



Supplement of

O₃-precursor relationship over multiple patterns of timescale: a case study in Zibo, Shandong Province, China

Zhensen Zheng et al.

Correspondence to: Kangwei Li (likangweizju@foxmail.com, kangwei.li@unibas.ch) and Zhipeng Bai (baizp@craes.org.cn)

The copyright of individual parts of the supplement might differ from the article licence.

31 **Content**

- 32 Section S1. Sensitivity test of different dilution rates.
- 33 Section S2. Determining the photochemical regime.
- Table S1. Summary of limit of detection, accuracy, precision of the measurementinstruments during whole campaign.
- 36 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.
- 39 Table S3. Summary of monthly averaged concentration or OH reactivity (with
- 40 standard deviation) of the measured VOCs, O₃ and its major precursors, as well as
- 41 TVOC/NOx ratios at the three sites in Zibo City.
- 42 Table S4. Summary of threshold values for photochemical regime classifications with
- 43 ratios of RIR_{NOx}/RIR_{AVOC}.
- 44 Table S5. Summary of box model performance using 3 statistical metrics.
- Table S6. Summary of averaged relative incremental reactivity (with standarddeviation) of major precursor groups over 4 patterns of timescale.
- 47 Table S7. Summary of averaged OH reactivity (k_{OH} , s⁻¹) or concentration, and
- 48 TVOC/NOx ratio (with standard deviation) of major O₃ precursor groups for four
- 49 patterns of timescale at the three sites.
- 50 Table S8. Number of box model calculation to derive RIR parameters at 3 sites over 4
- 51 patterns of timescale.
- 52 Figure S1. Geographical locations of the study.
- 53 Figure S2. A daily check of peak fitting and baseline of the chromatogram, which is a
- 54 case selected at TZ site.
- Figure S3-S8. Time series of modeled and observed O_3 at 3 sites over 4 patterns of timescale.
- 57 Figure S9. Time series of monthly OH reactivity (k_{OH}) or concentration for O₃ and its
- 58 precursors as well as the ratios of TVOC/NOx at the three sites in Zibo.
- 59 Figure S10. Time series of weekly OH reactivity (k_{OH}) or concentration for O₃ and its
- 60 precursors as well as the ratios of TVOC/NOx at the three sites in Zibo.
- 61 Figure S11-S13. Time series of daily RIR of major precursor groups and ratios of
- $62 RIR_{NOx}/RIR_{AVOC}$ at 3 sites.

- 63 Figure S14. Distributions of the standard deviations (Std.) for OH reactivity (k_{OH}) or
- 64 concentration of O_3 precursor groups for multiple patterns of timescale at the three
- 65 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 O₃ concentration and TVOC/NOx ratio at three sitesin Zibo.
- 70 Figure S18. Comparison between measured and simulated O₃ at different dilution
- rates, which was obtained through a stepwise sensitivity test by adjusting it from
- 72 $1/86400 \text{ s}^{-1}$ to $5/86400 \text{ s}^{-1}$ using diurnal average of five-month pattern as model input
- at the three sites.

Section S1 Sensitivity test of different dilution rates 74

75 Dilution rate is a technical parameterization for box model, and many 0-D box 76 model simulations include this parameter for all non-constraint species to avoid 77 secondary species building up to unreasonable levels (Dillon et al., 2002; Wolfe et al., 78 2016). Following the method proposed by Wolfe et al., (2016), the dilution rate (k_{dil}) 79 is represented as a first order reaction in the box model, designated as:

dt

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

where k_{dil} is a 1st order dilution rate coefficient, $[X]_b$ is a fixed background 81 82 concentration.

(1)

As showed in **Figure S19**, a stepwise sensitivity test of k_{dil} was performed by 83 adjusting it from 1/86400 s⁻¹ to 5/86400 s⁻¹ using diurnal average of five-month 84 pattern as model input. It is found that as k_{dil} was adjusted to a higher level, the 85 simulated O₃ declined accordingly as a result of faster dilution process. By comparing 86 the modeled O_3 with observed O_3 for the three sites, we obtained an optimized k_{dil} of 87 $3/86400 \text{ s}^{-1}$, and assigned it to all non-constraint species for all simulation days, 88 89 which is the only model parameter that was tuned to fit the measured O₃ data. In 90 general, this optimized k_{dil} is conductive to ensuring the rationality and comparability 91 of model performance for all modeled days at the three sites, and it is also worth for 92 further investigation about how different k_{dil} values affect the trends in photochemical 93 regime.

Section S2 Determining the photochemical regime 94

95 In this study, RIR_{NOx}/RIR_{AVOC} was used as a metric to classify the photochemical 96 regime (Li et al., 2021). Generally, the classification can be divided into two regimes 97 (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 98 99 ppbC/ppbv) can be used as a classic and simplified method for classifying the 100 photochemical regimes (National Research Council, 1991). Specifically, the TVOC/NOx ratios <4, 4 to 15, and >15 are defined as VOC-limited, transitional, and 101 NOx-limited regime, respectively; a cut-off value of "8" was used for two-regime 102 103 classification (i.e., TVOC/NOx ratios <8 and >8 were defined as VOC-limited and 104 NOx-limited, respectively). Note that the uncertainty range (i.e., -50% to +87.5%105 here) of the "cut-off value = 8" was therefore considered as transitional regime for 106 three-regime classification.

107 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., 108 RIR_{NOx}/RIR_{AVOC} ratio <1 and >1 are defined as VOC-limited and NOx-limited, 109 respectively) (Lu et al., 2010). Li et al., (2021) assigned the uncertainty range of "-50% 110 to $\pm 100\%$ to the cutoff value = 1 for three-regime classification based on 111 112 RIR_{NOx}/RIR_{AVOC} ratio method, which was not exactly but very close to the uncertainty 113 range (-50% to +87.5%) in the traditional TVOC/NOx ratio method (with threshold 114 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 115 116 classification determined by the RIR_{NOx}/RIR_{AVOC} method was used in the present 117 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. 118
- 119

Table S1. Summary of limit of detection, accuracy, precision of the measurement instruments duringwhole 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
VOC	GC-FID; Thermo Scientific GC5900	< 0.05 nnhu	< 10	< 10
vocs	GC-FID/PID, Syntech Spectras GC 955-615/815	< 0.03 pp0v	< 10	< 10

122 Table S2. Summary of the correlation coefficient of five-point calibration (i.e., 2, 4, 6, 8, 10 ppbv) for

123 the 55 VOC species during the May and August of 2019 at the three sites in Zibo city. Alkenes*

124 denotes anthropogenic alkenes, excluding isoprene in this study. "Non-listed in box model" represents

125

ten measured VOC species that cannot be simulated in box model.

