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DYNAMICS OF AUTOMOTIVE SULFATE EMISSIONS



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DYNAMICS OF AUTOMOTIVE SULFATE EMISSIONS

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ABSTRACT

A preliminary assessment of the potential environmental impact of automotive sulfuric acid (or sulfate) aerosol has been made by analyzing the aerosol dynamics. This analysis leads to the prediction of ambient automotive sulfuric acid aerosol concentrations over and around a large, ten-lane highway (48 m. x 20 km.), some ten or so years hence, when almost all cars in the United States will be fitted with catalytic converters. The attachment rate of fine automotive sulfuric acid aerosols to ambient aerosols is examined. The dispersion and deposition of automotive sulfate are modelled over the highway for "worst case" meteorology using K-theory. The neutralizing effect of ambient ammonia on sulfuric acid concentrations around the highway is examined by a direct simulation procedure for dispersion calculations. These calculations indicate that adverse environmental effects of automotive sulfuric acid emissions may be important under the stated conditions of this study.

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LIST OF ABBREVIATIONS AND SYMBOLS

Roman Letters

$b(\mu, \mu')$	coagulation coefficient
b_{11}	coagulation coefficient of the automotive sulfate with itself
b_{12}	coagulation coefficient of the automotive sulfate with ambient aerosol
c_1	number concentration of the automotive sulfate
c_2	number concentration of the ambient aerosol
$D(\mu)$	particle diffusivity
D	particle diameter
$dM/d\log D$	particle mass density function
G	gravitational settling velocity
$g.m.d.$	geometric mean diameter
K	eddy diffusivity tensor
K_x	x-component of eddy diffusivity
K_y	y-component of eddy diffusivity
K_z	z-component of eddy diffusivity
M	aerosol mass distribution
$n(\mu; \vec{r}, t)$	number density function of aerosol particles having mass μ in the range $(\mu, \mu + d\mu)$ at \vec{r} and at time t
\vec{v}	coordinate vector
t	time
u	time average wind velocity
v_d	deposition velocity
z_o	roughness length

Greek letters

δ	removal rate
μ	particle mass
ν_j	rate of production by nucleation of j-th component
$\psi(\mu;r,t)$	condensation coefficient
σ_i	rate of production from i-th source
σ_g	geometric standard deviation
σ_y	Gaussian dispersion parameter
σ_z	Gaussian dispersion parameter

SECTION 1

INTRODUCTION

Although the widespread introduction of catalytic converters on new cars in the United States in 1975, reduces carbon monoxide and hydrocarbon emissions, there are many uncertainties concerning possible adverse health and welfare effects of this new technology. Among these uncertainties is the environmental impact of the sulfuric acid emissions from catalytic converters.

Gasoline in the United States normally contains 0.03 weight percent sulfur, which may be converted to sulfur dioxide on combustion. The catalytic converter oxidizes part of the sulfur dioxide in the automotive exhaust to sulfur trioxide, which in turn rapidly reacts with water vapor to form sulfuric acid. In the atmosphere, sulfuric acid is believed to nucleate to form a sulfuric acid aerosols (1,2).

The adverse effects of environmental sulfuric acid aerosol on man, animals, plants, and materials have been known for some time (3). A recent study (4) indicates the critical role of the sulfuric acid aerosol size distribution. Particles in the size range ~ 0.1 to $1 \mu\text{m}$ equivalent diameter are deposited with the poorest efficiency in the lung, but are capable of penetrating efficiently to the critical lower lung regions.

This paper gives a preliminary assessment of the potential environmental impact of automotive sulfuric acid (or sulfate) aerosol by analyzing the dynamics of this aerosol and predicting the ambient automotive sulfuric acid aerosol concentration.

It will be assumed that in approximately 10 years almost all cars in the U.S. will be fitted with a catalytic converter. "Worst case" meteorology is considered for dispersion of the automotive sulfuric acid aerosol from a ten-lane divided highway 48 m. wide and 20 km long.

First, the procedure followed in the analysis is described. Then, the dynamics of the automotive sulfuric acid aerosol are examined. The relevant processes included are advection, dispersion, dry deposition, coagulation, and chemical reaction. For roadway regions, this leads to predicting the sulfuric acid aerosol concentration under conditions of "worst case" meteorology.

SECTION 2

CONCLUSIONS

The results presented for the attachment of automotive sulfate aerosol to the ambient aerosol are based on currently accepted formulations of the relevant rate processes.

The calculations based on AROSOL of automotive sulfate concentrations around the 48 m. x 20 km. highway are believed to represent the "state of the art" for this particular application. For the states conditions and assumptions, the calculated concentration levels are reliable.

The calculations based on EPOSOD of neutralization of automotive sulfuric acid by ambient ammonia provide only a qualitative guide; however, the results are internally consistent, and provide a basis for some qualitative conclusions concerning the possible role of ambient ammonia in the neutralization of automotive sulfuric acid.

The following forecasts are based on the stated emission rates for automotive sulfuric acid of 1.025×10^{-5} gm/m-sec for the 10 lane, 48 m. x 20 km. highway under very stable meteorological conditions. Emission rates of this order could occur in 10 years if all cars travelling the highway are equipped with catalytic converters which produce sulfuric acid.

1. For parallel winds and in the absence of ammonia, sulfuric acid concentrations over 90% of the length of the highway at the 2 m. level are, in the range 115-240 $\mu\text{g}/\text{m}^3$.

2. For parallel winds and very stable meteorological conditions, maximum sulfuric acid concentrations over the highway at the 2 m. level are not strongly influenced by ambient ammonia concentrations at the 3 ppb level and would be reduced by around 50% at the 30 ppb level.

3. On and adjacent to large highways, adverse health effects may be experienced by sensitive individuals (3). Increased rates of corrosion are likely to occur.

These preliminary studies suggest that the adverse environmental effects of automotive sulfuric acid emissions may be important.

SECTION 3

PROCEDURE

Two models developed here in our group have been used: AROSOL (5) and EPOSOD (6). The part of AROSOL dealing with atmospheric dispersion has been adapted from the computer code of Shir and Shieh (7). AROSOL described the transport, dispersion, and deposition of the automotive sulfuric acid aerosol. EPOSOD accounts qualitatively for the sulfate transport and chemical reaction with ambient ammonia.

Computer code AROSOL gives a numerical solution of the single density function of an aerosol:

$$\begin{aligned} \partial n(\mu; \vec{r}, t) / \partial t + \nabla \cdot \vec{U} n(\mu; \vec{r}, t) = & (K_x + K_y) \nabla^2 n(\mu; \vec{r}, t) + \nabla \cdot K_z \nabla n(\mu; \vec{r}, t) \\ & + 1/2 \int_0^\mu d\mu' b(\mu - \mu', \mu') n(\mu'; \vec{r}, t) n(\mu - \mu'; \vec{r}, t) \\ & - n(\mu; \vec{r}, t) \int_0^\infty d\mu' b(\mu, \mu') n(\mu'; \vec{r}, t) - \frac{\partial}{\partial \mu} [\Psi(\mu; \vec{r}, t) n(\mu; \vec{r}, t)] \\ & + \vec{G} \cdot \nabla n(\mu; \vec{r}, t) + \Sigma_i \sigma_i(\mu; \vec{r}, t) + \Sigma_j \nu_j(\mu; \vec{r}, t) \end{aligned} \quad (1)$$

Boundary and initial conditions are set as a particular physical system demands, and include phenomena such as dry deposition and resuspension at boundary surfaces.

Boundary conditions for highway calculations are:

$$\frac{\partial^2 n}{\partial x^2} = 0, \quad x=0, \quad x=x \text{ max.} \quad (2)$$

$$\frac{\partial^2 n}{\partial y^2} = 0, \quad y=0, \quad y=y \text{ max.} \quad (3)$$

$$nv_{\alpha} = -(K_z + D(\mu))\frac{\partial n}{\partial z} - Gn, \quad z=0 \quad (4)$$

$$\frac{\partial n}{\partial z} = 0, \quad z=z \text{ max.} \quad (5)$$

$$n = 0, \quad t=0 \quad (6)$$

$n(\mu; \vec{r}, t)$ represents the number of aerosol particles having mass μ in the range $\mu, d\mu$ at a point in space \vec{r} at time t . In the atmosphere \vec{U} is the time average wind velocity. K_x, K_y , and K_z are the turbulent eddy diffusivities (a rectangular Eulerian coordinate system is used) in the x, y , and z directions, respectively. The fourth and fifth terms on the right hand side of eq. (1) account for particle coagulation; the sixth term represents condensation; and the seventh, gravitational sedimentation. The last two terms allow for input of primary source aerosol, σ_i , and homogeneous nucleation of trace gaseous species v_i . In eq. (4), V_d is the deposition velocity and G the magnitude of the gravitational sedimentation velocity.

Eq. (1) is coupled to the corresponding conservation equations of those trace gaseous species which act as sources for secondary aerosol (5). The appropriateness of eq. (1) for describing the evolution of an aerosol under conditions of atmospheric turbulence has been verified (8,9).

EPOSOD (6) was specifically designed to study turbulent dispersion and chemical reaction in plumes from elevated point sources. This model separates the processes of dispersion and chemical reaction over small time increments, and treats each process separately in a sequential, step-wise manner. The model is formulated by defining a number of large, infinitesimally thin grids, normal to and centered about a plume axis. Each grid is located at a particular downward distance (x) from the source. The concentration levels of the various chemical species at all points on a grid at x_j are evaluated as a function of the concentration levels on the grid at $x = x_j$. A chemically reactive species in the grid at x_j is advected and diffused to the position $x_j + \Delta x$ with the reaction process inhibited. The reaction is allowed to take place for a time, $\Delta x/U$, where U is the advective wind speed. The error introduced by this stepwise procedure is controlled by choosing Δx (and hence Δt) sufficiently small.

SECTION 4

RESULTS AND DISCUSSION

This investigation assumes that in approximately ten years, all U.S. cars will be fitted with a catalytic converter. Hopefully, modelling of expected roadway conditions will serve as an early indication of future problems.

The use of AROSOL for predictions of roadway sulfuric acid aerosol concentrations eliminates the principal objections which have been raised to previous Gaussian-type model predictions (10). Variable winds at different heights and plume rise due to heated exhaust are explicitly accounted in AROSOL according to best current micrometeorological (7) and roadway information (11).

The importance of automobile traffic in regard to mixing *immediately* above the highway and vertical dispersion is widely recognized (e.g. 11). However, much more remains to be done to arrive at quantitative relationships between mixing, dispersion, traffic speed, and vehicle characteristics. Before presenting the results of the circulation of automotive sulfate concentration based on the AROSOL model, we discuss, in a highly simplified fashion, some factors affecting the size of the automotive sulfate aerosol. After this preliminary discussion, the results of AROSOL calculations for roadway sulfate concentration are given. This is followed by results obtained from EPOSOD for roadway sulfate concentrations in the presence of significant ambient ammonia concentrations.

