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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. 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.

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.

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; $k_{\text{OH-R}}$, $k_{\text{OH-Benzene}}$, $k_{\text{OH-Xylene}}$, and $k_{\text{OH-Styrene}}$ represents the reaction rate coefficients between R and OH radicals, benzene, xylene, and styrene.

The uncertainties associated with the method primarily stem from three key aspects. Firstly, variations in source emissions of VOCs can significantly alter the concentration ratios of different VOC species between the two sites. In urban Beijing, vehicular exhausts are the dominant contributor to ambient VOCs, a fact corroborated by an average toluene-to-benzene ratio (T/B) of 1.45—a T/B ratio around 2 typically signifies vehicle emissions, as illustrated in Figure S2. Consequently, it can be inferred that there are no substantial disparities in VOC sources between the two sites.

Secondly, differences in vertical concentration gradients among VOC species pose another uncertainty. During daylight hours within the boundary layer, NMHCs are primarily removed through reactions with OH radicals. The magnitude of these vertical gradients is strongly influenced by the reaction rate constants of NMHCs with OH radicals, as depicted in Figure 4. Conversely, at night, NMHC removal mainly occurs via reactions with O_3 and NO_3 radicals, which have much lower reaction rates compared to OH and hence exert lesser impact on the vertical distribution of NMHCs. To mitigate this issue, our study employs a strategy where the concentrations of unmeasured NMHCs across various altitudes are inferred from those of measured aromatic compounds with analogous k_{OH} values. By using this method, the effects of the differences in VOCs vertical gradients on the estimation of unmeasured NMHCs can be minimized.

Lastly, advection transport effects introduce variability, representing the most challenging uncertainty to address in estimating NMHC concentrations. Given the

relatively short geographical separation (5 km) between the two sites, however, it is reasonable to assume that transport-induced changes in NMHC concentrations would exhibit minimal differences. Thus, while acknowledging this potential source of uncertainty, we contend that its impact on estimating NMHC concentrations at different altitudes on the BMT site would be marginal.

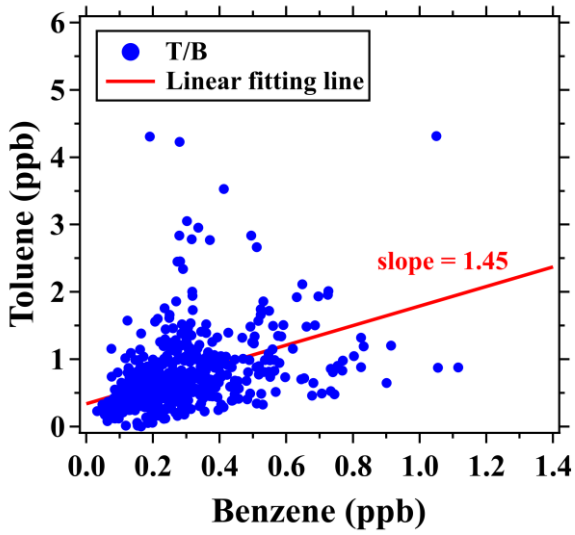

Figure S2. Scatter plot of toluene to benzene mixing ratios at ground level at the BMT site during the field campaign.

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. S5). 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)*.

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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}.

