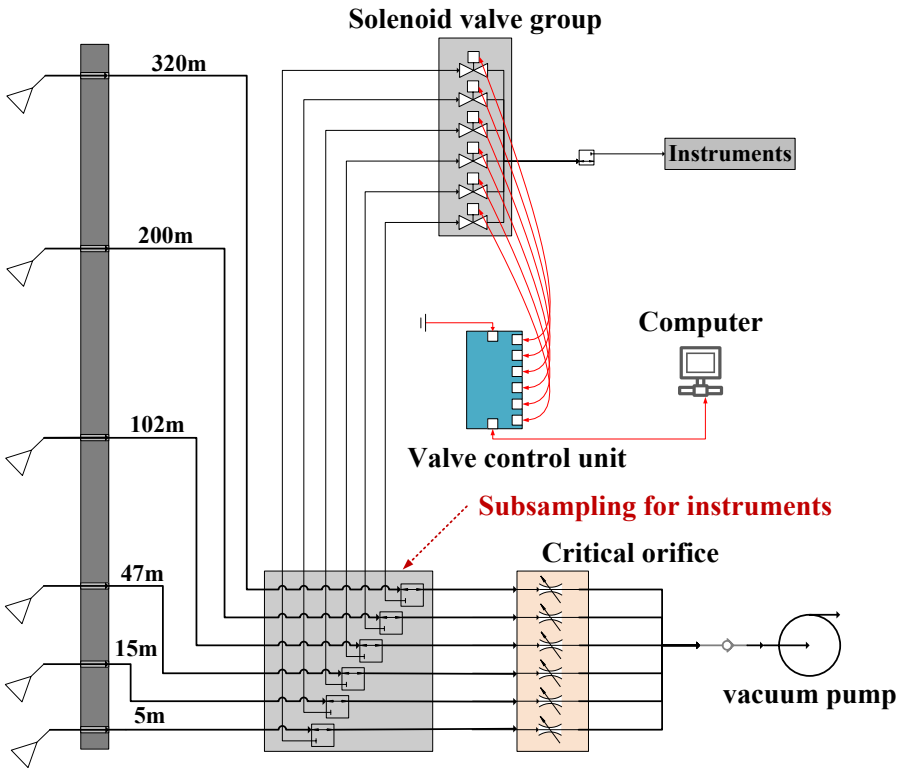

Figure S2. A simple schematic illustration of the vertical observation system on the BMT.

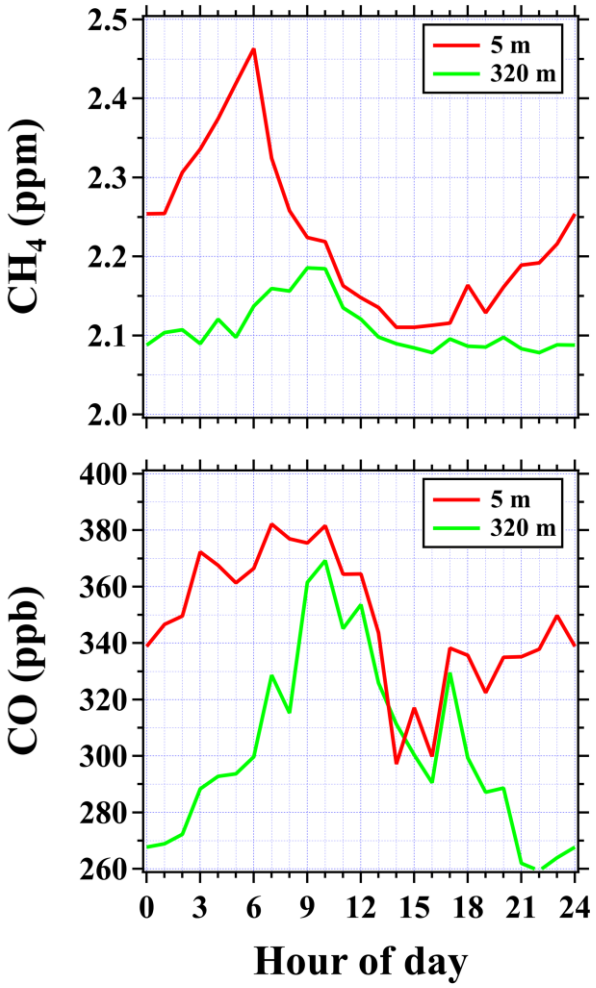

Figure S3. Average diurnal profiles of CH_4 and CO at 5 and 320 m on BMT during the campaign.

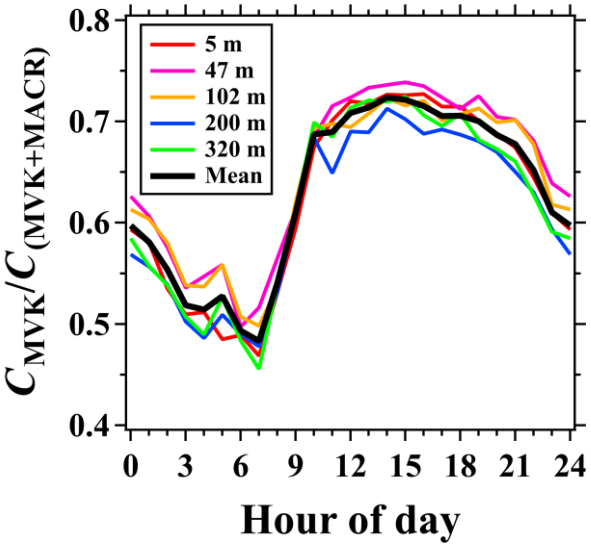

Figure S4. Average diurnal profiles of the concentration ratios of MVK to MVK+MACR (m/z 71, $C_4H_6OH^+$) at different altitudes measured by PTR-ToF-MS using the NO^+ mode from July 14 to August 4, 2021.

