



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 part of 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 concentrations. 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 amount 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 concentrations.

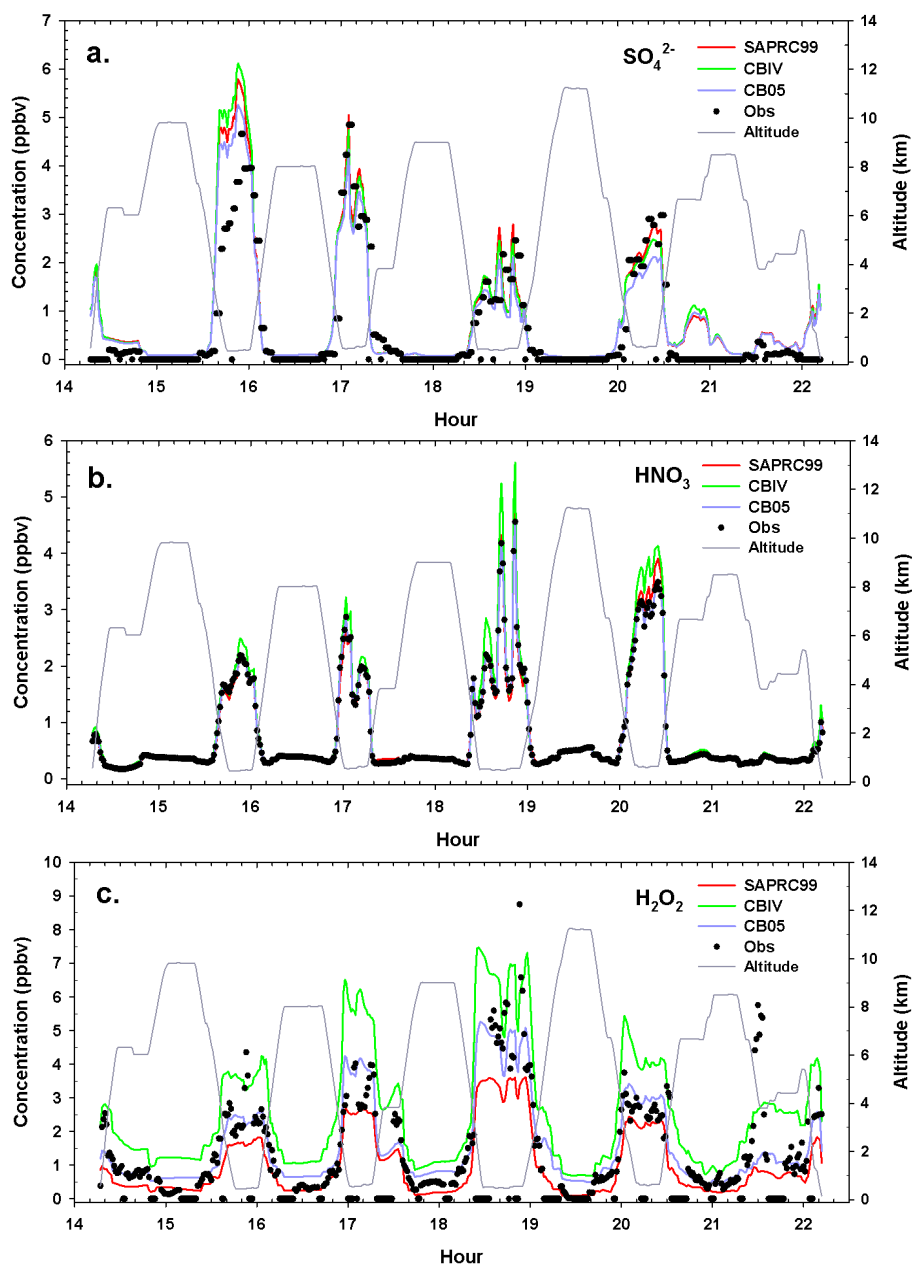


Fig. 1. Comparison of modeled vs. observed (a) $\text{PM}_{2.5}$ sulfate; (b) total nitrate; and, (c) hydrogen peroxide concentrations along the path of the DC8 flight on 20 July 2004.

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 14–23 July 2004.

