Supplement of Atmos. Chem. Phys., 25, 7467–7484, 2025
https://doi.org/10.5194/acp-25-7467-2025-supplement

Atmospheric Chemistry and Physics Open Access

Supplement of

Significant influence of oxygenated volatile organic compounds on atmospheric chemistry: a case study in a typical industrial city in China

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Text S1 Adjustments of model parameter

The base parameter settings of the OBM were shown in Sec 2.2. As formal studies have reported, PKU-Mo as a catalytic converter for NO_2 measurement can cause interferences from other nitrogen–oxygen compounds (e.g., PAN, HNO_3), which can lead to an overestimation NO_2 by 30%~50% (Kim et al., 2015; Tan et al., 2017, 2019; Xu et al., 2013). In addition, strong anthropogenic emissions (such as vehicle emissions) around these sites, the model might not be able to reach the steady state resulting in positive deviation (Li et al., 2014). Therefore, the observed NO_2 concentrations among those 5 sites were reduced by 30%~40% (40% for ZL and CQ, 30% for CD, TZ and XD) to compensate for interferences from catalytic converter (Xu et al., 2013), and NO steady-state approximations (NO_{ss}) was calculated (Equation (S1))(Del Negro et al., 1999; Jaeglé et al., 1994), which were then used for OBM inputs. Simulation constrained by all observed parameters including OVOCs and adjusted NO_2 and NO serves as the Base scenario. In order to investigate the impacts of model with OVOCs observationally constrained, scenario Free was conducted on top of the Base scenario by excluding observation constraints of OVOCs so that they were mainly generated by the oxidation of precursor VOCs in OBM. The time series plot of modeled and observed O_3 (Figure S6) and the model validation parameters were shown in Table S7. The modeled O_3 remain underestimate or overestimate at some times during the daytime, and significantly underestimate at night (Figure S6 (a)). This discrepancy may be due to the limitations of the 0-D model to express the transport processes in the atmosphere due to its simplification of atmospheric physical processes. The simplification of physical process is acceptable for modeling of in situ photochemistry.

$$NO_2 + h\nu \xrightarrow{R_1} NO + O \qquad \text{R1}$$

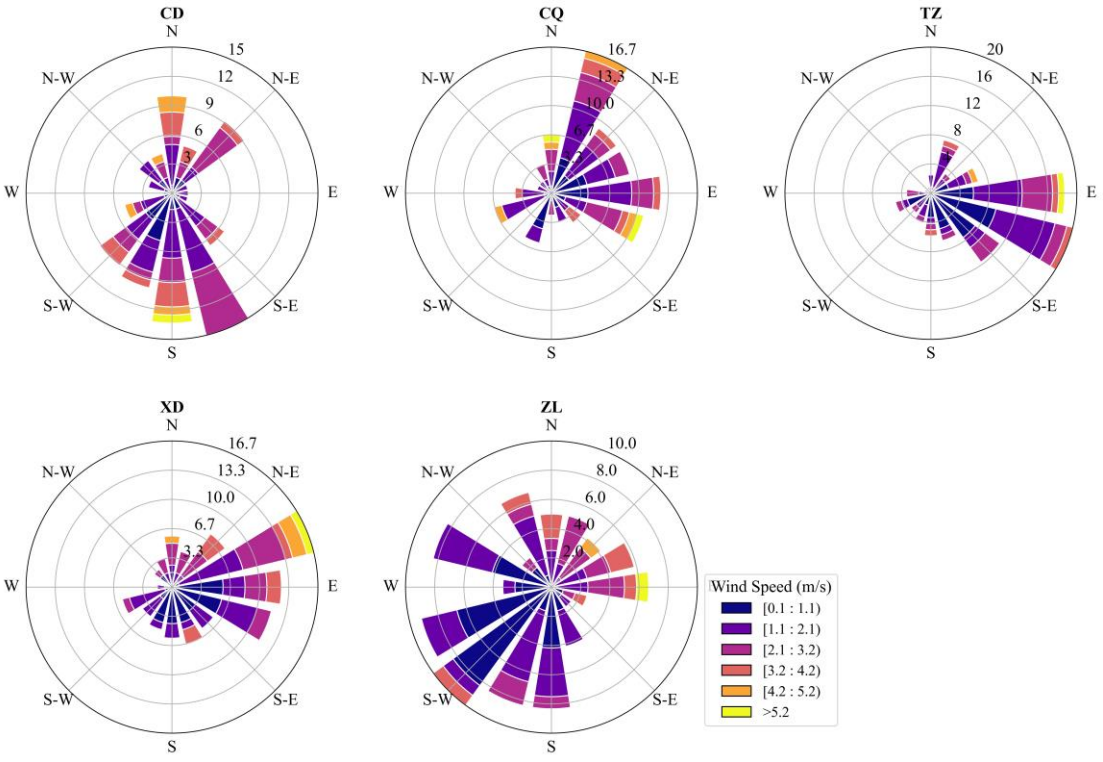
$$NO_2 + h\nu \xrightarrow{R_2} NO + O \qquad \text{R2}$$

$$[NO_{ss}] = \frac{J_{NO2} * [NO_2]}{k_{NO+O3} * [O_3]} \qquad \text{(S1)}$$

Where J_{NO2} represents the photolysis rate coefficient for reaction R1, k_{NO+O3} represents the reaction rate coefficient for the reaction R2, $[NO_{ss}]$, $[NO_2]$, and $[O_3]$ represents the mixing ratios of NO steady-state approximations, NO_2 and O_3, respectively.

Text S2 Simulations of OVOCs in the Free scenario

Similar to Base scenario but without OVOCs observationally constraints in the Free scenario, the hourly average concentration of OVOCs at five sites was 24.7±7.2 × 10^{-9}, with a 59.1% overpredict of observations (15.5±11.3 × 10^{-9}). OVOCs at CD (18.7±4.1 × 10^{-9}), CQ (26.3±6.6 × 10^{-9}), XD (24.7±7.0 × 10^{-9}), and ZL (32.1±6.2 × 10^{-9}) sites were overestimated in Free scenario by 81.4%, 88.4%, 42.1%, and 126.5%, respectively. The OVOCs concentrations in the atmosphere are subject to a combination of emission/transport, chemical process, and deposition. Given that direct emissions of OVOCs are not considered in the Free scenario, the OVOCs concentrations in the model are determined by the chemical process and deposition. In terms of the chemical production process, it can be influenced by the emission of precursor VOCs indirectly. It has shown that in the presence of strong emission sources of VOCs, the model might not be able to reach an steady state, leading to a significant overestimation (Li et al., 2014). The observed OVOCs at TZ during August 8 were unusually high due to transient emissions (Figure S6 (c)), pulling up the average levels. However, during the later days, the modeled OVOCs (15.5±10.7 × 10^{-9}) were also higher (15.3%) than the observed concentrations (13.4±11.5 × 10^{-9}) consisting with the other sites.



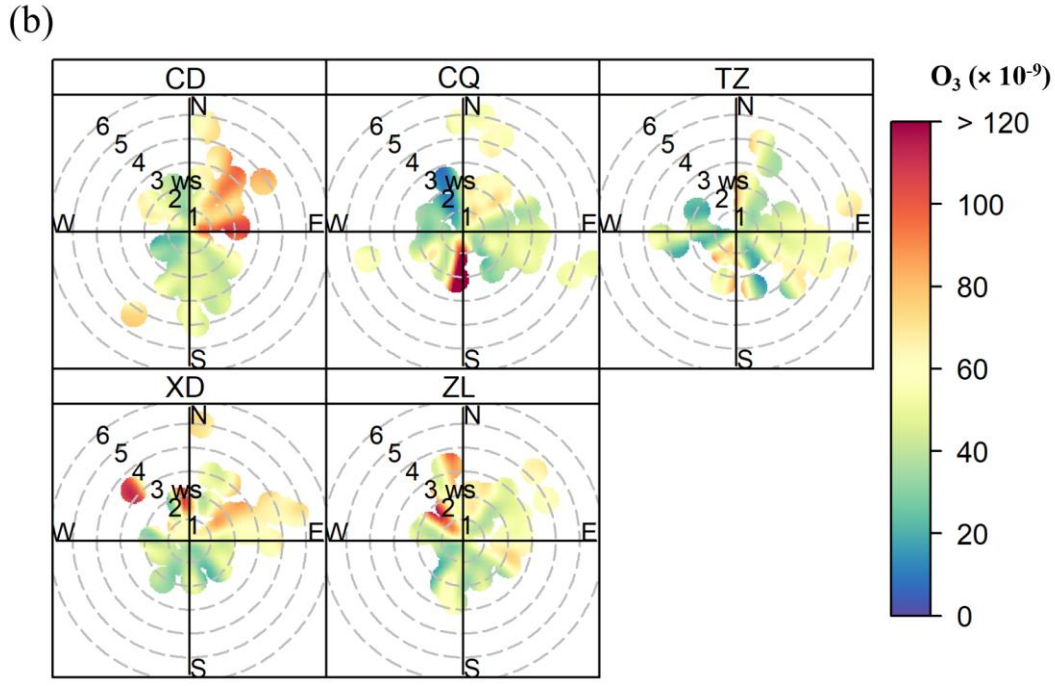


Figure S1 (a) Wind rose and (b) O_3 pollution rose diagram of each site during the observation period.

