Atmos. Chem. Phys. Discuss., 13, C3667–C3677, 2013
www.atmos-chem-phys-discuss.net/13/C3667/2013/


Atmospheric Chemistry and Physics Discussions
Open Access

ACPD
13, C3667–C3677, 2013

Interactive Comment

# *Interactive comment on* "A comparison of atmospheric composition using the Carbon Bond and Regional Atmospheric Chemistry Mechanisms" *by* G. Sarwar et al.

**G. Sarwar et al.**

sarwar.golam@epamail.epa.gov

Received and published: 14 June 2013

Comment: Chemical mechanisms are needed to simulate atmospheric chemistry in 3-D chemical transport models (CTMs) and this manuscript compares a newly developed mechanism (RACM2) to another mechanism (CB05TU) that is widely used. Mechanism comparisons are useful in providing information to guide mechanism selection for particular model applications, providing context for interpreting model results, and assessing overall uncertainties in atmospheric chemistry by comparing results from two independently derived mechanisms. RACM2 is a larger mechanism than CB05TU containing roughly twice the numbers of reactions and chemical species. Both mechanisms produce predict similar concentrations for chemical species of concern in air quality management, with average differences of: ozone (6%); nitrate (6%); sulfate (10%); ammonium (10%); PM2.5 (7%). These differences are comparable to or smaller than uncertainties expected from other CTM components such as emissions and meteorological input data, deposition algorithms or modeling grid resolution. Both mechanisms provide nearly identical responses to anthropogenic emission reductions.

Response: We appreciate the reviewer's thoughtful comments and suggestions to improve the article.

Comment: 1. On page 6931, line 20, modeled OH concentrations are compared to measurements for an urban location in Houston. The authors do not explain whether the median model predictions are for the 12 x 12 km grid cell containing the monitor – I assume this is the case. Later in the manuscript (page 6941, line 20) the authors point out substantial model under-predictions of VOCs in Houston which will strongly influence OH production. Realistically, the authors lack an objective basis for concluding whether one mechanism matches the observed OH concentrations better than the other.

Response: Indeed, model predictions from a single grid-cell containing the monitor are compared to the observations. Certain VOCs, especially ethene and propene, have been found to be underpredicted in the model compared to observations. However, such under-predictions do not occur at all times and locations since VOC emissions in Houston have been found to be intermittent due to episodic releases (Murphy and Allen, 2005). While the instantaneous OH production is influenced by available VOCs, the median value is not likely to be affected by spikes in VOCs. We believe the comparison of model and observed median value is robust and can be used to distinguish chemical mechanisms.

Reference: Murphy, C. G., Allen, D.: Hydrocarbon emissions from industrial release events in the Houston-Galveston area and their impact on ozone formation, Atmo-



ACPD
13, C3667–C3677, 2013

spheric Environment, 39, 3785-3798, 2005.

Comment: 2. On page 6932, line 16, modeled $H_2O_2$ concentrations for 2006 are compared to observed concentrations from 2001. The RACM2 and CB05TU predictions differ one from another by 10% but are less than half the observed concentration. The authors invoke a scaling factor of 2.5 from another modeling study to conclude that RACM2 agrees better than CB05TU with the observations. The uncertainties in this comparison are so great that it is unreasonable to conclude that one mechanism matches the observed $H_2O_2$ concentrations better than the other.

Response: We agree that the difference between the model predictions is small and the uncertainty in this comparison is likely to be similar to or greater than this difference. Thus, we will remove the related paragraph in the final article.

Comment: 3. On page 6933, line 12, modeled peroxyacyl acid concentrations for the US are compared to measured peroxyacetic acid concentrations from China with the stated assumption (on line 25) that concentrations will be similar for the US and China. How can this assumption be justified and then used to support a conclusion that RACM2 agrees better than CB05TU with the observations?

