Supplement of Atmos. Chem. Phys., 17, 10919–10935, 2017
https://doi.org/10.5194/acp-17-10919-2017-supplement

Supplement of

Long-term O_3–precursor relationships in Hong Kong: field observation and model simulation

Yu Wang et al.

Correspondence to: Hai Guo (ceguohai@polyu.edu.hk) and Hairong Cheng (chenghr@whu.edu.cn)

Text S1. The VOC species and categorizations.

Alkanes: propane, *n*/*i*-butanes, *n*/*i*-pentanes, *n*/*i*-hexanes, *n*-heptane

Alkenes: propene, *trans-2*-butene, *cis-2*-butene, 1,3-butadiene, isoprene

Aromatics: benzene, toluene, ethylbenzene, *m*/*p*/*o*-xylenes, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,2,3-trimethylbenzene

Note: C_2 hydrocarbons were not included in this study due to high missing rates of the C_2 data.

Text S2. Definition of TVOC reactivity.

TVOC reactivity, calculated as the product of the rate constant with OH and the mixing ratio, is widely used as an estimate of the potential for a single VOC to consume OH (Kleinman *et al*. 2000 and 2005; Lou *et al*. 2010):

$$\mathrm{TVOC}_R = \sum k_i \, [\mathrm{VOC}]_i \quad \text{(Eq. S1)}$$

where k_i is the rate constant for reaction of OH with VOC_i. Reaction rate constants are from Atkinson and Arey (2003).

Table S1. Limit of detection, accuracy and precision of VOC species measured by the Synspec GC 955 on-line analyzer (Feng *et al*. 2013).

Species	**Limit of detection (pptv)**	**Accuracy (%)**	**Precision (%)**
Propane	56	2	6
***i*-Butane**	47	3	5
***n*-Butane**	49	3	4
***i*-Pentane**	46	1	4
***n*-Pentane**	28	1	4
***n*-Hexane**	53	7	6
***i*-Hexane**	5	2	10
***n*-Heptane**	46	4	2
Propene	3	1	3
***trans*-2-Butene**	3	4	4
***cis*-2-Butene**	3	3	3
1,3-Butadiene	2	1	2
Isoprene	3	2	9
Benzene	6	3	5
Toluene	7	1	2
***m,p*-Xylene**	9	3	2
***o*-Xylene**	9	3	2
Ethylbenzene	8	1	1
1,3,5-Trimethylbenzene	6	2	2
1,2,4-Trimethylbenzene	7	2	3
1,2,3-Trimethylbenzene	7	3	4

Table S2. Matrix of assignments from real compounds to carbon bond 05 (CB05) model species (Yarwood *et al*. 2005). Species names for the CB05 mechanism: AKA = alkane carbon bond (C-C), AKE = terminal alkene carbon bond (R-C=C), TOL = toluene and other monoalkyl aromatics, XYL = xylene and other polyalkyl aromatics, ISOP = isoprene, NR = not reactive, IOLE = Internal alkene carbon bond (R-C=C-R), MW = molecular weight, Carbons = number of carbon atoms.

Name	AKA	AKE	TOL	XYL	ISOP	NR	IOLE	MW	Carbons
Propane	1.5	0	0	0	0	1.5	0	44.1	1.5
Propene	1	1	0	0	0	0	0	42.08	3
***n*-Butane**	4	0	0	0	0	0	0	58.12	4
***i*-Butane**	4	0	0	0	0	0	0	58.12	4
***trans*-2-Butene**	0	0	0	0	0	0	1	56.11	4
***cis*-2-Butene**	0	0	0	0	0	0	1	56.11	4
***n*-Pentane**	5	0	0	0	0	0	0	72.15	5
***i*-Pentane**	5	0	0	0	0	0	0	72.15	5
1,3-Butadiene	0	2	0	0	0	0	0	54.09	4
Isoprene	0	0	0	0	1	0	0	68.12	5
***n*-Hexane**	6	0	0	0	0	0	0	86.18	6
***i*-Hexane**	5.83	0	0	0	0	0.17	0	86.18	5.83
Benzene	1	0	0	0	0	5	0	78.11	1
***n*-Heptane**	7	0	0	0	0	0	0	100.21	7
Toluene	0	0	1	0	0	0	0	92.14	7
Ethylbenzene	1	0	1	0	0	0	0	106.17	8
***m*-Xylene**	0	0	0	1	0	0	0	106.17	8
***p*-Xylene**	0	0	0	1	0	0	0	106.17	8
***o*-Xylene**	0	0	0	1	0	0	0	106.17	8
1,3,5-Trimethylbenzene	1	0	0	1	0	0	0	120.2	9
1,2,4-Trimethylbenzene	1	0	0	1	0	0	0	120.2	9
1,2,3-Trimethylbenzene	1	0	0	1	0	0	0	120.2	9

Table S3. Overview of the 2688 days with available air-quality data at Tung Chung Air Quality Monitoring Station during 2005-2014.

	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Jan.					31	31	31	31	30	31
Feb.				29	27	26	28	26	28	28
Mar.		26		29	29	29	31	30	31	31
Apr.	7	28		28	28	27	27	29	28	30
May	29	27		29	30	30	30	29	28	31
Jun.	30	30			30	30	30	29	30	30
Jul.	29	29		29	31	31	30	31	28	31
Aug.	30	31		31	31		31	31	30	31
Sept.	21	30		29	28		26	28	28	
Oct.	25	29	31	31	30		23	30	31	
Nov.	30		30	30	30		29	27	29	
Dec.	29		30	31	31		31	30	19	
Total	252	230	91	296	356	204	347	351	340	238

Table S4. Means (±95% confidence intervals) of the initial concentrations of ozone precursors used in the OBM model (unit: ppbv for NO_2 and pptv for VOCs).

Precursors	Spring	Summer	Autumn	Winter
NO_2	17.11±1.8	8.66±1.71	20.97±1.66	25.88±2.24
Propane	559.64±22.88	282.59±18.63	625.52±22.11	1341.91±30.14
Propene	307.99±3.24	251.73±2.09	395.04±3.82	505.63±6.13
***n*-Butane**	699.14±18.23	338.3±17.13	797.07±15.83	1135.61±25.07
***i*-Butane**	478.51±11.51	229.8±11.27	433.56±10.98	951.14±17.08
1-Butene	56.29±0.78	26.61±0.76	57.96±1.98	65.17±2.49
***trans*-2-Butene**	131±0.88	96.11±0.77	72.93±1.06	216.2±1.75
***cis*-2-Butene**	54.02±0.57	25.74±0.72	17.64±2.09	102.61±1.8
1,3-Butadiene	85.82±0.83	42.87±0.54	72.61±1.76	137.15±1.52
***n*-Pentane**	191.99±7.74	84.96±7.72	133.68±5.9	255.14±6.48
***i*-Pentane**	219.78±9.5	195.38±12.05	101.67±8.02	312.37±8.96
***n*-Hexane**	230.75±8.98	127.26±5.63	381.72±6.28	425.7±19.74
***i*-Hexane**	162.01±5.66	43.6±5.39	172.46±9.4	283.3±7.11
***n*-Heptane**	63.09±2.47	16.03±1.44	69.24±3.31	102.5±5.28
Benzene	96.83±8.35	48.91±2.88	25.66±7.69	124.52±20.71
Toluene	1012.32±22.41	410.53±11.1	959.76±23.93	1340.78±52.09
Ethylbenzene	180.98±5.82	74.12±2.56	179.42±6.76	281.02±12.52
***m/p*-Xylene**	296.36±7.85	137.88±3.1	189.04±11.08	356.2±19.02
***o*-Xylene**	103.91±2.81	39.86±1.85	87.79±3.31	141.4±5.89
1,2,3-Trimethylbenzene	13.99±0.2	3.23±0.3	7.28±0.01	13.45±0.42
1,2,4-Trimethylbenzene	46.65±0.43	19.09±1.12	43.66±0.57	62.23±1.31
1,3,5-Trimethylbenzene	20.13±0.2	6.31±0.22	19.02±0.18	20.92±0.26

Table S5. The difference of locally-produced O_3 (simulated) before and after removing regional background NO_2.

	HKUST (Suburban site)	**Tung Chung (Suburban site)**	**Yuen Long (Urban site)**	**Mong Kok (Roadside site)**
Spring		-33.1%	-33.1%	-11.7%
Summer	-8.3%	-12.9%	-7.5%	-2.6%
Autumn	-14.8%	-17.7%	-13.9%	-5.6%
Winter	-26.6%	-46.0%	-47.9%	-21.9%

Note: Online VOC data was available at five sites from April 2011 to January 2012; Only four months trace gases data at HKUST site were available in 2011; Totally, the simulation days at TC, YL, MK and UST are 286, 273, 233 and 105 days.

Table S6. The difference of locally-produced O_3 (simulated) before and after removing regional background VOCs.

	HKUST (Suburban site)	**Tung Chung (Suburban site)**	**Yuen Long (Urban site)**	**Mong Kok (Roadside site)**
Spring		-2.6%	-2.6%	-1.2%
Summer	-2.4%	-2.7%	-2.1%	-0.3%
Autumn	-1.8%	-1.8%	-4.0%	-3.0%
Winter	-0.6%	-4.0%	-4.8%	-4.5%

Note: Online VOC data was available at five sites from April 2011 to January 2012; Only four months trace gases data at HKUST site were available in 2011; Totally, the simulation days at TC, YL, MK and UST are 286, 273, 233 and 105 days.

Table S7. The difference of locally-produced O_3 (simulated) before and after removing both regional background NO_2 and VOCs.

	HKUST (Suburban site)	Tung Chung (Suburban site)	Yuen Long (Urban site)	Mong Kok (Roadside site)
Spring		-33.5%	-33.2%	-12.6%
Summer	-9.8%	-13.7%	-7.9%	-2.7%
Autumn	-15.5%	-17.8%	-14%	-6.0%
Winter	-27.1%	-46.2%	-48.4%	-22.1%

Note: Online VOC data was available at five sites from April 2011 to January 2012; Only four months trace gases data at HKUST site were available in 2011; Totally, the simulation days at TC, YL, MK and UST are 286, 273, 233 and 105 days.

Table S8. Seasonal averages of TVOC (C_3-C_8) in 2013 at five sites in Hong Kong.

	Hok Tsui (Background site)	HKUST (Suburban site)	Tung Chung (Suburban site)	Yuen Long (Urban site)	Mong Kok (Roadside site)
Spring	5.9±0.2	2.6±0.2	4.1±0.2	6.3±0.4	11±0.5
Summer	4.5±0.2	1.5±0.2	2.5±0.2	2.9±0.2	11±0.3
Autumn	7.6±0.2	2.7±0.1	4.7±0.2	7.3±0.3	16.1±0.4
Winter	13.6±0.4	6.7±0.3	7±0.3	16±0.7	24.6±0.7

Note: Hok Tsui is a well-known regional background site at the southeastern tip of Hong Kong. The Hong Kong University of Science and Technology (HKUST) is an Air Quality Research Supersite located on the shorefront of the HKUST campus in the Hong Kong suburban area. Yuen Long (YL) is a typical urban site adjacent to main traffic roads and surrounded by residential and industrial blocks. Mong Kok is a typical roadside site with high traffic density.

