Response to Referee 1’s comments

General comment

A valuable long term dataset is described as a basis for an interesting long term trend study on ozone and its precursors, which can be used to track how emission changes and some abatement strategies are effecting air quality in Hong Kong, and how best to deal with air quality issues into the future. However, much more detail on the scientific approaches and applied methods (measurement techniques, modelling and data analysis/filtering) are needed as detailed below. Once these issues have been adequately addressed, this study can be accepted for publication in ACP.

We highly appreciate the reviewer for the positive comments and constructive suggestions. In general, all these comments have been addressed properly with addition of required words, figures and tables in the revised manuscript, particularly with great details of the methods. Furthermore, a number of modelling sensitivity tests have been conducted and the new results have been added to support our conclusions. Also, many sentences have been reorganised to either reduce confusing or improve readability. In the following section, the author’s responses (in blue) are immediately after the reviewer’s comments (in black), with the changes in manuscript at the end (in italic).

Specific comments

Comment 1.1

More details of the measurement techniques, in particularly the QA/QC methodologies and approaches for the GC analysis is needed (stating computer programme used for auto calibration is not good enough). I find a detection limit of 2 pptv using this technique quite low, especially for an hourly measurement.

Response:

More detailed description about the measurement techniques, such as instrumentation, detection limit, resolution, and QA/QC, has been added in the revised manuscript. In addition, it is not surprising to achieve a detection limit of 2 pptv for using this technique. In many previous studies (not only in Hong Kong), a comparable low detection limit was reported by using the same measurement techniques, such as Xie *et al*. (2008) and Yuan *et al*. (2009).

References:

Xie, X., *et al*. (2008), "Estimation of initial isoprene contribution to ozone formation potential in Beijing, China", Atmos. Environ., 42, 6000–6010, doi:10.1016/j.atmosenv. 2008.03.035.

Yuan, Z., *et al*. (2009). "Source analysis of volatile organic compounds by positive matrix factorization in urban and rural environments in Beijing." Journal of Geophysical Research Atmospheres 114(16).

Revision in the manuscript:

Page 4, Line 6:

"2.2 Measurement techniques

Hourly observations of O_3, CO, SO_2, NO-NO_2-NO_x and meteorological parameters at TC from 2005 to 2014 were obtained from the HKEPD (http://epic.epd.gov.hk/ca/uid/airdata). Briefly, O_3 was measured using a commercial UV photometric instrument (Advanced Pollution Instrumentation (API), Model 400A) with a detection limit of 0.6 ppbv. CO was measured with a gas filter correlation CO analyser (Thermo ElectronCorp. (TECO), Model 48C) with a detection limit of 0.04 ppm. SO_2 was measured using a pulsed fluorescence analyser (TECO, Model 43A) with a detection limit of 1.0 ppbv. NO-NO_2-NO_x were detected using a commercial chemiluminescence with an internal molybdenum converter (API, Model 200A) and a detection limit of 0.4 ppbv. All the time resolutions for these gas analysers were 1 hour. To ensure a high degree of accuracy and precision, the QA/QC procedures for gaseous pollutants were identical to those in the US air quality monitoring program (http://epic.epd.gov.hk/ca/uid/airdata). The accuracy of the monitoring network was assessed by performance audits, while the precision, a measure of the repeatability, of the measurements was checked in accordance with HKEPD's quality manuals. For the gaseous pollutants, the accuracy and precision within the limits of ±15 and ±20 % were adopted, respectively (HKEPD 2015).

Real-time VOC data at TC were also measured by the HKEPD. An online GC-FID analyser (Synspec GC 955, Series 600/800) was used to collect VOC speciation data continuously with a time resolution of 30 minutes. The VOC analyser consists of two separate systems for detection of C_2–C_5 and C_6–C_{10} hydrocarbons, respectively. Detailed description about the real-time VOC analyser can be found in Lyu et al. (2016). Twenty-eight C_3-C_{10} VOC species were identified and quantified using this method. In terms of the QA/QC for VOC analysis, built-in computerized programs of quality control systems such as auto-linearization and auto-calibration were used. Weekly calibrations were conducted by using NPL standard gas (National Physical Laboratory, Teddington, Middlesex, UK). In general, the detection limits of the target VOCs ranged from 2 to 56 pptv. The accuracy of each species measured by online GC-FID was determined by the percentage difference between measured mixing ratio and actual mixing ratio based on weekly span checks and monthly calibrations. The precision was based on the 95% probability limits for the integrated precision check results. The accuracy *of the measurements was about 1-7%, depending on the species, and the measurement precision was about 1-10% (Table S1). In addition, the quality of the real-time data was assured by regular comparison with whole-air canister samples collected and analysed by University of California at Irvine (UCI). More details can be found from previous studies in Hong Kong (Xue et al., 2014; Ou et al., 2015; Lyu et al., 2016).*

For data analysis, linear regression and error bars represented as 95% confidence intervals were used. Trends of O_3 and its precursors with a p value < 0.05 were considered significant (Guo et al., 2009).”

Comment 1.2

Different speciated sets of VOCs have been targeted in previous studies, such as 30 C_2 –C_{10} in previous studies at MK and HT (Lyu *et al*., 2016). Why have you focused on a different speciation of 21 species in the present study?

Response:

The main reason why not all detected species were included in the present study is because of high percentage of missing data for several species at TC site over 2005-2014. This problem was very serious in some years and also existed for other sites, such as MK and HT, over the years. As this study looks into the trend of O_3, those species with high missing data were excluded to eliminate the influence caused by different input of VOC species.

We admitted that the limited number of species would underestimate the O_3 production. To assess this impact, the missing reactivity has been examined and the results are presented in the Response to Comment 1.9.

In addition, *m*-xylene listed in Tables S1 and S2 actually represents *m/p*-xylene (*i.e.*, *m*-xylene and *p*-xylene) as the VOC analysis method used in this study could not divide the two species apart. To reflect this fact, the number of VOC species adopted in the study has been corrected from 21 to 22. It is noteworthy that this change would not affect our results and conclusion, because the three xylene isomers have the same CB05 model specie (*i.e.*, XYL, see Table S2).

Revision in the manuscript:

Page 8, Line 10: “The TVOCs were defined as the sum of the 22 VOC species listed in Text S1. Note that not all detected VOCs were included in this study because of high rates of missing data.”

Text S1 & Table S1 & Table S2 & Table S4 & Table S10: p-xylene has been added.

Comment 1.3

Given the extensive annual VOC information available at other sites (local and regional) it would be useful to compare seasonally averaged measurements at as many different sites as possible (in a Table?).

Response:

As suggested, a comparison of seasonally averaged total VOCs (TVOC) at five different sites (1 background, 2 suburban, 1 urban and 1 roadside sites) in Hong Kong has been conducted. The results are presented in Table S8. The table demonstrates the seasonal trends of TVOC were similar at these different sites, with highest values in winter and lowest in summer, though the TVOC levels varied over the sites. In addition, as expected, the TVOC levels were higher at urban and roadside sites, while lower at suburban sites.

Revision in the manuscript:

Supplementary:

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.

Page 10, Line 6: *"Generally, all precursors showed low values in summer and high levels in winter, mainly due to typical Asian monsoon circulations, which brought in clean marine air in summer and delivered pollutant-laden air from mainland*

China in winter (Wang et al., 2009). Subject to this reason, a similar seasonal variation was observed for the averages of TVOC at different locations over Hong Kong (see Table S8).”

Comment 1.4

Difficult to separate the background and regional effects on observed ozone formation from the local chemical production and more detail into how the authors have done this is needed.

The authors agree that it is indeed difficult to separate regional effects on O_3 observation from local production due to two assumptions: (1) the background/regional effects we deducted at HT or TM may not be the same as those at TC (TC may have higher or lower regional air than at HT/TM), or (2) HT/TM is also affected by local air mass (what we deducted as background/regional air may contain local emissions). However, we think the approach we used in this study is acceptable and did give reasonable results. To make it clearer, more details on the method have been provided in the revised manuscript. The sensitivity and uncertainty associated with this approach have also been investigated and the results are discussed in Responses to Comment 1.5 and 1.14.

Revision in the manuscript:

Page 6, Line 7:

” The measured precursors (i.e., VOCs, NO and NO_2) at TC are a mixture of regional background values augmented by local source influences, and the two parts are very difficult to be fully separated. It is worth noting that the regional background values are those observed at locations where there is little influence from urban sources of pollution, while the baseline values mentioned in Section 3.2 are observations made at a site when it is not influenced by recent, locally emitted or produced pollution (TF HTAP, 2010). To minimize the influence of regional transport from the inland PRD region, the real-time regional background values in this study were simply subtracted off from the observations at TC. …… In this study, mixing ratios of 21 anthropogenic VOC species with relatively long lifetimes (5h – 14d) at HT were selected as the background values for deducting from the observed data at TC. The lifetimes of these VOCs were estimated based on the reactions with OH radicals (Simpson et al., 2010). Isoprene was considered as not having a regional impact due to its short lifetime (1-2 h) (Ling et al., 2011). Furthermore, the lifetime of NO_2 is determined by the main sinks of OH+NO_2 reaction

and the hydrolysis of N_2O_5 at the surface of wet aerosols, which highly depends on meteorological conditions, such as temperature and humidity (Dils et al. 2008; Evans and Jacob, 2005). Previous experimental studies showed an exponential relationship between the NO_2 lifetime and temperature (Dils et al., 2008; Merlaud et al., 2011; Rivera et al., 2013), which was used to estimate the lifetime of NO_2 in this study."

Comment 1.5

What are the sensitivities in the model to these (potentially high) uncertainties in initial concentrations of ozone precursor?

Response:

Thanks for raising this issue. The uncertainties in initial concentrations of ozone precursors are considered into two parts: uncertainties caused by measurement data themselves, and uncertainties caused by the deduction of background/regional values. For the first part, the upper and lower limits of initial precursor concentrations with uncertainties (±95% confidence intervals, see Table S4) have been used for testing the sensitivity in the model. For this test, a small dataset with randomly selected days in 2012 is used. The sensitivity results are shown in Figure S4 and Figure S5 for model runs with varying NO_2 only or VOCs only, respectively. As it is believed that NO_2 had little influence on Hong Kong in summer and autumn through regional transport (see Page 6 in the original manuscript for the reasoning), the sensitivity tests of NO_2 were only conducted for spring and winter. For the sensitivity tests of VOCs, only the variations of anthropogenic VOCs were considered as the biogenic VOCs have much shorter lifetimes and are considered as negligible source of regional transport in this study. The results demonstrate that the variations in the modelled O_3 production are about ±13% and ±3.9% for NO_2 and VOCs, respectively, when the precursors change in the range of ±95% confidence intervals.

In addition, the changes in ozone precursors, which are caused by removing their regional background concentrations and are considered as the maximum uncertainties in initial concentrations, have also been investigated by modelling tests. Three scenarios (i.e. removing NO_2 only, removing VOCs only, and removing both NO_2 and VOCs) are included. Please refer to Response to Comment 1.14 for details.

Revision in the manuscript:

Page 8, Line 1: "Furthermore, the sensitivities in the OBM model to the uncertainties in initial concentrations of ozone precursors have been examined by running the model with varying NO_2 *or VOCs initial concentrations in the range of ±95% confidence intervals, respectively. The results demonstrate that the modelled* O_3 *production was more sensitive to* NO_2 *than VOCs, with a percentage variation about ±13% and ±3.9%, respectively (see Table S4, Figure S4 & Figure S5)."*

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	6.73 ±1.8	5.89 ±1.71	5.56 ±1.66	8.18 ±2.24
Propane	666.33 ±22.88	193.75 ±18.63	841.16 ±22.11	1444.59 ±30.14
Propene	68.65 ±3.24	18.77 ±2.09	62 ±3.82	175.59 ±6.13
_n_-Butane	331.36 ±18.23	175.87 ±17.13	399.96 ±15.83	682.38 ±25.07
_i_-Butane	253.15 ±11.51	116.7 ±11.27	309.77 ±10.98	549.66 ±17.08
1-Butene	6.73 ±0.78	3.03 ±0.76	20.96 ±1.98	26.59 ±2.49
trans-2-Butene	6 ±0.88	3.04 ±0.77	5.76 ±1.06	15.71 ±1.75
cis-2-Butene	4.14 ±0.57	2.7 ±0.72	24.23 ±2.09	17.9 ±1.8
1,3-Butadiene	6.49 ±0.83	2.22 ±0.54	11.97 ±1.76	22.05 ±1.52
_n_-Pentane	115.98 ±7.74	64.34 ±7.72	121.87 ±5.9	177.07 ±6.48
_i_-Pentane	192.06 ±9.5	122.53 ±12.05	228.66 ±8.02	300.24 ±8.96
_n_-Hexane	138.87 ±8.98	53.85 ±5.63	87.7 ±6.28	295.35 ±19.74
_i_-Hexane	36.22 ±5.66	18.72 ±5.39	50.39 ±9.4	84.59 ±7.11
_n_-Heptane	24.38 ±2.47	12.73 ±1.44	16.45 ±3.31	41.84 ±5.28
Benzene	279.94 ±8.35	68.04 ±2.88	399.86 ±7.69	872.04 ±20.71
Toluene	497.33 ±22.41	114.85 ±11.1	657.38 ±23.93	1337.9 ±52.09
Ethylbenzene	80.38 ±5.82	18.98 ±2.56	119.87 ±6.76	246.93 ±12.52
_m/p_-Xylene	78.13 ±7.85	20.57 ±3.1	161.13 ±11.08	316.45 ±19.02

***o*-Xylene**	23.14 ±2.81	9.46 ±1.85	40.92 ±3.31	85.85 ±5.89
1,2,3-Trimethylbenzene	1.72 ±0.2	1.96 ±0.3	1.51 ±0.01	2.55 ±0.42
1,2,4-Trimethylbenzene	2.85 ±0.43	3.22 ±1.12	3.17 ±0.57	8.28 ±1.31
1,3,5-Trimethylbenzene	1.91 ±0.2	1.81 ±0.22	1.71 ±0.18	1.88 ±0.26

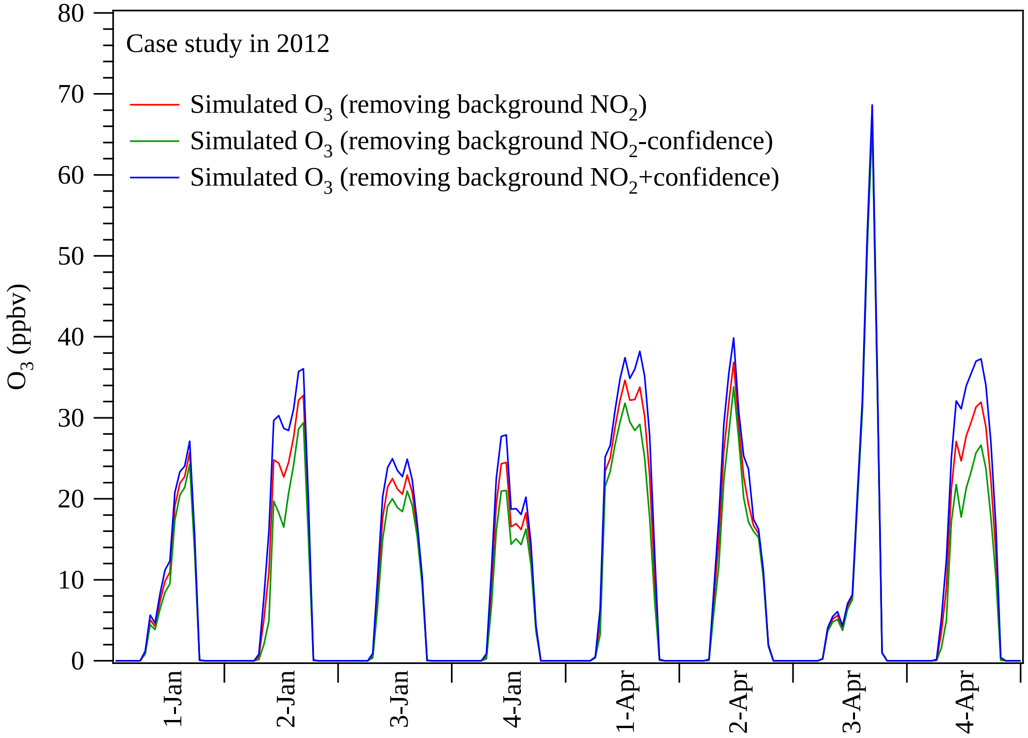

Figure S4. Comparison of locally-produced O_3 (simulated) at TC site in spring and winter with input of varying initial concentrations of NO_2 by subtracting the mean background NO_2 (red line), the mean background NO_2 plus 95% confidence intervals (C.I, blue line), and the mean background NO_2 minus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

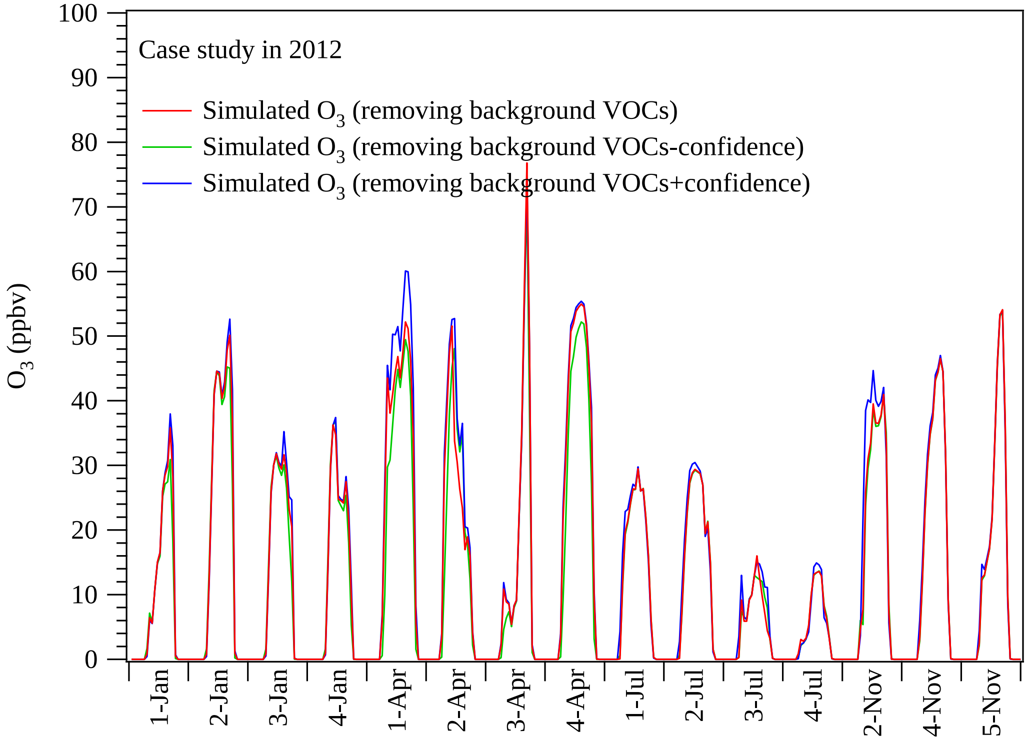

Figure S5. Comparison of locally-produced O_3 (simulated) at TC site over the year with input of varying initial concentrations of VOCs by subtracting the mean background VOCs (red line), the mean background VOCs plus 95% confidence intervals (C.I, blue line), and the mean background VOCs minus 95% C.I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

Comment 1.6

Set the overall air quality picture in HK in perspective - How do the observed precursor trends and ratios (e.g. NO_2/NO_x*) compare to other high population industrial urban areas of the world on a year by year seasonal basis? There is a wide range of comparable data in the literature.*

Response:

Thanks for the nice suggestion. Regional and global comparisons between this study and the literature have been added in a few places to set the overall air quality picture in HK.

Revision in the manuscript:

Page 8, Line 18: "…indicating increasing O_3 pollution in Hong Kong. This finding is consistent with other big cities and regions in the world, such as Beijing (Tang et al., 2009), west plains of Taiwan (Chou, et al., 2006), and Osaka (Itano et al., 2007)."

Page 8, Line 19: "The annual average O_3 concentration in Hong Kong has increased by 0.56 ppbv yr^{-1} in 2004-2015 which is close to that reported for Osaka (0.6 ppbv yr^{-1}) in 1985-2002, and in agreement with Lin et al. (2017) who found the annual mean ozone over Hong Kong increased by about 0.5 ppbv yr^{-1} over 2000-2014. "

*Page 8, Line 23: "The decreasing trends of NOx and CO, also observed in many other high population industrial urban areas (*Geddes *et al., 2009; Tang et al., 2009), suggest effective reduction of local emissions from transportation, power plants and other industrial activities (HKEPD, 2016)"*

*Page8, Line 26: "Unlike O_3 and NO_x, the trend of TVOCs varied across different areas, for example, increasing in Beijing (Tang et al., 2009), decreasing in Toronto (*Geddes *et al., 2009) and Taiwan (Chou et al., 2006), while almost remained unchanged ($p > 0.05$) for Hong Kong (Figure 2)."*

Reference:

Lin, M., W. Horowitz, R. Payton, A.M. Fiore, G. Tonnesen (2017). US surface ozone trends and extremes from 1980 to 2014: Quantifying the roles of rising Asian emissions, domestic controls, wildfires, and climate. Atmos. Chem. Phys., doi:10.5194/acp-17-2943-2017.

Comment 1.7

Difficult to relate specific plots with specific trends discussed in the main text.

Response:

Thanks for pointing out this inconvenience. Efforts have been made to improve the description of each figure caption and cite the plots as many as needed.

Comment 1.8

Confusing in parts and difficult to read/follow.

Response:

Not sure which parts the referee specified. However, the readability of the revised manuscript has been greatly improved with help from English native speakers.

Comment 1.9

Missing reactivity – This study is linked to the measurement of 21 VOC precursors, which may be the main source of ozone in the region in the inventories (show this?). However, how much primary reactivity is potentially missing (e.g. long chain/branched alkanes and alkenes?), on a year by year basis? Some discussion on the missing reactivity and how this may affect the presented results is warranted.

Response:

Thanks for pointing out this important issue. Although much more number of VOC precursors could be quantified in Hong Kong (*i.e.*, over 60+ NMHC species reported in our previous studies), only 21 VOC species (actually 22, please see the Response to Comment 1.2 for reasons) were available for the trend study subject to the capability of the online VOC analyser used at TC site and the completeness of the dataset over the years of interest.

The authors admit that the limited number of VOC precursors would cause missing of reactivity. Luckily, individual VOC species have different photochemical reactivity, and the selected VOCs in this study covered the majority of the total reactivity. Guo et al. (2004) calculated the individual reactivity of VOC species (including 97 hydrocarbons) at two sites in Hong Kong and found that the total reactivity of 21 hydrocarbons (*i.e.*, 1-butene, *i*-butene, isoprene, propene, toluene, *m*-xylene, *p*-xylene, *trans*-2-butene, *n*-butane, *cis*-2-butene, *i*-pentane, *2*-methylpentane, hexane, *i*-butane, propane, *n*-pentane, heptane, ethylbenzene, 3-methylpentane, *o*-xylene, and benzene) contributed over 80% reactivity by OH radicals. Compared to the present study, only 1-butene, *i*-butene and 3-methylpentane from this list were not included, leading to about 27% reactivity missing. In addition, it was found that carbonyls would also contribute to the total photochemical reactivity (Cheng et al., 2010). The lack of carbonyl species may also cause some reactivity missing. This information has been added into the text to state the limitation of this study.

Reference:

Cheng, H., et al. (2010). "On the relationship between ozone and its precursors in the Pearl River Delta: application of an observation-based model (OBM)." Environmental Science and Pollution Research 17(3): 547-560.

Guo, H., et al. (2004). "Characterization of hydrocarbons, halocarbons and carbonyls in the atmosphere of Hong Kong." Chemosphere 57(10): 1363-1372.

Revision in the manuscript:

Page 8, Line 11: "The limited number of VOC precursors would cause missing of reactivity which was estimated < 30% for total hydrocarbons based on our previous study (Guo et al., 2004). The missing reactivity would increase if carbonyls are considered (Cheng et al., 2010)."

Technical comments

Comment 1.10

Fig 1 – "cities" of regions? A more detailed map/maps of the local and regional environs including distance to downtown HK would be useful. What are the prevailing wind directions in each season?

Response:

Sorry for the confusing. Although many cities were labelled on the map (Figure 1), we did not mean that "cities" are "regions". As mentioned in the text, the PRD region consists of nine cities, two of which (*i.e.*, Guangzhou and Shenzhen) have a large population over 10 million. To minimise the confusing, only the two megacities are labelled on the revised map. In addition, a sub-map has been supplied to show more detailed environmental information around Hong Kong.

The prevailing wind directions at the measurement site in each season are summarised in Figure S1. As seen in the graph, east wind is the most prevailing in spring and autumn with southwest winds for summer and northeast for winter. This information has been briefly introduced in the revised manuscript with the reference being cited.

Revision in the manuscript:

Section 2.1: Site description

Page 3, line 14-15: "The sampling site (22.29 °N, 113.94 °E) is located at about 24 km southwest of downtown Hong Kong and about 3 km south of the Hong Kong International Airport (Figure 1)"

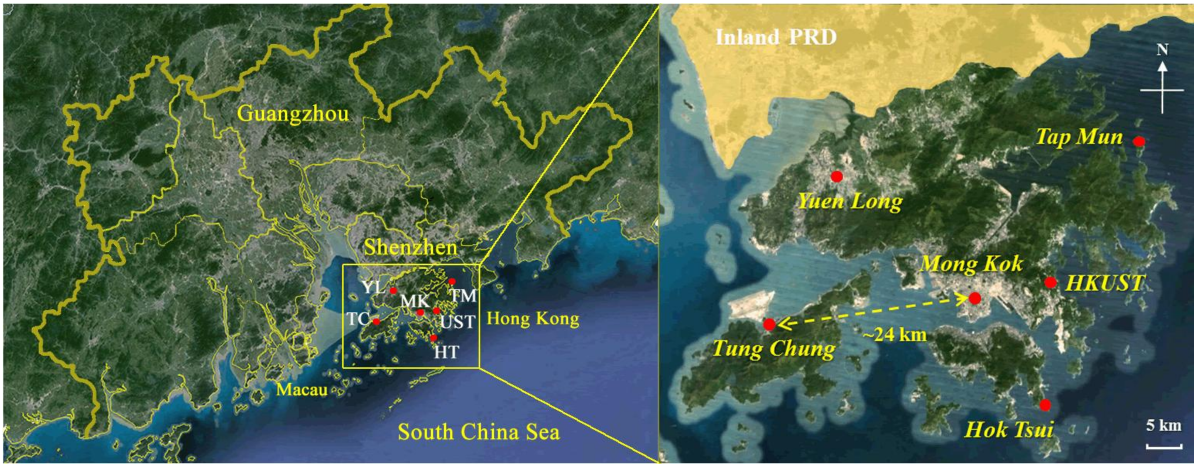

Figure 1. Location of the sampling sites and surrounding environments. Guangzhou and Shenzhen are the two biggest cities in the inland PRD region with a population over 10 million for each city. Hok Tsui (HT) and Tap Mun (TM) are regional background sites. The Hong Kong University of Science and Technology (HKUST) is an Air Quality Research Supersite located in 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.

Supplementary:

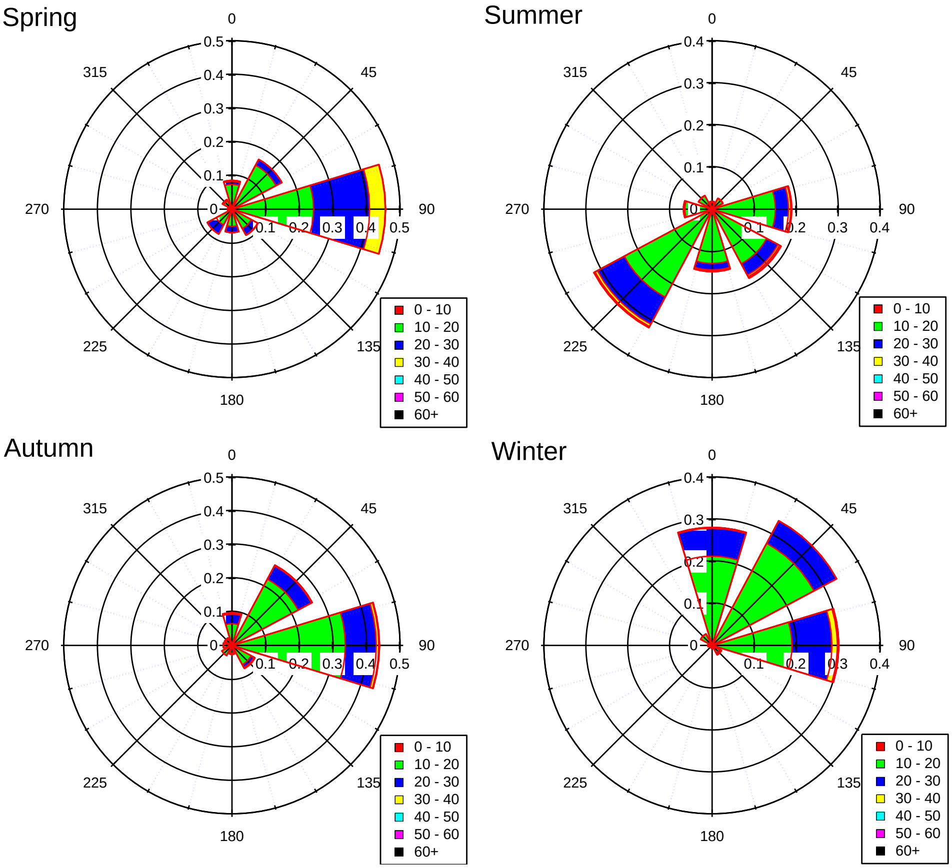

Figure S1. Wind rose plots showing prevailing winds in Hong Kong for each season. The daily data of 2005-2014 is obtained from the Hong Kong airport (https://www.wunderground.com). Colour indicates wind speed (unit: km h^{-1}).

Page 3, Line 17: "At TC, the prevailing wind varies by seasons, with east winds for spring and autumn, southwest winds for summer and northeast for winter (see Figure S1)."

Comment 1.11

Page 5 (modelling) - Reference for TUV photolysis modelling needed – model sensitivity to cloud and haze days? Loss of radicals to aerosol sensitivity studies? MCM is not an "explicit" mechanism. It is described as "semi-explicit" – more complex and complete chemistry than CB05.

Response:

Selected references have been cited in the text to provide the readers more information on the sensitivity of TUV photolysis model to cloud and haze days, as well as radical loss to aerosol studies. With regard to MCM, the description about its mechanism `has been corrected from "explicit" to "near-explicit" as the reviewer suggested.

Revision in the manuscript:

Page 5, Line 13: "… the photolysis rates of different species in the OBM model was determined using the output of the Tropospheric Ultraviolet and Visible Radiation model (TUV v5) (Madronich and Flocke, 1999) based on the actual conditions of Hong Kong, i.e., meteorological parameters, location, and time period of the field campaign."

Page 5, Line 16:" However, it is noteworthy that the atmospheric physical processes (i.e., vertical and horizontal transport), the deposition of species, and the radical loss to aerosol (George et al., 2013; Lakey et al., 2015) were not considered in the OBM model."

Page 5, Line 30: "Since the MCM utilizes the near-explicit mechanism describing the degradation of 143 primary VOCs and contains around 16,500 reactions involving 5,900 chemical species…"

Reference:

George, I. J., et al. (2013). "Measurements of uptake coefficients for heterogeneous loss of HO_2 onto submicron inorganic salt aerosols." Physical Chemistry Chemical Physics 15(31): 12829-12845.

Lakey, P. S. J., et al. (2015). "Measurements of the HO_2 Uptake Coefficients onto Single Component Organic Aerosols." Environ Sci Technol 49(8): 4878-4885.

Madronich S, Flocke S. 1999. The Role of Solar Radiation in Atmospheric Chemistry [M] // Boule P. Handbook of Environmental Chemistry. New York: Springer-Verlag, 1–26.

Comment 1.12

Why was a simple BLH/deposition sensitivity run not performed?- sensitivity?

Response:

Thanks for the nice suggestion. Unfortunately, the module of BLH/deposition is not included in the OBM model used in this study, as mentioned in the original manuscript (Page 5, Line 16). This factor will be incorporated into the model in the future.

Comment 1.13

Did the model runs include a "spin up" time to get the radical intermediates into steady state? i.e. run for 2-4 consecutive days and then taking the data for the last 24 hours? This could significantly affect the model O_3 coming from the model secondary chemistry and the RIR calculations if the intermediates are not in steady state.

Response:

We admit that the addition of a "spin up" time would get the radical intermediates steady quicker and reduce the modelling uncertainty. However, the influence might be limited for modelling the O_3 production. According to a study by Ren *et al*. (2013), running the model for 24 hours would be enough to allow most calculated reactive intermediates to reach steady state.

To further understand such an influence in this study, sensitivity tests have been conducted with a small dataset, which includes randomly selected four days from each season in 2012, with or without a 4-day "spin up" time. As seen in Figure S2, the results demonstrate that the method without the "spin-up" time (red line) 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.

The influence of "spin-up" time on RIR calculations has also been tested using the same small dataset. It shows that our approach (without spin-up time) systematically underestimates the RIR values, but it does not change the results in each season (Figure S3). In addition, it seems that the RIR of TVOCs is more sensitive to this method. This statement has been added into the text.

