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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

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We thank the referee for his/her comments, but strongly disagree with many of the points raised as detailed below.

Re: “Unsupported Conclusion.” It is apparent from the referee’s comments that he/she is not familiar with the widely known concept of NO_x-VOC sensitivities and the use of indicator ratios to gauge sensitivities in the formation of secondary atmospheric species. Although not directly relevant to the current work, we refer the referee to the work of Sillman (Sillman, 1995; <http://www-personal.umich.edu/~sillman/obm.htm>) for details of this concept as it relates to ozone formation. In the context of sensitivities to sulfate

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formation, we have already cited the work of Stein and Lamb (2002) which explains in great detail the foundational concepts referred to in this work. The referee also seems to be unfamiliar with the pioneering work of Stockwell et al. (1988) and Stockwell (1994) in defining potential sulfate as the most appropriate quantity for gauging the maximum amount of sulfate aerosol that is potentially achievable in either the “real” or “modeled” atmosphere. Given this fundamental background, the interpretation of the results in Figure 2 is straightforward and compelling; i.e., the three mechanisms exhibit a pronounced difference in potential sulfate formation sensitivity to NO_x and VOC concentration changes. This is most clearly evidenced by the difference in the value of the indicator where the potential sulfate changes for NO_x reductions and VOC reductions first “cross” (~4.0 for CBIV, < 1 for SAPRC99, and ~3.0 for CB05). The referee is correct in noting that the three mechanisms do not produce the same amount of H₂O₂ nor do they produce sulfate with “equal efficiency” – this is exactly the point being made in Figure 2. Contrary to the referee’s suggestion, presenting fields of delta sulfate between the NO_x and VOC reduction scenarios and the baseline would not add clarity to the paper beyond the already elegant and compact presentation of Figure 2. For readers familiar with these concepts, the presentation of Figure 2 is sufficient.

Re: “Flaky Indicator.” Taking a closer look at Figure 2a corresponding to the CBIV mechanism, it can be observed that for indicator values lower than 4 the potential sulfate gets reduced as VOC is reduced while a reduction in NO_x produces an increase in the levels of potential sulfate. This is, by definition, a VOC sensitive regime (see Sillman 1995 and Stein and Lamb 2002) and is not most sensitive to NO_x as pointed by the referee. On the other hand, in figure 2b all the modeled points that are shown in this particular figure happened to be NO_x sensitive and that is why there are no points corresponding to indicator values lower than 1. Please refer to figure 3 of Stein and Lamb (2002) for an example of VOC sensitive modeled points. One of the central points of this paper is to show that 3 widely used photochemical mechanisms give such noticeable different responses to changes in NO_x and VOC. The fact that they don’t give a consistent value for the transition between the NO_x- and VOC- sensitive regimes

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shows that the underlying chemical processing of the formation of sulfate are markedly different among the mechanisms and perhaps some of them are not correct. For instance, it is well known that the CBIV mechanism overestimates H₂O₂. Therefore, we should expect artificially higher transition values from VOC to NO_x sulfate sensitivity.

Re: “Scholarship.” The referee is correct in saying that he/she is “not intimately familiar with the work of Mathur et al. (2008)”. If they were, they would realize that this work is a significant extension and represents an entirely new interpretation of new results. Just to mention two differences between the studies: i) Mathur et al 2008 use only 2 chemical mechanisms (CBIV and SAPRC99) and we use 3 (CBIV, CB05, and SAPRC99). ii) Mathur et al 2008 use an earlier version of CMAQ (4.5) and we use version 4.6. Frankly, we are personally offended by the referee’s intimation that this work usurps proper credit from Mathur and co-authors and suggest that the referee in the future be more certain of the facts before making such an accusation.

Miscellaneous comment #1: We have changed the text to now read “. . . all three chemical mechanisms capture the levels of boundary layer H₂O₂, SO₄ . . .”

Miscellaneous comment #2: We have changed the text, where it says “measurements” it should read “modeled” in that particular sentence. We apologize for the mistake.

References Sillman, S. (1995) The use of NO_y, H₂O₂, and HNO₃ as indicators for ozone-NO_x-hydrocarbon sensitivity in urban locations, J. Geophys. Res., 100, D7, 14175-14188. Stein A.F. and Lamb D. (2002), Chemical Indicators of Sulfate Sensitivity to Nitrogen Oxides and Volatile Organic Compounds. Journal of Geophysical Research, Vol. 107, No. D20, 4449, doi:10.1029/2001JD001088. Stockwell, W. R., Milford, J. B., McRae, G. J., Middleton, P., Chang, J. S. (1988) Nonlinear coupling in the NO_x-SO_x-reactive organic system, Atmos. Environ., 22, 2481-2490. Stockwell, W. R. (1994) The effect of gas-phase chemistry on aqueous-phase sulfur dioxide oxidation rates, J. Atmos. Chem., 19, 317-329.

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