Supplementary Material for:

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

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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*/*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, 2005; Lou *et al*. 2010):

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

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 Synspec GC 955 on-line analyzer (Feng *et al*. 2013).

Species	**Limit of detection (ppt)**	**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-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
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. 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 S5. 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	14.3
n-pentane	3.94	*o*-xylene	13.7
i-pentane	3.9	1,3,5-trimethylbenzene	57.25
1,3-butadiene	66.6	1,2,4-trimethylbenzene	32.5
isoprene	101	1,2,3-trimethylbenzene	32.5
n-hexane	5.61		

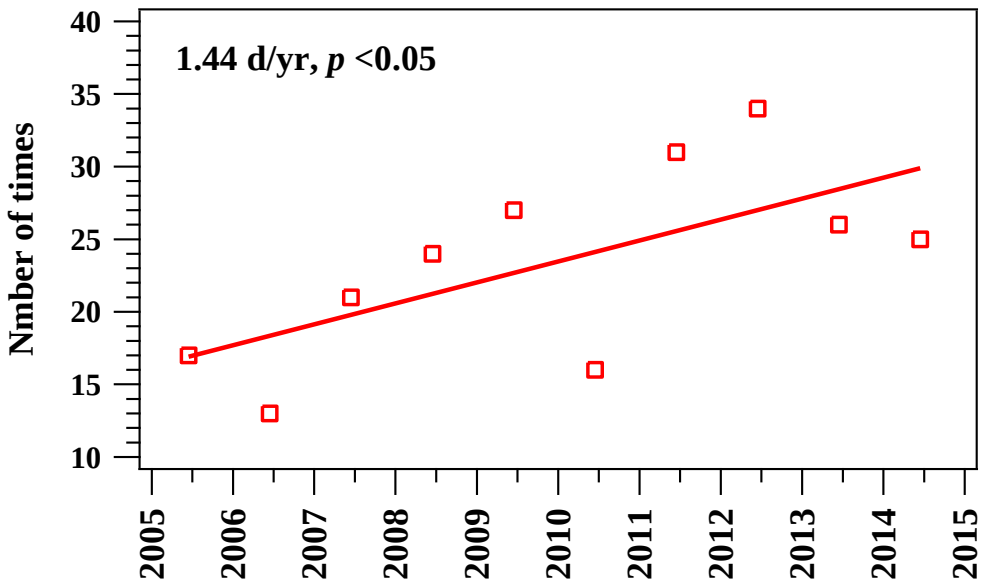


Figure S1. Annual trend of number of days per year that the daily 8-hour O_3 maximum (DMA8) exceeded 75 ppbv at TC during 2005–2014.

