Supplement to:

O_3-precursor relationship over multiple patterns of time scale: A case study in Zibo, Shandong Province, China

Zhensen Zheng[1], Kangwei Li[2*], Bo Xu[3], Jianping Dou[4], Liming Li[1], Guotao Zhang[1], Shijie Li[1], Chunmei Geng[1], Wen Yang[1], Merched Azzi[5], Zhipeng Bai[1*]

[1] *State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China*
[2] *Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626 Villeurbanne, France*
[3] *Zibo Eco-Environmental Monitoring Center, Zibo 255000, China*
[4] *Zibo Ecological Environment Quality Control Service Center, Zibo 255095, China*
[5] *New South Wales Department of Planning, Industry and Environment, PO Box 29, Lidcombe, NSW 1825, Australia*

*__Corresponding authors__:
Kangwei Li (likangweizju@foxmail.com) and Zhipeng Bai (baizp@craes.org.cn)

Contents of this file

Number of pages: 35

Number of text sections: 3

Number of tables: 8

Number of figures: 18

Content

Figure S13 Time series of monthly OH reactivity (k_{OH}) or concentration for O_3 and its precursors as well as the ratios of TVOC/NOx at the three sites in Zibo.

Figure S14 Time series of weekly OH reactivity (k_{OH}) or concentration for O_3 and its precursors as well as the ratios of TVOC/NOx at the three sites in Zibo.

Figure S15-S16 Time series of daily OH reactivity (k_{OH}) or concentration for major O_3 precursor groups at the three sites in Zibo.

Figure S17 Time series of daily O_3 concentration and TVOC/NOx ratio at three sites in Zibo.

Figure S18. Comparison between measured and simulated O_3 at different dilution rates, which was obtained through a stepwise sensitivity test by adjusting it from 1/86400 s^{-1} to 5/86400 s^{-1} using diurnal average of five-month pattern as model input at the three sites.

Text S1 RIR calculation of different hypothetical changes

To assess the influence of different hypothetical changes (i.e., 5%, 10%, and 15%) on RIR values, we performed box model sensitivity test with the three scenarios. **Figure S12** shows the model-derived RIR values at the three hypothetical changes using averaged diurnal pattern of five-month time scale as model input. In general, the RIR values of O_3 precursor groups and RIR_{NOx}/RIR_{AVOC} ratios were overall consistent at the different hypothetical changes. Given the fact that 10% was widely employed in the previous studies (Lyu et al., 2016; Wang et al., 2017a, 2018b), we applied this hypothetical change of 10% in our RIR calculation for consistency.

Text S2 Determining the photochemical regime

In this study, RIR_{NOx}/RIR_{AVOC} was used as a metric to classify the photochemical regime (Li et al., 2021). Generally, the classification can be divided into two regimes (i.e., VOC-limited and NOx-limited) and three regimes (i.e., VOC-limited, transitional, and NOx-limited). It is well-known that the TVOC/NOx ratio (in ppbC/ppbv) can be used as a classic and simplified method for classifying the photochemical regimes (see https://www.nap.edu/read/1889/chapter/8#165). Specifically, the TVOC/NOx ratios <4, 4 to 15, and >15 are defined as VOC-limited, transitional, and NOx-limited regime, respectively; a cut-off value of "8" was used for two-regime classification (i.e., TVOC/NOx ratios <8 and >8 were defined as VOC-limited and NOx-limited, respectively). Note that the uncertainty range (i.e., –50% to +87.5% here) of the "cut-off value = 8" was therefore considered as transitional regime for three-regime classification.

In parallel, the RIR_{NOx}/RIR_{AVOC} method has also been proposed to classify the photochemical regime, with the cutoff value of "1" for two-regime classification (i.e., RIR_{NOx}/RIR_{AVOC} ratio <1 and >1 are defined as VOC-limited and NOx-limited, respectively) (Lu et al., 2010). Li et al., (2021) assigned the uncertainty range of "–50% to +100%" to the cutoff value = 1 for three-regime classification based on RIR_{NOx}/RIR_{AVOC} ratio method, which was not exactly but very close to the uncertainty range (–50% to +87.5%) in the traditional TVOC/NOx ratio method (with threshold values of 4, 8, 15). **Table S5** summarizes threshold values for the photochemical regime classification indicated by RIR_{NOx}/RIR_{AVOC} (Li et al., 2021). The three-regime classification determined by the RIR_{NOx}/RIR_{AVOC} method was used in the present study. Specifically, a RIR_{NOx}/RIR_{AVOC} value of less than 0.5 was considered as VOC-limited regime, above 2 was considered as NOx-limited regime, and from 0.5 to 2 was defined as transitional regime.

Text S3 Sensitivity test of different dilution rates

Dilution rate is a technical parameterization for box model, and many 0-D box model simulations include this parameter for all non-constraint species to avoid secondary species building up to unreasonable levels (Dillon et al., 2002; Wolfe et al., 2016). Following the method proposed by Wolfe et al., (2016), the dilution rate (k_{dil}) is represented as a first order reaction in the box model, designated as:

$$\frac{d[X]}{dt} = -k_{dil}([X] - [X]_b) \quad (1)$$

where k_{dil} is a 1st order dilution rate coefficient, $[X]_b$ is a fixed background concentration.

As showed in **Figure S18**, a stepwise sensitivity test of dilution rate was performed by adjusting it from 1/86400 s^{-1} to 5/86400 s^{-1} using diurnal average of five-month pattern as model input. It is found that as the dilution rate was adjusted to a higher level, the simulated O_3 declined accordingly as a result of faster dilution process. By comparing the modeled O_3 with observed O_3 for the three sites, we obtained an optimized dilution rate of 3/86400 s^{-1}, and assigned it to all non-constraint species for all simulation days. In general, this optimized dilution rate is conductive to ensuring the rationality and comparability of model performance for all modeled days at the three sites.

126 Table S1. Summary of limit of detection, accuracy, precision of the measurement instruments during
127 whole campaign

Parameter	Instrument	Limit of detection	Accuracy (%)	Precision (%)
O_3	Thermo Scientific 49i	0.5 ppbv	1	<1
CO	Thermo Scientific 48i	40 ppbv	1	<1
SO_2	Thermo Scientific 43i	1 ppbv	1	<1
NO & NO_2	Thermo Scientific 42i	0.4 ppbv	1	<1
VOCs	GC-FID; Thermo Scientific GC5900 GC-FID/PID, Syntech Spectras GC 955-615/815	< 0.05 ppbv	< 10	< 10

Table S2. Summary of the correlation coefficient of five-point calibration (i.e., 2, 4, 6, 8, 10 ppbv) for the 55 VOC species during the May and August of 2019 at the three sites in Zibo city

Category	Species	TZ		BJ		XD	
		May 12th	Aug 8th	May 8th	Aug 9th	May 25th	Aug 6th
Alkanes	Ethane	0.9943	0.9990	0.9943	0.9976	0.9971	0.9992
	Propane	0.9972	0.9987	0.9972	0.9969	0.9972	0.9109
	n-Butane	0.9933	0.9969	0.9933	0.9992	0.9968	0.9996
	Isobutane	0.9961	0.9931	0.9961	0.9993	0.9931	0.9635
	n-Pentane	0.9958	0.9921	0.9958	0.9996	0.9903	0.9610
	Isopentane	0.9988	0.9944	0.9988	0.9969	0.9932	0.9406
	n-Hexane	0.9939	0.9810	0.9939	0.9957	0.9999	0.9999
	Cyclohexane	0.9970	0.9917	0.9970	0.9995	0.9990	0.9989
	2,2-Dimethylbutane	0.9973	0.9937	0.9973	0.9956	0.9879	0.9206
	2,3-Dimethylbutane	0.9965	0.9945	0.9965	0.9982	0.9844	0.9553
	2-Methylpentane	0.9970	0.9897	0.9970	0.9979	0.9985	0.9975
	3-Methylpentane	0.9916	0.9925	0.9916	0.9989	0.9991	0.9998
	n-Heptane	0.9902	0.9995	0.9986	0.9974	0.9997	0.9998
	2-Methylhexane	0.9942	0.9909	0.9942	0.9995	0.9991	0.9999
	3-Methylhexane	0.9961	0.9880	0.9961	0.9997	0.9998	0.9998
	n-Octane	0.9848	0.9991	0.9944	0.9981	0.9993	0.9973
	n-Nonane	0.9833	0.9980	0.9844	0.9998	0.9985	0.9802
	n-Decane	0.9924	0.9959	0.9976	0.9979	0.9960	0.9987
	n-Undecane	0.9946	0.9954	0.9881	0.9828	0.9870	0.9949
	n-Dodecane	0.9808	0.9976	0.9861	0.9878	0.9822	0.9536
Alkenes*	Ethene	0.9995	0.9984	0.9995	0.9864	0.9897	0.9987
	Propene	0.9980	0.9977	0.9980	0.9984	0.9977	1.0000
	1-Butene	0.9970	0.9964	0.9970	0.9968	0.9848	0.9759
	trans-2-Butene	0.9969	0.9960	0.9969	0.9982	0.9837	0.9519
	cis-2-Butene	0.9931	0.9867	0.9931	0.9973	0.9882	0.9705
	1-Pentene	0.9837	0.9893	0.9837	0.9887	0.9809	0.9566
	trans-2-Pentene	0.9940	0.9888	0.9940	0.9966	0.9908	0.9680
	cis-2-Pentene	0.9820	0.9905	0.9820	0.9938	0.9918	0.9632
BVOC	Isoprene	0.9845	0.9944	0.9845	0.9938	0.9864	0.9474
Alkynes	1-Hexene	0.9854	0.9815	0.9854	0.9995	0.9866	0.9994
	Acetylene	0. 9474	0.9949	0. 9474	0.9825	0.9904	0.9985
	Benzene	0.9940	0.9936	0.9940	0.9993	0.9994	0.9998
	Toluene	0.9936	0.9984	0.9946	0.9901	0.9990	0.9990
	Ethylbenzene	0.9986	0.9972	0.9821	0.9989	0.9973	0.9995
	m,p-xylene	0.9824	0.8660	0.9914	0.9999	0.9966	0.9994
	o-xylene	0.9887	0.9994	0.9963	0.9982	0.9955	0.9994
	Styrene	0.9948	0.9997	0.9941	0.9859	0.9885	0.9978
	n-Propylbenzene	0.9847	0.9993	0.9973	0.9868	0.9931	0.9992
	Isopropylbenzene	0.9863	0.9990	0.9992	0.9925	0.9951	0.9988
Aromatics	m-Ethyltoluene	0.9871	0.9982	0.9954	0.9924	0.9906	0.9986
	p-Ethyltoluene	0.9826	0.9983	0.9924	0.9903	0.9928	0.9992
	o-Ethyltoluene	0.9802	0.9972	0.9962	0.9962	0.9906	0.9983
	1,2,3-Trimethylbenzene	0.9965	0.9956	0.9931	0.9915	0.9857	0.9972

	1,2,4-Trimethylbenzene	0.9920	0.9965	0.9924	0.9886	0.9902	0.9969
	1,3,5-Trimethylbenzene	0.9829	0.9962	0.9954	0.9900	0.9906	0.9985
	2,4-Dimethylpentane	0.9868	0.9928	0.9868	0.9999	0.9995	0.9990
	2,3-Dimethylpentane	0.9872	0.9919	0.9872	0.9910	0.9995	0.9991
	2,2,4-Trimethylpentane	0.9967	0.9945	0.9967	0.9911	0.9995	0.9943
non-listed	2,3,4-Trimethylpentane	0.9919	0.9986	0.9912	0.9924	0.9996	0.9999
in box	Methylcyclohexane	0.9978	0.9991	0.9902	0.9885	0.9997	1.0000
model	2-Methylheptane	0.9904	0.9986	0.9977	0.9968	0.9996	0.9999
	3-Methylheptane	0.9945	0.9948	0.9945	0.9980	0.9995	1.0000
	p-Diethylbenzene	0.9924	0.9946	0.9919	0.9968	0.9856	0.9963
	Cyclopentane	0.9882	0.9977	0.9882	0.9980	0.9811	0.9362
	Methylcyclopentane	0.9972	0.9921	0.9972	0.9970	0.9831	0.9851

130

Table S3. Summary of monthly averaged concentration or OH reactivity (with standard deviation) of the measured VOCs, O_3 and its major precursors, as well as TVOC/NOx ratios at the three sites in Zibo City

