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Establishing a conceptual model for photochemical ozone pollution in subtropical Hong Kong

Z.H. Ling, H. Guo, J.Y. Zheng, P.K.K. Louie, H.R. Cheng, F. Jiang, K. Cheung, L.C. Wong, X.Q. Feng

A conceptual model is for the first time developed for ozone in Hong Kong. Tropical cyclones are most conducive to the occurrence of high O_3 episodes. Super-regional and regional transports are other factors that contribute to high O_3 levels in Hong Kong.

Highlights
- A conceptual model is for the first time developed for ozone in Hong Kong.
- Tropical cyclones are most conducive to the occurrence of high O_3 episodes.
- Super-regional and regional transports are other factors that contribute to high O_3 levels in Hong Kong.

Abstract
Photochemical ozone (O_3) formation is related to its precursors and meteorological conditions. A conceptual model of O_3 air pollution is developed based on the analysis of data obtained at Tung Chung (TC) in Hong Kong. By comparing meteorological parameters between O_3 and non-O_3 episode days, it was found that high temperatures, strong solar radiation, low wind speeds and relative humidity, northeasterly and/or northwesterly prevailing winds were favorable for the O_3 formation, while tropical cyclones were most conducive to the occurrence of O_3 episodes. Backward trajectories simulation and graphical illustration of O_3 pollution suggested that super-regional (i.e. central and eastern China) and regional (i.e. Pearl River Delta, southern China) transport was another factor that contributed to high O_3 levels in Hong Kong. The photochemical O_3 formation, generally VOC-limited in Hong Kong, was controlled by a small number of volatile organic compounds (VOCs). Furthermore, the positive matrix factorization (PMF) simulation suggested that solvent usage and vehicular emissions are the major contributors to ambient VOCs in Hong Kong. Finally, this paper presents recommendations for further O_3 research and implementation of O_3 control strategies.

1. Introduction
Ozone (O_3), a major component of photochemical smog which impairs visibility and human health, is formed by a complex series of chemical reactions involving volatile organic compounds (VOCs) and nitrogen oxides (NO_x) in the presence of sunlight (Seinfeld and Pandis, 2006; Zheng et al., 2010). In most urban areas, ambient concentrations of photochemically formed O_3 are related to its precursors, while favorable meteorological conditions are required for the occurrence of high O_3 concentrations (Ding et al., 2004; Guo et al., 2009). In Hong Kong, high O_3 concentrations or “O_3 episodes” are commonly observed in late summer and autumn, and are closely associated with local photochemical production and long-range transport (Guo et al., 2009; Wang et al., 2009).

In order to understand the factors that influence photochemical O_3 formation, conceptual models of O_3 air pollution have been developed in recent years for different regions. A conceptual model is a qualitative explanation of the formation and accumulation of O_3 in a given area based on the chemical characteristics of the ambient atmosphere, as well as the physical transport and removal process observed in given locations (Tom et al., 2006; Pun et al., 1998). Pun et al. (1998) developed a conceptual model to investigate the O_3 formation in San Joaquin Valley in the USA and found that the high O_3 concentrations observed resulted from both the transport of O_3 and precursors from upwind locations, and the local production of O_3 in urban areas within the valley. Tom et al. (2006) developed...
a conceptual description of the nature of the O\textsubscript{3} air quality problem in the O\textsubscript{3} transport region (OTR), including Connecticut, Delaware, the District of Columbia, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, Vermont and north Virginia in USA and concluded that a severe O\textsubscript{3} episode in the OTR can contain elements of long-range air pollution transport from outside the OTR, regional scale transport within the OTR from channeled flows in nocturnal low level jets, and local transport along coastal shores due to bay, lake, and sea breezes.

To formulate and implement effective control strategies for O\textsubscript{3} pollution, the major objective of this study is to develop a conceptual model for the formation, transport and accumulation of O\textsubscript{3} in subtropical Hong Kong by integrated data analysis at Tung Chung (TC) between 2005 and 2010. We chose the TC site because only at this site the most comprehensive dataset including real-time O\textsubscript{3}, CO, NO\textsubscript{x}, SO\textsubscript{2}, VOCs and meteorological parameters has been systematically collected so far. In addition to the influence of local emission sources, the sampling site is also affected by polluted continental air masses from the highly industrialized PRD region of mainland China (Guo et al., 2009; Zhang et al., 2007). Thus, this site is capable of monitoring air pollutants transported from the inland PRD region and is suitable for assessing their impact on local air quality. A variety of aspects, including meteorological conditions, source apportionments of O\textsubscript{3} precursors, O\textsubscript{3}-precursor relationships, and the characteristics of air masses in Hong Kong are evaluated. The conceptual model in this study tries to answer the following questions: (1) what meteorological conditions are favorable to photochemical O\textsubscript{3} formation? (2) Does regional transport have an important influence on high O\textsubscript{3} levels? (3) Is the O\textsubscript{3} formation limited by VOCs, or NO\textsubscript{x}, or both, and therefore which sources of precursors are the most important ones to be controlled? (4) What are the main sources of O\textsubscript{3} precursors i.e. VOCs and NO\textsubscript{x}?

