

Interactive comment on “Modeling of HCHO and CHOCHO at a semi-rural site in southern China during the PRIDE-PRD2006 campaign” by X. Li et al.

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Reply to Referee #1

We thank Referee #1 for his/her comments on our paper, which helped us to improve the quality of the paper. Below, we answer the reviewer's question point by point.

Specific Comments:

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This manuscript describes their box modeling work constrained by the measurements acquired during PRIDE-PRD2006 campaign. They focused on the importance of source and sink mechanisms to reconcile the observed and modeled HCHO and CHOCHO concentration. The authors claim that fresh emission, vertical and horizontal transport, and aerosol uptake processes are the major reason in the overestimation of HCHO and CHOCHO with respect to the observation. Also, they argue that care needs to be carried out in RGF factor analysis due to its complicated dependence on NMHC composition, OH, NO, NO₂, and physical/chemical processes.

I generally agree with the authors basic claims but to keep the reader motivated and make this manuscript more interesting, I suggest re-organizing the flow along with revisiting the points addressed below.

Comment: I suggest discussing the result of sensitivity analysis related with missing sinks (section 4.3) first and then describing the time of day dependence in production and loss rate of HCHO and CHOCHO later. Readers may likely get lost their interest somewhere in section 4.1 and 4.2, since it is not convincing to talk about the diurnal pattern of controlling mechanisms when the model cannot reproduce neither the diurnal pattern nor the magnitude of those species. Also, the discussion associated with night time process undermines the importance of this manuscript since the MAX-DOAS deployed on PRIDE mission did not provide any of the data during night time. I suggest keeping the analysis focuses on day time results.

Answer: We changed the flow of the manuscript according to the advice of the reviewer. The description of processes generating and removing HCHO and CHOCHO has been moved to the results section. We think the understanding of the model base-case is the foundation on which we base further investigations about the question why the model overpredicts HCHO and CHOCHO concentrations at the BG

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site. For example, the analysis of the model base-case shows that isoprene oxidation is the major contributor to HCHO and CHOCHO production at the BG site. With this information, we can further deduce that the overprediction of HCHO and CHOCHO concentration might be related to transport and vertical dilution of isoprene which is not well treated in the model. In the discussion section, we are now focusing on the causes of the discrepancy between the model and the measurement. Lengthy discussions on the nighttime chemistry and the day-to-day variations are removed. The discussion on the CHOCHO to HCHO ratio is moved to the end of the discussion section.

Comment: Some model run comparisons by constraining HO₂ vs OH and NO vs NO₂ along with current scenario would be also interesting to explore since HCHO and CHOCHO are very sensitive to these radical precursors. Moreover, if the authors can provide some results showing a comparison of oxidation product between model and measurement, will make this paper more logical (i.e. MVK, MACR as a secondary product of isoprene, etc.).

Answer: As described in Lu et al. (2012), our box model could not well reproduce the measured OH concentrations unless when we included an additional OH recycling mechanism. This effect was huge since OH concentrations calculated by the base model were a factor 3-5 off the observations during most of the day. In the expanded mechanism, a NO like species X was proposed to convert RO₂ to HO₂ and HO₂ to OH. In the model used by Lu et al. (2012), HCHO and CHOCHO were also produced during reactions involving X, which might not be correct. The exact properties of X was further investigated in our SAPHIR chamber. For isoprene degradation, X could have been a mean to describe unimolecular reactions (Fuchs et al., 2013). However, Fuchs et al. (2013) also showed that those unimolecular reactions of isoprene were far not enough to explain the observed OH concentrations at the BG site. Therefore, without

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knowing the property of X, we think it is better to constrain the model with measured OH.

Also, as described in Lu et al. (2012), measured HO₂ during the campaign was actually HO₂^{*}, i.e., HO₂ + RO₂ interferences. The amount of RO₂ interferences changes with the change of VOCs concentration and composition. Since we did not have RO₂ measurement during the campaign, we are not able to separate HO₂ from HO₂^{*} and constrain the model with measured HO₂ without assumptions about the unknown concentration and composition of the RO₂ family. Interestingly, even if RO_x would have been measured, the situation would not be better, since RO₂ would have been inferred from RO_{x_{obs}}-HO_{2_{obs}}, so even RO₂ would have an uncertainty related to that artifact problem.

Concerning NO and NO₂, they are strongly influenced by direct emissions at the BG site especially during night and early morning hours. Instead of by constraining the model base case by NO vs NO₂, we checked the sensitivity of HCHO and CHOCHO simulation to NO and NO₂ by changing their measured concentration by 1%. The results are described in section 4.2 in the revised manuscript.

