Concurrent observations of air pollutants at two sites in the Pearl River Delta and the implication of regional transport

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Abstract

An intensive field measurement study was conducted simultaneously at a site within the inland Pearl River Delta (PRD) region (WQS) and a site in Hong Kong (TC) between 22 October and 1 December 2007. Ambient air pollutants measured included \( \text{O}_3 \), \( \text{NO}_x \), CO, \( \text{SO}_2 \), NMHCs, and carbonyls. The purpose is to improve our understanding of the interplay among local and regional air pollutants in the Hong Kong area, and the influence of regional transport on local air pollutants. The results indicate that the mean levels of air pollutants at the WQS site were much higher than those at the TC site, except \( \text{NO}_x \). Elevated CO levels were measured when the northerly monsoons enhanced mixing ratios at both sites, whereas high \( \text{O}_3 \) episodes were usually observed when weather systems were relatively stable. Thirteen \( \text{O}_3 \) episode days (daily \( \text{O}_3 \) peak in excess of 122 ppbv) were monitored at WQS during the study period, while only 2 days were recorded at TC. The diurnal variations of air pollutants at the two sites were found to be rather different, suggesting different local and regional contributions. Ratio analyses for VOCs revealed that the air masses arriving at WQS were more aged than those arriving at TC, confirmed by the back trajectories analysis. In addition, the influence of regional transport from eastern China on the primary pollutants of Hong Kong was noticeable, whereas the air masses from the inland PRD region (e.g. Dongguan) had significant influence on the air pollutants at WQS. These results confirm that regional transport of air pollution has a complex and significant impact on local air pollutants in this region.

1 Introduction

One of the major problems facing the environmental society is photochemical smog. Photochemical smog is the result of the interaction of sunlight with certain chemicals in the atmosphere, which leads to ground-level ozone (\( \text{O}_3 \)) and airborne particles (NRC, 1991; Seinfeld and Pandis, 2006). Photochemical smog is a concern in most major
urban centers but, because it travels with the wind, it can affect sparsely populated areas as well. Smog can be formed in almost any climate where industries or cities release large amounts of air pollution. However, it is worse during periods of warmer, sunnier weather when the upper air is warm enough to dampen or inhibit vertical circulation. Photochemical smog is especially prevalent in geologic basins encircled by hills or mountains. It often stays for an extended period of time over densely populated cities, such as Hong Kong, and can build up to dangerous levels. The photochemically formed O$_3$ at ground level can have adverse effects on human health and also affects the oxidizing capacity of the atmosphere, while the secondary organic aerosols formed have direct effects on climate change through modification of radiative budgets (Warneck, 2000; Godish, 2004). Globally, the carbon load is strongly influenced by anthropogenic activity, and future changes in emissions will continue to be a central consideration in air quality policy and climate change.

In recent years, the Pearl River Delta (PRD) region on the coast of southern China has become one of the world's fastest growing industrial areas. The PRD region consists of nine cities within Guangdong Province, namely Guangzhou, Shenzhen, Zhuhai, Dongguan, Zhongshan, Foshan, Jiangmen, Huizhou and Zhaoqing (usually these nine cities are considered to comprise the inland PRD region), plus Hong Kong and Macau Special Administrative Regions (Fig. 1). A consequence of the rapid development is the sacrifice of environmental quality. Photochemical O$_3$ has been studied in Southern China for over a decade. Lam et al. (1998) analyzed the behavior of background surface O$_3$ measured at a coastal site in Hong Kong. Chan et al. (1998a, 1998b) compared background and urban O$_3$ in Hong Kong. They focused on seasonal variations of O$_3$ and related the observed trends to the large-scale Asian monsoon circulation. Low O$_3$ during summer was attributed to the inflow of maritime air, whereas abundant O$_3$ in autumn-winter was due to the outflow of polluted continental air. Wang, T., et al. (1998) found that the local-scale re-circulation was an important mechanism in transporting O$_3$ to a rural/coastal monitoring site (Tai O) near Hong Kong. The temporal variability and emission patterns related to photochemical smog episodes in Hong Kong were also

In addition, many O$_3$ episodes were analyzed in combination with the meteorological conditions in Hong Kong using numerical simulations (e.g. Lee et al., 2002; Wang and Kwok, 2003; Ding et al., 2004; Lam et al., 2005; Wang, T. J., et al., 2006; Huang et al., 2006). These studies suggested the importance of regional transport from the inland PRD region. Lee and Savtchenko (2006) found that air pollution in Hong Kong was correlated with that in the inland PRD region in 2003 and 2004. Huang et al. (2006) surveyed 54 O$_3$ episodes that occurred over Hong Kong during 2000–2004 and found that O$_3$ episodes were dominated by regional transport when a tropical cyclone/typhoon was located over the northwestern Pacific or the South China Sea to the east or southeast and when an anticyclone appeared over mainland China to the north. Sensitivity studies even revealed that, in some O$_3$ episodes, 40–90% of the ambient O$_3$ at urban and rural areas of Hong Kong was attributed to horizontal transport (Lam et al., 2005; Wang, T. J., et al., 2006). However, all of these studies were carried out within Hong Kong. The relative contributions of local photochemical formation and regional transport to O$_3$ episodes in Hong Kong are not fully understood. Furthermore, the causes of O$_3$ episodes in the inland PRD, which was considered as a major reason for O$_3$ episodes in Hong Kong, remain unclear, though some studies have been undertaken inside the inland PRD region (e.g. Zhang, Y., et al., 1999, 2008). Therefore, in order to improve our understanding of the correlation between air pollution in Hong Kong and the inland PRD region, simultaneous measurements of O$_3$ and its precursors (i.e. volatile organic compounds and nitrogen oxides) were conducted at both sites in October–December, 2007 (autumn is the period that O$_3$ episodes are often observed).

Volatile organic compounds (VOCs) and nitrogen oxides (NO$_x$) are important precursors of tropospheric O$_3$. Studies have shown that the formation of O$_3$ in the PRD region is limited by VOCs (So and Wang, 2004; Zhang, J., et al., 2007; Zhang, Y., et al., 2008). A number of studies have been conducted to understand the spatial and temporal characteristics of VOCs in the inland PRD region (e.g. Chan et al., 2006;
Tang et al., 2007; Barletta et al., 2008; Liu et al., 2008) and in the Hong Kong area (e.g. Sin et al., 2000; Lee et al., 2002; Guo et al., 2004, 2007; So and Wang, 2004; Zhang, J., et al., 2007). The regional and local source contributions to ambient VOCs in Hong Kong have been studied by measurements at a rural/coastal site near Hong Kong (Wang, T., et al., 2005; Guo et al., 2006). These previous studies mainly focused on the speciation, spatial and temporal variations, source characterization and identification of VOCs either in Hong Kong or in the inland PRD. To better understand the relationship of VOCs between inland PRD and Hong Kong during O$_3$ episodes, and the photochemistry of VOCs in the formation of O$_3$, it is necessary to undertake concurrent field measurements in these two different areas.

In this study, we present the measurement data of the main air pollutants simultaneously collected between 22 October and 1 December 2007 at two sampling sites which are located in the inland PRD region and in Hong Kong, respectively. The levels of individual trace gases, total non-methane hydrocarbons (NMHCs), and total carbonyls in both areas are reported here, and the differences and relationships of the air pollutant concentrations at the two sites are discussed. Temporal patterns of total NMHCs and other trace gases are compared between high and low O$_3$ pollution days. In particular, high O$_3$ episodes are analyzed in combination with the meteorological conditions. Finally, we discuss the influence of regional transport on these study areas by examining the relationship between selected VOC species ratios and the age of air masses, and by analyzing their backward trajectories.