Catagomy	Spacing	T	Z	B	J	XI)
Category	Species	May 12 th	Aug 8 th	May 8 th	Aug 9 th	May 25 th	Aug 6 th
	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
A 11-0-1-0-0	2-Methylhexane	0.9942	0.9909	0.9942	0.9995	0.9991	0.9999
Alkanes	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
	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
	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
Alkonoc*	Ethylbenzene	0.9986	0.9972	0.9821	0.9989	0.9973	0.9995
AIRCHES	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
Alkynes	m-Ethyltoluene	0.9871	0.9982	0.9954	0.9924	0.9906	0.9986
Aromatics	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

87.1	Group														Alkanes													
	Specie	Ethane	Propane	n-Butane	Isobutane	n-Pentane	Isopentane	n-Hexane	Cyclohexane	2,2-Dimethylbutane	2,3-Dimethylbutane	2-Methylpentane	3-Methylpentane	n-Heptane	2-Methylhexane	3-Methylhexane	n-Octane	n-Nonane	n-Decane	n-Undecane	n-Dodecane	Ethene	Propene	1-Butene	trans-2-Butene	cis-2-Butene		1-Pentene
	Mav	8.86 ± 11.72	8.06 ± 11.88	3.68 ± 5.84	2.24 ± 2.93	1.37 ± 1.95	2.13 ± 2.16	0.70 ± 0.82	0.49 ± 0.85	2.1 ± 3.48	0.40 ± 0.59	0.70 ± 0.74	0.37 ± 0.41	0.18 ± 0.16	0.22 ± 0.27	0.27 ± 0.23	0.39 ± 0.53	0.25 ± 0.53	0.03 ± 0.04	0.07 ± 0.08	0.06 ± 0.07	2.24 ± 1.64	0.74 ± 0.75	0.11 ± 0.17	0.06 ± 0.11	0.42 ± 0.53	0.06 ± 0.09	
	J	11.95 ± 13.63	10.45 ± 11.47	5.22 ± 5.48	2.7 ± 2.61	1.76 ± 1.75	2.65 ± 2.34	0.87 ± 0.73	0.26 ± 0.26	1.87 ± 2.73	0.15 ± 0.15	0.67 ± 0.47	0.44 ± 0.37	0.53 ± 0.44	0.21 ± 0.15	0.25 ± 0.16	0.09 ± 0.07	0.08 ± 0.08	0.03 ± 0.05	0.13 ± 0.13	0.05 ± 0.05	1.55 ± 1.15	0.91 ± 0.66	0.11 ± 0.09	0.05 ± 0.05	0.43 ± 0.45	0.06 + 0.05	0.00 ± 0.00
	Jul	10.21 ± 12.03	10.78 ± 11.46	4.87 ± 5.60	2.83 ± 2.800	2.07 ± 2.01	2.91 ± 2.40	0.90 ± 0.81	0.30 ± 0.61	1.34 ± 2.25	0.41 ± 0.37	0.59 ± 0.8	0.61 ± 0.39	0.43 ± 0.31	0.16 ± 0.24	0.13 ± 0.23	0.10 ± 0.10	0.07 ± 0.10	0.11 ± 0.17	0.27 ± 0.34	0.18 ± 0.34	1.94 ± 1.58	0.92 ± 0.84	0.08 ± 0.13	0.03 ± 0.06	0.32 ± 0.54	0 04 + 0 08	0.04 ± 0.00
	Aug	11.57 ± 13.14	9.42 ± 10.24	4.62 ± 5.09	3.31 ± 3.88	1.80 ± 2.01	2.96 ± 3.28	0.79 ± 0.81	0.49 ± 0.64	1.66 ± 2.45	0.32 ± 0.32	0.82 ± 0.78	0.64 ± 0.56	0.63 ± 0.47	0.26 ± 0.22	0.25 ± 0.21	0.14 ± 0.15	0.09 ± 0.10	0.07 ± 0.06	0.14 ± 0.19	0.13 ± 0.19	1.81 ± 1.12	0.70 ± 0.55	0.09 ± 0.09	0.06 ± 0.05	0.37 ± 0.43		0.07 ± 0.06
	Sep	15.33±14.79	20.99 ± 22.07	8.20 ± 8.32	4.53 ± 4.07	3.19 ± 3.47	4.08 ± 3.67	1.38 ± 1.18	1.20 ± 1.46	1.43 ± 1.67	0.22 ± 0.20	0.82 ± 0.68	1.03 ± 1.16	0.64 ± 0.50	0.43 ± 0.29	0.47 ± 0.33	0.24 ± 0.30	0.12 ± 0.11	0.11 ± 0.09	0.17 ± 0.19	0.15 ± 0.18	2.50 ± 1.77	1.30 ± 1.69	0.16 ± 0.16	0.07 ± 0.06	1.12 ± 2.05	0 05 + 0 05	0.00 ± 0.00
ratios	whole	11.57 ± 13.28	11.88 ± 14.82	5.30 ± 6.35	3.12 ± 3.41	2.02 ± 2.40	2.94 ± 2.90	0.92 ± 0.91	0.55 ± 0.92	1.69 ± 2.61	0.30 ± 0.38	0.72 ± 0.71	0.61 ± 0.69	0.48 ± 0.43	0.26 ± 0.25	0.27 ± 0.26	0.19 ± 0.31	0.12 ± 0.27	0.07 ± 0.10	0.15 ± 0.21	0.11 ± 0.20	2.01 ± 1.51	0.91 ± 1.01	0.11 ± 0.14	0.06 ± 0.07	0.52 ± 1.01	0.06 + 0.07	0.00 - 0.07
at the thre	Mav	3.98 ± 2.94	3.45 ± 3.82	2.26 ± 3.05	0.89 ± 1.15	0.79 ± 1.01	0.52 ± 1.01	1.91 ± 2.77	0.46 ± 0.55	0.78 ± 1.44	0.20 ± 0.17	0.69 ± 0.94	0.50 ± 0.73	2.07 ± 2.96	0.78 ± 0.72	0.78 ± 0.66	0.05 ± 0.05	0.08 ± 0.05	0.04 ± 0.03	0.59 ± 0.97	0.10 ± 0.20	2.41 ± 2.41	1.03 ± 1.34	0.37 ± 0.44	0.48 ± 0.56	0.33 ± 0.42	0.08 + 0.14	0.00 ± 0