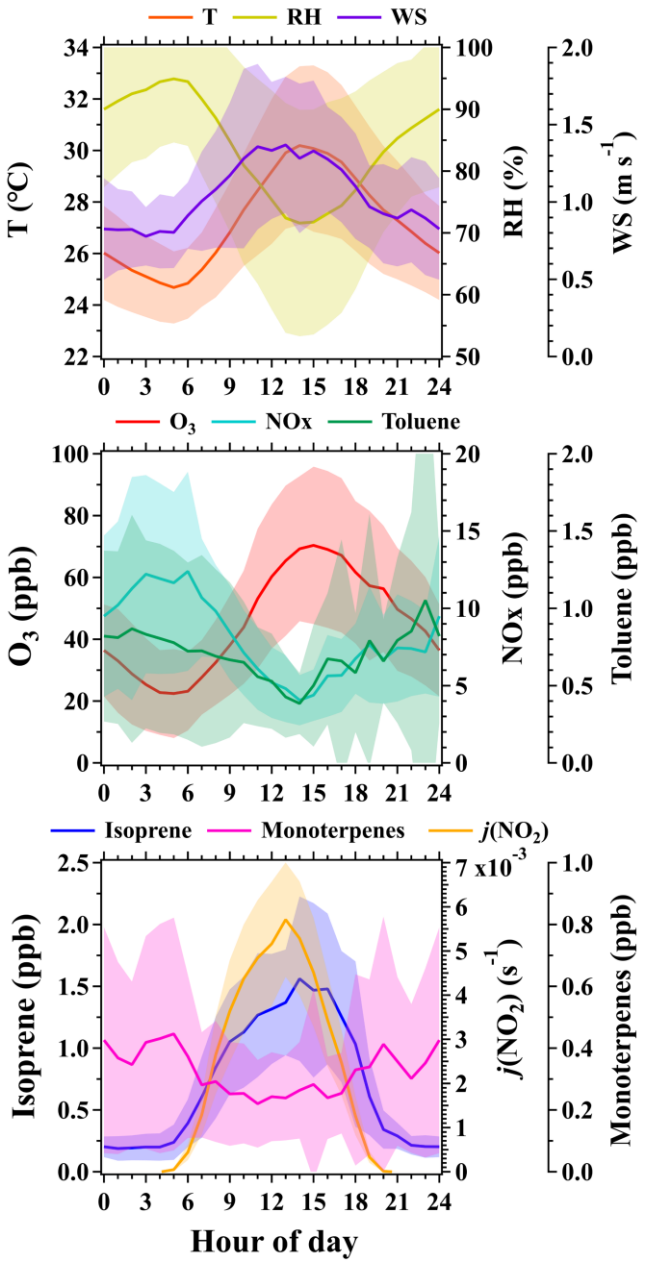

Figure S5. Average diurnal profiles of meteorological parameters, ozone, and precursor gases along with $j(NO_2)$ at ground level during the campaign.

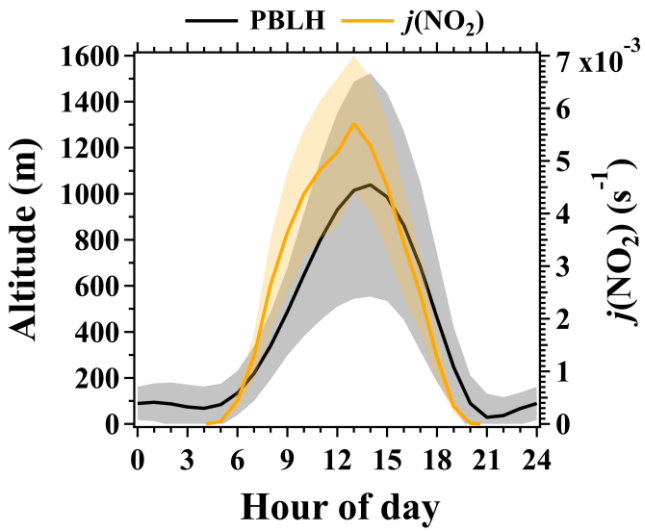

Figure S6. Average diurnal profiles of PBLH and $j(NO_2)$ at the BMT site during the campaign.

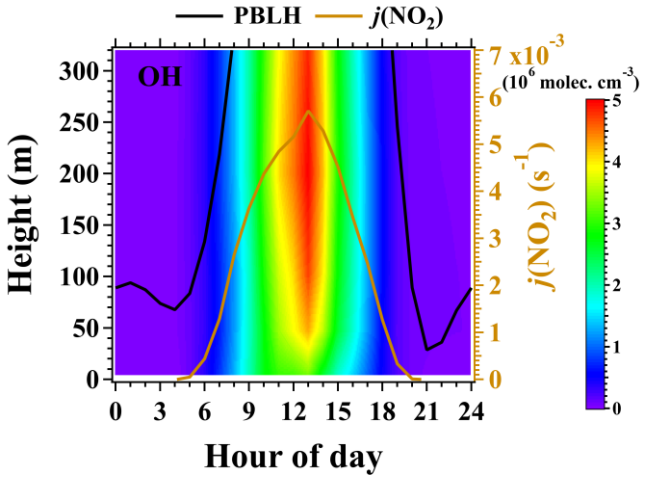

Figure S7. Average diurnal and vertical variations in concentrations of OH radical obtained from the box model results during the campaign.