Response: PACD is a secondary pollutant and formed from the reactions of acetyl peroxy and higher acyl peroxy radicals with $HO_2$. Many studies have already reported that current air pollution levels in China are greater than the US. Thus, PACD levels in China are likely to be greater than those in the US. In the absence of any measurements in the US, we compare our predictions to the higher observed values in China and suggest that CB05TU predictions in the US are an order of magnitude greater than the higher observations in China. We believe the uncertainty in this comparison is lower than the difference of the two model predictions. Thus, we plan to keep the paragraph and add the following sentences:

Many studies have reported that current air pollution levels in China are much greater than the US. Thus, PACD levels in China are likely to be greater than those in the

US. In the absence of any measurements in the US, we compare our predictions to the higher observed values in China and find that CB05TU predictions are an order of magnitude greater than the higher observed values in China. While the CB05TU predictions are too high, the RACM2 predictions appear to be similar in magnitude for such a comparison. Measurements of atmospheric PACD levels in the US are needed for a more robust comparison with the model predictions.

Comment: 4. On page 6934, line 14, modeled $CH_3OOH$ concentrations for 2006 are compared to observed concentrations from 2001. The RACM2 and CB05TU predictions differ one from another by 25% (0.20 vs. 0.15 ppb) but are half of the observations (0.4 ppb). The authors invoke a scaling factor of 1.96 from another modeling study to conclude that RACM2 agrees better than CB05TU with the observations. The uncertainties in this comparison are so great that it is unreasonable to conclude that one mechanism matches the observed $CH_3OOH$ concentrations better than the other.

Response: We agree that the difference between the model predictions is small and the uncertainty in this comparison is likely to be equal to or greater than this difference. Thus, we will remove the related paragraph in the final article.

Comment: 5. On page 6940, modeled $O_3$ concentrations are compared to observed concentrations in four cities and then by selecting some days with high $O_3$ the authors conclude that RACM2 is "improving the comparison at high observed O3" (line 28) compared to CB05TU. In reviewing the underlying data presented in Figures 7a-d it seemed that a systematic comparison could lead to a different conclusion. Selecting the 3 days that appear to have the highest observed $O_3$ in each city (Los Angeles, September 3, 4, 10; Houston, September 1, 7, 14; Atlanta, September 16, 15, 27; New York, September 9, 8, 18 and 27) reveals that in Los Angeles RACM2 over-predicts by more than CB05TU, in Houston RACM2 improves upon under-prediction by CB05TU, in Atlanta both mechanisms over and under-predict, and in New York RACM2 over-predicts consistently whereas CB05TU over and under-predicts. In summary, RACM2 improved performance in one city (Houston) but degraded performance in two cities

(Los Angeles and New York). Reliance upon the Houston result is questionable because the authors point out substantial model under-predictions of VOCs in Houston (page 6941, line 20). The authors should revise their conclusion.

Response: Figure 7 showed average values of all monitors in four specific urban-areas while Figure 5 was created using all monitoring data in the US. As shown in Figure 5, RACM2 improves performance at the high-end and exacerbates high-bias at the low-end and the overall conclusion drawn from Figure 5 is robust. We decided to replace Figure 7 and the related discussion. We now compare results of average daily maximum 8-h O3 predicted by the two mechanisms and observations from all AQS sites (only using 8-hr O3 > 75 ppbv) in Fig. 7. We revise the discussion as follows:

High concentrations occur during O3 episodes. Thus, it is important that air quality models capture these high observed values. Results of average daily maximum 8-h O3 predicted by the two mechanisms are compared to observations from all AQS sites in Fig. 7. We use data only when observed 8-h O3 values are greater than 75 ppbv. While both mechanisms tend to under-predict high observed concentrations, RACM2 captures the data better than CB05TU. The CB05TU captures the observed data better only on 7 days while RACM2 captures the observed data better on 19 days. Values do not appear in the Figure on days when no observed data exceeded the threshold. Mean bias for CB05TU was –6.6 ppbv while mean bias for RACM2 was only -2.2 ppbv for the entire period. RACM2 improves mean bias by 4.4 ppbv when observed daily maximum 8-h O3 >75 ppbv. Thus, CB05TU underpredicts O3 at the higher end of observed concentrations while RACM2 enhances and improves O3 predictions at such conditions. On the other hand, RACM2 predictions are greater than the CB05TU predictions and observed concentrations at the lower end of observed values.

Comment: 6. Page 6941. I found Section 3.3.3 difficult to follow because several concepts are combined in a single long paragraph. I suggest re-writing this paragraph to focus on vertical O3 distributions in the mid to upper troposphere.



