SENSITIVITY STUDY OF THE RESPONSE OF SULFATE AEROSOLS TO CHANGES IN PRIMARY SOURCES

Ariel F. Stein*

Earth Resources and Technology on assignment to the Air Resources Laboratory, NOAA, Silver Spring MD, USA

1. INTRODUCTION

The study of the formation of aerosol particles, specifically sulfate (SO_4^{2-}) aerosols, involves a complicated coupling among gas-phase chemical reactions (as in the formation of ozone), aqueous-phase photochemical, and meteorological processes within the simulation framework. The formation of SO_4^{2-} is chemically linked to primary emissions of sulfur dioxide (SO_2) via atmospheric oxidants such as the hydroxyl radical (OH) and hydrogen peroxide (H_2O_2) and therefore also to the emissions of nitrogen oxides (NOx) and volatile organic compounds (VOC). The SO_4^{2-} production depends in part on the resulting changes in oxidant levels and the competition that naturally exists between the gas- and aqueous-phase pathways for SO_2 oxidation. In this work we investigate the response of SO_4^{2-} production to variations in oxidant levels. In order to vary the oxidant abundances we have chosen to change the levels of primary NOx and VOC.

2. SULFATE SENSITIVITY TO OXIDANT ABUNDANCES

We can identify two photochemical regimes exhibiting a different response of SO_4^{2-} production to oxidant levels depending on the main sink of odd-hydrogen (HOx), defined as the sum of OH, HO_2, and organic peroxyl (RO_2) radicals. When the formation of HNO_3 dominates the loss of odd-hydrogen, a decrease in NOx frees up OH that can react with SO_2, CO, and VOC, which thus increases the abundance of HO_2 and in turn favors the formation of H_2O_2. Consequently, the interaction of these reactions tends to increase the formation of SO_4^{2-} via both the clear-air and aqueous-phase pathways. A decrease in VOC levels would reduce OH by making it available to form more HNO_3. As a consequence, the H_2O_2 production would also be reduced, thus decreasing the formation of SO_4^{2-}. Under this photochemical regime, called "VOC-sensitive", potential SO_4^{2-} (SO_4^{2-} + H_2O_2) decreases with decreasing VOC and increases with decreasing NOx.

By contrast, when the formation of HNO_3 can be regarded as a small odd-hydrogen sink, a decrease in NOx concentrations would slow down the conversion of HO_2 to OH, thereby decreasing the overall SO_4^{2-} formation. When the VOC levels are lowered, a small additional amount of OH would be available to react with SO_2, slightly increasing the gas-phase production of SO_4^{2-}. Lowering the VOC concentrations would not significantly affect the formation of H_2O_2, however, due to the fact that the system is saturated with hydrocarbons. Under this condition, changes in VOC levels would have little effect on HO_2 and hence on H_2O_2 formation. Therefore, the aqueous-phase SO_2 oxidation would remain unaltered. This scenario constitutes the "NOx-sensitive" photochemical regime, in which aerosol SO_4^{2-} concentrations would decrease with decreasing NOx and would be largely independent of VOC. The highly nonlinear and coupled nature of the sulfate production process is responsible for this somewhat counter-intuitive behavior.

Stein and Lamb (2002) proposed the use of a combination of afternoon concentrations of HNO_3, H_2O_2, and ambient SO_4^{2-} as "indicator species" of the ambient SO_4^{2-}-VOC-NO_x sensitivity. The link between the indicator value and the NO_x-VOC chemistry can be understood in terms of the dominant sinks and sources for odd-hydrogen. The NO_x-sensitive regime favors the formation of potential sulfate over the production of HNO_3. Under this condition the production of H_2O_2 constitutes the main loss of HO_x. Also, under NO_x-sensitive conditions the gas-phase SO_2 oxidation is favored over the formation of HNO_3. On the other hand, the VOC-sensitive regime is characterized by a high production rate of HNO_3 that overwhelms the formation of potential sulfate. Therefore, high values of the indicator ratio, $\{[H_2O_2]+[SO_4^{2-}]\}/\{[HNO_3]+[NO_3^-]\}$, are associated with NO_x-sensitive conditions while low values for

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*Corresponding author: Ariel F. Stein, 1315 East West Hwy, Silver Spring, MD 20910, USA; e-mail: ariel.stein@noaa.gov

the indicator can be identified with a VOC sensitive regime.

3. MODEL AND MEASUREMENTS

The CMAQ (Byun and Schere, 2006) Version 4.6 has been used to simulate the study period that extended from July 14-23, 2004. The model configuration included 3-D advection, cloud processes, aqueous chemistry, scavenging and wet deposition and dry deposition. Three different chemical mechanisms have been used to test the model response to changes in the NOx and VOC levels, namely CB-IV, CB05, and SAPRC-99. The model domain covered the Eastern US with a horizontal resolution of 12 km and 22 variably thickness layers in the vertical. The meteorological data used to drive CMAQ is based on the Eta model (Black, 1994) output. The emissions include point, mobile, area, and biogenic sources (Mathur, 2008).

