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> Interactive Comment

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

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The manuscript presents an analysis of ozone formation in Hong Kong, based on an ensemble of measured ambient concentrations, including NO, NO_y and VOC. The manuscript uses an "Observation-Based Model" to determine whether ozone formation is primarily sensitive to NOx or to VOC, and also evaluates the extent to which ozone in Hong Kong is due to local production as opposed to regional transport from Guangdong Province.

The manuscript is useful because it attempts to derive critical information about ozone formation directly from observations. Analyses of urban ozone formation based on 3-d Eulerian models are common, but analyses with a strong measurement-based component are rare and worth publishing. Other results (e.g. HONO) are also interesting.



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The major weakness of the manuscript is that the Observation-Based Model is used as a 'black box" to provide a simple policy recommendation. The manuscript concludes that ozone in Hong Kong is VOC-sensitive, but the manuscript does not show results in a form that would identify why ozone formation is VOC-sensitive or allow comparisons with other urban areas. The manuscript also does not show results that would identify uncertainties in their analysis. In effect, the manuscript tells readers to accept the results of the calculation on faith.

There is also a possible serious problem because the analysis relies on 24-hour average measurements for VOC. The authors have done the best they can with the 24-hour average data, but the resulting uncertainties might compromise the results.

In the comments below I will suggest ways to address these issues.

Acceptability for publication: The comments below includes suggestions for significant additions. I believe that the publication would be more convincing if the issues cited below are addressed, but I do not view them as absolute requirements for publication.

Specific comments

(1) The manuscript begins with a description of the problems with Eulerian models ("emission-based models") as a basis for evaluating ozone formation. This is accurate as far as it goes, but it is also necessary to acknowledge the weaknesses of the Observation-Based Model.

The model consists of a series of 0-d calculations that determine ozone production rates at specific locations, based on ambient measurements of primary pollutants (CO, VOC and NOx). The individual calculations are summed to provide an estimate of ozone production throughout the metropolitan region, and the sums are used to evaluate sensitivity to VOC and NO_x.

As pointed out in the manuscript, this approach has the advantage of linking model cal-

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culations directly to measurements and because it avoids the uncertainties of emission inventories. However, the approach also has disadvantages.

This approach makes it difficult to evaluate the effects of variations in ozone chemistry throughout the region, since the calculation is limited to locations with measurements. Results are presented as an area-wide sum, which fails to identify differences in NO_x -VOC sensitivity among the sites. When results are presented as an area-wide sum it is also difficult to provide estimates of uncertainty in the calculation. Suggestions below are given for dealing with this weakness.

A second weakness of the method is that surface measurements of primary pollutants are strongly influenced by near-surface dynamics and local emission sources. The method effectively assumes that average concentrations of NO_x and VOC throughout the boundary layer are identically equal to the surface measurements. This problem is especially severe in this study because of the reliance on 24-hour average measurements (see next comment).

These uncertainties are not insurmountable, but they need to be recognized in order to properly understand the method and its results. (No change is needed to the manuscript. This is background information for subsequent suggestions.)

(2) The analysis relies on 24-hour average measurements for VOC. This is a major weakness and could seriously compromise the results of the study. The 24-hour average values for anthropogenic VOC are determined primarily by concentrations at night and in the early morning, when peak values usually occur. These peak values are critically sensitive to mixing rates in the stable boundary layer and to micrometeorology in the vicinity of measurement sites. The method used to derive hour-by-hour concentrations is reasonable, but there are still large uncertainties in the conversion from 24-hour average values to hourly values.

The manuscript needs to do more to demonstrate the validity of this approach and to quantify the uncertainties. In the current version the text (Section 3.2.2) states that

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"encouraging similarity is found between the calculated profile at YL and the observed profile at TO". The manuscript does not show this. Figure 3 shows that the observed diurnal profile at TO varies greatly from day to day. The manuscript needs to show that this day-to-day variation can be reproduced in the calculation.

I suggest that the authors calculate the diurnal profile at TO based on 24-hour average VOC and using the methods of Section 3.2.2, and compare the calculated profiles to the observed values. They could also compare calculated versus measured CO diurnal profiles at all sites, also using 24-hour average values and the methods of Section 3.2.2 to derive calculated values.

I also suggest that the authors adopt a quantitative method for evaluating the calculated versus measured diurnal profiles. For example: they could compare calculated versus measured values at 12 noon (the hour of peak photochemical activity) or the ratio between concentrations at 7am versus 12 noon. The difference between model and measured values of VOC (at TO) and CO (at all sites) can provide a quantitative estimate of the uncertainty.

(3) The 24-hour average measurements also cast doubt on the analysis of anthropogenic versus biogenic VOC (Figures 5 and 6). The biogenic VOC are usually zero at night and reach their maximum values during the daytime. Thus, the comparison of anthropogenic versus biogenic VOC effectively represents a comparison of nighttime and early morning anthropogenic VOC versus midday biogenic VOC.