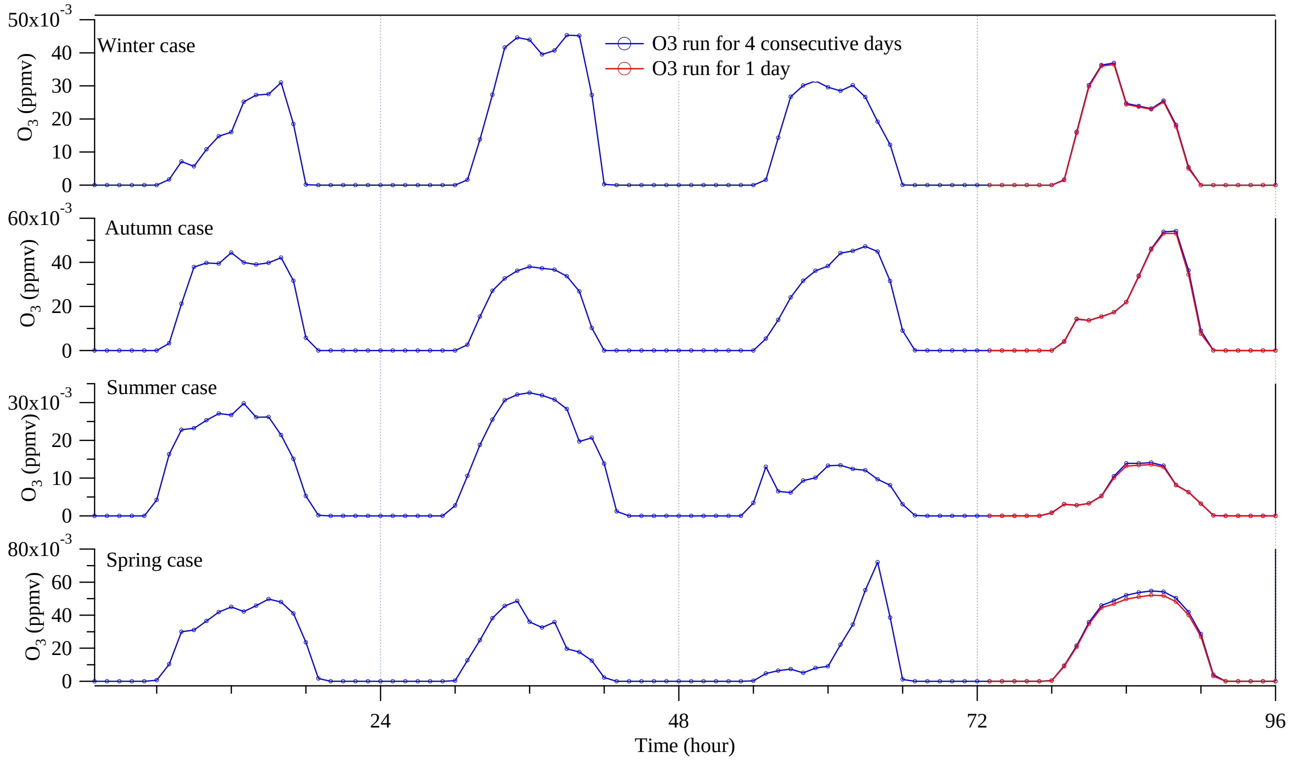

Figure S2. Comparison of O_3 production simulated by with (blue line) or without (red line) a 4-day "spin-up" time in different seasons. In the tests, four days data were randomly selected from each season in 2012 as an example. The results demonstrate that the method without the "spin-up" time indeed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

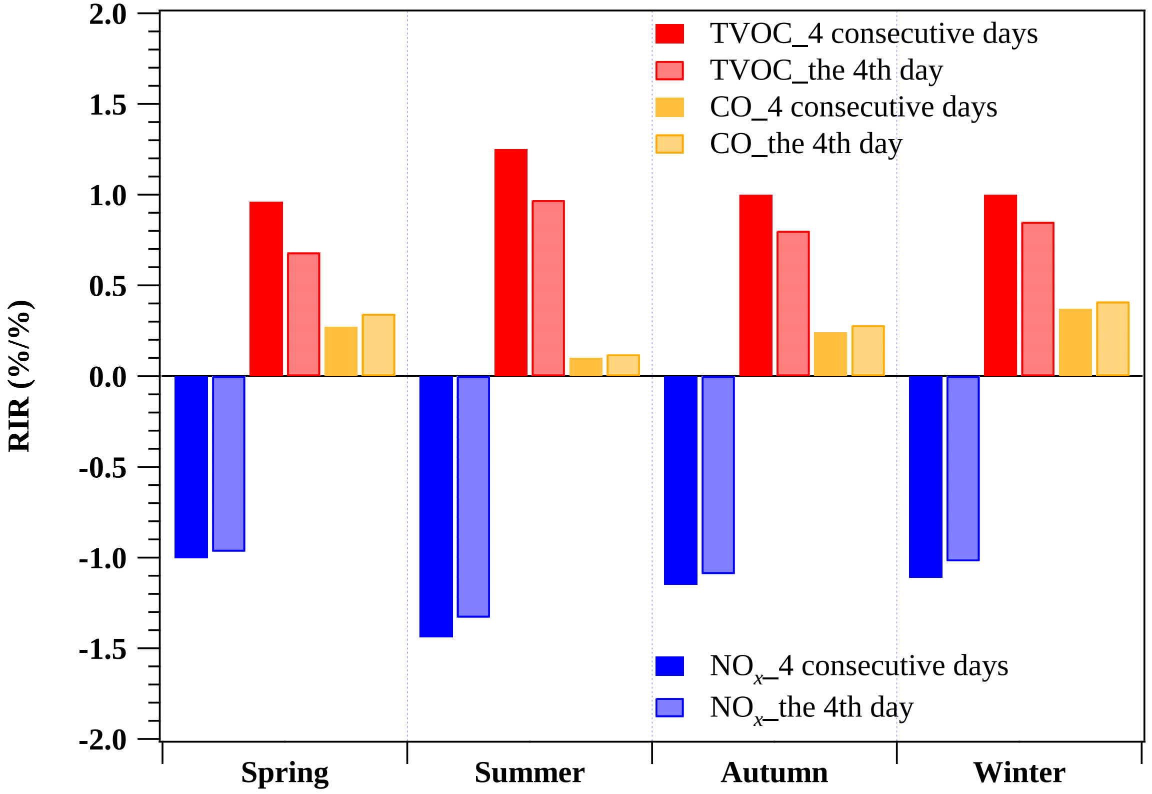

Figure S3. Comparison of RIR calculated by with (solid bar) or without (light bar) a 4-day "spin-up" time in different seasons. In the tests, one-day data was randomly selected from each season in 2012 as an example. It shows that the approach (without spin-up time) systematically underestimates the 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.

Revision in the manuscript:

Page 5, Line 18: "In addition, a "spin-up" time was not applied in the model to get the radical intermediates well steady which might have caused a slight underestimation on the simulated O_3 *production (Figure S2) and its sensitivity to precursors (Figure S3)."*

Reference:

Ren et al., 2013. Atmospheric oxidation chemistry and ozone production: Results from SHARP 2009 in Houston, Texas. Journal of Geophysical Research: Atmospheres 118(11), 5770-5780.

Comment 1.14

The reasoning behind the removal of "background" and "local" concentrations to give an "observed" value are vague and questionable. (1) Their influence will be highly variable with respect to the meteorology and time of the year. (2) What are these concentrations and how were they derived (by wind direction? hourly, monthly, seasonally?). (3) Again, I would like to see the ***seasonal concentrations o****f VOC measurements at other regional and local sites compared and contrasted to the current data set in some detail and (4) how sensitivity to this calculation effects the deconvolution of local photochemical ozone formation. (5) The authors state that the "NO_2 emitted from the inland PRD is slightly more likely (?) to arrive at TC in winter and spring than in summer and fall, the differences in travel time among the seasons are relatively small and it is difficult to be precise with seasonal average estimates of NO2 lifetime and travel time". Therefore, the errors and limitations in understanding the effect of regional/background NO2 on the observed O3 are high here (which the authors acknowledge) – what are the uncertainties associated with this and what is the sensitivity to the model runs?*

Response:

Thanks for the comments. However, we get a bit confused as we did not remove the "background" and "local" concentrations to get an "observed" value. Actually, what we did was to get "pure" local concentrations of precursors by subtracting the "background" concentrations, which were measured at a background site and were assumed being highly influenced by regional transport, from the observations at the receptor site. Then the calculated "local" concentrations were used for simulation of locally-produced O_3. This confusing on the method description has been resolved by changing the wording (see Response to Comment 1.4).

(1) Although the meteorology and time of the year are variable, the influence of background removal approach on the results would be minor for the hourly observation at the regional sites was considered as "regional background" and deducted from the data observed at the receptor site (TC). In other words, the variable meteorological and seasonal factors had already been considered in our method.

(2) As mentioned above, the concentrations obtained by subtracting off the regional background from the observations are the "pure" locally-produced concentrations. They were derived by hourly observations at the regional site and at the receptor site.

(3) The seasonal concentrations of VOC measurements at five different sites (namely HT, TC, YL, MK and HKUST) are summarised in Table S8. It shows that the seasonal variations are quite similar though their levels are different. Please see Response to Comment 1.3 for details.

(4) The authors are a bit confused by this comment, as the deconvolution of local photochemical ozone formation was not discussed in the paper. As mentioned above, the background removal method was applied to get a "pure" locally-produced O_3 which was considered as a part of observed O_3. For the sensitivity of locally-produced O_3 to initial VOC concentrations, please see the Response to Comment 1.5.

(5) As stated in the text, the authors admit that this approach dealing with NO_2 may cause uncertainty on simulation of locally-produced O_3. The sensitivity tests on initial NO_2 levels (see Response to Comment 1.5) also confirm this point. The maximum uncertainties associated with this, for 4 different sites (*i.e.*, HKUST, TC, YL and MK) in Hong Kong, have been assessed by comparing the changes in locally-produced O_3 (simulated) before and after removing the background NO_2 only (scenario 1) or the background TVOCs only (scenario 2) or both background NO_2 and TVOCs (scenario 3). The results for scenarios 1, 2 and 3 are given in Table S5, S6 and S7, respectively. Compared to the removal of VOCs, the removal of NO_2 had a much bigger influence on the simulation of locally-produced O_3. The influence was higher in spring and winter than in summer and autumn, consistent with our assumption based on calculation of precursor's lifetime: stronger regional transport in spring and winter. Therefore, the results support our approach to remove background NO_2 only in spring and winter seasons. In addition, the seasonal variations of the influence are similar across different sites.

Furthermore, we have compared annual trends of local O_3 production simulated with original precursor observations and with background removed precursor concentrations (see Figure S6). A similar trend is observed between with and without removing background values. Therefore, our method does not change the conclusion at least, though it might be associated with some degree of uncertainty.

Revision in the manuscript:

Page 8, Line 4: "In addition, the uncertainties associated with removing the background concentrations are also evaluated, suggesting a similar trend for simulated locally O_3 *production for both approaches (See Figure S6 & Tables S5-S7)."*

Supplementary:

5 **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.

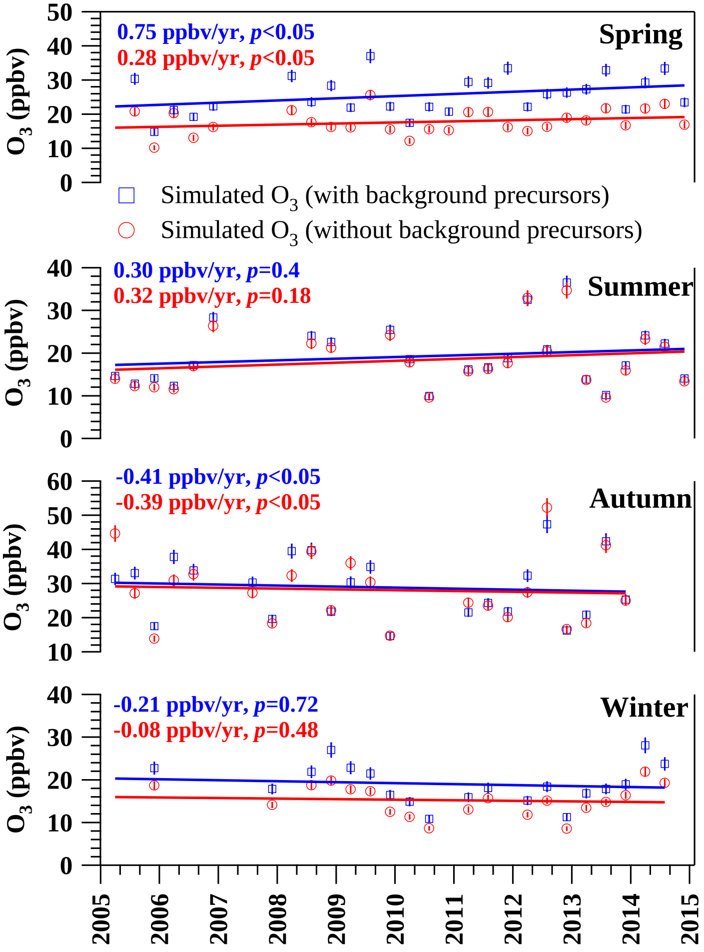

Figure S6. Annual trends of simulated local O_3 production (blue line: with background precursors; red line: without background precursors) in four seasons at TC during 2005–2014. Error bars represent 95% confidence interval of the averages.

Comment 1.15

Eq 7 – delta kro2+no[RO2][NO]?

Response:

Thanks for pointing out this error.

Revision in the manuscript:

Page 7, Line 17: The equation 7 has been revised as follows:

$$G^{S}_{O_3\text{-}NO} = k_{HO_2+NO}[HO_2][NO] + \sum k_{RO_{2i}+NO}[RO_{2i}][NO]$$

Comment 1.16

Fig 3. Not sure how significantly different the inter-annual trends of the TVOC in spring and autumn are?

Response:

As shown in Figure 3, the inter-annual trends of TVOCs in spring and autumn significantly decreased, however it is difficult to quantify how significantly different these trends were in the two seasons. What we can only conclude is that the TVOCs in autumn decreased slightly quicker than those in spring as the decreasing rates were -0.32 and -0.26, respectively. In addition, the inter-annual trends of the TVOC reactivity in spring showed no significant change, while the trends in autumn decreased significantly (see Figure S16), indicating some sort of difference in VOC concentration and composition in the two seasons. Please refer to line 23, page 12 for details.

Comment 1.17

Fig 4. Why are the locally produced simulated and filtered trends so different in most seasons?

Response:

The two types of locally-produced O_3 were obtained by two different approaches, that is, photochemical simulation with “pure” local precursors and simple filtering by wind speed. So it is not surprising to see a difference between the trends of the simulated and filtered data, though theoretically higher percentage of locally-produced O_3 observed at lower wind speed. On the other hand, both results were at a similar level, indicating that they were comparable.

Comment 1.18

Page 10 – “The different inter-annual trends of NO_x and TVOCs in spring/autumn from those in summer/winter were probably because marine air significantly diluted air pollution in summer while continental air masses remarkably burdened *air pollution in winter, which concealed the decreased local emissions of NO_x and TVOCs in summer and winter (Wang et al., 2009)" – do you have winder sector data to show evidence for this?*

Response:

Wind rose plots for each season have been given in Figure S1 which shows more southwest winds (*i.e.*, marine air) in summer and more northeast winds (*i.e.*, continental air) in winter. Please refer to the Response to Comment 1.10 for more information.

Comment 1.19

Define and show NO titration reaction as a separate Equation.

Response:

This comment has been well accepted.

Revision in the manuscript:

Page 10, Line 27: The following reactions related to NO titration have been added in the text.

$NO_2 + hv \rightarrow NO + O$ (R1)

$O + O_2 + M \rightarrow O_3 + M$ (R2)

$NO + O_3 \rightarrow NO_2 + O_2$ (R3)

Page 10, Line 21: "Here the NO titration refers to the ‘‘titration reaction’’ between NO and O_3. Although $NO–NO_2–O_3$ reaction cycling (including the effects of NO titration, see reactions R1-R3) can be theoretically regarded as a null cycle and provides rapid cycling between NO and NO_2, the NO titration effect can retard the accumulation of O_3 in an urban environment by means of substantial NO emissions (Chou et al., 2006)."

Comment 1.20

Further investigation found that temperature and solar radiation in summer indeed increased in these years ($p<0.05$)" Show this data.

Response:

This data was included in the original supplementary. Please refer to Figure S9 for details.

Revision in the manuscript:

Page 10, Line 27: "Further investigation found that temperature and solar radiation in summer indeed increased ($p<0.05$) in these years (see Figure S9), whereas they had no significant change in other seasons (the reasons remained unclear),…"

Comment 1.21

Page 11 – Section 3.2 repeats itself somewhat

Response:

This comment has been well accepted, and the first sentence has been revised to minimise the confusing.

Revision in the manuscript:

Page 12, Line 2: "In this study, the OBM (CB05) model was used to simulate the long-term trends of O_3 produced by in-situ photochemical reactions (hereinafter locally-produced O_3 (simulated))."

Comment 1.22

Page 12 – the MCM is not "explicit". Should also be ($p<0.05$)?

Response:

Thanks for the suggestion. In the text (page 5, line 31), "explicit" has been replaced by "near-explicit" to describe the mechanism applied in MCM.

For the *p*-value, though the MCM considers much more detailed chemical reactions than CB05, the simulated temporal patterns of O_3 were similar, which should be. So we do not think that "$p>0.05$" in the sentence, "*because the simulated results of both CB05 and MCM models followed similar temporal patterns ($p>0.05$)*", should be changed to "$p<0.05$".

Comment 1.23

"locally-produced O_3 (filtered) values clearly showed similar trends to locally-produced O_3 (simulated) in spring, autumn and winter (p=0.07, 0.09 and 0.93, respectively)" - where is the plot showing these trends?

Response:

Sorry for this confusing. Please refer to Figure 4 for these trends. In addition, we have realised that these *p*-values were used inappropriately. They only suggest the average levels of the type of data in these seasons were similar. This error has been fixed in the revised manuscript.

Revision in the manuscript:

Page 12, Line 27: "locally-produced O_3 (filtered) values clearly showed similar trends to locally-produced O_3 (simulated) in spring, autumn and winter (see Figure 4)"

Comment 1.24

"Unlike in spring, though the observed and locally-produced O3 (filtered) displayed increasing trends in summer (0.70±0.34 ppbv/yr and 0.66±0.41 ppbv/yr, respectively; p<0.05)," – these trends are not the same as shown in Fig 4?

Response:

Sorry for this error. Only the values in Figure 4 are correct. This inconsistence problem has been resolved.

Revision in the manuscript:

Page 13, Line 4: "Unlike in spring, though the observed and locally-produced O_3 (filtered) displayed increasing trends in summer (0.67±0.34 ppbv/yr and 0.61±0.41 ppbv/yr, respectively; p<0.05)…"

Comment 1.25

Page 13 – "the total solar radiation (0.24±0.16 MJ·m-2yr-1, p<0.01) and temperature (0.095±0.034 oC/yr, p<0.05) in summer significantly increased during the past 10 years" – odd units! Solar radiation should be given as irradiance in W m-2. Temperature in K. Be consistent as to how you write units – K/y or K y-1. Why has the solar radiation increased in the summer over 10 years? Less haze?

Response:

Thanks for pointing out these issues. The unit of temperature has been changed to "K". However, MJ·m^{-2} is a unit for the integration of solar radiation in a certain amount of time. This unit has been widely used in literature to show a general level of solar radiation. More important, the only solar radiation data available in this study are recorded in this unit and we have no way to convert them back to data with a unit of "W m^{-2}".

The statement on the increase of solar radiation in summer along the 10 years was based on measurements from Hong Kong Observation, but frankly speaking, the reasons remain unknown. It might be due to less haze as the air quality has been getting better in Hong Kong and the PRD. To make this point clear, the text has been improved accordingly.

Revision in the manuscript:

Page 13, Line 8: "Indeed, the total solar radiation (0.24±0.16 MJ m^{-2} yr^{-1}, $p<0.01$) and temperature (0.095±0.034 K yr^{-1}, $p<0.05$) in summer significantly increased during the past 10 years (see Figure S9), subsequently resulting in the enhanced in-situ photochemical reactivity of VOCs, although their quantitative contributions remain unknown and require further investigation. The increase of solar radiation might be due to the decreasing haze as the air quality has been getting better in Hong Kong and the PRD (Louie et al., 2013)."

Reference:

Louie, P. K. K., et al. (2013). "A Special Issue of Atmospheric Environment on "Improving Regional Air Quality over the Pearl River Delta and Hong Kong: From Science to Policy" Preface." Atmospheric Environment 76: 1-2.

Comment 1.26

Fig 9. Why is the data not presented as monthly averages or even by season – which would be clearer and possibly give more information?

Response:

Thanks for this suggestion. Figure 9 has been redrawn to make it clearer and more informative. The values have also been updated accordingly.

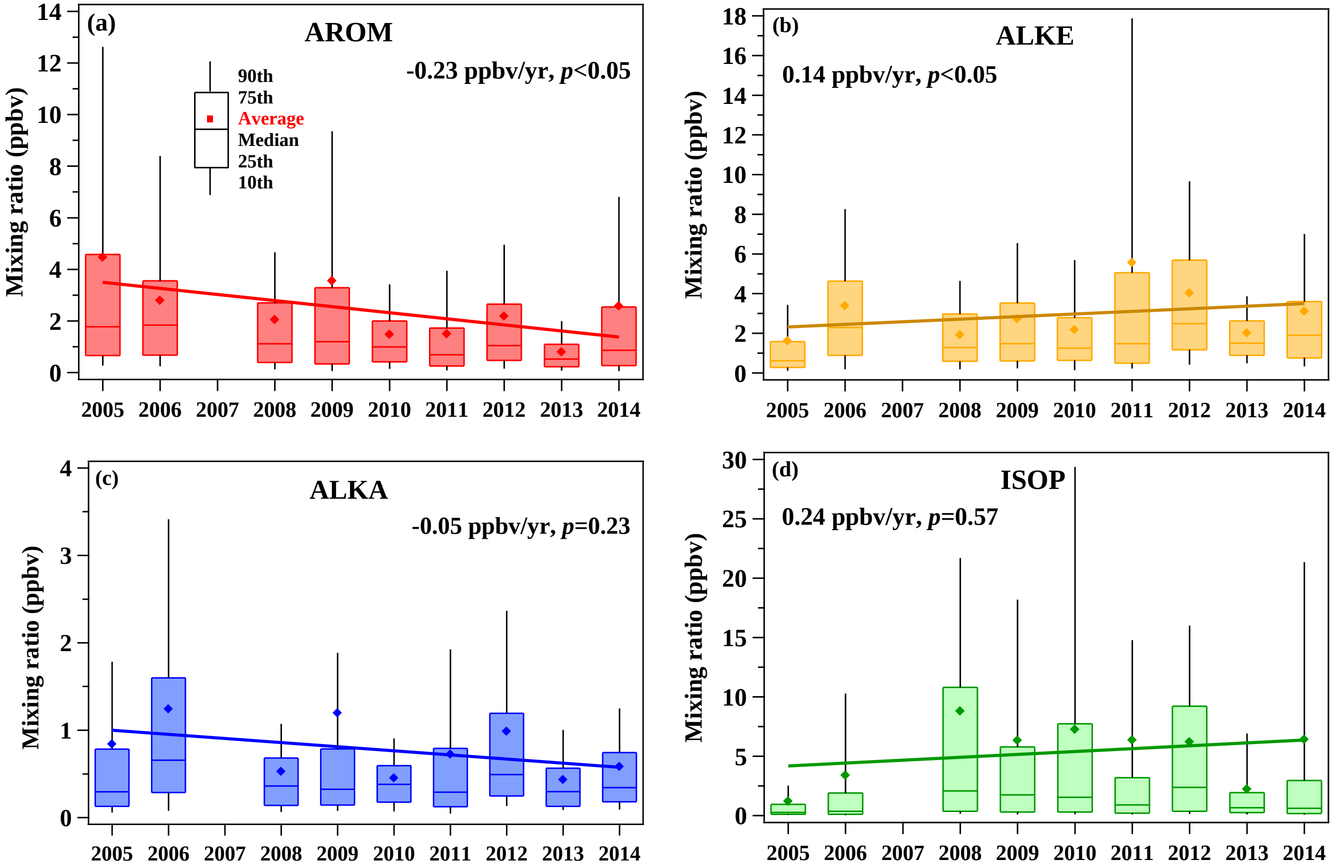

Figure 9. Trends of the daytime averaged contribution of four VOC groups to O_3 mixing ratio: (a) AVOC (Aromatics), (b) AVOC (Alkenes), (c) AVOC (Alkanes) and (d) BVOC at TC during 2005–2014.

Revision in the manuscript:

Page 21, Line 34: "Unlike AVOC (Aromatics/Alkanes), the contribution of AVOC (Alkanes) to O_3 formation during 2005-2014 showed no significant change (p=0.23), …"

Page 22, Line 4: "Furthermore, BVOC showed no evident change in the contribution to O_3 mixing ratios during the last decade (p=0.57), …"

Comment 1.27

Page 20 (contribution of VOC groups) – I would have liked to see the year by year seasonal trends of the individual TVOC groups plotted – i.e. aromatics, alkanes, alkenes and BVOC. This would give a more comprehensive overview of the TVOC trend and how it evolved/is evolving.

Response:

Thanks for the suggestion. A new graph has been supplied in the supplementary to show the year by year seasonal trends of the individual VOC groups (Figure S18). Text has been added to describe the new plot accordingly.

Revision in the manuscript:

Page 8, Line 29: "Moreover, the long-term trends of individual VOCs, except for BVOC, were different from that of TVOCs (see Figure S18) because many control measures were taken in the last decade, which altered the composition of VOCs in the atmosphere, such as the reduction of toluene by solvent usage control and the increase of alkanes in Liquefied Petroleum Gas (LPG) in 2005-2013 (Ou et al., 2015) and the decrease of LPG-alkanes in 2013-2014 (Lyu et al., 2016)."

Supplementary:

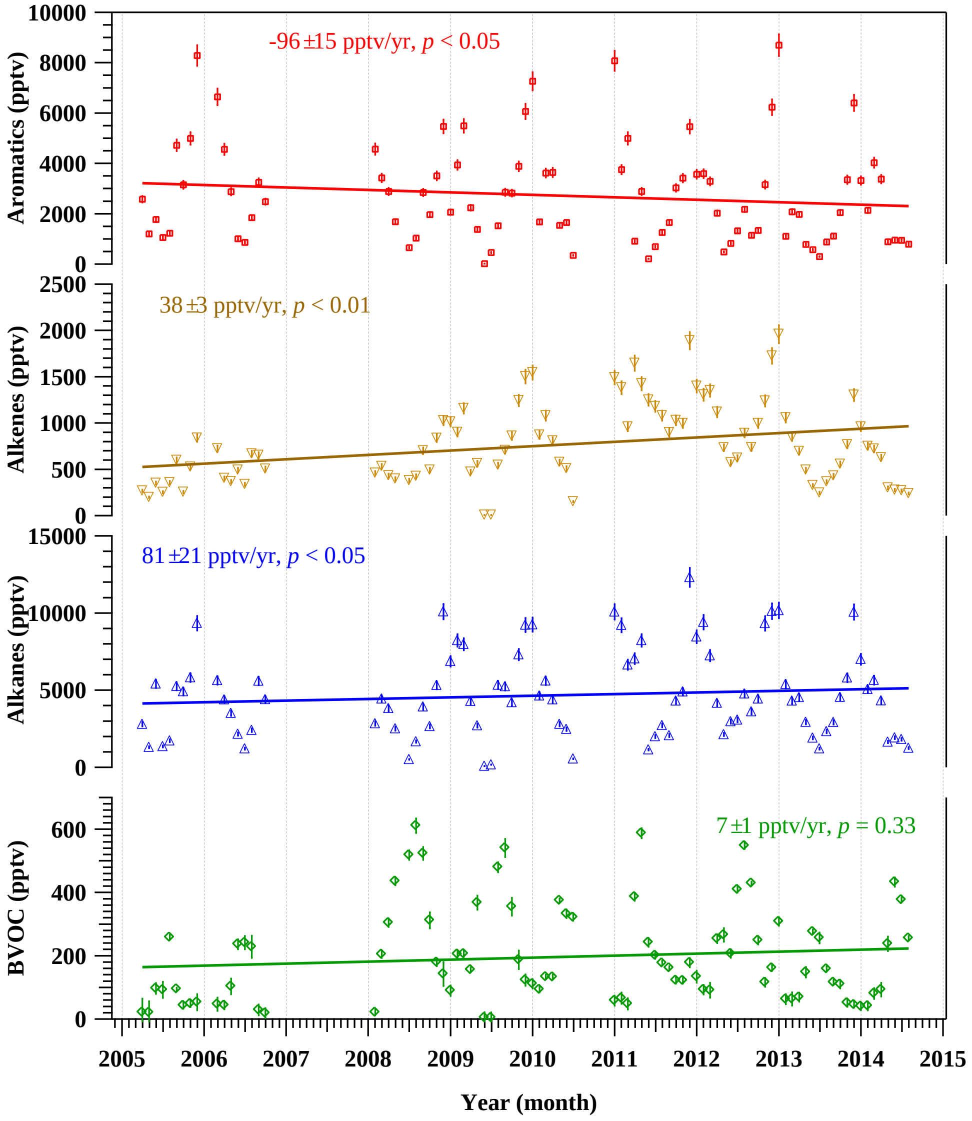

Figure S18. Trends of monthly average of individual VOC groups (*i.e.*, aromatics, alkenes, alkanes and BVOCs) at TC during 2005-2014.

Comment 1.28

5 *Page 21. Basic detail of the HK government emissions reduction plan need to be outlined (with the reference website placed in the References section).*

Response:

Thanks for this suggestion. Actually, there were a few places already describing the HK government emissions reduction plan in the original manuscript. For example,

"In fact, the Hong Kong Government has implemented a series of VOC-control measures since 2007 (HKEPD, 2016). From April 2007, the Air Pollution Control (VOCs) Regulation was implemented to control VOC emissions from regulated products, including architectural paints/coatings, printing inks and six selected categories of consumer products. In January 2010, the regulation was extended to control other high VOC-containing products, namely vehicle refinishing paints/coatings, vessel and pleasure craft paints/coatings, adhesives and sealants." (Page 21, Line 14-18), and

"During 2005-2014, the Hong Kong government launched a series of measures to reduce vehicular emissions, including diesel, LPG and gasoline vehicles (http://www.epd.gov.hk/epd/english/environmentinhk/air/prob_solutions/air_problems.html)." (Page 21, Line 25-26).

To provide more background information to readers, a reference has been added in the revised manuscript.

Revision in the manuscript:

Page 21, Line 14: "In fact, the Hong Kong Government has implemented a series of VOC-control measures since 2007 (HKEPD, 2016)."

Reference:

HKEPD (Hong Kong Environmental Protection Department): 2014 Hong Kong Emission Inventory Report, available at: http://www.epd.gov.hk/epd/sites/default/files/epd/2014Summary_of_Updates_eng_2.pdf, (available on 2017-06-15).

Comment 1.29

"photolysis rates of alkanes" – I am sure alkanes do not photolyse in the atmosphere!

Response:

Sorry for the confusing. What we attempted to say is the reaction rate of alkanes with OH radicals.

Revision in the manuscript:

Page 22, Line 2: "In addition, the seasonal variation of O_3 formation, of which the reaction rates of alkanes with OH radicals were high in summer and low in winter, would also blur the trend".

Responses to Referee 2's comments

General comment

The authors report an analysis of time series for O3, NOx, TVOCs and CO for Hong Kong for the years 2005-2014. Based on a seasonal analysis of observed and modelled data using an observation-based box model coupled with CB05 mechanism the authors find different trends of these pollutants for each season. Overall, they state that locally produced O3 increased in spring and decreased in autumn over the years. The authors suggest that different decreasing rates in O3 precursors NOx and TVOC as well as changes in VOC composition and/or VOC reactivity (mainly caused by decrease of aromatic compounds) might have led to these O3 trends. For the autumn season the authors state that regional O3 might have been a dominant factor in the O3 trend. An analysis of incremental reactivity showed decreasing contribution from aromatic compounds, while the contribution from alkenes appeared to increase over the years. This might have been due to changing VOC source contributions (less solvents, more traffic emissions). Overall, this paper shows some valuable material and associated discussion. However, there are some important issues which need to be addressed before this paper can be accepted.

We highly appreciate the reviewer for the positive comments and constructive suggestions. In general, all these comments have been addressed properly with addition of great details of the methods and in-depth discussion in the revised manuscript. Also, many sentences have been reorganised to clear confusing and improve readability. In the following section, the author's responses (in blue) are immediately after the reviewer's comments (in black), with the changes in manuscript at the end (in italic).

Major issues:

Comment 2.1

In most figures intra- and inter-annual variations are significantly larger than the 2005-2014 trend. For instance, the O3 trend shows the highest increase from 2005-2014 (0.67 ppb/yr) in autumn (Fig. 3). However, this trend is only determined by 3 "outlier" months of the years 2012, 2013, 2014. These 3 months are just 10% of this specific data set. Another example is

Fig. 5 which shows very large scatter in O3 data for the autumn season. Also, for instance Fig. S10 about the annual trends of VOC/NOx ratios is largely determined by the last two years. The question is: how robust are all the trends shown in this paper?

Response:

Thanks for raising this issue. We agree that the validity of the results is very important for a study. For a trend study using statistical techniques, however, it is not surprising to have a larger variation than the trend. In general, the robustness of the trends can be judged by the *p*-value for the regression model. A *p*-value less than 0.05 was considered as acceptable in this study.

The outliers are another issue. What we want to argue here is whether they are real outliers or not. For example, the three extremely high monthly averages of O_3 in autumn (see Figure 3), in the point of our view, might be not outliers, because each of them represents one month of data with relative small uncertainty. In other words, each point represents many valid observations during that period. We cannot simply consider them as outliers and exclude them from the dataset. To further clarify this point, monthly averages of O_3 observations over 2005-2014, as well as the ratios of TVOCs to NOx, are shown in Figure S10 and Figure S17, respectively.

The Figures have been added into the Supplementary and noted in the main text.

