Interactive comment on "Characterization of photochemical pollution at different elevations in mountainous areas in Hong Kong" by H. Guo et al.

Anonymous Referee #1

Referee 1

Surface ozone has been intensively studied in the Pearl River Delta region in South China in past decades, and many studies showed that mesoscale circulations like sealand breezes and mountain valley breezes play important roles in air pollution transport in such a region with complex topography and land-use/land cover. However, there were very few works conducting field measurements at mountain site in this region. This study presents latest results from a well-designed field campaign at a mountain site and concurrently at an urban site at foot of the mountain. The measurements were conducted in autumn, a typical period of photochemical pollution in South China. These data are very valuable for improving current understanding of photochemistry and multi-scales air pollution transport in such a region with severe ozone pollution for decades. Generally speaking, the manuscript is well-written and can be accepted for publication on Atmos. Chem. Phys. in its current form. However, this referee would like to encourage the authors to make some revision according to the following comments:

Major comments.

1)The authors presented data collected at the two sites equally in a comparative way, but the referee thinks that the difference of ozone levels between the two sites doesn't deserved such a long discussion in Section 3.2. The author should focus on the mountain site, which gives more valuable information in regional perspectives of air pollution transport. Section 3.2 can be re-organized by condensing the first half and adding more discussion on the long-range/regional transport issue. Here the long-range transport of air pollutions can influence the Hong Kong's local air quality by downward transport from upper-PBL through valley breezes at night and vertical mixing during the day time.

Reply: The review's comment is highly appreciated. In order to strengthen the analysis of regional transport, more discussion on the influence of regional transport has been added in the revised manuscript. To assess the impact of the long-range transport, ratios of different trace gases, including SO_2/NO_x, CO/NO_x, ethyne/propane, benzene/propane, toluene/benzene and *n*-butane/propane were investigated in the revised manuscript. Moreover, the influence of regional air masses was further confirmed by the correlation between VOC variability and the atmospheric lifetime. As such, the following discussion was added in the revised manuscript:

"……*Previous studies (So and Wang, 2003; Wang and Kwok, 2003; Guo et al., 2009) have reported that ratios of SO_2/NO_x and CO/NO_x were lower in Hong Kong than in PRD due to the use of low sulfur-containing fuel and more efficient combustion technology in Hong Kong. In this study, the ratios of SO_2/NO_x and CO/NO_x were 0.13 ± 0.04 and 12.85 ± 0.37 ppbv/ppbv at TW, within the ranges of 0.02 ~ 0.19 and 5.21 ~ 19.25 ppbv/ppbv from September to November 2010 observed in Hong Kong urban air (data from HKEPD, http://www.epd.gov.hk), respectively. This suggested that air masses at TW were mainly influenced by Hong Kong local emissions. On the other*

hand, the ratios of SO_2/NO_x and CO/NO_x were much higher at TMS, with the values of 0.40 ± 0.01 and 46.38 ± 0.71 ppbv/ppbv, respectively, which were within the values reported in the PRD region (0.40 ~ 1.26 and 11.9 ~ 52.0 ppbv/ppbv, respectively) (Wang et al., 2005; Guo et al., 2009; Zhao et al., 2011). Hence, the relatively higher ratios of SO_2/NO_x and CO/NO_x at TMS indicated the possible influence of PRD emissions."

"……In addition, the relationship between VOC variability and the atmospheric lifetime was analyzed to estimate the distance of the sources of air pollutants with/without the influence of regional transport (Jobson et al., 1998; Warneke and de Gouw, 2001; Wang et al., 2005). This relationship is expressed as follows (equation 6):

$S_{lnx} = A\tau^{-b}$ (6)

where S_{lnx} is the standard deviation of the natural logarithm of the mixing ratio X, τ is the atmospheric lifetime, and A and b are fit parameters. The detailed description for this function can be referred to Wang et al. (2005). In brief, the constant b is related to the source-receptor distances and lies between 0 and 1. The closer the sampling site is from the air pollutant sources, the smaller the exponent b (Ehhalt et al., 1998; Wang et al., 2005). Figure 6 presents the relationship of variability with lifetime for different VOC species under the influence of scenarios 1 and 2. It can be found that the b exponent was higher in scenario 1 than in scenario 2 ($p < 0.05$), indicating that air masses at TMS were more frequently impacted by regional transport, particularly under prevailing northerly winds with high speeds (Wang et al., 2005)."

"Therefore, to further assess the possible influence of PRD air masses on the air quality at TMS, ambient concentration ratios of VOCs i.e., ethyne/propane, benzene/propane, toluene/benzene and n-butane/propane, were compared among the TMS samples affected by regional transport, the Hong Kong urban air samples and samples collected in the PRD region (Table 2). Compared with those in Hong Kong urban areas, higher ratios of ethyne/propane and benzene/propane were found in the PRD region due to the high combustion emissions and solvent usage (Barletta et al., 2008; HKEPD, 2010; Zhang et al., 2012). On the other hand, n-butane and propane are generally Liquefied Petroleum Gas (LPG) tracers. The ratio of n-butane/propane was lower in the PRD than that in Hong Kong urban areas because of the high percentage of n-butane in the composition of LPG used in Hong Kong (Tsai et al., 2006; Tang et al., 2008; Ho et al., 2009; Zhang et al., 2012). Moreover, higher ratio of toluene/benzene was found in Hong Kong urban air as toluene was a distinct emission from Hong Kong due to the high toluene content in unleaded gasoline (So and Wang et al., 2003; Ho et al., 2004, 2009). In this study, for the TMS samples affected by regional air masses, the above four pair ratios were between the values observed in Hong Kong urban air and the PRD region. These results confirmed that the air pollutants at TMS were somewhat influenced by air masses from the highly polluted PRD region, apart from the influence of Hong Kong urban air by mesoscale circulations (discussed in section 3.2.4.2)."

For details, please refer to lines 499-512, pages 19 and lines 533-574, pages 20-22 in the revised manuscript.

2) In Fig.2, the authors give some results of MOZAIC measurement to explain the possible difference in the vertical distribution. However, for selected cases, the vertical distribution might also be misled by horizontal difference of plumes as the airplane may fly over different cities in the Pearl River Delta during the ascend/descend stage. A solid result should be averaged with very large number of profiles. In fact, previous studies with relatively large number of MOZAIC aircraft profiles have already made typical PBL ozone patterns, i.e., a higher ozone in upper PBL, in some cities.

Reply: We thank the reviewer for the valuable comment. According to the reviewer's comments, the vertical profile of O_3 has been revised in the revised manuscript. The profile shown in Figure 2 was the average concentrations together with standard deviations for the data extracted from MOZAIC aircraft project in 2005-2010.

3) In Section 2.4, for the Mbox modeling of TMS, problems may be existed if assuming air parcel moved from the foot site TW to TMS, because wind data at TMS generally come from North, i.e. from the Pearl River Delta region. For this case, the model maybe initiated by using previous measurements in the inland Pearl River Delta region.