Group	Specie	TZ						BJ						XD					
		May	Jun	Jul	Aug	Sep	whole	May	Jun	Jul	Aug	Sep	whole	May	Jun	Jul	Aug	Sep	whole
Alkanes	Ethane	8.86 ± 11.72	11.95 ± 13.63	10.21 ± 12.03	11.57 ± 13.14	15.33 ± 14.79	11.57 ± 13.28	3.98 ± 2.94	1.98 ± 1.69	3.37 ± 1.55	2.05 ± 1.36	3.74 ± 1.98	3.02 ± 2.17	2.23 ± 1.44	2.48 ± 1.68	3.37 ± 1.90	3.02 ± 2.07	4.28 ± 2.31	3.00 ± 2.00
	Propane	8.06 ± 11.88	10.45 ± 11.47	10.78 ± 11.46	9.42 ± 10.24	20.99 ± 22.07	11.88 ± 14.82	3.45 ± 3.82	3.43 ± 2.6	3.62 ± 2.79	3.87 ± 2.66	4.91 ± 3.35	3.88 ± 3.14	4.85 ± 4.92	4.41 ± 3.89	4.64 ± 3.87	6.11 ± 6.91	7.83 ± 5.7	5.52 ± 5.37
	n-Butane	3.68 ± 5.84	5.22 ± 5.48	4.87 ± 5.60	4.62 ± 5.09	8.20 ± 8.32	5.30 ± 6.35	2.26 ± 3.05	2.1 ± 2.07	1.60 ± 1.80	1.71 ± 1.89	3.25 ± 4.01	2.21 ± 2.80	1.58 ± 1.38	2.24 ± 2.05	2.47 ± 1.89	2.79 ± 2.98	5.3 ± 4.17	2.74 ± 2.84
	Isobutane	2.24 ± 2.93	2.7 ± 2.61	2.83 ± 2.800	3.31 ± 3.88	4.53 ± 4.07	3.12 ± 3.41	0.89 ± 1.15	1.3 ± 1.27	1.29 ± 1.09	1.58 ± 1.52	1.75 ± 1.64	1.37 ± 1.40	0.83 ± 0.84	1.52 ± 1.31	1.52 ± 1.60	2.03 ± 2.28	2.55 ± 2.01	1.65 ± 1.76
	n-Pentane	1.37 ± 1.95	1.76 ± 1.75	2.07 ± 2.01	1.80 ± 2.01	3.19 ± 3.47	2.02 ± 2.40	0.79 ± 1.01	1.08 ± 1.01	0.96 ± 0.90	1.86 ± 1.84	1.10 ± 1.18	1.18 ± 1.32	1.04 ± 1.10	1.7 ± 1.90	1.5 ± 1.44	1.98 ± 2.96	2.95 ± 2.44	1.77 ± 2.15
	Isopentane	2.13 ± 2.16	2.65 ± 2.34	2.91 ± 2.40	2.96 ± 3.28	4.08 ± 3.67	2.94 ± 2.90	0.52 ± 1.01	2.04 ± 1.45	1.66 ± 2.32	1.64 ± 1.68	2.70 ± 3.41	1.72 ± 2.28	1.48 ± 1.08	2.12 ± 2.2	2.14 ± 1.49	2.13 ± 2.37	3.10 ± 2.89	2.13 ± 2.11
	n-Hexane	0.70 ± 0.82	0.87 ± 0.73	0.90 ± 0.81	0.79 ± 0.81	1.38 ± 1.18	0.92 ± 0.91	1.91 ± 2.77	0.96 ± 1.35	0.33 ± 0.42	1.18 ± 1.30	2.19 ± 3.36	1.34 ± 2.24	0.69 ± 0.79	0.63 ± 0.96	1.23 ± 1.65	0.76 ± 0.87	1.23 ± 1.04	0.88 ± 1.11
	Cyclohexane	0.49 ± 0.85	0.26 ± 0.26	0.30 ± 0.61	0.49 ± 0.64	1.20 ± 1.46	0.55 ± 0.92	0.46 ± 0.55	0.19 ± 0.26	0.04 ± 0.07	0.53 ± 0.79	0.77 ± 1.32	0.42 ± 0.82	0.09 ± 0.14	0.18 ± 0.2	0.13 ± 0.27	0.14 ± 0.23	0.19 ± 0.26	0.14 ± 0.22
	2,2-Dimethylbutane	2.1 ± 3.48	1.87 ± 2.73	1.34 ± 2.25	1.66 ± 2.45	1.43 ± 1.67	1.69 ± 2.61	0.78 ± 1.44	0.41 ± 0.66	0.13 ± 0.32	1.77 ± 3.18	1.89 ± 3.10	1.08 ± 2.35	0.07 ± 0.14	0.22 ± 0.27	0.47 ± 0.53	0.36 ± 0.77	0.39 ± 0.5	0.29 ± 0.51
	2,3-Dimethylbutane	0.40 ± 0.59	0.15 ± 0.15	0.41 ± 0.37	0.32 ± 0.32	0.22 ± 0.20	0.30 ± 0.38	0.20 ± 0.17	0.23 ± 0.39	0.26 ± 0.25	0.22 ± 0.18	0.84 ± 1.10	0.36 ± 0.61	0.17 ± 0.19	0.39 ± 0.42	0.18 ± 0.37	0.44 ± 0.66	0.58 ± 0.58	0.34 ± 0.49
	2-Methylpentane	0.70 ± 0.74	0.67 ± 0.47	0.59 ± 0.8	0.82 ± 0.78	0.82 ± 0.68	0.72 ± 0.71	0.69 ± 0.94	0.53 ± 0.56	0.18 ± 0.22	0.31 ± 0.34	1.31 ± 1.79	0.62 ± 1.06	0.62 ± 0.57	0.87 ± 0.74	0.76 ± 0.75	0.76 ± 1.17	0.94 ± 0.72	0.78 ± 0.83
	3-Methylpentane	0.37 ± 0.41	0.44 ± 0.37	0.61 ± 0.39	0.64 ± 0.56	1.03 ± 1.16	0.61 ± 0.69	0.50 ± 0.73	0.78 ± 0.77	0.05 ± 0.09	0.24 ± 0.54	0.89 ± 1.32	0.50 ± 0.87	0.25 ± 0.24	0.35 ± 0.37	0.27 ± 0.22	0.21 ± 0.2	0.39 ± 0.31	0.29 ± 0.30
	n-Heptane	0.18 ± 0.16	0.53 ± 0.44	0.43 ± 0.31	0.63 ± 0.47	0.64 ± 0.50	0.48 ± 0.43	2.07 ± 2.96	1.38 ± 2.27	0.16 ± 0.15	0.74 ± 1.12	1.76 ± 2.12	1.25 ± 2.12	0.18 ± 0.36	0.24 ± 0.41	0.2 ± 0.21	0.17 ± 0.31	0.19 ± 0.18	0.20 ± 0.32
	2-Methylhexane	0.22 ± 0.27	0.21 ± 0.15	0.16 ± 0.24	0.26 ± 0.22	0.43 ± 0.29	0.26 ± 0.25	0.78 ± 0.72	0.57 ± 0.62	0.03 ± 0.08	0.15 ± 0.42	0.66 ± 1.19	0.42 ± 0.78	0.04 ± 0.07	0.05 ± 0.08	0.04 ± 0.06	0.05 ± 0.05	0.08 ± 0.06	0.05 ± 0.07
	3-Methylhexane	0.27 ± 0.23	0.25 ± 0.16	0.13 ± 0.23	0.25 ± 0.21	0.47 ± 0.33	0.27 ± 0.26	0.78 ± 0.66	0.31 ± 0.4	0.18 ± 0.24	0.55 ± 0.86	1.06 ± 2.01	0.59 ± 1.14	0.09 ± 0.16	0.09 ± 0.09	0.08 ± 0.1	0.12 ± 0.32	0.1 ± 0.07	0.10 ± 0.18
	n-Octane	0.39 ± 0.53	0.09 ± 0.07	0.10 ± 0.10	0.14 ± 0.15	0.24 ± 0.30	0.19 ± 0.31	0.05 ± 0.05	0.06 ± 0.06	0.04 ± 0.10	0.13 ± 0.13	0.31 ± 0.51	0.13 ± 0.27	0.04 ± 0.05	0.04 ± 0.06	0.07 ± 0.09	0.06 ± 0.08	0.03 ± 0.03	0.05 ± 0.07
	n-Nonane	0.25 ± 0.53	0.08 ± 0.08	0.07 ± 0.10	0.09 ± 0.10	0.12 ± 0.11	0.12 ± 0.27	0.08 ± 0.05	0.09 ± 0.09	0.02 ± 0.09	0.47 ± 0.64	0.06 ± 0.07	0.16 ± 0.36	0.01 ± 0.05	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.02	0.02 ± 0.02	0.01 ± 0.03
	n-Decane	0.03 ± 0.04	0.03 ± 0.05	0.11 ± 0.17	0.07 ± 0.06	0.11 ± 0.09	0.07 ± 0.10	0.04 ± 0.03	0.05 ± 0.14	0.07 ± 0.10	0.58 ± 0.73	0.10 ± 0.13	0.18 ± 0.42	0.04 ± 0.1	0.02 ± 0.05	0.06 ± 0.48	0.01 ± 0.03	0.01 ± 0.02	0.03 ± 0.21
	n-Undecane	0.07 ± 0.08	0.13 ± 0.13	0.27 ± 0.34	0.14 ± 0.19	0.17 ± 0.19	0.15 ± 0.21	0.59 ± 0.97	0.42 ± 0.57	0.13 ± 0.16	1.52 ± 2.13	0.19 ± 0.26	0.60 ± 1.25	0.01 ± 0.03	0.09 ± 0.22	0.05 ± 0.16	0.09 ± 0.12	0.05 ± 0.07	0.06 ± 0.14
	n-Dodecane	0.06 ± 0.07	0.05 ± 0.05	0.18 ± 0.34	0.13 ± 0.19	0.15 ± 0.18	0.11 ± 0.20	0.10 ± 0.20	0.16 ± 0.25	0.13 ± 0.22	1.13 ± 1.58	0.17 ± 0.20	0.36 ± 0.87	0.37 ± 0.37	0.33 ± 0.42	0.07 ± 0.19	0.1 ± 0.14	0.06 ± 0.07	0.19 ± 0.31
	Ethene	2.24 ± 1.64	1.55 ± 1.15	1.94 ± 1.58	1.81 ± 1.12	2.50 ± 1.77	2.01 ± 1.51	2.41 ± 2.41	2.21 ± 2.16	2.35 ± 1.68	2.38 ± 2.03	2.43 ± 1.77	2.36 ± 2.03	4.16 ± 2.96	3.09 ± 3.28	3.23 ± 3.21	2.25 ± 2.72	4.77 ± 3.01	3.46 ± 3.18
	Propene	0.74 ± 0.75	0.91 ± 0.66	0.92 ± 0.84	0.70 ± 0.55	1.30 ± 1.69	0.91 ± 1.01	1.03 ± 1.34	0.83 ± 0.92	0.43 ± 0.47	0.67 ± 0.73	0.82 ± 0.73	0.77 ± 0.92	1.97 ± 2.98	2.1 ± 3.86	1.48 ± 2.16	1.36 ± 2.35	1.69 ± 1.77	1.77 ± 2.84
	1-Butene	0.11 ± 0.17	0.11 ± 0.09	0.08 ± 0.13	0.09 ± 0.09	0.16 ± 0.16	0.11 ± 0.14	0.37 ± 0.44	0.18 ± 0.16	0.04 ± 0.07	0.98 ± 1.22	0.13 ± 0.15	0.37 ± 0.73	0.46 ± 0.32	0.82 ± 0.34	0.66 ± 0.46	0.4 ± 0.48	0.44 ± 0.58	0.56 ± 0.47
	trans-2-Butene	0.06 ± 0.11	0.05 ± 0.05	0.03 ± 0.06	0.06 ± 0.05	0.07 ± 0.06	0.06 ± 0.07	0.48 ± 0.56	0.13 ± 0.16	0.05 ± 0.08	1.28 ± 3.05	0.23 ± 0.34	0.46 ± 1.58	0.47 ± 0.34	0.8 ± 0.55	0.82 ± 0.91	0.44 ± 0.45	0.5 ± 0.53	0.60 ± 0.59
	cis-2-Butene	0.42 ± 0.53	0.43 ± 0.45	0.32 ± 0.54	0.37 ± 0.43	1.12 ± 2.05	0.52 ± 1.01	0.33 ± 0.42	0.18 ± 0.24	0.06 ± 0.15	0.21 ± 0.52	0.19 ± 0.42	0.19 ± 0.40	0.55 ± 0.45	0.47 ± 0.31	0.54 ± 1.06	0.3 ± 0.39	0.22 ± 0.22	0.43 ± 0.56
	1-Pentene	0.06 ± 0.09	0.06 ± 0.05	0.04 ± 0.08	0.07 ± 0.06	0.05 ± 0.05	0.06 ± 0.07	0.08 ± 0.14	0.12 ± 0.13	0.06 ± 0.09	0.15 ± 0.16	0.10 ± 0.08	0.10 ± 0.13	0.06 ± 0.16	0.09 ± 0.11	0.06 ± 0.11	0.09 ± 0.20	0.08 ± 0.07	0.08 ± 0.14
	trans-2-Pentene	0.05 ± 0.09	0.04 ± 0.04	0.03 ± 0.09	0.05 ± 0.04	0.10 ± 0.12	0.06 ± 0.08	0.14 ± 0.26	0.09 ± 0.10	0.03 ± 0.05	0.14 ± 0.32	0.09 ± 0.08	0.10 ± 0.20	0.10 ± 0.15	0.17 ± 0.10	0.07 ± 0.09	0.09 ± 0.15	0.06 ± 0.09	0.10 ± 0.13