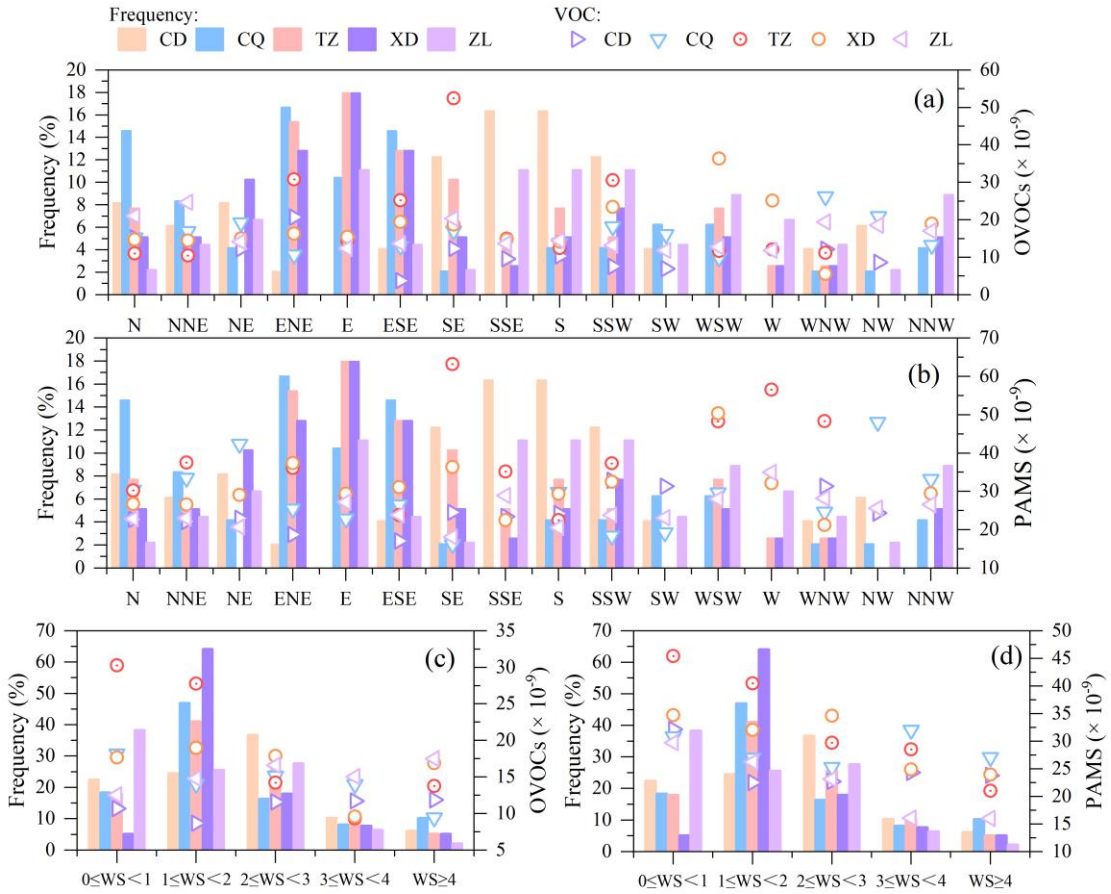
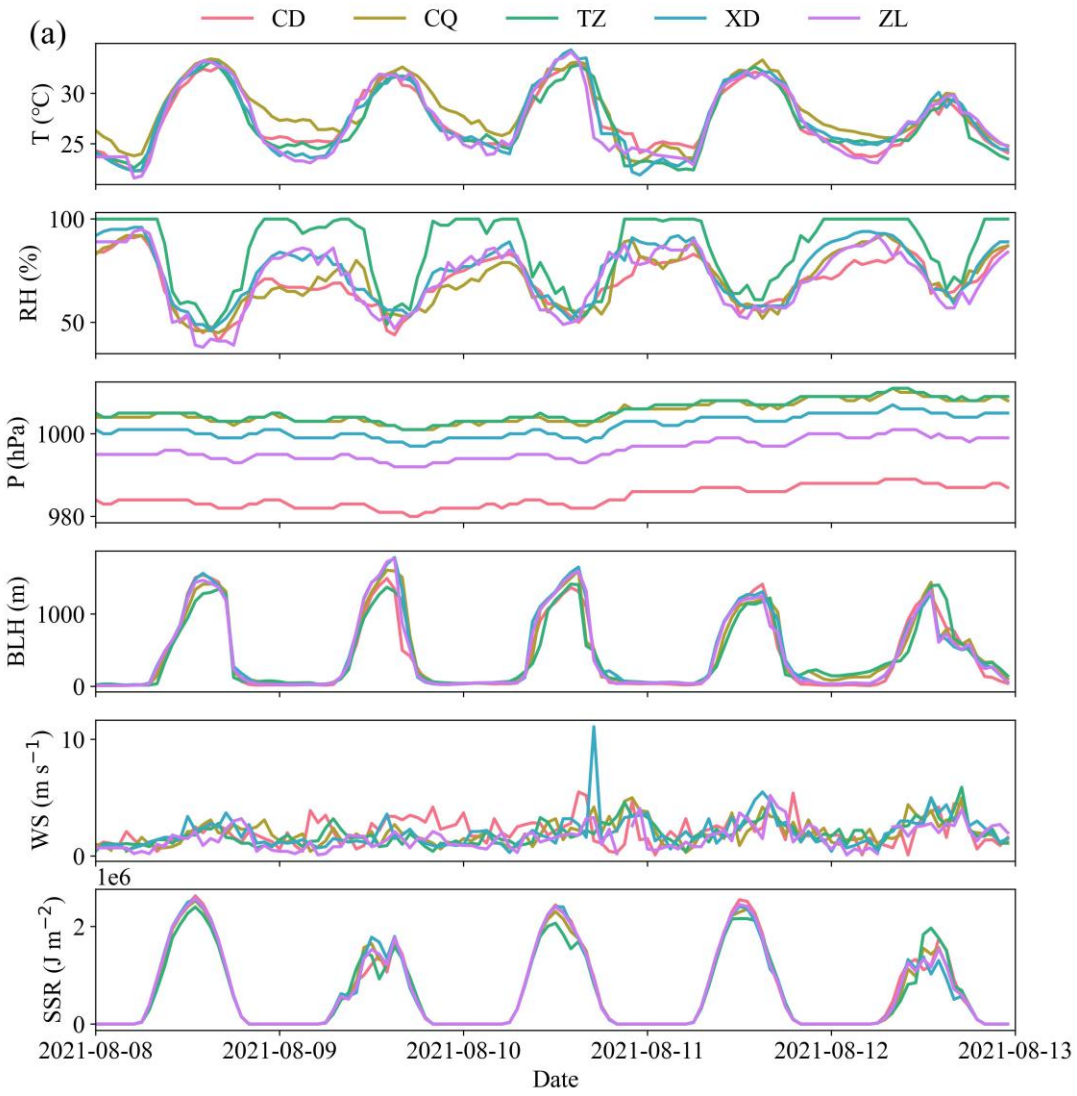
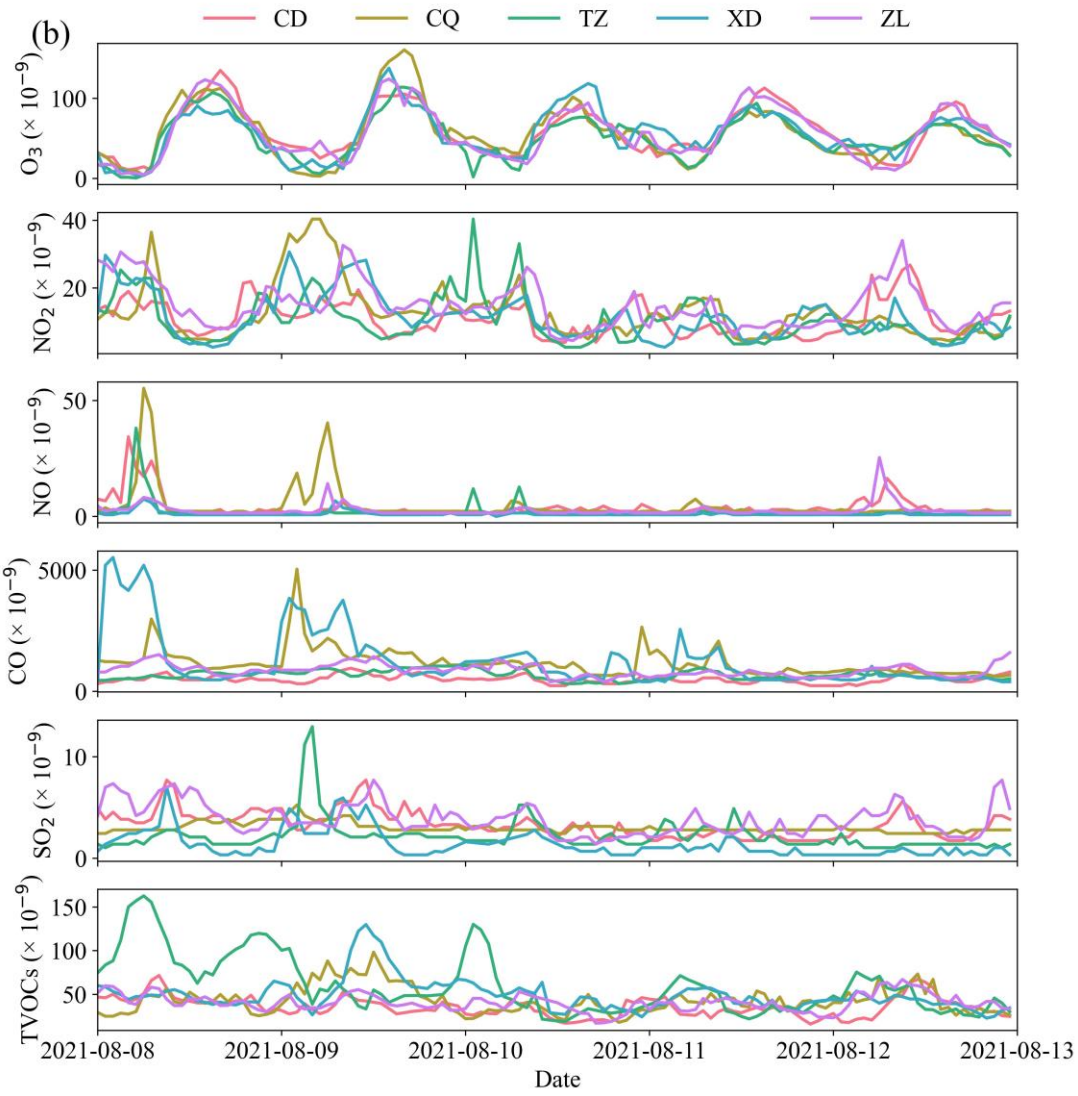


Figure S2 Concentration statistics of OVOCs (a, c) and PAMS (b, d) at different wind speed (WS) and wind direction (WD) intervals, respectively.


(a)
CD
CQ
TZ
XD
ZL
T (℃)
30
25
RH (%)
100
50
P (hPa)
1000
980
BLH (m)
1000
0
WS (m s^{-1})
10
0
1e6
SSR (J m^{-2})
2
0
2021-08-08
2021-08-09
2021-08-10
2021-08-11
2021-08-12
2021-08-13
Date

53



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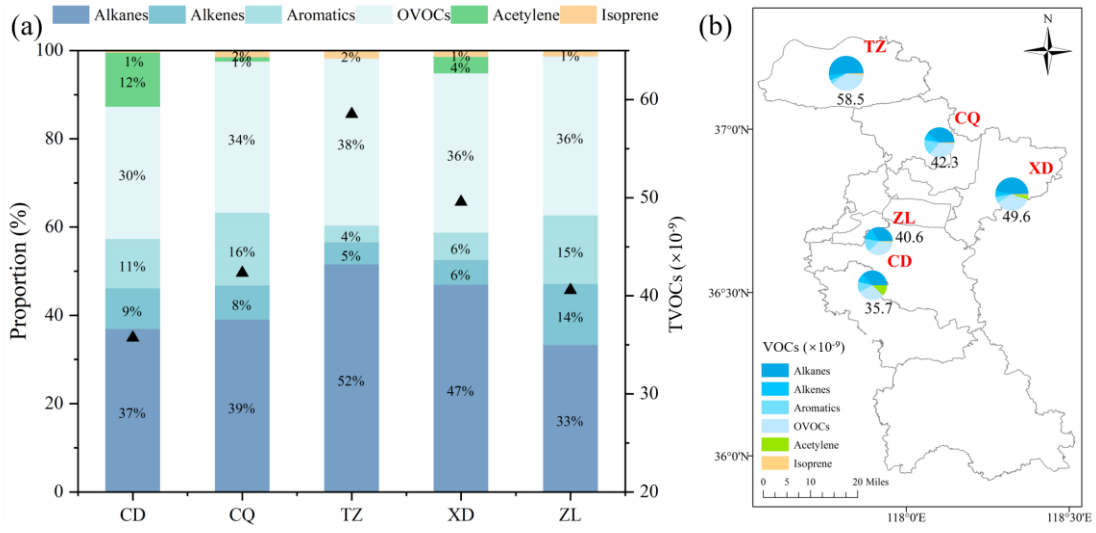
55 **Figure S3 Time series of (a) meteorological parameters and (b) major pollutant mixing**
56 **ratios at five sites in Zibo.**



57

58 **Figure S4 (a) Comparison and (b) spatial distribution of VOCs components among five sites.**