The measurements used for this work correspond to the ICARTT field campaign (Fehsenfeld, et al., 2006). The data have been obtained from http://www-air.larc.nasa.gov/cgi-bin/arcstat. Results for July 18, 20, and 22, 2004 along the path of the DC8 flight have been analyzed in this work.

Sulfate-NOx-VOC sensitivities have been calculated from a series of photochemical model simulations with varying rates of NO_x and VOC emissions to produce variations in oxidant abundances for each chemical mechanism; namely, a base case simulation, a simulation with 35% reduction in anthropogenic NO_x emissions, and a run with 35% reduction in anthropogenic VOC emissions.

Comparison of the model and the measurements shows that the simulations with the three chemical mechanisms capture the levels of H_2O_2, SO_4^{2-} and HNO_3/NO_3^- within 50% for July 20, 2004(Figure 1). For July 18 and 22, 2004 similar results have been obtained. Figure 2 shows the percentage normalized reduction in $\{[H_2O_2]+[SO_4^{2-}]\}$ concentration as a consequence of either a NO_x or a VOC emission reduction for each chemical mechanism along the path of the flight for July 20, 2004. Similar results have been obtained for July 18 and 22, 2004. The change in potential sulfate is plotted as a function of the concurrent ratio, $\{[H_2O_2]+[SO_4^{2-}]\}/\{[HNO_3]+[NO_3^-]\}$. High values of the ratio are associated with NO_x-sensitive conditions while low values for the indicator can be identified with a VOC sensitive regime. As can be inferred, the three chemical mechanisms have different responses in

$H_2O_2+SO_4^{2-}$ when the sources of NOx and VOC are reduced reflecting different photochemical regimes under which the formation of sulfate occurs. Therefore, under different oxidation conditions, (i.e. changes in sun radiation, seasons, primary emissions, etc.) the three chemical mechanisms will respond in an ambiguous way. In particular, the SAPRC99 chemical mechanism shows that reductions in NOx are more effective in reducing $H_2O_2+SO_4^{2-}$ than lowering VOCs showing that the preferential odd hydrogen sink seems to be the formation of H_2O_2. On the other hand, the runs with CB-IV shows that $H_2O_2+SO_4^{2-}$ will be reduced more effectively if VOCs are reduced revealing that the formation of nitric acid/nitrate would constitute the main sink for odd hydrogen species. This result is compatible with the fact that CB-IV tends to overestimate the levels of H_2O_2, artificially increasing the indicator levels. Finally, the CB-05 chemical mechanism shows an intermediate behavior between the other two mechanisms.
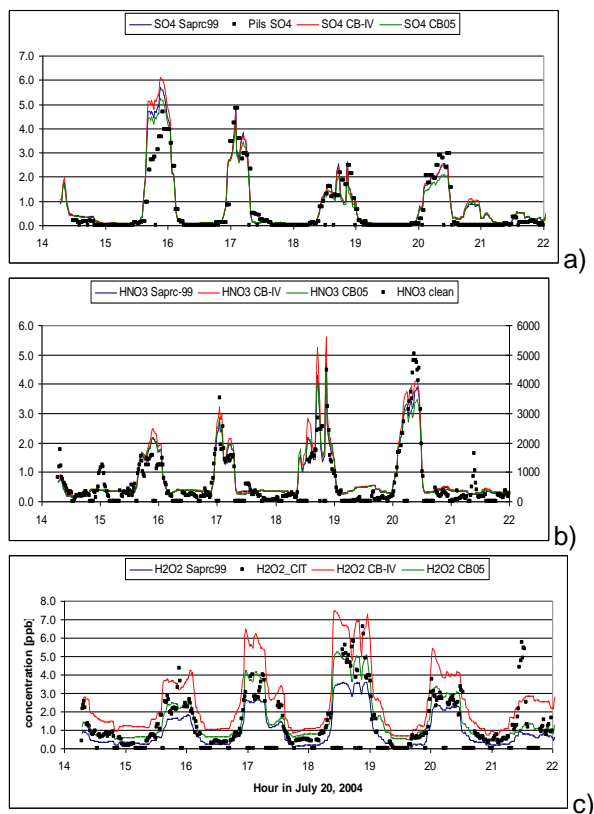