To avoid this problem, the comparison between anthropogenic and biogenic VOC (Figure 6) should be given for 12 noon (the time of maximum ozone production) rather than as a 24-hour average. Alternatively, the propy-equivalent VOC in Figure 6 might also be shown as diurnal profiles. The text should also warn readers about the difficulty of comparing 24-hour average values for anthropogenic versus biogenic VOC.

(4) In previous efforts it was found that results of the OBM are often compromised because measured NO during the daytime are near the lower detection limit of the in-

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struments (typically, 1 ppb) [Cardelino et al., 2000]. Significant amounts of ozone are produced at the hours when NO is near the detection limit, and the resulting uncertainties in the OBM calculation are high.

The text (Section 3.1.3) states that "generally large concentrations of NO ... were encountered; daytime NO concentrations of several ppbv were the norm." In figure 3 it appears that NO is zero on most days between the hours of 12 and 18. The authors could clarify this by converting Figure 3b to a log scale. The text should refer to the problems reported by Cardelino et al. [2000].

The hours from 12 to 18 are especially important because these hours are most likely to have NOx-sensitive chemistry. Since the authors concludes that Hong Kong is VOC-sensitive, they must make sure that the possible NO_x -sensitive hours are represented properly. The VOC-sensitive conclusion may change if different assumptions were made about the hours with apparent zero NO.

(5) The problems identified in comments 1 and 4 above might be addressed by showing a display of the calculated rates of ozone production at each daytime hour as a function of measured NO_x and VOC, rather than just the final sum of delta-O₃.

Hourly ozone production rates based on measured VOC and NO_x were calculated by Kleinman et al. [2005, J. Geophys Res.] for several cities (see their Figure 14). Their results showed a distinction between some cities (e.g. Phoenix) in which the hourly PO₃ were almost all VOC-sensitive, and other cities that included both VOC-sensitive and NO_x-sensitive conditions. Their results also showed that ozone production rates were sensitive to NO_x when the ratio of reactivity-weighted VOC was high (rVOC/NO_x>1 in their units), and sensitive to VOC when the ratio rVOC/NO_x was lower. (Others, e.g. Tonnessen and Dennis [2000], have similar findings.)

This type of display is important because the calculation of ozone production rates from ambient NO_x and VOC is the basis of the model used in the manuscript. If this type of display were shown, it would identify whether the measured VOC and NO_x is Hong

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Kong is consistent with VOC-sensitive chemistry everywhere or whether there are large areas of transitional or NO_x -sensitive chemistry. It would also allow a comparison between measured VOC and NO in Hong Kong and results from other cities.

The authors might be able to obtain rates of ozone production directly from their model calculation, since this is a central part of the procedure.

Alternatively, the authors could simply display the variation of measured reactivityweighted VOC versus NO, and compare the range of values with those reported by Kleinman et al. for different cities.

(6) The text refers to measured NO_y . If this is available, the authors should consider showing a plot of the measured correlation between O_3 and NO_y during the afternoon hours. Previous results (Sillman and He, 2002) have shown that these correlations appear very different for VOC-sensitive versus NO_x -sensitive locations. This could provide corroboration of the claim that the region is VOC-sensitive.

(7) Section 3.1.3 analyzes local versus regional production based on the measured ratio dCO/dNOy and based on back trajectories. The manuscript shows back-trajectories, but it never shows any results for dCO/dNOy.

The text states that "these plots (of back trajectories)" generally corroborate the results from the ratio dCO/dNOy." It should be possible to show this - for example, by showing a plot of CO vs. NOy (afternoon hours only, since morning values reflect local emissions on all days) identified by category.

(8) There are some confusing aspects in the analysis of HONO and aldehydes (section 3.2.3).

Figure 10 (b) shows production of OH from aldehydes and concludes that their impact on OH is small. This is confusing. Aldehydes do not produce OH directly, but they photolyze to produce HO_2 and RO_2 radicals (resulting in a net source of total odd hydrogen or summed OH+HO₂+RO₂). In a VOC-sensitive environment this affects ACPD

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OH. OH increases in direct proportion with the radical source [e.g. Sillman et al., 1990, J. Geophys. Res.].

If Figure 10(b) were changed to show radical production (rather than OH production), then the aldehydes would probably be a significant source.

Figure 10(c) compares OH with and without HONO or aldehydes. If I understand correctly, the authors conclude that the enhanced OH in the figure is due entirely to HONO because direct production of OH from aldehydes is small. It is possible that much of the enhanced OH in the figure is due to aldehydes rather than HONO.

/bf Technical corrections

The text needs to describe the methods used to measure NO, NO₂ and NO_y and give the detection limit for NO.

The text uses 'propy-equivalent carbon' as a measure of VOC reactivity. I suggest including the formula for the propy-equivalent carbon sum. (This would also let readers convert from propy-equivalent carbon to more familiar units such as summed OH reactivity.)

In section 3.2.3 the text states that in the simulation without HONO and aldehydes "we assume that no HONO and aldehydes are present in the morning." Please clarify this statement. I assume that HONO and aldehydes were set to zero at a specific morning hour and then allowed to accumulate in the model calculation. Is that correct?

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