e sites in	Jun	1.98 ± 1.69	3.43 ± 2.6	2.1 ± 2.07	1.3 ± 1.27	1.08 ± 1.01	2.04 ± 1.45	0.96 ± 1.35	0.19 ± 0.26	0.41 ± 0.66	0.23 ± 0.39	0.53 ± 0.56	0.78 ± 0.77	1.38 ± 2.27	0.57 ± 0.62	0.31 ± 0.4	0.06 ± 0.06	0.09 ± 0.09	0.05 ± 0.14	0.42 ± 0.57	0.16 ± 0.25	2.21 ± 2.16	0.83 ± 0.92	0.18 ± 0.16	0.13 ± 0.16	0.18 ± 0.24	0.12 ± 0.13	
Zibo City	Jul	3.37 ± 1.55	3.62 ± 2.79	1.60 ± 1.80	1.29 ± 1.09	0.96 ± 0.90	1.66 ± 2.32	0.33 ± 0.42	0.04 ± 0.07	0.13 ± 0.32	0.26 ± 0.25	0.18 ± 0.22	0.05 ± 0.09	0.16 ± 0.15	0.03 ± 0.08	0.18 ± 0.24	0.04 ± 0.10	0.02 ± 0.09	0.07 ± 0.10	0.13 ± 0.16	0.13 ± 0.22	2.35 ± 1.68	0.43 ± 0.47	0.04 ± 0.07	0.05 ± 0.08	0.06 ± 0.15	0.06 ± 0.00	0.00 ± 0.02
	Aug	2.05 ± 1.36	3.87 ± 2.66	1.71 ± 1.89	1.58 ± 1.52	1.86 ± 1.84	1.64 ± 1.68	1.18 ± 1.30	0.53 ± 0.79	1.77 ± 3.18	0.22 ± 0.18	0.31 ± 0.34	0.24 ± 0.54	0.74 ± 1.12	0.15 ± 0.42	0.55 ± 0.86	0.13 ± 0.13	0.47 ± 0.64	0.58 ± 0.73	1.52 ± 2.13	1.13 ± 1.58	$\textbf{2.38} \pm \textbf{2.03}$	0.67 ± 0.73	0.98 ± 1.22	1.28 ± 3.05	0.21 ± 0.52	012.016	0.13 ± 0.16
	Sep	3.74 ± 1.98	4.91 ± 3.35	3.25 ± 4.01	1.75 ± 1.64	1.10 ± 1.18	2.70 ± 3.41	2.19 ± 3.36	0.77 ± 1.32	1.89 ± 3.10	0.84 ± 1.10	1.31 ± 1.79	0.89 ± 1.32	1.76 ± 2.12	0.66 ± 1.19	1.06 ± 2.01	0.31 ± 0.51	0.06 ± 0.07	0.10 ± 0.13	0.19 ± 0.26	0.17 ± 0.20	2.43 ± 1.77	0.82 ± 0.73	0.13 ± 0.15	0.23 ± 0.34	0.19 ± 0.42	0.10 ± 0.08	
	whole	3.02 ± 2.17	3.88 ± 3.14	2.21 ± 2.80	1.37 ± 1.40	1.18 ± 1.32	1.72 ± 2.28	1.34 ± 2.24	0.42 ± 0.82	1.08 ± 2.35	0.36 ± 0.61	0.62 ± 1.06	0.50 ± 0.87	1.25 ± 2.12	0.42 ± 0.78	0.59 ± 1.14	0.13 ± 0.27	0.16 ± 0.36	0.18 ± 0.42	0.60 ± 1.25	0.36 ± 0.87	2.36 ± 2.03	0.77 ± 0.92	0.37 ± 0.73	0.46 ± 1.58	0.19 ± 0.40	0 10 + 0 12	0.10 ± 0.13
	Mav	2.23 ± 1.44	4.85 ± 4.92	1.58 ± 1.38	0.83 ± 0.84	1.04 ± 1.10	1.48 ± 1.08	0.69 ± 0.79	0.09 ± 0.14	0.07 ± 0.14	0.17 ± 0.19	0.62 ± 0.57	0.25 ± 0.24	0.18 ± 0.36	0.04 ± 0.07	0.09 ± 0.16	0.04 ± 0.05	0.01 ± 0.05	0.04 ± 0.1	0.01 ± 0.03	0.37 ± 0.37	4.16 ± 2.96	1.97 ± 2.98	0.46 ± 0.32	0.47 ± 0.34	0.55 ± 0.45	0.06 ± 0.16	
	Ju	2.48 ± 1.68	4.41 ± 3.89	2.24 ± 2.05	1.52 ± 1.31	1.7 ± 1.90	2.12 ± 2.2	0.63 ± 0.96	0.18 ± 0.2	0.22 ± 0.27	0.39 ± 0.42	0.87 ± 0.74	0.35 ± 0.37	0.24 ± 0.41	0.05 ± 0.08	0.09 ± 0.09	0.04 ± 0.06	0.01 ± 0.01	0.02 ± 0.05	0.09 ± 0.22	0.33 ± 0.42	3.09 ± 3.28	2.1 ± 3.86	0.82 ± 0.34	0.8 ± 0.55	0.47 ± 0.31	0.00 ± 0.11	0.07 ± 0.11
	Je XD	3.37 ± 1.90	4.64 ± 3.87	2.47 ± 1.89	1.52 ± 1.60	1.5 ± 1.44	2.14 ± 1.49	1.23 ± 1.65	0.13 ± 0.27	0.47 ± 0.53	0.18 ± 0.37	0.76 ± 0.75	0.27 ± 0.22	0.2 ± 0.21	0.04 ± 0.06	0.08 ± 0.1	0.07 ± 0.09	0.01 ± 0.01	0.06 ± 0.48	0.05 ± 0.16	0.07 ± 0.19	3.23 ± 3.21	1.48 ± 2.16	0.66 ± 0.46	0.82 ± 0.91	0.54 ± 1.06	0.06 ± 0.11	0000 = 0010
	Aug	3.02 ± 2.07	6.11 ± 6.91	2.79 ± 2.98	2.03 ± 2.28	1.98 ± 2.96	2.13 ± 2.37	0.76 ± 0.87	0.14 ± 0.23	0.36 ± 0.77	0.44 ± 0.66	0.76 ± 1.17	0.21 ± 0.2	0.17 ± 0.31	0.05 ± 0.05	0.12 ± 0.32	0.06 ± 0.08	0.01 ± 0.02	0.01 ± 0.03	0.09 ± 0.12	0.1 ± 0.14	2.25 ± 2.72	1.36 ± 2.35	0.4 ± 0.48	0.44 ± 0.45	0.3 ± 0.39	0.00.000	0.09 ± 0.20
	Sep	4.28 ± 2.31	7.83 ± 5.7	5.3 ± 4.17	2.55 ± 2.01	2.95 ± 2.44	3.10 ± 2.89	1.23 ± 1.04	0.19 ± 0.26	0.39 ± 0.5	0.58 ± 0.58	0.94 ± 0.72	0.39 ± 0.31	0.19 ± 0.18	0.08 ± 0.06	0.1 ± 0.07	0.03 ± 0.03	0.02 ± 0.02	0.01 ± 0.02	0.05 ± 0.07	0.06 ± 0.07	4.77 ± 3.01	1.69 ± 1.77	0.44 ± 0.58	0.5 ± 0.53	0.22 ± 0.22		0.08 ± 0.07
	whole	3.00 ± 2.00	5.52 ± 5.37	2.74 ± 2.84	1.65 ± 1.76	1.77 ± 2.15	2.13 ± 2.11	0.88 ± 1.11	0.14 ± 0.22	0.29 ± 0.51	0.34 ± 0.49	0.78 ± 0.83	0.29 ± 0.30	0.20 ± 0.32	0.05 ± 0.07	0.10 ± 0.18	0.05 ± 0.07	0.01 ± 0.03	0.03 ± 0.21	0.06 ± 0.14	0.19 ± 0.31	3.46 ± 3.18	1.77 ± 2.84	0.56 ± 0.47	0.60 ± 0.59	0.43 ± 0.56		0.08 ± 0.14

