MATHEMATICAL MODELING OF THE DYNAMICS AND THERMODYNAMICS OF MULTICOMPONENT ATMOSPHERIC AEROSOLS

Thesis by:

Christodoulos Pilinis

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Ο ισχυροs ανθρωποs εχει δουλουs, ο πλουσιοs κολακαs και ο συνετοs φιλουs. (Ισοκρατηs)

A powerful man is surrounded by slaves, a rich man by flatterers, while a wise man is surrounded by friends. **(Isocrates)**

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ABSTRACT

Atmospheric aerosols consist of particles with sizes between 0.01 and 10μm. These particles, when occurring in urban areas, consist, in general, of aqueous solutions of sulfate, nitrate, ammonium, chloride, sodium and other ionic species, as well as of primary and secondary organics.

This thesis attempts to describe the evolution and fate of atmospheric aerosol particles. The size-composition distribution of atmospheric aerosols is governed by a combination of kinetics and thermodynamics, which, because of their complexity, can be analyzed only with computer simulations. At first, a solution of the General Dynamic Equation in the case of small coagulation, using perturbation techniques, is developed.

In subsequent work, a comprehensive size-sectionalized trajectory aerosol model was developed for simulating the evolution of a multicomponent aerosol size-composition distribution through homogeneous heteromolecular nucleation, condensational growth, coagulation and deposition. The model was employed along a trajectory from Anaheim to Rubidoux, California.

In the process of analyzing this model it became apparent that a detailed treatment of the thermodynamics of the sodium/ sulfate/ nitrate/ ammonium/ chloride/ water system is very important in aerosol predictions. Thus, an equilibrium model for this system that takes into account differences in the composition among particles of different sizes was developed and tested.

Finally, the same theory was used in a Eulerian framework, thus producing a three-dimensional Eulerian Urban Gas-Aerosol Model, which was used to predict the aerosol concentration and size distribution throughout the Los Angeles Basin on August 30, 1982. Its prediction is compared with measured values and a statistical evaluation study is presented.

TABLE OF CONTENTS

LIST OF TABLES

Chapter 2

Chapter 3

Chapter 4

Chapter 5

LIST OF FIGURES

Chapter 2

Chapter 3

Chapter 4

Chapter 5

CHAPTER 1

INTRODUCTION

INTRODUCTION

The air pollution problem in Southern California has for many years been primarily associated with photochemical smog. Ozone and nitrogen dioxide concentrations still exceed National Ambient Air Quality Standards in the South Coast Air Basin. As a result, major modeling efforts have historically focused on the study of gas-phase photochemical smog. Ozone and nitrogen dioxide are not the only pollution problem in Los Angeles. High concentration levels of particulate matter with a diameter of less than $10\mu m$ cause visibility degradation and may lead to acid deposition.

The main aerosol effects depend not only on their size distribution but also on their chemical composition. Thus, to study the possible visibility and health effects of the ambient aerosol, mathematical models that predict the evolution of the size and chemical composition of the particulate matter are required. That is the subject of this thesis.

Atmospheric aerosol particles are divided between primary and secondary. Primary particles are those directly injected into the atmosphere. Significant natural sources of primary particles include soil and rock debris, fuel combustion byproducts and sea aerosol transported by the wind. Once primary particles exist in the atmosphere, their mass increases by gas-to-particle conversion of condensible species, while their size distribution changes via coagulation, deposition and production of new particles by nucleation. Sulfate, nitrate, ammonium and condensible organics are involved in this complex process. The formation of secondary aerosol mass, as sulfate, nitrate and organics, is strongly dependent on the amount of both the species precursors, i.e., SO_2, NO_x and hydrocarbons, and the species available to oxidize them, such as ozone and the hydroxyl radical. Hence, there is a coupled, highly nonlinear relationship between aerosol formation and gas-phase photochemical smog. As a result, both problems have to be considered concurrently in order to provide a comprehensive picture of the pollution phenomena in the South Coast Air Basin.

In this work we address the integrated problem, that is, gas-phase chemistry, gas-to-particle conversion via nucleation and condensation, transport, coagulation and chemical thermodynamics. The thrust of this research, though, is mainly in simulating the evolution of the size distribution and chemical composition of atmospheric aerosols.

The dynamic behavior of a spatially homogeneous aerosol undergoing particle growth, coagulation, augmentation by particle sources, and first-order removal is governed by the general dynamic equation. In Chapter 2 an asymptotic solution of the general dynamic equation for small coagulation is obtained. The solution provides a framework for the modeling of situations in which coagulation is expected to have a minor, but not insignificant, influence on the aerosol size distribution. It can also be used for verification of a model's accuracy.

In Chapter 3 a trajectory aerosol model that simulates the dynamics of inorganic multicomponent atmospheric aerosols, including new particle formation, gas-to-particle conversion, coagulation and dry deposition is presented. The sectional representation of an aerosol distribution, that approximates the continuous size distribution function with a series of step functions, is used, and both equilibrium and non-equilibrium aspects are considered.

Two important results are extracted from this analysis. The first is that homogeneous nucleation is predicted to be suppressed by preexisting aerosol through bulk vapor depletion and the second is that to predict accurate nitrate aerosol concentrations, a detailed equilibrium model for the sodium/ sulfate/ nitrate/ ammonium/ chloride/ water system must be developed. Chapter 4 discusses a detailed equilibrium thermodynamic model for this system. Using this model, it is shown that the size distribution of sulfates and sodium chloride are very important in determining the equilibrium aerosol concentrations of both ammonium and nitrates, as well as the existence of water in the aerosol phase at low relative humidities.

In Chapter 5 a Eulerian urban multicomponent aerosol model is developed. This model resulted from the coupling of the two models described in the two previous chapters with the Caltech airshed model. New gas-phase reactions are included to account for the formation of the various organic aerosol precursors. The aerosol particles are assumed to consist of an insoluble core, basically primary organics, covered by either an aqueous solution or a solid inorganic phase, which is surrounded by a secondary organic film. Because of the intensity of the calculations, a supercomputer is required for this code's running in realistic time. The model is used to predict the size-composition distribution throughout the Los angeles Basin for the 30^{th} of August 1982. Comparison between measured and simulated concentrations is made and statistical performance of the model is discussed.

Finally, in the Appendix all the subroutines developed for the models are listed in alphabetical order and a brief description of their variables is presented.

CHAPTER 2

ASYMPTOTIC SOLUTION OF THE AEROSOL GENERAL DYNAMIC EQUATION FOR SMALL COAGULATION

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Asymptotic Solution of the Aerosol General Dynamic Equation for Small Coagulation

CHRISTODOULOS PILINIS AND JOHN H. SEINFELD

Department of Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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The aerosol general dynamic equation is solved in the limit of small coagulation. The solution includes particle growth by gas-phase diffusion, surface and volume reaction, particle production, and loss by deposition to surfaces. © 1987 Academic Press, Inc.

INTRODUCTION

The dynamic behavior of a spatially homogeneous aerosol undergoing particle growth, coagulation, augmentation by particle sources, and first order removal such as that by deposition onto surfaces is governed by the general dynamic equation (4, 9, 10)

$$\frac{\partial n(D,t)}{\partial t} = -\frac{\partial}{\partial D}[I(D,t)n(D,t)] + \frac{D^2}{2}\int_{D_a}^{D} \times \frac{\beta[(D^3-D'^3)^{1/3},D']n[(D^3-D'^3)^{1/3},t]n(D',t)}{(D^3-D'^3)^{1/3}} \times dD' - n(D,t)\int_{D_a}^{D_b}\beta(D,D')n(D',t)dD' + S_0(D,t) - a(D,t)n(D,t), \quad [1]$$

where D is the particle diameter; D_b and D_a are the upper and lower limits on D, respectively; $n(D, t)$ is the size distribution density function at time t, such that $n(D, t)dD$ is the number concentration of particles having diameters in the range $[D, D + dD]$; $\beta(D, D')$ is the coagulation coefficient for particles with diameter D and D'; $I(D, t)$ is the rate of change of particle diameter, dD/dt, due to gas-to-particle conversion by vapor condensation; $S_0(D, t)$ is the rate of particle production from external sources, such that $S_0(D, t)dD$ is the rate of introduction per unit volume in the system of particles having diameters in the range $[D, D + dD]$; and $a(D, t)$ is the first order coefficient for particle removal by deposition on container surfaces.

When all the phenomena represented in Eq. [1] are important, Eq. [1] must generally be solved numerically (2, 5, 11). If particle growth or evaporation is not occurring, then $I(D, t) = 0$. Additionally, in the absence of sources or deposition, Eq. [1] reduces to the coagulation equation

$$\frac{\partial n(D,t)}{\partial t} = \frac{D^2}{2}\int_{D_a}^{D} \times \frac{\beta[(D^3-D'^3)^{1/3},D']n[(D^3-D'^3)^{1/3},t]n(D',t)}{(D^3-D'^3)^{1/3}} \times dD' - n(D,t)\int_{D_a}^{D_b}\beta(D,D')n(D',t)dD'. \quad [2]$$

There exist a number of studies of analytical (1, 8, 13) and numerical (2, 5, 7, 11) solutions of Eq. [2]. On the other hand, in the absence of coagulation, one obtains the condensation equation

$$\frac{\partial n(D,t)}{\partial t} = -\frac{\partial}{\partial D}[I(D,t)n(D,t)] + S_0(D,t) - a(D,t)n(D,t) \quad [3]$$

which may be solved by the method of characteristics (3, 12).

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In a number of important aerosol processes, such as formation and growth of aerosols in atmospheric photochemical reactions, the dominant physical processes influencing the aerosol size distribution are those represented in Eq. [3], namely condensation, sources, and removal, while coagulation exerts only a minor influence on the dynamics of the distribution. This observation suggests that it might be useful to seek a solution of the general dynamic equation, Eq. [1], for the case in which the effect of coagulation is small relative to those of the other phenomena represented in the equation, but not small enough to be neglected. Such a solution is the objective of the present work.

DIMENSIONLESS GENERAL DYNAMIC EQUATION

It is useful to cast Eq. [1] in an appropriate dimensionless form (3),

$$\begin{aligned}\frac{\partial \bar{n}(\mathrm{Kn},\tau)}{\partial \tau} &= \sigma(\tau)\frac{\partial}{\partial \mathrm{Kn}}[\mathrm{Kn}^2 \bar{I}(\mathrm{Kn},\tau)\bar{n}(\mathrm{Kn},\tau)] \\ &+ \xi\left\{\frac{1}{2}\int_{\mathrm{Kn}_b}^{\mathrm{Kn}} \beta[\mathrm{Kn}', (\mathrm{Kn}^{-3}-\mathrm{Kn}'^{-3})^{-1/3}]\right. \\ &\times \bar{n}(\mathrm{Kn}',\tau)\bar{n}[(\mathrm{Kn}^{-3}-\mathrm{Kn}'^{-3})^{-1/3},\tau] \\ &\times \left[\frac{(\mathrm{Kn}^{-3}-\mathrm{Kn}'^{-3})^{-1/3}}{\mathrm{Kn}}\right]^4 d\mathrm{Kn}' - \bar{n}(\mathrm{Kn},\tau) \\ &\times \left.\int_{\mathrm{Kn}_b}^{\mathrm{Kn}_a} \beta(\mathrm{Kn},\mathrm{Kn}')\bar{n}(\mathrm{Kn}',\tau)d\mathrm{Kn}'\right\} \\ &- \bar{S}_0(\mathrm{Kn},\tau) - \alpha(\mathrm{Kn},\tau)\bar{n}(\mathrm{Kn},\tau), \qquad [4]\end{aligned}$$

with initial condition

$$\bar{n}(\mathrm{Kn},0) = \bar{f}(\mathrm{Kn}), \qquad [5]$$

where

$$\bar{n}(\mathrm{Kn},\tau) = -\frac{\lambda n(D,t)}{N_0 \mathrm{Kn}^2}$$

$$\bar{S}_0(\mathrm{Kn},\tau) = \frac{S_0(D,t)\lambda^3}{\mathbf{D} N_0 \mathrm{Kn}^2}$$

$$\alpha(\mathrm{Kn},\tau) = \frac{a(D,t)\lambda^2}{\mathbf{D}}$$

$$\xi = \frac{N_0 k T \lambda^2}{\mathbf{D}\eta}$$

$$\bar{I}(\mathrm{Kn},\tau) = \phi I(D,t)$$

$$\tau = \frac{\mathbf{D}t}{\lambda^2},$$

and Kn is the Knudsen number, $2\lambda/D$; T is the absolute temperature; ϕ is a growth coefficient depending on the growth mechanism, $\phi = N_1 v_1 \mathbf{D}/\lambda$; **D** is the diffusivity of the vapor molecules; λ is the mean free path; $\sigma(\tau)$ is the coefficient accounting for any temporal variation of the growth rate; N_1, v_1 are the gas phase concentration and the volume of the condensing molecules, respectively; N_0 is the initial total particle number concentration; and η = viscosity. The dimensionless Brownian coagulation coefficient is (10)

$$\beta(\mathrm{Kn}_i,\mathrm{Kn}_j) = \frac{2/3Q(P_i\mathrm{Kn}_i + P_j\mathrm{Kn}_j)}{\dfrac{Q}{Q+(H_i^2+H_j^2)^{1/2}} + \dfrac{\pi A(P_i\mathrm{Kn}_i + P_j\mathrm{Kn}_j)}{2Q(\mathrm{Kn}_i^3+\mathrm{Kn}_j^3)^{1/2}}}$$

with

$$Q = \frac{1}{\mathrm{Kn}_i} + \frac{1}{\mathrm{Kn}_j}$$

$$H_i = \frac{\mathrm{Kn}_i^{3/2}}{6AP_i}\left[\left(\frac{2}{\mathrm{Kn}_i} + \frac{AP_i}{\mathrm{Kn}_i^{1/2}}\right)^3 - \left(\frac{4}{\mathrm{Kn}_i^2} - \frac{A^2P_i^2}{\mathrm{Kn}_i}\right)^{3/2}\right] - \frac{2}{\mathrm{Kn}_i}$$

$$A = \left[\frac{8\rho k T}{27\pi^2\eta\lambda}\right]^{1/2}$$

$$P_i = 1 + \mathrm{Kn}_i[1.257 + 0.4\exp(-1.1/\mathrm{Kn}_i)].$$

ASYMPTOTIC SOLUTION OF THE GENERAL DYNAMIC EQUATION FOR SMALL COAGULATION

The coagulation terms in Eq. [4] are multiplied by the parameter ξ. This parameter depends on the conditions in the system and the total particle concentration. If ξ is small, then the coagulation contribution to the evolution of $\bar{n}(\mathrm{Kn}, \tau)$ is correspondingly small.

In the case of small ξ we can express the solution of Eq. [4] in terms of a regular perturbation series (6),

$$\bar{n}(\mathrm{Kn},\tau)=\sum_{i=0}^{\infty}\bar{n}_i(\mathrm{Kn},\tau)\xi^i. \qquad [6]$$

Substituting Eq. [6] into Eq. [4] and equating terms containing like powers of ξ we obtain the following system of equations

$$\frac{\partial\bar{n}_0}{\partial\tau}=\sigma(\tau)\frac{\partial}{\partial\mathrm{Kn}}[\bar{n}_0(\mathrm{Kn},\tau)\mathrm{Kn}^2\bar{I}(\mathrm{Kn})] - \bar{S}_0(\mathrm{Kn},\tau)-\alpha(\mathrm{Kn},\tau)\bar{n}_0(\mathrm{Kn},\tau) \qquad [7]$$

$$\frac{\partial\bar{n}_i}{\partial\tau}=\sigma(\tau)\frac{\partial}{\partial\mathrm{Kn}}[\bar{n}_i(\mathrm{Kn},\tau)\mathrm{Kn}^2\bar{I}(\mathrm{Kn})] + G_i(\mathrm{Kn},\tau)-\alpha(\mathrm{Kn},\tau)\bar{n}_i(\mathrm{Kn},\tau) \qquad i=1,2,\ldots, \qquad [8]$$

subject to

$$\bar{n}_0(\mathrm{Kn},0)=\bar{f}(\mathrm{Kn}) \qquad [9]$$

$$\bar{n}_i(\mathrm{Kn},0)=0, \quad i=1,2,3,\ldots, \qquad [10]$$

where

$$G_i(\mathrm{Kn},\tau)=\frac{1}{2}\int_{\mathrm{Kn}_b}^{\mathrm{Kn}}\beta(\mathrm{Kn}',\mathrm{Kn}'')\left(\frac{\mathrm{Kn}''}{\mathrm{Kn}}\right)^4 \times\left[\sum_{\rho=0}^{i-1}\bar{n}_{i-\rho-1}(\mathrm{Kn}'',\tau)\bar{n}_\rho(\mathrm{Kn}',\tau)\right]d\mathrm{Kn}' - \int_{\mathrm{Kn}_b}^{\mathrm{Kn}_a}\beta(\mathrm{Kn},\mathrm{Kn}')\left[\sum_{\rho=0}^{i-1}\bar{n}_{i-\rho-1}(\mathrm{Kn},\tau) \times\bar{n}_\rho(\mathrm{Kn}',\tau)\right]d\mathrm{Kn}' \qquad [11]$$

and where $\mathrm{Kn}''=(\mathrm{Kn}^{-3}-\mathrm{Kn}'^{-3})^{-1/3}$.

We note that for each i, $G_i(\mathrm{Kn},\tau)$ is a known function of Kn and τ, since it depends only on lower orders of $\bar{n}_i(\mathrm{Kn},\tau)$. As a result, the system of equations [7] and [8] can be solved sequentially for successively higher values of i by the method of characteristics. The characteristic equations for the system [7] and [8] are

$$\frac{d\mathrm{Kn}}{d\tau}=-\sigma(\tau)\mathrm{Kn}^2\bar{I}(\mathrm{Kn}) \qquad [12]$$

$$\frac{d\bar{n}_0}{d\tau}=\left[\sigma(\tau)\frac{d(\mathrm{Kn}^2\bar{I}(\mathrm{Kn}))}{d\mathrm{Kn}}-\alpha(\mathrm{Kn},\tau)\right] \times\bar{n}_0(\mathrm{Kn},\tau)-\bar{S}_0(\mathrm{Kn},\tau) \qquad [13]$$

subject to

$$\bar{n}_0(\mathrm{Kn},0)=\bar{f}(\mathrm{Kn}) \qquad [14]$$

and

$$\frac{d\bar{n}_i}{d\tau}=\left[\sigma(\tau)\frac{d(\mathrm{Kn}^2\bar{I}(\mathrm{Kn}))}{d\mathrm{Kn}}-\alpha(\mathrm{Kn},\tau)\right] \times\bar{n}_i(\mathrm{Kn},\tau)+G_i(\mathrm{Kn},\tau) \qquad [15]$$

subject to

$$\bar{n}_i(\mathrm{Kn},0)=0 \quad i=1,2,\ldots. \qquad [16]$$

Integrating Eqs. [13] and [15] along the characteristic curves of Eq. [12] we obtain

$$\bar{n}_0(\mathrm{Kn},\tau) = \frac{\bar{f}(\mathrm{Kn}(0))\mathrm{Kn}^2(0)\bar{I}(\mathrm{Kn}(0))-H(\tau-\tau_0)\int_{\tau_0}^{\tau'}\bar{S}_0(\mathrm{Kn},\tau')\mathrm{Kn}^2\bar{I}(\mathrm{Kn})\exp\left[\int_{\tau_0}^{\tau'}\alpha(\mathrm{Kn},\tau'')d\tau''\right]d\tau'}{\mathrm{Kn}^2\bar{I}(\mathrm{Kn})\exp\left[\int_{\tau_0}^{\tau}\alpha(\mathrm{Kn},\tau')d\tau'\right]} \qquad [17]$$

and

$$\bar{n}_i(\mathrm{Kn},\tau)=\frac{H(\tau-\tau_0)\int_{\tau_0}^{\tau}G_i(\mathrm{Kn},\tau')\mathrm{Kn}^2\bar{I}(\mathrm{Kn})\exp\left[\int_{\tau_0}^{\tau'}\alpha(\mathrm{Kn},\tau'')d\tau''\right]d\tau'}{\mathrm{Kn}^2\bar{I}(\mathrm{Kn})\exp\left[\int_{\tau_0}^{\tau}\alpha(\mathrm{Kn},\tau')d\tau'\right]}, \qquad [18]$$

where τ_0 is the time at which the particles are introduced into the system, and

$$H(x) = \begin{cases} 1 & \text{for} \quad x \geqq 0 \\ 0 & \text{for} \quad x < 0 \end{cases}$$

The zeroth-order solution, $\bar{n}_0(\mathrm{Kn}, \tau)$, accounts only for the condensation, sources, and removal mechanisms in shaping the size distribution. The effect of coagulation appears then in the first order term $\bar{n}_1(\mathrm{Kn}, \tau)$. As τ increases, the effect of coagultion increases relative to those of the other principal processes, so the perturbation solution is expected to hold for values of τ that satisfy the constraint,

$$\frac{\xi}{2}\int_{\tau_0}^{\tau}\left[\int_{\mathrm{Kn}_b}^{\mathrm{Kn}_a}\beta(\mathrm{Kn}(\tau'), \mathrm{Kn}')\bar{n}_0(\mathrm{Kn}', \tau')d\mathrm{Kn}'\right]d\tau' < 1. \quad [19]$$

For a smooth zeroth-order solution Eq. [19] can be reduced to

$$\frac{\xi}{2}\max(\beta(\mathrm{Kn}, \mathrm{Kn}'))\int_{\tau_0}^{\tau}\bar{N}(\tau')d\tau' < 1, \quad [19a]$$

where $\bar{N}(\tau)$ is the dimensionless total particle number concentration, $\bar{N}(\tau) = N(\tau)/N_0$.

In the initial value problem $\bar{N}(\tau) < 1$, since particles are consumed due to deposition and coagulation. Therefore Eq. [19a] reduces to

$$\tfrac{1}{2}\xi\tau \max(\beta(\mathrm{Kn}, \mathrm{Kn}')) < 1. \quad [19b]$$

For temperature T = 300 K and pressure p = 1 atm, in air, $\lambda \approx 0.065$ μm and $\eta \approx 1.8 \times 10^{-5}$ kg m^{-1} s^{-1}. For a diffusion coefficient for typical condensible species in air, $\mathbf{D} \sim 10^{-5}$ m^2 s^{-1} and ξ is of order $\xi \sim 10^{-26} N_0$, where N_0 is in m^{-3}. For particles in the range 0.1–10 μm the maximum value of the dimensionless coagulation coefficient is of the order $\max(\beta(\mathrm{Kn}, \mathrm{Kn}')) \sim 10^2$. Using these values for the various parameters and Eq. [19b], and upper limit of τ for which the perturbation solution gives accurate results can be estimated. Table I shows $\tau_{\max}$, as well as the corresponding $t_{\max}$, in hours, for different values of N_0. Physically, the reason for this behavior can be understood by considering a system in which condensation and coagulation are the only processes occurring. As time progresses, while condensation is primarily shaping the distribution, coagulation is slowly reducing the number of particles and hence the surface area available for condensation. Eventually a point is reached at which the effect of coagulation relative to that of condensation is no longer small. The smaller the value of ξ, the longer the perturbation solution of Eq. [6] remains valid.

TABLE I

Estimates of Maximum Dimensionless and Real Time Corresponding to Initial Aerosol Number Concentrations for Which Asymptotic Solution Is Expected to be Valid

N_0 (m^{-3})	$\tau_{\max}$	$t_{\max}$ (h)
10	10^{23}	10^{10}
10^2	10^{22}	10^9
10^4	10^{20}	10^7
10^6	10^{18}	10^5
10^8	10^{16}	10^3
10^{10}	10^{14}	10^1
10^{12}	10^{12}	10^{-1}

EVOLUTION OF A MONODISPERSE AEROSOL BY GROWTH AND COAGULATION

A general expression for the dimensionless condensation growth law $\bar{I}$ that incorporates diffusion-, surface reaction-, and volume reaction-limited growth is (12)

$$\bar{I} = \sigma \mathrm{Kn}^{\gamma}, \quad [20]$$

where

$\gamma = 1$ diffusion-control
$\gamma = 0$ surface reaction control
$\gamma = -1$ volume reaction control

and where σ can be assumed independent of time τ.

With $\bar{I}$ given by Eq. [20] the characteristic growth curves given by the solution of Eq. [12] are

$$\mathrm{Kn}(\tau) = \begin{cases} [\sigma(\gamma+1)(\tau-\tau_0) \\ \quad + \mathrm{Kn}(\tau_0)^{-(\gamma+1)}]^{-1/(\gamma+1)} & \gamma \neq -1 \quad [21] \\ \mathrm{Kn}(\tau_0)e^{-\sigma(\tau-\tau_0)} & \gamma = -1, \quad [22] \end{cases}$$

where $\mathrm{Kn}(\tau_0)$ is the Knudsen number of the particles at τ_0. We note that in Eq. [21] only particles with the Knudsen number satisfying

$$\mathrm{Kn}(\tau) < [\sigma(\gamma+1)(\tau-\tau_0)]^{-1/(\gamma+1)}$$

have $\mathrm{Kn}(\tau_0) > 0$, i.e., follow real characteristics.

We now consider an initially monodisperse aerosol,

$$\bar{n}(\mathrm{Kn},0) = \delta(\mathrm{Kn}-\mathrm{Kn}^*), \qquad [23]$$

that undergoes growth and coagulation. Thus, particle sources and deposition losses are neglected. Using Eq. [17], for $\gamma \neq -1$, we obtain

$$\bar{n}_0(\mathrm{Kn},\tau) = [1-\sigma(\gamma+1)\tau\mathrm{Kn}^{\gamma+1}]^{-(\gamma+2)/(\gamma+1)} \times \delta[(\mathrm{Kn}^{-(\gamma+1)} - \sigma(\gamma+1)\tau)^{-1/(\gamma+1)} - \mathrm{Kn}^*]. \qquad [24]$$

Since

$$G_1(\mathrm{Kn},\tau) = \frac{1}{2}\int_{\mathrm{Kn}_b}^{\mathrm{Kn}} \beta(\mathrm{Kn}',\mathrm{Kn}'')\left(\frac{\mathrm{Kn}''}{\mathrm{Kn}}\right)^4 \bar{n}_0(\mathrm{Kn}',\tau)\bar{n}_0(\mathrm{Kn}'',\tau)d\mathrm{Kn}' - \int_{\mathrm{Kn}_b}^{\mathrm{Kn}_a} \beta(\mathrm{Kn},\mathrm{Kn}')\bar{n}_0(\mathrm{Kn},\tau)\bar{n}_0(\mathrm{Kn}',\tau)d\mathrm{Kn}',$$

we obtain

$$\bar{n}_1(\mathrm{Kn},\tau) = \frac{\beta(2^{1/3}\mathrm{Kn}, 2^{1/3}\mathrm{Kn})}{2\sigma\left(2^{(\gamma+1)/3}-1\right)\mathrm{Kn}^{(\gamma+2)}} H\left(\left[2^{(\gamma+1)/3}\mathrm{Kn}^{*-(\gamma+1)} + \sigma(\gamma+1)\tau\right]^{-1/(\gamma+1)} - \mathrm{Kn}\right)$$
$$\times H(\mathrm{Kn} - 2^{-1/3}[\mathrm{Kn}^{*-(\gamma+1)} + \sigma(\gamma+1)\tau]^{-1/(\gamma+1)}) - [1-\sigma(\gamma+1)\tau\mathrm{Kn}^{(\gamma+1)}]^{-(\gamma+2)/(\gamma+1)}$$
$$\times \int_0^\tau \beta(\mathrm{Kn}(\tau'), [\mathrm{Kn}^{*-(\gamma+1)} + \sigma(\gamma+1)\tau]^{-1/(\gamma+1)})d\tau'\delta[(\mathrm{Kn}^{-(\gamma+1)} - \sigma(\gamma+1)\tau)^{-1/(\gamma+1)} - \mathrm{Kn}^*]. \qquad [25]$$

Therefore, the dimensionless size distribution function is given to first order by

$$\bar{n}(\mathrm{Kn},\tau) = \left[1 - \xi\int_0^\tau \beta(\mathrm{Kn}(\tau'), [\mathrm{Kn}^{*-(\gamma+1)} + \sigma(\gamma+1)\tau]^{-1/(\gamma+1)}d\tau'\right]$$
$$\times [1-\sigma(\gamma+1)\tau\mathrm{Kn}^{(\gamma+1)}]^{-(\gamma+2)/(\gamma+1)} \times \delta[(\mathrm{Kn}^{-(\gamma+1)} - \sigma(\gamma+1)\tau)^{-1/(\gamma+1)} - \mathrm{Kn}^*]$$
$$+ \xi\frac{\beta(2^{1/3}\mathrm{Kn}, 2^{1/3}\mathrm{Kn})}{2\sigma\left(2^{(\gamma+1)/3}-1\right)\mathrm{Kn}^{(\gamma+2)}} \times H\left(\left[2^{(\gamma+1)/3}\mathrm{Kn}^{*-(\gamma+1)} + \sigma(\gamma+1)\tau\right]^{-1/(\gamma+1)} - \mathrm{Kn}\right)$$
$$\times H(\mathrm{Kn} - 2^{-1/3}[\mathrm{Kn}^{*-(\gamma+1)} + \sigma(\gamma+1)\tau]^{-1/(\gamma+1)}). \qquad [26]$$

If $\xi = 0$, Eq. [26] reduces to the solution for the size distribution function in the presence of pure growth. In that case, with the initial distribution given by Eq. [23] the aerosol remains monodisperse with time.

The dimensionless total particle number concentration, $\bar{N}(\tau) = N(\tau)/N_0$, is given by

$$\bar{N}(\tau) = \int_{\mathrm{Kn}_b}^{\mathrm{Kn}_a} \bar{n}(\mathrm{Kn},\tau)d\mathrm{Kn}. \qquad [27]$$

In general the integral in Eq. [27] must be evaluated numerically. In the special case of $\beta(\mathrm{Kn}', \mathrm{Kn}'') \equiv 2C$ the integral can be evaluated analytically to give

$$\bar{N}(\tau) = 1 - \xi C\tau + O(\xi^2). \qquad [28]$$

The exact result for the total number in the case of a constant coagulation coefficient is

$$\bar{N}(\tau) = \frac{1}{1 + \xi C\tau}. \qquad [29]$$

Equation [28] is just the first two terms in the Taylor series expansion of Eq. [29].

EVOLUTION OF A LOG-NORMALLY DISTRIBUTED AEROSOL BY GROWTH, DEPOSITION, AND COAGULATION

We now consider the case of an initially log-normally distributed aerosol,

$$\bar{n}(\mathrm{Kn}, 0) = -\frac{1}{\sqrt{2\pi}\,\mathrm{Kn}\,\ln\sigma_g} \times \exp\left[-\frac{\ln^2(\mathrm{Kn}_g/\mathrm{Kn})}{2\ln^2\sigma_g}\right], \qquad [30]$$

with $\mathrm{Kn}_g = 0.65$ and $\sigma_g = 1.4$, evolving by growth, as described in Eq. [21] with $\gamma = 1$, i.e., diffusion-limited growth, deposition with α = constant and coagulation with $\xi = 10^{-4}$.

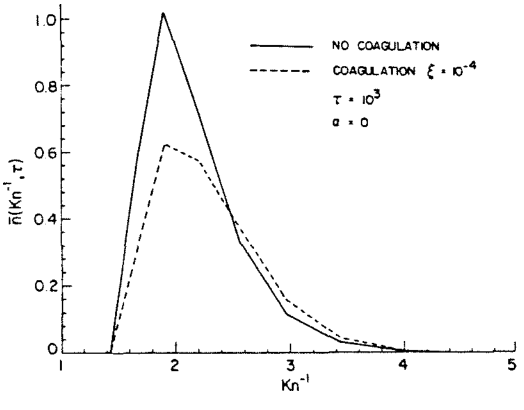

FIG. 1. Normalized aerosol size distribution function at a dimensionless time of $\tau = 10^3$ in the cases of no coagulation and small coagulation ($\xi = 10^{-4}$). No deposition ($\alpha = 0$).

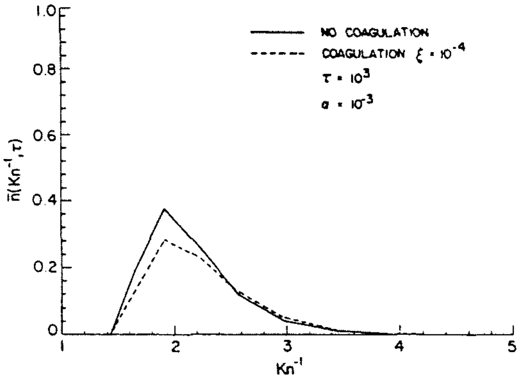

FIG. 2. Normalized aerosol size distribution function at a dimensionless time of $\tau = 10^3$ in the cases of no coagulation and small coagulation ($\xi = 10^{-4}$). Deposition occurring at a dimensionless rate of $\alpha = 10^{-3}$.

Two cases will be considered:

(i) Growth and coagulation without deposition, i.e., $\alpha = 0.0$;

(ii) Growth, coagulation, and deposition, with $\alpha = 10^{-3}$.

It is customary to plot the data so that the particle size increases along the x axis. Therefore plots of the dimensionless volume distribution $\bar{n}(\mathrm{Kn}^{-1}, \tau)$ and dimensionless volume distribution $\bar{V}(\mathrm{Kn}^{-1}, \tau)$ versus Kn^{-1} will be presented. In term of the previously defined distribution,

$$\bar{n}(\mathrm{Kn}^{-1}, \tau) = -\mathrm{Kn}^2\bar{n}(\mathrm{Kn}, \tau)$$

$$\bar{V}(\mathrm{Kn}^{-1}, \tau) = \frac{4\pi}{3}\mathrm{Kn}^{-3}\bar{n}(\mathrm{Kn}^{-1}, \tau).$$

Figure 1 shows the number distribution for $\tau = 10^3$, for Case (i) with and without coagulation. Comparison between the two curves in Fig. 1 shows that the number of small particles has been decreased, while the number of larger particles has been increased; compare this to the case in which coagulation is neglected. Figure 2 shows exactly the same situation for Case (ii). Comparison between the two curves in Fig. 2 shows that the coagulation process is not as important as in Case (i). Since a substantial number of small particles is consumed due to deposition on surfaces, fewer can participate in the coagulation process, with the immediate result being a decrease in the importance of coagulation on the evolution of the number density function.

We expect that the particles will shift to higher diameters due to the growth and coagulation processes. Figures 3 and 4 show this shift as a function of dimensionless time for Cases (i) and (ii), respectively. We find in Fig. 4 that a steady-state condition for large particles, $Kn^{-1} > 3$, is achieved. Thus the flux of particles to the large particle domain balances the loss from that domain due to deposition. The volume distribution for Case (i) is shown in Fig. 5. Figure 5 shows the development of a sharp peak, which is the result of the large number of small particles growing to an appreciable size.

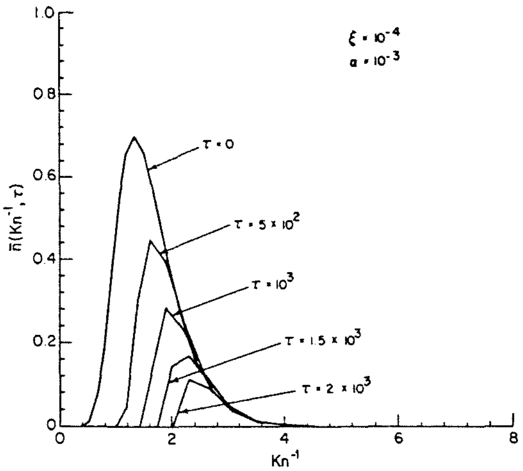

FIG. 4. Normalized aerosol size distribution function at a series of times in the case of small coagulation ($\xi = 10^{-4}$). Deposition occurring at a dimensionless rate of $\alpha = 10^{-3}$.

CONCLUSIONS

A solution of the dimensionless aerosol general dynamic equation in the limit of small coagulation has been obtained. The expressions for the particle sources, removal, and growth mechanisms can be quite general.

The case of initially monodisperse aerosol undergoing growth and coagulation was tested. Comparison between the solution via perturbation series and the analytical solution for the total particle number evolution shows that the series describes accurately the fate of the aerosol, the accuracy depending on the number of terms of the series evaluated.

The evolution of a log-normally distributed aerosol by growth, deposition, and coagulation was also presented and in which our solution predicts the "expected" aerosol behavior for

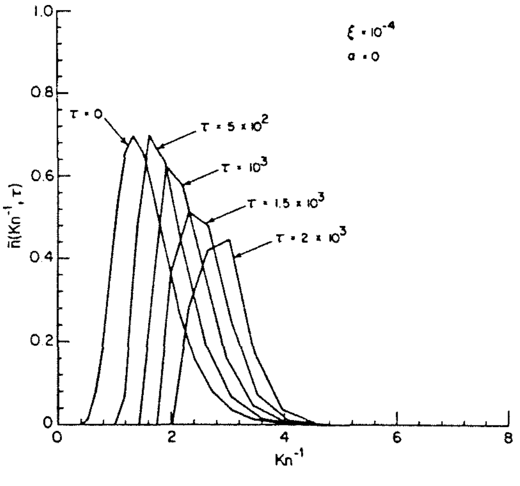

FIG. 3. Normalized aerosol size distribution function at a series of times in the case of small coagulation ($\xi = 10^{-4}$). No deposition ($\alpha = 0$).

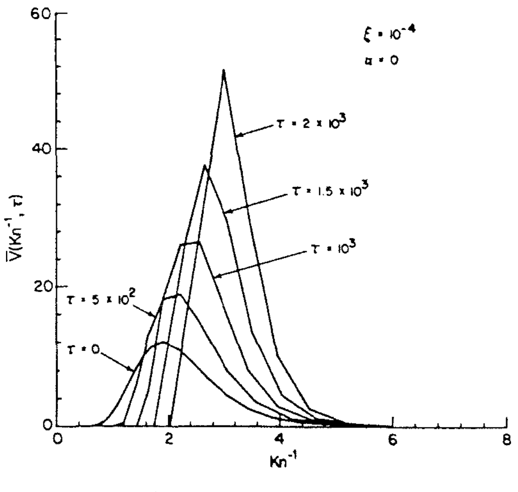

FIG. 5. Normalized aerosol volume distribution function at a series of times in the case of small coagulation ($\xi = 10^{-4}$). No deposition ($\alpha = 0$).

the number and volume density functions. A steady-state phenomenon for large particles that is the consequence of the competition between growth and coagulation on the one hand, and deposition on the other, is demonstrated by the solution. The solution presented here can provide a framework for the modeling of situations in which coagulation is expected to exert only a minor influence on the aerosol size distribution.

ACKNOWLEDGMENT

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CHAPTER 3

MATHEMATICAL MODELING OF THE DYNAMICS OF MULTICOMPONENT ATMOSPHERIC AEROSOLS

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MATHEMATICAL MODELING OF THE DYNAMICS OF MULTICOMPONENT ATMOSPHERIC AEROSOLS

Christodoulos Pilinis and John H. Seinfeld
Department of Chemical Engineering
California Institute of Technology
Pasadena, CA 91125
and
Christian Seigneur
Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903

ABSTRACT

A model is developed to simulate the dynamics of multicomponent atmospheric aerosols, including new particle formation by homogeneous heteromolecular nucleation, gas-to-particle conversion, coagulation, and dry deposition. Both equilibrium and non-equilibrium aspects involving sulfate, nitrate, and ammonium compounds are considered. The model is used to predict the dynamics of the composition of the aerosol observed on an air trajectory in the Los Angeles basin on August 31, 1982.

Indexing Key Words

Aerosols, Mathematical model.

INTRODUCTION

Atmospheric aerosols are, in general, multicomponent particles with sizes ranging roughly from 0.01 to 10 μm in diameter. These particles evolve as a result of gas-to-particle conversion and coagulation, are augmented through the formation of fresh particles by nucleation and through the continuous introduction of primary particles, and are removed by wet and dry deposition.

To predict how atmospheric aerosol levels depend on gaseous and particulate source emissions, and specifically how such levels might be expected to vary given changes in primary emissions, requires the development of aerosol air quality models. Whereas the development, evaluation and use of gas-phase air quality models have received considerable attention, there has not been available an air quality model capable of simulating the dynamics of multicomponent atmospheric aerosols that includes new particle formation by nucleation, growth or evaporation due to gas-to-particle or particle-to-gas conversion, and coagulation. The object of the present work is to present the first urban, multicomponent, aerosol model and to illustrate its application to the Los Angeles basin.

A considerable body of work has preceded the model we will present and it is useful to review that work briefly to provide the context within which the current model lies.

A spatially uniform, dynamic multicomponent aerosol can be characterized by its size-composition distribution function $n(m,t)$, where $m = (m_1, m_2, ..., m_k)^T$, such that $n(m,t)dm$ is the number of particles per volume of gas with mass composition in the range $[m_1, m_1 + dm_1]$, $[m_2, m_2 + dm_2]$, etc.(Specification of the complete chemical composition of a particle in principle specifies the particle's size.) For an aerosol that can be completely characterized by its size , e.g., one comprised of a single chemical component, its size distribution function is just $n(D_p, t)$, where $n(D_p, t)dD_p$ is the number of particles per volume of gas with diameters in the range $[D_p, D_p + dD_p]$ .The dynamic behavior of n is governed by the so-called general dynamic equation (Gelbard and Seinfeld 1979; Seinfeld 1986). The numerical solution of the general dynamic equation serves as the central core of a model simulating the evolution of aerosols. Significant work has been carried out on techniques for the numerical solution of the general dynamic equation, largely devoted to its form for $n(D_p, t)$ (Gelbard and Seinfeld 1978; Middleton and Brock 1976; Tsang and Brock 1983) Recently, several of these approaches have been reviewed and compared (Seigneur et al. 1986). Some previous work does exist on the numerical simulation of single-component atmospheric aerosols through solution for $n(D_p, t)$ (Bassett et al. 1981; Eltgroth and Hobbs 1979; Middleton and Kiang 1978; Seigneur 1982; Suck and Brock 1979; Tsang and Brock 1982).

An approximate composition of the Los Angeles aerosol is 20% sulfates, 25% nitrates, 10% elemental carbon, 20% organic carbon (primary and secondary), 25% soil, metals and water. The following picture is considered to represent the evolution of such a "typical" particle. Say that a primary carbonaceous particle is emitted and advected from its source by the wind. In the gas-phase, photochemical reactions are occurring converting NO_x to nitric acid (HNO_3), SO_2 to sulfuric acid (H_2SO_4), and reactive organic gases to low vapor pressure condensable species. Water vapor is ubiquitous, and ammonia (NH_3) may also be present in the gas phase. Gas-to-particle conversion of sulfate, nitrate, ammonium and organics occurs as these gas-phase reactions proceed, with the composition of the aerosol continuously adjusting to maintain equilibrium at the local relative humidity and temperature. At high relative humidity, the aerosol consists of an aqueous solution of sulfate, nitrate and ammonium ions, while at low relative humidity the resulting aerosol may be completely dry. In the latter case, the solid phase is a mixture of four simple salts, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $(NH_4)_2SO_4$ and NH_4NO_3, as well as two mixed salts, $(NH_4)_2SO_4 \bullet 2NH_4NO_3$ and $(NH_4)_2SO_4 \bullet 3NH_4NO_3$ (Stelson and Seinfeld 1982c; Harrison and Sturges 1984). It is this overall process that we seek to simulate.

We begin with a brief summary of the calculation of aerosol thermodynamic equilibria, followed by a discussion of the simulation of multicomponent aerosol dynamics. The remainder of the paper is devoted to a detailed application of the model developed to simulate the evolution of aerosol along a particular air trajectory in the Los Angeles basin on August 31, 1982.

AEROSOL THERMODYNAMIC EQUILIBRIUM

When the multicomponent nature of the aerosol is considered, one must account for the individual rates of transfer of the various species between the gas and particulate phases. If the sticking coefficient is equal to one, then the characteristic time for gas-particle transport for certain species is short enough that chemical equilibrium is established on a time scale much shorter than that over which other changes are taking place. This situation is, in fact, estimated to be the case for species such as water and ammonium nitrate(Hildelmann et al. 1984; Tanner 1983;

Russell et al. 1983; Russell and Cass 1984). Consequently, chemical equilibrium can be assumed to be instantaneously established for such species. Considerable effort has been devoted to developing the capability to predict the equilibrium chemical composition and physical state of atmospheric sulfate, nitrate, and ammonium aerosols (Bassett and Seinfeld 1983, 1984; Saxena et al. 1986; Stelson et al. 1979; Stelson and Seinfeld 1982 a, b, c). As noted above, to simulate the evolution of an atmospheric aerosol containing water, sulfates, nitrates, and ammonium, it will be necessary to merge the thermodynamic equilibrium calculation into the dynamic solution of the multicomponent general dynamic equation.

From the point of view of numerical simulation, we can divide the aerosol evolution into a short time step of non-equilibrium, gas-to-particle conversion and coagulation, followed by an instantaneous relaxation to equilibrium. Then more gas-to-particle conversion and coagulation occur over the next time step, followed again by adjustment of the particle composition (and size) to equilibrium. Thus, the structure of the numerical solution will consist of successive steps of non-equilibrium transport and coagulation, followed by the reestablishment of gas and particulate phase chemical equilibrium.

Sulfate is produced in the gas phase by oxidation of SO_2 (Middleton et al. 1980), and it is transferred to the particulate phase by either condensation on already existing particles or nucleation. Because of the relatively low vapor pressure of sulfuric acid, the gas-to-particle conversion process can be assumed to be irreversible. In addition, sulfate may be formed through oxidation of SO_2 on the surface of soot aerosol or in aqueous aerosols.

Volatile compounds, such as ammonia, nitric acid, and water, on the other hand, are distributed between the gas and aerosol phases as determined by thermodynamic equilibrium. The distribution by particle size of non-volatile species, such as sulfate, serves as a "core" upon which the distribution of volatile species can be determined.

In considering the equilibrium in the sulfate, nitrate, ammonium, system the following components are possible(Bassett and Seinfeld 1983, 1984; Harrison and Sturges 1984; Saxena et al. 1986):

gas phase NH_3, H_2O, HNO_3

liquid phase NH_4^+, H^+, HSO_4^-, SO_4^{2-}, NO_3^-, H_2O

solid phase NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, $(NH_4)_2SO_4$, NH_4NO_3
$(NH_4)_2SO_4 \bullet 2NH_4NO_3$, $(NH_4)_2SO_4 \bullet 3NH_4NO_3$.

Three methods have been developed to determine the thermodynamic equilibrium in this system, and the computer codes that have resulted are summarized in Table 1. The basic idea of each method is, given the sulfate, nitric acid, and ammonia concentrations, as well as relative humidity and temperature, to determine the equilibrium phases and their composition by minimizing the total Gibbs free energy of the system, i.e.

$$\min_{n_i} G_{total}$$

subject to

a) conservation of mass

$b)$ $n_i \geq 0$ for all i.

AEROSOL DYNAMICS

A spatially homogeneous aerosol undergoing nucleation, condensation and coagulation is simulated by numerical solution of the general dynamic equation. A particularly powerful technique for solving the multicomponent general dynamic equation is the so-called sectional method(Gelbard and Seinfeld 1980; Gelbard et al. 1980; Gelbard 1984; Warren and Seinfeld 1985).

The sectional representation of an aerosol distribution approximates the continuous size distribution function with a series of step functions. The particle size may be represented by x, the natural logarithm of the mass of a particle. If one defines $q(x)$ as the continuous aerosol mass distribution function, i.e., $q(x)dx$ is the mass corresponding to particles with logarithm of mass in the range $[x, x + dx]$, then the total mass within each section is given by

$$Q^l = \int_{x_l}^{x_{l+1}} q(x)\, dx \qquad l = 1, 2, \cdots, \tag{1}$$

where x_l, x_{l+1} are the lower and upper bounds of section l, respectively. One assumes that the mass is uniformly distributed within each section.Thus,

$$\bar{q}_l(x) = \frac{Q^l}{x_{l+1} - x_l} \qquad l = 1, 2, \cdots, \tag{2}$$

The number of particles in each section is linearly related to the total aerosol mass within the section , specifically

$$N^l = Q^l \, \frac{e^{-x_l} - e^{-x_{l+1}}}{x_{l+1} - x_l}. \tag{3}$$

Thus, the sectional general dynamic equation that describes the evolution of the concentration of species i in the l^{th} section, Q_i^l, takes the following form,

$$\frac{\partial Q_i^l}{\partial t} = \left[\frac{\partial Q_i^l}{\partial t}\right]_{cond./evap.} + \left[\frac{\partial Q_i^l}{\partial t}\right]_{coag.} + \left[\frac{\partial Q_i^l}{\partial t}\right]_{sources/sinks}, \tag{4}$$

where the first term on the right-hand side represents growth due to condensation or shrinkage due to evaporation, the second term represents coagulation and the third term represents sources of new particles through nucleation and primary emissions and removal through wet and dry deposition.

Multicomponent condensation/evaporation

The flux of vapor molecules of species i onto an aerosol particle of diameter d_p, F_i in the case that gas-phase diffusion is the rate-determining step, can be described by the Fuchs-Sutugin formula (Fuchs and Sutugin 1971),

$$F_i = 2\pi d_p \mathbf{D_i} \frac{(p_i - p_{di}) f_o(Kn)}{kT} \qquad [5]$$

with

$$f_o(Kn) = \frac{1 + Kn}{1 + 1.71Kn + 1.33Kn^2}, \qquad [6]$$

where Kn is the Knudsen number, $\mathbf{D_i}$ is the diffusion coefficient of species i in the gas phase and $(p_i - p_{di})$ is the difference between the partial pressure of species i in the bulk phase and that at the particle surface. The rate of change of the mass of species i in particles of diameter d_p due to the flux F_i is

$$\frac{dM_i}{dt} = H_i M_{tot}, \qquad [7]$$

where

$$H_i = \frac{12\mathbf{D_i}(p_i - p_{di}) f_o(Kn) m_{1i}}{\rho_l d_p^2 kT}, \qquad [8]$$

and where M_{tot} is the total aerosol mass at time t, ρ_l is the species density as a liquid or a solid, and m_{1i} is the molecular mass of species i. An assumption associated with Eq.[7] is that ρ_l remains constant as a function of time.

When the aerosol mass distribution has been represented by sections, the growth rate of the mass of component i in section l,

$$\overline{H}_i^l = \frac{\int_{x_l}^{x_{l+1}} q(x) H_i \, dx}{\int_{x_l}^{x_{l+1}} q(x) \, dx} \qquad [9]$$

from Eq.[2] becomes

$$\overline{H}_i^l = \frac{\int_{x_l}^{x_{l+1}} H_i \, dx}{x_{l+1} - x_l}. \qquad [10]$$

Therefore, $\overline{H}_i^l Q^l$ is the rate of change of the mass of species i on particles in section l. This growth causes some of the largest particles of the section to migrate into the $(l+1)^{th}$ section while, at the same time, some of the largest particles in the $(l-1)^{th}$ section grow into section l. Exactly the reverse behavior takes place in the case of evaporation. To account for this phenomenon, the intersectional condensation rate, $\overline{I}_i^{l+1}$, is defined, such that $\overline{I}_i^{l+1} dt$ is the mass of species i that goes from section l to section $l+1$ in the time interval $[t, t+dt]$. As a result the net rate of change of the mass of species i, in section l, is given by

$$\left[\frac{dQ_i^l}{dt}\right]_{condensation} = \overline{H}_i^l Q^l - \overline{I}_i^{l+1} + \overline{I}_i^l. \qquad [11]$$

Particle number conservation for an aerosol undergoing condensational growth can be used to set the rates of the intersectional condensation (Warren and Seinfeld 1985). The overall intersectional mass flux from the l^{th} section, defined as $\overline{I}^{l+1} = \sum_i \overline{I}_i^{l+1}$, is given by

$$\overline{I}^{l+1} = \frac{\sum_i \overline{H}_i^l Q^l}{1 - e^{-(x_{l+2} - x_l)/2}} \qquad [12]$$

in the case of condensation, and

$$\overline{I}^{l+1} = \frac{\sum_i \overline{H}_i^{l+1} Q^{l+1}}{1 - e^{(x_{l+2} - x_l)/2}} \qquad [13]$$

in the case of evaporation.