AUTOMOTIVE SULFATE SIZE DISTRIBUTION

Because of the important relationship between particle size and deposition efficiency in the lung, some attention has been given to the rate processes affecting the automotive sulfate size distribution.

Details of the initial growth stages of the automotive sulfate are lacking. It seems reasonable to suppose that sulfuric acid vapor is formed in the exhaust system, in or immediately after the catalytic converter undergoes homogeneous heteromolecular nucleation as the hot sulfuric acid vapor (at several hundreds of degrees Celsius exits from the exhaust tail pipe, and is rapidly mixed with the much cooler ambient air (1). The initial aerosol growth period (including condensation of water vapor and coagulation), to a particle geometric mean diameter of $0.01\text{ }\mu\text{m}$ is completed in a few tenths of a second, as is evident from an order of magnitude calculation of coagulation of condensation aerosol in the free molecule region (12). Of primary interest is the subsequent growth period-when the automotive sulfate coagulates with the ambient aerosol. We have frequently taken the initial geometric mean diameter to be $0.02\text{ }\mu\text{m}$; which appears to be in agreement with data from the GM sulfate experiment (13).

Figs. 1-7 illustrate the simplest case of the interaction by Brownian coagulation between automotive sulfuric acid aerosol and ambient aerosol. Automotive aerosol ($0.02\text{ }\mu\text{m}$ g.m.d. $\sigma_g = 2.2$) is mixed initially with ambient aerosol ($0.3\text{ }\mu\text{m}$ g.m.d. $\sigma_g = 2.2$), and coagulation is initiated. Therefore, only the time dependent coagulation process is considered in eq. (1).

The figures giving $dM/d\log D$ as a function of particle diameter (d) are arranged in order of increasing ambient mode at $0.3\text{ }\mu\text{m}$; M is the aerosol mass distribution, of the solution droplets. The initial mode for the automotive sulfuric acid solution is held fixed at a peak modal value of 155 pg/cc . The initial peak modal values for the ambient aerosol: 25, 52, 105, 200, and 520 pg/cc for Figs. 1, 2, 3, 4, and 5, respectively.

The plots of $dM/d\log D$ as a function of $\log D$ (as in Figs. 1-7) have the property that the area beneath a particular curve gives the total aerosol mass concentration in that size range. In all cases for Figs. 1-5, the automotive sulfuric acid mass $< 0.1\text{ }\mu\text{m}$ decreases with time as the sulfuric acid aerosol coagulates with the ambient aerosol that lies in the size range $> 0.1\text{ }\mu\text{m}$. Per unit time, as would be expected, the mass of sulfuric acid solution which attaches to the ambient mode is greater, the larger is the mass concentration of the ambient mode at $\sim 0.3\text{ }\mu\text{m}$.

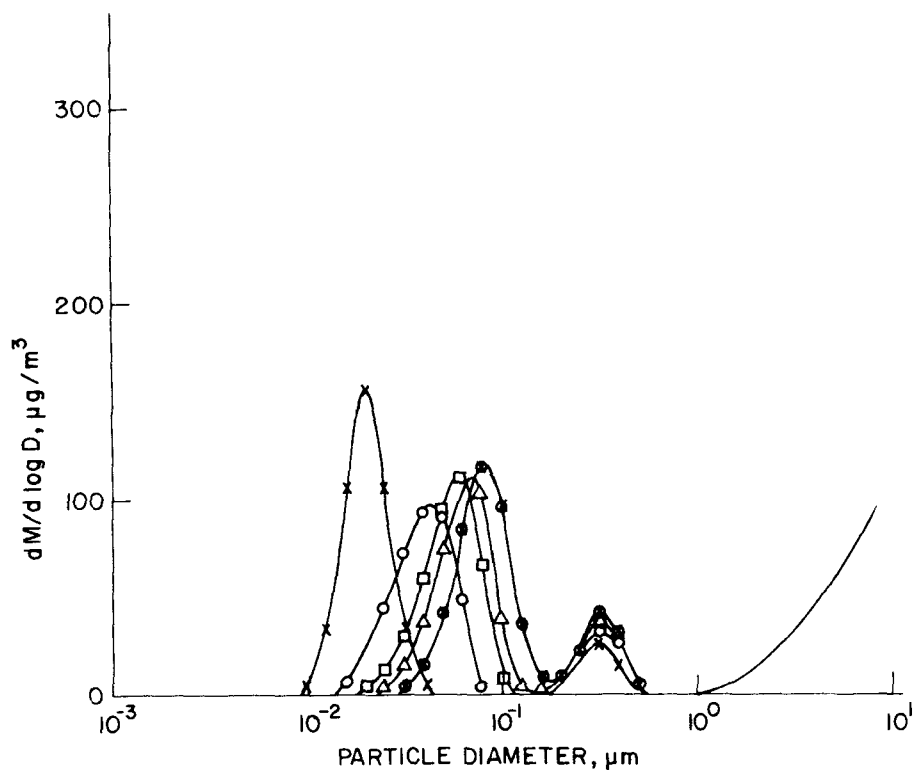


Figure 1. Coagulation of exhaust aerosol with ambient, Case I. Mass density functions ($dM/d\log D$) resulting from coagulation of automotive sulfuric acid aerosol with ambient aerosol with negligible dispersion. Initial automotive sulfuric acid: mode = $0.02 \mu\text{m}$, $\sigma_g = 2.2$, dry mass = 155 pg/cm^3 . Initial ambient aerosol: mode = $0.3 \mu\text{m}$, $\sigma_g = 2.2$, mass = 25 pg/cm^3 . Automotive and ambient aerosol mixing time: X = 0 min.
 O = 2 min.
 □ = 6 min.
 Δ = 10 min.
 ⊗ = 20 min.

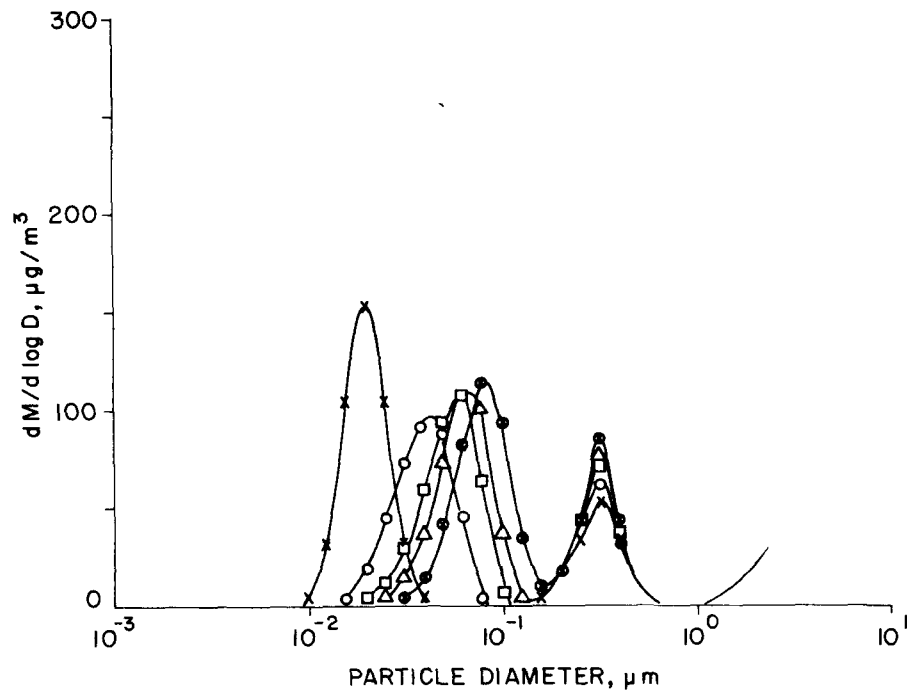


Figure 2. Coagulation of exhaust aerosol with ambient, Case II. Same as Fig. 1, except that initial ambient aerosol mass = 52 $\mu\text{g}/\text{cm}^3$.

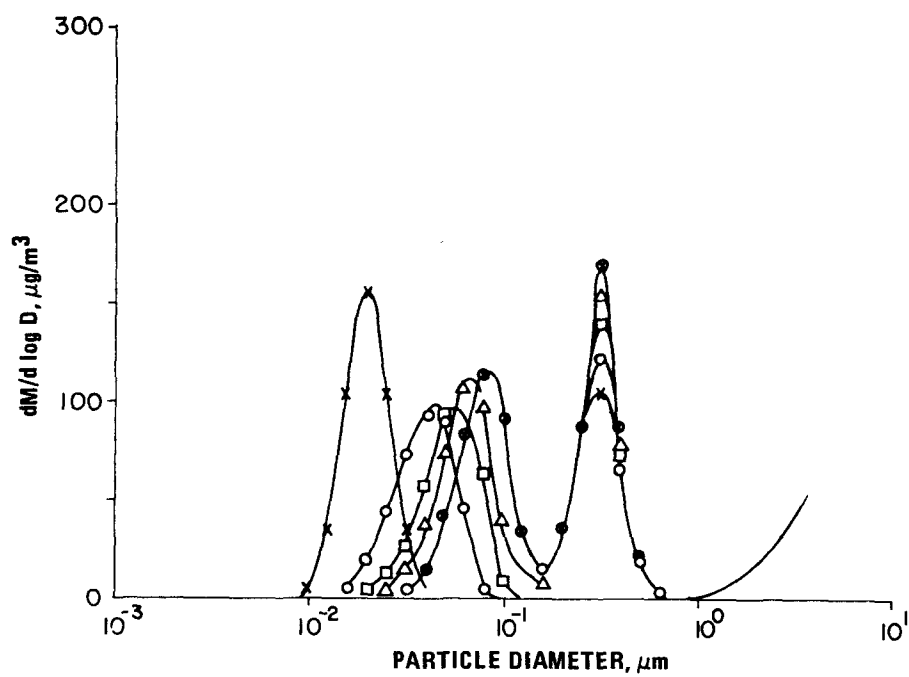


Figure 3. Coagulation of exhaust aerosol with ambient, Case III. Same as Fig. 1, except that initial ambient aerosol mass = $105 \text{ pg}/\text{cm}^3$.

