

Simulation and analysis of high ozone episodes observed in the Hong Kong airshed: An explicit model approach

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Keywords: Hong Kong; VOC oxidation; tropospheric ozone; Air quality modelling.

EXTENDED ABSTRACT

The analysis and forecast of elevated boundary layer ozone is of particular concern since it is known to have adverse effects on health, vegetation and material. The main contributors to the formation of photochemical smog, and high ozone levels are the emissions of Volatile Organic Compounds (VOC) and NO_x. There is a complex relationship between VOC and NO_x leading to ozone generation, which varies greatly depending on the geographic and regional setting. Modelling based on observational data provides one way to determine the major components, which have the greatest impact on ozone formation. Only through a combination of measurements, emission data and modelling is it possible to perform analysis, forecast, and develop sound strategies to minimize the occurrence of these high ozone events.

Hong Kong as a metropolitan city in Asia has been suffering from poor air quality for more than two decades. Therefore, the Hong Kong Environmental Protection Department (HKEPD, 2003) has developed a comprehensive monitoring network. Through this network, air pollutants including many VOC, NO_x and ozone are routinely monitored.

This study has analysed the available monitoring data on a series of high ozone episode days in 2003, to define the conditions for the development of an explicit airshed box model. High ozone episodes occurred from the

mid-October through to November, where daily peak ozone levels exceeded 100 ppb at the most easterly monitoring station on several days. The series of high ozone day observations, supported by back trajectory analyses are used to indicate the ozone episodes are single day events.

For this analysis an initial airshed model tailored to the Hong Kong environment is developed, based on the Master Chemical Mechanism (MCM) approach, to provide a comparison with the observational data. It is aimed towards gaining a detailed understanding of the sensitivities of photochemical ozone formation under the prevailing conditions in Hong Kong. Sensitivity analysis is performed on ozone development, following targeted reductions in NO_x and VOC emissions. The analysis has determined that ground level ozone production in Hong Kong is neither VOC nor NO_x limited, but in a transition zone between the two.

1. BACKGROUND

In this study, data from three monitoring stations are investigated to define the conditions for the development of an explicit airshed model and provide a comparison with the simulated ozone levels. The monitoring station locations are Central Western (CW), Tsuen Wan (TW) and Tung Chung (TC), as shown in Figure 1.

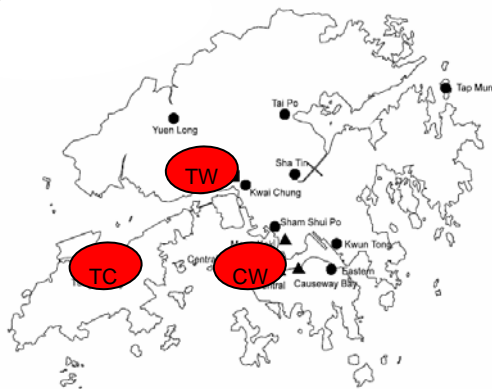


Figure 1: Location of HKEPD's Air Quality Monitoring Stations (2003)

Both CW and TW are situated in the densely populated urban areas of Hong Kong. They comprise a mixture of residential and business areas where vehicular related pollutants, e.g. NO, NO₂ and SO₂, are observed to be relatively high. During the analysis period peak ozone levels at these sites do not exceed 100ppb, however the highest ozone levels observed during the same period are at the TC monitoring station, with ozone levels in excess of 100ppb. TC is a comparatively less populated residential area where NO_x levels are relatively lower than the other urban sites. In addition, the prevailing Easterly winds in Hong Kong makes TC accumulate air pollutants from the urban areas in the East. The geographic location, as well as site characteristics of TC results in the highest ozone concentration observations, as can be seen in Figure 2A, 2B and 2C.

2. MONITORING DATA

The measurements of both ozone and NO_x from the three separate monitoring stations are given in Figures 2A, 2B and 2C.