The intersectional condensation rate of species i is proportional to the overall intersectional mass flux, and it is also proportional to the mass fraction of species i in the l^{th} and $(l+1)^{th}$ sections for condensation and evaporation, respectively; i.e.,

$$\overline{I}_i^{\,l+1} = \frac{Q_i^l}{Q^l}\,\overline{I}^{\,l+1} \qquad [14]$$

for condensation, and

$$\overline{I}_i^{\,l+1} = \frac{Q_i^{l+1}}{Q^{l+1}}\,\overline{I}^{\,l+1} \qquad [15]$$

for evaporation. Substitution of [12] and [13] into [14] and [15], respectively, gives

$$\overline{I}_i^{\,l+1} = \frac{Q_i^l \sum_i \overline{H}_i^{\,l}}{1 - e^{-(x_{l+2}-x_l)/2}} \qquad [16]$$

for the case of condensation, and

$$\overline{I}_i^{\,l+1} = \frac{Q_i^{l+1} \sum_i \overline{H}_i^{\,l+1}}{1 - e^{(x_{l+2}-x_l)/2}} \qquad [17]$$

for the case of evaporation.

Note that the largest section must be specified large enough so that no particles can grow out of it. Also, the lower bound of the first section must be larger than the size of the critical nucleus for homogeneous nucleation, so that freshly nucleated particles grow into the first section. It is assumed here that the rate of growth of aerosols into the lowest size section is equal to the rate of nucleation of fresh aerosols.

One difficulty that arises when applying the sectional method to atmospheric aerosols is dealing with those species the mass of which in the aerosol phase is thermodynamically controlled. We need to estimate the intersectional coefficients of the non-volatiles due to condensation or evaporation of the equilibrium species, the volatiles. Let $Q(t)$ be the overall aerosol mass at time t; i.e, $Q(t) = \sum_l Q^l(t)$. Then, one can define a time average rate of aerosol change due to condensation or evaporation of the volatiles, $\overline{H}_v$, so that Equation [7] is satisfied; i.e,

$$\frac{dQ}{dt} = \overline{H}_v Q \qquad [18]$$

subject to $Q(t_o) = Q_o$. Eq.[18] gives

$$\overline{H}_v = \frac{1}{\Delta t} \ln \left[\frac{Q(t_o + \Delta t)}{Q_o} \right], \qquad [19]$$

where $Q(t_0 + \Delta t)$ is the sum of the non-volatile species mass, obtained from the non-equilibrium computation, and the volatile species mass, found from the equilibrium portion of the computation, at time $(t_0 + \Delta t)$.

The distribution of the volatiles between sections depends, in general, on the particle size in each section, because the tendency for molecules to escape a small drop into the vapor phase will depend on the size of the drop. If, though, one neglects the effect of surface curvature on vapor pressure, the Kelvin effect, an assumption reasonable for particles for which $d_p \geq 0.01\,\mu$m, the mass of volatiles that condenses in one section is proportional to the mass fraction of the total non-volatiles in that section. As a result, the intrasectional time average rate of aerosol mass change in the l^{th} section, because of condensation or evaporation of volatile species, is given by

$$\overline{H}_v^l = \frac{1}{\Delta t} \frac{Q_{nv}^l}{Q_{nv}} \ln \left[\frac{Q(t_o + \Delta t)}{Q_o} \right], \qquad [20]$$

where ${Q^l}_{nv}$ is the mass of the non-volatiles in the l^{th} section, and Q_{nv} is the total non-volatile mass in the aerosol phase.

Given $\overline{H}_v^l$, Eqs. [16] and [17] can be used to determine the intersectional rates.

Coagulation

Assuming that only binary collisions occur, the coagulation part of Eq.[4] has the form

$$\frac{dQ^l}{dt} = \sum_{n=1}^{l-1} \beta^a_{n,l-1}\, Q^l\, Q^n - \sum_{n=1}^{L} \beta^b_{n,l}\, Q^l\, Q^n, \qquad [21]$$

where $\beta^a_{n,l-1}$ and $\beta^b_{n,l}$ are the sectional coagulation coefficients, depending on the total masses of the coagulating particles, and L is the total number of sections. (Gelbard and Seinfeld 1980; Gelbard et al 1980; Gelbard 1984). These coagulation calculations are simplified if a geometric constraint for the sectional boundaries is imposed; namely, $x_{l+1} - x_l \geq \ln 2$.

Homogeneous heteromolecular nucleation

New particles may form by homogeneous nucleation. In the system we are considering, nucleation may be either homomolecular or heteromolecular. The candidates for nucleation are H_2SO_4, HNO_3 and secondary organics formed from the atmospheric conversion of hydrocarbons.

Under atmospheric conditions, H_2SO_4 and HNO_3 heteromolecular nucleation with H_2O occurs at a rate many orders of magnitude above that of homogeneous homomolecular nucleation, because heteromolecular nucleation can take place when a mixture of vapors is undersaturated with respect to the pure vapors, as long as it is supersaturated with respect to the critical solution (Middleton and Kiang 1978; Mirabel and Katz 1974; Yue and Hamill 1979).

Since $H_2SO_4 - H_2O$ nucleates at 6 to 8 orders of magnitude lower concentration than does nitric acid at the same relative humidity, we account for only homogeneous heteromolecular nucleation of sulfuric acid with water here. For the present study, we neglect any nucleation that might be occurring involving secondary organics.

The classical rate of binary nucleation of $H_2SO_4 - H_2O$, when the vapor number concentration of water is much larger than that of sulfuric acid, is given by (Middleton and Kiang 1978; Mirabel and Katz 1974; Yue and Hamill 1979).

$$J = 4\pi r^{*2} \frac{p_{H_2SO_4}}{(2\pi m_{H_2SO_4} kT)^{1/2}} exp\left[- \frac{\Delta G^*}{kT} \right], \qquad [22]$$

where r^* and ΔG^* are the critical cluster radius and free energy, respectively, and where $p_{H_2SO_4}$ and $m_{H_2SO_4}$ are the partial pressure and molecular mass of sulfuric acid, respectively.

To calculate J from Eq.[22], one needs to know the quantities ΔG^* and r^*. The free energy of formation of a cluster containing n_1 and n_2 molecules of H_2SO_4 and H_2O, respectively, is given by

$$\Delta G = n_1(\mu_{1l} - \mu_{1g}) + n_2(\mu_{2l} - \mu_{2g}) + 4\pi r^2 \gamma, \qquad [23]$$

where μ_{1l}, μ_{2l}, μ_{1g}, μ_{2g} are the chemical potentials of the two components in the liquid and gas phase, respectively, for a macroscopic amount of liquid, and γ is the surface tension.

To find the Gibbs free energy, the radius, and the composition of the critical cluster, one has to solve Eq.[23] together with the saddle point conditions (Middleton and Kiang 1978; Mirabel and Katz 1974; Yue and Hamill 1979).

$$\left.\frac{\partial \Delta G}{\partial n_1}\right)_{n_2} = \mu_{1l} - \mu_{1g} + \frac{2\gamma V_1}{r^*} - \left.\frac{3X^* V}{r^*}\frac{d\gamma}{dX}\right)_{X=X^*} = 0 \qquad [24]$$

$$\left.\frac{\partial \Delta G}{\partial n_2}\right)_{n_1} = \mu_{2l} - \mu_{2g} + \frac{2\gamma V_2}{r^*} + \left.\frac{3(1-X^*)V}{r^*}\frac{d\gamma}{dX}\right)_{X=X^*} = 0 \qquad [25]$$

$$X = \frac{n_2}{n_1 + n_2} \qquad [26]$$

$$\frac{4}{3}\pi r^{*3} = (n_1^* + n_2^*)\,V, \qquad [27]$$

where V_1 and V_2 are the partial molar volumes, and V is the molar volume of the binary solution, at critical composition.

The location of the saddle point is obtained by solving the system of equations [23]-[27] numerically, using Newton's method. Since in the atmosphere the gas densities of sulfuric acid and water are very low, the ideal gas law can be used to obtain the terms $\mu_{ig} - \mu_{il}$ appearing in Eqs.[24]and [25]. Molar volumes have been calculated from the data on density and composition given in Perry (Perry and Chilton 1973). Calculated values were then fitted by a fifth degree polynomial. Partial molar volumes were determined by calculating the intercepts of the tangent to the polynomial with the axes. Vapor pressure data for aqueous sulfuric acid have been taken from the work of Gmitro and Vermeulen (1964) and were fitted with a logarithmic function. Surface tensions for the mixture of sulfuric acid and water were obtained from the data of Sabinina and Terpugow (1935) and have been fitted by a fifth degree polynomial.

TRAJECTORY AEROSOL MODEL

A form commonly used for air quality models is the Lagrangian trajectory model used to simulate the changes occurring in a hypothetical air parcel advected by the mean wind field(Liu and Seinfeld 1975; Tilden and Seinfeld 1982). The model is particularly useful in providing a means to examine the sensitivity of air quality to changes in key variables without incurring the computational requirements of a three-dimensional grid model. As applied to the aerosol model, the governing equations for Q_i^l are

$$\frac{\partial Q_i^l}{\partial t} = \frac{\partial}{\partial z}(K_{zz}\frac{\partial Q_i^l}{\partial z}) + \left[\frac{\partial Q_i^l}{\partial t}\right]_{growth/shrinkage}$$

$$+\left[\frac{\partial Q_i^l}{\partial t}\right]_{coagulation} - \left[\frac{\partial Q_i^l}{\partial t}\right]_{deposition} + S_i^l(x,y,z,t), \qquad [28]$$

with initial conditions

$$Q_i^l(x,y,z,0) = Q_{i0}^l(x,y,z) \qquad [29]$$

and boundary conditions

$$K_{zz}\frac{\partial Q_i^l}{\partial z} = 0 \qquad for \qquad z = H \qquad [30]$$

$$E_i^l + K_{zz}\frac{\partial Q_i^l}{\partial z} - v_{gi}Q_i^l = 0 \qquad for \qquad z = 0, \qquad [31]$$

where $K_{zz}(z)$ is the eddy vertical diffusion coefficient, H is the height of the vertical column, E_i^l is the emission flux-per-unit area of species i in the l^{th} section, v_{gi} is the deposition velocity, and $S_i^l(x,y,z,t)$ is the rate of increase of species i in the l^{th} section due to nucleation or direct injection of aerosol into the atmosphere.

Given the emission inventory, meteorological conditions and concentrations of all the gaseous pollutants at time t, the trajectory model calculates the concentrations of the various gases at time $t + \Delta t$, as well as the evolution of Q_i^l in the aerosol phase due to eddy diffusion and deposition. Then the non-equilibrium portion of the aerosol model is used to update the sulfate distribution in the aerosol phase through the condensation, coagulation, and nucleation portions of the general dynamic equation. Subsequently the equilibrium solution is used to calculate the total aerosol mass and chemical composition, as well as to update the size distribution of the aerosol, by calculating the intersectional movement of particles, due to reestablishment of the equilibrium of the volatile species. The resulting aerosol size and chemical composition distribution at time $t + \Delta t$ is used as input for the subsequent step.

The initial size and chemical composition distribution of the aerosol is required. Since the rates of generation of various condensable organics are not yet well established, we neglect here the organic contribution to gas-to-particle conversion, although the model has the ability to include organics as data become available. For convenience, the initial sulfate distribution is assumed to be lognormal. At the prevailing gas-phase conditions at the beginning of the trajectory, the volatiles are assumed to be distributed between the gaseous and the aerosol phase so that equilibrium is achieved.

A compromise between reasonable accuracy and computational cost is obtained by assuming that the aerosol size distribution is described by nine sections in the range between 0.01 and 20 μm, while the air parcel is divided into ten equally spaced vertical grids.

The vertical diffusion coefficient depends on atmospheric stability and height. The gas-phase chemical kinetics are simulated using the reaction mechanism presented by Russell et al. (1983). Dry deposition of aerosols is calculated on the basis of a single, size-independent deposition velocity v_g (Russell et al. 1983). Nitrate aerosol results from the formation of nitric acid vapor by a variety of paths, including reaction of NO_2 with hydroxyl radical. Formation of sulfuric acid takes place through the gas-phase oxidation of SO_2:

$$SO_2 + OH \xrightarrow{H_2O,O_2} H_2SO_4 + HO_2.$$

Oxidation of SO_2 in the aerosol phase by catalytic reactions with O_2 and H_2O_2 is not considered here, but could easily be included in the model formulation.

MODEL APPLICATION

We will compute the formation of aerosol along an air trajectory in the Los Angeles basin on August 31, 1982, which started at about 1300 (PST) at Anaheim and arrived at Rubidoux between 1700 and 1800 (Fig. 1). For the simulation of the thermodynamic equilibrium between the particulate and gas phases, the Kelvin effect has been neglected. The EQUIL model will be used for the base case calculation. A simulation will also be performed with the MARS model to compare the relative prediction accuracy and computational cost of these two thermodynamic submodels.

Gas and aerosol phase monitoring data are available at these locations against which to compare the predictions of our model. Emission rates, relative humidity, temperature, mixing depth and wind speed data are available for August 31, 1982

(Hildelmann et al. 1984). Temperature was in the range 25 to 31° C, while relative humidity varied from 30% to 40%. Fig. 2 shows the initial size composition distribution determined on the basis of chemical equilibrium at Anaheim at 1300.

The measured and predicted concentrations at Rubidoux are given in Table 2. The predicted NO_2 concentrations have been corrected to include the other nitrogen-containing species that interfere with the NO_2 measurement (Winer et al. 1974). The resulting NO_2 prediction is slightly lower than the measured concentrations at Rubidoux. The predicted concentration for O_3 matches the observed value, while NH_3 matches the measured values at Rubidoux within the measurement uncertainties. Comparison of the predicted and observed sulfate, nitrate, and ammonium concentrations at Rubidoux indicates that we have adequately represented the formation of those aerosol species along the trajectory.

The evolution of the total sulfate-nitrate-ammonium concentrations along the trajectory is presented in Fig 3. The first few hours, because of the substantial quantity of hydroxyl radical in the atmosphere, SO_2 is predicted to react relatively rapidly to produce sulfuric acid in the gas phase, which then transfers to the aerosol phase. Thus, the sulfate aerosol mass keeps increasing until it reaches a maximum of about 7 $\mu g\, m^{-3}$ at about 1600, between Anaheim and Rubidoux. Late in the afternoon, the reduction in the photochemical activity causes a decrease in the hydroxyl radical concentration, resulting in a reduction of the production rate of sulfuric acid in the gas-phase. Hence, turbulent diffusion and deposition predominate and the sulfate aerosol concentration declines smoothly to about 6.5 $\mu g\, m^{-3}$ at Rubidoux.

As shown in Table 5, condensation of sulfuric acid is the predominant source of sulfate mass increase in the aerosol phase, while dry deposition and eddy diffusion to the upper layers are the major removal mechanisms for aerosol sulfates. Since the ambient relative humidity on August 31, 1982, was very low, about 40%, the rate of particle formation due to binary nucleation is negligible, and no new particles are predicted to be produced.

The predicted aerosol nitrate has its minimum at about 1330, near Anaheim. At that time the ambient temperature reaches its maximum of about 31^o C. Such high temperature does not favor the formation of aerosol ammonium nitrate, and most of the nitrate exists in the gas-phase as nitric acid.

Later in the afternoon, near Rubidoux, the substantial increase in the ammonia concentration, due to production near Riverside, combined with a decrease of the ambient temperature to about 25^o C, causes ammonia and nitric acid to condense as ammonium nitrate. Thus, both the ammonium and nitrate concentrations increase sharply and reach their maxima at about 1800, near Rubidoux.

Effect of Thermodynamic Submodel

In Table 1 we indicated that two size-independent thermodynamic submodels are available, EQUIL and MARS. Figure 3 shows the aerosol sulfate, nitrate, and ammonium concentrations calculated by using both these submodels. Since the sulfate concentration is controlled by gas-phase reaction and gas-to-particle diffusion, the sulfate prediction is unaffected by the choice of a thermodynamic model.

The nitrate predictions differ between the two thermodynamic submodels. The curve corresponding to MARS shows lower nitrate concentrations along the course of the trajectory until close to Rubidoux. The reason for this difference is that EQUIL takes into account the existence of two mixed salts, $(NH_4)_2SO_4 \bullet 2NH_4NO_3$ and $(NH_4)_2SO_4 \bullet 3NH_4NO_3$, whereas MARS does not. As a result, at low relative humidities, whenever ammonia is in high enough concentration to form $(NH_4)_2SO_4$, but not so abundant as to form pure solid NH_4NO_3, MARS predicts that no nitrates should be present in the aerosol phase. On the other hand, under the same conditions, EQUIL predicts that nitrates exist in the solid phase in the form of mixed salts.

Near Rubidoux, because of the large production of ammonia in the eastern portion of the Los Angeles basin, the ammonium nitrate solid phase becomes thermodynamically favored. As a result, MARS predicts fairly well the existence of nitrates in the aerosol phase. EQUIL also predicts accurately the nitrate concentration over Rubidoux, showing, as presented in Fig. 4, that most of the nitrate is in the form of $(NH_4)_2SO_4 \bullet 3NH_4NO_3$.

Computationally, the program that uses MARS is considerably faster than the one using EQUIL. For the specific trajectory examined here, the first one consumed 3 hours of CPU time, while the second one consumed 4.5 hours of CPU time, on a VAX 11/780 . Therefore, MARS, even though less accurate than EQUIL, might be preferred in a Eulerian regional air quality model, where computational efficiency is of paramount importance.

ANALYSIS OF MODEL SENSITIVITY

We now focus on an analysis of parameters that affect the aerosol chemical composition and size distribution. This sensitivity analysis was conducted using the EQUIL submodel. The parameters studied are NH_3 initial conditions and emissions, ambient temperature and relative humidity, together with initial aerosol and SO_2 concentrations. Table 3 summarizes the sensitivity tests we will present with the changes of the various parameters from their base case values, while Table 4 presents the results of the sensitivity runs for major species and aerosol concentrations, at Rubidoux.

The first sensitivity test examines the effect of the ammonia concentration on the formation of aerosols. In this test both the initial ammonia concentration and the ammonia emissions along the course of the trajectory were reduced by 50%. The resulting size-composition distribution at Rubidoux is shown in Figure 5. As expected, the sulfate concentration remains unaffected. An interesting point is that the pure ammonium nitrate phase decreases more than 50%, causing an overall 30% reduction of the nitrate mass and a 23% reduction in the ammonium mass, while the ammonium nitrate that is contained in the mixed salt remains, practically, unaffected.

The second sensitivity test was designed to examine the influence of temperature on the aerosol formation and chemical composition. The ambient temperature was increased by 3^o C. The resulting size-composition distribution at Rubidoux is shown in Figure 6. The sulfate mass in the aerosol phase is not seriously affected (only 1.5% increase from the base case). The pure ammonium nitrate phase decreases more than 50% as the result of the increase in temperature, due to the strong temperature dependence of the ammonium nitrate dissociation constant.

In these two sensitivity tests, condensational growth is the only route of gas-to-particle conversion (Table 5). The last sensitivity test was designed to investigate conditions under which nucleation is a pathway for gas-to-particle conversion; thus, we selected a high-humidity situation with the initial concentration of preexisting aerosol very low. The initial sulfate concentration was reduced to 0.004 $\mu g\, m^{-3}$, while the SO_2 concentration was increased by a factor of ten and the relative humidity, maintained at 95%.

The resulting size-composition distribution at Rubidoux is presented in Figure 7. It is clear that the physical state of the resulting aerosol is completely different from the previous cases. Since the relative humidity is higher than the deliquescence humidity of all the possible salts, the aerosol consists of an aqueous solution of sulfate, nitrate and ammonium ions. The increased SO_2 concentration causes a substantial increase in the sulfate mass, and, as presented in Table 4, the overall sulfate concentration has been tripled, as compared to the previous cases. The total aerosol mass has been increased by an order of magnitude, as compared to the base case, basically because of the 400 $\mu g\, m^{-3}$ of condensed water.

As is shown in Table 5, in contrast to the previous cases, nucleation does take place here. High relative humidity provides a more favorable condition for nucleation. The critical cluster contains many more water molecules per molecule of sulfuric acid than it does in low relative humidities. Therefore, lower sulfuric acid partial pressure is necessary for binary nucleation to occur, at the same rate, in humid environments than in dry ones.

What is crucial, though, for the formation of new particles by nucleation is the concentration of preexisting aerosol particles. The cleaner environment provides less total surface area of aerosols; hence, there is less consumption of sulfuric acid vapors by condensation and, therefore, more H_2SO_4 available for nucleation

(Middleton and Kiang 1978). In this sensitivity test, all the new particle production by nucleation took place in the first thirty minutes of the simulation, when the concentration of preexisting aerosol was relatively low. After that time, the increasing aerosol mass accelerated the condensation process, resulting in no further particle production by nucleation. Under urban conditions, though, since background aerosol is always present, homogeneous nucleation of H_2SO_4-H_2O appears to be negligible.

New particles formed by nucleation are very small and do not contribute substantially to the total aerosol mass. They do, though, affect the number concentration density function in the range below 0.01 μm. In this sensitivity test, for example, the 0.023 $\mu g\, m^{-3}$ of sulfate produced by nucleation corresponds to about 10^{11} particles per cubic meter, one order of magnitude more than that initially existing in the system. Since the coagulation process is strongly dependent on the particle number density, these small particles move rapidly into the higher sections by coagulating among themselves and with preexisting small particles. This is the reason no particles smaller than 0.05 μm are predicted to exist when the trajectory reaches Rubidoux, as presented in Fig. 7.

CONCLUSIONS

A mathematical model that describes the evolution of the size and chemical composition distribution of atmospheric aerosols has been developed. The model, based on a sectional representation of the size distribution, treats dynamics and thermodynamics of multicomponent atmospheric aerosols, including new particle formation by homogeneous heteromolecular nucleation, gas-to-particle conversion, coagulation and dry deposition.

The aerosol model was used to simulate the aerosol size and chemical composition on a trajectory from Anaheim to Rubidoux in the Los Angeles basin, for which measured particulate concentrations were available. Comparison between the predicted and observed aerosol concentrations showed that the model adequately predicted the concentrations of the major particulate compounds along that trajectory.

The particular day of the trajectory in question was characterized by low relative humidity, and as a result the aerosol consisted solely of dry ammonium sulfate and ammonium nitrate. The results of the simulation showed that mixed salts rather than pure phases were thermodynamically favored along the course of the trajectory.

Three tests were conducted to investigate the sensitivity of the model to various atmospheric parameters. As expected, reduction of the ammonia and increase in the ambient temperature cause a decrease in the aerosol ammonium nitrate concentration. Although a condition of high relative humidity, combined with very low initial aerosol concentration, leads to the formation of new particles, by nucleation, condensation is predicted to be the predominant mechanism for gas-to-particle conversion.

Future studies to be carried out with the model include extension to organic aerosols and evaluation of the effect of proposed control strategies on atmospheric aerosol levels.

ACKNOWLEDGMENTS

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Table 1. Computer Codes for Aerosol Sulfate/ Nitrate/ Ammonium/ Water Equilibria.

	KEQUIL[a]	EQUIL[b]	MARS[c]
Method used	Minimization of the Gibbs free energy,using conjugate gradient and Newton's methods. Use of homotopy method, to include the Kelvin effect.	Minimization of the Gibbs free energy,using conjugate gradient and Newton's methods.	The domain of feasible solutions is divided into several subdomains. Then the Gibbs free energy is minimized into the specific subdomain that corresponds to the given atmospheric conditions.
Kelvin effect	Included	Not included	Not included
Mixed salts	Included	Included	Not included
Aqueous phase reactions	Not included	Not included	Included
Typical simulation time for an equilibrium calculation[d]. (CPU sec.)	72	10	0.2

a) Bassett and Seinfeld (1984)

b) Bassett and Seinfeld (1983)

c) Saxena et al. (1986)

d) Saxena et al. (1986)

Table 2. Measured and Predicted Gaseous and Particulate Concentrations at Rubidoux, CA, at 1700-1800 hours on August 31, 1982.

Species	Concentration	
	Measured	Predicted
NO_3^- ($\mu g\,m^{-3}$)	14.2-29.8	24.9
NH_4^+ ($\mu g\,m^{-3}$)	11.2-14.7	9.6
SO_4^{2-} ($\mu g\,m^{-3}$)	4.3-16.9	6.5
O_3 (ppb)	130.0	125.0
NO_2 (ppb)	50.0	31.0
SO_2 (ppb)	10	7.1
HNO_3 (ppb)	1.8-5.3	1.0
NH_3 (ppb)	59.8-89.0	58.0

Table 3. Parameters Varied in Sensitivity Study.

Sensitivity Study	Parameter	Variation
1	NH_3 initial conc. and emissions	50% decrease
2	Temperature	3° C increase
3	Relative humidity	increase to 95%
	SO_2 initial concentration	factor of 10 increase
	Initial sulfate concentration	factor of 10^3 decrease

Table 4. Predicted Gaseous and Particulate Concentrations at Rubidoux, CA, for the Sensitivity Studies.

	Base case	**Test 1**	**Test 2**	**Test 3**
SO_4^{2-} ($\mu g\,m^{-3}$)	**6.5**	**6.5**	**6.6**	**20.7**
NO_3^- ($\mu g\,m^{-3}$)	**24.9**	**17.6**	**20.0**	**30.8**
NH_4^+ ($\mu g\,m^{-3}$)	**9.6**	**7.4**	**8.2**	**16.5**
H_2O ($\mu g\,m^{-3}$)	**0.0**	**0.0**	**0.0**	**400.0**
Total mass ($\mu g\,m^{-3}$)	**41.0**	**31.5**	**34.8**	**468.0**
SO_2 (ppb)	**7.1**	**7.0**	**7.0**	**42.0**
HNO_3 (ppb)	**1.0**	**2.1**	**1.8**	**0.04**
NH_3 (ppb)	**58.0**	**25.0**	**60.0**	**43.8**

Table 5. Contribution of Nucleation, Condensation, and Loss by Deposition.

($\mu g\, m^{-3}$)

		Sensitivity study		
	Base case	1	2	3
Initial	4.0	4.0	4.0	0.004
Nucleation	0.0	0.0	0.0	0.023
Condensation	4.85	4.85	4.96	29.06
Loss by deposition	-2.35	-2.35	-2.36	-8.38
Final	6.50	6.50	6.60	20.71

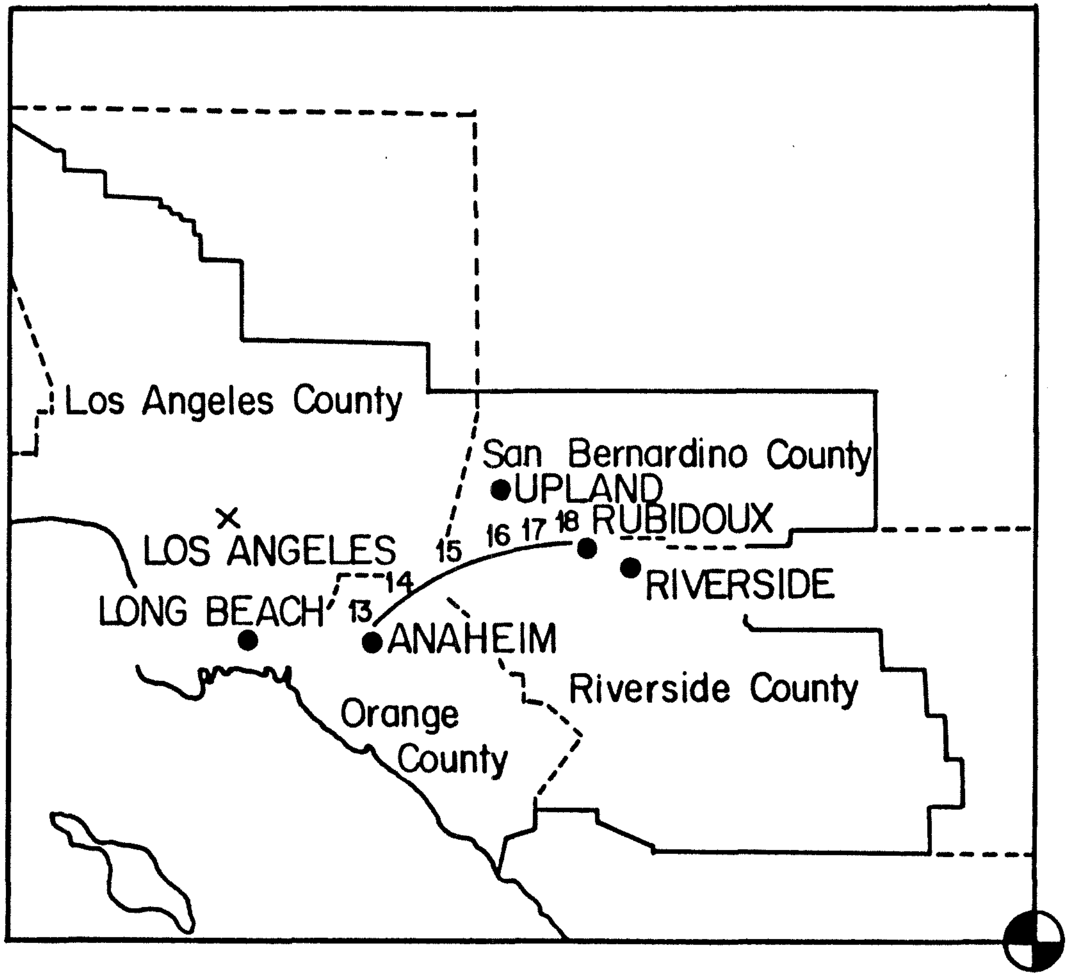

Fig. 1 Trajectory of the air mass that started on August 31,1982, at 1300 (PST) at Anaheim, CA, and arrived at Rubidoux, CA, at about 1800.

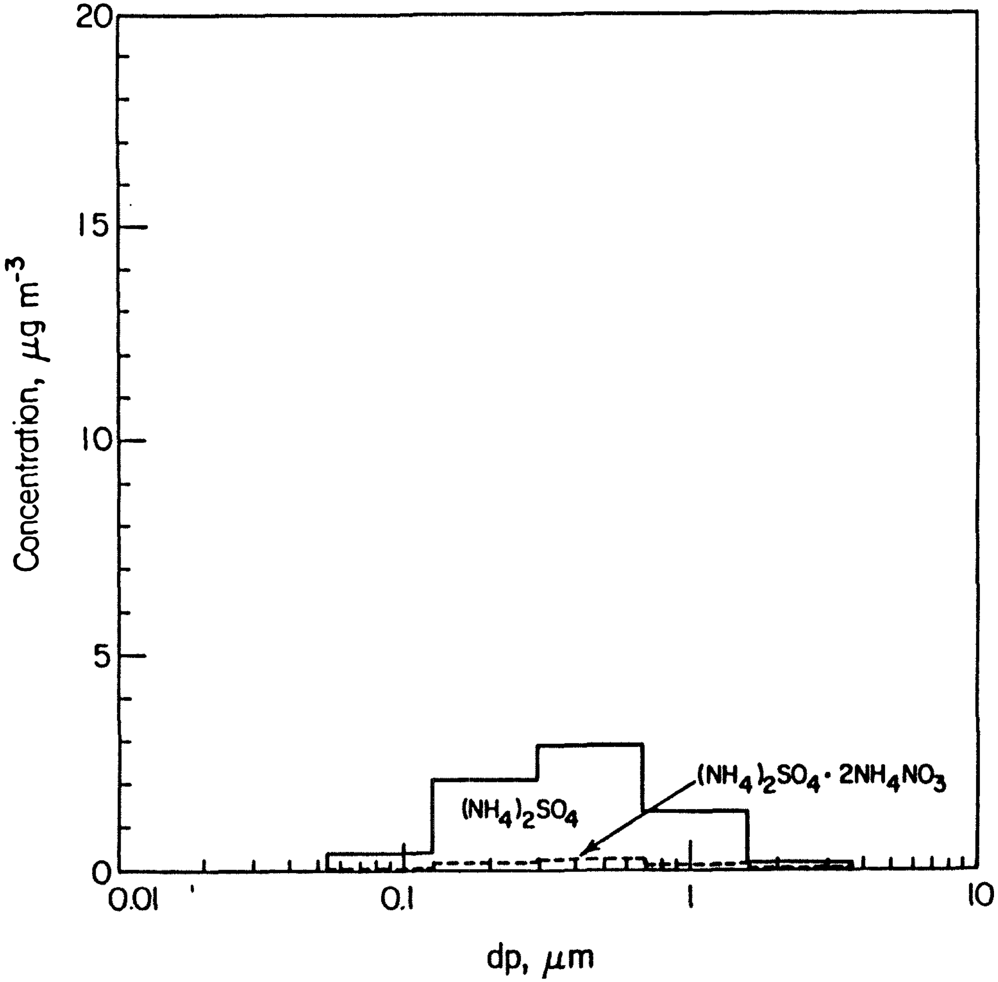

Fig. 2 Calculated aerosol size-composition distribution at Anaheim, CA, at 1300 hours on August 31, 1982. The mass below the solid line indicates the total amount of aerosol, and the incremental components of that total are indicated.

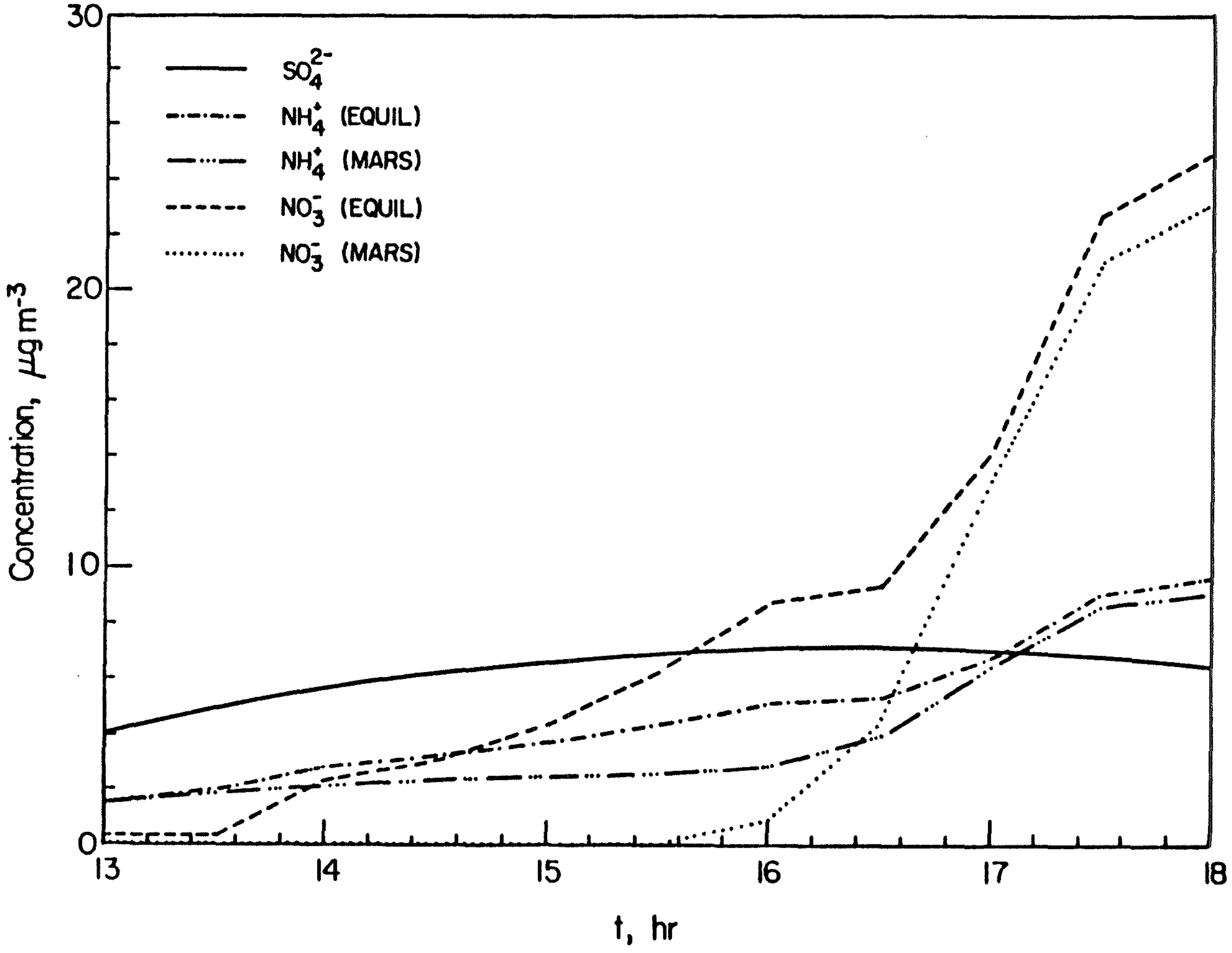

Fig. 3 Predicted evolution of total aerosol nitrate, ammonium and sulfate along the trajectory from Anaheim to Rubidoux, CA, from 1300 to 1800 hours on August 31, 1982. Predictions are shown for the two thermodynamic models, EQUIL and MARS (Table 1).

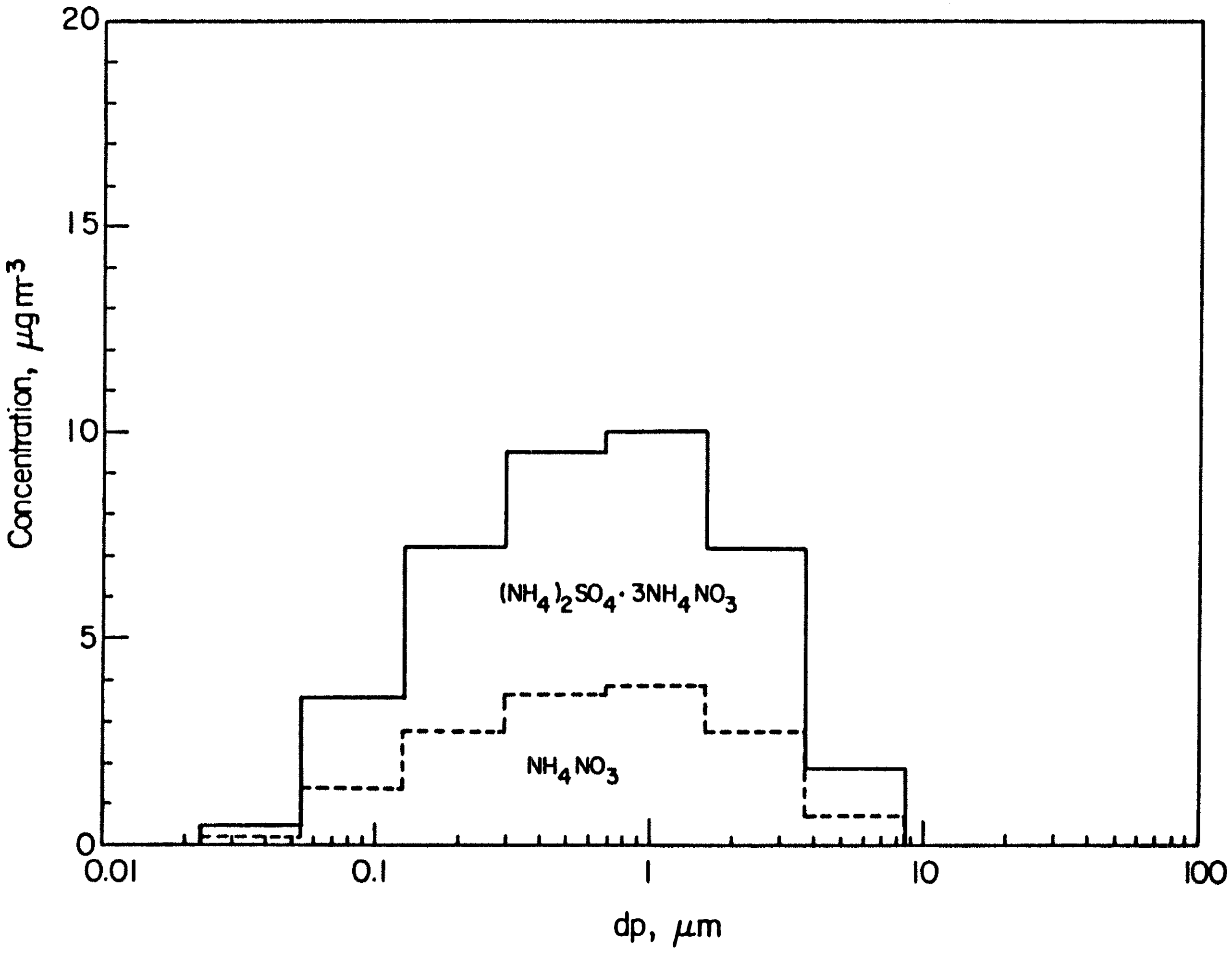

Fig. 4 Predicted size-composition distribution at Rubidoux, CA, at 1800 hours on August 31, 1982. The mass below the solid line indicates the total amount of aerosol, and the incremental components of that total are indicated.

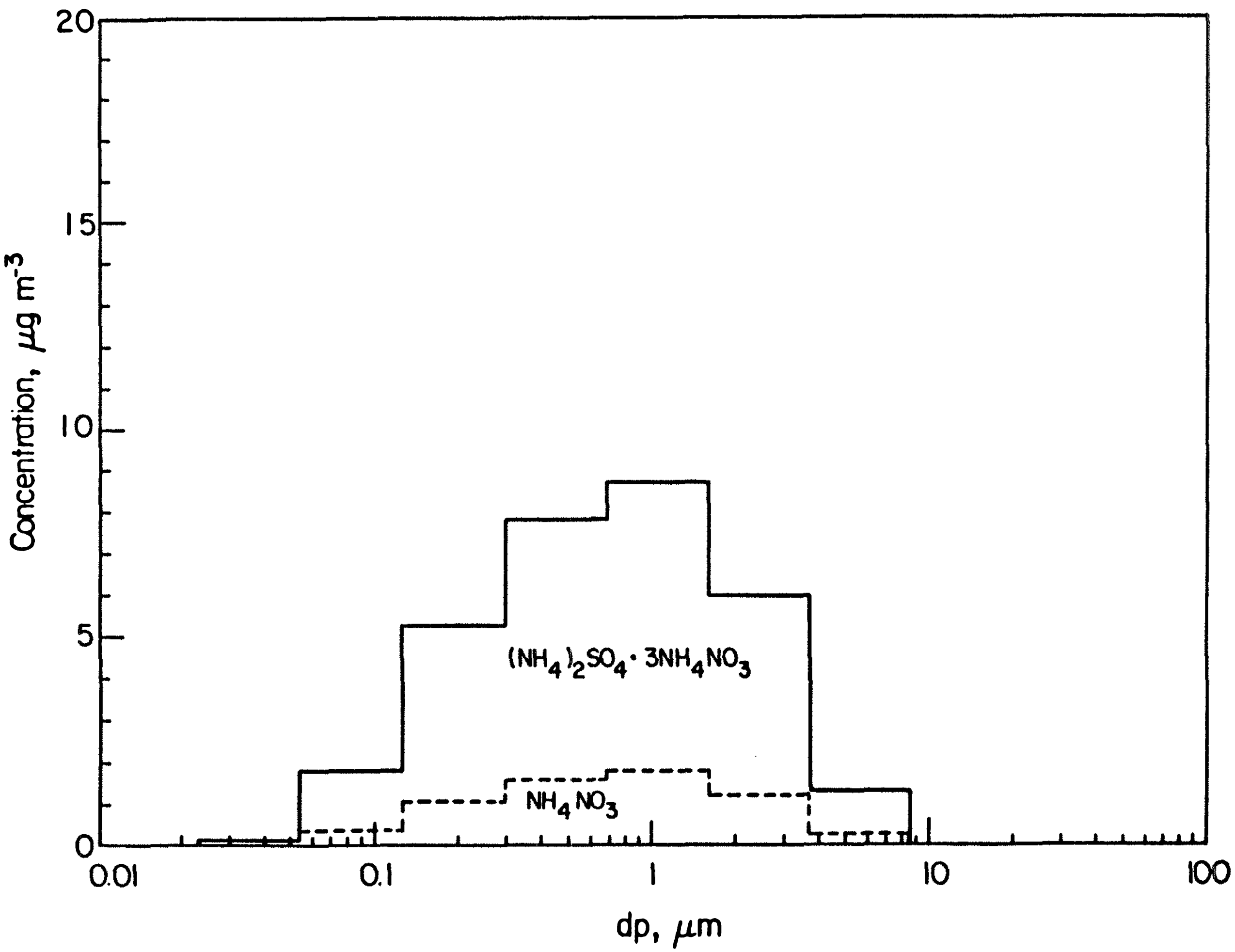

Fig. 5 Predicted size-composition distribution at Rubidoux, CA, at 1800 hours on August 31, 1982. Conditions changed according to Test 1 in Table 3. The mass below the solid line indicates the total amount of aerosol, and the incremental components of that total are indicated.

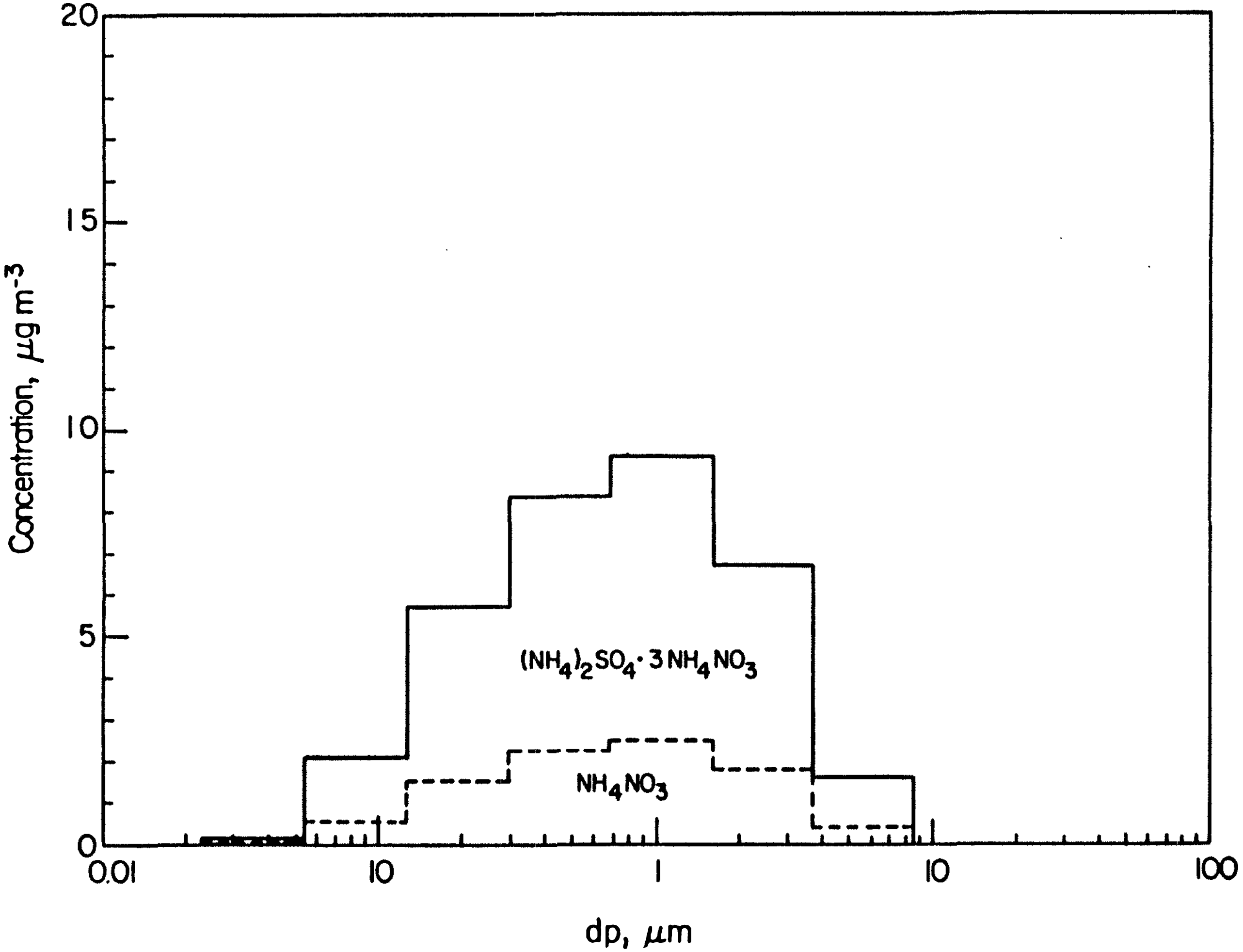

Fig. 6 Predicted size-composition distribution at Rubidoux, CA, at 1800 hours on August 31, 1982. Conditions changed according to Test 2 in Table 3. The mass below the solid line indicates the total amount of aerosol, and the incremental components of that total are indicated.

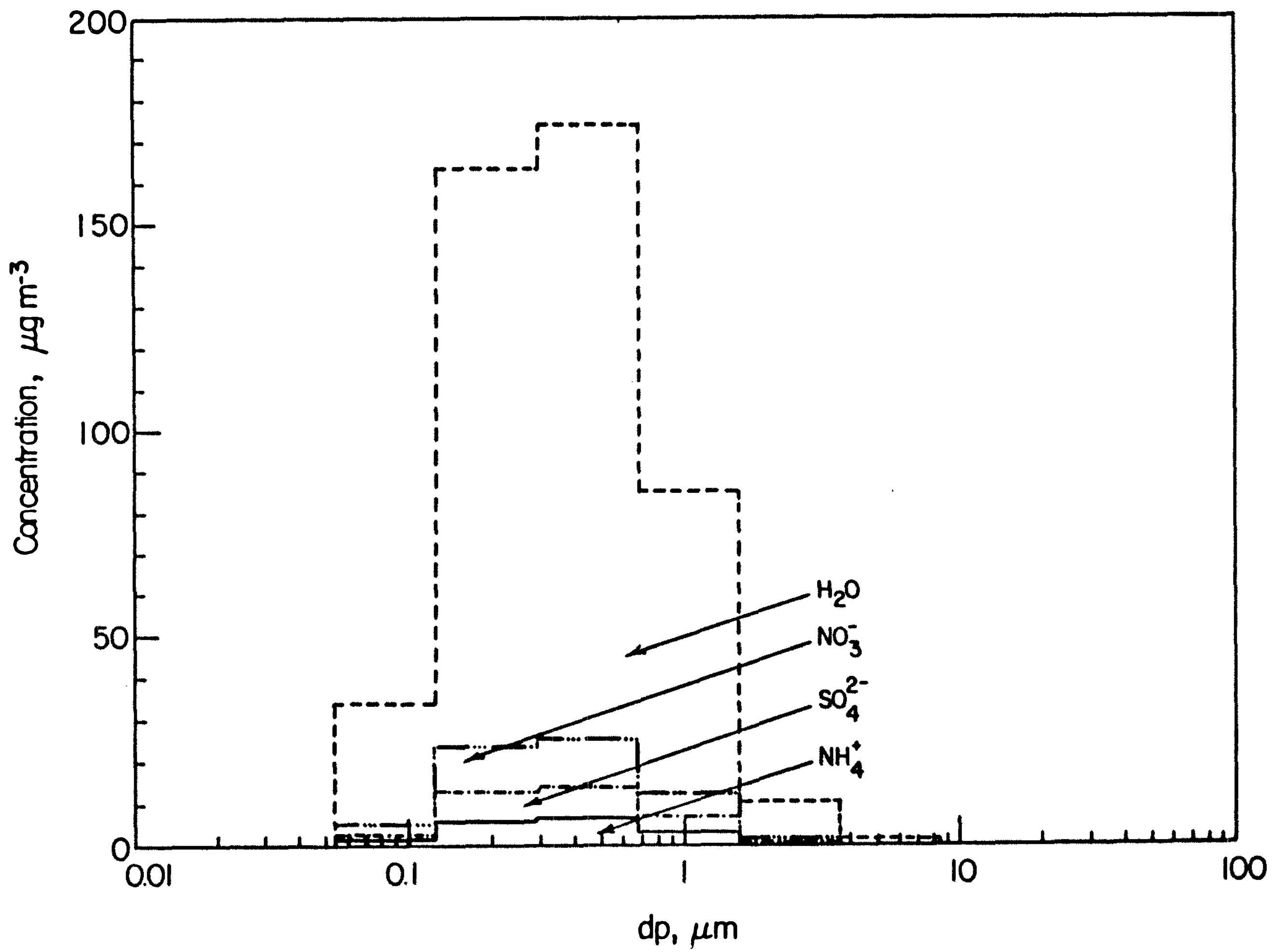

Fig. 7 Predicted size-composition distribution at Rubidoux, CA, at 1800 hours on August 31, 1982. Conditions changed according to Test 3 in Table 3. The mass below the upper line indicates the total amount of aerosol, and the incremental components of that total are indicated.