4

Fig. 4

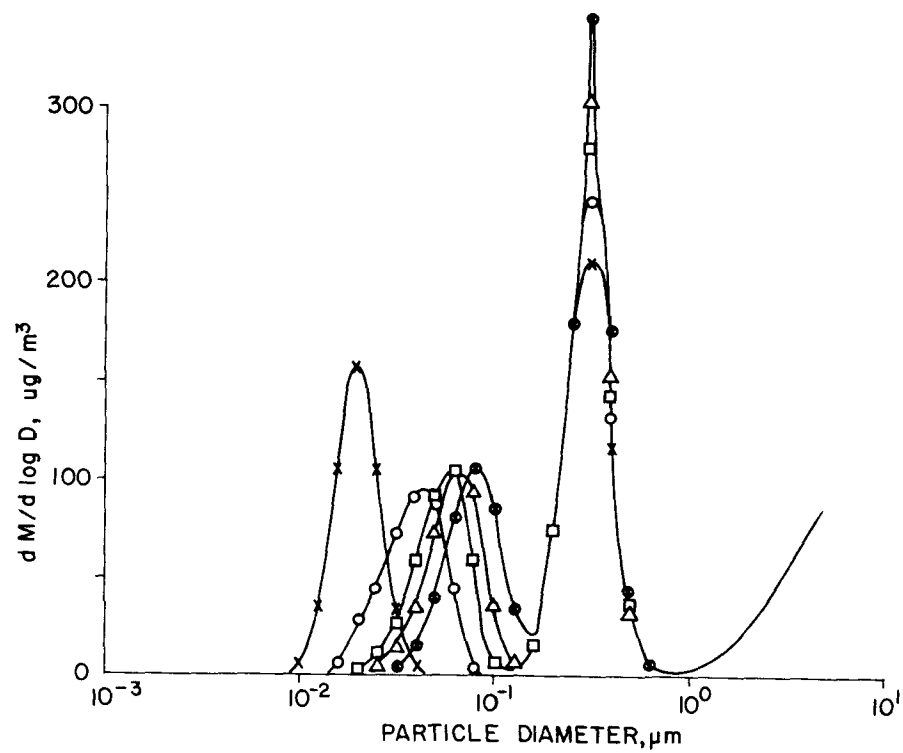


Figure 4. Coagulation of exhaust aerosol with ambient, Case IV. Same as Fig. 1, except that initial ambient aerosol mass = 200 $\mu\text{g}/\text{cm}^3$.

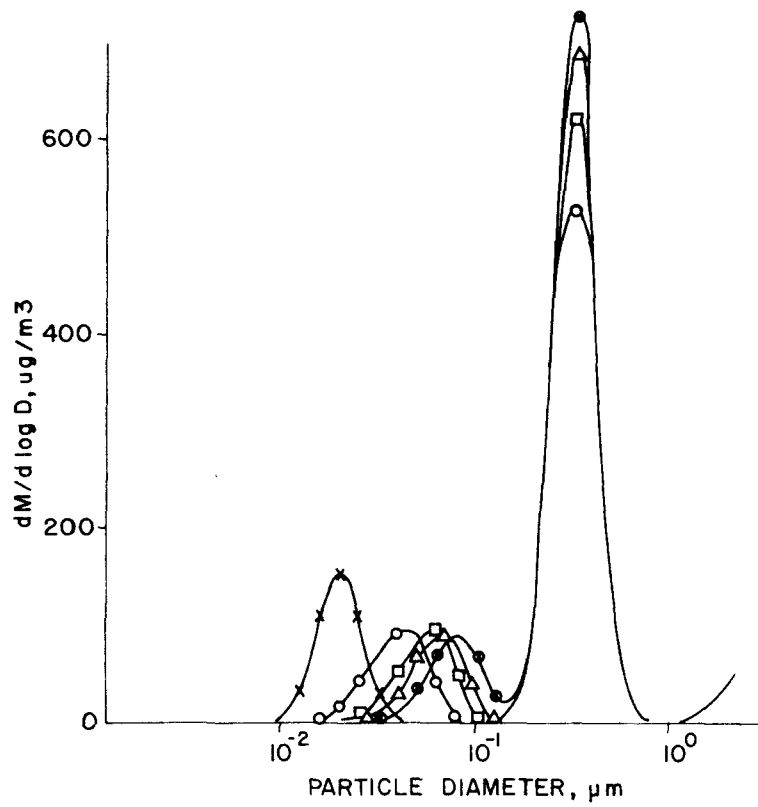


Figure 5. Coagulation of exhaust aerosol with ambient, Case V. Same as Fig. 1, except that initial ambient aerosol mass = 520 $\mu\text{g}/\text{cm}^3$.

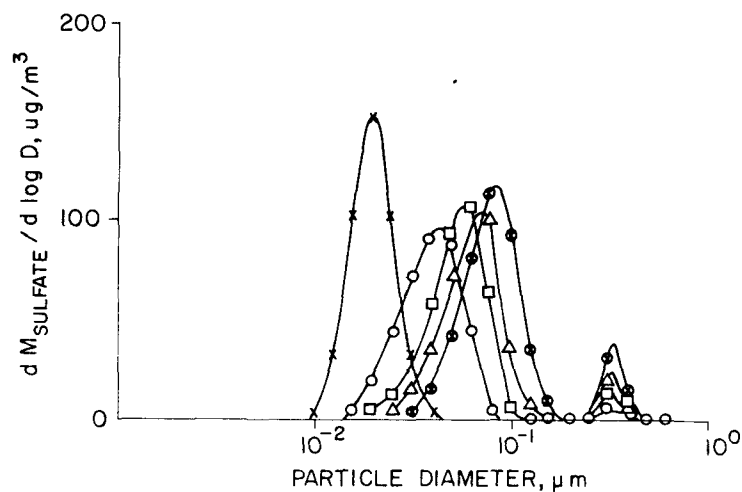


Figure 6. Coagulation of exhaust aerosol with ambient, Case VI. Mass density functions ($dM_{\text{sulfate}}/d \log D$) for automotive sulfuric acid aerosol as a function of particle diameter (D). Growth of upper sulfate mode ($\sim 0.4 \mu\text{m}$) results from attachment of automotive sulfuric acid particles to ambient aerosol. Initial ambient modal concentration = 52 pg/cm^3 .

<u>Mixing time</u>	<u>H_2SO_4 mass concentration not attached to ambient aerosol</u>
X = 0 min.	103 pg/cm^3
○ = 2 min	100 pg/cm^3
□ = 6 min.	97 pg/cm^3
Δ = 10 min.	95 pg/cm^3
⊗ = 20	91 pg/cm^3

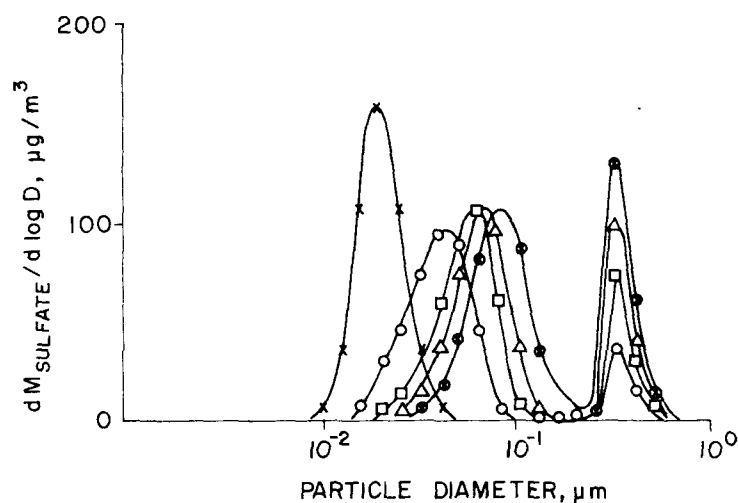


Figure 7. Coagulation of exhaust aerosol with ambient, Case VII. Mass density functions ($dM_{\text{sulfate}}/d \log D$) for automotive sulfuric acid as a function of particle diameter (D). Growth of upper sulfate mode ($\sim 0.4 \mu\text{m}$) results from attachment of automotive sulfuric acid aerosol particles to ambient aerosol. Initial ambient modal concentration = 200 pg/cm^3 .

Mixing time

x = 0 min.
 o = 2 min.
 □ = 6 min.
 Δ = 10 min.
 ⊗ = 20 min.

H₂SO₄ mass concentration not attached to ambient aerosol

103 pg/cm^3
 94 pg/cm^3
 83 pg/cm^3
 75 pg/cm^3
 61 pg/cm^3

Figs. 6 and 7 show the attachment process for sulfuric acid clearly. Initially, it is assumed that there is no sulfuric acid in the ambient mode. As coagulation proceeds, sulfuric acid begins to accumulate in the ambient mode. The accumulation occurs at a faster rate, as the mass concentration of the initial ambient mode at 0.3 μm increases.

From Figs. 1-6, a very simplified picture can be presented of the dynamics of the automotive sulfate. First, neglecting advection and dispersion, a control volume containing sources of automotive sulfate and ambient aerosol is considered. Assume that the automotive sulfate aerosol may be approximately represented by c_1 , the single number concentration, (initial particle diameter $\sim 0.02 \mu\text{m}$); assume also that the ambient aerosol is represented by c_2 , the number concentration (particle diameter $\sim 0.3 \mu\text{m}$), the rate of change of c_1 can be given by the qualitative relation:

$$dc_1/dt = -b_{11}c_1^2 - b_{12}c_1c_2 - \delta c_1 + \sigma \quad (7)$$

where b_{11} is the coagulation coefficient of the automotive sulfate with itself, and b_{12} is the coefficient for coagulation of automotive sulfate with ambient aerosol. δ is the removal rate coefficient of automotive sulfate from the control volume by processes such as deposition and dispersion. σ is the source input rate of automotive sulfate. It is evident, after an initial period that eq. (2) possesses quasistationary solutions in which, with a steady source, σ , and removal coefficient, δ , the automotive sulfate will be maintained at a given size, and will attach to the ambient aerosol at a particle diameter of $\sim 0.3 \mu\text{m}$.

Since the automotive sulfate aerosol undergoes advection and dispersion over a roadway, one must consider the following partial differential equation instead of eq. (2):

$$\partial c_1 / \partial t + \nabla \cdot \vec{U}c_1 = \nabla \cdot \vec{K} \cdot \nabla c_1 - b_{11}c_1^2 - b_{12}c_1c_2 \quad (8)$$

where sources and removal (deposition) appear as boundary conditions. If c_2 is relatively large, it may be supposed that, for short times, it is approximately independent of time and position. c_1 , however, is decreasing due to spatial dispersion, with the result that the term $b_{11}c_1^2$ can be

neglected in comparison with $b_{12}c_1c_2$. Therefore, dispersion decreases the importance of coagulation of the automotive sulfate with itself. Under these circumstances, we assume that b_{12} and c_2 are approximately independent of position; therefore, for steady state conditions for a point source, eq. (8) would have the solution:

$$c_1 = F(x,y,z)\exp\{-b_{12}c_2X/U\} \quad (9)$$

where x is in the direction of the advective flow with mean speed U , and $F(x,y,z)$ is a function representing the diffusion processes of eq. (8). As is to be expected, the decay of c_1 owing to attachment to the ambient aerosol is exponential.

The accurate representation of all the processes discussed here in eqs. (7), (8), and (9) is much more complex-and is given by eq. (1).