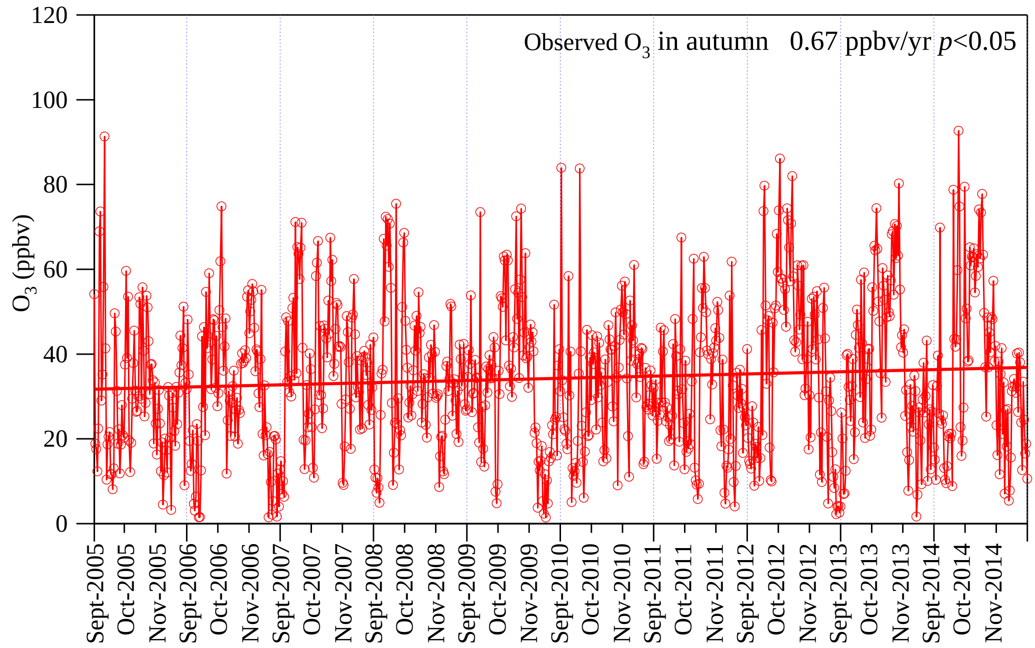

Figure S10. Monthly trend of observed O_3 at TC in 2005-2014

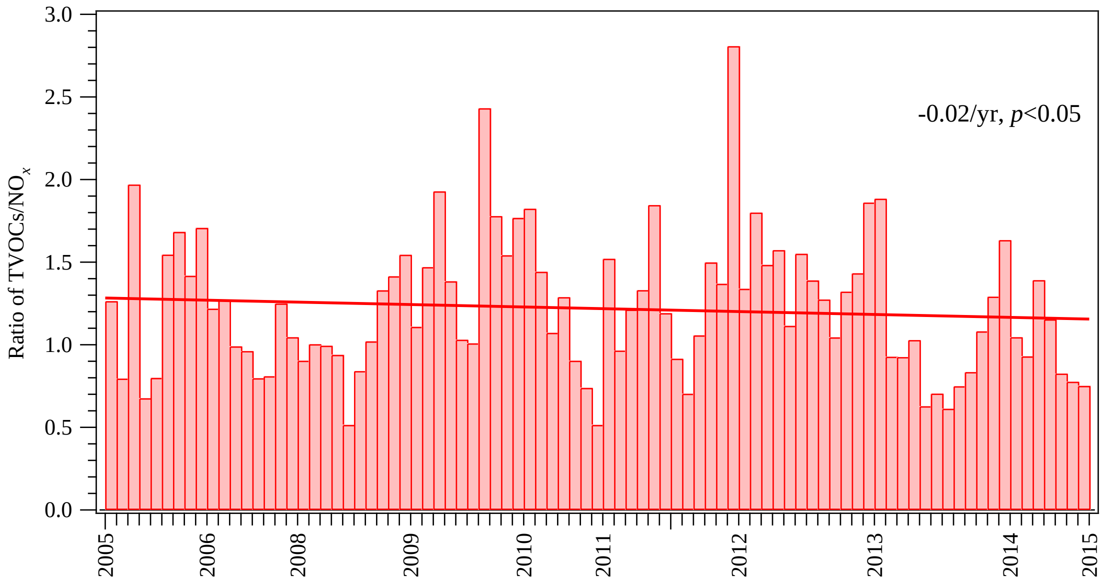

Figure S17. Monthly trend of VOCs/NOx ratio at TC in 2005-2014

Revision in the manuscript:

Page 11: Caption for Figure 3

"In the sub-plot for O_3 trend in autumn, the three extremely high values are not considered as outliers as each of them represents one month of data with relatively small uncertainty (see Figure S10)."

Page 20, Line 2:

"Furthermore, the monthly variation of VOC/NO_x ratios showed a significant decreasing trend at a rate of -0.02 yr-1 ($p<0.05$) (see Figure S17), indicating that VOC reduction became more effective in reducing O_3 in the past 10 years, which is consistent with the conclusions from the above modeling results."

Comment 2.2

According to HKEPD (2015) long-term trends for O3, NOx, and CO may have been different within the Hong Kong area and not necessarily the same as at the TC site. For O3, annual values at the rural site were highest, but did not change that much over the years, while urban and New Town sites show some increase at overall lower levels than at the rural site. Apart from that NOx values did not change that much for New Town sites, while urban sites indeed showed some slight decrease. For CO there were actually some increases at urban sites over the last years in contrast to New Town sites. The question is: how representative is the TC site for a trend analysis for Hong Kong?

Response:

The authors admit that spatial variations in the levels of O_3 and precursors may be significant across Hong Kong, and that the trends observed at TC might be different with other locations in the city. However, TC site was the best choice for us to select for analysing the trend of O_3 and precursors in Hong Kong. The reasons are as follows:

(1) TC is characterized as a polluted receptor site as it receives urban plumes from Hong Kong and inland PRD region under prevailing north-easterly winds in autumn when most heavy O_3 pollution often occurs in the region. Therefore, the trend of pollutant levels at TC site can generally represent the overall trend of pollutants in Hong Kong with regional impact.

(2) TC site is located in the area of Hong Kong that experiences the most serious O_3 pollution (Zhang et al. 2007; Xue et al., 2014). So understanding the trend of O_3 and precursors at this site will provide critical information to the government for initiation of effective emission reduction plans in future, and

(3) The measurements taken at TC site comprised the most comprehensive source of data, including long-term observations of hydrocarbons, which is very important for a high-quality trend study.

The aforementioned reasons for site selection have been added into the section of site description (section 2.1).

Reference:

Xue et al., Increasing external effects negate local efforts to control ozone air pollution: a case study of Hong Kong and implications for other Chinese cities, Environ. Sci. Technol., 48, 10769-10775, 2014.

Zhang et al., Ozone production and hydrocarbon reactivity in Hong Kong, Southern China, Atmos. Chem. Phys., 7, 557-573, 2007.

Revision in the manuscript:

Page 3, Line 19: "The selection of this site for the trend study was due to its downwind location being a good receptor for urbane plume, suffering from high O_3 pollution and having the most comprehensive dataset."

Comment 2.3

I think the most interesting results are shown in Figs 6 and 7. Fig 6 shows that O_x has remained unchanged over the last years. This is basically in line with the trends shown in HKEPD (2015), i.e. some slight decrease of NO_2 compensated by some slight increase of O_3. Actually, the authors' statement on page 16 L6-18 could be a valid reason for changes in ambient O_3 as it has been shown that NO_2/NO_x ratios may have increased due to a changing traffic fleet (e.g. Carslaw, 2005; Rappengluck et al., 2013). I recommend that the authors elaborate on this, as it may be the larger fraction of directly emitted NO_2 which may cause an increase in O_3, even at overall decreasing NO_x mixing ratios. I was wondering, whether Fig 7 shows day- and night-time data? An enhanced traffic related NO_2/NO_x ratio would be better discernable at night excluding secondarily produced NO_2 at daytime.

Response:

Thanks for the nice suggestion. Figure 7a and 7b present the NO_2/NO_x ratios in day-time and night-time, respectively. They demonstrate that the NO_2/NO_x ratio increases in both time periods, with higher values and increasing rates during night-time.

The results suggest that the increase in O_3 was at least partially due to the larger fraction of directly emitted NO_2. This statement has been added in the main text.

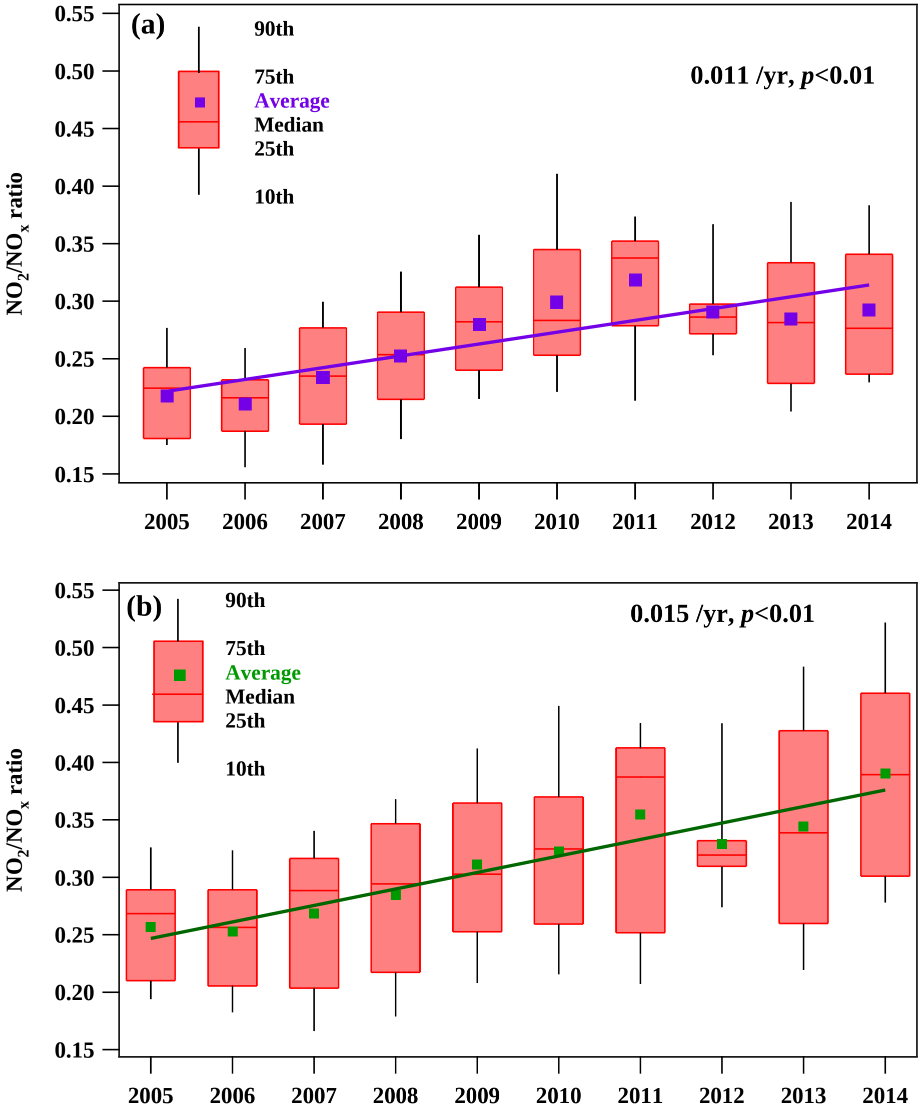

Figure 7. Annual trend of monthly averaged NO_2/NO_x ratios at MK site in daytime **(a)** and night-time **(b)** in Hong Kong in 2005–2014. Hourly observations of NO_2 and NO_x are obtained at MK from the HKEPD (http://epic.epd.gov.hk/ca/uid/airdata). Note that data of October in 2014 are excluded due to the impact of Occupy Central event in Hong Kong.

Revision in the manuscript:

Page 16, Line 15: "Indeed, the NO_2/NO_x ratio at Mong Kok significantly increased, with an enhanced traffic related NO_2/NO_x ratios observed at night, from 2005 to 2014 ($p<0.01$), leading to increased local O_3 levels (Figure 7)"

Comment 2.4

Fig. 3 shows some interesting feature. Not only all O_3 precursor values are lowest in summer, but also O_3 values in summer are lower than in spring and lower than in autumn. They are just slightly higher than in winter. This is a bit astonishing as one would expect highest O3 values in summer. I was wondering whether the authors can shed some light on this and explain the specific summertime conditions.

Response:

Although the solar radiation in summer is generally higher, it is not uncommon to see low O_3 levels in summer in a coastal region, like Hong Kong, where the east Asian monsoon brings in clean ocean air masses with less O_3 precursors to this area in this season, just like what we described in the original manuscript (Page 10, Lines 6-8):

"*Generally, all precursors showed low values in summer and high levels in winter, mainly due to typical Asian monsoon circulations, which brought in clean marine air in summer and delivered pollutant-laden air from mainland China in winter (Wang et al., 2009).*"

In addition, the high frequency of rainy days in summer was also not in favour of O_3 formation. This point has been added in the revised text.

Revision in the manuscript:

Page 10, Line 9: "With lower (diluted) precursor concentrations, together with high frequency of rainy days, it is not uncommon for Hong Kong to see lowest O_3 values in summertime (see Figure 3)."

Other comments:

Comment 2.5

Page 4 L5-8: The reference HKEPD (2015) lists various instruments being used in the Hong Kong network. What instruments were actually installed at TC, what were their detection limits, what their resolutions? Was NO_2 measured directly?

Response:

The instruments installed at TC site, as well as the detailed description (*i.e.*, detection limit and resolution), have been amended in the method section. In addition, NO_2 and NO_x were directly measured by the instrument, while NO was obtained by the difference of NO_x and NO_2.

Revision in the manuscript:

Page 4, Line 6:

"2.2 Measurement techniques

Hourly observations of O_3, CO, SO_2, NO-NO_2-NO_x and meteorological parameters at TC from 2005 to 2014 were obtained from the HKEPD (http://epic.epd.gov.hk/ca/uid/airdata). Briefly, O_3 was measured using a commercial UV photometric instrument (Advanced Pollution Instrumentation (API), Model 400A) with a detection limit of 0.6 ppbv. CO was measured with a gas filter correlation CO analyser (Thermo ElectronCorp. (TECO), Model 48C) with a detection limit of 0.04 ppm. SO_2 was measured using a pulsed fluorescence analyser (TECO, Model 43A) with a detection limit of 1.0 ppbv. NO-NO_2-NO_x were detected using a commercial chemiluminescence with an internal molybdenum converter (API, Model 200A) and a detection limit of 0.4 ppbv. All the time resolutions for these gas analysers were 1 hour. To ensure a high degree of accuracy and precision, the QA/QC procedures for gaseous pollutants were identical to those in the US air quality monitoring program (http://epic.epd.gov.hk/ca/uid/airdata). The accuracy of the monitoring network was assessed by performance audits, while the precision, a measure of the repeatability, of the measurements was checked in accordance with HKEPD's quality manuals. For the gaseous pollutants, the accuracy and precision within the limits of ±15 and ±20 % were adopted, respectively (HKEPD 2015).

Real-time VOC data at TC were also measured by the HKEPD. An online GC-FID analyser (Synspec GC 955, Series 600/800) was used to collect VOC speciation data continuously with a time resolution of 30 minutes. The VOC analyser *consists of two separate systems for detection of C_2–C_5 and C_6–C_{10} hydrocarbons, respectively. Detailed description about the real-time VOC analyser can be found in Lyu et al. (2016). Twenty-eight C_3-C_{10} VOC species were identified and quantified using this method. In terms of the QA/QC for VOC analysis, built-in computerized programs of quality control systems such as auto-linearization and auto-calibration were used. Weekly calibrations were conducted by using NPL standard gas (National Physical Laboratory, Teddington, Middlesex, UK). In general, the detection limits of the target VOCs ranged from 2 to 56 pptv. The accuracy of each species measured by online GC-FID was determined by the percentage difference between measured mixing ratio and actual mixing ratio based on weekly span checks and monthly calibrations. The precision was based on the 95% probability limits for the integrated precision check results. The accuracy of the measurements was about 1-7%, depending on the species, and the measurement precision was about 1-10% (Table S1). In addition, the quality of the real-time data was assured by regular comparison with whole-air canister samples collected and analysed by University of California at Irvine (UCI). More details can be found from previous studies in Hong Kong (Xue et al., 2014; Ou et al., 2015; Lyu et al., 2016).*

For data analysis, linear regression and error bars represented as 95% confidence intervals were used. Trends of O_3 and its precursors with a p value < 0.05 were considered significant (Guo et al., 2009).”

Comment 2.6

Page 4 L9: I am surprised to see that only 21 VOCs were identified and quantified at TC given the fact that it is an urban site. Looking into the CO data, which varies between 400 ppb and more than 1 ppm as monthly means (Fig 2), I would expect significantly higher number of VOCs. I doubt the authors can consider the sum of the quantified VOCs as the total VOCs (TVOCs). What do the authors estimate is the fraction of the quantified VOCs on the entire mass of VOCs in ambient air at TC?

Response:

The main reason why only 21 (actually 22 in the revised manuscript) species were included in the present study is because of high percentage of missing data for several species at TC site over 2005-2014. As this study looks into the trend of O_3, those species with high missing data were excluded to eliminate the influence caused by different input of VOC species.

The authors admit that the limited number of VOC precursors would cause missing of reactivity. Luckily, individual VOC species have different photochemical reactivity, and the selected VOCs in this study covered the majority of the total reactivity. Guo et al. (2004) calculated the individual reactivity of VOC species (including 97 hydrocarbons) at two sites in Hong Kong and found that the total reactivity of 21 hydrocarbons (*i.e.*, 1-butene, *i*-butene, isoprene, propene, toluene, *m*-xylene, *p*-xylene, *trans*-2-butene, *n*-butane, *cis*-2-butene, *i*-pentane, *2*-methylpentane, hexane, *i*-butane, propane, *n*-pentane, heptane, ethylbenzene, 3-methylpentane, *o*-xylene, and benzene) contributed over 80% reactivity by OH radicals. Compared to the present study, only 1-butene, *i*-butene and 3-methylpentane from this list were not included, leading to about 27% reactivity missing. In addition, it was found that carbonyls would also contribute to the total photochemical reactivity (Cheng et al., 2010). The lack of carbonyl species may also cause some reactivity missing. This information has been added into the text to state the limitation of this study.

In addition, *m*-xylene listed in Tables S1 and S2 actually represents *m/p*-xylene (*i.e.*, *m*-xylene and *p*-xylene) as the VOC analysis method used in this study could not divide the two species apart. To reflect this fact, the number of VOC species adopted in the study has been corrected from 21 to 22. It is noteworthy that this change would not affect our results and conclusion, because the three xylene isomers have the same CB05 model specie (*i.e.*, XYL, see Table S2).

Revision in the manuscript:

Page 8, Line 10: "The TVOCs were defined as the sum of the 22 VOC species listed in Text S1. Note that not all detected VOCs were included in this study because of high rates of missing data."

Page 8, Line 11: "The limited number of VOC precursors would cause missing of reactivity which was estimated < 30% for total hydrocarbons based on our previous study (Guo et al., 2004). The missing reactivity would increase if carbonyls are considered (Cheng et al., 2010)."

Text S1 & Table S1 & Table S2 & Table S4 & Table S10: p-xylene has been added.

Reference:

Cheng, H., et al. (2010). "On the relationship between ozone and its precursors in the Pearl River Delta: application of an observation-based model (OBM)." Environmental Science and Pollution Research 17(3): 547-560.

Guo, H., et al. (2004). "Characterization of hydrocarbons, halocarbons and carbonyls in the atmosphere of Hong Kong." Chemosphere 57(10): 1363-1372.

Comment 2.7

Page 4 L13-14: How was the accuracy of 1-7% determined?

Response:

The accuracy of each species measured by online GC-FID was determined by the percentage difference between measured mixing ratio and actual mixing ratio based on weekly span checks and monthly calibrations. For more details on the method description, please refer to the Response to Comment 2.5 above.

Comment 2.8

Page 5 L25-29: The authors only measured 21 VOCs. What assumptions did the authors have on other VOCs not measured, but needed as an input for MCM?

Response:

It was assumed that the measured VOCs contributed a dominant fraction to O_3 production, and that the initial concentrations of those VOCs not measured but needed by MCM were zero. We admit that the use of a limited number of VOCs would cause photochemical reactivity missing. Please refer to Response to Comment 2.6 above for more details on this issue.

Comment 2.9

Page 5 L30-31. It sounds like MCM has been developed by the authors referenced in this sentence. This should be clarified.

Response:

Sorry for this misleading. We admit that the MCM was originally developed by the University of Leeds (http://mcm.leeds.ac.uk/MCM/). Only some developments on localization of the model for Hong Kong and addition of chemical reaction pathways of more biogenic VOC species and alkyl nitrates have been made by our group. This point has been added in the revised text.

Revision in the manuscript:

Page 6, Line 3: "A more detailed description of the MCM can refer to Jenkin et al. (1997 and 2003) and Saunders et al. (2003). Some developments on localization of the MCM for Hong Kong and addition of chemical reaction pathways of more biogenic VOC species and alkyl nitrates are given in our previous papers (Lam et al., 2013; Cheng et al., 2013; Ling et al., 2014; Lyu et al., 2015)."

Reference:

Cheng, H. R., Saunders, S. M., Guo, H., Louie, P. K., and Jiang, F.: Photochemical trajectory modeling of ozone concentrations in Hong Kong, Environ. Pollut., 180, 101-110, 2013.

Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, Atmos. Environ., 31, 81-104, 1997.

Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 181-193, 2003.

Lam, S. H. M., et al. (2013). "Modelling VOC source impacts on high ozone episode days observed at a mountain summit in Hong Kong under the influence of mountain-valley breezes." Atmospheric Environment 81: 166-176.

Ling, Z. H., Guo, H., Lam, S. H. M., Saunders, S. M., and Wang, T.: Atmospheric photochemical reactivity and ozone production at two sites in Hong Kong: Application of a Master Chemical Mechanism-photochemical box model, J. Geophys. Res., 119, 10567–10582, 2014.

Lyu, X. P., Ling, Z. H., Guo, H., Saunders, S. M., Lam, S. H. M., Wang, N., Wang, Y., Liu, M., and Wang, T.: Re-examination of C1–C5 alkyl nitrates in Hong Kong using an observation-based model, Atmospheric Environment, 120, 28-37, 10.1016/j.atmosenv.2015.08.083, 2015.

Comment 2.10

Page 6 L2-4: The way the authors describe I can hardly understand the difference between "background" and "baseline" values. While the definition of "baseline values" is literally taken from the reference TF HTAP (2010) the term "background values" the authors use is different from what is defined in TF HTAP (2010).

Response:

We apologise for the confusing. In the reference of TF HTAP (2010), “background concentration” can refer to “global or hemispheric background concentration”, “urban background” and “rural or regional background”. In this study, the term “background values” actually refers to “rural or regional background” which is defined as those observed at locations where there is little influence from urban sources of pollution. To make this clear, the definition was improved in the revised text.

Revision in the manuscript:

Page 6, Line 7: “The measured precursors (i.e., VOCs, NO and NO_2) at TC are a mixture of regional background values augmented by local source influences, and the two parts are very difficult to be fully separated. It is worth noting that the regional background values are those observed at locations where there is little influence from urban sources of pollution, while the baseline values mentioned in Section 3.2 are observations made at a site when it is not influenced by recent, locally emitted or produced pollution (TF HTAP, 2010).”

Comment 2.11

Page 6, L16-18: How were these VOC lifetimes based on: on reactions with OH, O_3, NO_3, Cl? What were the concentration assumptions on these species? Did the authors consider that the VOC lifetimes might be different during the course of the day, in particular at night?

Response:

The lifetimes of these VOCs were referred to Simpson et al. (2010). According to this reference, the lifetime estimations of these VOCs were based on the reactions with OH radicals. The rate constants used were from Atkinson and Arey (2003) by assuming a 12-h daytime average OH radical concentration of 2.0×10^6 molecules cm^{-3}. Although VOC lifetime at night was not considered in this estimation, it did not affect our results as only daytime average O_3 production was simulated in the study. The reference has been cited in the revised manuscript.

References:

Simpson, I. J., et al. (2010): Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C2–C10 volatile organic compounds (VOCs), CO2, CH4, CO, NO, NO2, NOy, O3 and SO2, Atmospheric Chemistry and Physics, 10(23), 11931-11954, doi:10.5194/acp-10-11931-2010.

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

Revision in the manuscript:

Page 6, Line 24: "The lifetimes of these VOCs were estimated based on the reactions with OH radicals (Simpson et al., 2010). The rate constants used were from Atkinson and Arey (2003) by assuming a 12-h daytime average OH radical concentration of 2.0 × 10^6 molecules cm^{-3}."

Comment 2.12

Page 6 L19: Meteorological conditions could be something like wind speed, humidity, temperature, radiation, something which is actually not unique to NO_2....What meteorological conditions do the authors exactly mean?

Response:

The meteorological conditions here refer to ambient temperature and humidity. To make it clear, this sentence has been revised accordingly.

Revision in the manuscript:

Page 6, Line 28: "...which highly depends on meteorological conditions, such as temperature and humidity (Dils et al. 2008; Evans and Jacob, 2005)."

Comment 2.13

Page 6 L18-20: What reaction exactly shows exponential relationship with temperature?

Response:

Sorry for the confusing. What we attempted to say is that, based on previous experimental studies, an exponential relationship was observed between the lifetime of NO_2 and temperature. To make this point clear, the sentence has been revised accordingly.

Revision in the manuscript:

Page 6, Line 29: "Previous experimental studies showed an exponential relationship between the NO_2 lifetime and temperature (Dils et al. 2008; Merlaud et al., 2011; Rivera et al., 2013), which was used to estimate the lifetime of NO_2 in this study."

Comment 2.14

Page 6 L21: Do these lifetimes for NO_2 include all NO_2 relevant reactions or do they refer to just one specific reaction? Please explain why uncertainties show up in these lifetimes. Why were those lifetimes calculated for each season, but not for each day, as the model is run for each day?

Response:

The two types of sink reactions were introduced in the text to provide background information only, and they were not used for the calculation of lifetime values. Actually, the NO_2 lifetimes were estimated using the observations and the reported experimental equation as a function of temperature. The uncertainty of the estimated lifetimes resulted from the variation of temperature over time.

In addition, the lifetimes of NO_2 were calculated for each day first based on hourly averaged temperatures. Then the seasonal averaged lifetimes were obtained by averaging the daily values.

Comment 2.15

Page 6 L25: Where do the uncertainties in the wind speed calculations come from?

Response:

The uncertainties in the calculation of the transport time from the inland PRD to the TC site came from the 95% confidence intervals of the seasonal average wind speeds.

Comment 2.16

Page 7 L7-8: Please explain how O_3 will be produced with titration by NO.

Response:

Thanks for pointing out this confusing. The sentence has been revised accordingly.

Revision in the manuscript:

Page 7, Line 15: "In both runs, O_3 production modulated by NO titration is considered during the evaluation period."

Comment 2.17

Page 7, L16: With regard to the precursors NO_x, total VOCs and CO did the authors calculate arithmetic means or medians? Would there be differences?

Response:

The levels of O_3 and precursors in this study were presented by arithmetic means. We agree that there would be some differences between the results from the two different statistical approaches. However, since the distributions of precursors were near normal distributions due to the relatively large number of samples, the difference in the results from the two average methods was not significantly large. In addition, the application of arithmetic means in this study would make our results easy to compare with other studies.

Comment 2.18

Page 7 L19-20: Please explain whether the monthly maximum O_3 level was the monthly averaged daily maximum 8-h O_3 average or something else?

Response:

In our manuscript, the monthly maximum O_3 level means the maximum of averaged daily maximum 8-h O_3 average in one month.

Revision in the manuscript:

Page 8, Line 15: "The monthly maximum O_3 level, which was defined the maximum of DMA8 O_3 in one month, increased from about 68 ppbv in 2005 to 86 ppbv in 2014, exceeding the ambient air quality standards in Hong Kong (i.e. 80 ppbv)."

Comment 2.19

Page 8 L6: It sounds like toluene was reduced in LPG. Please verify, if this was meant, as usually most significant toluene emission sources are solvent and traffic exhaust related emissions. What about other aromatics apart from toluene?

Response:

Sorry for the misleading. The reduction of toluene was due to the control of solvent usage, and the increase of alkanes was due to the LPG usage.

Revision in the manuscript:

Page 8, Line 31: "…such as the reduction of toluene by solvent usage control and the increase of alkanes in Liquefied Petroleum Gas (LPG) in 2005-2013 (Ou et al., 2015) and the decrease of LPG-alkanes in 2013-2014 (Lyu et al., 2016)."

Comment 2.20

Page 8 L8-10: Given the fact that TVOCs almost remained unchanged it is not that much surprising to see O_3 increases in VOC limited areas. It would be different in NO_x limited regimes.

Response:

We agree with the reviewer. This sentence and the one after have been removed from the text.

Comment 2.21

Page 8 L9: It sounds like the references cited here were the first to find that urban areas in general are VOC limited. Please verify whether this is true or whether this statement refers to recent findings in Chinese cities only.

Response:

Sorry for the misleading. That the precursor - O_3 relationship in urban areas are generally VOC limited has been well documented before 1990s. The references cited here verified the phenomena in Hong Kong. It is noteworthy that the related sentence has been removed for other reasons (see Response to Comment 2.20).

Comment 2.22

Page 12 L11: I was just wondering if the definition of daytime (0700-1900 LT) is valid regardless what season is concerned.

Response:

Considering weak photochemical reactions in the early morning and in the late afternoon, as well as the convenience in data calculation, the daytime period was arbitrarily defined as 0700-1900 LT. The authors admit that the duration of daytime varies by seasons, and this approach would add some uncertainty into the modelling results. However, the change in daytime duration is about 1-2 hours in Hong Kong (see Hong Kong Observation). The expected uncertainty from this would be limited.

Comment 2.23

Page 12 L15-16: While this statement is true for the modelled data, the observations show a completely different result.

Response:

In this study, it was assumed that the O_3 observation included both locally-produced O_3 and regional transported O_3. So it is not necessary for the modelled data (the simulated locally-produced O_3) and the observations to have a similar trend.

Comment 2.24

Page 12 L28: "...who attributed the increasing O_3 *trend ....to local contribution and regional transport". Isn't this statement always and at any given site true?*

Response:

Sorry for the misleading. The sentence has been revised accordingly.

Revision in the manuscript:

Page 12, Line 33: "The spring pattern of O_3 *in this study is consistent with the findings of Li et al. (2014) who reported the increasing* O_3 *trend (2.0 ppbv/yr) in spring at urban clusters of PRD from 2006 to 2011."*

Comment 2.25

Page 12 L31-32: "... (0.70±0.34 ppbv/yr and 0.66±0.41 ppbv/yr)"... I do not see any of these values in Fig 4.

Response:

Sorry for this error. The values in Figure 4 are correct. This inconsistence problem has been resolved.

Revision in the manuscript:

Page 13, Line 4: "Unlike in spring, though the observed and locally-produced O_3 *(filtered) displayed increasing trends in summer (0.67±0.34 ppbv/yr and 0.61±0.41 ppbv/yr, respectively;* $p<0.05$*)..."*

Comment 2.26

Page 12 L33-34: I am astonished to read that the model did not consider the influence of solar radiation. Isn't this a crucial parameter which has not been considered?

Response:

This sentence was misleading. Actually we used the TUV model to simulate the diurnal variation of solar radiation and then calculate the photolysis rate of different chemicals (see Section 2.3). However, the annual variations of solar radiation over the years were not considered in the model.

Revision in the manuscript:

Page 13, Line 6: "Note that the influence of annual variation in solar radiation over the 10 years was not considered while the TUV model was used to calculate the photolysis rates, which could mask the actual trends of O3 mixing ratios."

Comment 2.27

Page 13 L1: What is the reason for the increase in solar radiation over the last years?

Response:

The statement on the increase of solar radiation in summer along the 10 years was based on measurements from Hong Kong Observation, but frankly speaking, the reasons remain unknown. It might be due to less haze as the air quality has been getting better in Hong Kong and the PRD. To make this point clear, the text has been improved accordingly.

Revision in the manuscript:

Page 13, Line 8: "Indeed, the total solar radiation (0.24±0.16 MJ m^{-2} yr^{-1}, $p<0.01$) and temperature (0.095±0.034 K yr^{-1}, $p<0.05$) in summer significantly increased during the past 10 years (see Figure S9), subsequently resulting in the enhanced in-situ photochemical reactivity of VOCs, although their quantitative contributions remain unknown and require further investigation. The increase of solar radiation might be due to the decreasing haze as the air quality has been getting better in Hong Kong and the PRD (Louie et al., 2013)."

Reference:

Louie, P. K. K., et al. (2013). "A Special Issue of Atmospheric Environment on "Improving Regional Air Quality over the Pearl River Delta and Hong Kong: From Science to Policy" Preface." Atmospheric Environment 76: 1-2.

Comment 2.28

Page 13 L2-3: What is the quantitative contribution of the increase in solar radiation for in-situ photochemical reactivity of VOCs?

Response:

Unfortunately, the contribution of the increase in solar radiation for in-situ photochemical reactivity of VOCs is hardly quantified in this study as the solar radiation data (unit: W m^{-2}) required for modelling are not available. The only solar radiation data available are recorded in this unit of MJ·m^{-2}. This type of data is an integration of solar radiation in a certain amount of time, for instance 24 hours. Although this data is widely used in literature to show a general level of solar radiation, we have no simple way to convert them back to the data with a unit of "W m^{-2}" due to the highly variable daily sunshine duration. If possible, we would like to do more work on this issue in the future.

Revision in the manuscript:

Page 13, Line 8:" Indeed, the total solar radiation (0.24±0.16 MJ m^{-2} yr^{-1}, $p<0.01$) and temperature (0.095±0.034 K yr^{-1}, $p<0.05$) in summer significantly increased during the past 10 years (see Figure S9), subsequently resulting in the enhanced in-situ photochemical reactivity of VOCs, although their quantitative contributions remain unknown and require further investigation."

Comment 2.29

Page 13 L6-7: What are the contributions quantitatively?

Response:

Please refer to the Response to Comment 2.28 above.

Comment 2.30

Page 18, L16-17: Fig 8a shows highest RIR from TVOC and CO, while NOx has the least negative RIR. Wouldn't this mean that O3 production would be most efficient in winter, which would be in contradiction to observed O3 values in winter (Fig. 3)?

Response:

The RIR value only shows the sensitivity of cutting precursors to O_3 formation and has been widely used to determine the future reduction plan of precursors. However, it is not necessary for RIR to reflect the efficiency of O_3 production.

