Supplement for the manuscript "Inter-comparison of O_3 formation and radical chemistry in the past decade at a suburban site in Hong Kong"

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Text S1. Set-up of the simulation scenarios

The base scenario (scenario A) was established to simulate the local production of O_3, with the observed concentrations of air pollutants (excluding O_3) as model inputs. The observed O_3 was not input because the simulated O_3 would be constrained to the observed values with the outputs exactly the same as the inputs otherwise. The scenario B was established to simulate O_3 under the assumption that a source of VOCs was totally removed. Namely, the VOCs emitted from a specific source were subtracted from the observed VOCs when allocating the model inputs. In this study, six sources of VOCs were identified (see section 3.4.1). Therefore, 6 sub-scenarios were included in scenario B, because the VOCs emitted from the individual sources were subtracted one by one. In this approach, the differences in simulated O_3 between scenario A and scenario B were the contributions of individual VOC sources to the local O_3 production.

Table S1. Summary of the sampling periods, VOC sampling dates and number of samples in the 2007, 2013 and 2016 sampling campaigns.

Year	Sampling period	Month	Date	Number of NMHC samples	Number of OVOC samples
2007	23 Oct.–1 Dec.	Oct.	26-27	96	28

		Nov.	13, 15-17, 23		
		Dec.	1		
2013	11 Aug.–22 Nov.	Sept.	11-12, 26	146	124
		Oct.	2-4, 9-10, 17, 22-25, 30-31		
		Nov.	15, 19-21		
2016	25 Sept. – 29 Nov.	Sept.	26	172	123
		Oct.	14-17, 23, 31		
		Nov.	1-7,14-18		
Total				414	275

Table S2. Instruments, analysis techniques, detection limits and time resolutions for the real-time measurements of trace gases at the TC air quality monitoring station.

Species	Instrument	Analysis technique	Detection limit	Time resolution
SO_2	API 100E	UV fluorescence	0.4 ppb	1 sec
CO	API 300	Non-dispersive infra-red absorption with gas filter correlation	<0.050 ppm	1 sec
NO-NO_2-NO_x	API 200A	Chemiluminescence	0.4 ppb	1 sec
O_3	API 400	UV absorption	0.6 ppb	1 sec

Table S3. Summary of limits of detection (LoDs), precisions and accuracies of the GC-MSD/FID/ECD systems used for NMHCs analyses of whole air samples collected in 2007, 2013 and 2016 (Simpson et al., 2010; Wang et al., 2018).

Institution	Year	Limit of Detection	Precision	Accuracy
UCI	2007	3-10 pptv	3%	5%
GIG	2013	3-57 pptv	2-5%	5%
HKPolyU	2016	3-10 pptv	5%	5%

Table S4. Statistics of VOC mixing ratios measured in 2007, 2013 and 2016. The 95% C.I., Max. and S.D. denote the 95% confidence interval, maximum and standard deviation of the mixing ratios of VOC species, respectively (Unit: pptv).

VOC species	2007			2013			2016		
	Mean ±95%CI	Max.	S.D.	Mean ±95%CI	Max.	S.D.	Mean ±95%CI	Max.	S.D.
Ethane	1587.6 ±37.3	1994.6	186.7	1918.9 ±140.1	5700.4	1123.4	1729.1 ±85.3	3951.2	655.6
Ethene	1388.7 ±53.5	2284.7	267.3	1074.9 ±94.3	4529.8	751.9	886.8 ±79.1	4335.5	605.3
Ethyne	1939.3 ±105.3	3855.4	526.3	1563.4 ±94.8	3339.0	760.0	1399.2 ±83.1	4254.7	637.5
Propane	2826.2 ±94.1	3889.6	472.0	1619.1 ±110.4	5826.3	883.4	2308.4 ±224.2	13269.8	1715.9
Propene	325.2 ±34.0	1036.7	169.9	296.1 ±20.3	1052.3	162.7	192.3 ±13.8	773.6	105.5
i-Butane	790.9 ±40.7	1269.3	203.6	1556.4 ±115.5	5778.5	922.7	901.5 ±67.5	3229.9	516.6
n-Butane	1562.4 ±124.3	3360.3	621.5	1402.6 ±95.8	5353.7	767.8	1403.8 ±116.3	5001.2	893.8
1-/i-Butene	275.1 ±71.2	2945.2	356.1	240.7 ±70.6	5944.6	566.2	98.0 ±9.4	715.8	71.7
trans-2-Butene	22.5 ±6.0	213.4	29.7	31.2 ±6.7	387.1	42.5	12.1 ±2.9	184.1	18.3
cis-2-Butene	24.4 ±6.0	201.9	29.7	25.2 ±5.0	275.2	32.4	9.3 ±2.8	178.5	17.5