ROADSIDE AUTOMOTIVE SULFATE ACCORDING TO AROSOL

"Worst case" meteorology is considered for dispersion of automotive sulfate from a ten-lane divided highway with a width of 48 m. and a length of 20 km. Dispersion is modelled under conditions analogous to F class stability and with a mean surface wind of 0.514 m/sec (at 10 m.). For each lane of the 10-lane highway, an emission rate of 1.025×10^{-5} gm/m-sec is assumed; a figure which could be justified by extrapolating to higher traffic densities the results of the GM sulfate experiment (2).

As previously stated, the use of AROSOL for modelling dispersion of automotive sulfate from a highway overcomes the principal objections which have been raised (10) to Gaussian-type models, such as HIWAY. AROSOL is a "K-theory" model which can account explicitly for: vertical variation of windspeed, traffic effects such as the highway "heat island" mixing over the highway and "shelter-belt" effects of traffic (11).

Detailed knowledge of parameters entering into AROSOL for automotive sulfate highway modelling is lacking. Consequently, we carried out model studies in which certain parameters are varied. These input data included:

- (1) Grid for highway calculation
- (2) Emission data

- (3) Wind data
- (4) Mixing height
- (5) Surface roughness
- (6) Particulate dry deposition
- (7) Eddy diffusivities

These will be discussed briefly in order.

(1) Grid for highway calculation: A rectangular Eulerian coordinate system is used with the origin at the upwind end of the straight, 20 km. highway, at pavement level, and at the center of the highway. X increases in the direction of the advective wind, which for the AROSOL calculations is always considered to be parallel to the highway. Z is the distance above the highway, and y is the distance from the center of the highway. In the x-y plane, 26 x 13 grid points were included, with a basic grid size of 200 m. x 50 m. Two-meter intervals were considered up to the mixing height.

(2) Emissions data: Total mass emission rate used was 1.025×10^{-5} g/m-sec for each lane of the 10-lane highway. The sulfate aerosol diameter was assumed to be 0.02 μm . Details of the interaction of these particles with ambient aerosol are not considered here.

(3) Wind data: The wind speed used was 0.514 m/sec at 10 m. and parallel to the highway. Vertical wind variation was calculated by a power law assumption (7).

(4) Mixing height: A value of 300 m. was arbitrarily selected.

(5) Surface roughness (z_0): Surface roughness was varied to reflect possible effects of highway traffic on vertical dispersion. It started with a value of 0.25 (15), other values used were 0.75 and 1.5.

(6) Particulate dry deposition: This process enters into the boundary condition of eq. (1) as the deposition velocity, (V_d). Several values of V_d were considered: 0, 0.5, and 2 cm/sec. The value of 2 cm/sec is the upper bound for the deposition velocity for automotive sulfate from the subsequent EPOSOD calculations. The value 0.5 cm/sec appears reasonable under the stated stability conditions based on the correlations of Sehmel and Hodgson (16).

(7) Eddy diffusivities: The vertical eddy diffusivity (K_z) was calculated by using the techniques employed by Shir and Shieh (7) up to a height of 1 m. Perfect vertical mixing was assumed over the highway.

Figs. 8-14 represent some of the results of our calculations employing AROSOL and the conditions stated above.

Figs. 8-9 show the approach to a steady state of the automotive sulfate above the highway at $x = 2$ km. At $t = 0$, the emission rate of 1.025×10^{-5} gm/m-sec was "switched on," and held constant. The sulfuric acid concentration at the two heights (2 m. and 10 m.), remains sensibly constant after 1-1/2 hours, and achieves around 80% of the steady state value in 30 min. In Fig. 8, for a roughness, (z_o), of 0.25 m., the acid concentration at 2 m. above the highway is approximately $218 \mu\text{g}/\text{m}^3$ under conditions of no dry deposition ($V_d = 0$). A value of $V_d = 0.5$ cm/sec lowers the steady state acid concentration at 2 km. to approximately $185 \mu\text{g}/\text{m}^3$. The value of $140 \mu\text{g}/\text{m}^3$ for $V_d = 2$ cm/sec is believed to be a "lower bound" for the stated conditions. In Fig. 9, the roughness (z_o) has been increased to 0.75 m.; all other conditions are the same as in Fig. 8. This results in a decrease of the steady state acid concentration at 2 m. above the highway at 2 km. to $163 \mu\text{g}/\text{m}^3$ ($V_d = 0$). The "lower bound" value is now $112 \mu\text{g}/\text{m}^3$ ($V_d = 2$ cm/sec). Figs. 10 and 11 show the buildup of acid proceeding downwind along the highway 2 hours after the start of traffic. At 2 hours, Figs. 8 and 9 indicate that steady state conditions have been achieved. As is evident from Fig. 10, acid concentration builds up very rapidly down the highway. After 1 km., around 70% of the maximum value has been achieved. Above the highway at 2 m., the maximum acid concentration for a roughness (z_o) of 0.25 m. is approximately $240 \mu\text{g}/\text{m}^3$ ($V_d = 0$) with a "lower bound" value of around $140 \mu\text{g}/\text{m}^3$ ($V_d = 2$ cm/sec). In Fig. 11, z_o has been increased to 0.75 m. which lowers the 2 m. highway concentration maximum to around $180 \mu\text{g}/\text{m}^3$ and the "lower bound" value to $115 \mu\text{g}/\text{m}^3$.

Figs. 12-15 give sulfuric acid concentration isopleths in a plane perpendicular to the highway at 5 km. from the upwind end of the highway. Figs. 12 and 13 are for a roughness (z_o) of 0.25 m., and 13 and 14, for a z_o of 0.75 m. Figs. 12 and 14 (for $V_d = 0$) show the important effect of

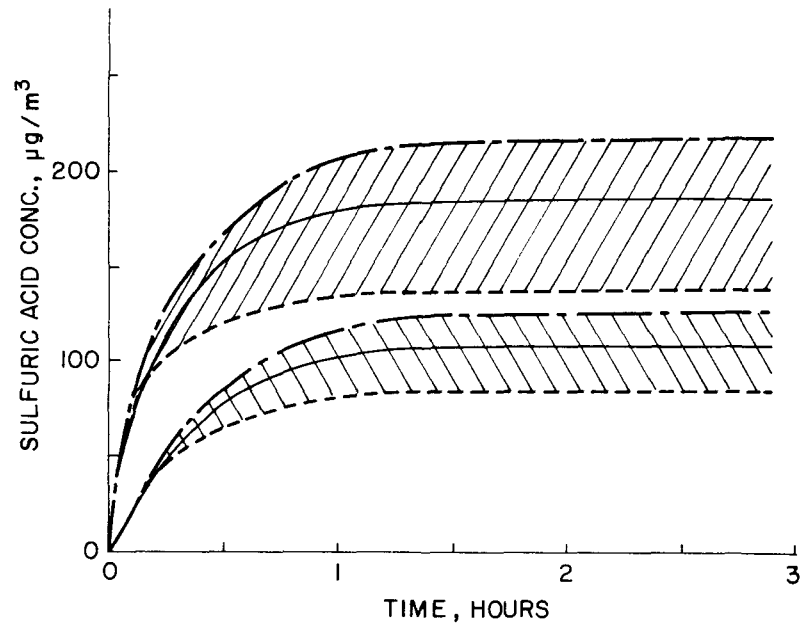


Figure 8. Dispersion of exhaust aerosol, Case VIII. AROSOL calculation for parallel winds for approach to steady state automotive sulfuric acid concentrations over highway at 2 km downwind from beginning of highway. Roughness (z_0) = 0.25 m. The upper band is for a height of 2m, and the lower band is for a height of 10m.

Dry deposition velocity

- 0 cm/sec
- 0.5 cm/sec
- .- 2 cm/sec

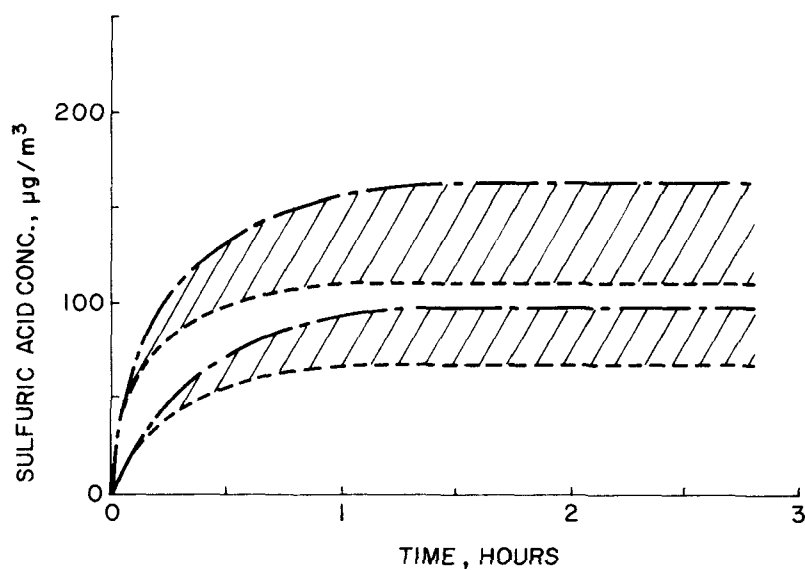


Figure 9. Dispersion of exhaust aerosol, Case IX. AROSOL calculation for parallel winds for approach to steady state automotive sulfuric acid concentrations over highway at 2 km. Roughness (z_0) = 0.75m. The upper band is for a height of 2m, and the lower band is for a height of 10m.

Dry deposition velocity

--- 0 cm/sec
 ---- 2 cm/sec

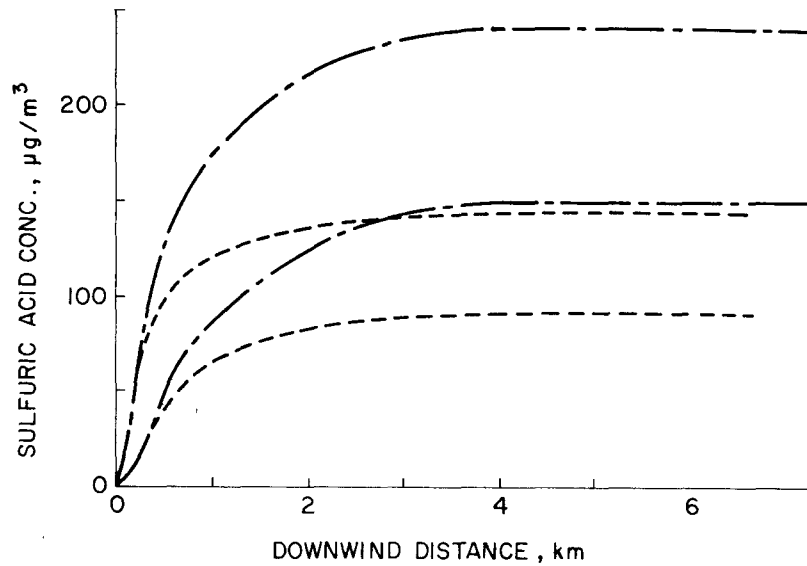


Figure 10. Dispersion of exhaust aerosol, Case X. AROSOL calculation for parallel winds of increase of automotive sulfuric acid concentration with downwind distance from beginning of highway 2 hours after start of traffic. Roughness (z_0) = 0.25m.

