Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2017

Ozone pollution around a coastal region of South China Sea: Interaction between marine and continental air

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Abstract

Marine atmosphere is usually considered to be a clean environment, while this study indicates that the near-coast waters of South China Sea (SCS) suffered from even worse air quality than coastal cities. The analyses were based on concurrent field measurements of target air pollutants and meteorological parameters conducted at a suburban site (TC) and a nearby marine site (WS) from August to November 2013. The observations showed that the levels of primary air pollutants were significantly lower at WS than those at TC, while ozone (O_3) value was greater at WS. Higher O_3 levels at WS were attributed to the weaker NO titration and higher O_3 production rate because of stronger oxidative capacity of the atmosphere. However, O_3 episodes were concurrently observed at both sites under certain meteorological conditions, such as tropical cyclones, continental anticyclones and sea-land breezes (SLBs). Driven by these synoptic systems and mesoscale recirculations, the interaction between continental and marine air masses had profoundly changed the atmospheric composition and subsequently influenced the formation and redistribution of O_3 in the coastal areas. When continental air intruded into marine atmosphere, the O_3 pollution was magnified over SCS, and the elevated O_3 (>100 ppbv) could overspread the sea boundary layer ~8 times the area of Hong Kong. In some cases, the exaggerated O_3 pollution over the SCS was re-circulated to the coastal inshore by sea breeze, leading to even aggravating O_3 pollution in coastal cities. The findings are applicable to similar mesoscale environments around the world where the maritime atmosphere is potentially influenced by severe continental air pollution.

Key words*:* Continental air pollution; Maritime atmosphere; Mesoscale recirculation; Ozone photochemistry

1 Introduction

Ozone (O_3) plays a central role in photochemical oxidation processes in the troposphere via direct reaction, photolysis and the subsequent reactions to produce the hydroxyl radical (Monks et al., 2015; Seinfeld and Pandis, 2016). As a strong oxidant, O_3 at surface level is recognized to be a threat to human health (WHO, 2003; Bell et al., 2007) and has a detrimental impact on vegetation (Fowler et al., 2009) and built infrastructure (Kumar and Imam, 2013). Tropospheric O_3 is also the third most important greenhouse gas (IPCC, 2014) and is referred to a short-lived climate pollutant (Shindell et al., 2012).

To mitigate O_3 pollution in the troposphere, tremendous efforts from both scientific and regulatory communities have been made since three decades ago (NRC, 1991; NARSTO, 2000; Monks et al., 2015). The O_3 levels started to decrease at many locations, such as Jungfraujoch in Switzerland, Zugspitze in Germany, Mace Head in Ireland, as well as parts of California and eastern US (Lefohn et al., 2010; Cui et al., 2011; Parrish et al., 2012; Lin et al., 2017). However, increasing studies showed that surface O_3 was elevated rapidly in East Asia in the last decade (Ding et al., 2008; Xu et al., 2008; Parrish et al., 2012; Zhang et al., 2014; Lin et al., 2017; Wang et al., 2017a). For example, the observational data revealed that regional O_3 concentrations increased at a rate of 0.86 ppbv yr^{-1} in Pearl River Delta (PRD) from 2006 to 2011 (Li et al., 2014), and at a rate of 0.56 ppbv yr^{-1} in Hong Kong from 2005 to 2014 (Wang et al., 2017a).

Hong Kong and the adjacent PRD is the most industrialized region along the coast of South China Sea (SCS), and is suffering from serious O_3 pollution (Zheng et al., 2010; Derwent et al., 2013; Ling et al., 2013). Numerous studies demonstrated that in addition to long-range transport (Chan, 2002; Guo et al., 2009; Wang et al., 2009) and local photochemical production (Ding et al., 2013a), tropical cyclones and mesoscale circulations are conducive to the occurrence of high O_3 events (Yin, 2004; Huang et al., 2005; Yang et al., 2012; Jiang et al., 2015; Wei et al., 2016). In a number of studies, tropical cyclone has been considered as the most conducive driver to the occurrence of O_3 episodes in Hong Kong (Yin, 2004; Ling et al., 2013) for it generally causes peripheral subsidence, stagnation air and inversion layer, which favor the production and accumulation of O_3.

Mesoscale circulations (*e.g.*, sea-land breezes (SLB) and mountain–valley breezes) also play important roles in O_3 distribution and transport in the coastal cities like Hong Kong with

complex topography and land cover (Liu and Chan, 2002; Ding et al., 2004; Lu et al., 2009a; Guo et al., 2013). For instance, Guo et al. (2013) demonstrated that upslope winds brought pollutants including O_3 from low-lying areas to the peak of Mt Tai Mo Shan (957 m a.s.l.) in Hong Kong. Ding et al. (2004) simulated a multi-day SLB related O_3 episode and discussed the influence of SLB circulation on the transport of oxidant precursors, the residence time and re-entry of photochemical compounds. Lu et al. (2010) simulated the SLB in the 2003/2004 winter and revealed that the urbanization of Shenzhen might significantly enhance the sea breeze to the west of Hong Kong in the early afternoon, which worsened the local air pollution.

Both coastal human activities and marine atmospheric cyclic behavior can significantly affect the air pollution level in coastal urban environments (Adame et al., 2010; Velchev et al., 2011). Exploring SLBs provides an important way to understand the interaction between continental air and marine atmosphere which has long been a focus of coastal air quality, global tropospheric chemistry and climate change research. Surprisingly, few studies investigated SLBs in Hong Kong though about 70 SLB days per year on average were observed in Hong Kong and the PRD region (Zhang and Zhang, 1997). Therefore, the association between mesoscale recirculation and air pollutants over the SCS and subtropical continental region is still not well established, which seriously limits our understanding on the interplay of continental and marine air masses in this region. Furthermore, previous O_3 studies carried out in this region neither paid enough attention to the variations of volatile organic compounds (VOCs, one important group of O_3 precursors) nor established any field measurements on an island, an ideal site for observation of marine air mass with less interference from local emissions, for understanding the O_3 pollution around the coastal region of the SCS (Parrish et al., 1998). So far, only a handful of studies deeply evaluated the chemical characteristics of air masses under various synoptic systems (Wang et al., 2005; Guo et al., 2009, 2013).

This study aimed to comprehensively characterize interaction between continental anthropogenic emissions and marine atmosphere over a coastal region of the SCS by concurrent measurements and in-depth analysis of air pollutants at a marine site over SCS and a suburban site in Hong Kong. Firstly, the spatial and temporal variations of measurements were described to give an overall picture of the campaign, as well as to directly evaluate how continental outflows polluted the marine atmosphere over the SCS.

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After that, the chemical and meteorological characteristics of air masses associated with high O_3 concentrations were explored. Finally, the interplay between the maritime and continental air masses and its influence on regional air quality were discussed.

2 Methodology

2.1 Sampling sites

Field measurements were carried out concurrently at a suburban site and a marine site over SCS (Figure 1). The suburban Tung Chung (TC, 22.29 °N, 113.94 °E) site, part of the Hong Kong Environmental Protection Department (HKEPD) air quality monitoring network, is located in southwestern Hong Kong, about 3 km south of the Hong Kong International Airport at Chek Lap Kok with Hong Kong urban center about 20 km to the southwest and Macau 38 km to the northeast. It is a newly-developed residential town adjacent to the busy highway and railway lines. The sampling instruments were installed on the rooftop of a building with a height of 27.5 m a.s.l. More detailed description of the TC site can be found in our previous publications (Cheng et al., 2010a; Jiang et al., 2010).

The marine site, Wan Shan island (WS, 21.93 °N, 113.73 °E), is located 40 km southeast of Zhuhai, and is bounded to the north by the Pearl River Estuary, with a straight distance of about 44 km to TC. WS has an area of 8.1 km^2 and a population of about 3,000 with sparse anthropogenic emissions at the island. The isolated island features a sub-tropical maritime climate. The measurement site was set up on the rooftop of the National Marine Environmental Monitoring Station with a height of about 65 m a.s.l.

High O_3 mixing ratios are frequently observed in Hong Kong in late summer and autumn (Ling et al., 2013) when the northeast monsoon prevails. During this period, WS is right in the downwind direction of TC, which facilitates the study of the interaction between the inland pollution and the marine environment.