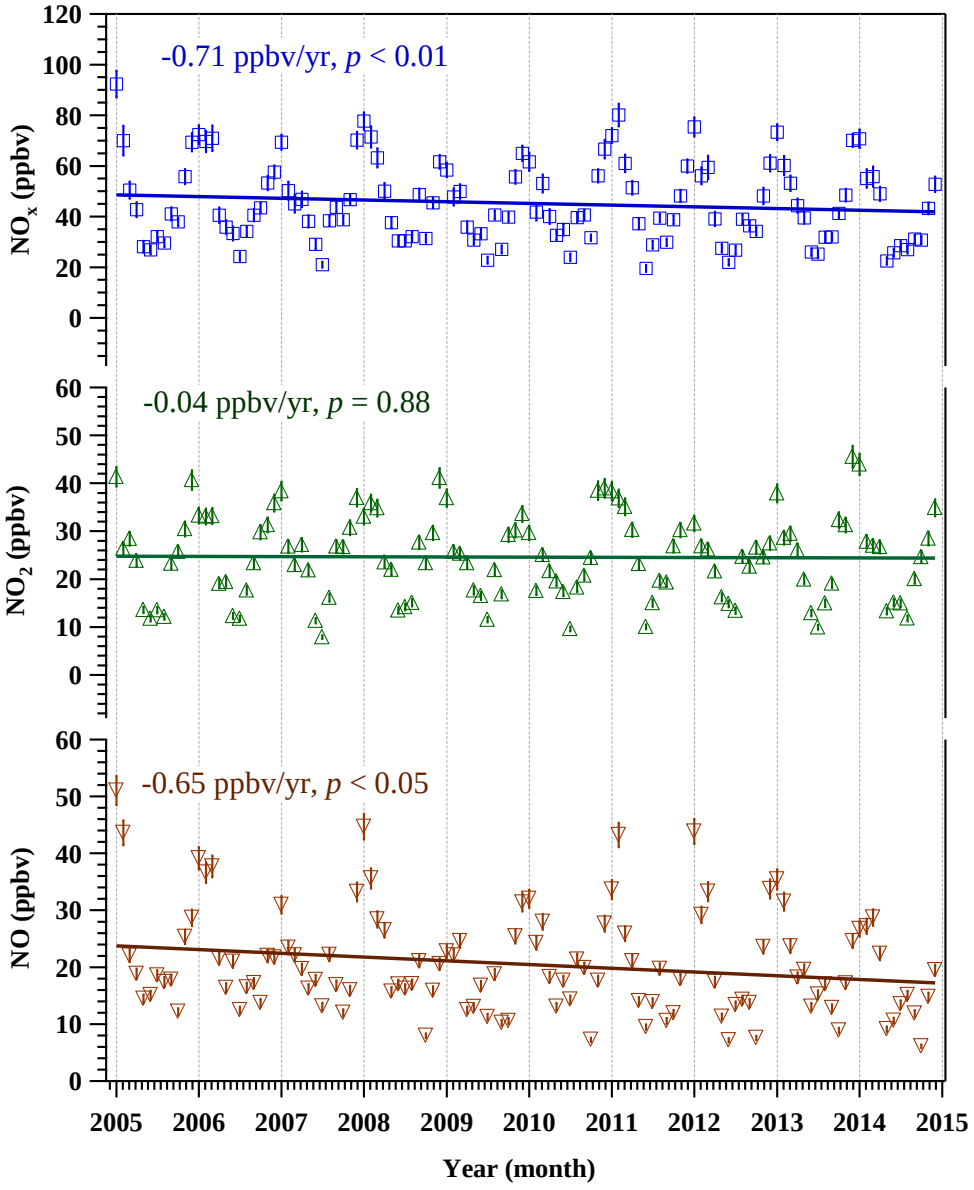
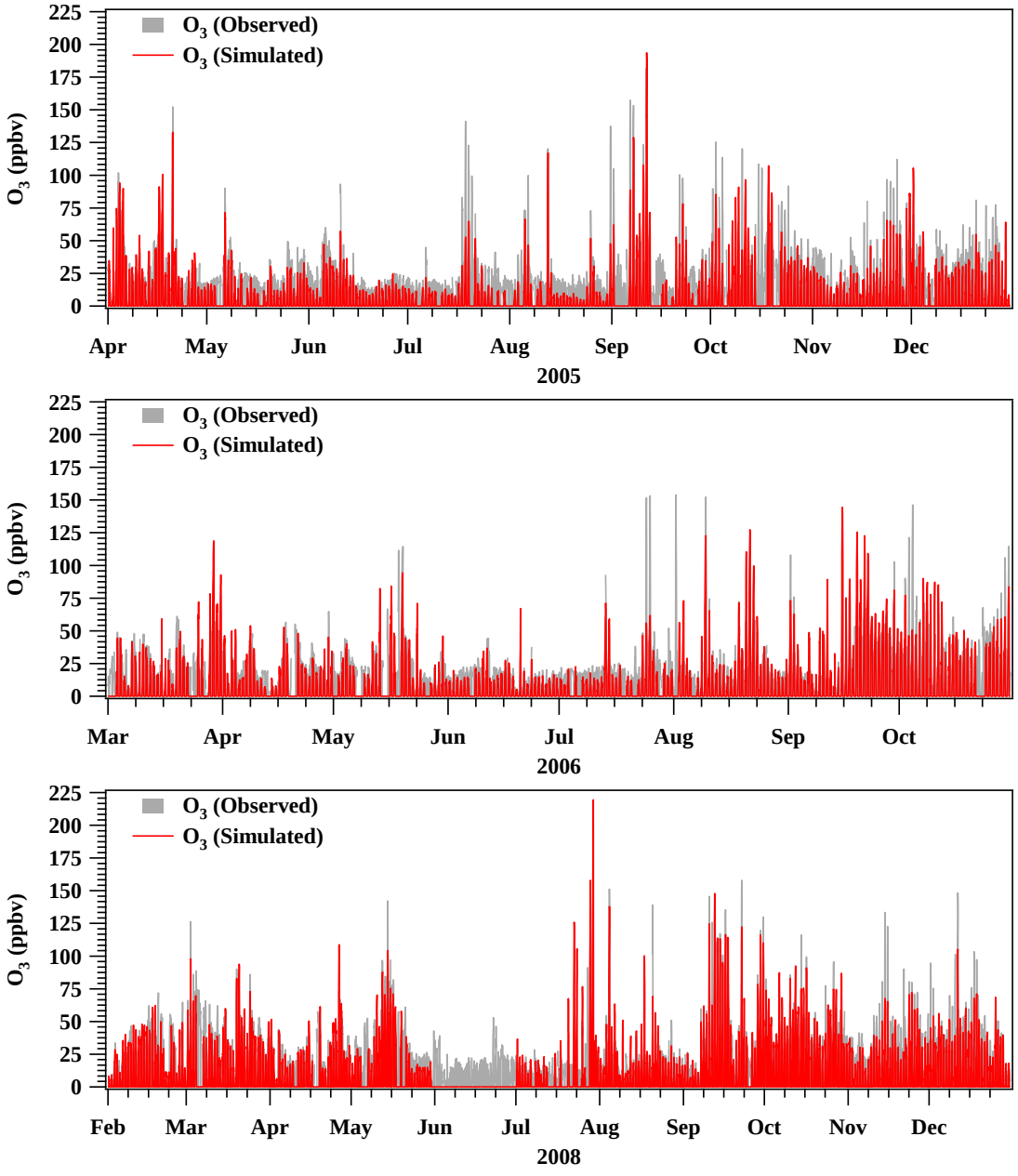
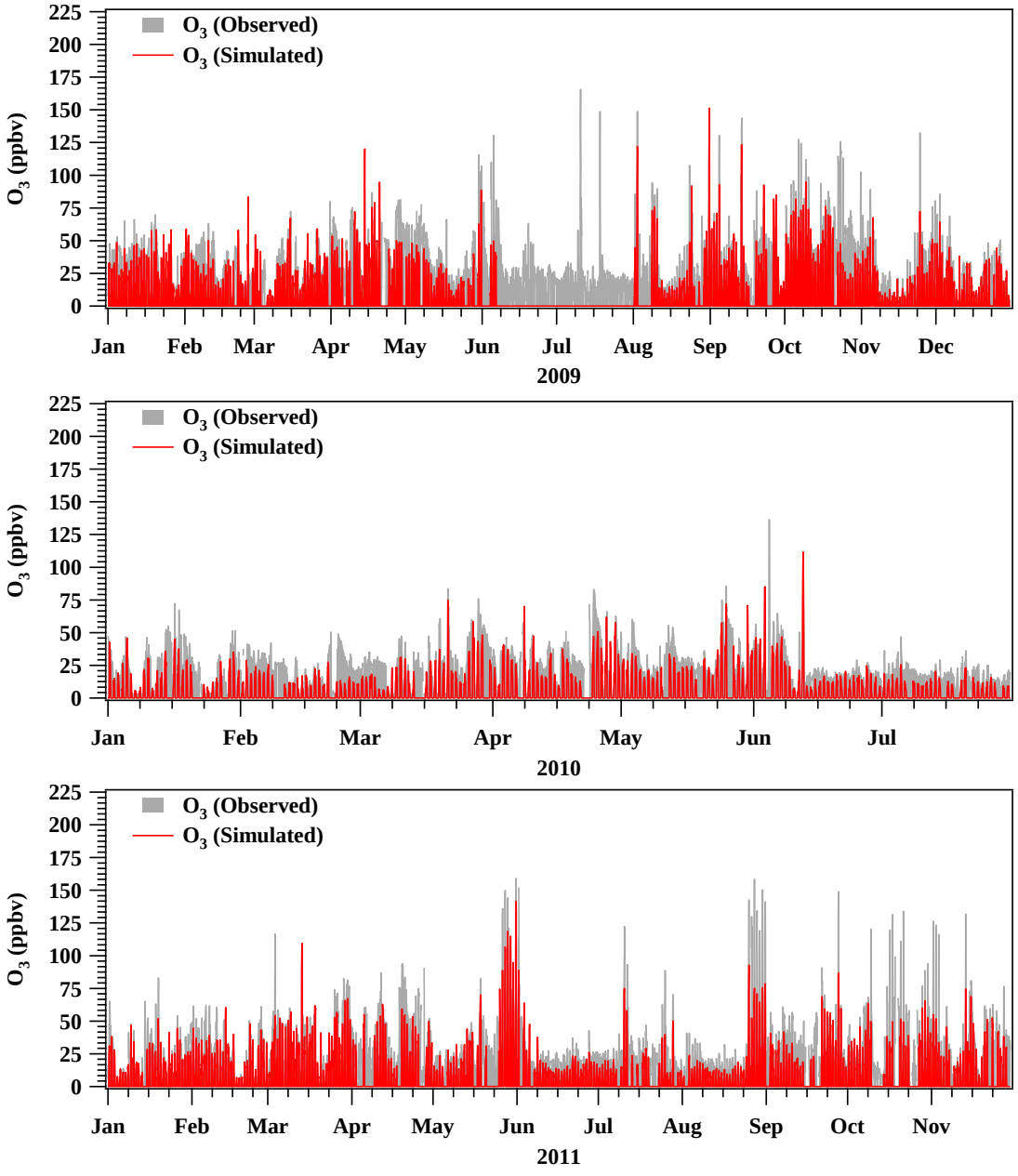


