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# Sensitivities of sulfate aerosol formation and oxidation pathways on the chemical mechanism employed in simulations

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## Abstract

The processes of aerosol sulfate formation are vital components in the scientific understanding of perturbations of earth's radiative balance via aerosol direct and indirect effects. In this work, an analysis of the influence of changes in oxidant levels and sulfur dioxide oxidation pathways was performed to study the underlying pathways for sulfate formation. Sensitivities of this constituent were calculated from a series of photochemical model simulations with varying rates of $NO_x$ and VOC emissions to produce variations in oxidant abundances using a photochemical model (CMAQ) that covers the Eastern US for the ICARTT 2004 campaign. Three different chemical mechanisms (CBIV, CB05, and SAPRC99) were used to test model responses to changes in $NO_x$ and VOC levels. Comparison of modeled results and measurements demonstrates that the simulations with all three chemical mechanisms capture the levels of sulfate reasonably well. However, the three mechanisms are shown to have significantly different responses in sulfate formation when the emissions of $NO_x$ and/or VOC are altered, reflecting different photochemical regimes under which the formation of sulfate occurs. Also, an analysis of the oxidation pathways that contribute to sulfur dioxide conversion to sulfate reveals substantial differences in the importance of the various pathways among the three chemical mechanisms. These findings suggest that estimations of the influence that future changes in primary emissions or other changes which perturb $SO_2$ oxidants have on sulfate abundances, and on its direct and indirect radiative forcing effects, may be dependent on the chemical mechanism employed in the model analysis.

## 1 Introduction

Since the 1970s, studies of particle sulfate ($SO_4^{2-}$) formation and fate have played a key role in advancing the scientific understanding of diverse phenomena such as acid precipitation, tropospheric particle matter composition, and, more recently, in the role $SO_4^{2-}$ particles play in the direct and indirect forcings of the earth's radiative budget. The study of the formation of $SO_4^{2-}$ aerosols involves a complex coupling among gas- and aqueous-phase photochemical reactions and meteorological processes. Formation of $SO_4^{2-}$ is chemically linked to primary emissions of sulfur dioxide $SO_2$ and to the abundance of atmospheric oxidants such as hydroxyl radical (OH), hydrogen peroxide ($H_2O_2$), ozone ($O_3$), methylhydroperoxide (MHP), and peroxyacetic acid (PAA) (Seinfeld and Pandis, 1998). All of these oxidant species are formed via photochemical reactions which originate from emissions of nitrogen oxides ($NO_x$) and volatile organic compounds (VOC). Therefore, it is expected that variations in primary emissions of $NO_x$ and VOCs may have an effect on the amount and distribution of sulfate (Stein and Lamb, 2002).

The aim of this work was to investigate the dependency of sulfate formation on oxidant levels and on the choice of the chemical mechanism employed to describe the processes by which these oxidants are produced. Towards that end, we present simulated $SO_4^{2-}$ concentrations calculated using a three-dimensional regional air quality model with three different photochemical mechanisms and compare results with airborne in situ measurements. Changes in the levels of primary emitted $NO_x$ and VOC were then introduced for each mechanism to understand the responses of sulfate formation processes to variations in $SO_2$ oxidant levels. In addition, an oxidation partitioning analysis was performed to delineate the main oxidation pathways participating in the conversion of gas-phase $SO_2$ to particle $SO_4^{2-}$ for each chemical scheme.

## 2 Model and measurements

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 the 14–23 July, 2004, corresponding to the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) field campaign (Fehsenfeld, et al., 2006). The





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model configuration included 3-D advection, cloud processes, gas and aqueous chemistry, cloud scavenging and wet and dry deposition. Three different chemical mechanisms were used to test model responses to changes in $NO_x$ and VOC levels, namely CBIV (Gery et al., 1989), CB05 (Yarwood et al., 2005), and SAPRC99 (Carter, 2000). The model domain covered the Eastern US with a horizontal resolution of 12 km and 22 vertical layers of variable thickness. The meteorological data used to drive CMAQ for this study was based on Eta model (Black, 1994) output. Emissions include point, mobile, area, and biogenic sources (Mathur, 2008).

The measurements used for this study from the ICARTT field campaign were obtained from www.air.larc.nasa.gov/cgi-bin/arcstat. Results for the 18, 20, and 22 July, 2004, along the path of the DC8 flight have been utilized in this analysis. Since the aim of this study is focused on sulfate formation, only species relevant to its formation have been included in the comparison. A more complete chemical comparison of CMAQ model results with ICARTT measurements can be found elsewhere (Yu et al., 2010).