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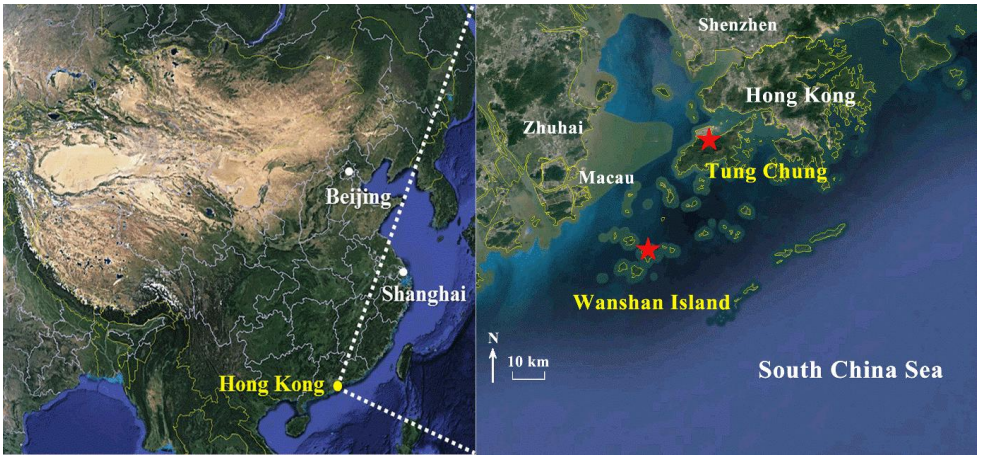

Figure 1. Locations of the sampling sites (red stars) and the surrounding environment.

2.2 Measurement techniques

2.2.1 Measurements of trace gases and meteorological parameters

The sampling campaign was conducted from 10 Aug. to 21 Nov. across late summer and autumn in 2013. At WS, trace gases (*i.e.*, NO_x, O_3, SO_2 and CO) were continuously monitored with a time resolution of 1 minute. NO-NO_2-NO_x was measured using a chemiluminescence analyzer (*Thermo Environmental Instruments (TEI), Model 42i*) with a range of 0-200 ppbv and a lower detection limit of 0.40 ppbv. O_3 was monitored with a commercial UV photometric analyzer (*TEI, Model 49i*) with a range of 0-0.050 to 200 ppm and a lower detection limit of 1.0 ppbv. SO_2 was measured using a pulsed UV fluorescence approach (*TEI, Model 43S*). CO was measured by a gas filter correlation, non-dispersive infrared analyzer (*API, Model 300*) with a heated catalytic scrubber to convert CO to CO_2 for baseline determination. Quality assurance and control procedures (*e.g.*, instrumental maintenance and calibration) for these devices have been described elsewhere (Guo et al., 2009, 2013). Meteorological parameters, including temperature, relative humidity, solar radiation, wind speed and wind direction, were routinely monitored by a weather station (Vantage Pro 2 plus, Davis Instruments) with a time resolution of 5 minutes. At TC, hourly data of the aforementioned trace gases and meteorological parameters were obtained from the

HKEPD (http://epic.epd.gov.hk/ca/uid/airdata). Detailed information of the quality assurance and control protocols is available in the HKEPD report (HKEPD, 2015).

2.2.2 Sampling and analysis of VOCs

Concurrent VOC samples (*i.e.*, non-methane hydrocarbons (NMHCs) and carbonyls) were collected on 21 selected days (including both non-O_3 episodes and O_3 episodes) at both sites. These days were selected on the basis of weather prediction and meteorological data analysis for potentially high and low O_3 days. An O_3 episode day is the day when the peak one-hour averaged O_3 mixing ratio exceeds 100 ppbv (Level II of China National Ambient Air Quality Standard). Please refer to our previous publication for details of this method (Guo et al., 2009).

The whole-air samples of NMHCs were collected using 2-L electro-polished stainless steel canisters. The canisters were cleaned, conditioned and evacuated before being used for sampling. A metal bellows pump was used to fill up the canisters with sample air over one-hour integration (with a flow restrictor) to a pressure of 40 psi. Seven one-hour VOC samples (every two hours during 7:00 – 19:00 inclusive) were collected simultaneously at each site. Intensive VOC sampling was also carried out at WS in selected seven days (*i.e.*, 3, 4, 9 and 22-25 October) with eleven one-hour samples (every two hours during 1:00 – 22:00 inclusive). Totally, 311 valid VOC samples (144 at TC and 167 at WS) were collected in addition to about 5% field blanks and 5% parallel samples for quality assurance purpose. The speciation and abundance of 59 C_2-C_{11} NMHCs in the canisters were determined by a Model 7100 preconcentrator (Entech Instruments Inc., California, USA) coupled with an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). The detection limit of NMHCs was 3 pptv with a measurement precision of 2-5%, and a measurement accuracy of 5%. Detailed information of the analysis system and quality control and quality assurance for VOC samples can be found elsewhere (Simpson et al., 2010).

Carbonyl samples were collected using silica gel filled cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH). Air samples were drawn through the cartridge at a flow rate of 0.8–0.9 L min^{-1} for 2 hours; the flow rate through the cartridges was monitored with a rotameter which was calibrated before and after each sampling. An O_3 scrubber was connected to the inlet of the DNPH–silica gel cartridge to prevent interference from O_3. In

total, 227 carbonyl samples (124 at TC and 103 at WS) were collected with 5 and 6 samples per non-O_3 and O_3 episode day (every two hours during 7:00 - 18:00 inclusive), respectively. All cartridges were stored in a refrigerator at 4 ℃ after sampling. The sampled carbonyl cartridges were eluted slowly with <5 ml of acetonitrile in the direction opposite to sampling flow into a 5-ml brown volumetric flask, followed by adding acetonitrile to a constant volume of 5 ml. A 20-μl aliquot was injected into the high performance liquid chromatography (HPLC) system through an auto-sampler. The operating conditions of the HPLC are shown in Table S1. Typically, C_1–C_9 carbonyl compounds were measured efficiently with a detection limit of ~0.2 ppbv.

2.3 Observation-based model (OBM)

A photochemical box model coupled with the Master Chemical Mechanism v3.2 (PBM-MCM) was applied to simulate the O_3 production at WS and TC for the VOC sampling days. The PBM-MCM model is a zero-dimension photochemical box model combined with a near explicit chemical mechanism consisting of 5,900 species and 16,500 reactions, which fully describes the mechanisms of homogeneous reactions in the atmosphere (Jenkin et al., 1997; Jenkin et al., 2003; Saunders et al., 2003). The simulation was constrained by hourly data of meteorological parameters (*i.e.*, temperature and relative humidity) and air pollutants (NO, NO_2, CO, SO_2 and 51 measured VOCs). Since the sampling interval was two hours for each sample, cubic spline interpolation was used to derive VOC concentrations at each hour for modeling purpose. Please see our previous publication for details (Wang et al., 2017a). It is noteworthy that the atmospheric physical processes (*i.e.*, vertical and horizontal transport) were not considered in this model. The PBM-MCM model has been successfully applied in previous studies (Cheng et al., 2010b; Lam et al., 2013; Ling et al., 2014). Details of the model construction can be found in Saunders et al. (2003) and Lam et al. (2013).

2.4 WRF-CMAQ simulation and backward particle release model

In this study, the Weather Research and Forecasting (WRF v3.7.1) model (Skamarock et al., 2008) was used to simulate vertical and horizontal wind fields for various weather systems observed in this campaign, and then provided meteorological parameters required by U.S. EPA Community Multiscale Air Quality (CMAQ v4.7.1) model (www.epa.gov/cmaq). CMAQ is a three-dimensional Eulerian atmospheric chemistry and transport modeling system, which includes complex physical and chemical processes, such as physical transport and diffuse, gas and aqueous chemical transformation, and so on; and it can treat multiple

pollutants simultaneously from local to continental scales. A domain system composed of four nested grids (81, 27, 9, 3 km) was adopted to better suit the simulation of mesoscale weather systems, as shown in Figure S1. The domain with finest resolution (3 km) covers the Pearl River Estuary region. Vertically, there were 31 sigma levels for all domains, with the model top fixed at 50 hPa. The major selected physical schemes invoked in WRF and chemical mechanisms used in CMAQ are shown in Table S2. The input meteorological data was made using NCEP FNL (final) data with a horizontal resolution of $1^{o}\times1^{o}$ (https://rda.ucar.edu/). In addition, the geographical data were obtained from the Research Data Archive of National Center for Atmospheric Research (NCAR) (http://www2.mmm.ucar.edu/wrf/users /downloads.html). The emission inventories (EI) used in this study included the 2000-based Regional Emission Inventory in ASia (REAS) (Kurokawa et al., 2013) and the 2010-based Multi-resolution Emission Inventory for China (MEIC) (He, 2012), both of which were processed by the Sparse Matrix Operating Kernel Emission (SMOKE) model. The biogenic emissions were calculated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther, 2006). The WRF modelling mainly focused on O_3 episodes with an additional 24hrs' preceding run as spin-up for each episode, and the integration was conducted separately. In addition, the spatiotemporal patterns of CO and O_3 were simulated by WRF-CMAQ during two O_3 episodes (see section 3.4). Table S3 gives the index of agreements (IOAs) between the simulated and observed meteorological parameters and air pollutants. Within the range of 0 – 1, higher IOAs represent better agreement between the simulated and observed values (Willmott, 1982). Here, IOA was between 0.51 and 0.84 for the simulation of meteorological parameters. Furthermore, it was not lower than 0.50 for primary air pollutants, and reached 0.81 for O_3 simulation at both sites. The model performances were comparable to those reported in previous studies (Cabaraban et al., 2013; Wang et al., 2015). Therefore, we accepted the modeling results, in view of the fact that the simulations were only used to qualitatively indicate the interactions between the continental and marine air in this study.