This modeling period encompasses three flights that took place on 18, 20, and 22 July 2004, corresponding to a portion of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) field campaign (Fehsenfeld et al., 2006). The flight patterns corresponding to the study period have been described in Singh et al. (2006). The 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

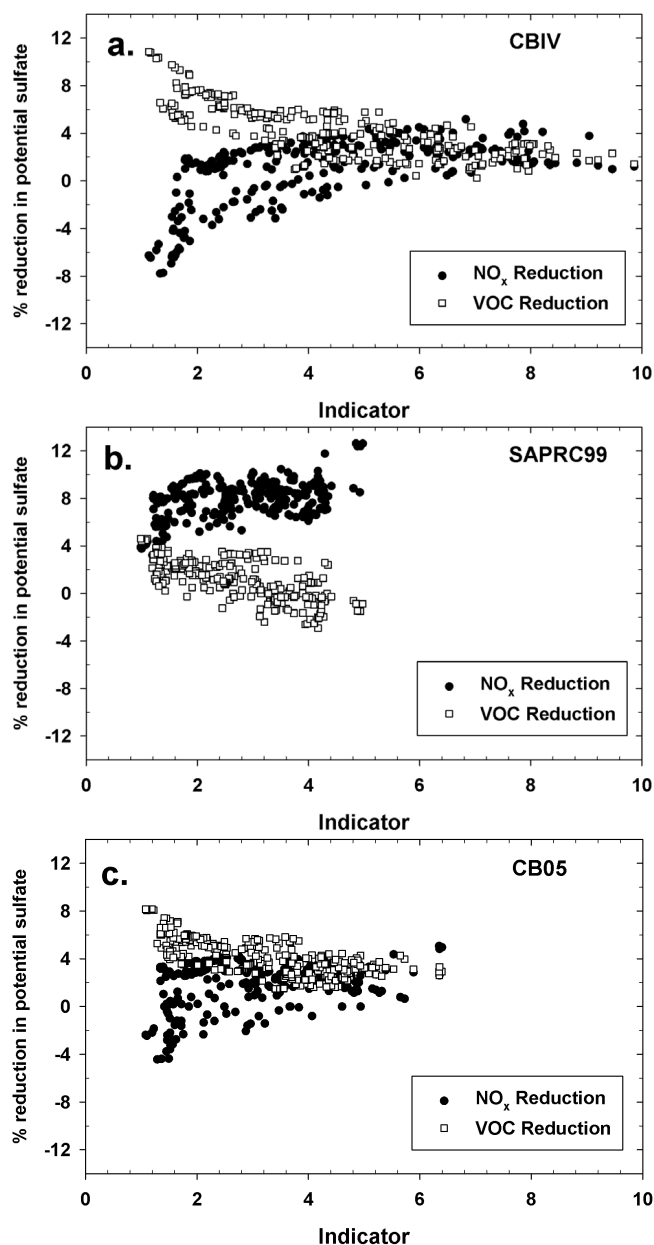


Fig. 2. Normalized percentage response of potential sulfate concentrations to changes in NO_x and VOC as a function of $I_{\text{SO}_4} = \frac{[\text{H}_2\text{O}_2] + [\text{SO}_4^{2-}]}{[\text{HNO}_3] + [\text{NO}_3^-]}$ for (a) CBIV; (b) SAPRC99; and, (c) CB05 for data along the path of the DC8 flight on 18, 20, and 22 July 2004.

VOC emission rates, namely CBIV (Gery et al., 1989), CB05 (Yarwood et al., 2005), and SAPRC99 (Carter, 2000). The aerosol calculation is based on the ISORROPIA v1.7 model (Nenes et al., 1998) and the aqueous phase simulation includes uptake of gases into the cloud droplets, aqueous oxidation of SO_2 by H_2O_2 , O_3 , MHP, PAA, and catalytic oxidation by iron and manganese (Binkowski and Roselle, 2003) and wet scavenging. The model domain covered the East-

ern US with a horizontal resolution of 12 km and 22 vertical layers of variable thickness. The meteorological data for this study was based on Eta model (Black, 1994) outputs linked to the CMAQ modeling system using the methodology described in Otte et al. (2005). Emissions include point, mobile, area, and biogenic sources (Mathur, 2008). The area emissions are based on the 2001 National Emissions Inventory. Emissions of SO_2 and NO_x from point sources were projected from 2001 to 2004 based on the Department of Energy's 2004 Annual Energy Outlook. Mobile sources were estimated based on the MOBILE6 model (Pouliot and Pierce, 2003) and biogenic emissions were calculated with the BEIS3.12 model (Pierce et al., 2002).

The measurements used for this study from the ICARTT field campaign were obtained from <http://www-air.larc.nasa.gov/cgi-bin/arcstat>. Results for 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 NO_x and VOC emission rates 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 boundary layer H_2O_2 , SO_4^{2-} and total nitrate (nitric acid/nitrate) ($\text{HNO}_3/\text{NO}_3^-$) within 50 % for 20 July 2004 (Fig. 1). (All results presented in this work for July 20 are representative of similar results obtained for July 18 and 22, 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 %. The similar sulfate concentrations obtained with the three different chemical mechanisms suggest that oxidant-limited conditions (i.e. the SO_2 oxidation is limited by the oxidant availability) prevailed during the study period. Therefore, 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.