CHAPTER 4

CONTINUED DEVELOPMENT OF A GENERAL EQUILIBRIUM MODEL FOR INORGANIC MULTICOMPONENT ATMOSPHERIC AEROSOLS

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CONTINUED DEVELOPMENT OF A GENERAL EQUILIBRIUM MODEL FOR INORGANIC MULTICOMPONENT ATMOSPHERIC AEROSOLS

CHRISTODOULOS PILINIS
Environmental Quality Laboratory
California Institute of Technology
Pasadena, CA 91125

and

JOHN H. SEINFELD
Department of Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

ABSTRACT

A model is presented that predicts the total quantities of ammonium, chloride, nitrate and water contained in atmospheric aerosols, their physical state and their distribution among aerosol particles of different sizes. The model is based on the thermodynamic equilibrium calculation of the ammonium chloride, nitrate, sodium, sulfate, water system. The existence of water in the aerosol phase at low relative humidities is shown to be explained. Observed aerosol concentrations at Long Beach, California, during August 30-31, 1982, are successfully predicted.

KEY WORD INDEX

Aerosol, inorganic. Water, in atmospheric aerosols. Sodium chloride.

INTRODUCTION

Atmospheric aerosols consist of solid and/ or liquid multicomponent particles. Prevalent compounds of both urban and natural aerosols are sulfate, nitrate, ammonium, sodium, chloride, water, organics and trace metals (Hitchcock et al., 1980; Russell and Cass, 1984; Jacob et al. 1985; John et al. 1987). A major question underlying understanding the chemical nature of the atmospheric aerosol is: What is the relationship among the chemical constituents of the aerosol? Early work by Stelson et al. (Stelson et al., 1979; Stelson and Seinfeld, 1982 a, b, c) and further work by others (Bassett and Seinfeld, 1983 and 1984; Saxena et al., 1983; Seigneur and Saxena 1984; Saxena et al. 1986) have postulated that the sulfate/ nitrate/ ammonium aerosol constituents should be in thermodynamic equilibrium with the local gas phase. Ambient measurements reported by a number of investigators (Hildelmann et al. 1984, John et al. 1985) have generally confirmed the equilibrium relationship among these species, although it has been shown that the thermodynamic equilibrium models for the sulfate/ nitrate/ ammonium system consistently underpredict the nitrate concentrations in the aerosol phase (Hildelmann et al., 1984; Jacob et al., 1986).

Drawing on previous work on the thermodynamics of the sulfate/ nitrate/ ammonium system (Bassett and Seinfeld, 1983, 1984; Saxena et al. 1986) Pilinis et al. (1987) presented an urban multicomponent aerosol model. Formulated in a trajectory framework, the model assumed that aerosol sulfate and organic levels are controlled by gas-to-particle conversion (condensation and nucleation), while particulate ammonium and nitrate concentrations are governed by thermodynamic equilibrium.

For a number of reasons, however, these thermodynamic models are incomplete in representing the general atmospheric aerosol. A notable omission is sodium chloride (NaCl). Ambient measurements have shown that NaCl is present at substantial concentrations in regions close to oceans (Russell and Cass, 1984; Orsini et al., 1986; John et al., 1987; Wall et al., 1987). Moreover it has been observed that marine aerosol can exhibit up to 100% loss of its chloride because of its reaction with strong acids (H_2SO_4 and HNO_3) (Hitchcock et al., 1980), providing evidence of chemical interaction between NaCl and other atmospheric constituents.

A shortcoming of the previous thermodynamic treatments is that they fail to predict the larger median diameter for nitrates than for sulfates (Hidy et al., 1975). Bassett and Seinfeld (1984) speculated that the Kelvin effect might be responsible for this phenomenon. Their calculations, though, showed that, if the Kelvin effect was the cause, then inordinately long times would be needed for the thermodynamic equilibrium to be established. Furthermore, there is a strong correlation between the coarse NaCl primary aerosol and the existence of nitrates in the large particles (Wall et al., 1987).

An additional shortcoming of the previous thermodynamic models is that they cannot treat cases where various non-volatile species are non-uniformly distributed among particles of different sizes. Since in their thermodynamic treatment, H_2SO_4 was the only non-volatile species, after the total amount of volatiles in the aerosol phase had been determined with thermodynamic arguments, they distributed the aerosol volatile species so that the ratio of volatiles to non-volatiles is constant for all the aerosol-size sections. This approach, though, is not applicable in the case where more than one non-volatile compound lies in the aerosol phase.

The goal of the present paper is to present a more comprehensive thermodynamic model of atmospheric aerosols. The system is ammonium/ chloride/ nitrate/ sodium/ sulfate/ water, including solid, liquid and gaseous phases. Since most of the particulate mass is associated with particles larger than $0.01\mu m$, the Kelvin effect will be neglected. The sectional representation of the aerosol-size composition distribution will be used, and differences in the primary composition among different sections will be taken into account. The aerosol population in each section will be assumed to be an internal mixture of all the species involved, which means that all the particles in each section have exactly the same composition. At relative humidities below the deliquescence point of each of the various salts, we include the equilibria between solid ions, using recent experimental values of binary activity coefficients and water activities of highly supersaturated solutions (Cohen et al., 1987ab). At relative humidities below the lowest deliquescence point of the thermodynamicaly possible salts, the aerosol is assumed to be completely solid.

In the next two sections the basic theory on which the thermodynamic model is based and its application on the specific system will be presented. The subsequent section describes in detail a general method with which the differences in the composition among particles of different sizes may be taken into account. The rest of the paper consists of application of the model. First, comparison is made with the previous models in terms of predicted concentrations, for just the ammonium/sulfate/nitrate system, for which the other models can be also applied. Then the model is used to predict the behavior of atmospheric aerosols and the significance of the inclusion of NaCl, while in the last section the predictions of the model are compared to ambient aerosol concentrations observed in Los Angeles, California. An attempt will also be made to explain the observed lack of deliquescent behavior of atmospheric aerosols, as well as the existence of water in the aerosol phase at low relative humidities (Hänel, 1970; Covert et al., 1972; Winkler, 1973 and Ho et al., 1974).

FORMULATION OF THE EQUILIBRIUM MODEL

The condition of chemical equilibrium in a closed system, such as the one under consideration, at constant temperature T and pressure p, is that the total Gibbs free energy of the system G is a minimum. Therefore, the problem addressed here, from a mathematical point of view, is a constrained minimization problem of the form:

$$\min_{n_i} G(T, p, n_i) \qquad \text{with} \quad n_i \geq 0, \tag{1}$$

where n_i, i =1,2,3... is the concentration of the $i^{\rm th}$ species in the system (in moles $\rm m^{-3}$ of air). Eq. (1) is satisfied for constant temperature and pressure if and only if (Denbigh, 1981)

$$\sum_i \nu_{ij}\mu_i = 0 \quad \text{for} \quad \text{all} \quad \text{reactions} \quad j, \tag{2}$$

where, ν_{ij} is the stoichiometric coefficient of the $i^{\rm th}$ species in the j^{th} reaction and $\mu_i = (\frac{\partial G}{\partial n_i})_{\rm T,P,\mathit{n_c}}$ is the chemical potential of species i. To solve the system, (2), expressions for the chemical potentials are needed, which are discussed in the next section.

1. Chemical Potentials and Equilibrium Constants

In general the chemical potential of species i is given by

$$\mu_i = \mu_i^0(T) + RT\ln a_i, \tag{3}$$

where $\mu_i^0(T)$ is the standard chemical potential for 1 atm and temperature T (in K), R is the gas constant and a_i is the activity of the i^{th} species. For pure solid phases $a_i = 1$, for ideal gases $a_i = p_i$ where p_i is the partial pressure of the i^{th} species (in atmospheres) and for aqueous solutions of electrolytes $a_i = \gamma_i^{(\nu_+ + \nu_-)} m_+^{\nu_+} m_-^{\nu_-}$, where γ_i is the activity coefficient of species i in water, ν_+ and ν_- are the moles of cations and anions, respectively, released by one mole of the electrolyte, and m_+, m_- are the molalities of the cation and anion, respectively. For electrolytes, the standard chemical potential is related to the standard chemical potentials $\mu_{i+}^0(T)$ and $\mu_{i-}^0(T)$ of the cations and anions, respectively; $\mu_i^0(T) = \nu_+\mu_{i+}^0(T) + \nu_-\mu_{i-}^0(T)$.

Substituting (3) into (2) for μ_i and rearranging terms we find

$$\prod_i a_i^{\nu_{ij}} = K_j(T), \tag{4}$$

where $K_j(T)$ is the equilibrium constant of the j^{th} reaction,

$$K_j(T) = exp[-\frac{\sum_i \nu_{ij}\mu_i^0(T)}{RT}]. \tag{5}$$

The system of equations (4) will be solved to determine the aerosol composition at thermodynamic equilibrium. To determine the activities of the various electrolytes, expressions for the activity coefficients of all the salts involved are needed.

At constant pressure, the equilibrium constant K is a function of only the temperature and it is expressed by the Van't Hoff's equation

$$\frac{d\ln K(T)}{dT} = \frac{\Delta H^o(T)}{RT^2}, \tag{6}$$

where $\Delta H^o(T)$ is the corresponding standard enthalpy change of the reaction at temperature T (Denbigh, 1981). A good approximation of $\Delta H^o(T)$ is

$$\Delta H^o(T) = \Delta H^o(T_o) + \Delta c_p^o(T - T_o), \tag{7}$$

where $\Delta H^o(T_o)$ is the corresponding standard enthalpy change at the base temperature ($T_o = 298.1\mathrm{K}$), and Δc_p^o is the change of the heat capacity at T_o. Substituting (7) for $\Delta H^o(T)$ in (6) and integrating, we obtain

$$K(T) = K_o\exp\left[-\frac{\Delta H^o(T_o)}{RT_o}\left(\frac{T_o}{T} - 1\right) - \frac{\Delta c_p^o}{R}\left(1 + \ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right], \tag{8}$$

where K_o is the equilibrium constant at T_o that can be found by (5) using tables of thermodynamic data (Wagman et al., 1968).

Finally, by applying the condition of phase equilibrium for water in (1) the water activity in the aqueous phase is found equal to the relative humidity RH; that is,

$$a_w = \mathrm{RH} \qquad (0 \leq \mathrm{RH} \leq 1). \tag{9}$$

In the situation of interest to us, the value of RH will be known (available from ambient measurements) and thus from (9) the water activity of any aqueous phase is fixed. The water activity a_w is a complex function of the individual ion and natural species concentrations, but that combination must be such that (9) is obeyed.

There are a number of theories that allow one to predict the water activity of a multicomponent aqueous electrolyte solution using binary data of solutions of either the same ionic strength or the same water activity as the multicomponent solution. Some of the widely used theories, such as RWR, RB, MK and ZSR, have been compared and tested with experimental data for many multicomponent solutions up to very high ionic strengths (Sangster and Lenzi, 1974; Saxena and Peterson, 1981; Cohen et al. 1987 a, b). In most of the cases, the water activities predicted with these methods do not differ by more than 5%. Thus, the computationally favorable ZSR method was selected to be used.

The ZSR method may be described as follows (Robinson and Stokes, 1965). Given a multicomponent solution of individual molalities m_i, let $m_{0i}(a_w)$ be the molality of the binary solution of the i^{th} electrolyte in water of the same water activity as the multicomponent solution. Then the following equation is satisfied at equilibrium

$$\sum_i \frac{m_i}{m_{0i}(a_w)} = 1. \tag{10}$$

Equations (9) and (10) combined can be used to calculate the water content of atmospheric aerosols.

2. Activity Coefficients

Most of the methods that predict the activity coefficients of an electrolyte in a multicomponent solution use, in one way or another, the activity coefficients of binary mixtures of the same ionic strength for their predictions.

We use Bromley's model (Bromley, 1973), which has been used up to very high ionic strengths (Saxena and Peterson, 1981, Sangster and Lenzi, 1974). According to this model,

$$\log\gamma_{12} = -A_\gamma \frac{Z_1 Z_2 I^{1/2}}{1+I^{1/2}} + \frac{Z_1 Z_2}{Z_1+Z_2}\left[\frac{F_1}{Z_1} + \frac{F_2}{Z_2}\right], \tag{11}$$

where γ_{12} is the activity coefficient of cation 1 and anion 2, Z_1 and Z_2 are the absolute values of the charges of the ions of the electrolyte 12, $I = \frac{1}{2}\sum_i m_i Z_i^2$ is the ionic strength, $A_\gamma = 0.511$ kg$^{1/2}$mole$^{-1/2}$, and where

$$F_1 = Y_{21}\log\gamma^o_{12} + Y_{41}\log\gamma^o_{14} + Y_{61}\log\gamma^o_{16} + ...+$$
$$+\frac{A_\gamma I^{1/2}}{1+I^{1/2}}[Z_1 Z_2 Y_{21} + Z_1 Z_4 Y_{41} + Z_1 Z_6 Y_{61} + ...] \tag{12}$$

and

$$F_2 = X_{12}\log\gamma^o_{12} + X_{32}\log\gamma^o_{32} + X_{52}\log\gamma^o_{52} + ...+$$
$$+\frac{A_\gamma I^{1/2}}{1+I^{1/2}}[Z_1 Z_2 X_{12} + Z_3 Z_2 X_{32} + Z_5 Z_2 X_{52} + ...] \tag{13}$$

with

$$Y_{21} = \left(\frac{Z_1+Z_2}{2}\right)^2 \frac{m_2}{I} \tag{14}$$

and

$$X_{12} = \left(\frac{Z_1+Z_2}{2}\right)^2 \frac{m_1}{I}. \tag{15}$$

In (11) through (15) the cations have the subscripts 1,2,3, etc. and the anions have 2,4,6, etc. Thus, to find the activity coefficients in the multicomponent solution with Bromley's method, one needs to know the binary activity coefficients of all the possible pairs of anions and cations in a solution of the same ionic strength.

A widely used method to calculate binary activity coefficients is Pitzer's method (Pitzer and Mayorga; 1973), according to which

$$\ln\gamma^o_{12} = Z_1 Z_2 f^\gamma + m_{12}\frac{2\nu_1\nu_2}{\nu_1+\nu_2}B^\gamma_{12} + m^2_{12}\frac{2(\nu_1\nu_2)^{3/2}}{\nu_1+\nu_2}C^\gamma_{12}, \tag{16}$$

where ν_1 and ν_2 are the numbers of cations and anions in the electrolyte formula, respectively, m_{12} is the molality of that electrolyte for the given ionic strength, and where

$$f^{\gamma} = -0.392\left[\frac{I^{1/2}}{1+1.2I^{1/2}} + \frac{2}{1.2}\ln(1+1.2I^{1/2})\right] \tag{17}$$

$$B_{12}^{\gamma} = 2\beta_{12}^{(0)} + \frac{2\beta_{12}^{(1)}}{4I}\left[1 - e^{-2I^{1/2}}(1 + 2I^{1/2} - 2I)\right]. \tag{18}$$

$\beta_{12}^{(0)}$, $\beta_{12}^{(1)}$ and C_{12}^{γ} are semiempirical parameters, the values of which have been extracted by curve fitting of experimental data for various binary electrolyte solutions. For many of the salts involved in atmospheric aerosols, these parameters have been recently updated so that they can apply up to very high ionic strengths (Cohen et al., 1987 a, b).

APPLICATION TO THE NH_3, NaCl, HCl, H_2SO_4, HNO_3, H_2O SYSTEM

The system we are considering consists of the following potential components:

Gas phase: NH_3, HCl, HNO_3, H_2O

Liquid phase: H_2O, NH_4^+, SO_4^{2-}, NO_3^-, H^+,
Na^+, Cl^-, HSO_4^- and H_2SO_4

Solid phase : Na_2SO_4, $NaHSO_4$, NaCl, $NaNO_3$, NH_4Cl,
NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4 and $(NH_4)_3H(SO_4)_2$.

Table 1 summarizes the equilibria and the equilibrium constants that are relevant for this system.

The approach followed for the above system is the following. Since sulfuric acid has a very low vapor pressure, it can be assumed to reside completely in the aerosol phase where it may react with NaCl and NH_3. Thus, the molar ratio of ammonia plus sodium chloride to sulfuric acid is of fundamental importance. The system is sulfate-deficient if the ratio $R_{H_2SO_4} = \frac{m_{NH_3}+m_{NaCl}}{m_{H_2SO_4}} \geq 2$. On the other hand, it is sulfate-rich, if $R_{H_2SO_4} < 2$.

In the sulfate-deficient case, sulfuric acid can be assumed to be completely neutralized, since there is an abundance of ammonia and sodium chloride. The sulfate-rich case can be divided into two subcases. When $1 \leq R_{H_2SO_4} < 2$, part of the H_2SO_4 is neutralized, while the rest of it reacts to produce HSO_4^-. The ratio of HSO_4^- to SO_4^{2-} is controlled by thermodynamic equilibrium. When $R_{H_2SO_4} < 1$, the solution is very acidic. Part of the H_2SO_4 dissociates to HSO_4^-, while the rest remains as $H_2SO_{4(l)}$, the distribution governed by thermodynamic equilibrium.

Another important variable is the relative humidity of deliquescence. Table 2 summarizes the deliquescence relative humidities for the nine possible solids. The RH above mixed, saturated solutions is less than or equal to the relative humidity of deliquescence of the individual salts involved. Thus, for relative humidities above the deliquescence of a specific solid, the solid may not exist. On the other hand, for humidities below the deliquescence RH, the solid phase may or may not exist, depending on the thermodynamic equilibrium. Thus, the equilibrium between solid and ions in aqueous solution for that specific salt must be considered in order to determine whether any solid exists. For RH's lower than the lowest deliquescence relative humidity of the salts involved, the aerosol is assumed to be dry and only the equilibrium between the gas and the solid phases is taken into account.

Thus, the entire range of relative humidities can be divided into several regimes. Tables 3 and 4 show the possible compounds as a function of the relative humidity for the sulfate-deficient and sulfate-rich cases, respectively.

Given the concentrations of NaCl, NH_3, HNO_3 and H_2SO_4, as well as the RH and temperature, the possible compounds at equilibrium are identified using Tables 3 and 4. Then a combination of Newton Raphson and bisection methods is used to solve the system of equations (4) together with the mass conservation and electroneutrality constraints and (9) and (10) to determine the equilibrium physical state and composition of the mixture.

Binary water activities and activity coefficient parameters for most of the electrolytes are taken from recent experimental work (Cohen et al., 1987 a, b), while those for the rest of the species from Bassett and Seinfeld (1983) and Pitzer and Mayorga (1973). Tables 5 and 6 present the water activities and binary activity coefficient parameters, respectively, used in our calculations.

THE SECTIONAL EQUILIBRIUM MODEL

In the case of atmospheric aerosols, the non-volatile species H_2SO_4 and NaCl are not uniformly distributed among particles of different sizes (Wall et al., 1987). As a result, different species might be thermodynamically favored in fine particles over coarse ones. Consider, for example, the case of an aerosol consisting of two sections, fine and coarse, with 0.1μmole of H_2SO_4 in the fine section and 0.2μmole of NaCl in the coarse section. If no specific account is made, the thermodynamic model will predict that, at equilibrium, the aerosol will consist of pure Na_2SO_4. We overcome this problem as follows.

At equilibrium, all the particles, regardless of their size are exposed to the same partial pressure of the volatile species. Let $p_0^{\mathrm{HNO_3}}$ and $p_e^{\mathrm{HNO_3}}$ be the initial and the equilibrium partial pressures of HNO_3, that is to say the pressure before any reaction takes place and after the thermodynamic equilibrium is established, respectively. Then the mass balance equation for nitrates can be written

$$\frac{p_0^{\mathrm{HNO_3}}}{RT} = \frac{p_e^{\mathrm{HNO_3}}}{RT} + \sum_{i=1}^{L} c_i^{\mathrm{HNO_3}}, \tag{19}$$

where $c_i^{\mathrm{HNO_3}}$ is the nitrate concentration in the i^{th} section and L is the total number of sections.

Let $w_i^{\mathrm{HNO_3}}$ be a new variable, defined by

$$w_i^{\mathrm{HNO_3}} = \frac{p_e^{\mathrm{HNO_3}}}{RT} + c_i^{\mathrm{HNO_3}}. \tag{20}$$

Substituting (20) for $c_i^{\mathrm{HNO_3}}$ into (19) one gets

$$\frac{p_0^{\mathrm{HNO_3}}}{RT} = \sum_{i=1}^{L} w_i^{\mathrm{HNO_3}} - (L-1)\frac{p_e^{\mathrm{HNO_3}}}{RT}. \tag{21}$$

Similarly, for NH_3

$$\frac{p_0^{\mathrm{NH_3}}}{RT} = \sum_{i=1}^{L} w_i^{\mathrm{NH_3}} - (L-1)\frac{p_e^{\mathrm{NH_3}}}{RT} \tag{22}$$

and for HCl

$$c_0^{\mathrm{HCl}} = \sum_{i=1}^{L} w_i^{\mathrm{HCl}} - (L-1)\frac{p_e^{\mathrm{HCl}}}{RT}, \tag{23}$$

where c_0^{HCl} is the total chloride concentration, that is, the sum of the sodium chloride and HCl in the system.

Physically, $w_i^{\mathrm{HNO_3}}$, $w_i^{\mathrm{NH_3}}$ and w_i^{HCl} are the hypothetical initial concentrations of HNO_3, NH_3 and HCl, respectively, which, in an atmosphere containing only the non-volatiles of the i^{th} section, give the same equilibrium composition of this aerosol section, as well as the same equilibrium partial pressures of the volatiles as when $p_0^{\mathrm{HNO_3}}$, $p_0^{\mathrm{NH_3}}$ and c_0^{HCl} are applied over the total aerosol population. This property of w_i's is the most useful one, because it enables us to use the method described in the previous section to find the equilibrium composition of all the size sections.

One solves (21), (22) and (23) together with

$$\begin{aligned} p_e^{\mathrm{HNO_3}} &= p_{ie}^{\mathrm{HNO_3}}(w_i^{\mathrm{HNO_3}}, w_i^{\mathrm{NH_3}}, w_i^{\mathrm{HCl}}) \\ p_e^{\mathrm{NH_3}} &= p_{ie}^{\mathrm{NH_3}}(w_i^{\mathrm{HNO_3}}, w_i^{\mathrm{NH_3}}, w_i^{\mathrm{HCl}}) \\ p_e^{\mathrm{HCl}} &= p_{ie}^{\mathrm{HCl}}(w_i^{\mathrm{HNO_3}}, w_i^{\mathrm{NH_3}}, w_i^{\mathrm{HCl}}) \\ &\text{for} \qquad i = 1, 2, ..., L, \end{aligned} \tag{24}$$

to find w's and p_e's, using the ZSPOW non-linear equation solver of the International Mathematical and Statistical Libraries (IMSL). In (24) $p_{ie}^{\mathrm{HNO_3}}$, $p_{ie}^{\mathrm{NH_3}}$ and p_{ie}^{HCl} are the equilibrium HNO_3, NH_3 and HCl partial pressures for the isolated system containing the H_2SO_4 and NaCl of the i^{th} section and the w_i's, at the given temperature and RH. These pressures are determined at each step of ZSPOW by solving, for each of the L size sections, the system of equations (4) together with the electroneutrality and mass balance conditions for each individual section; thus finding the physical state and chemical composition at equilibrium for each of the sections, for the current values of the w' s.

COMPARISON WITH EXISTING AEROSOL MODELS

We have presented a model to predict the equilibrium composition of the ammonium/sodium/sulfate/nitrate/water system, given the initial concentrations of H_2SO_4, HNO_3, NH_3, NaCl and HCl, the ambient RH and the ambient temperature. In the case of one section and zero NaCl concentration, we should obtain results similar to the other two existing aerosol equilibrium models, MARS and EQUIL, which treat the NH_3, H_2SO_4, HNO_3 and H_2O system (Bassett and Seinfeld, 1983; Saxena et al., 1986). Table 7 shows the results of the simulations by the current program, SEQUILIB, together with the results of both MARS and EQUIL for relative humidities ranging from 51-91%. The input data are typical ambient concentrations, i.e., 10 μg m^{-3} H_2SO_4, 10 μg m^{-3} NH_3 and 30 μg m^{-3} HNO_3, while the ambient temperature was assumed to be 25^{o}C (298 K).

As shown in Table 7, SEQUILIB gives results similar to both EQUIL and MARS over the whole range of relative humidities for all the species. MARS disagrees with the predictions of the other two programs in the case of 66% RH, where it predicts dry aerosol without any nitrate in the solid phase. Since for both 61% and 71% RH's, MARS predicts the existence of aerosol nitrates, numerical difficulties in MARS probably are the cause of the discrepancy at 66% RH. The small differences of the water content in the aerosol phase for RH's higher than 66% are due to differences in the methods used to calculate the activity coefficients. For all the runs of Table 7, SEQUILIB needed 21 CPUs, while MARS needed 3CPUs and EQUIL 113CPUs on a VAX-11/780.

THE ROLE OF NaCl IN ATMOSPHERIC AEROSOLS

The model we have developed can be used to find out how NaCl affects the concentration and physical state of a typical urban aerosol at both high and low relative humidities. The input data were again 10 $\mu g\ m^{-3}$ H_2SO_4, 0 $\mu g\ m^{-3}$ HCl, 10 $\mu g\ m^{-3}$ NH_3 and 30 $\mu g\ m^{-3}$ HNO_3, while the ambient temperature was assumed to be 25°C (298 K). The NaCl concentration was varied from 0-30 $\mu g\ m^{-3}$. Relative humidities of 90% and 40% will be considered. Only one aerosol size section is assumed.

Figure 1 shows the predicted aerosol composition for 90% relative humidity. Even at 0 $\mu g\ m^{-3}$ NaCl, the high concentrations of H_2SO_4 and HNO_3 force all the ammonia into the aerosol phase. Since the relative humidity is high (90%), the aerosol is predicted to be an aqueous solution of sulfate, nitrate, chloride, sodium and ammonium ions. As the NaCl concentration increases, the nitrate concentration increases almost linearly with the increase in NaCl. This increase in nitrate is directly correlated with the increase of the NaCl concentration, because all the NH_3 already lies in the aerosol phase. As the NaCl concentration increases, water condenses to satisfy the thermodynamic equilibrium. As is shown in Fig. 1, the liquid water content also increases with the NaCl. One should mention at this point that, even though the relative humidity in this example is below the deliquescence point for Na_2SO_4, no solid sodium sulfate is predicted to coexist with the aqueous phase.

Figure 2 shows the predicted aerosol composition under the same conditions, but for 40% RH. Because the ambient humidity is very low, the aerosol is predicted to be completely dry. We note that the effect of increasing NaCl concentration on the aerosol composition is quite different from the previous case. As the NaCl increases, it reacts with the H_2SO_4 existing in the aerosol phase, forming Na_2SO_4. Thus, less H_2SO_4 is available to react with NH_3, resulting in a decreasing concentration of $(NH_4)_2SO_4$, until it becomes zero at about 12 $\mu g\ m^{-3}$ NaCl. At this point NaCl consumes the total available H_2SO_4. The available NH_3 reacts primarily with HNO_3, producing NH_4NO_3. This is the reason the NH_4NO_3 concentration is predicted to have its maximum at exactly the same point, where the available H_2SO_4 is consumed. Beyond this point the NaCl concentration increase causes different results. Since H_2SO_4 has been completely consumed, the Na_2SO_4 concentration remains constant. The excess NaCl reacts with HNO_3 to produce $NaNO_3$. As more and more HNO_3 reacts to form $NaNO_3$, less remains to form NH_4NO_3, resulting in a decrease of the NH_4NO_3 concentration. At very high NaCl concentrations, the HCl produced by the reactions involving NaCl reaches high enough levels to react with NH_3 to produce NH_4Cl.

The next figure shows the predicted aerosol composition by equivalents (%) for 15 $\mu g\ m^{-3}$ NaCl, 10 $\mu g\ m^{-3}$ NH_3 and 30 $\mu g\ m^{-3}$ HNO_3, 90% RH and ambient temperature 298 K. The initial H_2SO_4 was 10 $\mu g\ m^{-3}$ and 50 $\mu g\ m^{-3}$ for cases (a) and (b), respectively. Case (a) corresponds to a sulfate-deficient environment; thus, the sulfates, as shown in Fig. 3a, are predicted to exist in the aerosol phase in the form of SO_4^{2-}. On the other hand, in case (b) the environment is sulfate-rich; thus, about 25% of the initial sulfuric acid is predicted to be in the aerosol phase in the form of HSO_4^-, while the rest as SO_4^{2-}. The increased concentration of H_2SO_4 in the aerosol phase in the latter case (Fig. 3b) causes a sharp decrease in both the NO_3^- and Cl^- concentrations in the particulate phase. In both cases the OH^- concentration is predicted to be negligible.

The next example demonstrates the dependence of the composition of the aerosol phase on the NaCl size distribution. In this set of runs the system was assumed to consist of 10 μg m^{-3} NaCl, 10 μg m^{-3} H_2SO_4, 0 μg m^{-3} HCl, 5 μg m^{-3} NH_3 and 5 μg m^{-3} HNO_3, while the ambient temperature was assumed to be 298 K and the relative humidity 40%. The aerosol was assumed to consist of two size sections, with 90% of the H_2SO_4 in the fine section and 10% in the coarse section. Figure 4 shows the predicted composition in the aerosol phase, as a function of the fraction of the total NaCl lying in the coarse section. As the fraction of NaCl in the coarse section increases, less NaCl is available in the fine section to react with the abudant H_2SO_4, thus reducing the produced Na_2SO_4. The inverse behavior is observed for $(NH_4)_2SO_4$. The remaining H_2SO_4 (after NaCl has been completely consumed in the fine section) reacts with ammonia, thus increasing the ammonium sulfate concentration.

In contrast to the Na_2SO_4 and $(NH_4)_2SO_4$, the behavior of which is controlled by reactions in the fine section, the concentration of $NaNO_3$ and NaCl is controlled by reactions in the coarse section. As NaCl increases in the coarse particles, part of it reacts completely with the H_2SO_4 in this section. The rest of it reacts directly with the HNO_3, until the equilibrium of the reaction

$$NaCl_{(s)} + HNO_{3(g)} \rightleftharpoons NaNO_{3(s)} + HCl_{(g)}$$

is established. One should note that no NH_4NO_3 is predicted to be formed. The total amount of ammonium is predicted to lie in the fine section as ammonium sulfate, while the total amounts of nitrate and chloride are predicted to lie in the coarse section, in the form of NaCl and $NaNO_3$.

SIMULATION OF AEROSOL COMPOSITION IN THE SOUTH COAST AIR BASIN OF CALIFORNIA

We will now apply our model to predict the behavior of the composition of inorganic aerosol in the South Coast Air Basin of California, and we will compare its predictions to observed values.

Measurements in the Los Angeles area during 1972 (Ho et al., 1974) showed that the liquid water content of atmospheric aerosols accounts for 10-40% of the total particulate mass, for relative humidities from 50-70%, while for RH above 70%, the liquid water fraction was increased significantly. Using typical values observed in the same area, we seek to predict the quantity of aerosol water. Figure 5 shows the measured water fraction in the aerosol phase in the Los Angeles area during 1972 (Ho et al., 1974), as well as the predicted water fraction for 1 and 10 $\mu g\ m^{-3}$ NH_3, as a function of the relative humidity. The rest of the input concentrations in the model were assumed to be 5 $\mu g\ m^{-3}$ NaCl, 20 $\mu g\ m^{-3}$ HNO_3, 10 $\mu g\ m^{-3}$ H_2SO_4 and 0 $\mu g\ m^{-3}$ HCl, while the ambient temperature is assumed to be 298 K. Such conditions were observed in Los Angeles, California, in August 1982 (Russell and Cass, 1984). The aerosol was assumed to consist of two size sections with 90% of the H_2SO_4 and 10% of the NaCl in the fine section.

Figure 5 shows the predicted water mass fraction for both cases. As is shown, for high relative humidities, higher than 62%, the predictions of both runs match the observed water fraction in Los Angeles in 1972 within the uncertainty of the measurements. An important observation from Fig. 5 is that for high relative humidities, the water fraction in the aerosol phase, in spite of being very sensitive to the relative humidity, is relatively robust to changes of the concentration of the inorganic condensible species. Physically, this behavior can be explained by the fact that, since the aqueous phase is thermodynamically favored at high humidities, the more sulfate, nitrate, ammonium and chloride that condense in the aerosol phase, the more water condenses to achieve thermodynamic equilibrium, given the ambient temperature and relative humidity.

Below 62% RH, the behavior between the two aerosols is quite different. The aerosol that corresponds to 10 μg m^{-3} of NH_3 shows a clear deliquescence behavior at 62%, which is the deliquescence relative humidity of NH_4NO_3, the lowest deliquescence point in the sulfate poor case. In contrast, the aerosol that corresponds to 1 μg m^{-3} of NH_3 shows the existence of water even at very low relative humidities, indicating hygroscopic behavior. This behavior can be explained with the help of Figure 6, which presents the size composition distribution of the aerosol at 36% RH in the case of 1 μg m^{-3} of NH_3. As shown in this figure, the assumed small quantity of atmospheric NH_3 is not enough to neutralize the sulfuric acid that is assumed to be in the fine section. Thus, the thermodynamic equilibrium predicts that $H_2SO_{4(l)}$ should exist, which, being hygroscopic, attracts water even at very low relative humidities. The coarse section, since it is completely neutralized by the NaCl reactions with the acids, is predicted to be dry. Thus, in this case, we have the interesting behavior of dry coarse and wet fine particles. Note that no deliquescent behavior is predicted, which may be a possible explanation of the lack of deliquescent behavior of atmospheric aerosols observed in many parts of the USA (Covert et al., 1972).

The large differences in the water content at low relative humidities, because of deliquescence and hydroscopic phenomena, indicate that the aerosol water fraction, in contrast to high relative humidities, is very sensitive to the ambient concentrations of the rest of the species.

Figure 7 shows the predicted aerosol composition and physical state as a function of the relative humidity for 10 μg m^{-3} initial NH_3. At low relative humidities, below 62%, the aerosol is predicted to consist of a mixture of solid Na_2SO_4, $(NH_4)_2SO_4$, NH_4NO_3 and $NaNO_3$. Above 62% RH, the critical humidity for NH_4NO_3, the ammonium nitrate is completely dissolved. The condensed water is predicted to be enough to cause the complete dissolution of the rest of the salts. Thus, above this RH the particle is predicted to be an aqueous solution of Na^+, NH_4^+, NO_3^-, Cl^-, and SO_4^{2-}, despite the fact that the deliquescence point of most of the rest of the thermodynamically favored salts is about 80% RH.

A field study took place throughout the California's South Coast Air Basin on August 30-31, 1982 (Russell and Cass, 1984; Hildelmann et al., 1984). During that study aerosol particles were collected and the amount of ionic material in the aerosol phase was determined. Thus, 4-hr and 2-hr average data for Aug. 30 and Aug. 31, respectively, are available for inorganic aerosol material, as well as NH_3, HNO_3 and ambient meteorological conditions. Unfortunately, neither HCl in the gas phase nor liquid H_2O was measured. We simulated the aerosol concentrations observed at Long Beach, California, throughout the 48 hrs that measured data exist.

The Long Beach prediction is a difficult test for aerosol equilibrium models, because during those 48 hrs the air mass stagnated for most of the day in an area of high NO_x and SO_2 emissions, resulting in high concentrations of sulfate and nitrate aerosols, despite the high ambient temperature, which, thermodynamically, does not favor aerosol formation (Russell et al., 1982; Russell and Cass, 1984).

Air masses from the Pacific Ocean cross the Long Beach coastline, carrying coarse aerosol, rich in sea salt, inland. Sulfur dioxide is produced in that area, the photooxidation of which produces H_2SO_4 which, by homogeneous nucleation and condensation, can be transferred into the aerosol phase. Hence, it is reasonable to consider that most of the NaCl at Long Beach lies in the coarse particles, while the H_2SO_4 lies in the fine ones. This assumption is supported by measurements of the aerosol size-composition distribution in many locations in California (Wall et al., 1987). Thus, we consider two size sections, assuming that 90% of the aerosol sodium exists in the coarse section, while 90% of the aerosol sulfate lies in the fine section.

Because no HCl data are available we assumed that all the sodium in the aerosol phase was initially in the form of NaCl and that NaCl was the only possible source of HCl. Whenever other cations, such as Ca^{2+}, Mg^{2+} and K^+, were present, their concentrations were reduced to equivalent sodium. Inputs to our calculation were the total measured H_2SO_4 and equivalent NaCl, distributed as described above, the total measured nitrates (i.e., $HNO_3 + NO_3^-$) and the total measured ammonium (i.e., $NH_4^+ + NH_3$), as well as the measured ambient temperature and relative humidity. Predicted were the total ammonium, chloride and nitrate concentrations in the aerosol phase, as well as the NH_3, HNO_3 and HCl in the gas phase at thermodynamic equilibrium. Also the water content and the thermodynamically favorable species for both the fine and coarse particles were predicted.

Figures 8, 9 and 10 show the predicted and observed total concentrations of nitrates, ammonium, and chlorides in the aerosol phase, respectively, for the Aug. 30-31, 1982 period at Long Beach, California. As shown in Fig. 8, we predict the nitrates in the aerosol phase within the uncertainty of the measurements throughout the 48-hr period, except for the peak between 800 and 1200 PDT of Aug. 31, 1982. For this time period the model predicts that the concentration of nitrates at Long Beach reaches a maximum, but the predicted nitrate concentration is lower than the mean observed value.

Fig. 9 shows the predicted and observed NH_4^+ for the same period of time. Despite the small consistent overprediction, the behavior of the ammonium concentration as a function of time is predicted. Chlorides, as shown in Fig. 10, are predicted quite well for many of the cases. For the others there is overprediction of the chloride concentrations, which is probably due to the lack of HCl data and to our assumption that all the sodium in the aerosol phase was initially in the form of NaCl.

Figure 11 shows the predicted distribution of the aerosol water between the fine and the coarse aerosol at 0-200 PDT of Aug. 31, 1982. Twice as much water is predicted to be in the large particles as in the small ones. Because of the high relative humidity, 81%, the aerosol is predicted to be an aqueous solution of ionic material. Figure 12 shows the distribution of the various ions between the two size sections, for the same case. Most of the Cl^- and NO_3^- is predicted to be in the coarse section, where most of the sodium exists, while most of the NH_4^+ is predicted to lie in the fine section, directly associated with the abudance of sulfate in that section.

Exactly the same behavior is noted in Fig. 13, which shows the predicted distribution between the two size sections, at Long Beach, California, for the period 1400-1600 PDT of Aug. 31, 1982. Because the relative humidity was only 43%, the aerosol was predicted to be a mixture of solid salts. Note that the aerosol nitrate and chloride are predicted to lie in the large particles, as $NaNO_3$ and NaCl, respectively, and that the ammonium is, again, predicted to be in the small size section, as $(NH_4)_2SO_4$, while no NH_4NO_3 is predicted to be formed during that 2-hr period at Long Beach, California.

CONCLUSIONS

An equilibrium model of the ammonium/ chloride/ nitrate/ sodium/ sulfate/ water aerosol system has been presented. Given the total quantities of HNO_3, NH_3 and HCl in the gas phase, as well as the distribution of NaCl and H_2SO_4 in the aerosol phase, the chemical composition-distribution and physical state of the aerosol are calculated, for the given temperature and relative humidity.

Using this model, we have shown that, in Los Angeles, the observed existence of liquid water in the aerosol phase at low relative humidities can be explained by the means of thermodynamic equilibrium. The model also successfully predicted the amount of the aerosol NO_3^-, NH_4^+ and Cl^- existing at Long Beach, California, during the episode of August 30-31, 1982.

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Table 1. Chemical reactions occurring in the NaCl-HCl-H$_2$SO$_4$-NH$_3$-HNO$_3$-H$_2$O system.

Reaction	Equilibrium Constant
$NaCl_{(s)} + HNO_{3(g)} \rightleftharpoons NaNO_{3(s)} + HCl_{(g)}$	$3.96 exp\left[5.50\left(\frac{T_o}{T}-1\right) - 2.180\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$
$NH_{3(g)} + HNO_{3(g)} \rightleftharpoons NH_4^+ + NO_3^-$	$3.99 \times 10^{17} exp\left[64.7\left(\frac{T_o}{T}-1\right) + 11.51\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol^2 Kg^{-2} atm^{-2}
$HCl_{(g)} \rightleftharpoons H^+ + Cl^-$	$2.03 \times 10^{6} exp\left[30.21\left(\frac{T_o}{T}-1\right) + 19.91\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol^2 Kg^{-2} atm^{-1}
$NH_{3(g)} + HCl_{(g)} \rightleftharpoons NH_4^+ + Cl^-$	$2.12 \times 10^{17} exp\left[65.08\left(\frac{T_o}{T}-1\right) + 14.51\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol^2 Kg^{-2} atm^{-2}
$Na_2SO_{4(s)} \rightleftharpoons 2Na^+ + SO_4^{2-}$	$0.4805 exp\left[0.98\left(\frac{T_o}{T}-1\right) + 39.57\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol^3 Kg^{-3}
$(NH_4)_2SO_{4(s)} \rightleftharpoons 2NH_4^+ + SO_4^{2-}$	$1.425 exp\left[-2.65\left(\frac{T_o}{T}-1\right) + 38.55\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol^3 Kg^{-3}
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	$1.031 \times 10^{-2} exp\left[7.59\left(\frac{T_o}{T}-1\right) + 18.83\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol Kg^{-1}
$HNO_{3(g)} \rightleftharpoons H^+ + NO_3^-$	$3.638 \times 10^{6} exp\left[29.47\left(\frac{T_o}{T}-1\right) + 16.84\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol^2 Kg^{-2} atm^{-1}
$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$	$1.039 \times 10^{-16} exp\left[-71.04\left(\frac{T_o}{T}-1\right) + 2.40\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ atm^2
$NH_{3(g)} + HNO_{3(g)} \rightleftharpoons NH_4NO_{3(s)}$	$3.349 \times 10^{16} exp\left[75.11\left(\frac{T_o}{T}-1\right) - 13.46\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ atm^{-2}
$NaNO_{3(s)} \rightleftharpoons Na^+ + NO_3^-$	$11.971 exp\left[-8.22\left(\frac{T_o}{T}-1\right) + 16.01\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol^2 Kg^{-2}
$NaCl_{(s)} \rightleftharpoons Na^+ + Cl^-$	$37.743 exp\left[-1.57\left(\frac{T_o}{T}-1\right) + 16.89\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol^2 Kg^{-2}
$NaHSO_{4(s)} \rightleftharpoons Na^+ + HSO_4^-$	$2.44 \times 10^{4} exp\left[0.79\left(\frac{T_o}{T}-1\right) + 4.53\left(1+ln(\frac{T_o}{T}) - \frac{T_o}{T}\right)\right]$ mol^2 Kg^{-2}

Table 2. Relative humidities of deliquescence of the nine possible solid compounds.

Species	Deliquesence RH
$NaCl$	76.0
Na_2SO_4	93.0
$NaHSO_4$	52.0
$NaNO_3$	74.0
NH_4Cl	80.0
$(NH_4)_2SO_4$	80.0
$(NH_4)_3H(SO_4)_2$	69.0
NH_4HSO_4	40.0
NH_4NO_3	62.0

Table 3. Aerosol chemical composition as a function of the ambient relative humidity for the sulfate-deficient case.

RH	SPECIES
100	
	Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, H_2O
93	
	$Na_2SO_{4(s)}$, H_2O Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-
80	
	$Na_2SO_{4(s)}$, $NH_4Cl_{(s)}$, $(NH_4)_2SO_{4(s)}$, H_2O Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-
76	
	$Na_2SO_{4(s)}$, $NH_4Cl_{(s)}$, $(NH_4)_2SO_{4(s)}$, $NaCl_{(s)}$, H_2O Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-
74	
	$Na_2SO_{4(s)}$, $NH_4Cl_{(s)}$, $(NH_4)_2SO_{4(s)}$, $NaNO_{3(s)}$, $NaCl_{(s)}$, H_2O Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-
62	
	$Na_2SO_{4(s)}$, $NH_4Cl_{(s)}$, $(NH_4)_2SO_{4(s)}$, $NH_4NO_{3(s)}$, $NaNO_{3(s)}$, $NaCl_{(s)}$
0	

Table 4. Aerosol chemical composition as a function of the ambient relative humidity for the sulfate-rich case.

	$1 \leq R_{H_2SO_4} < 2$	$0 \leq R_{H_2SO_4} < 1$
RH	SPECIES	SPECIES
100		
	Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, H_2O H^+, $HNO_{3(l)}$, HSO_4^-	
93		
	$Na_2SO_{4(s)}$, H_2O Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^- H^+, $HNO_{3(l)}$, HSO_4^-	
80		
	$Na_2SO_{4(s)}$, $(NH_4)_2SO_{4(s)}$, H_2O Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^- H^+, $HNO_{3(l)}$, HSO_4^-	H^+, $HNO_{3(l)}$, HSO_4^-, $H_2SO_{4(l)}$ NO_3^-, Na^+, Cl^-, NH_4^+, H_2O
69		
	$Na_2SO_{4(s)}$, $(NH_4)_2SO_{4(s)}$, $(NH_4)_3H(SO_4)_{2(s)}$ Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^- H^+, $HNO_{3(l)}$, HSO_4^-, H_2O	
52		
	$Na_2SO_{4(s)}$, $(NH_4)_2SO_{4(s)}$, $(NH_4)_3H(SO_4)_{2(s)}$ $NaHSO_{4(s)}$, H_2O Na^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^- H^+, $HNO_{3(l)}$, HSO_4^-	$NaHSO_{4(s)}$, H_2O Na^+, Cl^-, NH_4^+, NO_3^- H^+, $HNO_{3(l)}$, HSO_4^-, $H_2SO_{4(l)}$
40		
	$Na_2SO_{4(s)}$, $(NH_4)_2SO_{4(s)}$, $(NH_4)_3H(SO_4)_{2(s)}$, $NaHSO_{4(s)}$, $NH_4HSO_{4(s)}$,	$NaHSO_{4(s)}$, H_2O, Na^+, Cl^-, NH_4^+, NO_3^- $NH_4HSO_{4(s)}$, H^+, HSO_4^-, $HNO_{3(l)}$, $H_2SO_{4(l)}$
0		

Table 5. Coefficients of the polynomial fit of the binary solution water activity, $a_w = \sum_{i=0}^{6} a_i m^i$.

Species	a_0	a_1	a_2	a_3	a_4	a_5	a_6
$NaNO_3$	0.9988	-2.6947×10^{-2}	1.9010×10^{-4}	2.8154×10^{-5}	-6.1359×10^{-7}	0.0	0.0
$NaHSO_4$	1.0614	−0.1014	1.5796×10^{-2}	-1.9501×10^{-3}	9.5147×10^{-5}	-1.5473×10^{-6}	0.0
NaCl	1.0084	-4.9390×10^{-2}	8.8880×10^{-3}	-2.1570×10^{-3}	1.6170×10^{-4}	-1.9900×10^{-6}	-1.1420×10^{-7}
Na_2SO_4	1.0052	-6.4840×10^{-2}	3.5190×10^{-2}	-1.3190×10^{-2}	1.9250×10^{-3}	-1.2240×10^{-4}	2.8700×10^{-6}
$(NH_4)_2SO_4$	0.9968	-2.9690×10^{-2}	1.7350×10^{-5}	-3.2530×10^{-4}	3.5710×10^{-6}	-9.7870×10^{-7}	0.0
NH_4Cl	0.9908	-2.6110×10^{-2}	-1.5990×10^{-3}	1.3550×10^{-4}	-2.3170×10^{-6}	-1.1130×10^{-8}	0.0
NH_4NO_3	1.0053	-2.4991×10^{-2}	4.4688×10^{-4}	1.6453×10^{-5}	-3.8940×10^{-7}	-4.7668×10^{-8}	1.3753×10^{-9}
NH_4HSO_4	1.0261	-4.9766×10^{-2}	3.2757×10^{-3}	-2.4477×10^{-4}	1.0766×10^{-5}	-1.8329×10^{-7}	0.0
$(NH_4)_3H(SO_4)_2$	1.0088	-5.3730×10^{-2}	1.4201×10^{-3}	-9.2484×10^{-4}	2.2796×10^{-4}	-1.5445×10^{-5}	0.0
H_2SO_4	1.0175	-3.2120×10^{-2}	-9.5203×10^{-3}	8.7831×10^{-4}	-2.8025×10^{-5}	3.0897×10^{-7}	0.0
HCl	0.9992	-3.0929×10^{-2}	-4.9896×10^{-3}	5.3711×10^{-5}	2.2489×10^{-5}	-7.7602×10^{-7}	0.0
HNO_3	0.9988	-3.0466×10^{-2}	-2.8124×10^{-3}	-3.8769×10^{-7}	1.0932×10^{-5}	-2.9014×10^{-7}	0.0

Table 6: Parameters of Pitzer's method.

Species	$\beta_{12}^{(0)}$	$\beta_{12}^{(1)}$	$\frac{2}{3}C_{12}^{\gamma}$
NaCl	0.10820	0.03127	-0.002469
Na_2SO_4	0.08610	0.13037	-0.003104
$NaNO_3$	0.00680	0.17830	-0.000720
$NaHSO_4$	0.35262	1.56403	-0.009978
NH_4Cl	0.04568	0.20431	-0.001731
$(NH_4)_2SO_4$	0.04763	0.44459	-0.001311
NH_4NO_3	-0.01540	0.11200	-0.000030
NH_4HSO_4	0.04494	0.23594	-0.002920
(H^+, HSO_4^-)	0.25713	0.35308	-0.002830
$(2H^+, SO_4^{2-})$	-0.09330	0.32381	0.021162
HNO_3	0.11190	0.32060	0.001000
HCl	0.17750	0.29450	0.000800

Table 7.

SO_4^{2-}, NO_3^-, NH_4^+ and H_2O concentrations

obtained by the aerosol equilibrium models SEQUILIB, EQUIL and MARS

for T=298 K, 10 $\mu g\ m^{-3}$ H_2SO_4, 10 $\mu g\ m^{-3}$ NH_3 and 30 $\mu g\ m^{-3}$ HNO_3.