Figure S2. Trends of monthly averages of NO_x, NO_2 and NO at TC during 2005–2014. Error bars represent 95% confidence interval of monthly averages.


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
O3 (Observed)
O3 (Simulated)
O3 (ppbv)
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
2006
O3 (Observed)
O3 (Simulated)
O3 (ppbv)
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
O3 (Observed)
O3 (Simulated)
O3 (ppbv)
Jan
Feb
Mar
Apr
May
Jun
Jul
2010
O3 (Observed)
O3 (Simulated)
O3 (ppbv)
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
2011

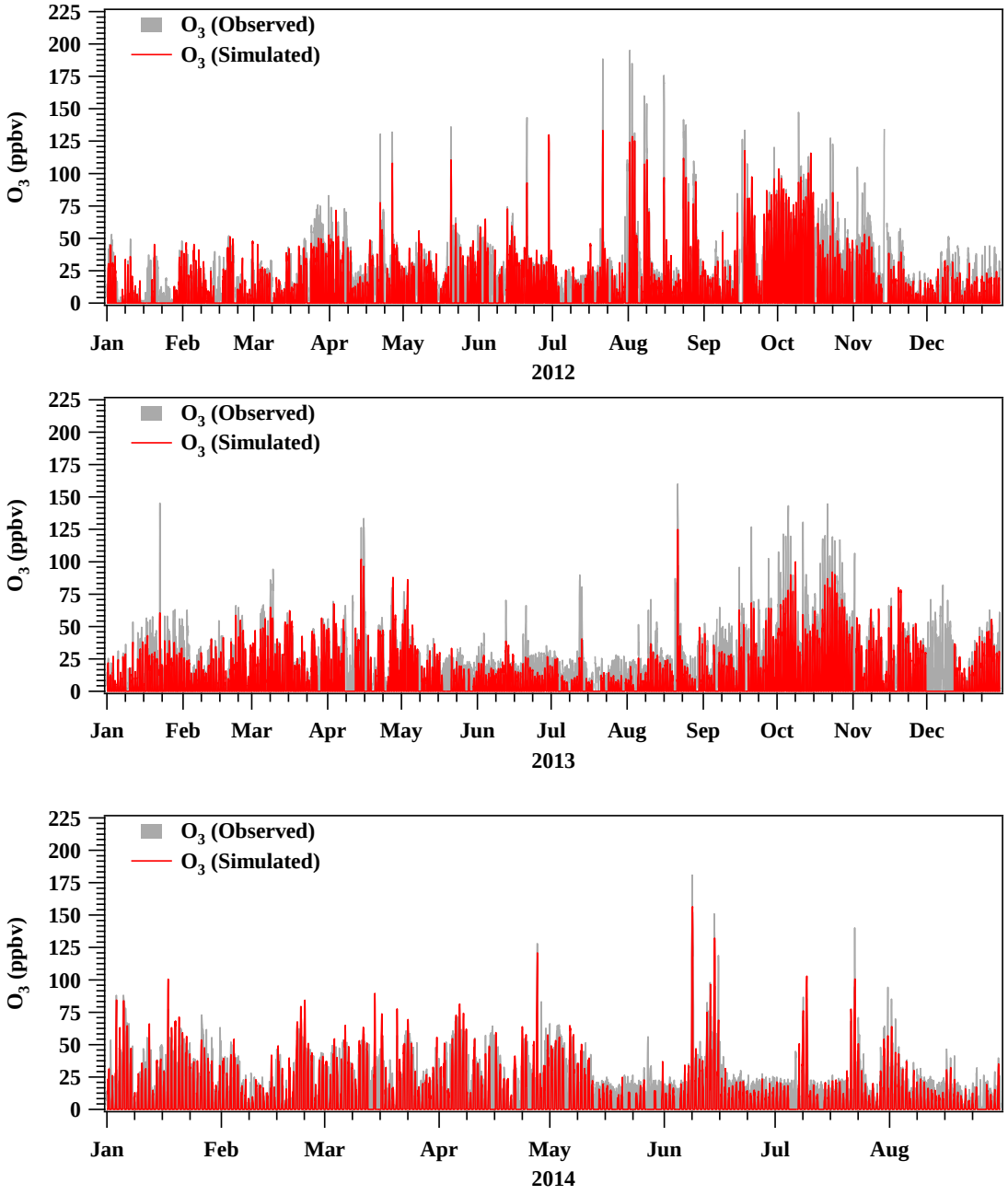
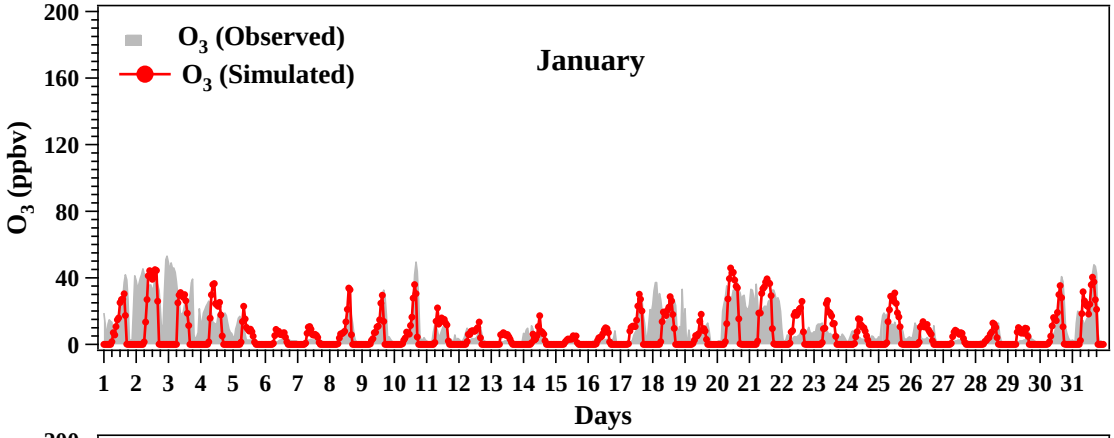
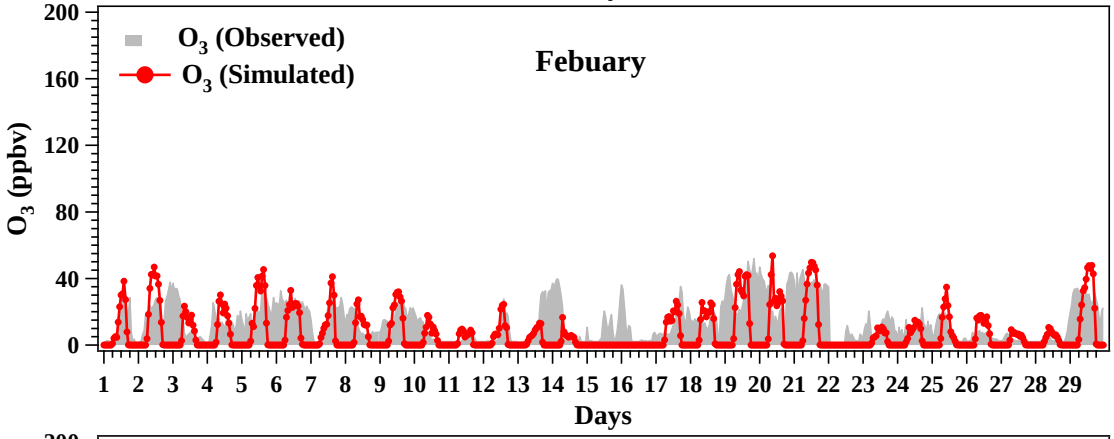
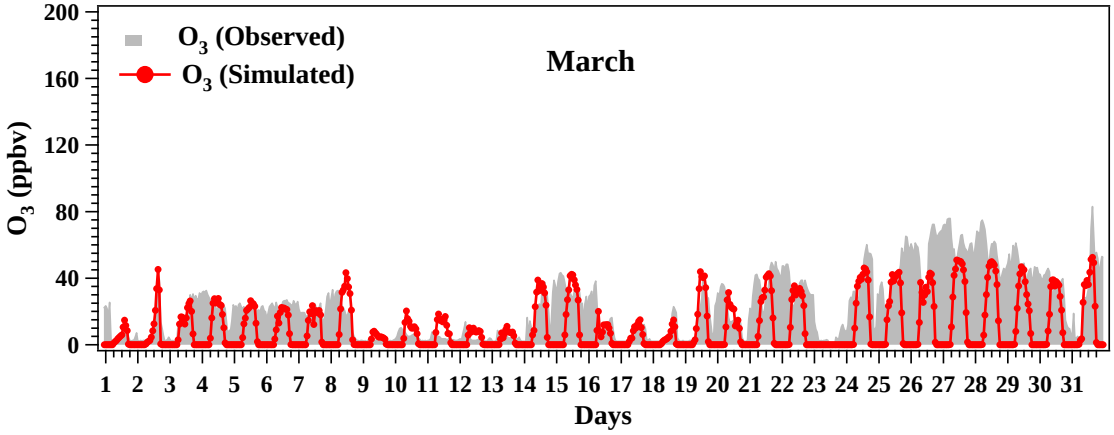
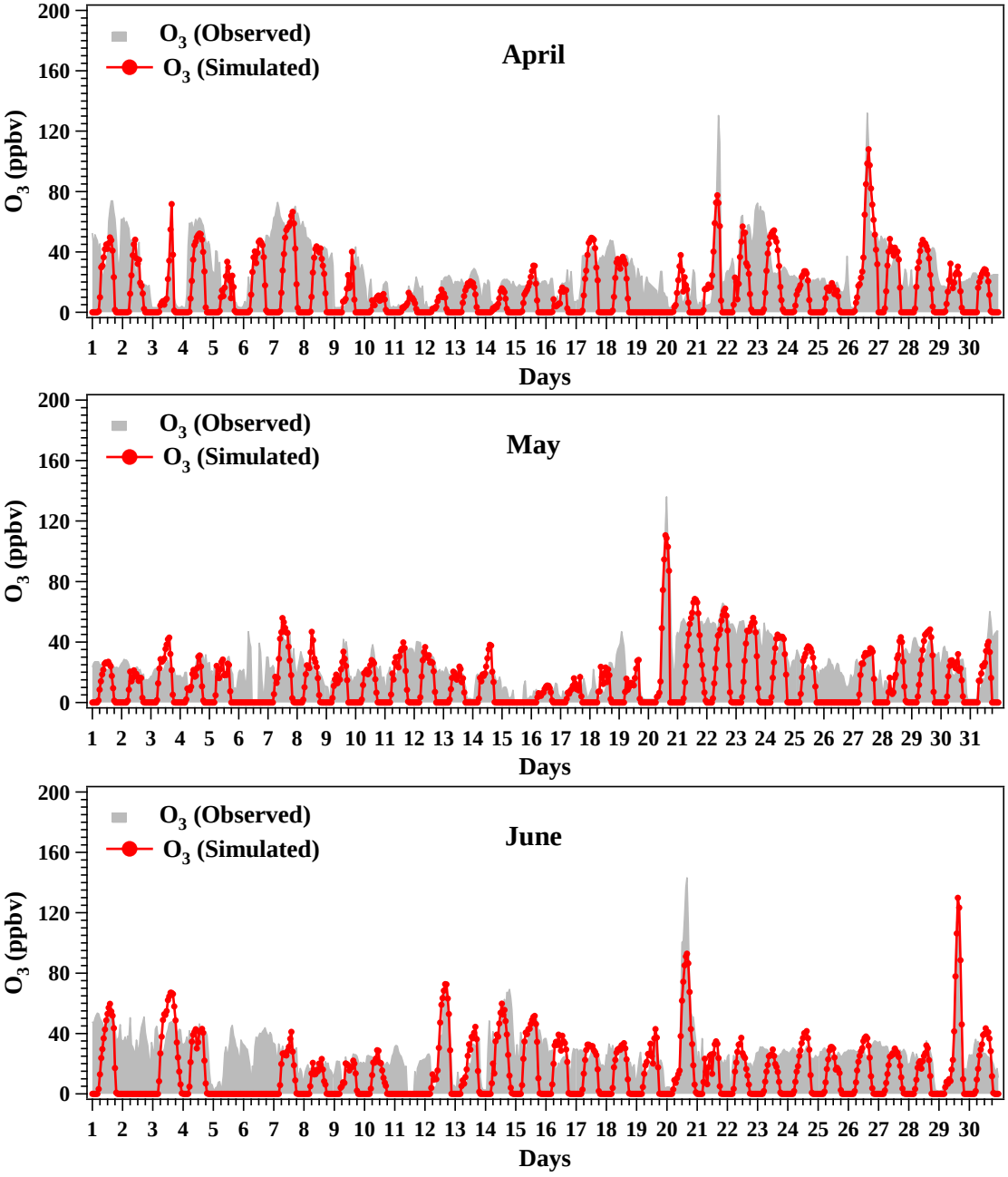