Comment 2.31

Page 19, L3-6: It looks like RIR values for BVOC (here only isoprene) in summer are higher than those for the remaining AVOCs for the same season. Would this mean that summertime O3 production critically depends on biogenic emissions in Hong Kong in summer?

Response:

Again, that RIR values for BVOC are higher than those for the remaining AVOCs in summer only indicates that O_3 production is more sensitive to the change in isoprene than the change in other AVOC species, from which one cannot directly derive that O_3 production largely depends on isoprene.

Comment 2.32

Page 19, L6-7: "The higher RIR of BVOCs in summer was due to the higher photochemical reactivity". Wouldn't it be higher biogenic emissions which cause higher BVOC RIR in summer?

Response:

The authors admit that, in addition to the higher photochemical reactivity, the higher biogenic emissions would be one of reasons for the higher BVOC RIR in summer.

Revision in the manuscript:

Page 19, Line 15: "The higher RIR of BVOCs in summer was mainly due to the higher biogenic emissions in summer. In addition, higher photochemical reactivity of BVOCs also contributed to higher RIR of BVOCs."

Comment 2.33

Page 19, L8-10: NO_x *RIR is less low in winter compared to spring and summer. Wouldn't this already lead to higher* O_3 *production in winter according to the authors?*

Response:

The fact of less low NO_x RIR does not warrant higher O_3 production in winter. Please refer to the Response to Comment 2.30 for reasons.

Comment 2.34

Page 19, L21: Is this statement valid for entire Hong Kong or just for the TC site?

Response:

Although the relationship between O_3 and precursors may vary by locations across Hong Kong, TC is a good representative site for the overall Hong Kong (please see the Response to Comment 2.2 above). Therefore, we think this statement would be generally valid for entire Hong Kong. Some specific locations, like those close to traffic sources, may need individual investigation, but that is out of the scope of this study.

Comment 2.35

Page 20, L9-10, Fig. 9: The trend analysis in Fig 9 is mostly driven by a few strong peaks. How robust is this analysis? Looking into the different y-scales of Fig. 9 I conclude that summertime O_3 mixing ratios are largely due to the high BVOC levels, which would be in line with Fig. 8. Again, is Hong Kong's O_3 pollution mostly caused by BVOCs?

Response:

In terms of robustness of this analysis, please refer to the Response to Comment 2.1. For the contribution of BVOCs to O_3 formation in summer, we agree with the reviewer's conclusion, that is, summertime O_3 mixing ratios are largely due to the high BVOC levels, given that Hong Kong has high BVOC emission in summer and low anthropogenic VOC levels due to the dilution by clean marine air mass. However, we do not think that Hong Kong's O_3 pollution is mostly caused by BVOCs. As reported by many previous studies (Zhang *et al*., 2012; Ou *et al*., 2015), anthropogenic VOCs, particularly reactive aromatics, play a critical role in O_3 formation in Hong Kong and in PRD region.

Reference:

Ou, J., et al. (2015). "Speciated OVOC and VOC emission inventories and their implications for reactivity-based ozone control strategy in the pearl river delta region, China." Science of the Total Environment 530-531: 393-402.

Zhang, Y., et al. (2012). "Aromatic hydrocarbons as ozone precursors before and after outbreak of the 2008 financial crisis in the Pearl River Delta region, south China." Journal of Geophysical Research Atmospheres 117(15).

Comment 2.36

Page 21, L17: "...increased emissions of alkenes from traffic related sources". Is this due to enhanced alkene emissions from changes in the composition of the traffic fleet or from increased traffic volume? If it is the latter, then emissions of aromatic compounds would also increase.

Response:

The increase of traffic related alkenes was due to both changes in the composition of the traffic fleet and in the traffic volume. In last decade, the traffic volume was increasing greatly with an increase of the fraction of gasoline vehicles. In addition, the main source of aromatics in Hong Kong was solvent usage according to the study by Ou *et al*. (2015).

Reference:

Ou, J., et al. (2015). "Speciated OVOC and VOC emission inventories and their implications for reactivity-based ozone control strategy in the pearl river delta region, China." Science of the Total Environment 530-531: 393-402.

Comment 2.37

Page 21, L20-21: Diesel driven vehicles emit significantly less VOCs than gasoline driven vehicles. In other words was the DCV program a significant contribution to the overall traffic related alkene emissions?

Response:

The reviewer is right. Diesel driven vehicles do emit significantly less VOCs than gasoline driven vehicles. That was part of reason why traffic-related alkenes still increased after introducing the DCV program which has been proved to be an effective measure to reduce alkene emissions (Lyu *et al*. 2017). The increase in number of LPG/gasoline vehicles likely contributed more traffic related alkene emissions leading the increased trend of alkenes.

Comment 2.38

Page 21, L26-28: Why would the AVOC (alkane) contribution to O_3 formation not increase with increasing alkane levels in 2005-2013?

Response:

There is a fact that alkanes include a bunch of compounds which have different but generally low reactivity with OH radicals. In this study, although the level of total alkanes increased over the years, it did not warrant the increase in its contribution to O_3 formation. For example, one possible case is that some alkanes with relatively high reactivity decreased with an increase of some low-reactivity alkanes.

Comment 2.39

Page 21, L29-30: "In addition...blur the trend". I do not understand this sentence. Also, what photolysis rates of alkanes do the authors exactly mean?

Response:

Sorry for the confusing. What we attempted to say is the reaction rate of alkanes with OH radicals.

Revision in the manuscript:

Page 22, Line 2: "In addition, the seasonal variation of O_3 formation, of which the reaction rates of alkanes with OH radicals were high in summer and low in winter, would also blur the trend".

Comment 2.40

Page 21, L34: Here you should add the Reiman et al paper, as this was one of the first to observe anthropogenic isoprene emissions.

Response:

The reviewer's advice is appreciated and the suggested reference has been added in the main text.

Revision in the manuscript:

Page 22, Line 6: "The main known sources of isoprene are biogenic and anthropogenic (Borbon et al. 2001; Barletta et al., 2002; Reiman et al., 2000)."

Reference:

Reimann et al. (2000), The anthropogenic contribution to isoprene concentrations in a rural atmosphere, Atmos. Environ., 34(1), 109–115, doi:10.1016/S1352-2310(99)00285-X

Comment 2.41

Page 22, L6-7: The authors state that 90% of isoprene was emitted from biogenic sources, while traffic sources were less than 5%. From what sources did the remaining 5% isoprene come from?

Response:

The remaining 5% isoprene may come from consumer products and printing processes, according to the source appointment study of Ou *et al*. (2015).

Reference:

Ou, et al. (2015). "Speciated OVOC and VOC emission inventories and their implications for reactivity-based ozone control strategy in the pearl river delta region, China." Science of the Total Environment 530-531: 393-402.

Comment 2.42

Figure 4: (1) There is no gold line (ΔO_3) for summer. (2) The observations (blue line) is always the highest. What is the model missing?

Response:

The regional O_3 (ΔO_3), the difference between overall observed and simulated O_3, was not shown for summer in Figure 4, because of a negligible impact of regional transport on summer O_3 trend in 2005-2014. It is evidenced by that the trend of locally-produced O_3 (filtered) was comparable to those of observed O_3 (p=0.12) and locally-produced O_3 (simulated) (p=0.32), respectively. To make this point clear, an explanation has been added to the caption of Figure 4.

In this study, it was assumed that the O_3 observation includes both local-produced and regional transported O_3. Thus it is not surprising to see that the observation is always higher. In addition, the regional transported O_3 was missing in the model as it was only used to simulate the locally-produced O_3.

Revision in the manuscript:

Caption for Figure 4: "…The regional O_3 in summer was negligible and is not shown in the graph."

Comment 2.43

Figure 8: Is this data day- or night-time data or both and why did the authors choose that specific time period?

Response:

Only daytime data are used in Figure 8 as the RIR values were calculated based on O_3 production in daytime. This information has been added into the description of RIR in Section 2.3.

Revision in the manuscript:

Page 7, Line 6: "The RIR is defined as the percent change in daytime O_3 *production per percent change in precursors."*

Comment 2.44

Figure S9: I am not sure about the units (M m^{-2}) for Solar Radiation here.

Response:

Thanks for pointing out this typo which has been corrected to "MJ m^{-2}".

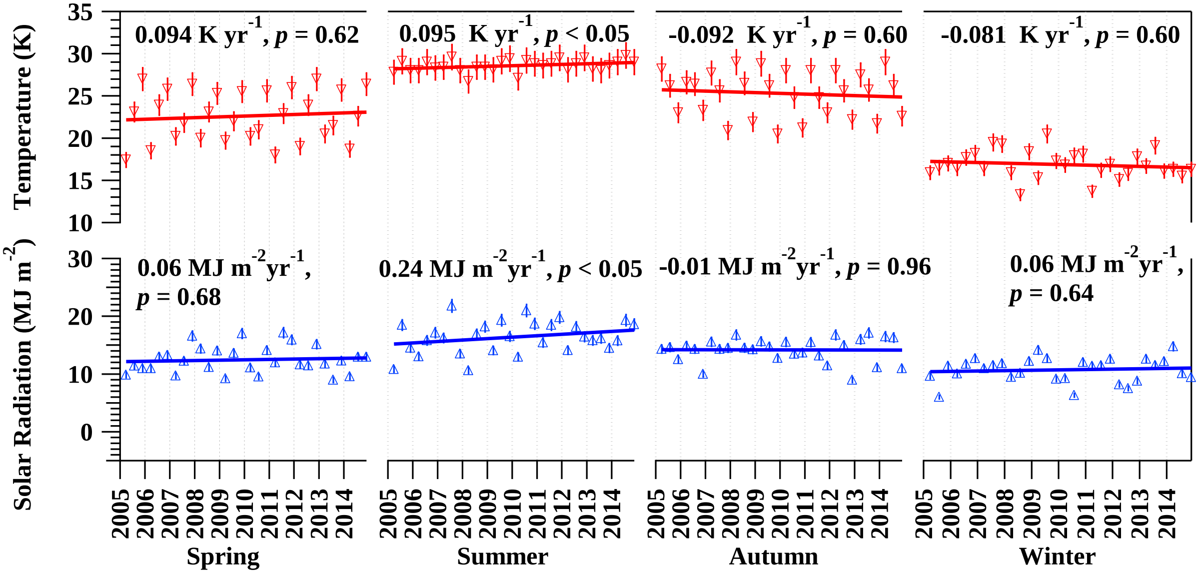

Figure S9. Variations of temperature (red) and solar radiation (blue) for the four seasons at TC during 2005–2014. Each data point in the figure is obtained by averaging hourly values into a monthly value. Error bars represent 95% confidence interval of monthly averages.

Literature cited:

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Rappengluck et al. (2013): Radical Precursors and Related Species from Traffic as Observed and Modeled at an Urban Highway Junction, J. Air Waste Man. Assoc., 63:11, 1270-1286, doi: 10.1080/10962247.2013.822438

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

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Abstract. Over the past ten years (2005-2014), ground-level O_3 in Hong Kong has consistently increased in all seasons except winter, despite the yearly reduction of its precursors, *i.e.*, nitrogen oxides (NO_x=NO+NO_2), total volatile organic compounds (TVOCs) and carbon monoxide (CO). To explain the contradictory phenomenon, an observation-based box model (OBM) coupled with CB05 mechanism was applied in order to understand the influence of both locally-produced O_3 and regional transport. The simulation of locally-produced O_3 showed an increasing trend in spring, a decreasing trend in autumn and no changes in summer and winter. The O_3 increase in spring was caused by the net effect of more rapid decrease of NO titration and unchanged TVOC reactivity despite decreased TVOC mixing ratios, while the decreased local O_3 formation in autumn was mainly due to the reduction of aromatic VOC mixing ratios and the TVOC reactivity and much slower decrease of NO titration. However, the decreased in-situ O_3 formation in autumn was overridden by the regional contribution, resulting in elevated O_3 observations. Furthermore, the OBM-derived relative incremental reactivity indicated that the O_3 formation was VOC-limited in all seasons, and the long-term O_3 formation was more sensitive to VOCs and less to NO_x and CO in the past 10 years. In addition, the OBM results found that the contributions of aromatics to O_3 formation decreased in all seasons of these years, particularly in autumn, likely due to effective control of solvent-related sources. In contrast, the contributions of alkenes increased, suggesting a continuing need to reduce traffic emissions. The findings provided updated information on photochemical pollution and its impact in Hong Kong.

Keywords: Ozone; VOCs; Long term; Observation-based model

1 Introduction

Ozone (O_3), one of the most important photochemical products influencing atmospheric oxidative capacity, human and vegetation health, and climate change, is formed through a series of photochemical reactions among volatile organic compounds (VOCs) and nitrogen oxides (NO_x) in the atmosphere (Seinfeld and Pandis, 2006). Due to the non-linear relationship between O_3 and its precursors, the development of appropriate control measures of O_3 is still problematic in mega cities (Sillman, 1999).

Distinguished from short-terms O_3 studies, investigation of long-term O_3 variations enables us to understand the seasonal and inter-annual characteristics of O_3, the influence of meteorological parameters on O_3 formation, and the O_3-precursor relationships in different years. Subsequently, more effective and sustainable O_3 control strategies can be formulated and implemented. Hence, earlier efforts have been made to investigate long-term variations of O_3 in different atmospheric conditions. For example, multi-year data analysis showed that the O_3 levels started to decrease around 2000 in Europe (*e.g.*, Jungfraujoch, Zugspitze, Mace Head) and North America excluding western US rural sites (*e.g.*, US Pacific, Lassen Volcanic National Park) (Lefohn *et al*., 2010; Cui *et al*., 2011; Parrish *et al*., 2012; Pollack *et al*., 2013; Lin *et al*., 2017), due to a decrease in the emissions of O_3 precursors since the early 1990s (Cui *et al*., 2011; Derwent *et al*., 2013). In contrast, the O_3 levels in East Asia increased at a rate of 1.0 ppbv yr^{-1} from 1998 to 2006, based on measurements at Mt. Happo, Japan (Parrish *et al*., 2012; Tanimoto, 2009). In China, with rapid economic growth and urbanization over the past three decades, increasing O_3 levels have been found in many locations. For instance, based on the data collected between 1991 and 2006 at Lin'an, a NO_x-limited rural area close to Shanghai, Xu *et al*. (2008) reported that the maximum mixing ratios of O_3 increased by 2.0% yr^{-1}, 2.7% yr^{-1}, 2.4% yr^{-1} and 2.0% yr^{-1} in spring, summer, autumn and winter, respectively, which were likely related to increased mixing ratios of NO_2. In the North China Plain (NCP), Ding *et al*. (2008) reported that O_3 in the lower troposphere over Beijing had a positive trend of ~2.0% yr^{-1} from 1995 to 2005, while Zhang *et al*. (2014) found that the daytime average O_3 in summer in Beijing significantly increased by 2.6 ppbv yr^{-1} from 2005 to 2011, due to decreased NO titration (-1.4 ppbv yr^{-1} of NO_x over the study period) and elevated regional background O_3 levels (~0.58 - 1.0 ppbv yr^{-1}) in the NCP.

Hong Kong, together with the inland Pearl River Delta (PRD) region of southern China, has suffered from high O_3 mixing ratios in recent years (Chan *et al*., 1998a; Chan *et al*., 1998b; Wang and Kwok, 2003; Ding *et al*., 2004; Zhang *et al*., 2007; Guo *et al*., 2009 and 2013). In 2014, O_3 exceeding the Chinese national air quality standard (80 ppbv, for the daily 8 hour maximum average, DMA8) was > 90 days in some areas of the PRD, with the highest DMA8 value of 165 ppbv (GDEMC and HKEPD, 2015). Based on the observational data at a newly-established regional monitoring network, Li *et al*. (2014) found that O_3 mixing ratios in the inland PRD region increased at a rate of 0.86 ppbv yr^{-1} from 2006 to 2011 because of the rapid reduction of NO in this VOC-limited region. Similarly, Wang *et al*. (2009) reported a continuous record of increased surface O_3 at Hok Tsui (HT), a regional background site in Hong Kong, with a rate of 0.58 ppbv yr^{-1} based on observations conducted from 1994 to 2007, concluding that the increased NO_2 column concentration in upwind eastern China might significantly contribute to the increased O_3 in Hong Kong. Even so, knowledge gaps still exist on long-term characteristics of O_3, long-term O_3-prescursor relationships, and the mechanisms for the varying O_3 trends in the PRD region, because of the lack of long-term observations of VOCs in the region, where photochemical O_3 formation is sensitive to VOCs in urban areas, and where the levels of VOCs and NO_x have varied significantly due to more stringent control measures since 2005 (Zhong *et al.*, 2013). It is noteworthy that although Xue *et al.* (2014) reported increasing O_3 trends in 2002-2013 in Hong Kong and investigated the roles of VOCs and NO_x in the long-term O_3 variations, only data in autumn were used, which could not provide a consistently full picture of the long-term variations of O_3, VOCs, NO_x and their relationships.

In this study, field measurements and model simulations were combined to characterize the long-term variations of O_3 and its precursors, the variations of locally-produced O_3, and the impact of regional transport in Hong Kong from 2005 to 2014. In addition, the long-term contribution of different VOC groups to the O_3 formation was explored. The findings aim at providing the most updated information on the characteristics of photochemical pollution and its impact in Hong Kong.

2 Methodology

2.1 Site description

Field measurements were carried out at the Tung Chung (TC) Air Quality Monitoring Station managed by the Hong Kong Environmental Protection Department (HKEPD). The sampling site (22.29 °N, 113.94 °E) is located at about 24 km southwest of downtown Hong Kong and about 3 km south of the Hong Kong International Airport (Figure 1). The elevation of TC is 37.5 m above sea level. It is surrounded by a newly-developed residential town on the northern Lantau Island, and is downwind of urban Hong Kong and the inland PRD region when easterly and northeasterly winds are prevailing (Ou *et al*., 2015). At TC, the prevailing wind varies by seasons, with east winds for spring and autumn, southwest winds for summer and northeast for winter (see Figure S1). The selection of this site for the trend study was due to its downwind location being a good receptor for urbane plume, suffering high O_3 pollution and having the most comprehensive dataset. More detailed description of the TC site can be found in our previous papers (Jiang *et al*., 2010; Cheng *et al*., 2010; Ling *et al*., 2013; Ou *et al*., 2015).

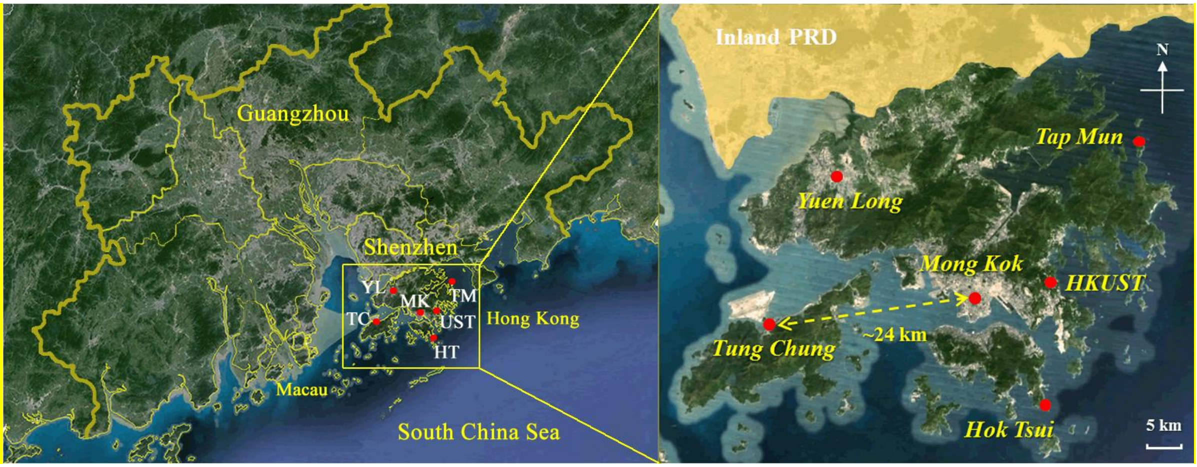

Figure 1. Location of the sampling sites and surrounding environments. Guangzhou and Shenzhen are the two biggest cities in the inland PRD region with a population over 10 million for each city. Hok Tsui (HT) and Tap Mun (TM) are regional background sites. The Hong Kong University of Science and Technology (HKUST) is an Air Quality Research Supersite located in 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 in downtown with high traffic density.

2.2 Measurement techniques

Hourly observations of O_3, CO, SO_2, NO-NO_2-NO_x and meteorological parameters at TC from 2005 to 2014 were obtained from the HKEPD (http://epic.epd.gov.hk/ca/uid/airdata). Briefly, O_3 was measured using a commercial UV photometric instrument (Advanced Pollution Instrumentation (API), Model 400A) with a detection limit of 0.6 ppbv. CO was measured with a gas filter correlation CO analyser (Thermo ElectronCorp. (TECO), Model 48C) with a detection limit of 0.04 ppm. SO_2 was measured using a pulsed fluorescence analyser (TECO, Model 43A) with a detection limit of 1.0 ppbv. NO-NO_2-NO_x were detected using a commercial chemiluminescence with an internal molybdenum converter (API, Model 200A) and a detection limit of 0.4 ppbv. All the time resolutions for these gas analysers are 1 hour. To ensure a high degree of accuracy and precision, the QA/QC procedures for gaseous pollutants were identical to those in the US air quality monitoring program (http://epic.epd.gov.hk/ca/uid/airdata). The accuracy of the monitoring network is assessed by performance audits, while the precision, a measure of the repeatability, of the measurements is checked in accordance with HKEPD's quality manuals. For the gaseous pollutants, the accuracy and precision within the limits of ± 15 and ± 20 % are adopted, respectively (HKEPD 2015).

Real-time VOC data at TC were also measured by the HKEPD. An online GC-FID analyser (Synspec GC 955, Series 600/800) was used to collect VOC speciation data continuously with a time resolution of 30 minutes. The VOC analyser consists of two separate systems for detection of C_2–C_5 and C_6–C_{10} hydrocarbons, respectively. Detailed description about the real-time VOC analyser can be found in Lyu *et al*. (2016). There were twenty-eight C_3-C_{10} VOC species identified and quantified with this method. In terms of the QA/QC for VOC analysis, built-in computerized programs of quality control systems such as auto-linearization and auto-calibration were used. Weekly calibrations were conducted by using NPL standard gas (National Physical Laboratory, Teddington, Middlesex, UK). In general, the detection limits of the target VOCs ranged from 2 to 56 pptv. The accuracy of each species measured by online GC-FID was determined by the percentage difference between measured mixing ratio and actual mixing ratio based on weekly span checks and monthly calibrations. The precision was based on the 95% probability limits for the integrated precision check results. The accuracy of the measurements was about 1-7%, depending on the species, and the measurement precision was about 1-10% (Table S1). In addition, the quality of the real-time data was assured by regular comparison with whole-air canister samples collected and analysed by University of California at Irvine (UCI). More details can be found from previous studies in Hong Kong (Xue *et al*., 2014; Ou *et al*., 2015; Lyu *et al*., 2016).

For data analysis, linear regression and error bars represented as 95% confidence intervals were used. Trends of O_3 and its precursors with a p value < 0.05 were considered significant (Guo *et al*., 2009).

2.3 Observation-based model

In this study, an observation-based box model (OBM) coupled with carbon bond mechanism (CB05) was used to simulate photochemical O_3 formation and to evaluate the sensitivity of O_3 formation to its precursors. The CB05 mechanism is a condensed mechanism with high computational efficiency and reliable simulation, and has been successfully applied in many emission-based modelling systems such as Weather Research and Forecasting with Chemistry (WRF/Chem) and the Community Multiscale Air Quality (CMAQ) (Yarwood *et al*. 2005; Coates and Butler, 2015). Unlike emission-based models, the OBM in this study is based on the real time observations at the TC site in Hong Kong. The simulation was constrained by observed hourly data of meteorological parameters (temperature, relative humidity and pressure) and air pollutants (NO, NO_2, CO, SO_2 and 22 C_3-C_{10} VOCs). In the CB05 module, VOCs are grouped according to carbon bond type and the reactions of individual VOCs were condensed using lumped structure technique (conversions from measured VOCs to CB05 grouped species are shown in Table S2). To better describe the photochemical reactions in Hong Kong, the photolysis rates of different species in the OBM model was determined using the output of the Tropospheric Ultraviolet and Visible Radiation model (TUV v5) (Madronich and Flocke, 1999) based on the actual conditions of Hong Kong, *i.e.*, meteorological parameters, location, and time period of the field campaign. However, it is noteworthy that the atmospheric physical processes (*i.e.*, vertical and horizontal transport), the deposition of species, and the radical loss to aerosol (George *et al*., 2013; Lakey *et al*., 2015) were not considered in the OBM model. In addition, a “spin-up” time was not applied in the model to get the radical intermediates well steady which might have caused a slight underestimation on the simulated O_3 production (Figure S2) and its sensitivity to precursors (Figure S3). In this study, we performed day-by-day OBM simulations for 2688 days during 2005−2014, where the missing days were due to lack of real-time VOC data (see Table S3). For each daily simulation, the model was run for a 24-hour period with 00:00 (local time, LT) as the initial time. The model output simulated mixing ratios of O_3, radicals (*i.e.*, OH, HO_2, RO and RO_2) and intermediates. The model performance was evaluated using the index of agreement (IOA) (Huang *et al*., 2005; Wang *et al*., 2015; Wang *et al*., 2013; Lyu *et al*., 2015).

$$\mathrm{IOA}=1-\frac{\sum_{i=1}^{n}(O_i-S_i)^2}{\sum_{i=1}^{n}(|O_i-\bar{O}|+|S_i-\bar{O}|)^2} \qquad \text{(Eq. 1)}$$

where S_i and O_i represent simulated and observed values, respectively, $\bar{O}$ represents the mean of observed values, and n is the number of samples. The IOA value lies between 0 and 1. The better agreement between simulated results and observed data, the higher the IOA (Huang *et al*., 2005).

Apart from the OBM (CB05), which is mainly for condensed VOC groups, a Master Chemical Mechanism (MCM, v3.2) was applied to inter-compare the modelling performance of OBM (CB05) (shown in section 3.2). Since the MCM utilizes the near-explicit mechanism describing the degradation of 143 primary VOCs and contains around 16,500 reactions involving

5,900 chemical species, it has a better performance in calculating the contribution of individual VOCs to O_3 production (Jenkin *et al*., 1997 and 2003; Saunders *et al*., 2003). The hourly input data of meteorological parameters, air pollutants and the photolysis rates in MCM were the same as in CB05. A more detailed description of the MCM can refer to Jenkin *et al*. (1997 and 2003) and Saunders *et al*. (2003). Some developments on localization of the MCM for Hong Kong and addition of chemical reaction pathways of more biogenic VOC species and alkyl nitrates are given in our previous papers (Lam *et al*., 2013; Cheng *et al*., 2013; Ling *et al*., 2014; Lyu et al., 2015).

The measured precursors (*i.e.*, VOCs, NO and NO_2) at TC are a mixture of regional background values augmented by local source influences, and the two parts are very difficult to be fully separated. It is worth noting that the regional background values are those observed at locations where there is little influence from urban sources of pollution, while the baseline values mentioned in Section 3.2 are observations made at a site when it is not influenced by recent, locally emitted or produced pollution (TF HTAP, 2010). To minimize the influence of regional transport from the inland PRD region, the real-time regional background values in this study were simply subtracted off from the observations at TC. Previous studies have reported that Tap Mun (TM, 22.47^{o} N, 114.36^{o} E) and Hok Tsui (HT, 22.217^{o} N, 114.25^{o} E), are two background sites of Hong Kong (Lyu *et al*., 2016; So and Wang, 2003 and 2004; Wang *et al*., 2005; Wang *et al*., 2009). TM is a rural site that is upwind of Hong Kong in autumn/winter seasons and HT is a background site at southeastern tip of Hong Kong. Good trace gas correlations were found between both sites (Lyu *et al*., 2016). Since not all the data during the entire 10-year period were available at one background site, the hourly measured VOCs at HT and NO_2 at TM were treated as background values. The background data were excluded using the equations:

$$[VOC]_{local} = [VOC]_{observed} - [VOC]_{background} \qquad \text{(Eq. 2)}$$

$$[NO]_{local} = [NO]_{observed} - [NO]_{background} \qquad \text{(Eq. 3)}$$

$$[NO_2]_{local} = [NO_2]_{observed} - [NO_2]_{background} \qquad \text{(Eq. 4)}$$

where $[xx]_{local}$, $[xx]_{observed}$, and $[xx]_{background}$ represent the local, observed and background values, respectively. In this study, mixing ratios of 21 anthropogenic VOC species with relatively long lifetimes (5h – 14d) at HT were selected as the background values for deducting from the observed data at TC. The lifetimes of these VOCs were estimated based on the reactions with OH radicals (Simpson *et al*., 2010). The rate constants used were from Atkinson and Arey (2003) by assuming a 12-h daytime average OH radical concentration of 2.0×10^{6} molecules cm^{-3}. Isoprene was considered as not having a regional impact due to its short lifetime (1-2 h) (Ling *et al*., 2011). Furthermore, the lifetime of NO_2 is determined by the main sinks of $OH+NO_2$ reaction and the hydrolysis of N_2O_5 at the surface of wet aerosols, which highly depends on meteorological conditions, such as temperature and humidity (Dils *et al*. 2008; Evans and Jacob, 2005). Previous experimental studies showed an exponential relationship between the NO_2 lifetime and temperature (Dils *et al*., 2008; Merlaud *et al*., 2011; Rivera *et al*., 2013), which was used to estimate the lifetime of NO_2 in this study. The lifetime of NO_2 was calculated to be approximately 3.4 ±0.3 h, 2.2 ±0.1 h, 2.8 ±0.2 h and 5.2 ±0.3 h in spring, summer, autumn and winter, respectively, consistent with the lifetimes of NO_2 in different seasons in the PRD region (Beirle *et al*., 2011). Considering the shortest distance between the inland PRD and TC (*i.e.*, from the center of Shenzhen to TC site, ~30 km) and the average wind speeds in different seasons (Ou *et al*., 2015), it would take approximately 3.4±0.3 h, 4.3±0.3 h, 4.0±0.5 h and 3.7±0.4 h in spring, summer, autumn and winter, respectively, for NO_2 originating in the inland PRD to arrive at TC. Hence, although NO_2 emitted from the inland PRD is slightly more likely to arrive at TC in winter and spring than in summer and fall, the differences in travel time among the seasons are relatively small and it is difficult to be precise with seasonal average estimates of NO_2 lifetime and travel time. We have excluded background NO_2 values in spring and winter in this study during model simulations, but we recognize the limitations in these calculations.

In addition to the simulation of O_3 formation, the precursor sensitivity of O_3 formation was assessed by the OBM using the relative incremental reactivity (RIR) (Cardelino and Chameides, 1995; Lu *et al*., 2010; Cheng *et al*., 2010; Ling *et al*., 2011; Xue *et al*., 2014). A higher positive RIR of a given precursor means a greater probability that reducing emissions of this precursor will more significantly reduce O_3 production. The RIR is defined as the percent change in daytime O_3 production per percent change in precursors. The RIR for precursor X is given by:

$$\mathrm{RIR\,(X)} = \frac{[\mathrm{P}^{\mathrm{S}}_{\mathrm{O_3-NO}}(\mathrm{X}) - \mathrm{P}^{\mathrm{S}}_{\mathrm{O_3-NO}}(\mathrm{X}-\Delta\mathrm{X})]/\mathrm{P}^{\mathrm{S}}_{\mathrm{O_3-NO}}(\mathrm{X})}{\dfrac{\Delta\mathrm{S(X)}}{\mathrm{S(X)}}} \qquad \text{(Eq. 5)}$$

X represents a specific precursor (*i.e.*, VOCs, NO_x, or CO); the superscript "s" is used to denote the specific site where the measurements were made; S(X) is the measured mixing ratio of species X (ppbv); ΔS(X) is the hypothetical change in the mixing ratio of X; $\mathrm{P}^{\mathrm{s}}_{\mathrm{O_3-NO}}(\mathrm{X})$ and $\mathrm{P}^{\mathrm{s}}_{\mathrm{O_3-NO}}(\mathrm{X}-\Delta\mathrm{X})$ represent net O_3 production in a base run with original mixing ratios, and in a run with a hypothetical change (ΔS(X); 10% S(X) in this study) in species X. In both runs, O_3 production modulated by NO titration is considered during the evaluation period. The O_3 production $\mathrm{P}^{\mathrm{S}}_{\mathrm{O_3-NO}}$ was calculated by the output parameters of the OBM.

$\mathrm{P}^{\mathrm{S}}_{\mathrm{O_3-NO}}$ is derived from the difference between O_3 gross production rate $\mathrm{G}^{\mathrm{S}}_{\mathrm{O_3-NO}}$ and O_3 destruction rate $D^{\mathrm{S}}_{\mathrm{O_3-NO}}$ (Eq. 6). $\mathrm{G}^{\mathrm{S}}_{\mathrm{O_3-NO}}$ is calculated by the oxidation of NO by HO_2 and RO_2 (Eq. 7), while $D^{\mathrm{S}}_{\mathrm{O_3-NO}}$ is calculated by O_3 photolysis, reactions of O_3 with OH, HO_2 and alkenes, and reaction of NO_2 with OH (Eq. 8).

$$\mathrm{P}^{\mathrm{S}}_{\mathrm{O_3-NO}} = \mathrm{G}^{\mathrm{S}}_{\mathrm{O_3-NO}} - \mathrm{D}^{\mathrm{S}}_{\mathrm{O_3-NO}} \qquad \text{(Eq. 6)}$$

$$\mathrm{G}^{\mathrm{S}}_{\mathrm{O_3\text{-}NO}} = \mathrm{k}_{\mathrm{HO_2+NO}}[\mathrm{HO_2}][\mathrm{NO}] + \sum \mathrm{k}_{\mathrm{RO_{2i}+NO}}[\mathrm{RO_{2i}}][\mathrm{NO}] \qquad \text{(Eq. 7)}$$

$$\begin{aligned}\mathrm{D}^{\mathrm{S}}_{\mathrm{O_3\text{-}NO}} = {} & \mathrm{k}_{\mathrm{HO_2+O_3}}[\mathrm{HO_2}][\mathrm{O_3}] + \mathrm{k}_{\mathrm{OH+O_3}}[\mathrm{OH}][\mathrm{O_3}] + \mathrm{k}_{\mathrm{o(^1D)+H_2O}}[\mathrm{O(^1D)}][\mathrm{H_2O}] + \\ & \mathrm{k}_{\mathrm{OH+NO_2}}[\mathrm{OH}][\mathrm{NO_2}] + \mathrm{k}_{\mathrm{OLE+O_3}}[\mathrm{alkenes}][\mathrm{O_3}]\end{aligned} \qquad \text{(Eq. 8)}$$

In Eq.7 and Eq.8, *k* constants are the rate coefficients of their subscript reactions. Values of radicals and intermediates are simulated by the OBM. Details of the calculation can be found in Ling *et al.* (2014) and Xue *et al.* (2014).