Reply: Thanks for the comment. In this study, Mbox model simulation was conducted during daytime hours (0800-1700 LT) on the selected days with VOC data, i.e., 24, 29 – 31 October, 1 – 3, 9 and 19 November, 2010, when evidence for the mesoscale circulation was clear based on the meteorological data and the levels of air pollutants. Mountain-valley breezes were simulated by the Weather Research and Forecasting (WRF) model on those days (Figure 9 as an example). The model results showed a valley breeze in the daytime (0900 LT) and a mountain breeze at night (2300 LT), suggesting the influence of mesoscale circulations on the redistribution of air pollutants between TMS and TW on those selected days. In addition, to determine whether regional transport had influence on the air pollutants on the selected days as stated above, wind speeds, ratios of SO_2/NO_x, CO/NO_x, toluene/benzene during daytime at TMS were compared with those influenced by the regional transport (in section 3.2.4.1). Previous studies (So and Wang, 2003; Guo et al., 2009) have reported that ratios of SO_2/NO_x and CO/NO_x were lower in Hong Kong than PRD due to the use of low sulfur-content fuel and more efficient combustion technology in Hong Kong. Toluene was a distinct emission from Hong Kong, which had much higher concentration than benzene due to the high toluene content in unleaded gasoline (So and Wang et al., 2003; Ho et al., 2004, 2009; Guo et al., 2009). If the mesoscale circulations were dominant during the Mbox modeling periods, lower wind speeds, lower ratios of SO_2/NO_x and CO/NO_x and higher ratio of toluene/benzene ratio would be observed, when compared to those observed for the periods influenced by regional transport (section 3.2.4.1). Indeed, the wind speed, ratios of SO_2/NO_x, CO/NO_x during the mesoscale modeling period were 1.57 $\pm$ 0.16 m/s, 0.37 $\pm$ 0.02 and 42.01 $\pm$ 1.08 ppbv/ppbv, respectively, which were much lower ($p < 0.05$) than those observed in the period influenced by regional transport at TMS, with values of 2.93 $\pm$

0.07 m/s, 0.45 ± 0.02 and 51.01 ± 1.28 ppbv/ppbv, respectively. In addition, the ratio of toluene/benzene (4.01 ± 0.28 pptv/pptv) was much higher ($p < 0.05$) during the selected days for MBox Modeling than that (3.14 ± 0.38 pptv/pptv) in the periods affected by regional transport, confirming the influence of Hong Kong urban air due to mesoscale circulations. Therefore, the above analysis demonstrated that the influence of mesoscale circulations was likely dominant on air pollutants on those selected days, when Mbox model was used correctly for the investigation on the influence of mesoscale circulations. The manuscript has been revised as follows:

"The correlation between the observation and the results of moving box (Mbox) model for TMS and TW developed by the PBM-MCM was also explored to evaluate the influence of mesoscale circulation. Since photochemical O_3 formation occurs during daytime hours, the photochemical processes between 0800 and 1700 LT were simulated using Mbox model on the selected VOC sampling days, i.e., 24, 29 – 31 October, 1 – 3, 9 and 19 November, 2010, when the potential influence of mesoscale circulations was dominant (Figure 9). In addition, to determine whether regional transport had influence on the air pollutants for the modeling periods as stated above, wind speeds, ratios of SO_2/NO_x, CO/NO_x and toluene/benzene during daytime hours (0800-1700 LT) at TMS were compared with those influenced by the regional transport (in section 3.2.4.1). If the mesoscale circulations were dominant during the Mbox modeling periods, lower wind speeds, lower ratios of SO_2/NO_x and CO/NO_x and higher ratio of toluene/benzene would be observed, when compared to those observed for the periods influenced by regional transport (section 3.2.4.1). Indeed, the wind speed, ratios of SO_2/NO_x, CO/NO_x during the mesoscale modeling periods were 1.57 ± 0.16 m/s, 0.37 ± 0.02 and 42.01 ± 1.08 ppbv/ppbv, respectively, which were much lower ($p < 0.05$) than those observed in the periods influenced by regional transport at TMS, with values of 2.93 ± 0.07 m/s, 0.45 ± 0.02 and 51.01 ± 1.28 ppbv/ppbv, respectively. Moreover, the ratio of toluene/benzene (4.01 ± 0.28 pptv/pptv) was much higher ($p < 0.05$) during the selected days for Mbox modeling than that (3.14 ± 0.38) in the periods affected by regional transport, confirming mesoscale circulations were dominant for the modeling periods. Figure 8 shows the correlation between observed and modeled O_3 during daytime hours. The time lag between the two sites was evaluated from dividing the distance between TMS and TW by the average value of the observed wind speeds during daytime hours. The value of time lag was factored in for pairs of data points used for correlation analysis, i.e. a sample collected at 0900 LT at TW corresponding to a sample at 1000 LT at TMS for a valley breeze during daytime hours if the time difference was one hour. Good correlation ($R^2 = 0.70$) between Mbox modeled O_3 and observed O_3 was found during daytime hours (Figure 8), suggesting that O_3 at TMS was related to the air pollutants at TW. This further indicated the influence of mesoscale circulations."

For details, please refer to lines 601-629, pages 23-24 in the revised manuscript.

On the other hand, we agreed with the reviewer about the regional impact on the air pollutants at TMS. Using the MCM-Mbox model to investigate the regional impact, typical trajectories and grid nudging from PRD to TMS on those days associated with

elevated O_3 concentrations at TMS should be obtained firstly from the output of WRF model and HYSPLIT model. Then the hourly measured data corresponding to the position of each grid should be input into the MCM model. As such, extensive sampling data, i.e. the hourly data, is pre-requisite for the modeling in the PRD region. Though a number of previous studies of VOCs have been conducted in the PRD region (e.g. Chan et al., 2006; Tang et al., 2007; Barletta et al., 2008; Liu et al., 2008; Guo et al., 2009; Zhang et al., 2012), these studies were only conducted in specific cities, i.e. Guangzhou and Dongguan, for specific time periods. The hourly data of VOCs is still lacking for the MCM-Mbox model input. In addition, comprehensive observation data of NO_x, CO and other trace gases is still limited in the PRD region, except for the emission inventory. Therefore, the data from previous studies in PRD was not appropriate for the MCM-Mbox modeling. However, the reviewer's suggestion does provide us a new idea about the assessment of the influence of regional transport. This will definitely be our future work when hourly data of trace gases in different gridded areas of PRD for the model input are available.

Minor issues.

1) Section 3.1.1, Paragraph 1. The authors tried to put the results of the mountain site into a global picture, however, because those results were obtained during different seasons, at different latitudes, and in regions with different emission characters. This part could be deleted or kept by adding more information about the experiments.

Reply: We agree with the reviewer's comments and the descriptions about comparison with other mountain sites were deleted. For details, please refer to lines 281-294, pages 10-11 in the revised manuscript.

Reference:

Chan, L. Y., Chu, K.W., Zou, S. C., Chan, C. Y., Wang, X. M., Barletta, B., Blake, D. R., Guo, H., and Tsai, W. Y.: Characteristics of nonmethane hydrocarbons (NMHCs) in industrial, industrial-urban,and industrial-suburban atmospheres of the Pearl River Delta (PRD) region of south China, J. Geophys. Res.-Atmos., 111, D11304, doi:10.1029/2005JD006481, 2006.

Ho, K. F., Lee, S. C., Guo, H., Tsai, W. Y.: Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong, Sci. Total Environ., 322, 155-166, 2004.

Ho, K. F., Lee, S. C., Ho, W. K., Blake, D. R., Cheng, Y., Li, Y. S., Ho, S. S. H., Fung, K., Louie, P. K. K., Park, D.: Vehicular emission of volatile organic compounds (VOCs) from a tunnel study in Hong Kong, Atmos. Chem. Phys., 9, 7491-7504, 2009.