Table S9. Index of agreement (IOA) between simulated and observed O_3.

Year	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
IOA	0.81	0.82	NA*	0.84	0.77	0.71	0.77	0.88	0.79	0.89

*VOCs data in 2007 are not available due to the maintenance of the instrument.

Table S10. Rate constants for reactions of OH with individual VOCs measured in this study (Atkinson and Arey, 2003).

Name	**Reactivity (10^{12} k_{OH}) (cm^{-3} $molecule^{-1}$ s^{-1})**	**Name**	**Reactivity (10^{12} k_{OH}) (cm^{-3} $molecule^{-1}$ s^{-1})**
Propane	1.15	***i*-Hexane**	5.6
Propene	26.3	**Benzene**	1.23
***n*-Butane**	2.54	***n*-Heptane**	7.15
***i*-Butane**	2.34	**Toluene**	6
***trans*-2-Butene**	64	**Ethylbenzene**	7.1
***cis*-2-Butene**	56.4	***m*-Xylene**	23.1
***n*-Pentane**	3.94	***p*-Xylene**	14.3
***i*-Pentane**	3.9	***o*-Xylene**	13.7
1,3-Butadiene	66.6	**1,3,5-trimethylbenzene**	57.25
Isoprene	101	**1,2,4-trimethylbenzene**	32.5
n-Hexane	5.61	**1,2,3-trimethylbenzene**	32.5

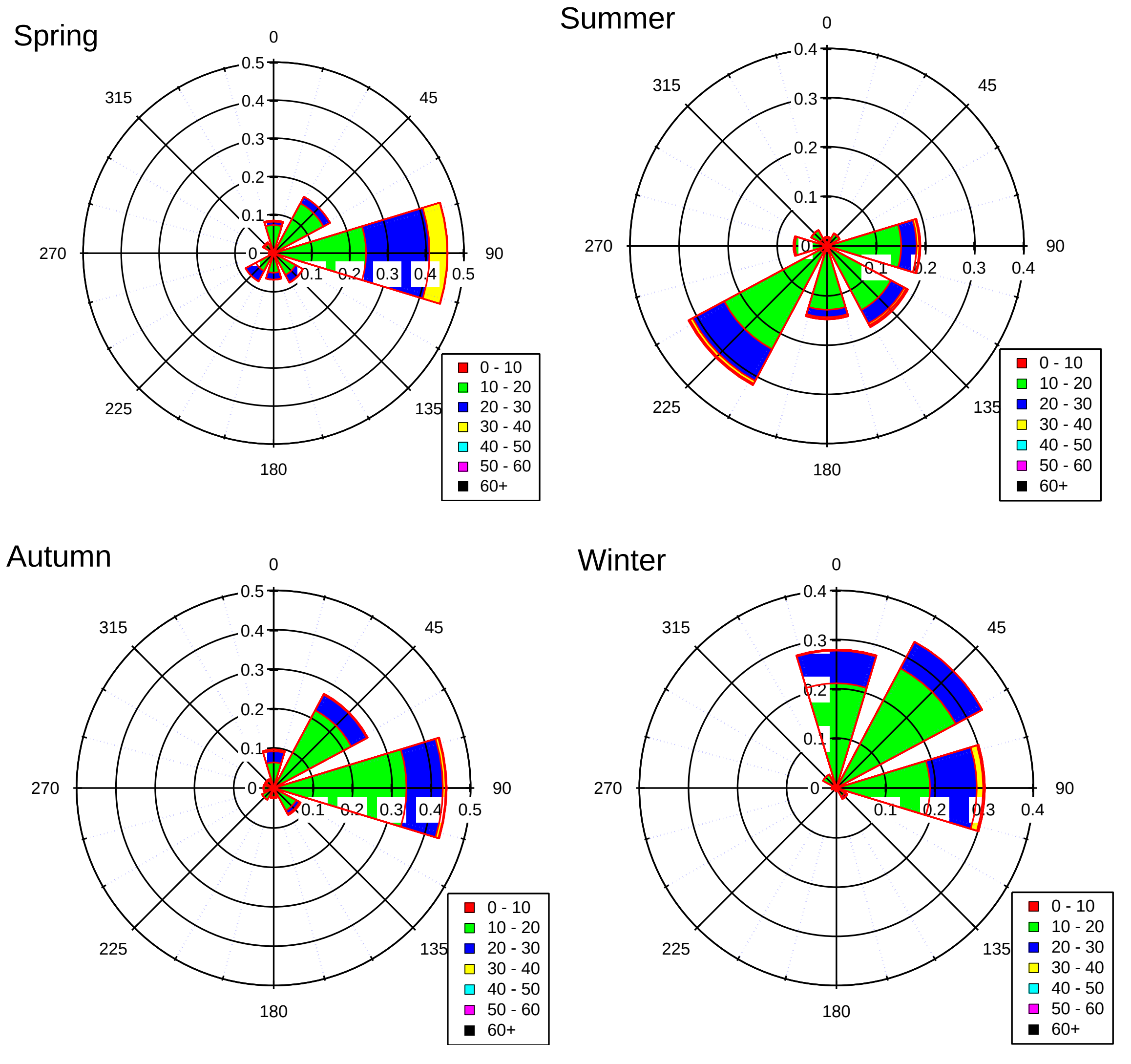


Figure S1. Wind rose plots showing prevailing winds in Hong Kong for each season. The daily data of 2005-2014 is obtained from the Hong Kong airport (https://www.wunderground.com). Colour indicates wind speed (unit: km h^{-1}).

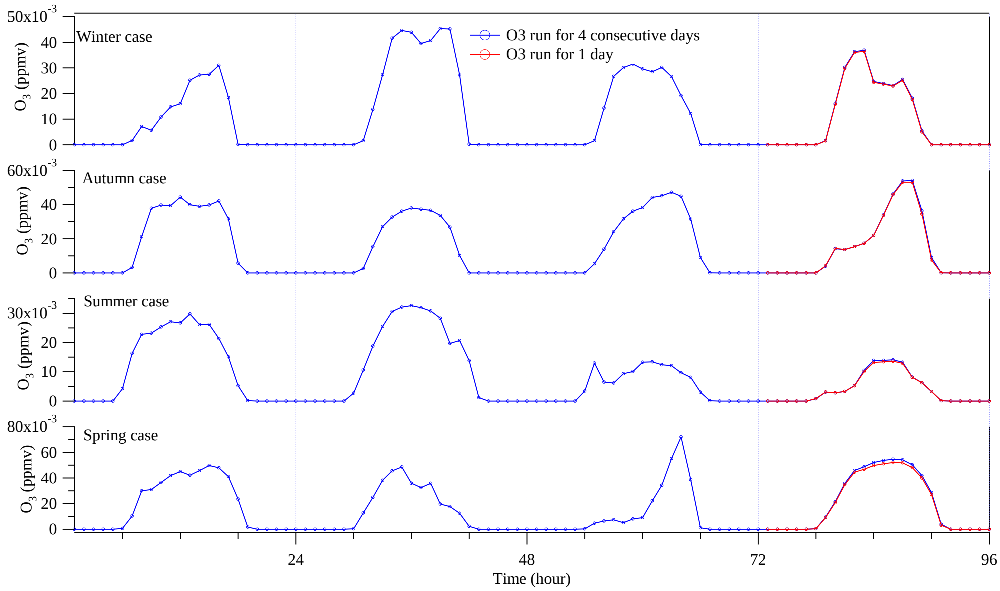


Figure S2. Comparison of O_3 production simulated by with (blue line) or without (red line) a 4-day "spin-up" time in different seasons. In the tests, four days data were randomly selected from each season in 2012 as an example. The results demonstrate that the method without the "spin-up" time indeed causes slight underestimation of the O_3 production with a maximum of 4.63% in spring and a minimum of 1.52% in winter.

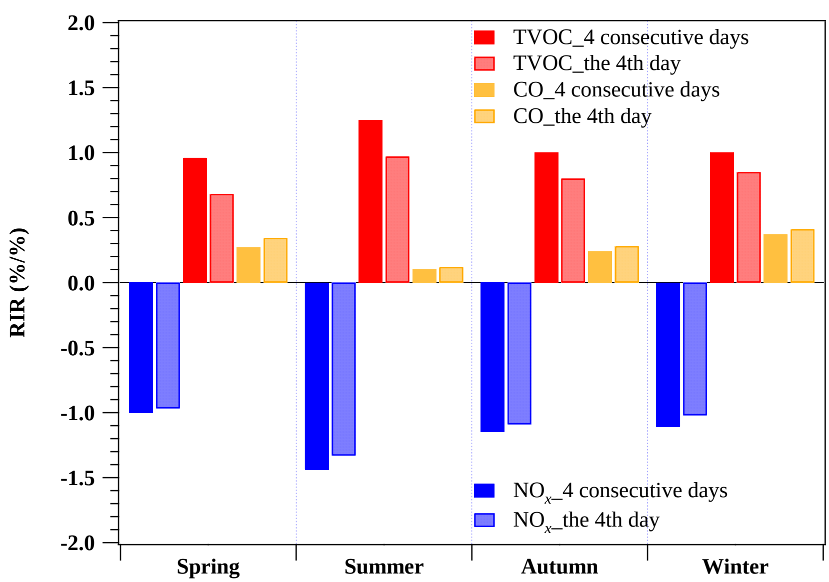


Figure S3. Comparison of RIR calculated by with (solid bar) or without (light bar) a 4-day "spin-up" time in different seasons. In the tests, one-day data was randomly selected from each season in 2012 as an example. It shows that the approach (without spin-up time) systematically underestimates the RIR values, but it does not change the results in each season. In addition, it seems that the RIR of TVOCs is more sensitive to this method.