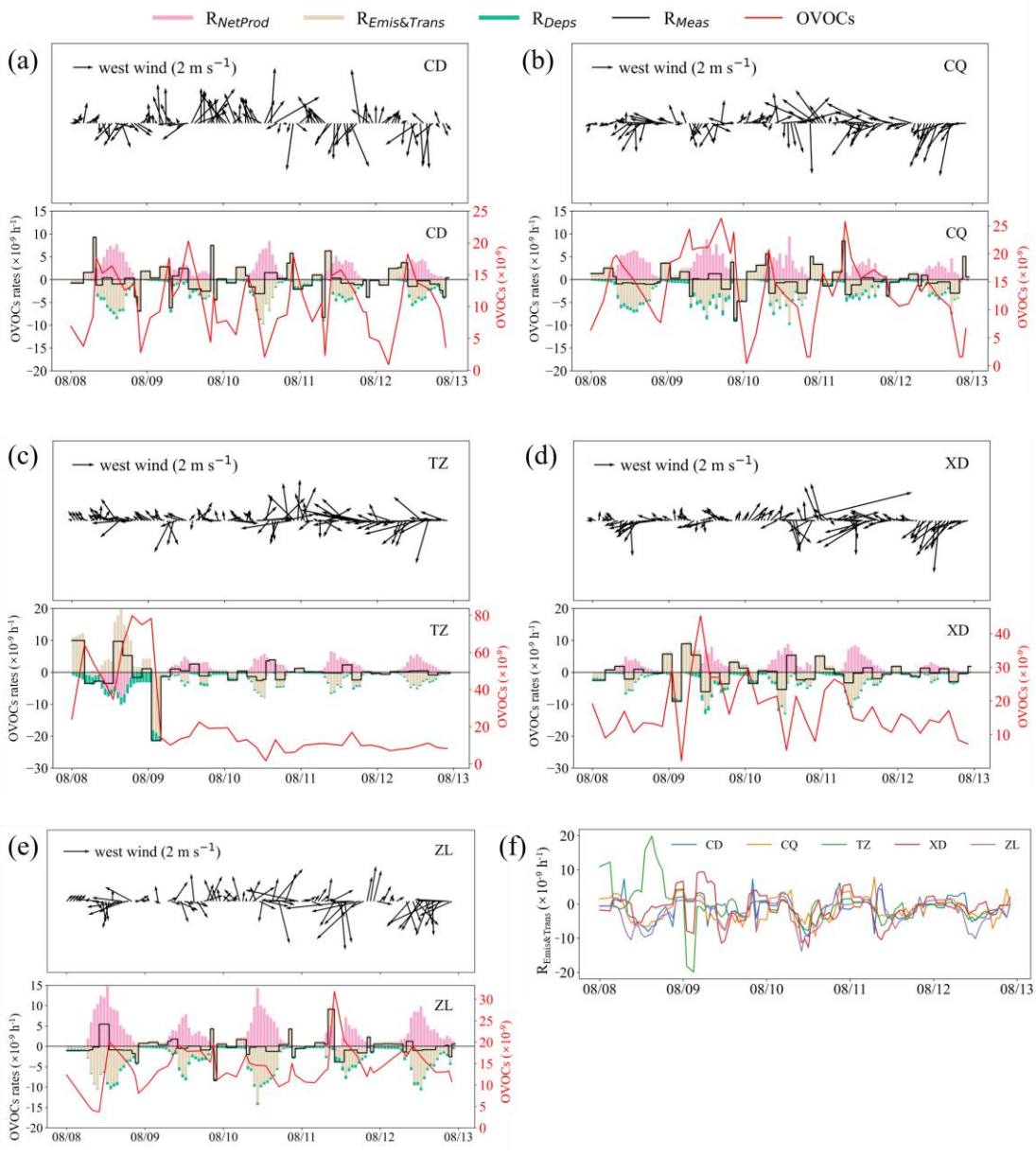


Figure S5 OVOCs accumulation and contributions from local net photochemical production and emissions/transport, and winds at (a) CD, (b) CQ, (c) TZ, (d) XD, and (e) ZL sites, respectively, and (f) time variations of $R_{Emis\&Trans}$ for all sites. $R_{NetProd}$, $R_{Emis\&Trans}$, R_{Deps} and R_{Meas} in the legend represent local net O_3 photochemical production, emissions and regional transport, deposition and observed OVOCs formation rates, respectively.

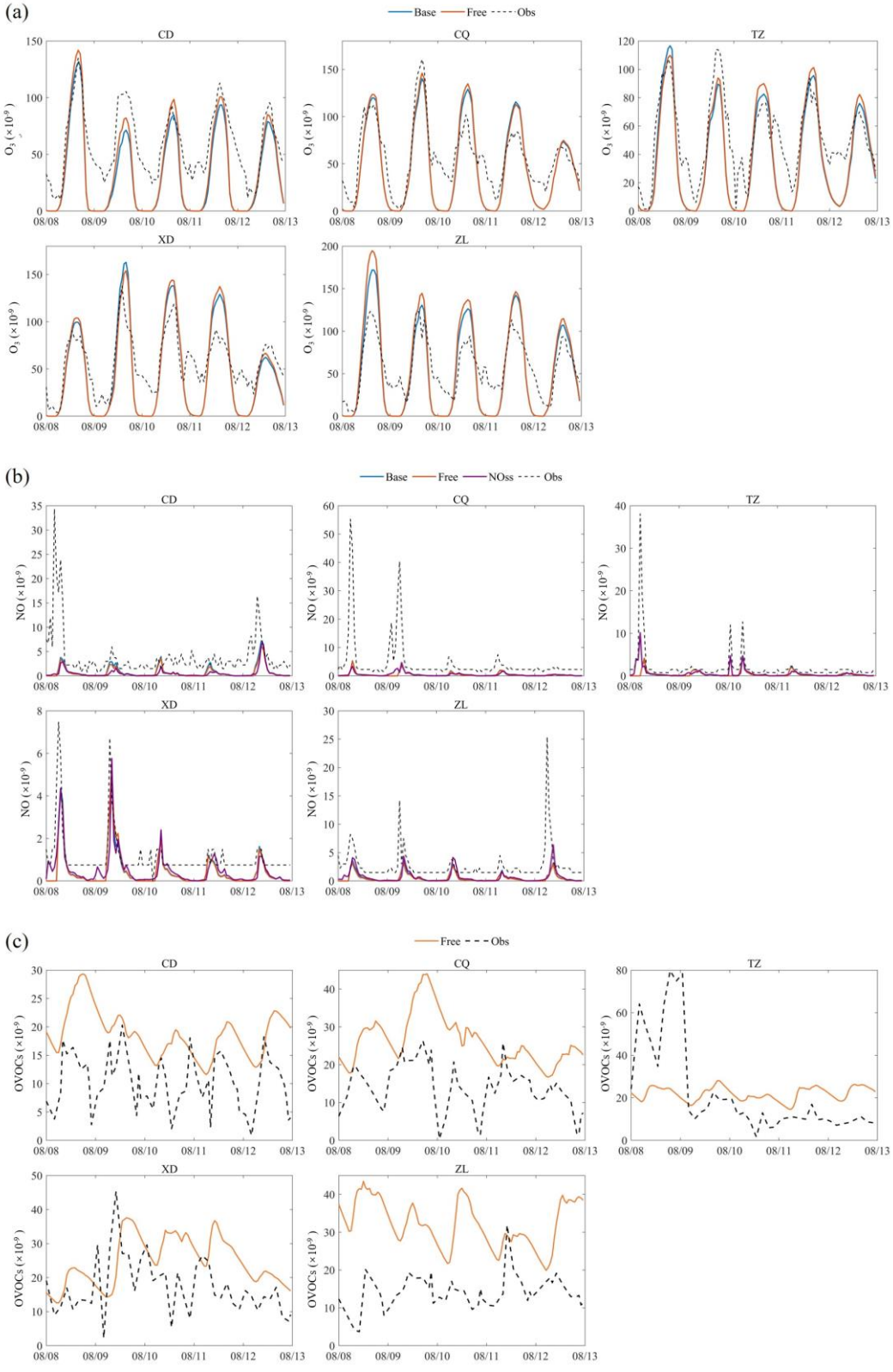


Figure S6 Time series mixing ratios of O_3, NO_x from observations (Obs), simulations (Base and Free scenarios) and NO steady state (NO_{ss}), and that of OVOCs only including input species from observation and Free scenario.

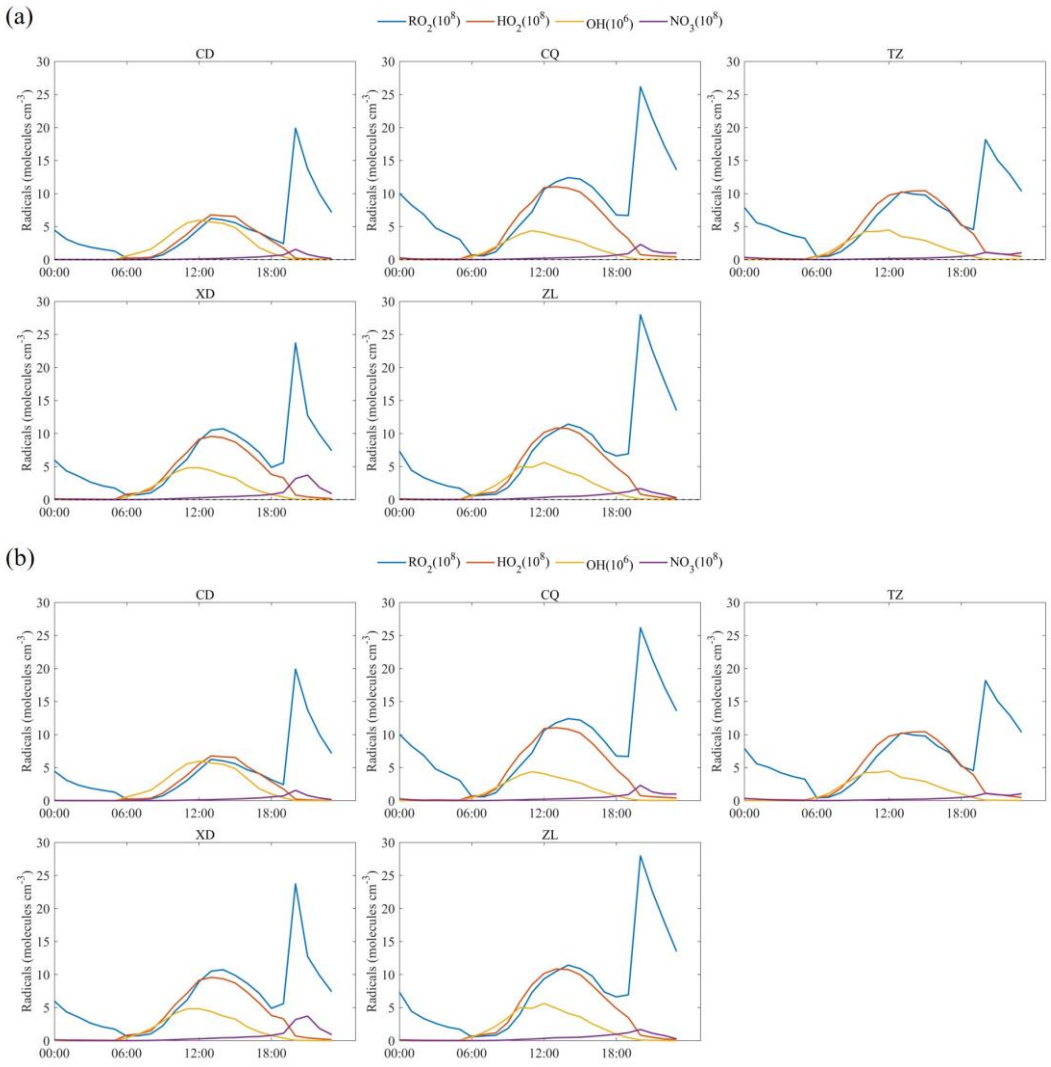


Figure S7 (a) Simulated average daytime variation of RO*x* (RO_2, HO_2, and OH) and NO_3 radicals at five sites, and (b) the effects of OVOCs observationally constrains on radical concentrations, calculated by (Free – Base).