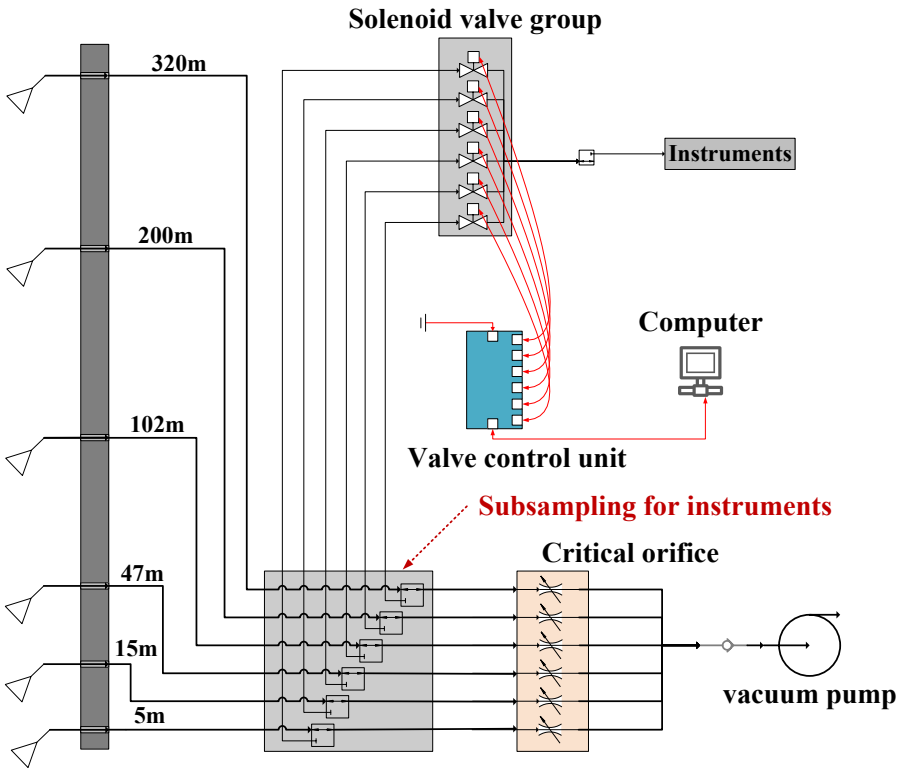

Figure S3. A simple schematic illustration of the vertical observation system on the BMT.

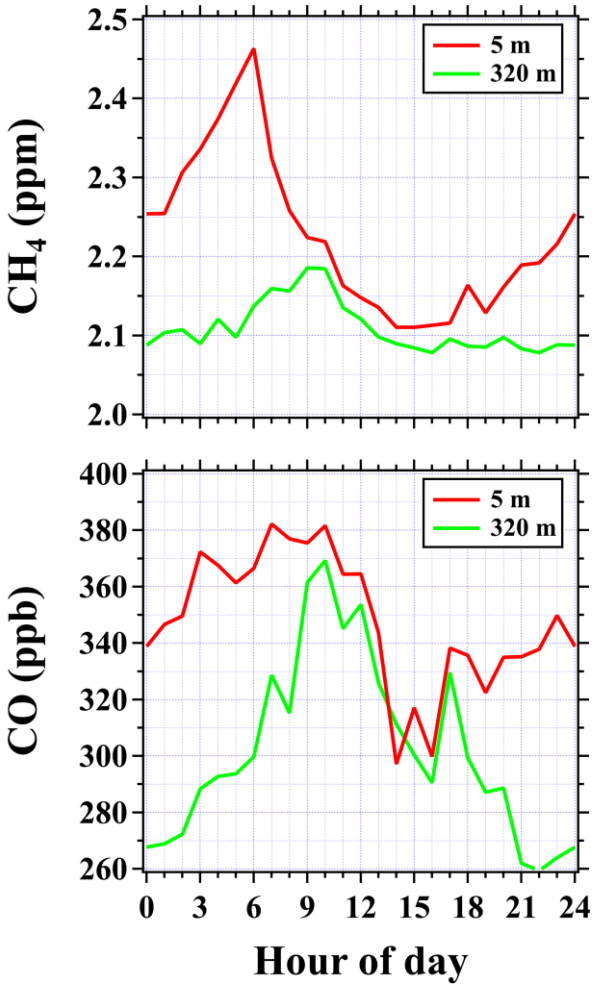

Figure S4. Average diurnal profiles of CH_4 and CO at 5 and 320 m on BMT during the campaign.

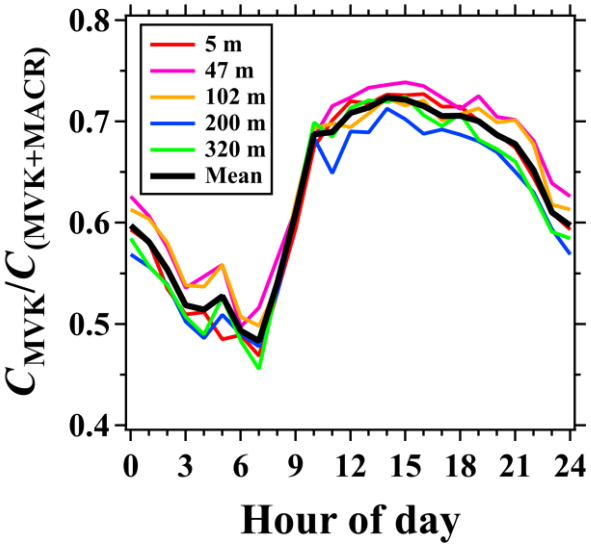

Figure S5. Average diurnal profiles of the concentration ratios of MVK to MVK+MACR (m/z 71, $C_4H_6OH^+$) at different altitudes measured by PTR-ToF-MS using the NO^+ mode from July 14 to August 4, 2021.