2 Methodology

2.1 Description of the sampling sites

The field measurement sampling sites – Wan Qing Sha (WQS) and Tung Chung (TC) – are shown in Fig. 1. The distance between the two sites is about 62 km. WQS (22.711° N, 113.549° E) is a small town located near the center of the PRD. This small
town is surrounded by farmlands and has very few textile and clothing workshops, so the local anthropogenic emissions are not remarkable. The major air pollutants are mainly from the surrounding cities. This site is 50 km to the southeast of the Guangzhou urban center, 40 km southwest of Dongguan, 50 km northwest of Shenzhen, and 25 km northeast of Zhongshan, making it a good location to characterize the air pollution in the inland PRD. Conversely, since WQS is at the northernmost boundary of the Pearl Estuary and to the northwest of Hong Kong, it is an appropriate site to investigate the influence of the inland PRD region on Hong Kong when northerly wind is prevalent. The measurements were carried out on the rooftop of a 15 m high building.

TC (22.30° N, 113.93° E) is located on northern Lantau Island, about 3 km south of the Hong Kong International airport at Chek Lap Kok. It is a newly-developed residential town, but adjacent to the highway and to railway lines. It is about 20 km to the southwest of Hong Kong urban center, and 38 km northeast of Macau. In addition to the influence of local emission sources, TC is also affected by polluted continental air masses from the highly industrialized PRD region of mainland China. 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. The samples were collected on the rooftop of a building with a height of 15 m.

2.2 Measurement techniques

2.2.1 Continuous measurements of trace gases

Measurement instruments were housed in a laboratory situated on the roof at both sites. Ambient air samples were drawn through a 10 m long PFA Teflon tube (outside diameter 12.7 mm; inside diameter: 9.6 mm). The sampling tube inlet was located 3 m above the rooftop of the laboratory, and the outlet was connected to a PFA-made manifold with a bypass pump drawing air at a rate of 15 L/min. Descriptions of the measurements of O₃, CO, SO₂ and NO-NO₂-NOₓ can be found in Wang, T., et al. (2003). In this study, continuous measurements of trace gases, including O₃, NO-NO₂-NOₓ,
CO and SO₂, were conducted from 22 October to 1 December 2007 at WQS, while at TC the hourly data of O₃, CO, SO₂, and NOₓ were obtained from the website of the Hong Kong Environmental Protection Department (HKEPD) (http://www.epd.gov.hk). Detailed information about the measurements and quality control and assurance at the TC site can be found in the HKEPD report (HKEPD, 2007). Here, we briefly describe the measurements at WQS. Ozone was measured using a commercial UV photometric instrument (Thermo Environmental Instruments (TEI), model 49C) that had a detection limit of 2 ppbv and a 2-sigma (2-σ) precision of 2 ppbv for a 2-min average. CO was measured with a gas filter correlation, non-dispersive infrared analyzer (API, Model 300) with a heated catalytic scrubber to convert CO to carbon dioxide (CO₂) for baseline determination. SO₂ was monitored by pulsed UV fluorescence (TEI, model 43S), with a detection limit of 0.06 ppbv and 2-σ precision of 3% for ambient levels of 10 ppbv (2-min average). NO and NOₓ were detected with a chemiluminescence NO-NO₂-NOₓ analyzer (Thermo Electron Corporation, Model 42i trace level). The analyzer has a detection limit of 0.05 ppbv. These analyzers were calibrated daily by injecting scrubbed ambient air (TEI, Model 111) and a span gas mixture. A NIST-traceable standard (Scott-Marrin, Inc.) containing 156.5 ppmv CO (±2%), 15.64 ppmv SO₂ (±2%), and 15.55 ppmv NO (±2%) was diluted using a dynamic calibrator (Environics, Inc., Model 6100). For the O₃, SO₂, NO and NOₓ analyzers, a data logger (Environmental Systems Corporation, Model 8816) was used to control the calibrations and to collect data, which were averaged to 1-min values.

### 2.2.2 Sampling and analyses of VOCs and carbonyls

Ambient NMHC samples were collected using cleaned and evacuated 2-L electropolished stainless steel canisters on selected days (26–27 October, 13 November, 15–17 November, 23 November, and 1 December). Details of the preparation and preconditioning of the canisters are described in Blake et al. (1994). During the sampling, a flow-controlling device was used to collect 1-h integrated samples. At both sampling sites, hourly NMHC samples were collected from 07:00 a.m. to 06:00 p.m. at TC, and
from 06:00 a.m. to 06:00 p.m. at WQS for the selected days. The samples were analyzed by an Entech Model 7100 Preconcentrator (Entech Instruments Inc., California, USA) coupled with a gas chromatography-mass selective detector (GC-MSD, Agilent 5973N). A HP-1 capillary column (60 m × 0.32 μm × 1.0 μm, Agilent Technologies, USA) was used with helium as carrier gas. The GC oven temperature was initially held at −50°C for 3 min, after which it was increased to 10°C at 15°C min⁻¹, then to 120°C at 5°C min⁻¹, and finally to 250°C at 10°C min⁻¹. The analysis was conducted after holding it at 250°C for 10 min. The MSD was used in selected ion monitoring (SIM) mode and the ionization method was electron impacting (EI). The detection limit of aromatics is 0.003 ppbv, and that of other NMHCs is 0.005 ppbv.

Carbonyl samples were collected simultaneously at both sites on the same selected days. Samples were collected at 0.4–0.5 L/min for 150 mins using a carbonyl sampler (ALDEHYDE, UNIT #7) by passing air through a silica cartridge impregnated with acidified 2, 4-dinitrophenylhydrazine, which is very reactive toward carbonyls. An O₃ scrubber was connected to the inlet of the cartridge during each sampling to eliminate the impact of O₃. About four carbonyl samples were collected during each sampling day. All cartridges were stored in a refrigerator at −4°C after sampling. Each sampled cartridge was eluted slowly with 5 mL of acetonitrile (ACN) into a 5 mL volumetric flask. A 20-μL aliquot was injected into the HPLC system through an auto-sampler. The operating conditions of the HPLC are shown in Table 1. Typically C₁–C₈ carbonyl compounds are measured effectively by this technique with a detection limit of ~0.2 ppbv.

2.2.3 Quality control and assurance for VOC and carbonyl analyses

Before sampling, all canisters were cleaned at least five times by repeatedly filling and evacuating humidified zero air. In order to check whether there was any contamination in the canister, we filled the evacuated canisters with pure N₂ and stored them in the laboratory for at least 24 h. These canisters were then checked by the same VOC analytical method to ensure that all the target compounds were not found or were under the method detection limit (MDL). In addition, duplicate samples were regularly
collected to check the precision and reliability of the sampling and analytical methods.

The eluted species were identified and quantified by MSD. The identification of each compound was based on its retention time and fragmentation pattern. The quantification of target VOCs was accomplished using multi-point external calibration curves. The calibration curves were updated every day and were prepared using 1000 ppbv standard calibration gases (TO-14 gases, Spectra Gases Inc.) at five different diluted concentrations plus humidified zero air (0–40 ppbv). The standard gases were analyzed in the same way as the field samples.