Backward particle release simulations were carried out using HYSPLIT model (Stein et al., 2015) for episode days at WS and TC sites during the entire sampling period (Draxler and Rolph, 2003). The backward particle release simulation, which considers the dispersion processes in the atmosphere, is capable of identifying the history of air masses (Guo et al., 2009; Ding et al., 2013a, 2013b). In this work, we applied the model following a method developed by Ding et al. (2013a).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2017

3 Results and Discussion

3.1 Spatio-termporal variations

Table 1 summarizes the meteorological conditions and chemical species observed at WS and TC. Lower temperature (25.7±0.1°C) and higher relative humidity (82.8±0.4%) were recorded at the marine site (WS) compared to the suburban site (TC) ($p < 0.01$) (temperature: 26.7±0.1°C and relative humidity: 67.7±0.5%). At WS, the solar radiation (635.8±46.9 Wm^{-2}) was much higher than that at TC (563.5±46.1 Wm^{-2}, $p < 0.01$), while the average wind speed at TC (4.6±0.1ms^{-1}) was significantly lower than that measured at WS (7.2±0.2ms^{-1}). The lower wind speed at TC was related to the roughness of underlying surfaces. However, no statistical differences were found for the average wind direction (about 81°, northeast wind) at the two sites, indicating that the two sites were probably under the influence of similar air masses in most cases.

The NO, NO_2, CO, SO_2 and total VOCs (the sum of NMHCs and carbonyls) had lower average and maximum mixing ratios at WS than those at TC. The lower levels of primary air pollutants at WS were likely the results of fewer local emission sources, faster photochemical consumption (as discussed later) and/or more favorable dispersion conditions (*e.g.*, higher wind speed). In contrast, O_3 was much higher at WS (Table 1), attributable to the enhancements by both meteorological and photochemical effects, as discussed in sections 3.2 and 3.3.

Table 1. Descriptive statistics of meteorological parameters and trace gases at the two sites during the sampling period.

Parameter	WS		TC	
	Mean±95% C.I.	*Max.*	*Mean±95% C.I.*	*Max.*
Temperature (°C)	25.7±0.1	32.8	26.7±0.1	35.4
Relative humidity (%)	82.8±0.4	98.9	67.7±0.5	96.8
Solar radiation (W m^{-2})*	635.8±46.9	1026.8	563.5±46.1	910.0
Wind speed (m s^{-1})	7.2±0.2	23.8	4.6±0.1	13.8
Wind direction (°)	81.3	-	80.9	-
O_3 (ppbv)	51.3±1.2	173.0	30.0±1.0	159.9
NO (ppbv)	0.7±0.1	21.0	14.0±0.8	115.7

NO_2 (ppbv)	4.3±0.3	49.3	25.0±0.6	104.2
CO (ppbv)	251.4±6.5	727.7	560.5±6.3	1047.9
SO_2 (ppbv)	2.4±0.1	12.2	5.9±0.1	19.1
NMHCs (ppbv)	12.7±1.1	32.9	17.7±1.7	60.0
Carbonyls (ppbv)	7.9±0.7	16.3	9.2±0.7	26.5

* Average of the daily maximum solar radiation. *C.I.* denotes confidence interval.

Time series of local meteorological parameters and hourly mixing ratios of air pollutants at the two sites are illustrated in Figures 2a-2b. The temporal patterns of wind directions were generally similar at both sites, with the dominance of the southerly winds in August and northeastern winds between September and November. Occasionally, the northwesterly winds from the PRD region were observed.

This sampling campaign witnessed 17 O_3 episodes and 7 near-O_3 episode days at TC, which refers to the days with maximum hourly mixing ratio of O_3 higher than 100 ppbv and within the range of 80-100 ppbv, respectively. (80 ppbv was Level I of China National Ambient Air Quality Standard for O_3). At WS, 21 O_3 episodes and 6 near-O_3 episodes were recorded. Specifically, 13 O_3 episode days were simultaneously observed at the two sites, with the rest occurred exclusively at one site. On one hand, the primary air pollutants (CO, SO_2 and NO_x) generally increased during O_3 episodes, implying enhanced O_3 formation potentials from the precursors. On the other hand, O_3 episodes were always accompanied by the synoptic conditions, *i.e.*, tropical cyclone (typhoon in the mature form) and continental anticyclone, and/or mesoscale circulations such as SLB, as detailed in Table S4. For example, the two multi-day O_3 episode events, *i.e.*, 1-8 Oct. and 19-27 Oct. (highlighted in blue in Figure 2), were strongly associated with continental high pressure. These episode days generally had high temperature, northerly winds, and intensive solar radiation, with air flows largely from the inland or the coastal areas. Also, the mixing ratios of CO, NO_2 and SO_2 usually increased during these days, suggesting the accumulation of local air pollutants and/or the increasing contribution from regional transport. In contrast, O_3 episodes under the influence of tropical cyclones (highlighted in orange in Figure 2) featured high temperature, strong solar radiation and typically calm or moderate northwesterly to northeasterly winds, except for typhoon

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
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"Haiyan" occurred on 9-12 Nov. (discussed in section 3.2.1). These conditions were all conducive to the formation and accumulation of O_3. Additionally, SLB was also an important factor regulating O_3 pollution in this region during O_3 episodes (Table S4). Detailed discussions can be found in section 3.2.3.

