**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Rates and regimes of photochemical ozone production over Central East China in June 2006: a box model analysis using comprehensive measurements of ozone precursors" *by* Y. Kanaya et al.

Anonymous Referee #2

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The manuscript by Kanaya et al. describes the analysis of the rate and regimes of the photochemical ozone production $(P(O_3))$ in a mountain top site of Central Eastern China (CEC) with a box model constrained by observed concentrations of non-radical species during the MTX2006 field campaign. The strategy of the analysis is clear and the manuscript has been relatively well organized for such a topic. It presents interesting information about the radical and ozone budgets at the Mount Tai site; the photochemical ozone production regime and impacts from several important trace gas compounds are investigated through sensitivity model runs; and the estimation of the

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impact of HO_2 radical losses through aerosol uptake looks interesting. Besides, this study could serve as an independent check of the corresponding diagnosed results from 3-D Eulerian model. Therefore it merits to be published in ACP. However, more detailed analysis are expected to make it complete and more convincing. In the following, I had a number of specific comments for the authors' reference to address before publication. The major weakness of the manuscript is that the uncertainty analysis of the model results is missing since the NMHCs measurements were done only for 2min once per day, PTR-MS were only available for the second half period of the campaign and the HONO measurement was not available. Possible ways to address this issue is given in the followed specific comments 1, 2 and 3.

Specific Comments

1. In section 3, the text describes qualitatively that how the interpolation of the canister measured NMHCs concentration is done by the correlations between NMHCs and CO. This kind of interpolation could come up with large uncertainties. Considering that the NMHCs measurements were done once per day and only for 2min duration, firstly, the data points utilized in the regression analysis are sparse (12 samples for the first period, 15 samples for the second period); secondly, the representative of the 2min sample is questionable; thirdly, the correlation analysis only support the consistency between CO and hydrocarbons for long term period not for the diurnal variations. Of course, the author probably had done the best they can for this kind of interpolation. But I think they should evaluate the possible uncertainties and that propagates to the estimated $P(O_3)$ and ozone formation regime. To solve this issue, I suggest: (1) present more detailed description and evaluation of the interpolation (the authors can add a supplement file which include the correlation analysis of CO and Hydrocarbons; and the benzene data set which had been measured by both PTR-MS and GC may be used to check uncertainty of the interpolation results); (2) based on the uncertainties

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estimated for the interpolated NMHCs, sensitivity model runs should be done to visualize the impacts.

2. In this study, the discussions are densely relied on the averaged diurnal variation model results. However, the model uncertainties should be significant different before and after June 12th, since the PTR-MS measurement were available afterwards. Thus, the authors had mixed up two groups of model results with potentially high and low uncertainties. I suggest the author to present them separately.

3. Atmospheric Nitrous Acid, HONO, has not been measured in this field campaign. Missing HONO as the model constrain, the ozone production rate could have been largely underestimated (Zhang et al., 2008) and it had been found that HONO could be a very important OH sources even in rural regions(Kleffmann et al., 2005). As indicated by the space observed NO_2 spatial distribution(Richter et al., 2005), the CEC region is covered by high NO_2 air. Thus, high HONO concentration at this region is expected. Sensitivity runs based on some typical HONO concentration values for rural regions or estimate the HONO concentration from the literature published value of HONO/NO_2 would be helpful to estimate the uncertainty of the calculated $P(O_3)$ rate.

4. The discussion of the ozone production regime (results shown in Fig. 5 and the sensitivity analysis of CO, ALD and biogenic hydrocarbons) is implicitly relied on the parameter, Relative Incremental Reactivity (RIR), which could be defined as

$$RIR = \frac{(P(O_3)_{sens} - P(O_3)_{base})/P(O_3)_{base}}{(E(X)_{sens} - E(X)_{base})/E(X)_{base}} \qquad (1)$$

$'X'$ could be NO_x, NMHCs, CO, ALD, Biogenic HCs, etc. $'E'$ means emission, subscript 'base' point to the standard calculations, subscript 'sens' point to the sensitivity model runs with increased or decreased emissions of substance $'X'$. RIRs define by equation (1) are pointed to the past time frame. If the change

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of emission rate of substance $'X'$ is replaced by the change of concentrations of substance $'X'$ (equation (2)), then the RIRs would be pointed to the present time frame.

$$RIR = \frac{(\mathrm{P(O_3)}_{sens} - \mathrm{P(O_3)}_{base})/\mathrm{P(O_3)}_{base}}{(\mathrm{C(X)}_{sens} - \mathrm{C(X)}_{base})/\mathrm{C(X)}_{base}} \qquad (2)$$

If Fig. 5 could be generated, the author should be able to calculate corresponding RIR value (present time frame, equation (2)) of NOx and NMHCs directly. The RIR values are much more straightforward than the demonstration of a set of sensitivity model runs.

5. Page 12979, line 6, the author depicted that L_N (OH + NO$_2$)/Q value corresponding to the transition ozone chemistry is about 0.2, the result is inconsistent with the theoretical investigations done by Kleinman and his co-workers (Kleinman, 2005;Kleinman et al., 1997). As Kleinman's work, if the Ozone-NOx-VOC sensitivity is derived through a box-model, then the L_N/Q value corresponding to transition ozone chemistry should be 0.5. More discussions are required to depict the reasons for this difference. I do not think the author stated in page 12979 lines 6 that "This is qualitatively consistent with the results of Kleinman et al. (2005)" is reasonable. This cutting off L_N/Q value itself is relatively critical and especially the difference is more than a factor of two.

6. In this manuscript, the PAN chemistry had been omitted in the discussion of the radical budget (Page 12974, line 9-14, and results presented in Table 2). Considering such a high mountain top site, the temperature should be low, then PAN would probably serve as a radical sink or source and influenced by transportation. From that point of view, bias must present in the model without constrained by PAN. Of course, PAN has probably not been measured in this field campaign as described. But the roles of PAN could be evaluated if meteorological parameters

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like temperature, pressure, wind direction and wind velocity had been recorded. I suggest the authors to briefly describe the characteristics of local meteorological conditions. If possible, the author should try to quantify the roles of PAN chemistry through inter-comparisons between high wind speed and low wind speed cases.

7. As indicated by table 1, many VOC compounds had been measured in this field campaign, hence a short analysis of the species contributions to total VOC reactivity may be valuable to be presented in this paper (probably in the style of Fig. 4 or a pie chart) so that the reader could notify that which kind of VOCs might be critical for $P(O_3)$ in CEC region.

8. Page 12970, when the canister sample was done daily should be presented in the experimental section.

9. Page 12974, line 25, the contribution of $OH + NO_2$ is missing in the calculation of $D(O_3)$ in equation (2) and probably in the followed analysis as well. The $D(O_3)$ calculation has been correctly done in their former publication of the Tokyo study (Kanaya et al., 2008).

10. Page 12989, Table 2, it is strange that the HO_2 budget has not reached balance for 6 hours averaged values (09:00 - 15:00). I think normally the box model should reach a steady state for radicals in a few minutes. The authors should give explanations about this point.

11. Page 12990, Fig. 1, the NMHCs is presented in the unit of ppbC while the OVOCs is presented in the unit of s^{-1}. I suggest the authors to unify them and better use the unit of s^{-1}.

Technical Suggestions:

1. Page 12974, line 24 - 26, the 'R' in the label of the three equations should be removed since they are not reactions.

2. Please use the same x-tickmark in Fig. 2 and Fig. 3 between the upper two panels and the lower panels.

3. Please enlarge the Fig. 7 horizontally so that the xlabel would not be so crowd.