Figure 1. Comparison of modeled vs. measured sulfate (a), nitrate (b), and (c) hydrogen peroxide concentrations along the path of the flight on July 20, 2004.
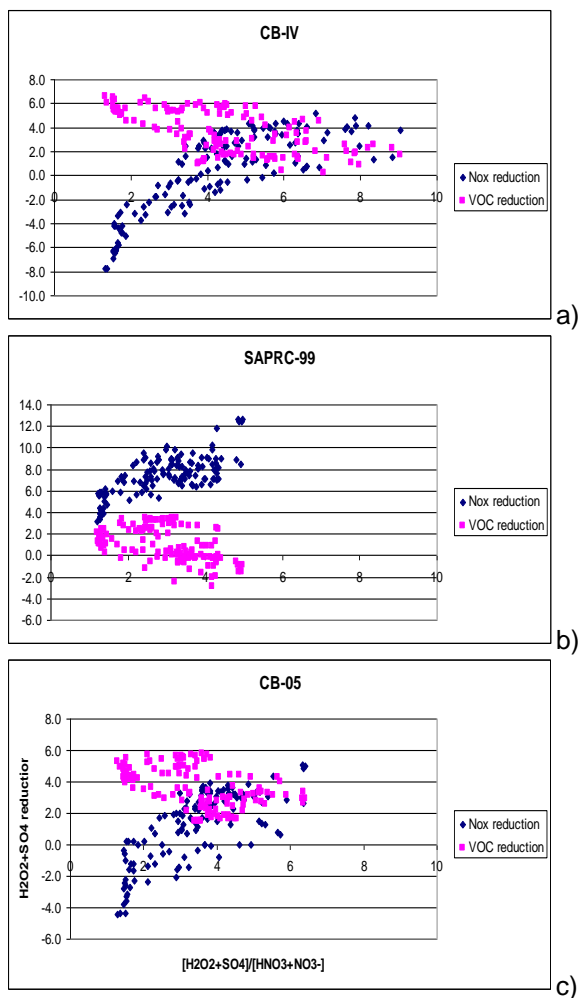
Figure 2. Percentage normalized reduction in $\{[H_2O_2]+[SO_4^{2-}]\}$ concentration as a consequence of either a NO_x or a VOC emission reduction for (a) CB-IV, (b) SAPRC99, and (c) CB-05 chemical mechanisms.

It is noted that the comparisons shown above are made along flight segments over the Northeastern states after the passage of a cold front. Differences in spatial distributions of sulfate productivity were also studied (Figure 3) to highlight the importance of aqueous-phase production. Significant differences in sulfate production paths between CB-IV vs. CB-05 and CB-4 vs. SAPRC99 mechanisms are present along the frontal cloud bands. Each chemical mechanism presents distinctively different sulfate productivity to different oxidation conditions. For the three chemical mechanisms the main oxidation paths for SO_2 are the gas phase OH and the aqueous phase H_2O_2 reactions. However, for the CB-IV mechanism up to 30% of the sulfate formation also occurs through aqueous phase oxidation by Methylhydroperoxide (MHP) from

15:00 to 16:00 PM (figure 3a). Comparison with measured MHP concentrations shows that the model tends to overestimate the levels of MHP by as much as an order of magnitude. Furthermore, for the CB05 and the SAPRC99 mechanisms the SO_2 oxidation mediated by Peroxyacetic acid (PAA) seems account for up to 20% of the sulfate formation from 15:00 to 16:00 PM (figure 3b and c). Comparison of PAA concentrations with measured values indicates that the model tends to overestimate the levels by as much as 4 times the observed values (figure 4). This can be understood in terms of the stoichiometric parameters used to describe the formation of PAA though the reaction of Peroxyacetyl (PA) radical and HO_2. In CB05 and SAPRC99 0.8 and 0.75 PAA molecules are formed for each PA + HO_2 respectively, while for the CBIV mechanism 0.21 PAA are formed.
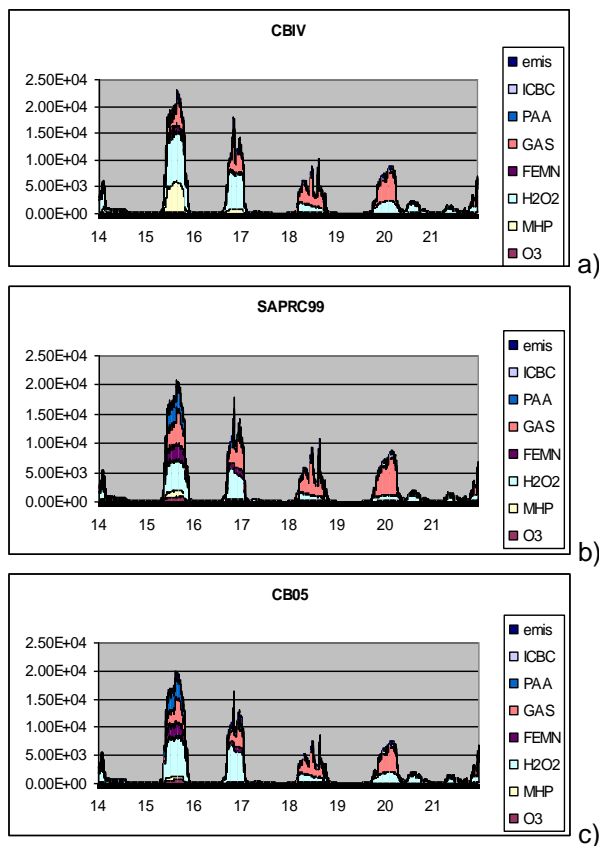

