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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozone production and hydrocarbon reactivity in Hong Kong, Southern China" *by* J. Zhang et al.

J. Zhang et al.

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Response to comments from Dr. Sillman (Referee)

On the use of OBM and 24-hour VOC:

For all the five areas examined in this study, OBM calculation indicated a VOC sensitive regime. Thus we did not miss the transition as suggested by the reviewer. The area-averaged RIR gives a mean value for Hong Kong providing initial guidance to control of ozone in the city.

In view of the difficulty in getting accurate emission inventories in Pearl River Delta with complex emission sources, we think the OBM method is particularly valuable in providing some insights into the NOx-VOC chemistry. However, OBM, like any other tools, has its own weakness as pointed out in Cardelino and Chameides (1995). We

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will add a summary of these limitations. One weakness is that OBM uses measurement at a point at surface to represent a larger area.

We used 24-hour average measurements for VOC because the hourly data were not available at some sites. While uncertainties exit in the conversion from 24-hour average values, sensitivity tests we carried in the study showed that the hourly VOC profile did not influence our final results on the RIRs. The conclusion on ozone formation limited by VOC-limiting based on OBM is also supported by the very small (2-4) VOC/NOx ratios as shown from a previous study in urban areas of Hong Kong (So and Wang, 2004, Science of the Total Environment).

We will add the figure for the derived hourly VOC profile in the text. In the figure we showed the derived hourly VOC reactivities at the four sites (YL, CW, TC and TM) and the VOC measurements at TO. At TO we have only VOC measurements at several hours but not 24-hour average. Therefore the comparison that we could do is between TO and YL. On other episode days, we used only measurements at TO since no 24-hour average measurements were available. The modeled VOC diurnal profiles are reasonable, capturing morning traffic and nighttime emissions in urban areas.

Since CO is used as inputs (like the 'standard' values) in OBM and the OBM-based derivation method, the derived CO diurnal profile is the same as the original input. Therefore, we did not compare the calculated CO and the measured CO at the sites.

On simulated VOC diurnal profiles:

The 24-hour average measurements were used to derive the hourly VOC profile. In the derivation, we considered the different patterns for anthropogenic and biogenic VOCs. For anthropogenic VOCs, we considered both nighttime and daytime emissions. For biogenic VOCs, we considered daytime emissions only. During the daytime, the biogenic VOCs reach maximum but during the nighttime their concentrations are almost zero.

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Except TO, the hourly VOC concentrations were not measured at the sites. To compare the measured (anthropogenic and biogenic) VOC concentrations among the sites, we have to use the 24-hour average. At TO, a rural site with more plants than at urban sites, the measured (anthropogenic and biogenic) VOC concentrations and the VOC reactivities are illustrated in two figures (Figure 6 and Figure 7). Even at rural TO, the biogenic VOCs plays less important role in ozone chemistry than the anthropogenic VOC. At other sites with fewer trees, anthropogenic VOCs are expected to be more important than biogenic VOCs.

On the detection limit of NO:

We will show Figure 3(b) on a log scale to better display the NO concentrations in the afternoon. It can be seen that the NO levels at 3 pm (approximately the time of maximum ozone) were in the range of 0.1-1 ppbv on the episode days at Tai O, which are much higher than the limit of detection of the NO analyzer (50 ppt for 5 minute average). Thus there is no problem measuring NO at Tai O. At the EPD stations using less sensitive instruments (detection limit: 0.4 ppbv), the afternoon concentrations of NO were in the range of 0.8 -18.6 ppb on Nov 7th, which can also be accurately measured. We will add this information in the revised manuscript.

On suggested different way to show ozone production rates:

The above suggestions are no doubt an alternative and a good way to show the ozone chemistry. We actually have planned to do a similar study by comparing the ozone production rates in HK, Beijing, and Shanghai in a separate work. The present study aims to provide some initial insights into the key factors that control ozone formation and ozone control in Hong Kong. To avoid a major deviation from the main theme and structure of present paper, we would like to keep our method of displaying NOx-VOC chemistry.

On afternoon O3/NOy result: We will include the results of an examination of the ratio of O3/NOy which indeed supports our OBM result on VOC limiting chemistry.

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On including dCO/dNOy result: We will add a figure to show the “24 hourly” ratio of dCO/dNOy.

On HONO as a dominant source of OH: We will modify the text to state that the OH illustrated was produced by photolysis and subsequent reactions. Similar result on the more important role of HONO has been reported in previous studies (Alicke et al., 2002, 2003).

Response to comments on technical corrections (itemized):

1. We will add the information on the detection limit for NO and mention that other HKEPD stations use instruments that are similar to those in the US.