	cis-2-Pentene	0.06 ± 0.12	0.12 ± 0.12	0.05 ± 0.17	0.07 ± 0.13	0.07 ± 0.07	0.07 ± 0.13	0.08 ± 0.15	0.09 ± 0.12	0.19 ± 0.23	0.71 ± 0.87	0.17 ± 0.21	0.27 ± 0.52	/	/	/	/	/	-
BVOC	Isoprene	0.95 ± 1.07	2.05 ± 2.04	1.86 ± 2.45	1.3 ± 1.41	1.22 ± 1.14	1.47 ± 1.74	0.62 ± 0.78	0.71 ± 0.70	0.59 ± 0.68	1.8 ± 1.47	0.77 ± 0.84	0.93 ± 1.07	0.48 ± 0.59	0.77 ± 0.74	1.01 ± 1.18	0.54 ± 0.50	0.29 ± 0.32	0.61 ± 0.75
Alkenes*	1-Hexene	0.05 ± 0.07	0.06 ± 0.05	0.01 ± 0.03	0.1 ± 0.06	0.12 ± 0.13	0.07 ± 0.09	0.16 ± 0.22	0.10 ± 0.13	0.16 ± 0.22	0.58 ± 1.07	0.17 ± 0.19	0.25 ± 0.58	0.08 ± 0.06	0.15 ± 0.16	0.04 ± 0.02	0.03 ± 0.03	0.05 ± 0.03	0.07 ± 0.09
	Acetylene	2.26 ± 3.43	2.88 ± 2.79	2.61 ± 3.52	3.25 ± 5.00	5.60 ± 4.85	3.32 ± 4.19	2.61 ± 2.21	3.72 ± 4.98	2.21 ± 2.07	2.56 ± 2.75	2.17 ± 2.38	2.65 ± 3.11	2.03 ± 1.4	2.17 ± 1.39	2.86 ± 2.39	1.6 ± 1.68	1.70 ± 1.51	2.06 ± 1.74
	Benzene	0.97 ± 0.98	1.32 ± 1.52	1.67 ± 2.69	0.82 ± 0.72	1.93 ± 2.09	1.33 ± 1.77	0.80 ± 0.62	0.89 ± 0.74	1.17 ± 0.79	1.19 ± 0.87	1.82 ± 1.37	1.19 ± 1.00	0.70 ± 0.53	0.65 ± 0.54	1.05 ± 0.79	0.71 ± 0.65	1.09 ± 0.66	0.81 ± 0.66
	Toluene	1.32 ± 1.85	0.98 ± 0.99	0.83 ± 0.71	1.11 ± 0.75	1.45 ± 1.42	1.14 ± 1.25	1.54 ± 1.68	2.29 ± 3.02	1.13 ± 2	2.07 ± 2.22	2.5 ± 3.29	1.94 ± 2.58	0.59 ± 0.97	0.63 ± 0.60	1.02 ± 0.96	0.75 ± 1.20	1.00 ± 0.74	0.77 ± 0.94
	Ethylbenzene	0.22 ± 0.22	0.19 ± 0.14	0.19 ± 0.12	0.24 ± 0.18	0.31 ± 0.24	0.23 ± 0.19	0.55 ± 0.74	0.43 ± 0.65	0.2 ± 0.22	0.32 ± 0.27	0.55 ± 0.7	0.42 ± 0.58	0.06 ± 0.09	0.06 ± 0.07	0.13 ± 0.13	0.09 ± 0.09	0.10 ± 0.08	0.08 ± 0.10
	m,p-xylene	0.55 ± 0.62	0.44 ± 0.38	0.43 ± 0.33	0.54 ± 0.40	0.79 ± 0.69	0.55 ± 0.52	1.66 ± 2.37	1.31 ± 2.27	0.44 ± 0.6	0.61 ± 0.64	1.49 ± 2.19	1.12 ± 1.88	0.27 ± 0.46	0.32 ± 0.40	0.68 ± 0.80	0.26 ± 0.25	0.37 ± 0.31	0.36 ± 0.49
	o-xylene	0.18 ± 0.19	0.18 ± 0.13	0.30 ± 0.18	0.23 ± 0.17	0.40 ± 0.31	0.25 ± 0.22	0.70 ± 1.01	0.58 ± 1.07	0.22 ± 0.29	0.18 ± 0.19	0.67 ± 0.91	0.48 ± 0.82	0.02 ± 0.04	0.05 ± 0.08	0.15 ± 0.32	0.07 ± 0.08	0.11 ± 0.10	0.07 ± 0.16
	Styrene	0.10 ± 0.14	0.07 ± 0.09	0.06 ± 0.10	0.12 ± 0.16	0.12 ± 0.15	0.10 ± 0.13	0.20 ± 0.31	0.16 ± 0.37	0.14 ± 0.25	0.15 ± 0.20	0.31 ± 0.55	0.19 ± 0.37	0.03 ± 0.07	0.04 ± 0.15	0.16 ± 0.32	0.13 ± 0.24	0.10 ± 0.17	0.09 ± 0.21
	n-Propylbenzene	0.04 ± 0.03	0.05 ± 0.05	0.08 ± 0.10	0.03 ± 0.03	0.06 ± 0.06	0.05 ± 0.06	0.05 ± 0.03	0.04 ± 0.09	0.02 ± 0.03	0.04 ± 0.04	0.04 ± 0.04	0.04 ± 0.05	0.01 ± 0.04	0.01 ± 0.03	0.04 ± 0.04	0.01 ± 0.02	0.01 ± 0.01	0.02 ± 0.03
	Isopropylbenzene	0.03 ± 0.06	0.03 ± 0.02	0.13 ± 0.12	0.04 ± 0.03	0.05 ± 0.05	0.05 ± 0.07	0.21 ± 0.14	0.08 ± 0.07	0.03 ± 0.03	0.03 ± 0.03	0.03 ± 0.03	0.07 ± 0.09	0.01 ± 0.09	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.03	0.01 ± 0.01	0.01 ± 0.05
Alkynes	m-Ethyltoluene	0.06 ± 0.08	0.09 ± 0.10	0.20 ± 0.24	0.09 ± 0.09	0.13 ± 0.19	0.11 ± 0.16	0.06 ± 0.06	0.03 ± 0.05	0.05 ± 0.07	0.06 ± 0.05	0.10 ± 0.11	0.06 ± 0.07	0.01 ± 0.05	0.01 ± 0.01	0.02 ± 0.03	0.02 ± 0.03	0.02 ± 0.03	0.01 ± 0.03
Aromatics	p-Ethyltoluene	0.03 ± 0.04	0.05 ± 0.06	0.14 ± 0.20	0.05 ± 0.05	0.07 ± 0.09	0.07 ± 0.11	0.03 ± 0.04	0.06 ± 0.17	0.02 ± 0.03	0.04 ± 0.05	0.04 ± 0.05	0.04 ± 0.09	0.01 ± 0.02	0.01 ± 0.01	0.03 ± 0.03	0.02 ± 0.03	0.02 ± 0.02	0.01 ± 0.02
	o-Ethyltoluene	0.06 ± 0.07	0.05 ± 0.06	0.11 ± 0.14	0.07 ± 0.09	0.07 ± 0.06	0.07 ± 0.09	0.03 ± 0.04	0.1 ± 0.18	0.03 ± 0.03	0.10 ± 0.13	0.04 ± 0.05	0.06 ± 0.11	0.01 ± 0.07	0.01 ± 0.01	0.01 ± 0.02	0.01 ± 0.02	0.02 ± 0.02	0.01 ± 0.04
	1,2,3-Trimethylbenzene	0.04 ± 0.05	0.07 ± 0.06	0.14 ± 0.13	0.04 ± 0.04	0.06 ± 0.07	0.07 ± 0.08	0.03 ± 0.02	0.09 ± 0.15	0.03 ± 0.04	0.06 ± 0.06	0.10 ± 0.13	0.06 ± 0.10	0.01 ± 0.04	0.01 ± 0.04	0.01 ± 0.02	0.02 ± 0.05	0.02 ± 0.02	0.01 ± 0.03
	1,2,4-Trimethylbenzene	0.10 ± 0.11	0.17 ± 0.16	0.46 ± 0.44	0.12 ± 0.10	0.26 ± 0.34	0.21 ± 0.29	0.16 ± 0.14	0.24 ± 0.33	0.14 ± 0.12	0.09 ± 0.09	0.24 ± 0.21	0.18 ± 0.20	0.02 ± 0.03	0.02 ± 0.02	0.01 ± 0.05	0.04 ± 0.06	0.04 ± 0.04	0.02 ± 0.04
	1,3,5-Trimethylbenzene	0.04 ± 0.05	0.05 ± 0.05	0.11 ± 0.15	0.04 ± 0.04	0.07 ± 0.09	0.06 ± 0.09	0.03 ± 0.05	0.02 ± 0.03	0.02 ± 0.03	0.07 ± 0.05	0.05 ± 0.06	0.04 ± 0.05	0.01 ± 0.11	0.01 ± 0.03	0.04 ± 0.05	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.06
non-listed in box model	2,4-Dimethylpentane	0.32 ± 0.34	0.49 ± 0.39	0.32 ± 0.59	0.58 ± 0.67	0.69 ± 0.64	0.48 ± 0.56	0.43 ± 0.40	0.12 ± 0.18	0.16 ± 0.15	1.22 ± 1.60	0.48 ± 0.84	0.51 ± 0.99	0.14 ± 0.10	0.20 ± 0.16	0.22 ± 0.23	0.23 ± 0.20	0.2 ± 0.12	0.20 ± 0.17
	2,3-Dimethylpentane	0.23 ± 0.22	0.24 ± 0.17	0.14 ± 0.28	0.21 ± 0.21	0.33 ± 0.29	0.23 ± 0.25	0.19 ± 0.24	0.15 ± 0.20	0.22 ± 0.23	0.20 ± 0.18	0.55 ± 0.79	0.27 ± 0.44	0.06 ± 0.06	0.05 ± 0.05	0.07 ± 0.09	0.04 ± 0.07	0.09 ± 0.12	0.06 ± 0.08
	2,2,4-Trimethylpentane	0.09 ± 0.17	0.71 ± 1.22	0.03 ± 0.18	0.22 ± 0.23	0.20 ± 0.17	0.26 ± 0.63	0.24 ± 0.34	0.14 ± 0.35	0.12 ± 0.30	0.65 ± 0.93	0.58 ± 1.33	0.38 ± 0.86	0.05 ± 0.05	0.06 ± 0.06	0.06 ± 0.07	0.08 ± 0.14	0.10 ± 0.10	0.07 ± 0.09
	2,3,4-Trimethylpentane	0.06 ± 0.09	0.08 ± 0.08	0.10 ± 0.11	0.11 ± 0.09	0.14 ± 0.14	0.10 ± 0.11	0.15 ± 0.14	0.07 ± 0.09	0.08 ± 0.18	1.17 ± 2.00	0.07 ± 0.08	0.34 ± 1.06	0.03 ± 0.11	0.06 ± 0.27	0.11 ± 0.19	0.31 ± 0.54	0.08 ± 0.11	0.12 ± 0.32
	Methylcyclohexane	0.16 ± 0.21	0.07 ± 0.07	0.06 ± 0.07	0.13 ± 0.16	0.11 ± 0.10	0.10 ± 0.14	0.08 ± 0.13	0.06 ± 0.05	0.04 ± 0.11	1.51 ± 2.65	0.05 ± 0.06	0.39 ± 1.40	0.18 ± 0.29	0.07 ± 0.11	0.14 ± 0.38	0.07 ± 0.12	0.09 ± 0.11	0.11 ± 0.23
	2-Methylheptane	0.04 ± 0.05	0.05 ± 0.04	0.04 ± 0.07	0.06 ± 0.05	0.08 ± 0.09	0.05 ± 0.06	0.03 ± 0.06	0.07 ± 0.08	0.12 ± 0.3	1.81 ± 2.44	0.09 ± 0.13	0.46 ± 1.37	0.02 ± 0.03	0.03 ± 0.04	0.02 ± 0.03	0.01 ± 0.04	0.02 ± 0.02	0.02 ± 0.03
	3-Methylheptane	0.34 ± 0.36	0.41 ± 0.30	0.49 ± 0.76	0.44 ± 0.46	0.71 ± 0.71	0.48 ± 0.56	0.35 ± 0.44	0.17 ± 0.21	0.28 ± 0.29	0.62 ± 0.6	0.44 ± 0.51	0.38 ± 0.47	0.01 ± 0.01	0.02 ± 0.02	0.01 ± 0.03	0.01 ± 0.02	0.01 ± 0.02	0.01 ± 0.02
	p-Diethylbenzene	0.03 ± 0.03	0.02 ± 0.02	0.09 ± 0.17	0.02 ± 0.02	0.03 ± 0.03	0.04 ± 0.08	0.02 ± 0.02	0.05 ± 0.08	0.02 ± 0.03	0.11 ± 0.15	0.09 ± 0.14	0.06 ± 0.11	0.02 ± 0.05	0.01 ± 0.02	0.01 ± 0.02	0.01 ± 0.05	0.01 ± 0.01	0.01 ± 0.04
	Cyclopentane	0.07 ± 0.16	0.20 ± 0.38	0.07 ± 0.22	0.10 ± 0.19	0.60± 0.82	0.20 ± 0.46	0.31 ± 0.36	0.11 ± 0.13	0.02 ± 0.05	0.25 ± 0.37	0.36 ± 0.86	0.22 ± 0.49	0.26 ± 0.37	0.86 ± 0.85	0.88 ± 0.79	1.17 ± 2.23	0.3 ± 0.41	0.70 ± 1.24
	Methylcyclopentane	0.51 ± 0.61	0.69 ± 0.97	0.69 ± 2.09	0.53 ± 0.74	0.84 ± 0.95	0.65 ± 1.17	0.80 ± 0.83	0.37 ± 0.31	0.04 ± 0.10	0.16 ± 0.18	0.58 ± 1.28	0.38 ± 0.76	0.13 ± 0.21	0.12 ± 0.18	0.05 ± 0.12	0.11 ± 0.23	0.04 ± 0.06	0.09 ± 0.18
Summary	k_{AVOC} (s^{-1})	4.7 ± 3.7	5.1 ± 3.4	5.3 ± 4.2	5.1 ± 3.5	8.4 ± 6.5	5.7 ± 4.6	6.2 ± 6.29	5.3 ± 4.3	3.3 ± 2.3	10.7 ± 8.4	7.3 ± 5.3	6.8 ± 6.3	5.5 ± 3.8	6.6 ± 4.3	6.4 ± 4.9	5.0 ± 4.8	6.0 ± 4.0	5.9 ± 4.4
	k_{BVOC} (s^{-1})	2.3 ± 2.6	4.9 ± 4.9	4.5 ± 5.9	3.1 ± 3.4	2.9 ± 2.7	3.5 ± 4.2	1.5 ± 1.9	1.7 ± 1.7	1.4 ± 1.6	4.3 ± 3.5	1.8 ± 2.0	2.2 ± 2.6	1.1 ± 1.4	1.8 ± 1.8	2.4 ± 2.8	1.3 ± 1.2	0.7 ± 0.8	1.5 ± 1.8
	$k_{Alkanes}$ (s^{-1})	2.0 ± 1.9	2.3 ± 1.8	2.3 ± 1.9	2.4 ± 2.1	3.7 ± 3.0	2.5 ± 2.3	1.9 ± 2.0	1.7 ± 1.3	1.0 ± 0.8	3.7 ± 3.5	2.9 ± 2.6	2.3 ± 2.5	1.1 ± 0.8	1.4 ± 1.1	1.4 ± 1.0	1.5 ± 1.6	1.9 ± 1.4	1.4 ± 1.2
	$k_{Alkenes*}$ (s^{-1})	1.9 ± 1.5	1.9 ± 1.2	1.7 ± 1.5	1.8 ± 1.1	3.2 ± 3.4	2.1 ± 2.0	2.5 ± 3.2	1.9 ± 1.4	1.5 ± 1.1	5.8 ± 6.0	2.3 ± 1.7	2.9 ± 3.7	4.1 ± 2.9	4.8 ± 3.3	4.2 ± 3.8	2.9 ± 3.0	3.6 ± 2.6	4.0 ± 3.2