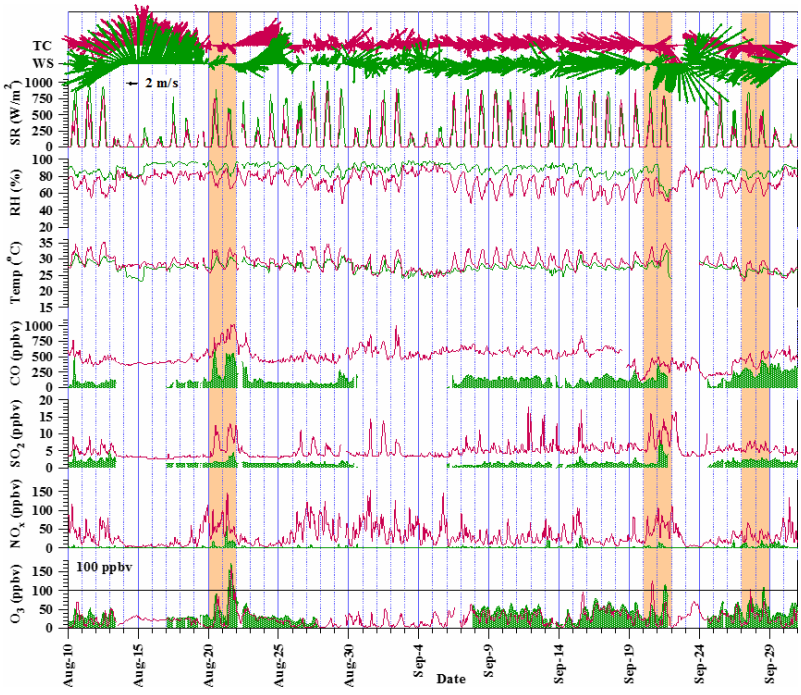

Figure 2a. Time series of trace gases and meteorological parameters observed for the sampling period of 10 Aug. - 30 Sept. at WS (green) and TC (red). The black line of 100 ppbv is the threshold for O_3 episode definition. The dates seriously affected by continental high pressure and tropical cyclones are shaded in blue and orange, respectively. Note that there are some data missing in these months due to extremely bad weather conditions and instrumental failure.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
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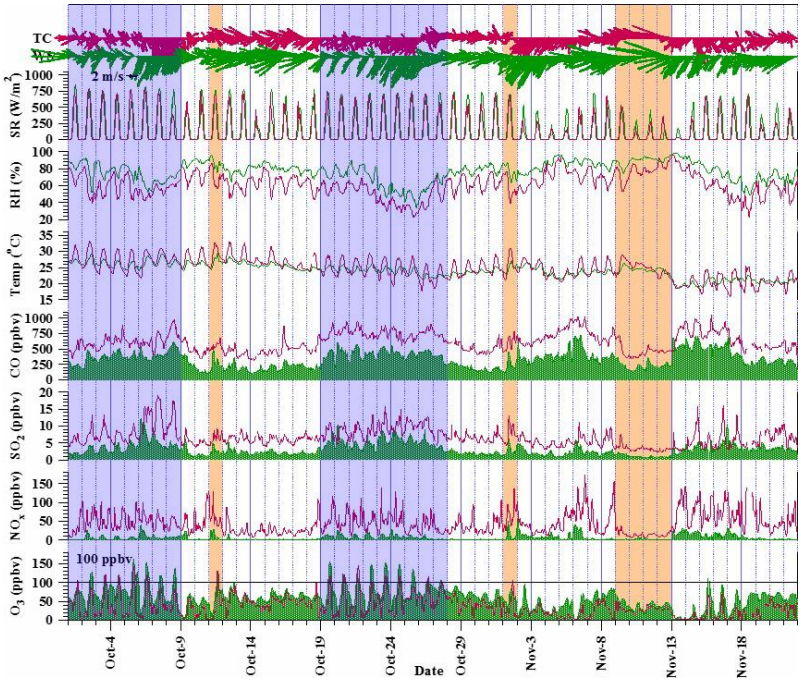

Figure 2b. Time series of trace gases and meteorological parameters observed for the sampling period of 1 Oct. - 21 Nov at WS (green) and TC (red). The black line of 100 ppbv is the threshold for O_3 episode definition. The dates seriously affected by continental high pressure and tropical cyclones are shaded in red and orange, respectively.

3.2 Meteorological influence on O_3 mixing ratios

Descriptive statistics of meteorological parameters during O_3 episode and non-episode days are summarized in Table 2. On episode days the wind speed and relative humidity were lower whereas solar radiation was stronger at both sites, suggesting that this type of weather condition was conducive to the formation and accumulation of tropospheric O_3. Furthermore, the wind direction during non-episodes was predominantly from the east (SCS), while on episodes the winds mainly came from the north and northeast which might bring more pollutants from the urban areas of Hong Kong and inland PRD to the sampling sites. The characteristics of O_3 pollution under different weather conditions were discussed below.

Table 2. Descriptive statistics (Mean ±95% C.I.) of meteorological parameters at the two sites during O_3 episodes and non-O_3 episodes days.

Parameter	**WS**		**TC**	
	O_3 episode	*Non-O_3 episode*	*O_3 episode*	*Non-O_3 episode*
Temperature (°C)	25.3 ±0.2	25.8 ±0.1	26.3 ±0.3	26.8 ±0.2
Wind speed (m s^{-1})	5.3 ±0.2	7.7 ±0.2	3.7 ±0.2	4.8 ±0.1
Wind direction (°)	45.1	89.1	19.5	86.8
Relative humidity (%)	71.7 ±1.2	85.7 ±0.4	58.4 ±1.4	69.6 ±0.6
Solar radiation (W m^{-2})*	723.2 ±26.1	613.7 ±57.6	699.0 ±29.1	537.0 ±53.1

* Average of the daily maximum solar radiation. *C.I.* denotes confidence interval.

3.2.1 Tropical cyclones

Tropical cyclone (low-pressure system) is one of the main meteorological conditions conducive to the occurrence of O_3 episodes in Hong Kong (Yin, 2004; Ling et al., 2013). In this study, 7 episode days and 3 near-episode days were closely associated with 5 tropical cyclones (*i.e.*, Trami, Usagi, Wutip, Nari and Krosa) (Table S4 and Figure S2). For example, Trami caused the worst O_3 episode on 21 Aug. with the highest peak hourly O_3 mixing ratios of 160 and 173 ppbv at TC and WS, respectively. These episode or near-episode days usually appeared 1-2 days before the arrival of the tropical cyclones, because the large-scale peripheral subsidence of the tropical cyclones usually creates the meteorological conditions favorable to the formation and accumulation of O_3, such as inversion layer, high temperature, low humidity, intensive light, and weak winds (Wang et al., 1998; Yin, 2004). The tropical cyclones also cause anti-clockwise air flows at their outskirt affecting the wind directions and subsequent the regional transport of air pollution. Figure 3 illustrates surface wind fields and air movement two days (*i.e.*, 20-21 Sept.) before the occurrence of Usagi as an example. It can be seen that when Usagi approached southeastern area of Hong Kong, it led to weak northeasterly and later northwesterly winds which potentially delivered O_3 and its precursors from highly polluted inland PRD region to the sampling sites (Yin, 2004; Wei et al., 2016; Wang et al., 2017a). The wind speed was lower than 4 m s^{-1} at the sampling sites and in their surrounding area on 20 Sept. (Figure 3a), and it gradually increased on the next day (21 Sept.)

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
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Discussion started: 20 December 2017

with the approaching of the tropical cyclone (Figure 3b). It is noteworthy that the rarely occurred westerly and northwesterly winds caused tropical cyclones resulted in unsynchronized occurrence of O_3 episodes between the two sites (Figures 3c & d). Namely, high O_3 values were observed at TC only on 20 Sept., while O_3 started to increase at WS on the next day (21 Sept.). This discrepancy might indicate the transport of O_3 and/or its precursors from terrestrial area to the offshore site driven by tropical cyclone.

Please note, not all tropical cyclones would cause high levels of O_3. For example, the tropical cyclone Haiyan observed on 9-12 Nov. over the SCS did not cause high O_3 levels (Figure 2b). Because the origin of Haiyan was at a lower latitude (southern Guam) and it moved on the waters southwest of PRD (Figure S2), the anti-clockwise air flow caused easterly and southeasterly winds in the north and northeast outer band of Haiyan. The winds originated from SCS brought in clean marine air to the sampling sites, resulting in dilution and dispersion of local air pollutants.

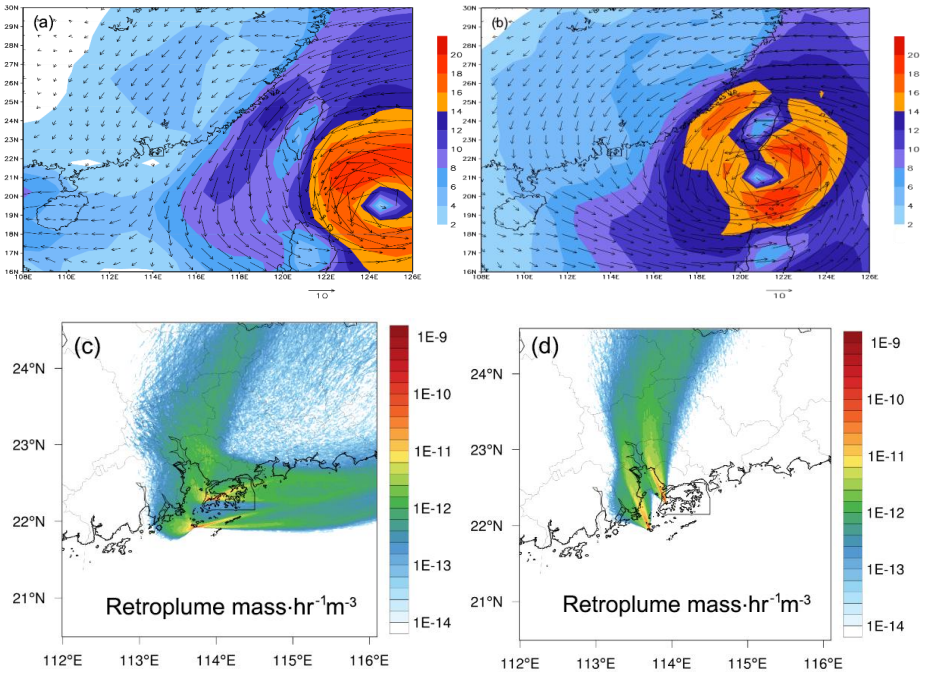

Figure 3. Model simulated 10 m wind vectors (arrows) and wind speed (shaded, unit: m s^{-1}), and the distribution of air mass concentrations (unit: mass hr^{-1} m^{-3}) within surface 100 m simulated by HYSPLIT Lagrangian backward particle release model with WS and TC as the

starting points two days (20 Sept. 2013) before (a, c) and one day (21 Sept. 2013) before (b, d) the arrival of Usagi.