Identification and quantification of carbonyl compounds were based on retention times and peak areas of the corresponding calibration standards, respectively. The instrument was calibrated using five standard concentrations covering the concentrations of interest for ambient samples. Excellent linear relationships ($R^2 > 0.998$) were observed between the concentrations and responses for all carbonyls identified. Cartridge collection efficiency was determined with two cartridges in series, and over 98% of carbonyl compounds were found in the first cartridge. Relative percent differences (RPDs) for duplicate analysis were within 10%.

### 2.2.4 Meteorological parameters

Several meteorological parameters were simultaneously measured using a mini weather station (Vantage Pro2™, Davis Instruments Corp., USA) during the study period at WQS, including wind speed, wind direction, temperature, relative humidity, total ultraviolet radiation (320–400 nm) and global solar radiation. The meteorological data at TC were obtained from the HKEPD for the sampling period.

### 2.3 Calculation of back trajectories

Backward trajectory has been widely used in the analysis of field measurements to learn the history of the observed air masses (e.g., Stohl, 1998; Cooper et al., 2001). In the present work, the trajectory model, NOAA-HYSPLIT4.8 (Draxler and Rolph, 2003),
was applied to calculate the respective backward trajectories to the WQS and TC sites during the study period. The hourly output data of Weather Research and Forecasting (WRF) model (V3.01, Skamarock et al., 2008) were used to drive the trajectory model. WRF simulation was conducted from 00:00 UTC on 22 October to 18:00 UTC on 1 December. Three nested domains were defined, with grid spacings of 27 km, 9 km, and 3 km, respectively. The finest domain covers the whole PRD region, while the outermost domain covers East and South China, the South China Sea as well as the Indo-China Peninsula. The vertical layers and the model’s physical parameterization configuration can be found in Jiang et al. (2008). Moreover, in order to improve the model performance, grid nudging on the 27 km grid was applied.

3 Results and discussion

3.1 Mean meteorological conditions

The mean sea level pressure and wind field on 1000 hPa for East Asia over the whole sampling period are shown in Fig. 2. The figure was made using NCEP FNL (final) data with a horizontal resolution of $1^\circ \times 1^\circ$ (http://dss.ucar.edu/datasets/ds083.2/). It shows that there was an intensive high-pressure system over northern China, while Hong Kong and the inland PRD region were in front of the high-pressure ridge. Due to the influence of the high-pressure system, the prevailing synoptic winds in Hong Kong and the inland PRD region were from the northeast. It is noted that the wind speeds over the ocean were much greater than those over the land. Since TC is much closer to the open ocean than WQS, the wind speed at TC was much higher than that at WQS. Statistical analysis of the ground meteorological observation data confirmed that the mean wind speed was $1.95 \pm 0.06$ (mean $\pm 95\%$ confidence interval) $\text{m s}^{-1}$ at TC and $1.32 \pm 0.08$ $\text{m s}^{-1}$ at WQS, and the average wind direction was $97^\circ$ (degrees azimuth, $0^\circ$ means North) at TC and $54^\circ$ at WQS (Table 2). The differences in wind speed and wind direction at the two sites implied that the air masses of the two sites may have
had different transport pathways. In contrast, no statistical differences were found for temperature and relatively humidity at the two sites, respectively (Table 2).

3.2 Spatial distributions and evidence of regional influence

3.2.1 Spatial variations of trace gases, total NMHCs and carbonyls

In this study, a total of 928 hourly trace gas averages (i.e. O\textsubscript{3}, NO\textsubscript{x}, CO, SO\textsubscript{2}) were collected at TC, with 920 hourly samples collected at WQS, except for CO (432 counts). Table 3 illustrates the data counts, average values, 95% confidence intervals and maximum values of O\textsubscript{3}, NO\textsubscript{x}, CO, SO\textsubscript{2}, total NMHCs and carbonyls measured at the two sites during the study period. In general, the average concentrations of target air pollutants at WQS were higher than those at TC, except for NO\textsubscript{x}. The mean mixing ratios of O\textsubscript{3}, CO, and SO\textsubscript{2} at the WQS site – 40, 1047, and 32 ppbv, respectively – were 1.3, 1.8, and 3.6 times those measured at TC site, respectively. However, the average NO\textsubscript{x} concentration was 31 ppbv at WQS, only 0.68 times that at TC. The elevated NO\textsubscript{x} level at TC is likely due to high traffic density in Hong Kong. The respective maximum mixing ratios of NO\textsubscript{x}, CO and SO\textsubscript{2} were 155, 2915 and 167 ppbv at the WQS site, and 178, 1204 and 35 ppbv at the TC site.

For NMHCs, 96 and 102 ambient VOC samples were collected at TC and WQS, respectively. A total of 61 NMHC species were quantified. The mean total NMHC mixing ratio was 34 and 40 ppbv at TC and WQS, respectively. The maximum total NMHC mixing ratio was 141 ppbv at TC, compared to 237 ppbv at WQS. We further divided NMHCs into four groups, namely alkanes, alkenes, aromatics, and biogenic VOCs (mainly isoprene), of which the first three groups were mainly emitted from anthropogenic sources. When the contribution of each VOC group to the total NMHC abundance was calculated, it was found that alkanes accounted for most of the NMHC abundance both at TC (63%) and WQS (40%), respectively. Alkenes, aromatics, and biogenic VOCs accounted for 16, 19, and 2% at TC, respectively. On the other hand, alkenes, aromatics and biogenic VOCs contributed 20, 39 and 0.7% to the total NMHCs...
at WQS, respectively. The total NMHC concentration and composition at WQS were similar to that at Xinken reported by Liu et al. (2008). The clear difference of the VOC composition at the TC and WQS sites suggested a difference in VOC sources. The high contribution of alkanes at TC may owe to widespread use of liquefied petroleum gas, whereas the high contribution of aromatics at WQS may be attributed to industrial emissions, which are mainly located in Dongguan, upwind of the WQS site. Liu et al. (2008) reported that about 52% of the total NMHCs in the atmosphere of Dongguan were aromatics.

For carbonyls, 26 and 32 ambient samples were simultaneously collected at TC and WQS, respectively. A total of 11 species of carbonyls were quantified and the average mixing ratios of total carbonyls at TC and WQS were 19 and 43 ppbv, respectively. Among the 11 species, formaldehyde was the most abundant compound at both sites, accounting for 40% at TC and 49% at WQS. Acetaldehyde and acetone accounted for 29 and 17% at WQS, respectively, whereas the proportions of acetaldehyde and acetone were basically the same at TC, accounting for 26 and 28%, respectively. The average concentrations of formaldehyde, acetaldehyde and acetone measured at TC were much lower than the mean values observed at WQS. Compared to other studies, the mean levels of formaldehyde (7.5±1.9 ppbv) and acetaldehyde (4.9±1.1 ppbv) at TC were close to the roadside values of Hong Kong in 2001–2002 (5.5–8.6 ppbv and 4.2–6.3 ppbv, respectively; Ho et al., 2006), indicating the importance of photochemical production at TC. On the other hand, the formaldehyde and acetaldehyde levels at WQS (20.9±2.1 ppbv and 12.6±2.6 ppbv, respectively) were much higher than those observed in Guangzhou (10.2 ppbv and 4.2 ppbv, respectively; Feng et al., 2005) during a study conducted from 15 July–20 September 2003. Since the WQS site is a rural site downwind of Guangzhou, much higher values observed at WQS than in Guangzhou were likely due to photochemical production. Air masses at the WQS site could also be affected by nearby carbonyl sources as well. Indeed, there is a power plant in Humen town of Dongguan, approximately 10 km to the southeast of WQS, which uses coal as fuel for power generation. Furthermore, as the sampling period in this study
was different from those in previous studies (Feng et al., 2005; Ho et al., 2006), the elevated values found at TC and WQS might imply increased emissions of carbonyls in the inland PRD region in recent years.