Liu, Y., Shao, M., Lu, S., Chang, C. C., Wang, J. L., and Chen, G.: Volatile Organic Compound (VOC) measurements in the Pearl River Delta (PRD) region, China, Atmos. Chem. Phys., 8, 1531–1545, 2008..

Tang, J. H. et al.: Characteristics and diurnal variations of NMHCs at urban, suburban, and rural sites in the Pearl River Delta and a remote site in South China, Atmos. Environ., 41,8620–8632, 2007.

Interactive comment on "Characterization of photochemical pollution at different elevations in mountainous areas in Hong Kong" by H. Guo et al.

Anonymous Referee #2

General comments:

The paper presents the characterization of photochemical pollution near the summit of Mt. Tai Mao. The pollutants and meteorological conditions of the summit site were compared with those of the urban site at the foot of the mountain to explore the possible reasons (NO titration, vertical meteorological conditions, regional transport, and mesoscale circulations) causing frequent O_3 episodes at the summit site in autumn, but only one O_3 episode at the foot of the mountain. Numerous methods and concepts were used in this study to explain the physical and chemical processes of the O_3 episode observed at the summit. Some of these approaches are reasonable and able to produce robust results (e.g., NO titration and meteorological conditions). Nevertheless, some inferences (e.g., high O_3 concentrations at TMS were mainly influenced by mesoscale circulations and photochemical O_3 formation was VOC-sensitive or both NOx and VOC-sensitive at TMS) derived from either unfit approaches (eg., Mbox without considering NO titration) or weak results are controversial or less persuasive (specific comments). In general, the study is beneficial for understanding photochemical pollution at the mountain site and serves as a complement to previous studies conducted in low-elevation areas of PRD. Thus, this manuscript can be considered for publication after the specific comments below have been addressed.

Reply: We thank the reviewer for his/her comments. Our responses to the reviewer are as follows, along with indications of how the manuscript has been further revised for the consideration by ACP. We hope that these changes will further strengthen the main points and make them clearer in the revised manuscript.

Specific comments:

Page 29035 Lines 5-12: Figure 2b shows that both TMS and TW had similar patterns of O3 with broad maximum values at approximately 1500 h. Moreover, O_x reached a maximum value at TW during 1500 h to 1600 h, which was later than that at TMS. In Lines 1 to 4 of Page 29010, the authors stated that the air mass arriving at TMS was generally more aged than that at TW, which may be attributed to regional transport and/or mesoscale circulations. In general, the maximum O_3 in the downwind area is usually a few hours later than that in the source area. In the source area, O_3 builds up after sunrise and usually reaches a maximum value at approximately 1300 h to 1400 h. It seems a bit late for maximum O_3 and O_x at TW. The authors need to clarify this phenomenon.

Reply: The excellent comment of the reviewer is greatly appreciated. As described in the text, the concentrations of "oxidant" O_x are equal to the concentrations of O_3 and NO_2. That is, the O_x value is determined by both O_3 and NO_2 values at the sampling site. The purpose of using O_x rather than O_3 was to eliminate the titration effect of NO on O_3. This method has been widely used in previous studies (Helmut, 1999; Jenkinet al., 2000; Chen et al., 2002; Godish et al., 2003; Lin et al., 2007; Jianget al., 2010). On one hand, NO_2 is generated via NO titration on O_3 while at the same time O_3 value

is reduced. On the other hand, NO_2 is directly emitted from combustion sources. Due to the complex NO_x chemistry and combined impact of primary and secondary NO_2, the maximum concentration of O_x does not necessarily appear with a delay in the downwind areas (Tang et al., 2006; Seinfeld and Pandis, 2006; Godish et al., 2003; Jiang et al., 2010).

In contrast, as a secondary pollutant, O_3 generally presents a peak value at noon and/or in early afternoon, and the maximum O_3 in the downwind area is usually a few hours later than that in the source area. Indeed, in this study, the maximum O_3 at TMS showed a delay, when compared with that at TW (Figure 1). The average daily maximum O_3 (35 ± 4 ppbv) at TW appeared at about 1400 local time (LT), while the peak O_3 value at TMS was observed at about 1500 LT with the average value of 70 ± 6 ppbv. A description has been added in the revised manuscript as follows:

"However, the maximum O_3 at TMS showed a delay, when compared to that at TW. The average daily maximum O_3 mixing ratio at TMS (70 ± 6 ppbv, 1500 LT) appeared one-hour later ($p < 0.05$) than that observed at TW (35 ± 4 ppbv, 1400 LT). The delayed daily maximum O_3 at TMS was due to the fact that the air mass arriving at TMS was generally more aged than that at TW, which may be attributed to regional transport (section 3.2.4.1) and/or mesoscale circulations (section 3.2.4.2)."

For details, please refer to lines 304-307, page 11 in the revised manuscript.

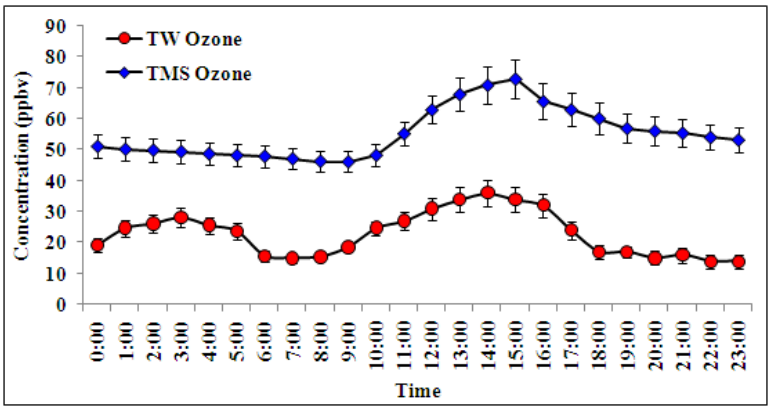

Figure 1 Diurnal variations of O_3 observed at TMS and TW

Page 29036 Line 26 - Page 29037 Line 14: Attaining the mixing ratios of OH radical through the relationship between isoprene and its oxidation products seems controversial. In urban areas, isoprene not only has biogenic sources but also anthropogenic emissions (Borbon et al., 2001). Defining the processing time t for isoprene would be difficult because of the different diurnal emission patterns of the two sources. Furthermore, adopting the identical processing time for isoprene ("precursor") and its "products" in Eqs. 4 and 5 seems unreasonable.

Reply: We thank the reviewer for the valuable comments. Although some previous studies have reported that isoprene in the urban areas may be attributed to both vehicular exhaust and biogenic emissions (Borbon et al., 2001; Barletta et al., 2002), isoprene was mainly emitted from biogenic sources in this study. This was due to the following facts:

1. The isoprene diurnal patterns: When isoprene was influenced by both anthropogenic and biogenic emissions, it would have a bimodal pattern corresponding to the rush hours with maximum traffic flow, in addition to a biogenic peak at noon/in early afternoon (Borbon et al., 2001). However, the diurnal pattern of isoprene in this study was totally different. The following figure (Figure 2) presents the average diurnal patterns of isoprene during O_3 and non-O_3 episode days at TW. It can be seen that on both O_3 and non-O_3 episode days, isoprene showed a broad peak value between 11:00 and 14:00, and low levels at night at TW, suggesting isoprene was dominated by biogenic emission at this urban site (i.e. TW). Similar findings have been widely reported in urban Hong Kong (Ho et al., 2004; Wang et al., 2005; Tang et al., 2007). Indeed, VOC composition in roadside samples in Hong Kong showed very low (or ignorable) level (0.3% in percentage, ppbC/ppbC) of isoprene (unpublished data).