3.2.2 Continental anticyclones

In addition to tropical cyclones, the continental anticyclone (high-pressure system) was frequently observed in the region, which often caused high O_3 concentrations. For example, two multi-day O_3 episodes (1-8 Oct. and 19-27 Oct.) occurred at the sampling sites when there were intensive continental anticyclones and weak Western Pacific Subtropical High (WPSH) to the north of Hong Kong (see Figure S3 as examples).

The main feature of the anticyclones is sinking air at the center with gentle clockwise winds in the northern hemisphere. The air warms up as it sinks by compression leading to warm, cloudless and dry weather, which is conducive to intensive photochemical O_3 formation. In addition, anticyclone is a large-scale weather system which produces long-lasting settled and calm weather for many days or weeks favorable to the accumulation of primary and secondary pollutants.

Indeed, the two continental high pressure systems observed in this campaign lasted 8 and 9 days, respectively, with the presence of SLBs occasionally (*i.e.*, 2-5 Oct. and 19-21 Oct.) on the first several days when the synoptic winds were relatively weak. The clockwise and slow movement of the air masses caused northeasterly and easterly winds to the sampling sites and brought in densely polluted air from the inland (Figure 2b) to the coastal areas of the SCS. For example, the CO mixing ratios were significantly elevated during these episode days, with an average of 409 and 683 ppbv at WS and TC, respectively, which were higher than other episode days. The continuous input of exotic air pollutants provided essential "fuel" to local photochemical production of O_3, leading to the severe multi-day O_3 episodes.

3.2.3 Sea-land breeze (SLB) circulation

During the sampling period, SLB circulations in the study area were identified on 21 out of 104 sampling days. The occurrence frequency was comparable to that reported by Zhang and Zhang (1997) who discovered 70 SLB days in a year in the same region. In this study, 12 O_3 episode days were thought to be influenced by SLB (see Table S4), with 5 of them (27-28 Sept., 11-12 Oct. and 1 Nov.) under the dominance of tropical cyclones (*i.e.*, Wutip, Nari and Krosa) and the other 7 days in association with the continental anticyclones. In addition to the

effects of tropical cyclones and continental anticyclones discussed above, SLB also posed non-negligible impact on O_3 pollution in these cases.

SLB circulation is driven by sea-land thermal difference and topographic conditions, and usually happens when the synoptic winds are weak (Liu et al., 2002; Lo et al., 2006; Lu et al., 2009b). In general, the temperature difference between the sea and the land is large on the SLB days. Taking 3 Oct. as an example, the maximum hourly temperature at TC was 3.2 ^{o}C higher than that at WS during daytime hours, whereas the minimum hourly temperature in the evening was 2.7 ^{o}C lower at TC than at WS. On a typical SLB day, wind blows onshore during the day (sea breeze) and offshore in the evening (land breeze). However, the transition time of breezes in this study was found to vary in a wide range. The sea breeze switched to land breeze between 00:00 and 08:00 with a median of 03:00 for breeze shifting, and 11:00 – 18:00 with the median of 14:00 was the time when land breeze turned to sea breeze. Ding et al. (2004) also reported this phenomenon and pointed out that the start time of sea breezes in Hong Kong was generally delayed to noontime due to the synoptic northerly winds blowing from the continental areas to SCS, particularly on O_3 episode days when northerly winds dominated in Hong Kong. For example, the sea breeze commenced at 15:00 on 3 Oct. and transited to land breeze at 4:00 on 4 Oct. (Figure 4). Figures 4a and 4b depict the surface wind fields with a sea breeze and a land breeze, respectively. The vertical wind fields with the sea breeze and land breeze are presented in Figures 4c and 4d, respectively. Surface and vertical SLB circulations were clearly seen in these panels of Figure 4. The mesoscale circulations caused by SLB might promote the interactions between the continental (TC) and marine (WS) atmospheres. Specifically, the primary air pollutants observed at TC could be transported to WS by land breeze. Moreover, the air masses could return to TC after sufficient photochemical evolutions over SCS, during which O_3 might also be elevated in the continental areas.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2017

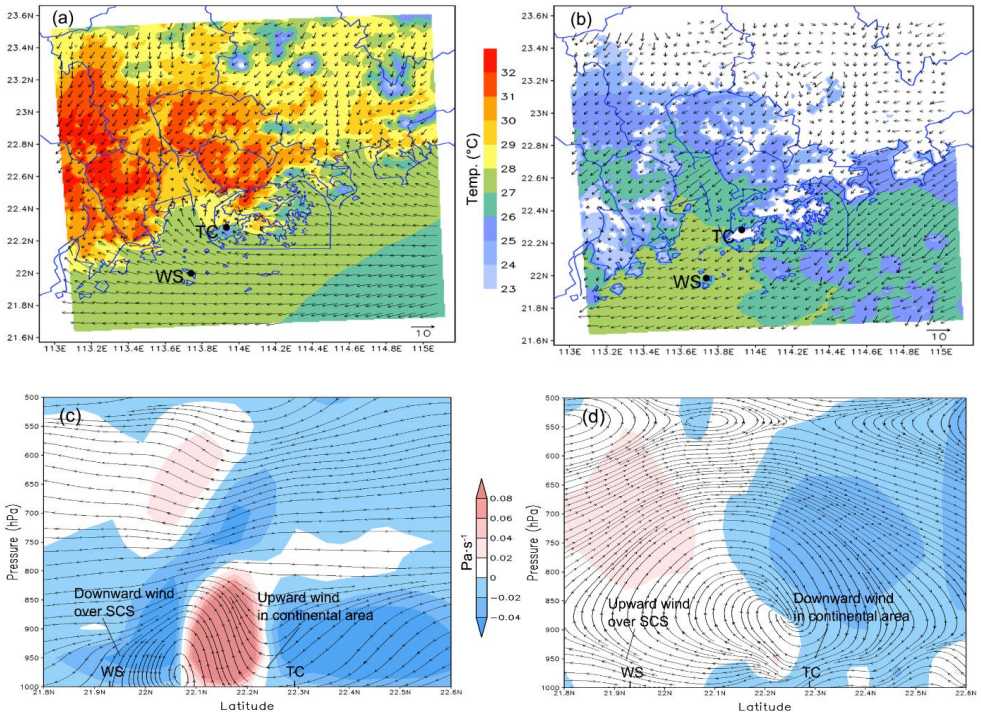

Figure 4. SLB circulation on 3-4 Oct. 2013, showing surface wind pattern (arrows) and temperature (color) at 17:00 on 3 Oct. (a) and at 04:00 on 4 Oct. (b). Vertical cross-section (taken over a longitude of 113.85 °E, mean of the longitudes of TC and WS) depicting the v–w wind stream (arrow) and the index of ω*100 (color) at 17:00 on 3 Oct. (c); and at 04:00 on 4 Oct. (d). For figures (c) and (d), the blue color (negative) and light red color (positive) present downward and upward winds, respectively. Figures (a) and (c) represent a sea breeze, and Figures (b) and (d) show a land breeze. Note that ω is the vertical velocity in isobaric coordinates.

3.3 Chemical characteristics of air masses

3.3.1 Chemical composition

To inspect the chemical characteristics of air masses on O_3 episode days and non-O_3 episode days, chemical species are statistically summarized at the two sites (Table 3). As expected, the levels of all pollutants (*i.e.*, O_3, NO_2, CO, SO_2, NMHCs and carbonyls) were significantly higher on O_3 episode days for both sites (p<0.05), except for the comparable or even lower

NO due to its titration to O_3 (see Section 3.3.2). Table S5 shows the top 10 NMHC species observed during O_3 episodes and non-episodes at the two sites. The dominant species were quite similar regardless of episode or non-episode days at both sites. The higher concentrations of both primary and secondary pollutants on episode days than those on non-episode days were likely due to more intense photochemical reactions, more local pollutant accumulation as well as the regional transport of more highly polluted air masses. On the other hand, the similar NMHCs composition at both sites during both episodes and non-episodes indicated somewhat interaction of air masses between the two sites regardless of O_3 levels.

It is worth to mention that O_3 was much higher at WS than that at TC during both episodes and non-episodes (p<0.01), with an average difference of 30.2 ppbv and 16.7 ppbv, respectively (Table 3), though the levels of O_3 precursors (*i.e.*, NO_x and VOCs) at WS were lower. Insight into VOC ratios found that ethene/ethane (0.5±0.04) and toluene/benzene (2.2±0.5) at WS were significantly (p<0.05) lower than those at TC (0.7±0.1 and 2.9±0.4, respectively), likely indicating that the air masses at WS were more aged (Guo et al., 2007). Therefore, the higher O_3 at WS might be partially attributable to the aging of air masses (*e.g.*, during the transport of continental air).