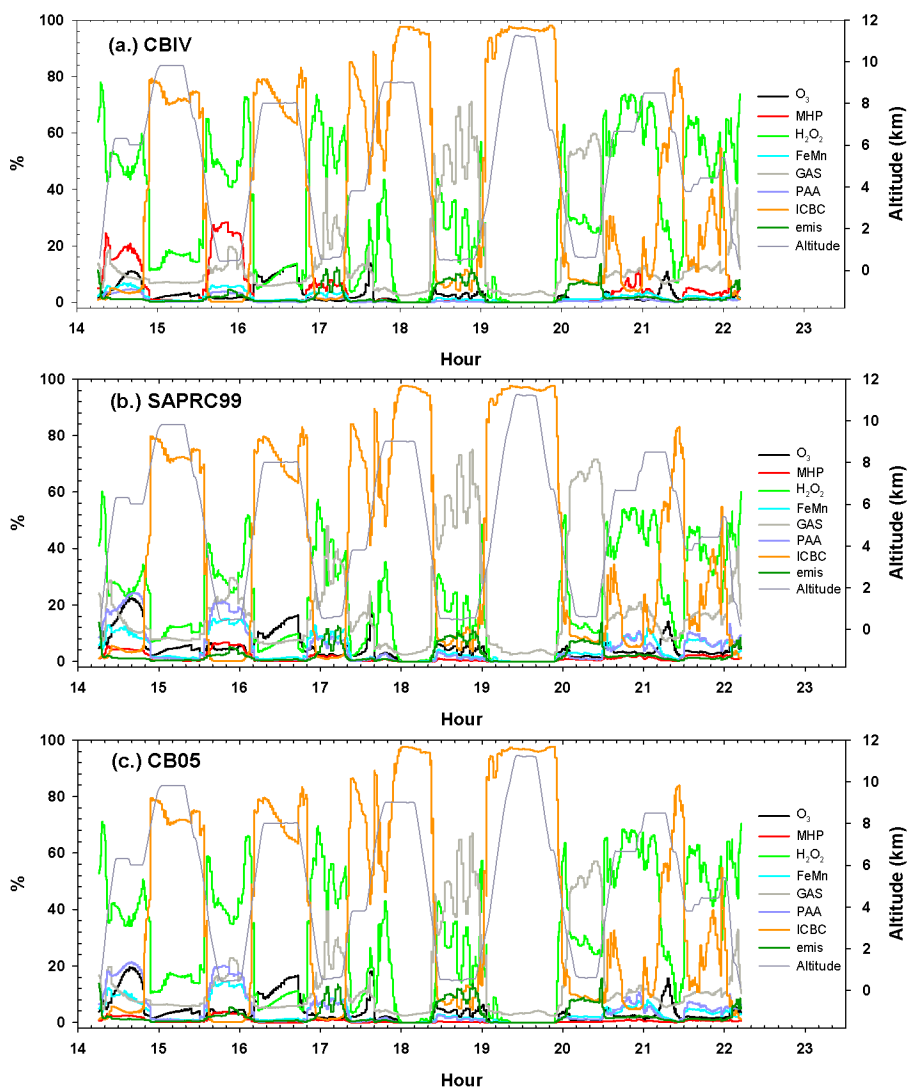


Fig. 3. Percent contribution of sulfate formation pathways to total sulfate for (a) CBIV, (b) SAPRC99, and (c) CB05 along the path of the flight of the DC8 on 20 July 2004. In the legend: ICBC stands for initial conditions and boundary conditions.

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 $[\text{SO}_4^{2-}] + [\text{H}_2\text{O}_2]$. The concept of potential sulfate was first proposed by Stockwell et al. (1988) and can be interpreted as the maximum concentration of SO_4^{2-} that could be produced in the gas and aqueous phases. This idea provides an integrated tool to deal with this complex chemical system. The link between the indicator ratio (defined as $\frac{[\text{H}_2\text{O}_2] + [\text{SO}_4^{2-}]}{[\text{HNO}_3] + [\text{NO}_3^-]}$ and hereafter denoted as I_{SO_4}) and NO_x -VOC chemistry can be understood in terms of the dominant sinks and sources for odd-hydrogen. A NO_x -sensitive regime, defined as the chemical conditions