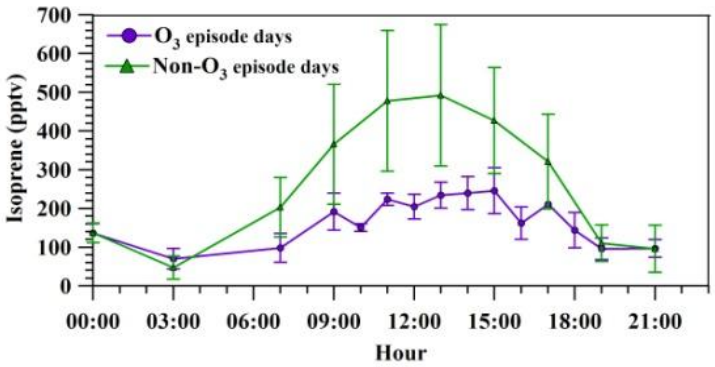

Figure 2 Average diurnal patterns of isoprene during O_3 and non-O_3 episode days at TW

2. Apart from the analyses of diurnal patterns, the correlations between isoprene and combustion tracers, i.e. CO, and acetylene were also investigated. Poor correlations were found for isoprene vs. CO (R^2 = 0.05) and isoprene vs. acetylene (R^2 = 0.03) at TW, indicating that vehicular exhaust was not a source of isoprene at TW.

Therefore, based on the above discussion, we concluded that isoprene was mainly emitted from biogenic sources at TW.

On the other hand, we agreed with the reviewer's comment on the calculation of the OH radical mixing ratio. As we did not measure OH radical in situ, we used the simulation results of two models, i.e., an observation-based model (OBM) and a Master Chemical Mechanism (MCM) model to investigate the mixing ratios of OH radical at the two sites, while the results of the calculation method were used as an additional evidence for variations of OH radicals. The calculations of OH radical via the parameterization between isoprene and MAC and MVK were based on the assumption that the processing time of the air mass was identical for MAC and MVK and there were no additional sources of MAC and MVK apart from the oxidation of isoprene. We have revised the text as follows:

"On the other hand, the levels of hydroxyl radical (OH radical) were further compared at the two sites. As we did not measure OH radical in situ, its mixing ratio during daytime hours (0700-1900 LT) was calculated using two models, i.e., an observation based model (OBM) and a Master Chemical Mechanism (MCM) model.

The detailed description of the OBM model can be found elsewhere (Zhang et al., 2007, 2008; Cheng et al., 2010a; Ling et al., 2011). Besides simulation results, the concentration of OH radical was also estimated from the parameterization method through the empirical relationship between isoprene (ISOP) and its oxidation products i.e. methacrolein (MAC) and methyl vinyl ketone (MVK) based on the assumption that the processing time of the air mass was identical for MAC and MVK and there were no additional sources of MAC and MVK apart from the oxidation of isoprene (equations 1 ~ 5 as follows),

ISOP + OH → 0.63 HCHO + 0.32 MVK + 0.23 MAC $k_1 = 1.0 \times 10^{-10}$ *cm*$^{-3}$ *s*$^{-1}$ *(1)*

MAC + OH → products $k_2 = 3.3 \times 10^{-11}$ *cm*$^{-3}$ *s*$^{-1}$ *(2)*

MVK + OH → products $k_3 = 1.9 \times 10^{-11}$ *cm*$^{-3}$ *s*$^{-1}$ *(3)*

$$\frac{[MAC]}{[ISOP]} = \frac{0.23k_1}{(k_2 - k_1)}(1 - e^{(k_1 - k_2)[OH]_{avg}t}) \quad (4)$$

$$\frac{[MVK]}{[ISOP]} = \frac{0.32k_1}{(k_3 - k_1)}(1 - e^{(k_1 - k_3)[OH]_{avg}t}) \quad (5)$$

where [MAC], [ISOP] and [MVK] were the measured values for MAC, isoprene and MVK, and t is the processing time. Details of this method can be found in Liu et al. (2009) and Yuan et al. (2012). Figure 3b presents the calculated and simulated OH radical concentrations at TMS and TW during daytime hours. At TMS, the average mixing ratios of OH radical simulated by OBM and MCM models were (2.31 ± 0.27) × 10^6 *and (3.93 ± 0.74) × 10*^{6} *molecule cm*$^{-3}$*, respectively, and (2.03 ± 0.28) × 10*^{6} *molecule cm*$^{-3}$ *from the calculations of the parameterization method. On the other hand, the average concentrations of OH at TW calculated by the corresponding three methods were (2.63 ± 0.29) × 10*^{6}*, (4.26 ± 0.74) × 10*^{6} *and (2.27 ± 0.31) × 10*^{6} *molecule cm*$^{-3}$*, respectively. Though variations were found for the results of different methods, the average mixing ratios of OH radical at the two sites were comparable (p > 0.05). In addition, by considering the factor of fractional conversion which represented the relative importance of photolysis reactions on OH radical formation in the atmosphere (Jenkin et al., 2000; Atkinson et al., 1997), the mean fraction conversion index at TMS (0.17 ± 0.03) was lower than that at TW (0.23 ± 0.04, p < 0.05). Based on the aforementioned analyses, it could be concluded that photochemical reactions at TMS were not stronger than at TW. Hence, the higher* O_3 *levels observed at TMS than those at TW were not induced by the different degrees of photochemical reactions."*

For details, please refer to lines 383-418, pages 15-16 in the revised manuscript.

Page 29040 Line 27 - Page 29041 Line 8: With regard to strengthening the conclusion of influence of air mass transport, numerous VOCs can be employed as tracers of specific source regions, and they might be helpful for assessing the influence by regional air masses from the highly polluted PRD.

Reply: This comment was highly appreciated. According to the reviewers' comments, ratios of different trace gases, including SO_2/NO_x, CO/NO_x, ethyne/propane, benzene/propane, toluene/benzene and *n*-butane/propane were further investigated in the revised manuscript in order to strengthen the conclusion of influence of air mass transport. Moreover, the influence of regional air masses was further confirmed by the correlation between VOC variability and the atmospheric lifetime of VOCs for the scenarios with and without the influence of regional transport at TMS during sampling period. The following text has been added in the revised manuscript:

"……Previous studies (So and Wang, 2003; Wang and Kwok, 2003; Guo et al., 2009) have reported that ratios of SO_2/NO_x and CO/NO_x were lower in Hong Kong than in PRD due to the use of low sulfur-containing fuel and more efficient combustion technology in Hong Kong. In this study, the ratios of SO_2/NO_x and CO/NO_x were 0.13 ± 0.04 and 12.85 ± 0.37 ppbv/ppbv at TW, within the ranges of 0.02 ~ 0.19 and 5.21 ~ 19.25 ppbv/ppbv from September to November 2010 observed in Hong Kong urban air (data from HKEPD, http://www.epd.gov.hk), respectively. This suggested that air masses at TW were mainly influenced by Hong Kong local emissions. On the other hand, the ratios of SO_2/NO_x and CO/NO_x were much higher at TMS, with the values of 0.40 ± 0.01 and 46.38 ± 0.71 ppbv/ppbv, respectively, which were within the values reported in the PRD region (0.40 ~ 1.26 and 11.9 ~ 52.0 ppbv/ppbv, respectively) (Wang et al., 2005; Guo et al., 2009; Zhao et al., 2011). Hence, the relatively higher ratios of SO_2/NO_x and CO/NO_x at TMS indicated the possible influence of PRD emissions."