3-methyl-1-Butene	12.0±2.4	76.6	11.9	35.6±16.0	332.0	67.2	8.7±5.5	207.0	26.6
2-methyl-1-Butene	16.4±3.3	89.0	16.3	47.4±25.3	1074.0	146.6	17.4±11.4	765.6	73.4
cis-2-Pentene	28.6±5.1	130.4	25.4	34.5±7.9	273.9	46.8	5.5±3.4	130.1	16.4
2-methyl-2-Butene	4.6±1.0	25.8	4.8	37.4±14.6	558.0	84.3	10.2±3.6	139.3	17.5
Butyne	41.0±6.3	171.2	31.5	40.5±12.1	406.7	58.6	18.5±2.8	142.2	18.5
i-Pentane	1809.6±339.6	7793.6	1697.8	827.5±63.3	4646.9	504.0	466.3±33.2	1681.2	254.1
n-Pentane	351.9±63.7	2271.2	318.7	50.1±8.6	416.2	59.9	265.1±25.1	1104.0	192.5
1-Pentene	20.4±5.7	244.3	28.2	50.1±8.6	416.2	59.9	15.6±2.9	182.5	20.3
trans-2-Pentene	15.3±4.1	182.0	20.8	23.6±7.7	302.1	41.4	9.8±4.9	189.6	24.1
2-Methylpentane	268.8±68.7	2253.0	343.6	257.1±29.6	1643.9	237.9	195.5±27.1	1171.6	204.9
n-Hexane	1785.2±547.3	17974.4	2736.1	930.6±147.7	9829.0	1182.2	163.4±23.8	1426.7	182.1
n-Heptane	113.8±39.3	1196.3	196.7	100.2±12.8	877.3	102.4	65.9±5.8	290.7	44.7
n-Octane	42.4±9.6	245.2	48.1	47.5±8.9	739.3	70.4	34.0±3.9	188.0	30.4
2,2-Dimethylbutane	18.7±2.2	64.8	11.3	52.7±8.7	719.6	65.0	20.2±2.0	91.9	14.2

2,3-Dimethylbutane	31.2 ±17.1	822.5	84.5	68.8 ±7.1	389.3	55.9	46.3 ±7.3	311.9	50.0
3-Methylpentane	1911.5 ±423.0	10292.0	2114.7	172.0 ±20.5	1260.3	164.4	131.8 ±18.9	1025.8	144.7
Cyclohexane	66.1 ±29.1	905.4	145.7	84.1 ±8.7	601.5	70.3	68.1 ±8.0	414.4	54.3
2-Methylhexane	49.0 ±16.4	557.0	82.1	85.7 ±9.7	429.6	77.5	205.8 ±19.2	492.8	89.9
3-Methylhexane	172.8 ±53.5	1651.2	266.3	171.5 ±19.4	1171.5	155.6	43.7 ±5.4	271.3	37.0
n-Nonane	29.1 ±6.4	226.8	32.2	47.6 ±8.1	621.6	64.4	39.9 ±7.3	477.2	56.4
n-Decane	457.3 ±138.9	3680.5	694.4	72.2 ±15.7	1198.3	126.3	34.0 ±3.9	188.0	30.4
n-Undecane	71.9 ±13.6	319.7	65.9	90.8 ±18.1	1367.5	145.4	--	--	--
Isoprene	270.6 ±53.0	2181.6	264.9	417.0 ±44.4	1561.0	343.4	409.1 ±52.5	3122.0	402.0
α-Pinene	261.8 ±191.5	6810.0	957.3	29.9 ±4.4	321.5	34.2	21.1 ±2.9	218.0	22.2
β-Pinene	30.3 ±10.1	306.4	50.6	53.8 ±7.3	314.5	57.5	9.9 ±0.7	32.0	5.4
Benzene	567.0 ±99.7	3761.2	498.5	493.1 ±33.2	2308.0	266.3	257.3 ±14.5	658.2	110.3
Toluene	2878.9 ±845.3	26556.8	4225.8	1445.3 ±149.2	6494.2	1196.5	1169.5 ±229.5	13376.0	1601.8
Ethylbenzene	358.8 ±63.2	1597.7	316.3	389.1 ±52.3	4274.0	419.5	193.6 ±20.7	1350.2	159.1