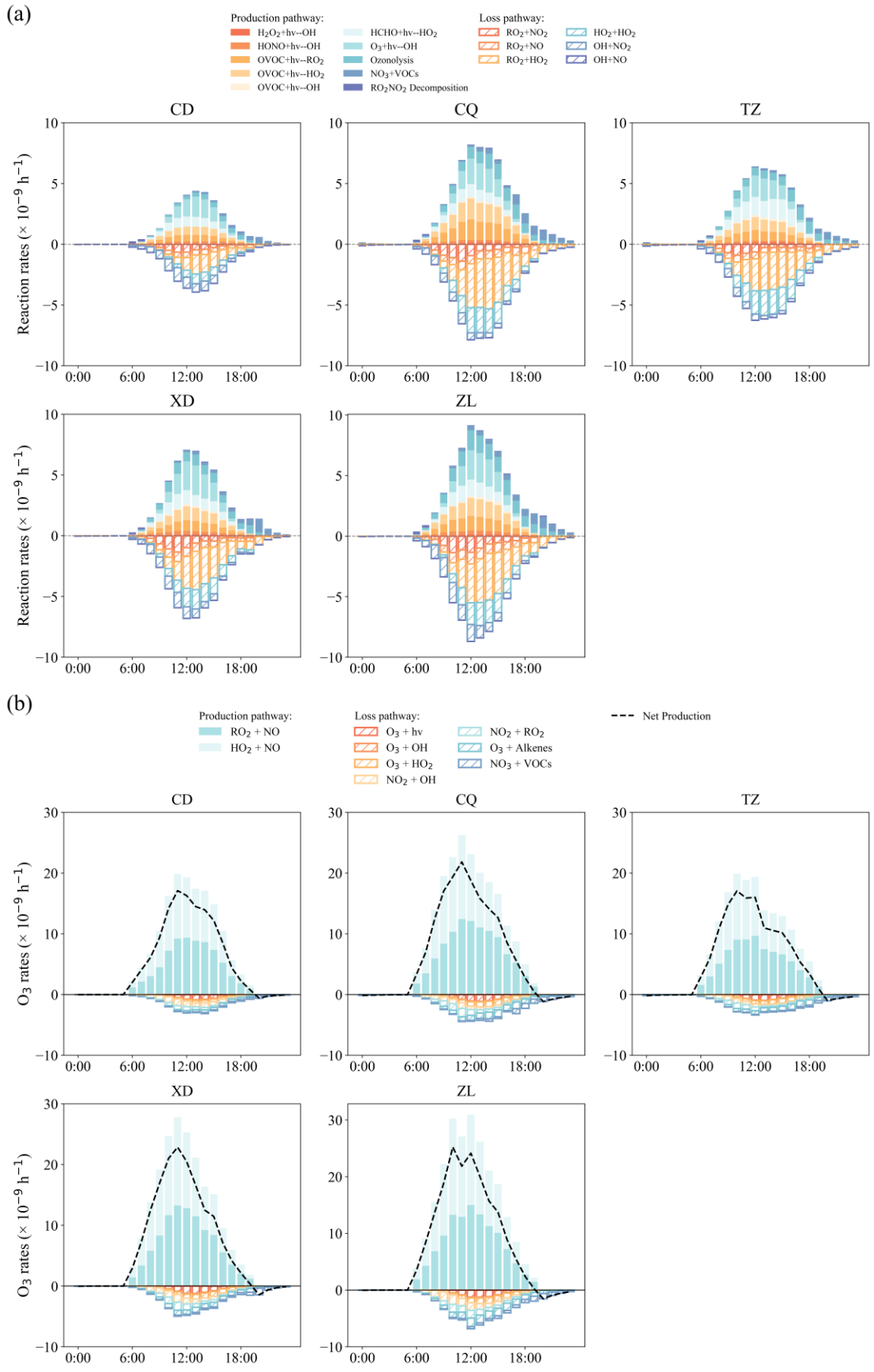


Figure S8 Average diurnal profiles of sources and sinks of (a) RO_x and (b) O_3 in the Base scenario.

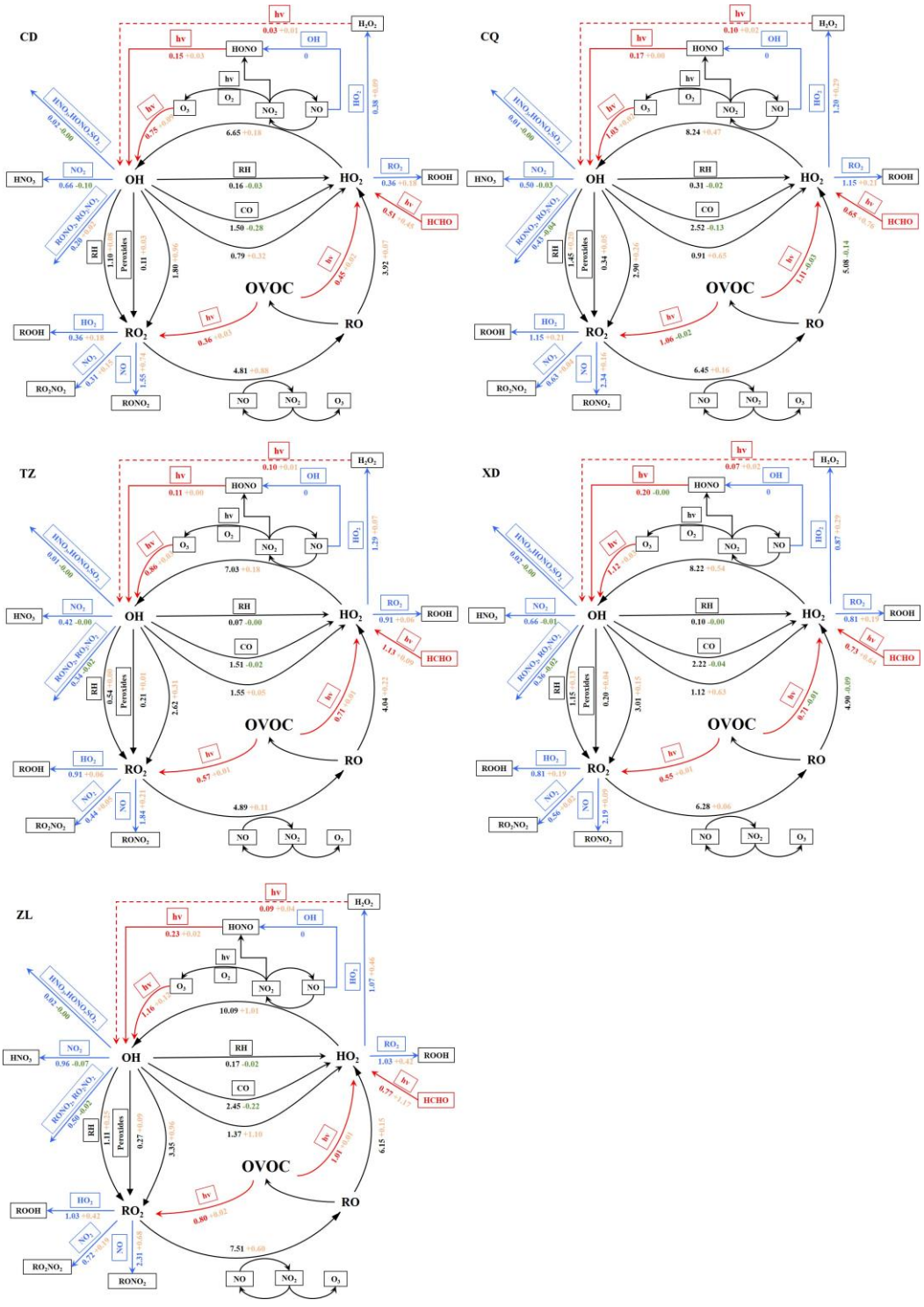


Figure S9 Daytime (8:00-18:00 LT) average budgets of RO_x radicals (in × 10^{-9} h^{-1}) at each site in Base scenario and the difference between Free and Base scenario. The first values were the rates of Base, followed by the difference between Free and Base, where '-' means that the rate of Free scenario is lower than that of Base (in green), and conversely '+' means that the rate of Free is higher than that of Base (in orange). Primary RO_x sources and sinks are in red and blue, respectively, and the black lines represent the processes in RO_x and NO_x recycling.

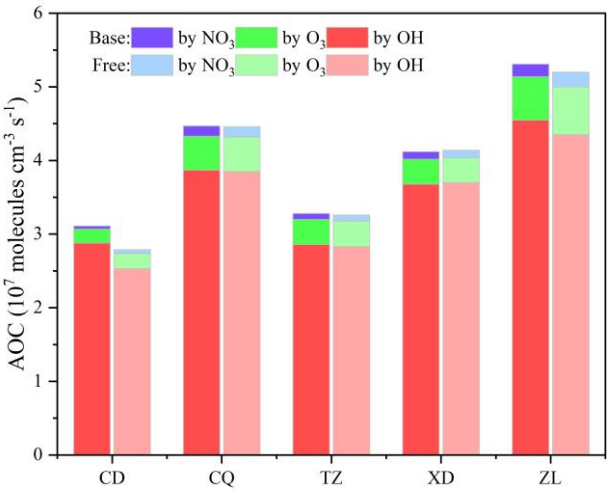


Figure S10 Comparison of daytime (8:00-18:00 LT) atmospheric oxidation capacity (AOC) between Base and Free scenario.