3.2.2 Characteristics of air masses in inland PRD and Hong Kong

Carbon monoxide can be considered as an air pollution transport indicator due to its relatively long lifetime (months). A scatter plot (not shown) of CO measured at TC vs. WQS showed that the correlation coefficient was 0.40. The poor correlation implies that the transport of air masses between Hong Kong and the inland PRD region during this study period may not be significant, or that local source influences are a dominant factor.

The concentration ratios of SO$_2$ to NO$_x$ and of CO to NO$_x$ can provide signatures of the air masses arriving at each site. In this study, the SO$_2$/NO$_x$ ratio was found to be 0.25±0.01 ppbv/ppbv at TC and 1.26±0.06 ppbv/ppbv at WQS, whereas the CO/NO$_x$ ratio was 15.8±0.5 ppbv/ppbv at TC and 52.0±3.8 ppbv/ppbv at WQS. That is, the SO$_2$/NO$_x$ and CO/NO$_x$ ratios at WQS were much higher than those at TC ($p<0.001$). This is because the air masses from mainland China are laden with relatively abundant CO and SO$_2$ while the air masses in Hong Kong have high NO$_x$ levels (Kok et al., 1997; Wang, T., et al., 2001, 2005). Compared to previous studies, the SO$_2$/NO$_x$ and CO/NO$_x$ ratios at WQS (1.26 and 52.0, respectively) were 3–4 times higher than the values reported in upwind Guangzhou urban areas (0.4 and 11.9, respectively) (Zhang, Y., et al., 1998; Wang, X. M., et al., 2005). The higher ratios were probably caused by the lower NO$_x$ level due to photochemical conversion at this rural site, as well as higher SO$_2$ and CO emissions from the nearby power plant in Humen town of Dongguan.

Likewise, the SO$_2$/NO$_x$ and CO/NO$_x$ ratios at TC (0.25 and 15.8, respectively) were higher than those measured in Hong Kong urban areas during a previous study (0.1 and 2.4 ppbv/ppbv, respectively; HKEPD, 2000), and they were higher than those measured at the same site in a previous study (0.18 and 5.2 ppbv/ppbv, respectively (So and Wang, 2003). This suggests that there might have been a temporal increase in the
two ratios in Hong Kong and/or an association with the seasonality. In this study, the sampling period was from October to December, in which the meteorological conditions were not favorable for the dispersion of air pollutants, whereas the ratios reported by HKEPD (2000) and So and Wang (2003) were based on one-year measurement data. Hence, seasonality is likely a reason for these higher ratios in this study. In order to further understand whether these higher ratios at TC were caused by regional transport from the inland PRD region or attributed to the temporal change of local source strength, the \( \text{SO}_2/\text{NO}_x \) ratios at nine Hong Kong urban air quality monitoring stations were calculated using the data collected in the same period as this study. The ratio from October to December 2007 ranged from 0.12 to 0.29 (data from HKEPD website, http://www.epd.gov.hk), suggesting that the air masses at TC (\( \text{SO}_2/\text{NO}_x \) ratio: 0.25) had similar chemical characteristics to that in Hong Kong urban areas. Similarly, we investigated the CO/\( \text{NO}_x \) ratios at Hong Kong urban air quality monitoring stations as well. Data at two stations were available, namely Tsuen Wan and Yuen Long, with ratios of 14.6±0.7 and 20.6±0.6 ppbv/ppbv, respectively, for the same autumn period as our study. The CO/\( \text{NO}_x \) ratio at TC (15.8 ppbv/ppbv) was between the values for the Tsuen Wan and Yuen Long stations. Moreover, Wang, T., et al. (2003) suggested that urban Hong Kong plumes typically contain a CO/\( \text{NO}_y \) ratio of 3.9–6 ppbv/ppbv, whereas regional air masses usually contained a much higher ratio of about 20 ppbv/ppbv. \( \text{NO}_y \) represents \( \text{NO}_x \) and its atmospheric oxidation products. Though the proportion of \( \text{NO}_x \) to \( \text{NO}_y \) varies spatially and temporally, \( \text{NO}_x \) generally accounts for about 40% of \( \text{NO}_y \) at rural sites (Aneja et al., 1996; Zhou et al., 2002). By conversion, the CO/\( \text{NO}_x \) ratio in urban Hong Kong plumes (9.8–15 ppbv/ppbv) was close to the measured value at TC (15.8 ppbv/ppbv). Therefore, both the \( \text{SO}_2/\text{NO}_x \) and CO/\( \text{NO}_x \) ratios suggest that the air masses at TC were mainly impacted by Hong Kong local emissions, and that there does not appear to have been a significant temporal change in these ratios during this decade for autumn values.

The ratios of VOCs with different photochemical lifetimes are useful tools to examine the atmospheric processes of air masses, including atmospheric transport and
photochemical aging. Due to different lifetimes of two given VOC species, their ratio may change during the course of air mass transport. Using the ratio of a more reactive VOC to a less reactive VOC, a higher ratio indicates relatively little photochemical processing of the air mass and major impact from local emissions. On the other hand, a lower ratio is reflective of more aged VOC mixes and thus presumably that the VOCs were emitted from more distant sources. Comparisons of the ratios among sites can be used to estimate the relative ages of air parcels and help provide evidence of transport histories. Moreover, this ratio analysis can further indicate whether the site is dominantly affected by pollutants from local or regional sources. In this study, we compared the ratios of \( m, p \)-xylene/ethylbenzene and \( i \)-butane/propane at the two sites as a measure of atmospheric processing in different air masses (e.g. Grosjean et al., 1999; So and Wang, 2004; Guo et al., 2007). \( m, p \)-Xylene and ethylbenzene are mainly emitted from vehicles and solvent usage, whereas \( i \)-butane and propane have an origin of liquefied petroleum gas emission (Guo et al., 2007). \( m, p \)-Xylene is more reactive than ethylbenzene, with lifetimes about 1 and 2 days, respectively; \( i \)-butane also has a shorter lifetime than propane, with lifetimes of about 6 and 12 days, respectively. Figure 3 shows the scatter plots of (a) \( m, p \)-xylene to ethylbenzene and (b) \( i \)-butane to propane at TC and WQS. Clearly, TC had higher slopes than WQS for both VOC ratios, with an \( m, p \)-xylene/ethylbenzene ratio of 1.07 (versus 0.91 at WQS), and an \( i \)-butane/propane ratio of 0.38 (versus 0.26 at WQS). The results suggested that the air masses at WQS were more aged than that at TC, reflecting the higher importance of regional transport at the WQS site.

3.3 Temporal variations

3.3.1 Day-to-day variations

Figure 4 shows the day-to-day variations of \( O_3 \), \( NO_x \), CO, \( SO_2 \), and total NMHCs at the two sites, which were sometimes similar on consecutive days such as 25–26 October: high concentrations of CO, \( SO_2 \), \( NO_x \) and \( O_3 \) were observed at both sites on both days.
In contrast, the day-to-day variations at the two sites showed differing daily patterns on other days such as 26–27 October: high levels of air pollutants were recorded on 26 October whereas the levels of air pollutants on 27 October were rather low. At the WQS site the maximum hourly average O\textsubscript{3} concentration during the study reached 182 ppbv, whereas the peak hourly value was 139 ppbv at the TC site (see Table 3). The number of O\textsubscript{3} episode days (the daily maximum value exceeds the Hong Kong Air Quality Objective of 122 ppbv) reached 13 days out of 41 sampling days at WQS, compared to only 2 days at TC.