Sulfate-$NO_x$-VOC sensitivities were calculated from a series of photochemical model simulations with varying rates of $NO_x$ and VOC emissions to produce responses in oxidant abundances. For each chemical mechanism three simulations were performed: a base case simulation, a simulation with 35 % reduction in anthropogenic $NO_x$ emissions, and a simulation with 35 % reduction in anthropogenic VOC emissions.

## 3 Discussion

Comparison of base case model results and measurements demonstrates that all three chemical mechanisms capture the levels of $H_2O_2$, $SO_4^{2-}$ and total nitrate (nitric acid/nitrate) ($HNO_3/NO_3^-$) within 50 % for the 20 July, 2004 (Fig. 1). (All results presented in this work for the 20 July are representative of similar results obtained for the 18 and 22 July, which are not shown for brevity.) These results are consistent with the model comparisons performed by Yu et al. (2010) for the same dataset. In particular, it is important to notice that all three chemical mechanisms show a very similar performance with regard to fine particle sulfate, with the largest differences occurring in the boundary layer where concentrations are highest. At their largest, the differences in sulfate between the mechanisms are less than 20 %. A sensitivity analysis and an $SO_2$ oxidant partitioning study were undertaken to investigate whether or not the three mechanisms form these similar sulfate concentrations via similar underlying processes.

In order to analyze the response of sulfate levels to changes in primary emissions of $NO_x$ and VOCs, Stein and Lamb (2002) proposed the use of a combination of afternoon concentrations of $HNO_3$, $H_2O_2$, and $SO_4^{2-}$ as "indicator species" of ambient "potential" $SO_4^{2-}$-VOC-$NO_x$ sensitivities, where potential sulfate is defined here, after Stockwell (1994), as $[SO_4^{2-}]$ + $[H_2O_2]$. The link between the indicator ratio (defined as $\{[H_2O_2]+[SO_4^{2-}]\}/\{[HNO_3]+[NO_3^-]\}$ and hereafter denoted as $I_{SO4}$) and $NO_x$-VOC chemistry can be understood in terms of the dominant sinks and sources for odd-hydrogen. A $NO_x$-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, larger values of $I_{SO4}$ are associated with $NO_x$-sensitive conditions while smaller values for the indicator are associated with VOC sensitive regimes.

Figure 2 presents the normalized percentage reduction in $\{[H_2O_2]+[SO_4^{2-}]\}$ (i.e., potential sulfate) concentration as a consequence of either a $NO_x$ or a VOC emission reduction for each chemical mechanism along the path of the DC8 flight for the 20 July, 2004. The change in potential sulfate is plotted as a function of the simultaneously measured $I_{SO4}$, $\{[H_2O_2]+[SO_4^{2-}]\}/\{[HNO_3]+[NO_3^-]\}$. As seen in Fig. 2, the three chemical mechanisms exhibit markedly different responses in potential sulfate formation when emissions of $NO_x$ and VOC are altered; these differing responses reflect different photochemical regimes under which the formation of sulfate occurs with the three chemical mechanisms. Therefore, for a given change in oxidation conditions, (i.e. changes in solar radiation, seasons, primary emissions, etc.) the three chemical mech-





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anisms will produce substantially different responses in sulfate formation. In particular, the SAPRC99 chemical mechanism shows that reductions in $NO_x$ are more effective in reducing $H_2O_2$+$SO_4^{2-}$ than are reductions in VOCs, suggesting that the preferential odd hydrogen sink seems to be the formation of $H_2O_2$. On the other hand, results using CBIV show that $H_2O_2$+$SO_4^{2-}$ will be reduced more effectively if VOCs are reduced, revealing that the formation of total nitrate constitutes the main sink for odd hydrogen species. This result is consistent with the fact that CBIV tends to overestimate concentrations of $H_2O_2$ (Fig. 1c), thereby artificially increasing the $I_{SO4}$ levels. Finally, the CB05 chemical mechanism exhibits an intermediate behavior somewhere between the other two mechanisms.