Dry deposition velocity

- 0 cm/sec (upper curve for height = 2m, lower curve for height = 10m)
- 2 cm/sec (upper curve for height = 2m, lower curve for height = 10m)

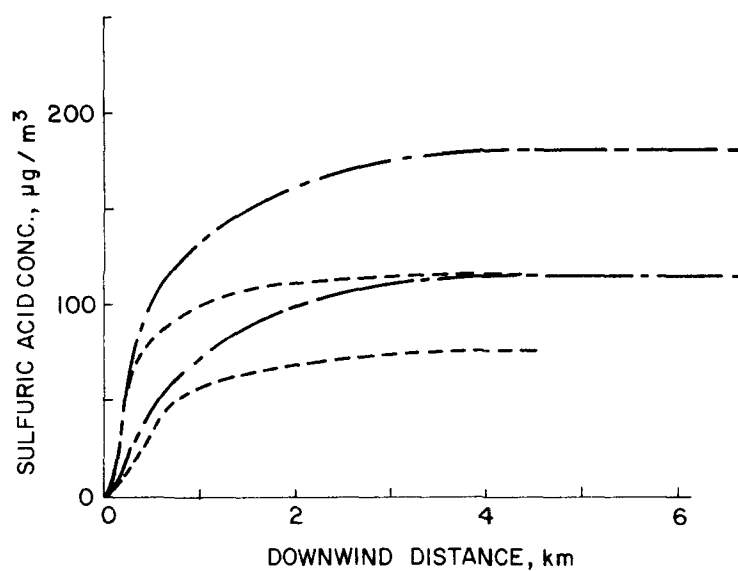


Figure 11. Dispersion of exhaust aerosol, Case XI. AROSOL calculation for parallel winds of increase of automotive sulfuric acid concentration with downwind distance from beginning of highway 2 hours after start of traffic. Roughness (z_0) = 0.75m.

Dry deposition velocity

— 0 cm/sec
 --- 2 cm/sec

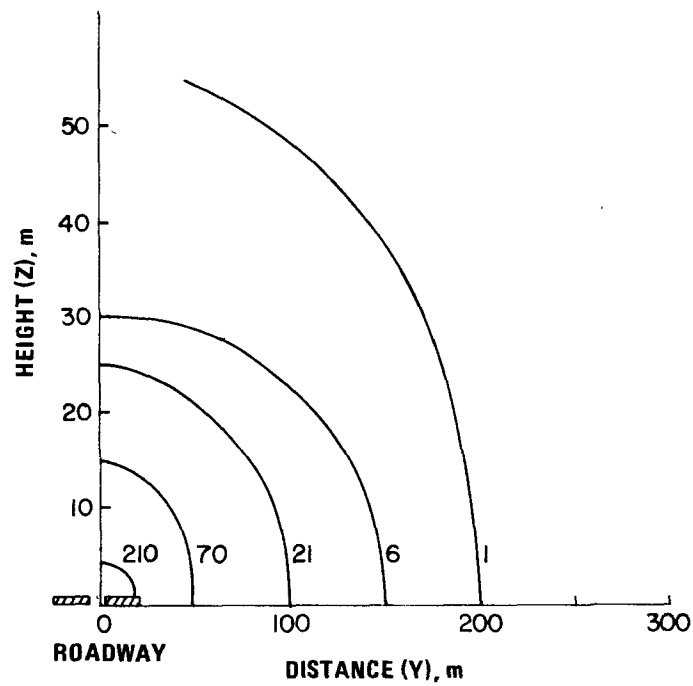


Figure 12. Dispersion of exhaust aerosol, Case XII. AROSOL calculation for parallel winds of sulfuric acid concentration ($\mu\text{g}/\text{m}^3$) isopleths 5 km downwind of beginning of highway.

Ammonia concentration = 0 ppb
 Roughness (z_0) = 0.25 m
 Deposition velocity = 0 cm/sec

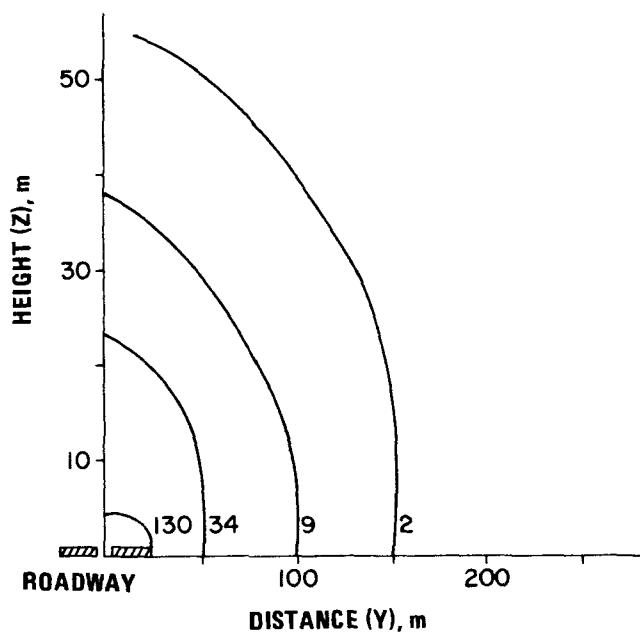


Figure 13. Dispersion of exhaust aerosol, Case XIII. AROSOL calculation for parallel winds of sulfuric acid concentration ($\mu\text{g}/\text{m}^3$) isopleths 5 km downwind of beginning of highway.

Ammonia concentration = 0
 Roughness (z_0) = 0.25 m
 Deposition velocity - 2 cm/sec

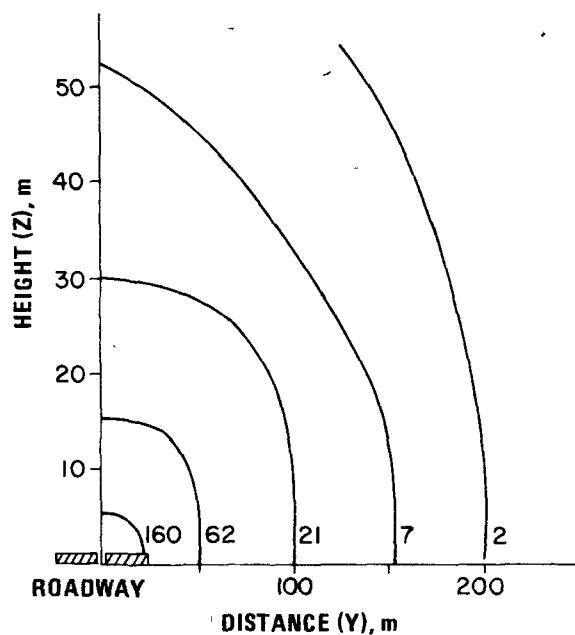


Figure 14. Dispersion of exhaust aerosol, Case XIV. AROSOL calculation for parallel winds of sulfuric acid concentration ($\mu\text{g}/\text{m}^3$) isopleths 5 km downwind of beginning of highway.

Ammonia concentration = 0 ppb
 Roughness (z_0) = 0.75 m
 Deposition velocity = 0 cm/sec

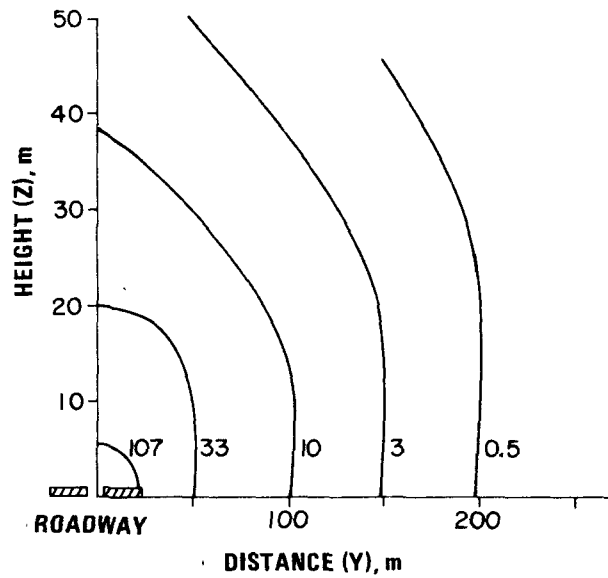


Figure 15. Dispersion of exhaust aerosol, Case XV. AROSOL calculation for parallel winds of sulfuric acid concentration ($\mu\text{g}/\text{m}^3$) isopleths 5 km downwind of beginning of highway.

Ammonia concentration = 0 ppb
 Roughness (z_0) = 0.75 m
 Deposition velocity = 2 cm/sec

z_o on the vertical transfer of acid sulfate. Increasing z_o , decreases the acid sulfate concentration immediately around the roadway, but increases it several hundred meters away. Comparison of Figs. 12 and 13 for $z_o = 0.25$ shows the important effect of dry deposition. The deposition velocity of $V_d = 2$ cm/sec of Fig. 13 is perhaps unrealistically high (providing a "lower bound"), but it shows the effect of deposition rather dramatically. Dry deposition at $V_d = 2$ cm/sec almost halves the acid sulfate concentrations. A large uncertainty is the possible resuspension of acid sulfate by the traffic. We are unable to assess this possibility, but the net effect would always be to lower the effective deposition velocity.

The general forms of the isopleths shown in Figs. 12-15, and particularly 14 and 15 for $z_o = 0.75$, resemble those found in the GM experiment with inert tracer (10). The isopleths of Figs. 12-15, differ considerably from isopleths based on the EPOSOD calculations discussed in the next section; this difference is expected.

REACTION OF AUTOMOTIVE SULFURIC ACID WITH AMBIENT AMMONIA ACCORDING TO EPOSOD

The results of the EPOSOD calculation provide only a qualitative picture of the reaction of automotive sulfuric acid with ambient ammonia. The calculations are internally consistent and indicate the variation of sulfuric acid concentration with ambient ammonia concentrations under the conditions of "worst case" meteorology.