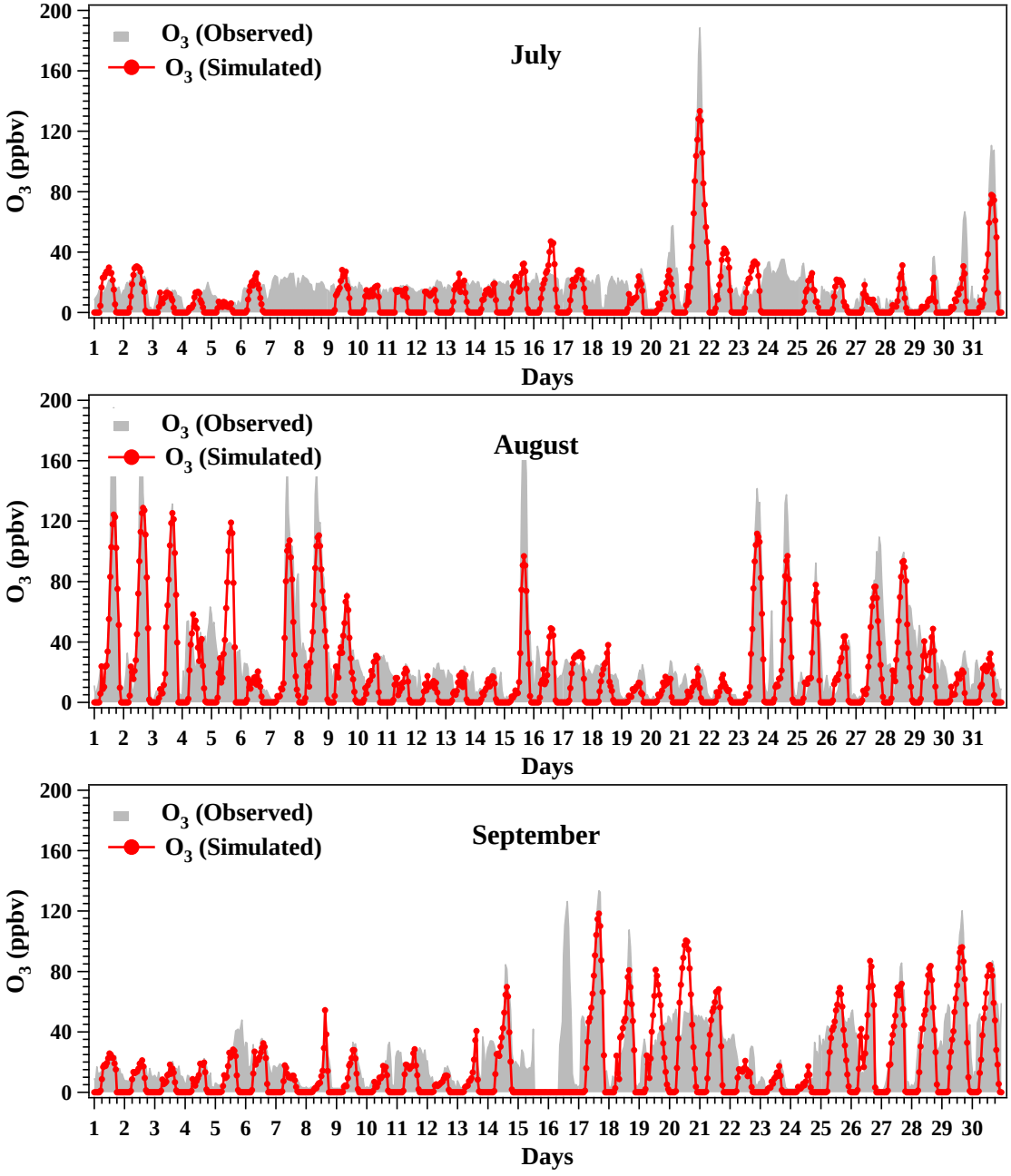
Figure S3. Comparison of simulated (red lines) and observed (grey areas) O_3 at TC from 2005–2014. Note: The plots are drawn by hourly data. O_3 simulations are not drawn in some days due to the lack of VOC real-time data (see Table S3).


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)
Days
May
June


O3 (Observed)
O3 (Simulated)
July
August
September
O3 (ppbv)
Days
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
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