Furthermore, the sensitivities in the OBM model to the uncertainties in initial concentrations of ozone precursors have been examined by running the model with varying NO_2 or VOCs initial concentrations in the range of ±95% confidence intervals, respectively. The results demonstrate that the modelled O_3 production was more sensitive to NO_2 than VOCs, with a percentage variation about ±13% and ±3.9%, respectively (see Table S4, Figure S4 & S5). In addition, the uncertainties associated with removing the background concentrations are also evaluated, suggesting a similar trend for simulated locally O_3 production for both approaches (see Figure S6 & Tables S5-S7).

3 Results and discussion

3.1 Long-term trends of O_3 and its precursors

Figure 2 shows trends of monthly-averaged mixing ratios of O_3 and its precursors, namely NO_x, total VOCs (TVOCs) and CO measured at TC in the past 10 years. The TVOCs were defined as the sum of the 22 VOC species listed in Text S1. Note that not all detected VOCs were included in this study because of high rates of missing data. The limited number of VOC precursors would cause missing of reactivity which was estimated < 30% for total hydrocarbons based on our previous study (Guo *et al.*, 2004). The missing reactivity would increase if carbonyls are considered (Cheng *et al.*, 2010). It was found that both monthly-averaged O_3 and monthly maximum O_3 increased with a rate of 0.56 ±0.01 ppbv yr^{-1} (p<0.01) and 1.92 ±0.15 (p<0.05), respectively. The monthly maximum O_3 level, which was defined as the maximum of DMA8 O_3 in one month, increased from about 68 ppbv in 2005 to 86 ppbv in 2014, exceeding the ambient air quality standards in Hong Kong (*i.e.*, 80 ppbv). Besides, the number of days per year (d yr^{-1}) that DMA8 exceeded 80 ppbv also increased during 2005-2014 (1.16 ±0.26 d yr^{-1}, p<0.05, see Figure S7), indicating increasing O_3 pollution in Hong Kong. This finding is consistent with other big cities and regions in the world, such as Beijing (Tang *et al.*, 2009), west plains of Taiwan (Chou, *et al.*, 2006), and Osaka (Itano *et al.*, 2007). The annual average O_3 concentration in Hong Kong has increased by 0.56 ppbv yr^{-1} in 2004-2015 which is close to that reported for Osaka (0.6 ppbv yr^{-1}) in 1985-2002, and in agreement with Lin *et al.* (2017) who found the annual mean O_3 over Hong Kong increased by about 0.5 ppbv yr^{-1} over 2000-2014. In contrast, NO_x and CO significantly decreased with an average rate of -0.71 ±0.01 ppbv yr^{-1} (p<0.01) and -29.4 ±0.05ppbv yr^{-1} (p<0.01), respectively, while TVOCs remained unchanged (p=0.71) in these years. The decreasing trends of NO_x and CO, also observed in many other high population industrial urban areas (Geddes *et al.*, 2009; Tang *et al.*, 2009), suggest effective reduction of local emissions from transportation, power plants and other industrial activities (HKEPD, 2016). Unlike O_3 and NO_x, the trend of TVOCs varied across different areas, for example, increasing in Beijing (Tang *et al.*, 2009), decreasing in Toronto (Geddes *et al.*, 2009) and Taiwan (Chou *et al.*, 2006), while almost remained unchanged (p>0.05) in Hong Kong (Figure 2). Although the 10-year TVOCs trend did not change, their levels showed clear inter-annual variations in spring and autumn (Figure 3). Moreover, the long-term trends of individual VOCs, except for BVOC, were different from that of TVOCs (see Figure S18) because many control measures were taken in the last decade, which altered the composition of VOCs in the atmosphere, such as the reduction of toluene by solvent usage control and the increase of alkanes in Liquefied Petroleum Gas (LPG) in 2005-2013 (Ou *et al.*, 2015) and the decrease of LPG-alkanes in 2013-2014 (Lyu *et al.*, 2016).

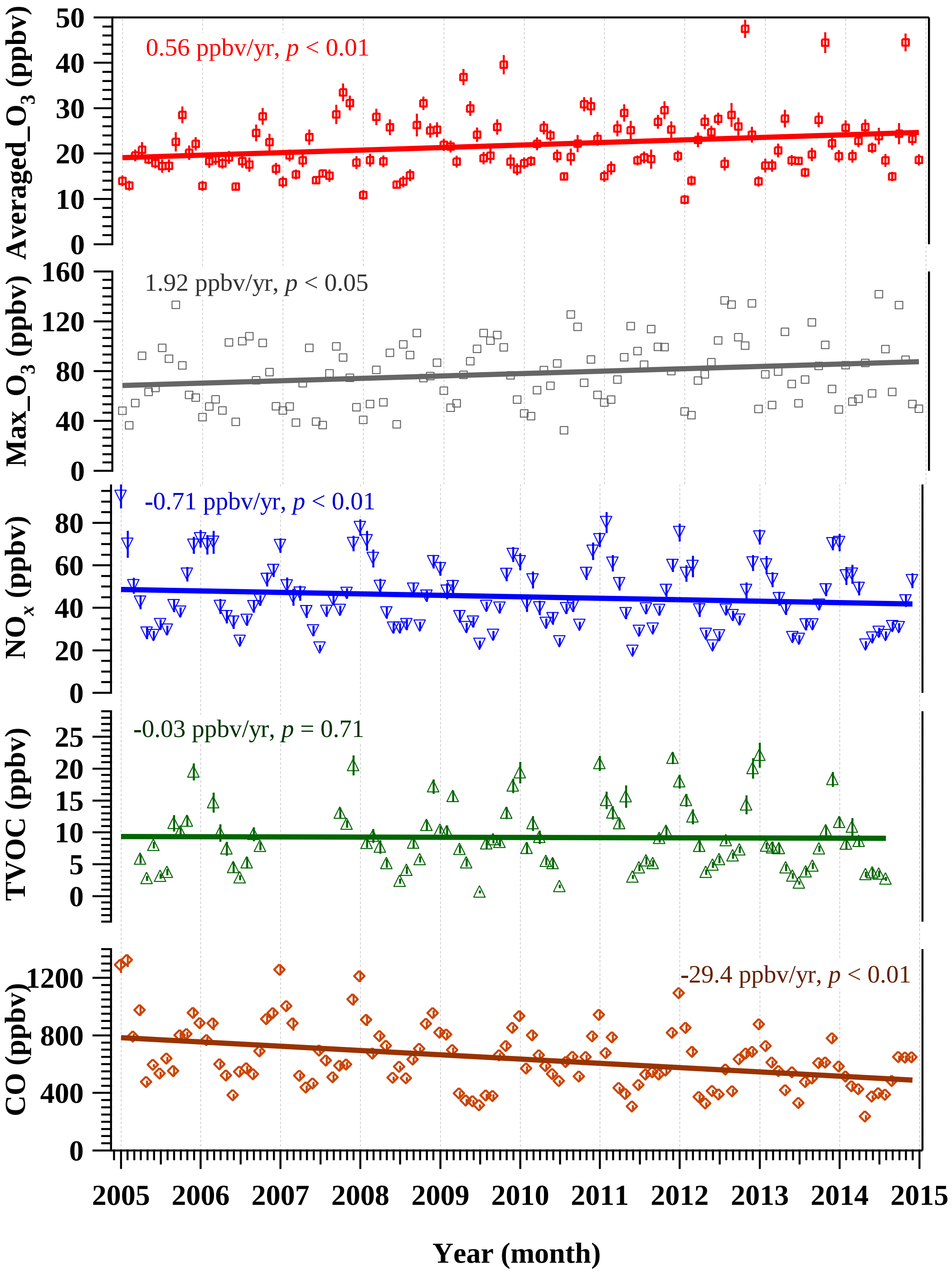

Figure 2. Trends of monthly averages of O_3 and its precursors, *i.e.*, NO_x, TVOCs and CO at TC during 2005–2014. Error bars represent 95% confidence interval of monthly averages.

Figure 3 displays variations of measured O_3 and its precursors (NO_x, TVOCs and CO) in four seasons in 2005-2014. Here we defined December–February, March–May, June–August and September–November as winter, spring, summer and autumn, respectively. Generally, all precursors showed low values in summer and high levels in winter, mainly due to typical Asian monsoon circulations, which brought in clean marine air in summer and delivered pollutant-laden air from mainland China in winter (Wang *et al*., 2009). Subject to this reason, a similar seasonal variation was observed for the averages of TVOCs at different locations over Hong Kong (see Table S8). With lower (diluted) precursor concentrations, together with high frequency of rainy days, it is not uncommon for Hong Kong to see the lowest O_3 values in summertime (see Figure 3).

The long-term trends of CO in all seasons (slopes from spring to winter: -39.2 ±0.20, -16.8 ±0.12, -14.4 ±0.16 and -50.3 ±0.23 ppbv yr^{-1}, respectively) and NO_x and TVOCs in spring (NO_x: -0.69 ±0.01 ppbv yr^{-1}; TVOCs: -0.26 ±0.01 ppbv yr^{-1}) and autumn (NO_x: -0.50 ±0.02 ppbv yr^{-1}; TVOCs: -0.32 ±0.01 ppbv yr^{-1}) showed significant decreases ($p<0.05$), whereas NO_x and TVOCs did not have statistical variations in summer and winter during the 10 years ($p>0.05$). The different inter-annual trends of NO_x and TVOCs in spring/autumn from those in summer/winter were probably because marine air significantly diluted air pollution in summer while continental air masses remarkably burdened air pollution in winter, which concealed the decreased local emissions of NO_x and TVOCs in summer and winter (Wang *et al*., 2009). In contrast, the measured O_3 trends significantly increased in spring, summer and autumn, with the rate of 0.51 ±0.05, 0.50 ±0.04 and 0.67 ±0.07 ppbv yr^{-1}, respectively ($p<0.05$), while winter O_3 levels showed no significant trend (0.23 ±0.05 ppbv yr^{-1}, $p=0.11$). Apart from the impact of regional transport, the increased spring and autumn O_3 in these years was likely due to the reduction of NO titration overrode the O_3 decrease owing to the reduction of TVOCs, leading to net O_3 increase. Here the NO titration refers to the ‘‘titration reaction’’ between NO and O_3. Although NO–NO_2–O_3 reaction cycling (including the effects of NO titration, see reactions R1-R3) can be theoretically regarded as a null cycle and provides rapid cycling between NO and NO_2, the NO titration effect can retard the accumulation of O_3 in an urban environment by means of substantial NO emissions (Chou *et al*., 2006). Indeed, the observed NO at TC site decreased significantly during 2005-2010 (shown in Figure S8), which mitigated the effects of NO titration and led to the increase of O_3.

$$NO_2 + hv \rightarrow NO + O \quad \text{(R1)}$$

$$O + O_2 + M \rightarrow O_3 + M \quad \text{(R2)}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R3)}$$

Interestingly, summer O_3 had a significant increase though NO_x and TVOCs showed no differences in these years. Further investigation found that temperature and solar radiation in summer indeed increased ($p<0.05$) in these years (see Figure S9), whereas they had no significant change in other seasons (the reasons remained unclear), consistent with the fact that the increase of temperature and solar radiation would enhance the photochemical reaction rates, partly resulting in O_3 increase in summer (Lee *et al*., 2014). On the other hand, the unchanged winter O_3 trend was in line with the unchanged NO_x and TVOCs values in winter of past 10 years. Again, the impact of regional transport could not be ignored. To better understand the mechanisms of long-term trends of O_3 in different seasons in this study, the source origins of O_3, *i.e.*, whether it was locally formed or transported from other regions, were explored.

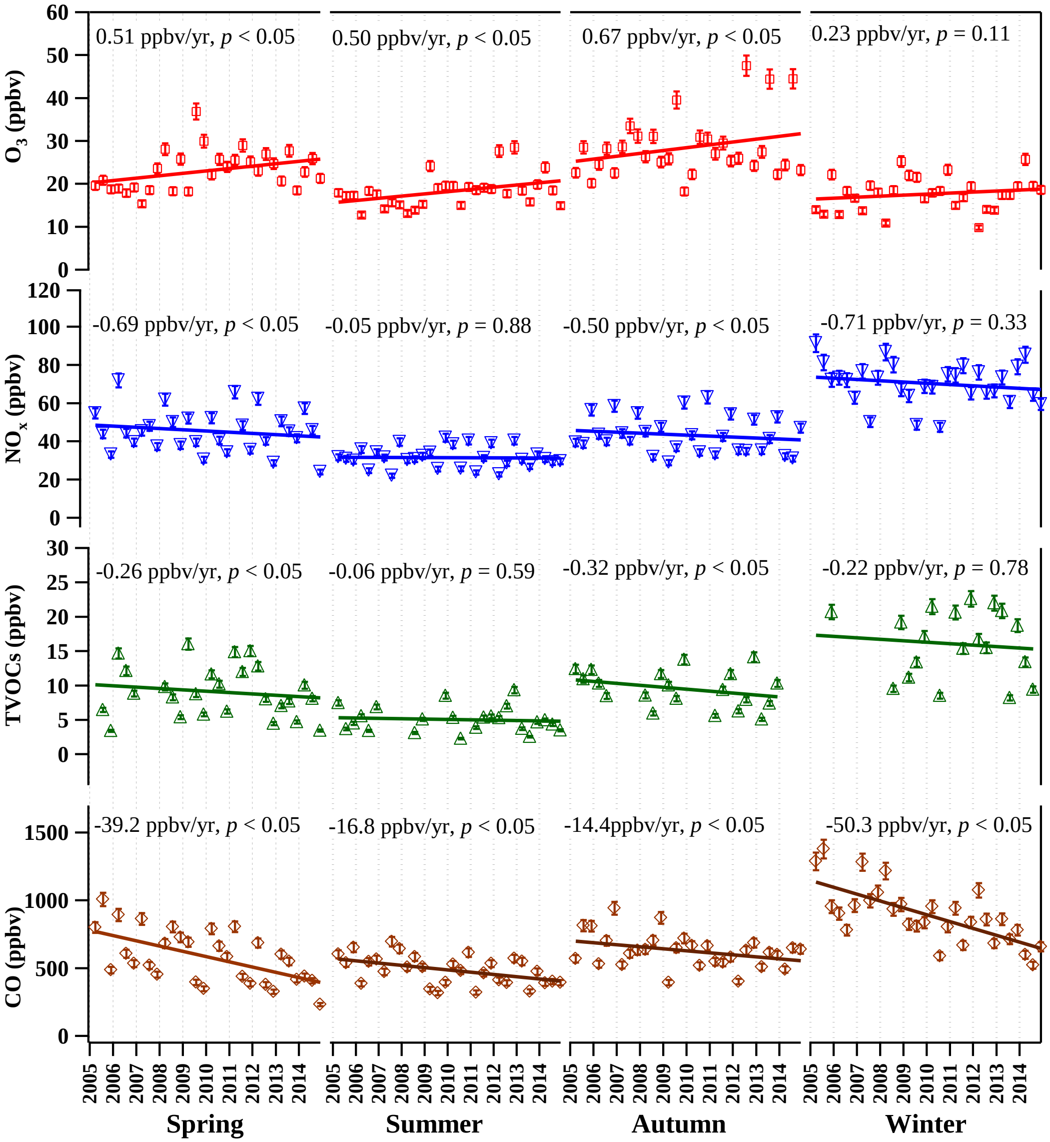

Figure 3. Variations of O_3 and its precursors in four seasons at TC during 2005–2014. Each data point in the figure is obtained by averaging hourly values into a monthly value. Error bars represent 95% confidence interval of the averages. In the sub-plot for O_3 trend in autumn, the three extremely high values are not considered as outliers as each of them represents one month of data with relatively small uncertainty (see Figure S10).

3.2 Long-term trends of locally-produced O_3 and regional contribution

In this study, the OBM (CB05) model was used to simulate the long-term trends of O_3 produced by in-situ photochemical reactions (hereinafter locally-produced O_3 (simulated)). The comparisons of simulated and observed O_3 at TC during 2005–2014 are shown in Figures S11 (by year) and S12 (by month). Besides, Table S9 lists the IOA values between observed and locally-produced O_3 (simulated) at TC site in each year. As shown, the IOA values ranged from 0.71 to 0.89, indicating that the performance of the OBM model on the O_3 simulation was acceptable.

It is noteworthy that MCM has better simulation performance than CB05 due to its near-explicit rather than condensed chemical mechanism. Indeed, the overall IOA of MCM modeling (0.89) was higher than that of CB05 (0.81), according to our test on the same sampling days of 2005-2014 (shown in Figure S13, rainy days were excluded). Despite this, the high computational efficiency OBM (CB05) was used for the 10-year day-by-day O_3 simulations to investigate the long-term trend of O_3 in this study, because the simulated results of both CB05 and MCM models followed similar temporal patterns ($p>0.05$), and the difference of simulated values between the two models was reasonable (IOA value: 0.89 vs. 0.81), revealing that the condensed mechanism of CB05 would not significantly affect the long-term trends of O_3 in this study (shown in Figure S14). Previous studies suggest that wind speed of 2 m/s could be used as a threshold to classify regional and local air masses in Hong Kong (Guo *et al*., 2013; Ou *et al*., 2015; Cheung *et al*., 2014). Namely, the O_3 values measured with < 2 m/s in this study were considered as locally-produced O_3 (hereinafter locally-produced O_3 (filtered)). Figure 4 presents the long-term trends of observed daytime O_3 (0700-1900LT) and locally-produced O_3 (filtered/simulated) in four seasons during 2005-2014. Please note, the trends of observed daytime O_3 in the four seasons were consistent with those of 24-hour observed O_3 (see Figure S15). It can be seen that the locally-produced O_3 (simulated) increased in spring (0.28 ± 0.01 ppbv yr^{-1}, $p<0.05$), decreased in autumn (-0.39 ± 0.02 ppbv yr^{-1}, $p<0.05$) and showed no change in summer and winter ($p>0.05$). Interestingly, the long-term trend of locally-produced O_3 (simulated) in autumn was opposite to that in spring though both NO_x and TVOCs decreased in the two seasons. The reasons were because 1) NO_x decreased faster while TVOCs slower (Figure 3) in spring than in autumn, leading to net increase of O_3 formation in spring and decrease in autumn; and 2) TVOC reactivity (described in Text S2 and Table S10) decreased in autumn ($-0.03\ s^{-1}y^{-1}$, $p<0.05$) but showed insignificant variations in other seasons ($p>0.1$) (Figure S16), resulting in the reduction of O_3 production in autumn. The simulated springtime O_3 increase and unchanged winter values were consistent with the observed trends, whereas the simulated autumn O_3 decrease was opposite to the observed trend for the overall observations. However, locally-produced O_3 (filtered) values clearly showed similar trends to locally-produced O_3 (simulated) in spring, autumn and winter (see Figure 4), confirming that locally-produced O_3 indeed increased in spring and decreased in autumn in these years.

In comparison, a significant difference ($\Delta O_3 = O_3$ overall$_{\text{observed}} - O_{3\ \text{simulated}}$, $p<0.01$) was found between measured and simulated O_3 in spring, implying the contribution of regional transport to the measured O_3. The 10-year average ΔO_3 was 8.26 ± 1.77 ppbv and the long-term trend of ΔO_3 showed no significant change ($p=0.91$), suggesting that the contribution of regional transport in spring was stable during last decade. The spring pattern of O_3 in this study is consistent with the findings of Li *et al*. (2014) who reported the increasing O_3 trend (2.0 ppbv yr^{-1}) in spring at urban clusters of PRD from 2006 to 2011. In conclusion, the increasing O_3 trend in spring at TC was caused by the increased local O_3 production, and the contribution of regional transport was steady in 2005-2014.

Unlike in spring, though the observed and locally-produced O_3 (filtered) displayed increasing trends in summer (0.67±0.34 ppbv yr^{-1} and 0.61±0.41 ppbv yr^{-1}, respectively; $p<0.05$), locally-produced O_3 (simulated) showed no significant change ($p=0.18$), consistent with the unchanged trends of precursors (NO_x and TVOCs) in summer (Figure 3). Note that the influence of annual variation in solar radiation over the 10 years was not considered while the TUV model was used to calculate the photolysis rates, which could mask the actual trends of O_3 mixing ratios. Indeed, the total solar radiation (0.24±0.16 MJ m^{-2} yr^{-1}, $p<0.01$) and temperature (0.095±0.034 K yr^{-1}, $p<0.05$) in summer significantly increased during the past 10 years (see Figure S9), subsequently resulting in the enhanced in-situ photochemical reactivity of VOCs, although their quantitative contributions remain unknown and require further investigation. The increase of solar radiation might be due to the decreasing haze as the air quality has been getting better in Hong Kong and the PRD (Louie *et al*., 2013). Moreover, the summertime wind speeds significantly decreased at a rate of -0.062±0.041 $m \cdot s^{-1} yr^{-1}$ ($p<0.05$), which might accumulate the locally-produced O_3. Lastly, the locally-produced O_3 (filtered) trend was comparable to observed O_3 ($p=0.12$) and locally-produced O_3 (simulated) ($p=0.32$), respectively, indicating a negligible impact of regional transport on summer O_3 trend in 2005-2014 (thereby ΔO_3 in summer not shown in Figure 4). As such, the increasing trend of summer O_3 was partly attributed to the increase of solar radiation and temperature from 2005 to 2014.

Consistent with the decreasing trends of NO_x and TVOCs in autumn, both locally-produced O_3 (simulated) ($p<0.05$) and locally-produced O_3 (filtered) ($p<0.1$) remarkably decreased, suggesting the dominant impact of VOC reduction over the reduction of NO titration. The decreased locally-produced O_3 in autumn was consistent with the results of Xue *et al*. (2014), who found local O_3 production decreased in autumn from 2002 to 2013. Furthermore, the 10-year average ΔO_3 was 7.35±3.16 ppbv and the long-term trend of ΔO_3 increased with a rate of 1.09±0.21 ppbv yr^{-1} ($p<0.05$), suggesting an increased contribution of regional transport in autumn during the last decade, in line with the fact that autumn O_3 level in inland PRD was higher and increased more rapidly than in Hong Kong (Figure 5), and high O_3 mixing ratios were frequently observed in this season due to stronger solar radiation, lower wind speeds, and less vertical dilution of air pollution than in other seasons in this region. In summary, locally-produced O_3 in autumn decreased due to the reduction of dominant VOC precursors, while an increased contribution of regional transport negated the local reduction, leading to an elevated O_3 observation.

In winter, locally-produced O_3 (filtered and simulated) had similar trends ($p=0.93$) and the trends showed no significant changes ($p>0.05$), confirming similar locally-produced O_3 in these years, due to insignificant variations of NO_x and TVOCs levels (Figure 3). Besides, locally-produced O_3 (both filtered and simulated) presented significant difference from the observed O_3 ($p<0.01$), implying the regional contribution in winter. The 10-year average ΔO_3 was 4.56±0.78 ppbv and the long-term trend of ΔO_3 was not significant ($p=0.98$).

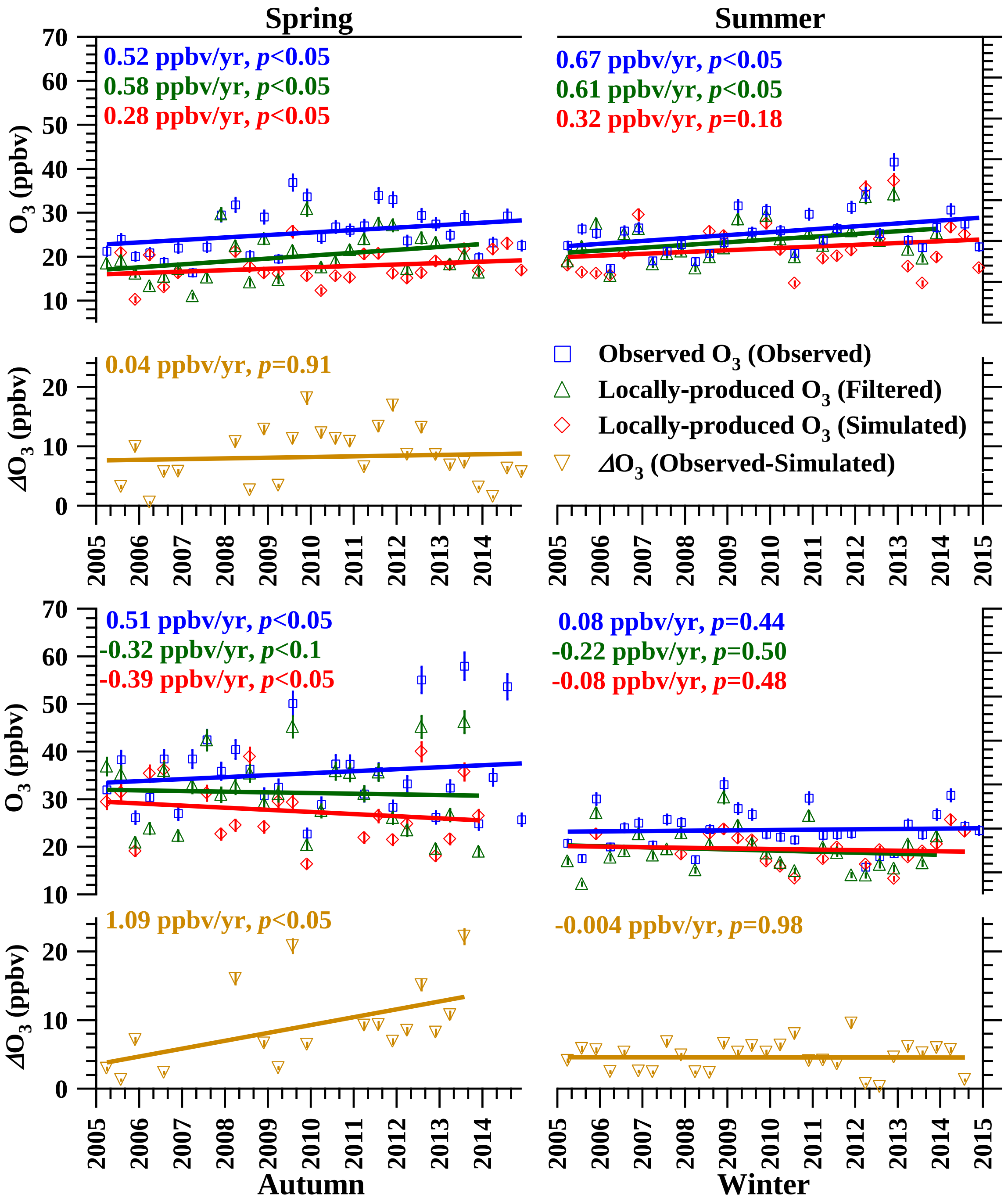

Figure 4. Trends of locally-produced O_3 simulated by OBM (red line), observed O_3 (blue line: overall observed O_3; green line: locally-produced O_3 (filtered), *i.e.*, observed O_3 with hourly wind speed <2 m/s), and regional O_3 (gold line, $\Delta O_3 = O_3$ overall observed – O_3 simulated) in four seasons at TC during 2005–2014. Note: all the data are based on daytime hours (0700-1900 LT). The regional O_3 in summer was negligible and is not shown in the graph. Error bars represent 95% confidence interval of the averages.

To further investigate the regional transport from the PRD region to Hong Kong, the observed O_3 values at PRD sites and at TC site in four seasons during 2006–2014 are compared (Figure 5). Generally, the observed O_3 levels in PRD were all higher than those at TC in four seasons ($p<0.05$). Considering that the PRD is upwind of Hong Kong in spring/autumn/winter (Ou *et al.* 2015), high O_3-laden air in the PRD region could transport to Hong Kong in the three seasons. Moreover, comparable long-term trends were found between the sites in PRD and the TC site in spring (PRD: 0.49 ±0.06 ppbv yr^{-1}; TC: 0.51 ±0.05 ppbv yr^{-1}) and winter (PRD: 0.30 ±0.06 ppbv yr^{-1}; TC: 0.23 ±0.05 ppbv yr^{-1}), indicating that regional transport in spring and winter was stable in these years. In comparison, autumn O_3 level in inland PRD increased (0.84 ±0.08 ppbv yr^{-1}) more rapidly than in Hong Kong (0.67 ±0.07 ppbv yr^{-1}), implying an elevated regional contribution to Hong Kong. Therefore, the differences of observed O_3 between PRD and TC in spring/autumn/winter were consistent with the above calculations of average ΔO_3, confirming regional contribution to the observed O_3 in Hong Kong. In contrast, though the increasing rate of O_3 level in PRD was much faster than at TC in summer, the impact of regional transport from PRD region was insignificant due to the dominance of southerly and southeasterly winds from the South China Sea.

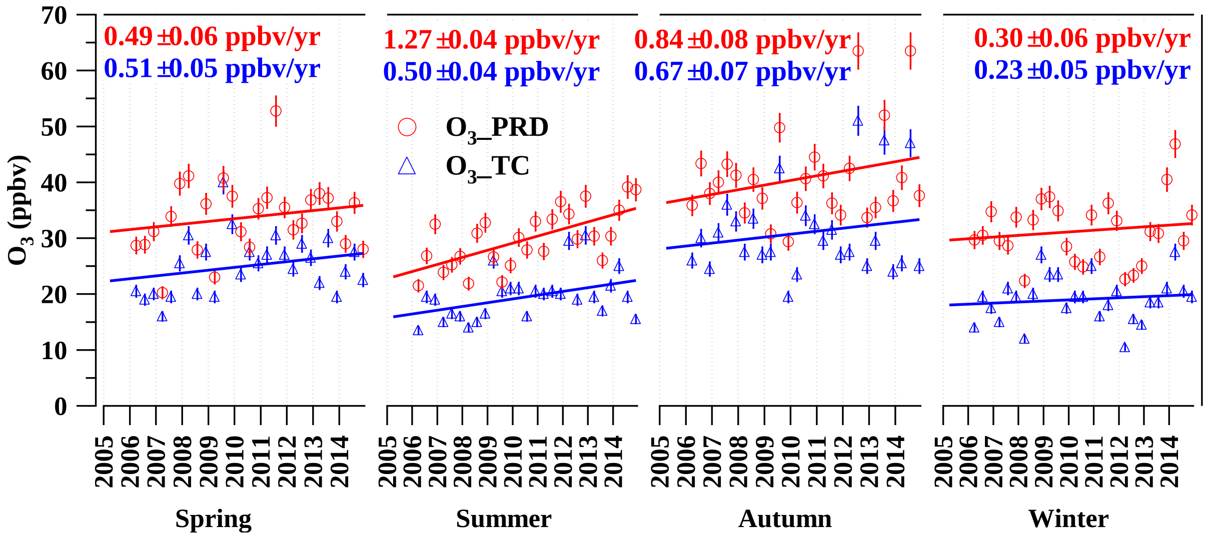

Figure 5. Trends of observed O_3 in inland PRD (red line) and at TC (blue line) in four seasons during 2006–2014. Each data point in the figure is obtained by averaging hourly values into a monthly value. Note: Due to the location of sites which might have O_3 transport to TC (Guo *et al*., 2009), three regional background sites (*i.e*., Wanqingsha, Jinguowan and Tianhu) and an urban site (*i.e*., Haogang) in Dongguan are used for comparison. Error bars represent 95% confidence interval of monthly averages.

Overall, locally-produced O_3 (simulated) in Hong Kong varied by season, showing an increase in spring, a decrease in autumn and no change in summer and winter. The elevated observed O_3 in spring/summer/autumn was mainly attributed to the increase of locally-produced springtime O_3 and constant regional contribution, increased summertime in-situ photochemical reactivity, and regional contribution in autumn. Moreover, since the NO_x and NO levels significantly decreased during the last decade (Figure S8), the reduced effect of NO titration, to a certain extent, made contribution to local O_3 levels. The effect of NO titration has also been reported in other areas (*i.e.*, Beijing, Taiwan, Guangdong Province in China and Osaka in Japan) (Chou *et al*., 2006; Itano *et al*., 2007; Tang *et al*., 2009; Li *et al*., 2014). To confirm the reduction of NO titration in this study, the variation of O_x, the total oxidant estimated by O_3+NO_2 was investigated. According to the reaction of NO titration ($NO+O_3 \rightarrow NO_2+O_2$), the sum of O_3 and NO_2 (*i.e.*, total oxidant O_x) remained essentially constant regardless the variation of NO (Chou *et al*., 2006). Indeed, the mixing ratio of local O_x (filtered by wind speed < 2m/s) showed no significant change (p=0.42) at TC site, during 2005-2013 (Figure 6), suggesting that the increase of O_3 was a result of the reduced NO titration. The reduction of NO titration was also confirmed by the increasing NO_2/NO_x ratio at a roadside site (Mong Kok) in Hong Kong. The NO_2/NO_x emission ratio is a parameter that can be used to examine the variation of NO titration (Carslaw, 2005; Yao *et al*., 2005; Dallmann *et al*., 2011; Tian *et al*., 2011; Ning *et al*., 2012; Lau *et al*., 2015). Generally, higher ratios of NO_2/NO_x mean a lower potential of O_3 titration by NO, resulting in higher O_3. Indeed, the NO_2/NO_x ratio at Mong Kok significantly increased, with an enhanced traffic related NO_2/NO_x ratios observed at night, from 2005 to 2014 (p<0.01), leading to increased local O_3 levels (Figure 7). This finding was supported by the Hong Kong emission inventory, which indicated that the NO_x emission decreased from 1997 to 2014 in Hong Kong (HKEPD, 2016), and studies conducted by Tian *et al.* (2011) and Lau *et al.* (2015), who found an increasing trend of primary NO_2 emission in Hong Kong due to several diesel retrofit programs in 1998-2008.