"……In addition, the relationship between VOC variability and the atmospheric lifetime was analyzed to estimate the distance of the sources of air pollutants with/without the influence of regional transport (Jobson et al., 1998; Warneke and de Gouw, 2001; Wang et al., 2005). This relationship is expressed as follows (equation 6):

$$S_{lnx} = A\tau^{-b} \quad (6)$$

where S_{lnx} is the standard deviation of the natural logarithm of the mixing ratio X, τ is the atmospheric lifetime, and A and b are fit parameters. The detailed description for this function can be referred to Wang et al. (2005). In brief, the constant b is related to the source-receptor distances and lies between 0 and 1. The closer the sampling site is from the air pollutant sources, the smaller the exponent b (Ehhalt et al., 1998; Wang et al., 2005). Figure 6 presents the relationship of variability with lifetime for different VOC species under the influence of scenarios 1 and 2. It can be found that the b exponent was higher in scenario 1 than in scenario 2 ($p < 0.05$), indicating that air masses at TMS were more frequently impacted by regional transport, particularly under prevailing northerly winds with high speeds (Wang et al., 2005)."

"Therefore, to further assess the possible influence of PRD air masses on the air quality at TMS, ambient concentration ratios of VOCs i.e., ethyne/propane, benzene/propane, toluene/benzene and n-butane/propane were compared among the TMS samples affected by regional transport, the Hong Kong urban air samples and samples collected in the PRD region (Table 2). Compared to those in Hong Kong urban areas, higher ratios of ethyne/propane and benzene/propane were found in the

PRD region due to the high combustion emissions and solvent usage (Barletta et al., 2008; HKEPD, 2010; Zhang et al., 2012). On the other hand, n-butane and propane are generally Liquefied Petroleum Gas (LPG) tracers. The ratio of n-butane/propane was lower in the PRD than that in Hong Kong urban areas because of the high percentage of n-butane in the composition of LPG used in Hong Kong (Tsai et al., 2006; Tang et al., 2008; Ho et al., 2009; Zhang et al., 2012). Moreover, higher ratio of toluene/benzene was found in Hong Kong urban air as toluene was a distinct emission from Hong Kong due to the high toluene content in unleaded gasoline (So and Wang et al., 2003; Ho et al., 2004, 2009). In this study, for the TMS samples affected by regional air masses, the above four pair ratios were between the values observed in Hong Kong urban air and the PRD region. These results confirmed that the air pollutants at TMS were somewhat influenced by air masses from the highly polluted PRD region, apart from the influence of Hong Kong urban air by mesoscale circulations (discussed in section 3.2.4.2).”

For details, please refer to lines 499-512, pages 19 and lines 533-574, pages 20-22 in the revised manuscript.

Page 29042 Lines 21-26: The model employed for calculating O_3 did not consider NO titration. However, the influence of NO titration must be significant at TW to affect O_3 levels seriously.

Reply: Thanks for pointing this out. The Mbox model applied in this study implemented the most up-to-date version of near-explicit photochemical mechanism which included the NO titration. To better introduce the model, a detailed description has been added as follows:

“In this study, a photochemical box model (PBM) implementing the most up-to-date version of near-explicit photochemical mechanism, namely the Master Chemical Mechanism version 3.2 (MCMv3.2), has been applied to simulate the O_3 pollution at the two sites (Lam et al., 2012)……Moving box (Mbox): this scenario was an over simplified mountain-valley breezes phenomenon with the grid sitting between TW and TMS monitoring stations and an air parcel moving on an idealized trajectory. During daytime hours (0800 - 1700, local time (LT)), the monitoring station at TW was assumed to be the centre of the box model and the concentrations of the targeted species were homogenous throughout the box. The air parcel from TW followed the valley breezes entering the grid simultaneously, which brought trace gases emitted from TW to the top of the mountain. Photochemical reaction occurred under abundant sunlight at the top of the mountain (TMS). At this scenario, the model was constrained with TW data only. If mesoscale circulations were dominated, the modeled O_3 levels compared well with the observations at TMS during daytime hours. When at dusk, the air parcel was carried back down by the mountain breezes into the grid until the next morning (1800 - 0700 LT). At this scenario, TMS was assumed to be the centre of the box model and the model was constrained with TMS data only……”

For details, please refer to lines 251-277, pages 9-10 in the revised manuscript.

Page 29044 Lines 26-27: VOC/NOx ratio should only give a rough ideal as to whether it is a NOx-sensitive or VOC-sensitive environment, which is crucial for ozone formation. However, VOCs are a complex mixture of compounds with large difference in reactivity with respect to ozone formation. The true impact of VOCs to ozone formation is more relevant to the reactivity of individual VOC species rather than to the total amount of VOCs.

Reply: We thank the reviewer for the invaluable suggestion. In addition to the analysis of VOC/NO_x ratios, an observation-based model (OBM) was applied to investigate the relationship of O_3 and its precursors in more details in this study. The measured data of O_3 and its precursors (i.e., VOCs, NO and CO), as well as the meteorological parameters were used as input of the model to calculate the relative incremental reactivity (RIR) value of each precursor of O_3. This RIR function extracted from the OBM model could be used to investigate the change of O_3 formation according to the change of its precursors' (i.e., VOC, NO and CO) concentrations. After model simulation, it was found that VOC showed the highest RIR values at the both sites, meaning that VOC was the most important group in O_3 production (Figure 13). In addition, relatively higher RIRs were found for CO at TMS, indicating that CO could have a significant impact on the O_3 formation when it transported from the upwind areas (Ling et al., 2011). Interestingly, the RIRs of NO at TMS were positive but small, indicating that NO also had some influence on O_3 production. On the other hand, the RIR_S of NO were negative at TW, indicating a strong VOC-limited regime. Therefore, based on the VOC/NO_x ratio analysis and the OBM results, we concluded that photochemical O_3 formation at TMS was mostly influenced by VOCs, with measurable influence of NO_x, while O_3 production at TW was generally limited by the concentrations of VOCs.

A detailed description has been added in the text as follows:

"Therefore, in order to investigate the O_3-precursors relationship in more details, an observation-based model (OBM) was applied in this study. The OBM model, developed by Cardelino and Chameides (1995), uses concentrations of O_3 and its precursors (i.e. VOCs, NO and CO), as well as meteorological data measured as a function of time at given sites. The calculated relative incremental reactivity (RIR) function extracted from the OBM model could be used to investigate the change of O_3 formation according to the change of its precursors' concentrations in different environments (Chameides et al., 2000; Chou et al., 2006; Zhang et al., 2007, 2008; Cheng et al., 2010a; Ling et al., 2011). In this study, measured data at 1000-1800 LT on the selected O_3 episode days at TMS and TW were input into the OBM model to calculate the sensitivity of O_3 production to its precursors, i.e., RIR. Figure 13 presents the RIRs for O_3 precursors at TMS and TW. It was found that VOC showed the highest RIR values at the both sites, meaning that VOC was the most important group in O_3 production. In addition, relatively higher RIRs were found for CO at TMS, indicating that CO could have a significant impact on the O_3 formation when it transported from the upwind areas (Ling et al., 2011). Interestingly, the RIRs of NO at TMS were positive but small, indicating that NO also had some influence on O_3 production. On the other hand, the RIRs of NO were negative at TW, indicating a

strong VOC-limited regime. Based on the VOCs/NO_x ratio analysis and the OBM results, it was concluded that photochemical O_3 formation at TMS was mostly influenced by VOCs, with measurable impact of NO, while O_3 production at TW was generally limited by the concentrations of VOCs."
For details, please refer to lines 733-758, pages 29-30 in the revised manuscript.