2. Methodology

2.1. Description of sampling site

Tung Chung (TC, 22.30°N, 113.93°E, Fig. 1) is a newly-developed residential town located on northern Lantau Island, about 3 km south of the Hong Kong International Airport at Chek Lap Kok with Hong Kong urban center 20 km to the southwest and Macau 38 km to the northeast. The TC site is adjacent to highway and railway lines that connect the airport with other islands of Hong Kong. The potential impact of the airport, highway and railway lines on VOC and NO\textsubscript{x} levels at the sampling site was demonstrated to be insignificant (AOAQS, 2011; Guo et al., 2007; So and Wang, 2004). In addition to the influence of local emission sources, TC is also affected by polluted continental air masses from the highly industrialized Pearl River Delta (PRD) region, south China. As such, the TC site is an ideal location to assess the O\textsubscript{3} pollution in Hong Kong.

2.2. Sampling data

In this study, real-time VOC data collected from 2005 to 2010 was provided by the Hong Kong Environmental Protection Department (HKEPD). The on-line VOC analyzer (Syntech Spectras GC 955, Series 600/800, Netherland) includes two sampling systems and two column separating systems: GC1 for the 16 C\textsubscript{2}eC\textsubscript{5} hydrocarbons, and GC2 for the 14 C\textsubscript{6}eC\textsubscript{10} hydrocarbons. Details can be found in HKEPD (2012). In this study, the GC system was operated continuously, with samples collected and analyzed every 30 min. Furthermore, in order to maintain the consistency for the input of different models, the 30-min data was averaged into hourly values.

In addition, built-in computerized programmes of quality control systems, i.e. auto-linearization and auto-calibration, and calibration with span gas were used. Before sampling, the analyzers were calibrated weekly by injecting certified calibration gas (NPL span gas, National Physical Laboratory). In addition, the quality of the real-time data was assured by comparison with the canister samples analyzed by the University of California at Irvine (UCI) (Colman et al., 2001). The accuracy and precision of the measurements were obtained using the following methods: the accuracy of GC was based on weekly span checks, monthly calibration and annual auto-linearization using NPL gas. The precision of GC was based on quarterly precision check results (the 95% probability limits for the integrated precision based on the weekly precision check results of the latest 3 months). The detection limits of the

![Fig. 1. Location of the sampling site and the surrounding region.](image-url)
above VOCs varied compound by compound, ranging from 0.002 to 0.787 ppbv. The accuracy of the measurements was 1–10% for the above VOCs, whereas the precision was 2.5–20%.

Furthermore, other trace gases, including O₃, CO, SO₂, NO–NO₂–NOₓ and meteorological parameters were also obtained from HKEDP (http://epic.epd.gov.hk/ca/uid/airdata).

2.3. Procedures for developing a conceptual ozone model

Fig. 2 illustrates three steps for developing a conceptual ozone model. The first step is to generalize the meteorological conditions, air mass transport characteristics, and precursor levels on O₃ episode days by analyzing the measurement data: first, we identified the O₃ episodes, especially multi-day O₃ episodes from 2005 to 2010; second, we analyzed and compared the meteorological conditions on O₃ and non-O₃ episode days; third, we investigated the characteristics of air masses on O₃ and non-O₃ episode days; fourth, we analyzed the source contributions of VOCs and investigated the O₃-precursor relationships. Based on the generalized requirements for an O₃ episode day in step 1, we proposed a conceptual model for O₃ pollution which considers atmospheric chemical and physical processes, emission sources of O₃ precursors and meteorological parameters during O₃ episode events (step 2). Once the conceptual model is established, O₃ episode events will be forecast by looking into the meteorological conditions, air mass transport and abundance and sources of precursors (step 3). The proposed conceptual model will be evaluated by case studies.

2.4. Simulation tools for the conceptual model development

2.4.1. Backward trajectories simulation

Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT 4.9, http://ready.arl.noaa.gov/HYSPLIT.php), developed by National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory, was applied to air masses at TC at every 3 h with the start time of 0000 LT (local time) at the ending point of 200 m above sea level. Furthermore, the trajectories were classified into different groups by using Hierarchical Clustering Method (Ward, 1963). Details can be found in Guo et al. (2009).

2.4.2. Positive matrix factorization (PMF) model

PMF model v 3.0 was applied to investigate the VOC source apportionments in this study. PMF is a multivariate factor analysis tool that decomposes a matrix of speciated data into two matrices, factor contributions and profiles, which can be interpreted by an analyst as to what sources are represented based on observations at the receptor site. A detailed description of this model can be found in Guo et al. (2011).

2.4.3. Observation-based model (OBM)

The OBM uses concentrations of O₃ and its precursors (i.e. VOCs, CO and NO), as well as meteorological data measured as a function of time at given sites. Detailed description of the OBM model can be found in Ling et al. (2011). Briefly, the relative incremental reactivity (RIR) functions simulated by the OBM model can be used to evaluate the sensitivity of O₃ photochemical production to the changes in the concentration of its individual precursors in the given areas.