Table 3. Descriptive statistics (Mean±95% *C.I.*) of measured air pollutants, simulated OH and O_3 production rates at the two sites during O_3 episodes and non-O_3 episodes days.

Parameter	WS		TC	
	O_3 episode	*Non-O_3 episode*	*O_3 episode*	*Non-O_3 episode*
O_3 (ppbv)	74.3±3.0	43.9±1.0	44.1±3.6	27.2±0.8
O_x (ppbv)	81.6±2.9	47.8±1.0	83.3±3.7	49.4±1.0
NO (ppbv)	0.6±0.1	0.7±0.1	11.5±1.4	14.5±0.9
NO_2 (ppbv)	7.3±0.6	3.3±0.3	39.2±1.7	22.2±0.6
CO (ppbv)	391.4±9.1	209.4±6.8	652.9±16.0	541.9±6.5
SO_2 (ppbv)	4.3±0.2	1.9±0.1	8.1±0.3	5.5±0.1
NMHCs (ppbv)	17.7±1.4	9.6±1.2	20.2±2.2	16.8±2.1
Carbonyls (ppbv)	10.3±0.8	5.4±0.4	12.0±1.3	8.1±0.7
NO_2/NO (ppbv/ppbv)	12.7±1.1	4.7±0.5	3.4±0.4	1.5±0.2
Simulated OH ($\times 10^6$ molecules cm^{-3})	5.4 ±1.0	3.3 ±0.8	1.2 ±0.3	1.5 ±0.3

* Average of the daily maximum solar radiation. *C.I.* denotes confidence interval. $O_x = O_3 + NO_2$.

3.3.2 Influence of NO titration

Apart from the age of air masses, NO titration is another important factor influencing O_3 concentration. In areas with high NO levels, the NO titration ($O_3 + NO \rightarrow NO_2 + O_2$) is a main process consuming O_3. In this study, the average NO mixing ratio at TC was 14.0±0.8 ppbv, compared to 0.7±0.1 ppbv at WS (Table 1). The much lower NO at WS implied weaker titration to O_3, which enabled the survival of O_3 in high concentration. A direct evidence of NO titration effect was the trough of O_3 during the morning rush hours (06:00-07:00), together with an increase of NO_2 (Figure S4). Furthermore, the total oxidants ($O_x = O_3 + NO_2$), which are usually adopted to take into account the NO titration influence, were comparable ($p > 0.05$) between TC and WS with mean values of 83.3±3.7 ppbv and 81.6±2.9 ppbv during O_3 episodes, and 49.4±1.0 ppbv and 47.8±1.0 ppbv during non-episodes, respectively (Table 3). This was reasonable in view of the interactions between the two sites. However, the remarkably higher O_3 and lower NO at WS indicated that NO titration was a determinant factor regulating the O_3 levels at both sites.

Moreover, NO titration is generally more significant on high O_3 days, resulting in higher NO_2/NO ratios due to the conversion of NO to NO_2 by O_3. Indeed, the mean NO_2/NO ratios increased from 4.7±0.5 at WS and 1.5±0.2 at TC during non-episodes to 12.7±1.1 and 3.4±0.4 during O_3 episodes, respectively, implying that more O_3 was titrated by NO during episodes. As a result, NO at TC was lower ($p < 0.01$) during O_3 episodes than during non-episodes (Table 3). It is noteworthy that NO at WS was on the same level between O_3 episode and non-O_3 episode days ($p > 0.05$). This probably related to the weak titration at this marine site due to the trivial NO concentrations in both periods, as well as the counteracting effect of the increased transport of NO under northerly winds against the enhanced titration during O_3 episodes.

The aforementioned discussion demonstrated that NO titration played an important role in altering O_3 distribution, especially on O_3 episodes days. The lower NO (weaker NO titration) partially resulted in the higher O_3 concentrations observed at WS.

3.3.3 Atmospheric oxidative capacity

The O_3 formation is generally initiated by the oxidations of VOCs by OH. Furthermore, the oxidative radicals (*e.g.*, RO_2) generated from these reactions experience an array of transformations, through which OH can be recycled. Thus, the OH concentration is an important indicator to evaluate the atmospheric oxidative capacity and the potential of O_3 formation. As shown in Table 3, the OH concentration simulated by PBM-MCM model was significantly higher (p<0.05) at WS than that at TC, regardless of O_3 episode ($5.4 \pm 1.0 \times 10^6$ molecules cm^{-3}) or non-episode days ($3.3 \pm 0.8 \times 10^6$ molecules cm^{-3}). This indicated that the oxidative capacity of the atmosphere at WS was stronger than that at TC, which might explain the higher O_3 at WS. Moreover, while the simulated OH remained unchanged (p>0.05) at TC, it increased largely (p<0.05) from non-episodes to episodes at WS, suggesting that the oxidative capacity of the atmosphere at WS was more enhanced during O_3 episodes.

Furthermore, we simulated the rates of O_3 production, destruction and net O_3 production at both sites, as presented in Figure 5. No significant change in net O_3 production was observed between O_3 episode ($1.1 \pm 0.6 \times 10^7$ molecules cm^{-3} s^{-1}) and non-episode days ($1.2 \pm 0.3 \times 10^7$ molecules cm^{-3} s^{-1}) at TC (p>0.05). Since previous studies (Cheng et al., 2010a; Wang et al., 2017a) repeatedly confirmed that O_3 formation at TC was limited by VOCs, the unchanged net O_3 production might be due to the balance between the increased O_3 production and O_3 destruction resulting from the elevated VOCs and NO_x during O_3 episodes, respectively. On the contrary, the net O_3 production increased remarkably from non-episodes ($1.2 \pm 0.2 \times 10^7$ molecules cm^{-3} s^{-1}) to O_3 episodes ($3.9 \pm 0.8 \times 10^7$ molecules cm^{-3} s^{-1}) at WS. Insight into the O_3 formation and destruction pathways found that the slight increases of O_3 destructions (mainly through $OH+NO_2$ and O^1D+H_2O) were overridden by the great enhancements of O_3 productions through RO_2+NO and HO_2+NO. Our recent study (Wang et al., 2017b) revealed that O_3 formation at WS was in a transition regime and much more sensitive to NO_x during non-episodes, when the principal photochemical reaction pathways to produce O_3 (*i.e.*, RO_2+NO and HO_2+NO) were seriously limited by the low NO_x levels. During O_3 episodes, with the increase of NO_x (Table 3), the contributions of the aforementioned two O_3 production pathways were significantly enhanced (Figure 5). In addition, the increased VOCs also contributed to the O_3 formation by producing more RO_2 radicals (not shown here) through OH-initiated reactions. Therefore, the combined effect of elevated VOCs and NO_x

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2017

during O_3 episodes at WS was the increase of O_3 production, which was insignificant at TC. Detailed discussion on the O_3 photochemistry at WS can be found in our recent publication (Wang et al., 2017b).

