Responses to Referee # 2

We appreciate the referee's comments. Below are our responses:

General comments:

Referee's comment: The simulation period is 8 days, yet the authors focus on one aircraft flight on one day. The authors do mention on page 8172 (line 25) that the results from July 20 are similar to 2 other days. It is not clear if these were the only other flights during the simulation period or not.

Response:

For clarification purposes we added the following phrase to the 1st paragraph of section 2.

"The Community Multiscale Air Quality (CMAQ) modeling system (Byun and Schere, 2006) Version 4.6 was used to simulate the study period that extended from July 14-23, 2004. This modeling period encompasses three flights that took place on July 18, 20, and 22, 2004, corresponding to a portion of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) field campaign (Fehsenfeld, et al., 2006)….."

Referee's comment: Perhaps there were flights in which the results shown in Fig.1 are not similar?

Response:

We explicitly state at the beginning of section 3:

"All results presented in this work for July 20 are representative of similar results obtained for July 18 and 22, which are not shown for brevity "

Referee's comment: If the behavior of the results for NOx and VOC sensitivity simulation are consistent from day to day, it would be useful to show some sort of spatial plot of the eastern US indicating changes in sulfate concentrations in terms micrograms per meter cubed. This sort of information would be more useful than Figure 2 by itself.

Response:

We do not agree with the reviewer's suggestion since figure 2 clearly depicts the nonlinear chemical behavior of the system independent of the geographical location.

Referee's comment: It seems rather fortuitous that CBIV, CB05, and SAPRC all lead to similar sulfate concentrations (Fig. 1), yet produce different results when the emission are changed. Is it just fortuitous? The discussion on this point is rather lacking in the paper.

Response:

One of the main points of the paper is to show that the three chemical mechanisms indeed achieve similar sulfate concentrations using different processes. In fact, it is not all that surprising that the mechanisms all produce similar sulfate concentrations, given the history of the mechanisms and the CMAQ modeling system. Section 3 is devoted to explain the different results obtained when emissions are changed using the concept of photochemical indicators. Also, the use of the sulfate tracking tool helps analyzing the different oxidation pathways that lead to different model responses.

We also added a phrase to the first paragraph of section 3 to address the reviewer's concern about the similarities in sulfate concentrations obtained with the different chemical mechanisms:

…."The similar sulfate concentrations obtained with the three different chemical mechanisms suggest that oxidant-limited conditions (i.e. the SO2 oxidation is limited by the oxidant availability) prevailed during the study period." ….

Specific comments:

Referee's comment: Page 8170, line 11: Change "levels" to "emission rates" or "concentration". "levels" is a rather generic term and the authors should be more specific to avoid confusion. The same comment applies to numerous instances in the text.

Response: Done

Referee's comment: Page 8717, line 17: Change "levels" to "amount" or "magnitude".

Response: Done

Referee's comment: Page 8171, line 19: Change "levels" to "concentration" or "mixing ratios".

Response: Done

Referee's comment: Page 8172, line 3: Change "levels" to something more specific.

Response: Changed to "emission rates"

Referee's comment: Page 8172, lines 13-14: The authors refer to another paper describing the performance of CMAQ, and seem to imply (although to not say specifically) that the current simulation is configured in the same way and thus the performance is the same. Is the model run exactly as in Yu at al. (2010)? If not, what are the differences. The authors should include a paragraph on how emissions were handled, e.g. what inventory was used? The authors refer to

Mathur (2008) for the emissions, but because of its importance to this paper more details are warranted here.

Response:

The model configuration is described in the first paragraph of section 2 and there is no mentioning of the Yu et al (2010) paper in that section.

We added the following description of the emissions at the end of the first paragraph of section 2:

…" The meteorological data for this study was based on Eta model (Black, 1994) outputs linked to the CMAQ modeling system using the methodology described in Otte et al. 2005. Emissions include point, mobile, area, and biogenic sources (Mathur, 2008). The area emissions are based on the 2001 National Emissions Inventory. Emissions of SO_2 and NOx from point sources were projected from 2001 to 2004 based on the Department of Energy's 2004 Annual Energy Outlook. Mobile sources were estimated based on the MOBILE6 model (Pouliot and Pierce, 2003) and biogenic emissions were calculated with the BEIS3.12 model (Pierce et al., 2002)."

We also added the following references:

Otte, T. L., et al. (2005), Linking the Eta model with the Community Multiscale Air Quality (CMAQ) modeling system to build a national air quality forecasting system, Weather Forecasting, 20, 367– 384.

Pouliot, G., and T. Pierce (2003), Emissions processing for an air quality forecasting model, 12th Intl. Conf. on Emission Inventories, San Diego, Calif., 28 April–1 May.

Pierce, T., C. Geron, G. Pouliot, E. Kinnee, and J. Vukovich (2002), Integration of the biogenic emission inventory system (BEIS3) into the community multiscale air quality modeling system, preprints, 12th Joint Conference on the Apps. of Air Pollut. Meteor. with the A&WMA, on Am. Meteorol. Soc., Norfolk, Va., 20–24 May 2002, J85–J86.

Referee's comment: Page 8172, line 16: Change "varying rates of NOx and VOC emissions" to "varying NOx and VOC emission rates".

Response: Done.

Referee's comment: Does this include both anthropogenic and biogenic emissions?

Response:

In the very next phrase it is stated: “For each chemical mechanism three simulations were performed: a base case simulation, a simulation with 35% reduction in anthropogenic NOx emissions, and a simulation with 35% reduction in anthropogenic VOC emissions.”