Table S3. Summary of monthly averaged concentration or OH reactivity (with standard deviation) of the measured VOCs, O3 and its major precursors, as well as TVOC/NOx

127

6S

Summary	non-listed in bax model	Alkynes Aromatics	Alkenes*	BVOC
k _A voc (s ⁻¹) k _B voc (s ⁻¹) k _{Alkans} (s ⁻¹) k _{Alkans} (s ⁻¹)	2.4-Dimethylpentane 2.3-Dimethylpentane 2.2.4-Trimethylpentane 2.3.4-Trimethylpentane Methyk yclohexane 2-Methylheptane 3-Methylheptane p-Diethylbenzene Cyclopentane Methyk yclopentane	m-Ethyltoluene p-Ethyltoluene o-Ethyltoluene 1.2.3-Trimethylbenzene 1.2.4-Trimethylbenzene 1.3.5-Trimethylbenzene	1-Hexene Acetylene Benzene Troluene Ethylbenzene m.p-xylene o-xylene o-xylene Styrene n-Propylbenzene Isopropylbenzene	cis-2-Pentene Isoprene
4.7±3.7 2.3±2.6 2.0±1.9 1.9±1.5	$\begin{array}{c} 0.32\pm0.34\\ 0.23\pm0.22\\ 0.09\pm0.17\\ 0.06\pm0.09\\ 0.16\pm0.21\\ 0.04\pm0.05\\ 0.34\pm0.36\\ 0.34\pm0.36\\ 0.07\pm0.16\\ 0.51\pm0.61\end{array}$	$\begin{array}{c} 0.06 \pm 0.08 \\ 0.03 \pm 0.04 \\ 0.06 \pm 0.07 \\ 0.04 \pm 0.05 \\ 0.10 \pm 0.11 \\ 0.04 \pm 0.05 \end{array}$	$\begin{array}{c} 0.05\pm 0.07\\ 2.26\pm 3.43\\ 0.97\pm 0.98\\ 1.32\pm 1.85\\ 0.22\pm 0.22\\ 0.55\pm 0.62\\ 0.18\pm 0.19\\ 0.10\pm 0.14\\ 0.04\pm 0.03\\ 0.03\pm 0.06\end{array}$	0.06 ± 0.12 0.95 ± 1.07
$5.1 \pm 3.4 \\ 4.9 \pm 4.9 \\ 2.3 \pm 1.8 \\ 1.9 \pm 1.2$	$\begin{array}{c} 0.49\pm 0.39\\ 0.24\pm 0.17\\ 0.71\pm 1.22\\ 0.08\pm 0.08\\ 0.07\pm 0.07\\ 0.05\pm 0.04\\ 0.41\pm 0.30\\ 0.41\pm 0.30\\ 0.42\pm 0.02\\ 0.22\pm 0.02\\ 0.20\pm 0.38\\ 0.29\pm 0.97\end{array}$	$\begin{array}{c} 0.09 \pm 0.10 \\ \\ 0.05 \pm 0.06 \\ \\ 0.07 \pm 0.06 \\ \\ 0.17 \pm 0.16 \\ \\ 0.17 \pm 0.16 \\ \end{array}$	$\begin{array}{c} 0.06\pm0.05\\ 2.88\pm2.79\\ 1.32\pm1.52\\ 0.98\pm0.99\\ 0.19\pm0.14\\ 0.44\pm0.38\\ 0.18\pm0.13\\ 0.07\pm0.09\\ 0.05\pm0.05\\ 0.05\pm0.02\\ \end{array}$	0.12 ± 0.12 2.05 ± 2.04
5.3 ± 4.2 4.5 ± 5.9 2.3 ± 1.9 1.7 ± 1.5	$\begin{array}{c} 0.32 \pm 0.59 \\ 0.14 \pm 0.28 \\ 0.03 \pm 0.18 \\ 0.10 \pm 0.11 \\ 0.06 \pm 0.07 \\ 0.04 \pm 0.07 \\ 0.04 \pm 0.07 \\ 0.49 \pm 0.76 \\ 0.49 \pm 0.17 \\ 0.07 \pm 0.22 \\ 0.69 \pm 2.09 \end{array}$	$\begin{array}{c} 0.20 \pm 0.24 \\ 0.11 \pm 0.20 \\ 0.11 \pm 0.14 \\ 0.14 \pm 0.13 \\ 0.46 \pm 0.44 \\ 0.11 \pm 0.15 \end{array}$	$\begin{array}{c} 0.01 \pm 0.03 \\ 2.61 \pm 3.52 \\ 1.67 \pm 2.69 \\ 0.83 \pm 0.71 \\ 0.19 \pm 0.12 \\ 0.43 \pm 0.33 \\ 0.30 \pm 0.18 \\ 0.06 \pm 0.10 \\ 0.08 \pm 0.10 \\ 0.13 \pm 0.12 \end{array}$	0.05 ± 0.17 1.86 ± 2.45