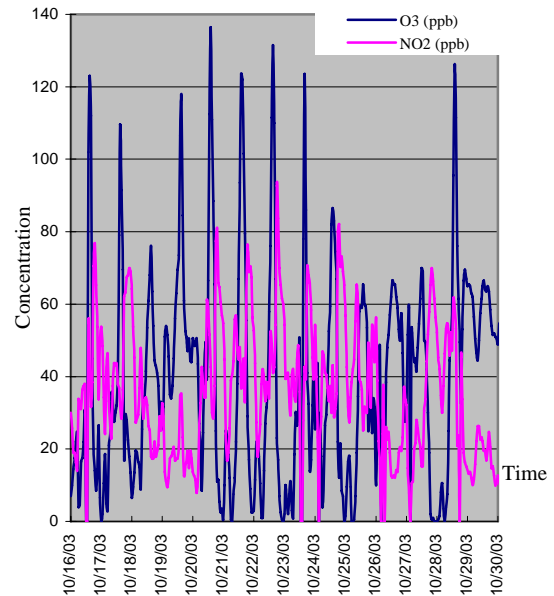


Figure 2A TC 16/10/03-30/10/03

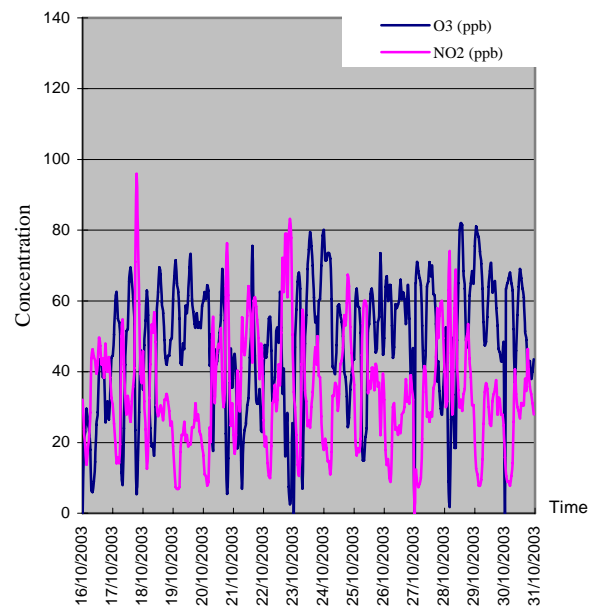


Figure 2B CW 16/10/03-30/10/03

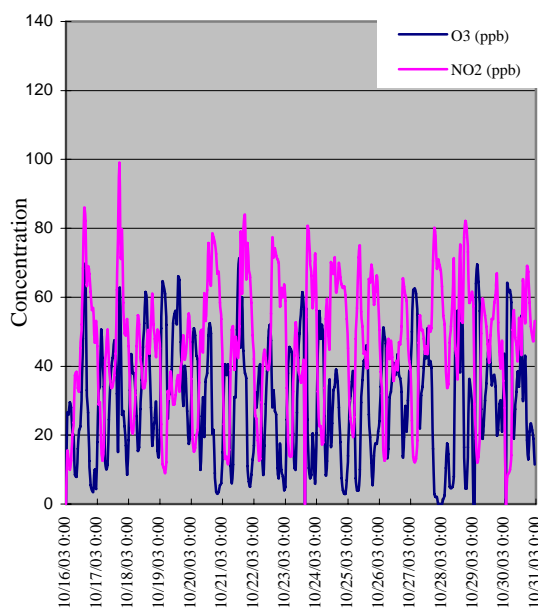


Figure 2C. TW 16/10/03-30/10/03

The measurements clearly demonstrate that peak ozone concentrations do not build up over a sequence of days. At TC, days in excess of 100ppb can be followed by days very much lower. From the 20th to 24th October, a series of high ozone days does not display a build up sequence. Peak daily ozone levels vary between 112 and 130 ppb. Indeed the 29th October stands out as a distinct exceedance day, whilst the days either side generate ozone levels around 75ppb. This suggests accumulating emissions transported over several days are not major contributors to ozone levels experienced. Therefore, this supports the development of an airshed box model that treats the ozone episodes as single day events.