$k_{Aromatics}$ (s^{-1})	0.9 ± 0.8	0.9 ± 0.7	1.4 ± 1.2	0.9 ± 0.6	1.3 ± 1.1	1.1 ± 0.9	1.7 ± 2.0	1.6 ± 2.1	0.9 ± 0.8	1.2 ± 0.8	2.1 ± 2.3	1.5 ± 1.8	0.3 ± 0.4	0.3 ± 0.4	0.8 ± 0.7	0.5 ± 0.5	0.6 ± 0.4	0.5 ± 0.5
k_{C2H2} (s^{-1})	0.04 ± 0.06	0.05 ± 0.05	0.05 ± 0.06	0.06 ± 0.09	0.1 ± 0.09	0.06 ± 0.08	0.05 ± 0.04	0.07 ± 0.09	0.04 ± 0.04	0.05 ± 0.05	0.04 ± 0.04	0.05 ± 0.06	0.04 ± 0.03	0.04 ± 0.03	0.05 ± 0.04	0.03 ± 0.03	0.03 ± 0.03	0.04 ± 0.03
CO (ppbv)	1053 ± 318	963 ± 288	1020 ± 294	943 ± 269	965 ± 269	989 ± 291	1063 ± 354	1207 ± 344	1449 ± 396	944 ± 415	939 ± 385	1121 ± 426	906 ± 938	726 ± 727	1194 ± 966	962 ± 777	1111 ± 737	980 ± 852
NOx (ppbv)	22.8 ± 17.3	16.4 ± 11.8	12.1 ± 8.5	18.2 ± 10.7	26.2 ± 18.5	19.1 ± 14.9	28.2 ± 24.8	20.7 ± 18.7	24.5 ± 22.8	32.4 ± 23.8	50.9 ± 38.7	31.1 ± 28.6	21.7 ± 15.7	18.2 ± 10.5	15.8 ± 10.0	21.9 ± 13.8	27.9 ± 14.4	21.0 ± 13.9
O_3 (ppbv)	45.0 ± 25.3	60.0 ± 32.7	60.2 ± 33.7	38.5 ± 27.3	38.4 ± 33.4	48.4 ± 32.2	45.0 ± 26.7	66.5 ± 36.3	54.7 ± 35.6	32.8 ± 25.5	37.1 ± 33.8	47.2 ± 34.1	49.1 ± 25.1	59.9 ± 29.4	56 ± 34.1	34 ± 25.3	46 ± 30.5	48.9 ± 30.4
TVOC/NOx[a]	8.5 ± 4.3	13.9 ± 4.8	19.1 ± 9.6	16.6 ± 9.4	15.0 ± 6.5	14.3 ± 7.9	7.2 ± 5.3	9.5 ± 6.1	5.5 ± 3.3	11.5 ± 10.0	6.2 ± 4.4	8.0 ± 6.6	8.0 ± 6.6	5.4 ± 2.0	7.6 ± 3.2	10.1 ± 4.1	7.7 ± 4.5	7.0 ± 3.3

133 [a]Unit of ppbC/ppbv;

Table S4. Summary of box model performance using three statistical metrics, *IOA*, *r*, and *RMSE*, at three sites in four patterns of time scale during the campaign

Site	Time scale		Simulation days	*IOA*[a]	*r*[b]	*RMSE*[c]
TZ	Five-month		1	0.98	0.98	8.7
	Month-to-month		5	0.96	0.95	11.8
	Week-to-week		21	0.93	0.91	15.5
	Day-to-day	May	21	0.90	0.84	17.4
		Jun	24	0.95	0.91	16.0
		Jul	15	0.87	0.87	21.3
		Aug	17	0.86	0.81	20.3
		Sep	23	0.86	0.83	22.1
		Total	100	0.90	0.85	19.4
BJ	Five-month		1	0.95	0.99	14.3
	Month-to-month		5	0.89	0.82	21.8
	Week-to-week		20	0.84	0.74	26.6
	Day-to-day	May	20	0.78	0.69	23.7
		Jun	15	0.86	0.77	28.2
		Jul	19	0.73	0.75	32.9
		Aug	11	0.83	0.72	25.4
		Sep	16	0.73	0.66	32.9
		Total	81	0.84	0.74	27.7
XD	Five-month		1	0.97	0.98	10.1
	Month-to-month		5	0.89	0.86	20.1
	Week-to-week		19	0.89	0.85	21.2
	Day-to-day	May	29	0.84	0.79	22.7
		Jun	24	0.87	0.84	25.6
		Jul	19	0.92	0.85	20.7
		Aug	22	0.79	0.68	22.8
		Sep	20	0.60	0.87	29.8
		Total	114	0.86	0.78	24.4

[a]Index of agreement
[b]Pearson's correlation coefficient
[c]Root mean square error (in ppbv)

Table S5. Summary of threshold values for photochemical regime classifications with ratios of RIR_{NOx}/RIR_{AVOC}

	Photochemical regime	RIR_{NOx}/RIR_{AVOC}
Two-regime classification	VOC-limited	<1
	NOx-limited	>1
Three-regime classification	VOC-limited	<0.5
	Transitional	0.5 to 2
	NOx-limited	>2

Table S6. Summary of averaged relative incremental reactivity (with standard deviation) of major precursor groups for four patterns of time scale

Site	RIR parameters	Five-month	Month-to-month	Week-to-week	Day-to-day
TZ	RIR_{AVOC}	0.25	0.29 ± 0.14	0.35 ± 0.28	0.37 ± 0.34
	RIR_{BVOC}	0.21	0.22 ± 0.06	0.23 ± 0.08	0.24 ± 0.11
	RIR_{CO}	0.08	0.06 ± 0.02	0.07 ± 0.04	0.07 ± 0.05
	RIR_{NOx}	0.30	0.30 ± 0.16	0.21 ± 0.34	0.19 ± 0.40
	$RIR_{Alkanes}$	0.03	0.02 ± 0.01	0.02 ± 0.02	0.02 ± 0.03
	$RIR_{Alkenes*}$	0.17	0.19 ± 0.10	0.21 ± 0.17	0.23 ± 0.23
	$RIR_{Aromatics}$	0.05	0.08 ± 0.03	0.11 ± 0.11	0.11 ± 0.11
	RIR_{NOx}/RIR_{AVOC}	1.20	1.43 ± 1.11	1.48 ± 1.33	1.34 ± 1.39
BJ	RIR_{AVOC}	0.48	0.56 ± 0.31	0.60 ± 0.44	0.80 ± 0.41
	RIR_{BVOC}	0.09	0.15 ± 0.09	0.17 ± 0.15	0.07 ± 0.11
	RIR_{CO}	0.12	0.10 ± 0.04	0.10 ± 0.05	0.15 ± 0.08
	RIR_{NOx}	0.23	0.11 ± 0.28	0.002 ± 0.56	–0.09 ± 0.47
	$RIR_{Alkanes}$	0.03	0.01 ± 0.01	0.01 ± 0.02	0.05 ± 0.03
	$RIR_{Alkenes*}$	0.37	0.42 ± 0.25	0.43 ± 0.32	0.54 ± 0.29
	$RIR_{Aromatics}$	0.07	0.12 ± 0.06	0.16 ± 0.19	0.19 ± 0.16
	RIR_{NOx}/RIR_{AVOC}	0.48	0.38 ± 0.48	0.33 ± 0.62	0.16 ± 0.65
XD	RIR_{AVOC}	0.46	0.62 ± 0.45	0.66 ± 0.49	0.69 ± 0.49
	RIR_{BVOC}	0.15	0.19 ± 0.09	0.17 ± 0.08	0.17 ± 0.11
	RIR_{CO}	0.12	0.10 ± 0.07	0.11 ± 0.07	0.11 ± 0.08
	RIR_{NOx}	0.15	–0.02 ± 0.56	–0.06 ± 0.64	–0.07 ± 0.60
	$RIR_{Alkanes}$	0.04	0.04 ± 0.04	0.05 ± 0.04	0.05 ± 0.05
	$RIR_{Alkenes*}$	0.39	0.51 ± 0.36	0.54 ± 0.40	0.56 ± 0.40
	$RIR_{Aromatics}$	0.03	0.06 ± 0.06	0.07 ± 0.06	0.08 ± 0.07
	RIR_{NOx}/RIR_{AVOC}	0.33	0.46 ± 0.95	0.84 ± 1.80	0.67 ± 1.49

Table S7. Summary of averaged OH reactivity (k_{OH}, s^{-1}) or concentration, and TVOC/NOx ratio (with standard deviation) of major O_3 precursor groups for four patterns of time scale at the three sites

Site	Species	Five-month	Month-to-month	Week-to-week	Day-to-day
TZ	AVOC	5.66 ± 2.53	5.67 ± 1.48	5.57 ± 1.78	5.70 ± 4.59
	BVOC	3.55 ± 2.64	3.59 ± 1.15	3.55 ± 1.52	3.50 ± 4.15
	CO[a]	989 ± 138	989 ± 46	997 ± 91	989 ± 291
	NOx[a]	18.6 ± 9.2	19.1 ± 5.5	18.9 ± 6.0	19.1 ± 14.9
	alkanes	2.48 ± 1.26	2.48 ± 0.68	2.44 ± 0.75	2.50 ± 2.26
	alkenes*	2.08 ± 0.8	2.07 ± 0.64	2.03 ± 0.9	2.09 ± 2.00
	aromatisc	1.05 ± 0.46	1.05 ± 0.25	1.04 ± 0.32	1.05 ± 0.93
	TVOC/NOx[b]	14.35 ± 1.20	14.78 ± 4.21	14.70 ± 5.33	14.31 ± 7.89
BJ	AVOC	6.74 ± 2.22	6.54 ± 2.74	6.61 ± 2.77	6.78 ± 6.32
	BVOC	2.23 ± 1.02	2.15 ± 1.21	2.09 ± 1.04	2.21 ± 2.56
	CO[a]	1121 ± 158	1120 ± 214	1123± 246	1121 ± 426
	NOx[a]	30.8 ± 16.4	31.4 ± 11.8	31.6 ± 13.2	31.1 ± 28.6
	alkanes	2.3 ± 0.59	2.22 ± 1.06	2.23 ± 1.13	2.31 ± 2.52
	alkenes*	2.89 ± 0.97	2.79 ± 1.71	2.81 ± 1.66	2.91 ± 3.71
	aromatics	1.5 ± 0.72	1.48 ± 0.50	1.53 ± 0.76	1.51 ± 1.78
	TVOC/NOx[b]	8.11 ± 2.43	8.10 ± 3.60	8.04 ± 4.20	8.02 ± 6.61
XD	AVOC	5.89 ± 2.32	5.92 ± 349.73	6.15 ± 1.09	5.91 ± 1.09
	BVOC	1.47 ± 0.6	1.48 ± 369.13	1.45 ± 0.87	1.47 ± 0.87
	CO[a]	980 ± 462	980 ± 391.6	985 ± 303	980 ± 290
	NOx[a]	20.2 ± 8.7	21.3 ± 4.3	20.3 ± 5.2	21.0 ± 5.0
	alkanes	1.42 ± 0.63	1.44 ± 0.27	1.47 ± 0.36	1.43 ± 0.36
	alkenes*	3.95 ± 1.49	3.95 ± 0.77	4.14 ± 0.96	3.96 ± 0.96
	aromatics	0.48 ± 0.21	0.50 ± 0.22	0.5 ± 0.22	0.48 ± 0.22
	TVOC/NOx[b]	7.52 ± 0.52	7.55 ± 1.76	7.54 ± 2.52	7.53 ± 3.87

[a]Unit of ppbv;
[b]Unit of ppbC/ppbv;

Table S8. Number of box model calculation to derive 2 types of RIR values in four patterns of time scale in this study. The first type of RIR contains 7 major precursor groups and one base run, and the second type of RIR contains 45 individual VOC species and one base run.