The concentrations of air pollutants have a close relationship with weather conditions, such as temperature, wind, solar radiation and so on (Wang, T., et al., 2001, 2003; Wang and Kwok, 2003). Figure 4 also shows the time series of temperature, relative humidity, solar radiation and wind observed at the two sites during the study period. It can be seen that there were four clearly cooling processes, which happened on 30 October–1 November, 7–8 November, 18–19 November, and 26–29 November. Each cooling process was generally associated with a decrease in relative humidity and solar radiation, along with an increase in wind speed, especially at WQS. The wind directions at WQS were relatively uniform, generally from northeast, whereas complex wind directions were found at TC. Inspection of the daily weather plots indicated that each cooling process generally corresponded with an intensely elevated northerly monsoon which brought dry and cold air from the inner Asian continent to the PRD region.

With the change of weather conditions, the concentrations of air pollutants changed correspondingly (see Fig. 4). Generally, when the northerly monsoons were enhanced, the CO levels were dramatically increased at both sites (for example, 30 October–1 November and 18–19 November). Chung et al. (1999) investigated the relationship between high CO episodes and synoptic conditions at a coastal station in Hong Kong and found similar features as well. In contrast to CO, the O\textsubscript{3} levels had a decreasing trend with enhanced northerly monsoons at both sites (for example, 30 October–1 November and 7–8 November), perhaps due to the precipitation and the decrease in
temperature and solar radiation. When the intense northerly monsoons were over, resulting in elevated temperature and solar radiation and a stable boundary layer, the photochemical reaction strengthened and the O$_3$ level increased rapidly. In addition, due to the stable boundary layer and lower surface wind, the dispersion of primary air pollutants was reduced, resulting in elevated levels of NO$_x$, SO$_2$, and CO (for example, 29–30 November), especially at WQS. This implies that the elevated O$_3$ levels may be dominantly affected by local production. Table 4 summarizes the synoptic conditions and the corresponding variations of air pollutants levels. The O$_3$ levels at the two sites during 11–17 November were very interesting. The O$_3$ levels were fairly high at WQS (daily peaks >150 ppbv) but rather low at TC (daily peaks ~50 ppbv), although the distance between these two sites is only 62 km. Similar phenomena were also observed during 23–29 October. This may be partly due to the relatively higher temperature, lower relative humidity, and much weaker wind speed during the daytime at WQS as well as stronger NMHC emissions in the inland PRD region. Detailed mechanisms for these phenomena will be further discussed in a separate paper.

### 3.3.2 Diurnal variations

By analyzing the diurnal variations of air pollutants, information about the contributions of emissions and chemical and physical processes to a diurnal cycle can be obtained. Figure 6 shows the mean diurnal variations of trace gases, total NMHCs (8-day average), and wind fields at WQS and TC between 23 October and 1 December. A clear diurnal shift in wind direction was found at TC: the winds were southeasterly at night and then became more northerly with increased speeds during the daytime. However, the mean winds at WQS basically reflected the large-scale air flow from the northeast, with increased speeds in the morning and decreased speeds in the afternoon and at night.

In general, O$_3$ showed a high peak in the afternoon and had relatively low concentrations at night at both sites (Fig. 6). However, different features were also observed at the two sites. Firstly, the maximum O$_3$ level was much higher and the diurnal change
was much faster at WQS than at TC, suggesting more significant photochemical production of O$_3$ at WQS than that at TC. Secondly, the O$_3$ concentration began to increase in the early morning (about 07:00) at WQS, whereas there was a low trough in early morning at TC followed by enhanced O$_3$ beginning at about 09:00, likely due to high concentrations of NO in the morning which titrated some O$_3$. Thirdly, the O$_3$ concentrations at nighttime at TC (27±4 ppbv) were higher than those measured at WQS (18±3 ppbv), which was probably attributed to the constant transport of O$_3$ to TC by southeasterly flows from the South China Sea where O$_3$ was consumed less. The average diurnal O$_3$ difference (the mean daytime minus nighttime concentration) was 8±4 ppbv and 41±6 ppbv at TC and WQS, respectively (Table 5).

The diurnal variation of NO$_x$ at the TC site showed a typical urban profile (obvious bimodal structure) with peaks at about 09:00 and 19:00, respectively (Fig. 6). This observation is consistent with the traffic pattern of Hong Kong. However, much weaker NO$_x$ peaks were found at WQS as it was a rural site. As observed at many rural and coastal sites, reduced mid-daytime concentrations of NO$_x$ were found at both TC and WQS, which can be explained by high photochemical conversion and elevated vertical turbulence dilution. The diurnal patterns of SO$_2$ and CO at the TC site were almost exactly the same, with a small and broad peak in the afternoon indicating the contribution of regional transport to Hong Kong by northerly winds. By contrast to TC, at the WQS site CO had an obvious bimodal structure profile, and SO$_2$ had a high morning peak and a low afternoon concentration. The diurnal variation of total NMHCs at WQS showed two major peaks, namely in early morning and in late afternoon; at TC the peaks were much weaker and were not statistically different from the troughs. These observations show that VOC-limited O$_3$ production is even more acute in the Hong Kong area than in the inland PRD region.

Figure 7 shows diurnal patterns of air pollutants observed on 26 and 27 October, which differed for primary species on high vs. low O$_3$ pollution days. On 26 October the O$_3$ level was very high, with peaks of 139 ppbv at TC and 159 ppbv at WQS. In contrast, on 27 October the O$_3$ concentrations remained relatively low and the afternoon O$_3$
peaks were weak at both sites (95 and 55 ppbv at WQS and TC, respectively). The prevailing daytime winds on 26 October were northerly and their speeds were much smaller than typical values recorded at both sites (Fig. 6). However, on 27 October the winds turned southerly at the two sites, consistent with the arrival of less polluted maritime air.

At the TC site, the diurnal patterns of NO$_x$, CO and SO$_2$ on 26 October were similar to the average profiles shown in Fig. 6, but with much sharper variations. On the other hand, on 27 October no daytime CO or SO$_2$ peaks were observed at TC and the morning NO$_x$ peak was seriously reduced. These findings confirmed that the elevated CO and SO$_2$ concentrations in the afternoon were due to regional transport by northerly winds. In addition, the difference in diurnal variation for total NMHCs between high O$_3$ pollution and low O$_3$ pollution days (i.e. a broader and higher peak near noon on 26 October than on 27 October) also revealed the regional transport influence.