5.1 ± 3.5 3.1 ± 3.4 2.4 ± 2.1 1.8 ± 1.1	$\begin{array}{c} 0.58 \pm 0.67\\ 0.21 \pm 0.21\\ 0.22 \pm 0.23\\ 0.11 \pm 0.09\\ 0.13 \pm 0.16\\ 0.06 \pm 0.05\\ 0.44 \pm 0.46\\ 0.02 \pm 0.02\\ 0.10 \pm 0.19\\ 0.53 \pm 0.74\end{array}$	$\begin{array}{c} 0.09 \pm 0.09 \\ 0.05 \pm 0.05 \\ 0.07 \pm 0.09 \\ 0.04 \pm 0.04 \\ 0.12 \pm 0.10 \\ 0.04 \pm 0.04 \end{array}$	$\begin{array}{c} 0.1\pm 0.06\\ 3.25\pm 5.00\\ 0.82\pm 0.72\\ 1.11\pm 0.75\\ 0.24\pm 0.18\\ 0.24\pm 0.40\\ 0.23\pm 0.17\\ 0.12\pm 0.16\\ 0.03\pm 0.03\\ 0.04\pm 0.03\\ 0.04\pm 0.03\end{array}$	0.07 ± 0.13 1.3 ± 1.41
8.4 ± 6.5 2.9 ± 2.7 3.7 ± 3.0 3.2 ± 3.4	$\begin{array}{c} 0.69 \pm 0.64 \\ 0.33 \pm 0.29 \\ 0.20 \pm 0.17 \\ 0.14 \pm 0.14 \\ 0.11 \pm 0.10 \\ 0.08 \pm 0.09 \\ 0.71 \pm 0.71 \\ 0.03 \pm 0.03 \\ 0.60 \pm 0.82 \\ 0.84 \pm 0.95 \end{array}$	0.13 ± 0.19 0.07 ± 0.09 0.07 ± 0.06 0.06 ± 0.07 0.26 ± 0.34 0.07 ± 0.09	$\begin{array}{c} 0.12\pm 0.13\\ 5.60\pm 4.88\\ 1.93\pm 2.09\\ 1.45\pm 1.42\\ 0.51\pm 0.24\\ 0.79\pm 0.69\\ 0.40\pm 0.31\\ 0.12\pm 0.15\\ 0.06\pm 0.06\\ 0.05\pm 0.05\\ \end{array}$	0.07 ± 0.07 1.22 ± 1.14
5.7 ± 4.6 3.5 ± 4.2 2.5 ± 2.3 2.1 ± 2.0	$\begin{array}{c} 0.48 \pm 0.56 \\ 0.23 \pm 0.25 \\ 0.26 \pm 0.63 \\ 0.10 \pm 0.11 \\ 0.10 \pm 0.14 \\ 0.05 \pm 0.06 \\ 0.48 \pm 0.56 \\ 0.04 \pm 0.08 \\ 0.20 \pm 0.46 \\ 0.20 \pm 0.46 \\ 0.20 \pm 1.17 \end{array}$	0.11 ± 0.16 0.07 ± 0.11 0.07 ± 0.09 0.07 ± 0.08 0.21 ± 0.29 0.06 ± 0.09	0.07 ± 0.09 3.32 ± 4.19 1.33 ± 1.77 1.14 ± 1.25 0.23 ± 0.19 0.25 ± 0.52 0.10 ± 0.13 0.05 ± 0.06 0.05 ± 0.07	0.07 ± 0.13 1.47 ± 1.74
6.2 ± 6.29 1.5 ± 1.9 1.9 ± 2.0 2.5 ± 3.2	$\begin{array}{c} 0.43\pm 0.40\\ 0.19\pm 0.24\\ 0.24\pm 0.34\\ 0.15\pm 0.14\\ 0.08\pm 0.13\\ 0.03\pm 0.06\\ 0.35\pm 0.44\\ 0.02\pm 0.02\\ 0.02\pm 0.02\\ 0.01\pm 0.36\\ 0.80\pm 0.83\\ \end{array}$	0.06 ± 0.06 0.03 ± 0.04 0.03 ± 0.04 0.03 ± 0.02 0.16 ± 0.14 0.03 ± 0.05	$\begin{array}{c} 0.16\pm 0.22\\ 2.61\pm 2.21\\ 0.80\pm 0.62\\ 1.54\pm 1.68\\ 0.55\pm 0.74\\ 1.66\pm 2.37\\ 0.70\pm 1.01\\ 0.20\pm 0.31\\ 0.05\pm 0.03\\ 0.21\pm 0.14\\ \end{array}$	0.08 ± 0.15 0.62 ± 0.78
5.3 ± 4.3 1.7 ± 1.7 1.7 ± 1.3 1.9 ± 1.4	$\begin{array}{c} 0.12\pm0.18\\ 0.15\pm0.20\\ 0.14\pm0.35\\ 0.07\pm0.09\\ 0.06\pm0.05\\ 0.07\pm0.08\\ 0.17\pm0.21\\ 0.05\pm0.08\\ 0.11\pm0.13\\ 0.37\pm0.31\end{array}$	$\begin{array}{c} 0.03 \pm 0.05 \\ 0.06 \pm 0.17 \\ 0.1 \pm 0.18 \\ 0.09 \pm 0.15 \\ 0.24 \pm 0.33 \\ 0.02 \pm 0.03 \end{array}$	0.10 ± 0.13 3.72 ± 4.98 0.89 ± 0.74 2.29 ± 3.02 0.43 ± 0.65 1.31 ± 2.27 0.58 ± 1.07 0.16 ± 0.37 0.04 ± 0.09 0.08 ± 0.07	0.09 ± 0.12 0.71 ± 0.70