RH	SEQUILIB				EQUIL				MARS			
	SO_4^{2-}	NO_3^-	NH_4^+	H_2O	SO_4^{2-}	NO_3^-	NH_4^+	H_2O	SO_4^{2-}	NO_3^-	NH_4^+	H_2O
51	10.0	12.9	7.4	0.0	10.0	14.0	7.7	0.0	10.0	13.0	7.4	0.0
56	10.0	12.9	7.4	0.0	10.0	14.0	7.7	0.0	10.0	13.0	7.4	0.0
61	10.0	12.9	7.4	0.0	10.0	14.0	7.7	0.0	10.0	13.0	7.4	0.0
66	10.0	14.0	7.8	19.0	9.90	15.1	8.1	5.3	10.0	0.00	3.7	0.0
71	10.0	15.5	8.2	26.0	9.70	16.9	8.6	28.8	10.0	15.6	8.2	25.7
76	10.0	16.8	8.6	35.1	9.70	18.0	8.9	36.7	10.0	17.2	8.7	35.9
81	10.0	18.3	9.0	49.1	9.70	19.1	9.2	49.5	10.0	18.6	9.1	50.5
86	10.0	19.7	9.4	73.1	9.70	20.3	9.5	73.8	10.0	19.1	9.5	75.5
91	10.0	21.2	9.8	124.0	9.50	21.9	9.9	131.0	10.0	21.4	9.9	131.9

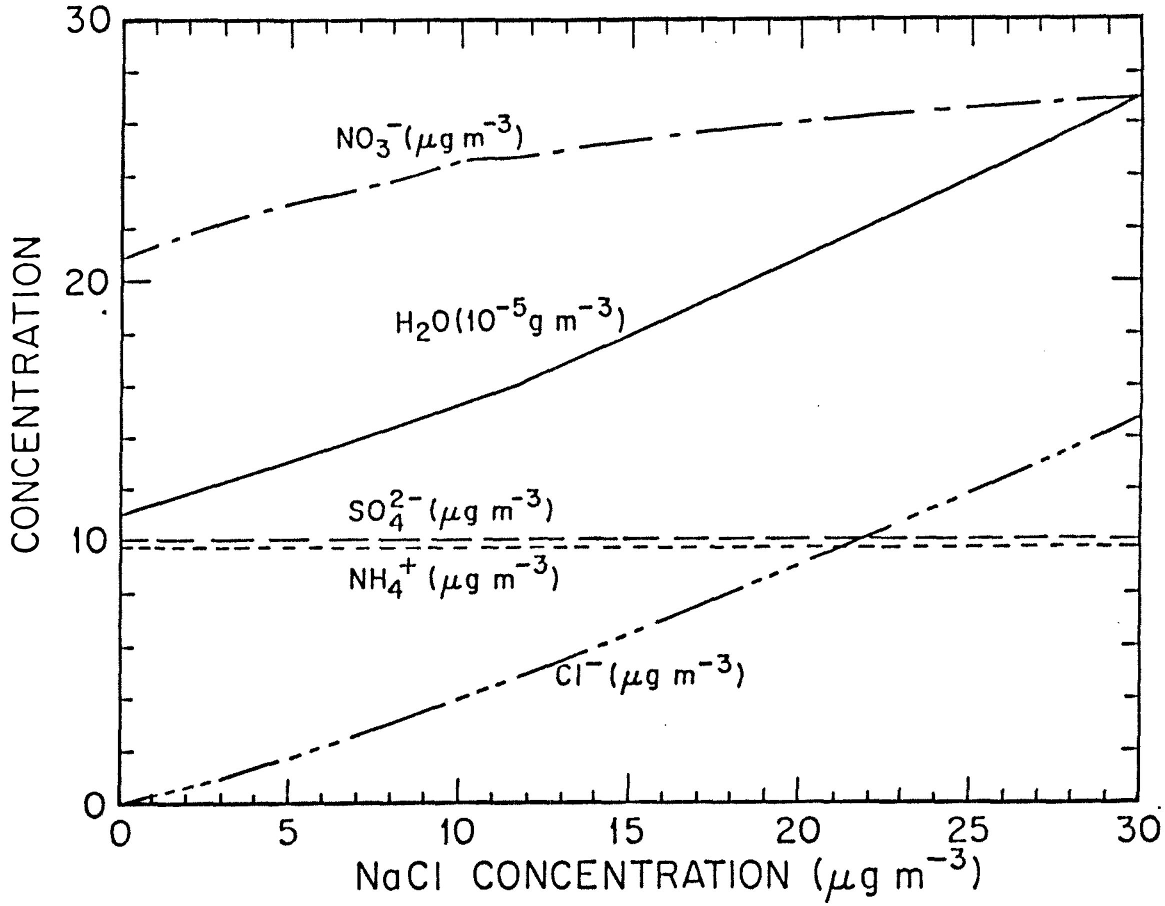

Fig. 1 Aerosol composition as a function of the NaCl concentration for 90% relative humidity. The conditions are 10 μg m^{-3} H_2SO_4, 0 μg m^{-3} HCl, 10 μg m^{-3} NH_3 and 30 μg m^{-3} HNO_3, ambient temperature is 298 K.

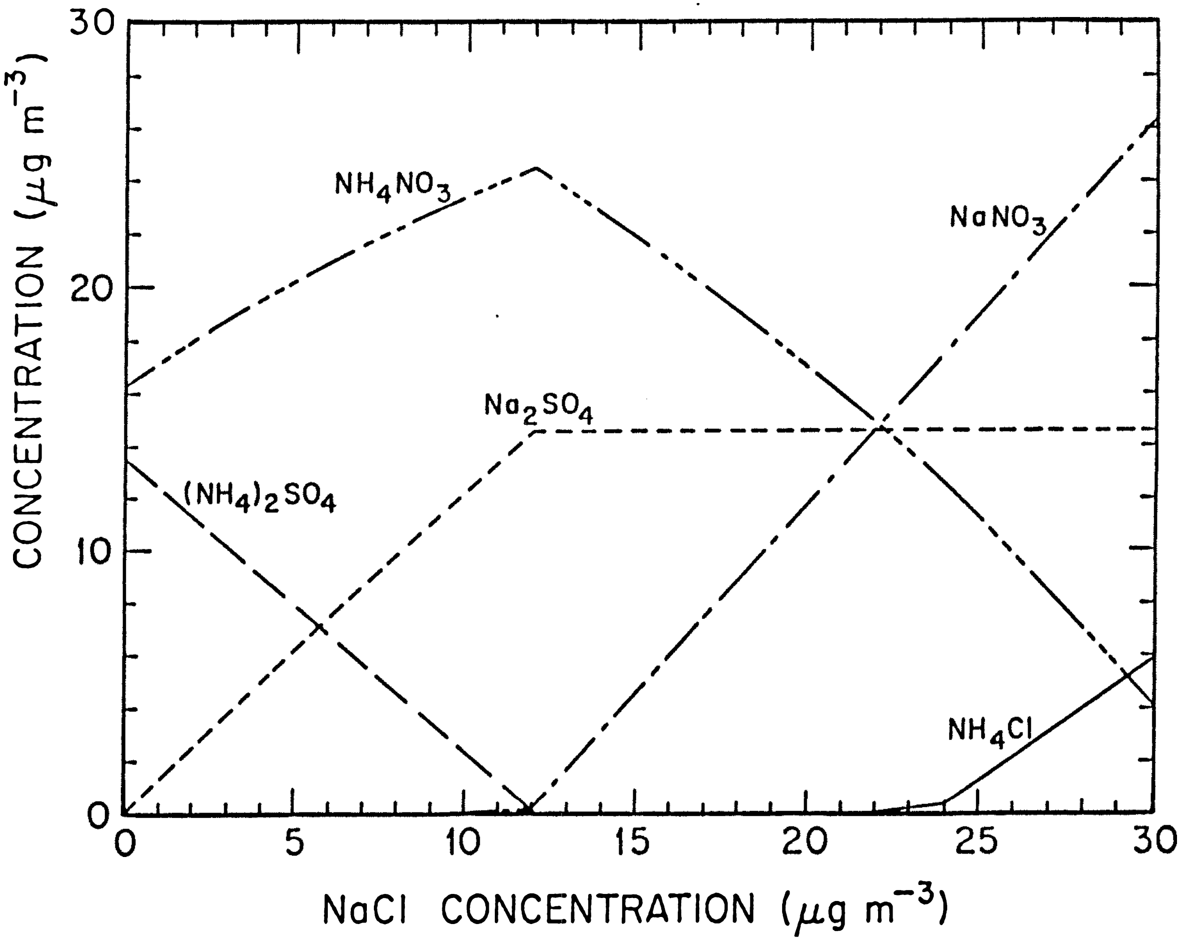

Fig. 2 Aerosol composition as a function of the NaCl concentration for 40% relative humidity. The conditions are 10 μg m^{-3} H_2SO_4, 0 μg m^{-3} HCl, 10 μg m^{-3} NH_3 and 30 μg m^{-3} HNO_3; ambient temperature is 298 K.

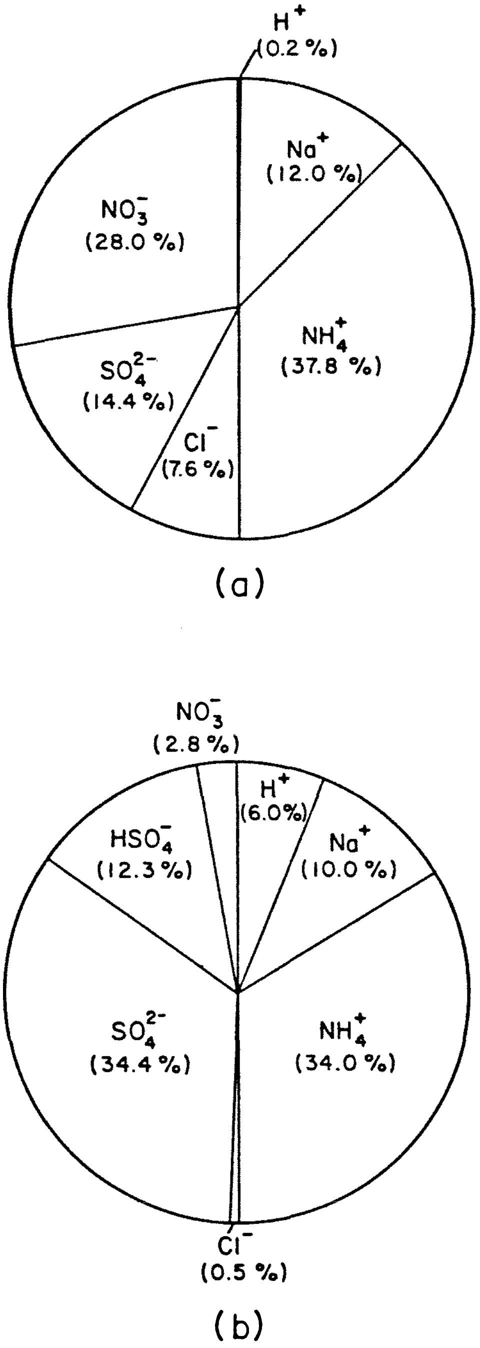

Fig. 3 Aerosol composition by equivalents (%). Case (a) corresponds to 10 μg m^{-3} H_2SO_4, while case (b) to 50 μg m^{-3} H_2SO_4. The other conditions are 15 μg m^{-3} NaCl, 0 μg m^{-3} HCl, 10 μg m^{-3} NH_3 and 30 μg m^{-3} HNO_3, ambient temperature is 298 K and ambient RH 90%.

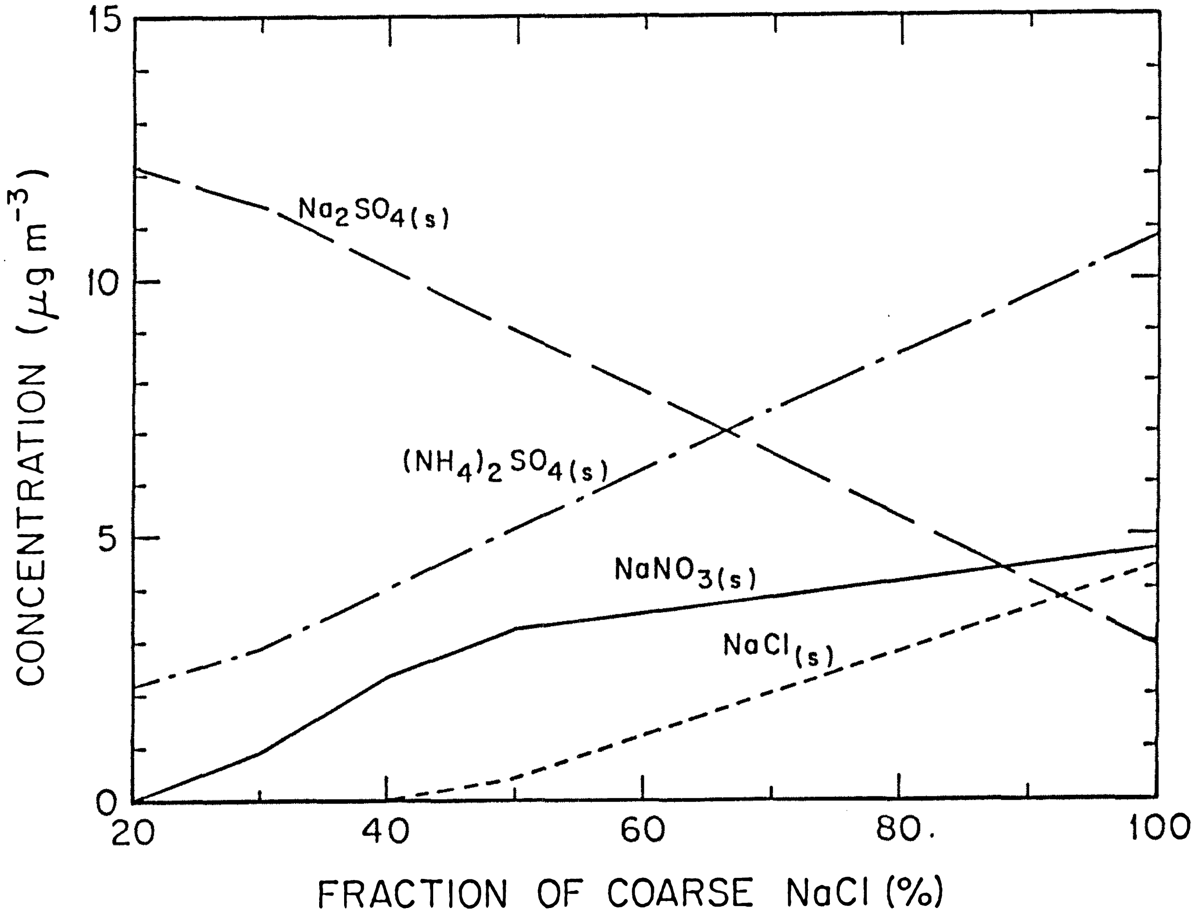

Fig. 4 Aerosol composition as a function of the fraction of NaCl in the coarse section of a two size section aerosol. The conditions are 10 μg m^{-3} NaCl, 10 μg m^{-3} H_2SO_4, 0 μg m^{-3} HCl, 5 μg m^{-3} NH_3 and 5 μg m^{-3} HNO_3, ambient temperature is 298 K and relative humidity is 40%.

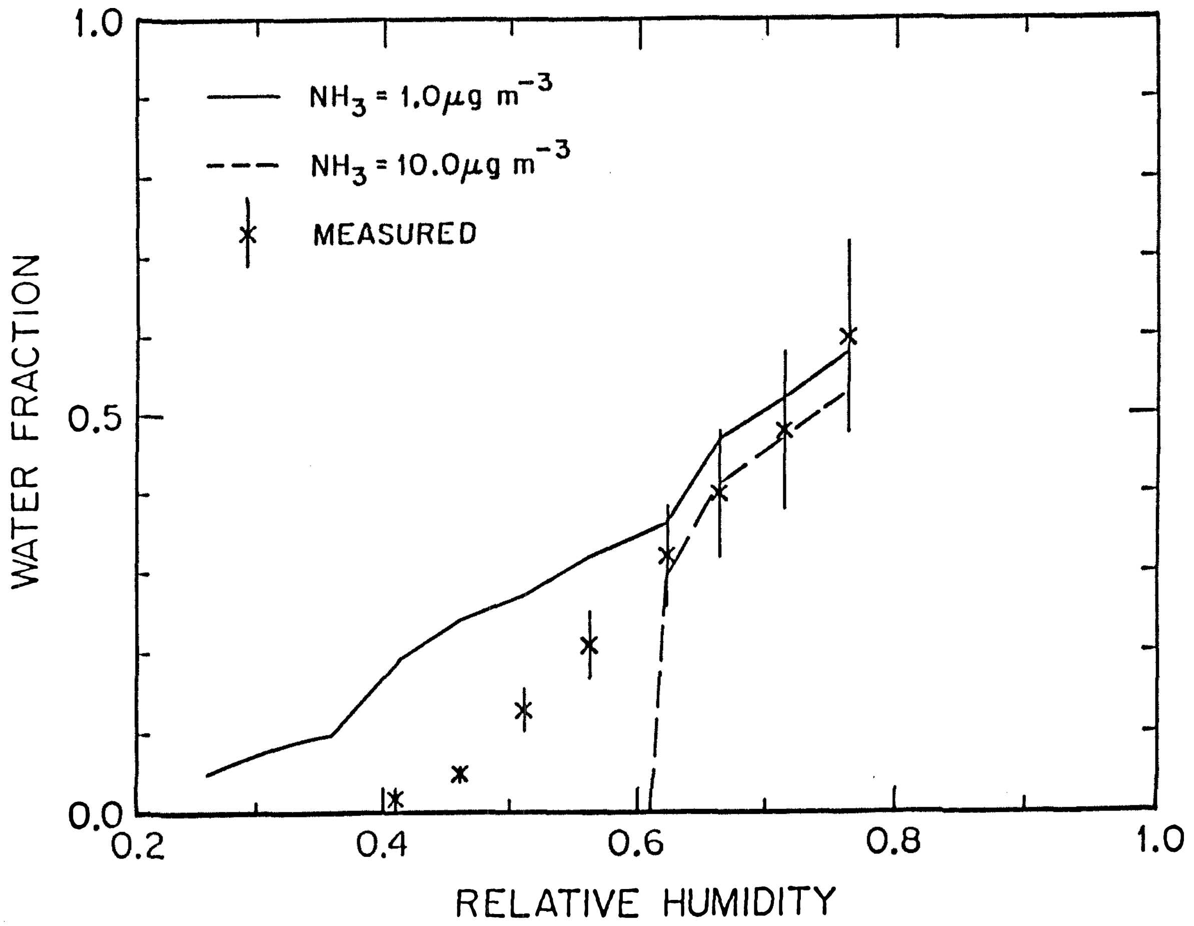

Fig. 5 Predicted water mass fraction as a function of the relative humidity for 1 and 10 μg m^{-3} NH_3. The other conditions are 5 μg m^{-3} NaCl, 20 μg m^{-3} HNO_3, 10 μg m^{-3} H_2SO_4 and 0 μg m^{-3} HCl. The error bars correspond to observed values in Los Angeles, CA. (Ho et al., 1974)

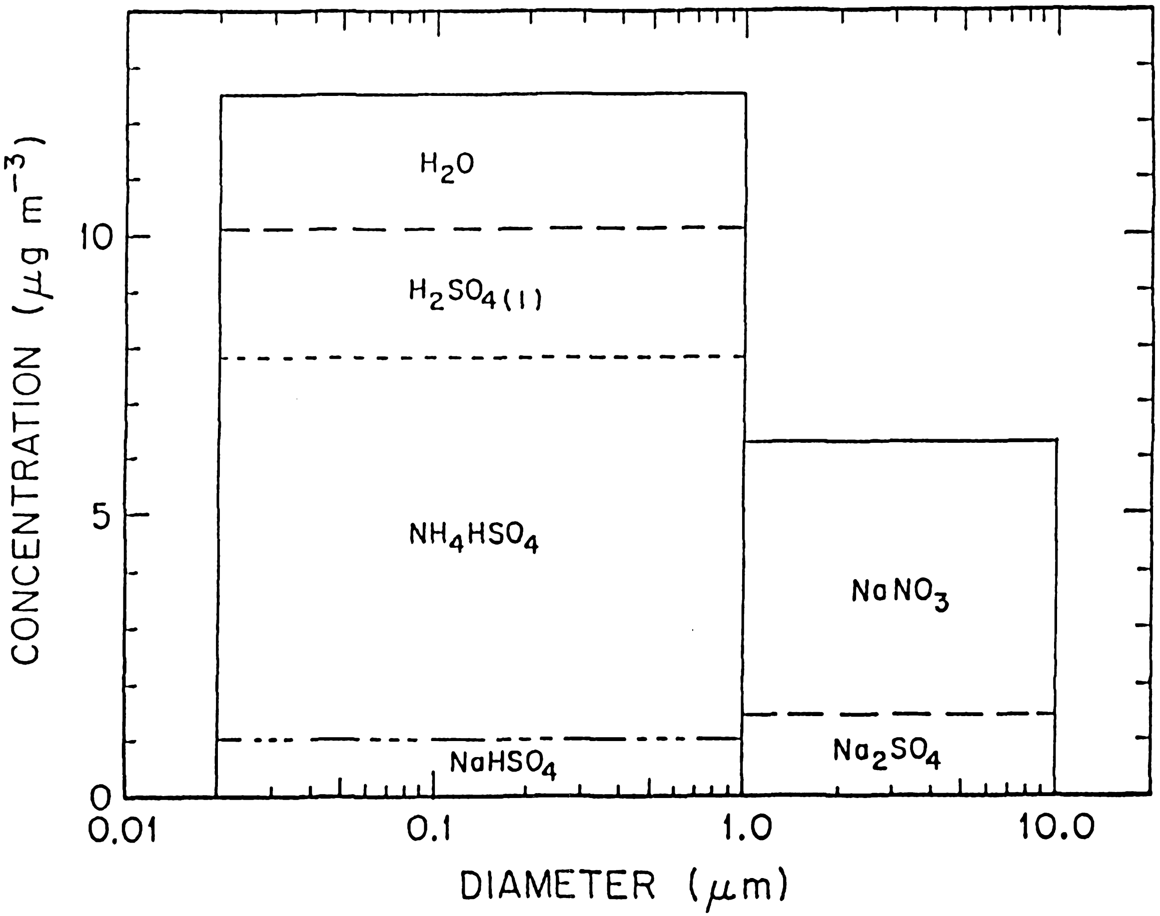

Fig. 6 Predicted size-composition distribution for 1 μg m^{-3} NH_3. The other conditions are 5 μg m^{-3} NaCl, 20 μg m^{-3} HNO_3, 10 μg m^{-3} H_2SO_4 and 0 μg m^{-3} HCl. The relative humidity is 36% and the temperature 298 K. The mass below the solid line indicates the total amount of aerosol, with the incremental components of that total as indicated.

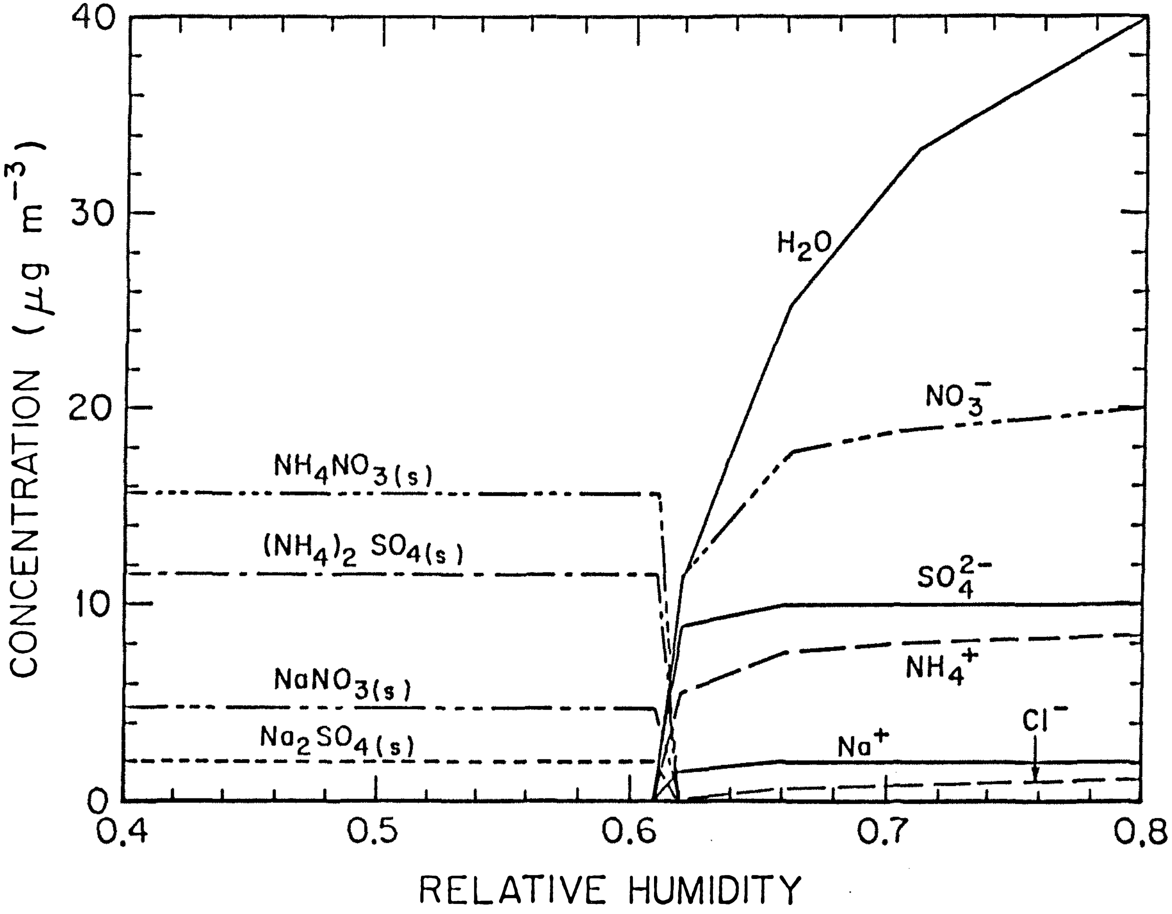

Fig. 7 Predicted aerosol composition as a function of the relative humidity for 10 μg m^{-3} NH_3. The other conditions are 5 μg m^{-3} NaCl, 20 μg m^{-3} HNO_3, 10 μg m^{-3} H_2SO_4 and 0 μg m^{-3} HCl, and the temperature is 298 K.

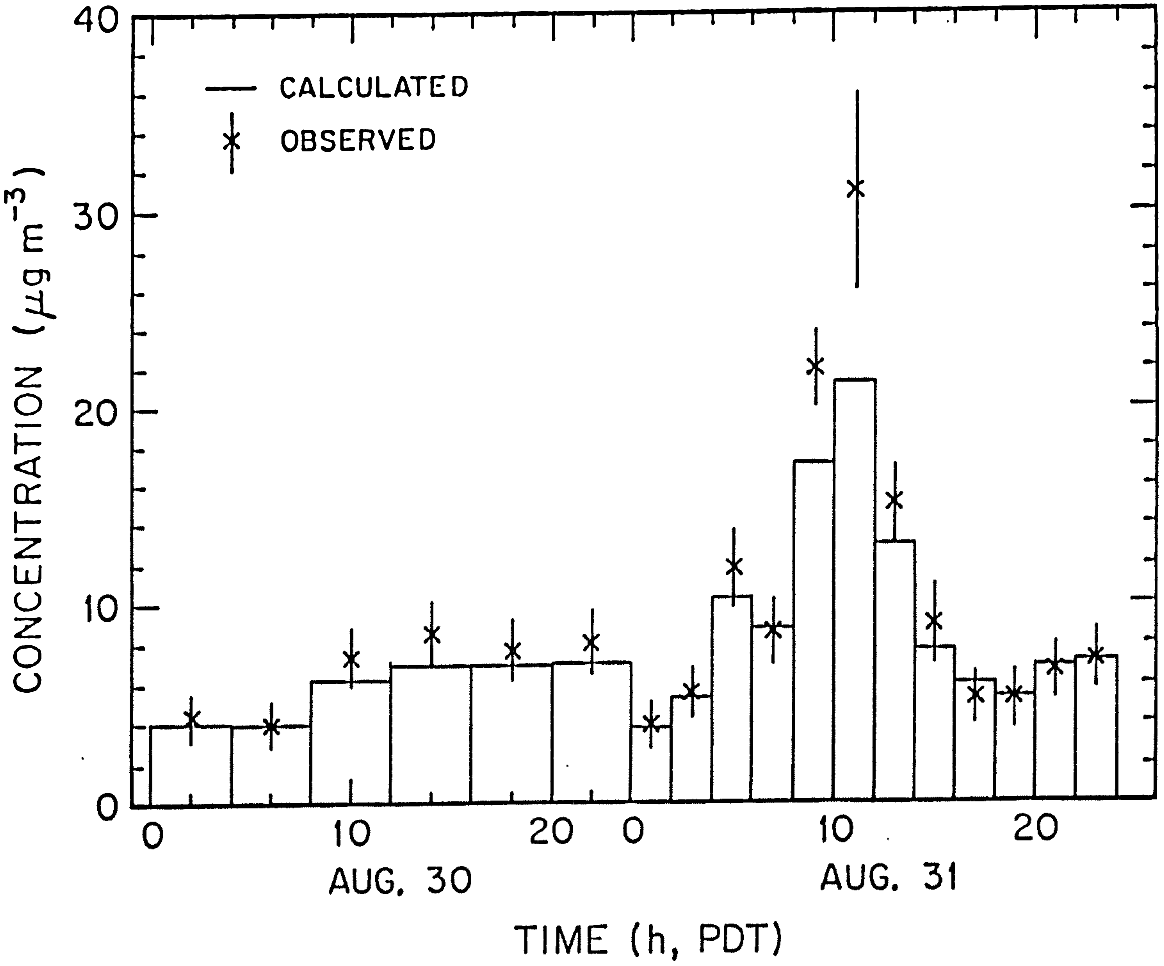

Fig. 8 Observed (Russell and Cass, 1984) and predicted nitrate concentrations at Long Beach, CA, on August 30 and 31, 1982.

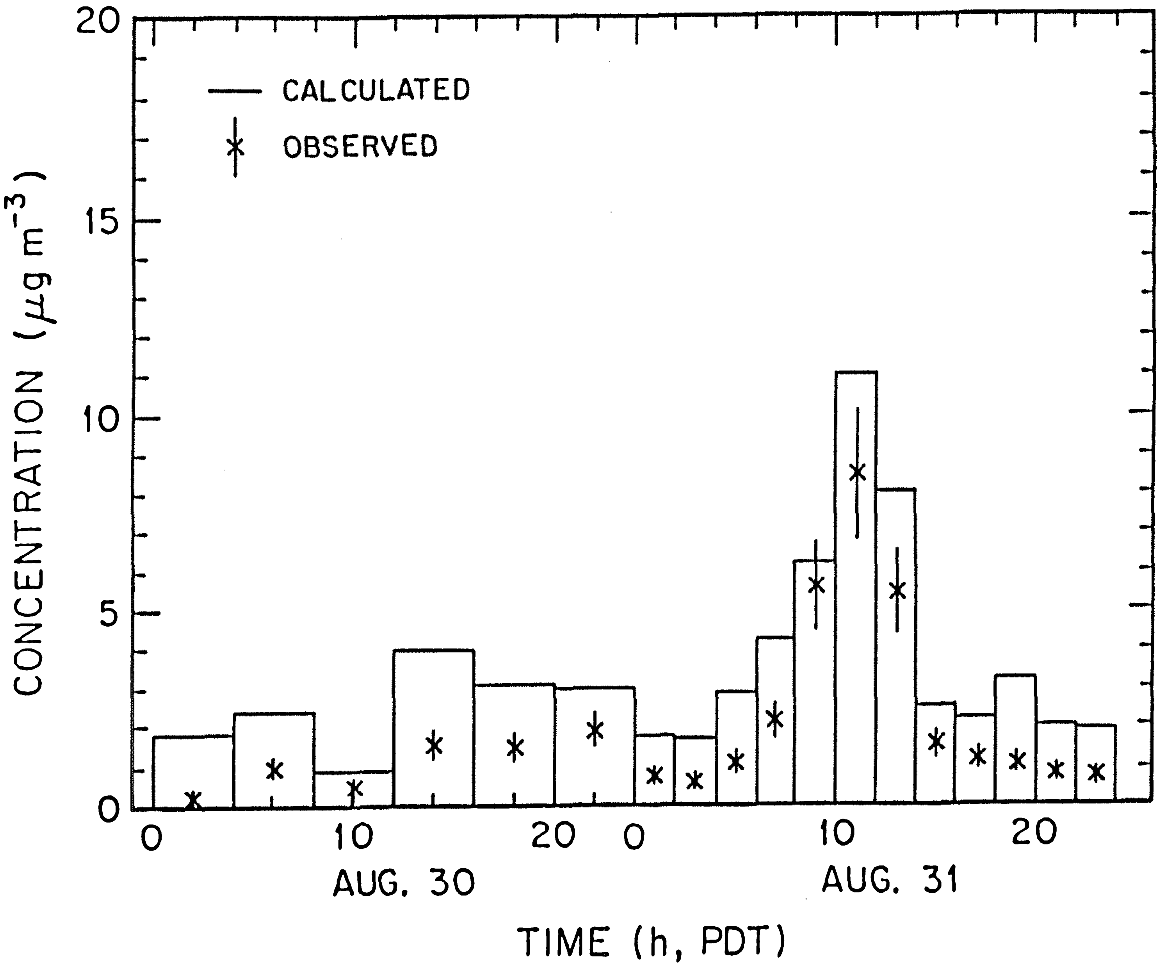

Fig. 9 Observed (Russell and Cass, 1984) and predicted ammonium concentrations at Long Beach, CA, on August 30 and 31, 1982.

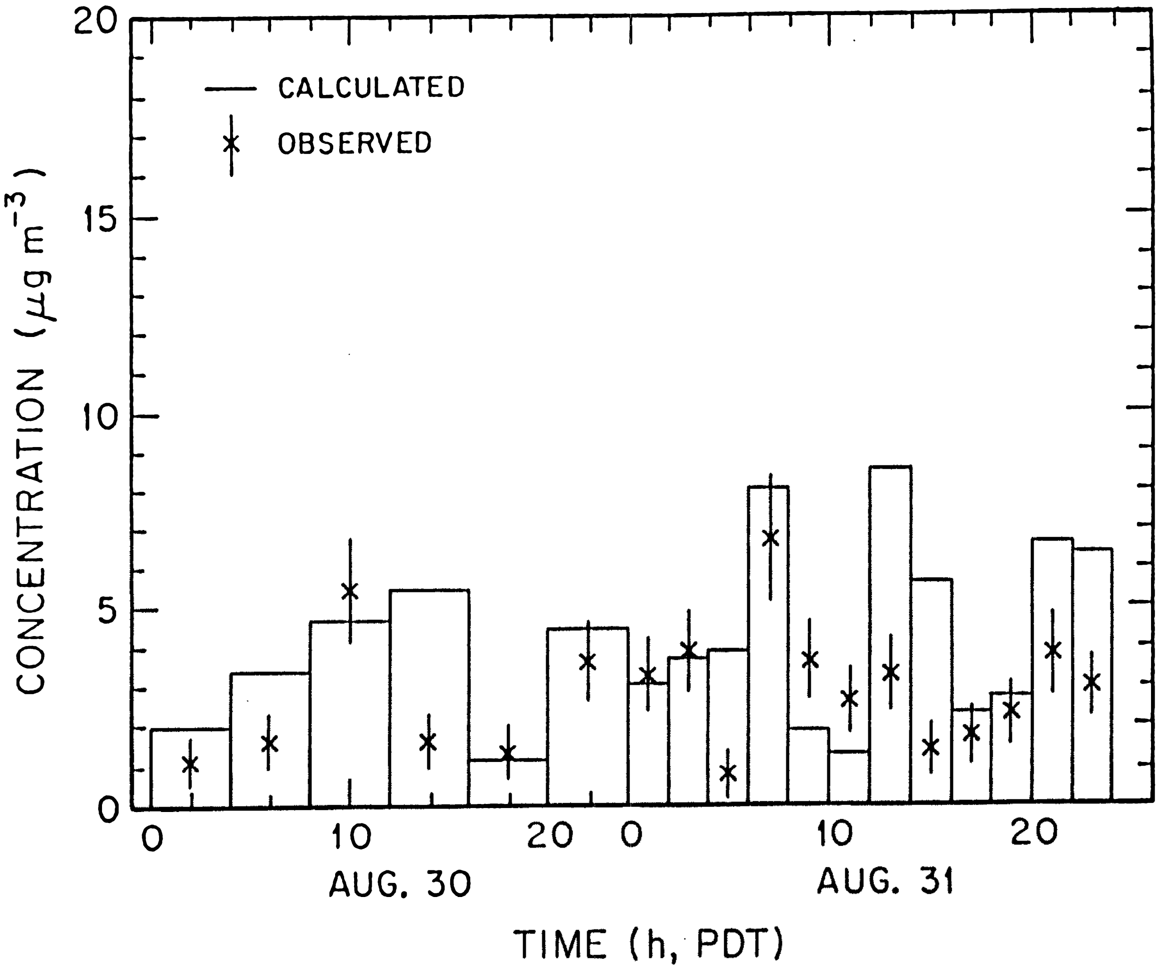

Fig. 10 Observed (Russell and Cass, 1984) and predicted chloride concentrations at Long Beach, CA, on August 30 and 31, 1982.

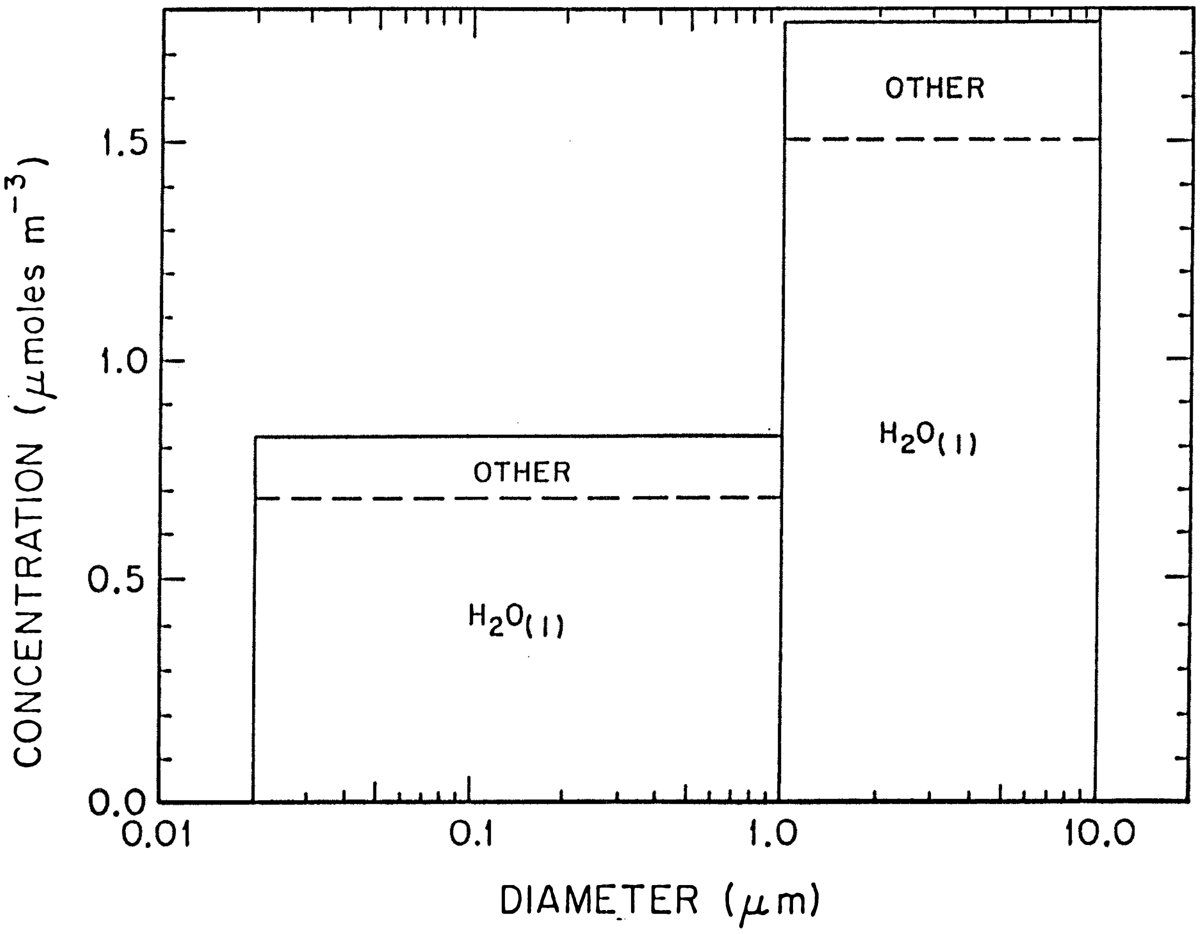

Fig. 11 Predicted size distribution of aerosol water at Long Beach, CA, during the period 0000-0200 hours PDT on August 31, 1982. The relative humidity was 81%. The mass below the upper line indicates the total amount of aerosol, with the incremental components of that total as indicated.

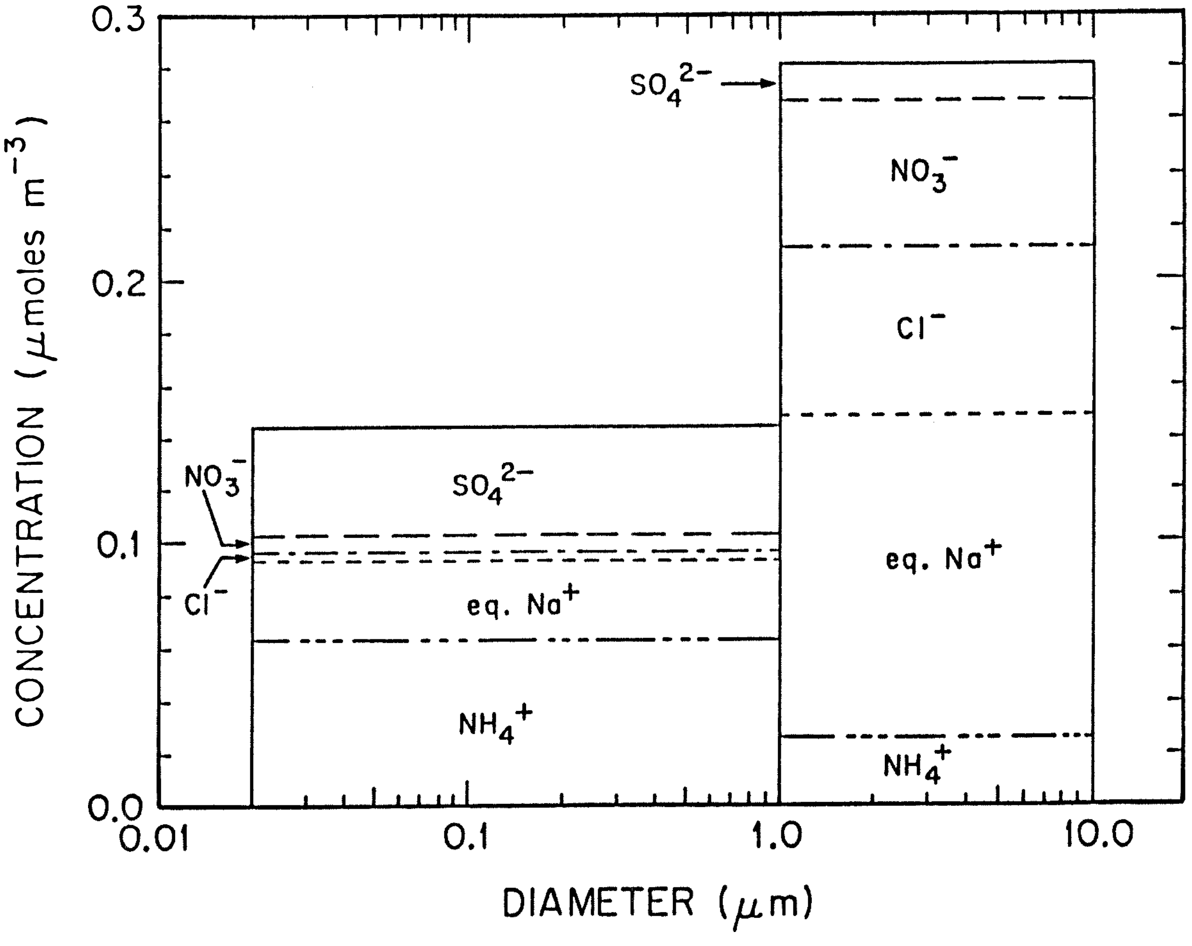

Fig. 12 Predicted size-composition distribution (exluding water) at Long Beach, CA, during the period 0000-0200 hours PDT on August 31, 1982. The relative humidity was 81%. The mass below the upper line indicates the total amount of aerosol (exluding water), with the incremental components of that total as indicated.

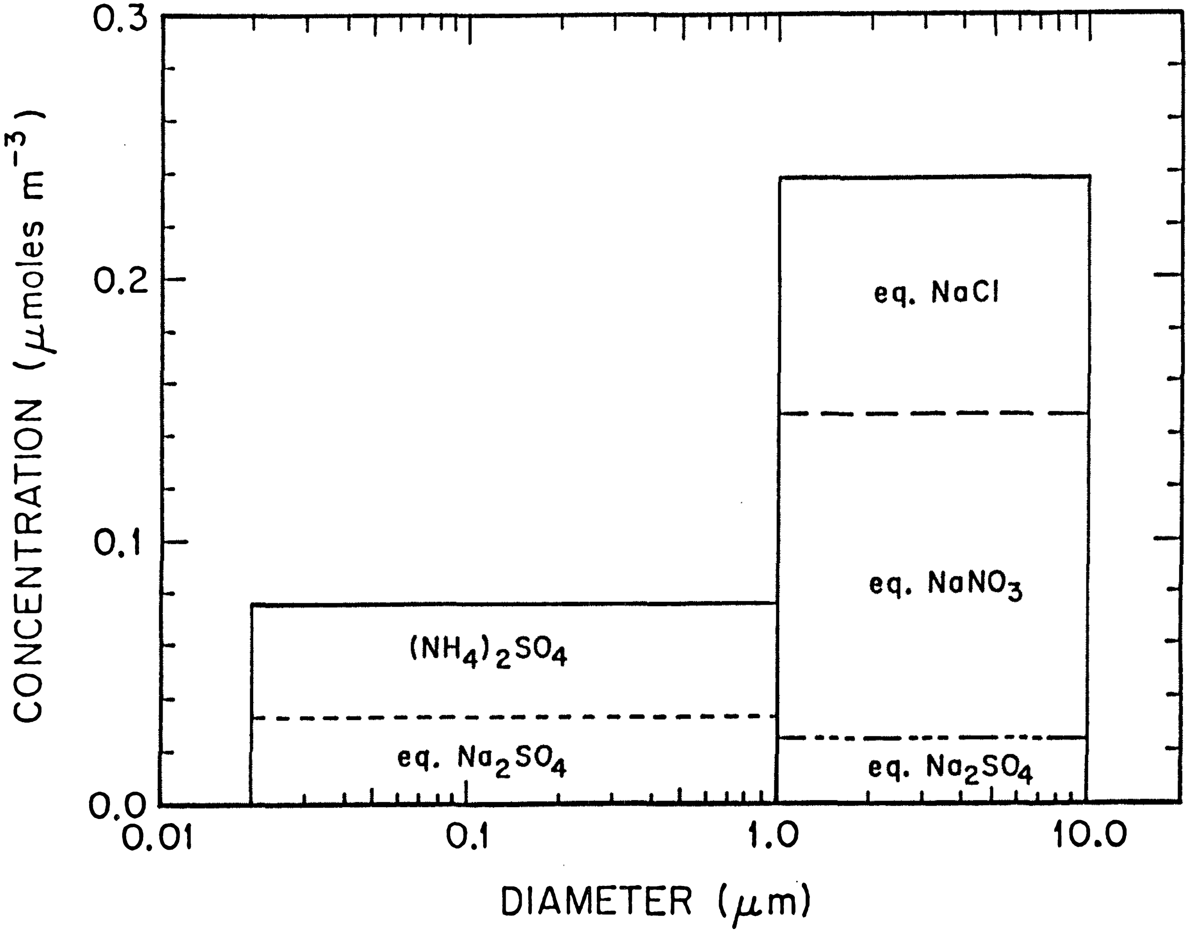

Fig. 13 Predicted size-composition distribution at Long Beach, CA, during the period 1400-1600 hours PDT on August 31, 1982. The relative humidity was 43%. The mass below the upper line indicates the total amount of aerosol, with the incremental components of that total as indicated.

CHAPTER 5

DEVELOPMENT AND EVALUATION OF A EULERIAN PHOTOCHEMICAL GAS-AEROSOL MODEL

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DEVELOPMENT AND EVALUATION OF AN EULERIAN PHOTOCHEMICAL GAS-AEROSOL MODEL

CHRISTODOULOS PILINIS
Environmental Quality Laboratory
California Institute of Technology
Pasadena, CA 91125

and

JOHN H. SEINFELD
Department of Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

ABSTRACT

A three-dimensional Eulerian model that simulates the concentrations of gaseous pollutants and the size-composition distribution of multicomponent atmospheric aerosols has been developed and used to study the evolution of the aerosol-size distribution and composition in the South Coast Air Basin of California. The predictions of the model are compared with ambient measurements of sulfate, nitrate, sodium, chloride and ammonium aerosol.

1. INTRODUCTION

To predict atmospheric aerosol size and composition, it is necessary to account for gas phase processes that lead to aerosol products, transport of gases to the surfaces of particles, formation of new particles by nucleation, shaping of the size distribution by coagulation and equilibration of particles with the local gaseous environment. Aerosols in the polluted urban atmosphere can be considered to consist of a mixture of sulfates, nitrates, water, ammonium, elemental and organic carbon and dust (Figure 1). Primary particles are emitted and advected from their sources by the wind, while gas-phase, photochemical reactions occur, converting NO_x to nitric acid (HNO_3), SO_2 to sulfuric acid (H_2SO_4) and reactive organic gases to low vapor pressure, condensable species. Water vapor is ubiquitous, and ammonia is generally also present in the gas phase. Gas-to-particle conversion of sulfate, nitrate, ammonium and organics may occur as these gas phase reactions proceed, either by homogeneous nucleation or condensation on existing particles.

In previous work (Pilinis et al., 1987) we have shown that non-equilibrium aerosol growth and coagulation, coupled with continuous reestablishment of gas and particulate phase chemical equilibrium, predicts the key features of the evolution of the urban aerosol size-composition distribution. We have also demonstrated the importance of ionic species, especially sodium, in shaping the aerosol size distribution, as well as in determining the nitrate concentration in the particulate phase (Pilinis and Seinfeld, 1987).

In this work we present an Eulerian, three-dimensional urban airshed atmospheric aerosol model that represents a merging of a three-dimensional Eulerian, gas-phase, air-quality model (McRae et al., 1982a) with the aerosol models developed by Pilinis and Seinfeld (1987). We begin with a description of the full Eulerian model, followed by a listing of its input data requirements. We then apply the model to simulate the aerosol evolution in the Los Angeles basin on August 30, 1982, and we conclude with a brief statistical evaluation of the model performance.

2. MODEL DESCRIPTION

The size and composition of particles undergoing nucleation, condensation, coagulation, transport and deposition are governed by the aerosol general dynamic equation (Seinfeld, 1986). The sectional approximation of the aerosol general dynamic equation, in which the continuous size distribution is approximated by a series of step functions, is particularly advantageous for numerical solution of the equation (Warren and Seinfeld, 1985; Pilinis et al., 1987). The evolution of the mass concentration of species i in the l^{th} section, Q_{il}, is described by the following integrated form of the general dynamic equation,

$$\frac{\partial Q_{il}}{\partial t} + \nabla \cdot (\mathbf{u} Q_{il}) = \nabla \cdot (\mathbf{K} \nabla Q_{il}) + \left[\frac{\partial Q_{il}}{\partial t}\right]_{cond./evap.} + \left[\frac{\partial Q_{il}}{\partial t}\right]_{coag.} + \left[\frac{\partial Q_{il}}{\partial t}\right]_{sources/sinks}, \tag{1}$$

where u is the wind velocity at the point of interest, **K** is the atmospheric eddy diffusivity, $\left[\frac{\partial Q_{il}}{\partial t}\right]_{sources/sinks}$ is the rate of change of aerosol mass of species i in section l due to nucleation, primary aerosol injection and removal, while $\left[\frac{\partial Q_{il}}{\partial t}\right]_{cond./evap.}$ and $\left[\frac{\partial Q_{il}}{\partial t}\right]_{coag.}$ are the rates of change due to condensation or evaporation and coagulation, respectively (Gelbard and Seinfeld, 1980; Gelbard et al., 1980; Warren and Seinfeld, 1985; Pilinis et al., 1987).