Patterns of time scale	Number of box model calculation (3 sites)		
	RIR of major groups	RIR of individual VOC	Total
five-month	24	138	162
month-to-month	120	690	810
week-to-week	480	2760	3240
day-to-day	2360	-	2360

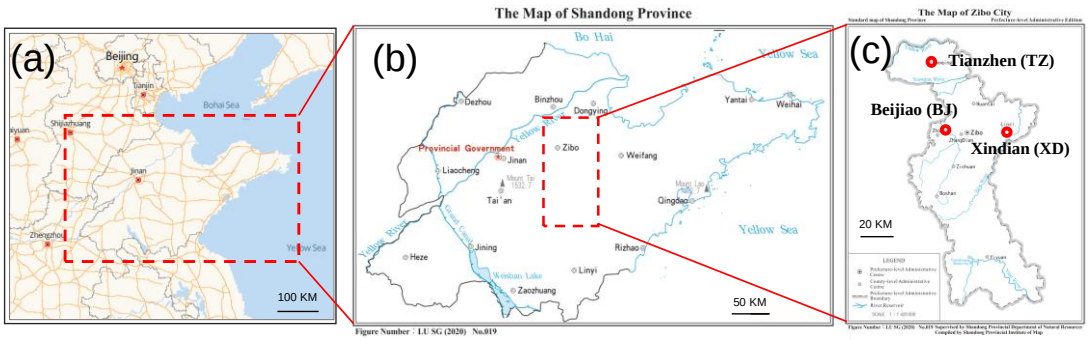

Figure S1. Geographical locations of the study: (a) North China Plain, (b) Shandong Province, and (c) Zibo City. Three measurement sites (TZ, BJ, and XD) in Zibo are marked in red. The map can be obtained from http://dnr.shandong.gov.cn/tplj_30790/sdsgtzytbzdtfw/.

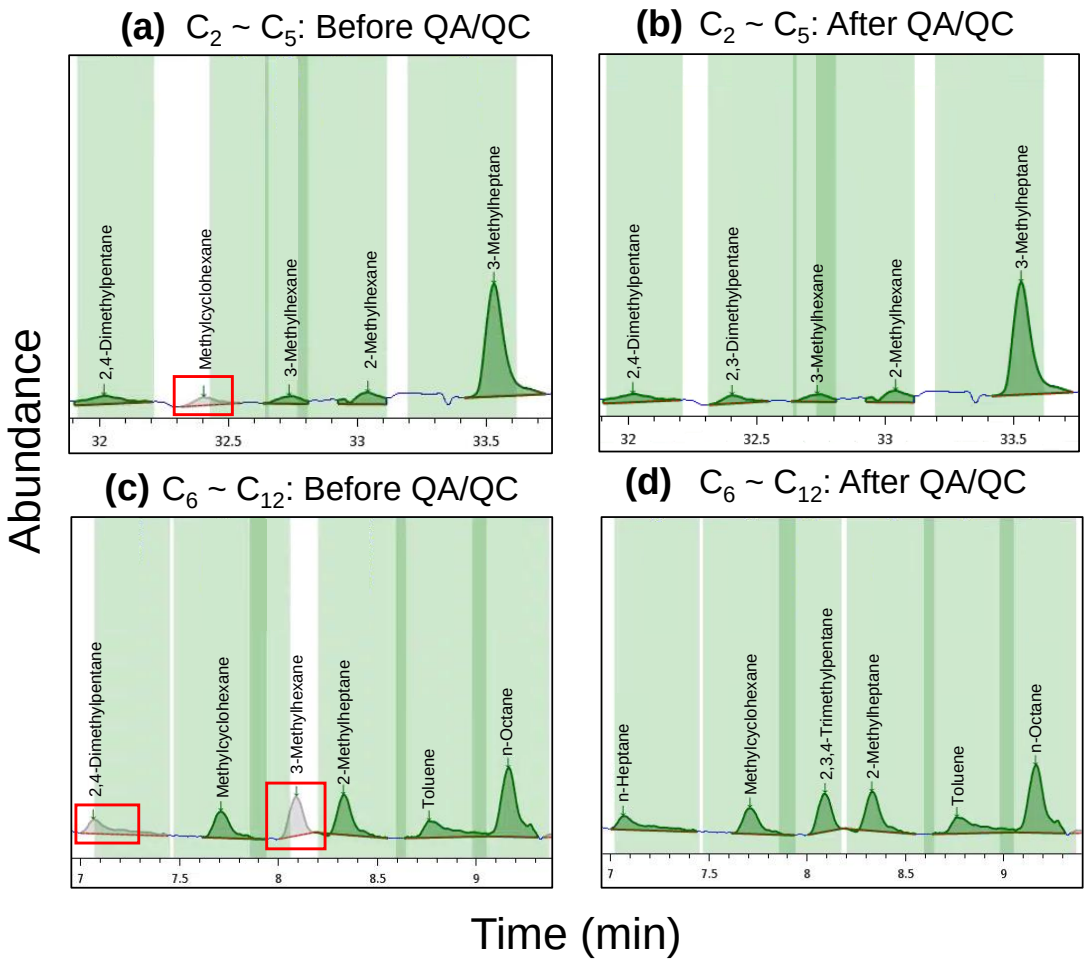

Figure S2. A daily check of peak fitting and baseline of the total ion current (TIC) chromatogram, which is a case selected at TZ site. Note that (a) and (c) are automatically performed by software, while (b) and (d) are manually checked and adjusted after QA/QC.

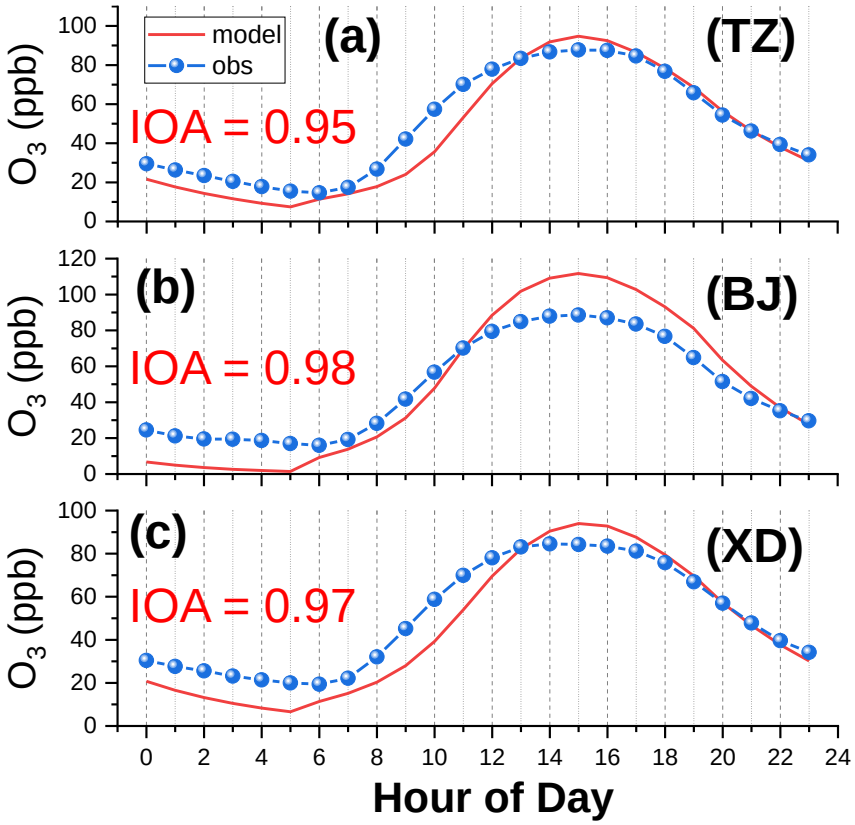

Figure S3. Time series of modeled and observed O_3 at three sites in Zibo at the five-month scale.

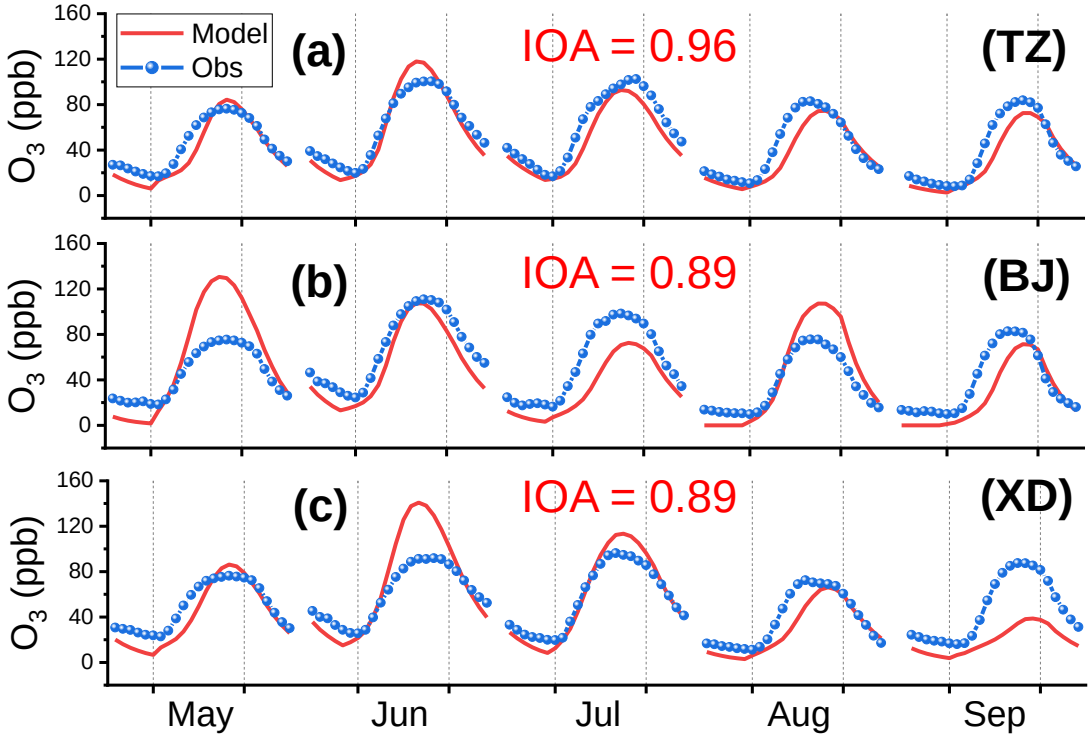

Figure S4. Time series of modeled and observed O_3 at three sites in Zibo at the monthly scale.

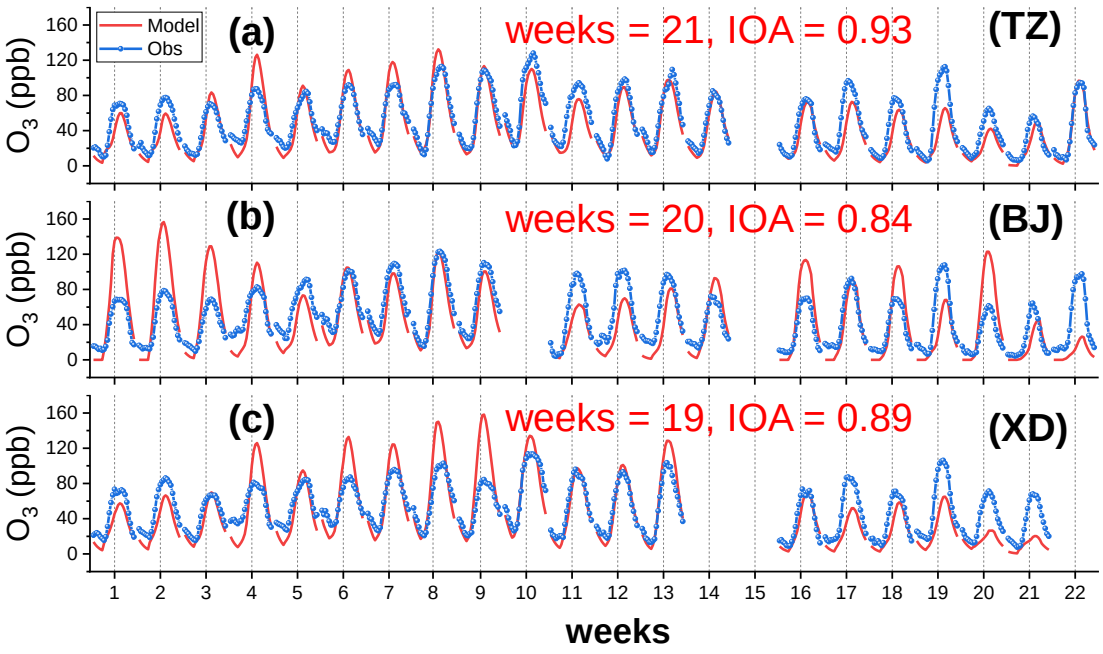

Figure S5. Time series of modeled and observed O_3 at three sites in Zibo at the weekly scale.