Page 29045 Lines 26-27: Observed anthropogenic VOCs at downwind remote or rural sites (e.g., TMS) are mostly transported from the upwind source areas and regarded as residues left from photochemical reactions during transport. These VOC residues are not suitable for the calculation of O3 formation potentials.
Reply: We agreed with the reviewer's comments. The VOC used for the calculation of O_3 formation potential at TMS could be the residues left from photochemical reaction during transport. As such, the section used propylene-equivalent concentration method to investigate the contributions VOCs of on photochemical O_3 formation was deleted.
For details, please refer to section 3.3, lines 663-755, pages 26-30 in the revised manuscript.

Page 29057 Figure 2b: An increase in O_3 was observed from nighttime to the next morning (before 0400 h LT) at TW. However, a decrease in NO titration was unable to enhance O3 levels before dawn. The authors should try to expound on the possible causes of this phenomenon.
Reply: Thanks for the comment. The diurnal variations of O_3 at TW had one peak at about 0300 and another at 1400 LT with a trough at about 0700 LT (Figure 3). The peaks and the trough of O_3 were corresponding to NO minimum and maximum, consistent with previous studies (Chan et al., 1998; So and Wang, 2003). After reaching the daily peak in the afternoon (1400 LT), O_3 gradually decreased and approached to the normal background level at night due to the fact that NO emitted at the rush hours could titrate some O_3 and the photochemical production of O_3 ceased at night. Then, O_3 started to buildup slowly and presented a peak in the early morning, which was more obvious when a trough was generated at 0700 LT. This trough was caused by the NO from the fresh vehicular emission which titrated part of the O_3 (Chan et al., 1998a; So and Wang et al., 2003). On the other hand, the small O_3 peak in the early morning may be caused by the decreased titration of NO (Figure 3). While NO started to decrease at 0000 LT and reached its lowest level at about 0400 LT, O_3 increased gradually and formed a peak from 0000-0500 LT. In addition, the small O_3 peak observed in the early morning might be also attributed to the constant transport of O_3 to TW by southeasterly flows from the South China Sea where O_3 was less consumed (So and Wang et al., 2003; Guo et al., 2009). This speculation was based on the fact that the winds changed from easterly to southeasterly from midnight until dawn. The imposed O_3 from the South China Sea and the minimum traffic activities caused higher O_3 concentrations in the early morning than the normal background level at night (So and Wang, 2003; Guo et al., 2009). The speculation was further evidenced by the diurnal variations of dimethyl sulfide (DMS), an ocean tracer. DMS

had a small peak observed from 0000 to 0300 LT (data not shown), corresponding to the small O_3 peak observed between midnight and dawn. Previous studies indeed reported that southeasterly winds from South China Sea could result in higher O_3 levels at night (So and Wang, 2003; Guo et al., 2009). A detailed discussion was added in the revised manuscript:

"The diurnal variations of O_3 at TW had one peak at about 0300 and another at 1400 LT with a trough at about 0700 LT (Figure 2b). The peaks and the trough of O_3 were corresponding to NO minimum and maximum, consistent with previous studies (Chan et al., 1998; So and Wang, 2003). The combination of photochemical formation and downward mixing from the overlying air masses could result in the O_3 daily peak in the afternoon (So and Wang, 2003; Guo et al., 2009). After reaching the daily peak (1400 LT), O_3 gradually decreased and approached to the normal background level at night due to the fact that NO emitted during the rush hours could titrate some O_3 and the photochemical production of O_3 ceased at night (Chan et al., 1998; So and Wang, 2003). Then, O_3 started to buildup slowly and presented a peak in the early morning, which was more obvious when a trough was generated at 0700 LT. This trough was caused by the NO from the fresh vehicular emission which titrated part of the O_3 (Chan et al., 1998a; So and Wang et al., 2003). On the other hand, the small O_3 peak in the early morning may be caused by the decreased titration of NO. While NO started to decrease at 0000 LT and reached its lowest level at about 0400 LT (data not shown), O_3 increased gradually and formed a peak at 0000-0500 LT. In addition, the small O_3 peak in the early morning might be also attributed to the constant transport of O_3 to TW by southeasterly flows from the South China Sea where O_3 was less consumed (So and Wang et al., 2003; Guo et al., 2009). This speculation was based on the fact that the winds changed from easterly to southeasterly from midnight until dawn. The imposed O_3 from the South China Sea and the minimum traffic activities caused higher O_3 concentrations in the early morning than the normal background level at night (So and Wang, 2003; Guo et al., 2009). The speculation was further evidenced by the diurnal variations of dimethyl sulfide (DMS), an ocean tracer. DMS had a small peak observed from 0000 to 0300 LT (data not shown), corresponding to the small O_3 peak observed between midnight and dawn. Previous studies indeed reported that southeasterly winds from South China Sea could result in higher O_3 levels at night (So and Wang, 2003; Guo et al., 2009)."

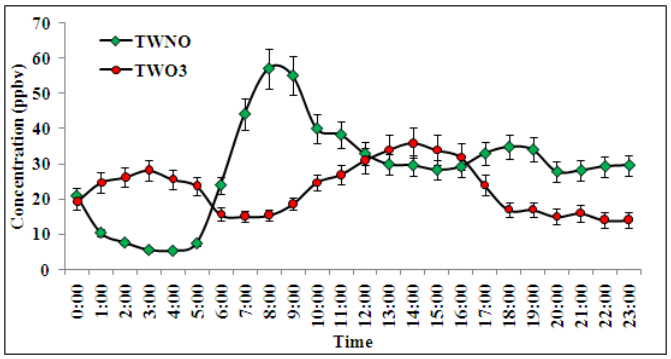

Figure 3 Diurnal patterns of O_3 and NO at TW

For details, please refer to lines 315-342, pages 12-13 in the revised manuscript.

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Interactive comment on "Characterization of photochemical pollution at different elevations in mountainous areas in Hong Kong" by H. Guo et al.

Customer Reviewer

Disclaimer: This peer review was written as an assignment for an Atmospheric Chemistry course. I've never written one before, so I would appreciate feedback on my technique. I would also like to apologies in advance for any mistakes or assumptions I've made, of which I've sure there are many. This paper outlines measurements of O_3 levels at varying altitudes, and the possible causes of the concentration differences found. It concluded that there were higher levels of O_3 at higher altitudes due to a variety of causes. These include: 1. the effects of NO titration- lower [NO] at higher altitudes lowers the removal rates of O_3; 2. vertical meteorological conditions- the height of the inversion layer changes the $[O_3]$ at higher altitudes; 3. valley-mountain breezes transporting newly emitted pollutants from urban areas to higher altitudes during daylight hours; 4. regional transport- the differing wind patterns at various altitudes bringing in changing concentrations of O_3 from nearby urban areas It was also found that the O_3 rate was dependant on both VOC and NOx concentration levels at higher altitudes, rather than just [VOC].