2.4.4. Photochemical trajectory model incorporated with master chemical mechanism (PTM-MCM model)

The PTM is a ground-level Lagrangian box model, simulating complex chemical reactions within a well mixed boundary layer air parcel, which extends from the Earth’s surface up to the top of a diurnally varying boundary layer. The chemical mechanism employed in the PTM is an extended version of MCM v3.1, which is a near-explicit chemical mechanism describing the detailed degradation of a large number of emitted organic compounds and the resulting generation of O₃ and other secondary pollutants under conditions appropriate to the atmospheric boundary layer. Furthermore, a photochemical O₃ creation potential (POCP) index is used to describe the relative contribution of VOCs to O₃ formation at the regional scale in the PTM model. The detailed model description and the initial concentrations for the majority of VOCs in the model can be found in Cheng et al. (2010a).

3. Conceptual model development for the O₃ pollution

3.1. What meteorological conditions are favorable to photochemical O₃ formation?

3.1.1. General characteristics of meteorological conditions conducive to O₃ formation

In this study, an O₃ episode day was defined when the highest hourly O₃ concentration of a given day exceeded 200 µg m⁻³ (~102 ppbv) based on the Ambient Air Quality Standard in China (China’s Grade II standard, http://english.mep.gov.cn/standards/reports/standards/). In addition, a multi-day O₃ episode referred to a period of at least 3 consecutive O₃ episode days. Table 1 identifies multi-day O₃ episodes and selected non-O₃ episodes at TC from 2005 to 2010. A total of 10 multi-day O₃ episodes were observed from 2005 to 2010 at TC. The non-O₃ episodes were selected as the days with the hourly maximum O₃ concentration lower than 102 ppbv in the same month as that for multi-O₃ episodes. To provide the representative characteristics of non-O₃ episode days, investigate the influence of different factors and improve the statistical significance, non-O₃ episode days were selected as many as possible for comparison. Table 2 shows statistical descriptions of air pollutants together with meteorological parameters for O₃ and non-O₃ episode days. Fig. 3 illustrates the mean diurnal variations of O₃ and meteorological parameters, including solar radiation, temperature, relative humidity, wind speed, and wind direction at TC on O₃ and non-O₃ episode days from 2005 to 2010. Much higher concentrations (p < 0.01) of O₃ and
some primary pollutants, i.e. SO2 and CO, were observed on the O3 episode days. However, NO level was comparable on both O3 episode and non-O3 episode days (\(p > 0.05\)), while higher NO2 (\(p < 0.01\)) was observed on O3 episode days. In addition, temperature and solar radiation were higher on the O3 episode days than non-O3 episode days (\(p < 0.01\)), while the relative humidity and wind speed were lower (\(p < 0.01\)), indicating that meteorological parameters had significant impact on O3 levels. Indeed, inspection of all the 10 multi-day O3 episodes found that high O3 levels were closely associated with high temperature (\(>28^\circ C\) at daytime), strong solar radiation (\(>700\) W m\(^{-2}\) at daytime), low wind speed (\(<2\) m s\(^{-1}\) at daytime) and relative humidity (\(<70\%\) at daytime).

On a regional scale, a high-pressure system over China may transport polluted continental air masses to Hong Kong, resulting in high O3 concentrations. Fig. 4 shows the mean sea level pressure and wind field on 1000 hpa for East Asia from 23 October to 1 December 2007, when five O3 episode days were observed (Guo et al., 2009). It is clear that there was an intensive high-pressure system over northern China, while Hong Kong was in the front of the high-pressure ridge. Due to the influence of the high-pressure system, the prevailing synoptic winds in Hong Kong were from the northeast, which might lead to high O3 levels. Indeed, on 24–26 October, an O3 episode event was found at TC. Furthermore, the diurnal patterns on the O3 episode days observed in 2005–2010 (Fig. 3) showed a clear diurnal shift in wind speed and direction at TC – southeasterner/northeaster at lower speeds at night and northerly/northwesterly at higher speeds during daytime when the O3 levels were usually high, confirming that synoptic winds were associated with high O3 concentrations. Previous studies demonstrated that the prevailing north and northeast winds brought VOC-laden air and O3 from inland PRD region to Hong Kong (Guo et al., 2009; Wang et al., 2009).

### 3.1.2. Impact of tropical cyclones

Table 1 shows the typical synoptic charts on the nine O3 episode events. It is remarkable that the nine severe O3 episode events from 2005 to 2009 were all influenced by tropical cyclones over the East and South China Sea. The tropical cyclones were also found to be most conducive to the occurrence of high O3 episodes from 1994 to 2003 (Lee et al., 2002; Huang et al., 2005). When a tropical cyclone was formed and its center was over the East and the South China Sea, it intensified the inflow in the lower atmospheric layer and the outflow in the upper atmosphere, which caused stagnation and subsidence air over Hong Kong, forming an inversion layer. Such an inversion layer is not favorable to the dispersion of air pollutants. Nevertheless, it should be noted that though all tropical cyclones over the East and the South China Sea caused high O3 levels, it does not mean that all the O3 episode days in Hong Kong were induced by tropical cyclones. Under stable meteorological conditions which include high temperature, strong solar radiation, and calm winds, high O3 levels could also be observed. Huang et al. (2005) counted that about 62% of O3 episodes from 1999 to 2003 resulted from cyclonic weather patterns.