$\begin{array}{c} 3.3 \pm 2.3 \\ 1.4 \pm 1.6 \\ 1.0 \pm 0.8 \\ 1.5 \pm 1.1 \end{array}$	$\begin{array}{c} 0.16\pm0.15\\ 0.22\pm0.23\\ 0.12\pm0.30\\ 0.08\pm0.18\\ 0.04\pm0.11\\ 0.12\pm0.3\\ 0.28\pm0.29\\ 0.02\pm0.03\\ 0.02\pm0.03\\ 0.02\pm0.05\\ 0.04\pm0.10\\ \end{array}$	$\begin{array}{c} 0.05 \pm 0.07 \\ 0.02 \pm 0.03 \\ 0.03 \pm 0.03 \\ 0.03 \pm 0.04 \\ 0.14 \pm 0.12 \\ 0.02 \pm 0.03 \end{array}$	$\begin{array}{c} 0.16 \pm 0.22 \\ 2.21 \pm 2.07 \\ 1.17 \pm 0.79 \\ 1.13 \pm 2 \\ 0.2 \pm 0.22 \\ 0.44 \pm 0.6 \\ 0.22 \pm 0.29 \\ 0.14 \pm 0.25 \\ 0.02 \pm 0.03 \\ 0.03 \pm 0.03 \end{array}$	0.19 ± 0.23 0.59 ± 0.68
10.7 ± 8.4 4.3 ± 3.5 3.7 ± 3.5 5.8 ± 6.0	$\begin{array}{c} 1.22\pm1.60\\ 0.20\pm0.18\\ 0.65\pm0.93\\ 1.17\pm2.00\\ 1.51\pm2.65\\ 1.81\pm2.44\\ 0.62\pm0.6\\ 0.11\pm0.15\\ 0.25\pm0.37\\ 0.16\pm0.18\\ \end{array}$	$\begin{array}{c} 0.06 \pm 0.05 \\ 0.04 \pm 0.05 \\ 0.10 \pm 0.13 \\ 0.06 \pm 0.06 \\ 0.09 \pm 0.09 \\ 0.07 \pm 0.05 \end{array}$	$\begin{array}{c} 0.58 \pm 1.07\\ 2.56 \pm 2.75\\ 1.19 \pm 0.87\\ 2.07 \pm 2.22\\ 0.32 \pm 0.27\\ 0.61 \pm 0.64\\ 0.18 \pm 0.19\\ 0.15 \pm 0.20\\ 0.04 \pm 0.04\\ 0.03 \pm 0.03\\ \end{array}$	0.71 ±0.87 1.8 ± 1.47
7.3 ± 5.3 1.8 ± 2.0 2.9 ± 2.6 2.3 ± 1.7	$\begin{array}{l} 0.48\pm 0.84\\ 0.55\pm 0.79\\ 0.58\pm 1.33\\ 0.07\pm 0.08\\ 0.05\pm 0.06\\ 0.09\pm 0.13\\ 0.44\pm 0.51\\ 0.09\pm 0.14\\ 0.36\pm 0.86\\ 0.58\pm 1.28\end{array}$	$\begin{array}{c} 0.10\pm0.11\\ 0.04\pm0.05\\ 0.04\pm0.05\\ 0.10\pm0.13\\ 0.24\pm0.21\\ 0.05\pm0.06\end{array}$	$\begin{array}{c} 0.17\pm 0.19\\ 2.17\pm 2.38\\ 1.82\pm 1.37\\ 2.5\pm 3.29\\ 0.55\pm 0.7\\ 1.49\pm 2.19\\ 0.67\pm 0.91\\ 0.31\pm 0.55\\ 0.04\pm 0.04\\ 0.03\pm 0.03\\ \end{array}$	0.17 ± 0.21 0.77 ± 0.84
6.8 ± 6.3 2.2 ± 2.6 2.3 ± 2.5 2.9 ± 3.7	$\begin{array}{c} 0.51 \pm 0.99\\ 0.27 \pm 0.44\\ 0.38 \pm 0.86\\ 0.39 \pm 1.40\\ 0.46 \pm 1.37\\ 0.38 \pm 0.47\\ 0.38 \pm 0.47\\ 0.06 \pm 0.11\\ 0.22 \pm 0.49\\ 0.38 \pm 0.76\end{array}$	0.06 ± 0.07 0.04 ± 0.09 0.06 ± 0.11 0.06 ± 0.10 0.18 ± 0.20 0.04 ± 0.05	0.25 ± 0.58 2.65 ± 3.11 1.19 ± 1.00 1.94 ± 2.58 0.42 ± 0.58 1.12 ± 1.88 0.48 ± 0.82 0.19 ± 0.37 0.04 ± 0.05 0.07 ± 0.09	0.27 ± 0.52 0.93 ± 1.07
5.5 ± 3.8 1.1 ± 1.4 1.1 ± 0.8 4.1 ± 2.9	$\begin{array}{c} 0.14\pm 0.10\\ 0.06\pm 0.06\\ 0.03\pm 0.11\\ 0.18\pm 0.29\\ 0.02\pm 0.03\\ 0.01\pm 0.01\\ 0.02\pm 0.03\\ 0.01\pm 0.01\\ 0.02\pm 0.05\\ 0.26\pm 0.37\\ 0.13\pm 0.21\end{array}$	$\begin{array}{c} 0.01 \pm 0.05 \\ \\ 0.01 \pm 0.02 \\ \\ 0.01 \pm 0.07 \\ \\ 0.01 \pm 0.04 \\ \\ 0.02 \pm 0.03 \\ \\ 0.01 \pm 0.11 \end{array}$	$\begin{array}{c} 0.08\pm0.06\\ 2.03\pm1.4\\ 0.70\pm0.53\\ 0.59\pm0.97\\ 0.06\pm0.09\\ 0.27\pm0.46\\ 0.02\pm0.04\\ 0.03\pm0.07\\ 0.01\pm0.04\\ 0.01\pm0.04\end{array}$	/ 0.48 ± 0.59