The evolution of the concentration of the i^{th} gaseous species, C_i is governed by the atmospheric diffusion equation

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (\mathbf{u} C_i) = \nabla \cdot (\mathbf{K} \nabla C_i) + R_i(C_1, C_2, \ldots\ldots, C_n), \tag{2}$$

where R_i is the rate of change of species i via chemical reactions.

2.1 Inorganic Aerosol Constituents

One must account for the rates of transfer of each species between the gas and the aerosol phases. For some species the characteristic time for gas-to-particle transport is sufficiently short that chemical equilibrium is established on a time scale much shorter than that over which other changes are taking place. This situation is, in fact, estimated to be the case for water, nitric acid and ammonia (Hildemann et al., 1984; Wall et al., 1987; Pilinis and Seinfeld, 1987). Therefore, whereas the gas-to-particle conversion of sulfuric acid and condensable organics is controlled by gas-phase diffusion, the distribution of the volatile inorganic species between the gaseous and particulate phases is calculated using thermodynamic equilibrium.

In the sulfate, nitrate, chloride, sodium, ammonium, water system, the following components are possible:

Gas phase: NH_3, HCl, HNO_3, H_2O

Liquid phase: H_2O, NH_4^+, SO_4^{2-}, NO_3^-, H^+,
Na^+, Cl^-, HSO_4^- and H_2SO_4

Solid phase : Na_2SO_4, $NaHSO_4$, NaCl, $NaNO_3$, NH_4Cl,

NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4 and $(NH_4)_3H(SO_4)_2$.

Mixed salts of NH_4NO_3 and $(NH_4)_2SO_4$ are not taken into account, because their inclusion is predicted not to affect significantly the distribution of ammonium and nitrate between the gas and the aerosol phases (Saxena et al., 1986). Which of these inorganic species are present at thermodynamic equilibrium depend on the relative humidity, ambient temperature, as well as on the ratio of the $([NH_3]+[NaCl])/[H_2SO_4]$ (Pilinis and Seinfeld, 1987). Because the inorganic portion of the aerosol has been thoroughly addressed by Pilinis and Seinfeld (1987), it will not be discussed further here.

2.2 Organic Constituents

Organic particulate matter consists of primary and secondary organic compounds. The primary aerosol is the product of combustion processes, while secondary organic aerosol results from condensation of various organic species, the products of gas-phase photooxidation of primary hydrocarbons.

The contribution of the various classes of primary hydrocarbons to the formation of particulate matter depends on their relative ambient concentrations, gas-phase reactivity and ability to form products whose vapor pressure is low enough to produce aerosol.

The oxidation of an atmospheric hydrocarbon HC can be expressed in a general way as (Grosjean, 1977):

$$\mathrm{HC} + \mathrm{X} \longrightarrow \mathrm{I} \longrightarrow \sum_i a_i P_i,$$

where X is the oxidizing species (e.g., OH and O_3), P_i is the i^{th} product resulting from reactions of the intermediate I, whose formation is the rate-determining step, and a_i is the molar yield.

A sufficiently low vapor pressure for aerosol formation is not thought to occur until the hydrocarbon oxidation products have approximately eight carbon atoms. Since straight chain olefins of such length exist in the atmosphere only in trace amounts (Grosjean and Fung, 1984) the role of the straight chain olefins as organic aerosol precursors can be neglected but can be easily added if future work indicates that their aerosol-forming potential is significant.

Cyclic olefins and diolefins have been found to produce aerosol upon photooxidation (Hatakeyama et al., 1985, 1987; Izumi et al., 1987). Among the cycloalkenes, cyclopentene and cyclohexene are of major importance, because they are found in gasoline and auto-exhaust. Studies to characterize the chemical identity of the condensable products of the photooxidation reactions of these two cycloalkenes have reported that dicarboxylic acids, dialdehydes and oxo-carboxylic acids are the major products in the aerosol phase (Hatakeyama et al., 1985, 1987; Izumi et al., 1987). Dialdehydes are the major primary species produced from the cycloalkene-O_3 reactions, but they are subsequently oxidized to produce oxo-carboxylic acids, the further oxidation of which gives the dicarboxylic acids. The latter species have been reported to be the major aerosol products of the cycloalkene-O_3 reactions (Hatakeyma et al., 1985, 1987). As shown in Table 1, glutaric acid and adipic acid, products of the photooxidation of cyclopentene and cyclohexene, respectively, have sufficiently low vapor pressures to form aerosols. Thus, it seems reasonable to assume that these two dicarboxylic acids are the only aerosol products of cyclopentene and cyclohexene and use overall reactions for their production, in the form shown in Table 2.

Product characterization has been attempted by many investigators (O' Brien et al., 1975; Niki et al., 1983) for the reactions of diolefins with O_3. The final products of the diolefin-O_3 reactions are dicarboxylic acids (Schwartz et al., 1974), which explains the observed high aerosol yields. Three diolefins, 1,5-hexadiene, 1,6-heptadiene and 1,7-octadiene, are included in the primary organic inventory of aerosol precursors. The overall reactions of the diolefins are shown in Table 2, and the physical properties of their condensable products are summarized in Table 1.

Another class of organics that gives aerosol products, upon atmospheric photooxidation, is aromatics. Aromatics currently comprise about 35% of the gasoline in the United States and are also used as industrial solvents. Among the various aromatics, toluene and the xylenes are of major importance, because they are present in substantial levels in urban air (Grosjean and Fung, 1984).

In spite of numerous experimental studies, the detailed reaction pathways of aromatic photooxidations are still not well understood (Atkinson et al., 1980; Leone and Seinfeld, 1984; Gery et al., 1985, 1987). Rate constant considerations indicate that aromatics will react predominantly with OH. Three reactions involving aromatic hydrocarbons are included in the current organic aerosol mechanism. Because of similarities in their reaction mechanisms and rate constants, o-,p-,m-xylenes are lumped together. The major products of the toluene-OH and xylene-OH reactions are cresols and dimethyl phenols. The molar yield of the cresol production from the first reaction is estimated to be about 24% of the reacted toluene, while the yield of the latter reaction is estimated to be about 17% of the reacted xylene (Atkinson and Lloyd 1984; Gery et al., 1985, 1987). Once cresols and dimethylphenols are formed, various nitrocresol and nitroxylene products result through addition of radicals (Gery et al., 1985, 1987). It is estimated that the yield of the nitro-cresol formation is about 30% of the cresols and of the phenols reacted.

Physical properties of the various condensable species produced by the aromatic hydrocarbons photooxidation reactions are not generally known. For the purpose of our calculations the diffusion coefficient, molecular weight and solubility of all aromatic aerosol organics were assumed to be those of nitro-cresol, while saturation vapor pressure data for the condensable species were taken from recent smog chamber experiments (Seinfeld et al., 1987) and are listed in Table 1.

2.3 Gas-Phase Chemistry

The chemical mechanism used in this model is that previously employed by Russell et al. (1987). Estimated emission rates of various hydrocarbons in the South Coast Air Basin of California in 1982 are listed in Table 3. Based on these estimated emission rates, cyclopentene, toluene and xylene are assumed to be the only organic aerosol precursors, from the ones discussed previously, present in the South Coast Air Basin. The potential though exists in the model to include the emissions of other organic precursors once their emission rates have been estimated. Because gridded hydrocarbon emissions and ambient concentrations are not generally speciated into the organic compounds needed by chemical mechanisms, splitting factors must be used so that the specific organic species emissions or concentrations can be determined as the product of the species splitting factor and the total emission rate or concentration of organics. Using the estimates of

Table 3 and results of previous work (Gray et al., 1986; Russell et al., 1987) a set of splitting factors for the non-methane organic species involved in the chemical reaction mechanism, including the organic aerosol precursors, has been developed and is listed in Table 4.

2.4 Computational Implementation

The region, for which the air quality is to be simulated, is part of the South Coast Air Basin of California (Figure 2). In the vertical direction the calculation is extended up to 1100 m above ground level. It has been shown in previous work (Russell et al., 1987) that five vertical layers, unequally distributed, provide a good compromise between computing time requirements and acceptable representation of the vertical variation of the predicted concentrations of the various major gas-phase pollutants. Each horizontal layer consists of 681 cells, as shown in Figure 2, with dimensions 5 km×5 km. Hence, 3405 cells are involved in the implementation of the model for this region.

The set of equations (1) and (2) is solved using an operator splitting technique, in order to decouple the horizontal transport, the vertical transport, the gas phase chemistry and the aerosol growth and coagulation (McRae et al., 1982b). The operator scheme used here to calculate the value of the variable vector F_i at time $t + 2h$ is

$$F_i^{(t+2h)} = A_x(h)A_y(h)A_{zc}(2h)A_y(h)A_x(h)F_i^{(t)} \tag{3}$$

for the non-condensable gases, while

$$F_i^{(t+2h)} = A_i(2h)A_{th}(2h)A_d(2h)A_x(h)A_y(h)A_{zc}(2h)A_y(h)A_x(h)F_i^{(t)} \tag{4}$$

for the aerosol species and the condensable gases. A_x, A_y, A_{zc} are the x-transport, y-transport, z-transport and gas-phase chemistry operators, respectively, while A_i, A_{th}, A_d are the operators for the intersectional movement of the aerosol particles, the aerosol thermodynamics and the aerosol dynamics, respectively.

The structure of the entire model is shown in Figure 3. For the advection part of A_x and A_y a linear finite element scheme with Crank-Nicholson time differencing and a noise filter is applied, while a finite difference scheme is used for the diffusion term of these operators (McRae et al., 1982b). In the A_{zc} operator, a simple explicit finite difference scheme is used for the transport, while a predictor-evaluation-corrector method is used for the gas-phase chemistry, which involves 33 gas-phase species (Russell et al., 1987). Thus, with 3405 cells in the modeling region, 112,365 ordinary differential equations have to be solved at each time step, for the gas-phase chemistry.

The aerosol operator A_d deals with the condensation of sulfuric acid and the four condensable organics of Table 1, the generation of new aerosol by homogeneous heteromolecular nucleation of H_2SO_4-H_2O, introduction of primary particles, such as sodium and primary carbon, as well as coagulation and intersectional motion of both volatile and non-volatile species (Pilinis et al., 1987). One ordinary differential equation is required for each species in each section to describe its evolution from the above processes. Thus, for each computational cell of the modeling region [8×(number of aerosol sections) + 5] ordinary differential equations have to be solved. For 3405 cells, with the aerosol assumed to consist of three sections, two fine and one coarse, 98,745 ordinary differential equations result, which are solved with the EPISODE O.D.E. solver routine (Hindmarsh and

Byrne, 1975).

A_{th} represents the equilibrium calculation. For each cell it is necessary to determine the equilibrium concentrations for the HNO_3-NH_3-H_2SO_4-NaCl-HCl-H_2O system, which involves 18 aerosol and three gaseous species. This equilibrium calculation involves $[3405\times(18\times3+3)]$ algebraic equations that have to be solved at each time step (Pilinis and Seinfeld, 1987). Finally, the A_i operator deals with the intersectional migration of the various species due to the condensation of the volatile components (Pilinis et al., 1987). Depending on the thermodynamically possible species predicted in the equilibrium calculation, in which up to 22 species are involved, this part may require the solution of as many as $3405\times3\times22 = 224{,}730$ ordinary differential equations. Output at the end of each time step is the new size-distributed aerosol chemical composition and the concentrations of the gas phase species. All the species predicted by the model are listed in Table 5.

3. INPUT DATA FOR THE MODEL

Input data include the region definition and its topography and surface roughness distribution, three-dimensional wind fields, spatial and temporal temperature and relative humidity profiles, solar radiation and cloud cover, surface and elevated area and point source emissions, as well as initial and boundary gas-phase concentrations and aerosol size-composition distributions. The input data used in this calculation, are listed in Table 6.

Because of the lack of any information about the size distributions of sulfate, sodium and organics throughout the South Coast Air Basin at 0000 PST (Pacific Standard Time) on the simulation day of August 30, 1982, default initial size distributions, based on observations in the Los Angeles area (Wolff and Klimisch, 1982; Wall et al., 1987), are used. From a computational point of view, the aerosol is assumed to consist of three size sections, two fine and one coarse, with ranges 0.05-0.3, 0.3-2.0 and 2.0-10.0 μm. Given these sections, the initial concentrations of HNO_3, NH_3, H_2SO_4, HCl and NaCl, and the initial temperature and relative humidity fields, the size-distributed composition and physical state of the aerosol at 0000 PST are predicted throughout the region of interest by the chemical equilibrium calculation, while the initial aerosol organic concentrations are calculated, using the splitting factors of Table 4.

4. APPLICATION OF THE MODEL TO THE SOUTH COAST AIR BASIN ON AUGUST 30, 1982

The Eulerian gas-aerosol model, using the initial conditions and emission inventories described above, has been applied to the South Coast Air Basin of California from 0000-2400 PST on August 30, 1982, for which 4 h average concentration data for sulfate, nitrate, ammonium, chloride,sodium, calcium and magnesium are available. Whenever Ca and Mg are present, their concentrations were reduced to equivalent Na in order to be included in the equilibrium calculation. About 8 CPU hours on the San Diego Supercomputer Center CRAY X-MP were required for the 24 h simulation.

Figures 4-5 show the predicted concentrations of sulfate, nitrate, ammonium, sodium, and chloride at Long Beach and Rubidoux, California. These figures also show the evolution of the water, total aerosol concentrations, and various organic species over the course of the day.

The predictions are seen to exhibit the same behavior as the observed aerosol species concentrations, generally within the uncertainty of the measurements. The predicted chloride concentrations at Rubidoux are much higher than those observed. This discrepancy could be attributable to our assumption concerning the total chloride concentration. Despite the fact that four-hour averaged aerosol chloride measurements were available, no gaseous HCl measurements were available. In the absence of HCl data it was assumed that the total airborne chloride concentration was equal to that for sodium. This assumption is no doubt more adequate for the coastal sites, where fresh NaCl flows inland, than inland, at locations like Rubidoux, where the total chlorides are overestimated, since the coastal NaCl reacts with H_2SO_4 and HNO_3 to produce more stable compounds than NaCl before it reaches those areas (Harrison and Pio, 1983). Predicted nitrate and ammonium concentrations vary from low values at the coastal sites to high values inland, consistent with the observed behavior.

As shown in Fig. 4(f)-5(f), the total aerosol concentration follows the amount of water in the aerosol phase. Early in the morning, because of high relative humidities, water is predicted to account for about 50% of the total aerosol mass. During the day, increasing temperature and decreasing relative humidity cause water to evaporate, thus reducing the total aerosol concentration, which is predicted to reach a minimum around 1600 PST at most of the sites. Later in the evening, because of increasing relative humidity, a second peak in the water concentration is predicted to cause a rapid increase in the total aerosol concentration. High temperatures during the day also cause the evaporation of the other volatile species, especially chloride, the concentration of which is predicted to reach a minimum between 1200 and 1600 PST.

Figures 6-7 show the predicted size-composition distributions at 0000, 1200 and 2400 PST at Long Beach and Rubidoux. A common characteristic of these size distributions is that early in the morning, when relative humidities $\geq$ 75%, sufficient water is predicted to exist in the aerosol phase to dissolve the ionic species. From 900 PST to 1800 PST the relative humidity falls below the deliquescence point of all the thermodynamically possible salts (Pilinis et al., 1987), resulting in dry particles. Predominant compounds in the aerosol phase during this period are predicted to be Na_2SO_4, $(NH_4)_2SO_4$, $NaNO_3$ and NH_4NO_3. A substantial quantity of nitrate is predicted to be associated with the existence of sodium in the coarse particles, providing an explanation why the median diameter for nitrates is generally observed to be larger than that of the sulfates (Hidy et al., 1975; Harrison and Pio, 1983; Wall et al., 1987).

After 1800 PST the ambient relative humidity again starts increasing, leading to the gradual dissolution of the various ionic species and the growth of the particles. At the end of the day, when the relative humidity is above 80%, most of the aerosol mass is predicted to lie in the coarse section, with water accounting for more than 50% of the aerosol mass, consistent with various observations in Los Angeles (Ho et al., 1974).

5. STATISTICAL EVALUATION OF MODEL PERFORMANCE

A statistical analysis of the deviation between model predictions and observations is a key element of model performance evaluation. Many statistical tests may be used to evaluate the performance of air quality models (Bencala and Seinfeld, 1979; Rao et al., 1985; Ku et al., 1987; Russell et al., 1987).

Table 7 contains a number of performance measures, their defining equations, and their values for the August 30, 1982 simulation. The mean of the residuals is positive for the sulfate and sodium, indicating underprediction, whereas it is negative for nitrates, ammonium and chlorides, indicating overprediction of the model with respect to those species.

We have also computed the correlation coefficient between observations and predictions, as well as the index of the agreement. The correlation coefficient, in general, shows the extent to which the predicted concentrations increase linearly with the observed ones. The index of agreement is a stricter test, because it is sensitive to differences between the measured and predicted means, as well as to changes in proportionality. Both of these statistical criteria show agreement between observations and predictions for all the species, except the chlorides. The performance for chlorides was poor, of the order of 0.2, for both the correlation coefficient and the index of agreement. This discrepancy may be a result of the assumed initial total chloride concentrations inland. This possibility is supported by the fact, that, if the predicted chloride concentrations at Upland and Rubidoux are not included, the correlation coefficient increases from 0.2 to 0.5, while the index of agreement increases from 0.23 to 0.7.

Figure 8 shows the linear-least squares lines for all the ionic species. Perfect agreement would have all points falling on the 45° line. The predicted lines are within 15° of the 45° line. Residual frequency plots (Figure 9) show that the residual differences between the predicted and observed concentrations for all the ionic aerosol species.

The last test performed and listed in Table 7 is the mean-square error, which consists of the systematic and unsystematic parts. These statistical measures can be used to indicate the extent to which a model may be improved (Rao et al., 1985; Ku et al., 1987). The contribution of the M.S.E.u to the mean-square error is seen in the present case to be more important than that of the M.S.E.s, which means that improvements in the model may not be as possible as if systematic errors were present.

6. CONCLUSIONS

An urban multicomponent Eulerian aerosol model has been developed by coupling a model that predicts the size-composition distribution of atmospheric aerosols to a grid-based, gas-phase urban airshed model. Model performance was evaluated by comparison against measured aerosol concentrations on August 30, 1982, in the South Coast Air Basin of California. The model has provided the first three-dimensional predictions of the concentrations and size distribution of inorganic and organic aerosol species over an urban airshed.

The inorganic aerosol phase was predicted to consist of an aqueous solution of various inorganic species during the early hours of the day and late at night, during which the relative humidity was high, and of a solid phase during the rest of the day, when the relative humidity was low. Water is predicted to play an important role in shaping the aerosol size distribution. Besides the fact that water is predicted to account for more than 50% of the aerosol mass at humidities above 80%, its condensation causes the growth of the particles into the coarse particle regime.

Volatile aerosol constituents are predicted to be quite sensitive to temperature changes. Sulfate and nitrate were predicted to be the major inorganic aerosol species, whose hygroscopicity causes the water condensation, while primary organics were the major organic species in the aerosol phase.

ACKNOWLEDGMENTS

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Table 1: Physical properties of condensable organics.

Species	Formula	MW	D (m^{2}sec^{-1})	p_o (Pa)
succinic acid	$HO_2C(CH_2)_2CO_2H$	118	8.22×10^{-6}	3.96×10^{-5}
glutaric acid	$HO_2C(CH_2)_3CO_2H$	132	7.51×10^{-6}	1.80×10^{-5}
adipic acid	$HO_2C(CH_2)_4CO_2H$	146	6.96×10^{-6}	8.19×10^{-6}
nitro-cresol	$NO_2CH_3C_6H_3OH$	153	7.13×10^{-6}	8.00×10^{-6}

Table 2: Organic aerosol-producing reactions.

Reaction	Rate Constant ($ppm^{-1}\ min^{-1}$)	Ref.
$CH_2 = CH - (CH_2)_2 - CH = CH_2 \xrightarrow{O_3} 0.11\ HCOO - (CH_2)_2 - COOH$	8.26×10^{-2}	(a)
$CH_2 = CH - (CH_2)_3 - CH = CH_2 \xrightarrow{O_3} 0.19\ HCOO - (CH_2)_3 - COOH$	5.25×10^{-2}	(a)
$CH_2 = CH - (CH_2)_4 - CH = CH_2 \xrightarrow{O_3} 0.15\ HCOO - (CH_2)_4 - COOH$	3.35×10^{-2}	(a)
cyclopentene $\xrightarrow{O_3}$ 0.39 $HCOO - (CH_2)_3 - COOH$	1.56	(b)
cyclohexene $\xrightarrow{O_3}$ 0.15 $HCOO - (CH_2)_4 - COOH$	0.328	(b)
toluene $\xrightarrow{OH}$ 0.20 cresol	9.10×10^{3}	(c)
xylene $\xrightarrow{OH}$ 0.25 cresoll	2.65×10^{4}	(c)
cresol $\xrightarrow{NO_x}$ 0.30 nitro – cresol	2.20×10^{4}	(c)

(a) Grosjean, *personal communication.*

(b) Grosjean and Friedlander, (1980); Hatakeyama et al., (1987).

(c) Atkinson et al., (1982).

Table 3: Estimated Organic Emission Rates in the South Coast Air Basin of CA[a].

Species	Emissions (tons/day)
Methane	1,202.8
Toluene	105.5
Pentane	89.6
Butane	66.7
Ethane	59.7
Ethylene	55.3
Octane	49.4
Xylene	43.9
Heptane	49.9
Propylene	36.8
Chloroethylene	33.2
Acetylene	32.7
Hexane	31.1
Propane	26.2
Benzene	19.0
1,1,1-Trichloroethane	16.1
Pentene	13.2
N-butyl acetate	13.1
Acetone	12.9
N-Pentadecane	12.4
Cyclohexane	12.4
Methyl-ethyl ketone	11.1
Acetalehyde	10.6
Trimethylbenzene	10.0
Ethylbenzene	8.4
Naphtha	8.0
Cyclopentene	0.4

Table 4: Hydrocarbon Splitting Factors[a].

Species[b]	Urban	Rural	Ocean
HCHO	3.7×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
RCHO	3.3×10^{-3}	2.0×10^{-3}	5.0×10^{-3}
OLE	4.2×10^{-3}	6.0×10^{-4}	1.0×10^{-4}
ALK	6.8×10^{-2}	2.3×10^{-2}	9.6×10^{-3}
C_2H_4	6.1×10^{-3}	4.0×10^{-3}	6.0×10^{-3}
TOLUENE[c]	1.1×10^{-2}	3.3×10^{-3}	1.1×10^{-3}
XYLENE[c]	3.9×10^{-3}	1.2×10^{-3}	3.8×10^{-4}
PRIM. ORG. AER.	7.0×10^{-3}	7.0×10^{-3}	7.0×10^{-3}
CYCLOPENTENE[d]	7.0×10^{-5}	1.0×10^{-5}	1.7×10^{-6}

a) When multiplied by the total organic concentrations, these splitting factors produce the individual species concentrations.

b) These are the organic species in the chemical reaction mechanism of Russell et al. (1987) appended with the primary organic aerosol and the organic aerosol precursors, toluene, xylene and cyclopentene.

(c) Based on Table 3, toluene and xylene emission rates are estimated to be about 63.4% and 22.3% of the total aromatic emissions, respectively. These values, when multiplied by the splitting factors for aromatics used by Russell et al. (1987), give the toluene and xylene splitting factors.

d) These factors have been derived from measurements taken by Grosjean and Fung (1984) of the speciated hydrocarbon composition in Los Angeles and the splitting factors of OLE used by Russell et al. (1987).

Table 5: Variables Predicted by the Model.

GAS PHASE

CO, O_3, NO, NO_2,PAN

HNO_3, NH_3, H_2SO_4, SO_2

Toluene, Xylene, Cyclopentene

Nitrocresol, Cyclohexene, Cresol

C_6H_{10}, C_7H_{12}, C_8H_{14}

$C_4H_6O_4$, $C_5H_8O_4$, $C_6H_{10}O_4$

AEROSOL PHASE

1. Size-Distributed:

H_2O, NH_4^+, SO_4^{2-}, NO_3^- , H^+

Na^+, Cl^-, HSO_4^-, H_2SO_4

Na_2SO_4, $NaHSO_4$, $NaCl$, $NaNO_3$, NH_4Cl

NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4

$(NH_4)_3H(SO_4)_2$

Primary and Secondary Organics

2. Total Concentration:

Sulfate

Nitrate

Chloride

Sodium

Ammonium

Water

Primary and Secondary Organics

3. Total Volatiles

4. Total Aerosol Mass

Table 6: Input data to the model for August 30, 1982.

Parameter	Source of Measured Data	Method of Derivation of Gridded-Data
3D-wind fields	SCAQMD[a], CARB[b], NWS[c]	Interpolation over the 80×30 grid of Fig. 2
Solar radiation	JPL[d], CARB, SCAQMD	
Cloud cover	JPL, CARB, SCAQMD	
Inversion height		Russell et al. (1987)
Emission inventory of gaseous pollutants (except of NH_3)		CARB, SoCAB 1982 forecast emission inventory
NH_3 emission inventory		Cass and Gharib (1984)
Ionic species (Ca and Mg) emissions (in equivalent Na)[e]		2.0×10^{-4} ppm m min^{-1}
RH and T	SCAQMD, CARB, NWS	Interpolation over the 80×30 grid of Fig. 2
Ground-level initial conditions (0000 PST)	SCAQMD for gases Hildemann et al., (1984) for aerosol species	Interpolation over the 80×30 grid of Fig. 2
Upper-level initial conditions		Interpolation between the ground-level initial conditions and background concentrations[f]
Initial concentrations of condensible organics		Set equal to zero.
Boundary conditions		Set to the concentrations of the various gas and aerosol species at the edge of the small region of Fig. 2. They are defined by the values of the interpolated conc. over the 80×30 grid, at the edge of the modeling region.

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a) SCAQMD stands for South Coast Air Quality Management District.

b) CARB stands for California Air Resources Board.

c) NWS stands for National Weather Service.

d) JPL stands for Jet Propulsion Laboratory.

e) Major sources of Ca and Mg on August 30, 1982 were soil dust particles emitted during construction and other anthropogenic activities (Cass, Personal Communication). Due to the lack of any data regarding dust emissions, the value of 2.0×10^{-4} ppm m min^{-1}, based on the maximum average concentration increase observed during that day (Hildemann et al., 1984), is used for these species.

f) Background concentrations of various gases are given by Russell et al. (1987). Background concentrations of organic aerosol precursors are calculated from the corresponding total background hydrocarbon concentrations using the splitting factors of Table 4, while those of sulfate and sodium chloride are set 0.5 ppb.

Table 7: Statistical Evaluation of Model Performance for Various Ionic Aerosol Species

Performance Measure	Definition	Species				
		SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-
Mean Observed (μg m^{-3})	$\mu_o = \frac{1}{n}\sum_{i=1}^{n} O_i$	10.54	8.91	2.11	6.89	1.36
Standard Deviation Observed (μg m^{-3})	$s_o = (\frac{1}{n-1}\sum_{i=1}^{n}(O_i - \mu_o)^2)^{1/2}$	6.10	6.64	1.75	6.63	1.47
Mean Predicted (μg m^{-3})	$\mu_p = \frac{1}{n}\sum_{i=1}^{n} P_i$	8.74	13.36	3.39	6.67	2.61
Standard Deviation Predicted (μg m^{-3})	$s_p = (\frac{1}{n-1}\sum_{i=1}^{n}(P_i - \mu_p)^2)^{1/2}$	5.59	9.54	3.31	4.86	4.79
Mean of Residuals (μg m^{-3})	$\mu_R = \frac{1}{n}\sum_{i=1}^{n}(O_i - P_i)$	1.80	-4.44	-1.28	0.23	-1.25
Slope	$m = \frac{\sum_{i=1}^{n} O_i P_i - \frac{1}{n}\sum_{i=1}^{n} O_i \sum_{i=1}^{n} P_i}{\sum_{i=1}^{n} O_i^2 - \frac{1}{n}(\sum_{i=1}^{n} O_i)^2}$	0.602	0.920	1.226	0.635	0.631
Intercept (μg m^{-3})	$b = \frac{1}{n}(\sum_{i=1}^{n} P_i - m\sum_{i=1}^{n} O_i)$	2.391	5.163	0.809	2.293	1.753
Correlation Coefficient	$\rho = \frac{m s_o}{s_p}$	0.66	0.64	0.65	0.86	0.20
Average Absolute Gross Error (μg m^{-3})	$A = \frac{1}{n}\sum_{i=1}^{n} \mid O_i - P_i \mid$	3.63	5.65	1.90	2.36	2.17
Index of Agreement	$I = 1 - \frac{\sum_{i=1}^{n}(O_i - P_i)^2}{\sum_{i=1}^{n}(\mid P_i - \mu_o\mid + \mid O_i - \mu_o\mid)^2}$	0.79	0.71	0.67	0.90	0.23
R.M.S.E. (μg m^{-3})	$\sigma = (\frac{1}{n}\sum_{i=1}^{n}(O_i - P_i - \mu_R)^2)^{1/2}$	4.82	7.29	2.53	3.40	4.69
M.S.E.u (μg m^{-3})^2	$mse_u = \frac{1}{n}\sum_{i=1}^{n}(mO_i + b - P_i)^2$	17.48	52.89	6.23	5.91	21.74
M.S.E.s (μg m^{-3})^2	$mse_s = \frac{1}{n}\sum_{i=1}^{n}(mO_i + b - O_i)^2$	9.05	20.02	1.81	5.70	1.85
M.S.E.u/M.S.E	%	65.9	72.5	77.5	50.9	92.1
M.S.E.s/M.S.E	%	34.1	27.5	22.5	49.1	7.9

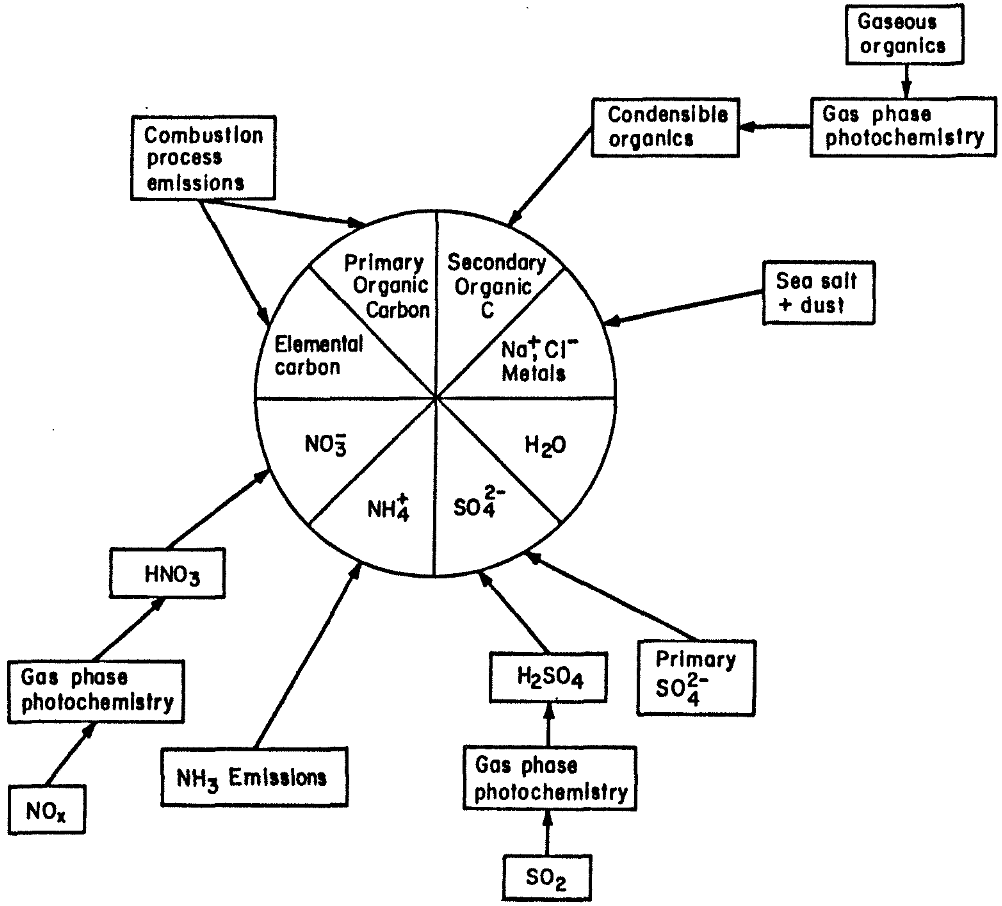

Fig. 1 Idealized schematic of the composition of atmospheric aerosols. The principal sources and particle formation mechanisms are indicated.

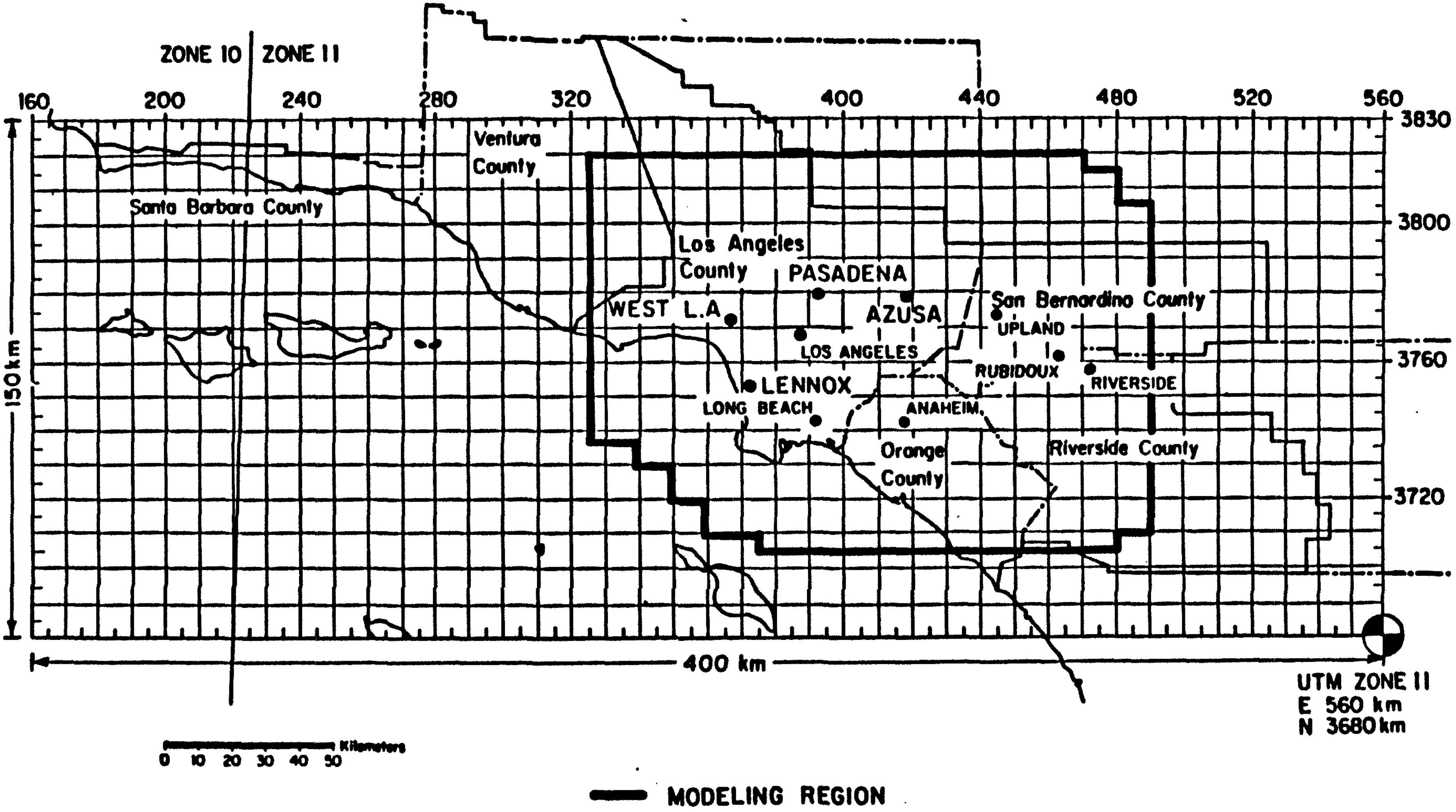

Fig. 2 The South Coast Air Basin of California. Emissions and meteorological data fields are developed over the 400 km×150 km gridded area. Air quality modeling calculations are performed within the region bounded by the heavy solid line.

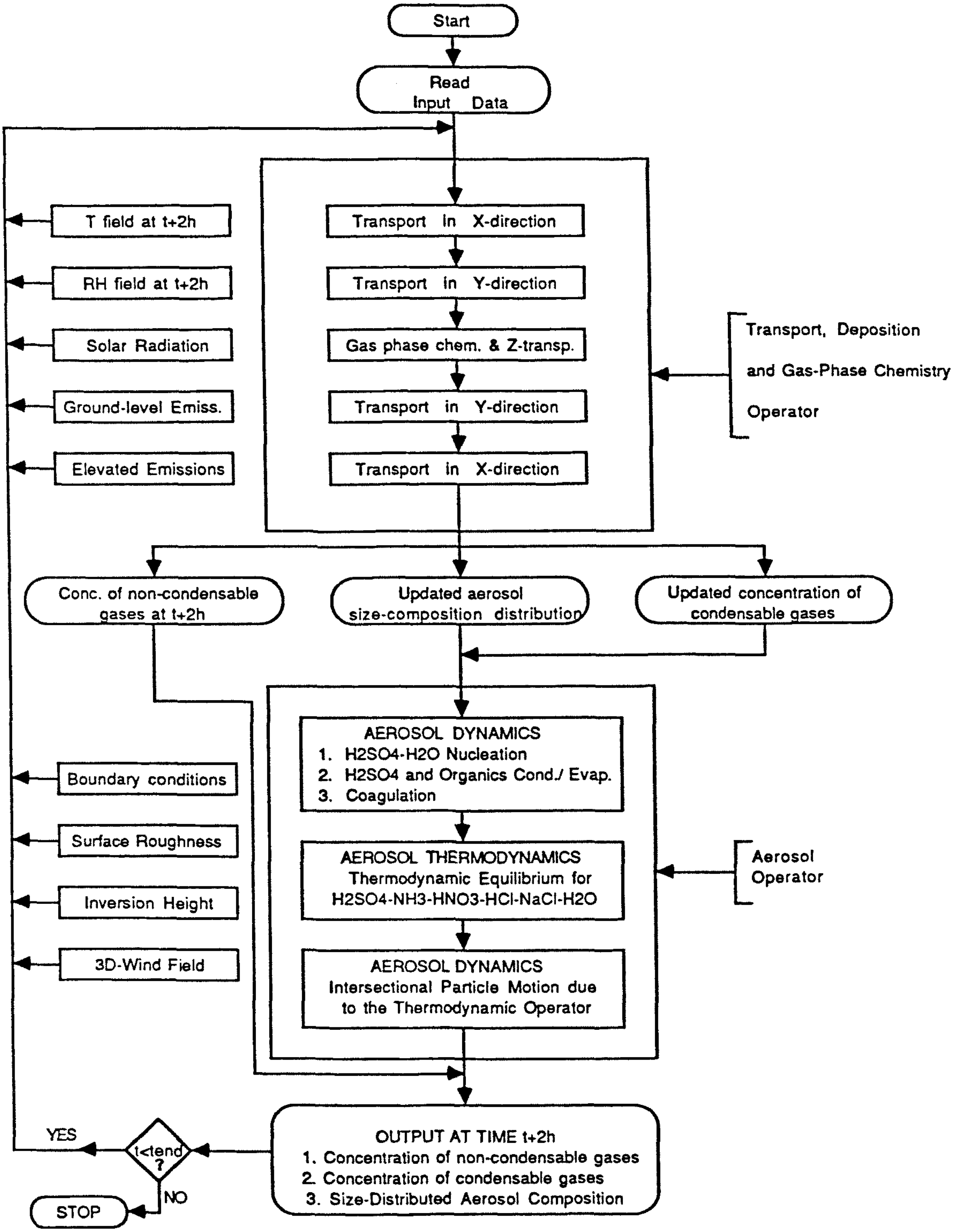

Fig. 3 Schematic representation of the structure of the numerical model.

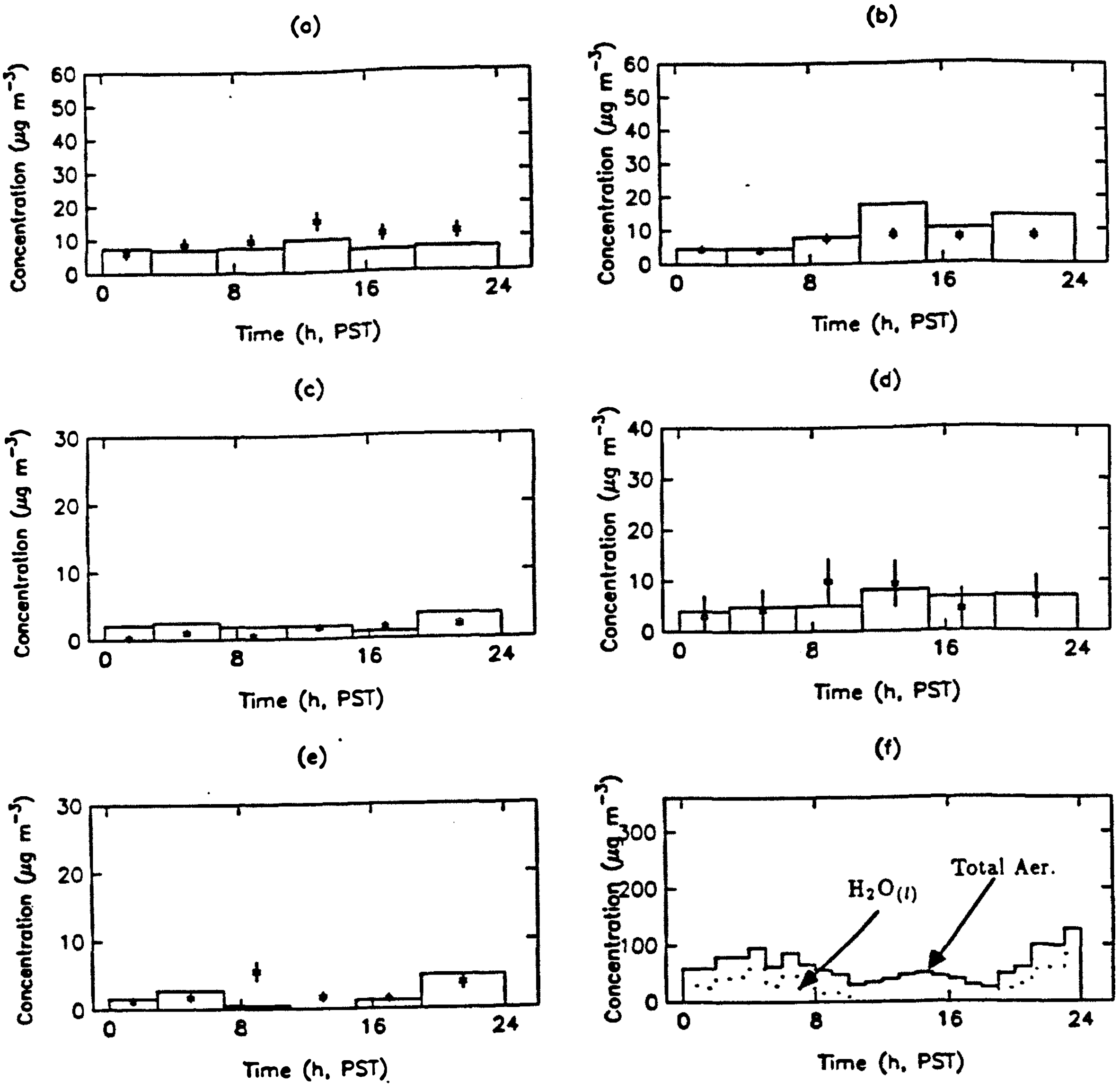

Fig. 4 Predicted and observed concentrations of (a) sulfate, (b) nitrate, (c) ammonium, (d) equivalent sodium and (e) chloride, as well as predicted concentrations of (f) aerosol water and total aerosol at Long Beach, CA on August 30, 1982.

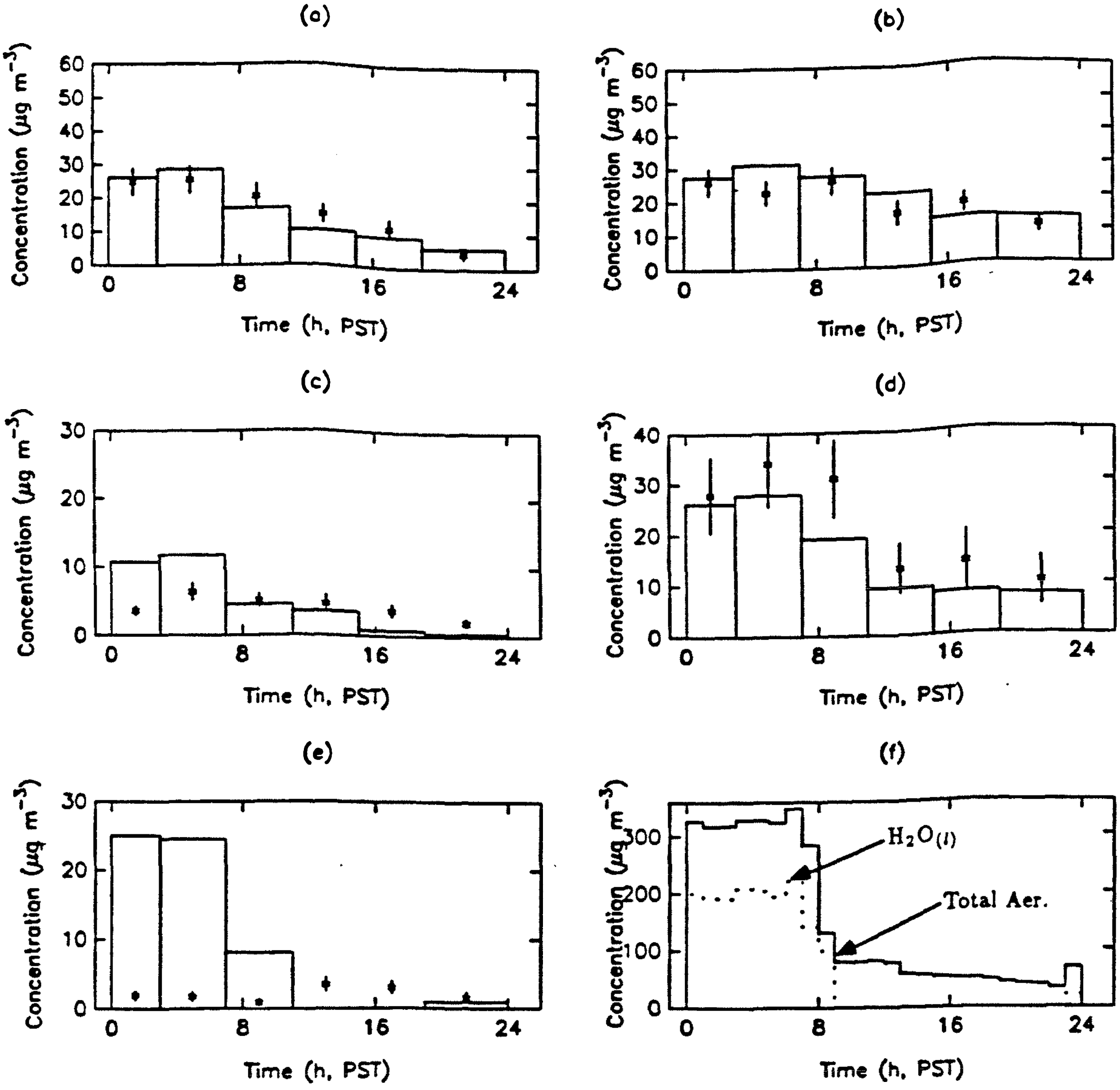

Fig. 5 Predicted and observed concentrations of (a) sulfate, (b) nitrate, (c) ammonium, (d) equivalent sodium and (e) chloride, as well as predicted concentrations of (f) aerosol water and total aerosol at Rubidoux, CA on August 30, 1982.

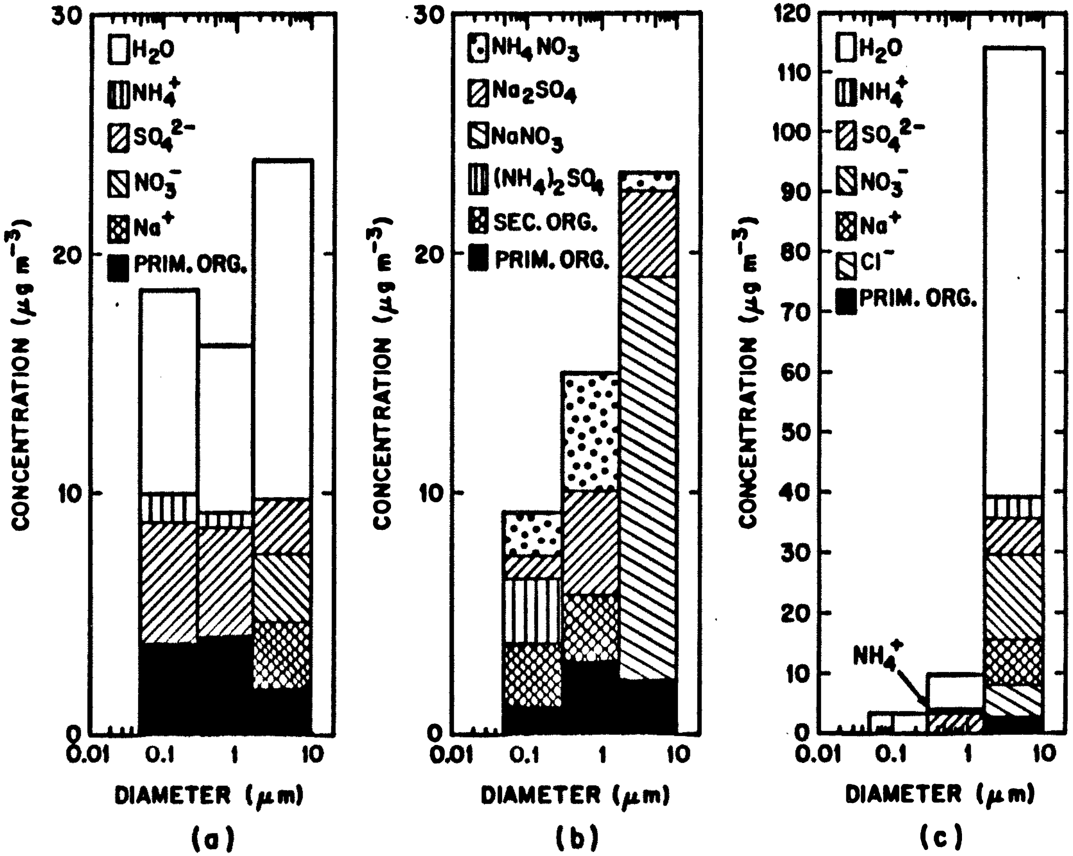

Fig. 6 Predicted aerosol size-composition distribution at Long Beach, CA, at (a) 0000 PST, (b) 1200 PST and (c) 2400 PST on August 30, 1982. The mass below the upper line indicates the total amount of aerosol, with the incremental components of that total indicated.