Unfortunately, we did not have on-line measurements of MVK and MACR during the campaign. However, we had direct observations of total OH reactivity (k_{OH}) during the campaign. As described by Lou et al. (2010), more than 50% of the measured k_{OH} is from oxygenated VOCs which are produced from the oxidation of measured NMHCs. In general, we found good agreement between the modeled (by the model base-case) and the measured k_{OH} (Fig. S4). Since most of these oxygenated products also predominately react with OH, the concentrations of these species are expected not to depend on the exact concentration of OH. So even if OH can not be reproduced by the base case model, k_{OH} can. The discrepancy between the model and the measurements in some periods can be reconciled by modifying the τ_D value in the model. We include this discussion in the revised manuscript.

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Comment: Authors keep mentioning G1 and G2 throughout the manuscript, however, the importance of grouping them only shows in RGF analysis. For example, figures 1 & 2 and their corresponding descriptions do not show discrepancy among those days. The measured data looks more likely daily variability; the measured CHOCHO does not show any systematic difference and the measured HCHO only shows some possible difference in the morning time which may due to the influence of previous night. If authors claim the importance in grouping, I suggest making figure 2 clearer to address this point.

Answer: In the revised manuscript, the grouping of the measurement days is removed and the figure 2 is modified.

Comment: In section 4.2, I suggest re-organizing the flow. The general description about RGF should come first (p. 33028 line 9 – line 14) to guide the readers who are not familiar with RGF. P. 33027 line 27, it would be interesting to describe why RGF varies with the amount of OH. Is it due to the difference in production rate or the loss process matter? How does it change with OH recycling processes?

Answer: We reorganized the flow of Section 4.2. Moreover, explanations about the reason, why RGF is depending on OH, are added.

Comment: Authors also mentioned about the sensitivity of PAN which is an indication of inhomogeneity of PRD site. Due to this reason, the importance of advection may need to re-visit.

Answer: The inclusion of measured PANs as a model constraint is aiming to improve the model prediction of NMHC oxidation processes. Since we only have measured

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PAN data at a single spot (i.e., BG site), it is difficult to assess the inhomogeneity of airmasses originating from surrounding areas. Moreover, since the lifetime of PANs is different to HCHO and CHOCHO, the advection effect inferred from PANs inhomogeneity might not be applicable to HCHO and CHOCHO. Due to the lack of an accurate emission inventory of VOCs for the area around the BG site, we are not able to check the horizontal transport of HCHO and CHOCHO in detail by applying a transport model [e.g., a truncated-Lagrangian-transport model used by Huisman et al. (2011)]. However, during the campaign, our visual observations showed a relative homogeneous land usage along the major wind directions (i.e., north or south) within a distance of around 10 km. This can also be identified from the new figure S1 which shows the land usage in PRD. Therefore, we expect little concentration gradients of HCHO and CHOCHO along the major wind direction. Given this information as well as the wind speed of $\approx 2 \text{ m s}^{-1}$ and the lifetime of HCHO and CHOCHO of $\approx 1.5 \text{ h}$, we conclude that the horizontal transport might only have a small influence on the HCHO and CHOCHO simulation.

Comment: Instead of using one deposition rate throughout the whole day, it is more realistic to have diurnally varying dilution rate which reflects the physical mixing due to the boundary layer changes, horizontal advection, and dry deposition. I suggest using concentrations and emission rates of some chemical species with long life time or black carbon, as used to describe the influence of vertical mixing, to estimate the time of day dependence in physical loss term. By that way, authors can merge M1, M2 and M3 to one scenario and can emphasize the importance in aerosol uptake loss of CHOCHO and HCHO with respect to the.

Answer: We did not merge M1–M3 because we would like to check the effect of production terms, dry deposition, and vertical dilution on the HCHO and CHOCHO simulation separately. We think that the loss of HCHO and CHOCHO on aerosols is

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an additional factor which could contribute to the removal of HCHO and CHOCHO in the model, but this factor remains some uncertainties especially for HCHO. Therefore, we would not emphasize the importance of this effect without giving more solid experimental evidence.

Technical comments:

Comment: 1. P.33015, line 24: Correct“Filed” to “Field”

Answer: Corrected.

Comment: 2. A site map represents the geographical features with major wind direction would be helpful to understand where the site is and how it is characterized for the readers who are not familiar with geography of China. Accordingly, authors may be able to add clarity to the p. 33020, line 25 – p. 33021. line 8.

Answer: A map showing the land cover of the surrounding areas of the measurement site is now provided in the supplement.

Comment: 3. P. 33018, line 20. Describe more about the systematic error in concentration retrieval.