### 3.2. Does regional transport have an important influence on high O3 levels?

Analysis of synoptic wind patterns above suggested the influence of regional transport of air pollutants at TC. In order to determine whether the air masses originated from local, regional and super-regional sources, 24-h backward trajectories were developed using the NOAA-HYSPLIT 4.9 model with the Global Data Assimilation System (GDAS) meteorological data for 3-h intervals at the ending point of 200 m above sea level. These air masses were classified into local, regional (from PRD region), oceanic and super-regional air masses according to their source origins (i.e. longitude and latitude). In addition, cluster analysis was applied to segregate the calculated trajectories into a number of groups for each month from 2005 to 2010 using the hierarchical Ward's method with a square Euclidean measure (Ward, 1963). In total, 55 cluster groups were obtained. Based on their pathways, air masses arriving at TC were classified into four categories for each month from 2005 to 2010. In order to characterize the four types of air masses, two cases are presented here. Taking September 2005 and June 2010 as examples (Fig. 7), in September 2005, four categories were described: (i) air masses originating from inland China, passing over Guangdong province and finally arrived at TC (track 1); (ii) air masses originating in the Hong Kong area (track 2); (iii) air mass originating in the South China Sea (track 3) with fast movement; and (iv) air masses originating from the eastern China coast, passing over the coast of eastern Guangdong with very slow movement (track 4). Hence, tracks 1 and 4 were identified as super-regional transport; track 2 was identified as local transport while track 3 originated from the South China Sea. In June 2010, four categories were obtained as well: (i) air masses originating from eastern China coast, passing over the coast of eastern Guangdong with very slow movement (track 1); (ii) air masses originating from the PRD region (track 2) with slow movement; (iii) air mass originating from South China Sea (tracks 3 and 4) with fast movement. Track 1 was identified as super-regional transport, while track 2 was classified as regional

| Table 1 |
|----------|
| Ozone episode and non-ozone episode days in 2005–2010. |
| **Ozone episode** | Period | Non-ozone episode\(^a\) | Period\(^b\) |
| 2005 Episode 1 | 18/19/20 Jul 2005 | 2005 Non-episode 1 | Jul 2005 |
| 2005 Episode 2 | 2/3/4 Oct 2005 | 2005 Non-episode 2 | 1–15 Oct 2005 |
| 2006 Episode 1 | 3/4/5 Nov 2006 | 2006 Non-episode 1 | 1–15 Nov 2006 |
| 2007 Episode 1 | 15–21 Sep 2007 | 2007 Non-episode 1 | Sep 2007 |
| 2007 Episode 2 | 5/6/7 Oct 2007 | 2007 Non-episode 2 | Oct 2007 |
| 2007 Episode 3 | 24/25/26 Oct 2007 | | |
| 2008 Episode 1 | 10–16 Sep 2008 | 2008 Non-episode 1 | Sep 2008 |
| 2009 Episode 1 | 6–9 Oct 2009 | 2009 Non-episode 1 | Oct 2009 |
| 2009 Episode 2 | 22–24 Oct 2009 | | |
| 2010 Episode 1 | 28–31 Aug 2010 | 2010 Non-episode 1 | Aug 2010 |

\(^a\) Days with low ozone concentration (<200 \(\mu\)g m\(^{-3}\)), used for comparison with ozone episode day (>200 \(\mu\)g m\(^{-3}\)).

\(^b\) Ozone episode days excluded if applicable.

### Table 2

Statistical description of air pollutants and meteorological parameters during the O3 episode events and the selected non-O3 episode days\(^b\) (mean ± 95% confidence interval).

| O3 (ppbv) | NO (ppbv) | SO2 (ppbv) | CO (ppbv) | Temperature (\(^\circ\)C)\(^a\) | NO2 (ppbv) | Wind speed (m s\(^{-1}\))\(^a\) | Solar radiation (W m\(^{-2}\)) | Humidity (%)\(^a\) |
|-----------|-----------|------------|-----------|-----------------|-----------|-----------------|-----------------|-----------------|
| 40.4 ± 2.4 | 11.5 ± 0.9 | 13.6 ± 0.7 | 793.1 ± 0.1 | 34.1 ± 2.6 | 37.9 ± 1.1 | 3.7 ± 0.2 | 764 ± 32 | 77.1 ± 1.9 |
| 22/24 Oct 2005 | 25.6 ± 0.6 | 12.5 ± 0.6 | 7.7 ± 0.4 | 570.1 ± 5.6 | 31.2 ± 1.1 | 21.5 ± 0.4 | 4.7 ± 0.2 | 705 ± 29 | 81.1 ± 1.1 |

\(^a\) Daily maximum average value.