Theoretical, as well as model-derived, estimates of the threshold value of $I_{SO4}$ for the transition from VOC to $NO_x$ sensitivity in the formation of potential sulfate were derived by Stein and Lamb (2002) to range from 1.4 to 2.2. In that work, the SAPRC99 chemical mechanism was used and the period of study was from 14–16 July, 1995, covering the Eastern US. Figure 2b shows that when SAPRC99 is used, although no points are simulated to be VOC sensitive for this particular day, the indicator transition seems to be in agreement with the estimated values from Stein and Lamb (2002). Indeed, for the 18 and 22 July, 2004, the model suggests transition values of around 1.2. On the other hand, Fig. 2a and c shows that the transition has approximate values of 7 and 5 for the CBIV and the CB05 chemical mechanisms, respectively.

The main chemical processes that drive behavior of the $SO_4^{2-}$-VOC-$NO_x$ sensitivities for the three chemical mechanisms are expected to be the gas-phase oxidation by OH and the aqueous-phase oxidation mediated by $H_2O_2$ while other oxidants are expected to play a minor role (Seifeld and Pandis, 1998). To determine the importance of the different formation pathways, the sulfate tracking diagnostic model configuration included in CMAQ (Mathur et al., 2008) was employed. Significant differences in sulfate production chemical pathways are observed to be present between the CBIV, CB05, and SAPRC99 mechanisms (Fig. 3). In general, for all three chemical mechanisms, oxidation pathways for $SO_2$ are dominated by the gas-phase OH and the aqueous-phase

$H_2O_2$ reactions. However, for the CBIV mechanism, up to 30 % of sulfate formation occurs through aqueous phase oxidation by methylhydroperoxide (MHP) from 15:00 to 16:00 p.m. (Fig. 3a). Comparison with measured MHP concentrations shows that the model (using CBIV) tends to overestimate levels of MHP by as much as an order of magnitude (not shown). Furthermore, for the CB05 and the SAPRC99 mechanisms, the aqueous $SO_2$ oxidation pathway mediated by peroxyacetic acid (PAA) accounts for up to 20 % of the sulfate formation from 15:00 to 16:00 p.m. (Fig. 3b, c). Comparison of PAA concentrations with observed values indicates that the model (using CB05 or SAPRC-99) tends to overestimate the levels of PAA by as much as 4 times the observed values (Fig. 4). This can be understood in terms of the stoichiometric parameters used to describe the formation of PAA though the reaction of peroxyacetyl radical (PA) 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 only 0.21 PAA are formed.

## 4 Conclusions

This study illustrates that, despite the close agreement between the observed and simulated sulfate concentrations, each of the three chemical mechanisms presents a different sensitivity response of sulfate formation to changes in oxidant levels. The SAPRC99 mechanism generally presents sulfate levels that are $NO_x$ sensitive along the path of the flights for the cases analyzed. On the other hand, CBIV and CB05 show VOC sensitivity to be dominant for the formation of sulfate. In addition, beyond the dominant pathways for $SO_2$ to sulfate conversion (aqueous $H_2O_2$ and gaseous OH oxidation), different secondary sulfate formation pathways are simulated among the three chemical mechanisms. For CBIV, the aqueous phase oxidation via MHP constitutes the third dominant reaction while for SAPRC99 and CB05 aqueous oxidation via PAA dominates.

These findings imply that good agreement between measured and modeled concentrations is a necessary but not a sufficient condition for an accurate depiction of sulfate





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chemical formation processes. Indeed, recent studies (e.g., Goto et al., 2011) highlight the importance of an accurate description of sulfate formation chemical pathways, in particular in global aerosol models. The more detailed formulation of sulfate chemical processes presented in Goto et al. (2011) showed an improvement in simulation performance when compared with observations and revealed a difference of approximately 50 % in the estimated radiative forcing with respect to the very simplified approaches generally utilized in the global simulations included in the IPCC-AR4 report. However, as shown in the present work, simulations of sulfate may agree with the measured values despite the use of completely different chemical mechanisms and consequent differing formation pathways. Our analysis of the influence of changes in oxidant levels and $SO_2$ oxidation pathways strongly suggests that the choice of chemical mechanism may produce noticeable differences in sulfate distributions given changes in primary emissions of $NO_x$ or VOCs, or given some other change which affects the amount or relative concentrations of $SO_2$ oxidants. This implies that estimations of the influence of future changes in emissions on sulfate levels, and therefore on its direct or indirect radiative forcing effects, may be highly dependent on the chemical mechanism employed in the model analysis. Further research is needed to establish the extent of influence of these findings in a global-scale modeling framework and to determine what impacts of these sensitivities may be potentially propagated to long-term climate scenario analyses.