Firstly I feel like the method for determining the concentrations should be moved to an appendix. While it is important to include this methodology, it has been done before and is not new science. Including it in the main article detracts from the purpose of the study, which was focused on reasons for the variation in concentration. It seemed like the paper could effectively be read from section 3.2, which starts with a summary of the previous findings and then begins an analysis of the causes.

Reply: For a scientific paper, it is important to include the methodology in the text rather than in an appendix as an accurate and reliable method is the solid base of a successful research work. By presenting the methods in the text, readers will judge whether the methods support the research objectives, are suitable for the research, and help to achieve the hypothesis. Although the methods may be not new, it is always necessary to report the instruments used, the sampling plan, the quality control and quality assurance for the whole study. Only by doing these, readers can clearly understand the full picture of the sampling campaign and subsequently the proper interpretation of the results. We suggest that you read more journal papers in order to get familiar with the format/style of scientific papers.

The Abstract contains a good and succinct summary of previous research and findings. It would have been interesting to read about the author's opinions on these findings, as they are often contradictory. A clear statement of intent would have been appreciated, as the paper's goal wasn't entirely clear. They state that it was the first time pollutant concentrations at varying altitudes had been investigated in mountainous regions, but don't present forth a hypothesis on what the causes might be, which would be an improvement. However it does give examples of previous findings, and confirms that their own match these.

Reply: The abstract is the first part of a scientific paper, which allows the authors to summarize each major aspect of the paper usually in one paragraph (normally 200-300 words), including the questions the authors investigated, the methods used, and the major findings of the study. The detailed information and description are provided in the text. For example, the detailed description of the research objectives and improvements of this study were presented in the induction section, while the methodology section provided elaborate introduction for the methods we applied in this study, including the description of instruments, the study sites, sampling plan, the quality control and assurance, and how the data were analyzed for the whole study. The results and discussion section presented the results of this study and explained what the results mean or why they differ from what other workers have found, while the conclusion part summarized the results obtained in this study.

The Methodology attempts to describe the layout of the site in several paragraphs. This is hard to visualise and the information could be better conveyed on a map in the appendices. A map of China is included, but it doesn't show any of the pertinent information. The map also didn't show height variations, which is obviously extremely relevant to this study and would have been helpful. They did provide a map of the wind movements, which will be useful for anyone looking to apply their own hypothesis to this data in the future. It was also mentioned that the distribution of urban land cover was replaced in their Weather Research and Forecasting model with the most current data, which I found impressive. In several cases the graphs would benefit from more explanation or notes as they are hard to follow.

Reply: Good suggestion. Although the existing 2D map is sufficient for experts to extract information, your suggestion is helpful. We provided a 3D map of the Hong Kong area, including the height variations of sampling locations, land use and the administrative areas of Hong Kong in Figure 1. In addition, all the figures in this work were drawn according to the author's guide of ACP journal and the explanation and notes for these figures were appropriate for us to present the specific results of this study clearly and for experts to follow and obtain the key message of each figure easily. We suggest that you read more journal papers in order to get a better understanding of the legends and the functions of the figures in scientific papers.

There was also some statistical analysis it would have been useful to include- for example the [O3] could be plotted against varying wind speeds on different days, to substantiate the claim that regional transport effects the concentration. These kind of results are easily plotted from the data obtained and would increase the original science presented in the paper exponentially.

Reply: Most likely the suggestion won't increase the original science of the paper. The regional transport impact is a complicated issue in this region and simply based on the correlation of O_3 with wind speeds would not help us fully understand the regional impact. The ambient concentration of O_3 is determined by a series of factors including the concentrations of its precursors, background air dilution, air masses transport and NO titration, while the wind speeds were related to different synoptic

conditions, i.e., tropical cyclones, anticyclone and air monsoon. The wind speeds do not necessarily have a correlation with O_3 concentration at a given site. Thus, it is not reasonable to assess the regional impact simply by plotting O_3 against wind speeds. However, for fully assessing the influence of regional transport, more discussion, i.e., ratios of different trace gases, the relationship between VOC variability and atmospheric lifetime were added in the revised manuscript. For details, please refer to section 3.2.4.1, pages 18-21 in the revised manuscript.

The details of the measurement techniques are good, giving details of the equipment model numbers and statistical precision limits in terms of δ. However, the Methodology fell down when discussing simulations (sections 2.3 and 2.4) which weren't explained in enough detail. In particular, including more information on the Moving box scenario would be relevant.
Reply: Thank you for the suggestion. The description for the models used in section 2.3 and 2.4 has been updated in the revised manuscript. More detailed information, including references, methods for the comparisons between modeled and observed results were added. For details, please refer to section 2.3 and 2.4, pages 8-10 in the revised manuscript.

When analyzing findings they compared their own suggestions with previous papers, which was good. They could have made it clearer that their results matched previous studies, as this was a success and was barely mentioned! Apart from this lack of clarity, the analysis was clear and understandable. In terms of the science, I had several concerns about the method used. The measurements were only taken over a period of 9/6/10 to 11/29/10. I worry that this isn't enough time to get a reliable average- if the O3 concentrations vary by season or if there was a particular outlier during this time period it wouldn't be picked up on. I also find it worrisome that the meteorological parameters used in the analysis- including temperature, relative humidity and wind speeds- were taken from a weather station. It would have been quite simple to take these measurements at the site itself, which would stop small fluctuations in temperature or wind going unnoticed, when they might affect the results. I would also point out that the instruments may not be at the same temperature as the environment, and this will have gone unmeasured. The VOC samples were 'collected at 2-h intervals from 7:00am to 7:00pm per day'. It should be noted that these sample times mean that there is no measurement taken at midday- when the concentration should be highest. It is also concerning that the O3 samples were taken more frequently than VOCs, and the number of samples taken at each altitude was also different- varying from 201 to 183. It seems strange to add in an unnecessary bias to the data by changing the sample number in this way, when it would have been more logical to keep all possible variables constant in the measurements. This makes statistical analysis of the data harder to process, and also means that the results will have different confidence levels – so they cannot be compared as easily.
Reply: Thanks for the suggestion. The results of atmospheric field measurements may be different in different studies because of different sampling time, different sampling

location, different sampling techniques and different emission characters. It is not necessary to have similar results to others. Thus, we have deleted the comparison part in the manuscript. For details, please refer to lines 271-287, page 10-11 in the revised manuscript.

For the sampling campaign, it is difficult to conduct intensive sampling campaign throughout the whole year, as the processes of sample collection and chemical analysis require advanced and expensive instruments and experienced professionals. By balancing the cost and the motivations of this study, field measurements were carried out simultaneously at TMS and TW, from 06 September to 29 November, 2010. We specifically chose these months as the frequency of O_3 episodes is expected to be the highest in this season (Guo et al., 2009; Wang et al., 2009; Huang et al., 2006). On the other hand, the meteorological conditions in this season are favorable for photochemical O_3 formation (Ling et al., 2012). In addition, we include the month of September because some of the worst O_3 air pollution can occur in this month when tropical cyclones cause air stagnation in the Hong Kong area. Moreover, polluted air from inland PRD often reaches the sampling sites under the influence of prevailing north/northeast synoptic winds, which could induce high levels of O_3 and its precursors observed in Hong Kong in this season (So and Wang, 2003; Huang et al., 2005, 2006; Wang et al., 2005; Cheng et al., 2010a, b; Guo et al., 2009).