\(^b\) The selected non-O3 episode days were presented in Table 1.
transport. The trajectory results confirmed that the air masses were of different origins during different periods.

Table 3 presents the average values of different pollutants of the four types of air masses from 2005 to 2010. SO2, NO and TVOCs showed higher concentrations in the local and regional air masses, and lower concentrations in the oceanic air masses, most likely due to the dilution of cleaner air from the ocean. However, O3 had the highest concentration in the super-regional air masses, followed by regional, oceanic and local air masses. The relatively higher O3 levels in super-regional and regional air masses indicated that long-range transport contributed significantly to the increase of background O3 levels in Hong Kong. Indeed, Wang et al. (2009) found that long-range transport made a significant contribution to the increase in "total ozone" in urban Hong Kong, and about 81% of the O3 increase in Hong Kong was due to the O3 increase in the background air. On the other hand, the lower O3 level (\( p < 0.01 \)) in the local air masses was due to the titration of NO at TC. To better understand the NO titration for local air masses, the "total ozone" O\(_x\) (i.e. O3 + NO2) was further examined. The mean concentration of O\(_x\) was 49.5 \( \pm \) 2.4 ppbv (mean \( \pm \) 95% confidence interval) for local air masses, while it was 44.5 \( \pm \) 0.5 ppbv and 54.7 \( \pm \) 0.5 ppbv for regional and super-regional air masses, respectively. This
confirmed that lower O₃ concentration in local air masses was attributed to high emissions of NO in urban Hong Kong (Guo et al., 2009; Wang et al., 2009). Further inspection found that over the six years, the transport regime at TC was dominated by the air originating from super-regional transport (about 65% to the total air masses), followed by oceanic air (29%), regional transport (5%) and local emissions (1%). Due to the influence of Asian monsoon circulations, most of the oceanic air arrived at TC in summer, bringing in clean marine air, while super-regional and regional transport were often observed in autumn and winter, leading to the movement of precursor-laden air from the Asian continent to Hong Kong. The high frequency of air masses from super-regional and regional transport is another factor that contributes to high O₃ levels in autumn in Hong Kong, confirmed by the highest O₃ mixing ratio in the super-regional air masses (Table 3). Indeed, a study conducted at TC in October–December 2007 also found that high O₃ levels were attributed to regional and super-regional transport (Guo et al., 2009; Cheng et al., 2010a).

Fig. 8 shows a conceptualization of the influence of different air masses on O₃ levels at TC. The figure was generated based on the following steps. First, the transport history of air masses was investigated and the air masses were classified for the sampling period. In this study, 24-h backward trajectories were carried out using the HYSPLIT model with the GDAS meteorological data. For each day in the sampling period, eight trajectories were generated corresponding to arrival times at TC of 0000, 0300, 0600, 0900, 1200, 1500, 1800, and 2100 LST at the ending point of 200 m above sea level. These air masses were classified into local, regional, super-regional and oceanic air masses according to their original positions (i.e., latitude and longitude). In addition, the air masses for other hours during the day were classified using the following method: if an air mass at 0300 was identified as regional transport, the air masses at 0200 and 0400 were also considered as regional transport; secondly, the dominant surface winds of different air masses on high O₃ days and non-O₃ episode days in summer and autumn were identified; Finally, the relative O₃ concentrations in different air masses (i.e. local, regional, super-regional and oceanic) with different dominant surface winds were determined. It should be noted that due to the consideration of the statistical power of the trajectory results, a high O₃ day is defined as the day with the highest hourly average O₃ mixing ratio exceeding 80 ppbv in the figure. In addition, only O₃ mixing ratios during daytime (0800–1800, local time) were considered due to the fact that O₃ is formed by VOCs and NOₓ reacting in the presence of sunlight. It is noteworthy that O₃ episode days usually occur in summer and autumn in Hong Kong. Inspection of the figure found that the dominant surface wind was generally from the northwest during high O₃ days, whereas the prevailing winds were generally from the south/southwest during summer (May–August) and autumn non-O₃ episode days (September–November), respectively. Moreover, the contributions of super-regional, regional, oceanic and local air masses to the average O₃ levels were 31–49%, 20–31%, 18–29% and 0–27%, respectively, during summer non-O₃ episode days, while they were 29–56%, 19–37%, 15–24% and 0–31%, respectively, on autumn non-O₃ episode days. The relatively low contribution of oceanic air may be attributed to the fact that the south/southeast winds from the South China Sea brought in clean oceanic air with less primary pollutants and thus led to lower O₃ concentrations (Zheng et al., 2010). On the other hand, during high O₃ days, super-regional, regional, and local air masses contributed 28–100%, 0–61% and 0–42% respectively to the O₃ mixing ratios in summer, while the respective contributions were 33–100%, 0–56% and 0–39% in autumn. However, no contribution of oceanic air masses was found on high O₃ days in summer and autumn. Overall, regional and super-regional air masses made the most significant contributions to the average O₃ mixing ratio, followed by local and oceanic air masses, consistent with previous studies (Wang et al., 2009; Zheng et al., 2010). The results further demonstrated that regional and super-regional air pollution had notable influence on the O₃ pollution in Hong Kong.