conducive to a stronger decrease in potential sulfate as a result of a NO_x reduction when compared with the same reduction in VOC (see Sillman, 1995 and Stein and Lamb, 2002), 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 and the gas-phase SO_2 oxidation is favored over the formation of HNO_3 . On the other hand, the VOC-sensitive regime, featuring a reduction in potential sulfate when reducing VOC and an increase in potential sulfate as NO_x is lowered, is characterized by a higher production rate of HNO_3 that overwhelms the formation of potential sulfate. Therefore, larger values of I_{SO_4} 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 $\frac{[\text{H}_2\text{O}_2] + [\text{SO}_4^{2-}]}{[\text{HNO}_3] + [\text{NO}_3^-]}$ (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 flights for 18, 20, and 22 July 2004. The difference in potential sulfate levels between the base case and the NO_x and VOC reduction scenarios is plotted as a function of the simultaneously modeled I_{SO_4} , $\{[\text{H}_2\text{O}_2]+[\text{SO}_4^{2-}]\}/\{[\text{HNO}_3]+[\text{NO}_3^-]\}$. Although each particular chemical mechanism shows a distinct response to NO_x and VOC changes, the shape of the sensitivity curves depicted in Fig. 2 share some common general features arising from the sensitivity of HO_x to changes in NO_x levels for all the chemical mechanisms. Each curve shows that for relative low values of I_{SO_4} (i.e. less than approximately 4, 1, and 3 for CBIV, SAPRC-99, and CB05, respectively) the potential sulfate concentrations tend to decrease when VOC levels are reduced and tend to increase when a reduction in NO_x levels occurs. This is, by definition, a VOC sensitive regime. Under these conditions, lowering VOC in the photochemical system will reduce HO_x producing less H_2O_2 . Furthermore, a reduction in NO_x increases the availability of HO_x , that otherwise will form HNO_3 , to form peroxides instead, therefore increasing the potential sulfate.

Even though VOC sensitive conditions exist for the three mechanisms, when comparing Fig. 2a, b, and c it can be observed that the range indicator values for which VOC conditions prevail differ among the mechanisms with I_{SO_4} values lower than about 4, 1, and 3 for the CBIV, SAPRC-99, and CB05 chemical mechanisms, respectively. Differences in these values cannot be attributed to a single component of the chemical mechanisms but to a complex interrelation among the radical cycles depicted by each mechanism. For instance, the increasingly higher formation rate of H_2O_2 from the SAPRC-99, CB05, and CBIV mechanisms (Luecken et al., 2008) explains the higher simulated H_2O_2 . Since in the CBIV mechanism the formation of H_2O_2 is the only sink of HO_2 a decrease in NO_x will free up more HO_x that will directly form even more H_2O_2 . In CB05 and SAPRC-99, on the other hand, the formation of organic peroxides diverts HO_2 from forming H_2O_2 , leading to less potential sulfate formation. The three chemical mechanisms give a more convergent picture when modeling HNO_3 , with the CBIV mechanism producing slightly more than the other two. SAPRC-99 and CB05 produce similar HNO_3 levels (Fig. 1b) because in SAPRC-99 the reaction rate for the formation of HNO_3 is lower but the OH levels are higher than in CB05 (Luecken et al., 2008). Therefore, when combining the increasingly higher H_2O_2 peroxide formation from CBIV, CB05 and SAPRC-99 with a small variation in the HNO_3 among the three mechanisms we end up with increasingly higher values of I_{SO_4} . Indeed, the linear regression coefficient of the I_{SO_4} calculated with the three chemical mechanisms against measurements shows values of 1.15, 0.79, and 0.89 for CBIV, SAPRC-99 and CB05, respectively.

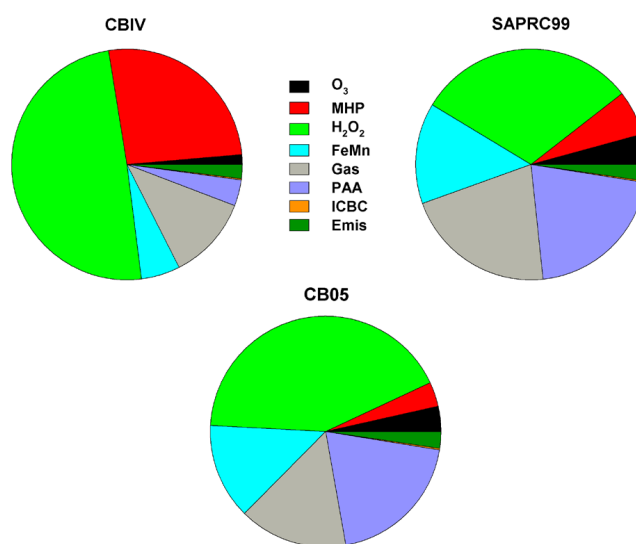


Fig. 4. Pie chart showing the percent contribution of sulfate formation pathways to total sulfate for CBIV, SAPRC99, and CB05 on 20 July 2004 at 15:45.

