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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sensitivities of sulfate aerosol formation and oxidation pathways on the chemical mechanism employed in simulations" *by* A. F. Stein and R. D. Saylor

Anonymous Referee #2

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General Comments:

The authors use a chemical transport model to show that while similar sulfate concentrations are produced from simulations that employ different photochemical mechanisms using a default emission inventory, the different photochemical mechanisms lead to different sulfate concentrations when the NOx or VOC emission rates were changed. As stated in the text, the NOx and VOC sensitivity simulations have implications for climate studies since sulfate contributes significantly to aerosol radiative forcing, emission rates and distributions are likely to change in the future, and climate models treatments of gas-phase chemistry currently is relatively simple. The paper is

scientifically relevant, well-organized, concise, and suitable for Atmospheric Chemistry and Physics. However, there are a number of points that need to be addressed before the paper is suitable for publication.

As described in my specific comments, there are a number of important details on how the study was conducted that need to be defined. There is insufficient details presented that allow other scientists to reproduce the results presented in this study. The most important omissions are a description of the aerosol model, and emissions inventory, and details on how the NOx and VOC sensitivity simulations were conducted.

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. Perhaps there were flights in which the results shown in Fig. 1 are not similar? 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.

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.

Specific Comments:

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.

Page 8717, line 17: Change "levels" to "amount" or "magnitude".

Page 8171, line 19: Change "levels" to "concentration" or "mixing ratios".

Page 8172, line 3: Change "levels" to something more specific.

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.

Page 8172, line 16: Change "varying rates of NOx and VOC emissions" to "varying NOx and VOC emission rates". Does this include both anthropogenic and biogenic emissions?

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.

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.

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.

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.

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

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.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 8169, 2012.