Answer: Origins of the systematic error are added, and the description of MAX-DOAS measurements and data retrieval is revised.

Comment: 4. P. 33019, line15 - line17: How does the estimated OH using JO1D C13686

differs from the measured OH during the time when measured OH concentration is available? If the estimated OH differs from the measured OH, how does it affect HCHO and CHOCHO modeling?

Answer: In general, the estimated OH concentration is within $\pm 50\%$ of the measured values (figure 1 in this file). We have shown in figure S3 of the supplement that 50% change of OH concentration can result in almost 50% change of the calculated HCHO and CHOCHO concentration. During our model calculation, the OH concentration was only estimated for occasions when the measured OH data was not available. For the 6 days shown in the manuscript, there were measured data available. Therefore, the uncertainty of OH estimation has minor influence on the HCHO and CHOCHO simulation in these 6 days.

Comment: 5. P. 33019, line 28: Correct “trance” to “trace”.

Answer: Corrected.

Comment: 6. P. 33028, line 19-line21: Add a reference related.

Answer: This sentence is the finding of this work, which has been described in some details in the following sentences.

Comment: 7. P. 33028, line 26: Add a reference.

Answer: This sentence is also the outcome of this work, which has been explained in the following sentences.

Comment: 8. P. 33031: I suggest changing the orders either the figures in supplement or the text description to match each other for the reader's convenience.

Answer: We changed the order of the figures in the supplement according to their occurrence sequence in the main text.

Comment: 9. P. 33050: the figure 2 is hard to read and the labels "a", "b", "c" and "d" is not noticeable. If the grouping of G1 and G2 has some meaning in this figure, even though I missed it, try to simplify these figures using the advantage of grouping them.

Answer: The figure has been modified.

Comment: 10. Figure S4, figure S5 and figure S6, all the bottom figures does not matching with legend. The some of the tracers in figure S4 and figure S5 might overlay each other and that might be the reason but double check that. For the bottom figure in figure S6, it has a missing or miss-colored marker; the graph contains yellow marker which is not shown in legend.

Answer: Because CHOCHO has little sensitivity to hydroperoxides and PANs, modeled CHOCHO concentrations represented by symbol "×" (i.e., model sensitivity run) overlap with those by "○" (i.e., model base case) in figure S4 and S5. The symbols and colors in the figures of the revised supplement have been modified.

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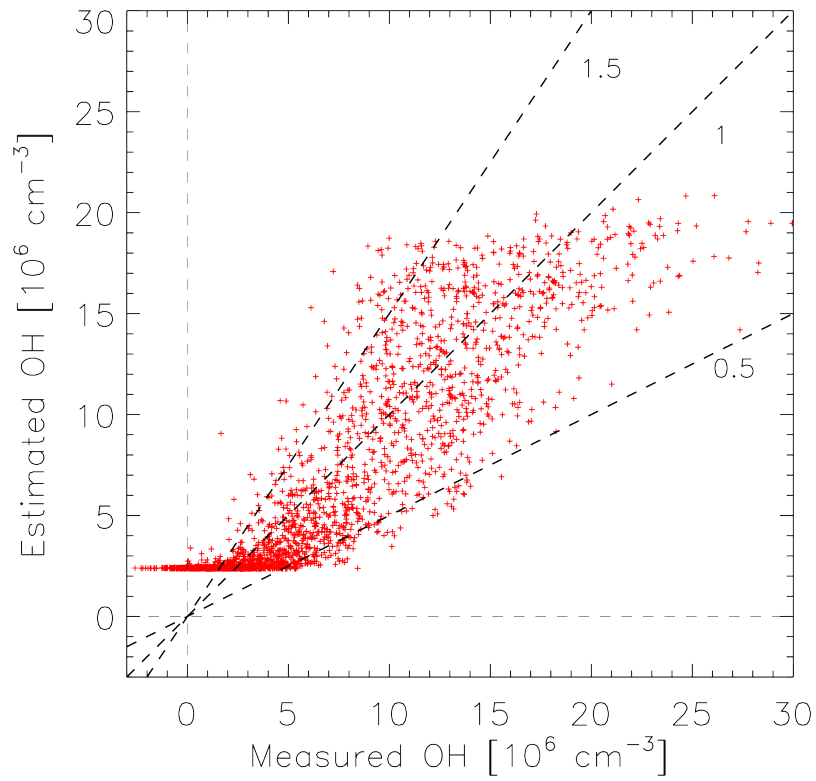


Fig. 1. Estimated OH concentration versus measured OH concentration during the PRD2006 campaign. The OH estimation was performed by using the empirical formula described by Lu et al. (2012).

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