3.3. Is photochemical O₃ formation limited by VOCs, or NOₓ or both?

Due to the complex O₃ chemistry, photochemical O₃ formation could be dominated by either VOCs or NOₓ or both. As such, it is important to understand the mechanisms of O₃ formation in a location. Moreover, since O₃ is a secondary pollutant, the regional influence should therefore be considered. On a regional scale, Zheng et al. (2010) reported that the O₃ production was controlled by VOCs in urban areas and possibly controlled by NOₓ in the northern/northeastern rural areas in the PRD region. Locally, Zhang et al. (2007) and Cheng et al. (2010b) found that the O₃ formation throughout Hong Kong was limited by VOCs, especially by reactive
Fig. 6. Synoptic charts for the nine O₃ episode events (source: http://envf.ust.hk/dataview/hko_wc/current/).
aromatics and some carbonyl compounds, and high NO concentrations suppressed O₃ production. In this section, measurement data for a total of 115 days (i.e. 17, 15, 13, 27, 23 and 20 days in years 2005–2010, respectively) with the maximum hourly O₃ mixing ratios above 80 ppbv were input into the OBM model to investigate the O₃-precursors relationship at TC. Fig. 9 presents the average RIR values for different precursors on those 115 high O₃ days. It is apparent that O₃ production was generally VOC-limited at TC, indicating that reducing VOCs decreased the O₃ formation and reducing NO could increase O₃ levels. The anthropogenic volatile organic compounds (AVOCs) made the most significant contributions to the O₃ formation, except for 2007 and 2009 when biogenic volatile organic compounds (BVOCs) had the highest contributions due to the high isoprene emissions in these two years. Among the top 10 VOC species, the average RIR value of isoprene was the highest, followed by aromatic compounds i.e. toluene and o-xylene, and alkenes i.e. propene and tran-2-butene (Fig. 10), revealing that the O₃ formation in Hong Kong was controlled by a small number of VOC species.

In the PTM-MCM model, another method was applied to evaluate the relative contribution of each VOC to O₃ formation, in which the importance of each VOC to O₃ production was ranked by POCP-weighted values (Cheng et al., 2010a). The POCP values were calculated by the PTM-MCM model, while the POCP-weighted values were calculated by combining the POCP value and emissions of each VOC (i.e. the emission rate of the VOC in Hong Kong (tonne yr⁻¹) multiplies by its POCP value). The 15 most abundant VOC species accounted for 51.7% of the total VOC emission rates in the PRD region (Cheng et al., 2013). Among these species, isoprene, cis-2-pentene, 1,3,5-trimethylbenzene, acetaldehyde, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene and propene had high POCP values, while toluene, benzene, ethene, isoprene had high emission rates, which are accounted for 6.2%, 5.8%, 5.5%, and 5.3% of the total emission rates, respectively.

After taking account into both the POCP and the emission amount of each VOC (POCP-weighted values), isoprene, ethene, toluene, formaldehyde, m-xylene, propene, acetaldehyde, 1,2,4-trimethylbenzene, o-xylene, 1-butene and ethylbenzene became the key precursors to photochemical O₃ formation in Hong Kong (Cheng et al., 2013). However, some highly reactive species, such as cis-2-pentene, 1,3,5-trimethylbenzene and 1,2,3-trimethylbenzene, had relatively lower contributions to the O₃ formation. This may be due to their low emissions, accounting for 0.1%, 0.5% and 0.4% of the total emission rates, respectively. In contrast, benzene and ethyne

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### Table 3

|          | 2005     | 2006     | 2007     | 2008     | 2009     | 2010     |
|----------|----------|----------|----------|----------|----------|----------|
| SO₂ (ppbv) |          |          |          |          |          |          |
| L⁺       | 3.6 (21) | 23.5 (48)|          | 6.9 (45) | 10.1 (36)| 8.2 (24) |
| R⁺       | 12.2 (321)| 16.6 (474)|          | 9.4 (690)| 9.5 (513)| 8.1 (497)|
| S⁺       | 6.1 (4242)| 10.9 (3855)|          | 8.7 (5310)| 5.8 (5160)| 4.6 (5208)|
| O⁺       | 4.3 (2740)| 4.4 (2520)|          | 3.4 (1977)| 2.5 (1999)| 2.4 (2181)|
| NO (ppbv) |          |          |          |          |          |          |
| L        | 26.4     | 61.3     |          | 33.2     | 25.3     | 78.3     |
| R        | 24.9     | 29.8     | 25.2     | 26.3     | 24.7     | 37.2     |
| S        | 11.6     | 13.6     | 13.2     | 14.1     | 11.2     | 14.7     |
| O        | 15.4     | 10.3     | 8.5      | 12.0     | 8.0      |          |
| O₃ (ppbv) |          |          |          |          |          |          |
| L        | 9.0      | 3.1      |          | 9.6      | 16.7     | 11.3     |
| R        | 19.8     | 11.0     | 11.0     | 14.6     | 21.7     | 9.5      |
| S        | 25.2     | 23.3     | 27.7     | 25.9     | 28.0     | 22.6     |
| O        | 15.7     | 15.7     |          | 18.6     | 16.8     | 20.4     |
| CO (ppbv) |          |          |          |          |          |          |
| L        | 499.3    | 948.0    |          | 704.3    | 584.9    | 918.3    |
| R        | 813.6    | 786.7    | 529.8    | 845.8    | 732.0    | 866.6    |
| S        | 769.9    | 640.4    | 739.7    | 809.4    | 589.2    | 677.6    |
| O        | 650.7    | 512.3    |          | 564.3    | 440.0    | 498.6    |
| TVOCs (μg m⁻³) |          |          |          |          |          |          |
| L        | 24.8     | 38.6     |          | 37.8     | 48.5     | 72.0     |
| R        | 33.5     | 56.0     | 15.7     | 40.7     | 48.6     | 78.6     |
| S        | 14.5     | 14.4     | 18.4     | 26.8     | 27.4     | 29.1     |
| O        | 7.8      | 8.8      |          | 5.7      | 11.8     | 6.3      |

