THE SENSITIVITY OF AEROSOL SULFATE TO CHANGES IN NITROGEN OXIDES AND VOLATILE ORGANIC COMPOUNDS

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1.0 INTRODUCTION

Traditionally, strategies to control sulfate formation have been focused on the response of sulfate (SO$_4^{2-}$) to reductions in sulfur dioxide (SO$_2$) emissions [e.g. Shin and Carmichael, 1992]. Much less attention has been devoted to assessing the effects on sulfate formation arising from changes in emissions of volatile organic compounds (VOC) and nitrogen oxides (NO$_x$), the chemical families largely responsible for the generation of the tropospheric ozone (O$_3$) and the oxidants needed to transform SO$_2$ to SO$_4^{2-}$. The response of ambient sulfate to reductions in NO$_x$ and VOC emissions depends in part on the resulting changes in oxidant levels and the competition that naturally exists between in-cloud (via hydrogen peroxide) and clear-air (via hydroxyl radical) SO$_2$ oxidation. Coupling of the different chemical families leads to complex and potentially non-linear behavior with non-intuitive consequences (Stein and Lamb, 2000).

2.0 SO$_4^{2-}$ SENSITIVITY TO NO$_x$ AND VOC

The idea of “potential” sulfate can be utilized to study the combined response of aqueous- and gas-phase sulfate formation to changes in NOx and VOC emissions using one conceptual species only. Potential sulfate, defined as the sum of ambient sulfate (i.e. total sulfate) and hydrogen peroxide (H$_2$O$_2$) [Stockwell, 1994], can be interpreted as the maximum concentration of SO$_4^{2-}$ that could be produced in the gas and aqueous phases. The usefulness of potential sulfate as a surrogate for ambient sulfate depends on the prevailing meteorological conditions and emission distributions. Nevertheless, this concept provides an integrated way to deal with this complex chemical system.

We can identify two photochemical regimes, each of which exhibits a different response of potential SO$_4^{2-}$ production to changes in NO$_x$ and VOC emissions, depending on the main sink of odd-hydrogen (HO$_x$), defined as the sum of hydroxyl (OH), hydroperoxyl (HO$_2$), and organic peroxy (RO$_2$) radicals [Sillman, 1995]. When the formation of nitric acid (HNO$_3$)

dominates the loss of odd-hydrogen, a decrease in NO$_x$ 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$_2$O$_2$. 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$_2$O$_2$ production would also be reduced, thus decreasing the formation of SO$_4^{2-}$. Under this photochemical regime, called “VOC-sensitive”, potential SO$_4^{2-}$ decreases with decreasing VOC and increases with decreasing NO$_x$.

By contrast, when the formation of HNO$_3$ can be regarded as a small odd-hydrogen sink, a decrease in NO$_x$ concentrations would slow down the conversion of HO$_x$ 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$_2$O$_2$, 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$_2$O$_2$ formation [Sillman et al., 1990]. Therefore, the aqueous-phase SO$_2$ oxidation would remain unaltered. This scenario constitutes the “NO$_x$-sensitive” photochemical regime, in which aerosol SO$_4^{2-}$ concentrations would decrease with decreasing NO$_x$ 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.

Milford et al [1994] and Sillman [1995] have developed a methodology to assess the sensitivity of a secondary pollutant (ozone) to changes in NO$_x$ and VOC. They found that model predictions for O$_3$-NO$_x$ sensitivity were associated with the concentrations of a number of key chemical species that differed from those linked to O$_3$-VOC sensitivity. Milford et al. [1994] showed that ozone simulated under an NO$_x$-sensitive regime was linked to afternoon values of total reactive nitrogen (NO$_x$ = NO + HNO$_3$ + Peroxyacetyl nitrites + alkyl nitrates) below a certain threshold concentration, while VOC-sensitive ozone was connected to higher NO$_x$ levels. Sillman [1995] extended that work to include species ratios, such as O$_3$/NO$_x$ and H$_2$O$_2$/HNO$_3$.

Following these ideas, we propose the use of a combination of afternoon concentrations of HNO$_3$, H$_2$O$_2$,
and ambient SO$_2$ as “indicator species” of the ambient SO$_2$ - 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$_2$O$_2$ 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$_2$O$_2$)+[SO$_2$]]/([(HNO$_3$)+[NO$_2$]]), are associated with NO$_x$-sensitive conditions while low values for the indicator can be identified with a VOC sensitive regime.