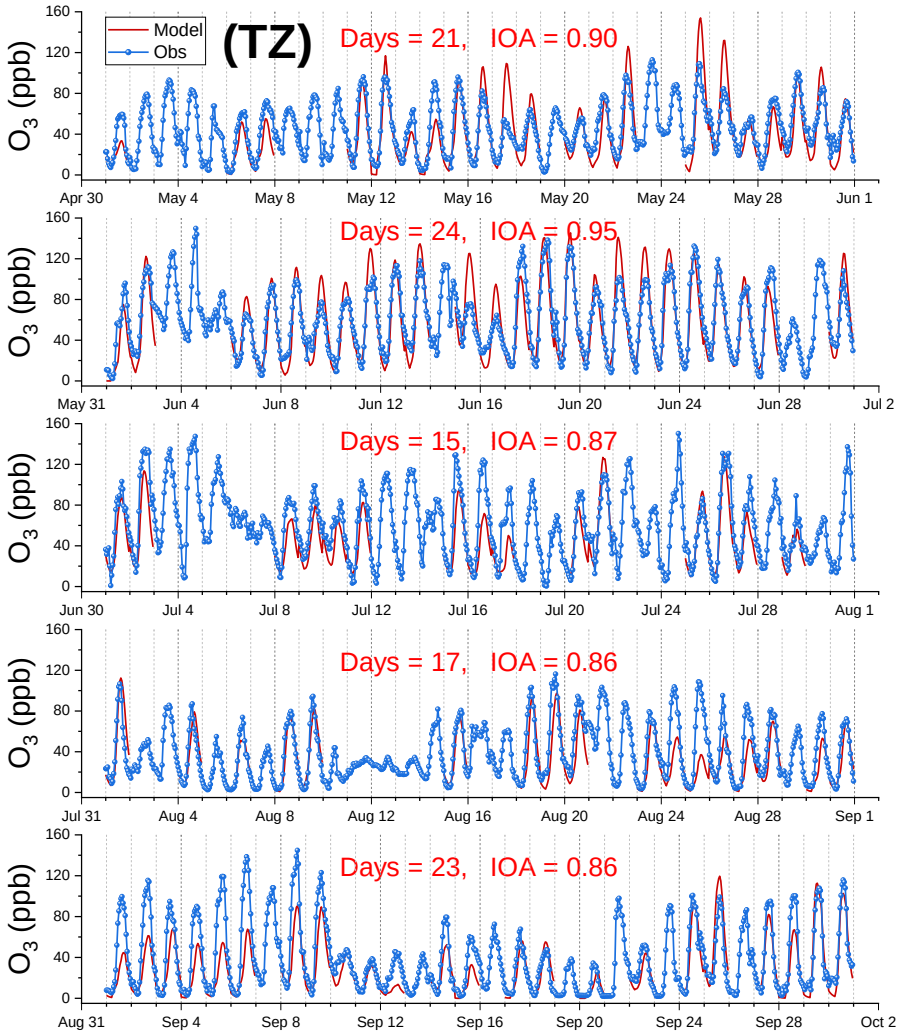

Figure S6. Time series of modeled and observed O_3 at the TZ site in Zibo at the daily scale.

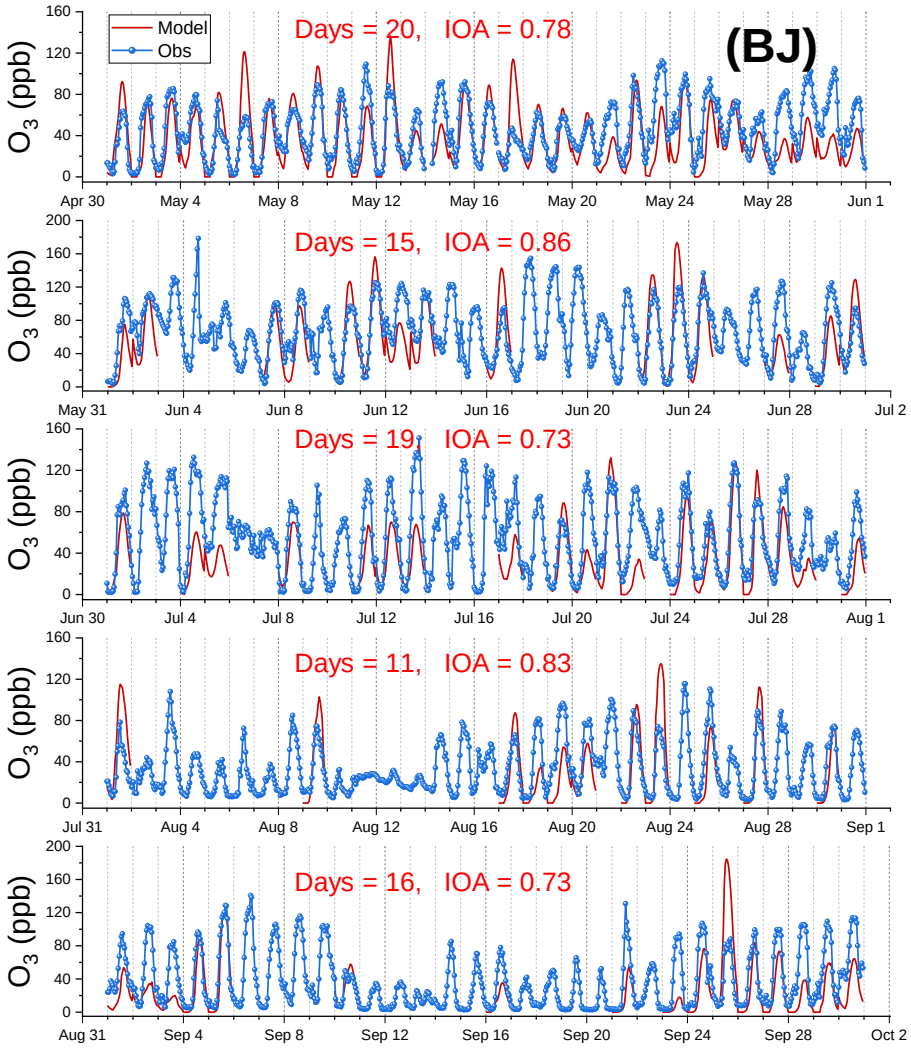

Figure S7. Time series of modeled and observed O_3 at the BJ site in Zibo at the daily scale.

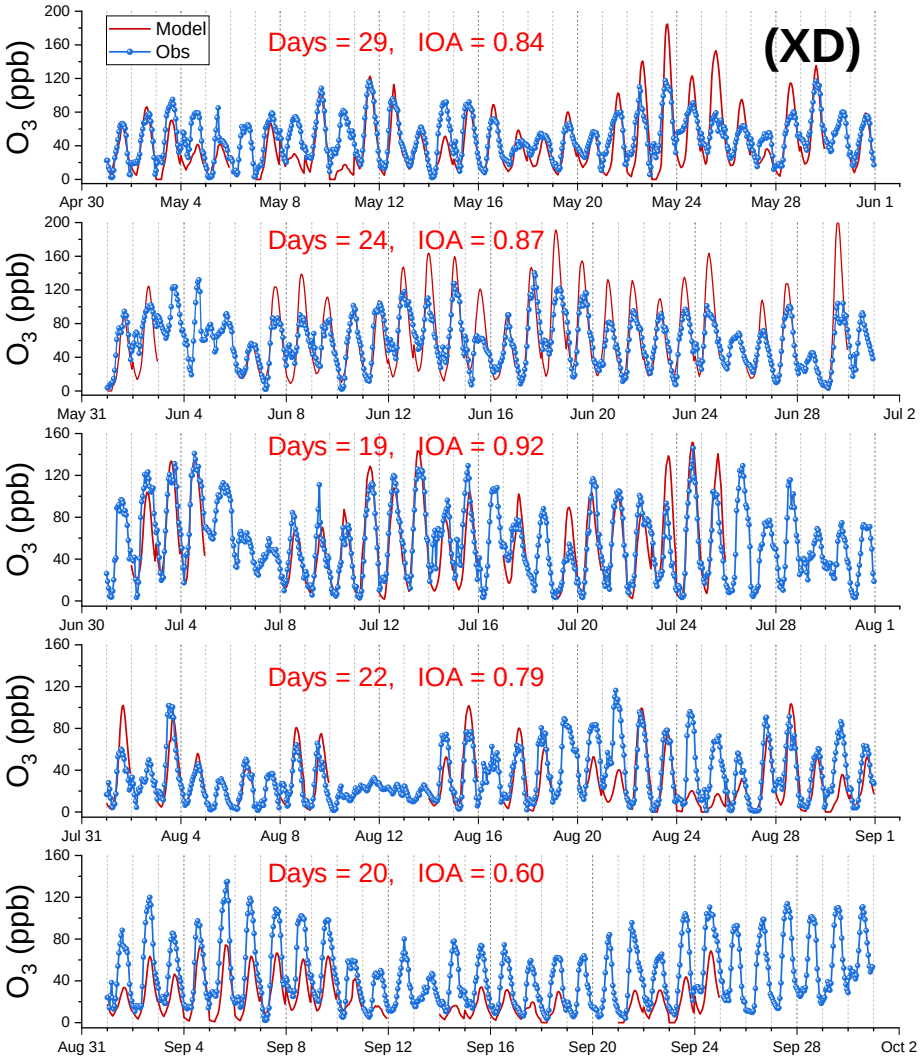

Figure S8. Time series of modeled and observed O_3 at the XD site in Zibo at the daily scale.

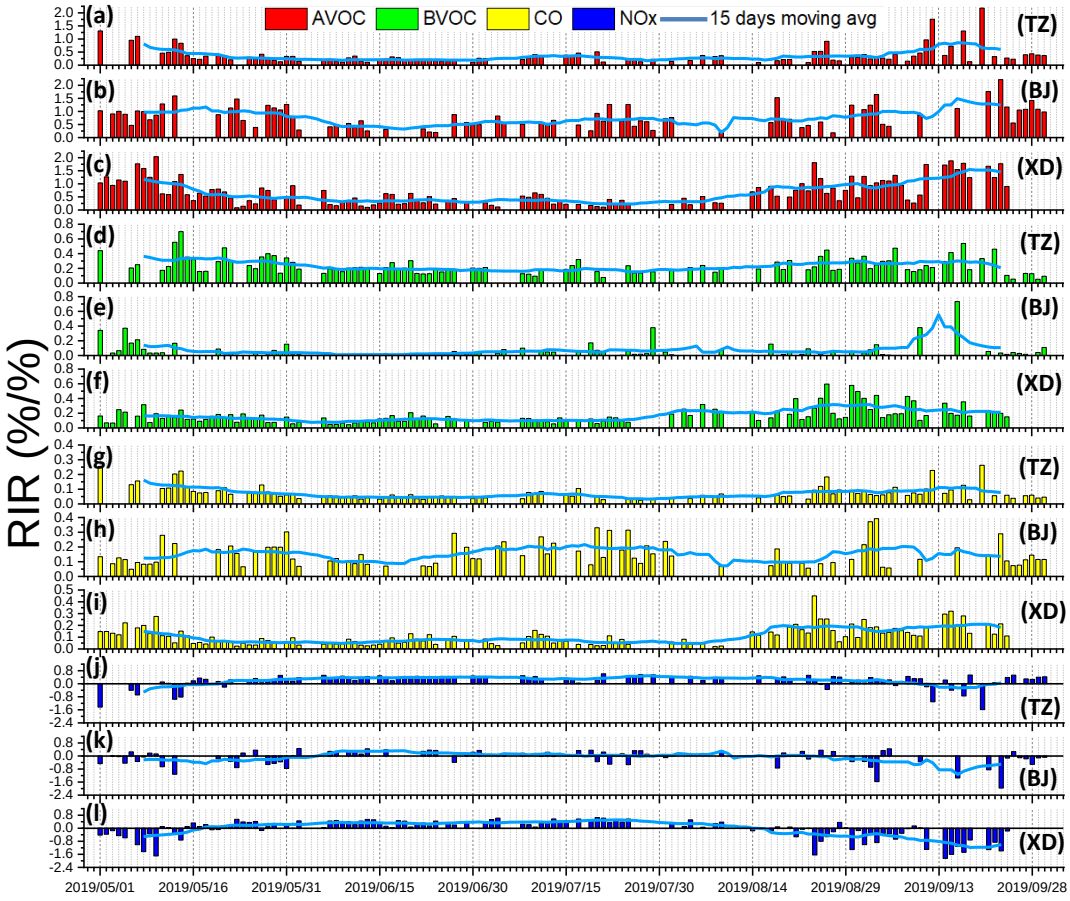

Figure S9. Time series of daily RIR values of major precursor categories at three sites in Zibo.