m/p-Xylene	411.1 ±82.1	1789.7	410.7	491.8 ±109.7	10168.0	879.8	299.4 ±28.4	1600.8	217.9
o-Xylene	168.1 ±30.0	773.5	150.3	231.3 ±34.1	2082.0	274.1	151.7 ±13.7	891.2	105.0
1,3,5-Trimethylbenzene	43.8 ±8.8	323.5	44.3	38.6 ±8.4	680.3	67.5	11.6 ±1.6	125.5	12.7
1,2,4-Trimethylbenzene	177.3 ±40.1	1527.5	200.6	143.3 ±25.1	1492.3	201.7	39.6 ±5.6	336.7	42.9
1,2,3-Trimethylbenzene	64.7 ±23.8	940.9	117.8	63.1 ±11.6	809.7	93.4	16.7 ±3.5	320.3	27.2
i-Propylbenzene	7.4 ±1.2	38.0	6.3	16.5 ±1.8	111.1	14.2	7.5 ±0.7	63.0	5.8
n-Propylbenzene	16.4 ±2.6	68.9	13.0	34.3 ±4.3	305.2	34.5	12.4 ±2.0	188.6	15.3
3-Ethyltoluene	34.6 ±7.2	212.4	36.1	74.0 ±10.6	653.0	85.5	24.7 ±2.9	171.4	22.4
4-Ethyltoluene	18.1 ±3.4	114.4	17.1	45.4 ±6.1	429.8	48.7	16.6 ±2.4	220.2	18.3
2-Ethyltoluene	23.2 ±4.3	143.0	21.5	40.4 ±6.7	476.3	53.9	14.0 ±2.1	186.1	16.3
Formaldehyde	8608.3 ±1298.0	30244.3	6352.3	2729.0 ±146.5	6403.5	1123.8	2673.3 ±283.1	13633.0	2171.5
Acetaldehyde	9853.8 ±1732.6	46380.0	8198.0	1395.9 ±81.1	3694.8	622.2	779.4 ±92.1	3126.0	649.4

Acetone	12786.4 ±2712.9	75590.0	13131.5	5156.2 ±421.3	22921.5	3231.7	4995.6 ±460.6	13370.9	3469.7
Propionaldehyde	--	--	--	325.0 ±38.2	1593.2	247.0	1547.9 ±547.2	3071.6	1081.3

Table S5. Comparison of meteorological conditions in the autumns of 2007, 2013 and 2016 (HKO, 2017).

	2007		2013		2016	
	Mean ± 95%C.I.	Max.	Mean ± 95%C.I.	Max.	Mean ± 95%C.I.	Max.
Temperature (℃)	23.5±0.4	30.0	25.2±0.3	33.9	25.0±0.3	32.7
Relative humidity (%)	64.4±1.4	80.0	58.6±1.3	83.1	77.1±0.7	94.5
Solar radiation (W/m^2)	190.3±37.7	788.9	159.2±21.3	869.1	119.8±18.2	829.3
Pressure (hPa)	1016.9±0.4	1024.3	1015.0±0.3	1023.1	1012.3±0.3	1020.2
Wind Speed (m/s)	2.3±0.2	5.3	1.0±0.1	3.2	0.9±0.1	4.3

Table S6. Number of O_3 episode days identified under the tropical cyclone, continental anticyclone and low pressure trough in the autumns of 2007, 2013 and 2016.

Year	Total No. of Episode	Tropical cyclone	Continental anti-cyclone	Low Pressure trough
2007	15*	8 (4 typhoons)	8	1
2013	16	11 (5 typhoons)	5	0
2016	5	4 (3 typhoons)	0	1

*Two O_3 episode days were under the combined influence of tropical cyclone and continental anticyclone.