a L, R, S, O stand for air masses from local, regional, super-regional and oceanic transport.
b Data in the bracket means the total number of air masses observed.

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**Fig. 7.** Backward trajectories for September 2005 and June 2010.
accounted for a relatively high percentage of the total VOC emissions (5.8% and 3.3%). Yet they had negligible contribution to the O3 formation because of their low reactivity. This feature suggests that the contribution of a VOC to the O3 formation is determined by the combination of its reactivity and emission.

Despite some variations, the results of both OBM and PTM-MCM models showed that some reactive VOCs including BVOCs i.e. isoprene, and AVOCs i.e. toluene, o-xylene and propene had the highest contributions to the O3 formation. Given that it is difficult to control BVOC emissions, the practical strategy to control O3 pollution is to effectively reduce AVOC emissions. In addition, POCP-weighted values calculated by PTM-MCM model suggest that the optimal strategy should also consider the emission quantity together with reactivity of individual VOCs when it is formulated and implemented.

3.4. Which emission sources are responsible for the volatile organic compounds in the atmosphere of Hong Kong?

Since photochemical O3 formation at TC was mostly VOC-limited, investigation of the characteristics of VOC source profiles and apportionments is the prerequisite for the formulation and
3.5. Application of the conceptual model — model verification

In the sections described above, a conceptual description for O₃ pollution in Hong Kong was developed. During O₃ episodes, the most frequent weather systems affecting Hong Kong were tropical cyclones over the East and the South China Sea (Scenario 1), followed by regional high-pressure systems (anticyclones) to the north over mainland China (Scenario 2), and low-pressure system (trough) to the south and east over the South China Sea (Scenario 3) (Huang et al., 2006; Guo et al., 2009). In this section, we conducted the model verification for four cases, i.e. 26 October 2007, 15 November 2008 and 04 June 2010 as examples for the high O₃ episode scenarios, and 29 July 2010 as an example for non-O₃ episode case.

Fig. 12 presents the diurnal variations of meteorological parameters for the four cases. It was found that there were some similarities in weather conditions at TC on the days of 26 October 2007, 04 June and 29 July 2010. First, the temperature and solar radiation were relatively high on these three days, which had daily maximum temperature of 30 °C with solar radiation of 806 W m⁻², 29 °C with solar radiation of 805 W m⁻², and 33 °C with solar radiation of 888 W m⁻², respectively. Second, the relative humidity on these three days was comparable (p > 0.05). However, some differences were also found on these days. Firstly, a tropical cyclone was found over the East China Sea on 26 October 2007 (Fig. 11a). On 04 June 2010, a low-pressure system (trough) to the south and east...
Fig. 11. Weather Charts on (a) 26 October 2007, (b) 15 November 2008, (c) 04 June 2010 and (d) 29 July 2010.

Fig. 12. Diurnal variations of meteorological parameters on 26 October 2007, 04 June 2010, 15 November 2008 and 29 July 2010.
was over the South China Sea (Fig. 11c), while an intense low-pressure system was found over Northern China and Hong Kong was in the front of the low-pressure ridge on 29 July 2010 (Fig. 11d). Secondly, the wind patterns were different on these three days. On 26 October 2007, the prevailing winds were southeasterly and northeasterly at night and northerly during daytime hours, while the dominant winds were southerly on 29 July 2010 with high wind speeds. However, the winds were calm (0.5–2 m s$^{-1}$) on 04 June 2010 with northerly and westerly winds during daytime hours and easterly winds at night. Thirdly, the backward trajectories analysis revealed that air masses arriving at TC were caused by super-regional transport on 26 October 2007, while the air masses were mainly from the ocean on 29 July 2010 (data not shown), indicating that high O$_3$ levels on 26 October 2007 (hourly peak value: 139 ppbv) and low O$_3$ level (30 ppbv) on 29 July 2010 were attributed to the influence of different air masses. Indeed, the OBM modeling results suggested that super-regional transport contributed as high as 50% to the O$_3$ pollution at TC on 26 October 2007. On the other hand, the conditions of high temperature, strong solar radiation, and the low wind speeds on 04 June 2010 created a relatively stable lower tropospheric layer, which was favorable to the O$_3$ formation and accumulation at TC. This was confirmed by the OBM modeling results, which revealed that high O$_3$ levels (i.e. peak value: 132 ppbv) on 04 June 2010 were mainly (50%) controlled by local formation.