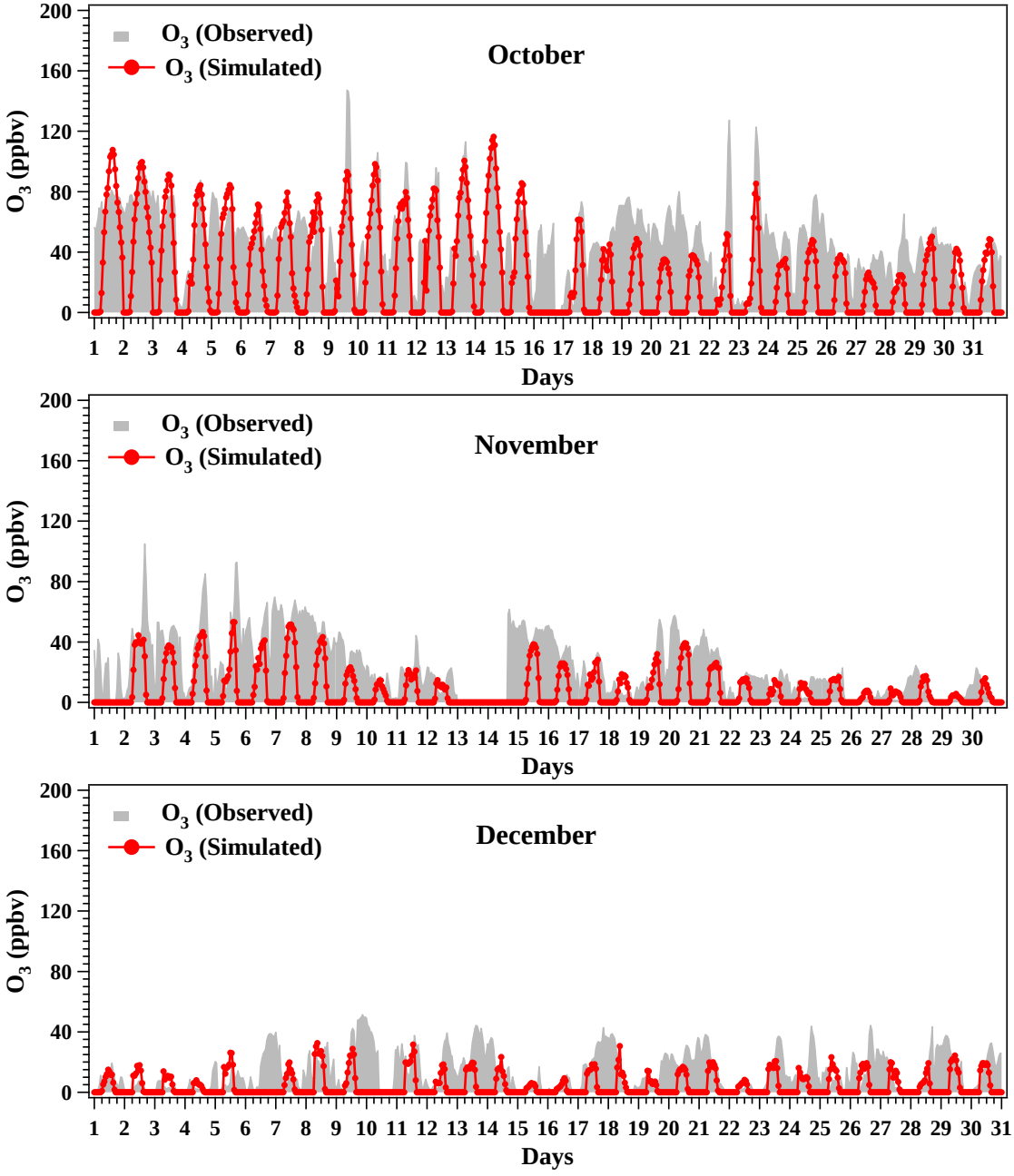


Figure S4. Comparison of simulated (red lines) and observed (grey areas) O_3 at TC in all 12 months in 2012. Note: The plots are drawn using hourly data. O_3 simulations are not drawn in some days due to the lack of VOC real-time data (see Table S3). Due to space constraints, only the data in 2012, the year with the most complete data, are selected to represent the simulation results.

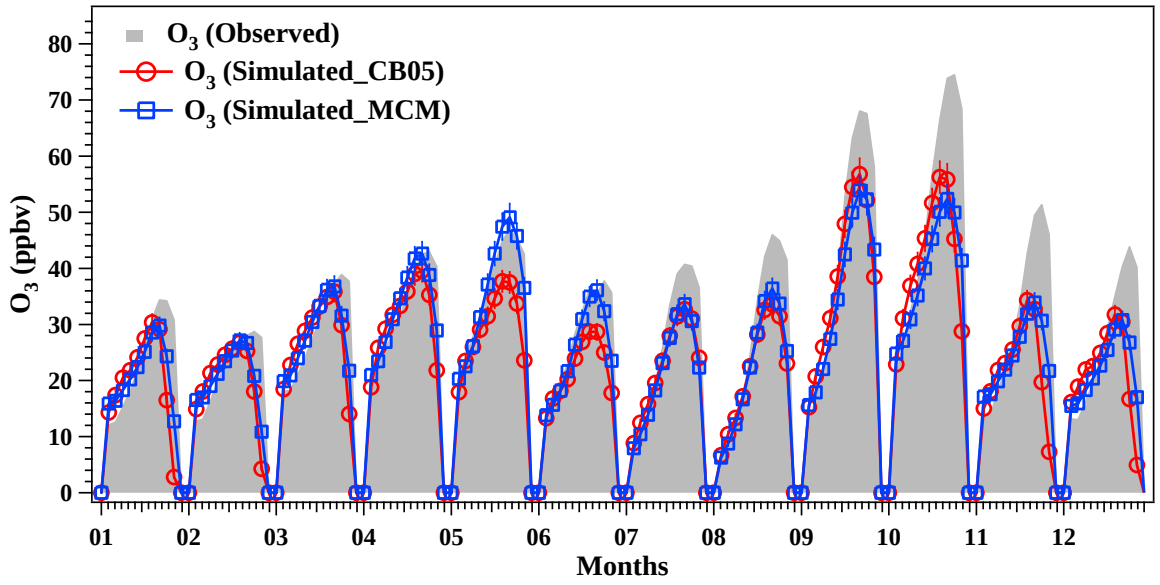


Figure S5. 12-month averaged diurnal variation of simulated O_3 by OBM (CB05, red line) and OBM (MCM, blue line); and observed O_3 (grey area) at TC during 2005–2014 (rainy days excluded). Note that the models were run for daily simulations. The daily simulated O_3 results and observed O_3 are further 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.