$\begin{array}{c} 6.6 \pm 4.3 \\ 1.8 \pm 1.8 \\ 1.4 \pm 1.1 \\ 4.8 \pm 3.3 \end{array}$	$\begin{array}{c} 0.20\pm0.16\\ 0.05\pm0.05\\ 0.06\pm0.06\\ 0.06\pm0.27\\ 0.07\pm0.11\\ 0.03\pm0.04\\ 0.03\pm0.04\\ 0.02\pm0.02\\ 0.01\pm0.02\\ 0.86\pm0.85\\ 0.12\pm0.18 \end{array}$	$\begin{array}{c} 0.01 \pm 0.01 \\ 0.01 \pm 0.01 \\ 0.01 \pm 0.01 \\ 0.01 \pm 0.04 \\ 0.02 \pm 0.02 \\ 0.01 \pm 0.03 \end{array}$	$\begin{array}{c} 0.15\pm0.16\\ 2.17\pm1.39\\ 0.65\pm0.54\\ 0.63\pm0.60\\ 0.06\pm0.07\\ 0.32\pm0.40\\ 0.05\pm0.08\\ 0.04\pm0.15\\ 0.01\pm0.01\\ 0.01\pm0.01\\ \end{array}$	/ 0.77 ± 0.74
6.4 ± 4.9 2.4 ± 2.8 1.4 ± 1.0 4.2 ± 3.8	$\begin{array}{l} 0.22\pm 0.23\\ 0.07\pm 0.09\\ 0.06\pm 0.07\\ 0.11\pm 0.19\\ 0.14\pm 0.38\\ 0.02\pm 0.03\\ 0.01\pm 0.03\\ 0.01\pm 0.03\\ 0.88\pm 0.79\\ 0.88\pm 0.79\end{array}$	$\begin{array}{c} 0.02\pm0.03\\ 0.03\pm0.03\\ 0.01\pm0.02\\ 0.01\pm0.02\\ 0.01\pm0.02\\ 0.01\pm0.05\\ 0.04\pm0.05\end{array}$	$\begin{array}{c} 0.04\pm 0.02\\ 2.86\pm 2.39\\ 1.05\pm 0.79\\ 1.02\pm 0.96\\ 0.13\pm 0.13\\ 0.68\pm 0.80\\ 0.15\pm 0.32\\ 0.16\pm 0.32\\ 0.04\pm 0.04\\ 0.01\pm 0.01\\ \end{array}$	/ 1.01 ± 1.18
5.0 ± 4.8 1.3 ± 1.2 1.5 ± 1.6 2.9 ± 3.0	$\begin{array}{c} 0.23\pm0.20\\ 0.04\pm0.07\\ 0.08\pm0.14\\ 0.31\pm0.54\\ 0.07\pm0.12\\ 0.01\pm0.04\\ 0.01\pm0.02\\ 0.01\pm0.05\\ 1.17\pm2.23\\ 0.11\pm0.23\end{array}$	$\begin{array}{c} 0.02 \pm 0.03 \\ 0.02 \pm 0.03 \\ 0.01 \pm 0.02 \\ 0.02 \pm 0.05 \\ 0.04 \pm 0.06 \\ 0.01 \pm 0.01 \end{array}$	$\begin{array}{c} 0.03\pm 0.03\\ 1.6\pm 1.68\\ 0.71\pm 0.65\\ 0.75\pm 1.20\\ 0.09\pm 0.09\\ 0.26\pm 0.25\\ 0.07\pm 0.08\\ 0.13\pm 0.24\\ 0.01\pm 0.02\\ 0.01\pm 0.03\\ \end{array}$	$^{/}$ 0.54 ± 0.50
6.0 ± 4.0 0.7 ± 0.8 1.9 ± 1.4 3.6 ± 2.6	$\begin{array}{l} 0.2\pm0.12\\ 0.09\pm0.12\\ 0.10\pm0.10\\ 0.08\pm0.11\\ 0.09\pm0.11\\ 0.02\pm0.02\\ 0.01\pm0.02\\ 0.01\pm0.02\\ 0.01\pm0.01\\ 0.3\pm0.41\\ 0.04\pm0.06\end{array}$	$\begin{array}{c} 0.02\pm0.03\\ 0.02\pm0.02\\ 0.02\pm0.02\\ 0.02\pm0.02\\ 0.04\pm0.04\\ 0.01\pm0.01 \end{array}$	0.05 ± 0.03 1.70 ± 1.51 1.09 ± 0.66 1.00 ± 0.74 0.10 ± 0.08 0.37 ± 0.31 0.11 ± 0.10 0.10 ± 0.17 0.01 ± 0.01 0.01 ± 0.01	$^{/}$ 0.29 \pm 0.32
5.9 ± 4.4 1.5 ± 1.8 1.4 ± 1.2 4.0 ± 3.2	$\begin{array}{c} 0.20\pm 0.17\\ 0.06\pm 0.08\\ 0.07\pm 0.09\\ 0.12\pm 0.32\\ 0.11\pm 0.23\\ 0.02\pm 0.03\\ 0.01\pm 0.02\\ 0.01\pm 0.02\\ 0.01\pm 0.02\\ 0.01\pm 0.04\\ 0.70\pm 1.24\\ 0.70\pm 1.24 \end{array}$	$\begin{array}{c} 0.01 \pm 0.03 \\ \\ 0.01 \pm 0.02 \\ \\ 0.01 \pm 0.03 \\ \\ 0.02 \pm 0.04 \\ \\ 0.02 \pm 0.06 \end{array}$	$\begin{array}{c} 0.07\pm 0.09\\ 2.06\pm 1.74\\ 0.81\pm 0.66\\ 0.77\pm 0.94\\ 0.08\pm 0.10\\ 0.36\pm 0.49\\ 0.07\pm 0.16\\ 0.07\pm 0.16\\ 0.09\pm 0.21\\ 0.02\pm 0.03\\ 0.01\pm 0.05\\ \end{array}$	- 0.61 ± 0.75