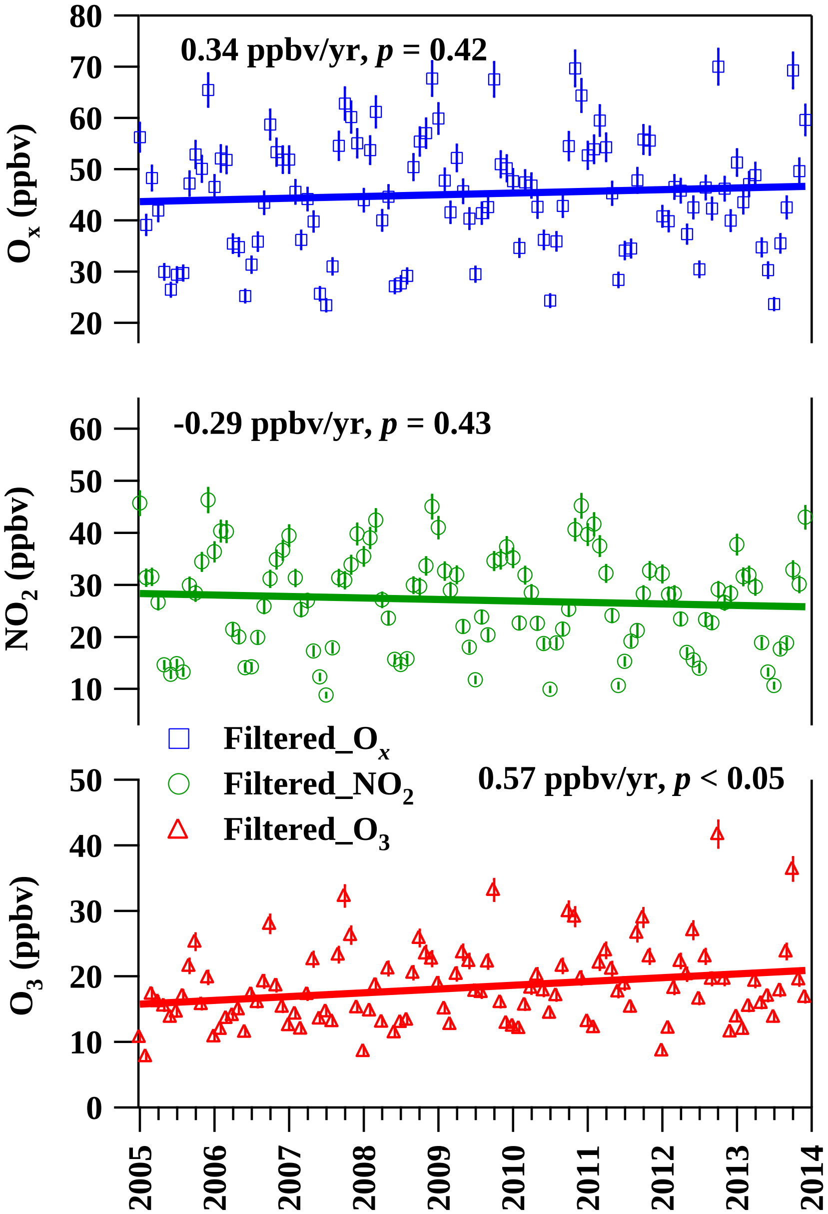

Figure 6. Annual trend of O_x, O_3 and NO_2 (filtered) at TC in 2005–2013. Error bars represent the 95% confidence interval of the averages.

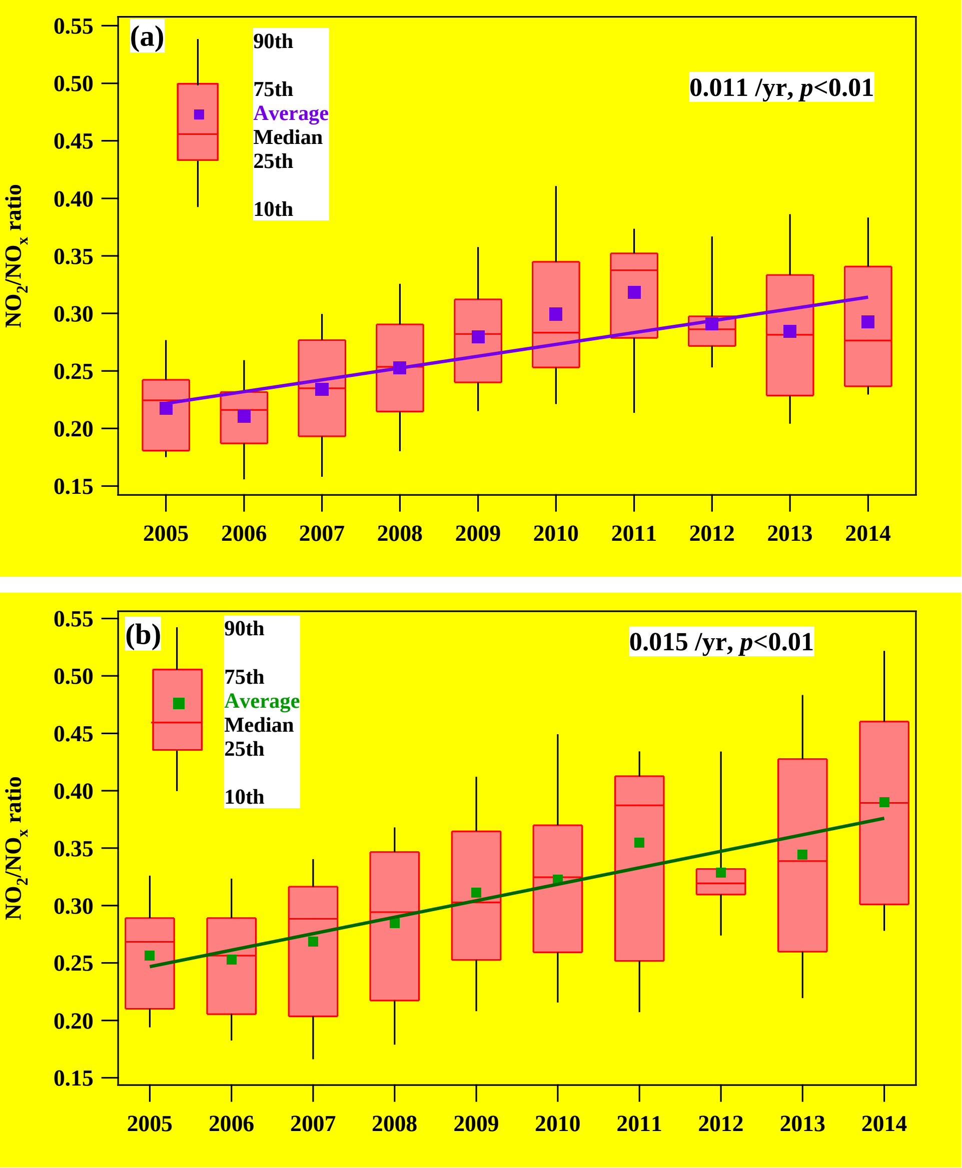

Figure 7. Annual trend of monthly average NO$_2$/NO$_x$ ratio at MK site in daytime **(a)** and night-time **(b)** in Hong Kong in 2005–2014. Hourly observations of NO$_2$ and NO$_x$ are obtained at MK from the HKEPD (http://epic.epd.gov.hk/ca/uid/airdata). Note that data of October in 2014 are excluded due to the impact of Occupy Central event in Hong Kong.

Apart from the regional and local impact on O$_3$ trends, the impact of variations of baseline O$_3$ was also considered. Oltmans *et al*. (2013) reported that O$_3$ at mid-latitudes of the Northern Hemisphere was flat or declining during 1996-2010 and the limited data in the subtropical Pacific suggested very little change during the same period. Thus, the O$_3$ trend in Hong Kong might be unaffected or underestimated given the flat or decline of baseline O_3. Therefore, the increasing trend of O_3 in Hong Kong over the last decade was the integrated influence of its precursors, meteorological parameters and regional transport.

3.3 Ozone - precursor relationships

Ozone - precursor relationships are critical to determine the reduction plan of precursors for future O_3 control. In this study, the RIR of major O_3 precursors was calculated by the OBM, to directly reflect the O_3 alteration in response to the percentage changes of its precursors (see Section 2.3). Furthermore, the long-term trend of RIR was used to evaluate the variation of the sensitivity of O_3 formation to each individual precursor. Figure 8(a) shows the average RIR values of O_3 precursors in the four seasons during the last decade. The RIR values of TVOCs (AVOC+BVOC, where AVOC = anthropogenic VOC and BVOC = biogenic VOC, see Section 3.4 for the definition of BVOC) ranged from 0.78 ±0.04 to 0.89 ±0.04, followed by CO (0.32 ±0.01 to 0.37 ±0.01) in all seasons, suggesting the dominant role of TVOCs in photochemical O_3 formation. Among TVOCs, AVOCs had their highest RIR value in winter (0.80 ±0.03, $p<0.05$) and lowest in summer (0.39 ±0.02, $p<0.05$). Since RIR values are highly dependent on precursor mixing ratios (Eq. 5), the difference of RIR values of AVOCs in the four seasons was mainly caused by seasonal variations of observed AVOC levels (Figure 3). In contrast, BVOCs had the highest RIR in summer (0.47 ±0.02, $p<0.05$), followed by autumn, spring and winter (0.30 ±0.02, 0.28 ±0.02 and 0.09 ±0.01, respectively). The higher RIR of BVOCs in summer was mainly due to the higher biogenic emissions in summer. In addition, higher photochemical reactivity of BVOCs also contributed to higher RIR of BVOCs (Atkinson and Arey, 2003; Tsui *et al*., 2009). The RIR values of NO_x, in contrast, were negative in all seasons, indicating that reducing NO_x would lead to an increase of photochemical O_3 formation. The RIR values of NO_x were lower in spring (-1.15 ±0.02) and summer (-1.22 ±0.02) than in autumn (-1.05 ±0.02) and winter (-1.00 ±0.01, $p<0.05$), suggesting that reducing NO_x would increase more O_3 in spring and summer. The aforementioned findings were consistent with the results of previous studies conducted in autumn in Hong Kong, which were based on modeled and observed VOC/NO_x ratios (Zhang *et al*., 2007; Cheng *et al*., 2010; Ling *et al*., 2013; Guo *et al*., 2013). The relationship analyses suggests that the O_3 formation in Hong Kong was VOC-limited in all seasons in these years; that is, the O_3 formation was dominated by AVOCs in winter and was sensitive to both AVOCs and BVOCs in the other three seasons, whereas reducing NO_x emissions enhanced O_3 formation, more so in spring and summer. The findings suggest that simultaneous cut of AVOCs and NO_x (which is often the case in real situation) would be most effective in O_3 pollution control in winter, but least efficient in summer.

Figure 8(b) presents the long-term trends of RIR values of O_3 precursors from 2005 to 2014. The RIR values of TVOCs and NO_x increased at an average rate of 0.014 ±0.012 yr^{-1} ($p<0.05$) and 0.009 ±0.01 yr^{-1} ($p<0.05$), respectively, while the RIR of CO decreased at an average rate of -0.014 ±0.007 yr^{-1} ($p<0.01$). The evolution of RIR values suggested that the O_3 formation was more sensitive to TVOCs and less to CO and NO_x, indicating that VOCs reduction strategies would be more effective on O_3 control. The decreasing sensitivities of both CO and NO_x to O_3 formation were consistent with the decrease of their mixing ratios during the last decade. The sensitivity of O_3 formation to TVOCs increased although the 10-year levels of TVOCs showed no significant trend, which might be attributed to the variations of speciated VOC levels and the VOC/NO_x ratios in these years (Ou *et al*., 2015). Furthermore, the monthly variation of VOC/NO$_x$ ratios showed a significant decreasing trend at a rate of -0.02 yr^{-1} (p<0.05) (see Figure S17), indicating that VOC reduction became more effective in reducing O$_3$ in the past 10 years, which is consistent with the conclusions from the above modeling results.

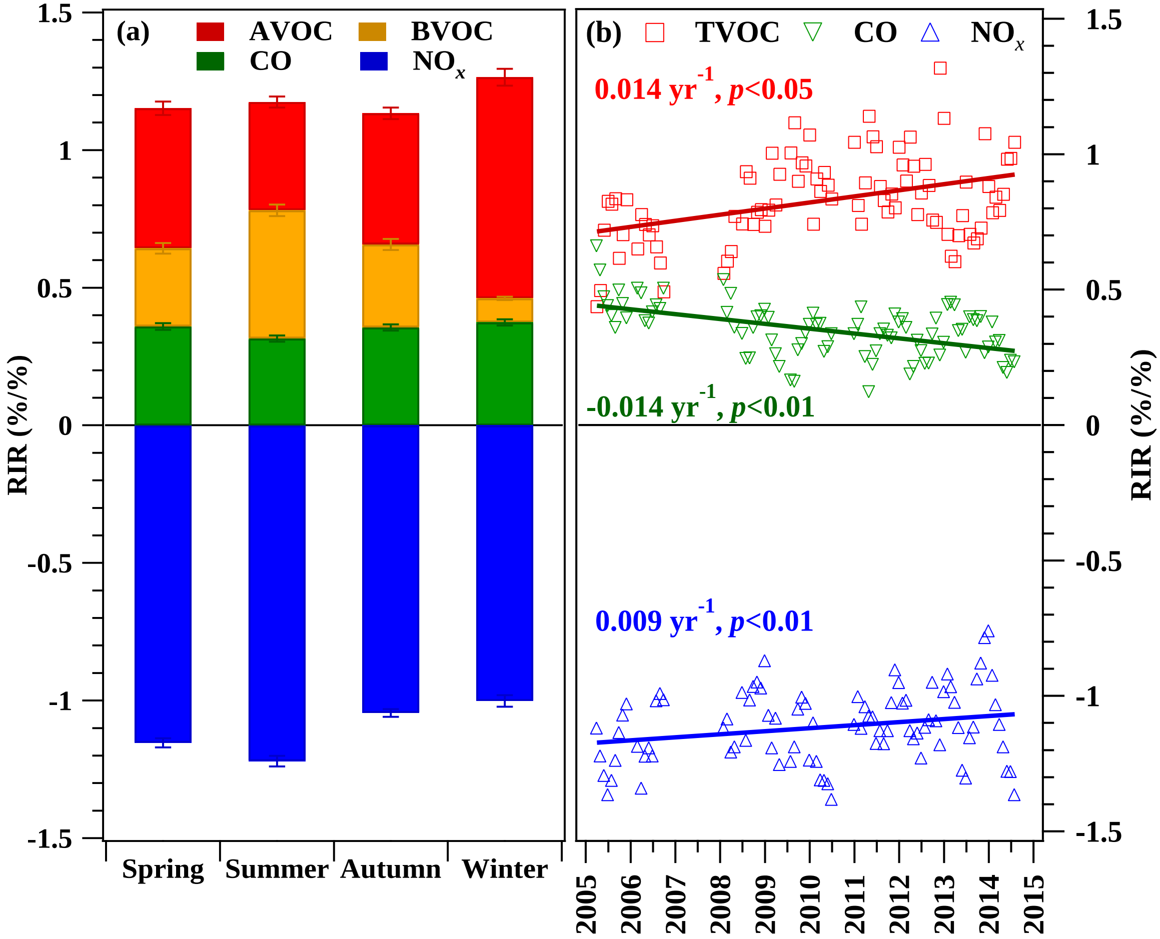

Figure 8. (a) Average RIR values of O$_3$ precursors in the four seasons; and (b) Trends of RIR values of O$_3$ precursors at TC from 2005 to 2014. AVOC represents anthropogenic VOCs, including 20 VOC species. BVOC means biogenic VOCs, including isoprene. Note: all the data are based on daytime hours (0700-1900 LT).

3.4 Contribution of VOC groups to O$_3$ formation

Since the local O$_3$ production was VOC-limited in Hong Kong, it is important to study the contribution of VOC species to the O$_3$ formation. To facilitate analysis and interpretation, AVOC species were categorized into three groups, namely, AVOC (Aromatics) (including benzene, toluene, *m/o*-xylenes, ethylbenzene and three trimethylbenzene isomers), AVOC (Alkenes) (including propene, three butene isomers and 1, 3-butadiene) and AVOC (Alkanes) (including propane, *n/i*-butanes, *n/i*-pentanes, *n/i*-hexanes and *n*-heptane). It is noteworthy that C_2 hydrocarbons were not included in the groups due to high missing rates of the C_2 data The variations of the daytime averaged contributions of four VOC groups (i.e., AVOC (Alkanes/Alkenes/Aromatics) and BVOC) to O_3 mixing ratios were calculated by OBM and shown in Figure 9. Two scenarios were selected for data analysis. The first scenario was "origin", which used all originally measured data as input. The second scenario was "AVOC (Aromatics/Alkenes/Alkanes) or BVOC group", which excluded each of the four VOC groups in turn from the input data in the "origin" scenario. Hence, the contributions of VOC groups ((AVOC (Aromatics/Alkenes/Alkanes) and BVOC) were obtained from the difference of simulated O_3 between the scenario "origin" and the related "VOCs group (AVOC (Aromatics/Alkenes/Alkanes) or BVOC))". Clearly, the contribution of AVOC (Aromatics) to O_3 mixing ratios significantly decreased with an average rate of -0.23±0.01 ppbv yr^{-1} ($p<0.05$), while AVOC (Alkenes) made increasing contribution to O_3 mixing ratio ($p<0.05$), and BVOC and AVOC (Alkanes) showed no significant changes ($p>0.05$). The decreased contribution of AVOC (Aromatics) to the O_3 mixing ratio was likely due to the decrease of C_6-C_8 aromatics, consistent with previous studies which found that aromatic levels decreased during 2005-2013 in Hong Kong (Ou *et al*., 2015). In fact, the Hong Kong Government has implemented a series of VOC-control measures since 2007 (HKEPD, 2016). From April 2007, the Air Pollution Control (VOCs) Regulation was implemented to control VOC emissions from regulated products, including architectural paints/coatings, printing inks and six selected categories of consumer products. In January 2010, the regulation was extended to control other high VOC-containing products, namely vehicle refinishing paints/coatings, vessel and pleasure craft paints/coatings, adhesives and sealants. The reduced contribution of AVOC (Aromatics) to O_3 formation in these years also agreed well with the decreasing O_3 production rate of aromatics in autumn at TC from 2002 to 2013 reported by Xue *et al*. (2014). Furthermore, source apportionment results from Lyu *et al*. (2017) showed that solvent related VOCs decreased at a rate of 204.7±39.7 pptv yr^{-1} at TC site, confirming that the reduction of solvent usage in these years was effective in decreasing the contribution of aromatics to the O_3 production.

In contrast, the contributions of AVOC (Alkenes) to O_3 production in these years showed a significant increasing trend with a rate of 0.14±0.01 ppbv yr^{-1} ($p<0.05$), perhaps attributed to the increased emissions of alkenes from traffic related sources. During 2005-2014, the Hong Kong government launched a series of measures to reduce vehicular emissions, including diesel, LPG and gasoline vehicles (http://www.epd.gov.hk/epd/english/environmentinhk/air_/prob_solutions/air_problems.html). Among the measures, the diesel commercial vehicle (DCV) program (2007-2013) was shown to be effective in reducing the emission of alkenes from diesel vehicles (Lyu *et al*., 2017). However, gasoline and LPG vehicular emissions caused ambient alkenes to increase during the same period due to the increasing of number of LPG/gasoline vehicles and some short-term/non-mandatory measures (Lyu *et al*., 2017). In consequence, the overall emissions of alkenes from traffic related sources increased during 2005-2014, leading to the increased contribution of AVOC (alkenes) to O_3 formation (Lyu *et al*., 2017).

Unlike AVOC (Aromatics/Alkanes), the contribution of AVOC (Alkanes) to O_3 formation during 2005-2014 showed no significant change ($p=0.23$), perhaps due to their low photochemical reactivities (see Table S10) despite the increase of total alkane levels in the atmosphere in 2005-2013 (Ou *et al*., 2015), and the decrease of LPG-related alkanes in 2013-2014 (Lyu *et* *al.*, 2016). In addition, the seasonal variation of O_3 formation, of which the reaction rates of alkanes with OH radicals were high in summer and low in winter, would also blur the trend.

Furthermore, BVOC showed no evident change in the contribution to O_3 mixing ratios during the last decade ($p=0.57$), which was likely attributed to the no significant change of isoprene levels at TC site during 2005-2014 (shown in Figure S18). In this study, isoprene was defined as biogenic VOCs. The main known sources of isoprene are biogenic and anthropogenic (Borbon *et al*. 2001; Barletta *et al*., 2002; Reiman *et al*., 2000). It is noteworthy that according to the tunnel study in Hong Kong (Ho *et al*., 2009), vehicular emissions of isoprene are not significant in this city. Another tunnel study in the PRD region (Tsai *et al*., 2006) found that isoprene was not present in diesel-fueled vehicular emissions in Hong Kong, likely related to variations of fuel types and vehicular engines used in different countries (Ho *et al*., 2009). In addition, in low latitude areas like Hong Kong, with a high level of plant coverage (more than 70%), isoprene is mainly produced by biogenic emissions. The source of isoprene at TC site has been also investigated and confirmed by previous long-term source appointment studies, which reported that during 2005-2013 about 90% of isoprene was emitted from biogenic emissions and the contribution of traffic sources was not significant (<5%) (Ou *et al*., 2015). Therefore, in this study the traffic sources of isoprene in Hong Kong was disregarded and isoprene was defined as biogenic VOCs.

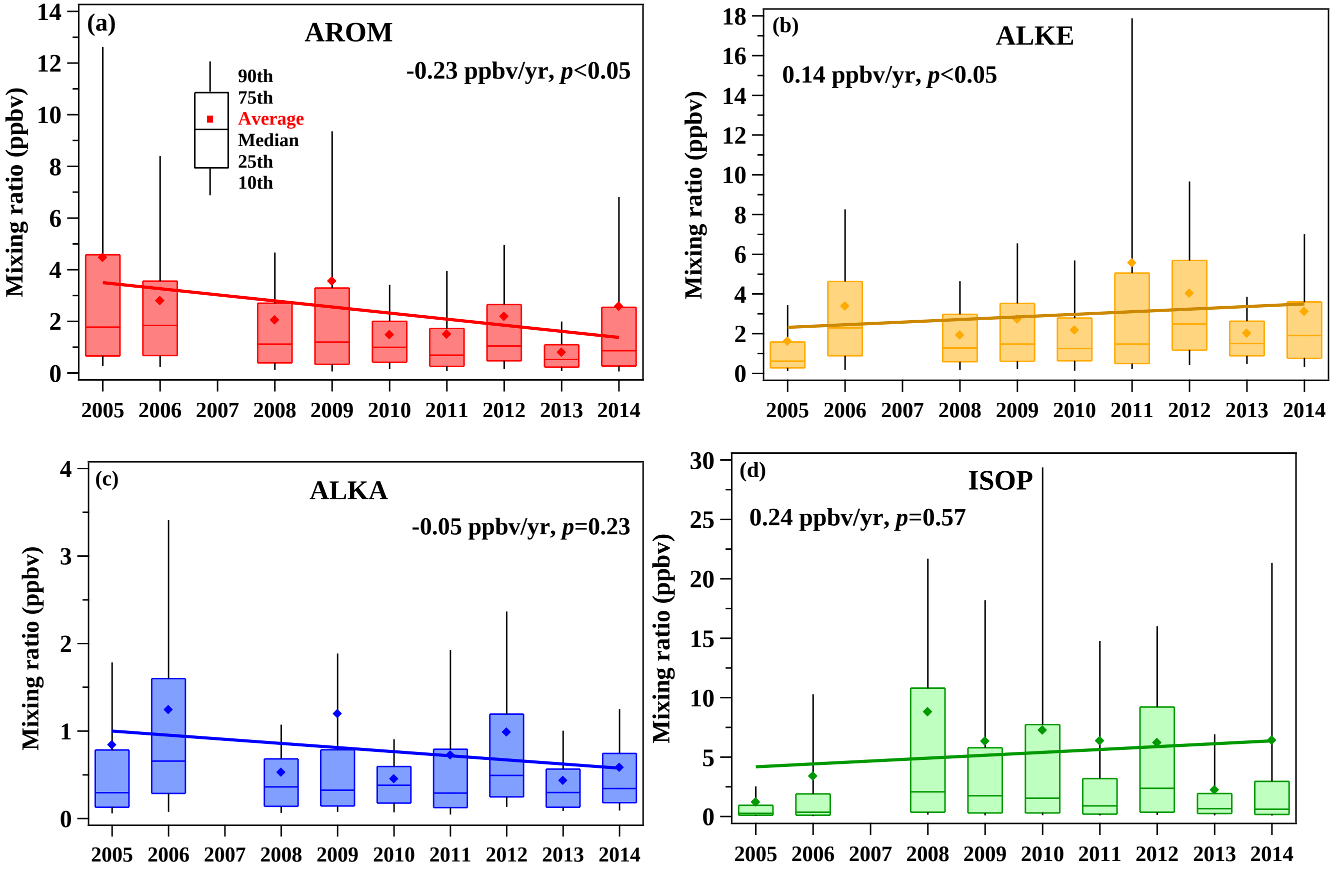

Figure 9. Trends of the daytime averaged contribution of four VOC groups to O_3 mixing ratio: (a) AVOC (Aromatics), (b) AVOC (Alkenes), (c) AVOC (Alkanes) and (d) BVOC at TC during 2005–2014.

4 Conclusions

In this study, the long-term trends of O_3 and its precursors (NO_x, TVOCs and CO) were analyzed at TC from 2005 to 2014. It was found that NO_x and CO decreased while TVOCs remained unchanged, suggesting the effective reduction of some emissions in Hong Kong. However, ambient O_3 levels increased in these years and the locally-produced O_3 showed different variations in the four seasons, reflecting the complexity of photochemical pollution in Hong Kong. To effectively control locally-produced O_3, VOC control plays a vital role, since O_3 formation in Hong Kong was shown to be VOC-limited in these years. Moreover, trend studies found that the sensitivity of O_3 formation gradually increased with VOCs and decreased with NO_x and CO, indicating that controlling VOCs will be increasingly effective for O_3 control in the future. Among the VOCs, the contribution of aromatics to O_3 formation decreased from 2005-2014, consistent with their declining abundance over this period and implying effective control measures of solvent-related sources. By contrast, the contribution of anthropogenic alkenes increased, suggesting a continuing need for the control of traffic-related sources. In addition, of the four seasons, the highest AVOC sensitivity and relatively low NO_x sensitivity to O_3 formation concurrently appeared in winter, suggesting that winter is the best time for O_3 control. Lastly, in addition to locally-produced O_3, regional transport of O_3 from the PRD region made a substantial contribution to ambient O_3 in Hong Kong and even increased in autumn. In the future, the Hong Kong government should collaborate closely with Guangdong province to mitigate O_3 pollution in this region.

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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*/*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):

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

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 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	6.73 ±1.8	5.89 ±1.71	5.56 ±1.66	8.18 ±2.24
Propane	666.33 ±22.88	193.75 ±18.63	841.16 ±22.11	1444.59 ±30.14
Propene	68.65 ±3.24	18.77 ±2.09	62 ±3.82	175.59 ±6.13
***n*-Butane**	331.36 ±18.23	175.87 ±17.13	399.96 ±15.83	682.38 ±25.07
***i*-Butane**	253.15 ±11.51	116.7 ±11.27	309.77 ±10.98	549.66 ±17.08
1-Butene	6.73 ±0.78	3.03 ±0.76	20.96 ±1.98	26.59 ±2.49
***trans*-2-Butene**	6 ±0.88	3.04 ±0.77	5.76 ±1.06	15.71 ±1.75
***cis-2*-Butene**	4.14 ±0.57	2.7 ±0.72	24.23 ±2.09	17.9 ±1.8
1,3-Butadiene	6.49 ±0.83	2.22 ±0.54	11.97 ±1.76	22.05 ±1.52
***n*-Pentane**	115.98 ±7.74	64.34 ±7.72	121.87 ±5.9	177.07 ±6.48
***i*-Pentane**	192.06 ±9.5	122.53 ±12.05	228.66 ±8.02	300.24 ±8.96
***n*-Hexane**	138.87 ±8.98	53.85 ±5.63	87.7 ±6.28	295.35 ±19.74
***i*-Hexane**	36.22 ±5.66	18.72 ±5.39	50.39 ±9.4	84.59 ±7.11
***n*-Heptane**	24.38 ±2.47	12.73 ±1.44	16.45 ±3.31	41.84 ±5.28
Benzene	279.94 ±8.35	68.04 ±2.88	399.86 ±7.69	872.04 ±20.71
Toluene	497.33 ±22.41	114.85 ±11.1	657.38 ±23.93	1337.9 ±52.09
Ethylbenzene	80.38 ±5.82	18.98 ±2.56	119.87 ±6.76	246.93 ±12.52
***m/p*-Xylene**	78.13 ±7.85	20.57 ±3.1	161.13 ±11.08	316.45 ±19.02
***o*-Xylene**	23.14 ±2.81	9.46 ±1.85	40.92 ±3.31	85.85 ±5.89
1,2,3-Trimethylbenzene	1.72 ±0.2	1.96 ±0.3	1.51 ±0.01	2.55 ±0.42
1,2,4-Trimethylbenzene	2.85 ±0.43	3.22 ±1.12	3.17 ±0.57	8.28 ±1.31
1,3,5-Trimethylbenzene	1.91 ±0.2	1.81 ±0.22	1.71 ±0.18	1.88 ±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

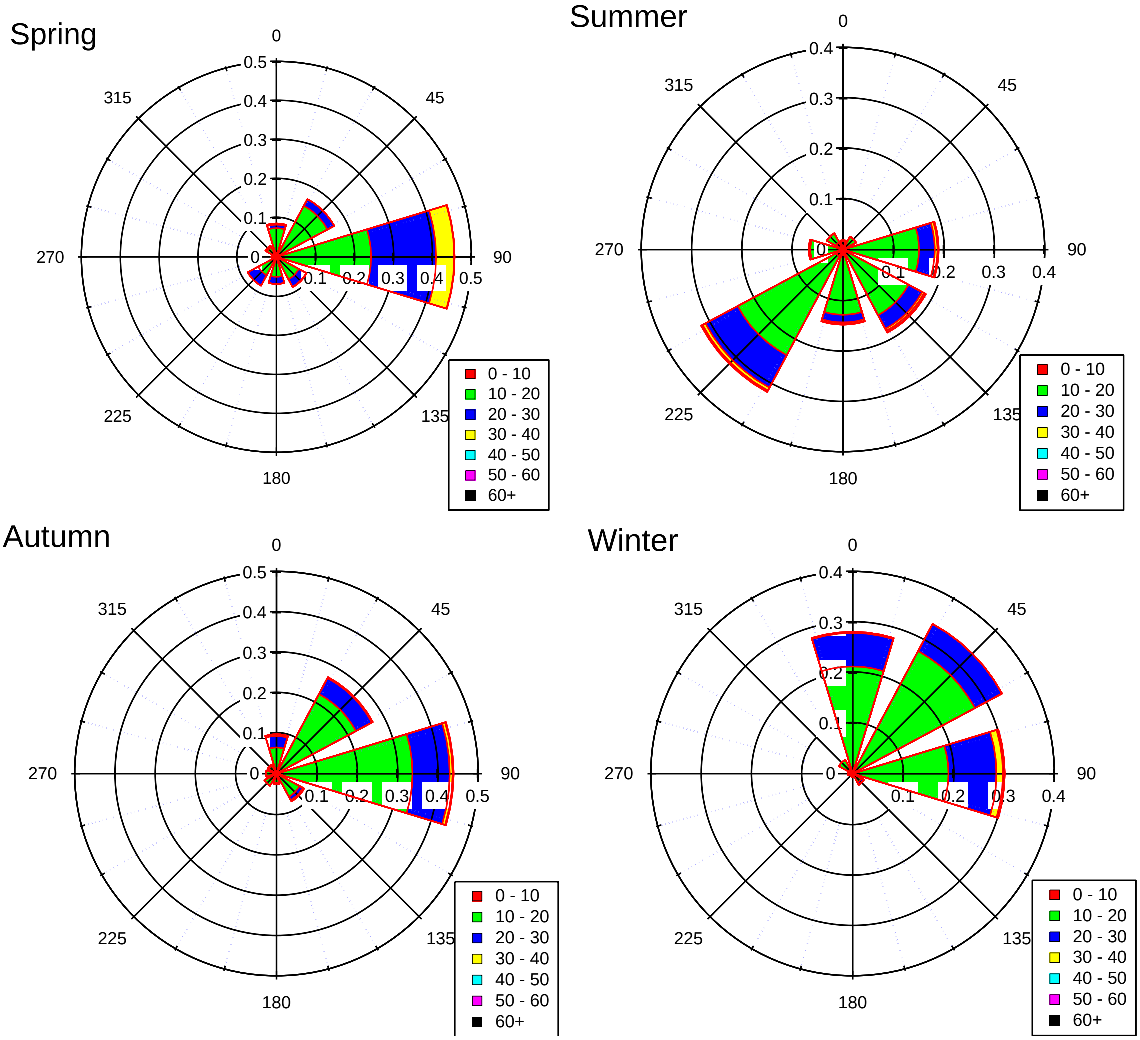


Figure S1. Wind rose plots showing prevailing winds in Hong Kong for each season. The daily data of 2005-2014 is obtained from the Hong Kong airport (https://www.wunderground.com). Colour indicates wind speed (unit: km h^{-1}).