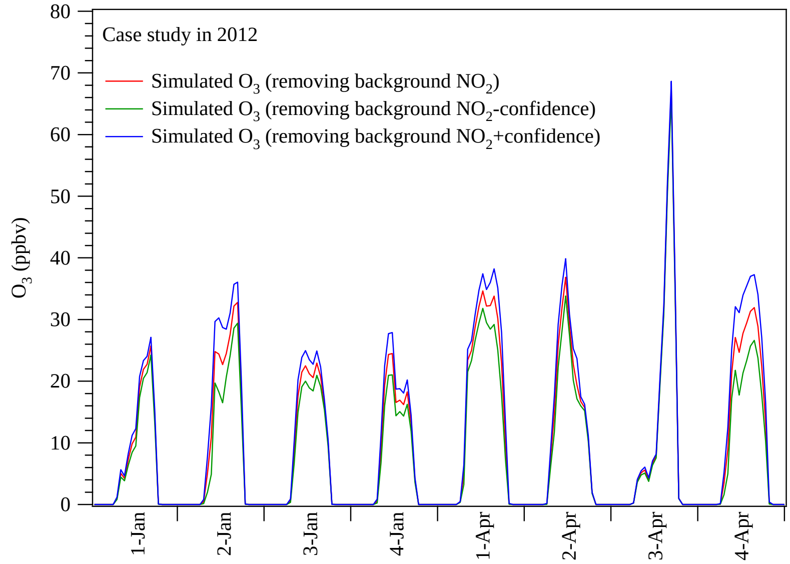


Figure S4. Comparison of locally-produced O_3 (simulated) at TC site in spring and winter with input of varying initial concentrations of NO_2 by subtracting the mean background NO_2 (red line), the mean background NO_2 plus 95% confidence intervals (blue line), and the mean background NO_2 minus 95% confidence intervals (green line).

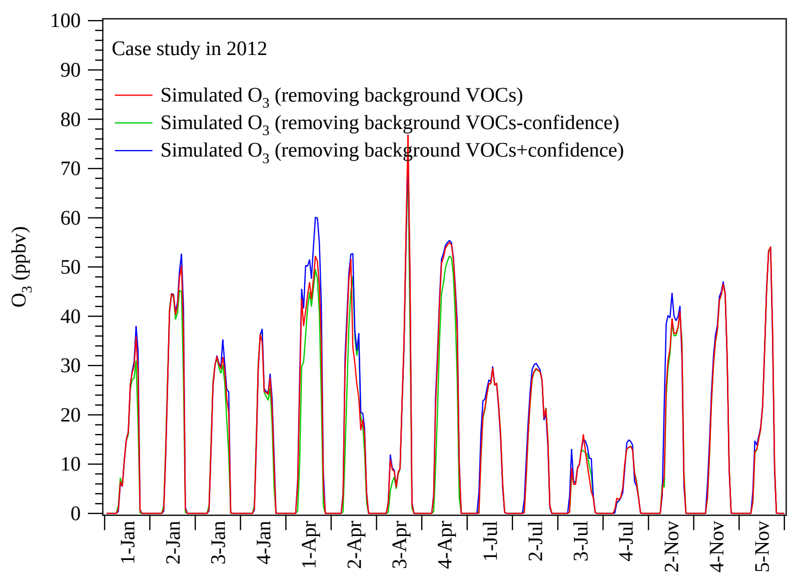


Figure S5. Comparison of locally-produced O_3 (simulated) at TC site over the year with input of varying initial concentrations of VOCs by subtracting the mean background VOCs (red line), the mean background VOCs plus 95% confidence intervals (blue line), and the mean background VOCs minus 95% confidence intervals (green line).

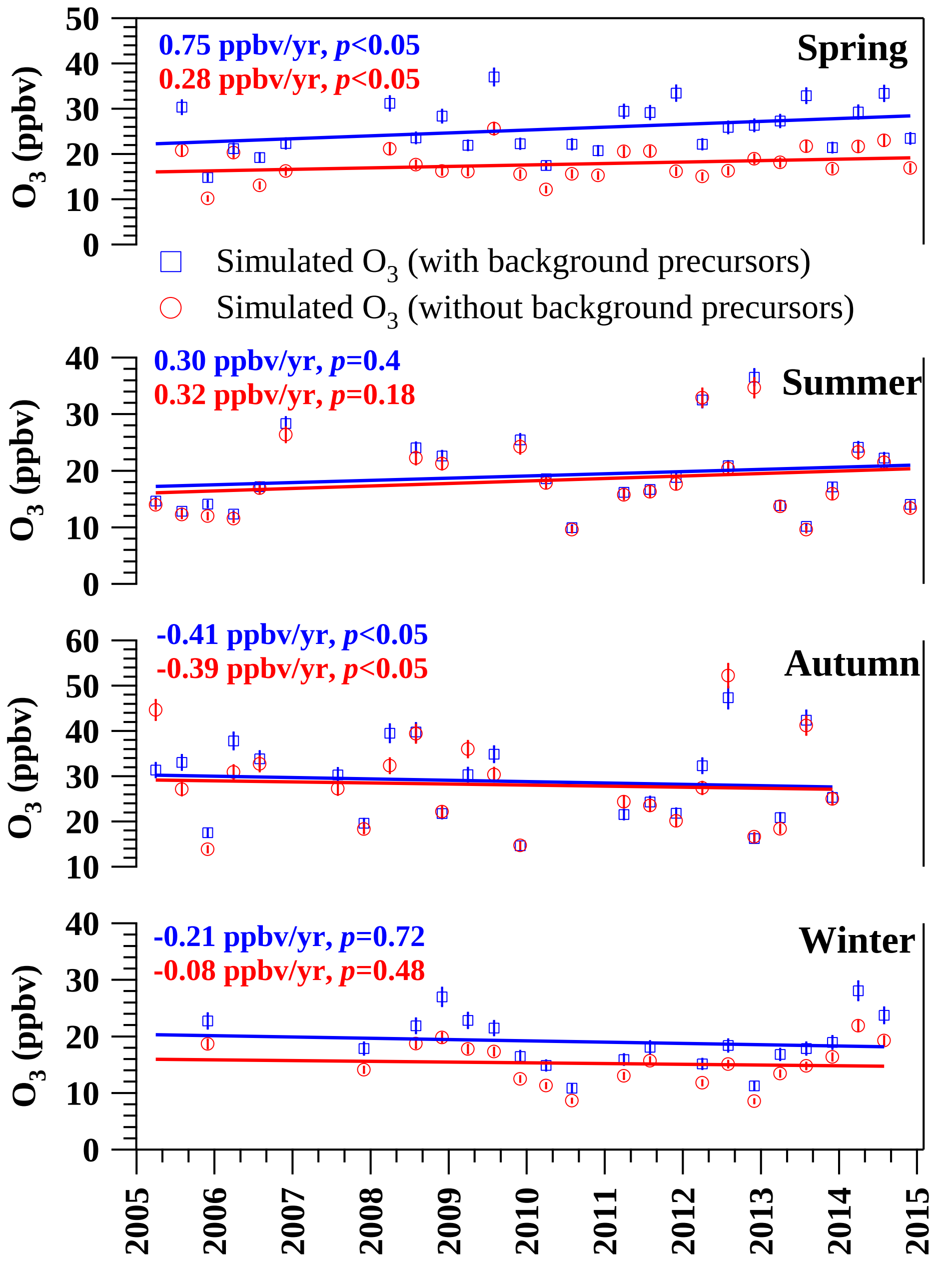


Figure S6. Annual trends of simulated local O_3 production (blue line: with background precursors; red line: without background precursors) in four seasons at TC during 2005–2014. Error bars represent 95% confidence intervals of the averages.

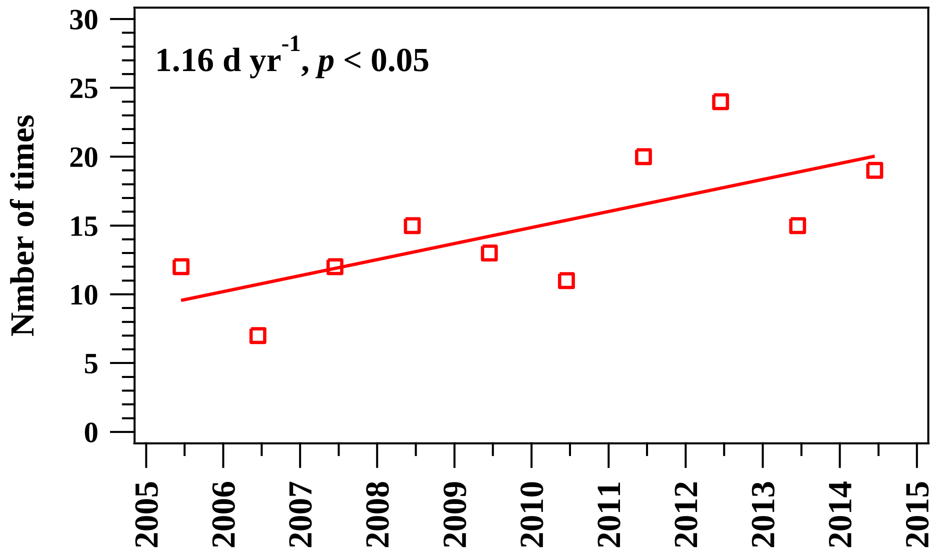


Figure S7. Annual trend of number of days per year that the daily 8-hour O_3 maximum (DMA8) exceeded 80 ppbv at TC during 2005–2014.