2. The ‘propy-equivalent carbon sum’ is just sum of the ‘propy-equivalent carbon’. This seems obvious, thus we did not show this formula.

3. Yes, correct. We will modify the sentence.

Response to comments from anonymous referee #3 (Number below refers to the order of paragraph in the referee’s report)

(1) We will add the information on frequent ozone episode in the autumn. (High ozone events also occurred in the summer but with a much lower frequency.)

(2) We will add a summary of the previous work.

(3) We will add the information on the detection limit for NO and point out other HKEPD stations use instruments that are similar to those in the US, and provide some references for details on the instruments.

(4) We will provide the info. to indicate no significant difference between 8 November and other episode days.

(5) We will indicate the strong titration of O3 by NO and eliminate the somewhat speculative statement on vertical mixing, as no observation data was able to support the

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statement.

(6) Given both reviewers made such a suggestion, we will add a figure of dCO/dNOy.

(7) Since the field campaign was carried out during the period of October to December, the biogenic emissions were not strong. A separate work (So and Wang, manuscript in preparation) discussed the biogenic VOC in summer compared to that in autumn. The peak of biogenic emissions in this region is in summer when the temperature is higher, and up to 5 ppbv of isoprene has been observed at Tai O.

(8) Biogenic VOC is not part of R-OLE. So here R-OLE is due to the anthropogenic emissions. We focus on the ozone episode days in this study. VOC concentrations at Tai O during non-episode days are generally similar to that for episode days, but with much lower concentrations compared to the episode days.

(9) We assumed the hydrocarbon concentrations above the boundary layer as zero in this study. There was no measurement of VOCs above boundary layer over HK. Aircraft study of other trace gases and aerosols (Kok et al., 1997, JGR) suggests that the outflow from the mainland was predominantly in the boundary layer. In the model calculation, however, we have considered all the possible VOC sources in the item of "source" when we derived the hourly VOC profile.

(10) We will include a figure to show the derived diurnal VOC profiles at the sites other than TO and compared with the measured VOC at TO. At TO no 24-hour average samples were collected, only measured daytime VOC concentrations are available. Therefore what we can do is to compare the derived VOC profiles at the sites other than TO with the measurements at TO. Result shows that the modeled diurnal profiles look reasonable, for instance, capturing morning traffic and continuous nighttime emissions at some urban sites.

(11) Reaction (3) occurs at night. We followed the method of Harrison et al. (1996) in determining the rate of HONO production and dry deposition during the nighttime.

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When the mixing height is small, generally the concentration of NO2 and H2O is high, and the reaction rate is high too. The opposite when the mixing height is large. We will add a sentence in the text to compare our results of HONO and HCHO in early morning with some published studies in Milan and Berlin (Alicke et al., 2002, 2003).

(12) Titration and radical scavenging by high NO is the reason for the negative RIR for NO. The NO concentration on 9 October is relatively low compared to other episode days. We don't have clear answer about a transition threshold between NOx-saturated and NOx-sensitive for a given VOC reactivity, but this should be investigated in future.

(13) Due to page limit, the details of the sensitivity tests are not shown in the text, but we will include a brief summary of the parameters tested and results. Although using 24-hour average concentrations to drive the OBM gives the similar RIR results as using hourly concentrations, there are still some differences. For a better understanding of daytime photochemistry, hourly data on VOC would be more desirable.

Technical corrections:

1. We will modify the relevant sentences.

2. They were meant to be subtitles.

3. We placed the OBM sensitivity to NO and CO approximations in Section 2 to better explain the influence of the data approximation on the results.

4. CO is also high on some non-episode days, but lack of favorable meteorological condition/transport pattern may be the reason for not very high ozone concentrations on these days.

5. TUV is relatively high on 7 November, but other days may have more UV but low ozone (e.g., Oct 21-22) due to very low levels of ozone precursors associated with inflow of maritime air. Thus high UV is only one of a set of conditions for high ozone to occur.

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6. We will change the title of Figure 3 to 'Diurnal variations of (a) nonmethane hydrocarbons and (b) NO observed at Tai O on the episode days.' The abnormally high concentrations in the early morning on Oct 11 and Nov 7 may be due unusual weather conditions preventing air-pollution dispersion and/or unusual nighttime transport patterns that brought more urban pollutants to TO.

7. The sentence should be "since its extremely low reactivity though its high concentration". We will correct it.

8. The observed O3 increment is defined here as the difference between the peak O3 concentration and the early morning O3 concentration. We will include percentage to better quantify "agreement".

9. Will only keep Figure 7b.

10. Will adopt the suggestion.

11. Will show Figure 3 in a log scale, which can be seen that the NO concentrations were all above zero.

12. Will adopt the suggestion.

13. Will add the date.

14. Will add the RIR information.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 8961, 2006.