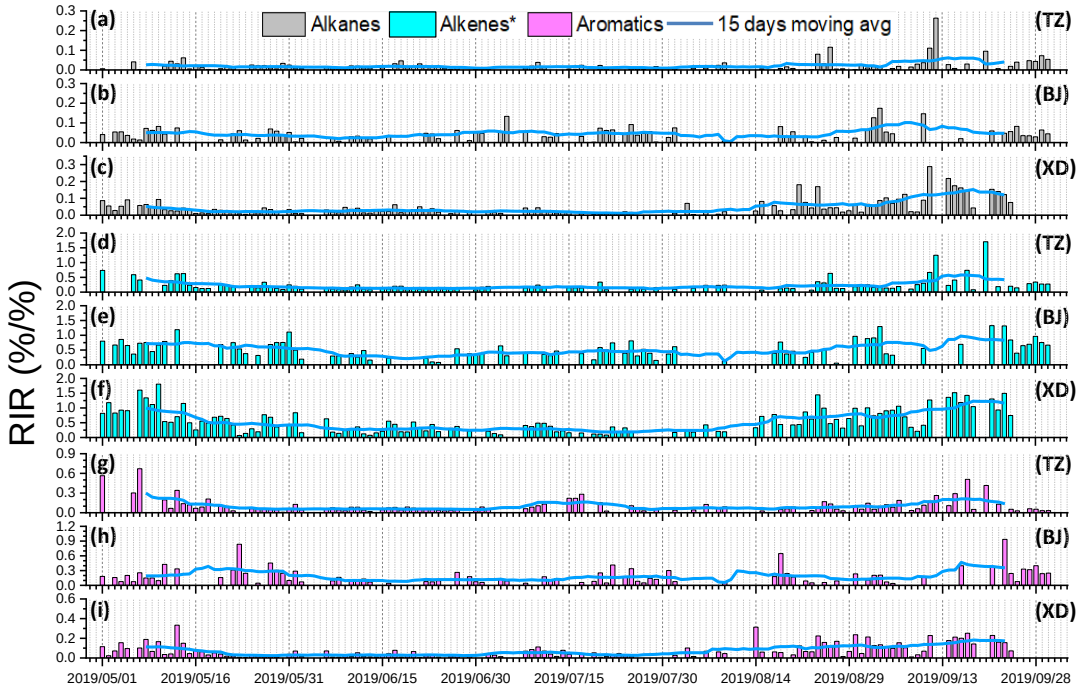

Figure S10. Time series of daily RIR values for subgroups of AVOC at three sites in Zibo.

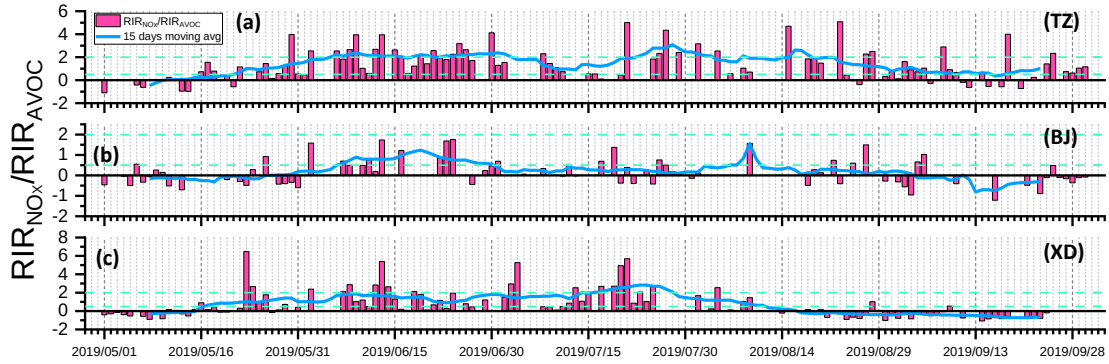

Figure S11. Time series of daily RIR_{NOx}/RIR_{AVOC} values at three sites in Zibo. The green dash line denotes to RIR_{NOx}/RIR_{AVOC} = 0.5 and 2.

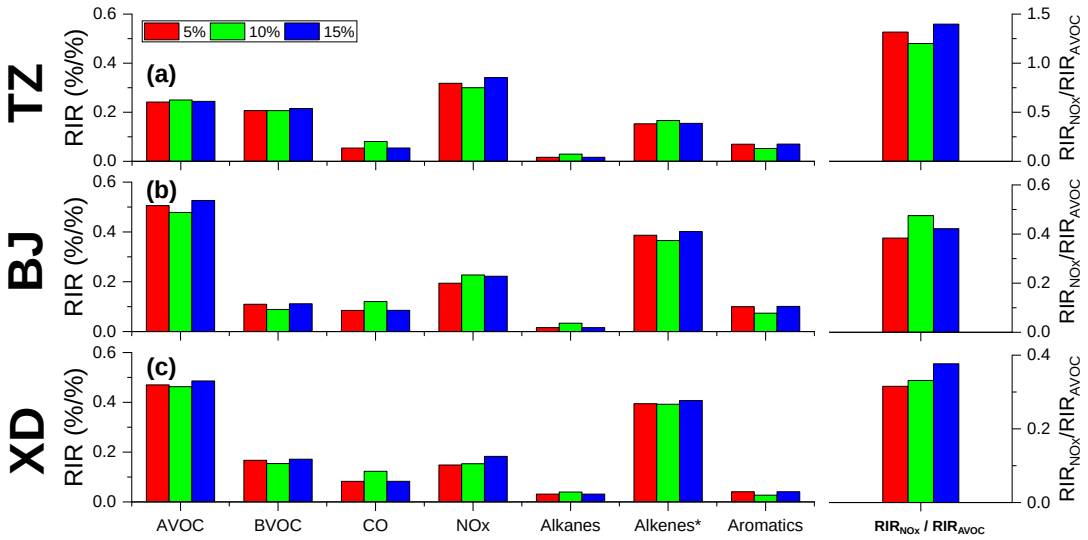

Figure S12. The RIR values of O_3 precursor groups and RIR_{NOx}/RIR_{AVOC} at different hypothetical changes (i.e., 5%, 10%, and 15%) using diurnal average of five-month pattern as model input at the three sites.

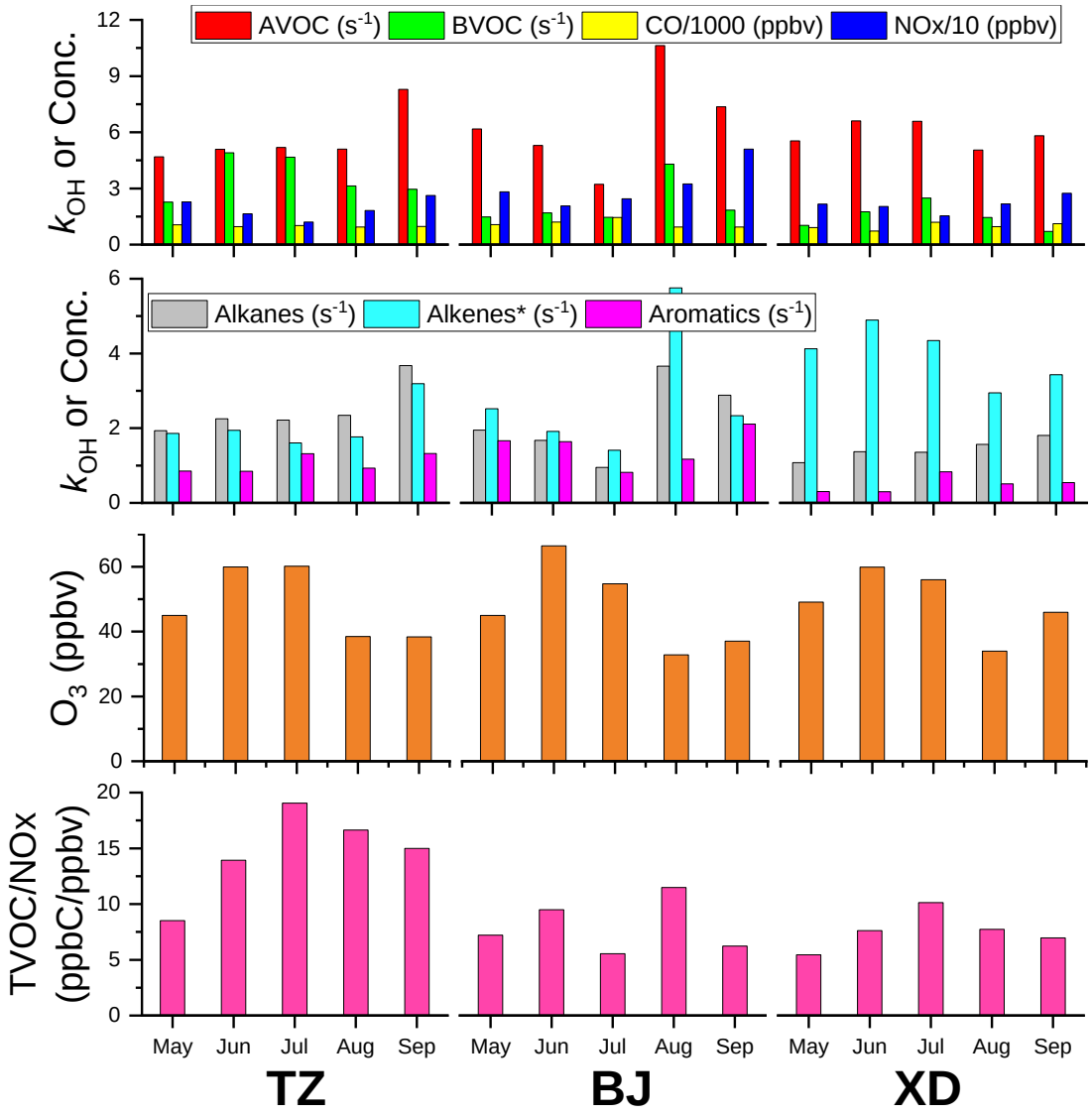

Figure S13. Time series of monthly OH reactivity (k_{OH}) or concentration for O_3 and its precursors as well as the ratios of TVOC/NOx at the three sites in Zibo.

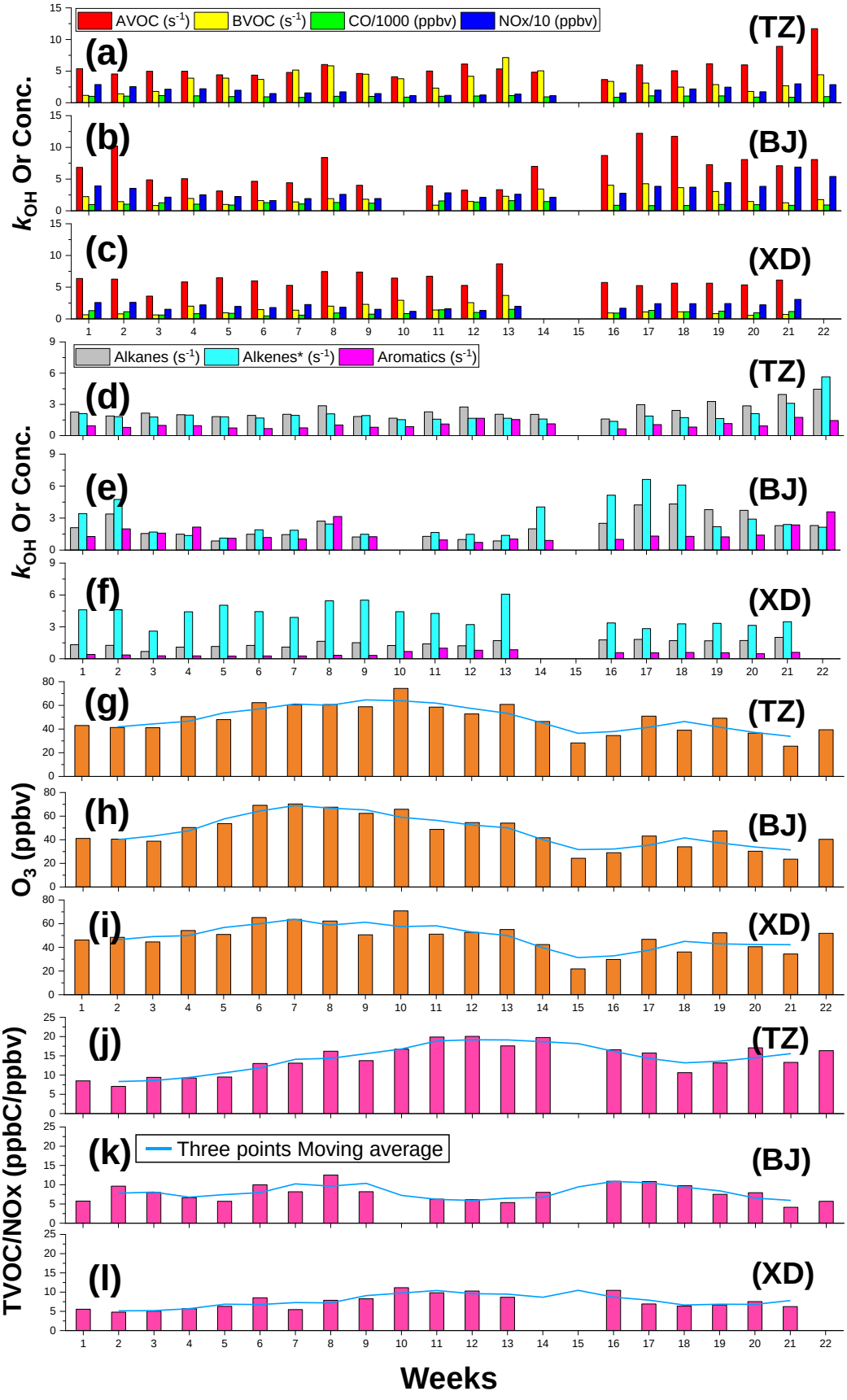

Figure S14. Time series of weekly OH reactivity (k_{OH}) or concentration for O_3 and its precursors as well as the ratios of TVOC/NOx at the three sites in Zibo.