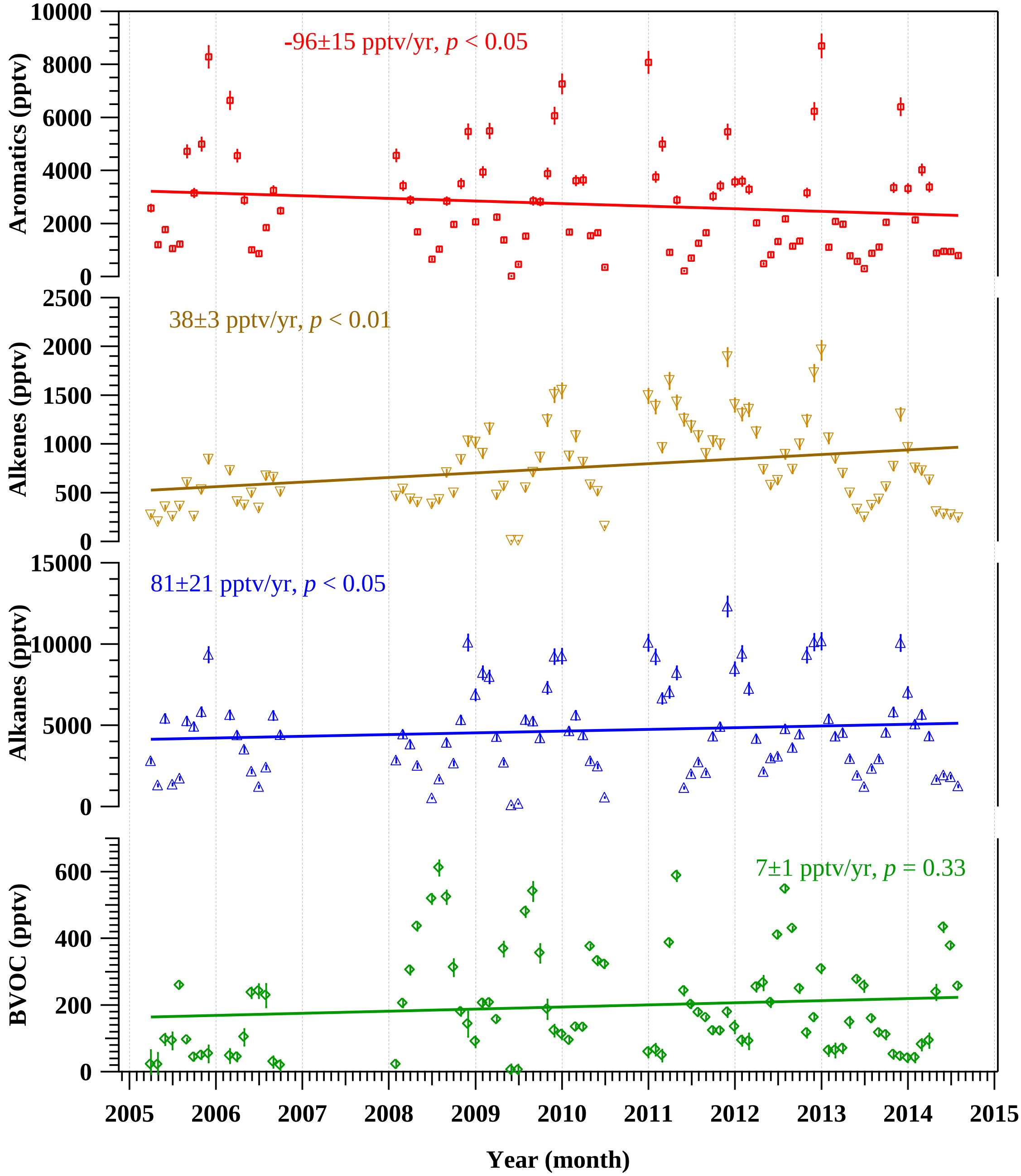


Figure S8. Trends of monthly average of individual VOC groups (*i.e.*, AVOC (aromatics/alkenes/alkanes) and BVOC) at TC during 2005-2014. Error bars represent the 95% confidence intervals of the averages.

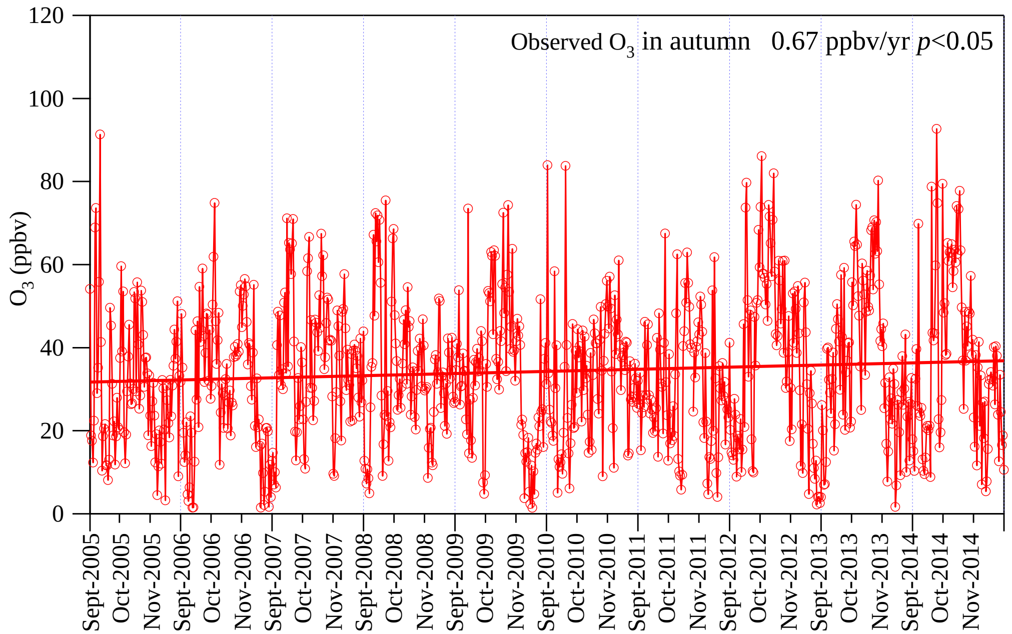


Figure S9. Variations of observed daily average O_3 at TC in autumns of 2005-2014.

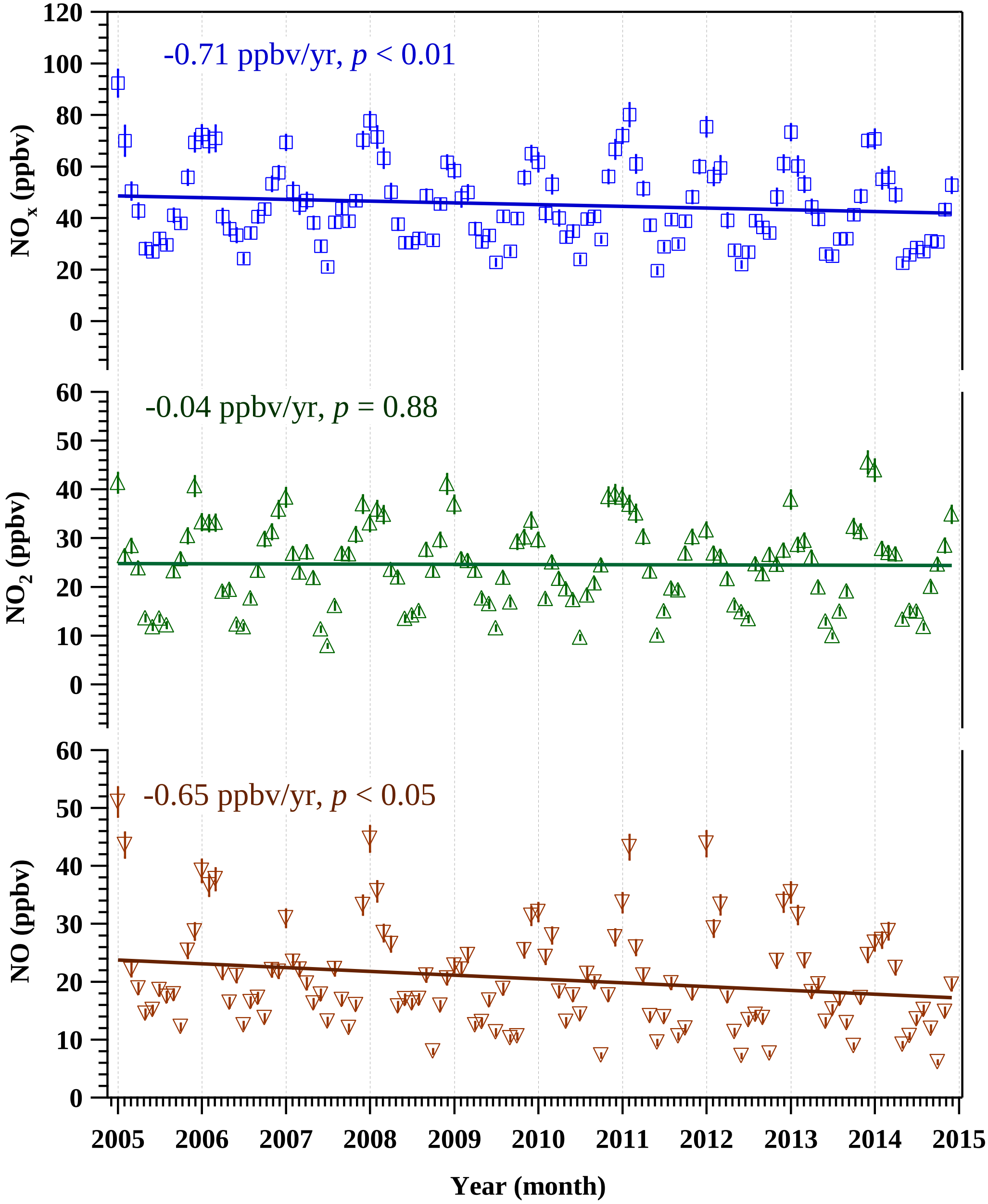


Figure S10. Trends of monthly averages of NO_x, NO_2 and NO at TC during 2005–2014. Error bars represent 95% confidence intervals of monthly averages.