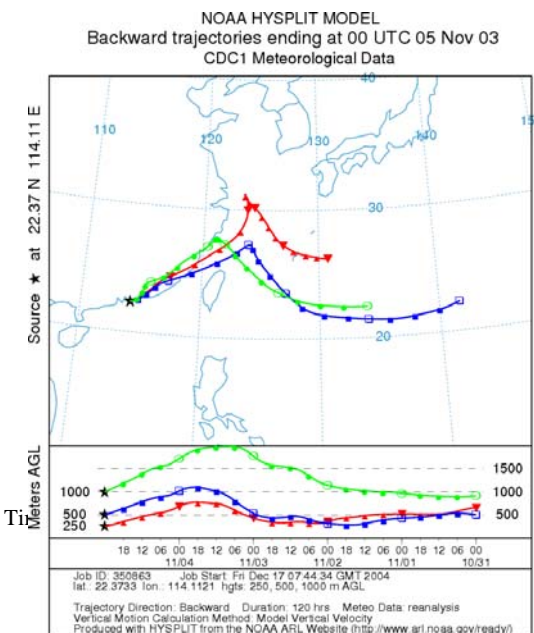


Figure 3. Back trajectory air mass

Further support for the source emissions have been considered by performing backward trajectory analysis, using the NOAA hysplit model (NOAA, 2005). This has been run to trace back air parcels during the analysis period, an example of which is given in Figure 3. Trajectories on other days in the analysis period are not as clearly marine in origin but follow Eastern coastal paths over 3 days. The trajectory analysis indicates that air parcels arriving at Hong Kong on high ozone episode days are mainly from marine trajectory paths. They are clearly not from those recognised densely populated and high emitting regions in southern part of China. As a result, the local 2003 (HKEPD, 2003) emissions inventory data for the Hong Kong region, as shown in figure 1, has been adopted in our preliminary model design (see Table 1).

From the emissions inventory, alkanes and aromatics constitute the major local VOC emissions. Toluene at 25% of total emissions is the predominant species, which is markedly difference from other airshed models in Europe and United States (Wagner et al. 2003 and Derwent et al. 2003).

Table 1. Hong Kong VOC emission inventory 2003. (Source HKEPD)

Reactive Organic Compounds (ROC)	Percentage of Total VOC
C4+ alkanes	40%
ethylene	5%
C3+alkenes	3%
Isoprene	1%
a-pinene	0%
Toluene	25%
Higher aromatics	20%
Alkynes	5%
Total ROC	100%

3. INITIAL HONG KONG PHOTOCHEMICAL MODEL

Based on local meteorology and emission source analysis a highly explicit photochemical model for the Hong Kong airshed has been developed to simulate the development of ozone and other photo-oxidants.

The model input meteorological conditions, emissions, aloft and initial concentration data represent an average of the monitored conditions at the TC monitoring station in Hong Kong through the analysis period. All data input are extracted from the Hong Kong Environmental Protection Department (HKEPD, 2003) monitoring network in 2003.

Solar declination and latitude are set at -14.221 and 22.18° respectively appropriate for Hong Kong. Initial concentrations were set for NO_x at 40ppb, CO at 360ppb, CH_4 at 1315ppb, HCHO at 2ppb and O_3 at 30ppb. The initial concentrations for remaining VOC were adapted from the information of the HKEPD monitoring network. For those VOCs not specified in the reactive organic compound emissions, however included in this model, an initial concentration of 1ppb, were assigned as baseline level.