Though the O_3, CO, SO_2 and NO-NO_2-NO_x data was collected continuously as 1-min intervals, they were averaged to hourly data in order to be consistent with the VOC data at the two sites. For the VOC sampling campaign, 201 and 183 hourly samples of VOCs were collected at TMS and TW, respectively. Seven hourly VOC samples were simultaneously collected on each of the ten selected non-O_3 episode days, while thirteen hourly VOC samples were simultaneously taken each day for the ten O_3 episode days at TMS and TW, respectively. This sampling design has no problem given that total 182 VOC samples were collected concurrently at TMS and TW, respectively. In addition to measurements of different chemicals, continuous measurements of meteorological parameters were carried out at the same sites as chemicals during the entire sampling period. These parameters could reflect the true meteorological conditions at the sampling sites. As such, in situ observations in this study could provide sufficient data for us to investigate the diurnal patterns of different chemicals, the variations of different chemicals during O_3 and non-O_3 episode days, the source apportionments of VOCs and the relationship between O_3 and its-precursors at both sites.

The presentation of the paper was good with very few mistakes. The spelling and grammar were generally good- although I found wrongly worded sentence in section 2.4, and a spelling error in the Conclusion. The paper repeatedly uses the term ‘O3 episode day’, but this isn’t defined until the results on page 5. The acronym ‘LT’ was also used throughout and not explained until page 6. It would benefit from another proof-read.

Reply: Thank you for pointing this out. We double-checked the manuscript and corrected the spelling and grammar errors in the manuscript. In addition, definitions

of "O_3 episode day" and "local time (LT)" were presented in their first appearance. For details, please refer to lines 189-191, page 7 and line 260, page 10 for details.

An equation was given in section 3.2.1 which wasn't given in integer proportions- it gave molecules in ratios of 1: 0.63: 0.32: 0.23. I found this odd, especially as a rate constant was quoted. This might lead to confusion in calculations when the k value is used.

Reply: Thanks for the comment. In the atmosphere, isoprene reacts with OH radical and produces methacrolein (MAC) and methyl vinyl ketone (MVK) through the following equations (Equation 1 in section 3.2.1), which is as follows:

ISOP + OH $\rightarrow$ 0.63 HCHO + 0.32 MVK + 0.23 MAC $k_1 = 1.0 \times 10^{-10}$ cm^{-3} s^{-1}

The k_1 in this equation is the rate constants for the reaction of isoprene with OH radical. In such a reaction, 1 mole isoprene can produce 0.32 mole and 0.23 mole MVK and MAC simultaneously. The function of this chemical equation in this study is to accurately illustrate the reaction mechanism of the sink of isoprene with OH radical to produce proportional HCHO, MAC and MVK, which could be used to calculate the mixing ratio of OH radical (Mckeen et al., 1990; de Gouw et al., 2005; Vrekoussis et al., 2007; Liu et al., 2009; Kim et al., 2011; Yuan et al., 2012).

The graphs were good- the sizing made it hard to see all the details but this isn't necessarily a problem if reading on a computer, when it can be zoomed. It might be pertinent to include the day and night boundary layer mixing heights on the graphs as a reference. In some places references are placed in brackets rather than the footnotes. They also didn't provide references for several models that were mentioned, although perhaps interested parties reading the paper would be familiar with all of these.

Reply: Thank you for pointing this out. We have increased the resolution for the graphs and the fonts used in figures. For the issue of providing day and night boundary layer mixing heights on the graph, it did provide some new idea for improving the graphs in the manuscript for further study. However, as the boundary layer was not monitored in this study, all the analysis of boundary layer in the manuscript was referred to previous studies (Guo et al., 2012). Though we can find the information of the boundary layer from other institute in Hong Kong (http://envf.ust.hk/dataview/others/current/), it was shown in figures day by day from 2003~2009 and 2011~2012, while no observed data was present in 2010. As such, it is hard to embed the height of boundary layer during daytime and nighttime into the graphs without measured data. In addition, we have double-checked the manuscript. All the references for the models that were mentioned in the revised manuscript were provided in the text. For the MCM model, please refer to section 2.4, page 9 for details. For WRF model, please refer to section 2.3, pages 8-9 for details. For OBM model, please refer to lines 727-734, page 29 for details.

The paper in general presented a few new ideas, but it was mainly a confirmation of existing findings. Section 3.3, for example, discusses the correlation between O3 and VOC/NOx* which are well known mechanisms. I would suggest that including more

fresh hypotheses would make this paper a more useful addition to previous research, however it does provide important data which can be analysed further to provide solid evidence for their claims. To summarise, this is a solid beginning on which further work is needed to make it a useful addition to the field. A lot of the data is now available and can be further analysed in regards to the different factors to find correlations. Whilst the Methodology is very detailed, the Analysis needs to be taken further before the paper can be considered an original finding.

Reply: We thank the reviewer's comment. Surface ozone has been intensively studied in the Pearl River Delta region in South China in past decades, and many studies showed that mesoscale circulations like sealand breezes and/or mountain valley breezes play important roles in air pollution transport in such a region with complex topography and land-use/land cover. The role of sea-land breezes in air pollution transport has been well-studied previously (Zhang and Zhang, 1997; Liu et al., 2000; Ding et al., 2004). For mountain-valley breezes, there were relatively few Hong Kong studies focusing on this topic, even though it is almost certainly very important to air pollution transport in Hong Kong. In addition, there were very few works conducting field measurements at mountain site, especially the concurrent measurements at the foot and summit of the mountain in this region. This study presents the latest results from a well-designed field campaign at a mountain site and concurrently at an urban site at foot of the mountain. The measurements were conducted in autumn, a typical period of photochemical pollution in Hong Kong. The characteristics of photochemical pollutions at different elevations in mountainous areas in this region would be presented by addressing the following questions: Is the degree of photochemical reactions different due to the variations of air pollutants at the two sites? Are the variations of O_3 between the mountain site and the low-elevation urban site only related to the vertical profiles of O_3? Is there any difference of the relationship between the two different sites due to the different levels of O_3 and its precursors due to the nonlinear dependency of O_3 formation on its precursors? If the relationship of O_3-precursor is different between the two sites, does it mean that O_3 formation is NO_x-limited and/or both VOC and NO_x-limited at the mountain site due to the fact that O_3 formation is VOC-limited in the Hong Kong urban areas. In addition, how is the influence of physical processes, regional transport and/or mesoscale circulations on the air pollutants in mountainous areas? In order to answer the above questions, the following work was conducted in this study: the characteristics of air pollutants and the causes of variations of air pollutants at the two sites were investigated; the relationships between the two sites and the influence of mesoscale circulations were explored by integrated data analysis and different models, and the relationships of O_3-precursors at the two different sites were further evaluated. To our best knowledge, this is the first attempt to conduct these concurrent measurements and comprehensive analysis of air pollutants in this region. These results are very valuable for improving current understanding of photochemistry and multi-scales air pollution transport in such a region with severe ozone pollution for decades. Furthermore, the study is beneficial for understanding photochemical

pollution at the mountain site and serves as a complement to previous studies conducted in low-elevation areas of PRD.

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