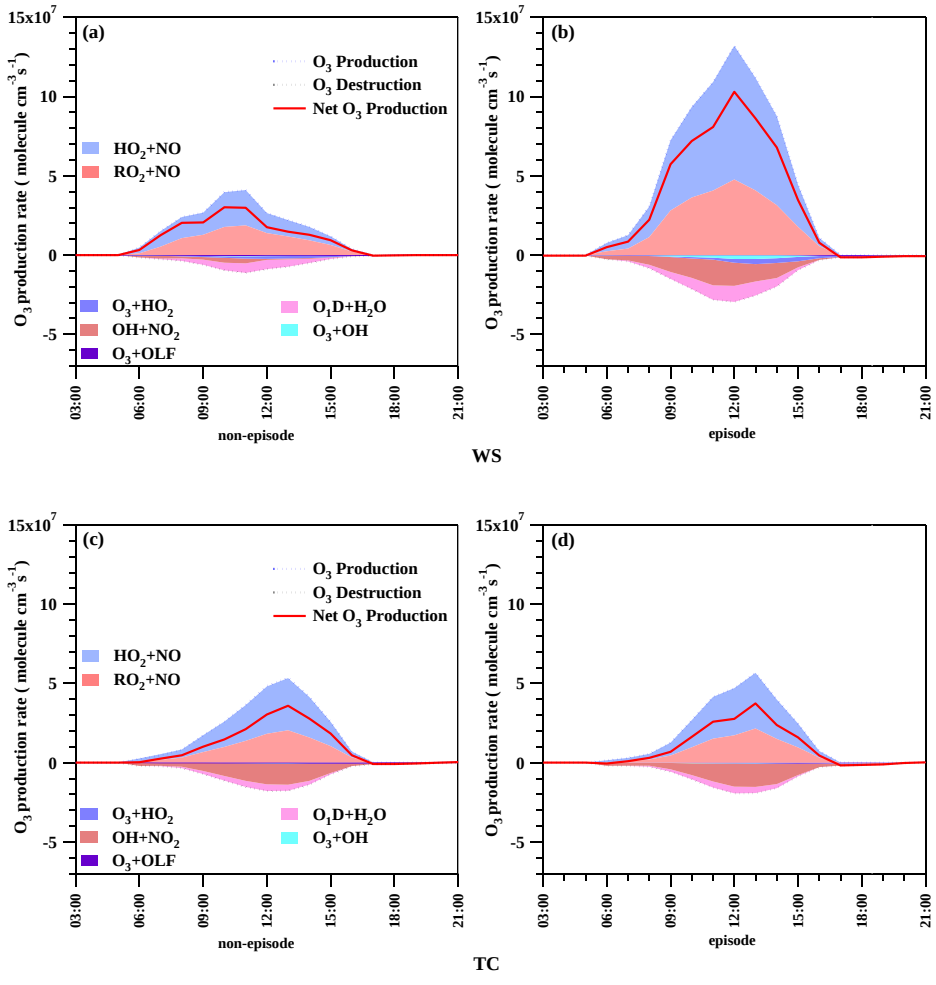

Figure 5. Simulated rates of O_3 production, destruction, and net O_3 production (unit: molecules cm^{-3} s^{-1}) on O_3 episode and non-episode days at WS (panels (a) and (b)) and TC (panels (c) and (d)). Panels (a) and (b) were adapted from our recent publication (Wang et al. 2017b).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2017

3.4 Impact of air mass interaction on O_3 pollution in coastal areas

Driven by various weather systems (*e.g.*, continental anticyclones, WPSH, tropical cyclones and SLBs), continental and marine air masses frequently interact with each other in the coastal areas. When continental air masses intrude into marine atmosphere, the chemical composition and atmospheric oxidative capacity over the marine atmosphere will be altered by the introduction of anthropogenic pollutants. Taken 21 Aug. as an example, when the sampling sites (TC and WS) were under northwesterly to southwesterly winds caused by tropical cyclone (Figure 2a), the maximum hourly O_3 reached 160 and 173 ppbv at TC and WS, respectively. Correspondingly, the primary air pollutants all stayed on high levels, compared to those during non-episodes (Figure 2a). Since WS was almost free of anthropogenic emissions, the great abundances of both primary and secondary air pollutants implied the influence of continental pollution on air quality at this site. Figures 6-7 depict the spatial distributions of CO and O_3 over the region of interest at selective time (08:00, 14:00, 19:00 and 23:00) on 21 Aug., respectively. CO is presented as an example of primary air pollutants emitted from anthropogenic sources. The spatiotemporal patterns of CO and O_3 were simulated by WRF-CMAQ. Noticeably, the model well reproduced high level of CO in PRD region at 08:00, which was reasonable in view of the vehicular emissions in urban areas during morning rush hours. However, under the dominance of northwesterly winds in the morning, the center of high CO moved to the coastal areas. Even though the winds changed to southwesterly at noon, CO concentration over SCS was still remarkably elevated according to the simulated results at 14:00. Further, the spatial distribution of CO at 19:00 and 23:00 confirmed the continuous movement of the polluted air masses away from the land under southwesterly winds. It should be noted that the increase of CO in PRD region at 19:00 and 23:00 were most likely caused by the vehicle emissions during evening rush hours. Overall, the dynamic distribution of CO in the study area clearly indicated the interaction between continental and marine atmospheres. As a result of the intrusion of continental air, high level of O_3 was simulated over SCS at 14:00 (Figure 7b), which was comparable to the observed value (148 ppbv) at WS. Moreover, O_3 was even higher over SCS than that in continental area, due mainly to the more aged air masses, lower NO titration and higher oxidative capacity of the atmosphere (see section 3.3). Consistent with CO, the center of high O_3 moved away from the land. At 19:00, the O_3-laden air mass penetrated into the SCS ~300 km, causing ~8,000 km^2 water area (8 times the area of Hong Kong) under high level of O_3 (>100

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2017

ppbv). This case provided solid evidence of the transport of continental air masses to SCS, which aggravated air pollution (particularly O_3 pollution) in this offshore area.

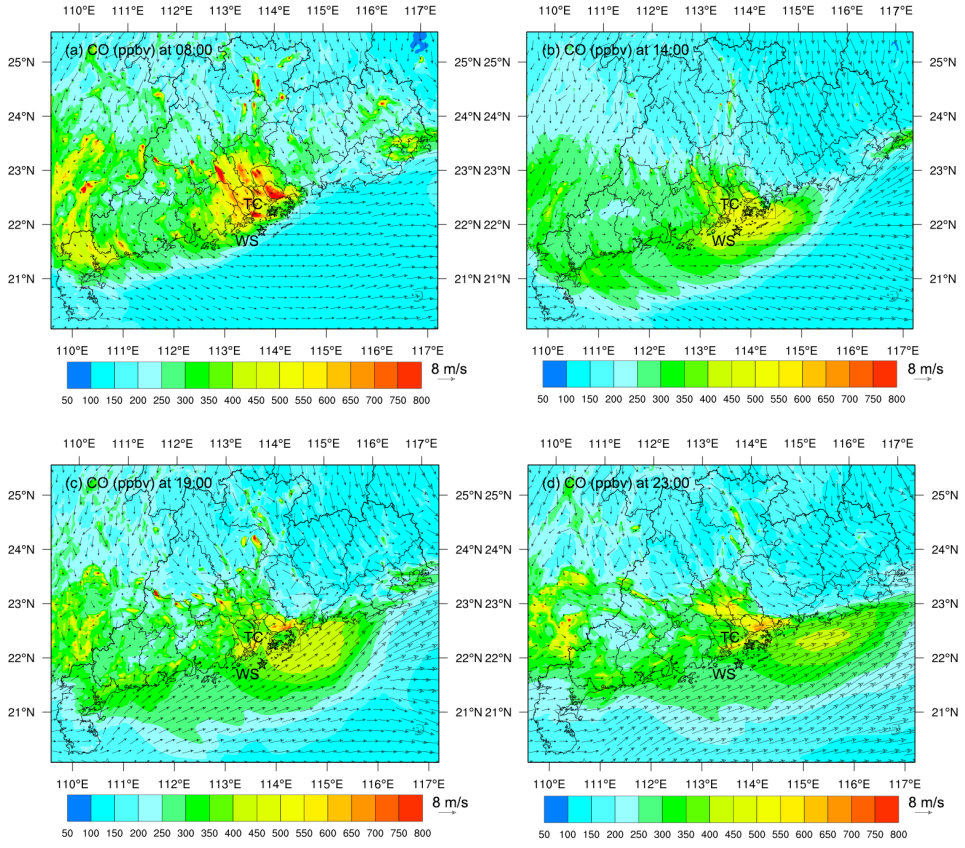

Figure 6. Spatial distribution of CO at 08:00 (a), 14:00 (b), 19:00 (c) and 23:00 (d) on 21 August simulated by WRF-CMAQ, taken as an example of the "Outflow" interaction pattern. Arrows in the figure represent the surface wind field.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2017