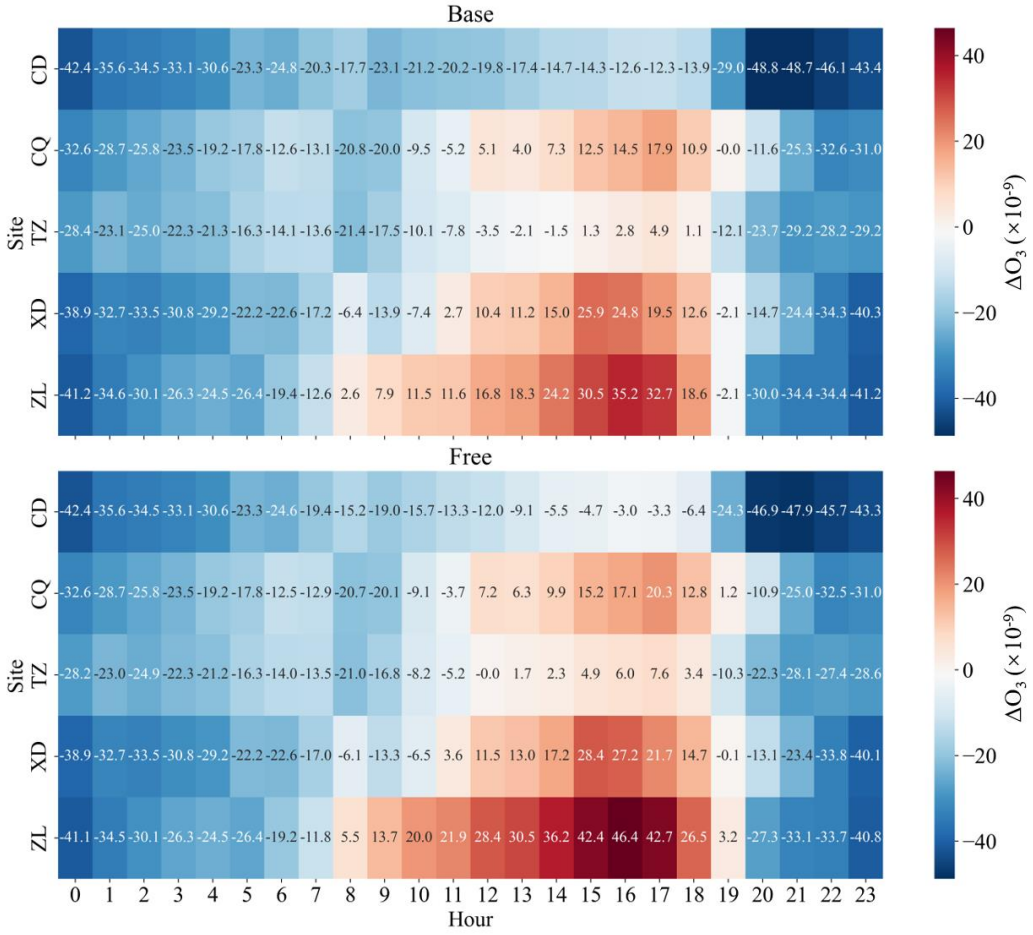
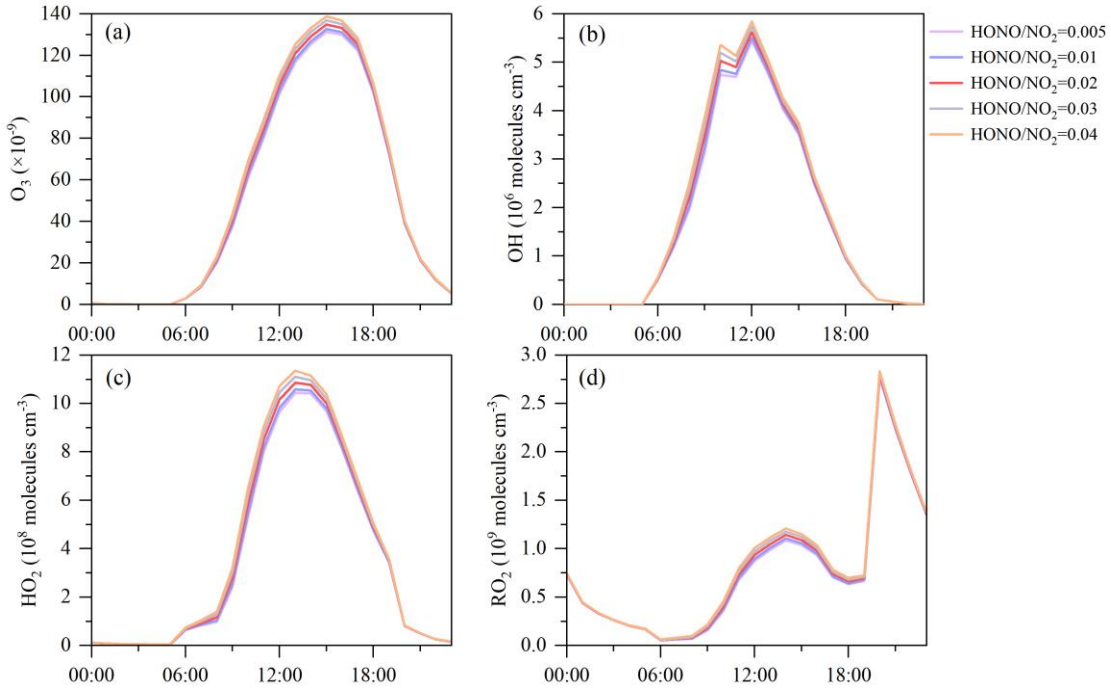
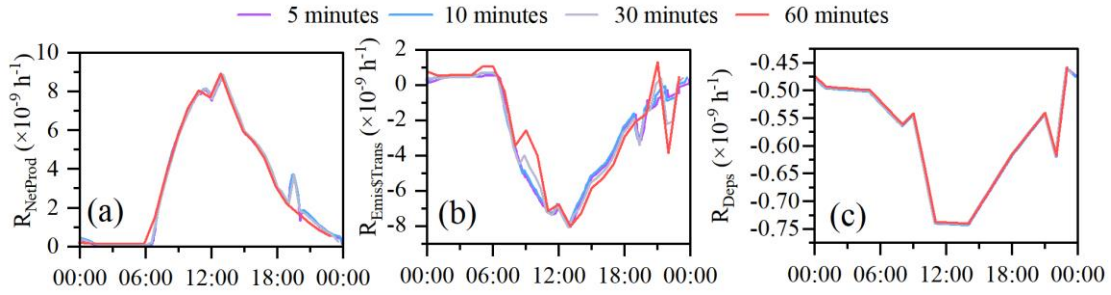


Figure S11 Heat map of O_3 concentration difference (ΔO_3 = Sim - Obs) between simulated and observed of Base and Free scenario



96

97 **Figure S12 Comparison of (a) O_3, (b) HO_2, (c) OH, (d) RO_2 concentrations under different**
98 **HONO/NO_2 ratios.**



99

100 **Figure S13 Comparison of $R_{NetProd}$, $R_{Emis\&Trans}$, and R_{Deps} contributed to OVOCs for different**
101 **time-step.**

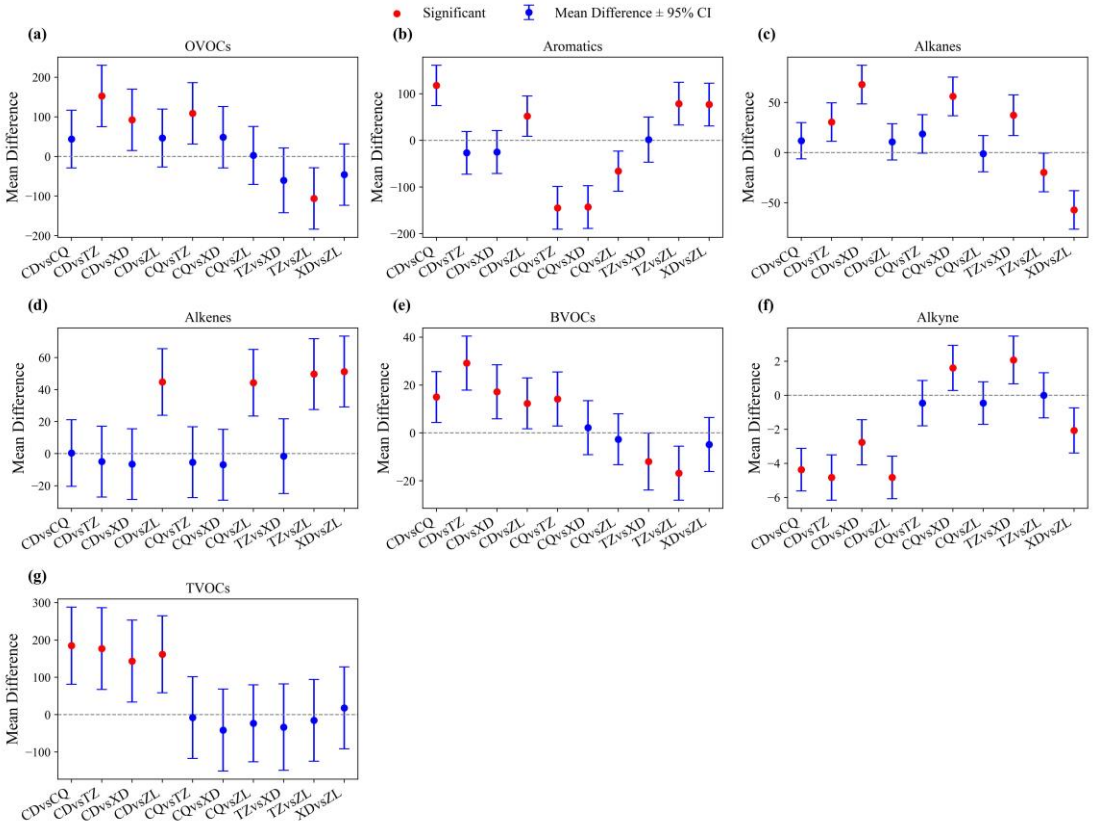


Figure S14 Comparison of Tukey honestly significant difference (HSD) tests for OFP of VOC and its subclasses between different sites. Blue Dots represent the mean difference between the two sites, blue error bar represents the 95th percentile confidence interval (CI), red dots indicate significant difference between the two sites.

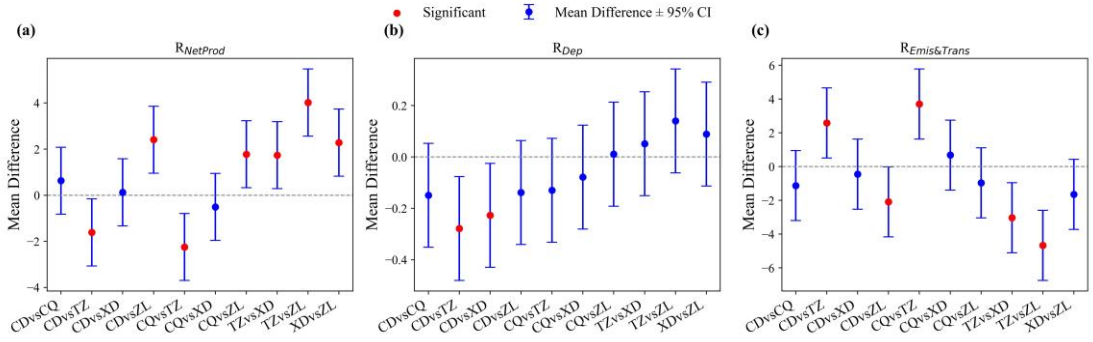


Figure S15 Tukey HSD tests for daytime (a) $R_{NetProd}$, (b) R_{Deps}, (c) $R_{Emis\&Trans}$ between sites.

Table S1 Location and site classification for the five different sites of Zibo

Site name	Site	Longitude	Latitude	Style	Meteorological sites
Chengdong	CD	117°53'E	36°31'N	Downwind	Boshan
Chengqu	CQ	118°60'E	36°57'N	Upwind	Huantai
Tianzhen	TZ	117°48'E	37°10'N	Suburban	Gaoqing
Xindian	XD	118°19'E	36°48'N	Industrial	Linzi
Zhonglou	ZL	117°54'E	36°39'N	Urban	Zichuan

Table S2 VOCs species and their names in Master Chemical Mechanism (MCMv3.3.1), minimum detection limits (MDL), and maximum incremental reactivity coefficient (MIR). "—" means that the species is not listed in the mechanism.