5

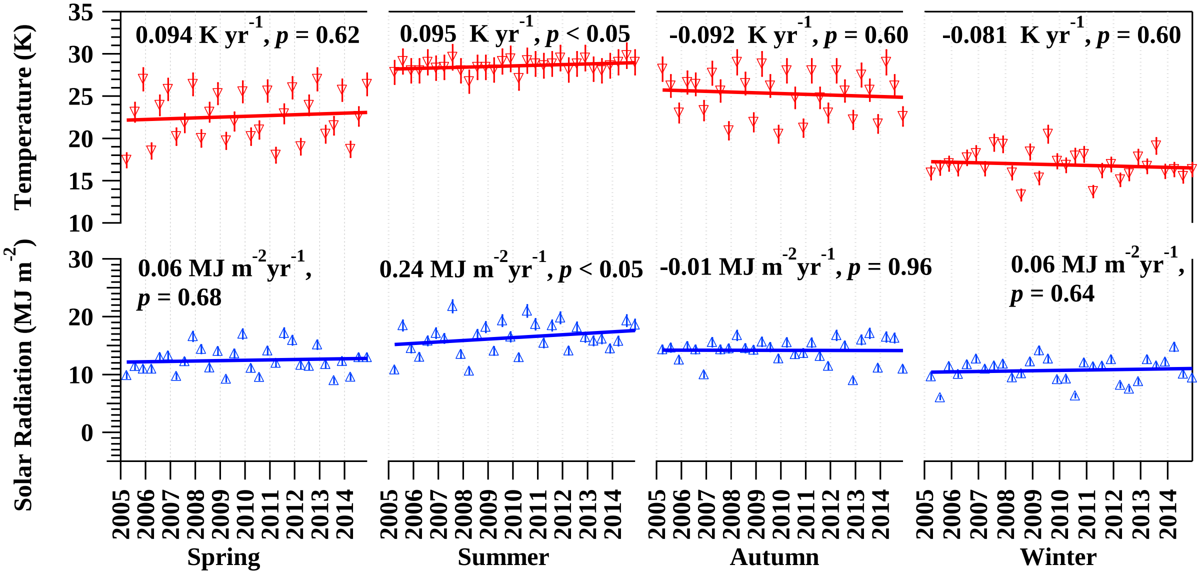
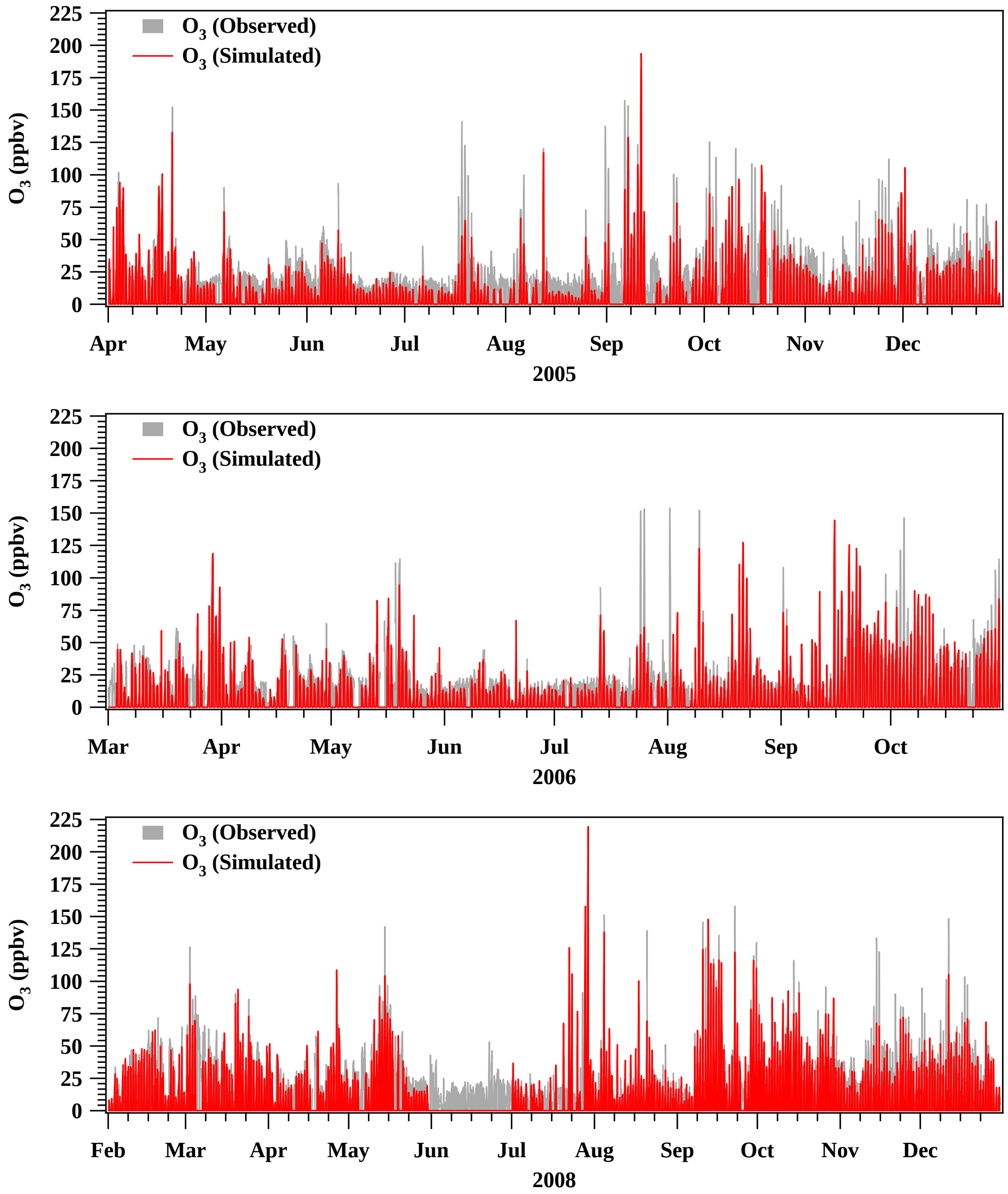
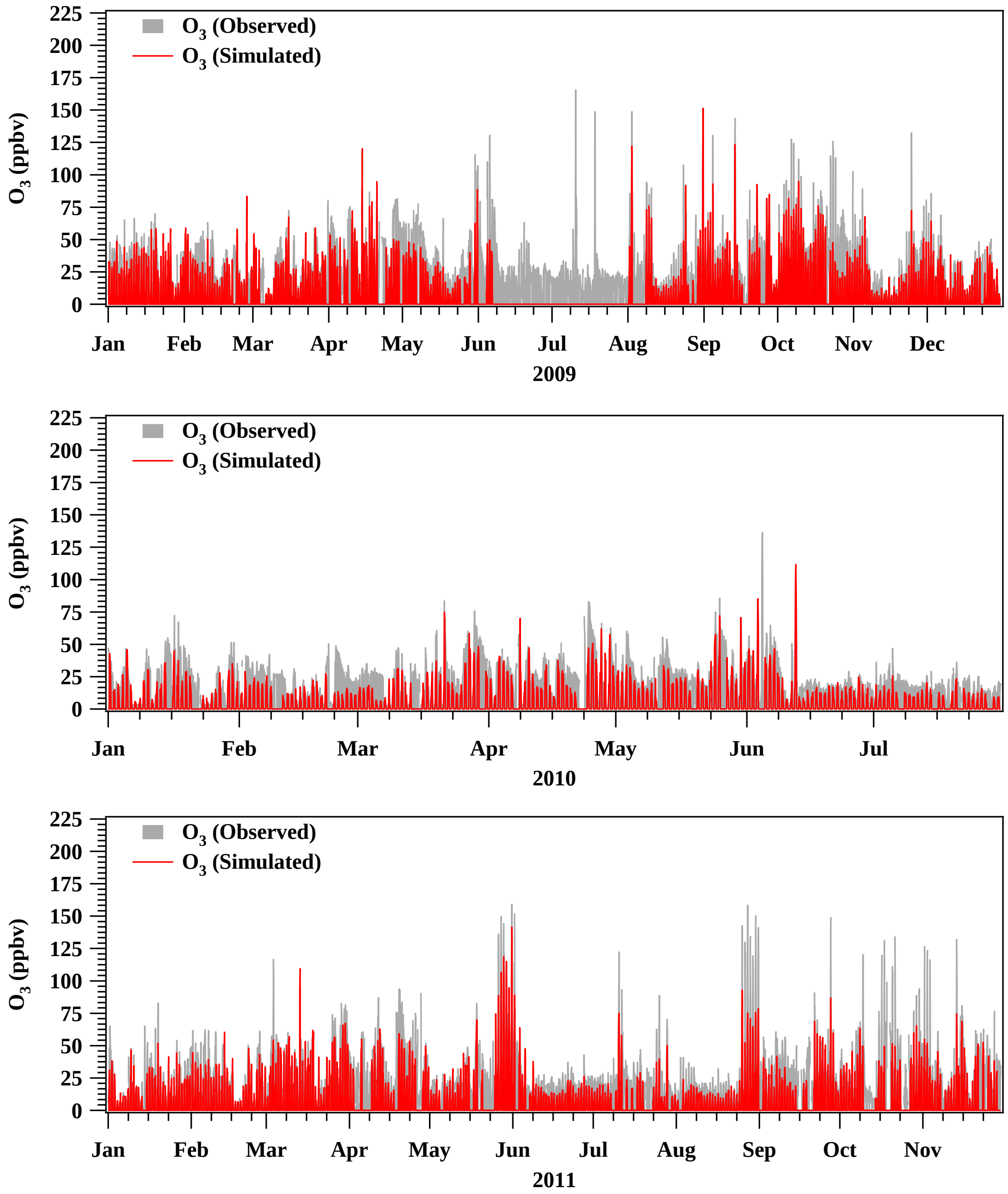


Figure S11. Variations of temperature (red) and solar radiation (blue) for the four seasons at TC during 2005–2014. Each data point in the figure is obtained by averaging hourly values into a monthly value. Error bars represent 95% confidence intervals of monthly averages.


O3 (Observed)
O3 (Simulated)
O3 (ppbv)
225
200
175
150
125
100
75
50
25
0
Apr May Jun Jul Aug Sep Oct Nov Dec
2005
Mar Apr May Jun Jul Aug Sep Oct
2006
Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
2008



O3 (Observed)
O3 (Simulated)
O3 (ppbv)
225
200
175
150
125
100
75
50
25
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
2009
2010
2011