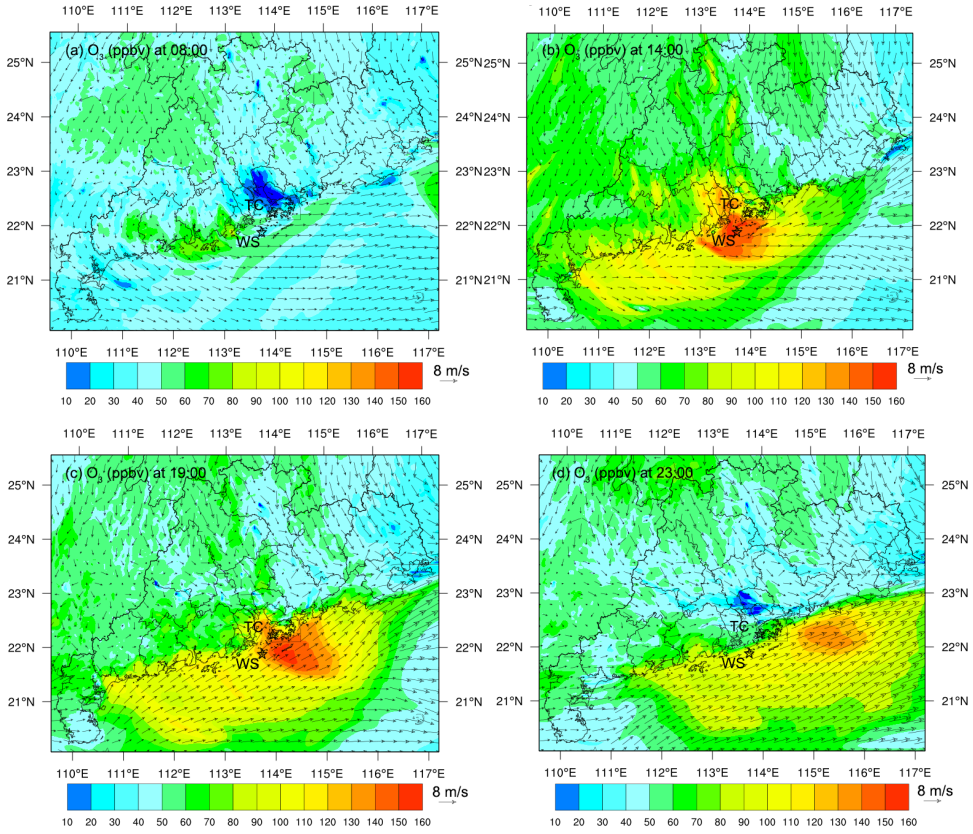

Figure 7 Spatial distribution of O_3 at 08:00 (a), 14:00 (b), 19:00 (c) and 23:00 (d) on 21 August simulated by WRF-CMAQ, taken as an example of the "Outflow" interaction pattern. Arrows in the figure represent the surface wind field.

In contrast to outflow of continental air masses, the continental area near the coast could also be immersed by oceanic air under sea breeze. Contrary to our general expectation that ocean airflow dilutes air pollution, the sea breeze carrying elevated O_3 formed over SCS might build up the terrestrial O_3 in the coastal area in some cases. Figure 8 shows the spatial distribution of O_3 over the study area on 3 Oct., as an example of SLB regulating O_3 formation and distribution (see Figure 4). Similar to the aforementioned scenario controlled by tropical cyclone, the simulated O_3 at 14:00 was generally higher over SCS than in the terrestrial area, indicating the transport of polluted air masses from the land to the sea area. This was confirmed by the prevailing northeasterly winds in the morning (08:00 here). However, the O_3-laden air did not move far away from the land subsequently. Instead, it progressively approached the land, leading to increase of O_3 concentration in most parts of

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-988
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 20 December 2017

Hong Kong. This is because the wind direction in the coastal region changed from northeasterly to southeasterly at 17:00. Namely, the sea breeze appeared in late afternoon, which delivered the high O_3 formed over SCS to the continental areas near the coast. In fact, the air quality monitoring stations deployed in southern Hong Kong by HKEPD also recorded the O_3 peak in the evening when O_3 could not be formed locally (Figure S5), further confirming the recirculation of O_3-laden air from SCS to coastal areas of Hong Kong under sea-breeze. However, the oceanic air did not penetrate further into the inland PRD, which was likely stopped by the strong northeasterly winds dominated in the inland areas. Overall, it can be seen that SLB as a common interaction between marine and continental atmospheres played important role in regulating O_3 formation and distribution in coastal region of SCS, which is also applicable to other similar mesoscale environments over the world.

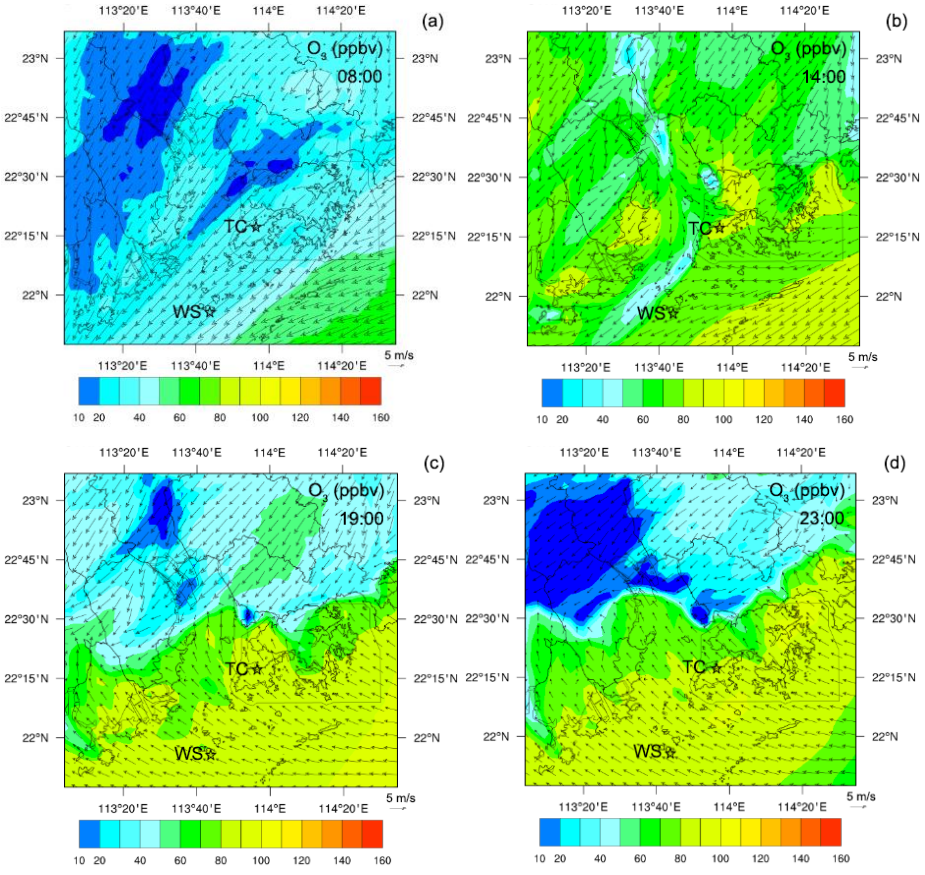

Figure 8. Spatial distribution of O_3 at 08:00 (a), 14:00 (b), 19:00 (c) and 23:00 (d) on 3 October, taken as an example of the "SLB" interaction pattern. Arrows in the figure represent the surface wind field.

4. Conclusions

Coastal regions with dense population, economic prosperity and environmental pollution are common in the world. This study provided an overview of O_3 pollution in warm seasons around a coastal region of SCS, focusing on the influences of interactions between marine and continental atmospheres on air quality in this subtropical region. The concurrent measurements of primary and secondary air pollutants at TC (a continental site) and WS (a marine site) from August to November 2013 indicated that O_3 was much higher at WS than that at TC, contrary to the more abundant primary air pollutants at TC. At the two sites, O_3 episodes and near-O_3 episodes were frequently observed, which were closely associated with continental anticyclone, tropical cyclone and SLB. In addition to high temperature, strong solar radiation and weak wind, the aforementioned meteorological conditions all favored the transport of polluted air masses from continental areas to SCS, during which the air pollutants were transformed with the aging of air masses. After arriving in SCS, the land-originated air pollutants further involved in intensive photochemical reactions with the trait of low NO titration to O_3 and high O_3 production rate, leading to higher O_3 level in marine atmosphere (WS) than that in coastal cities (TC). In addition to the continental outflow that aggravated O_3 pollution over SCS, SLB as a common interaction in coastal areas also often facilitated the recirculation of O_3 formed over SCS to the continental areas, building up O_3 concentration in coastal cities under sea breeze. The findings can be extended to other similar regions to advance our understanding of O_3 pollution.

Acknowledgements

This project was supported by the Natural Science Foundation of China (Grant No. 41275122), the Research Grants Council (RGC) of the Hong Kong Government of Special Administrative Region (PolyU5154/13E, PolyU152052/14E, PolyU152052/16E and CRF/C5004-15E), the Guangdong special fund for science and technology development (2017B020216007), and partly by the Hong Kong PolyU internal grant (G-SB63, 1-BBW4 and 4-ZZFW). The authors thank HKEPD for provision of the air quality and meteorological data at TC site, and are grateful to Po On Commercial Association Wan Ho Kan Primary

School at Tung Chung and the National Marine Environmental Monitoring Station at Wanshan Island for their generous support on the field study. Contributions to field measurements by Kalam Cheung, Dawei Wang, Bo Liu, Nan Wang, Jiamin Ou, Huanghuang Yan and Xiaoxin Fu are also highly appreciated. The authors also gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication.

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