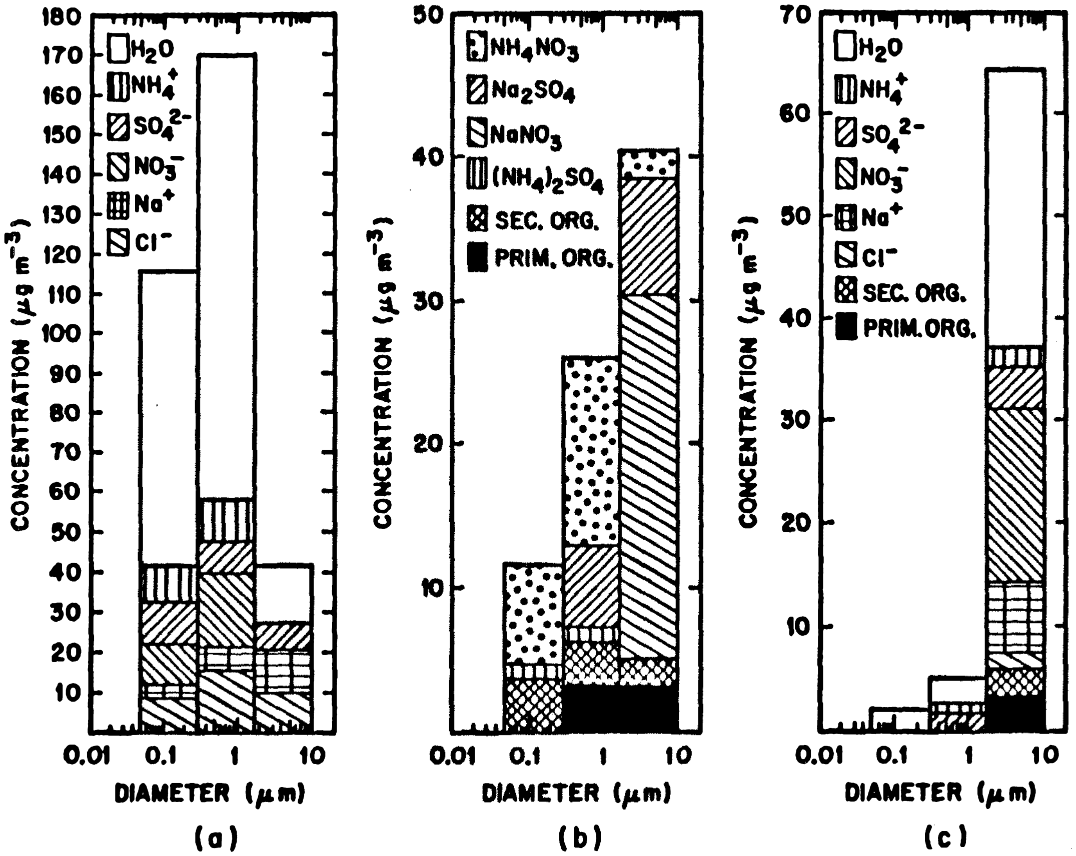

Fig. 7 Predicted size-composition distribution at Rubidoux, CA, at (a) 0000 PST, (b) 1200 PST and (c) 2400 PST on August 30, 1982. The mass below the upper line indicates the total amount of aerosol, with the incremental components of that total indicated.

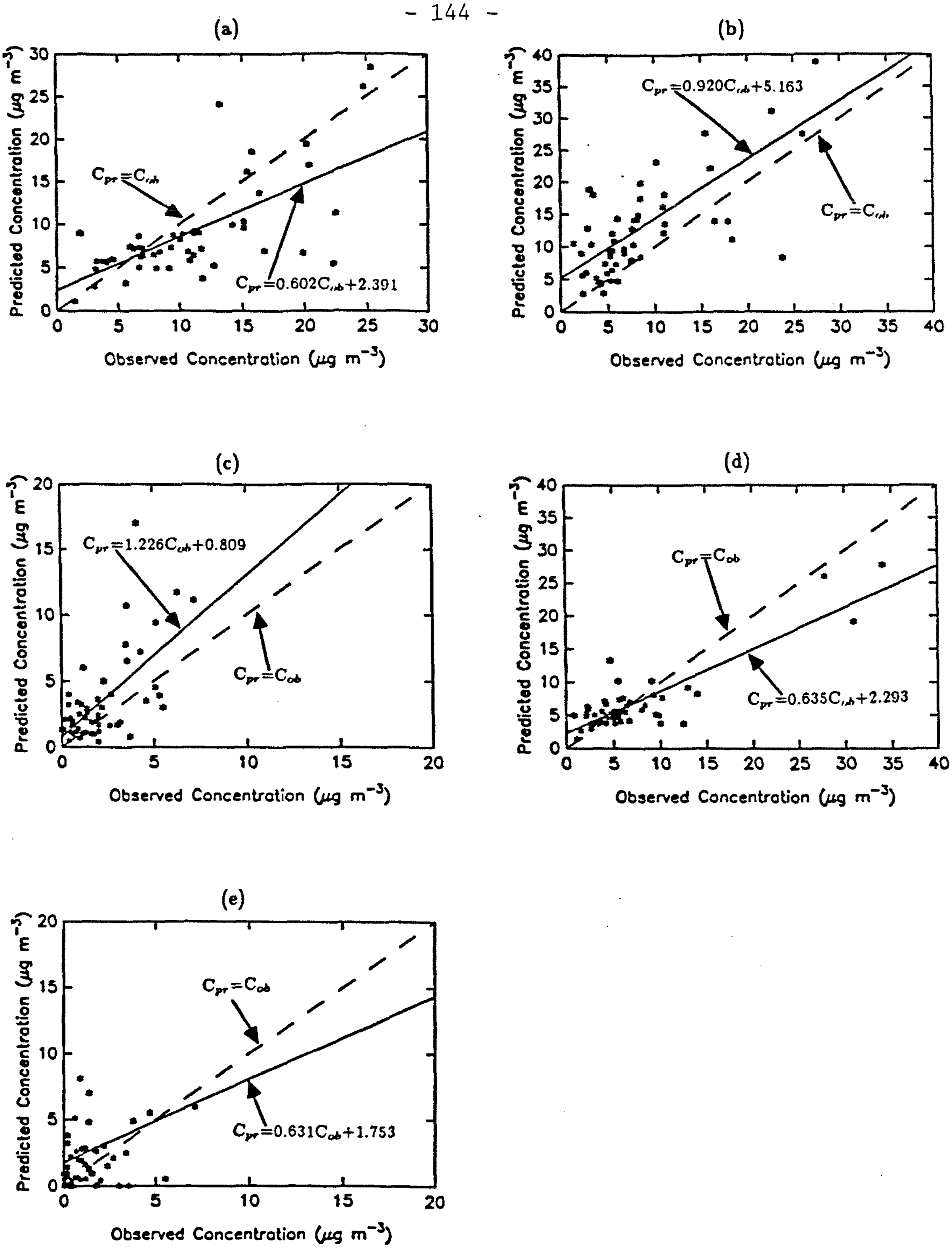

Fig. 8 Linear least-squares lines for predicted and observed concentrations of (a) sulfate, (b) nitrate, (c) ammonium, (d) equivalent sodium and (e) chloride determined over all times and locations of the 24 h application of the model in the SoCAB on August 30, 1982.

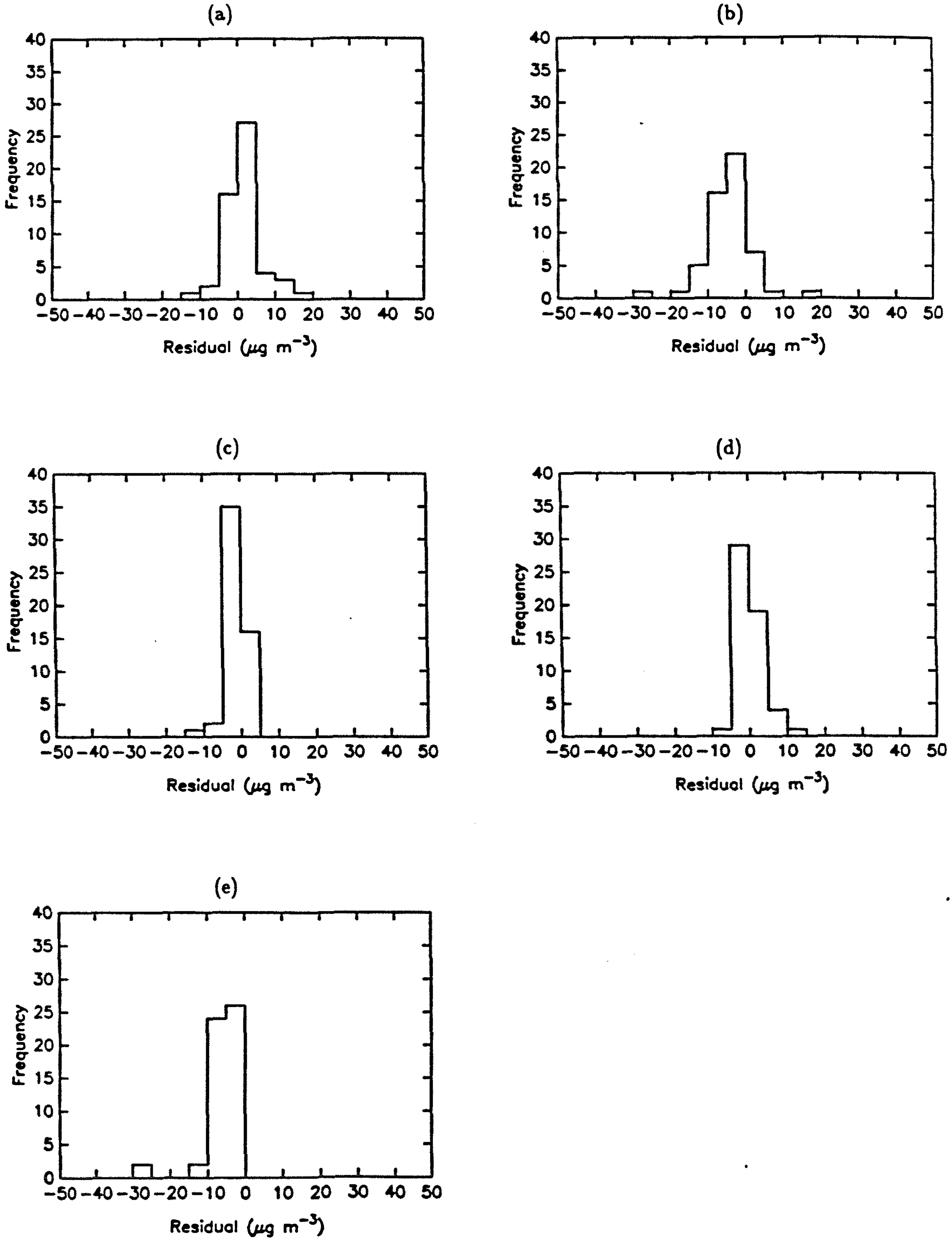

Fig. 9 Histograms of concentration residuals (observed minus predicted) for (a) sulfate, (b) nitrate, (c) ammonium, (d) equivalent sodium and (e) chloride determined over all times and locations of the 24 h application of the model in the SoCAB on August 30, 1982.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The behavior of multicomponent atmospheric aerosols has been studied using mathematical modeling.

At first, a mathematical model that describes the evolution of the size and chemical composition distribution of atmospheric aerosols has been developed. The model, based on a sectional representation of the size distribution, treats dynamics and thermodynamics of multicomponent atmospheric aerosols, including new particle formation by homogeneous heteromolecular nucleation, gas-to-particle conversion, coagulation and dry deposition. Implementation of this model along the trajectory from Anaheim to Rubidoux showed that, using classical nucleation theory, no new particles are generated, because condensation onto preexisting particles is the predominant process for gas-to-particle conversion.

Studying the aerosol behavior with this model it became apparent that ionic species, like NaCl, play an important role in the aerosol composition. Thus, a size-sectionalized thermodynamic equilibrium model for the sodium-sulfate-ammonium-nitrate-chloride-water system has been developed. Given the total quantities of HNO_3, NH_3 and HCl in the gas phase, as well as the distribution of NaCl and H_2SO_4 in the aerosol phase, the chemical composition-distribution and physical state of the aerosol is calculated for given temperature and relative humidity. Using this model, we have shown that the observed tendency of nitrates to be found in larger particles than the sulfates can be explained by the means of thermodynamic equilibrium, via the reactions of HNO_3 with sea salt. It has also been shown how the existence of water in atmospheric aerosols is governed by thermodynamic equilibrium.

By coupling the sectional aerosol model that simulates aerosol dynamics and the model that simulates aerosol thermodynamics to a grid-based, gas-phase, airshed model, an urban multicomponent Eulerian gas-aerosol model has been developed. Model performance was evaluated by comparison against measured aerosol concentrations on August 30, 1982, in the South Coast Air Basin of California. The model has provided the first three-dimensional predictions of the size-composition distribution of inorganic and organic aerosol species over an urban airshed.

Using this model it has been shown that non-equilibrium aerosol growth and coagulation, coupled with continuous reestablishment of gas and particulate phase chemical equilibrium, predict the key features of the evolution of the urban aerosol size-composition distribution. It has also been predicted that water plays an important role in shaping the aerosol size-composition distribution at high relative humidities.

With this work the prospect now exists to calculate the acidic composition of the gas and the aerosol phases and the rates of deposition of both gaseous and particulate acidic species. The models developed in this project are key elements in a comprehensive acid deposition assessment that accounts for both gaseous and particulate acidic species.

APPENDIX

PROGRAM DOCUMENTATION

EXTENDED AIRSHED GAS-AEROSOL MODEL DOCUMENTATION MANUAL

This is a preliminary user's guide for the AIRSHED GAS-AEROSOL package.

TIME REQUIREMENTS

The time required depends strongly on the ambient conditions (especially RH). On average, this program needs about 20 CPU minutes of CRAY-XMP for each hour it simulates.

WARNING

This version of the program is written specifically for a CRAY-XMP computer with the CFT 1.14 compiler. When the program is compiled, using the CFT 1.14 compiler, the compiler option OFF=P must be used. The use of a different computer or a different CFT compiler may require extensive revisions to the code.

PURPOSE

This model solves the atmospheric diffusion equation for 46 gas and aerosol species in order to find their concentrations as a function of time and space. The method used is based on an operator splitting technique. The aerosol size composition distribution is approximated by a number of sections.

SPECIES TREATED BY THE MODEL

01) NO

02) NO_2

03) O_3

04) HCHO

05) RCHO

06) OLEFINES

07) ALKANES

08) AROMATICS

09) C_2H_4

10) CO

11) H_2O_2

12) PAN

13) HNO_2

14) RONO

15) RNO_4

16) HNO_3

17) NH_3

18) NIT (used only to input the initial aerosol ammonium nitrates)

19) N_2O_5

20) NO_3

21) SO_2

22) H_2SO_4 (gas phase sulfuric acid)

23) HCl

24) $C_4H_6O_4$ (gas phase succinic acid)

25) $C_5H_8O_4$ (gas phase glutaric acid)

26) $C_6H_{10}O_4$ (gas phase adipic acid)

27) cC_5H_8 (cyclopentene)

28) cC_6H_{10} (cyclohexene)

29) C_6H_{10} (1,5 hexadiene)

30) C_7H_{12} (1,6 heptadiene)

31) C_8H_{14} (1,7 octadiene)

32) TOL (toluene)

33) XYLN (xylene)

34) CRESOL

35) CRENO2 (gas phase nitro-cresols)

36) AER (total aerosol concentration)

37) AER1 (concentration of volatiles in the aerosol phase)

38) AER2 (aerosol sulfates)

39) AER3 (aerosol sodium)

40) AER4 (aerosol phase succinic acid)

41) AER5 (aerosol phase glutaric acid)

42) AER6 (aerosol phase adipic acid)

43) AER7 (Primary Carbon in the aerosol phase)

44) AER8 (Nitro-cresols in the aerosol phase)

45) NaCl (used only to input the initial NaCl)

46) PRIM (used only to input the initial primary C)

INPUT FILES

unit 01: Surface roughness (gmsurf)

unit 02: Mixing depth field (deptha30)

unit 04: Temperature field (tema30)

unit 05: Region definition field (regdlab)

unit 08: Relative Humidity field (rha30)

unit 09: Point Source field (pntbsa)

unit 11: Initial Conditions (aira30)

unit 12: Area Source file (gridbsa)

unit 13: General Command file (gmcomd)

unit 19: Default Upper concentrations (gmupa30)

unit 21: Upper-level concentrations (agrvrt)

unit 31: Region Definition (rurlab)

unit 50: U, V, W Wind fields (w3da30)

OUTPUT FILES

unit 03: Error Messages (er1)

unit 06: Error Messages (er2)

unit 14: Main gas concentration output file (output)

unit 15: Restart file (Not needed on a Cray, restart)

unit 16: Commands processed (comd1)

unit 17: Average Concentrations (avgas)

unit 30: Average Concentrations (avgas1) unit 71: Aerosol species Concentrations (aerosol)

unit 72: Aerosol Size Composition Distrib. (distrib)

unit 73: Print Messages and CPU time (time)

SUBROUTINES

function ABSMAX(NVALS, ARRAY)

PURPOSE

This program calculates the maximum absolute value of the elements in a string vector. This function is very useful for calculating stability limits for the advection schemes.

CALLED BY: gmamod

CALLS: none

MAIN VARIABLES

NVALS = number of array elements

ARRAY = array of data values

ABSMAX = absolute value of the maximum array element

subroutine ACTIVITY

PURPOSE

This subroutine establishes the activity coefficients of the various species in a multicomponent solution, using Pitzer's and Bromley's methods.

CALLED BY: FCN1, FCN2, FCN4, FCN7, FCN8

CALLED BY: FCN9, FCN11, FCN14, FCN15, FCN16, FCN18

CALLS: ION

MAIN VARIABLES

molal= ion concentrations (in moles m^{-3})

molal(1)= H^+

molal(2)= Na^+

molal(3)= NH_4^+

molal(4)= Cl^-

molal(5)= SO_4^{2-}

molal(6)= HSO_4^-

molal(7)= NO_3^-

molalr= concentrations of the various electrolytes used in the ZSR method (in moles m^{-3})

molalr(1)=NaCl

molalr(2)=Na_2SO_4

molalr(3)=$NaNO_3$

molalr(4)=$(NH_4)_2SO_4$

molalr(5)=NH_4NO_3

molalr(6)=NH_4Cl

molalr(7)=(2H,SO_4)

molalr(8)=(H,HSO_4)

molalr(9)=NH_4HSO_4

molalr(10)=(H,NO_3)

molalr(11)=(H,Cl)

molalr(12)=$NaHSO_4$

molalr(13)=$(NH4)_3H(SO_4)_2$

rmw= molecular weights of the various ions

gama= activity coefficients

z = absolute values of the charges of the various ions

niu = number of ions per molecule of a specific electrolyte

zz = $z_+ \times z_-$

bingam= logarithms of the binary activity coefficients

gama0= logarithms of the binary activity coefficients

f1 = F_1 in Bromley's method

f2 = F_2 in Bromley's method

x(i , j) = X_{ij} in Bromley's method

y(j , i) = Y_{ji} in Bromley's method

ionic = ionic strength

subroutine ADVECT (CN, U, DIFF, FNCTNL, FNCTNR, DX, DT, IMAX)

PURPOSE

This program has been designed to solve the one-dimensional, advection-diffusion equation. The program can be used to solve multidimensional problems by using time-splitting procedures. The numerical method employs a fourth order (space) finite element scheme as part of an implicit procedure to solve the advection part of the problem following an advection step. A non-linear noise filter is used to remove most of the computational noise generated by the scheme. The final step in the program is to calculate the diffusion step with an explicit second-order, finite difference scheme.

CALLED BY: transc

CALLS: none

MAIN VARIABLES

A = vector used in tridiagonal matrix solution

B = vector used in tridiagonal matrix solution

BETA = vector used in tridiagonal matrix solution

C = vector used in tridiagonal matrix solution

D = vector used in tridiagonal matrix solution

CN = vector of C values at time level N+1

CNM1 = vector of C values at current time level

DIFF = vector of diffusion coefficients

DENOM = temporary variable

PROGRAM RESTRICTIONS AND NOTES

1. GRID SPACING IN THIS VERSION IS CONSTANT
2. AT LEAST FOUR(4) GRID POINTS MUST BE USED
3. TRY TO RUN THE SCHEME AT ITS COURANT LIMIT OF 0.5
4. BE VERY CAREFUL OF SITUATIONS IN WHICH THE BOUNDARY CONDITIONS AT EACH END OF THE GRID ARE EQUAL.
5. THE CURRENT MAXIMUM NUMBER OF GRID POINTS IS 50
6. THE ROUTINE DOES NOT PRESERVE SIGN OF THE C FILED BUT THE ERRORS ARE MINIMAL (LESSS THAN 2% IN MOST CASES)

```
subroutine AEROBON (NSPEC,IHNO3,INH3,INIT,ISO4,inacl,ihcl
1      ,ic4h6o4,ic5h8o4,ic6h10o4,icreno2,iprimc,tmpc,rhi,
2      iaer,iaer1,iaer2,iaer3,iaer4,iaer5,iaer6,iaer7,iaer8,
```

```
3     NROWS,NCOLS,NVERT,NIC,ICORD,IRHCP,ITHCP,
4     ITSPP,NRHC,IRHC,THCS,RHCS,BW,BE,BS,BN )
```

PURPOSE

This subroutine establishes the boundary aerosols for the modeling region in the correct string format and allocates the data on the input file in the required form for the reaction mechanism.

CALLED BY: gmamod

CALLS: equilib

MAIN VARIABLES

BW=array containing the concentrations of the west boundary

BE=array containing the concentrations of the east boundary

BN=array containing the concentrations of the north boundary

BS=array containing the concentrations of the south boundary

tw=array containing the temperatures of the west boundary

te=array containing the temperatures of the east boundary

tn=array containing the temperatures of the north boundary

ts=array containing the temperatures of the south boundary

rhw=array containing the RH's of the west boundary

rhe=array containing the RH's of the east boundary

rhn=array containing the RH's of the north boundary

rhs=array containing the RH's of the south boundary

gmolwt= molecular weights of the various aerosol species (ions and salts)

NSPEC = the number of species in the mechanism

NROWS = the number of rows in the modeling region

NCOLS = the number of columns in the modeling region

NVERT = the number of vertical grids

I......= the index of the various species (See SUBROUTINE DOCUMS)

W, W1 arrays containing the total concentrations

of the various components μg m^{-3}

W(1)	NaCl concentration
W(2)	H_2SO_4 concentration
W(3)	NH_3 concentration
W(4)	HNO_3 concentration
W(5)	HCl concentration

nh3= ammmonia concentration at equilibrium

hcl= HCl concentration at equilibrium

hno3= HNO_3 concentration at equilibrium

subroutine AEROMAIN (w,temp,rh,kk,begin)

PURPOSE

This subroutine is the main driver for the equilibrium calculation. Given the initial sulfate and sodium-size distribution, as well as the gas phase NH_3, HCl and HNO_3 concentrations and the ambient temperature and relative humidity the size-composition distribution of the aerosol at equilibrium is calculated.

CALLED BY: aerosol, rodos

CALLS: equilib, c05nbf

MAIN VARIABLES

W, W1 arrays containing the total concentrations

of the various components μg m^{-3}

W(1)	NaCl concentration
W(2)	H_2SO_4 concentration
W(3)	NH_3 concentration
W(4)	HNO_3 concentration
W(5)	HCl concentration

equl(l,i,kk)=concentration of the lth aerosol species of the ith section in the kkth grid

in μg m^{-3}

begin = logical variable.

(if begin is .false. then the solution of the previous cell is

used as an initial guess in the equilibrium calculation)

initial= variable used for relative humidities above 50%

(if rh > 50%, a good initial guess is required because otherwise

the program is slow. This guess is found for rh < 50% and then

the iteration with the real relative humidity is performed)

temp = temperature (K)

rh = relative humidity

nsec = number of sections

nz = number of vertical cells

n = number of equations to be solved by c05nbf

lwa = dimension of the working array needed by c05nbf

wa = working array needed by the non-linear equation solver c05nbf

ff = array containing the values of the functions whose zeros we want to find

xtol = accuracy we require for the solution

ifail= error criteria (on input always 1. If ifail not 1 or 0 on output no convergence)

x = the values of the independent variables

subroutine AEROM1 (w,temp,rh,kk)

PURPOSE

This subroutine is used to find an approximate solution of the equilibrium problem. It is used for the upper layers ($nz \geq 3$) where the exact size composition distribution is not needed. The subroutine is used to save CPU time. Sensitivity analysis has shown that the accuracy of its results is satisfactory.

CALLED BY: aerosol, rodos

CALLS: equilib

MAIN VARIABLES

See subroutine AEROMAIN

subroutine AEROSOL (NSPEC,IHNO3,INH3,INIT,ISO4,inacl,ihcl
1 ,ic4h6o4,ic5h8o4,ic6h10o4,icreno2,iprimc,tmpc,rhi,
2 iaer,iaer1,iaer2,iaer3,iaer4,iaer5,iaer6,iaer7,iaer8,
3 lenlay,lenavg)

PURPOSE

To find the initial aerosol size composition distribution, based on the thermodynamic equilibrium between the gas and the aerosol phase.

CALLED BY: gmamod

CALLS: aeromain,aeroml,calsiz

MAIN VARIABLES

NSPEC = the number of species in the mechanism

I......= the index of the various species (See SUBROUTINE DOCUMS)

lenlay= number of grids in each layer

lenavg= lenlay× NSPEC

ms, ns, nsec=number of aerosol sections

gmolwt= molecular weights of the various aerosol species (ions and salts)

conmw = molecular weights of the main aerosol species (ie AER1....AER8)

begin = logical variable.

(if begin is .false. then the solution of the previous cell is

used as an initial guess in the equilibrium calculation)

aernh3(i)= total ammonium in the aerosol phase in the i^{th} grid.

aerno3(i)= total nitrate in the aerosol phase in the i^{th} grid.

aercl(i) = total chloride in the aerosol phase in the i^{th} grid.

aerh2o(i)= total water in the aerosol phase in the i^{th} grid.

RAT the relative amount of non-volatiles in each section

1 = NaCl

2 = H_2SO_4

3 = ORGANICS

RH.... the relative humidity for the various cases

t the grid temperature (K)

W, W1 arrays containing the total concentrations

of the various components μg m^{-3}

W(1)	NaCl concentration
W(2)	H_2SO_4 concentration
W(3)	NH_3 concentration
W(4)	HNO_3 concentration
W(5)	HCl concentration

equl(l,i,kk)=concentration of the lth aerosol species of the ith section in the kkth grid

in μg m^{-3}

equl(1,i,kk)= NH_4NO_3

equl(2,i,kk)= $NaHSO_4$

equl(3,i,kk)= NH_4HSO_4

equl(4,i,kk)= clc

equl(5,i,kk)= Na_2SO_4

equl(6,i,kk)= $NaNO_3$

equl(7,i,kk)= NaCl

equl(8,i,kk)= $(NH_4)_2SO_4$

equl(9,i,kk)= NH_4Cl

equl(10,i,kk)= $H_2O_{(l)}$

equl(11,i,kk)= NH_4^+

equl(12,i,kk)= H_2SO_4

equul(13,i,kk)= HSO_4^-

equl(14,i,kk)= SO_4^{2-}

equl(15,i,kk)= NO_3^-

equl(16,i,kk)= Na^+

equl(17,i,kk)= Cl^-

equl(21,i,kk)= $C_4H_6O_4$

equl(22,i,kk)= $C_5H_8O_4$

equl(23,i,kk)= $C_6H_{10}O_4$

equl(24,i,kk)= PRIMARY C

equl(25,i,kk)= nitro-cresols

Concentration of the various inorganic condensable gases in the kk^{th} grid

equl(18,nsec,kk)=NH_3

equl(19,nsec,kk)=HNO_3

equl(20,nsec,kk)=HCl

subroutine ALOCEM(DTMIN,H,NSPEC,C,NE,IEM,EMISS)

PURPOSE

This program has been designed to allocate area source emissions to copmutational cells. The program accepts emissions in flux units, i.e., ppm m min^{-1} and converts them to concentration additions in the appropriate grid cells.

CALLED BY: poinal

MAIN VARIABLES

DTMIN = computational time step (min)

H = height of the computational cell (m)

NSPEC = number of species in chemical mechanism

C = species concentration at time T on output at T+DT

NE = number of emission species

IEM = index array for the emission species in C

EMISS = array of emissions (ppm m min^{-1})

subroutine ALOCIC(NSPEC,C,NIC,CI,ICIND,IRHC,ITHC,ITSP,NHYCAR,

1 IHYS,THCS,RHCS)

PURPOSE

This subroutine has been designed to allocate the initial conditions for the concentration array, given measured or interpolated grid values. In addition, the program will take total or reactive hydrocarbon values and allocate them to the correct positions in the species array corresponding to the chemical split used in the reaction mechanism.

CALLED BY: bond

CALLS: none

MAIN VARIABLES

NSPEC = number of species in the mechanism

C = species array

NIC = number of initial conditions

CI = array containing initial conditions

ICIND = initial condition index array (i.e., where CI is in C)

IRHC = position in CI of reactive hydrocarbons (-1 for no RHC)

ITHC = position in CI of total hydrocarbons (-1 for no THC)

ITSP = position in CI of total suspended particulates

NHYCAR = number of reactive hydrocarbons in chemical mechanism

IHYS = index array for the reactive hydrocarbons

THCS = total hydrocarbon splits

RHCS = reactive hydrocarbon splits

subroutine ALOCICR(NSPEC,C,NIC,CI,ICIND,IRHC,ITHC,ITSP,NHYCAR,
1 IHYS,THCS,RHCS,IRL)

PURPOSE

This subroutine has been designed to allocate the initial conditions for the concentration array, given measured or interpolated grid values. In addition, the program will take total or reactive hydrocarbon values and allocate them to the correct positions in the species array corresponding to the chemical split used in the reaction mechanism. Besides what subroutine ALOCIC performs, this subroutine examines whether a specific cell is over urban areas or over the ocean and uses different splitting factors for different cases.

CALLED BY: icfldr

CALLS: ruralsp

MAIN VARIABLES

NSPEC = number of species in the mechanism

C = species array

NIC = number of initial conditions

CI = array containing initial conditions

ICIND = initial condition index array (i.e. where CI is in C)

IRHC = position in CI of reactive hydrocarbons (-1 for no RHC)

ITHC = position in CI of total hydrocarbons (-1 for no THC)

ITSP = position in CI of total suspended particulates

NHYCAR = number of reactive hydrocarbons in chemical mechanism

IHYS = index array for the reactive hydrocarbons

THCS = total hydrocarbon splits

THC2 = total hydrocarbon splits for rural or ocean areas

RHCS = reactive hydrocarbon splits

IRL = 2 for rural, = 3 for ocean areas

function AMEAN(NVALS,ARRAY)

PURPOSE

This program has been designed to calculate the mean value of a scalar string containing NVALS.

CALLED BY: astdv

CALLS: none

MAIN VARIABLES

NVALS = number of array elements

ARRAY = array of data values

AMEAN = mean value of the scalar string

subroutine APREP(NEMAX,TEMP,KHOUR,IEMS,NT,
1 NROWS,NCOLS,NCELLS,KAMAX,
2 NXSQR,NYSQR,ILEFT,IRIGHT,IMIN,JMIN)

PURPOSE

This program processes area emissions and creates input arrays used by the airshed aerosol model. The data must have hours in sequential order 0 to 2300.

CALLED BY: gmamod

CALLS: strip

MAIN VARIABLES

NEMAX = maximum number of emission species

TEMP = array to hold the emission string vector

KHOUR = hour for the required emissions

IEMS = file number of emission file

NT = length of the string vector

NROWS = number of rows in computational region

NCOLS = number of columns in computational region

NCELLS= number of vertical cells

NXSQR = number of x-cells in master grid

NYSQR = number of y-cells in master grid

ILEFT = left-hand x-indices of each row in computational grid

IRIGHT= right-hand x-indices of each row in computational grid

IMIN = minimum I index for the computational region

JMIN = minimum J index for the computational region

EMTOT = total emissions for this hour

ITYPE = 1 x-dimension loaded first

ITYPE = 2 y-dimension loaded first

ITYPE = 3 z-dimension loaded first

function ASTDV(NVALS,ARRAY)

PURPOSE

This program has been designed to calculate the standard deviation of a scalar string containing NVALS.

MAIN VARIABLES

NVALS = number of array elements

ARRAY = array of data values

ASTDV = standard deviation of scalar string

subroutine BACKGN(NIC,CINAM,BCKGRN,IREAD,IPRN,MODHT)

PURPOSE

This subroutine reads in the background concentrations of the different species. First, it reads in the species name and background concentration. Then it compares it to the species name list to find the correct point in the background array.

CALLED BY: gmamod, dprep

CALLS: none

MAIN VARIABLES

NIC = number of input species

CINAM = array of species names

BCKGRN = array of background concentrations

IREAD = input unit number

IPRN = output unit number

function BETA(Y,X,TGAS,PGAS,NBTYPE)

PURPOSE

To calculate the coagulation coefficient. In addition to simple Brownian motion, gravity and turbulence are included mechanisms, with additivity assumed.

CALLED BY: betcal, gaus3, checke

CALLS: rhodd, setgas

MAIN VARIABLES

Y = Log Mass of first particle

X = Log Mass of second particle

TGAS = Gas Temperature [K]

PGAS = Gas Pressure, Total [Pa]

NBTYPE = Type of Coefficient Needed

DENAIR = Background Gas Density [kg m^{-3}]

FREEMP = Background Gas Mean Free Path [m]

VISCOS = Background Gas Viscosity

BETA = Coagulation Coefficient

V,U = Particle Masses (of X and Y) [kg]

DX,DY = Particle Diameters (of X and Y) [m]

function BETCAL(X,RELER,ABSER,ROUND,IPRNT,FIXSZ,BASESZ,INNER,
1 TGAS,PGAS,NBTYPE)

PURPOSE

To calculate the inner integral of the sectional coagulation coefficients.

CALLED BY: gausbt

CALLS: beta, gaus3

MAIN VARIABLES

X = Outer Integral Size Value [log10(mass)]

RELER = Relative Error Tolerance for Sectional Integral

ABSER = Absolute Error Tolerance for Sectional Integral

ROUND = Unit Round-Off Error (largest X that 1.+X=1.)

IPRNT = Logical Unit Number for Output Device or File

FIXSZ = Size Limit for Inner Integral

BASESZ = Size Limit for Inner Integral

INNER = Flag (0,1,2) for Type of Sectional Coefficient:

Inner Integral Has Following Range (where z=exp(x)):

INNER=0 : BASESZ to FIXSZ

INNER=1 : log(BASESZ-z) to FIXSZ

INNER=2 : FIXSZ to log(BASESZ-z)

TGAS = Gas Temperature [K]

PGAS = Gas Pressure [Pa]

NBTYPE = Type of Sectional Coefficient

BETCAL = Inner Integral

subroutine BINUCL(rh,t,p2,j,x,n1,n2,r,dG)

PURPOSE

This subroutine calculates the rate of the homogeneous bimolecular nucleation of H_2O-H_2SO_4.

CALLED BY: diffun

CALLS : mole, numer

MAIN VARIABLES

rh = relative humidity

t = temperature (K)

p1= partial vapor pressure of water

p2= partial vapor pressure of sulfuric acid

na= number concentration of water molecules

nb= number concentration of H_2SO_4 molecules

j = rate of new particle formation

gamma = surface tension

r = cluster radius

x = cluster mole fraction

subroutine BISECT(aa1,aa2,root,rmax)

PURPOSE

To find the root of a function of the form

$f(x)=x^2+aa1\ x+aa2$

in the [0, rmax] domain using bisection

CALLED BY: equilib

```
subroutine BOND( NSPEC,NROWS,NCOLS,NVERT,NIC,ICORD,IRHCP,
1 ITHCP,ITSPP,NRHC,IRHC,THCS,RHCS,CW,BW,CE,BE,CS,BS,CN,BN )
```

PURPOSE

This program establishes the boundary conditions for the modeling region in the correct string format and allocates the data on the input file in the required form for the reaction mechanism. This feature saves recoding of input programs for different inventories or air quality data formats.

CALLED BY: gmamod

CALLS: alocic, setpan

MAIN VARIABLES

NSPEC = number of species in reaction mechanism

NROWS = number of computational rows

NCOLS = number of computational columns

NVERT = number of vertical layers used in calculation

NIC = number of initial condition species

ICORD = location of initial conditions in species order

IRHCP = location of total reactive hydrocarbons in I.C. array

ITHCP = location of total hydrocarbon in I.C. array

ITSPP = location of total suspended particulates in I.C. array

NRHC = number of reactive hydrocarbons in reaction mechanism

IRHC = location of hydrocarbons in list of mechanism species

THCS = split factors for total hydrocarbons

RHCS = split factors for reactive hydrocarbons

CW, CE, CS, CN = B. C.'s read from files

BW, BE, BS, BN = B.C.'s used for the reaction mechanism species

subroutine BOUND(CONC,DEPTH,CELLHT,HTMOD,BN,BS,BE,BW,ILEFT,
1 IRIGHT,JMIN,IMIN,JBOT,JTOP,CINAME,BKGRND,NOSPEC,NX,NY,NZ,
2 NUMX,NUMY,NB1,NB2)

PURPOSE

Extract subgrid boundary values from full concentration grid and write to BN, BS, BE, BW. This subroutine works as follows:

For those species for which elevated B. C.'s are NOT given from files, linear interpolation between the ground-level and the background concentrations is performed for the cells above the mixing layer, while ground-level, boundary conditions are used below the inversion. If no ground-level, boundary conditions are given, the closest region cell concentration is used as ground level boundary condition.

CALLED BY: dprep

CALLS: none

MAIN VARIABLES

IMIN = minimum I index for the computational region

NOSPEC = number of species in reaction mechanism

NUMX = number of computational rows

NUMY = number of computational columns

NZ = number of vertical layers used in calculation

BW, BE, BS, BN = B.C.'s used for the reaction mechanism species

BKGRND = array of background concentrations

CINAME = array containing species names

DIR = array containing directions

ILEFT = left-hand x-indices of each row in computational grid

IRIGHT= right-hand x-indices of each row in computational grid

JBOT = array containing the global y-coordinate of the bottom cell of each column

JTOP = array containing the global y-coordinate of the top cell of each column

CB = array containing the vertical profile of B.C.'s read from files (dflt = -1)

NB1 = 4800

NB2 = 1800

subroutine BTEMRH(NSPEC,NROWS,ILEFT,IRIGHT,NCOLS,IBOT,ITOP,
1 ngx,ngy,LENLAY,ILX,ILY)

PURPOSE

To find the temperature and relative humidity values at the four boundaries

CALLED BY: gmamod

CALLS: none

MAIN VARIABLES

NSPEC = the number of species in the mechanism

NROWS = the number of rows in the modeling region

ILEFT = array containing the global x-coordinate of the first cell of each row

IRIGHT = array containing the global x-coordinate of the last cell of each row

NCOLS = number of columns

IBOT = array containing the global y-coordinate of the bottom cell of each column

ITOP = array containing the global y-coordinate of the top cell of each column

lenlay= number of grids in each layer

ilx = The global x-coordinate of the far left cell of the modeling region

ily = The global y-coordinate of the far bottom cell of the modeling region

tempc = array containing the temperatures (C)

relh = array containing the relative humidities

tw=array containing the temperatures of the west boundary

te=array containing the temperatures of the east boundary

tn=array containing the temperatures of the north boundary

ts=array containing the temperatures of the south boundary

rhw=array containing the RH's of the west boundary

rhe=array containing the RH's of the east boundary

rhn=array containing the RH's of the north boundary

rhs=array containing the RH's of the south boundary

subroutine CALSIZ(DPMIN,DPMAX)

PURPOSE

To Calculate Sectional Size Boundaries. It generates Geometrically Evenly Spaces Sections, so DEL is constant. This is a convenient situation, but not necessary.

CALLED BY: aerosol

CALLS: rhodd

MAIN VARIABLES

DPMIN = Smallest Sectional Particle Diameter [m]

DPMAX = Largest Sectional Particle Diameter [m]

MS = Number of Size Sections

DS(MMAX1) = Sectional Particle Diameter [m]

VS(MMAX1) = Sectional Particle Mass [kg]

XS(MMAX1) = Sectional Log (Particle Mass)

DEL(MMAX) = Sectional Range in log(mass): XS(I-1)-XS(I)

function CELLVG(VG,USTAR,DZ,ZR,RMOL)

PURPOSE

This program has been designed to calculate the cell average deposition velocity, given the value of VG at some reference height ZR which is much smaller than the cell height DZ.

CALLED BY: depvel

CALLS : none

MAIN VARIABLES

VG = deposition velocity at the reference height

USTAR = friction velocity

RMOL = reciprocal of the MONIN-OBUKHOV length

ZR = reference height

DZ = cell height

CELLVG = cell average deposition velocity

VK = Von Karman constant

subroutine CHMSET(A1,A2,A3,A4,A5,A6,B1,B2,B3,B1M)

PURPOSE

This subroutine sets the default values for the stoichiometric coefficients

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

A1, A2, A3, A4, A5, A6 = stoichiometric coefficients for the reaction

$$OLE + O_3 \rightarrow (A1)RCHO + (A2)HCHO + (A3)HO_2 + (A4)RO_2 + (A5)OH + (A6)RO$$

B1M, B1, B2, B3 = stoichiometric coefficients for the reaction

$$RO \longrightarrow (B1M)RO_2 + (B1)HO_2 + (B2)HCHO + (B3)RCHO$$

```
subroutine CHMSOL2(NSPEC,NEQNT,CNT,TIN,DTMIN,EPS,IERROR,
1 MF,INDEX)
```

PURPOSE

This is the buffer subroutine to interact with the subroutines that are used by the trajectory model. It sets up the common blocks and calls INTEGR2 to integrate the system of N equations, where N is the number of species times the number of cells. (Up to 10 vertical cells and up to 50 species.)

CALLED BY: gmamod

CALLS : integr2

MAIN VARIABLES

neqnt = number of equations

tinn = initial time

toutt= output time

cnt = concentration string for the trajectory model

vg = deposition velocity

emt = area emissions

akzzt= eddy diffusion coefficients

subroutine COEF(NEWCOF,TGAS,PGAS,IPRNT)

PURPOSE

To Calculate the Sectional Aerosol Coefficients

CALLED BY: maeros

CALLS : gausbt, gaus2, gaus3, setgas, growth, betcal, depost

MAIN VARIABLES

NEWCOF= Flag Tells Which Coefficients are Needed: (See MAEROS for description)

TGAS = Gas Temperature [K]

PGAS = Gas Pressure [Pa]

IPRNT = Logical Unit Number for Output

MS = Number of Size Sections

VS = Particle Mass Array [kg]

XS = Log of Particle Mass Array

DEL = Array containing XS range of section

COEFAV= Array containing the various coefficients

subroutine CONCN (NC,CNAME,ITHC,IRHC,ITSP)

PURPOSE

This program returns the names and order of chemical species stored on the initial and boundary condition files. Special provision for THC, RHC and TSP has been included to account for the fact that they may not be explicitly treated in the chemical mechanism but are nevertheless needed.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

NC = number of species

CNAME= species names

ITHC = index for total hydrocarbons

IRHC = index for reactive hydrocarbons

ITSP = index for total suspended particulates

subroutine CONCPR(IPRIN,IOPT,TOUT,NSPEC,SNAM,C)

PURPOSE

This subroutine prints the species concentrations corresponding to a particular output time TOUT.

CALLED BY: limprt

CALLS : times

MAIN VARIABLES

IPRIN = logical unit number of the line printer

IOPT = option to skip to a new page, = 0 NO, =1 YES.

TOUT = time corresponding to concentration output

NSPEC = number of species

SNAM = species names

C = concentration vector

NDAYS = current day number of simulation

NHRS = hour component of 24 HR clock time

NMINS = minute component of 24 HR clock time

T = a dummy variable to save current time

```
subroutine CONFLD(IPRIN,TIMEM,NSPEC,SNAM,NPICS,NSICS,NLAY,
1 NGX,NGY,ILY,NROWS,ILEFT,IRIGHT,LENLAY,LENCON,C,CTEMP)
```

PURPOSE

This program has been designed to print the concentration field and a shaded map for each species required. The area of display is the computational region defined by the boundaries ILEFT and IRIGHT.

CALLED BY: gmamod

CALLS : times, pload, shade, matout

MAIN VARIABLES

IPRIN = logical unit number of the output device

TIMEM = time in minutes from midnight

NSPEC = maximum number of species

SNAM = species names

NPICS = flag array for species to be printed =0 NO, =1 YES

NSICS = flag array for species to be shaded =0 NO, =1 YES

NLAY = number of layers

NGX,NGY = dimensions of the global grid

ILY = Y row number of bottom of computational region

NROWS = number of rows in computational grid

ILEFT = left row numbers of computational region

IRIGHT = right row numbers of computational region

LENLAY = scalar length of a single layer

LENCON = length of the concentration array

C = concentration vector

CTEMP = temporary storage vector

```
subroutine CONPRT(IPRIN,TIMEM,NSPEC,SNAM,NPICS,NSICS,OPTION,
1 NLAY,NGX,NGY,ILX,ILY,NROWS,NCOLS,ILEFT,IRIGHT,
2 LENLAY,LENCON,C,CTEMP)
```

PURPOSE

This program has been designed to print the concentration field and a shaded map for each species requested. The area of display is the computational region defined by the boundaries ILEFT and IRIGHT.

CALLED BY: gmamod

CALLS : pload, print, filli, powr, fillln, shade, times

MAIN VARIABLES

IPRIN = logical unit number of the output device

TIMEM = time in minutes from midnight

NSPEC = maximum number of species

SNAM = species names

NPICS = flag array for species to be printed =0 NO, =1 YES

NSICS = flag array for species to be shaded =0 NO, =1 YES

NLAY = number of layers

NGX,NGY = dimensions of the global grid

ILY = Y row number of bottom of computational region

NROWS = number of rows in computational grid

ILEFT = left row numbers of computational region

IRIGHT = right row numbers of computational region

LENLAY = scalar length of a single layer

LENCON = length of the concentration array

C = concentration vector

CTEMP = temporary storage vector

subroutine CONSPP(IPRIN,IOPT,TOUT,NSPEC,SNAM,C)

PURPOSE

This subroutine prints the species concentrations corresponding to a particular output time TOUT. This program is simply a single precision version of the routine "CONCPR.".

MAIN VARIABLES

(see subroutine CONCPR)

subroutine COURNT(CMAX,U,DX,DTMIN,DTMAX,DT)

PURPOSE

This program calculates the maximum time step for advection using the Courant-Fredrich-Levy (CFL) numerical stability condition. In addition, the program checks to see if the time step is between certain upper and lower limits.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

CMAX = maximum number at which to operate numerical scheme

U = maximum velocity in grid

DX = grid cell size

DTMIN = minimum acceptable step size

DTMAX = maximum acceptable step size

DT = step size consistent with constraints of stability.

subroutine C05NBF(section,n,x,ff,xtol,wa,lwa,ifail)

PURPOSE

To find the root of a system of non-linear equations.

No Jacobian is needed as input.

CALLED BY: aeromain

CALLS : various subroutines of the nag library

MAIN VARIABLES

n = number of equations to be solved by c05nbf

lwa = dimension of the working array needed by c05nbf

wa = working array needed by the non-linear equation solver c05nbf

ff = array containing the values of the functions whose zeros we want to find

xtol = accuracy we require for the solution

ifail= error criteria (on input always 1. If ifail not 1 or 0 on output no convergence)

x = the values of the independent variables

section = the name of the subroutine that calculates ff for given x

function DEPOST(X,DUMMY,TGAS,PGAS,NBTYPE,k)

PURPOSE

To Calculate the Deposition Coefficients Due To Gravity and Diffusion. The Coefficient is Given For the Overall Container.

CALLED BY: coef

CALLS : olddep, rhodd

MAIN VARIABLES

X = Log of Particle Mass

DUMMY = Not Used

TGAS = Gas Temperature [K]

PGAS = Gas Total Pressure [Pa]

NBTYPE = Type of Sectional Coefficient; Should Be 7 Here

DENAIR = Background Gas Density [kg m^{-3}]

FREEMP = Background Gas Mean Free Path [m]

VISCOS = Background Gas Viscosity [kg/m/sec]

DELDEP = Boundary Layer [m] or Flag (if negative):

-1 Spherical Container

-2 Box with equal length sides

≤ -4 No Deposition

DEPOST = Deposition Coefficient

function DEPVEL(CZR,CZD,RMOL,ZR,Z0,SC,PR,UBAR)

PURPOSE

This function has been designed to evaluate an upper limit for the pollutant deposition velocity as a function of the surface roughness and meteorological conditions. Then it calculates the cell average deposition velocity, given the value of VG at some reference height ZR, which is much smaller than the cell height DZ.

CALLED BY: diffld

CALLS: cellvg, us

MAIN VARIABLES

CZD = concentration at the ground

CZR = concentration at the reference height

RMOL = reciprocal of the Monin Obukhov length

ZR = reference height

Z0 = surface roughness height

SC = turbulent Schmidt number

PR = Prandtl number

UBAR = absolute value of surface wind speed

DEPVEL = pollutant deposition velocity

K = Von Karman constant

USTAR = friction velocity U_*

POLINT = pollutant integral

subroutine DIFF2 (NEQN,C,DT,A,B,F)

PURPOSE

This subroutine establishes the right-hand side spatial derivatives to the one-dimensional atmospheric diffusion equation.

CALLED BY: integr2

CALLS: diffr

MAIN VARIABLES

A = vector with (A) coefficients of the differential equations

AKB = diffusivity at the bottom of the cell

AKT = diffusivity at the top of the cell

AKZ = array of the face diffusivities

ATEMP = temporary storage array for (A) coefficients

B = vector with (B) coefficients of the differencial equations

BTEMP = temporary storage array for (B) coefficients

C = concentration array at time T

CTEMP = temporary array for holding concentrations

DKDZT = diffusion coefficient D(KZZ)/DZ

DZ = array containing the cell heights

F = DC/DT at time T

FTEMP = temporary storage array for reaction rates

FAC = diffusion coefficient factor for boundary conditions

IND = index pointer

INDEX = index pointer

NEQN = number of equations

NSPEC = number of species

NZ = number of vertical cells

NZM1 = number of vertical cells - 1

NZP1 = number of vertical cells + 1

SCDOTA = source term associated with production

VG = species deposition velocities

T = current time

```
subroutine DIFFLD( SRAD,LV,Z0,U,V,FCLOUD,HMODEL,ZI,SLA,
1 INDX,ZREFH,KXXFLD,KZZFLD,NVERT,CELLB,
2 IAFF,ZREFVG,VGFLD)
```

PURPOSE

This program calculates the horizontal diffusion coefficients and deposition velocities, using the surface wind speeds at each grid point, and in addition it calculates the vertical diffusivity profile.

CALLED BY: gmamod

CALLS: stabpm, us, ws, kxxyy, kzprof, depvel

MAIN VARIABLES

SRAD = solar radiation

LV = length of the string vectors

Z0 = surface roughness field

U,V = velocity field over modeling region

FCLOUD = fraction cloud cover (=0 no clouds)

ZI = mixing depth

SLA = latitude of the modeling region (degrees, negative if south)

INDX = index array for unloading V-velocity components

ZREFH = reference height for wind velocity (typically 10 m)

CELLB = cell boundaries in physical coordinates

NVERT = number of vertical cells

VGFLD = deposition velocity field

subroutine DIFFR (N,CON,TIN,A,B,F)

PURPOSE

This program has been designed to calculate the differential rate of the chemical kinetics over a time step DT.