Conversely, for I_{SO_4} values higher than 7, 2, and 5 for CBIV, SAPRC-99 and CB05, respectively, the curves in Fig. 2 show features corresponding to NO_x sensitive conditions, i.e. potential sulfate is reduced more when NO_x levels are reduced than when VOC are. Differences in the VOC speciation and more reactivity of the aromatic fragments (Faraji et al., 2008) can help explain why the SAPRC-99 mechanism tends to show more NO_x -sensitivity than the CB05 and CBIV. In SAPRC-99, the relative higher abundance of reactive VOC species with respect to NO_x leads to VOC saturated conditions. Under these conditions, a reduction in NO_x slows down the cycling between HO_2 and OH lowering the formation of potential sulfate (Stein and Lamb, 2002).

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 mechanisms 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 $\text{H}_2\text{O}_2+\text{SO}_4^{2-}$ than are reductions in VOCs. On the other hand, results using CBIV show that $\text{H}_2\text{O}_2+\text{SO}_4^{2-}$ will be reduced more effectively if VOCs are reduced. Finally, the CB05 chemical mechanism exhibits an intermediate behavior somewhere between the other two mechanisms but with closer similarities to CBIV given their common formulation.

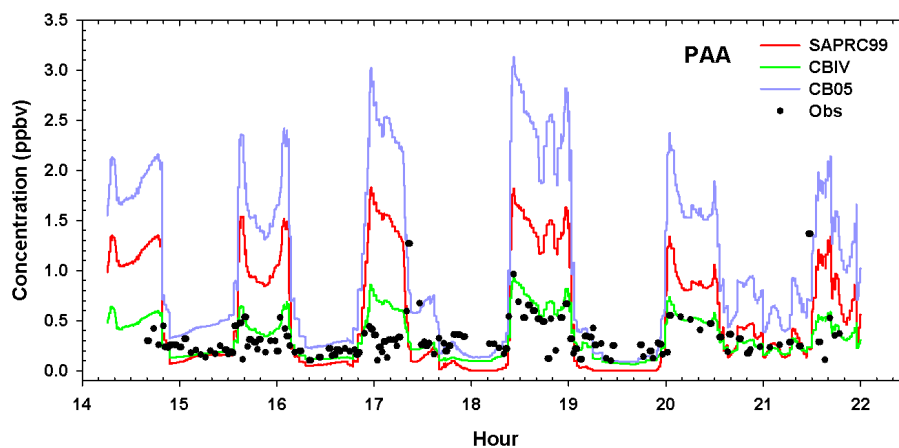


Fig. 5. Comparison of modeled and observed PAA concentrations for CBIV, SAPRC99, and CB05 along the path of the flight of the DC8 on 20 July 2004.

Theoretical, as well as model-derived, estimates of the threshold value of I_{SO_4} 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, the indicator transition seems to be in agreement with the estimated values from Stein and Lamb (2002). 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 (Seinfeld 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 15:30 to 16:00 p.m. (Figs. 3a and 4). 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 15:30 to 16:00 p.m. (Figs. 3b, c and 4). 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. 5). This can be understood in terms of the stoichiometric parameters used to describe the formation of PAA through the reaction of peroxyacetyl radical (PA) and HO_2 . In CB05 and SAPRC-99, 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. When interpreting these results it has to be taken into account that CBIV, CB05, and SAPRC-99 are condensed mechanisms that have originally been developed to model ozone concentrations and its precursors (mostly focused on hydrocarbons and NO_x) by replicating smog chamber experiments. The use of lumping techniques to condense the complex atmospheric processes into these chemical mechanisms produces reasonably good representations of the ozone formation (Carter, 2010). However, the description of the formation of other species, like PAA, does not appear to be as accurate.

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 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 SO₂ 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 SO₂ 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. Giving the limited time and space scales examined in the present study, 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.

An additional conclusion that can be drawn from this work is one which is well known among three-dimensional atmospheric chemistry modelers in the context of tropospheric ozone simulation, namely that the right answer can be obtained for the wrong reasons. In other words, compensating errors within the modeling framework can lead to results which compare well with measurements, but the model errors can remain hidden unless the right measurement-model comparisons are undertaken. In this work, we have identified a potential source of compensating errors in the simulation of fine particle sulfate. Further research is necessary to understand the full implications of this finding.

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