3.0 SIMULATION

In order to investigate the response of “potential” sulfate to changes in the NO$_x$ and VOC source strengths we make use of U.S. Environmental Protection Agency (EPA)’s MODELS-3 [Dennis et al., 1996] Personal Computer (PC) version. This system constitutes a state-of-the-art tool for regional-scale simulations of photochemical smog, visibility and fine particulates. MODELS-3 is a versatile software system that includes a Community Multiscale Air Quality (CMAQ) model [EPA, 1999], a three-dimensional Eulerian chemical transport model that accounts for horizontal and vertical advection, eddy diffusion, gas-phase chemical transformations, emissions, cloud mixing, aqueous-phase chemical reactions, and aerosol processes. The meteorological data used by this simulation are obtained as output fields from the Mesoscale Model Version 5 (MMS) [Grell et al., 1994, Seaman and Michelson, 2000]. Emissions are calculated by the MODELS-3 Emissions Processing and Projection System (MEPPS) [EPA, 1999]. A detailed description of the equations and algorithms of each component of MODELS-3 are given by EPA [1999].

The simulation results presented here are based on an air pollution event that took place over the eastern United States during July 12-14, 1995. This episode featured concentrations exceeding the 1-h National Ambient Air Quality Standards (NAAQS) for ozone with a maximum of 175 parts per billion (ppb) measured at a Connecticut site on July 14 [Sistla et al., 2001]. In order to allow the model to build up the chemical species concentrations, thus minimizing the influence of initial conditions, the first two simulation days were treated as an initialization period. Therefore, only the results for July 14 are discussed here. The model domain covered an area of 2268 x 2808 km$^2$ from the Great Lakes and northern New England to the Gulf of Mexico with a 36-km resolution. The simulation utilized 15 non-hydrostatic sigma-pressure vertical layers. Initial concentrations and boundary conditions were set to near-rural conditions [Chang et al., 1990]. The RAMD2 chemical mechanism [Stockwell et al., 1990] was used to simulate the gas-phase chemical reactions. The aerosol processes were calculated based on the Regional Particulate Model (RPM) [Binkowski and Shankar, 1995]. Area and point emissions were estimated using MEPPS, which is based on the 1995 National Emissions Trends [EPA, 1999]. Emissions data from motor vehicles and vegetation were simulated using the Mobile5a [EPA, 1996] and BEIS-2 [Pierce et al., 1998] models, respectively.

The meteorological data used for the present case study have been described in detail in Seaman and Michelson [2000], so only a brief summary is given here. This event featured light winds, restricted vertical mixing and high temperatures, conditions typically associated with a Bermuda high. Mesoscale structures associated with an Appalachian lee trough played a key role in determining the geographical distribution of photochemical smog. Low mixing depths and south-south-westerly flow favored the accumulation of photochemical precursors to the east of the trough [Seaman and Michelson, 2000], further explaining the observed ozone concentrations in excess of 120 ppb along the northeastern U.S. urban corridor.

The data used to verify the model predictions are a subset of measurements made during the North American Research Strategy for Tropospheric Ozone-Northeast (NARSTO-NE) 1995 intensive field campaign [Mueller, 1998]. A total of 327 measurement sites distributed throughout the Northeastern United States were selected to make the model comparison. The modeled and measured ozone concentrations were paired spatially by performing a bi-linear horizontal interpolation of the simulated values to the corresponding monitor locations.

4.0 RESULTS AND DISCUSSION

Good agreement is found between modeled and observed maximum 1-h ozone concentrations for the Northeastern U.S. The simulation captures the broad features of the geographical distribution of this episode, but not the detailed spatial variability. In particular, the highest ozone peaks are under-predicted by the model. The simulation shows a raw bias of -9.7 ppb, a normalized bias of -7.3%, a raw gross error of 18.3 ppb, and a normalized gross error of 18.5% for the spatially paired maximum 1-h ozone mixing ratios. These simulation results are within the performance “goals” suggested by Tesche et al. [1990] and by Hanna et al. [1996].

In order to build further confidence in the ability of the model to predict sensitivities of photochemical species to changes in VOC and NO$_x$, we performed three separate series of runs, each with 35% reductions in emission rates separately for VOC and NO$_x$. The first simulation (BASECASE) corresponds to the base case scenario with standard emission rates. In the second run (DBLSO2) the SO$_2$ emissions rates were doubled from those of the base case. In the third scenario (DBLWOC) the anthropogenic VOC emission rates were doubled with respect to the base case. Subsequently, we calculated the values for two concentration ratios, namely O$_3$/NO$_x$ (NO$_x$ = NO$_y$+NO$_x$) and H$_2$O$_2$/HNO$_3$, that
are associated with ozone- NOx and VOC-sensitive locations at 16:00 EDT (20:00 UTC). VOC-sensitive locations are defined as those where the O3 concentration in the simulation with reduced VOC is lower than the levels of O3 in both the base case scenario and in the simulation with an equivalent reduction in NOx by at least 5 ppb [Sillman et al., 1997]. NOx-sensitive locations are classified analogously. The median values along with the 5th and 95th percentiles for the indicator ratios corresponding to NOx- and VOC-sensitive locations are not substantially different from those calculated by Sillman [1995, 1997]. NOx-sensitive locations are associated with O3/NOx > 12 and H2O2/HNO3 > 0.5, while VOC-sensitive stations are linked to O3/NOx < 9 and H2O2/HNO3 < 0.3.