Two examples are discussed: winds parallel and perpendicular to the highway. In the former case, grids in the EPOSOD calculation are 50 m. apart; in the latter, they are 10 m. apart. Empirically, these spacings were found to be optimal from the standpoints of numerical error and computer time. Diffusion from an upwind grid element to the next grid (50 m. downwind) was assumed to occur with the constant Gaussian dispersion parameters:

$$\sigma_y = 14.4 \text{ m.} \quad \sigma_z = 3.2 \text{ m.}$$

These values correspond roughly to the Pasquill-Gifford correlations for F-class stability (6). The effect of traffic on mixing was accounted for by assuming that automotive sulfate was vertically mixed in a region 48 m. wide and 6 m. high. Owing to the rapid reaction between sulfuric acid

aerosol and ammonia, no distinction was made as to particle size in the calculation of reaction rate. Also, dry deposition was assumed to occur at a rate independent of particle size and to be irreversible; as in the AROSOL calculation, the principal uncertainty is the effect of traffic on deposition rate. Consequently, deposition rate is a variable parameter in our model studies.

Figs. 16 to 28 are a sample of the results from our EPOSOD calculations. Figs. 16 to 26 are the results for parallel winds and Figs. 27 to 28 are for perpendicular winds. The neutralization of the automotive sulfate is a diffusion limited rate process, as is apparent from the figures. The attenuation of acid sulfate concentration has been studied for ammonia concentrations of 0, 3, and 30 ppb. Although accurate ambient levels for ammonia have not yet been established, 3 ppb. would appear to be a representative ambient value. 30 ppb. is believed to be unrealistically large, but is included for comparison. The 0 ppb. case is studied to provide a basis of comparison with the more accurate AROSOL dispersion calculations.

In the parallel wind case for the 20 km. highway, the origin of the Cartesian coordinate system is located at the upwind end of the highway, at pavement level, and at the center of the highway.

Figs. 16-17 for ambient ammonia concentration of 3 ppb. show the build-up of sulfuric acid over the roadway at a point (y), 20 m. from the center of the highway, and a height (z), of 2 m. This is shown for a deposition velocity, (V_d) of 0 and 0.03 cm/sec. Figs. 18-21 present sulfuric acid isopleths for 3 ppb. ambient ammonia in a plane 10 km. downwind and perpendicular to the highway. These isopleths are for deposition velocities (V_d) of 0, 0.03, and 0.4 and 2 cm/sec. The value of 2 cm/sec represents a possible upper bound based on the assumed vertical diffusion rate corresponding approximately to F-class stability. These values may be compared to corresponding values for 0 ppb. ambient ammonia. The sulfuric acid concentrations immediately above the roadway for "worst case" meteorology are not strongly influenced by the addition of 3 ppb. ambient ammonia; however, the roadway concentrations are significantly influenced by the deposition rate.

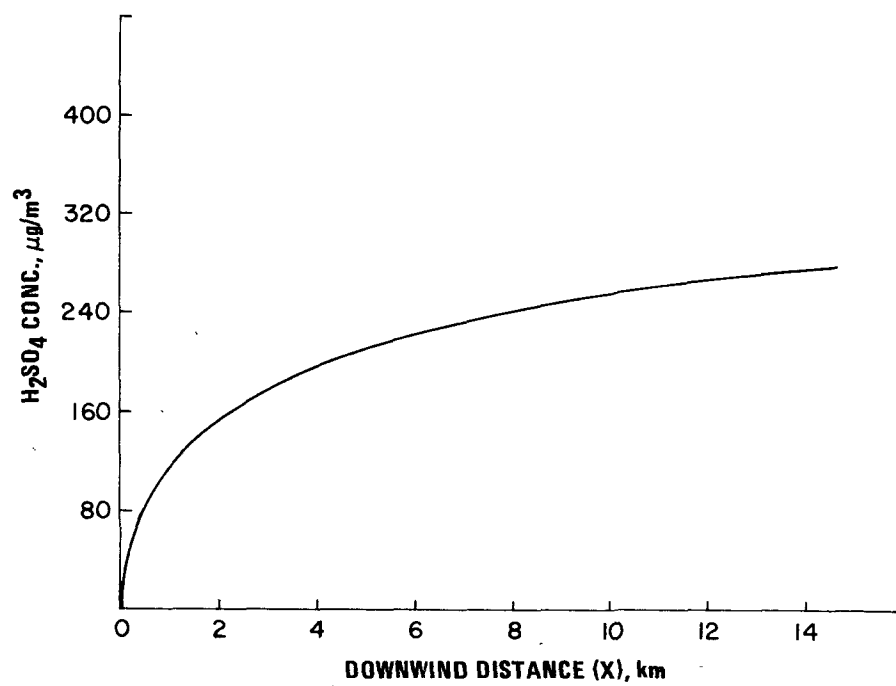


Figure 16. Transport and reaction of exhaust aerosol, Case XVI. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway as function of downwind distance at 2m above surface of highway and 20m from highway center.

Ammonia concentration = 3 ppb
Deposition velocity = 0 cm/sec

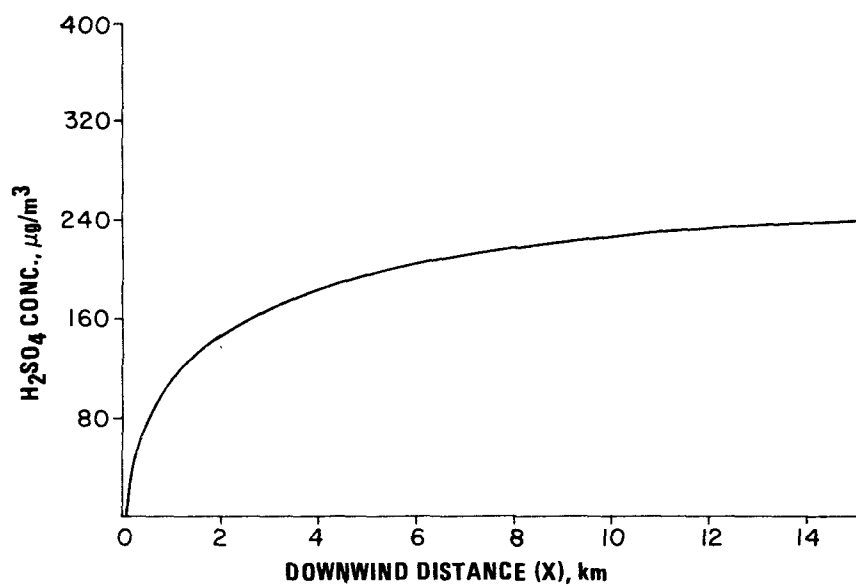


Figure 17. Transport and reaction of exhaust aerosol, Case XVII. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway as function of downwind distance at 2m above surface of highway and 20m from highway center.

Ammonia concentration = 3 ppb
 Deposition velocity = 0.03 cm/sec

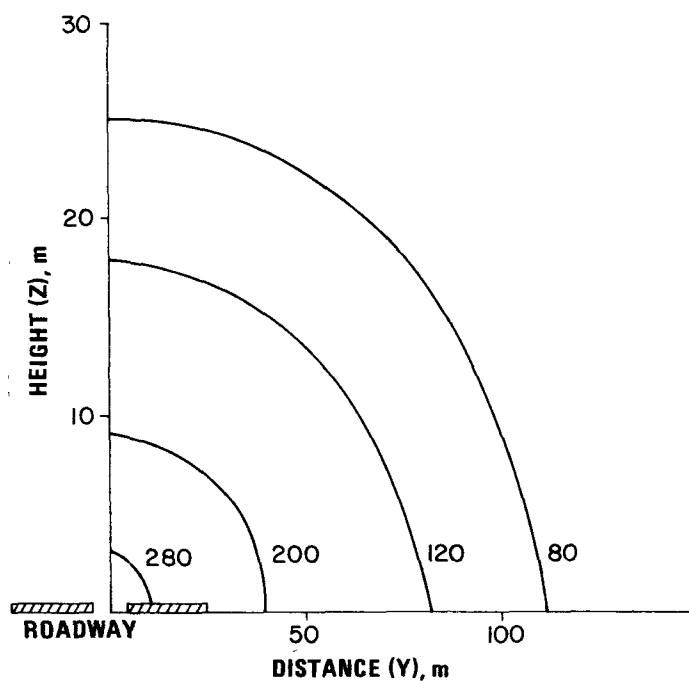


Figure 18. Transport and reaction of exhaust aerosol, Case XVIII. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway. Sulfuric acid concentration isopleths ($\mu\text{g}/\text{m}^3$) at cross-section perpendicular to highway at 10km downwind.

Ammonia concentration = 3 ppb
Deposition velocity = 0 cm/sec

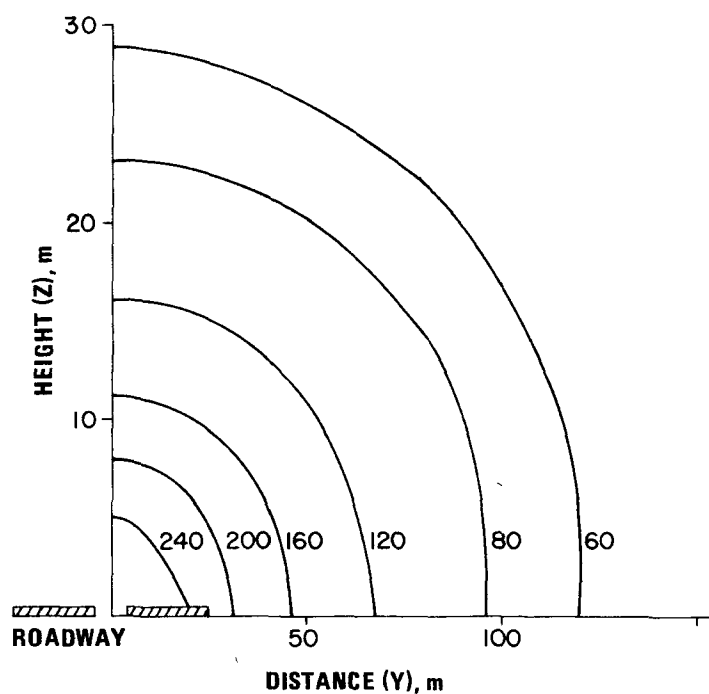


Figure 19. Transport and reaction of exhaust aerosol, Case XIX. EPOSOD calculations of neutralization of automotive sulfuric and by ambient gaseous ammonia for wind parallel to highway. Sulfuric acid concentration isopleths ($\mu\text{g}/\text{m}^3$) at cross-section perpendicular to highway at 10 km downwind.

Ammonia concentration = 3 ppb
 Deposition velocity = 0.03 cm/sec

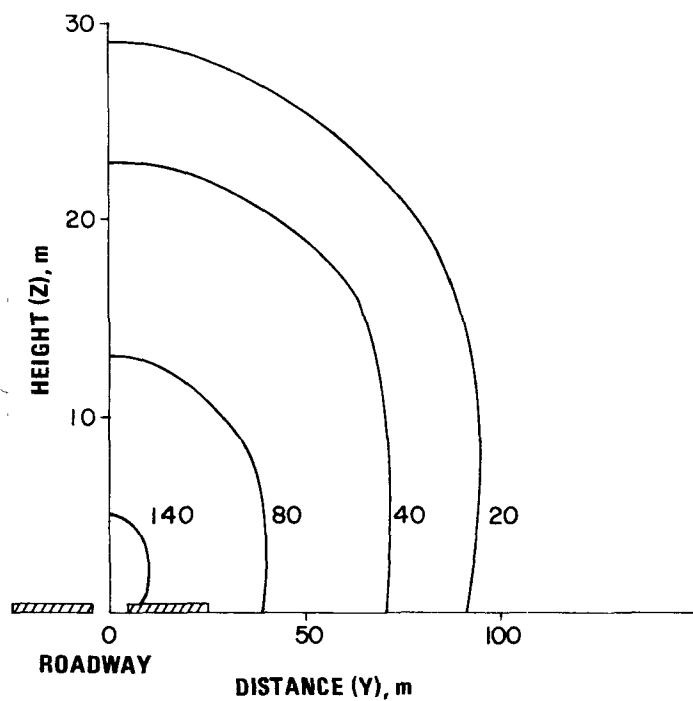


Figure 20. Transport and reaction of exhaust aerosol, Case XX. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway. Sulfuric acid concentration isopleths ($\mu\text{g}/\text{m}^3$) at cross-section perpendicular to highway at 10 km downwind.

Ammonia concentration = 3 ppb
 Deposition velocity = 0.4 cm/sec

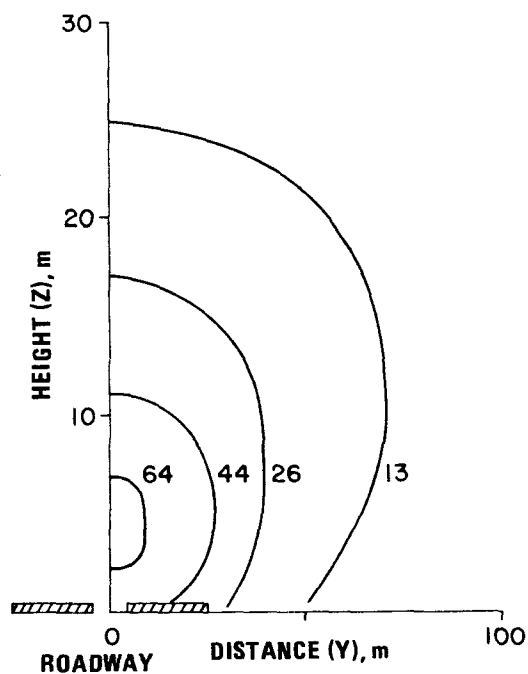


Figure 21. Transport and reaction of exhaust aerosol, Case XXI. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway. Sulfuric acid concentration isopleths ($\mu\text{g}/\text{m}^3$) at cross-section perpendicular to highway at 10 km downwind.

Ammonia concentration = 3 ppb
 Deposition velocity = 2 cm/sec

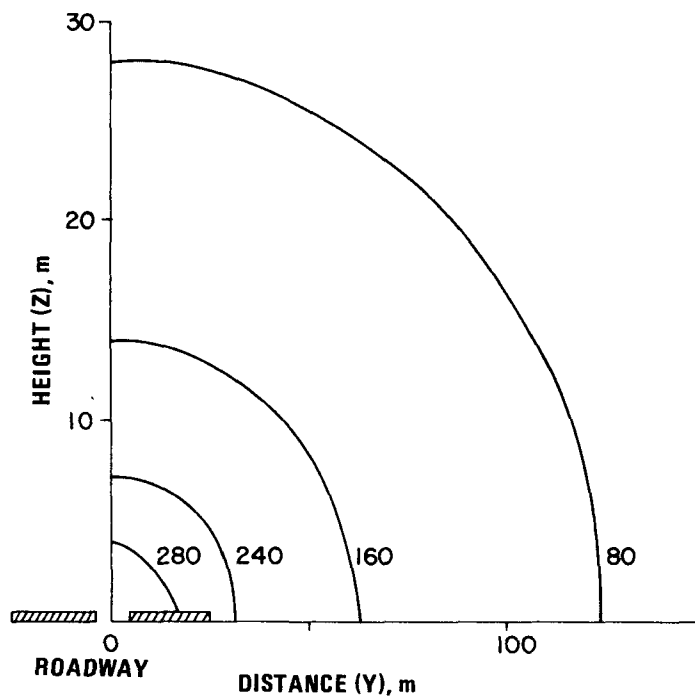


Figure 22. Transport and reaction of exhaust aerosol, Case XXII. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway. Sulfuric acid concentration isopleths ($\mu\text{g}/\text{m}^3$) at cross-section perpendicular to highway at 10 km downwind.

Ammonia concentration = 0 ppb
 Deposition velocity = 0 cm/sec

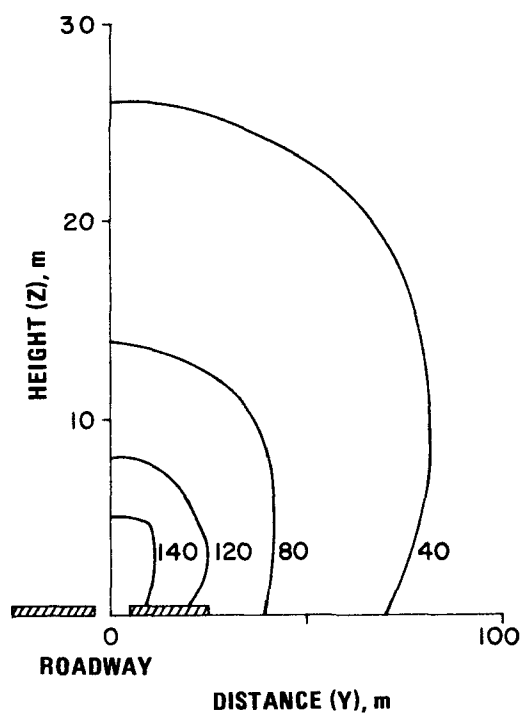


Figure 23. Transport and reaction of exhaust aerosol, Case XXIII. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway. Sulfuric acid concentration isopleths ($\mu\text{g}/\text{m}^3$) at cross-section perpendicular to highway at 10 km downwind.

Ammonia concentration = 0 ppb
 Deposition velocity = 0.4 cm/sec

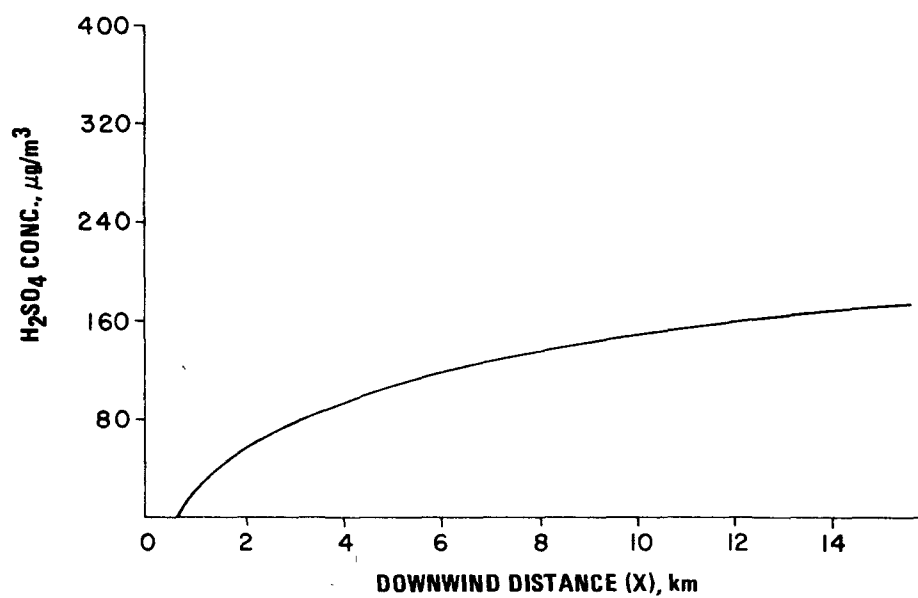


Figure 24. Transport and reaction of exhaust aerosol, Case XXIV. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway as a function of downwind distance at 2m above surface of highway and 20m from highway center.

Ammonia concentration = 30 ppb
Deposition velocity = 0 cm/sec

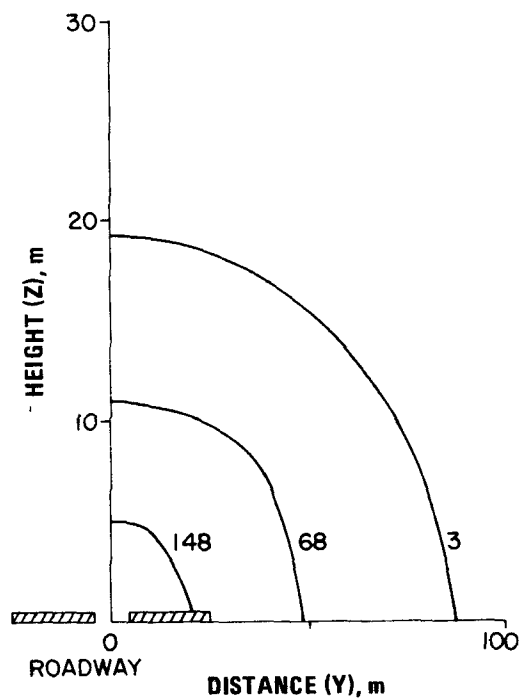


Figure 25. Transport and reaction of exhaust aerosol, Case XXV. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway. Sulfuric acid concentration isopleths ($\mu\text{g}/\text{m}^3$) at cross-section perpendicular to highway at 10 km downwind.

Ammonia concentration = 30 ppb

Deposition velocity = 0 cm/sec

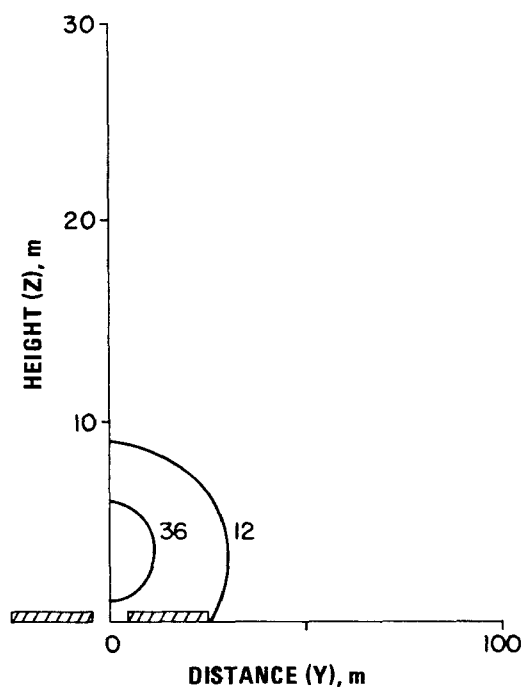


Figure 26. Transport and reaction of exhaust aerosol, Case XXVI. EPOSOD calculations of neutralization of automotive sulfuric acid by ambient gaseous ammonia for wind parallel to highway. Sulfuric acid concentration isopleths ($\mu\text{g}/\text{m}^3$) at cross-section perpendicular to highway at 10 km downwind.