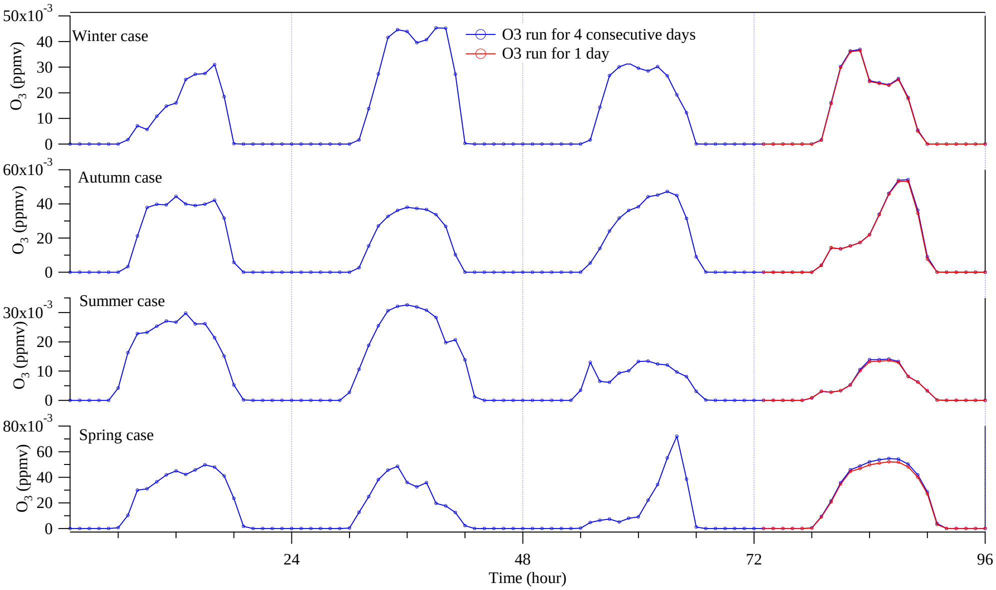


Figure S2. Comparison of O_3 production simulated by with (blue line) or without (red line) a 4-day "spin-up" time in different seasons. In the tests, four days data were randomly selected from each season in 2012 as an example. The results demonstrate that the method without the "spin-up" time indeed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

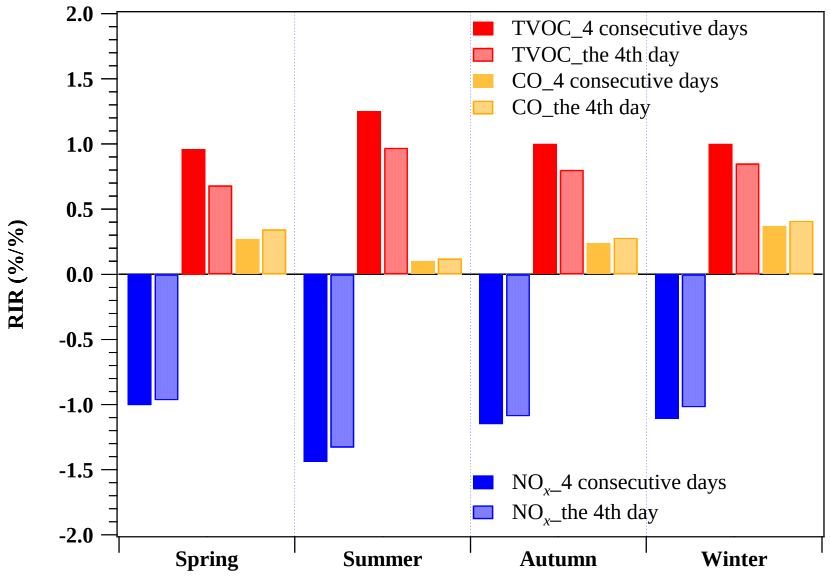


Figure S3. Comparison of RIR calculated by with (solid bar) or without (light bar) a 4-day "spin-up" time in different seasons. In the tests, one-day data was randomly selected from each season in 2012 as an example. It shows that the approach (without spin-up time) systematically underestimates the 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.

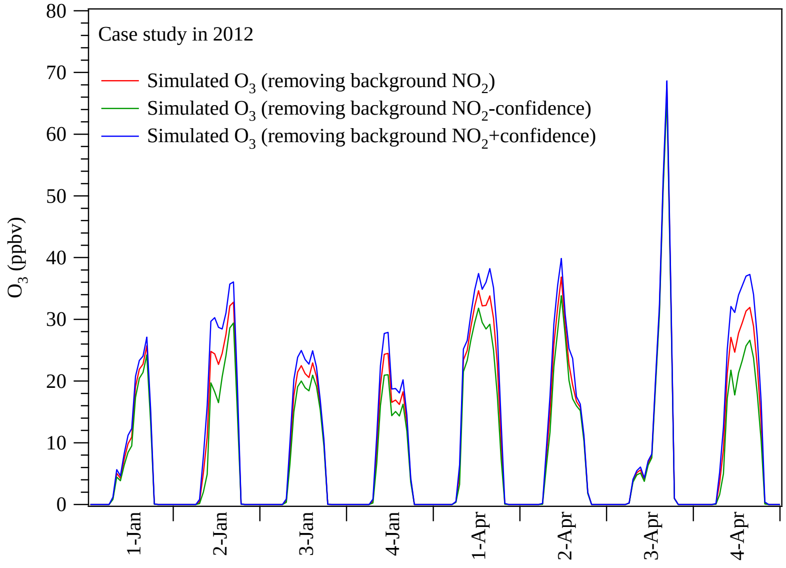


Figure S4. Comparison of locally-produced O_3 (simulated) at TC site in spring and winter with input of varying initial concentrations of NO_2 by subtracting the mean background NO_2 (red line), the mean background NO_2 plus 95% confidence intervals (C.I, blue line), and the mean background NO_2 minus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

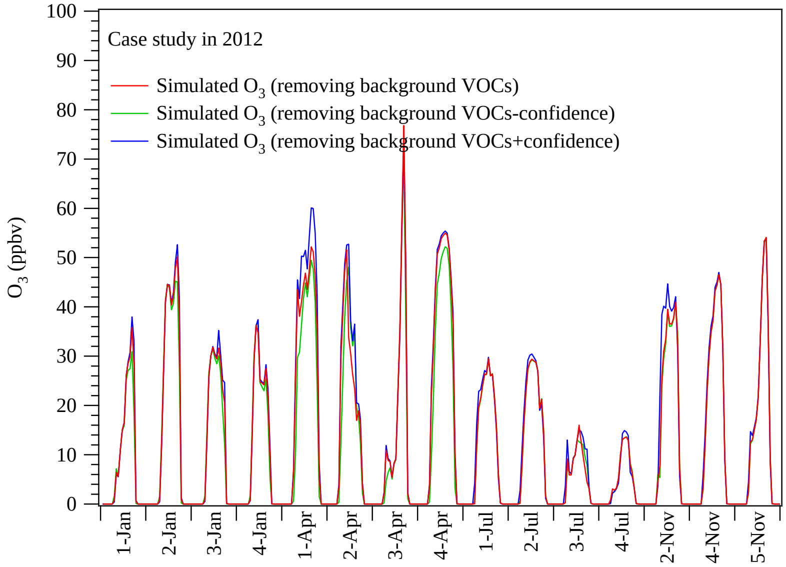


Figure S5. Comparison of locally-produced O_3 (simulated) at TC site over the year with input of varying initial concentrations of VOCs by subtracting the mean background VOCs (red line), the mean background VOCs plus 95% confidence intervals (C.I, blue line), and the mean background VOCs minus 95% C.I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

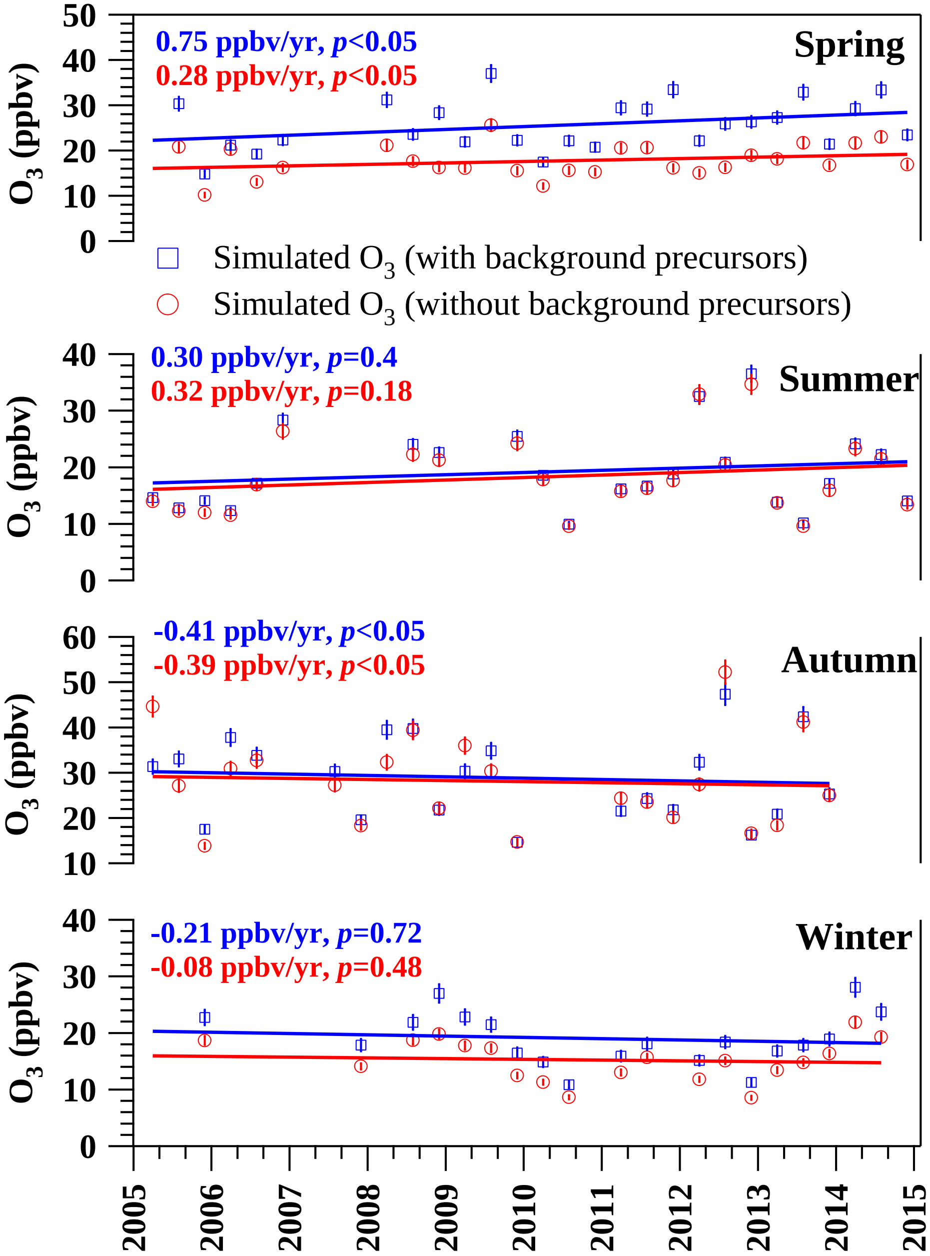


Figure S6. Annual trends of simulated local O_3 production (blue line: with background precursors; red line: without background precursors) in four seasons at TC during 2005–2014. Error bars represent 95% confidence interval of the averages.

5

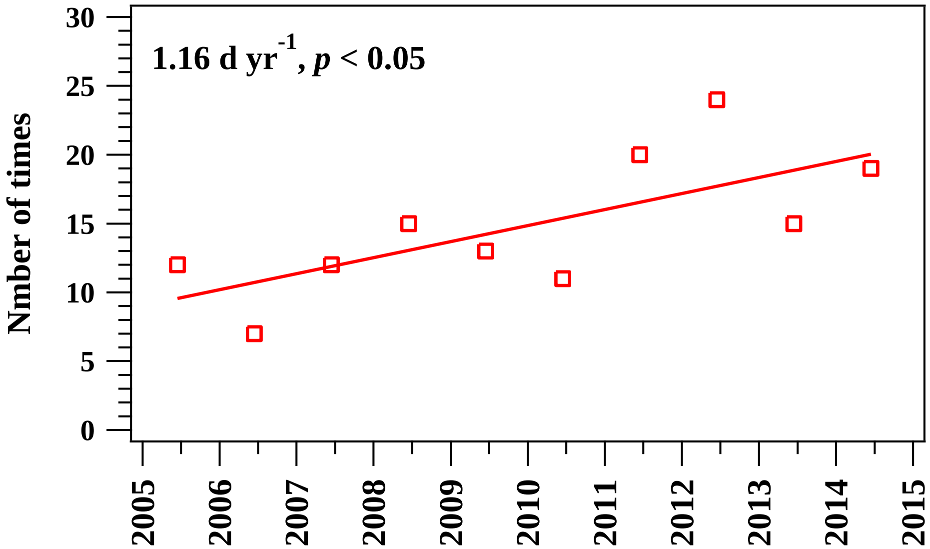


Figure S7. Annual trend of number of days per year that the daily 8-hour O_3 maximum (DMA8) exceeded 80 ppbv at TC during 2005–2014.

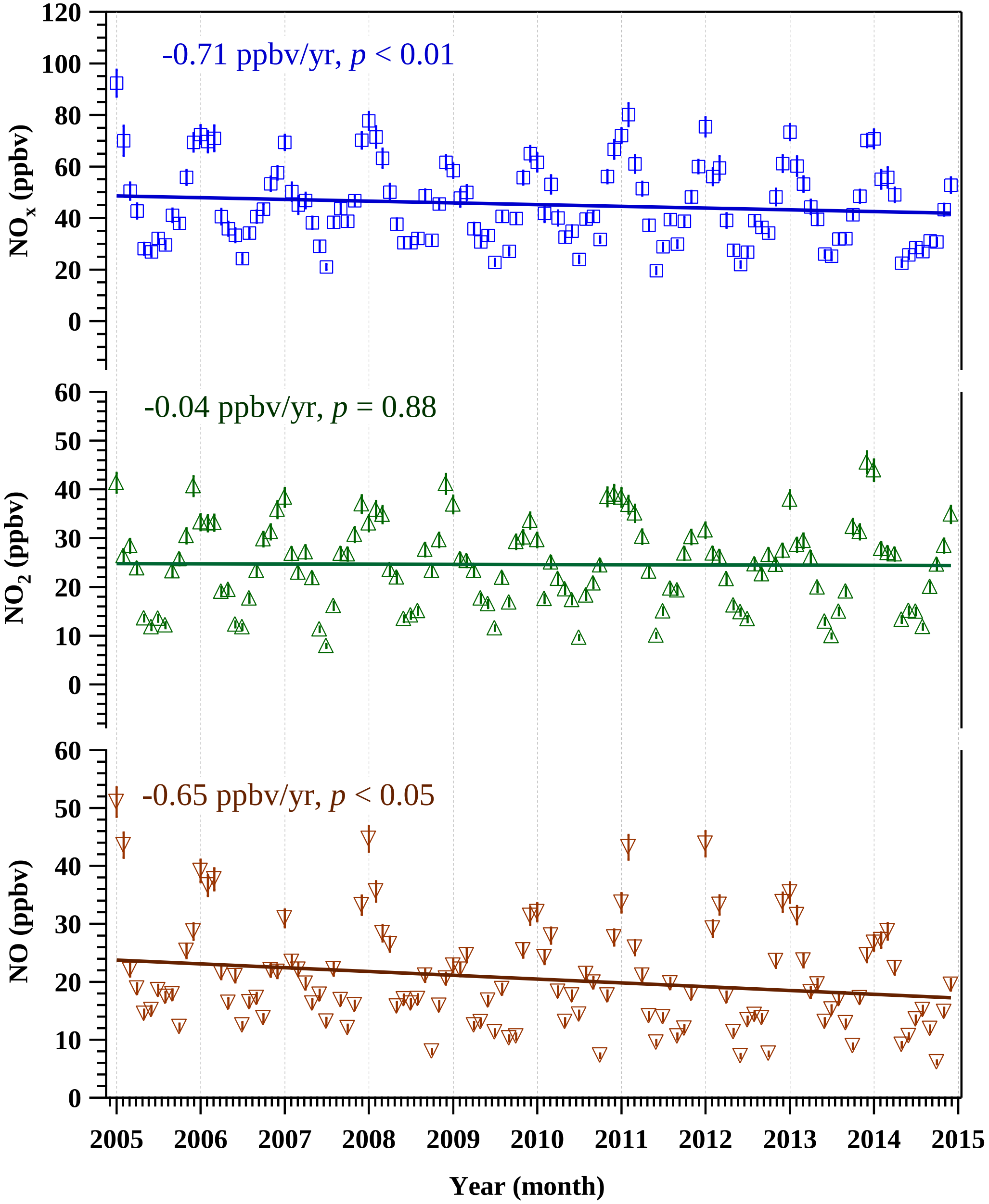


Figure S8. Trends of monthly averages of NO_x, NO_2 and NO at TC during 2005–2014. Error bars represent 95% confidence interval of monthly averages.

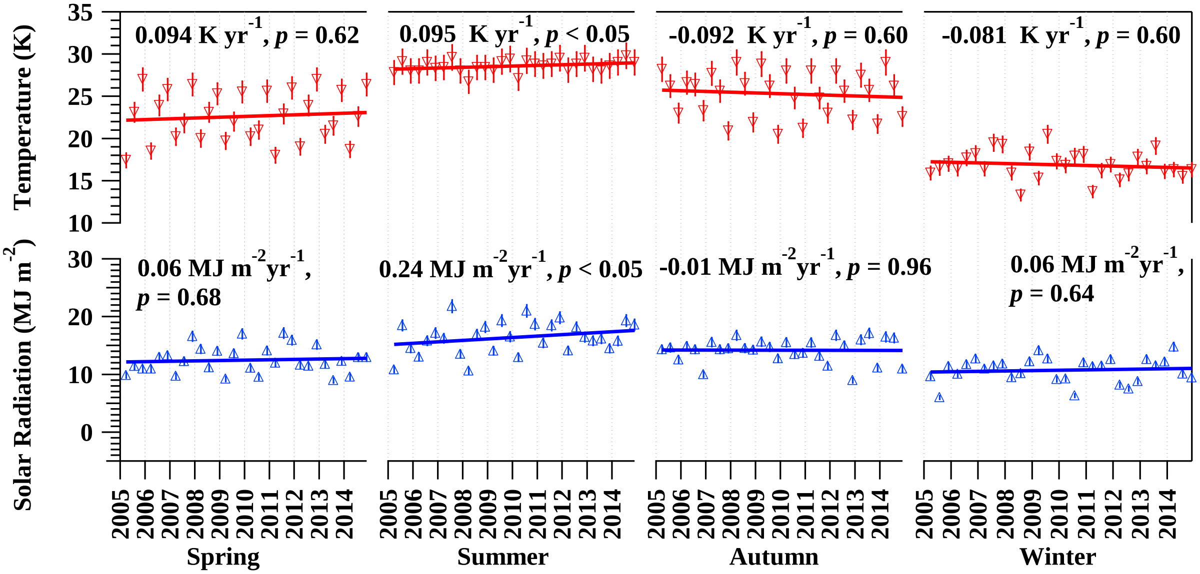


Figure S9. Variations of temperature (red) and solar radiation (blue) for the four seasons at TC during 2005–2014. Each data point in the figure is obtained by averaging hourly values into a monthly value. Error bars represent 95% confidence interval of monthly averages.

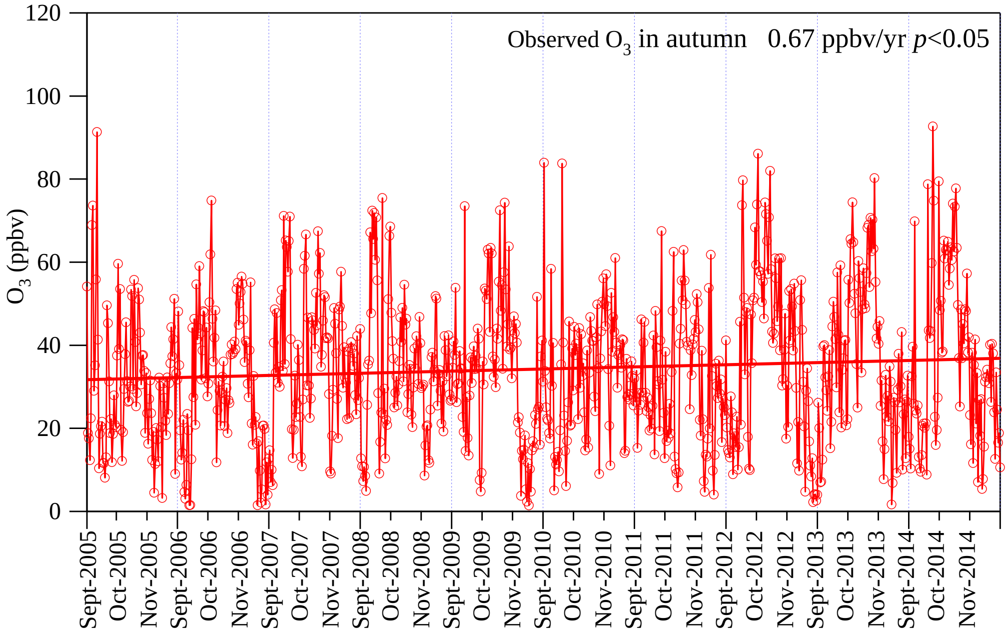
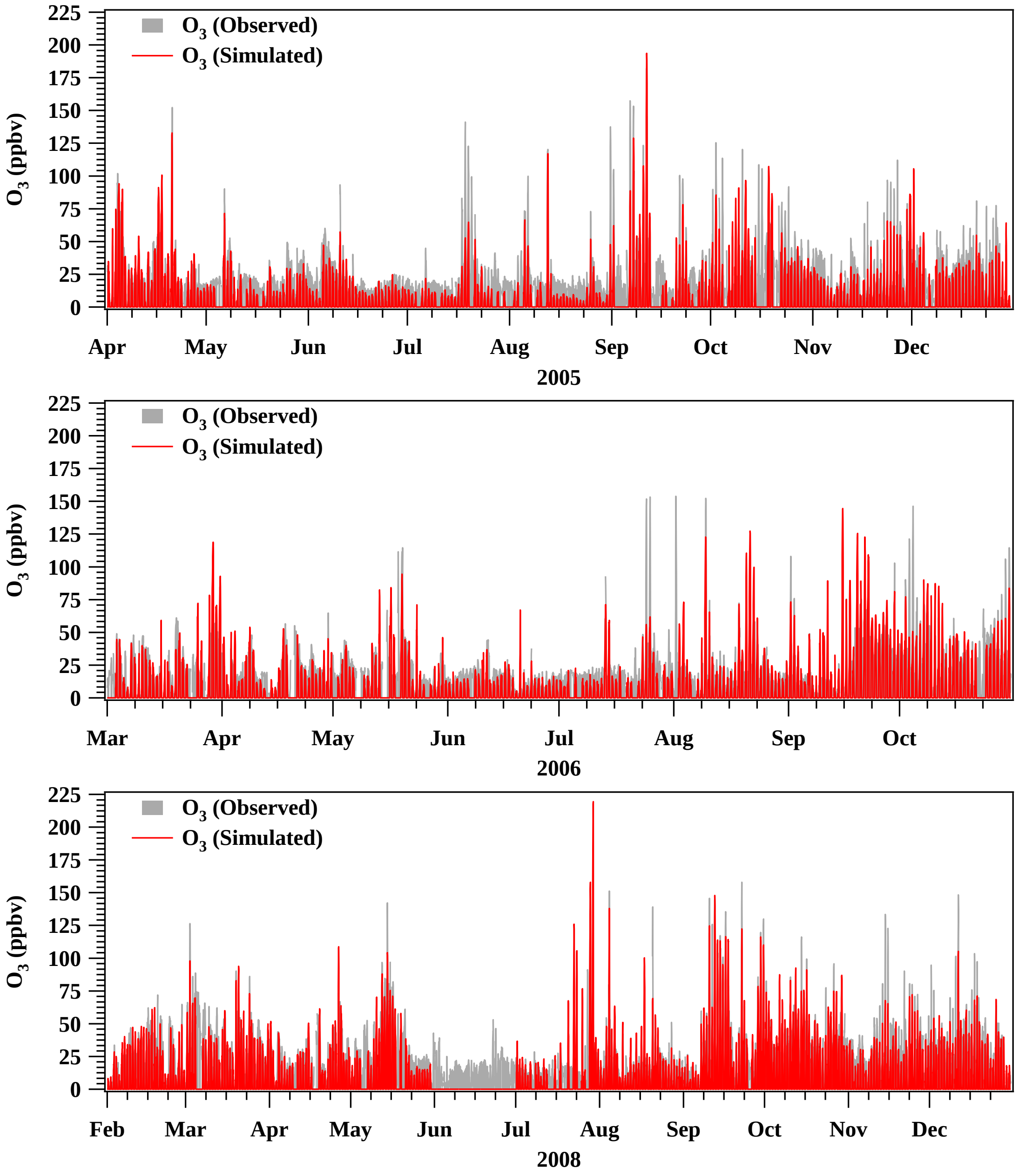
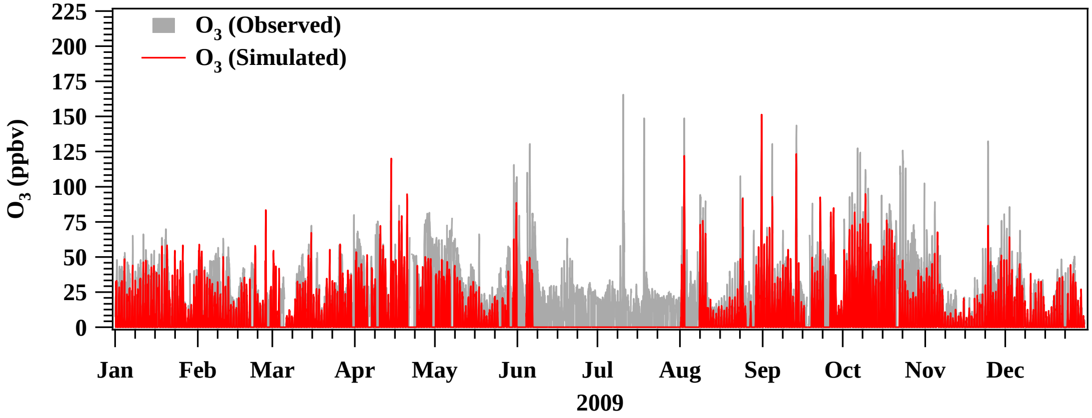
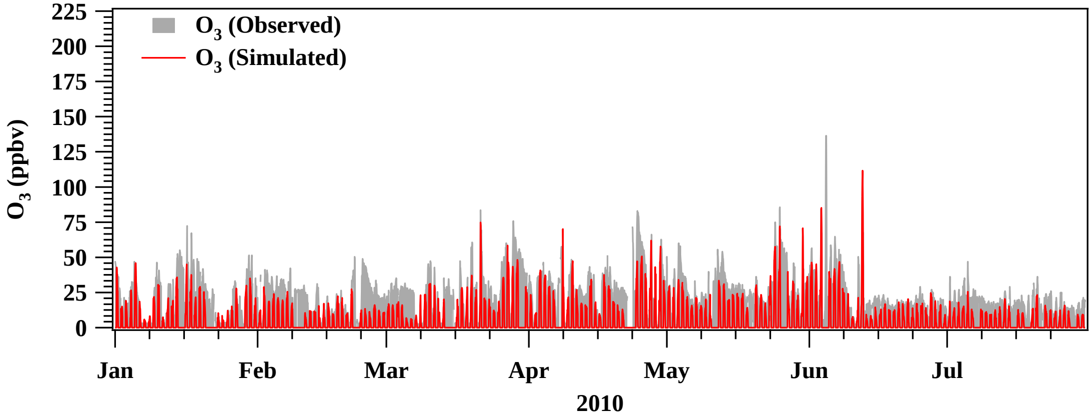
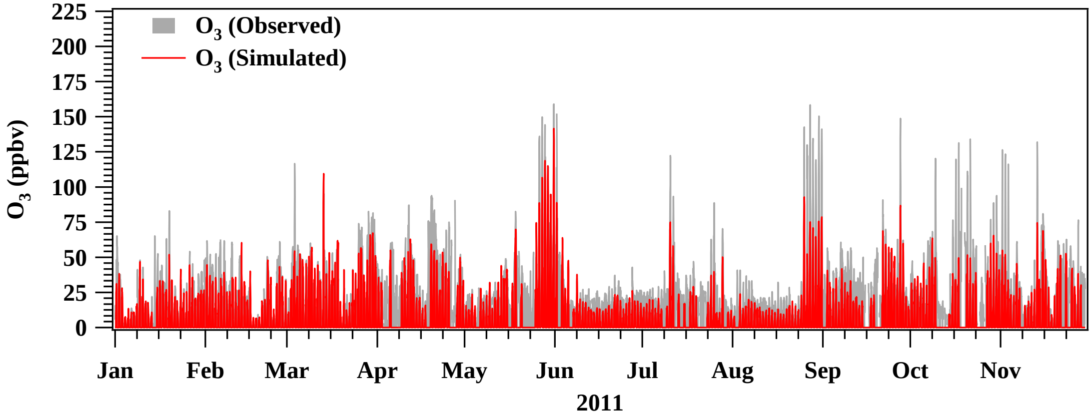


Figure S10. Monthly trend of observed O_3 at TC in 2005-2014.