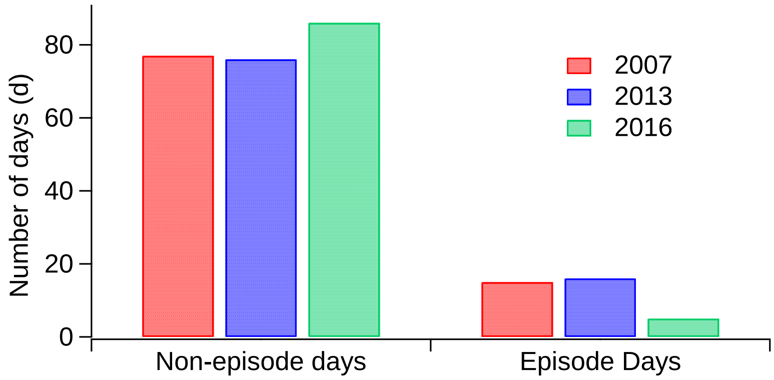

Figure S1. Number of O_3 episode days and non-O_3 episode days in the autumns of 2007, 2013 and 2016.

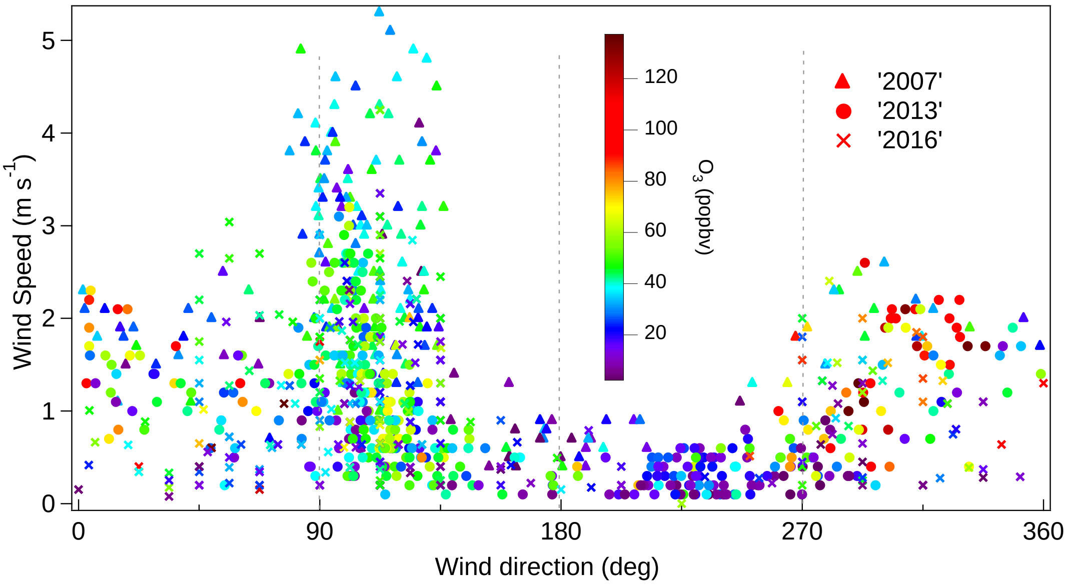

Figure S2. Relationship between the hourly observed O_3 and the wind fields at TC in the three sampling campaigns.