S10

																ppbC/ppbv;	129 ^a Unit of
0.1 ± 4.1	-	7.6 ± 3.2	5.4 ± 2.0	8.0 ± 6.6	8.0 ± 6.6	6.2 ± 4.4	11.5 ± 10.0	5.5 ± 3.3	9.5 ± 6.1	7.2 ± 5.3	14.3 ± 7.9	15.0 ± 6.5	16.6 ± 9.4	19.1 ± 9.6	13.9 ± 4.8	8.5±4.3	TVOC/NOx ^a
± 25.3	34	56 ± 34.1	59.9 ± 29.4	49.1 ± 25.1	47.2 ± 34.1	37.1 ± 33.8	32.8 ± 25.5	54.7 ± 35.6	66.5 ± 36.3	45.0 ± 26.7	48.4 ± 32.2	38.4 ± 33.4	38.5 ± 27.3	60.2 ± 33.7	60.0 ± 32.7	45.0 ± 25.3	O3 (ppbv)
9±13.8	21.	15.8 ± 10.0	18.2 ± 10.5	21.7 ± 15.7	31.1 ± 28.6	50.9 ± 38.7	32.4 ± 23.8	24.5 ± 22.8	20.7 ± 18.7	28.2 ± 24.8	19.1 ± 14.9	26.2 ± 18.5	18.2 ± 10.7	12.1 ± 8.5	16.4 ± 11.8	22.8 ± 17.3	NOx (ppbv)
± 777	962	1194 ± 966	726 ± 727	906 ± 938	1121 ± 426	939 ± 385	944 ± 415	1449 ± 396	1207 ± 344	1063 ± 354	989 ± 291	965 ± 269	943 ± 269	1020 ± 294	963 ± 288	1053 ± 318	CO (ppbv)
3 ± 0.03	0.0	0.05 ± 0.04	0.04 ± 0.03	0.04 ± 0.03	0.05 ± 0.06	0.04 ± 0.04	0.05 ± 0.05	0.04 ± 0.04	0.07 ± 0.09	0.05 ± 0.04	0.06 ± 0.08	0.1 ± 0.09	0.06 ± 0.09	0.05 ± 0.06	0.05 ± 0.05	0.04 ± 0.06	$k_{C2H2} (s^{-1})$
± 0.5	0.5 :	0.8 ± 0.7	0.3 ± 0.4	0.3 ± 0.4	1.5 ± 1.8	2.1 ± 2.3	1.2 ± 0.8	0.9 ± 0.8	1.6 ± 2.1	1.7 ± 2.0	1.1 ± 0.9	1.3 ± 1.1	0.9 ± 0.6	1.4 ± 1.2	0.9 ± 0.7	0.9 ± 0.8	k _{Aromatics} (s ⁻¹)

130 131

Table S4. Summary of threshold values for photochemical regime classifications with ratios of RIR_{NOx}/RIR_{AVOC}

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

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

133 Table S5. Summary of box model performance using three statistical metrics, IOA, r, and RMSE, at 134 three sites in four patterns of timescale during the campaign

^aIndex of agreement

^bPearson's correlation coefficient ^cRoot mean square error (in ppbv)

135

137 138

Table S6. Summary of averaged relative incremental reactivity (with standard deviation) of majorprecursor groups for four patterns of timescale

Site	RIR parameters	Five-month	Month-to-month	Week-to-week	Day-to-day
	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
T 7	RIR _{NOx}	0.30	0.30 ± 0.16	0.21 ± 0.34	0.19 ± 0.40
1Z	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
	RIRAromatics	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
	RIRAVOC	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
DI	RIR _{NOx}	0.23	0.11 ± 0.28	0.002 ± 0.56	-0.09 ± 0.47
DJ	RIRAlkanes	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
	RIRAromatics	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
	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
VD	RIR _{NOx}	0.15	-0.02 ± 0.56	-0.06 ± 0.64	-0.07 ± 0.60
ХD	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
	RIRAromatics	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 140 141 standard deviation) of major O₃ precursor groups for four patterns of timescale at the three sites

Site	Species	Five-month	Month-to-month	Week-to-week	Day-to-day
	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
ΤZ	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
	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
ы	NOx ^a	30.8 ± 16.4	31.4 ± 11.8	31.6 ± 13.2	31.1 ± 28.6
Bl	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
	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
VD	NOx ^a	20.2 ± 8.7	21.3 ± 4.3	20.3 ± 5.2	21.0 ± 5.0
XD	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

^aUnit of ppbv; ^bUnit of ppbC/ppbv; 143

144Table S8. Number of box model calculation to derive 2 types of RIR values in four patterns of145timescale in this study. The first type of RIR contains 7 major precursor groups and one base run, and146the second type of RIR contains 45 individual VOC species and one base run.

Dettorne of timescale	Number of box	model calculation (3 sites)	
Fatterns of timescale	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



149Figure S1. Geographical locations of the study: (a) North China Plain, (b) Shandong Province, and (c)150Zibo City. Three measurement sites (TZ, BJ, and XD) in Zibo are marked in red. The map can be151obtained from http://dnr.shandong.gov.cn/tplj_30790/sdsgtzytbzdtfw/.



152 153 154 Figure S2. A daily check of peak fitting and baseline of the 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 O₃ at three sites in Zibo at the five-month scale.



Figure S4. Time series of modeled and observed O₃ at three sites in Zibo at the monthly scale.

164

165 Figure S6. Time series of modeled and observed O₃ at the TZ site in Zibo at the daily scale.

166 167

Figure S7. Time series of modeled and observed O₃ at the BJ site in Zibo at the daily scale.

168 169

Figure S8. Time series of modeled and observed O₃ at the XD site in Zibo at the daily scale.

Figure S9. Time series of monthly OH reactivity (k_{OH}) or concentration for O₃ and its precursors as well as the ratios of TVOC/NOx at the three sites in Zibo.

173 174

Figure S10. Time series of weekly OH reactivity (k_{OH}) or concentration for O₃ and its precursors as well as the ratios of TVOC/NOx at the three sites in Zibo.

Figure S11. Time series of daily RIR values of major precursor categories at three sites in Zibo.

178 179

Figure S12. Time series of daily RIR values for subgroups of AVOC at three sites in Zibo.

S29

Figure S14. Distributions of the standard deviations (Std.) for OH reactivity (k_{OH}) or concentration of O₃ precursor groups for multiple patterns of timescale at the three sites in Zibo. For example, there would be 24 standard deviation values when averaging into five-month diurnal patter; and months×24 standard deviation values (n=120 for all sites) when averaging into monthly pattern; and weeks×24 standard deviation values (n=504, 480, 456 for TZ, BJ, XD) when averaging into weekly pattern.

193 194

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

198

199Figure S18. Comparison between measured and simulated O_3 at different dilution rates, which was200obtained through a stepwise sensitivity test by adjusting it from 1/86400 s⁻¹ to 5/86400 s⁻¹ using diurnal201average of five-month pattern as model input at the three sites.

202 **Reference**

- Council, N. R.: Rethinking the Ozone Problem in Urban and Regional Air Pollution, The National
 Academies Press, Washington, DC., 1991.
- 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.