Ammonia concentration = 30 ppb
 Deposition velocity = 2 cm/sec

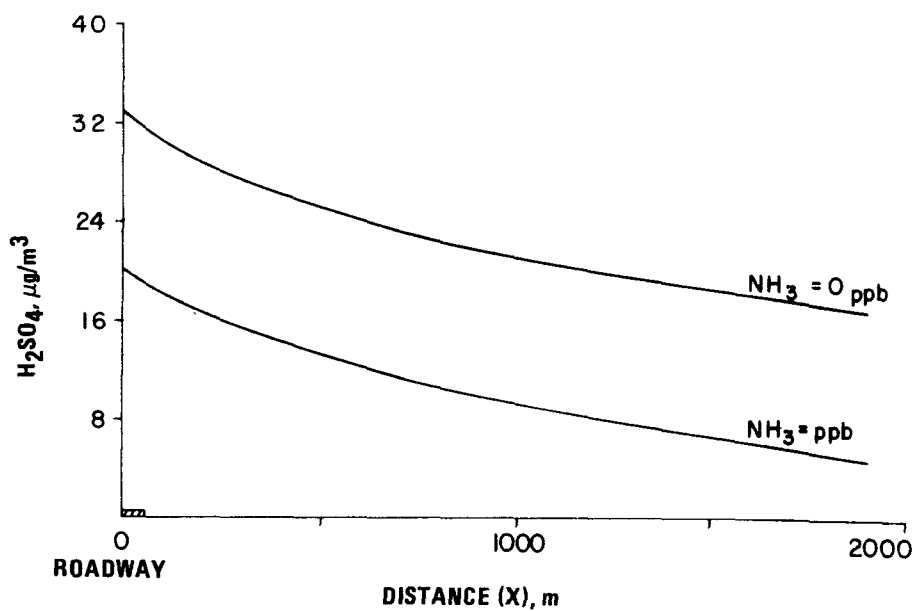


Figure 27. Transport and reaction of exhaust aerosol, Case XXVII. EPOSOD calculation of neutralization of automotive sulfuric acid by ambient gaseous ammonia with wind perpendicular to highway. Downwind distance measured from nearest upwind border of highway. Sulfuric acid concentration is at 2m above ground.

Deposition velocity = 0 cm/sec

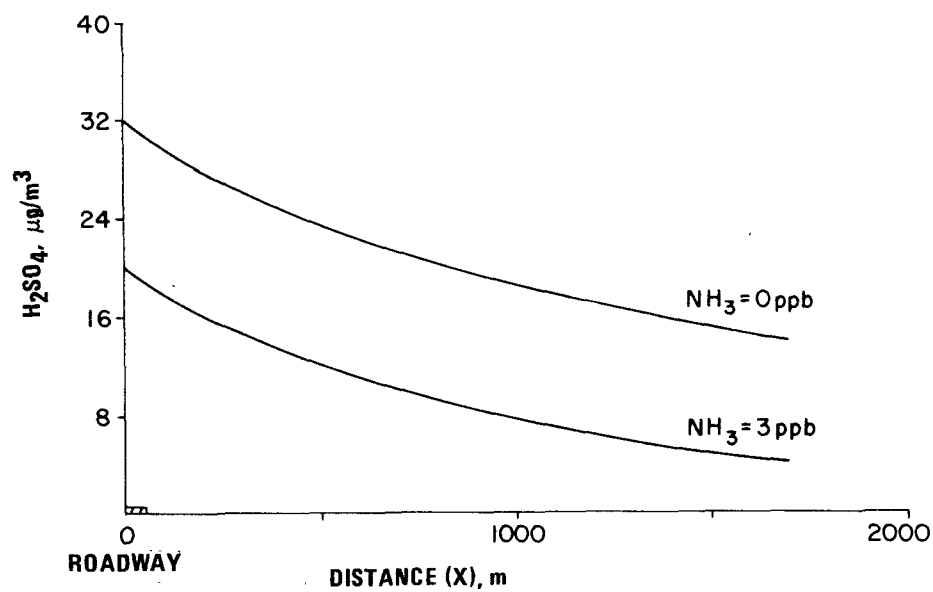


Figure 28. Transport and reaction of exhaust aerosol, Case XXVIII. EPOSOD calculation of neutralization of automotive sulfuric acid by ambient gaseous ammonia with wind perpendicular to highway. Downwind distance measured from nearest upwind border of highway. Sulfuric acid concentration is at 2m above ground.

Deposition velocity = 0.03 cm/sec

Even when, as in Figs. 24 to 26, ambient ammonia is increased to 30 ppb., sulfuric acid concentrations immediately above the roadway are only reduced to about one-half the sulfuric acid concentrations for 0 ppb. ambient ammonia. Again, the sulfuric acid concentration above the roadway is most strongly influenced by the dry deposition rate.

For winds perpendicular to the highway, Figs. 27 and 28 give the sulfuric acid concentrations at a height of 2 m. ($z = 2$ m.) as a function of downwind distance. The origin of the Cartesian co-ordinate system is located at the 10 km. point of the highway, at the upwind edge and pavement level. For the two deposition velocities, 0 and 0.3 cm/sec, it is clear that, irrespective of the ambient ammonia concentration, the downwind sulfuric acid concentrations are very small. The trend of these predicted concentration levels appear to be consistent with some of the measurements from the GM Sulfate Dispersion Experiment (14).

A comparison between AROSOL and EPOSOD calculations is given in Figs. 12 and 22.* Under equivalent conditions, EPOSOD predicts a larger roadway concentration ($\sim 280 \mu\text{g}/\text{m}^3$) than AROSOL ($\sim 210 \mu\text{g}/\text{m}^3$). EPOSOD, when compared with AROSOL, underestimates the concentrations some distance away from the roadway.

*For sulfuric acid, units in ppb. multiplied by 4 give $\mu\text{g}/\text{m}^3$.

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APPENDIX A

THE RATE OF REACTION BETWEEN AMBIENT AMMONIA AND SULFURIC ACID SOLUTION AEROSOL

The analysis of the reaction of dispersing automotive sulfuric acid with ambient ammonia assumed that the reaction was rapid compared to the characteristic diffusion time. The diffusion time was in the range 1-10 minutes. This section gives estimates of the reaction rate.

The automotive sulfuric acid solution aerosol is found in particle sizes less than 1 μm diameter. For such particle sizes the rate of collision N of ammonia molecules with a sulfuric acid solution droplet is approximately (12):

$$N \approx \frac{6 \times 10^4 D^2 n}{1 + 2.3 \times 10^4 D} \quad (\text{A-1})$$

where D is the droplet diameter in centimeters and n is the number density (cm^{-3}) of ammonia molecules surrounding the droplet.

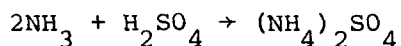
Under the assumption that the reaction occurs on the surface of the droplet, a collision efficiency for reaction, α can be introduced so that αN gives the number of ammonia molecules per second undergoing reaction with the sulfuric acid droplet.

An upper bound for this reaction rate is given by setting $\alpha = 1$. A lower bound is not easily established. Evidence exists that in the atmosphere sulfuric acid solution droplets can exist in the presence of ambient ammonia (17); this phenomenon has been attributed to the presence of relatively impermeable surface films on the sulfuric acid solution droplets.

It is not the aim of this section to explore the question of surface accommodation and reaction of ammonia molecules with sulfuric acid solution droplets. It will be assumed that in the absence of further information, $\alpha = 1$.

Under this assumption, the characteristic reaction time is of the order N^{-1} which for ammonia concentration at the ppb level is seen to be very short compared to the characteristic diffusion time.

In addition an estimate of the minimum time, t_N , for complete neutralization of a single sulfuric acid solution droplet by ammonia according to the overall reaction:



is given by:

$$t_N \approx 10^{17} D_O^3 (1 + 2.3 \times 10^4 D) / D^2 n \quad (\text{A-2})$$

In this equation D_O is the diameter of the water-free sulfuric acid droplet and D is the actual diameter of the sulfuric acid solution droplet at a given ambient relative humidity. As the reaction proceeds D will actually vary with time; this refinement is not included in the estimate of eq. A-2. Also, of course, n , the number density of ammonia molecules, will vary during the course of the reaction. However, n also varies in our calculations because of dispersion so that integration of the rate equation under the assumption of spatial homogeneity is meaningless. Hence, eq. A-2 provides an estimate of the minimum time for neutralization at a given ammonia concentration.

Table A-1 gives some values for neutralization times for 3 ppb ammonia and at 50% and 70% relative humidity. The automotive sulfuric acid aerosol has been shown to be in the size range 0.01 - 0.5 μm . Therefore, even the time for complete neutralization is less than the characteristic diffusion time for these particles.

Table A-1. Estimate of Time for Complete Neutralization of a Single Sulfuric Acid Solution Droplet. Ammonia Concentration = 3ppb.

Dry Particle Diameter		
<u>T</u> <u>(sec)</u>	<u>D_O</u> <u>μm</u>	<u>Relative</u> <u>Humidity</u>
0.6	0.01	70%
7.4	0.1	70%
254	1.0	70%
0.84	0.01	50%
10.7	0.1	50%
328	1.0	50%

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
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4. TITLE AND SUBTITLE DYNAMICS OF AUTOMOTIVE SULFATE EMISSIONS	5. REPORT DATE April 1978	6. PERFORMING ORGANIZATION CODE
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16. ABSTRACT A preliminary assessment of the potential environmental impact of automotive sulfuric acid (or sulfate) aerosol has been made by analyzing the aerosol dynamics. This analysis leads to the prediction of ambient automotive sulfuric acid aerosol concentrations over and around a large, ten-lane highway (48 m. x 20 km.), some ten or so years hence, when almost all cars in the United States will be fitted with catalytic converters. The attachment rate of fine automotive sulfuric acid aerosols to ambient aerosols is examined. The dispersion and deposition of automotive sulfate are modelled over the highway for "worst case" meteorology using K-theory. The neutralizing effect of ambient ammonia on sulfuric acid concentrations around the highway is examined by a direct simulation procedure for dispersion calculations. These calculations indicate that adverse environmental effects of automotive sulfuric acid emissions may be important under the stated conditions of this study.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution Catalytic converters		13B
*Aerosols *Mathematical models		07D
*Sulfuric acid Highways		07B
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