Species	MCM name	MDL ($\times 10^{-9}$)	MIR	Species	MCM name	MDL ($\times 10^{-9}$)	MIR
Alkanes				**BVOCs**			
Ethane	C2H6	0.079	0.28	Isoprene	C5H8	0.02	10.61
Propane	C3H8	0.046	0.49	**Alkynes**			
Isobutane	IC4H10	0.022	1.23	Acetylene	C2H2	0.032	0.95
n-Butane	NC4H10	0.027	1.15	**Aromatics**			
Cyclopentane	—	0.016	1.15	Benzene	BENZENE	0.012	0.72
Isopentane	IC5H12	0.087	2.39	Toluene	TOLUENE	0.013	4.00
n-Pentane	NC5H12	0.031	1.31	Ethylbenzene	EBENZ	0.014	3.04
2,2-Dimethylbutae	M22C4	0.014	1.17	m-Xylene	MXYL	0.027	9.75
2,3-Dimethylbutane	M23C4	0.019	0.97	Styrene	STYRENE	0.014	1.73
2-Methylpentane	M2PE	0.031	1.50	o-Xylene	OXYL	0.012	7.64
3-Methylpentane	M3PE	0.012	1.80	Isopropylbenzene	IPBENZ	0.014	2.52
n-Hexane	NC6H14	0.011	1.24	n-Propylbenzene	PBENZ	0.013	2.03
Methylcyclopentane	—	0.011	2.19	m-Ethyltoluene	METHTOL	0.032	7.39
2,4-Dimethylpentane	—	0.013	1.55	p-Ethyltoluene	PETHTOL	0.014	4.44
Cyclohexane	CHEX	0.016	1.25	1,3,5-Trimethylbenzene	TM135B	0.012	11.76
2-Methylhexane	M2HEX	0.012	1.19	1,2,4-Trimethylbenzene	TM124B	0.011	8.87
3-Methylhexane	M3HEX	0.013	1.61	1,2,3-Trimethylbenzene	TM123B	0.011	11.97
2,3-Dimethylpentane	—	0.013	1.34	o-Ethyltoluene	OETHTOL	0.013	5.59
2,2,4-Trimethylpentane	—	0.012	1.26	m-Diethylbenzene	—	0.011	7.10
n-Heptane	NC7H16	0.012	1.07	p-Diethylbenzene	—	0.011	4.43
Methylcyclohexane	—	0.011	1.70	**OVOCs**			

2,3,4-Trimethylpentane	—	0.013	1.03	Formaldehyde	HCHO	0.007	9.46
2-Methylheptane	—	0.013	1.07	Acetaldehyde	CH3CHO	0.016	6.54
3-Methylheptane	—	0.013	1.24	Acetone	CH3COCH3	0.009	0.36
n-Octane	NC8H18	0.012	0.90	Acrolein	ACR	0.008	7.45
n-Nonane	NC9H20	0.013	0.78	Propionaldehyde	C2H5CHO	0.026	7.08
n-Decane	NC10H22	0.011	0.68	Crotonaldehyde	C4ALDB	0.042	9.39
n-Undecane	NC11H24	0.018	0.61	Butanal	C3H7CHO	0.048	5.97
n-Dodecane	NC12H26	0.048	0.55	Benzaldehyde	BENZAL	0.055	-0.67
Alkenes				Cyclohexanone	CYHEXONE	0.058	1.35
Ethylene	C2H4	0.057	9.00	3-Methylbutyraldehyde	C3ME3CHO	0.058	4.97
Propylene	C3H6	0.022	11.66	Valeraldehyde	C4H9CHO	0.038	5.08
trans-2-Butene	TBUT2ENE	0.013	15.16	o-Tolualdehyde	OXYLAL	0.072	-0.59
1-Butene	BUT1ENE	0.023	9.73	m-Tolualdehyde	MXYLAL	0.089	-0.59
cis-2-Butene	CBUT2ENE	0.016	14.24	Hexaldehyde	C5H11CHO	0.060	4.35
trans-2-Pentene	TPENT2ENE	0.012	10.56	Heptaldehyde	C6H13CHO	0.034	3.69
1-Pentene	PENT1ENE	0.093	7.21	Octanal	—	0.029	3.16
cis-2-Pentene	CPENT2ENE	0.011	10.38	Nonanal	—	0.032	0.00
1-Hexene	HEX1ENE	0.014	5.49	Decanal	—	0.035	0.00

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Table S3 Uncertainty in sensitive model runs performed with different NO_x settings

Parameter	Site	Corrected $[NO_2]$ [a] and $[NO_{ss}]$ [b] (the Base scenario) ($\times\ 10^{-9}$ or $\times\ 10^{-9}\ h^{-1}$) [c]	Changes based on the Base scenario				
			0.5*$[NO_2]$	0.6*$[NO_2]$	0.7*$[NO_2]$	$[NO_2]$	corrected $[NO_2]$ and NO_{obs} [d]
Daytime O_3	CD	60.9	-6.9%	-2.8%	—	2.8%	5.3%
	CQ	82.4	-8.3%	—	7.4%	25.1%	19.2%
	TZ	66.2	-15.3%	-7.3%	—	18.2%	8.4%
	XD	85.2	-12.1%	-5.6%	—	12.0%	2.9%
	ZL	96.8	-5.9%	—	4.8%	13.9%	7.5%
Daytime $R_{NetProd}$	CD	3.5	-10.2%	-4.4%	—	6.0%	8.7%
	CQ	4.1	-11.5%	—	10.3%	35.9%	27.1%
	TZ	1.9	-30.9%	-14.7%	—	36.7%	17.0%
	XD	3.6	-17.2%	-7.9%	—	17.4%	4.4%
	ZL	5.9	-7.2%	—	5.8%	17.1%	9.8%
$R_{Emis\&Trans}$	CD	-1.3	-13.6%	-5.9%	—	8.2%	10.8%
	CQ	-1.5	-16.0%	—	14.5%	51.3%	37.6%
	TZ	-0.2	-122.4%	-58.1%	—	146.2%	67.2%
	XD	-1.2	-26.9%	-12.5%	—	28.1%	7.1%
	ZL	-2.5	-9.1%	—	7.5%	22.5%	12.2%

Note: [a] $[NO_2]$ represents the mixing ratios of NO_2, the corrected $[NO_2]$ of CD, TZ and XD are 0.7*$[NO_2]$, and those of CQ and ZL are 0.6*$[NO_2]$ (Text S1). [b] NO_{ss} and NO_{obs} [d] represent the mixing ratios of NO steady-state approximations and observed NO, respectively. [c] The $\times\ 10^{-9}$ is for O_3, and $\times\ 10^{-9}\ h^{-1}$ for $R_{NetProd}$ and $R_{Emis\&Trans}$.

117 **Table S4 Comparison of VOC mixing ratios and compositions in this study with former studies. Unit is 10^{-9}.**

City	Site	Type	Period	Species	TVOCs	Alkanes	Alkenes	Aromatics	Acetylene	OVOCs	Halocarbons	References
Zibo	CD	Downwind	August 8-13, 2021	74	35.3	13.4	3.4	4.1	4.0	10.4		This study
	CQ	Upwind			42.6	16.9	3.9	7.5	0.5	13.9		
	TZ	Suburban			55.1	29.4	3.8	2.1	0.0	19.7		
	XD	Industrial			47.0	22.3	3.4	2.9	1.6	16.8		
	ZL	Urban			41.3	14.3	5.8	6.2	0.0	14.9		
	TZ	Suburban	High-O_3 episodes in July 2019	56	58.1	43.8	3.7	5.5	3.1			(Li et al., 2021)
	BJ	Urban			23.8	13.8	3.2	3.7	2.4			
	XD	Suburban			38.1	22.5	7.8	3.4	3.2			
Qingdao		Rural	October 5 to November 10, 2018	106	7.6	4.7	1.6	0.6	0.2	0.4		(Liu et al., 2021a)
Rizhao		Urban	December 2021 to October 2022	111	19.7	8.6	2.1	1.4	0.7	4.0	3.6	(Zhang et al., 2023)
Jinan		Downtown	June 2010 to May 2012	55	25.3	14.3	7.0	4.0				(Wang et al., 2016)
Shanxi	LL	Urban	2019-2020	115	44.4	19.4	5.3	4.5	1.8	10.8	2.7	(Liu et al., 2023)
	LF				45.7	14.3	9.1	3.2	2.9	13.2	2.6	
	YC				37.5	13.9	5.9	2.4	3.1	9.6	2.7	
Beijing		Urban	2018	99	29.1	12.4	2.9	2.1	2.1	6.4	3.0	(Li et al., 2022)
Tianjing		Suburban	November 1, 2018 to March 15, 2019	54	30.6	17.3	6.5	3.9	2.9			(Gu et al., 2020)
Xianghe		Suburban	August 7-25, 2018	65	28.1	13.5	3.1	6.0		5.5		(Yang et al., 2021)
			December 1, 2018 to January 5, 2019		58.0	28.6	9.8	8.3		11.3		

City	Site	Type	Period	Species	TVOCs	Alkanes	Alkenes	Aromatics	Acetylene	OVOCs	Halocarbons	References
Wangdu	WD	Rural	2014 and 2016(June–July)	17	52.4					46.9		(Han et al., 2019)
Shenzhen	YMK	Rural			11.1					8.2		
Heshan		Suburban	October 20 to November 22, 2014	56	46.6	19.7	5.6	9.1		12.3		(Yang et al., 2017)
Beijing		Urban	August 10-27, 2013		50.4	23.8	5.6	9.1		11.9		
Zhengzhou		Urban	May 3-24, 2018	103	29.1	9.0	3.1	1.6		9.1	6.0	(Li et al., 2020)
Zhengzhou		Urban	July 2019	106	38.6	15.9	2.0	4.5	2.2	6.2	7.1	(Wang et al., 2022)
Xi'an		Whole city	June 20 to July 20, 2019	99	29.1	10.4	3.0	1.8	1.3	9.3	3.2	(Song et al., 2021)
Shanghai		Urban	2017.12.5-2018.1.15	113	63.6	26.2	6.8	7.3	3.2	14.9	5.1	(Liu et al., 2021b)
Ningde		Urban	March-May, 2019	94	25.0	15.0	3.0	1.6	2.0	1.7	1.7	(Chen et al., 2024)
			June-August, 2019		20.0	9.5	2.6	1.5	1.4	3.0	1.9	
			September-November, 2019		22.4	12.2	2.3	1.9	1.4	2.1	2.5	
			January-February, 2019		36.5	22.3	4.1	2.5	3.1	2.3	2.1	
Fujian	Mt. Wuyi	Background	August-October 2016	70	6.1	1.9	1.1	1.3			1.8	(Hong et al., 2019)
	XM	Urban		70	17.9	9.1	2.1	4.1			2.6	
	FZ	Urban		70	14.1	6.8	1.7	3.1			2.5	
Shenzhen	SZ-U	Urban	December 2017	18	35.7			8.6		26.2		(Huang et al., 2019)
	NA-R	Regional	December 20, 2015 to January 15, 2016		13.5			4.1		8.7		
	NL-B	Background	October 31, 2016 to November 14, 2016		8.2			0.9		6.5		

City	Site	Type	Period	Species	TVOCs	Alkanes	Alkenes	Aromatics	Acetylene	OVOCs	Halocarbons	References
Chongqing	JYS	Urban	August-September 2015	96	23.0	6.1	1.4	16.1	1.8	6.8	4.9	(Li et al., 2018)
	CJZ	Urban		96	49.9	17.7	7.1	5.8	5.2	7.6	4.8	
	NQ	Urban		96	34.1	12.9	4.1	4.6	3.8	5.1	3.1	
Chengdu		Urban	October 2016 to September 2017	55	41.8	23.6	8.2	7.2	2.7			(Song et al., 2018)
Chengdu		Whole city	May 2016 to January 2017	99	57.5	22.4	5.8	5.9	4.3	12.6	6.0	(Simayi et al., 2020)
Wuhan		Urban	January 2021	106	37.4	13.8	5.4	4.0	4.2	5.3	4.8	(Xu et al., 2023)
Wuhan		Urban	September 2016 to August 2017	102	34.7	15.9	4.2	3.2	2.4	4.9	3.7	(Hui et al., 2018)
Shenyang		Urban	August 20 to September 16, 2017	58	40.4	28.5	6.3	5.6		9.8		(Ma et al., 2019)

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Table S5 Measured mixing ratios, ozone formation potential from VOC species and groups.