At the WQS site, the NO$_x$ profile showed 2 peaks (the average value for the small afternoon peak was 30.2±1.3 ppbv, higher than the baseline level of 16.7±0.3 ppbv) on the high O$_3$ pollution day (26 October), but these were 1–2 h earlier than those recorded at TC, whereas these peaks disappeared on 27 October and NO$_x$ concentrations fell. The patterns of CO and SO$_2$ were virtually identical on 26 October, with both gases showing a sharp peak in early morning and a relatively lower peak in late afternoon. However, on 27 October, the CO concentrations remained at a low level without any obvious elevation during the daytime, whereas the SO$_2$ concentrations became significantly enhanced in the afternoon. This indicates that the CO concentrations at WQS were basically attributed to regional transport, while the high SO$_2$ concentration was partly due to local SO$_2$ emission, perhaps from coal or biomass burning. On 26 October, total NMHCs at WQS had a high peak in early morning and concentrations remained high during the morning, followed by a sharp drop at noon. However, on 27 October, the low O$_3$ pollution day, the total NMHC morning peak was reduced and the deep trough at noon disappeared, suggesting less transport and weaker source emissions in the morning and reduced photochemical consumption of NMHCs at noon.
3.4 Transport of the air masses

To further investigate the regional transport of air pollutants, back trajectories were used to examine the typical air masses arriving at TC and WQS during this study period. Two-day back trajectories run every 3 hours at 200 m height at both sites were calculated using the HYSPLIT model and the 27 km resolution WRF output data were adopted. From 00:00 LT 25 October to 21:00 LT 1 December, a total of 304 back trajectories (8 tracks per day) were calculated at each site, and then they were classified by using cluster analysis, which is a relatively objective method to investigate different transport patterns of air masses (Stohl, 1998). In this work, we classified the trajectories into 3 groups at both sites by using the Hierarchical Clustering Method (Ward, 1963) as shown in Fig. 8. The typical back trajectories at TC and WQS were similar: the first trajectory was along the eastern China coast (Track 1); the second originated from inland China (Track 2), passing over Fujian and Jiangxi provinces; and the third (Track 3) was also from inland China, but more northerly (over Jiangxi province) and with much higher transport speeds than Track 2. The proportion of air masses associated with each track and the corresponding concentrations of air pollutants are shown in Table 6. At TC, the air masses were mainly from Track 1 (44%), followed by Track 3 (39%) and Track 2 (17%). By comparison, the air masses arriving at WQS were mainly from Track 2 (41%), then Track 3 (34%) and Track 1 (25%). These results confirm the discussion in Section 3.1 that the air masses sources of the two sites differed somewhat, and illustrate that not all air parcels were transported from the inland PRD region to Hong Kong.

As anticipated at TC, air masses from Track 1 had the lowest concentrations for primary pollutants (i.e. NO$\textsubscript{x}$, CO, SO$\textsubscript{2}$), and those from Track 3 had the highest concentrations of trace gases ($p<0.01$). In contrast, the mean O$\textsubscript{3}$ concentration for Track 1 (35±3 ppbv) was significantly higher than that for Track 3 (27±3 ppbv) ($p<0.01$). Inspecting the corresponding times of the Track 1 and Track 3 air masses, we found that the transport pathways of air masses were mainly dominated by Track 3 when
the northerly monsoons were elevated, while Track 1 air masses were basically observed under fine weather conditions. As discussed before, enhanced monsoons corresponded with low \( \text{O}_3 \) levels. The concentrations of primary pollutants in Track 2 were close to that in Track 3. The results suggest that the influence of regional transport from inland China (mainly eastern China) on the levels of primary pollutants found within Hong Kong cannot be ignored. It should be noted that all three tracks passed over urban Hong Kong areas before arriving at TC, suggesting that the air masses from the three tracks were also affected by urban Hong Kong emissions.

At WQS, Track 2 air masses had the highest concentrations of \( \text{NO}_x \) (37\( \pm \)4 ppbv) and \( \text{SO}_2 \) (38\( \pm \)4 ppbv), which were significantly higher than the concentrations of Track 3 \((p<0.05)\). The higher \( \text{NO}_x \) and \( \text{SO}_2 \) concentrations were most likely caused by chimney emissions of the power plant in Humen town of Dongguan, because Track 2 passes over the power plant area (labeled in Fig. 1). As was the case with TC, the air masses from Track 1 had the lowest concentrations of \( \text{CO} \) (894\( \pm \)64 ppbv) compared to Tracks 2 and 3 \((p<0.001)\), and the CO concentrations from Track 2 and Track 3 had no obvious difference \((p=0.26)\), indicating strong transport influences of CO from eastern China regions. For \( \text{O}_3 \), there were no statistical difference among the three tracks, suggesting that the long-range transport of \( \text{O}_3 \), such as from eastern China, was not important during this study period. This is consistent with our earlier \( \text{O}_3 \) analysis in Sect. 3.3.1 that \( \text{O}_3 \) levels were dominantly affected by local production.

In contrast to the trace gases \( \text{CO} \), \( \text{SO}_2 \), \( \text{NO}_x \) and \( \text{O}_3 \), which were continuously measured, the NMHCs were manually monitored for 8 sampling days within the study period. All samples were found to originate from Track 1 and Track 2, and no samples were observed from Track 3. Furthermore, there was no statistical difference in NMHC concentration between the two tracks at both sites \((p>0.05)\). In order to obtain a more detailed signature of NMHCs in different air masses, much a finer back trajectory analysis was conducted to better understand the influence of regional transport on NMHCs. Nine-km resolution WRF output data were used in the HYSPLIT model, and 12-hour back trajectories at a 50 m height level were calculated for each hour during the VOC
sampling period at both sites. Four groups of air masses were identified at each site, namely, Tracks A, B, C, and D (Fig. 9). The corresponding concentrations of NMHCs for each track were calculated as well (Table 7).

At the TC site, the air masses from Track C (passing over the inland region) had a higher total NMHC concentration than air masses from Tracks B and D ($p<0.05$), which originated from the coast and the South China Sea, respectively, suggesting the significant influence of emission from the inland PRD region (mainly the northeastern part, i.e. Huizhou and Shenzhen) on NMHC levels at TC (Table 7). Further inspection of the anthropogenic NMHCs (i.e. alkenes, alkanes and aromatics) shows that the concentrations of alkanes for Track C were much higher than for Tracks B and D, mainly due to the contribution of 2-methylpentane, 3-methylpentane, $n$-hexane, and methylcyclopentane, with mean concentrations 4–6 times those for Tracks B and D. In contrast, the total NMHC concentration for Track A ($27.8\pm6.5$ ppbv) was similar to that for Tracks B and D, although Track A also originated from the inland region. Its value was between the levels for Track C ($42.6\pm12.7$ ppbv) and Tracks B ($23.2\pm3.2$ ppbv) and D ($22.6\pm2.1$ ppbv), perhaps due to the fact that the air masses from Track A were intersected by air masses from the inland region and the southern China coast. However, the concentration of alkenes for Track A ($4.9\pm0.6$ ppbv) was significantly higher than that for Tracks B ($3.9\pm0.2$ ppbv) and D ($3.5\pm0.6$ ppbv).