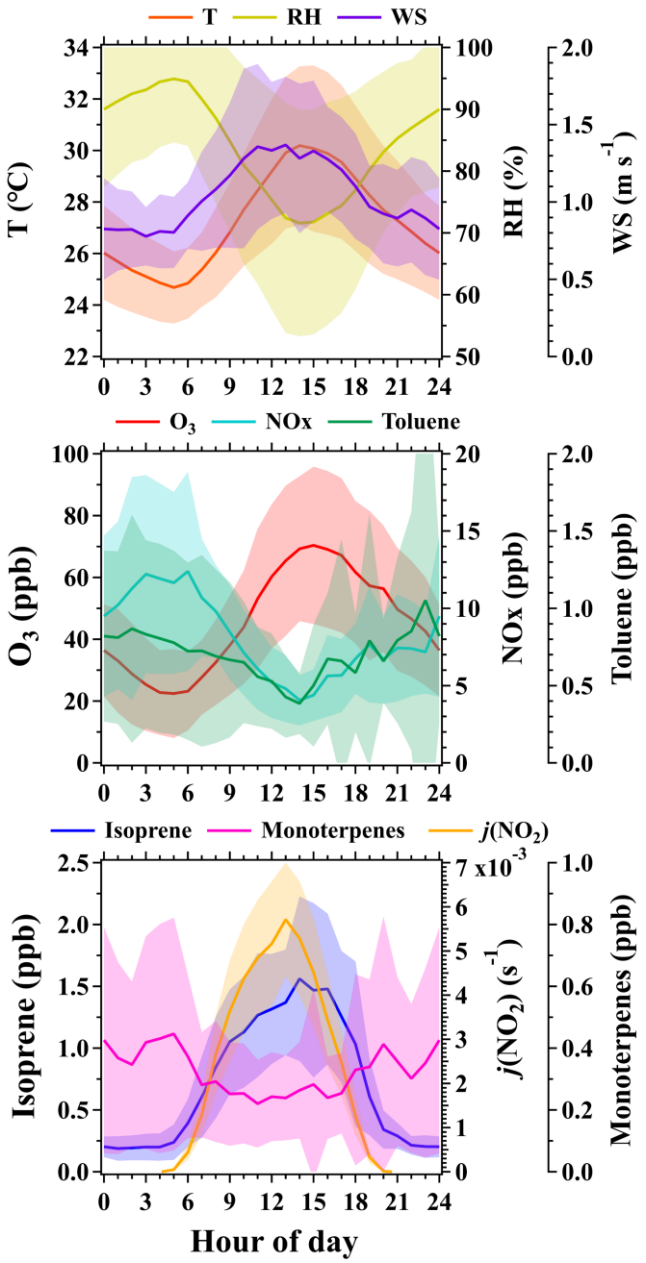

Figure S6. Average diurnal profiles of meteorological parameters, ozone, and precursor gases along with $j(NO_2)$ at ground level during the campaign.

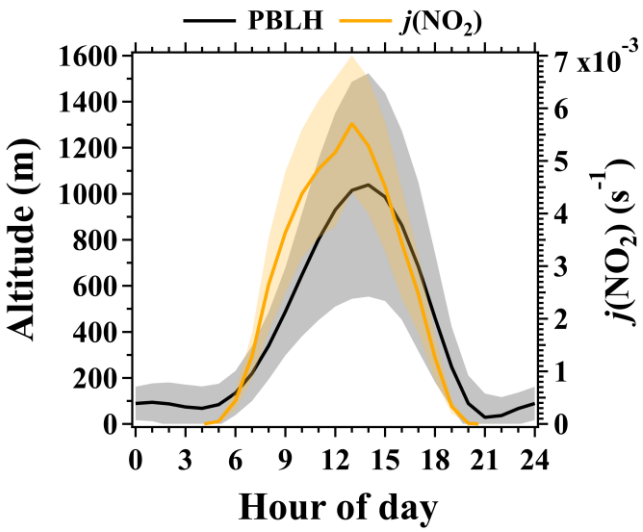

Figure S7. Average diurnal profiles of PBLH and $j(NO_2)$ at the BMT site during the campaign.