Species/Groups	VOC mixing ratios (mean±std) ($\times 10^{-9}$)					OFP (mean±std) ($\mu g\ m^{-3}$)				
	CD	CQ	TZ	XD	ZL	CD	CQ	TZ	XD	ZL
TVOCs	35.7±12.5	42.3±15.4	58.5±35.0	49.6±19.0	40.6±10.3	279.4±101.2	464.2±162.3	456.3±295.3	422.9±166.9	441.1±174.5
Alkanes	13.2±6.2	16.5±8.5	30.2±21.0	23.3±11.2	13.5±5.6	36.0±19.3	47.8±25.4	66.5±39.9	103.9±51.7	46.7±21.9
Alkenes	3.3±1.8	3.3±1.6	2.9±1.7	2.8±1.3	5.6±3.0	57.1±30.4	57.5±30.5	52.1±30.8	50.6±27.2	101.8±56.8
Aromatics	4.0±1.7	7.0±3.6	2.2±1.2	3.1±1.5	6.3±4.7	73.4±29.1	191.3±111.3	46.6±24.8	48.4±23.0	125.3±116.2
OVOCs	10.7±5.0	14.5±6.7	22.1±22.5	17.9±8.5	14.6±4.8	102.3±51.2	146.2±70.7	254.9±276.1	194.7±101.0	148.9±55.7
Acetylene	4.4±4.1	0.4±0.7	0.0±0.0	1.9±1.6	0.0±0.0	4.8±4.5	0.5±0.8	0.0±0.1	2.1±1.7	0.0±0.1
Isoprene	0.2±0.2	0.6±0.6	1.1±0.8	0.7±0.5	0.6±0.7	5.8±7.7	20.8±17.8	34.9±25.8	23.0±16.3	18.1±23.6
Benzene	1.0±0.5	0.3±0.2	0.2±0.3	1.1±0.6	1.2±0.5	2.4±1.3	0.6±0.4	0.4±0.7	2.7±1.5	3.0±1.3
Toluene	1.2±0.5	1.2±0.9	1.4±1.0	0.9±0.5	1.6±1.3	19.3±7.5	20.0±15.2	23.6±15.9	14.5±8.2	25.8±21.4
Ethylbenzene	0.3±0.2	0.4±0.5	0.1±0.1	0.2±0.1	0.7±0.3	4.4±2.7	6.3±7.7	0.9±0.8	3.0±1.0	9.5±4.8
m-Xylene	0.4±0.2	1.2±1.2	0.1±0.1	0.4±0.2	0.3±0.1	17.2±9.0	53.8±56.1	3.6±2.6	16.7±8.0	12.5±5.9
Styrene	0.5±0.4	0.8±1.1	0.1±0.0	0.3±0.3	0.6±0.4	3.7±3.4	6.8±8.5	0.6±0.3	2.3±2.5	4.6±3.0
o-Xylene	0.2±0.1	0.7±0.8	0.1±0.0	0.1±0.1	1.5±2.2	6.0±3.9	23.6±29.3	2.1±1.4	5.1±2.4	53.2±79.4
Isopropylbenzene	0.0±0.1	0.4±0.5	0.0±0.1	0.0±0.1	0.2±0.1	0.2±0.4	5.3±6.9	0.2±0.3	0.1±0.2	2.8±1.7
n-Propylbenzene	0.0±0.1	0.4±0.5	0.0±0.1	0.0±0.1	0.0±0.1	0.5±0.4	4.0±5.3	0.1±0.3	0.2±0.4	0.0±0.1
m-Ethyltoluene	0.1±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.1	4.1±1.8	0.0±0.1	1.0±1.2	1.0±1.5	0.3±0.6
p-Ethyltoluene	0.0±0.1	0.3±0.3	0.0±0.1	0.0±0.1	0.1±0.1	1.0±0.6	7.1±6.6	0.3±0.5	0.0±0.1	1.3±1.8
1,3,5-Trimethylbenzene	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.0±0.1	2.6±2.3	13.6±15.3	1.2±2.0	0.0±0.1	0.0±0.1
1,2,4-Trimethylbenzene	0.1±0.1	0.3±0.3	0.2±0.1	0.0±0.1	0.0±0.1	2.6±3.1	13.7±13.4	7.4±3.6	2.3±2.4	0.2±0.7
1,2,3-Trimethylbenzene	0.0±0.1	0.3±0.3	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.0	18.1±17.2	3.1±2.1	0.0±0.1	6.5±4.9
o-Ethyltoluene	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.0±0.1	1.2±1.4	7.0±7.0	0.8±0.8	0.6±0.9	0.7±0.9
m-Diethylbenzene	0.1±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.1±0.1	6.0±2.6	7.2±10.2	1.1±1.5	0.0±0.1	2.4±2.9

Species/Groups	VOC mixing ratios (mean±std) (× 10^{-9})					OFP (mean±std) (μg m^{-3})				
	CD	CQ	TZ	XD	ZL	CD	CQ	TZ	XD	ZL
p-Diethylbenzene	0.1±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.1±0.1	2.0±1.4	4.1±5.5	0.3±0.5	0.0±0.1	2.7±1.1
Ethylene	1.4±1.2	1.8±0.9	1.6±1.2	1.4±0.6	2.7±1.4	15.5±13.6	20.4±9.6	17.9±13.1	15.3±6.7	29.9±15.3
Propylene	0.4±0.4	0.9±0.7	0.7±0.5	0.6±0.4	1.6±1.5	8.8±8.0	20.7±15.6	14.6±11.8	12.5±8.2	36.0±33.9
trans-2-Butene	0.1±0.1	0.0±0.1	0.0±0.1	0.2±0.2	0.4±0.2	2.0±2.4	0.0±0.1	1.6±2.5	6.5±7.8	14.0±8.5
1-Butene	0.0±0.1	0.0±0.1	0.0±0.1	0.1±0.2	0.2±0.2	1.2±1.6	1.0±1.1	1.0±1.7	3.2±4.1	5.0±3.7
cis-2-Butene	0.0±0.1	0.3±0.2	0.0±0.1	0.1±0.1	0.1±0.1	0.7±1.9	10.2±8.0	0.3±0.8	3.7±4.8	2.3±4.0
trans-2-Pentene	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.1	0.0±0.1	0.7±1.5	1.0±1.3	2.0±2.5	0.1±0.3	0.0±0.1
1-Pentene	0.0±0.1	0.1±0.1	0.0±0.1	0.0±0.1	0.2±0.2	0.2±0.7	1.8±1.3	0.9±1.6	0.5±0.6	3.9±4.8
cis-2-Pentene	0.0±0.1	0.1±0.1	0.3±0.3	0.0±0.1	0.0±0.1	0.0±0.1	1.9±3.2	10.6±9.5	0.3±0.9	0.6±1.4
1-Hexene	1.4±1.0	0.0±0.1	0.2±0.2	0.4±0.7	0.5±0.4	28.1±20.3	0.4±0.6	3.2±3.5	8.4±13.7	10.1±8.9
Ethane	4.0±1.5	3.3±1.6	4.4±3.9	2.4±0.8	0.0±0.1	1.5±0.6	1.2±0.6	1.7±1.5	0.9±0.3	0.0±0.1
Propane	2.8±1.7	3.9±2.4	13.3±11.1	4.1±2.3	3.2±0.8	2.7±1.6	3.7±2.3	12.8±10.7	4.0±2.2	3.1±0.8
Isobutane	0.8±0.6	1.4±1.4	1.0±1.2	1.3±1.1	3.2±1.4	2.6±1.9	4.5±4.6	3.2±3.9	4.1±3.4	10.3±4.5
n-Butane	1.6±0.9	2.4±2.4	4.4±3.6	2.9±2.5	0.9±0.5	4.7±2.8	7.0±7.2	13.0±10.9	8.7±7.6	2.7±1.6
Cyclopentane	0.1±0.1	0.3±0.2	2.5±2.2	0.3±0.5	1.6±0.9	0.3±0.3	0.9±0.8	8.9±7.8	1.2±1.7	5.9±3.1
Isopentane	1.3±0.7	0.4±0.8	0.0±0.1	8.6±5.0	0.1±0.1	10.3±5.5	3.4±5.9	0.0±0.1	66.2±38.5	0.6±0.5
n-Pentane	0.7±0.6	0.3±0.5	0.0±0.1	1.3±1.2	1.4±0.8	3.1±2.4	1.4±2.3	0.0±0.1	5.5±5.0	6.0±3.2
2,2-Dimethylbutae	0.1±0.1	0.1±0.1	0.0±0.1	0.0±0.1	0.8±0.6	0.6±0.6	0.4±0.6	0.2±0.5	0.0±0.1	3.8±2.7
2,3-Dimethylbutane	0.1±0.2	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.5±0.6	0.1±0.1	0.9±0.8	0.1±0.2	0.1±0.1
2-Methylpentane	0.2±0.1	0.2±0.2	0.0±0.1	0.4±0.3	0.4±0.2	0.9±0.8	1.0±0.9	0.0±0.1	2.4±1.8	2.0±0.9
3-Methylpentane	0.3±0.2	0.3±0.2	0.0±0.1	0.3±0.1	0.3±0.2	1.9±1.4	2.0±1.6	0.0±0.1	2.3±1.0	2.0±1.1
n-Hexane	0.6±0.4	0.2±0.3	0.0±0.1	0.6±0.2	0.1±0.1	2.7±2.0	0.9±1.4	0.1±0.4	2.7±1.1	0.4±0.4