ACPD
13, C3667–C3677, 2013

Response: We agree that the comparison of model predictions to aircraft observations complicates the paragraph. Thus, we will eliminate the discussion related to the comparison of model predictions to the aircraft measurements [along with Figure 8(b)]. Please note that we found Figure 8 was created using older simulation results and thus we have re-created the Figure using newer simulation results which is consistent with other Figures presented in the article. The new Figure also show similar differences in vertical profiles of O3 obtained with CB05TU and RACM2. We will revise the paragraph as follows:

3.3.3 Impact on vertical distribution of O3 Vertical profiles of O3 obtained with CB05TU and RACM2 at 18 UTC on September 13 are presented in Figure 8. Data shown in the figure are obtained by averaging the domain-wide O3 at 18 UTC. These vertical profiles reveal that RACM2 enhances O3 up to 11,000-meters. RACM2 enhances O3 by 3-4 ppbv from surface to 7,000 meters and 1-2 ppbv above 7,000 meters. Predictions on other days are also similar. Thus, RACM2 consistently enhances O3 from surface to upper troposphere compared to those obtained with CB05TU.

Comment: 7. Page 6943. Section 3.5.2 discusses SOA. Table 3 shows RACM2 producing 42% higher anthropogenic SOA concentrations than CB05TU which is opposite a 22% decrease reported by a comparison for Europe (page 6926, line 1). Some discussion of this difference needs to be added.

Response: We agree and will add the following discussion to section 3.5.2: The difference in anthropogenic SOA response over Europe and US lies primarily in differences in the SOA and gas-phase chemical mechanisms used in the two studies. In our study, RACM2 leads to higher anthropogenic and biogenic SOA concentrations due to higher oxidant levels. In the European simulation, higher anthropogenic SOA is predicted with CB05, in spite of lower OH predictions, due to higher precursor levels. The European study specifically highlighted the higher cresol concentrations predicted with CB05 as a major contributor to increased anthropogenic SOA over RACM2 (Kim et al, 2011). Not only is cresol not included as an explicit precursor in CMAQ's SOA module (any SOA



ACPD
13, C3667–C3677, 2013

formed from cresol is assumed to be accounted for in the toluene SOA parameterization), but CB05TU is known to lead to significantly lower cresol concentrations than CB05. Kim et al. (2011) indicated that the discrepancy in aromatic SOA formation between CB05 and RACM2 would be significantly reduced with CB05TU, the mechanism used here.

Comment: 8. Page 6946, line 9. Conclusions about the accuracy of predictions for H2O2, MEPX and PACD cannot be supported due to uncertainties in the comparisons (discussed in points 2-4 above) and should be removed.

Response: We plan to remove the comparison of predicted H2O2 and MEPX with observed data in section 3.1.2 and 3.1.4 based comments # 2 and #4. Line 9 on page 6946 deals with mechanism to mechanism comparison. Thus, we believe no other changes are necessary.

Comment: 9. Page 6946, line 16. Data presented by the authors contradict a conclusion that RACM2 improves O3 predictions when observed O3 is high (point 5 above) and this conclusion should be modified or deleted.

Response: We have revised the paragraph related to Figure 7 (point 5 above) and believe that the overall conclusion drawn from Figure 5 and current Figure 7 is robust. Overall, RACM2 improves O3 predictions at the higher end of observed values and we will revise the sentence as follows:

However, CB05TU under-predicts O3 at the higher end of observed values while RACM2 improves the predictions for such conditions.

Comment: 10. Page 6946, line 20. A summary statement is made that "the two mechanisms produce relatively large differences in the predictions of O3 and secondary particles" when the differences range from 6% to 10%. These are small differences in the context of other uncertainties in the modeling such as the emissions and meteorological input data. The statement should be revised to the mechanism predictions are similar.

Response: We agree and plan to revise as follows: RACM2 and CB05TU predict similar O3 and PM2.5 concentrations, thus any air pollution control strategies are not expected to be noticeably different either.

Comment: 11. Page 6924, line 9. The statement "RACM2 predictions generally agree better with the observed data than the CB05TU predictions" is broad and unqualified and should be deleted.

Response: We agree and will delete it.

Comment: 12. Page 6946, line 11. Data presented by the authors contradict a conclusion that RACM2 improves O3 predictions when observed O3 is high (point 5 above) and this conclusion should be modified or deleted.