O$_3$ (Observed)
O$_3$ (Simulated)
O$_3$ (ppbv)
225
200
175
150
125
100
75
50
25
0
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
2005
O$_3$ (Observed)
O$_3$ (Simulated)
O$_3$ (ppbv)
225
200
175
150
125
100
75
50
25
0
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
2006
O$_3$ (Observed)
O$_3$ (Simulated)
O$_3$ (ppbv)
225
200
175
150
125
100
75
50
25
0
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
2008


O$_3$ (Observed)
O$_3$ (Simulated)
O$_3$ (ppbv)
225
200
175
150
125
100
75
50
25
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
2009


O$_3$ (Observed)
O$_3$ (Simulated)
O$_3$ (ppbv)
225
200
175
150
125
100
75
50
25
0
Jan
Feb
Mar
Apr
May
Jun
Jul
2010


O$_3$ (Observed)
O$_3$ (Simulated)
O$_3$ (ppbv)
225
200
175
150
125
100
75
50
25
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
2011

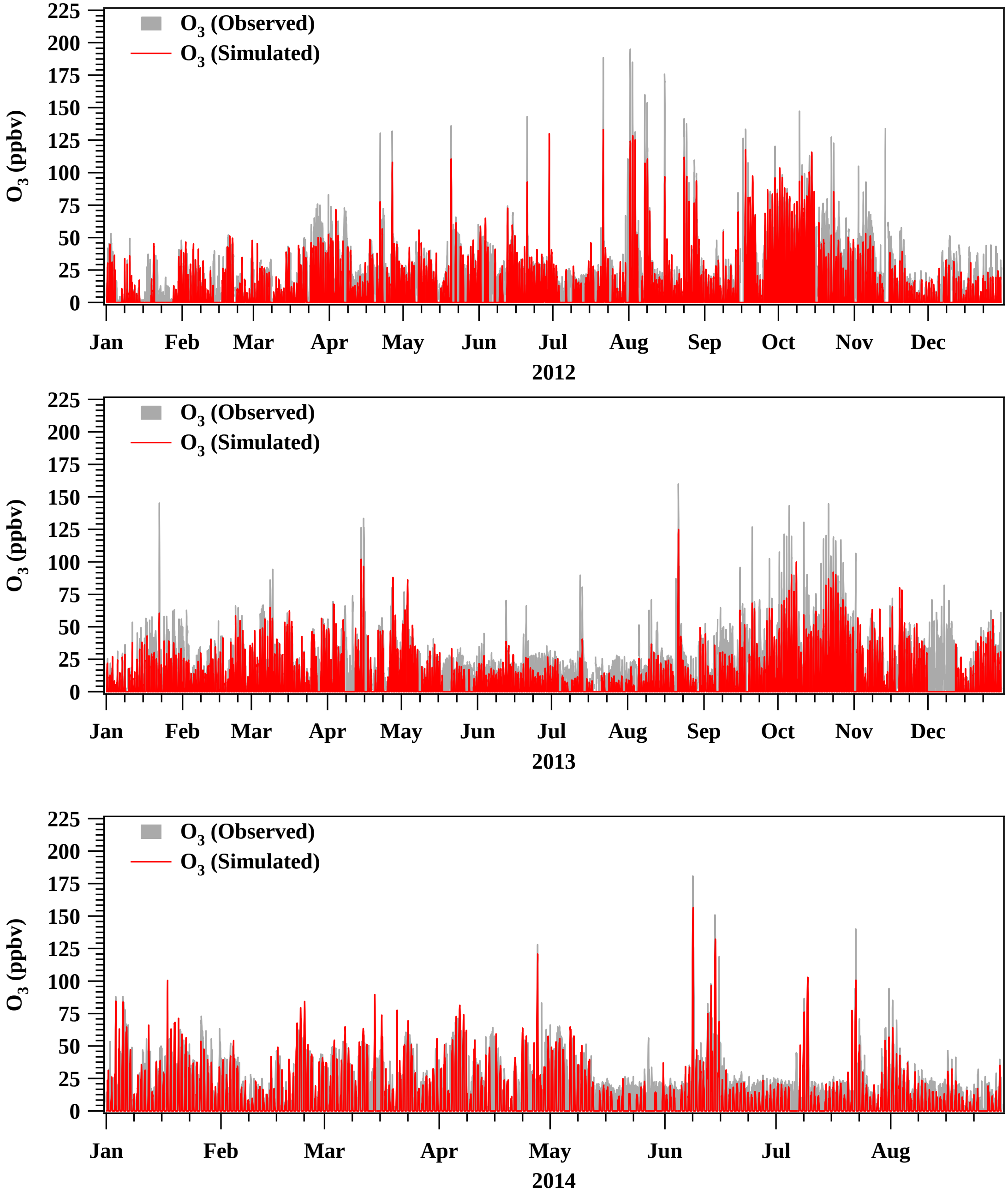
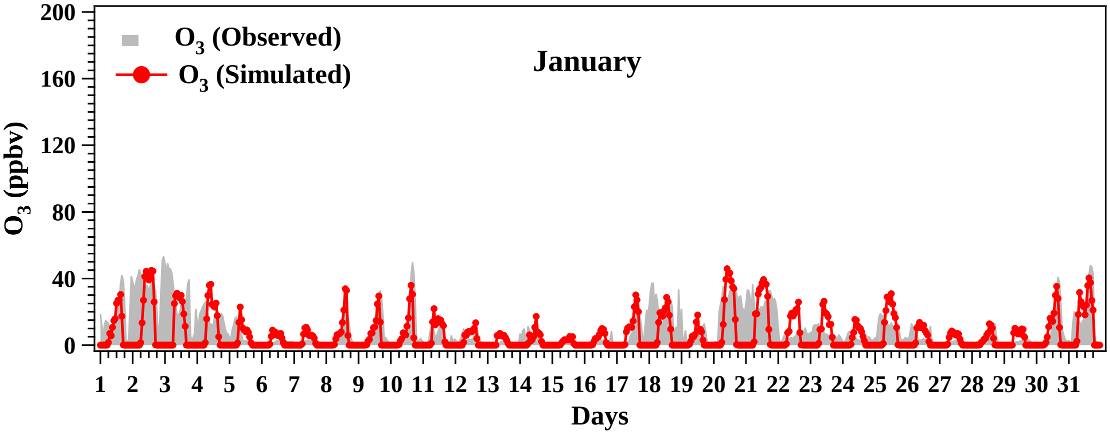
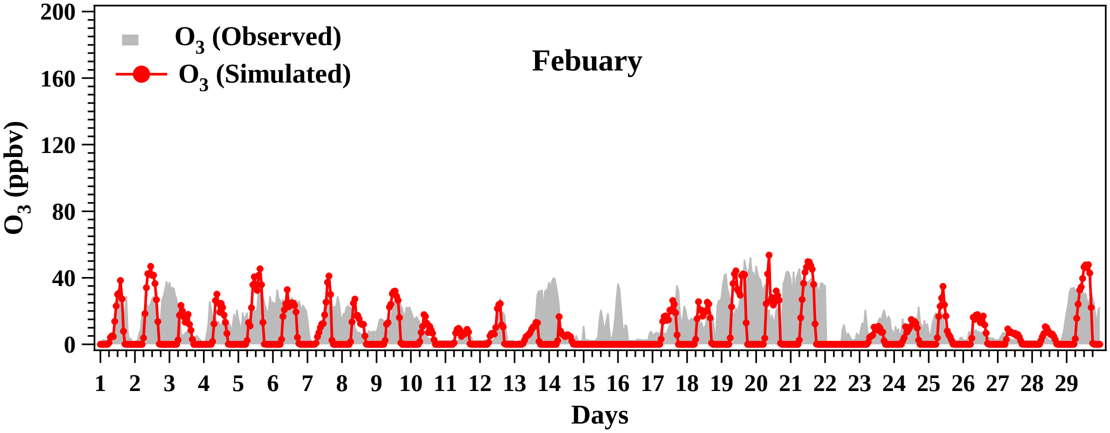
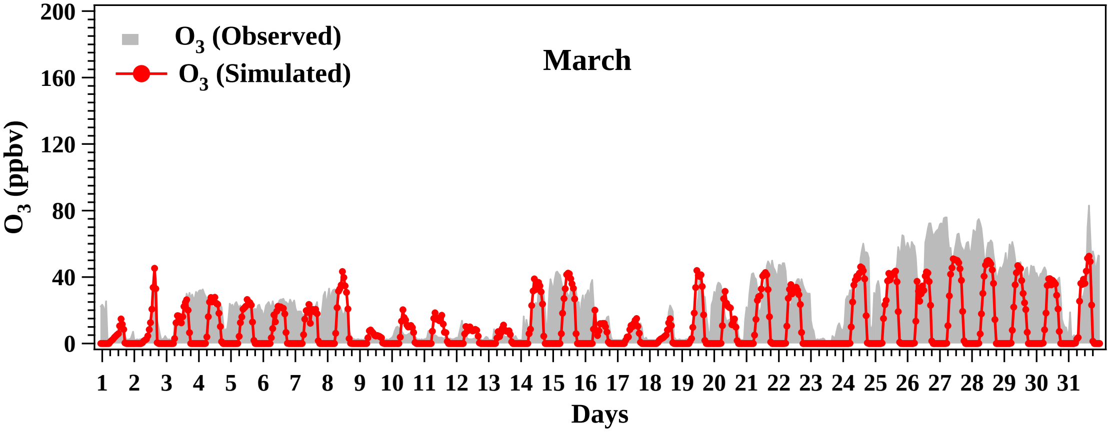
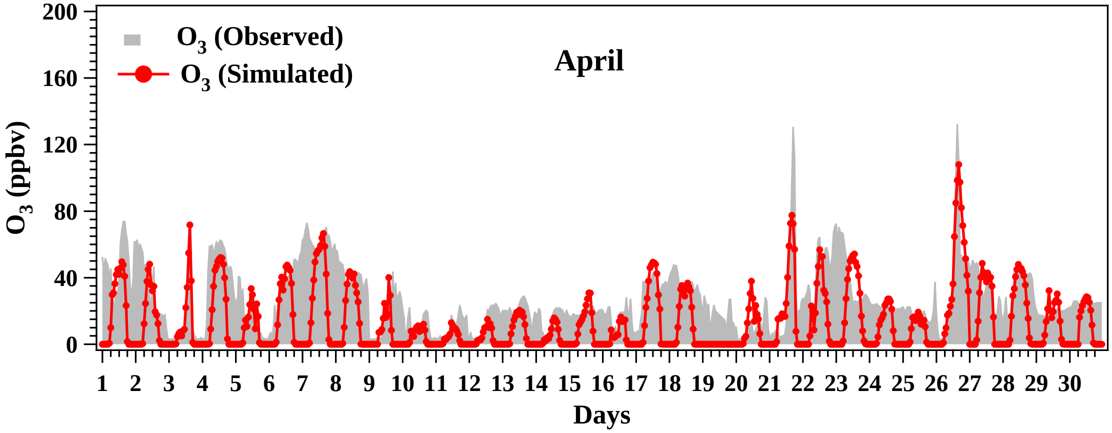


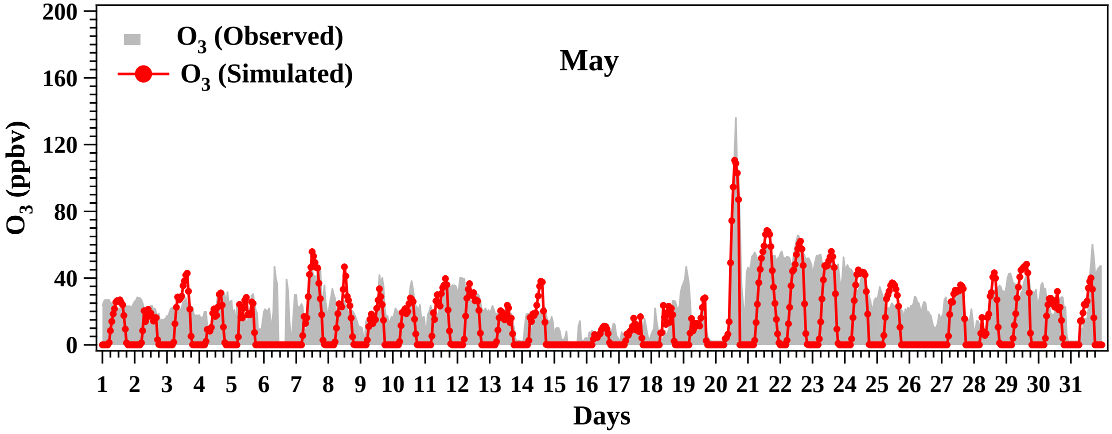
Figure S11. Comparison of simulated (red lines) and observed (grey areas) O$_3$ at TC from 2005–2014. Note: The plots are drawn by hourly data. O$_3$ simulations are not drawn in some days due to the lack of VOC real-time data (see Table S3).

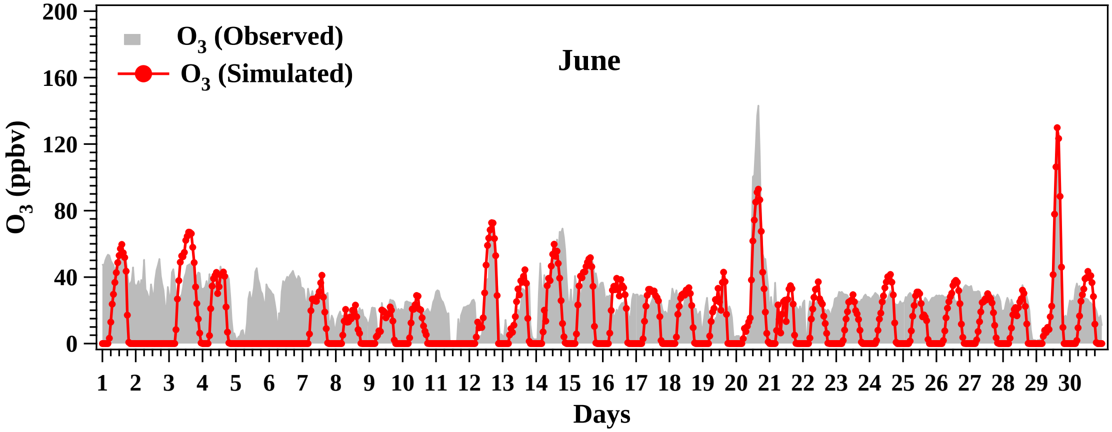

O$_3$ (Observed)
O$_3$ (Simulated)
January
O$_3$ (ppbv)
200
160
120
80
40
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
Days

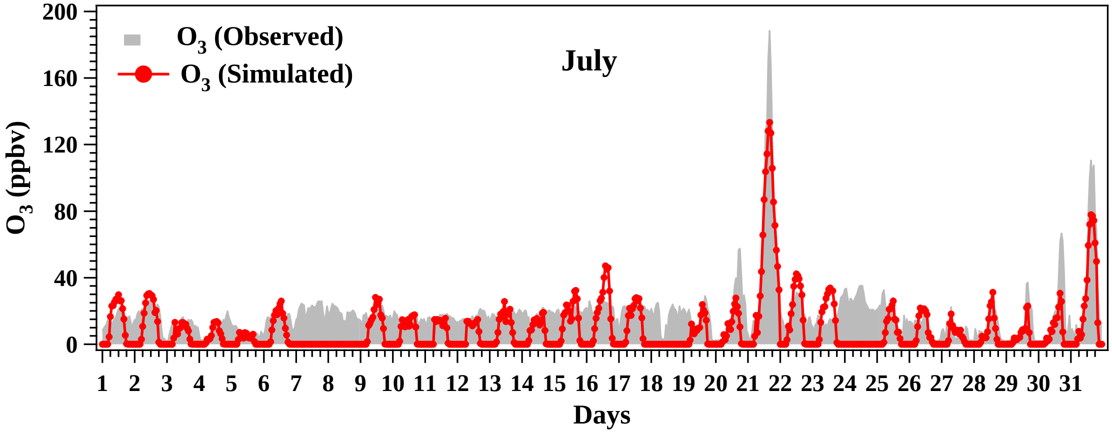

O$_3$ (Observed)
O$_3$ (Simulated)
Febuary
O$_3$ (ppbv)
200
160
120
80
40
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29
Days

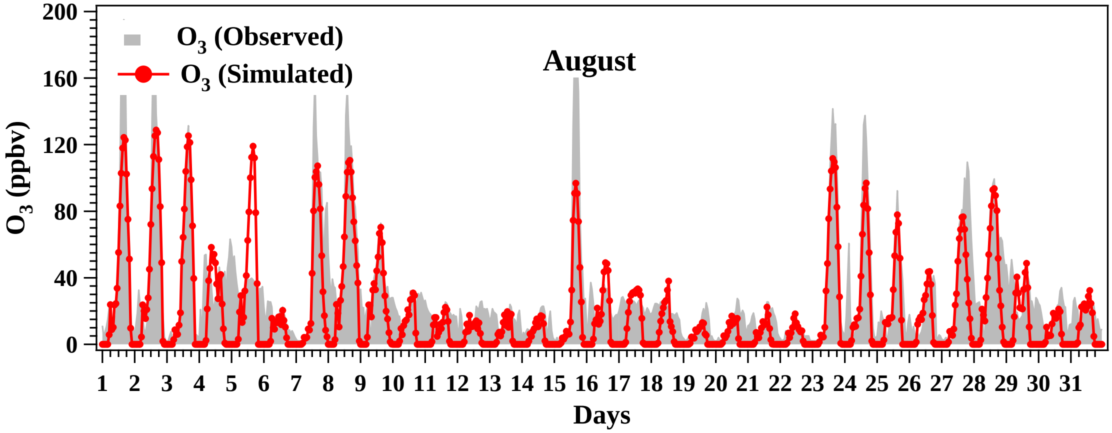

O$_3$ (Observed)
O$_3$ (Simulated)
March
O$_3$ (ppbv)
200
160
120
80
40
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
Days

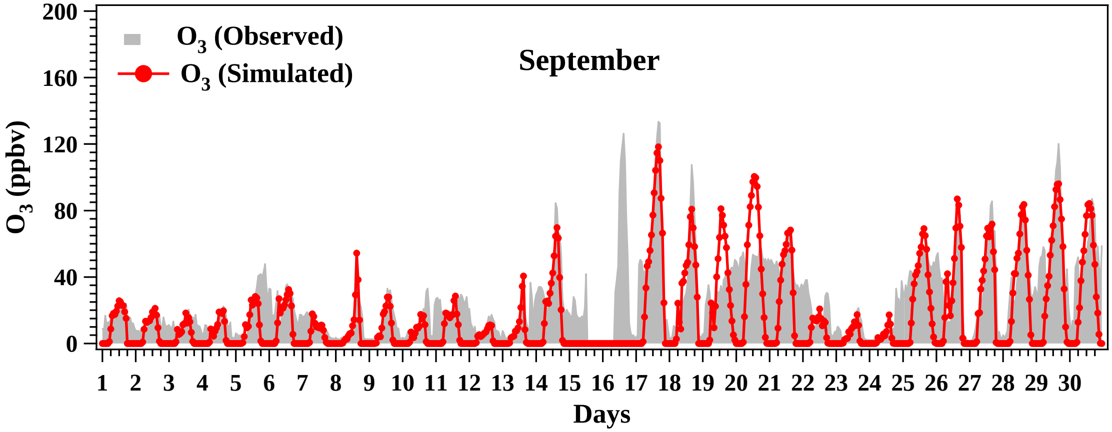

O$_3$ (Observed)
O$_3$ (Simulated)
April
O$_3$ (ppbv)
0
40
80
120
160
200
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
Days


O$_3$ (Observed)
O$_3$ (Simulated)
May
O$_3$ (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


O$_3$ (Observed)
O$_3$ (Simulated)
June
O$_3$ (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


O$_3$ (Observed)
O$_3$ (Simulated)
July
O$_3$ (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


O$_3$ (Observed)
O$_3$ (Simulated)
August
O$_3$ (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


O$_3$ (Observed)
O$_3$ (Simulated)
September
O$_3$ (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

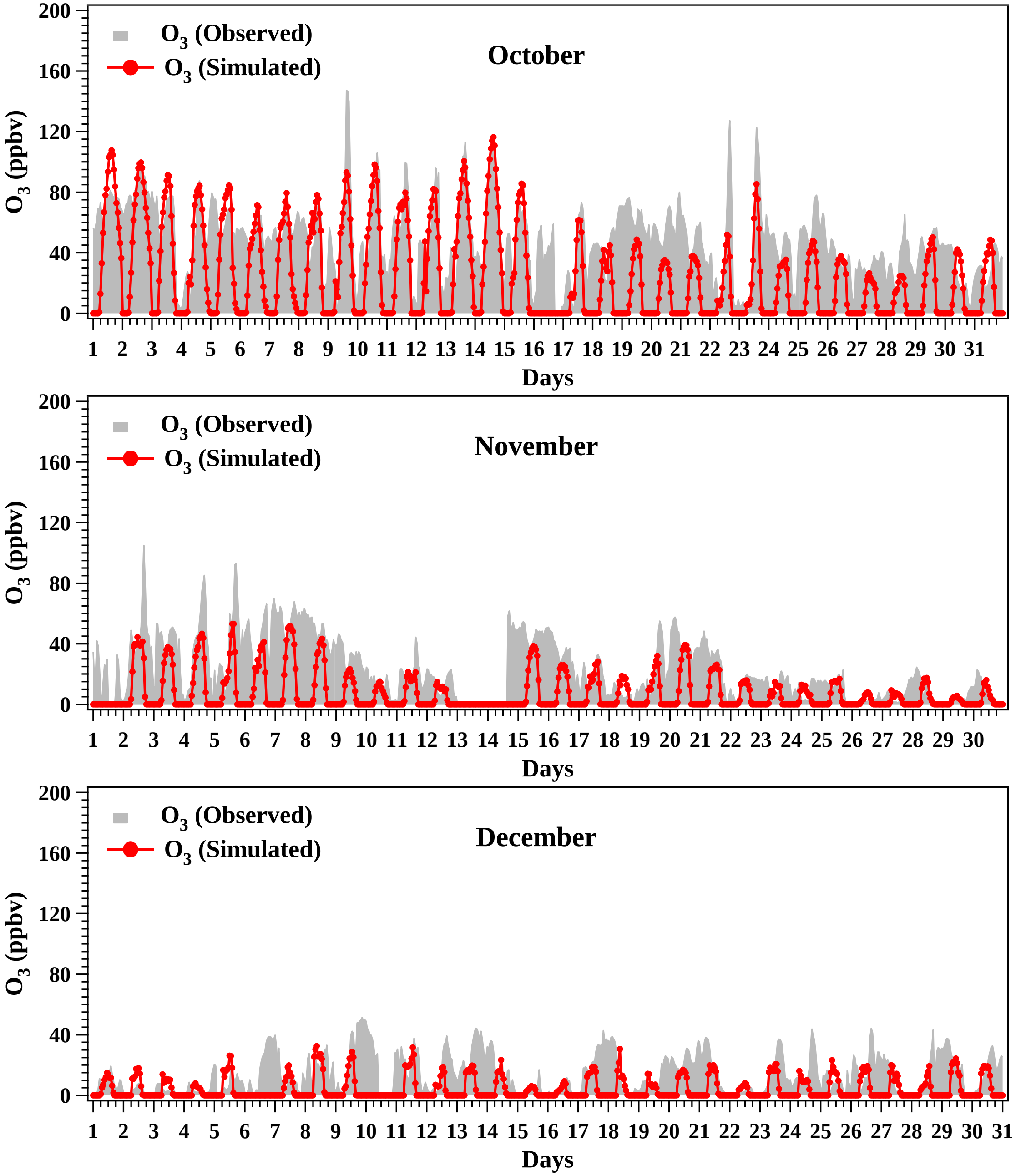


Figure S12. Comparison of simulated (red lines) and observed (grey areas) O_3 at TC in all 12 months in 2012. Note: The plots are drawn using hourly data. O_3 simulations are not drawn in some days due to the lack of VOC real-time data (see Table S3). Due to space constraints, only the data in 2012, the year with the most complete data, are selected to represent the simulation results.

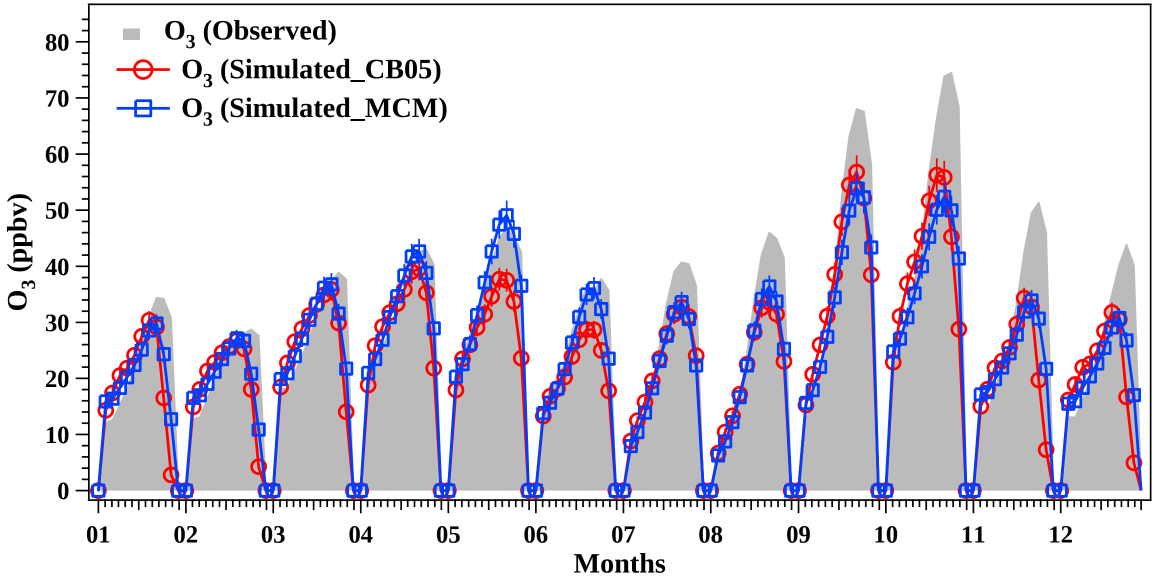


Figure S13. 12-month averaged diurnal variation of simulated O_3 by OBM (CB05, red line) and OBM (MCM, blue line); and observed O_3 (grey area) at TC during 2005–2014 (rainy days excluded). Note that the models were run for daily simulations. The daily simulated O_3 results and observed O_3 are further 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.

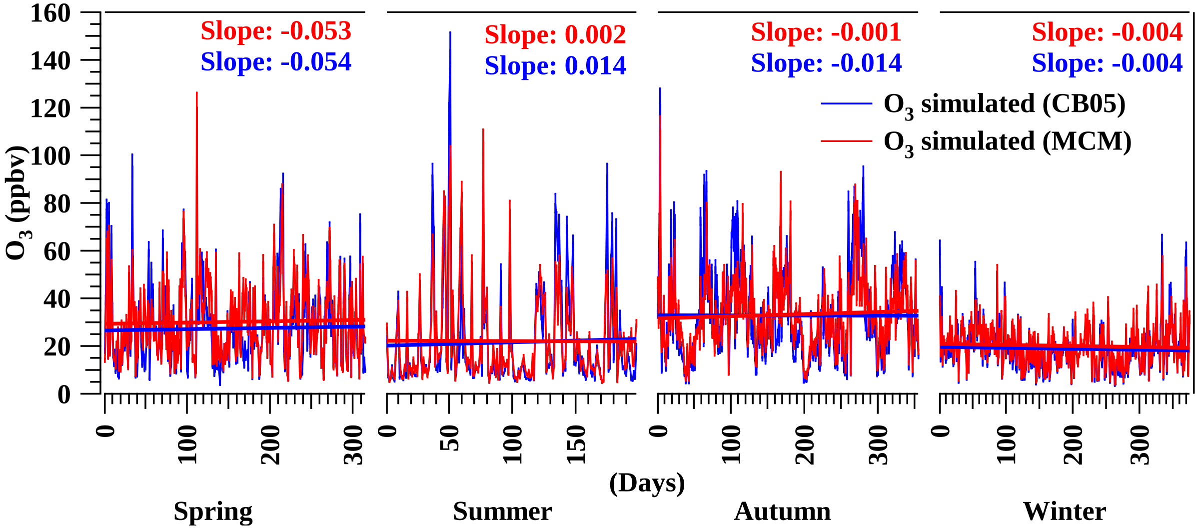


Figure S14. Trends of daily averaged locally-produced O_3 simulated by OBM (CB05, blue line) and by OBM (MCM, red line) in four seasons at TC during 2005–2014 (rainy days excluded). Note: all the data are based on daytime hours (0700-1900 LT).

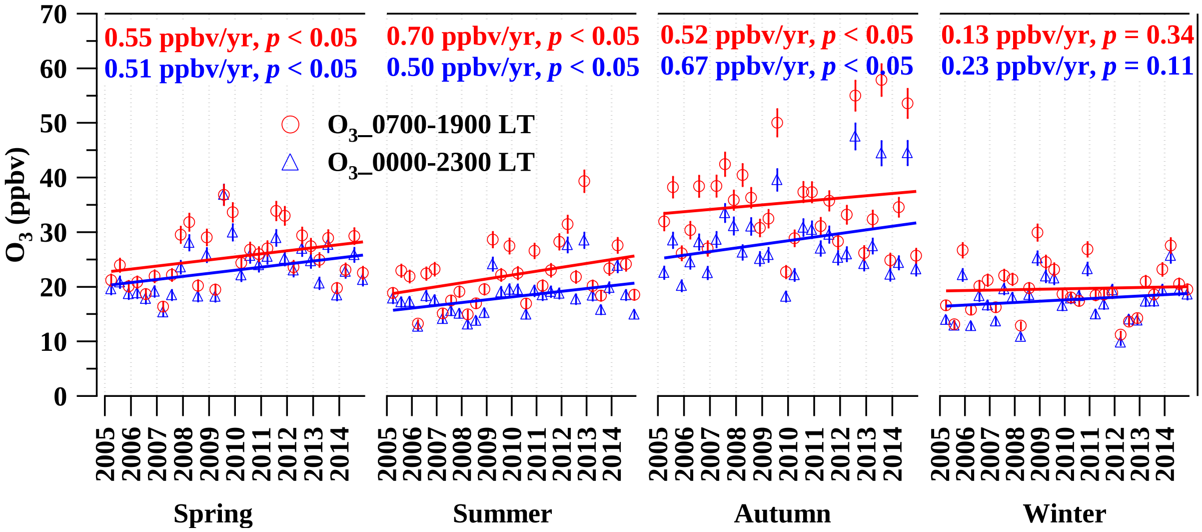


Figure S15. Trends of observed O_3 (blue line: 24-hour observed O_3, 0000-2300 LT; red line: daytime observed O_3, 0700-1900 LT) in four seasons at TC during 2005–2014. Error bars represent 95% confidence interval of the averages.

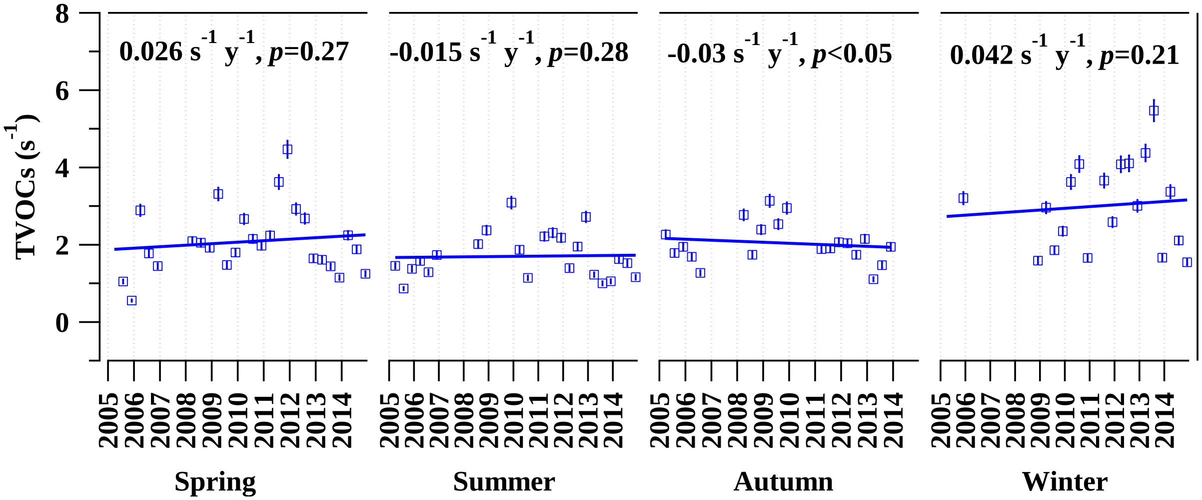


Figure S16. Annual variations of TVOC reactivity in four seasons at TC during 2005–2014. Each data point in the figure is obtained by averaging hourly values into a monthly value. Error bars represent 95% confidence interval of the averages. The rate constants with OH (k_{OH}) of VOC species are from Atkinson and Arey (2003).

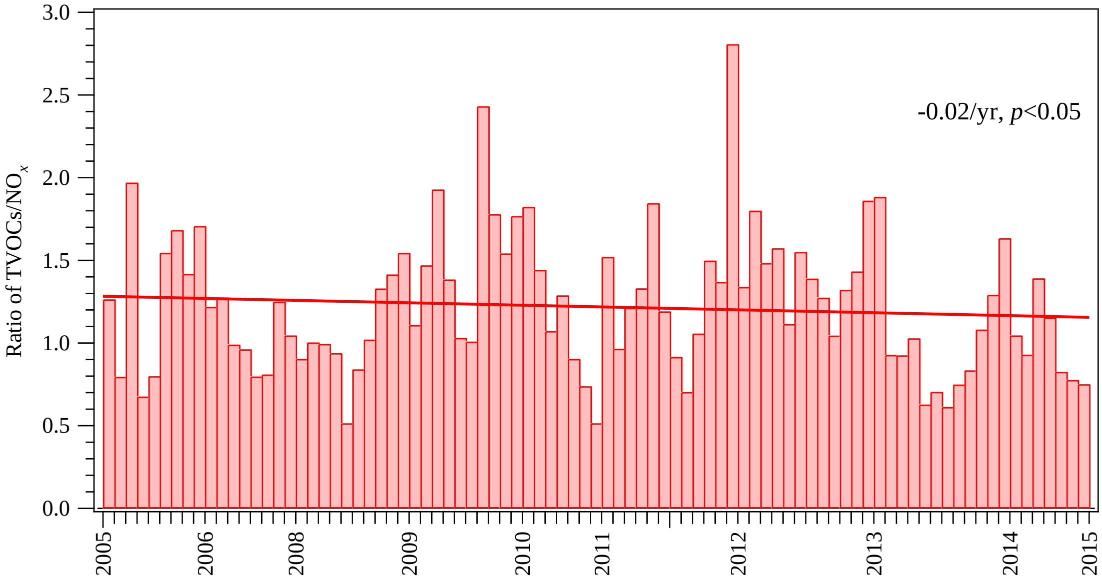


Figure S17. Monthly trend of VOCs/NO$_x$ ratio at TC in 2005-2014.

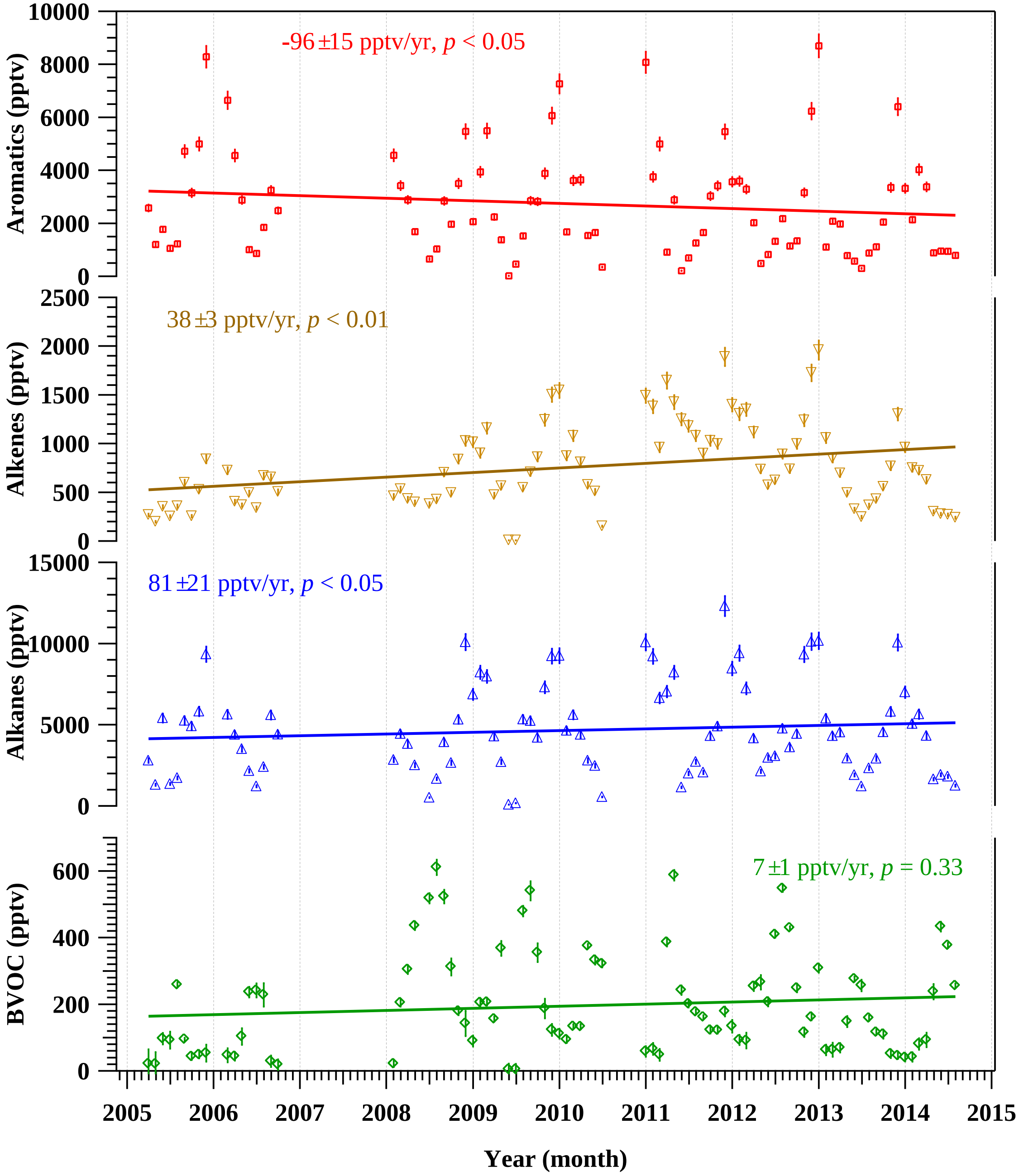


Figure S18. Trends of monthly average of individual VOC groups (*i.e.*, AVOC (aromatics/alkenes/alkanes) and BVOC) at TC during 2005-2014. Error bars represent the 95% confidence interval of the averages.

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