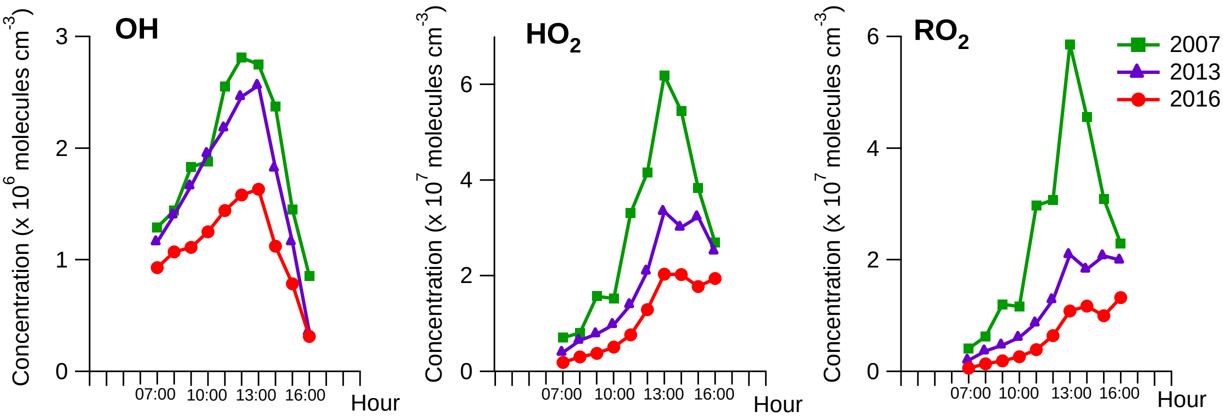

Figure S3. Average diurnal profiles of the simulated OH, HO_2 and RO_2 concentrations on VOC sampling days in 2007, 2013 and 2016.

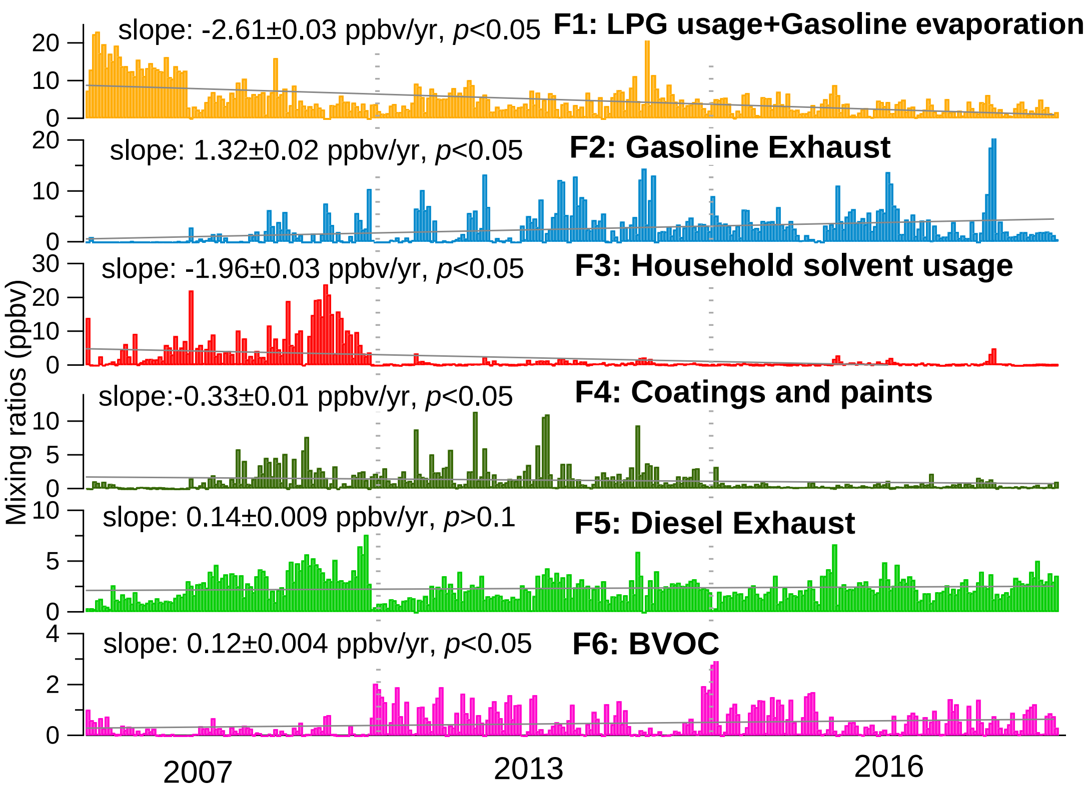

Figure S4. Total mixing ratio of VOCs emitted from each individual source extracted from PMF in the 2007, 2013 and 2016 sampling campaigns. The solid lines represent the linear regressions of the VOC mixing ratios against the sequence number of the samples, with the slope being converted to yearly rates.