At the WQS site the concentrations of total NMHCs, alkanes, alkenes and aromatics in Track A were similar to those in Track C (both over Dongguan and Huizhou). The concentrations of total NMHCs for these two tracks were significantly higher than those for Track B ($p<0.05$), which came along the coast and passed over the north of Shenzhen, indicating the influence of Dongguan and Huizhou on the WQS site. Further inspection found that the higher total NMHCs in Tracks A and C were mainly attributed to the higher aromatic concentrations. For example, the mean concentrations of toluene, ethylbenzene, $m/p$-xylene, and $o$-xylene for Track C were 3–6 times those for Track B. This result also confirms the discussion in Sect. 3.2.1 that Dongguan made a significant contribution to aromatics at WQS.
4 Summary and conclusions

We analyzed measurement data collected concurrently at a site in the inland PRD region (WQS) and a site in greater Hong Kong (TC). The average levels of air pollutants at the WQS site were much higher than those at the TC site, with the exception for NO\textsubscript{x}. The respective mean mixing ratios (±95% confidence interval) at WQS and TC were 40±2 and 32±1 ppbv (O\textsubscript{3}), 31±2 and 45±2 ppbv (NO\textsubscript{x}), 1047±38 and 574±13 ppbv (CO), 32±1 and 9±0.3 ppbv (SO\textsubscript{2}), 40±6 and 33±4 ppbv (total NMHCs), and 43±6 ppbv and 19±4 ppbv (total carbonyls). The relatively high CO levels at WQS were attributed to regional emissions, and the high SO\textsubscript{2} levels at WQS were attributed to local power plant emissions in Humen of Dongguan. By comparison, the high traffic density in Hong Kong contributed to the elevated NO\textsubscript{x} levels at TC. In addition, the results from this study indicate that carbonyl levels in the region have increased in recent years.

Northerly monsoons bring cold, dry air from the inner Asian continent to the PRD region. Whereas elevated CO levels were generally observed at both sites when northerly monsoons were enhanced, the monsoons were associated with a decreasing O\textsubscript{3} trend. Instead, O\textsubscript{3} episodes usually occurred when weather systems were relatively stable. Analysis of the synoptic weather conditions and variations of air pollutants indicated that high O\textsubscript{3} levels were mainly attributed to local photochemical production. However, significant differences in diurnal variations of air pollutants were also observed at the two sites, indicating different local and regional contributions. In particular, ozone episodes were stronger and more frequent at WQS than TC. During the sampling period the daily maximum O\textsubscript{3} value exceeded 122 ppbv 13 times at WQS compared to 2 times at TC, with maximum O\textsubscript{3} levels of 182 ppbv at WQS vs. 139 ppbv at TC. Diurnal variations of O\textsubscript{3} showed higher nighttime levels of O\textsubscript{3} at TC than at WQS as well as more photochemical activity at WQS than TC. At each site, remarkable differences in diurnal variations were also found between high and low O\textsubscript{3} pollution days. An important conclusion from this work is that Hong Kong is more acutely VOC-limited than the inland PRD region.
A detailed look at the NMHCs showed that the composition of NMHCs and carbonyls were different at the two sites, with relatively higher levels of alkanes at TC that were attributed to LPG usage, and relatively higher levels of aromatics at WQS that were due to industry. Various air pollutant ratios (SO$_2$/NO$_x$, CO/NO$_x$, m, p-xylene/ethylbenzene, $i$-butane/propane) further suggested that air masses arriving at TC were mainly affected by local emissions superimposed by regional transport, whereas the air at WQS was highly influenced by regional emissions and was therefore more aged. Indeed, backward trajectory analysis showed that air masses arriving at these two sites had different transport pathways. This finding was corroborated by higher wind speeds and different wind directions at TC than WQS. The back trajectories showed that air masses arriving at WQS were mainly affected by inland China, including Dongguan and Huizhou, whereas air masses arriving at TC were primarily from the East China Coast, which brought lower levels of pollutants to Hong Kong. Therefore another important conclusion from this research is that despite the separation of the two study sites by only 62 km, not all parcels arriving in Hong Kong have been influenced by the PRD. Instead, strong local emissions from urban Hong Kong impacted the TC site, although the influence of East China emissions on Hong Kong cannot be ignored. By contrast to TC, inland influences contributed to the trace gas signatures at WQS, including significant regional transport from Dongguan.

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Environmental Protection Department (EPD): Air Quality in Hong Kong 2006, Air Science Group, Environmental Protection Department, the Government of the Hong Kong Special Administrative Region, 2007.


**Table 1.** The operating conditions of HPLC.

<table>
<thead>
<tr>
<th>Column</th>
<th>Nava-Pak C18 3.9x150 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobile phase</td>
<td>A: Water/Acetonitrile/Tetrahydrofuran 60/30/10</td>
</tr>
<tr>
<td>Gradient</td>
<td>B: Water/Acetonitrile 40/60</td>
</tr>
<tr>
<td>Flow rate</td>
<td>100% A for 2 min then a linear gradient from 100% A to 100% B in 18 min, 100% B for 4 min</td>
</tr>
<tr>
<td>Injection volume</td>
<td>20 µL</td>
</tr>
<tr>
<td>Detection</td>
<td>Absorbance at 360 nm</td>
</tr>
</tbody>
</table>
Table 2. Statistics of meteorological parameters at the TC and WQS sites.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Count</th>
<th>Average</th>
<th>Max value</th>
<th>Min value</th>
<th>95% confidence interval</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TC</td>
<td>WQS</td>
<td>TC</td>
<td>WQS</td>
<td>TC</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>954</td>
<td>791</td>
<td>21.8</td>
<td>21.9</td>
<td>31.6</td>
</tr>
<tr>
<td>Wind speed (m s⁻¹)</td>
<td>945</td>
<td>702</td>
<td>1.95</td>
<td>1.32</td>
<td>5.3</td>
</tr>
<tr>
<td>Wind direction (°)</td>
<td>945</td>
<td>682</td>
<td>96.8</td>
<td>57.4</td>
<td>–</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>947</td>
<td>800</td>
<td>65.6</td>
<td>66.3</td>
<td>97.0</td>
</tr>
<tr>
<td>Solar radiation (W m⁻²)</td>
<td>954</td>
<td>783</td>
<td>665*</td>
<td>585*</td>
<td>789</td>
</tr>
</tbody>
</table>

* Average of the daily maximum solar radiation
### Table 3. Statistics of total NMHCs, total carbonyls and other trace gases at the TC and WQS sites.

<table>
<thead>
<tr>
<th>Units: ppbv</th>
<th>TC Count</th>
<th>Average ± 95% confidence interval</th>
<th>Max value</th>
<th>WQS Count</th>
<th>Average ± 95% confidence interval</th>
<th>Max value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃</td>
<td>928</td>
<td>32±1</td>
<td>139</td>
<td>920</td>
<td>40±3</td>
<td>182</td>
</tr>
<tr>
<td>NOₓ</td>
<td>928</td>
<td>45±2</td>
<td>179</td>
<td>920</td>
<td>31±2</td>
<td>155</td>
</tr>
<tr>
<td>CO</td>
<td>928</td>
<td>574±13</td>
<td>1204</td>
<td>432</td>
<td>1047±38</td>
<td>2915</td>
</tr>
<tr>
<td>SO₂</td>
<td>928</td>
<td>9±0.3</td>
<td>35</td>
<td>920</td>
<td>32±1</td>
<td>167</td>
</tr>
<tr>
<td>Total NMHCs</td>
<td>96</td>
<td>26±3</td>
<td>141</td>
<td>102</td>
<td>39±6</td>
<td>237</td>
</tr>
<tr>
<td>Total Carbonyls</td>
<td>26</td>
<td>19±4</td>
<td>52</td>
<td>32</td>
<td>43±6</td>
<td>92</td>
</tr>
</tbody>
</table>
Table 4. Summary of synoptic weather conditions and the corresponding variations of air pollutants during the sampling period.