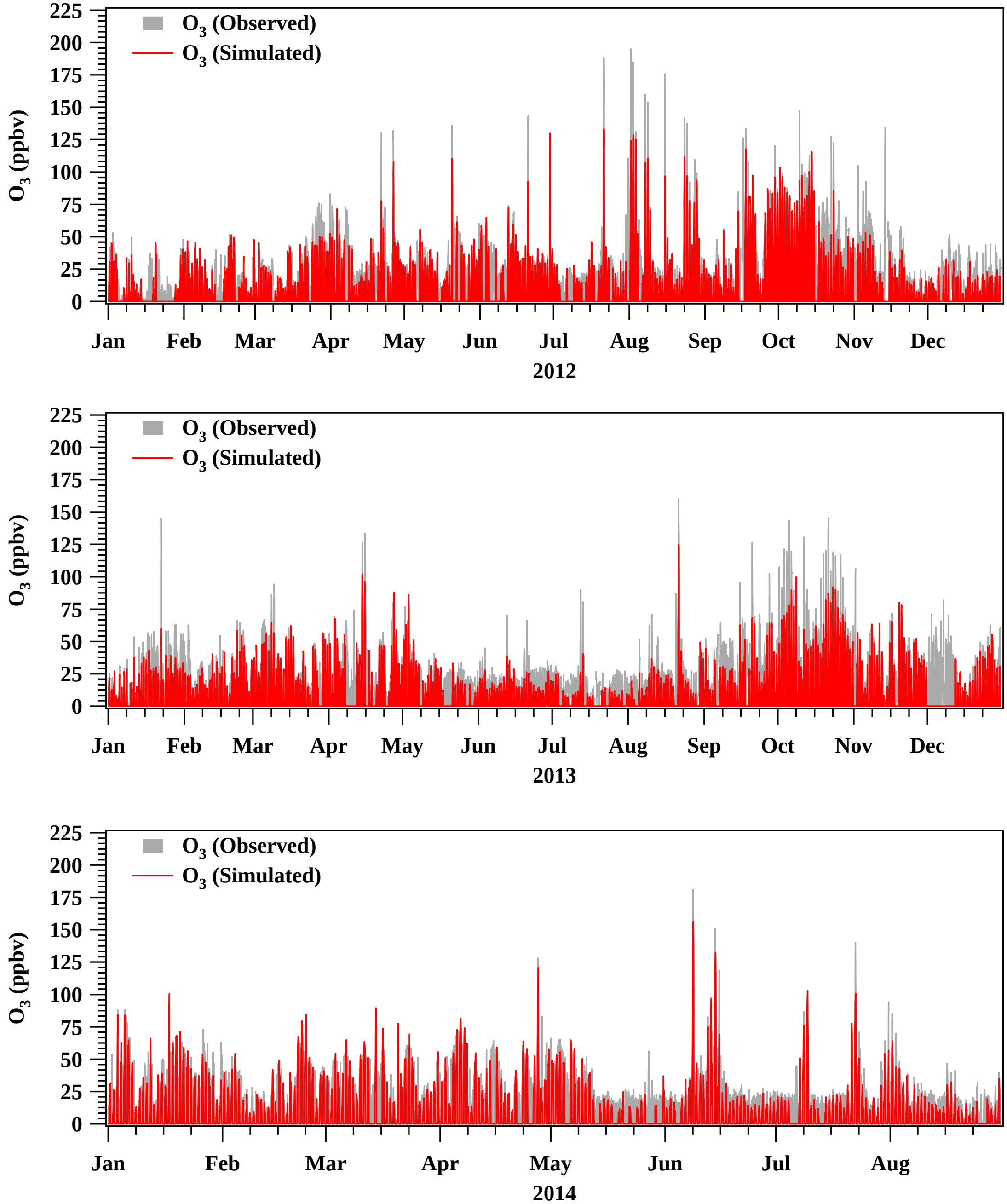
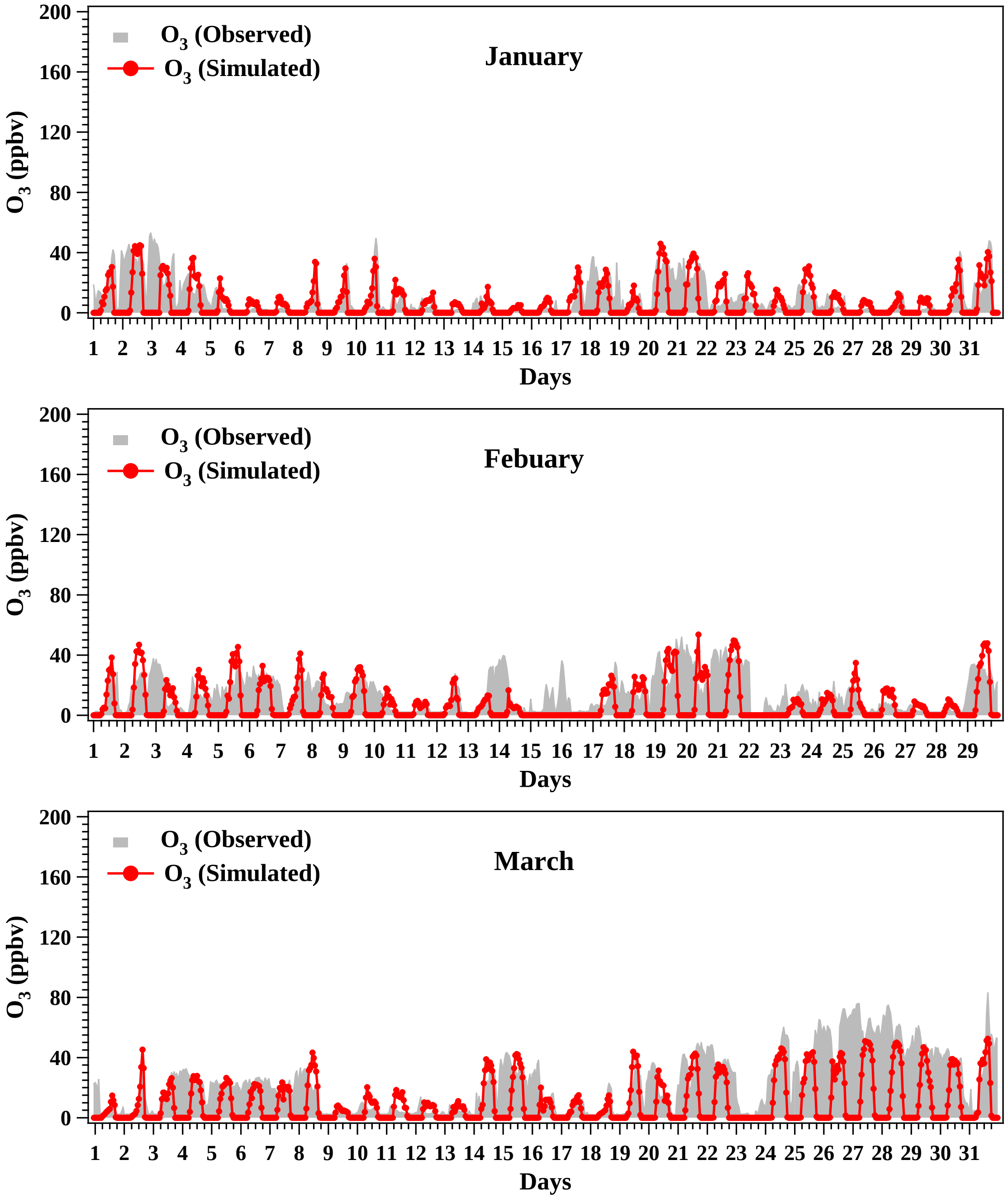
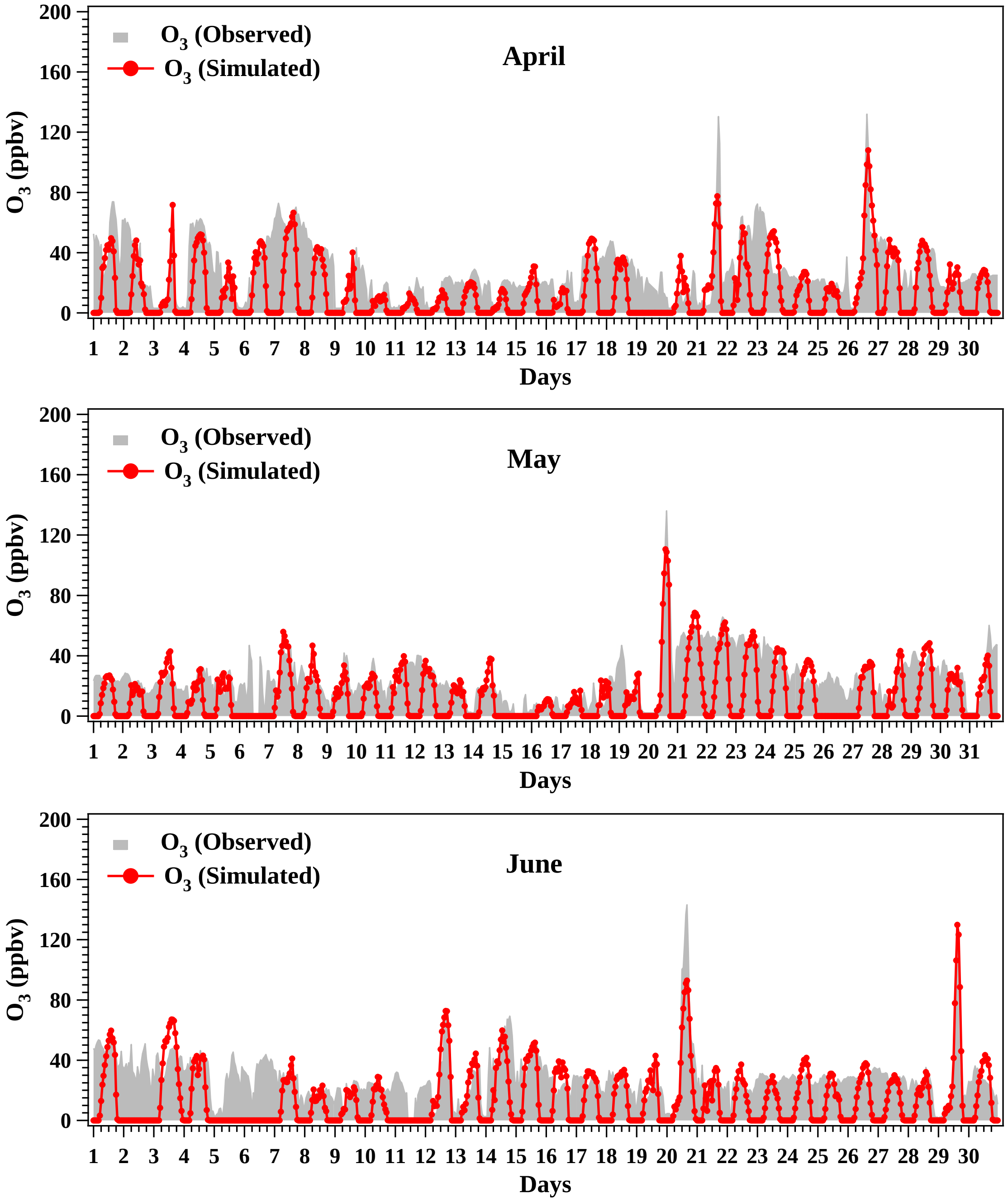


