**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.

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Reply to the Referee 2

We thank the reviewer very much for reading our paper carefully and giving us valuable comments. Detailed responses to the comments are given below.

Comment 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(O3) 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 estimated for the interpolated NMHCs, sensitivity model runs should be done to visualize the impacts.

Reply 1. The uncertainty in the NMHC concentrations used in the model could be large but it does not produce large errors in the estimated ozone production rates, under the NOx-limited conditions generally applicable for this field campaign. The short time period (2 min) for the canister sampling was chosen to reduce the risk of possible contamination by local sources during the sampling period. The 2-min NMHC concentrations need not be representative for a longer period, because the correlation with the CO data is taken into account. Anthropogenic VOCs with short lifetimes of several hours (and thus undergo significant diurnal variation in comparison to that of CO) had limited contribution to the ozone formation in this region, somewhat distant from urban areas. Hence neglecting diurnal variations in the NMHC/CO concentration ratios would not lead to fatal errors. In contrast, biogenic hydrocarbons with short lifetimes are important in our analysis and thus we made a sensitivity study for them as shown in section 4.4.3. As suggested, we compared (A) the benzene concentrations estimated from the correlation between canister-GC-based benzene concentrations and CO to (B) the benzene concentrations directly observed by a PTR-MS for the period after 12

June. The result is shown in Figure S1 in the supplement file. The temporal variation patterns are quite similar to each other (with a correlation coefficient of 0.81), and the (A)/(B) concentration ratio ranged from 0.80 (10th percentile) to 1.67 (90th percentile). Additionally, we found that 84% of [estimated NMHC]/[true NMHC] ratios were within a range between 0.5 and 2 for selected hydrocarbons that showed large reactivity toward OH (ethene, acetylene, propane, propene, i-pentane, toluene, and o-xylene). (Here the [estimated NMHC] is that estimated from [CO] and the linear regression parameters between [CO] and [GC-based NMHC].) On the basis of these analyses, we estimated that the uncertainty in the NMHC concentrations was a factor of 2. It propagated to the uncertainty in the daily production of ozone (on the basis of F-D(O3)) of a factor of only 1.15, because of the dominance of the NOx-limited condition.

Comment 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.

Reply 2. As mentioned above, the uncertainty in the NMHC concentration is estimated to be a factor of 2 even in the early part of the field campaign (when the PTR-MS was not in operation) and the uncertainty did not produce significant errors in the estimated ozone production rate.

Comment 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 NO2 spatial distribution(Richter et al., 2005), the CEC region is covered by high NO2 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/NO2 would be helpful to estimate the uncertainty of the calculated P(O3) rate.

Reply 3. An additional model run with heterogeneous production of HONO upon NO2 deposition on the ground assuming a HONO yield of 0.5 was made (Aumont et al., 2003; Kanaya et al., 2007). In the run, HONO/NO2 ratio was typically 5-10% in the nighttime, similar to the reported value for Milan and near Berlin (Alicke et al., 2002, 2003). The ozone amount produced in a day increased only by < 1 ppb from the base run. The small sensitivity is due to the low NO2 concentrations (and thus HONO concentrations) at the mountaintop in comparison to the typical values at urban sites at ground level (e.g., Zhang et al., 2008). We should note that Acker et al. (2006) suggested the presence of HONO at higher concentrations during midday rather than in the nighttime at the Meteorological Observatory Hohenpeissenberg (980ma.s.l.) in summer. However, the production process is unclear and we cannot take this into account in the simulations. Future studies to clarify the HONO formation in the upper part of the boundary layer are required.

Comment 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). 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.

Reply 4. We agree but simultaneously suppose that the F-D(O3) dependence on NMHCs and NOx concentrations as displayed in Figure 5 contains sufficient information to draw our conclusion and thus RIR values are not necessary.

Comment 5. Page 12979, line 6, the author depicted that LN (OH + NO2)/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 LN/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 LN/Q value itself is relatively critical and especially the difference is more than a factor of two.

Reply 5. We found that the NOx-related termination in our model mainly occurred via the XO2 (parameterized RO2 in RACM) + NO reaction in addition to via the OH + NO2 + M reaction, and thus the L_N/L(radical) cannot be approximated by the k[OH][NO2]/L(radical) rate. Figure 7d is replaced with the one showing L_N/L(radical) that includes the XO2 + NO term. Now the transition of the regime occurs at a L_N/L(radical) value of around 0.5 and closer agreement with other studies is obtained.

Comment 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 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.

Reply 6. We found that the net imbalance flux between the radical group (OH+HO2+RO2) and the reservoirs (HNO4 and PANs) was less than 4% of the gross production/loss of the radical group (as shown in Table 2; calculated without the flux between the radical group and the reservoirs) and thus the influence of the imbalance

on the ozone production rate would be small. We were not able to take into account the temporal variations in the PANs concentrations in the real atmosphere because they were not measured during the campaign.

Comment 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(O3) in CEC region.

Reply 7. The information is contained in Table 2, where the breakdown of the OH loss is shown, although some hydrocarbons are grouped into RACM species in this case. On the individual NMHC basis, isoprene, limonene, ethene, alpha-pinene, propene, toluene, acetylene, o-xylene, benzene, i-pentane, and propane showed large reactivity to OH. We conclude that the information in Table 2 is sufficient and do not include the detailed ranking of individual hydrocarbons in the revised manuscript, because the ozone production is not normally limited by VOC.

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

Reply 8. The typical timing (14:40 CST) is included in text.

Comment 9. Page 12974, line 25, the contribution of OH + NO2 is missing in the calculation of D(O3) in equation (2) and probably in the followed analysis as well. The D(O3) calculation has been correctly done in their former publication of the Tokyo study (Kanaya et al., 2008).

Reply 9. Because the site is not near urban areas and thus the [NO2]/[O3] ratio is very low (typically <2%), we did not define Ox (as a group of NO2 and O3) for this study, as opposed to our previous paper for the city center of Tokyo. The daily net production of Ox was typically only 1.5 ppb lower than that of O3 (the difference was calculated from

the OH + NO2 + M reaction rate).

Comment 10. Page 12989, Table 2, it is strange that the HO2 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.

Reply 10. The values are the averages of 10-min-based HO2 production and loss rates included in the daytime 6-hour period. For each 10 min, we average radical concentrations at five timings with 2-min intervals and then the budget is calculated on the basis of the averaged radical concentrations. The small imbalance (2%) is probably affected by the radical budget not in a full balance immediately (ca. 2 min) after the new boundary conditions are introduced to the box model.

Comment 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 $s-1$.

Reply 11. Figure 1h is revised to include the following three series; (1) the reactivity of CO, CH4, H2, SO2, and NMHCs toward OH, (2) same as (1) but the contribution from oxygenated VOCs is added, and (3) the reactivity from CO, CH4, H2, and SO2 only. The contributions of NMHCs and OVOCs can be recognized as differences between (1) and (3) and between (1) and (2).

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

Reply 1. The equations are labeled as (1), (2) and (3) and the former equation (1) for the heterogeneous loss rate of HO2 will be labeled as (4) in the revised manuscript.

Suggestion 2 and 3. Please use the same x-tickmark in Fig. 2 and Fig. 3 between the upper two panels and the lower panels. Please enlarge the Fig. 7 horizontally so that the xlabel would not be so crowd.

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Reply 2 and 3. The figures are revised as suggested. The aspect ratio of Figure 7 will be improved according to the layout in ACP.

References

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Please also note the Supplement to this comment.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 12965, 2009.

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