

Modeled Role of Heterogeneous Chemistry in Regional Sulfate Formation

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Summary

Models of aerosol sulfate formation must include two primary chemical pathways. One involves the homogeneous oxidation of SO₂ in the gas phase through reaction with OH. This is the mechanism that is believed to be most prevalent because it is active as long as sufficient sunlight is available. The other reaction of importance is the heterogeneous reaction of SO₂ in aqueous solution with ozone and/or peroxides. To be active, this mechanism requires the presence of a solution particle, either as a hygroscopic haze aerosol or cloud droplet. The second mechanism is only important when and where atmospheric water vapor levels are very high. Thus, a larger volume of the atmosphere is normally available for sulfate formation by way of the homogeneous mechanism. A confounding factor, however, in determining the relative importance of these two mechanisms is their relative oxidation rates. The homogeneous mechanism is relatively slow compared to other gas-phase reactions. By comparison, the heterogeneous reaction can be very fast and efficient. The latter is true, in part, because SO₂ and peroxides are highly water soluble. This paper presents the results of a study into the relative roles of the homogeneous and heterogeneous mechanisms as represented in an atmospheric model.

Research Approach – An atmospheric chemistry model developed at the Georgia Institute of Technology, referred to as the URM-1ATM model, is the vehicle used to investigate the relative role of heterogeneous sulfate formation. This model was developed to study the relationships between pollutant emissions and atmospheric levels of ozone, aerosols and wet deposition cations and anions. The model is well suited for this analysis because it simulates all the necessary chemistry. The model uses the SAPRC set of chemical reactions and the Reactive Scavenging Model (RSM), the latter originally developed for use during NAPAP (National Acid Precipitation Assessment Program). Aerosol dynamics are modeled explicitly for discrete particle size bins. The aqueous-phase chemistry in non-precipitating particles is computed using the same chemical reactions simulated in RSM for precipitating clouds.

The roles of the two SO₂ oxidation pathways were examined through a series of model simulations in which different mechanisms were activated. For a given episode, one simulation was made with all the chemical modules activated. Another simulation was made with the RSM (homogeneous chemistry and precipitation scavenging) deactivated. A third simulation was made with both the RSM and the non-precipitating heterogeneous chemistry deactivated. A comparison between results from the first and second simulations provided information on the contribution of precipitation systems to sulfate formation and deposition. A comparison between the first and third simulations yielded information on the incremental role played by the non-precipitating clouds and haze particles in sulfate formation.

Model Simulation of Cloud Cover – An understanding of the role of clouds must first examine how well clouds are simulated. This work has been done, but a detailed description of such an analysis is beyond the scope of this paper. Four modeling episodes were examined to determine the model's ability to reproduce cloud cover. These multi-day episodes occurred in April-May 1995, June 1992, August 1993 and July 1995, and represent a range of cloudiness and precipitation. Cloud observations were acquired for 14 National Weather Service (NWS) ground stations within the finest (12 km) modeling grid. One of the parameters routinely observed is the fractional cloud cover (FCC). FCC has values ranging from zero (for no clouds) to 10 tenths (complete overcast) with one-tenth increments in between. A similar parameter was determined in the vicinity of each model grid cell containing a NWS station. Modeled FCC was then compared with observed FCC values for each location.

This comparison revealed that the URM-1ATM, coupled with the RAMS meteorological model, produced realistic hourly grid-averaged FCC for each of the episodes. However, the model performed poorly when its FCC values were paired with

NWS data in space and time. Hence, the relative importance of sulfate oxidation mechanisms may not be accurately identified by the model at specific locations, but should be fairly well represented when averaged over the grid.

Heterogeneous vs. Homogeneous Sulfate Formation – The influence of precipitation on sulfate levels can be quite pervasive. Precipitation scavenging of both SO₂ and sulfate aerosol can not only influence sulfate levels during the hours that precipitation occurs but during subsequent hours at downwind locations. For this reason, this analysis restricted itself to examining only those grid cells for which the precipitation influence was judged to be very small. In over 90 percent of the time the presence of precipitating clouds reduced sulfate below what it otherwise would have been. Thus, for these cloud systems scavenging was dominant over in-cloud heterogeneous sulfate production, producing a net reduction in sulfate aerosol concentrations.

The ratio of sulfate produced homogeneously to total sulfate, R_{ho} , was computed for grid cells not significantly impacted by precipitation. R_{ho} was determined for each hour at every grid cell within a model subdomain centered on the southern Appalachians. The fraction of total possible grid cells used for this calculation varied widely among the episodes. The two episodes with the most precipitation (June 1992 and August 1993) only had <10% of the grid cells available. The two driest episodes had over 50% of the grid cells available. This variability was also influenced in part by the winds that occurred. Episodes with strong winds are more likely to see a precipitation influence transported outside the region of interest.

Overall, R_{ho} was highest, 76%, for the rainy August 1993 episode. This is a direct consequence of the prevalent precipitation scavenging that occurred. Grid cells were classified according to their computed sulfate concentrations: “low,” “medium” and “high.” Nearly 80% of the grid cells examined for the August 1993 episode fell into the low sulfate category.

The April 1995 episode, which was not very productive for sulfate, had the second highest value for R_{ho} (57%) and over 80% of its analyzed grid cells were in the low sulfate category. R_{ho} was near 35% for both the July 1995 and June 1992 episodes, even though the former was extremely dry and the latter had some rainy periods. Both had over half of their analyzed grid cells in the “high” sulfate category. Thus, homogeneous sulfate production was very important for these two periods.

In general, the low sulfate cells had the smallest relative contribution (~30%) from heterogeneous sulfate formation. Heterogeneous chemistry accounted for roughly 60% of the sulfate in medium sulfate cells. In high sulfate cells the cloud influence was dominant (>75%). The average relative contribution of heterogeneous sulfate formation was about 50% across all episodes, but ranged from an episodic low of 24% to a high of 67%.

Summary – Model results for four episodes were analyzed to determine the role of heterogeneous sulfate formation. The focus was on areas that were relatively unaffected by precipitation. The role of heterogeneous chemistry varied greatly according to the meteorological circumstances. Heterogeneous oxidation produced less than a quarter of the sulfate during a rainy summer period, but two-thirds of the sulfate during an extremely dry summer period. Regions modeled to have low sulfate levels were less likely to have active heterogeneous chemistry than areas computed to have high sulfate. Overall, heterogeneous sulfate formation accounted for about half of the total sulfate produced.