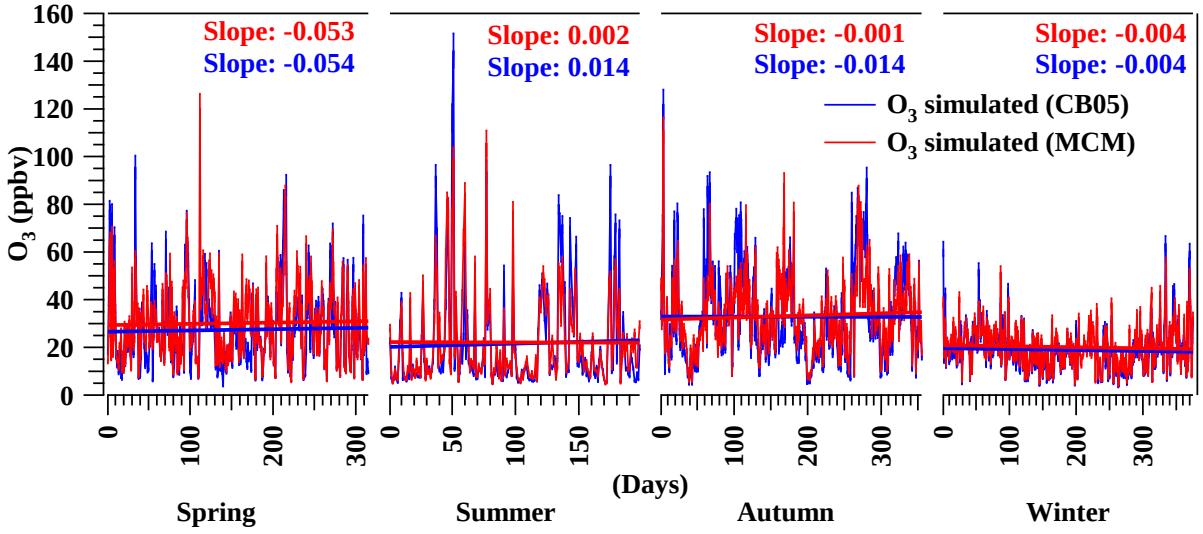


Figure S6. Trends of daily averaged locally-produced O_3 simulated by OBM (CB05, blue line) and by OBM (MCM, red line) in four seasons at TC during 2005–2014 (rainy days excluded). Note: all the data are based on daytime hours (0700-1900 LT).

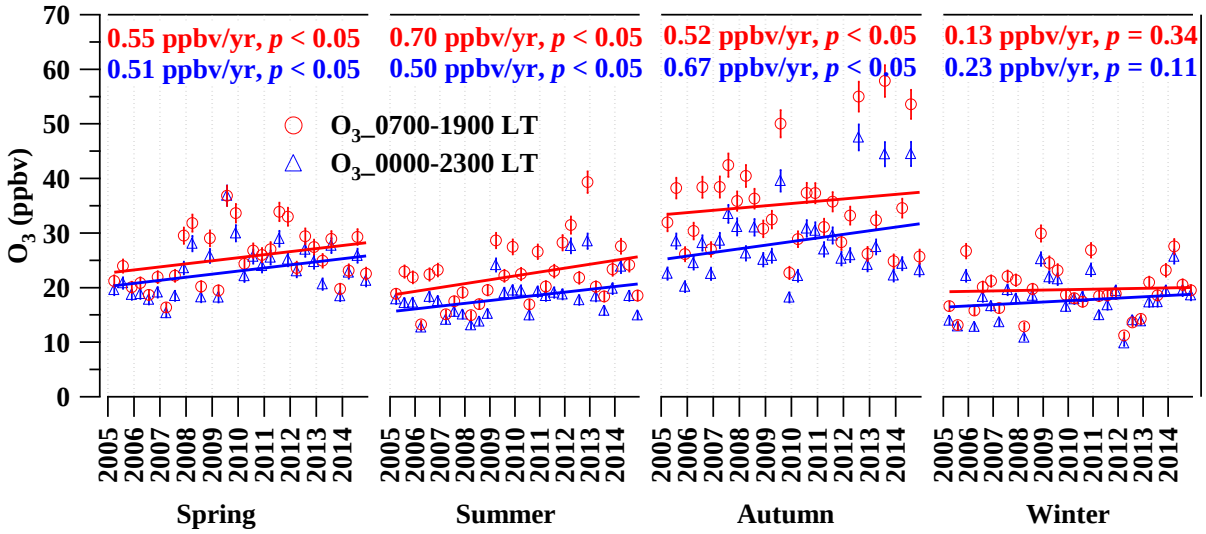


Figure S7. Trends of observed O_3 (blue line: 24-hour observed O_3, 0000-2300 LT; red line: daytime observed O_3, 0700-1900 LT) in four seasons at TC during 2005–2014. Error bars represent 95% confidence interval of the averages.

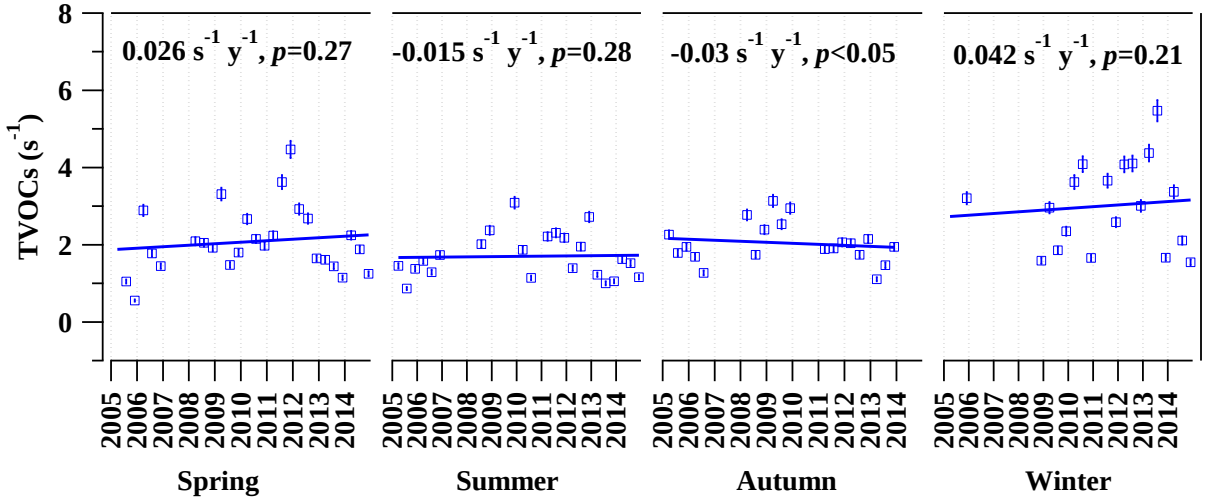


Figure S8. Annual variations of TVOC reactivity in four seasons at TC during 2005–2014. Each data point in the figure is obtained by averaging hourly values into a monthly value. Error bars represent 95% confidence interval of the averages. The rate constants with OH (k_{OH}) of VOC species are from Atkinson and Arey (2003).

