**Atmospheric
Chemistry
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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 #3**

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## General comments

The authors apply 3 different chemical mechanisms within the CMAQ model to simulate air quality over the eastern U.S. for a 10-day summer period. All 3 simulations yield similar sulfate concentrations but, when they are repeated with lower emissions of $NO_X$ and VOC, the authors report "significantly different responses in sulfate formation." The manuscript is succinct, which is a refreshing change compared to recent papers in *ACPD*, and the writing quality is quite good. However, the authors fail to make a strong case that supports their main conclusion. Instead, they launch into a rather confusing discussion about indicator ratios. I have no reason to doubt the validity of the authors'

conclusions so, with a little work, I expect this manuscript to be publishable in *ACP*.

*Unsupported Conclusion.* The authors state in their abstract, "... the three mechanisms are shown to have significantly different responses in sulfate formation when the emissions of $NO_X$ and/or VOC are altered." This is reasserted at the bottom of p8173, but it is never shown. Fig. 2 shows responses in "potential sulfate" formation, where potential sulfate is defined as the sum of $SO_4$ and $H_2O_2$. This may be a useful metric in field studies, but its appropriateness in this modeling study is questionable because CBIV produces an unrealistically large amount of $H_2O_2$ (Fig. 1c) and it's not apparent that all 3 mechanisms convert $H_2O_2$ to $SO_4$ with equal efficiency. It would be more convincing if the authors were to display spatial fields of $\Delta SO_4$ from the 3 mechanisms for both the $\Delta NO_X$ and $\Delta VOC$ scenarios. Also, these fields should be presented with the longest possible averaging period (e.g., 10 days) to ensure robustness of their conclusion rather than just the 8-hour flight duration shown in Fig. 2.

*Flaky Indicator.* The authors explain on p8173 that, "larger values of $I_{SO4}$ are associated with $NO_X$-sensitive conditions while smaller values for the indicator are associated with VOC sensitive regimes." This is inconsistent with Fig. 2, which suggests that potential $SO_4$ in CBIV is most sensitive to $NO_X$ at low $I_{SO4}$ values (Fig. 2a) and in SAPRC99 is entirely insensitive to VOC even at the lowest $I_{SO4}$ levels (see Fig. 2b). In short, the authors' simplistic conceptual model is not upheld by their more complex numerical modeling. I strongly urge the authors to recast their results in a manner that does not rely so heavily on the concept of potential sulfate and to also reduce the emphasis on $I_{SO4}$ because those terms are not lending much clarity to their analysis.

*Scholarship.* The authors appear to make extensive use of the simulations by Mathur et al. (2008), in which the same 3 chemical mechanisms were applied in CMAQ for this same time period and domain. Though I'm not intimately familiar with the work of Mathur et al., I did see a related presentation of theirs from an ICARTT data workshop. From what I recall, those authors also applied the sulfate-tracking model in CMAQ to diagnose which chemical pathways were producing sulfate in this same domain and time

period. In the grand scheme, the present work seems to be a rather modest extension of the material presented by those authors. Therefore, I question whether the authorship is appropriately shared among all who contributed to this study and if sufficient acknowledgements have been given. At the very least the authors need to present the work of Mathur et al. (2008) as a critical step toward their current investigation.

**Miscellaneous comments**

• On p8172, the authors state that all 3 mechanisms capture the levels of $H_2O_2$ within 50%. Fig. 1c shows this to be true at the higher $H_2O_2$ mixing ratios, but not at lower levels. For example, CBIV appears to overestimate $H_2O_2$ by a factor of 5 or more at hours 15, 16.5, and 19.5.
• In the description of Fig.2 on p8173, the authors state that changes in "potential sulfate are plotted as a function of the simultaneously measured $I_{SO4}$." If these are measurements of $I_{SO4}$, why does their range of values change when different mechanisms are applied in the model (e.g., narrow range for SAPRC99 and wide range for CBIV)?

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