Species/Groups	VOC mixing ratios (mean±std) ($\times 10^{-9}$)					OFP (mean±std) ($\mu g\ m^{-3}$)				
	CD	CQ	TZ	XD	ZL	CD	CQ	TZ	XD	ZL
Methylcyclopentane	0.1±0.1	0.1±0.2	0.0±0.0	0.0±0.1	0.7±0.5	0.9±0.9	0.9±1.3	0.0±0.1	0.1±0.5	5.5±3.8
2,4-Dimethylpentane	0.1±0.1	0.0±0.1	0.2±0.2	0.2±0.1	0.1±0.1	0.8±0.4	0.2±0.3	1.2±1.3	1.2±0.9	1.0±1.0
Cyclohexane	0.1±0.1	0.2±0.3	0.0±0.1	0.1±0.1	0.2±0.1	0.6±0.3	1.1±1.3	0.0±0.1	0.4±0.4	0.9±0.4
2-Methylhexane	0.0±0.1	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.1	0.2±0.3	0.3±0.3	0.0±0.1	0.3±0.3	0.2±0.3
3-Methylhexane	0.1±0.1	0.3±0.3	0.0±0.1	0.1±0.1	0.0±0.1	0.7±0.5	2.1±2.4	0.0±0.1	0.7±0.6	0.1±0.1
2,3-Dimethylpentane	0.0±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.0±0.1	0.6±0.7	0.8±0.8	0.4±0.5	0.7±0.3
2,2,4-Trimethylpentane	0.0±0.1	0.1±0.1	2.5±1.7	0.0±0.1	0.0±0.1	0.1±0.2	0.9±0.7	16.4±10.7	0.2±0.3	0.0±0.1
n-Heptane	0.1±0.1	0.4±0.3	0.6±0.4	0.2±0.1	0.0±0.1	0.4±0.4	2.1±1.6	2.8±2.1	0.8±0.4	0.2±0.2
Methylcyclohexane	0.0±0.1	0.2±0.2	0.0±0.1	0.1±0.1	0.1±0.1	0.2±0.4	1.3±1.5	0.2±0.5	1.0±0.9	0.7±0.6
2,3,4-Trimethylpentane	0.0±0.1	0.2±0.2	0.2±0.4	0.0±0.1	0.0±0.1	0.0±0.1	1.2±1.2	1.2±2.0	0.0±0.1	0.0±0.1
2-Methylheptane	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.1	1.1±1.1	0.2±0.5	0.1±0.1	0.3±0.4
3-Methylheptane	0.0±0.1	0.8±0.5	0.2±0.2	0.0±0.1	0.0±0.1	0.2±0.3	4.9±3.2	1.5±1.3	0.1±0.2	0.0±0.1
n-Octane	0.0±0.1	0.3±0.3	0.1±0.1	0.0±0.1	0.0±0.1	0.1±0.1	1.2±1.4	0.4±0.5	0.2±0.2	0.1±0.2
n-Nonane	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.0±0.1	0.1±0.1	0.9±1.0	0.1±0.3	0.2±0.2	0.1±0.2
n-Decane	0.0±0.1	0.2±0.3	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.9±1.4	0.1±0.1	0.0±0.1	0.1±0.1
n-Undecane	0.0±0.1	0.2±0.2	0.1±0.0	0.0±0.1	0.0±0.1	0.1±0.1	0.8±0.9	0.3±0.2	0.1±0.2	0.0±0.1
n-Dodecane	0.0±0.1	0.2±0.2	0.1±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.8±0.9	0.3±0.2	0.0±0.0	0.0±0.1
Formaldehyde	4.5±2.3	6.6±3.5	15.9±20.0	8.1±4.3	7.8±3.8	56.6±29.1	83.3±44.4	202.0±253.8	103.2±54.8	99.1±48.0
Acetaldehyde	2.1±1.7	3.1±2.1	2.4±1.1	4.3±3.4	2.1±0.7	27.6±21.4	39.4±27.5	31.0±14.7	55.6±44.2	27.4±8.8
Acetone	2.6±1.5	2.9±1.8	1.9±1.2	2.6±1.0	2.7±1.6	2.4±1.4	2.7±1.6	1.8±1.2	2.4±0.9	2.5±1.5
Acrolein	0.0±0.1	0.0±0.1	0.0±0.1	0.1±0.2	0.0±0.1	0.0±0.1	0.2±0.6	0.0±0.2	1.4±4.6	0.1±0.3
Propionaldehyde	0.3±0.1	0.4±0.2	0.3±0.1	0.4±0.3	0.3±0.1	5.0±2.4	7.3±3.9	5.5±2.1	7.5±5.2	5.6±2.2
Crotonaldehyde	0.1±0.1	0.1±0.2	0.0±0.1	0.1±0.1	0.1±0.2	1.8±3.1	2.4±5.9	0.2±0.6	1.8±2.8	3.9±4.9
Butyraldehyde	0.2±0.1	0.2±0.3	0.2±0.1	0.8±0.9	0.1±0.1	3.5±2.6	4.7±5.2	3.4±2.3	14.7±16.7	2.8±2.4

Species/Groups	VOC mixing ratios (mean±std) ($\times 10^{-9}$)					OFP (mean±std) ($\mu g\ m^{-3}$)				
	CD	CQ	TZ	XD	ZL	CD	CQ	TZ	XD	ZL
Benzaldehyde	0.1±0.1	0.2±0.1	0.2±0.1	0.3±0.6	0.2±0.1	-0.4±0.4	-0.8±0.4	-0.5±0.3	-1.0±1.9	-0.6±0.4
Cyclohexanone	0.0±0.1	0.1±0.2	0.1±0.1	0.1±0.1	0.2±0.2	0.1±0.2	0.9±0.9	0.7±0.6	0.5±0.4	1.1±1.2
Isovaleraldehyde	0.1±0.2	0.1±0.1	0.1±0.2	0.1±0.1	0.0±0.1	1.9±4.0	1.1±1.1	2.5±4.1	1.2±0.6	0.9±1.0
Pentanal	0.0±0.1	0.0±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.5±0.8	0.7±0.8	1.8±1.2	1.3±0.7	1.6±1.4
o-Tolualdehyde	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
m-Tolualdehyde	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
Hexaldehyde	0.1±0.2	0.2±0.2	0.3±0.2	0.3±0.2	0.2±0.2	2.7±3.0	2.9±4.0	4.9±3.2	4.9±3.3	3.5±3.7
Heptaldehyde	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.2±0.5	1.3±1.0	0.3±0.5	0.2±0.4
Octanal	0.0±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.6±1.3	1.4±1.3	1.6±1.4	1.2±1.0	1.3±1.4
Nonanal	0.3±0.2	0.3±0.1	0.3±0.3	0.3±0.1	0.3±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
Decanal	0.2±0.1	0.1±0.1	0.1±0.1	0.2±0.1	0.2±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0

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Table S6 Summary of main meteorological parameters and average levels of pollutants during the observation period.

Parameters	CD	CQ	TZ	XD	ZL
WS (m/s)	2.1±1.2	2.0±1.0	1.9±1.0	1.9±1.1	1.5±1.0
T (℃)	27.3±2.9	28.2±2.9	27.1±3.1	27.4±3.3	27.3±3.4
RH (%)	69.1±11.8	70.4±13.1	85.4±17.0	74.6±13.9	70.9±14.9
P(hPa)	984.6±2.5	1005.2±2.6	1005.6±2.6	1001.6±2.6	996.1±2.5
BLH (m)	421.2±512.2	451.5±510.1	421.3±465.1	463.9±541.2	443.8±528.3
SSR (10^5 J m^{-2})	6.7±8.3	6.5±8.1	6.3±7.7	6.6±8.2	6.6±8.2
NO (× 10^{-9})	3.9±4.7	4.5±7.8	1.9±4.1	1.1±1.1	2.6±2.9
NO_2 (× 10^{-9})	10.8±5.1	12.7±8.1	10.4±6.7	11.4±6.7	14.8±6.6
SO_2 (× 10^{-9})	3.4±1.3	3.0±0.5	2.2±1.6	1.4±1.3	3.9±1.5
CO (× 10^{-9})	508.0±173.6	1176.4±578.4	674.3±190.9	1261.4±1174.1	868.0±258.3
O_3 (× 10^{-9})	58.6±30.0	56.4±34.2	51.0±27.8	56.1±29.4	57.4±32.2

Table S7 Modeled O_3 assessment of Base and Free scenario.

Site	Base		Free	
	IOA	R	IOA	R
CD	0.80	0.88	0.90	0.88
CQ	0.90	0.87	0.86	0.87
TZ	0.88	0.88	0.85	0.88
XD	0.86	0.88	0.83	0.89
ZL	0.88	0.89	0.88	0.87

Table S8 Comparison concentrations of the Base and Free scenario modeling parameters, including OVOCs, O_3, RO_2, HO_2, and OH at the five sites.

Parameter	site	Conc		Parameter	site	Conc	
		Base	Free			Base	Free
OVOCs	CD	10.3	18.7	Daytime OH	CD	3.87E+06	3.06E+06
	CQ	14.0	26.3		CQ	2.78E+06	2.64E+06
	TZ	21.9	21.9		TZ	2.99E+06	2.94E+06
	XD	17.4	24.7		XD	3.10E+06	3.01E+06
	ZL	14.2	32.1		ZL	3.56E+06	3.20E+06
Daytime O_3	CD	60.9	68.2	Daytime HO_2	CD	4.13E+08	4.67E+08
	CQ	82.4	84.1		CQ	7.75E+08	8.58E+08
	TZ	66.2	68.8		TZ	7.56E+08	7.96E+08

	XD	85.2	86.7		XD	6.45E+08	7.34E+08
	ZL	96.8	106.3		ZL	7.26E+08	8.74E+08
Daytime $\|\Delta O_3\|$	CD	18.1	14.6	Daytime RO_2	CD	3.67E+08	4.96E+08
	CQ	18.0	18.1		CQ	8.25E+08	8.79E+08
	TZ	12.3	13.1		TZ	6.74E+08	7.29E+08
	XD	18.6	19.8		XD	6.79E+08	7.26E+08
	ZL	21.0	29.1		ZL	7.26E+08	8.72E+08

Note: Concentrations of OVOCs and O_3 in $\times 10^{-9}$, RO_2, HO_2 and OH in molecules cm^{-3}.; $|\Delta O_3|$ = |Sim – Obs|.

Table S9 Model sensitivity testing due to HONO mixing ratios. The change is based on a ratio of $HONO/NO_2$ of 0.02.

$HONO/NO_2$ ratio	Change in O_3	Change in OH	Change in HO_2	Change in RO_2
0.005	-3.4%	-4.6%	-4.8%	-6.0%
0.01	-2.2%	-3.0%	-3.1%	-4.0%
0.03	2.0%	2.7%	2.8%	3.6%
0.04	3.8%	5.4%	5.6%	7.2%

Table S10 Changes in $R_{NetProd}$, $R_{Emis\&Trans}$, and R_{Deps} contributions to OVOC in different time-step scenarios relative to the Base scenario (1-hour time-step).

Time-step	$R_{NetProd}$	$R_{Emisa\&Trans}$	R_{Deps}
5 minutes	4.3%	5.0%	-0.2%
10 minutes	4.2%	4.8%	-0.1%
30 minutes	2.8%	3.2%	-0.1%

Table S11 The one-way analysis of variance (ANOVA) results for pollutants level, OFP of different VOC groups, and daytime contributions of OVOC budget.

Type	Group	F-stat[a]	p-value[b]
Mixing ratio	O_3	1.08	3.66E-01
	NO_2	8.52	1.09E-06
	NO	10.74	2.07E-08
	CO	33.52	3.09E-25
	TVOCs	8.78	1.35E-06
OFP	OVOCs	8.28	3.06E-06
	Aromatics	28.56	4.06E-19
	Alkanes	28.23	6.21E-19
	Alkenes	15.48	3.55E-11
	BVOCs	13.11	1.36E-09
	Alkyne	39.91	4.09E-25
	TVOCs	8.10	4.15E-06
Daytime OVOC budget	$R_{NetProd}$	14.87	5.42E-11
	R_{Deps}	4.13	2.89E-03
	$R_{Emis\&Trans}$	10.74	4.35E-08

Note: [a] F-statistic (F-stat) measures the ratio of OFP variance between VOC groups to the variance within the groups. A higher F-stat indicates a larger difference between the groups relative to the variation within the groups. This suggests that OFP is more likely to differ across VOCs categories.

[b] p-value indicates the probability that the observed difference (or a more extreme difference) occurred by chance. A p-value less than 0.05 typically indicates that the observed differences are statistically significant, meaning there is a high likelihood that the differences are not due to random variation.

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