On 15 November 2008, there was an intensive high-pressure system over northern China, while Hong Kong was in the front of the high-pressure ridge. Due to the influence of this high-pressure system, more frequent northerly winds with higher speeds (maximum velocity: 6 m s$^{-1}$) were observed on 15 November 2008. In addition, the temperature and solar radiation (daily maximum value: 730 W m$^{-2}$) on 15 November 2008 were lower ($p < 0.05$) and the relative humidity was comparable to those on 29 July 2010. This implied that the O$_3$ levels could be lower on 15 November 2008, however the O$_3$ mixing ratio was actually higher on 15 November 2008 (hourly peak value: 123 ppbv). Further inspection showed that the discrepancy between O$_3$ levels on 15 November 2008 and 29 July 2010 was also attributed to the influence of different air masses. The higher O$_3$ levels on 15 November 2008 were caused by the regional and super-regional transport. Backward trajectory analysis demonstrated that regional and super-regional air masses were frequently observed on 15 November 2008, and the OBM modeling simulations further confirmed that 90% of O$_3$ was caused by regional/super-regional transport on that day.

In summary, the above discussion indicated that tropical cyclone was mostly conducive to the occurrence of high O$_3$ mixing ratios. In addition, meteorological conditions such as high temperature, intense solar radiation, low relative humidity and wind speed were favorable to photochemical O$_3$ formation. Furthermore, polluted continental air masses brought by the northerly winds facilitated the O$_3$ production in Hong Kong.

5. Implications for ozone control measures

By considering the meteorological conditions, atmospheric chemistry and physics, and source apportionment of O$_3$ precursors, a conceptual description of O$_3$ pollution problem at TC in Hong Kong was presented above. However, some details remain to be thoroughly understood.

(1) A key factor for the occurrence of O$_3$ episodes in Hong Kong is the influence of tropical cyclones which cause subsidence, stagnation air and inversion layer. However, the mechanisms of such influence are not fully understood.

(2) Photochemical O$_3$ formation was generally VOC-limited and related to a small number of VOC species in Hong Kong, and solvent usage and vehicular emissions are the two major VOC sources. It appears that an effective control measure on the emissions of solvent usage and vehicles is an optimal strategy for controlling O$_3$ pollution in Hong Kong. In addition, the optimal strategy should also consider the emission quantity together with reactivity of individual VOCs when it is formulated and implemented.

(3) Many VOC sources are located in the PRD region and regional transport from the inland PRD region has significant influence on the amount of air pollutants in Hong Kong (Tang et al., 2007; Guo et al., 2009). As such, more concurrent field measurements should be conducted in these two closely interactive areas. In addition, air quality control strategies formulated in Hong Kong should consider the emissions from distant sources together with local sources.

(4) In Hong Kong, the combination of the coastline and the mountains gives a terrain with many complex physical features. The role of sea-land breezes in air pollution transport has been well studied previously (Ding et al., 2004). However, there are relatively few studies on mountain-valley breezes in Hong Kong, though it is very important to air pollution transport in Hong Kong.

(5) Although remarkable improvements in the VOC emission inventory and VOC measurements have been made in Hong Kong, significant uncertainties still exist in the source profiles and apportionments of VOC data. Hence, further survey on the VOC emission sources and accurate VOC source profile measurements and analyses are essential to better understand the VOC emissions from different sources in Hong Kong and its surrounding areas i.e. inland PRD region, to provide more reliable results on VOC sources and species which contribute the most to photochemical O$_3$ formation in Hong Kong.

(6) Though photochemical O$_3$ formation is generally VOC-limited in Hong Kong, the influence of other highly reactive chemicals such as HONO, PAN, H$_2$O$_2$ and other reactive oxidants on the O$_3$ formation should not be ignored. Besides VOCs, the characteristics of other precursors, i.e. NO$_x$ and products, i.e. particles, are required in order to better understand the specific atmospheric chemistry. Flux measurements of O$_3$ and its precursors over different areas, i.e. Hong Kong and inland PRD, under different conditions are required to better understand the specific atmospheric chemistry. Flux measurements of O$_3$ and its precursors over different areas, i.e. Hong Kong and inland PRD, under different
meteorological conditions, i.e. anticyclones and cyclones, mixing heights and transport processes are also necessary.

(7) Since the conceptual model was developed based on the data collected at one site, i.e. TC, it is suggested that this model should be further confirmed and improved by using data from other sites in Hong Kong.

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