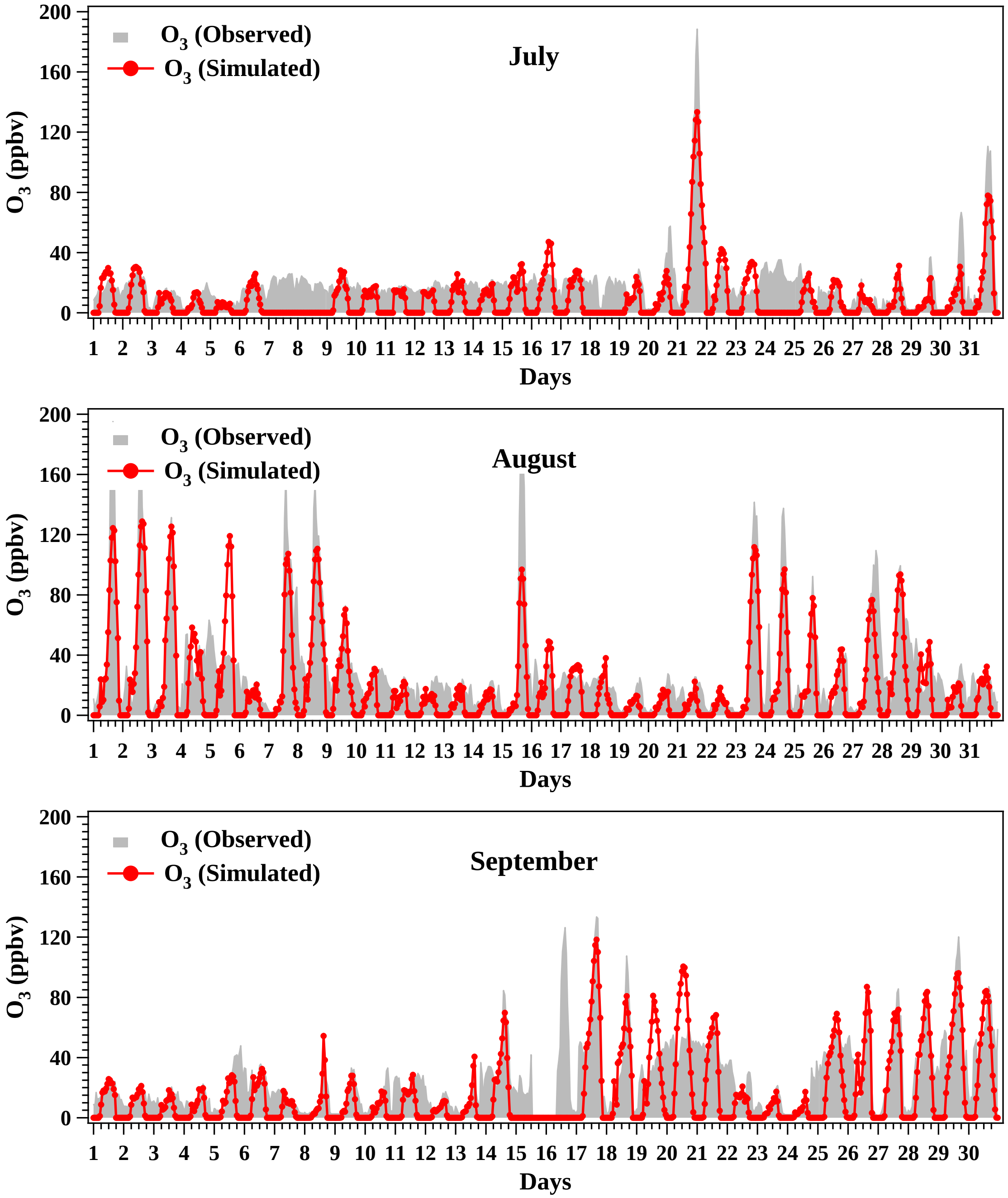
Figure S12. Comparison of simulated (red lines) and observed (grey areas) O_3 at TC from 2005–2014. Note: The plots are drawn by hourly data. O_3 simulations are not drawn in some days due to the lack of VOC real-time data (see Table S3).



O3 (Observed)
O3 (Simulated)
January
O3 (ppbv)
0
40
80
120
160
200
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
Days
O3 (Observed)
O3 (Simulated)
Febuary
O3 (ppbv)
0
40
80
120
160
200
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29
Days
O3 (Observed)
O3 (Simulated)
March
O3 (ppbv)
0
40
80
120
160
200
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
Days



O3 (Observed)
O3 (Simulated)
April
O3 (ppbv)
0
40
80
120
160
200
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
Days
O3 (Observed)
O3 (Simulated)
May
O3 (ppbv)
0
40
80
120
160
200
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
Days
O3 (Observed)
O3 (Simulated)
June
O3 (ppbv)
0
40
80
120
160
200
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
Days


O3 (Observed)
O3 (Simulated)
July
August
September
O3 (ppbv)
Days
200
160
120
80
40
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

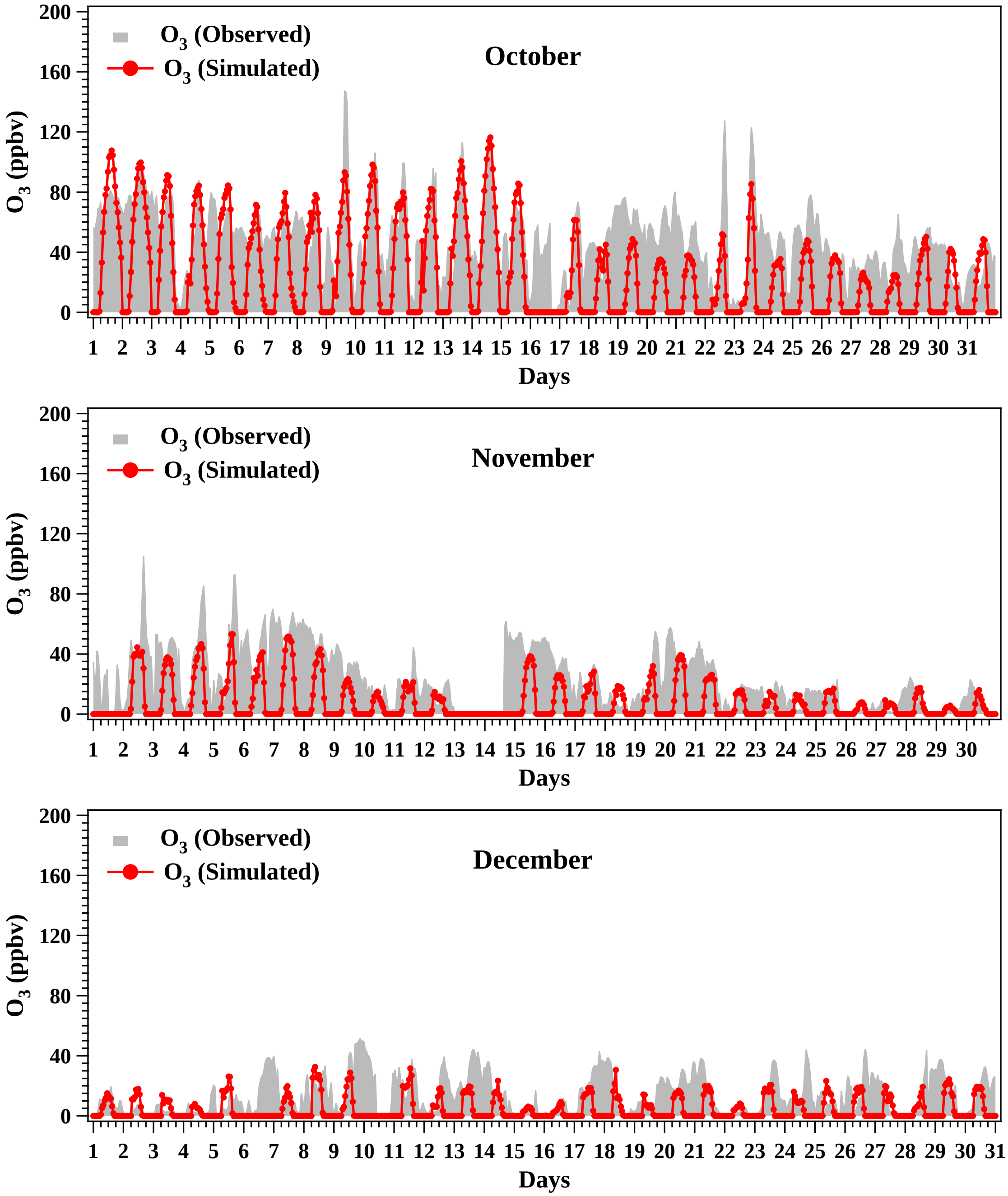


Figure S13. Comparison of simulated (red lines) and observed (grey areas) O_3 at TC in all 12 months in 2012. Note: The plots are drawn using hourly data. O_3 simulations are not drawn in some days due to the lack of VOC real-time data (see Table S3). Due to space constraints, only the data in 2012, the year with the most complete data, are selected to represent the simulation results.

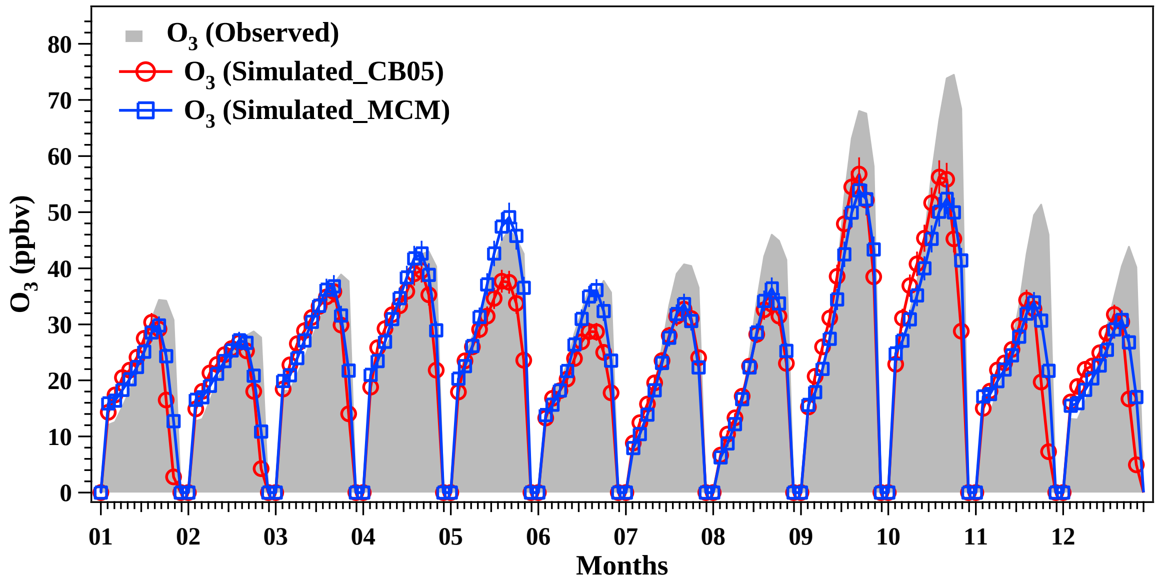


Figure S14. 12-month averaged diurnal variation of simulated O_3 by OBM (CB05, red line) and OBM (MCM, blue line); and observed O_3 (grey area) at TC during 2005–2014 (rainy days excluded). Note that the models were run for daily simulations. The daily simulated O_3 results and observed O_3 are further calculated into monthly-average diurnal profiles for the comparison. All daily simulated results in each month were averaged to one diurnal variation for that month.