Figure 3. Contribution of sulfate formation paths for (a) CB-IV, (b) SAPRC99, and (c) CB-05 chemical mechanisms along the path of the flight on July 20, 2004. Concentrations units are in mg m⁻³.

3. CONCLUSIONS

This study shows that, despite the close agreement between the measured and simulated sulfate concentrations, each of the three chemical mechanisms presents a different sensitivity response to changes in oxidant levels. The SAPRC99 mechanism generally presents sulfate levels that are NOx sensitive along the path of the flight for the cases analyzed. On the other hand, the CBIV and CB05 show the VOC sensitivity to be dominant for the formation of sulfate.

Different formation pathways are observed among the three chemical mechanisms besides the dominant paths for SO_2 conversion to sulfate that are the aqueous H_2O_2 and gaseous OH oxidation. For the CBIV mechanism, the aqueous phase oxidation via MHP constitutes the third dominant reaction while for SAPRC99 and CB05 the oxidation via PAA dominates.
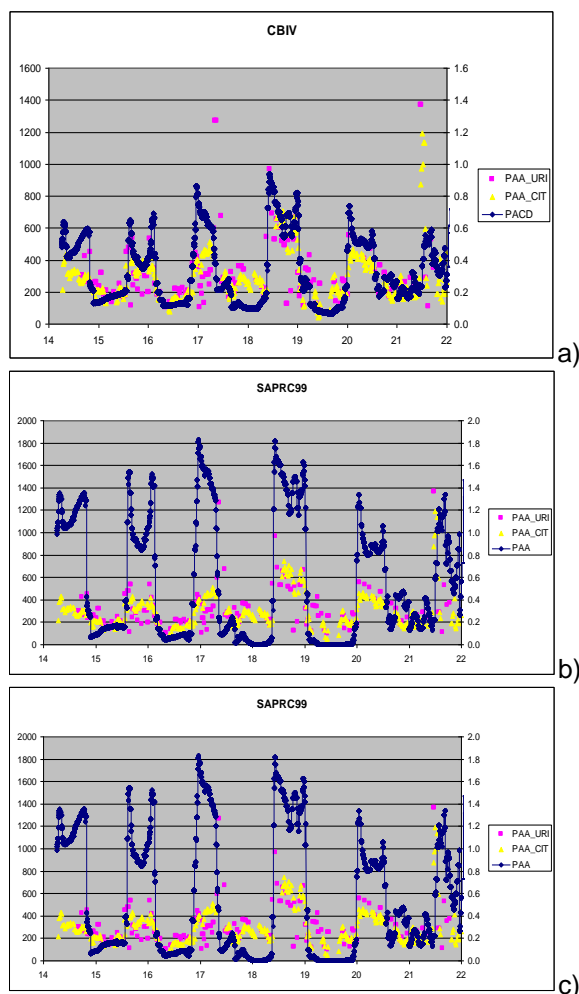

a)

b)

c)

Figure 4. Modeled and measured PAA concentrations for (a) CB-IV, (b) SAPRC99, and (c) CB-05 chemical mechanisms along the path of the flight on July 20, 2004.

4. REFERENCES

Black, T. (1994), The new NMC mesoscale Eta Model: description and forecast examples. *Weather and Forecasting*, 9, 265-278.

Byun, D.W., and K.L. Schere (2006), Review of governing equations, computational algorithms, and other components of the models-3 Community Multiscale Air Quality (CMAQ) modeling system, *Applied Mechanics Review*, 59, 51-77.

Fehsenfeld, F. C., et al. (2006), International Consortium for Atmospheric Research on Transport and Transformation (ICARTT): North America to Europe—Overview of the 2004 summer field study, *J. Geophys. Res.*, 111, D23S01, doi:10.1029/2006JD007829.

Mathur, R. (2008), Estimating the impact of the 2004 Alaskan forest fires on episodic particulate matter pollution over the eastern United States through assimilation of satellite-derived aerosol optical depths in a regional air quality model, *J. Geophys. Res.*, 113, D17302, doi:10.1029/2007JD009767.

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.