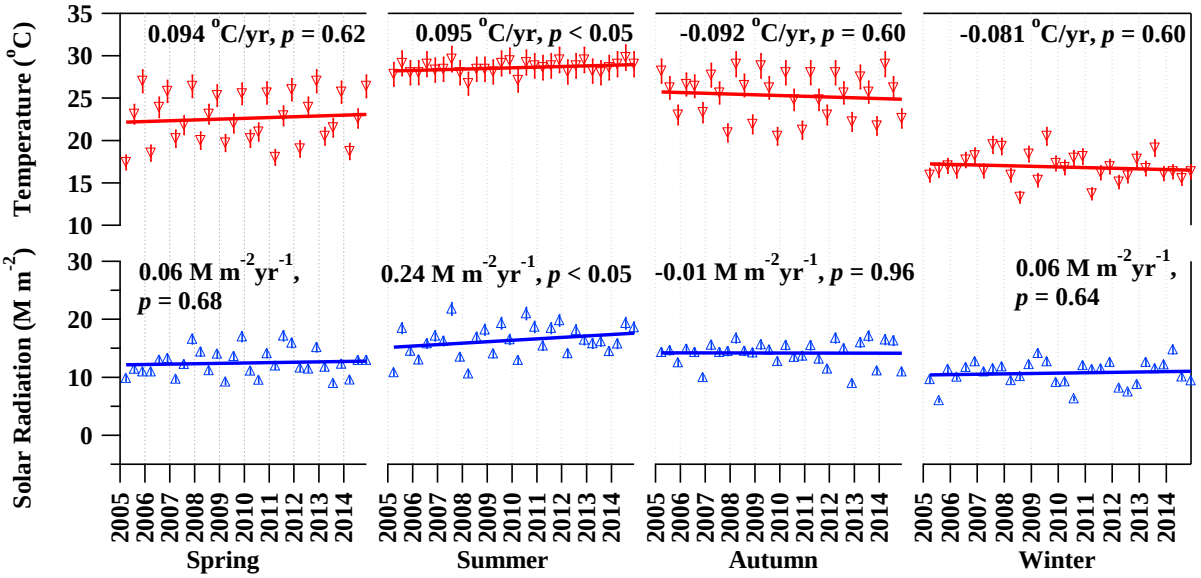


Figure S9. Variations of temperature (red) and solar radiation (blue) for the four seasons at TC during 2005–2014. Each data point in the figure is obtained by averaging hourly values into a monthly value. Error bars represent 95% confidence interval of monthly averages.

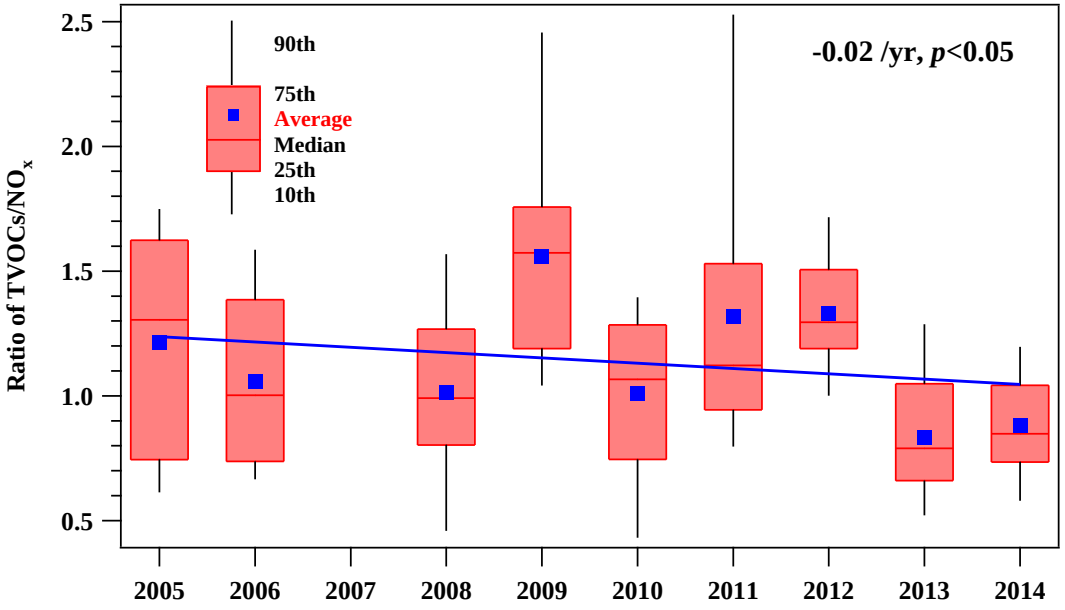


Figure S10. Annual trend of VOCs/NO_x ratio at TC in 2005–2014.

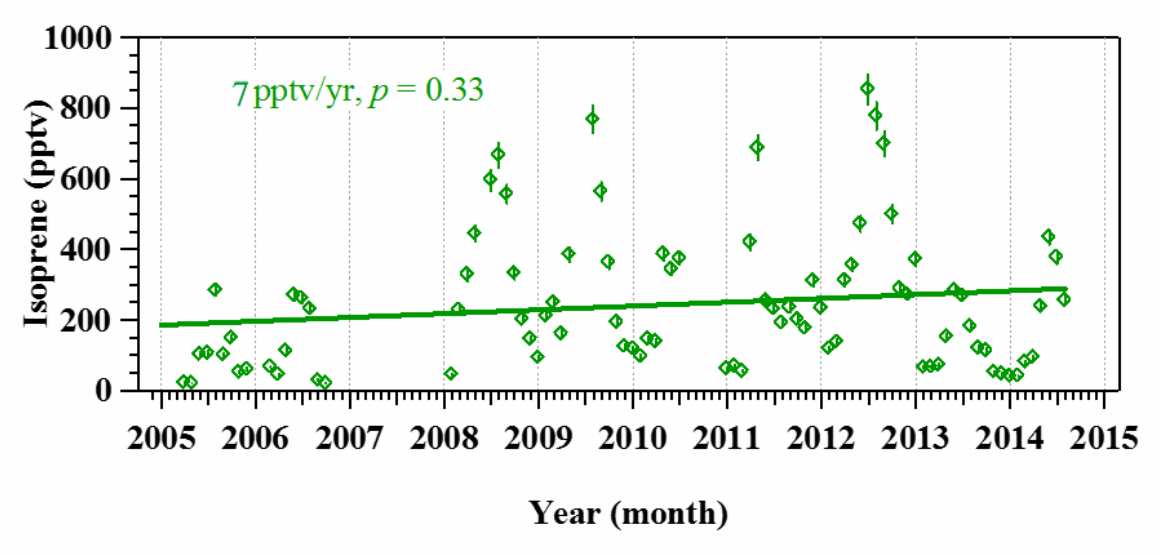


Figure S11. Trend of monthly average isoprene at TC during 2005–2014. Error bars represent the 95% confidence interval of the averages.

References

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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.

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