<table>
<thead>
<tr>
<th>Period</th>
<th>Synoptic weather conditions</th>
<th>Variation of pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 October ~1 November</td>
<td>An intense northeast monsoon and a rain-band over southern China due to a high-pressure system moving toward eastern China which brought cool and rainy weather to Hong Kong and the inland PRD region. The temperature decreased to about 16°C at night on 1 November, and the daily maximum solar radiation decreased to about 180 W/m².</td>
<td>CO peaks reached 1197 ppbv at TC and 1811 ppbv at WQS; O₃ concentrations decreased to a very low level at both sites.</td>
</tr>
<tr>
<td>2~3 November</td>
<td>The weather turned fine again; a high-pressure center was present near the Guizhou and Hunan provinces, and the temperature began to increase.</td>
<td>O₃ levels increased slowly at both sites; CO concentrations had a decreasing trend.</td>
</tr>
<tr>
<td>7~8 November</td>
<td>It turned cloudy on 8 November as the cloud band associated with Tropical Storm Peipah over the South China Sea reached the south China coast. The temperature decreased to about 21°C.</td>
<td>O₃ levels decreased slowly; the O₃ peaks at TC and WQS decreased from 75 and 82 ppbv (6 November) to 29 and 59 ppbv (8 November), respectively.</td>
</tr>
<tr>
<td>9~17 November</td>
<td>On the south edge of the high-pressure system located in North China, the weather was fine.</td>
<td>O₃ peaks reached 124 (TC) and 138 ppbv (WQS) on 10 November. SO₂ and CO peaks reached 101 and 2158 ppbv at WQS, respectively.</td>
</tr>
<tr>
<td>18~19 November</td>
<td>Northerly monsoons were elevated due to the moving high-pressure system, which was present in Hunan province on 19 November.</td>
<td>CO mixing ratios were intensely elevated; their peaks reached 1204 ppbv at TC and 2915 ppbv at WQS.</td>
</tr>
<tr>
<td>26~29 November</td>
<td>The northerlies strengthened on 26 November when a surge of the intense northeast monsoon reached southern China. The weather became progressively cool and very dry with the relative humidity falling below 40%. Temperatures dropped to about 14°C on 28 November.</td>
<td>CO mixing ratios were elevated at TC. SO₂ and NOₓ both decreased to a low level at WQS. O₃ levels had a decreasing trend at both TC and WQS.</td>
</tr>
<tr>
<td>30 November ~1 December</td>
<td>The weather turned fine again; Hong Kong and the inland PRD region were located near the high-pressure ridge.</td>
<td>O₃ peak reached 138 ppbv at WQS, but remained low at TC.</td>
</tr>
</tbody>
</table>
### Table 5. Mean concentrations of trace gases at daytime and nighttime and the diurnal difference.

<table>
<thead>
<tr>
<th>Units: ppbv</th>
<th>Daytime*</th>
<th>Nighttime**</th>
<th>Daytime–Nighttime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TC</td>
<td>WQS</td>
<td>TC</td>
</tr>
<tr>
<td><strong>O₃</strong></td>
<td>35±3</td>
<td>59±7</td>
<td>27±4</td>
</tr>
<tr>
<td><strong>NOₓ</strong></td>
<td>48±4</td>
<td>27±3</td>
<td>42±5</td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td>601±62</td>
<td>1118±115</td>
<td>545±55</td>
</tr>
<tr>
<td><strong>SO₂</strong></td>
<td>10±1</td>
<td>32±3</td>
<td>7±1</td>
</tr>
</tbody>
</table>

* From 06:00 to 18:00; ** from 19:00 to 05:00
### Table 6. Proportion of air masses associated with each track and the corresponding concentrations of trace gases.

<table>
<thead>
<tr>
<th></th>
<th>Track 1</th>
<th>Track 2</th>
<th>Track 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TC</td>
<td>WQS</td>
<td>TC</td>
</tr>
<tr>
<td>Proportion (%)</td>
<td>44</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>$O_3$ (ppbv)</td>
<td>35±3*</td>
<td>47±11</td>
<td>31±7</td>
</tr>
<tr>
<td>$NO_x$ (ppbv)</td>
<td>40±5</td>
<td>30±5</td>
<td>48±7</td>
</tr>
<tr>
<td>CO (ppbv)</td>
<td>470±30</td>
<td>894±64</td>
<td>648±45</td>
</tr>
<tr>
<td>$SO_2$ (ppbv)</td>
<td>8±1</td>
<td>27±4</td>
<td>9±1</td>
</tr>
<tr>
<td>Total NMHCs (ppbv)</td>
<td>22±5</td>
<td>40±9</td>
<td>30±15</td>
</tr>
</tbody>
</table>

*Mean ±95% confidence interval
Table 7. Proportion of each air mass associated with each track and the corresponding concentrations of NMHCs during the VOC sampling period.

<table>
<thead>
<tr>
<th></th>
<th>Track A</th>
<th></th>
<th>Track B</th>
<th></th>
<th>Track C</th>
<th></th>
<th>Track D</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TC</td>
<td>WQS</td>
<td>TC</td>
<td>WQS</td>
<td>TC</td>
<td>WQS</td>
<td>TC</td>
<td>WQS</td>
</tr>
<tr>
<td>Proportion (%)</td>
<td>18</td>
<td>55</td>
<td>65</td>
<td>9</td>
<td>11</td>
<td>24</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Total NMHCs (ppbv)</td>
<td>27.8±6.5</td>
<td>42.5±9.2</td>
<td>23.2±3.2</td>
<td>22.2±7.5</td>
<td>42.6±12.7</td>
<td>42.6±15.1</td>
<td>22.6±2.1</td>
<td>30.8±6.3</td>
</tr>
<tr>
<td>Alkene (ppbv)</td>
<td>4.9±0.6</td>
<td>8.2±0.7</td>
<td>3.9±0.2</td>
<td>5.8±0.8</td>
<td>3.8±0.8</td>
<td>7.7±1.6</td>
<td>3.5±0.6</td>
<td>8.3±1.3</td>
</tr>
<tr>
<td>Alkane (ppbv)</td>
<td>15.6±3.3</td>
<td>15.8±1.8</td>
<td>14.5±2.0</td>
<td>12.5±6.1</td>
<td>30±10.7</td>
<td>17.6±6.1</td>
<td>15.3±2.0</td>
<td>14.5±3.5</td>
</tr>
<tr>
<td>Aromatic (ppbv)</td>
<td>6.5±3.2</td>
<td>18.3±8.7</td>
<td>4.0±1.3</td>
<td>3.6±1.1</td>
<td>6.7±2.2</td>
<td>17.0±8.5</td>
<td>3.7±0.7</td>
<td>7.7±2.3</td>
</tr>
</tbody>
</table>
Fig. 1. Location of the sampling sites, Pearl River Delta of Southern China.
Fig. 2. Mean sea level pressure and wind field on 1000 hPa between 22 October and 1 December 2007.
Fig. 3. Scatter plots of (a) \( m, p \)-xylene to ethylbenzene (b) \( i \)-butane to propane at TC and WQS during the VOC sampling period.
Fig. 4. Time series of trace gases and total NMHCs between 22 October and 1 December 2007.
Fig. 5. Time series of the main meteorological factors between 22 October and 1 December 2007.
Fig. 6. Mean diurnal variations of total NMHCs, other trace gases and wind fields between 23 October to 1 December (total NMHCs were averaged using all VOC samples from 8 sampling days).
Fig. 7. Diurnal variation of total NMHCs, other trace gases and wind fields on 26 and 27 October.
Fig. 8. Three typical back trajectories for each site at the 200 m height level.
Fig. 9. Four typical back trajectories for each site at the 50 m height level during the VOC sampling period.