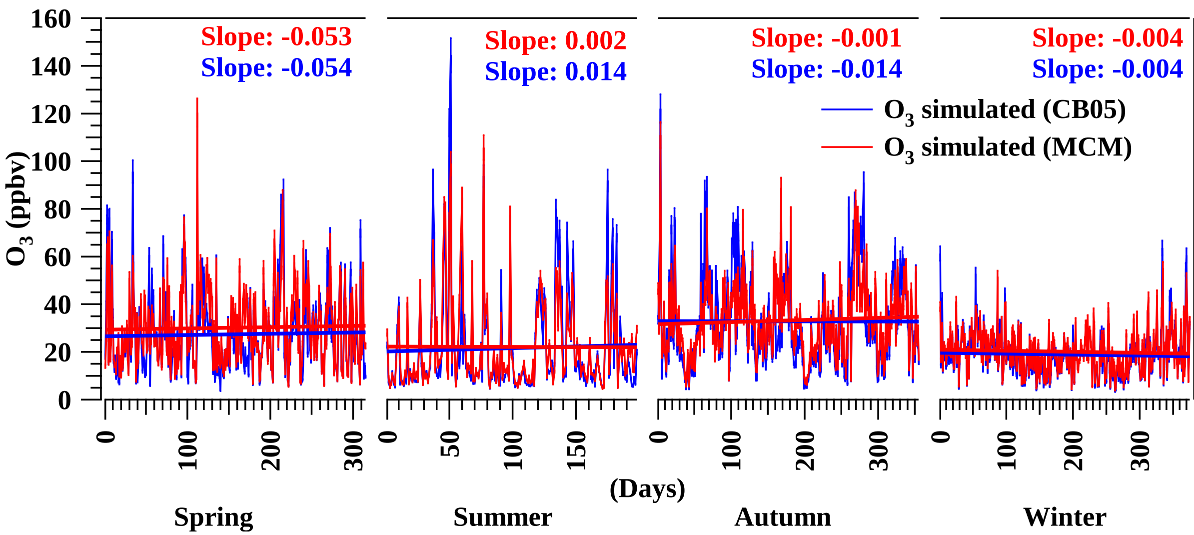


Figure S15. Trends of daily averaged locally-produced O_3 simulated by OBM (CB05, blue line) and by OBM (MCM, red line) in four seasons at TC during 2005–2014 (rainy days excluded). Note: all the data are based on daytime hours (0700-1900 LT).

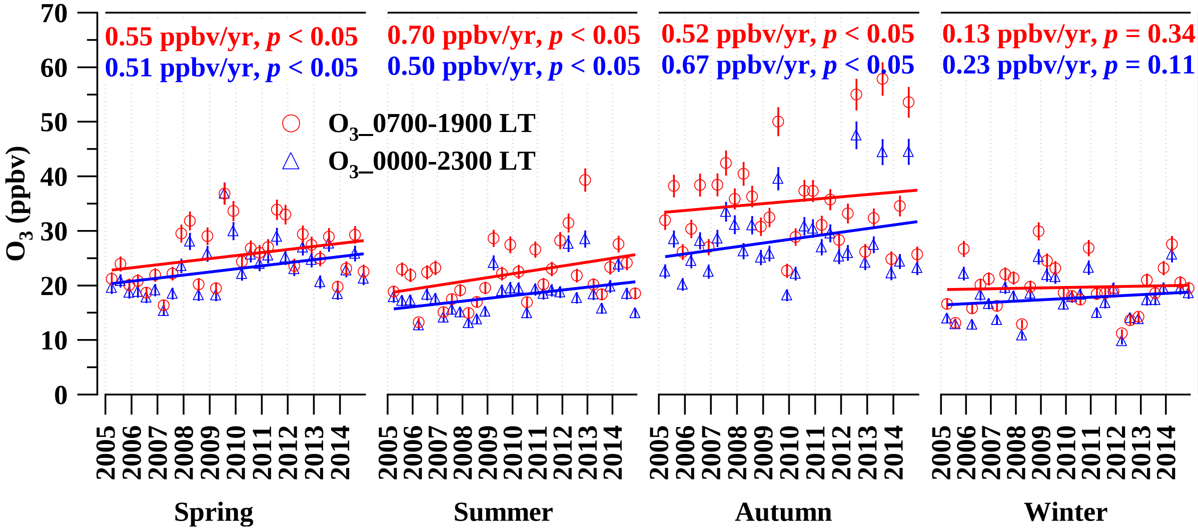


Figure S16. Trends of observed O_3 (blue line: 24-hour observed O_3, 0000-2300 LT; red line: daytime observed O_3, 0700-1900 LT) in four seasons at TC during 2005–2014. Error bars represent 95% confidence intervals of the averages.

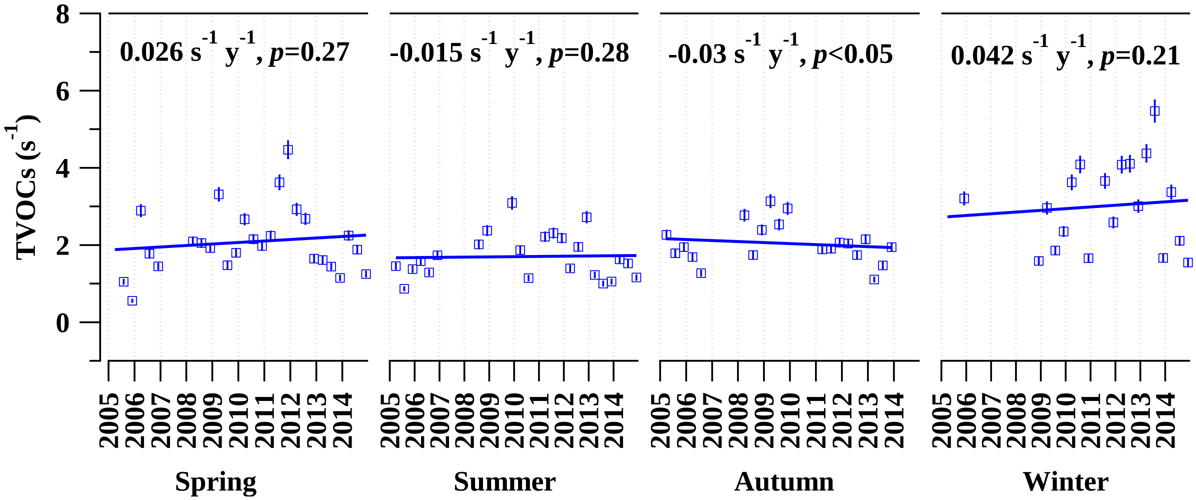


Figure S17. Annual variations of TVOC reactivity in four seasons at TC during 2005–2014. Each data point in the figure is obtained by averaging hourly values into a monthly value. Error bars represent 95% confidence intervals of the averages. The rate constants with OH (k_{OH}) of VOC species are from Atkinson and Arey (2003).

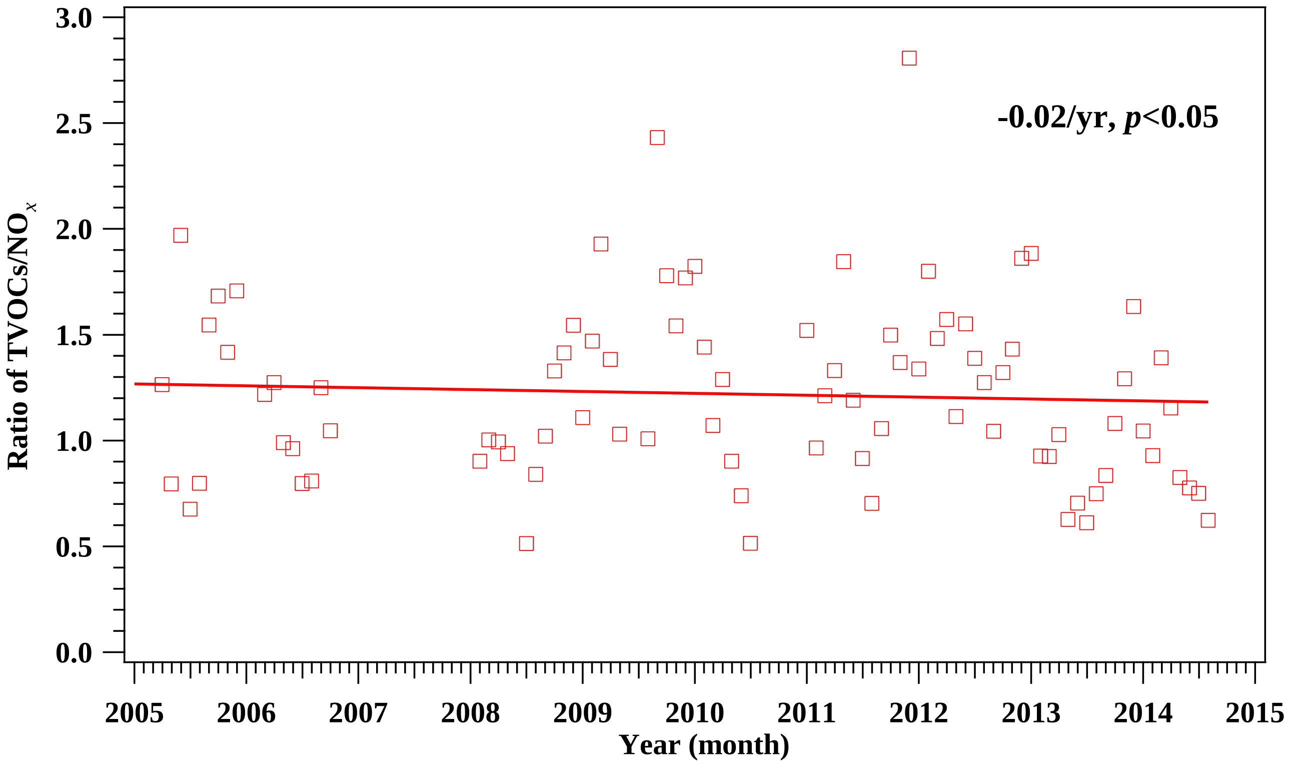


Figure S18. Monthly trend of TVOCs/NO_x ratio at TC in 2005-2014.

5

References

Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605-4638, 2003.

Kleinman, L. I.; Daum, P. H.; Imre, D. G.; Lee, J. H.; Lee, Y. N.; Nunnermacker, L. J.; Springston, S. R.; Weinstein-Lloyd, J. and Newman, L.: Ozone production in the New York City urban plume, J. Geophys. Res. Atmos., 105, 14495-14511, 2000.

Kleinman, L. I.; Daum, P. H.; Lee, Y. N.; Nunnermacker, L. J.; Springston, S. R.; Weinstein-Lloyd, J. and Rudolph, J.: A comparative study of ozone production in five U.S. metropolitan areas, J. Geophys. Res. Atmos., 110, D02301, 2005.

Lou, S.; Holland, F.; Rohrer, F.; Lu, K.; Bohn, B.; Brauers, T.; Chang, C. C.; Fuchs, H.; Haseler, R.; Kita, K.; Kondo, Y.; Li, X.; Shao, M.; Zeng, L.; Wahner, A.; Zhang, Y.; Wang, W. and Hofzumahaus, A.: Atmospheric OH reactivities in the Pearl River Delta - China in summer 2006: measurement and model results, Atmos. Chem. Phys., 10, (22), 11243-11260, 2010.

Feng, X. Q.; Peng, K.; Ling, Z. H.; Zheng, J. Y.; Guo, H.: Source apportionments and characteristics of VOCs from 2005 to 2010 in Hong Kong, Acta. Sci. Circumst., 33(1):173-180, 2013.

Yarwood, G., Rao, S.,Yocke, M., and Whitten, G. Z.: Updates to the Carbon Bond Chemical Mechanism: CB05, Tech. rep., US Environmental Protection Agency, Novato, California, USA, 2005.