CALLED BY: diff2

CALLS: none

REACTION MECHANISM

$$NO_2 + HV \longrightarrow NO + O \tag{1}$$

$$O + O_2 + M \longrightarrow O_3 + M \tag{2}$$

$$O_3 + NO \longrightarrow NO_2 + O_2 \tag{3}$$

$$NO_2 + O \longrightarrow NO + O_2 \tag{4}$$

$$NO + O \longrightarrow NO_2 \tag{5}$$

$$NO_2 + O \longrightarrow NO_3 \tag{6}$$

$$O_3 + NO_2 \longrightarrow NO_3 + O_2 \tag{7}$$

$$NO_3 + NO \longrightarrow NO_2 + NO_2 \tag{8}$$

$$NO + OH \rightarrow HNO_2 \tag{9}$$

$$HNO_2 + HV \longrightarrow OH + NO \tag{10}$$

$$HO_2 + NO_2 \longrightarrow HNO_2 + O_2 \tag{11}$$

$$HNO_2 + OH \longrightarrow H_2O + NO_2 \tag{12}$$

$$NO_2 + HO_2 \longrightarrow HNO_4 \tag{13}$$

$$HNO_4 \longrightarrow HO_2 + NO_2 \tag{14}$$

$$HO_2 + NO \longrightarrow NO_2 + OH \tag{15}$$

$$RO_2 + NO \longrightarrow NO_2 + RO \tag{16}$$

$$RCO_3 + NO \longrightarrow NO_2 + RO_2 + CO_2 \tag{17}$$

$$NO_2 + OH \longrightarrow HNO_3 \tag{18}$$

$$CO + OH \longrightarrow HO_2 + CO_2 \tag{19}$$

$$O_3 + HV \longrightarrow O + O_2 \tag{20}$$

$$HCHO + HV \longrightarrow HO_2 + HO_2 + CO \tag{21}$$

$$HCHO + HV \longrightarrow H_2 + CO \tag{22}$$

$$HCHO + OH \longrightarrow HO_2 + H_2O + CO \qquad (23)$$

$$RCHO + HV \longrightarrow RO_2 + HO_2 + CO \qquad (24)$$

$$RCHO + OH \longrightarrow RCO_3 + H_2O \qquad (25)$$

$$C_2H_4 + OH \longrightarrow RO_2 \qquad (26)$$

$$C_2H_4 + O \longrightarrow RO_2 + HO_2 \qquad (27)$$

$$OLE + OH \longrightarrow RO_2 \qquad (28)$$

$$OLE + O \longrightarrow RO_2 + RCO_3 \qquad (29)$$

$$OLE + O_3 \rightarrow (A1)RCHO + (A2)HCHO + (A3)HO_2 + (A4)RO_2 + (A5)OH + (A6)RO \qquad (30)$$

$$ALK + OH \longrightarrow RO_2 \qquad (31)$$

$$ALK + O \longrightarrow RO_2 + OH \qquad (32)$$

$$ARO + OH \longrightarrow RO_2 + RCHO \qquad (33)$$

$$RO \longrightarrow (B1M)RO_2 + (B1)HO_2 + (B2)HCHO + (B3)RCHO \qquad (34)$$

$$RONO + HV \longrightarrow NO + RO \qquad (35)$$

$$RO + NO \longrightarrow RONO \qquad (36)$$

$$RO + NO_2 \longrightarrow RNO_3 \qquad (37)$$

$$RO + NO_2 \longrightarrow RCHO + HNO_2 \qquad (38)$$

$$NO_2 + RO_2 \longrightarrow RNO_4 \qquad (39)$$

$$NO_2 + RO_2 \longrightarrow RCHO + HNO_3 \qquad (40)$$

$$RNO_4 \longrightarrow NO_2 + RO_2 \tag{41}$$

$$RCO_3 + NO_2 \longrightarrow PAN \tag{42}$$

$$PAN \longrightarrow RCO_3 + NO_2 \tag{43}$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \tag{44}$$

$$N_2O_5 \longrightarrow NO_3 + NO_2 \tag{45}$$

$$H_2O + N_2O_5 \longrightarrow HNO_3 + HNO_3 \tag{46}$$

$$O_3 + OH \longrightarrow HO_2 + O_2 \tag{47}$$

$$O_3 + HO_2 \longrightarrow OH + O_2 + O_2 \tag{48}$$

$$O_3 \longrightarrow LOSS \tag{49}$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 \tag{50}$$

$$H_2O_2 + HV \longrightarrow OH + OH \tag{51}$$

$$RO_2 + RO_2 \longrightarrow RO + RO \tag{52}$$

$$NO_3 + HCHO \longrightarrow HNO_3 + HO_2 + CO \tag{53}$$

$$NO_3 + RCHO \longrightarrow HNO_3 + RCO_3 \tag{54}$$

$$NO_3 + HV \longrightarrow NO_2 + O \tag{55}$$

$$NO_3 + OLE \longrightarrow HNO_3 + RCO_3 \tag{56}$$

$$NO_2 + NO_3 \longrightarrow NO_2 + NO + O_2 \tag{57}$$

$$HNO_3 \longrightarrow LOSS \tag{58}$$

$$SO_2 + OH + M \longrightarrow HOSO_2 + M \tag{59}$$

$$\mathrm{CYCLOHEXENE} + O_3 \longrightarrow 0.39 \quad \mathrm{COOH} - (\mathrm{CH_2})_4 - \mathrm{COOH} \tag{60}$$

$$\mathrm{CYCLOPENTENE} + O_3 \longrightarrow 0.15 \quad \mathrm{COOH} - (\mathrm{CH_2})_3 - \mathrm{COOH} \tag{61}$$

$$\mathrm{CH_2} = \mathrm{CH} - (\mathrm{CH_2})_2 - \mathrm{CH} = \mathrm{CH_2} + O_3 \longrightarrow 0.11 \quad \mathrm{HOOC} - (\mathrm{CH_2})_2 - \mathrm{COOH} \tag{62}$$

$$\mathrm{CH_2} = \mathrm{CH} - (\mathrm{CH_2})_3 - \mathrm{CH} = \mathrm{CH_2} + O_3 \longrightarrow 0.19 \quad \mathrm{HOOC} - (\mathrm{CH_2})_3 - \mathrm{COOH} \tag{63}$$

$$\mathrm{CH_2} = \mathrm{CH} - (\mathrm{CH_2})_4 - \mathrm{CH} = \mathrm{CH_2} + O_3 \longrightarrow 0.15 \quad \mathrm{HOOC} - (\mathrm{CH_2})_4 - \mathrm{COOH} \tag{64}$$

$$\mathrm{C_6H_5} - \mathrm{CH_3} + \mathrm{OH} \longrightarrow 0.24 \quad \mathrm{CRESOL} + \mathrm{OTHER} \quad \mathrm{PRODUCTS} \tag{65}$$

$$\mathrm{C_6H_4} - (\mathrm{CH_3})_2 + \mathrm{OH} \longrightarrow 0.17 \quad \mathrm{CRESOL} + \mathrm{OTHER} \quad \mathrm{PRODUCTS} \tag{66}$$

$$\mathrm{CRESOL} + \mathrm{NO_3} \longrightarrow 0.30 \quad \mathrm{NITRO} - \mathrm{CRESOL} + \mathrm{OTHER} \quad \mathrm{PRODUCTS} \tag{67}$$

subroutine DIFFUN(NEQ,T,Q,DQDT)

PURPOSE

To Calculate the Derivatives dQ/dt for the Multicomponent Aerosol Model.

CALLED BY: DRIVE and other EPISODE subroutines

CALLS: pr1, press, binucl

MAIN VARIABLES

NEQ = Number of elements in Q or DQDT (augmented) arrays

T = Time at which derivatives are to be evaluated [sec]

Q = Array of Sectional Masses [Kg m^{-3}]

DQDT= Array of Sectional Mass Time Derivatives [Kg m^{-3} sec^{-1}]

nz = number of vertical cells

nemax = maximum number of equations

qt = total mass in each section

coefav= coefficients for growth and coagulation

psrate= source rate of particles

dmean = geometric mean diameter of each section

gammal= surface tension

dens =density

temp = temperature

dikelv= Kelvin diameter

pl = partial pressure of the condensable species in the bulk phase

ps = vapor pressure of the species over a flat surface of

. a solution having the same composition with the aerosol

ps0 = vapor pressure of the pure liquid

z = driving force for condensation

kc, kcon = number of condensable species

h(kcon $(l$-1)$+k$)=H^l_k

avhtq(l)=H^l

subroutine DIFFUN1(NEQ,T,Q,DQDT)

PURPOSE

To Calculate the Derivatives dQ/dt for the Multicomponent Aerosol Model. It is written in the same fashion with DIFFUN and its goal is to calculate the rates of intersectional motion due to condensation of volatiles that are treated with thermodynamics.

CALLED BY: DRIVE and other EPISODE subroutines

CALLS : none

MAIN VARIABLES

NEQ = Number of elements in Q or DQDT (augmented) arrays

T = Time at which derivatives are to be evaluated [sec]

Q = Array of Sectional Masses [Kg m^{-3}]

DQDT= Array of Sectional Mass Time Derivatives [Kg m^{-3} sec^{-1}]

nz = number of vertical cells

qmin = minimum non-zero mass

trans = intersectional coefficients

fp = intersectional coefficients

subroutine DIRECT(NSPEC,T,C,NZ,TZ,ZI,NT,TA,EF,SCDOT)

PURPOSE

This subroutine calculates the contribution of direct emissions to the source term in the material balance equation.

CALLED: none

CALLS: tint

MAIN VARIABLES

NSPEC = number of species

T = current time in minutes since 00:00 of the current day

C = concentration of species

NZ = number of mixing depth values

TZ = times for the mixing depth values

ZI = mixing depths

NT = number of the points for the emissions

TA = time array for the emissions

EF = emission flux array

SCDOT = source contribution term

ZIT = mixing depth at the current time

RECIPZ = 1.0 $ZI(T)^{-1}$

```
subroutine DOCUMS (ICODEN,NSPECS,NREACS,SNAM,SMW,ITYPE,
1 IOPT,IPRIN,INO,INO2,IO3,IHNO3,INH3,INIT,NRHC,IRHC,THCS,RHCS,
2 ISO2,ISO4,iHCl,iC4H6O4,iC5H8O4,iC6H10O4,iCRENO2,inacl,iPRIMC,
3 iaer,iaer1,iaer2,iaer3,iaer4,iaer5,iaer6,iaer7,iaer8)
```

PURPOSE

This program documents the species names, and types for both the gas and the aerosol phases. A secondary feature of the program is to identify those species that can be classified as either reactive hydrocarbons or part of NO_x, i.e., $NO + NO_2$. The program also supplies default values for the hydrocarbon splits for atmospheric conditions, if only THC or RHC are available. The default values are based on air quality data from Los Angeles.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

ICODE = code number to identify the reaction mechanism

NSPEC = number of species

NREACT = number of reactions

SNAM = species names

ITYPE = species type (= 1 differential, = 2 pssa = 3 constant)

SMW = species molecular weights

IOPT = options (=1 recall data, =2 print data,=3 change MW's)

IPRIN = logical unit number of the line printer

INO,INO2 = species numbers for NO AND NO_2, respectively

iaer = species number for total aerosol mass

iaer1 = species number for volatiles

iaer2 = species number for H_2SO_4

iaer3 = species number for Na

iaer4 = species number for aerosol $C_4H_6O_4$

iaer5 = species number for aerosol $C_5H_8O_4$

iaer6 = species number for aerosol $C_6H_{10}O_4$

iaer7 = species number for primary C

iaer8 = species number for aerosol nitro-cresol

NRHC = number of reactive hydrocarbons in mechanism

IRHC = array of species numbers for the reactive hydrocarbons

THCS = array of splitting factors for total HC

RHCS, NUMRHC= array of splitting factors for reactive hydrocarbons

01) NO

02) NO_2

03) O_3

04) HCHO

05) RCHO

06) OLEFINES

07) ALKANES

08) AROMATICS

09) C_2H_4

10) CO

11) H_2O_2

12) PAN

13) HNO_2

14) RONO

15) RNO_4

16) HNO_3

17) NH_3

18) NIT (used only to input the initial aerosol ammonium nitrates)

19) N_2O_5

20) NO_3

21) SO_2

22) SO4 (gas phase sulfuric acid)

23) HCl

24) SUCC (gas phase succinic acid)

25) GLUT (gas phase glutaric acid)

26) ADIP (gas phase adipic acid)

27) C5EN (cyclopentene)

28) C6EN (cyclohexene)

29) C6H1 (1,5 hexadiene)

30) C7H1 (1,6 heptadiene)

31) C8H1 (1,7 octadiene)

32) TOL (toluene)

33) XYLN (xylene)

34) CRES (cresol)

35) CREN (gas phase nitro-cresols)

36) AER (total aerosol concentration)

37) AER1 (concentration of volatiles in the aerosol phase)

38) AER2 (aerosol sulfates)

39) AER3 (aerosol sodium)

40) AER4 (aerosol phase succinic acid)

41) AER5 (aerosol phase glutaric acid)

42) AER6 (aerosol phase adipic acid)

43) AER7 (Primary Carbon in the aerosol phase)

44) AER8 (Nitro-cresols in the aerosol phase)

45) NACL (used only to input the initial NaCl)

46) PRIM (used only to input the initial primary C)

subroutine DPREP(ARRAY,WORK,ITYPE,NHOUR,BN,BS,BE,BW,CINAME,
1 KMAX,NX,NY,NZ,NIC,NA,IREAD,IDREAD,IPRINT,IOPT1,CELLHT)

PURPOSE

This program inputs concentration, wind and mixing depth data from the master grid and then it generates initial conditions, boundary conditions, wind fields and mixing depth fields for any subsection of the full grid.

CALLED BY: gmamod

CALLS : region, fread, strip, backgn, intrp, bound

MAIN VARIABLES

BKGRND = vector of pollutant background concentrations

BE = vector of boundary concentrations at east boundary

BN = vector of boundary concentrations at north boundary

BS = vector of boundary concentrations at south boundary

BW = vector of boundary concentrations at west boundary

CELLHT = vector of cell heights

CONC = array of pollutant concentrations

DEPTH = array of mixing depths

DX = grid spacing in X-direction

DY = grid spacing in Y-direction

DZ = vector of non-dimensional cell heights

IBCOND = subgrid boundary concentration data file

ICODE = code word written on file

ICOND = subgrid initial concentration data file number

IDEPTH = mixing depth data file number

IDEP1 = subgrid mixing depth data file

IEND = right end of subgrid

ILEFT = vector of left limits of subgrid

IPRINT = file number for printed output

IQUAL = pollutant concentration data file number

IREAD = file number for card input

IRIGHT = vector of right limits of subgrid

IMIN = far left end of subgrid

ITEXT = descriptive information read from main files

IWIND = wind data file number

IWIND1 = subgrid wind data file

JBOT = vector of lower limits of subgrid

JEND = top of subgrid

JMIN = bottom of subgrid

JTOP = vector of upper limits of subgrid

KMAX = number of elements in subgrid vector

LDAY = day for which data are to be processed

LMONTH = month for which data are to be processed

LYEAR = year for which data are to be processed

HTMOD = height of model above terrain

NCELLS = number of vertical cells

NHOUR = current hour of mixing depth data

NHRS = current hour of wind data

NLINES = number of lines of text

NOSPEC = number of pollutant species

NXSQR = number of grid points in X-direction (full grid)

NUMY = number of grid points in X-direction (subgrid)

NYSQR = number of grid points in Y-direction (full grid)

NUMX = number of grid points in Y-direction (subgrid)

POLNAM = vector of pollutant names

TEMP = temporary vector

TEXT = descriptive information to be written on file

VX = X-component of velocity

VY = Y-component of velocity

VZ = Z-component of velocity

subroutine DRIVE(diffun,N,T0,H0,Y0,TOUT,EPS,IERROR,MF,INDEX)

PURPOSE

To Solve a System of Stiff ODEs, with custom modifications to handle a non-negativity constraint and to keep error limited, where neither simple relative nor absolute error bounds are appropriate.

CALLED BY: maeros, intersec

CALLS : various EPISODE subroutines, diffun, diffunl

MAIN VARIABLES

N = the number of differential equations (used only on first call, unless index = -1). N must never be increased during a given problem.

T0 = the initial value of T, the independent variable (used for input only on first call).

H0 = the step size in T (used for input only on the first call, unless INDEX = 3 on input). When INDEX = 3, H0 is the maximum absolute value of the step size to be used.

Y0 = a vector of length N containing the initial values of Y (used for input only on first call).

TOUT = the value of T at which output is desired next. Integration will normally go beyond TOUT and interpolate to T = TOUT (used only for input).

EPS = The relative error bound (used only on first call, unless INDEX = -1). This bound is used as follows. Let R(I) denote the estimated relative local error in Y(I), i.e., the error relative to YMAX(I), as measured per step (of size H) or per SS units of T. Then EPS is a bound on the root-mean-square norm of the vector R; i.e., $N^{-1} \sum_1^N R(I)^2 < EPS$. The vector YMAX is computed in DRIVE as described under IERROR below. If error control per SS units of T is desired, set SS to a positive number after statement 10 (where it is now set to zero) and update it after statement 60. See also the comments on SS and YMAX below.

IERROR = The error flag with values and meanings as follow.

1 absolute error is controlled. YMAX(I) = 1.0.

2 error relative to ABS(Y) is controlled. If Y(I) = 0.0 a divide error will NOT occur. YMAX(I) = ABS(Y(I)).

3 error relative to the largest value of ABS(Y(I)) seen so far is controlled. If the initial value of Y(I) is 0.0, then YMAX(I) is set to 1.0 initially and remains at least 1.0.

4 same as 2 except if Y(I) initially < YMIN, YMAX(I)=YMIN

5 same as 3 except if Y(I) currently < YMIN, YMAX(I)=YMIN

6 same as 4 except if Y(I) < 0., Error Criteria Not Met

7 same as 5 except if Y(I) < 0., Error Criteria Not Met

8 same as 4 except if Y(I) < -YMIN, Error Criteria Not Met

9 same as 5 except if Y(I) < -YMIN, Error Criteria Not Met

Note: For 6-9, Special Modification so Y(N)<0. rejected 4 and 5 were added for problems when IERROR=2 fails because of divide by zero and IERROR=3 scales poorly to ONE -DRW. Note 4 and 5 require user to set YMIN reasonably in DRIVE

MF = The method flag (used only on first call, unless INDEX = -1). Allowed values are 10, 11, 12, 13, 20, 21, 22, 23. MF is an integer with two decimal digits, METH and MITER (MF = 10× METH + MITER). (MF can be thought of as the ordered pair (METH,MITER).) METH is the basic method indicator.

METH = 1 indicates variable-step size, variable-order ADAMS method, suitable for non-stiff problems.

METH = 2 indicates variable-step size, variable-order, backward differentiation method, suitable for stiff problems.

MITER indicates the method of iterative correction (non-linear system solution).

MITER = 0 indicates functional iteration (no partial derivatives needed).

MITER = 1 indicates a chord or semistationary NEWTON method with closed form (EXACT) JACOBIAN, which is computed in the user supplied subroutine PEDERV(N,T,Y,PD,N0).

MITER = 2 indicates a chord or semistationary NEWTON method with an internally computed finite difference approximation to the JACOBIAN.

MITER = 3 indicates a chord or semistationary NEWTON method with an internally computed DIAGONAL matrix approximation to the JACOBIAN, based on a directional derivative.

INDEX = Integer used on input to indicate type of call, with the following values and meanings:

1 this is the first call for this problem.

0 this is not the first call for this problem, and integration is to continue.

-1 this is not the first call for the problem, and the user has reset N, EPS, AND/OR MF.

2 same as 0 EXCEPT that TOUT is to be hit EXACTLY (no interpolation is done). assumes TOUT > the current T.

3 same as 0 EXCEPT control returns to calling program after one step. TOUT is ignored.

7 this is not the first call but the Y array has changed slightly, so the derivatives must be recomputed (NEW by DRW)

After the initial call, if a normal return occurred and a normal continuation is desired, simply reset TOUT and call again. All other parameters will be ready for the next call. A change of parameters with INDEX = -1 can be made after either a successful or an unsuccessful return.

THE OUTPUT PARAMETERS ARE AS FOLLOWS.

T0 = The output value of T. If integration was successful, T0 = TOUT. Otherwise, T0 is the last value of T reached successfully.

H0 = The step size H used last, whether successfully or not.

Y0 = The computed values of Y at T = T0.

INDEX = Integer used on output to indicate results, with the following values and meanings:

0 Integration was completed to TOUT or beyond.

-1 The integration was halted after failing to pass the error test even after reducing H by a factor of 10^{10} from its initial value.

-2 After some initial success, the integration was halted either by repeated error test failures or by a test on EPS. Possibly too much accuracy has been requested, or a bad choice of MF was made.

-3 The integration was halted after failing to achieve corrector convergence even after reducing H by a factor of 10^{10} from its initial value.

-4 Immediate halt because of illegal values of input parameters.

-5 INDEX was -1 on input, but the desired changes of parameters were not implemented because TOUT was not beyond T. Interpolation to T = TOUT was performed as on a normal return. To continue, simply call again with INDEX = -1 and a new TOUT.

-6 INDEX was 2 on input, but TOUT was not beyond T. No action was taken.

-7 Integration suspended because a $Y(I) < 0$ found, with $NRMIN \leq I \leq NRMAX$, and IERROR of 6 or 7 had proscribed against negative values –DRW

subroutine DYNAMIC(rh,ntime,tmpc,newcof)

PURPOSE

To perform the aerosol dynamic part. Specifically, it treats condensation, homogeneous nucleation and coagulation

CALLED BY: rodos

CALLS : setgas and maeros

MAIN VARIABLES

rh = relative humidity

ntime = time interval for integration

tmpc = temperature

newcof= flag to calculate coefficients

nz= number of vertical cells

ns, ms = number of sections

kc, kcon = number of different species

nemax= maximum number of equations that can be treated by EPISODE

q= string with the species concentrations

DO...= flags for the various options of the aerosol model

source = average source rate of the various condensable gases.

siniti = initial concentrations of the condensable gases

p1 = partial pressure of the various gases

ps = vapor pressure of the various species over a solution surface

ps0 = saturation vapor pressure

equl= array containing the size composition distribution

gmolwt= molecular weights of the species contained in (equl)

conmw= molecular weights of the species contained in (Q)

1 = H_2O

2 = H_2SO_4

3 = Na

4 = $C_4H_6O_4$

5 = $C_5H_8O_4$

6 = $C_6H_{10}O_4$

7 = prim C (assume carbon)

8 = nitro-cresol

sratio = ratio of the current aerosol concentration over the aerosol concentration of the previous step

RAT the relative amount of non-volatiles in each section

1 = NaCl

2 = H_2SO_4

3 = ORGANICS

qgas = concentrations of the condensable species in the gas phase

qtotal(i,j) = total aerosol concentration in section j in cell i

qnonvola = sectional concentration of the non-volatiles (Kg m^{-3})

diffus = diffusion coefficients

gasmw = molecular weight of air

qmin = minimum non-zero concentration

psrate= source rate of particles

plsat = saturation pressure of water

pwater = partial vapor pressure of water

rateg = source rate of the various condensable gases (Kg sec^{-1})

h0 = initial time step for EPISODE

HMAXMX = maximum time step for EPISODE

time = starting time

deltim = time increment

tout = output time

index = error messages from EPISODE

subroutine EMISN(NE,SNAME)

PURPOSE

This program has been designed to get the order of the species names as they are stored on the emission files.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

NE = number of emission species

SNAME = vector of emission species names

subroutine END1(IPRIN)

PURPOSE

This subroutine prints the "END" message for the airshed aerosol model.

CALLED BY: gmmain

CALLS : none

MAIN VARIABLES

iprin = unit number for the printer.

```
subroutine EQUILIB(temp1,rh,w1,rwater,ammon,sodium,
1 sulfate,nitrate,chloride,hno3,nh3,rhcl,rna2so4,rnh42s4,
2 rnh4cl,rnacl,rnano3,rnh4no3,bisulf,clc,rh2so4,
3 cnh4hso4,rnahso4)
```

PURPOSE

This subroutine finds the equilibrium composition of a closed system. Given the initial sulfate and sodium concentrations, as well as the gas phase NH_3, HCl and HNO_3 concentrations and the ambient temperature and relative humidity the concentration of the various species at equilibrium is calculated.

CALLED BY: aeromain, aeroml, aerobon, section

CALLS : FCN1,FCN2,FCN4,FCN7,FCN8,FCN9,FCN10,FCN11

CALLS : FCN12,FCN13,FCN14,FCN15,FCN16,FCN18,bisect

MAIN VARIABLES

awas= water activity of the $(NH_4)_2SO_4$-H_2O binary solution as a function of the RH

awan= water activity of the NH_4NO_3-H_2O binary solution as a function of the RH

awab= water activity of the NH_4HSO_4-H_2O binary solution as a function of the RH

awss= water activity of the Na_2SO_4-H_2O binary solution as a function of the RH

awsn= water activity of the $NaNO_3$-H_2O binary solution as a function of the RH

awsa= water activity of the H_2SO_4-H_2O binary solution as a function of the RH

awac= water activity of the NH_4Cl-H_2O binary solution as a function of the RH

awsb= water activity of the $NaHSO_4$-H_2O binary solution as a function of the RH

awlc= water activity of the $(NH_4)_3H(SO_4)_2$-H_2O solution as a function of the RH

awsc= water activity of the NaCl-H_2O binary solution as a function of the RH

molal= ion concentrations (in moles m^{-3})

molal(1)= H^+

molal(2)= Na^+

molal(3)= NH_4^+

molal(4)= Cl^-

molal(5)= SO_4^{2-}

molal(6)= HSO_4^-

molal(7)= NO_3^-

molalr= concentrations of the various electrolytes used in the ZSR method (in moles m^{-3})

molalr(1)=NaCl

molalr(2)=Na_2SO_4

molalr(3)=$NaNO_3$

molalr(4)=$(NH_4)_2SO_4$

molalr(5)=NH_4NO_3

molalr(6)=NH_4Cl

molalr(7)=$(2H,SO_4)$

molalr(8)=(H,HSO_4)

molalr(9)=NH_4HSO_4

molalr(10)=(H,NO_3)

molalr(11)=(H,Cl)

molalr(12)=$NaHSO_4$

molalr(13)=$(NH4)_3H(SO_4)_2$

rmw= molecular weights of the various ions

gama= activity coefficients

z = absolute values of the charges of the various ions

niu = number of ions per molecule of a specific electrolyte

zz = $z_+ \times z_-$

rk...= equilibrium constants of the various reactions

subroutines FCN1,FCN2,FCN4,FCN7,FCN8,FCN9

subroutines FCN10,FCN11,FCN12,FCN13,FCN14

subroutines FCN15,FCN16,FCN18

PURPOSE

Find the thermodynamically favorable species for different relative humidities and H_2SO_4/ (NH_3 + NaCl) ratios

subroutine FILLI(ARRAY, IARRAY, NGX, NGY, OPTION, IDEF, ADEF,

1 NAME, UNITS)

PURPOSE

This program fills an integer array with values from a real array. The values are factored so that a proper factor is chosen.

CALLED BY : CONPRT, PRINT

CALLS: IFLD, POWR

MAIN VARIABLES

ARRAY = real array with concentrations

IARRAY = integer array with concentrations

NGX,NGY = dimensions of the global grid

OPTION = unit option (currently not used)

IDEF, ADEF = default unit values

NAME = name of the species to be printed

subroutine FILLLN(LINE,N,IVALS,IDEF,IL,IR,J)

PURPOSE

This program fills a line of characters with integer values from an array. This is used to print the data in a "map" form

CALLED BY : CONPRT, PRINT

CALLS: ifld

MAIN VARIABLES

LINE = line with characters

N = number of grids in the x direction

IVALS= integer array containing the concentrations

IDEF = default value (no concentration)

IL = global index of the first cell of the line

IR = global index of the last cell of the line

J = index in the y-axis of the current line

subroutine FILTER (NXSQR, NYSQR, FIELD)

PURPOSE

This program has been designed to smooth discrete two-dimensional vector and scalar fields using a five-point averaging operator. The edges and corner points are handled with four- and three-point formulae. Multiple applications of the filter effectively increase the radius of influence of the averaging process.

MAIN VARIABLES

NXSQR = number of grid cells in the x direction

NYSQR = number of grid cells in the y direction

FIELD = field to be smoothed or filtered

TEMP = temporary array to prevent initial overwriting

subroutine FIND(ICALL,IPRIN,NSPEC,SNAM,SMW,NE,SNAME, IORD,IERR)

PURPOSE

This program has been designed to create a pointer array, which will enable the emissions or initial conditions to be allocated to the correct location in the species array. This feature allows the chemical mechanism to be changed without affecting the emission or I.C. processing programs.

CALLED BY : gmamod

CALLS: none

MAIN VARIABLES

ICALL = call type indicator, =1 emissions, =2 I.C.'s

IPRIN = logical unit of line printer

NSPEC = number of chemical species in the mechanism

SNAM = species names

SMW = species molecular weights

NE = number of emission species

SNAME = names of emission species

IORD = order of species for chemical mechanism

IERR = error flag

=0 no error

=1 emission species could not be found in the mechanism

subroutine FREAD(TEMP,NXSQR,NYSQR,NCELLS,NPOL,IHOUR,ITYPE,
1 IREAD,IPRINT,IOPT1)

PURPOSE

This subroutine reads the input files and returns the values for the particular hour.

CALLED BY : dprep

CALLS: header

MAIN VARIABLES

Look at main variables in subroutine DPREP

subroutine GAUS2(F,XL,XU,RELER,ABSER,ROUND,ANSWR,IER,EXTRA1,
1 EXTRA2,EXTRA3,NEXTRA,k)

PURPOSE

This routine computes the integral of F(X,EXTRA1,EXTRA2,EXTRA3, NEXTRA) from XL to XU. A two-point GAUSS-LEGENDRE QUADRATURE formula is used. Convergence is checked by dividing the domain in half and reapplying the formula in each half. If the value of the integral calculated over the entire domain is not equal to the sum of the integrals in each half (within the user specified error tolerance), each half is further divided into halves and the GAUSS-LEGENDRE formula is reapplied. The procedure will continue iterating (i.e., subdividing), until convergence is achieved or the maximum number of iterations is reached. The maximum number of iterations is either the set defualt value of 20 (where the first iteration is for evaluation over the entire domain), or the largest number of iterations possible without severe machine round-off errors, whichever is smaller.

NOTE:The user must supply a function subroutine F(X,EXTRA1,EXTRA2, EXTRA3,NEXTRA), which must be declared external in the routine that calls GAUS2. The variable of integration is the first argument of the function F.

CALLED BY: coef

CALLS : F (growth)

MAIN VARIABLES

F = external function routine for integrand

F(X, EXTRA1, EXTRA2, EXTRA3, NEXTRA, k)

XL= lower limit of integration (REAL)

XU= upper limit of integration (REAL)

RELER= relative error tolerance (REAL)

ABSER= absolute error tolerance (REAL)

EXTRA1= variable that may be passed to function F (REAL)

EXTRA2= variable that may be passed to function F (REAL)

EXTRA3= variable that may be passed to function F (REAL)

NEXTRA= variable which may be passed to function F (INTEGER)

IER = normally set to zero, but may be set to 1 for the integral to be computed by a single application of GAUSS-LEGENDRE formula.

ANSWR= value of integral unless ier.ne.0 IER = integer error flag

0 no errors, convergence obtained

-2 integration domain is too small. ANSWR computed by single application of GAUSS-LEGENDRE formula

-1 integration domain is too small for given machine round-off error. ANSWR computed by single application of GAUSS-LEGENDRE formula

$\geq$ 1 number of times divided into halves before reaching maximum number of subdivisions. ANSWR determined by single application of GAUSS-LEGENDRE formula

A(I,N) = integral in left half (corresponding to I=1), or right half (corresponding to I=2) at the N^{th} level. For N=1, integral is contained in A(2,1) and A(1,1) is never used

H(N) = step size at N^{th} level

ISIDE(N)= side at N^{th} level where N=1 or 2 corresponding to the left or right half, respectively

N = level of region

NMAX = maximum number of levels

X(N) = smallest X value at the N^{th} level

k = level of grid (for growth)

subroutine GAUS3(F,XL,XU,RELER,ABSER,ROUND,ANSWR,IER,EXTRA1,
1 EXTRA2,EXTRA3,NEXTRA

PURPOSE

This routine computes the integral of F(X,EXTRA1,EXTRA2,EXTRA3, NEXTRA) from XL to XU. Everything is similar to GAUS2. This subroutine is used to calculate all the coefficients except of growth, that is calculated by gaus2.

CALLED BY: COEF, BETCAL

CALLS : F (BETA)

subroutine GAUSBT(F,XL,XU,RELER,ABSER,ROUND,ANSWR,IER,IPRNT,
1 FIXSZ,BASESZ,INNER,TGAS,PGAS,NBTYPE)

PURPOSE

To Calculate the Outer Sectional Integral for Sectional Coagulation Coefficients.

CALLED BY: coef

CALLS : F (betcal)

MAIN VARIABLES

F = Function to be integrated

XL = Lower Limit on Outer Integral

XU = Upper Limit on Outer Integral

RELER = Relative Error Tolerance for Integration

ABSER = Absolute Error Tolerance for Integration

ROUND = Unit Round-Off Error (largest X that 1.+X=1.)

IPRNT = Logical Unit Number for Output Messages

FIXSZ = Inner Integral Size Limit

BASESZ = Inner Integral Size Limit

INNER = Flag to Interpret Inner Size Limits

TGAS = Gas Temperature [K]

PGAS = Gas Total Pressure [Pa]

NBTYPE = Flag for Type of Sectional Integral

ANSWR = Double Integral Value

IER = Error Return Flag

```
subroutine GMAMOD ( LSCAL,LWIND,NEMAX,LWORK,NSMAX,NIMAX
1 ,LC,LIC,LAVG,NPMAX,NDWC,NMROWS,NMCOLS,LBR,LBC,LBRIC,
2 LBCIC,LAREAS,
3 NGMX,NGMY,NGMZ )
```

PURPOSE

This program has been designed to calculate the air quality distribution over an airshed by solving the species conservation equations for a chemically reacting system. Numerically, this approach assumes that the vertical pollutant distribution within a computational cell is well mixed. A special feature of this particular program is that it contains, as a subset, a vertically integrated form of the governing equations.

CALLED BY : gmmain

CALLS: Most of the subroutines of the airshed aerosol model

MAIN VARIABLES

ZI = mixing depth

Z0 = surface roughness

U,V,W = X,Y, and Z components of the wind field

TEMP = temperature field

RELH = relative humidity field

AKXXYY = horizontal diffusion field

DZIDT = temporal gradient in mixing depth field

VGFLD = deposition velocity field

AKZZ = vertical diffusion field

EMISS = area source emissions

IPHOUR = string index for point source locations

ICELLI = X cell location of point sources

ICELLJ = Y cell location of point sources

HF = plume rise from point sources

STKHT = point source stack height

EGTEMP = exhaust gas temperatures

EGRATE = volumetric gas flow rate

PEMISS = point source emissions by species

ISQ,JSQ = X,Y locations for downwind source allocation

SRCE = source contributions to downwind cells

PTSEMP = point source emissions

ILEFT = left or west side of modeling region

IRIGHT = right or east side of modeling region

ITOP = top or north side of modeling region

IBOT = bottom or south side of modeling region

IPINDX = species index array for string vectors

INDX = scalar index for string vectors

C = concentration array for all species

CI = array of initial conditions read from files

BN..BW = arrays containing N,S,E and W B.C.'s for all species

CN..CW = boundary conditions derived from measurements

WORK = work vector for input and output

PTEMP = temporary two-dimensional storage array (real)

ITEMP = temporary two-dimensional storage array (integer)

starti = logical variable to indicate that initial aerosol

. conditions must be calculated

aernh3(i)= total ammonium in the aerosol phase in the i^{th} grid

aerno3(i)= total nitrate in the aerosol phase in the i^{th} grid

aercl(i) = total chloride in the aerosol phase in the i^{th} grid

aerh2o(i)= total water in the aerosol phase in the i^{th} grid s)

sourcl =average production in gas phase

siniti =initial gas concentration

nspec =number of species

twest=array containing the temperatures of the west boundary

teast=array containing the temperatures of the east boundary

tnorth=array containing the temperatures of the north boundary

tsouth=array containing the temperatures of the south boundary

rhwest=array containing the RH's of the west boundary

rheast=array containing the RH's of the east boundary rhnorth=array containing the RH's of the north boundary

rhsouth=array containing the RH's of the south boundary

aern, aernam = vectors containing the names of the aerosol species
to be printed

kpics, lpics = vectors containing the order to print aerosol species

cnt = concentration string for the trajectory model

rk = rates of the reactions

emt = area emissions for the trajectory model

vgt = deposition velocities for the trajectory model

taersm = time step for the aerosol part

PROGRAM GMMAIN

PURPOSE

This is the main data allocation program for the photochemical modeling system and has been designed to establish the length or dimension of the master arrays. Because most of the storage allocation is done in this program, this considerably simplifies the task of implementing dynamic dimensioning on different types of large-scale computers.

CALLED BY: none

CALLS : end1, gmamod, start1

MAIN VARIABLES

ZI = mixing depth

Z0 = surface roughness

U,V,W = X,Y, and Z components of the wind field

TEMP = temperature field

RELH = relative humidity field

AKXXYY = horizontal diffusion field

DZIDT = temporal gradient in mixing depth field

VGFLD = deposition velocity field

AKZZ = vertical diffusion field

EMISS = area source emissions

IPHOUR = string index for point source locations

ICELLI = X cell location of point sources

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HF = plume rise from point sources

STKHT = point source stack height

EGTEMP = exhaust gas temperatures

EGRATE = volumetric gas flow rate

PEMISS = point source emissions by species

ISQ,JSQ = X,Y locations for downwind source allocation

SRCE = source contributions to downwind cells

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ILEFT = left or west side of modeling region

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IBOT = bottom or south side of modeling region

IPINDX = species index array for string vectors

INDX = scalar index for string vectors

C = concentration array for all species

CI = array of initial conditions read from files

BN..BW = arrays containing N,S,E and W B.C.'s for all species

CN..CW = boundary conditions derived from measurements

WORK = work vector for input and output

PTEMP = temporary two-dimensional storage array (real)

ITEMP = temporary two-dimensional storage array (integer)

subroutine GRADZI(DTAVG,LENG,ZIT,DZIDT)

PURPOSE

This program has been designed to calculate the time derivative associated with changing mixing heights. The program accepts two fields and the averaging time DTAVG and then calculates the gradients, assuming a linear variation between end points.

CALLED BY : gmamod

CALLS: none

MAIN VARIABLES

DTAVG = averaging time of the fields (typically 60 min)

LENG = array size of the vector

ZIT = array of mixing heights at time T

DZIDT = time derivative of mixing height. On input to this program DZIDT contains the mixing height at time T+DTAVG; i.e., this array is overwritten on output.

function GROWTH(X,DUMMY,TGAS,PGAS,NBTYPE,k)

PURPOSE

To Calculate the Condensational Growth Rate of a Particle

CALLED BY: coef, gaus2

CALLS : RHODD

MAIN VARIABLES

X = Log of Particle Mass

DUMMY = Not used

TGAS = Gas Temperature [K]

NBTYPE = Flag for coefficient type

DIFFUS = Condensing Species Vapor Diffusivity [m^2 sec^{-1}]

conmw= molecular weights of the species contained in (Q)

DENSTY = Density of Liquid Condensing [kg m^{-3}]

GROWTH = Particle Growth Rate [sec^{-1}]

subroutine HEADER(IRNCDE,KDAY,KMONTH,KYEAR,NLINES,NXSQR,
1 NYSQR,DX,DY,NCELLS,HTMOD,NPOL,DELRHO,ITEXT,POLNAM,
2 ITYPE,IOPT,IREAD,IPRINT)

PURPOSE

This subroutine reads the header records from the input files needed by the airshed model and returns the information to the calling program.

CALLED BY: fread

CALLS : none

MAIN VARIABLES

ITYPE=CODE FOR TYPE OF HEADER (1,2,3= winds, 4 = mixing depth, 5 = air quality, 6 = topography, 7 = surface roughness, 8 = temperature and 9 = relative humidity)

IOPT = 0 do not print the header

IOPT = 1 print the header

subroutine ICFLDR(NSPEC,LENLAY,NVERT,NIC,ICORD,IRHCP,ITHCP,
1 ITSPP,NRHC,IRHC,THCS,RHCS,CI,C,IRURAL)

PURPOSE

This program establishes the initial conditions for the modeling region in the correct string format and allocates the data on the input file in the required form for the reaction mechanism. This feature saves recoding of input programs for different inventories or air quality data formats.

CALLED BY: gmamod

CALLS : alocicr

MAIN VARIABLES

NSPEC = number of species in the reaction mechanism

LENLAY = number of computational cells in a layer

NVERT = number of vertical layers used in calculation

NIC = number of initial condition species

ICORD = location of initial conditions in species order

IRHCP = location of total reactive hydrocarbons in I.C. array

ITHCP = location of total hydrocarbons in I.C. array

ITSPP = location of total suspended particulates in I.C. array

NRHC = number of reactive hydrocarbons in reaction mechanism

IRHC = location of hydrocarbons in list of mechanism species

THCS = split factors for total hydrocarbons

RHCS = split factors for reactive hydrocarbons

CI = I.C.'S read from files

C = I.C.'S used for the reaction mechanism species

subroutine IFLD(IWIDE, NUMBER, ALPHA)

PURPOSE

This subroutine returns an alpha field with a width of IWIDE containing the concentration field

CALLED BY: filli

CALLS: none

subroutine INDEX(NROWS,ILEFT,IRIGHT,NCOLS,IBOT,ITOP,
1 NGX,NGY,ITEMP,INDVEC,LENVEC,ILX,ILY)

PURPOSE

This program has been designed to develop a vector of indices corresponding to the location of points normal to the X-axis in arrays that have components stored parallel to the Y-axis

CALLED BY: none

CALLS : none

MAIN VARIABLES

IPRIN = logical unit number of the line printer

ILEFT = array of the left most indices

IRIGHT = array of the right most indices

NCOLS = number of computational columns

IBOT = array of the bottom indices

ITOP = array of the top indices

NGX,NGY= dimensions of the global grid

ILX,ILY= coordinates of the corner grid cell

ITEMP = work array used to construct the index vector

INDVEC = index vector

LENVEC = length of the index vector

subroutine INTEGR2(N,C,TIN,TOUT)

PURPOSE

This subroutine integrates coupled stiff differential equations, using a hybrid integration technique. While the method is very fast, it is very important to recognise that certain of the numerical constants have been tailored to the characteristics of the particular reaction mechanism.

The form of the differential expressions assumed by this program is:

$$\frac{dC}{dT} = A(C,T) - B(C,T) \times C.$$

A subroutine of the form DIFF(N,C,TIN,A,B,F) must be provided for the system of interest to compute the A and B arrays from the concentrations, C and the input time, TIN. The array F, which contains the values of DC/DT, must also be computed.

CALLED BY: chmsol2

CALLS : diff2

MAIN VARIABLES

A, A2 = vectors with (A) coefficients of the differential equations

B, B2 = vectors with (B) coefficients of the differential equations

BTEMP = temporary storage array for (B) coefficients

C, C2, C3 = concentration arrays

CMIN = minimum non-zero concentrations

F, F2 = arrays containing DC/DT

IS = index pointer for stiff equations (=0 non-stiff, =1 stiff)

N = number of equations

TIN = input time

TOUT = output time

subroutine INTERSEC(ntime)

PURPOSE

To update the size composition of the aerosol species. It takes into account the intersectional motion of particles due to the condensation of the various volatiles. This subroutine uses the number conservation argument to minimize numerical diffusion.

CALLED BY: rodos

CALLS : DRIVE (EPISODE)

MAIN VARIABLES

ntime = time interval for integration

ms, ns = number of sections

nz = number of vertical cells

kc, kcon = number of different species

uround = round-off error (needed for EPISODE)

rele = relative error

abse = absolute error

MFEPI= method of integration used by EPISODE

ktol = (see DRIVE comments for explanations)

diffun1 = name of the subroutine that calculates the derivatives

qmin = minimum non-zero mass

equl = array containing the various species at equilibrium

q = array that will be processed

h0 = initial time step for EPISODE

HMAXMX = maximum time step for EPISODE

time = starting time

deltim = time increment

tout = output time

subroutine INTRP(CONC,DEPTH,CELLHT,HTMOD,TEMP,ILEFT,IRIGHT,

1 CINAME,BKGRND,JMIN,NOSPEC,NX,NY,NZ,JJ,KMAX,NUMX)

PURPOSE

This subroutine calculates upper-level concentration values, assuming surface values up to the inversion base and linear decrease to background values within inversion

CALLED BY: dprep

CALLS: none

MAIN VARIABLES

conc = species concentrations

NOSPEC = number of species in reaction mechanism

NUMX = number of computational rows

NUMY = number of computational columns

NZ = number of vertical layers used in calculation

BKGRND = array of background concentrations

CINAME = array containing species names

ILEFT = left-hand x-indices of each row in computational grid

IRIGHT= right-hand x-indices of each row in computational grid

subroutine ION(ionic)

PURPOSE

To calculate the ionic strength

CALLED BY: activity

MAIN VARIABLES

ionic = ionic strength

water = H_2O concentration (Kg m^{-3})

function IPOSN(IGX,IGY,NROWS,ILEFT,IRIGHT,ILY)

PURPOSE

This program has been designed to calculate the index location in the modelling region, given the global data coordinates of a point in the master data storage grid.

CALLED BY: plumht

CALLS : none

MAIN VARIABLES

IGX,IGY = coordinates of the point in the global grid

NROWS = number of rows in the modeling region

ILEFT = left column indices for each row (from bottom up)

IRIGHT = right column indices for each row

ILY = Y index of the bottom of the modeling region

IPOSN = position of point in scalar string vector

subroutine JNDEX (NROWS,ILEFT,IRIGHT,NCOLS,IBOT,ITOP,
1 NGX,NGY,ITEMP,INDVEC,LENVEC,ILX,ILY)

PURPOSE

This program has been designed to develop a vector of indices corresponding to the locations of points in the string arrays, which are normal to the x-axis.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

NROWS = number of rows in the modeling region

ILEFT(I) = X index for the far left cell of the I^{th} row (from bottom up)

IRIGHT(I)= X index for the far right cell of the I^{th} row (from bottom up)

NCOLS = number of columns in the modeling region

IBOT(I) = bottom Y index for the I^{th} column (from left to right)

ITOP(I) = top Y index for the I^{th} column (from left to right)

NGX,NGY = dimensions of the global data region

ITEMP = integer work array

ILX = The global x-coordinate of the far left cell of the modeling region

ILY = The global y-coordinate of the far bottom cell of the modeling region

subroutine KXXYY (SRAD,Z0,USURF,FCLOUD,HMODEL,HMIXL,ALAT,
1 ZREFH,HKXXYY)

PURPOSE

This program has been designed to calculate the horizontal variation of the turbulent eddy diffusivity. In the present program, the key stability parameter is the Monin-Obukhov length, which is estimated by using Golder's method. This procedure uses only commonly available meteorological data and as such should be easily implemented in diverse geographical areas.

CALLED BY: diffld

CALLS : stabpm, us

MAIN VARIABLES

SRAD = solar radiation

Z0 = surface roughness (m)

USURF = wind velocity at reference height (m sec^{-1})

FCLOUD = fraction cloud cover =0 no cloud, =1 total coverage

HMODEL = height to top of the modeling region (m)

HMIXL = height of mixed layer (m)

ALAT = latitude of region (degrees, (+ for north, - for south))

ZREFH = reference height for surface winds (m)

HKXXYY = horizontal eddy diffusivity (constant with Z)

VK = Von Karman constant

RMOLEN = reciprocal of Monin-Obukhov length (1/L)

USTAR = surface friction velocity (m $\sec^{-1}$)

WSTAR = convective velocity scale (m $\sec^{-1}$)

H = scale height for stable scale

F = coriolis parameter

```
subroutine KZPROF( SRAD,Z0,USURF,FCLOUD,HMODEL,HMIXL,ALAT,
1 ZREFH,NKZL,HKZ,VKZ,HKXXYY )
```

PURPOSE

This program has been designed to calculate the vertical variation of the turbulent eddy diffusivity. In the present program, the key stability parameter is the Monin-Obukhov length, which is estimated by using Golder's method. This procedure uses only commonly available meteorological data and as such should be easily implemented in diverse geographical areas.

CALLED BY: diffld

CALLS : stabpm, us

MAIN VARIABLES

SRAD = solar radiation

Z0 = surface roughness (m)

USURF = wind velocity at reference height (m sec^{-1})

FCLOUD = fraction cloud cover =0 no cloud, =1 total coverage

HMODEL = height to top of the modelling region (m)

HMIXL = height of mixed layer (m)

ALAT = latitude of region (degrees, (+ for north, - for south))

ZREFH = reference height for surface winds (m)

HKXXYY = horizontal eddy diffusivity (constant with Z)

VK = Von Karman constant

RMOLEN = reciprocal of Monin-Obukhov length (1/L)

USTAR = surface friction velocity (m sec^{-1})

WSTAR = convective velocity scale (m sec^{-1})

H = scale height for stable scale

F = coriolis parameter

NKZL = number of levels at which K(Z) is required

HKZ = array of heights for K(Z) determinations

VKZ = vertical eddy diffusivity at each height (m^2 sec^{-1})

B0..B4 = polynomial coefficients for unstable case

PSI = non-dimensional height parameter (Z/HMIXL) subroutine LIMPRT(IPRIN,IOPT,TOUT,NSPEC,SNAM,IPRINT,C)

PURPOSE

This subroutine has been designed to print the concentration output for only those species requested on input; the default is simply to print all the species.

CALLED BY: none

CALLS: CONCPR

MAIN VARIABLES

IPRIN = logical unit number of the line printer

IOPT = option to skip to a new page =0 no, =1 yes

TOUT = time in minutes since the start

NSPEC = number of species

SNAM = species names

IPRINT = print indicator = 1 yes, = 0 no

C = concentration vector for all species

PNAM = names to be printed

subroutine LOAD(ITYPE,ADEF,NUM,ILEFT,IRIGHT,VECTOR,LENVEC,
1 IK,NGX,NGY,ARRAY)

PURPOSE

This program takes data stored in string format and loads the information into a two-dimensional array for output display processing.

CALLED BY: gmamod

CALLS: none

MAIN VARIABLES

ADEF = default value to load into the non modeling region

NUM = number of rows or columns in the modeling region

ILEFT = X indices for the left-hand ends of each row

= or Y indices for the bottom ends of each column

IRIGHT = X indices of the right-hand ends of each row or

= Y indices of the top ends of each column

VECTOR = vector of data values stored in string form

LENVEC = length of the vector

IK = lowest row or column number in global data region

ITYPE = 1 loads with X varying fastest

ITYPE = 2 loads with Y varying fastest

NGX,NGY= dimensions of global data region

ARRAY = two-dimensional array holding the string data

subroutine MAEROS(TIME,DELTIM,Q,TGAS,

1 TGAS,PGAS,IPRNT,IFLAG,NEWCOF,h0)

PURPOSE

To Calculate an Aerosol Size Distribution, at a Future Time, Using a Sectional Representation.

CALLED BY: dynamic

CALLS : coef, setgas, pr1, press, drive

MAIN VARIABLES

TIME = Current Time [sec]

DELTIM = Time Step, after which MAEROS returns [sec]

Q(NEQ) = Sectional Mass Array [kg m^{-3}]

TGAS = Gas Temperature [K]

PGAS = Pressure, total [Pa]

IPRNT = Logical Unit Number for Output (often 6)

IFLAG = Flag for Integration Routine

NEWCOF = Flag that controls which coefficients are calculated; Negative values cause use of current coefficients.

TGAS1,TGAS2 = Min and Max Temperatures [K]

PGAS1,PGAS2 = Min and Max Pressures [Pa]

PSRATE(NEMAX)= Sectional Particle Source Rates [kg m^{-3} sec^{-1}]

DEPSIT(3,KC) = Mass Deposited on (Surface,Component) [kg]

UROUND = Machine Unit Round-Off Error

ms,kc,kcon = Number of Size Sections and Components

TIME = Updated to new Time.

subroutine MAPCOM(NGX,NGY,NGZ,NROWS,IROWN,IS,IF,

1 NCOLS,JTOP,JBOT,IPRIN,NCELLS)

PURPOSE

This program has been designed to print a map of the distribution of computational grid cells within the global grid system.