Following the methodology developed by Sillman [1995], we used the ([H2O2]+[SO4]2-)/([HNO3]+[NO3]) ratio as an indicator for the sensitivity of potential sulfate to changes in NOx and VOC emissions. Figure 1 depicts the potential SO42- VOC-NOx sensitivity for the BASECASE simulation at 16:00 EDT (20:00 UTC). This figure shows the percentage normalized reduction in ([H2O2]+[SO4]2-) concentration as a consequence of either a NOx or a VOC emission reduction for each grid within the model domain. The change in potential sulfate is plotted as a function of the concurrent indicator ratio, ([H2O2]+[SO4]2-)/([HNO3]+[NO3]). As can be inferred, there is well-defined contrast between NOx and VOC sensitive locations. High ([H2O2]+[SO4]2-)/([HNO3]+[NO3]) ratios are associated with reduced ([H2O2]+[SO4]2-) concentrations as NOx emissions are reduced, while no sensitivity is observed for changes in VOC (NOx sensitive regime). On the other hand, low indicator ratios are linked to a decrease in “potential” sulfate as the VOC emissions are reduced and an increase in the ([H2O2]+[SO4]2-) concentrations when the NOx emissions decrease (VOC sensitive regime).

![Fig 1 Normalized percentage response of potential sulfate concentrations to changes in NOx and VOC versus ([H2O2]+[SO4]2-)/([HNO3]+[NO3]) ratios for 20:00 UTC, July 14, 1995.](image_url)

The correspondence between the SO42- VOC-NOx sensitivity and the indicator ratio was evaluated quantitatively by calculating the 95th and 5th percentiles for the ([H2O2]+[SO4]2-)/([HNO3]+[NO3]) ratios associated with VOC- and NOx-sensitive locations respectively (Table 1). We define NOx-sensitive locations as those where the normalized ([H2O2]+[SO4]2-) calculated in the simulation with a 35% reduction in NOx is lower than the normalized potential sulfate concentrations modeled with a 35% reduction in VOC by at least 5%. VOC-sensitive stations are defined in an analogous way. Table 1 also shows that the median values of the ([H2O2]+[SO4]2-)/([HNO3]+[NO3]) ratios linked to NOx-sensitive stations are at least four times higher than those associated with VOC-sensitive locations. The 95th percentile of the collection of indicator values corresponding to VOC-sensitive stations, which identifies the highest values for this distribution, along with the 5th percentile of indicator values associated with NOx-sensitive locations, reflecting the lowest values of the indicator distribution, identify the threshold interval of the ([H2O2]+[SO4]2-)/([HNO3]+[NO3]) ratio for the transition from VOC to NOx sensitivity. The choice of these percentile cutoffs are based on Sillman et al. (1997). We find similar transition points for the three different model scenarios that range between 1.4 to 2.2.

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<th>Run</th>
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Table 1 Distribution of ([H2O2]+[SO4]2-)/([HNO3]+[NO3]) ratios for NOx- and VOC-sensitive regimes.

5.0 CONCLUSIONS

MODELS-3 constitutes a suitable and powerful tool to assess the sensitivity of particulate sulfate to changes in primary pollutant source strength. In particular, the simulation results show that the response of potential sulfate levels to changes in VOC and NOx emissions is strongly correlated with afternoon values of the ([H2O2]+[SO4]2-)/([HNO3]+[NO3]) indicator ratio. The relatively narrow range of the transition values unequivocally identifies either a VOC- or NOx-sensitive regime despite the three different scenarios used in this modeling exercise. Under VOC-sensitive conditions (when the indicator ratio is less than approximately 1.4) potential sulfate is reduced when VOC emissions are reduced, but it is *increased* when NOx emissions are reduced. On the other hand, under NOx-sensitive conditions (values higher than 2.2 for the non-dimensional indicator) potential sulfate is reduced when NOx emissions are reduced, while it is only weakly sensitive to changes in VOC.
6.0 REFERENCES


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