Response: We have revised the paragraph related to Figure 7 (point 5 above) and believe that the overall conclusion drawn from Figure 5 and current Figure 7 is robust. Overall, RACM2 improves O3 predictions at the higher end of observed values while it deteriorates the performance at the lower observed values. We will revise the sentences as follows:

A comparison of model predictions with the available observed data suggests that predictions obtained with RACM2 for many species agree better with the observed data. However, it deteriorates the model performance for O3 at lower observed values.

Comment: 13. Page 6946, line 20. A summary statement is made that "RACM2 enhances ozone and secondary aerosols by relatively large margins" when the differences range from 6% to 10%. These differences are small in the context of other uncertainties in the modeling such as the emissions and meteorological input data. I suggest changing this statement to "RACM2 and CB05TU predict similar concentrations for ozone and secondary aerosols" which would then help to explain why the mechanisms produce similar responses to emission reductions.

Response: We agree and will revise as follows: RACM2 and CB05TU predict similar O3 and PM2.5 concentrations, thus any air pollution control strategies are not expected to be noticeably different either.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 6923, 2013.



ACPD

13, C3667–C3677, 2013

Interactive Comment

ACPD
13, C3667–C3677, 2013

Interactive Comment

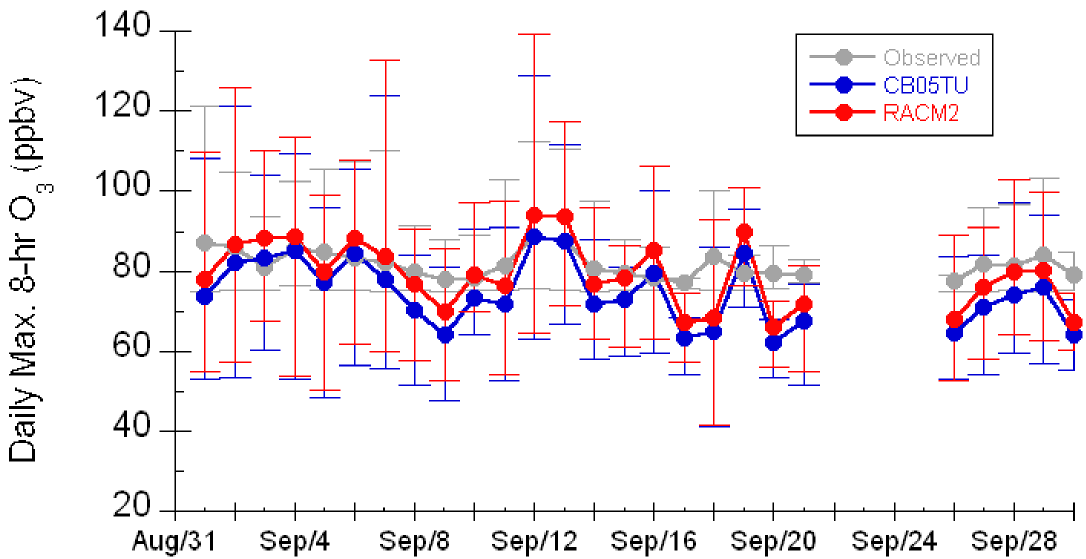


**Fig. 1.** Figure 7: A comparison of predicted daily maximum 8-hr O3 with observations from the Air Quality System (when 8-hr O3 > 75 ppbv). Error bars represent minimum and maximum values

ACPD

13, C3667–C3677, 2013

Interactive Comment

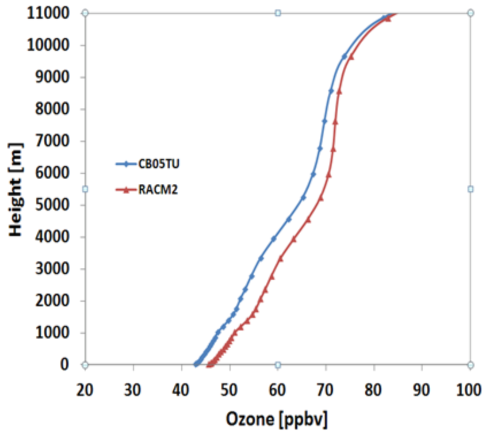


**Fig. 2.** Figure 8: Predicted vertical O3 profiles obtained with CB05TU and RACM2 at 18UTC on September 13



Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper