

NO_x and VOC Control and Its Effects on the Formation of Aerosols

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This research analyzes the qualitative and quantitative behavior of aerosol dynamics resulting from the control of nitrogen oxide (NO_x) and volatile organic compound (VOC) emissions by calculating detailed pollutant isopleths. Several emission scenarios are evaluated using various norms to study the nonlinear impact of control strategies. The modeling episode studied is the Southern California Air Quality Study on August 27, 28, and 29, 1987. The modeling domain is the South Coast Air Basin of California. Research suggests that the reduction of NO_x and VOC emissions traditionally implemented to control ozone also controls particulate matter, but to a limited extent. Furthermore, the effects of reducing NH₃ are more effective in PM control than reducing both NO_x and VOC. Simulations indicate that the combined control of NH₃, NO_x, and VOC emissions is most effective to reduce particulate matter and ozone in the South Coast Air Basin of California.

INTRODUCTION

Atmospheric aerosols have significant impact on the quality of life on Earth. The U.S. Environmental Protection Agency (EPA) created the National Ambient Air Quality Standards for particulate matter (PM) in 1996 to prevent health problems arising from high PM intake. In addition to the 0.08 parts per million (ppm) 8 h average ozone standard, the 24 h PM standard for PM with diameters <2.5 μm (PM_{2.5}) is set to 50 μgm^{-3} and for PM with diameters <10 μm (PM₁₀) is set to 150 μgm^{-3} (Fed. Reg. 1996). Conditions in urban areas like the South Coast Air

Basin of California have traditionally been in violation of both PM and ozone standards on a 24 h and 8 h average basis, respectively (EM 1997). However, much progress has been made to improve ozone levels in urban areas due to the control of NO_x and volatile organic compounds (VOC) emissions. The effectiveness of such control measures are generally analyzed through sensitivity studies with the aid of three-dimensional air quality models (Chock et al. 1999; Meng et al. 1997; Milford et al. 1994). The use of three-dimensional air quality models is the method of choice for analyzing control strategies (Milford et al. 1989). Current models incorporate a comprehensive set of physical and chemical processes. Various attempts have been made to quantify the effects of emissions reduction upon aerosol formations. However, these attempts are predominantly from trajectory models due to computational constraints (Farber et al. 1994). In light of parallel computers and efficient algorithms, the creation of aerosol isopleths using fully developed three-dimensional models is now feasible and provides valuable information on control strategies.

The control measures that are effective for ozone reduction have been NO_x and VOCs (Milford et al. 1989). Following similar principles, the control of aerosols by varying the emissions of NO_x and VOCs is analyzed. This work uses the CIT Airshed Model (Harley et al. 1993), a state-of-the-science air quality model, to provide the framework in quantifying the effectiveness of various control strategies. This framework is used to study the impact of detailed emissions control strategies on nitrates, sulfates, ammonium, organic and inorganic compounds, and gas-phase pollutants. A variety of norms to evaluate the effectiveness of controls are computed to produce informative isopleths. The design of control strategies using isopleths started by the Empirical Kinetics Modeling Approach (EKMA) (Gipson et al. 1981) has been on the basis of peak ozone concentrations. However, the coupling of aerosols and gaseous species like ozone are complex and highly nonlinear (Meng et al. 1997). Therefore multiple control objectives are presented in this research. In addition, peak ozone and aerosol PM minimization may not provide the optimal control strategy for the entire domain due to spatial variations in the effects of the control. Quantitative effectiveness of control strategies by

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different norms is presented to account for spatial and temporal variations.

METHODOLOGY

Control Parameters

Air quality models are considered the preferred approach to analyze the impact of control strategies on pollution dynamics. Numerous researchers have analyzed the abatement of ozone by reduction of NO_x and VOC (Chock et al. 1999; Meng et al. 1997; Milford et al. 1994). To quantify the effects of such control measures on the production of aerosols, computation of aerosol and gas isopleths are performed. The computation of isopleths in this research uses the CIT Airshed Model's base case conditions. The development of the base case has been thoroughly analyzed by Meng et al. (1998). The sensitivity of aerosol and gaseous pollutants to NO_x and VOC emissions is computed by varying the amount of emissions over the modeling domain. The base case emissions of NO_x and VOCs are each amplified by factors of 0, 0.4, 0.8, 1.0, 1.2, 1.6, and 2.0. Aerosols and gas-phase concentrations are computed for each amplification factor, giving rise to 49 emission scenarios. Control measures affect different parts of the airshed differently. Therefore the effects of the control measure on specific locations are also analyzed. Several norms are evaluated for a comprehensive assessment of the

control strategies,

$$\text{MAX}[\text{species}] = \max \{ \text{species}(x, y, t) \}, \quad [1]$$

$$\text{MAX24}[\text{species}] = \frac{1}{24} \max \left\{ \sum_{t=0}^{23} \text{species}(x, y, t) \right\}, \quad [2]$$

$$\text{MAX}_{\text{city}}[\text{species}] = \max \{ \text{species}(x = x_0, y = y_0, t) \}, \quad [3]$$

$$\text{CONC}_{\text{city}, \text{hour}}[\text{species}] = \max \{ \text{species}(x = x_0, y = y_0, t = t_0) \}, \quad [4]$$

where x and y are the space variables and t represents time.

Traditionally, the MAX norm has been considered in earlier models (Gipson et al. 1981; Meyer 1986). Minimizing the MAX norm so that the peak concentrations comply with regulations would ensure that other locations are also in compliance. The MAX24 norm is used to measure compliance with the EPA's National Ambient Air Quality Standard. The MAX24 present the 24 h averaged exposure of particulates. To quantify the impact of control measures on different locations, the MAX_{city} norm is evaluated to pinpoint the effects of the various control strategies upon a particular city. Further resolution into the dynamics of aerosol can be attained with the $\text{CONC}_{\text{city}, \text{hour}}$ norm, which computes the isopleths for a particular city and time. The CONC norm is able to resolve not only the spatial variations but also temporal variations that exist in complex aerosol systems.

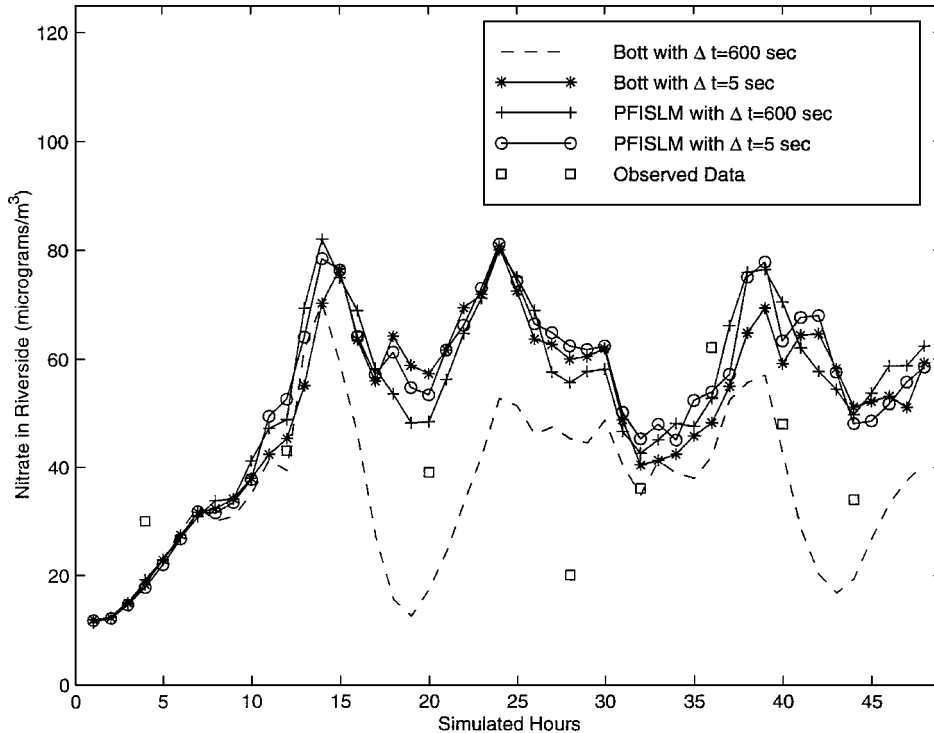


Figure 1. Results in Riverside for nitrate indicate similarity between Bott solver with a maximum time step of 5 s and PFISLM with 5 and 600 s maximum time steps. The Bott solver using the maximum time step of 600 s is substantially different from the other schemes.

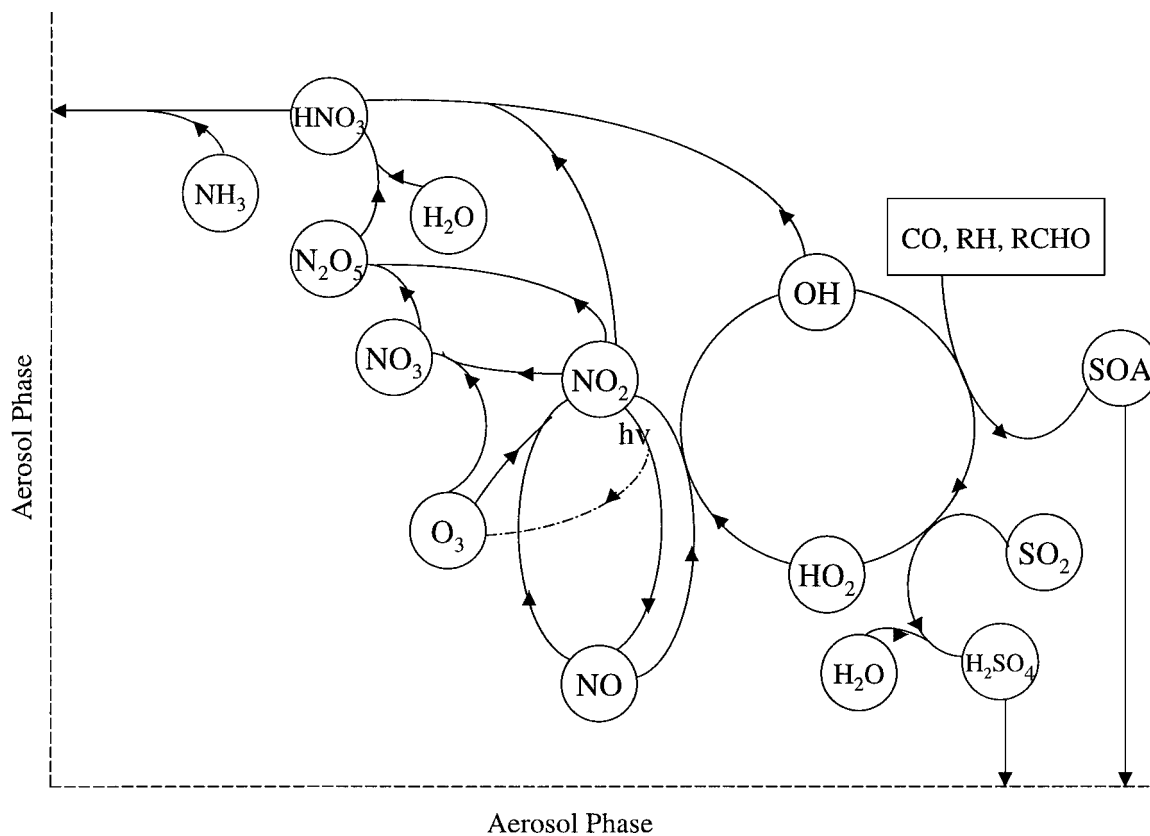


Figure 2. The chemical mechanism describing interactions of ozone and aerosols. The 2 main paths of forming ammonium and nitrate is through NO_2 with OH and NO_2 with O_3 ; the former occurs during the day while the latter is dominant at night.

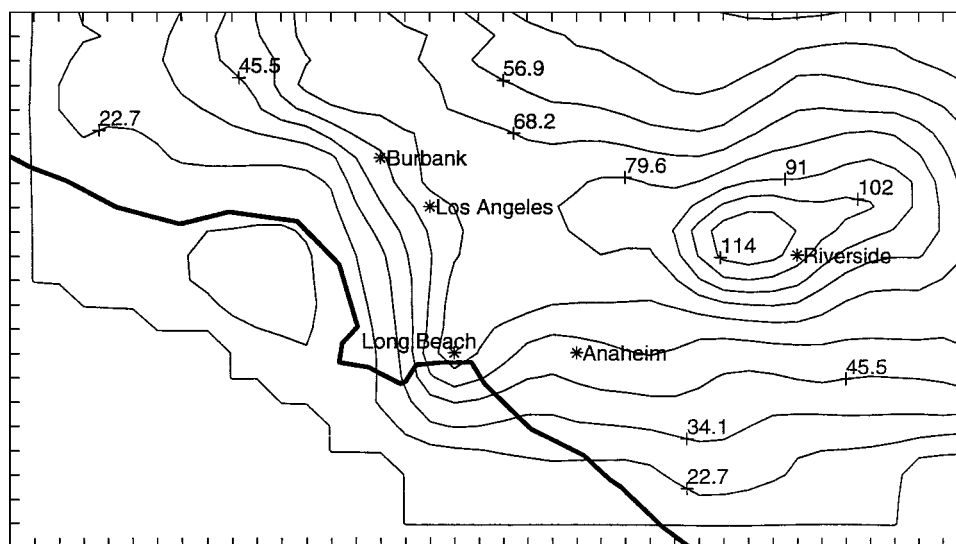


Figure 3. Predicted 24 h averaged total mass $\text{PM}_{2.5}$ (μgm^{-3}) contour on August 28, 1987, for the South Coast Air Basin of California shows similar forms as ammonium and nitrate contours. In the geographical region modeled, the dominant form of $\text{PM}_{2.5}$ is ammonium and nitrate.

The results presented by Meng et al. (1997) show the quantitative effects of reducing NO_x and VOC emissions using 9 emission scenarios evaluated with one norm, the $\text{MAX}_{\text{Riverside}}$ norm. With only 9 data points, the qualitative behavior of PM under various emission scenarios cannot be analyzed. Furthermore, as detailed in the results section of this research, the complex behavior of aerosol dynamics cannot be thoroughly described using one norm. The impact of various chemical reactions upon aerosol dynamics requires substantially more data points and several norms. The behavior of the isopleths presented in the results section can be rigorously explained using existing chemical reactions and dynamical equations as dictated by their mathematical, physical, and chemical computational representation. However, those reactions' qualitative and quantitative contribution to the PM behavior are not evident with the data presented in Meng et al. (1997). In particular, Meng et al. computes only a few data points of one quadrant of the isopleth presented in this research. In this quadrant of the isopleth, the behavior of PM isopleths when reducing NO_x and VOC emissions is linear with the emission factors of NO_x . The nonlinear behavior of the PM isopleths arises outside this quadrant as described later in further detail.

In addition, there are computational differences between the results presented in this research and those presented by Meng et al. (1997). The major computational difference is between the mathematical modeling. This work uses substantially smaller time steps in the computation of aerosol dynamics. The smaller time steps are taken to insure accuracy when solving the aerosol dynamics equations. The maximum allowable time step to solve the aerosol dynamics is set to 5 s, whereas the simulations performed by Meng et al. were set to 600 s. The reduction in maximum allowable time increments is to anticipate the numerical instabilities that might arise when varying emissions for a wide range of factors. Furthermore, the condensation/evaporation solver used in Meng et al. is the modified Bott solver (Dhanyala and Wexler 1996), which is inaccurate under stringent conditions used in the condensation/evaporation equation (Yang et al. 1999). The accuracy of the Bott solver is compared with that of the Partitioned Flux Integrated Semi-Lagrangian Method (PFISLM) solver used in this research. Nguyen and Dabdub (2001) present a full derivation and description of the new solver. The difference among the use of various time steps and solvers is shown in Figure 1. A difference of 25% in the temporal peak is observed. Even greater differences are observed at other times. The underpredictions of the Bott solver (when addressing aerosol growth) found here confirm those reported by Yang et al. (1999).

Finally, another major difference in the chemical simulations is the inclusion of a more detailed semivolatile organic emission inventories from the California Air Resources Board (Wagner and Allen 1990). The chemical path describing the formation of major aerosol compounds is shown in Figure 2. These emissions contribute to PM_{10} mass near Los Angeles, with an increase of up to 12% in the 24 h average PM_{10} concentrations near Los Angeles.

The total mass $\text{PM}_{2.5}$ results from the base case simulations for August 28 are presented in Figure 3. The spatial maximum occurs 15 km west of Riverside, where the emissions of ammonia are concentrated. The objective of this research is to specify qualitatively and quantitatively the impact of NO_x , VOC, and NH_3 emissions and their chemical mechanisms on the formation of aerosols in the South Coast Air Basin. The influence of the chemical mechanism between NO_x , VOC, NH_3 , and aerosols is important to reducing the PM in the South Coast Air Basin.

RESULTS

Preliminaries

The simulation scenarios in this research are for SCAQS 87. However, only the data for the second day of simulations (August 28, 1987) are analyzed to reduce effects of initial conditions. A Lagrangian model used to compute trajectories confirmed that more than 90% of the initial conditions have left the computational domain on the second day of simulation.

A schematic of the coupling between gas and aerosol components is presented in Figure 2 to aid in the understanding of PM isopleths. Figure 2 details the major paths of aerosol formations that pertain to the South Coast Air Basin of California. In particular, the production of ammonium and nitrate aerosols follow 2 major production routes that occur in the daytime and nighttime. The aerosol and gas species analyzed by isopleths in this research are nitrate, ammonium, $\text{PM}_{2.5}$ total mass, PM_{10} total mass, and ozone. These components are the main contributors to the South Coast Air Basin air quality as presented by Meng et al. (1998). The maximum 1 h averaged and 24 h averaged aerosol concentrations in the South Coast Air Basin for SCAQS 87 are composed primarily of ammonium and nitrate, which contribute 70% of the mass in $\text{PM}_{2.5}$ and 53% in PM_{10} . Secondary nitrates contribute <10% of the aerosol composition. Sulfates contribute roughly 12%. While the control of SO_2 would also be beneficial, especially at a low NO_x emissions level, the chemical composition of aerosols in the South Coast Air Basin of California is not dominated by sulfates. Another important emissions control species is primary aerosol emissions. The control of primary PM emissions is important to PM_{10} and the formation of secondary organic aerosols. These lumped organics and inorganics primary emissions contribute up to 35% of the total mass PM_{10} . However, more research is needed to model adequately the behavior of those lumped primary aerosol emissions. This research focuses on the behavior of ammonium and nitrate due to their strong dominance in PM total mass in the South Coast Air Basin of California.

The Impact of NO_x and VOC on the Formation of Aerosols

The resulting MAX24 isopleths for ammonium $\text{PM}_{2.5}$, nitrate $\text{PM}_{2.5}$, total mass $\text{PM}_{2.5}$, and total mass PM_{10} are displayed in

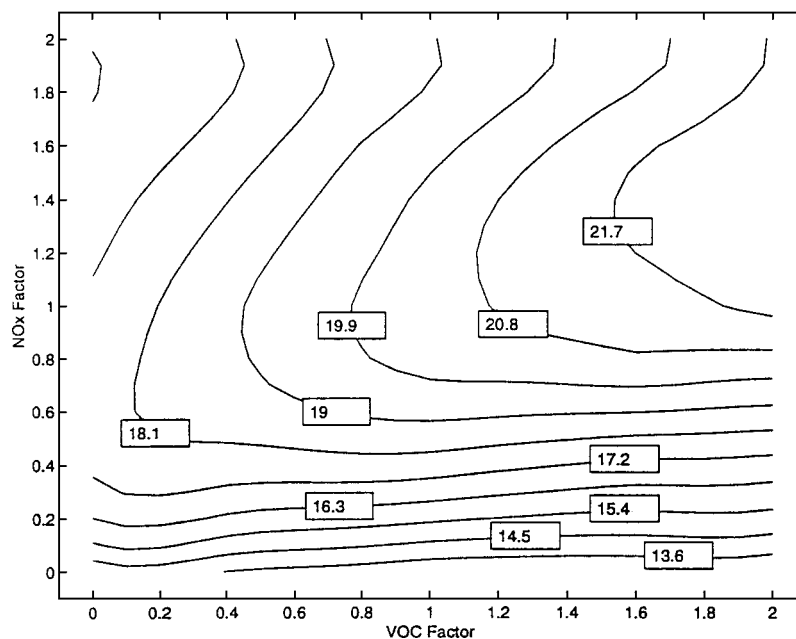


Plate 1a. Spatial maximum 24 h averaged ammonium $\text{PM}_{2.5}$ (μgm^{-3}) isopleth on August 28, 1987, for the entire South Coast Air Basin of California. All maxima occur 15 km west of Riverside. The plot has similar behavior to ozone isopleths for the South Coast Air Basin due to the coupling between ozone and ammonium nitrate as shown in Figure 2.

Plates 1a–d, respectively. The MAX24 isopleths for nitrates and ammonium $\text{PM}_{2.5}$ are similar due to their shared path of formation through ammonia and nitric acid as depicted in Figure 2. Plate 1d also displays the location at which the spatial maximum occurs. For MAX24 $\text{PM}_{2.5}$ ammonium, nitrate, and total mass $\text{PM}_{2.5}$, the maximum 24 h averaged concentrations all occur ap-

proximately 15 km west of Riverside. The MAX24 isopleth for total mass PM_{10} in Plate 1d occurs near Riverside (denoted by the letter R) for the conditions of rich NO_x and rich VOC emissions. Otherwise, the MAX24 total mass PM_{10} occurs near Los Angeles (denoted by the letter L). The occurrence of the MAX24 total mass PM_{10} at Los Angeles is not attributed to ammonium

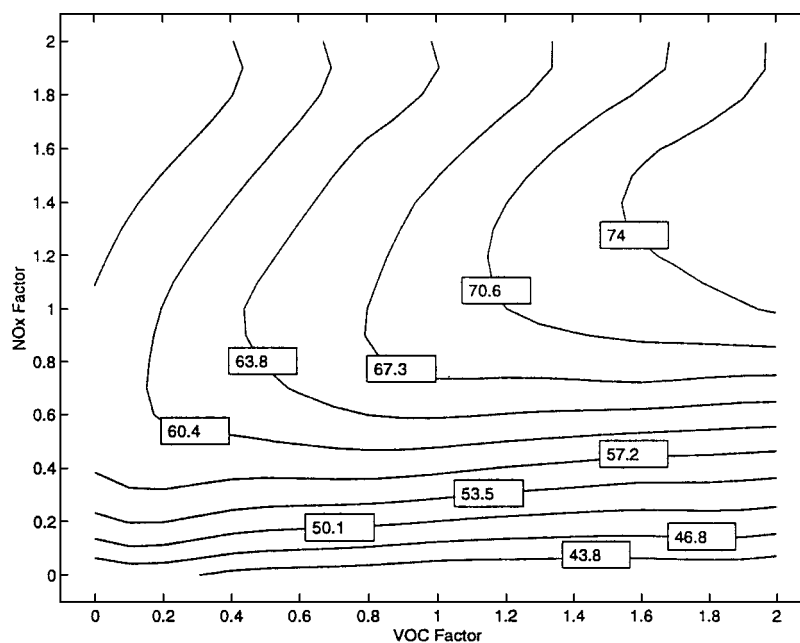


Plate 1b. Spatial maximum 24 h averaged nitrate $\text{PM}_{2.5}$ (μgm^{-3}) isopleth on August 28, 1987, for the entire South Coast Air Basin of California. The nitrate $\text{PM}_{2.5}$ isopleth shows similar behavior to the ammonium $\text{PM}_{2.5}$ isopleth due to their shared path of formation as shown in Figure 2. All spatial maxima occur 15 km west of Riverside.

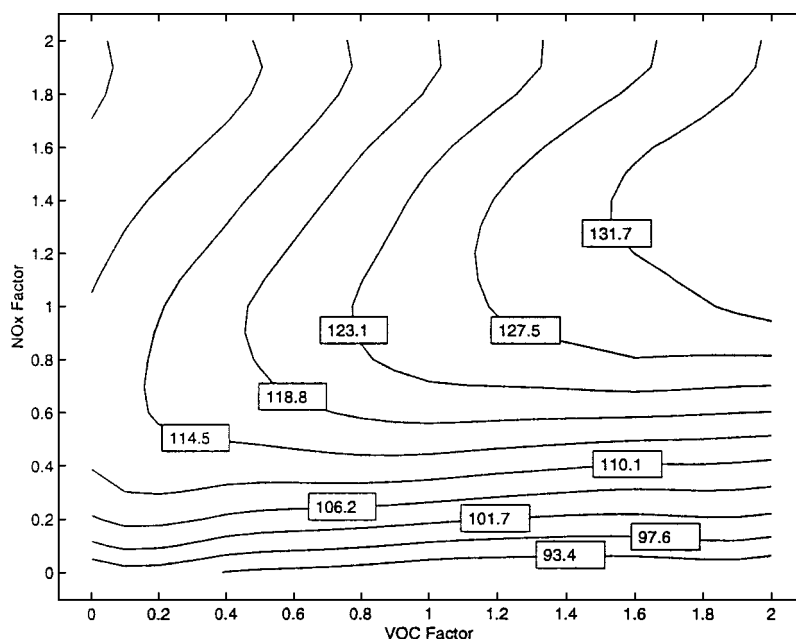


Plate 1c. Spatial maximum 24 h averaged $\text{PM}_{2.5}$ (μgm^{-3}) total mass isopleth on August 28, 1987, for the entire South Coast Air Basin of California. The total mass $\text{PM}_{2.5}$ isopleth shows similar behavior to the ammonium and nitrate since the chemical composition of $\text{PM}_{2.5}$ is dominated by ammonium and nitrate.

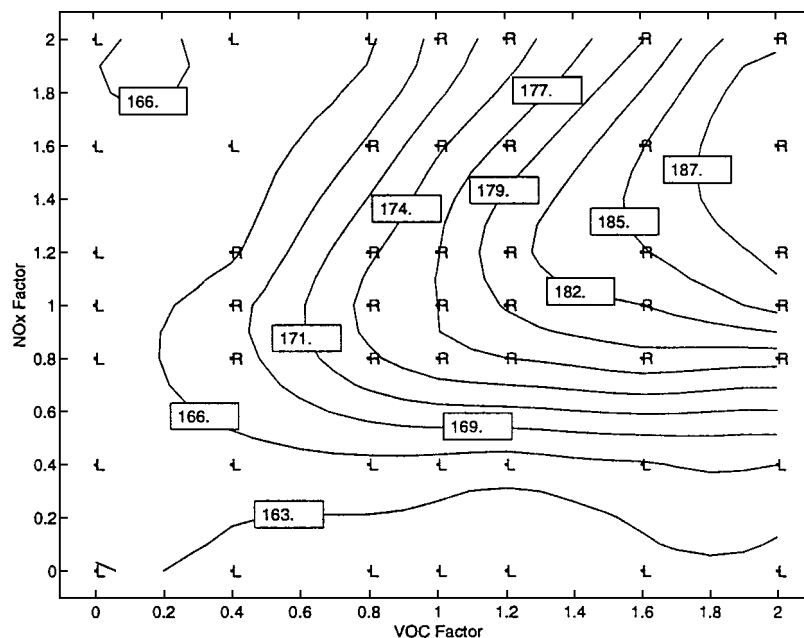


Plate 1d. Spatial maximum 24 h averaged PM_{10} (μgm^{-3}) total mass isopleth on August 28, 1987, for the entire South Coast Air Basin of California. The spatial maxima of total mass PM_{10} occurs at 2 different locations. At higher NO_x and VOC emissions the maximum occurs near Riverside (denoted by the letter R), otherwise it occurs near the city of Los Angeles (denoted by the letter L). Total mass PM_{10} aerosol levels are not sensitive to NO_x at low NO_x emissions. This is due to the aerosol composition near Los Angeles. The dominant component of PM_{10} aerosols near Los Angeles is lumped organics and inorganics.

and nitrate but to lumped organics and inorganics. The emissions of these lumped organics and inorganics all occur in the vicinity of Los Angeles. Plate 1d shows that the MAX24 total mass PM_{10} at Los Angeles is insensitive to controls of NO_x and VOC emissions. The control of PM_{10} requires the reduction in primary emissions of lumped organics and inorganics near the city of Los Angeles.

The general trend for the MAX24 $PM_{2.5}$ ammonium and nitrate isopleths in Plates 1a and b dictates that an increase of NO_x emissions increases nitrates and ammonium in the NO_x poor regime. However, as NO_x emissions increase over the base case conditions, a decrease in the formation of $PM_{2.5}$ ammonium and nitrate occurs. To understand the nonlinear relation between NO_x emissions and PM levels in the rich NO_x emission scenarios requires the use of other norms that are more appropriate and resolved: MAX and CONC. The MAX (maximum 1 h average) isopleth for nitrate $PM_{2.5}$ is displayed in Plate 2b. The time at which the MAX $PM_{2.5}$ nitrate occurs is labeled next to the data points in Plate 2b. The MAX norm has more resolving power than the MAX24 norm since it does not average over time. The location of MAX ammonium and nitrate aerosol is uniform across the isopleth. The MAX $PM_{2.5}$ nitrate and ammonium occur 15 km west of Riverside, where ammonia emissions are concentrated. The research and computation on the effects of NO_x and VOC emissions by Meng et al. (1997) are a part of the lower left-hand quadrant in Plate 1b. In this region, the MAX $PM_{2.5}$ nitrate increases linearly with NO_x emissions and occurs at noon. However, the MAX nitrate isopleth in Plate 1b indicates that the MAX $PM_{2.5}$ nitrate occurs at different times, at noon and midnight. In the VOC-rich regime of the MAX iso-

pleth in Plate 2b, the occurrence of the maximum is at night, while at other parts of the isopleth the occurrence is at noon. The 2 different times of the maxima are due to 2 different paths of formation of nitric acid, as shown in Figure 2. In the lower half of the isopleth in Plate 2b, the behavior of the MAX nitrate depends linearly on the amount of NO_x and is insensitive to the emissions of VOC. However, NO_x emission conditions surpassing the base case show stagnant and decreasing MAX nitrate $PM_{2.5}$. Clearly, the effects of nighttime chemistry are important for regions of the isopleth where the MAX $PM_{2.5}$ nitrate occurs at night. However, nighttime chemistry is also important in the isopleth regions where the MAX $PM_{2.5}$ nitrate occurs in the daytime. To understand the importance of nighttime chemistry and further resolve the isopleth, the CONC norm is used to pinpoint the behavior of these aerosol components at a particular time and place. Since the location of the MAX $PM_{2.5}$ nitrate is uniform across the isopleth, the CONC norm is evaluated at Riverside for 12 pm and 1 am. The $CONC_{Riverside, 1\text{ am}}[\text{nitrate}]$ and $CONC_{Riverside, 12\text{ pm}}[\text{nitrate}]$ are displayed in Plates 3a and b, respectively. The MAX isopleths for nitrate in Plate 2b is a merger between the 2 CONC isopleths for nitrate at midnight and midnoon. At noon, in Plate 3b, the increase in NO_x emissions increases nitric acid up to the base case emissions factors. This behavior results from the reaction of OH with NO_2 to form nitric acid. With additional emissions of NO_x in excess of the base case, the sensitivity of ammonium and nitrate decreases. This lack of sensitivity in high NO_x levels is due to the reduction of ozone. The $CONC_{Riverside, 12\text{ pm}}[\text{ozone}]$ isopleth is presented in Plate 2a. In the NO_x rich regime, increasing NO_x reduces ozone concentration at Riverside. With the decrease in ozone,

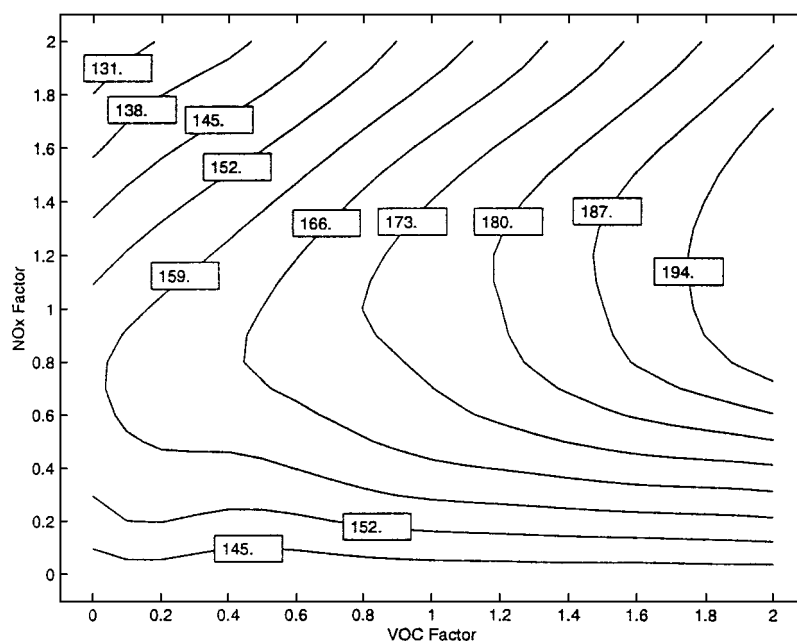


Plate 2a. The temporal maximum 1 h averaged ozone (parts per billion) concentrations near Riverside on August 28, 1987.

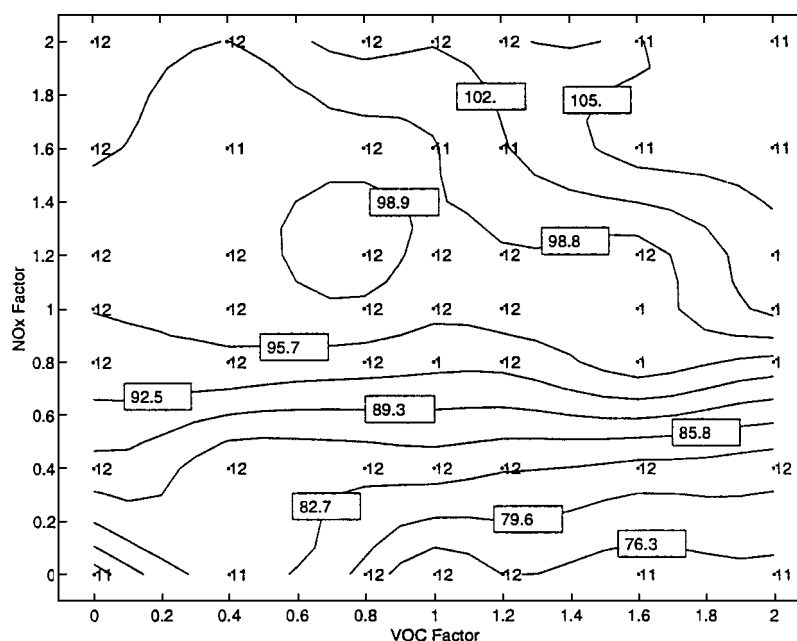


Plate 2b. Spatial and temporal maximum 1 h averaged nitrate $\text{PM}_{2.5}$ (μgm^{-3}) isopleth on August 28, 1987, for the entire South Coast Air Basin of California. The spatial location of the peak is uniform over all values of NO_x and VOC emissions factors and occurs 15 km west of Riverside. The nitrate $\text{PM}_{2.5}$ isopleth shows 2 competing chemical dynamics that occur at 2 different times. The hour when the maximum occurs is indicated next to the data points on the graph and varies between midday and midnight. At higher VOC factors the maximum occurs at midnight due to increased ozone to oxidize NO_2 as presented in Figure 2. For the region of the isopleth where the maximum occurs at midday, increases in NO_x emissions increases nitrate to a certain extent, after which nitrate would decrease. This is due to the decrease in noon ozone when NO_x emissions exceed the base case as depicted in Plate 2a. The decrease in ozone hinders the production of OH to combine with NO_2 .

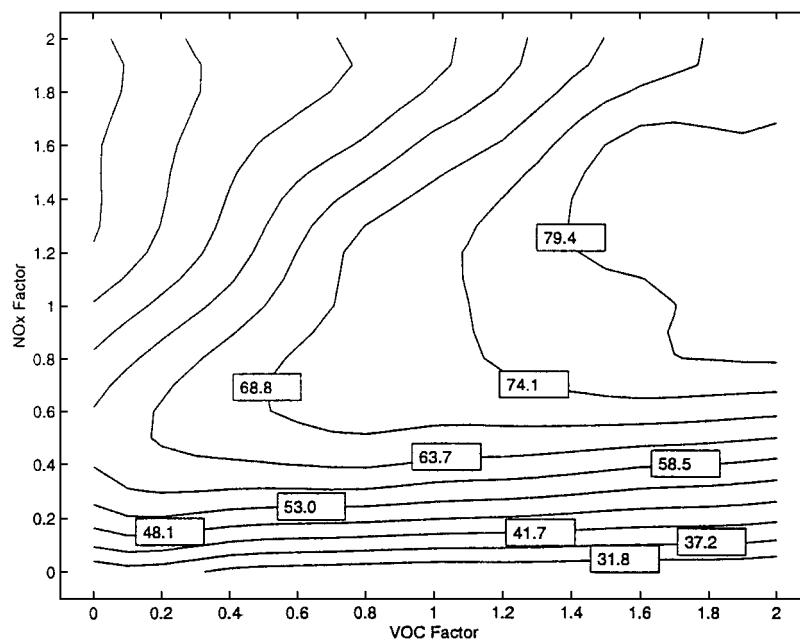


Plate 3a. Isopleth for nitrate $\text{PM}_{2.5}$ (μgm^{-3}) 15 km west of Riverside at 1 am on August 28, 1987. The nitrate $\text{PM}_{2.5}$ isopleth is similar to that of ozone, as in Plate 2a. The similarity is due to the nighttime production of nitrate, which results from the oxidation of NO_2 by O_3 .

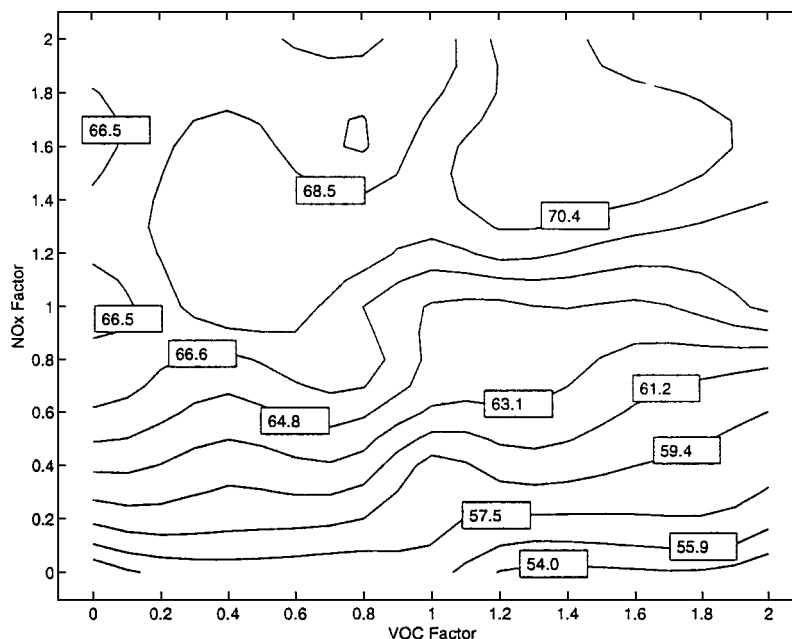
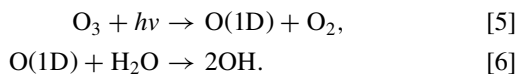


Plate 3b. Isopleth for nitrate $\text{PM}_{2.5}$ (μgm^{-3}) 15 km west of Riverside at 12 pm on August 28, 1987. The nitrate $\text{PM}_{2.5}$ isopleth indicates a higher sensitivity to NO_x emissions at low NO_x emissions. At a higher NO_x emissions regime, the decrease in ozone hinders the production of OH, which combines with NO_2 to form nitric acid.

the formation of OH also decreases due to the reactions



The photolysis of O_3 in the presence of water is a major tropospheric source of OH radical (Atkinson 2000). The decrease in OH limits its reaction with NO_2 to form nitric acid. Due to the decrease in ozone, Plate 3b shows a reduction of nitrate formation with high NO_x emissions. The $\text{CONC}_{\text{Riverside}, 1 \text{ am}}[\text{nitrate}]$ isopleth, in Plate 3a, follows the isopleth for ozone at Riverside as shown in Plate 2a. The similarity is due to the role of ozone as the major oxidant for NO_2 to form N_2O_5 at night as depicted in Figure 2. From Plate 2b, the increase in VOC causes the maximum nitrate at Riverside to occur at night. As VOC emissions increase, the nighttime $\text{PM}_{2.5}$ nitrate peak surpasses the daytime peak. Comparing the MAX24 isopleths in Plate 1 and the MAX isopleth in Plate 2b, the MAX24 isopleths follow the nighttime isopleth for $\text{PM}_{2.5}$ nitrate. This is due to the time averaging computation of the MAX24 norm. The contribution from the cumulative nighttime concentrations surpasses that of the daytime concentrations in the computation of the MAX24 norm. The domination of nighttime chemistry determines the behavior of the MAX24 isopleths shown in Plate 1 and the $\text{CONC}_{\text{Riverside}, 1 \text{ am}}[\text{nitrate}]$ isopleth in Plate 3a. These isopleths have similar behavior to the ozone isopleth in Plate 2a. This is the first time that such nonlinear regions of the isopleth have been analyzed.

The Control of Urban Aerosols in the South Coast Air Basin of California

Research indicates that another route should be examined to provide more effective impact upon reducing PM during the SCAQS 87 simulations. Since ammonium and nitrate dominate aerosol compositions and their path of formation is from the interactions between ammonia and nitric acid, an advantageous strategy would be to control ammonia. PM total mass isopleths are computed by modifying the base case emissions of NO_x and NH_3 by factors of 1.0, 0.8, 0.4, and 0.0. Plates 4a and b show the MAX24 isopleths for total mass $\text{PM}_{2.5}$ and total mass PM_{10} , respectively. With no ammonia emissions, 50% of the MAX24 $\text{PM}_{2.5}$ total mass is reduced. The effectiveness of ammonia control is expected since most of the ammonium nitrate is produced from ammonia emissions near Riverside. The total mass PM_{10} isopleth shown in Plates 4b is less sensitive to ammonia emissions. Only a 16% decrease in MAX24 PM_{10} is attained with zero ammonia emissions. At low NH_3 emission levels the location of the MAX24 PM_{10} transfers to the vicinity of Los Angeles, where different aerosol components dominate.

The effect of control measures upon the entire airshed is vital since control measures might adversely affect other parts of the domain. The contours displaying the effect of reducing NO_x and VOC by 60% and 0%, respectively, and reducing NO_x and NH_3 by 0% and 60%, respectively, for 24 h averaged $\text{PM}_{2.5}$ and PM_{10} are presented in Plate 5. The reason for these particular reduction control scenarios is that MAX24 total mass $\text{PM}_{2.5}$ and PM_{10} isopleths are insensitive to VOC when NO_x is reduced by 60% as Plate 1 indicates. Due to this insensitivity, the most

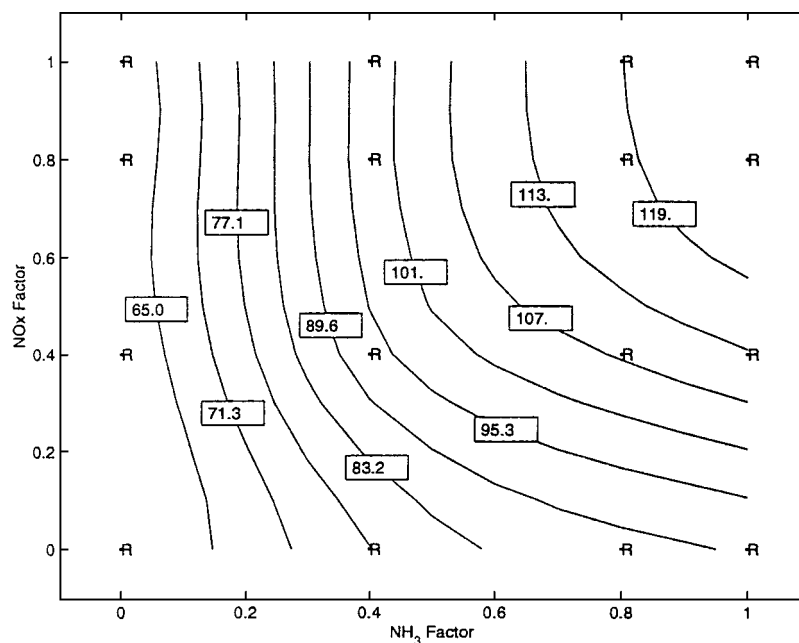


Plate 4a. Spatial maximum 24 h averaged total mass $\text{PM}_{2.5}$ (μgm^{-3}) isopleth on August 28, 1987, for the entire South Coast Air Basin of California. The total mass $\text{PM}_{2.5}$ isopleth with NO_x and NH_3 controls shows a strong response to ammonia emissions. The spatial occurrence of the peak $\text{PM}_{2.5}$ is at Riverside, even with more than twice the reduction of ammonium and nitrate.

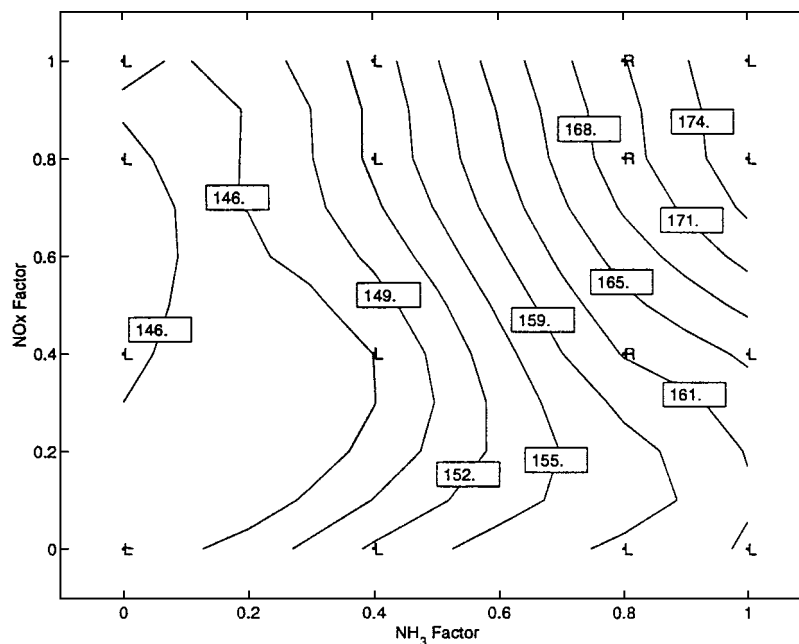


Plate 4b. Spatial maximum 24 h averaged total mass PM_{10} (μgm^{-3}) isopleth on August 28, 1987, for the entire South Coast Air Basin of California. The total mass PM_{10} isopleth with NO_x and NH_3 controls is not sensitive to NH_3 and NO_x control at low NH_3 emissions. This behavior is similar to Plate 1d, as the geographical location of the peak shifts from the vicinity of Riverside to Los Angeles.

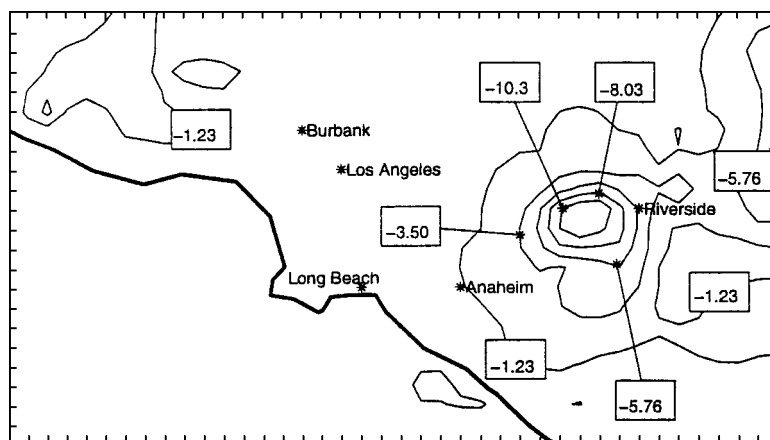


Plate 5a. Predicted difference in the 24 h averaged $\text{PM}_{2.5}$ (μgm^{-3}) from base case conditions on August 28, 1987, for the South Coast Air Basin of California by reducing 60% of NO_x . The contours show greatest impact near the ammonia emissions area 15 km west of Riverside.

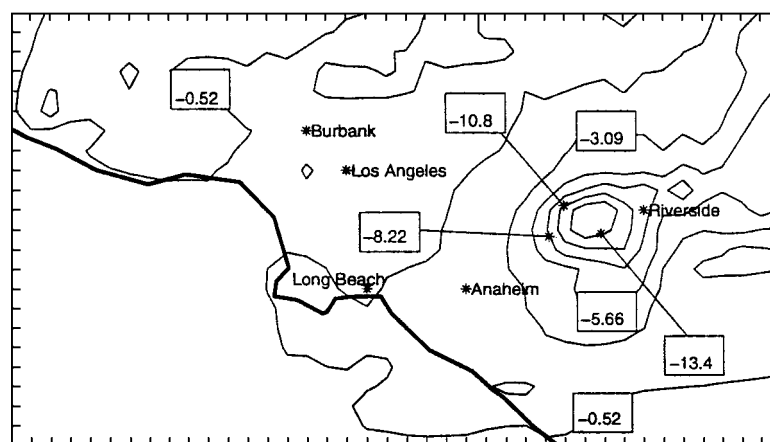


Plate 5b. Predicted difference in the 24 h averaged $\text{PM}_{2.5}$ (μgm^{-3}) from base case conditions for the South Coast Air Basin of California by reducing 60% of NO_x . The contours show similar trends as those for $\text{PM}_{2.5}$.