CALLED BY: region

CALLS: none

MAIN VARIABLES

NGX,NGY,NGZ = number of X,Y,Z cells in global grid

NROWS = number of rows in computational grid

NCOLS = number of columns in computational grid

IBROWN = bottom row number of computational grid

JTOP,JBOT = top and bottom row indices for each column

IS,IF = start and finish column indices for each row

IROWN = array of row numbers for computational cells

ITROWN = top row number of the computational grid

NCELLS = number of computational cells

IPRIN = logical unit number of the line printer

NGCELL = number of cells in global grid

FRAC = fraction of cells used for computation

IND = row number

INDS,INDF = start and stop column indices for row indices

IDOT,IAST = line printer symbols ‘ . ’ and ‘ * ’

IPLUS = ‘+’

subroutine MASCAL(IPRIN,NSPEC,NLEVEL,LENLAY,DX,HEIGHT,SMW,
1 SNAM,DZRHO,NPMASS,C)

PURPOSE

This subroutine is designed to calculate the total mass of the various species in each of the of the grids.

CALLED BY: gmamod

MAIN VARIABLES

C = concentration of various species

SMW = molecular weights

SNAM = name of the various pollutants

IPRIN = logical unit number of the line printer

NSPEC = number of species

nlevel = level

LENLAY = number of computational cells in a layer

DZRHO = array of dimensionless grid cell heights

subroutine MATOUT(IPRIN,A,N,M,LINS,IPOS,ISP,IUP,ITYPE,IW,ID,ISKIP,
1 NC,TITLE)

PURPOSE

This subroutine has been designed to print rectangular matrices in a user specified format. The program accepts the number of print positions and if the matrix is too large the subroutine will print the results over multiple pages.

CALLED BY: gmamod

CALLS : RECFMT

MAIN VARIABLES

IPRIN = Logical unit number of the line printer

A = matrix to be printed

N,M = dimensions of matrix A(N,M)

LINS = number of lines per page (typically 60)

IPOS = number of print positions across the page(usually 132)

IUP = option to print row number (N first = 0 ,N last =1)

ISP = line spacing required (=0 single, =1 double)

ITYPE = format type =0 'E', =1 'F', =2 'G'

IW,ID = print format in form Fw.d OR Ew.d

ISKIP = option to skip to a new page =0 NO, =1 YES

NC = number of characters in the title

TITLE = title to be printed on the page

subroutine MLTDAY(ISHR,ISMIN,LENCON,IPRINT,IFILE,C)

PURPOSE

This program picks up the initial concentrations to perform a multiday simulation of the AIRSHED model.

CALLED BY: gmamod

CALLS: none

subroutine MOLE(p1,p2,rh,na,nb,t)

PURPOSE

This subroutine calculates the partial vapor pressure of H_2O in the atmosphere,given R.H and T. it also calculates the number concentration of H_2O and H_2SO_4 molecules.

CALLED BY: binucl

CALLES : phys

MAIN VARIABLES

rh = relative humidity

t = temperature (K)

p1= partial vapor pressure of water

p1s= saturation vapor pressure of water

p2= partial vapor pressure of sulfuric acid

na= number concentration of water molecules

nb= number concentration of H_2SO_4 molecules

subroutine NOXMIN(NZ,NSPEC,INO,INO2,C)

PURPOSE

This subroutine has been designed to test if the NO_x values fall below a preset minimum value. The NO_x values can become very small in the late part of the day and as a result can cause severe problems with the numerical error control procedures.

CALLED BY: (not used in this version)

CALLS : none

MAIN VARIABLES

NZ = number of vertical layers

NSPEC = number of species

INO,INO2 = indices for NO and NO_2 in the species list

C = concentration array

ANOXMN = minimum NO_x concentration

subroutine NUMER(p1,p2,x,t,r,gamma,v)

PURPOSE

This subroutine solves numerically the system $\frac{dG}{dn_1} = 0.0$ $\frac{dG}{dn_2} = 0.0$ to find (x,r) at the saddle point.

CALLED BY: binucl

CALLS : phys

MAIN VARIABLES

p1=actual partial vapor pressure of H_2O in the atmosphere (Pa)

p2=actual partial vapor pressure of H_2SO_4 in the atmosphere (Pa)

x=mole fraction of H_2SO_4 in the critical nuclei

r= radius of the critical nuclei (m)

t=temperature (K)

function OLDDEP(X,DUMMY,TGAS,PGAS,NBTYPE)

PURPOSE

To Calculate the Surface Deposition Coefficients, for the processes of gravity (settling), diffusion (boundary layer), and thermophoresis.

CALLED BY: depost

CALLS : rhodd

MAIN VARIABLES

X = Log Particle Mass

DUMMY = Not Used

TGAS = Gas Temperature [K]

PGAS = Gas Total Pressure [Pa]

NBTYPE = Flag for Type of Section Coefficient:

7=Ceiling 8=Vertical Walls 9=Floor

DENAIR = Background Gas Density [kg m^{-3}]

FREEMP = Background Gas Mean Free Path [m]

VISCOS = Background Gas Viscosity [kg $m^{-1}sec^{-1}$]

OLDDEP = Deposition Coefficient

```
subroutine PAEROS(iaeros,TIMEM,NSPEC,SNAM,NPICS,NSICS,OPTION,
1 NLAY,NGX,NGY,ILX,ILY,NROWS,NCOLS,ILEFT,IRIGHT,
2 LENLAY,LENCON)
```

PURPOSE

To print the size composition distribution

CALLED BY: gmamod

CALLS : times

MAIN VARIABLES

iaeros = unit number for the output of the aerosol size composition distribution

TIMEM = current time

NSPEC = the number of species in the mechanism

NLAY = number of layers to be printed

NROWS = the number of rows in the modeling region

ILEFT = array containing the global x-coordinate of the first cell of each row

IRIGHT = array containing the global x-coordinate of the last cell of each row

NCOLS = number of columns

lenlay= number of grids in each layer

ilx = The global x-coordinate of the far left cell of the modeling region

ily = The global y-coordinate of the far bottom cell of the modeling region

ns = number of sections

nz = total number of cells in the modeling region

nvert = number of vertical cells

ds = array containing the sectional diameter boundaries of the aerosol

equl = array containing the aerosol species concentrations (See AEROSOL)

subroutine PHEAD(IPAGE,IPRIN)

PURPOSE

This subroutine has been designed to print page headings and to increment the page number each time it is called.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

IPAGE = page number to be printed

IPRIN = logical unit number of the output device

subroutine PHORAT(SLA,SLO,TZ,IY,IM,ID,T24MIN,NRATES,PRATES)

PURPOSE

This program calculates photolysis rate constants as a function of location and time for a variety of species that occur in photochemical modeling applications. The photodissociation rates as a function of the zenith angle have been previously calculated by a theoretical integration over UV wavelengths of the product actinic irradiance × absorption cross section × quantum yield.

CALLED BY: rate

CALLS : solar

MAIN VARIABLES

ZENITH = array of zenith angles corresponding to K values

Z = zenith angle

ZK......= array of photolysis rates for the various reactions as a function of Z.

IHR = number of hours since midnight

T24HR = 24hr standard clock time

SOLANG = solar elevation angle

RH0 = linear interpolation parameter

IUP,ILOW= upper and lower indices for array interpolation

subroutine PHYS(xstar,t,vv,vv1,vv2,gamma,dgamma,p1,p2,dens)

PURPOSE

This subroutine calculates all the physical properties of the mixture H_2SO_4-H_2O as function of the mole ratio of the H_2SO_4.

(1) = H_2O and (2) = H_2SO_4

NOTE:: All the equations used are fitting polynomials on experimental data.

CALLED BY: press, mole, numer

CALLS : none

MAIN VARIABLES

t =temperature (on entry in K)

V =molar volume of the solution

V1 =partial molar volume of the water in a solution with mole ratio (x) of H_2SO_4

V2 =partial molar volume of the H_2SO_4 in a solution with mole ratio (x) of H_2SO_4

GAMMA=surface tension of a solution H_2O-H_2SO_4 with mole ratio (x) of H_2SO_4

dGAMMA=derivative of the surphase tension of a solution H_2O-H_2SO_4 with respect to the mole ratio (x) of H_2SO_4

d =density of a solution H_2O-H_2SO_4 with mole ratio (x) of H_2SO_4

p1 =equilibrium vapor pressure of H_2O over a flat surface of a solution with mole ratio (x)

p2 =equilibrium vapor pressure of H_2SO_4 over a flat surface of a solution with mole ratio (x)

DPR =first derivative of d

vpr =first derivative of V

subroutine PLOAD(ADEF,ICNUM,NSPEC,ILAY,NROWS,ILEFT,IRIGHT,
1 ,CVEC,LENLAY,LENVEC,ILY,NGX,NGY,ARRAY)

PURPOSE

This program takes concentration data stored in string format and loads a requested species for a particular layer into an output array for display processing.

CALLED BY: conprt, confld

CALLS : none

MAIN VARIABLES

ADEF = default value to load into the non modeling region

ICNUM = species number to be loaded into output array

NSPEC = maximum number of species in the mechanism

ILAY = layer to be processed for output

NROWS = number of rows in the modeling region

ILEFT = array containing the global x-coordinate of the first cell of each row

IRIGHT = array containing the global x-coordinate of the last cell of each row

CVEC = concentration vector

LENLAY = length of the scalar string for one layer

LENVEC = length of the vector

ILY = lowest y-axis coordinate in global data region

NGX,NGY= dimensions of global data region

ARRAY = two-dimensional array holding the string data

```
subroutine PLUMER(HP,TS,VS,D,VF,PSTAB,U,X,DTHDZ,DTHDZI,ZI,
1 TA,PA,HX,HF,DISTF,QMW,F,M,IERR )
```

PURPOSE

This program calculates the plume rise from an elevated sorce of momentum and buoyancy. The formulas are based on the correlations of BRIGGS.

CALLED BY: plumht

CALLS : none

MAIN VARIABLES

HP = physical stack height (m)

TS = stack gas temperature (K)

VS = stack gas exit velocity (m $\sec^{-1}$)

D = inside stack diameter (m)

VF = volumetric flow rate (m^3 $\sec^{-1}$)

PSTAB = Pasquill-Gifford stability

RMOL = reciprocal of Monin-Obukhov length

U = wind speed (m $\sec^{-1}$)

X = downwind distance (m)

DTHDZ = potential temperature lapse rate, surface layer (K m^{-1})

DTHDZI = potential temperature lapse rate in inversion (K m^{-1})

TA = ambient temperature (K)

PA = ambient pressure (mb)

ZI = depth of mixed layer (m)

G = gravitational acceleration (m $\sec^{-2}$)

CP = specific heat of air

AMW = molecular weight of air

QC = heat conversion factor (4.1855×10^{-6} MW/CAL $\sec^{-1}$)

HX = plume height at downwind distance X (m)

HF = final plume height (m)

DISTF = downwind distance to final plume height (m)

QMW = heat output of the source (MW)

F = buoyancy flux parameter (m^4 $\sec^{-3}$)

M = momentum flux parameter (m^4 $\sec^{-3}$)

IERR = error return from subroutine

```
subroutine PLUMHT( NPTSRC,ICELLI,ICELLJ,STKHT,EGTEMP,EGRATE,
1 NROWS,ILEFT,IRIGHT,LENLAY,INDX,Z0,ZI,TEMPC,
2 LENWIN,U,V,APRESS,SRAD,FCLOUD,DX,HF,ILY,HEIGHT )
```

PURPOSE

This program has been designed to calculate the plume rise for each point source inside the modeling region.

CALLED BY: gmamod

CALLS : plumer, stabpm

MAIN VARIABLES

NPTSRC = number of point sources

ICELLI = I or X cell location in the global grid

ICELLJ = J or Y cell location in the global grid

STKHT = physical stack height

EGTEMP = exhaust gas temperature (K)

EGRATE = exhaust gas flow rate (m^3 sec^{-1})

NSPEC = maximum number of species in the mechanism

ILAY = layer to be processed for output

NROWS = number of rows in the modeling region

ILEFT = array containing the global x-coordinate of the first cell of each row

IRIGHT = array containing the global x-coordinate of the last cell of each row

LENLAY = length of the scalar string

INDX = index array to locate V components

Z0 = surface roughness

ZI = mixing height

TEMPC = ambient temperature (C)

LENWIN = length of the wind vector

U,V = U and V components of the wind FIELD

APRESS = atmospheric pressure (mb)

SRAD = solar radiation (w m^{-2})

FCLOUD = fraction cloud cover = 0 no cloud

DX = basic grid cell size

HF = plume rise for each of the sources

subroutine PNDEX (NSPEC,NROWS,ILEFT,IRIGHT,NCOLS,IBOT,ITOP,
1 NGX,NGY,ITEMP,INDVEC,LENVEC,ILX,ILY)

PURPOSE

This program has been designed to develop a vector of indices corresponding to the locations of points in the string arrays that are normal to the X-axis. The program is designed to handle the concentration array.

CALLED BY: gmamod

CALLS: none

MAIN VARIABLES

NROWS = number of rows in the modeling region

ILEFT(I) = X index for the far left cell of the I^{th} row (from bottom up)

IRIGHT(I)= X index for the far right cell of the I^{th} row (from bottom up)

NCOLS = number of columns in the modeling region

IBOT(I) = bottom Y index for the I^{th} column (from left to right)

ITOP(I) = top Y index for the I^{th} column (from left to right)

NGX,NGY = dimensions of the global data region

ITEMP = integer work array

ILX = The global x-coordinate of the far left cell of the modeling region

ILY = The global y-coordinate of the far bottom cell of the modeling region

NSPEC = number of chemical species in array

INDVEC = vector of indices

LENVEC = length of the index vector

subroutine POINAL(NPTSRC,ICELLI,ICELLJ,EGRATE,PEMISS,HF,NE,
1 IEMORD,C,LENLAY,NSPEC,NVERT,DX,HEIGHT,DZRHO,U,V,ZI,Z0,ILY,
2 NROWS,ILEFT,IRIGHT,FCLOUD,SRAD,DTCHMM,IERROR)

PURPOSE

This program has been designed to act as a simple point source module for the injection of pollutant emissions into a three-dimensional computational grid.

CALLED BY: gmamod

CALLS : alocem, stabpm

MAIN VARIABLES

PEMISS = emissions from the point sources

NE = number of emission species

IEMORD = index array for the emission species

C = concentration array

NVERT = number of vertical layers

DX = grid cell size

HEIGHT = height of the modeling region

DZRHO = array of dimensionless grid cell heights

ILY = The global y-coordinate of the far bottom cell of the modeling region

DTCHMM = time step (min)

IERROR = error flag (=0 no error)

NPTSRC = number of point sources

ICELLI = I or X cell location in the global grid

ICELLJ = J or Y cell location in the global grid

EGRATE = exhaust gas flow rate (m^3 sec^{-1})

NSPEC = maximum number of species in the mechanism

ILAY = layer to be processed for output

NROWS = number of rows in the modeling region

ILEFT = array containing the global x-coordinate of the first cell of each row

IRIGHT = array containing the global x-coordinate of the last cell of each row

LENLAY = length of the scalar string

INDX = index array to locate V components

Z0 = surface roughness

ZI = mixing height

TEMPC = ambient temperature (C)

LENWIN = length of the wind vector

U,V = U and V components of the wind FIELD

APRESS = atmospheric pressure (mb)

SRAD = solar radiation (w m^{-2})

FCLOUD = fraction cloud cover = 0 no cloud

DX = basic grid cell size

HF = plume rise for each of the sources

integer function POWR(ARRAY, NX, NY, DEFALT, IWIDTH)

PURPOSE

This function choses a power of 10 by which all elements of a 2-d array may be multiplied to produce an integer value with a maximum number of digits of IWIDTH.

CALLED BY: FILLI, CONPRT

CALLS: none

MAIN VARIABLES

powr = power of 10 used in scaling

array = concentration array

xmax = max concentration

xmin = min concentration

iwidth= number of significant digits (typically 4)

subroutine PPREP(KHOUR,NEMAX,IHOUR,ICELLI,ICELLJ,ISID,STKHT,

1 EGTEMP,EGRATE,PEMS,NPMAX,IEMS,IMIN,JMIN,

2 NROWS,ILEFT,IRIGHT)

PURPOSE

This program processes emission records and creates input arrays for the Caltech model. Multiple calls of the module must have hours in sequential order 0 to 2300.

CALLED BY: gmamod

CALLS: none

MAIN VARIABLES

EMTOT = total emissions for this hour

NEMAX = maximum number of emission species

IPHOUR = string index for point source locations

ICELLI = X cell location of point sources

ICELLJ = Y cell location of point sources

STKHT = point source stack height

EGTEMP = exhaust gas temperatures

EGRATE = volumetric gas flow rate

PEMS = point source emissions by species

ILEFT = left or west side of modeling region

IRIGHT = right or east side of modeling region

NROWS = number of rows in the modeling region

IMIN = minimum I index for the computational region

JMIN = minimum J index for the computational region

subroutine press(q)

PURPOSE

This subroutine updates the physical properties of the various species.

CALLED BY: maeros, diffun

CALLS: phys

MAIN VARIABLES

ps = vapor pressure of the various species over a solution surface

ps0 = saturation vapor pressure

solub= solubilities of the various organics in water [g-organic/ g-water]

qmin= minimum non-zero concentration

suml= total organic mass

sq = total inorganics in aqueous solution

conmw= molecular weights of the species contained in (Q)

sum = total organics in separate phase (μg m^{-3})

smole = total organics in separate phase (kmole m^{-3})

undis(i)= concentration of species i in separate phase

subroutine PRINT(ADEF, NAME, LEVEL, OPTION, ARRAY, NROWS,
1 ,NCOLS, ILEFT, IRIGHT, ILX, ILY, TIME, NGX, NGY, IPRINT)

PURPOSE

This subroutine prints an array of NGX by NGY dimension starting at the ILX AND ILY position for only the number of columns and rows that have actual data. All positions in the array that have no data (i.e., the value adef) and are within the specified bounds are left blank on the printout.

CALLED BY: conprt

CALLS : ttl, fillln

MAIN VARIABLES

ARRAY = real array with concentrations

IARRAY = integer array with concentrations

NGX,NGY = dimensions of the global grid

ADEF = default unit values

NAME = name of the species to be printed

NAME1, NAME2 = names of the aerosol species to be printed

FACTOR = scaling factor

ILX = The global x-coordinate of the far left cell of the modeling region

ILY = The global y-coordinate of the far bottom cell of the modeling region

subroutine PR1(q)

PURPOSE

This subroutine calculates the partial pressure at infinity of the condensable species, given the concentration

CALLED BY: maeros, diffun

CALLS: none

MAIN VARIABLES

tgas = temperature

nz= number of vertical cells

ns, ms = number of sections

kc, kcon = number of different species

nemax= maximum number of equations that can be treated by EPISODE

q= string with the species concentrations

nz= number of vertical cells

pl = partial pressure of the various gases

conmw= molecular weights of the species contained in (Q)

subroutine RATE(SLA,SLO,TZ,IY,IM,ID,TIME,SCALE)

PURPOSE

This program calculates the reaction rate constants for the photochemical reaction mechanism implemented within the airshed model.

CALLED BY: gmamod

CALLS : phorat

MAIN VARIABLES

HUMID = relative humidity (not used)

INUM = array of reaction rate numbers that are to be changed

IY,IM,ID= year month and day of the simulation

NPRATE = number of photolytic species reactions stored in PHORAT

NRATES = number of rate constants

NUPDAT = number for rate constants to be updated

PR = vector of photolysis rate constants

PRESS = pressure (not used)

RAT = values that are to be substituted

RK = vector of rate constants

SCALE = scale factor to be applied to photolysis rate constants

SLA,SLO = latitude and longitude of the modeling region (deg)

TEMPC = temperature (C)

TEMP = temperature (K)

TIME = standard time (min)

TZ = time zone for the modeling region

subroutine RATEM(DTMIN,H,NSPEC,EMT,NE,IEM,EMISS)

PURPOSE

This program has been designed to allocate area source emissions to computational cells. The program accepts emissions in flux units, i.e., (ppm m min-1) and converts them to concentration emissions in the appropriate grid cells.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

DTMIN = computational time step (min)

H = height of the computational cell (m)

NSPEC = number of species in the mechanism

NE = number of emission species

IEM = index array for the emission species in C

EMISS = array of emissions

EMT = array of emission rates in the cell

subroutine RATEP (IPRIN,IOPT,TOUT,NRATES,RK)

PURPOSE

This subroutine prints the reaction rate constants corresponding a particular output time TOUT.

CALLED BY: gmamod

CALLS : times

MAIN VARIABLES

IPRIN = logical unit number of the line printer

IOPT = option to skip to a new page = 0 NO, =1 NEW PAGE

TOUT = time corresponding to rate constant output

NRATES = number of rate constants

RK = array of the rate constants

NDAYS = current day number of simulation

NHRS = hour component of 24 hr clock time

NMINS = minute component of 24 hr clock time

T = a dummy variable to save current time

subroutine READ24(ICARD,NT,TA,VAL)

PURPOSE

This subroutine reads 24 hourly averaged values and assigns the data point to the half-hour point.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

ICARD = logical unit number of the card reader

TA = time array

VAL = array of data values

NT = number of time points

subroutine RECFMT(ITYPE,ISKIP,IW,ID,NVALS,ROW,COL)

PURPOSE

This subroutine has been designed to set up the format statements for the matrix print routine.

CALLED BY: matout

CALLS : none

MAIN VARIABLES

ITYPE = format type =0 ‘E’, =1 ‘F’, =2 ‘G’

IW,ID = format(IW.ID) note ID must be less than 10, IW $\geq$ 3

ISKIP = line spacing =0 single, =1 double spacing (default single)

NVALS = number of values to be printed on a line

ROW = format for each output row

COL = format for the column

DIGIT = array of numerical digits

IE,IF = characters ‘E’,‘F’ for format statement

IBLNK = blank character

ROWFMT= default row format

COLFMT= default column format

NPOSN = number of positions for field width

IFD = first digit

ISD = second digit

```
subroutine REGION(LYEAR,LMONTH,LDAY,NROWS,NCOLS,NCELLS,
1 NXSQR,NYSQR,ILEFT,IRIGHT,JBOT,JTOP,IMIN,JMIN,
2 IOPTR,IREAD,IPRINT)
```

PURPOSE

This routine reads in the definition of the computational region within the master data grid. The program accepts only convex modeling regions (i.e., no reentrant boundaries). The computational region is defined in terms of the start and stop column indices (x-direction) for each row (y-direction). The row indices may be entered in either increasing or decreasing order.

CALLED BY: gmamod, rural, dprep

CALLS : mapcom

MAIN VARIABLES

NROWS = number of rows in modeling region

ILEFT = array of far left indices for each row

IRIGHT = array of far right indices for each row

NCOLS = number of columns in the modeling region

JBOT(I) = bottom Y index for the I^{th} column (from left to right)

JTOP(I) = top Y index for the I^{th} column (from left to right)

IMIN = minimum I index for the computational region

JMIN = minimum J index for the computational region

LYEAR = year read from region definition file

LMONTH = month read from region definition file

LDAY = day read from region definition file

NCELLS = number of vertical cells

NXSQR = number of cells in x-direction of master grid

NYSQR = number of cells in y-direction of master grid

IOPTR = option to print the computational cell map (=1 yes, =0 no)

IPRINT = logical unit number of output device for the map subroutine REHEAD(IDM,IPRINT,IDUM)

PURPOSE

This file is used just as a dummy file to read the file headers the first time through.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

subroutine RESTAR(ILRES,IPOSN)

PURPOSE

This is a simple program to indicate the position in the calling program for the purposes of restarting after a system crash. (Not important for CRAY use)

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

ILRES = logical unit number of the restart file

IPOSN = position in the code from where restar was called

subroutine RESTRT(ISHR,ISMIN,IPRINT,IAVG1,INST,LENCON,NVERT,C)

PURPOSE

This program is needed for restarting the airshed model. (Not important for CRAY use)

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

ISHR = starting hour

ISMIN = starting minutes

IPRINT = logical unit number of output device for the map

LENCON = length of the concentration array

C = concentration vector

NVERT = number of vertical layers

subroutine RHODD(V,D,RHO)

PURPOSE

To Interconvert Particle Mass and Diameter. Whichever one is set to zero will be calculated from the other.

CALLED BY: beta, calciz, coef, depost, growth, olddep

CALLS : none

MAIN VARIABLES

V = Particle Mass [kg] Note: Set to 0.0 if to be found from D

D = Particle Diameter [m] Note: Set to 0.0 if to be found from V

RHO = (Constant) Particle Density [kg m^{-3}]

```
subroutine ROD(NSPEC,IHNO3,INH3,iaer,ISO4,inacl,ihcl,
1 ic4h6o4,ic5h8o4,ic6h10o4,icreno2,iprimc,dt,
2 newcof,iaer1,iaer2,iaer3,iaer4,iaer5,iaer6,iaer7,iaer8,
3 lenlay)
```

PURPOSE

This program is the main driver of the aerosol calculations. It transfers all the necessary data from the global elements to the "trajectory" kind ones and then it calls RODOS to perform the actual calculations.

CALLED BY: gmamod

CALLS : rodos

MAIN VARIABLES

aernh3(i)= total ammonium in the aerosol phase in the i^{th} grid (global elements)

aenh3(i)= total ammonium in the aerosol phase in the i^{th} grid (local elements)

aerno3(i)= total nitrate in the aerosol phase in the i^{th} grid (global elements)

aeno3(i)= total nitrate in the aerosol phase in the i^{th} grid (local elements)

aercl(i) = total chloride in the aerosol phase in the i^{th} grid (global elements)

aecl(i) = total chloride in the aerosol phase in the i^{th} grid (local elements)

aerh2o(i)= total water in the aerosol phase in the i^{th} grid (global elements)

aeh2o(i)= total water in the aerosol phase in the i^{th} grid (local elements)

sourcl =average production in gas phase (global elements)

sinitl =initial gas concentration (global elements)

source =average production in gas phase (local elements)

siniti =initial gas concentration (local elements)

dt =time step of the trajectory model

nspec =number of species

nz =number of grids

I.... =index corresponding to various species

c = array containing the species concentrations (global elements)

cnt= array containing the species concentrations (local elements)

taer = array containing the aerosol concentrations of the previous step (global)

taerl = array containing the aerosol concentrations of the previous step (local)

equl = size composition distribution (global elements)

equll = size composition distribution (local elements)

```
SUBROUTINE RODOS(NSPEC,IHNO3,INH3,iaer,ISO4,inacl,ihcl,
1 ic4h6o4,ic5h8o4,ic6h10o4,icreno2,iprimc,tmpc,rhi,
2 dt,newcof,iaer1,iaer2,iaer3,iaer4,iaer5,iaer6,iaer7,iaer8,
3 begin)
```

PURPOSE

To perform the aerosol dynamic and thermodynamic calculations

CALLED BY: rod

CALLS : dynamic, aeromain, aeroml, intersec

MAIN VARIABLES

aernh3(i)= total ammonium in the aerosol phase in the i^{th} grid (local elements)

aerno3(i)= total nitrate in the aerosol phase in the i^{th} grid (local elements)

aercl(i) = total chloride in the aerosol phase in the i^{th} grid (local elements)

aerh2o(i)= total water in the aerosol phase in the i^{th} grid (local elements)

dt =time step of the trajectory model

nspec =number of species

nz =number of vertical grids

I.... =index corresponding to various species

c= array containing the species concentrations (local elements)

taer = array containing the aerosol concentrations of the previous step (local)

equl = size composition distribution (local elements)

ns, ms, nsec = number of sections

nemax= maximum number of ODE's that the subroutines can handle

sratio = ratio of the current aerosol concentration over the aerosol concentration of the previous step

q = string of the aerosol species in the various sections (Kg m^{-3})

qgas = concentrations of the condensable species in the gas phase

hvqst= average intrasectional condensation rate of the volatile species (sec^{-1})

qtotal(i,j) = total aerosol concentration in section j in cell i

qnonvola = sectional concentration of the non-volatiles (Kg m^{-3})

qmin, qmin1 = minimum masses used to avoid overflows

kc, kcon = number of condensable species

subroutine RURAL(IRURAL,NX,NY,NIC,NA,IREAD,IDREAD,IPRINT,
1 IOPT1,LENLAY)

PURPOSE

This program reads a file defining the rural and ocean areas over the master grid for use in generating initial conditions.

CALLED BY: gmamod

CALLS : region, strip

MAIN VARIABLES

DX = grid spacing in X-direction

DY = grid spacing in Y-direction

DZ = vector of non-dimensional cell heights

IBCOND = subgrid boundary concentration data file

ICODE = code word written on file

ICOND = subgrid initial concentration data file number

IEND = right end of subgrid

ILEFT = vector of left limits of subgrid

IPRINT = file number for printed output

IREAD = file number for card input

IRIGHT = vector of right limits of subgrid

IMIN = far left end of subgrid

ITEXT = descriptive information read from main files

JBOT = vector of lower limits of subgrid

JEND = top of subgrid

JMIN = bottom of subgrid

JTOP = vector of upper limits of subgrid

KMAX = number of elements in subgrid vector

LDAY = day for which data are to be processed

LMONTH = month for which data are to be processed

LYEAR = year for which data are to be processed

HTMOD = height of model above terrain

NCELLS = number of vertical cells

NLINES = number of lines of text

NXSQR = number of grid points in X-direction (full grid)

NUMY = number of grid points in X-direction (subgrid)

NYSQR = number of grid points in Y-direction (full grid)

NUMX = number of grid points in Y-direction (subgrid)

TEMP = temporary vector

TEXT = descriptive information to be written on file

VX = X-component of velocity

VY = Y-component of velocity

VZ = Z-component of velocity

subroutine RURALSP(THC2,IRL,NHYCAR)

PURPOSE

This program sets the rural and ocean splits for splitting the hydrocarbons

CALLED BY: alocicr

CALLS : none

MAIN VARIABLES

THC2 = array containing the output hydrocarbon split

THCR = array containing the rural hydrocarbon split

THCO = array containing the ocean hydrocarbon split

subroutine SECTION(n,x,ff,ifal)

PURPOSE

Calculates the values of the functions, whose zeros we want to find

CALLED BY: c05nbf

CALLS : equilib

MAIN VARIABLES

temp = temperature (K)

rh = relative humidity

nsec = number of sections

n = number of equations to be solved by c05nbf

ff = array containing the values of the functions whose zeros we want to find

x = the values of the independent variables

subroutine SETGAS(TGAS,PGAS)

PURPOSE

To set gas properties kept in /GAS/ COMMON.

CALLED BY: beta, coef, dynamic, maeros, depost, olddep

CALLS : none

MAIN VARIABLES

TGAS = Gas Temperature [K]

PGAS = Gas Total Pressure [Pa]

TEMP = Gas Temperature [K]

PRES = Gas Total Pressure [Pa]

DENAIR = Gas Density [kg m^{-3}]

FREEMP = Gas Mean-Free Path [m]

VISCOS = Gas Viscosity

subroutine SETPAN(CN,NSPEC,IPAN,IO3,ICO)

PURPOSE

This subroutine sets the initial PAN concentrations to be a fraction of the O_3 concentration

CALLED BY: bond, gmamod

CALLS : none

MAIN VARIABLES

CN = species concentrations

NSPEC = number of species in the mechanism

IPAN = index for PAN in the species list

IO3 = index for O_3 in the species list

RAT = ratio of PAN over O_3 (now 0.10)

subroutine SHADE(A,NX,NY,IUP,LAW,IL,IH,NEG,IPRIN,ISKIP,NC,TITLE)

PURPOSE

This subroutine has been designed to produce a shaded image on the line printer through the use of a 32 level grey scale. The program produces the shading through the use of overprinting up to five characters. The algorithm can perform linear, square-root and logarithmic scaling of input data, as well as create negative images.

CALLED BY: conprt, confld

CALLS : none

MAIN VARIABLES

IA = integer array to be scaled

NX,NY = number of rows and columns

IUP = option to print row number (N first = 0 ,N last =1)

LAW = grey level scale translation variable

IL,IH = minimum and maximum grey levels to be used

NEG = image type (=0 normal, =-1 negative image)

IPRIN = logical unit number for the line printer

NC = number of characters in the title

ISKIP = option to skip to a new page (=0 NO, =1 YES)

TITLE = title to be annotated on the output

subroutine SOLAR (SLA,SLO,TZ,IY,IM,ID,TIME,D,NV)

PURPOSE

This subroutine computes, for a given location and time, a variety of parameters related to attributes of the earth-sun relationships.

CALLED BY: solcal, sunud, phorat

CALLS : none

MAIN VARIABLES

SLA = latitude (deg., south= minus)

SLO = longitude (deg., east = minus)

TZ = time zone

IY = year

IM = month

ID = day

TIME = local standard time

D = returned value

NV = value to be returned, selected as follows:

1... declination (deg.)

2... equation of time adjustment (hrs.)

3... true solar time (hrs.)

4... hour angle (deg.)

5... solar elevation (deg.)

6... optical airmass

subroutine SOLCAL(SOL,IHOUR,IOPT,IPRIN,SLA,SLO,TZ,IY,IM,ID,

1 RADMAX)

PURPOSE

This subroutine calculates total solar intensity, solar zenith angle, sunrise and sunset times for an arbitrary hour and location.

CALLED BY: gmamod

CALLS : solar

MAIN VARIABLES

SOL = total solar intensity (watts m^{-2})

IHOUR = hour for which solar intensity is calculated

IOPT = print option flag (0=no print, 1=print)

IPRIN = unit number for the print file

SLA = latitude

SLO = longitude

TZ = time zone

IY = year

IM = month

ID = day

RADMAX = maximum solar radiation factor (LA = 1000.)

SUNR = sunrise time

SUNS = sunset time

subroutine SOURCE(ICARD,NSPEC,IERR,SNAM,NT,TA,EF)

PURPOSE

This subroutine reads the source data for each species

CALLED BY: none

CALLS : none

MAIN VARIABLES

ICARD = logical unit number of the card reader

NSPEC = number of species

IERR = error flag

SNAM = array of valid species names

NT = number of times

EF = array of direct emissions

END = character string to indicate end of the data

SNAME = species name read from the card

ICOD = code to indicate single values for emissions(=1)

VALUE = emission rate to hold for all times subroutine SOURCZ(ICARD,NZ,NSPEC,IERR,SNAM,NT,TA,EE)

PURPOSE

This subroutine reads the elevated source data for each species

CALLED BY: none

CALLS : none

MAIN VARIABLES

ICARD = logical unit number of the card reader

NSPEC = number of species

IERR = error flag

SNAM = array of valid species names

NT = number of times

EE = array of direct elevated emissions

END = character string to indicate end of the data

SNAME = species name read from the card

ICOD = code to indicate single values for emissions(=1)

VALUE = emission rate to hold for all times

NZ = number of vertical layers

subroutine SOURPT(IPRIN,NSPEC,SNAM,NZ,EA,EE)

PURPOSE

This program has been designed to print the source contributions from both point and area sources. A special feature of the routine is that it prints only the non-zero source terms.

CALLED BY: none

CALLS : none

MAIN VARIABLES

IPRIN = logical unit number for the line printer

NSPEC = number of species

SNAM = species names

NZ = number of layers

EA = area source emissions

EE = elevated emissions

subroutine SPACE(NCELLS,DZRHO,HEIGHT,DZDIM,CELCEN)

PURPOSE

This subroutine has been designed to calculate the physical cell heights and the elevation of the cell centers above the ground, given the region height and the corresponding set of RHO values. The RHO coordinate is the non-dimensional form of the Z-axis.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

NCELLS = number of vertical cells

DZRHO = RHO dimension of each cell

HEIGHT = region height

DZDIM = cell sizes in dimensional form

CELCEN = height of the center of each cell above the ground subroutine SPECIN(ICARD,NSPEC,IERR,SNAM,CDATA)

PURPOSE

This program reads species cards and data. The program reads integer flags to set print and plot requests. A feature of the program is that it checks to see that each species has the correct 4-character code. The principal use of the program is to avoid preparing input cards for species that have no data or zero data.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

ICARD = logical unit number of the input device

NSPEC = number of species

IERR = error code (= 0 no error)

SNAM = array of species names

CDATA = array of data values on return

END = characters to signify the end of data for this input

SNAME = species name read from the card

VALUE = data value for this species

subroutine SPECRD(ICARD,NSPEC,IERR,SNAM,NRHC,IRHC,THCS,RHCS,
1 CDATA)

PURPOSE

This subroutine reads species cards and data. The program can be used to input initial conditions, deposition velocities, background and entrained concentration levels.

A feature of the program is that it checks to see that each species has the correct 4-character code. The principal use of the program is to avoid preparing input cards for species that have no data or zero data. The program also has the option to apportion either THC or RHC hydrocarbon splits if no detailed speciation data are available.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

ICARD = logical unit number of the input device

NSPEC = number of species

IERR = error code (= 0 no error)

SNAM = array of species names

CDATA = array of data values on return

END = characters to signify the end of data for this input

SNAME = species name read from the card

VALUE = data value for this species

NRHC = number of reactive hydrocarbons

IRHC = array containing the array indices for the hydrocarbons

THCS = splitting factors for the total hydrocarbons

RHCS = splitting factors for the reactive hydrocarbons

subroutine SPECRZ(ICARD,NZ,NSPEC,IERR,SNAM,
1 NRHC,IRHC,THCS,RHCS,CDATA)

PURPOSE

This subroutine reads species cards and data. The program can be used to input initial conditions, deposition velocities, background and entrained concentration levels. A feature of the program is that it checks to see that each species has the correct 4-character code. The principal use of the program is to avoid preparing input cards for species that have no data or zero data. The program also has the option to apportion either THC or RHC hydrocarbon splits if no detailed speciation data are available.

CALLED BY: none

CALLS : none

MAIN VARIABLES

ICARD = logical unit number of the input device

NSPEC = number of species

IERR = error code (= 0 no error)

SNAM = array of species names

CDATA = array of data values on return

END = characters to signify the end of data for this input

SNAME = species name read from the card

VALUE = data value for this species

NRHC = number of reactive hydrocarbons

IRHC = array containing the array indices for the hydrocarbons

THCS = splitting factors for the total hydrocarbons

RHCS = splitting factors for the reactive hydrocarbons

subroutine STABPM(SRAD,Z0,USURF,FCLOUD,RMOLEN,PASQIL)

PURPOSE

This program has been designed to calculate the Pasquill-Gifford stability class and the Monin-Obukhov length corresponding to given surface conditions. Both stability parameters are useful in determining turbulent diffusion coefficients.

CALLED BY: plumht, kzprof, kxxyy, diffld, poinal

CALLS : none

MAIN VARIABLES

SRAD = Total solar radiation (watts m^{-2})

Z0 = surface roughness

USURF = surface wind speed (m sec^{-1})

FCLOUD = fraction cloud cover

RMOLEN = resiprocal of the Monin-Obukhov length

PASQIL = Pasquill-Gifford stability number

UBAR = absolute value of the wind velocity

PSTAB = array of Pasquill stability conditions A=1, B=2, ...F=6.

A,B = coefficients for straight line fit to Golder's plot

ZMAX = maximum surface roughness

NCLASS = Pasquill - Gifford stability class number subroutine START1(IPRIN)

PURPOSE

This program prints the first page for the airshed aerosol model as an indication of the page start and program beginning.

CALLED BY: gmmain

CALLS : none

MAIN VARIABLES

iprin = unit number of line printer

subroutine STEP(DTM,UMAX,DTMIN,DTMAX,

CMAX,DX,NSTEPS,DTA,DTC)

PURPOSE

This function calculates the number of steps required to complete an integration step over the chemistry and the transport components so that total time is consistent with the averaging time for emissions and meteorology. The program uses the Courant-Fredrichs-Lewy (CFL) condition to determine the maximum step size.

CALLED BY: none

CALLS : none

MAIN VARIABLES

DTM = averaging time for meteorology or emissions

UMAX = maximum absolute velocity in model region

DTMIN = minimum acceptable time step

DTMAX = maximum acceptable time step

CMAX = maximum courant number at which to run scheme

DX = grid cell size

NSTEPS = number of time steps

DTA = size of the advection step

DTC = size of chemistry or total step

subroutine STOIC(RK1,INO,INO2,IO3,C)

PURPOSE

This subroutine adjusts the initial NO, NO_2 AND O_3 values when K1 is zero (no sunlight), so that they are stoichiometrically correct before the integration process begins.

CALLED BY: none

CALLS : none

MAIN VARIABLES

c = concentration of various species

ino = number for NO

ino2 = number for NO_2

io3 = number for O_3

subroutine STOICH(RK1,INO,INO2,IO3,C)

PURPOSE

Finds the ammonium nitrate concentration

CALLED BY: none

CALLS : none

MAIN VARIABLES

AM = input ammonia concentration

NIT = input ammonium nitrate concentration

E = equilibrium dissociation constant

AN = ammonium nitrate

NITC= corrected nitric acid

AMC = corrected ammonia

subroutine STRIP(TEMP,ARRAY,ITYPE,LLEFT,LRIGHT,MIN,NT,NUM,

1 KMAX,NX,NY,NZ)

PURPOSE

This subroutine strips off subregions of multidimensional arrays and loads the values into a one-dimensional array

CALLED BY: aprep, dprep, rural

CALLS : none

MAIN VARIABLES

ITYPE = 1 X-dimension loaded first

ITYPE = 2 Y-dimension loaded first

ITYPE = 3 Z-dimension loaded first

LLEFT(I) = X index for the far left cell of the I^{th} row (from bottom up)

LRIGHT(I)= X index for the far right cell of the I^{th} row (from bottom up)

NZ = number of vertical layers

NUM = number of rows in the modeling region

MIN = y-coordinate of the farther bottom cell

subroutine SUNUD(SLA,SLO,TZ,IY,IM,ID,SUNR,SUNS,DAYLEN,
1 ISRHR,ISRMN,ISSHR,ISSMN,DECLN)

PURPOSE

This program has been designed to calculate the time for sunrise and sunset at the modeling location. The results are expressed in terms of minutes from midnight standard time. So if the routine is used during periods of daylight saving time, be careful to take the time shift into account.

CALLED BY: gmamod

CALLS : solar

MAIN VARIABLES

SLA,SLO = latitude and longitude of location in degrees

TZ = time zone for the region

IY,IM,ID = date in the form year-month-day

SUNR,SUNS = time in minutes from midnight for sunrise and sunset

DAYLEN = length of the day in minutes

DECLN = declination angle in degrees

ISRHR = sunrise time in hours

ISRMN = sunrise time in minutes

ISSHR = sunset time in hours

ISSMN = sunset time in minutes

subroutine SZERO(NSPEC, SCDOT, SJAB)

PURPOSE

This subroutine puts the source terms equal to zero.

CALLED BY: none

CALLS : none

MAIN VARIABLES

NSPEC = number of species

SCDOT = source term array

SJAB = array of elements for the Jacobian terms

subroutine TIMES(TMIN, NDAY, NHRS, NMINS)

PURPOSE

This subroutine accepts a time (TMIN) expressed in minutes from 00:00 and converts it to the appropriate number of 24 hrs. clock time to the nearest minute on the current day.

CALLED BY: ratep, conspz, conspp, conprt, paeros

CALLED BY: confld, concpr

CALLS : none

MAIN VARIABLES

TMIN = time in minutes from the beginning of the start day

NDAY = current day number for the simulation

NHRS = hour component of the 24 hrs. clock time

NMINS = minute component of the 24 hrs. clock time

T = a dummy variable to save modifying TMIN function TINT(T,NT,TA,YA)

PURPOSE

This function performs a linear interpolation of tabulated data with special treatment at the start and end points, if T is beyond the bounds of the time array, the AINT is set to the value of the appropriate end points.

CALLED BY: direcz, direct

CALLS : none

MAIN VARIABLES

N = number of tabulated values

T = time at which interpolation is performed

TA = array of time values

YA = array of function values

TINT = interpolated table values

subroutine TMSTP(DTSTAB,NCT,DTADV,DTCHM)

PURPOSE

This program has been designed to calculate the integral number of time steps, during one hour, for numerical integration of both the chemistry and the transport, subject to the stability limits.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

DTSTAB = maximum time step based on stability for advection

NCT = number of composite time steps

DTADV = advection time step

DTCHM = chemistry time step

TSTEPS = time steps to give integral number of minutes

NSTEPS = number of time steps associated with TSTEPS

NINCS = number of divisions of the hour

function TNORM(T)

PURPOSE

This function normalizes a time in minutes from the start of a simulation to a 24hr period.

CALLED BY: none

CALLS : none

MAIN VARIABLES

T = time in minutes from the start of the simulation

TNORM = 24hr time in minutes from 00:00

function TNOX(INO,INO2,NSPEC,C)

PURPOSE

This function calculates the total NO_x ($NO + NO_2$)

CALLED BY: none

CALLS : none

MAIN VARIABLES

NSPEC = number of species

C = concentration vector

TNOX = total NO_x ($NO+ NO_2$) expressed as NO_x

INO2 = index of NO_2 in C

INO = index of NO in C

```
subroutine TRANSC( IXORY,NSPEC,IPINDT,NROWS,ILEFT,IRIGHT,
1 LENVEC,INDPI,INDX,U,ZI,KXXYY,CL,CR,DT,DX,C,IERR,NLEVEL,
2 DZRHO,HEIGHT,IFLUX,NPFLUX,SMW,ILX,ILY,
3 FLUXL,FLUXR )
```

PURPOSE

This program performs the transport calculations in the X-Y plane, using a fourth-order finite element numerical integration. The routine has the capability to transport multiple species and can be used for multiple layers in the atmosphere.

CALLED BY: gmamod

CALLS : advect

MAIN VARIABLES

IXORY = flag to indicate X or Y direction (= 1 X, = 0 Y)

NSPEC = number of chemical species

IPINDT = index to denote transport option for species (=0 NO, =1 Y)

NROWS = number of rows in modeling region

ILEFT = array of far left indices for each row

IRIGHT = array of far right indices for each row

LENVEC = length of a single layer scalar array

INDPI = index array for the pollutants

INDX = index array for integration in Y - direction

U = wind magnitude in direction of vector

ZI = mixing height

KXXYY = field of diffusion coefficients

C = concentration field at time T

CL,CR = boundary values at each end of the rows

DT = time step for integration

DX = cell grid size

function TRHC(NSPEC,C,NRHC,IRHC)

PURPOSE

This function calculates the total reactive hydrocarbon concentration from the species vector C. This routine is useful for atmospheric applications in which comparisons can be made only against non-methane hydrocarbom measurements.

CALLED BY: none

CALLS : none

MAIN VARIABLES

C = concentration vector

NSPEC = number of species

NRHC = number of reactive hydrocarbon species

IRHC = array of reactive hydrocarbon indices

TRHC = total reactive hydrocarbon concentrations subroutine TRIDAG (N, A, B, C, X, Y, BETA, GAMMA)

PURPOSE

This subroutine solves a set of N tridiagonal equations, using LU decomposition and back substitution.

CALLED BY: none

CALLS : none

MAIN VARIABLES

N = number of equations

A,B,C = coefficients of the tridiagonal matrix

X = required solution vector

Y = right-hand side vector

BETA = intermediate vector

GAMMA = intermediate vector

subroutine TTL(IPRINT)

PURPOSE

To print the character '1'.

CALLED BY: print

CALLS : none

MAIN VARIABLES

IPRINT = file number for printed output

function UCFL(NDIM,UMIN,UMAX,VMIN,VMAX,WMIN,WMAX)

PURPOSE

This function has been designed to calculate the maximum absolute velocity in the modeling region for use in determining the step-size base on the Courant-Fredrichs-Lewy (CFL) condition.

CALLED BY: none

CALLS : none

MAIN VARIABLES

NDIM = number of dimensions

UMIN,VMIN,WMIN = minimum velocities in each direction

UMAX,VMAX,WMAX = maximum velocities in each direction

UCFL = maximum velocity over whole region

function US(ZR,Z0,UBAR,RMOLEN)

PURPOSE

This program has been designed to calculate the surface level friction velocity U* for a range of meteorological conditions. The calculations are based on the integral form of the Businger PHI functions for the stable and unstable cases.

CALLED BY: depvel, kxxyy, kzprof

CALLS : none

MAIN VARIABLES

ZR = reference height for the wind measurements

Z0 = surface roughness height

UBAR = absolute value of the wind velocity at height ZR

US = friciton velocity U*

RMOLEN= reciprocal of the Monin-Obukhov length

VK = Von Karman constant

subroutine WATER(TEMP,PRESS,RH,PSAT,PPMH2O,UGMH2O)

PURPOSE

This program has been designed to calculate the atmospheric water vapor concentration, given the ambient temperature, pressure and relative humidity. The formulation is based on the assumption that the perfect gas laws apply to the air-water vapor mixture.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

TEMP = ambient temperature (C)

PRESS = atmospheric pressure (mb)

RH = relative humidity (%)

PSAT = saturation pressure (mb)

PPMH2O = water concentration (ppm)

UGMH2O = water concentration (μg m^{-3})

TDEGK = temperature (K)

PA = standard atmospheric pressure (1013.25 mb)

TS = steam temperature (373.15 K)

function WS(ZR,Z0,UBAR,RMOLEN,ZI)

PURPOSE

This program has been designed to calculate the surface level convective velocity scale W* for use in determining mixing times. The calculations are based on the integral form of the Businger PHI function for unstable meteorological conditions.

CALLED BY: diffld

CALLS : none

MAIN VARIABLES

ZR = reference height for the wind measurements

Z0 = surface roughness height

UBAR = absolute value of the wind velocity at height ZR

US = friciton velocity U*

RMOLEN= reciprocal of the Monin-Obukhov length

VK = Von Karman constant

WS = convective velocity scale W*

ZI = mixed layer height

subroutine WTEXT(ICARD,IPRIN,IOPT)

PURPOSE

This subroutine has been designed to write descriptive text on the line printer when called by any other routine. The program reads input records until an '*' is encountered in column 1 and then returns to the calling program.

CALLED BY: none

CALLS : none

MAIN VARIABLES

ICARD = logical unit number of card reader

IPRIN = logical unit number of line printer

IOPT = option to skip a page (=0 NO, =1 YES)

IAST = test character for the end of data (*)

IA = input array

subroutine WTEXT2(ICARD,IPRIN,IOPT,NLINED,IDTEXT)

PURPOSE

This subroutine has been designed to write descriptive text on the line printer when called by any other routine. The program reads input records until an '*' is encountered in column 1 and then returns to the calling program.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

ICARD = logical unit number of card reader

IPRIN = logical unit number of line printer

IOPT = option to skip a page (=0 NO, =1 YES)

IAST = test character for the end of data (*)

IA = input array

NLINED - number of lines of descriptive text

IDTEXT - up to 50 lines of descriptive text subroutine ZIMIND(ZIMIN,LENG,ZIT)

PURPOSE

This subroutine has been designed to test the mixing depth field and to check to see if any values are less than a preset minimum value. The principal purpose of this program is to avoid the problems that can be caused by zero mixing heights arising from spatial interpolation and topographic intersection.

CALLED BY: gmamod

CALLS : none

MAIN VARIABLES

ZIMIN = minimum acceptable mixing depth (set to 10.0 m)

LENG = length of the mixing depth vector

ZIT = mixing depth array

subroutine ZMIXD(DT,LENG,ZIMIN,ZIT,DZIDT)

PURPOSE

This program has been designed to calculate the current value of the mixing height, given the value for ZI at the previous time step and the rate of change of ZI with time. The routine overwrites the new value of ZI into the old array.

CALLED BY: none

CALLS : none

MAIN VARIABLES

ZIMIN = minimum acceptable mixing depth (set to 10.0 m)

LENG = length of the mixing depth vector

ZIT = mixing depth array

DT = time step

DZIDT = differential rate of change of ZI at time T

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