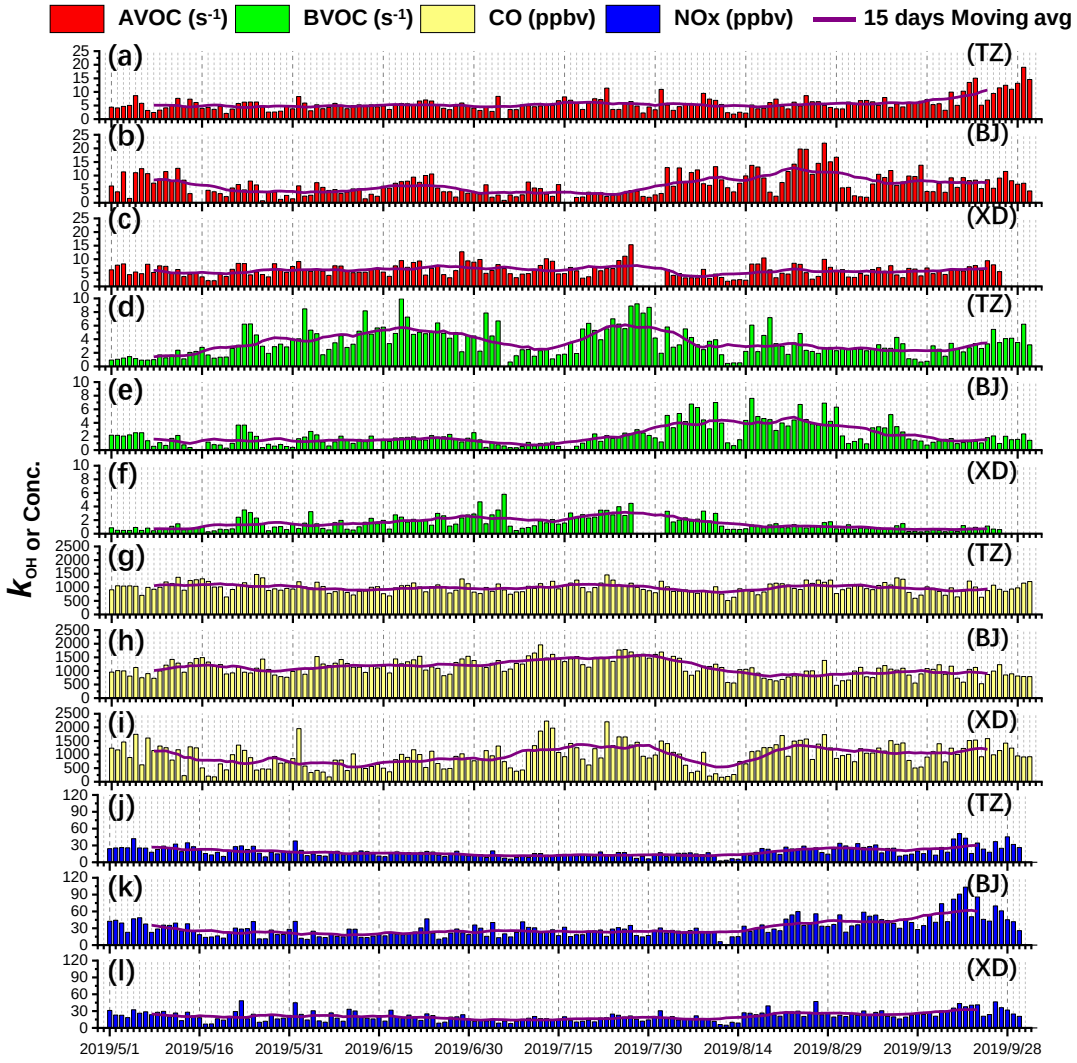

Figure S15. Time series of daily OH reactivity (k_{OH}) or concentration for major O_3 precursor categories at the three sites in Zibo.

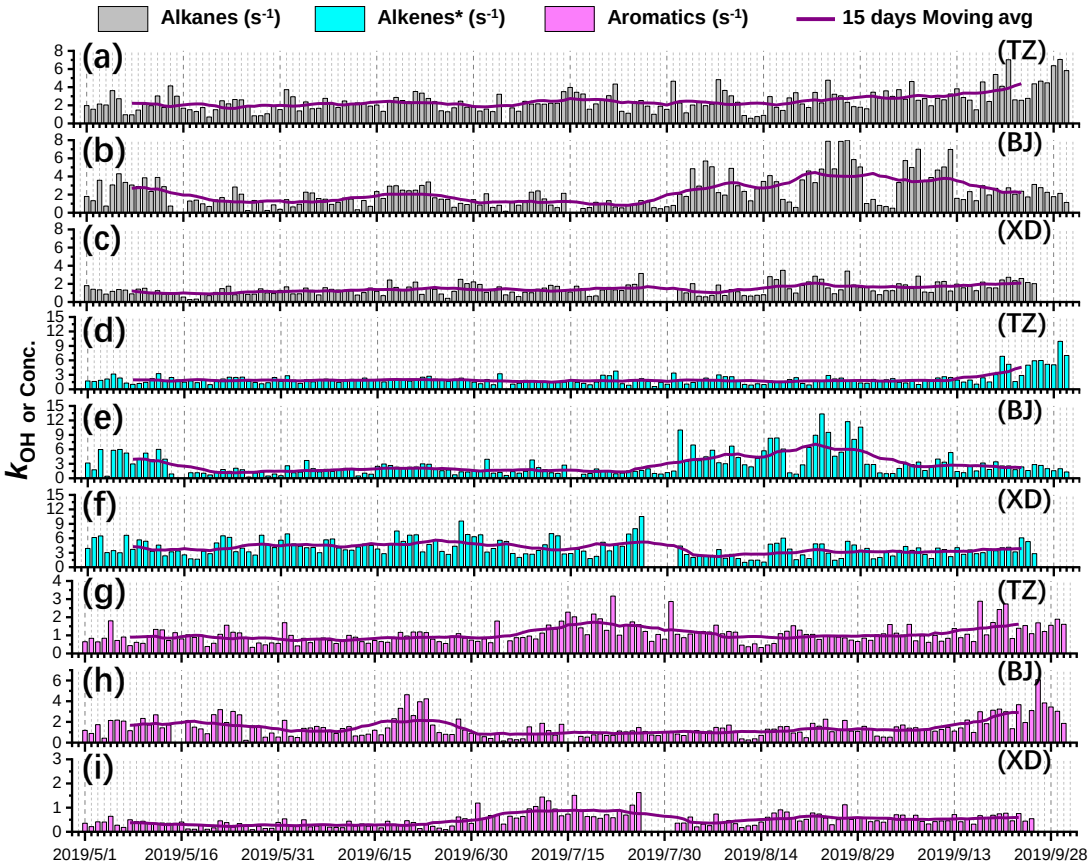

Figure S16. Time series of daily OH reactivity (k_{OH}) for subgroups of AVOC at the three sites in Zibo.

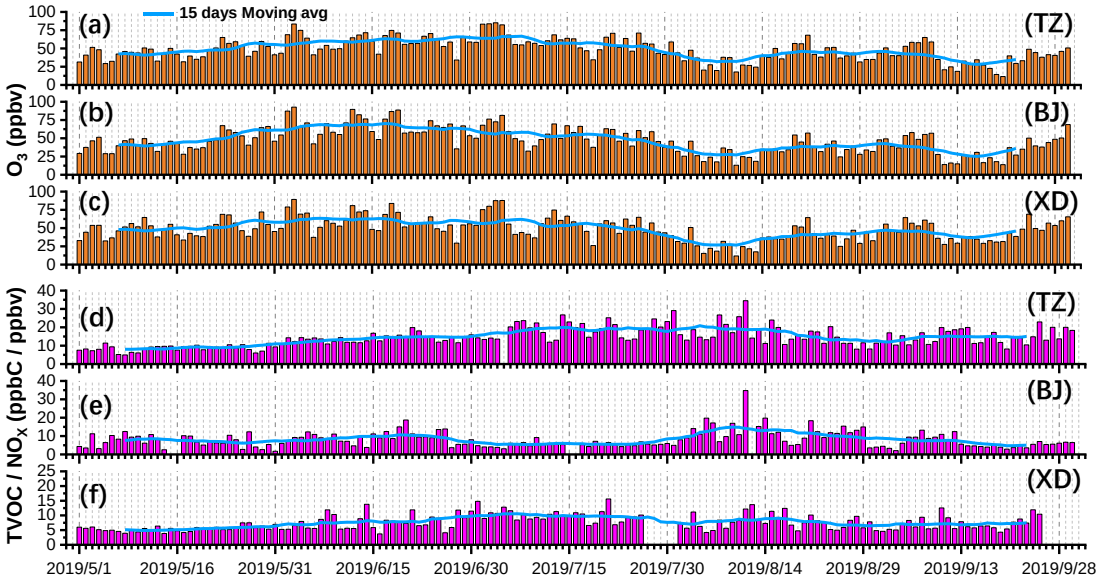

Figure S17. Time series of daily O_3 concentration and TVOC/NOx ratio at three sites in Zibo.

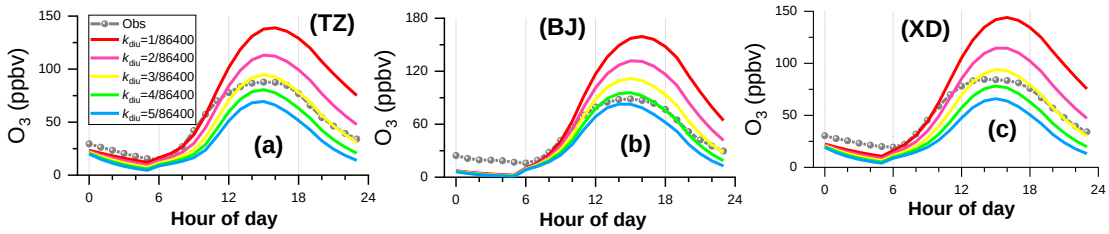

Figure S18. Comparison between measured and simulated O_3 at different dilution rates, which was obtained through a stepwise sensitivity test by adjusting it from 1/86400 s^{-1} to 5/86400 s^{-1} using diurnal average of five-month pattern as model input at the three sites.

Reference

Dillon, M. B., Lamanna, M. S., Schade, G. W., Goldstein, A. H. and Cohen, R. C.: Chemical evolution of the Sacramento urban plume: Transport and oxidation, J. Geophys. Res. Atmos., 107(D5), ACH-3, 2002.

Li, K., Wang, X., Li, L., Wang, J., Liu, Y., Cheng, X., Xu, B., Wang, X., Yan, P., Li, S., Geng, C., Yang, W., Azzi, M. and Bai, Z.: Large variability of O3-precursor relationship during severe ozone polluted period in an industry-driven cluster city (Zibo) of North China Plain, J. Clean. Prod., 316, 128252, doi:https://doi.org/10.1016/j.jclepro.2021.128252, 2021.

Lu, K. D., Zhang, Y. H., Su, H., Shao, M., Zeng, L. M., Zhong, L. J., Xiang, Y. R., Chang, C. C., Chou, C. C. K. and Andreas, W.: Regional ozone pollution and key controlling factors of photochemical ozone production in Pearl River Delta during summer time, Sci. China Chem., 53(3), 651–663, doi:10.1007/s11426-010-0055-6, 2010.

Lyu, X. P., Chen, N., Guo, H., Zhang, W. H., Wang, N., Wang, Y. and Liu, M.: Ambient volatile organic compounds and their effect on ozone production in Wuhan, central China, Sci. Total Environ., 541, 200–209, doi:10.1016/j.scitotenv.2015.09.093, 2016.

Wang, Y., Wang, H., Guo, H., Lyu, X., Cheng, H., Ling, Z., Louie, P. K. K., Simpson, I. J., Meinardi, S. and Blake, D. R.: Long-term O3-precursor relationships in Hong Kong: Field observation and model simulation, Atmos. Chem. Phys., 17(18), 10919–10935, doi:10.5194/acp-17-10919-2017, 2017.

Wang, Y., Guo, H., Zou, S., Lyu, X., Ling, Z., Cheng, H. and Zeren, Y.: Surface O3 photochemistry over the South China Sea: Application of a near-explicit chemical mechanism box model, Environ. Pollut., 234, 155–166, doi:10.1016/j.envpol.2017.11.001, 2018.

Wolfe, G. M., Marvin, M. R., Roberts, S. J., Travis, K. R. and Liao, J.: The framework for 0-D atmospheric modeling (F0AM) v3. 1, Geosci. Model Dev., 9(9), 3309–3319, 2016.