The chemical development of the species in the air parcel is described by a series of differential

equations:

$$\frac{dC_i}{dt} = P - L \cdot C_i - \frac{VC_i}{h} + \frac{E_i}{h} - (C_i - B_i) \frac{1}{h} \frac{dh}{dt} \quad (1)$$

Where C_i is the species concentration in the air parcel, P is the instantaneous production from photochemistry, $L \cdot C_i$ is the instantaneous loss rate by photochemistry, V is the species-dependent dry deposition velocity, h is the time-dependent boundary layer depth, E is the local emission rate from pollution sources, and B_i is the background concentration of the species aloft.

The system, which includes 4644 simultaneous stiff differential equations, was integrated with a variable order Gear's method (Curtis et al. 1987).

The air parcel, which encompasses the regions emissions, extends from Earth's surface to the top of the boundary layer to a 33 x 33 km grid horizontally. The depth of the model boundary layer starts at 300m at 06:00hrs and rises at a constant rate of increase throughout the morning reaching a height of 1800m by 14:00hrs. As the boundary layer depth expands, air is entrained from the free troposphere above, and this process is described by the last term on the right hand side of equation 1.

4. MASTER CHEMICAL MECHANISM (MCM)

The Hong Kong photochemical model uses the entire master chemical mechanism, Version 3.1 to describe the oxidation of CH_4 , 134 additional Hydrocarbons (VOC), CO, SO_2 and NO_x , which gives a reasonable representation of the pollutants in the atmosphere.

It has been written specifically to describe the contribution to ozone as other secondary oxidant formation (e.g. peroxyacetyl nitrate, PAN) from a large number of individual hydrocarbon species and their degradation products. The most updated mechanism is composed of 4644 chemical

species and more than 13500 chemical equations.

The MCM consists of a number of identifiable and separate elements.

- ◆ The inorganic chemical reactions of the simple atoms and radicals, which contains hydrogen, oxygen, sulphur, nitrogen and carbon monoxide.
- ◆ The photolytic reactions of the photochemically labile species and a large number of oxygenated organic compounds.
- ◆ The atmospheric degradation of CH₄ and 134 additional organic compounds.

The chemistry of the aromatic hydrocarbons has been updated considerably recently in MCM v3.1 The most updated mechanism can be viewed and downloaded via the World Wide Web at <http://chem.leeds.ac.uk:80/atmospheric/MCM/mcmproj.html>.

5. MODEL VALIDATION

In order to have confidence in the results concerning O₃ formation from anthropogenic hydrocarbon sources, the model needs to be checked, verified and validated (Saunders, 2003). A rigorous testing approach could not be accomplished within this initial model development time frame. Nonetheless, related work and testing of the sub parts of the mechanism have been shown to be entirely satisfactory (Hayman et al. 1999, Derwent et al. 2001). These studies provide confidence in the description of the degradation schemes of the VOC and the associated ozone production.

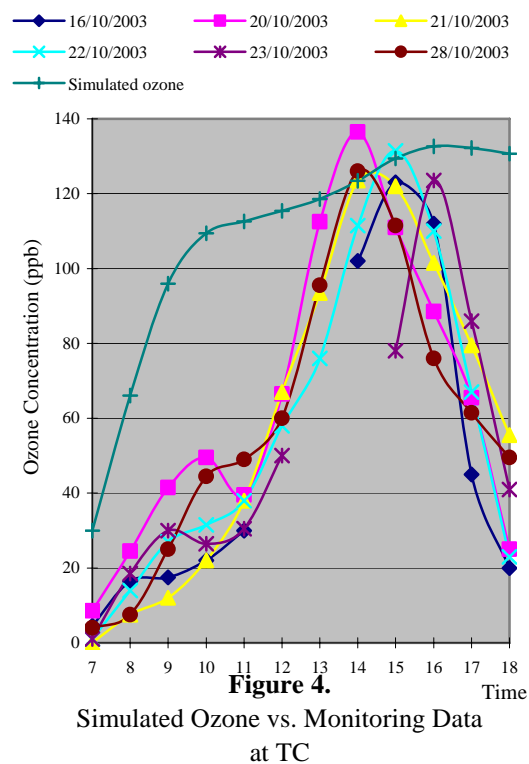


Figure 4 presents a comparison of the ozone development in the base case of the Hong Kong photochemical model simulation with the monitoring levels determined on high ozone days at the TC monitoring station, (defined as monitoring ozone concentrations higher than 100ppb).