Referee’s comment: Page 8172, section 2: Later in the text the authors mention aqueous phase chemistry, but not description is included here. The authors should include a brief description on how aqueous chemistry is simulated in the model. Also, there is no mention of which aerosol model is being used in CMAQ. They do mention which gas-phase mechanisms are employed, and it seems like a serious oversight to not inform the reader which aerosol model is used.

Response:

We added the following phrases into the first paragraph of section 2:

“The aerosol calculation is based on the ISORROPIA v1.7 model (Nenes et al, 1998) and the aqueous phase simulation includes uptake of gases into the cloud droplets, aqueous oxidation of SO2 by H2O2, O3, MHP, PAA, and catalytic oxidation by iron and manganese (Binkowski and (2003) and wet scavenging.”

We also added the following references:

Nenes A., Pilinis C., and Pandis S.N. (1998) Continued Development and Testing of a New Thermodynamic Aerosol Module for Urban and Regional Air Quality Models, Atmos. Env., 33,1553-1560

Binkowski, F. S., and S. J. Roselle (2003), Models-3 community multi-scale air quality (CMAQ) model aerosol component: 1. Model description, J. Geophys. Res., 108(D6), 4183, doi:10.1029/2001JD001409.

Referee’s comment: Page 8173, line 2: The authors mention that the highest concentrations are largest in the boundary layer. It would be useful to modify Figure 1 to include the altitude of the aircraft so that the readers can see what altitude the measurements are collected at. How did you infer that those measurements were in the boundary layer? Just because the concentrations are high does not mean they are all within the boundary layer. A figure depicting the spatial flight path is also needed.

Response: We added the flight altitude into Figure 1.

We infer the measurements were in the boundary layer because they were taken close to the ground. With the addition of the flight altitude into Figure 1 this becomes apparent.

The spatial flight path has been published elsewhere. We added a phrase to the first paragraph of section 2 and a reference where the geographical flight pattern is shown for the period of our study.

…."The flight patterns corresponding to the study period have been described in Singh et al. (2006)."….

We also added the following reference:

Singh, H. B., W. H. Brune, J. H. Crawford, D. J. Jacob, and P. B. Russell (2006). Overview of the summer 2004 Intercontinental Chemical Transport Experiment–North America (INTEX-A). Journal of Geophysical Research, Vol. 111, D24S01, doi:10.1029/2006JD007905

Referee's comment: Page 8173, lines 18-19: The authors being to discuss the NOx and VOC sensitivity test they will perform; however, they do not mention how those simulations are conducted and need to provide more details. For example, by how much as NOx and VOC emissions changed? Were just two simulations performed (one increasing and one decreasing the emissions) or were there a range of simulations performed? Expressing the emissions in terms of a total amount rather than just a percentage is needed.

Response:

We clearly state in the last paragraph of section 2:

"For each chemical mechanism three simulations were performed: a base case simulation, a simulation with 35% reduction in anthropogenic NOx emissions, and a simulation with 35% reduction in anthropogenic VOC emissions."

We do not agree with the reviewer's comments regarding the need to show absolute instead of relative magnitudes of the emission reductions. It does not add any new information.

Referee's comment: Page 8173, line 25: The authors state that the three mechanisms are markedly different; however, the results for CBIV and CB05 look rather similar to me except that there are no results when the indicator is greater than 6.

Response:

We do not agree with the assessment of the reviewer. Not only there are no results when the indicator is greater than 6 for CBIV but also the transition point between NOx- and VOC- limited

sulfate formation is different and the magnitude of the change in potential sulfate is quite different between CBIV and CB05.

Referee's comment: Page 8174, line 9: Same comment previously. CB05 looks similar to CBIV and not between CBIV and SAPRC as the authors state.

Response:

We see the point the reviewer is trying to make and we made a slight change into the statement to address the concern:

….."Finally, the CB05 chemical mechanism exhibits an intermediate behavior somewhere between the other two mechanisms but with closer similarities to CBIV given their common formulation."

Referee's comment: Page 8175, end of section 3: The last paragraph in this section discusses the performance of the 3 mechanisms in simulating PAA. The last sentence provides a reason why CB05 and SAPRC produce higher concentrations than CBIV, but some additional discussion of these results are needed. Does this imply that the newer mechanisms are worse? The performance of PAA depends on other factors that are not evaluated here. It is possible that CB05 and SAPRC perform better for other trace gases, so this comparison may not really say which mechanism is better overall – only that there are differences in the mechanisms. Also the differences in how many molecules are formed for the PA+HO2 reaction is based on some science, so which is more accepted? Some references here on how those were defined is warranted.

Response:

The reviewer is correct to say that it is not possible from this analysis to say which mechanism is "best", only that there are differences between the mechanisms. That is exactly the point we are trying to make with this manuscript. We are not advocating one mechanism over the others, but simply pointing out that further investigation needs to be done to fully understand these differences. Moreover, we are also suggesting that the mechanism sensitivities we have identified may have important implications for studies of sulfate formation in future changed climates. Any additional discussion of PAA formation differences between the mechanisms, although scientifically interesting, is not actually germane to the focus of this work.

Referee's comment: Figure 3: The lines are defined in the text, but they should also be defined in the figure caption or figure itself. It is also difficult to see differences in the models from these plots, since the aircraft flew in the free atmosphere much of the time and the models seem to be more similar in that region. I highly recommend to also show the results in terms of

averaged pie charts, divided into two categories: within the boundary layer and the free atmosphere.

Response:

We added the flight altitude to Figure 3 to address the reviewer's concern. We don't think it is necessary to add a pie chart that will give the same information as the flight altitude.