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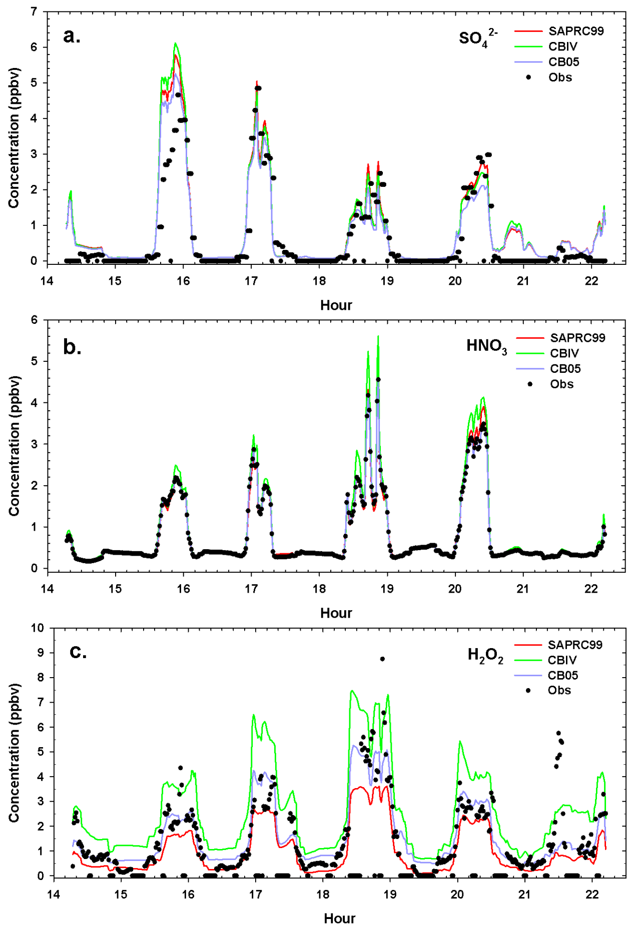


**Fig. 1.** Comparison of modeled vs. observed **(a)** $PM_{2.5}$ sulfate; **(b)** total nitrate; and, **(c)** hydrogen peroxide concentrations along the path of the DC8 flight on 20 July, 2004.





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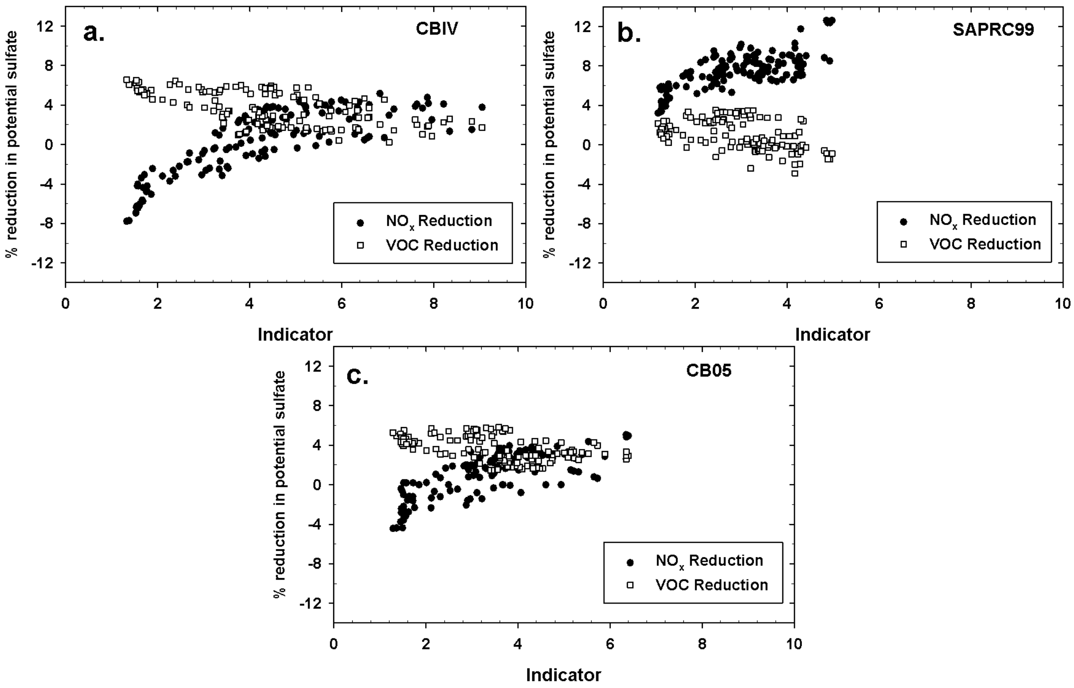


**Fig. 2.** Normalized percentage response of potential sulfate concentrations to changes in $NO_x$ and VOC as a function of $I_{SO4} = \{[H_2O_2]+[SO_4^{2-}]\}/\{[HNO_3]+[NO_3^-]\}$ for **(a)** CBIV; **(b)** SAPRC99; and, **(c)** CB05.