The peak model ozone concentration (133ppb) is in close agreement with the observed ozone concentrations, while the largest peak difference is 6ppb. As a box model the level of ozone generated defines a maximum possible from the defined emissions, boundary and initial conditions, and the chemical mechanism representing the degradation of emitted compounds of the airshed, and makes no account of the movement of the air parcel.

The simulated peak ozone occurs in the late afternoon. It is not expected to match the time frame of the observed ozone peaks at the TC monitoring station, as this will depend on the site characteristics as well as prevailing

meteorological conditions (HKEPD, 2003).

6. BASE CASE MODEL RESULT

Figure 5 illustrates the time development of the O_3 and NO_x ($NO + NO_2$) concentrations in the base case model experiment for the averaged Hong Kong conditions.

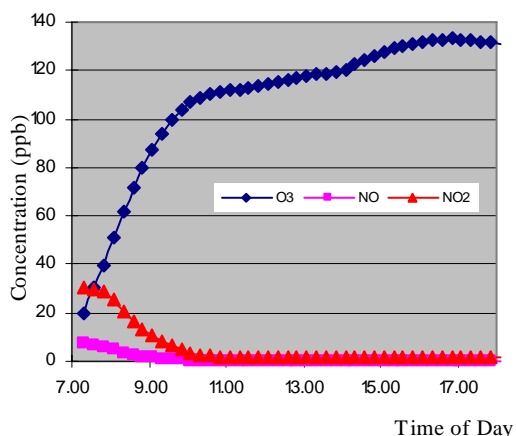


Figure 5. Time development of ozone formation of Hong Kong Base case model

Ozone concentrations in the air parcel increase rapidly from the starting value of 20ppb and reach a maximum of 133ppb at the end of the afternoon at around 5:00p.m. The $O_3 - NO_2$ crossover point was reached at around 7:30a.m.

According to VOC and NO_x sensitivity analysis (Sillman et al, 1997), the air parcel should be in the transition region between VOC and NO_x control. This was confirmed by comparing the O_3 reductions calculated following, firstly 25% then 50% reductions in NO_x and VOC emissions sequentially. These O_3 reductions were identical within the precision of the numerical model used; showing that neither NO_x nor VOC control is more efficient at reducing ozone. This strongly suggests that the air parcel is, indeed in the transition region between the two regimes.

7. CONCLUSION

This study gives an initial development and preliminary testing of a highly detailed Hong Kong Tropospheric Photochemical Model. With reference to the monitoring data in 2003, the high

ozone episodes in Hong Kong do not build up over a sequence of days in general. It implies accumulating emissions transported over several days are not major contributor to ozone levels experienced. Therefore, ozone episodes have been treated as single day events in a box model.

Backward trajectory calculations have shown that air parcels arriving at Hong Kong on high ozone episode days, mainly arise from coastal marine trajectory paths and not those recognised densely populated and high emitting regions in southern part of China. As a result, the local emissions inventory data has been adopted in our model design.

The base case model has produced comparable simulated peak ozone concentrations to the HKEPD monitoring network, where ozone levels monitored exceed 100ppb. The model will continue to be developed and ongoing investigations will be to assess the impact of toluene and other aromatic emissions on ozone formation in Hong Kong, and compare with model results for other regions.

8. ACKNOWLEDGEMENTS

The authors are grateful for the data provided by Peter Louie of the HKEPD and acknowledge continued support from colleagues involved in MCM development and applications.

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