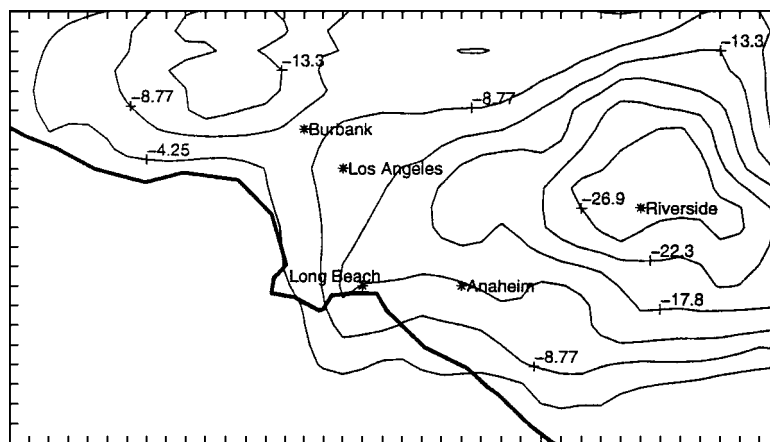


Plate 5c. Predicted difference in the 24 h averaged $\text{PM}_{2.5}$ (μgm^{-3}) from base case conditions for the South Coast Air Basin of California by reducing 60% of NH_3 . The contours show significantly more effectiveness in controlling $\text{PM}_{2.5}$ by NH_3 than by NO_x , as shown in Plate 5a.

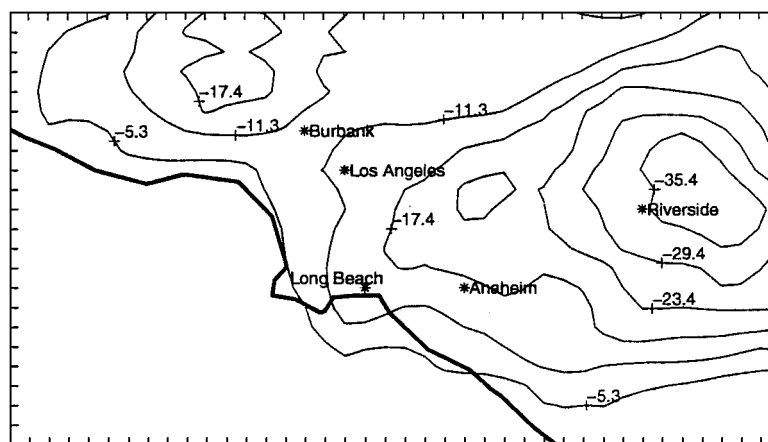


Plate 5d. Predicted difference in the 24 h averaged $\text{PM}_{2.5}$ (μgm^{-3}) from base case conditions for the South Coast Air Basin of California by reducing 60% of NH_3 . The contours show results similar to Plate 5c.

cost effective approach to suppressing aerosols is not to reduce VOC. Similarly, the isopleths in Plate 4 with NO_x and NH_3 control indicates that at 60% reduction in NH_3 , there is little gain in reducing NO_x . Decreasing NO_x emissions leads to local reduction in aerosol concentrations near Riverside as displayed in Plate 5a. When decreasing NO_x emissions by 60%, the peak 24 h average $\text{PM}_{2.5}$ is reduced by $10.3 \mu\text{gm}^{-3}$ and the PM_{10} peak is reduced by $13.4 \mu\text{gm}^{-3}$ as shown in Plates 5a and b, respectively. The reductions in $\text{PM}_{2.5}$ and PM_{10} are also seen to the east of the ammonia emissions location due to advection of the pollutants eastward. The contours corresponding to ammonia control show more effectiveness with a reduction of $26.9 \mu\text{gm}^{-3}$ near Riverside and $13.3 \mu\text{gm}^{-3}$ in the northwestern part of the domain. For the emissions reduction scenarios studied, the most effective control strategy for PM in the South Coast Air Basin of California is the reduction of ammonia emissions. Furthermore, the second most effective approach is to control NO_x .

CONCLUSION

The formation of aerosols in urban areas like the South Coast Air Basin of California is the result of complex chemical and physical interactions of pollutants in the atmosphere. Aerosol concentration levels have contributed to violations of the EPA's air quality standards. To understand the role of NO_x and VOC in aerosol formation, this work presents detailed isopleths to gauge the sensitivity of aerosol concentrations upon NO_x and VOC emission levels. Traditional control measures for ozone are determined by examining the effects of NO_x and VOC (Milford et al. 1989) emissions. Those control measures impact aerosol formations due to the coupling between ozone and aerosols (Meng et al. 1997). This research elucidates in greater detail the coupling mechanisms that occur during daytime hours, and nighttime hours, as well as their effects on the behavior of PM isopleths.

There are several new scientific findings resulting from the analysis performed by this study for the South Coast Air Basin of California during the 1987 SCAQS episode.

First, the highest concentrations of PM occur at the highest emissions rates of VOC and NO_x studied, as expected. However, the maximum 24 h average PM levels depend nonlinearly on NO_x and VOC concentrations. In fact, near the base case scenario, an increase in NO_x emissions decreases the maximum 24 h average PM concentrations. This nonlinear region of the isopleth is not considered in any previous studies.

Second, nighttime chemistry plays a pivotal role in the production of PM. This study is the first to quantify the role of nighttime chemistry dynamics on the behavior of PM isopleths. In fact, under polluted conditions, the maximum 1 h average PM concentrations occur at night. Furthermore, even at base case conditions (when the maximum 1 h average occurs at noon), the maximum 24 h average PM levels are highly influenced by nighttime chemistry. In other words, control strategies implemented to reduce nighttime PM concentrations present similar effects on the reduction of the maximum 24 h average PM concentrations.

Third, the quantitative effects of reducing NO_x and VOC emissions upon the reduction of PM are not substantial. A reduction of 20% in the maximum 24 h average $\text{PM}_{2.5}$ levels is possible with no NO_x emissions. Furthermore, at a reduction of 20% or higher in emitted NO_x , the reduction or increase in emitted VOC has no substantial impact on the maximum 24 h average $\text{PM}_{2.5}$ levels. The effect of ammonia reduction has a greater impact in the maximum 24 h average $\text{PM}_{2.5}$ levels than NO_x reductions. A reduction of 50% in the maximum 24 h average $\text{PM}_{2.5}$ levels is possible with no ammonia emissions. At 20% or higher reduction in emitted ammonia, the reduction of NO_x emissions does not decrease the maximum.

Finally, this study has found that the reduction of PM_{10} at a NO_x poor region of the isopleths (where the maximum 24 h average PM_{10} levels occur at Los Angeles) are independent of NO_x , VOC, and NH_3 . Control with NO_x , VOC, and ammonia have the highest impact near the Riverside area. Reductions of maximum 24 h average PM_{10} near Los Angeles are more effective when controlling primary lumped organic and

inorganic emissions near Los Angeles. The chemical dynamics of lumped primary aerosols emissions and the formation of secondary organic aerosols should be addressed rigorously in future research.

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