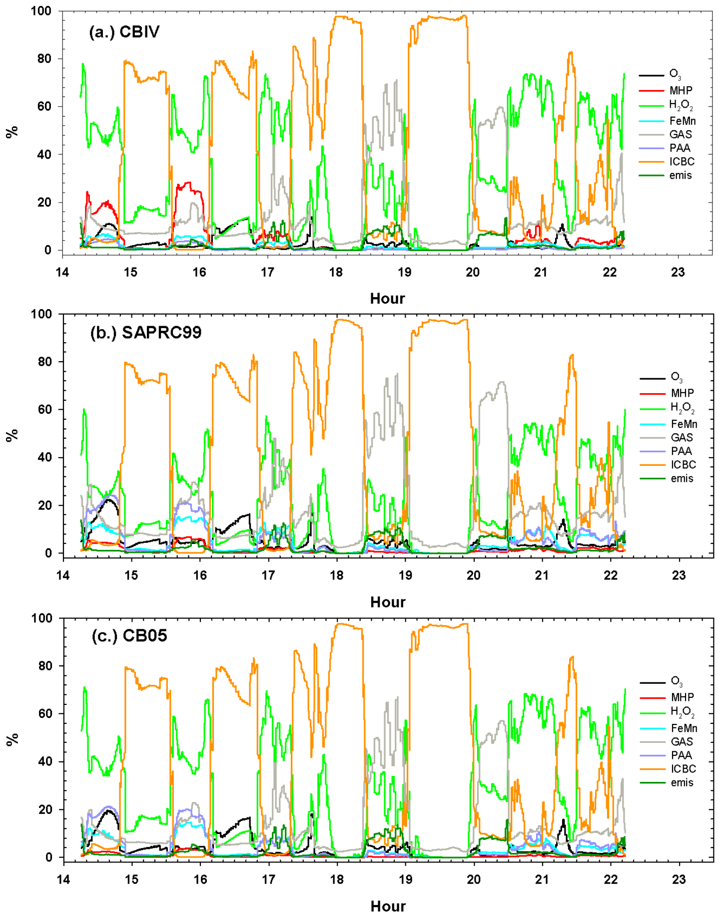


**Fig. 3.** Percent contribution of sulfate formation pathways to total sulfate for **(a)** CBIV, **(b)** SAPRC99, and **(c)** CB05 along the path of the flight of the DC8 on 20 July, 2004.





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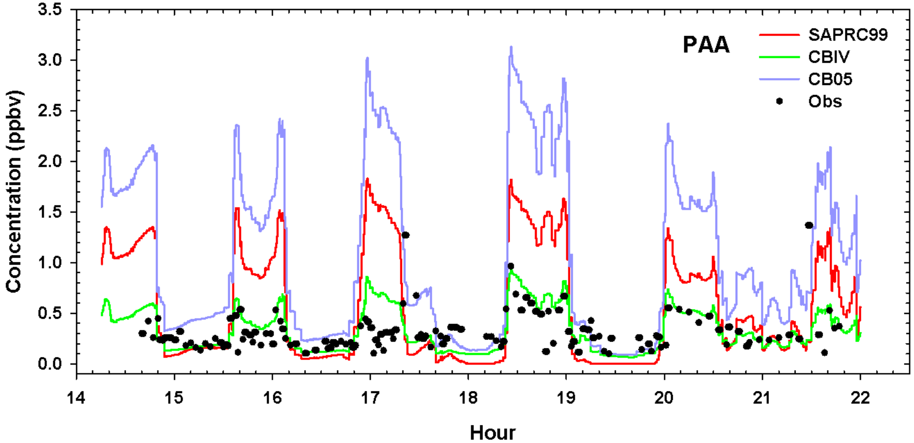


**Fig. 4.** Comparison of modeled and observed PAA concentrations for CBIV, SAPRC99, and CB05 along the path of the flight of the DC8 on 20 July, 2004.





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