

# COMPUTATIONAL CHALLENGES OF MODELING INTERACTIONS BETWEEN AEROSOL AND GAS PHASE PROCESSES IN LARGE SCALE AIR POLLUTION MODELS

GREGORY R. CARMICHAEL, ADRIAN SANDU, CHUL H. SONG,  
SHAN HE, MAHESH J. PHANDIS, DACIAN DAESCU, VALERIU DAMIAN-IORDACHE AND  
FLORIAN A. POTRA

*Center for Global & Regional Environmental Research and the  
Department of Chemical & Biochemical Engineering University  
of Iowa. Iowa City, Iowa 52240, Tel: 319/335-1399  
FAX: 319/335-1415 EMAIL: gcarmich@icaen.uiowa.edu*

In this paper we discuss computational challenges in air quality modeling (as viewed by the authors). The focus of the paper will be on the “current” state-of-affairs. Due to limitation of space the discussion will focus on only a few aspects of air quality modeling; i.e., chemical integration, sensitivity analysis and computational framework; with particular emphasis on aerosol issues.

KEY WORDS: Air quality, atmospheric chemistry, sensitivity analysis

## 1. Introduction

A detailed understanding of the relationships between the emissions and the resulting distribution of primary and secondary species in the atmosphere is a requisite to designing actions for the maintenance of a healthy environment. Scientific efforts to understand the atmospheric processes governing these relationships involve a combination of laboratory experiments, field studies, and modeling analysis. Laboratory experiments provide basic data on individual physical and chemical processes. Field studies are designed to investigate a limited number of processes under conditions in which a few processes dominate. Unlike controlled laboratory experiments, field studies cannot be parametrically controlled. Since laboratory experiments and field studies by themselves cannot fully elucidate complex atmospheric phenomena, comprehensive models that allow multiple processes to occur simultaneously are required for data analysis and scientific inquiry.

The models by Carmichael et al. (0), Jacob et al. (0), Dentener and Crutzen (0) are examples of regional and global scale atmospheric chemistry models in use today. These models treat transport, chemical transformations, emissions and deposition processes in an integrated framework, and serve as representations of our current understanding of the complex atmospheric processes. They provide a means to perform parametric studies for quantitative analysis of the relationships between emissions and the resulting distribution, and can also be used to study the response of the pollutant distributions to system perturbations, and to link pollutant distributions to environmental effects.

As our scientific understanding of atmospheric chemistry and dynamics has expanded in recent years, so has our ability to construct comprehensive models which describe the relevant processes. However, these comprehensive atmospheric chemistry models are computationally intensive because the governing equations are nonlinear, highly coupled, and extremely stiff. As with other computationally intensive problems, the ability to fully utilize these models remain severely limited by today's computer technology.

The scientific issues associated with analysis of our chemically perturbed atmospheres are dominated by a number of underlying considerations. Several of the more important ones are: (a) the anthropogenic sources of trace species are quite localized and occur only over a fraction of the Earth's land area; (b) natural sources of trace species are, for the most part, very disperse and are not in the same areas as the anthropogenic sources (although this trend may be changing in regions such as tropical rain forests and the savannahs); (c) in virtually no case can an individual species be studied in isolation from other species; (d) many of the mechanisms that effect transformation of the species are non-linear (e.g., chemical reactions and nucleation processes); and (e) species of importance have atmospheric lifetimes that range from milliseconds and shorter to years (e.g.,  $OH$  radical to  $CH_4$ ). These considerations require: finer grid resolutions than currently existing ones in present-day models; simultaneous treatment of many species; and long simulation times (i.e. months to years) to assess the impacts. These demands present considerable challenges to the air quality modeling community.

Aerosols are an area of increased importance that put additional computational burden on air quality models. Atmospheric particles have various influences on the earth-atmospheric system, including the scattering and absorption of solar and terrestrial radiation (Charlson et al. (0)) and visibility impairment (Waggoner et al. (0)). In order to better quantify the role of aerosols in the chemistry and physics of the atmosphere, it is necessary to improve our ability to predict aerosol composition as a function of size. However, the modeling of aerosol processes is difficult because of the

strong spatial and temporal variability in aerosol composition and size distributions, and the complexities and uncertainties in aerosol micro-physical processes, transport characteristics, and chemical interactions between the particulate and gas phases.

Atmospheric aerosols are formed in two ways: (i) direct emissions from natural sources; and (ii) gas-to-particle conversion. Aerosol particles from natural sources tend to be in the coarse mode with diameters larger than  $1\mu m$ . In contrast, particles formed by gas-to-particle conversion, such as nucleation and absorption (Wexler et al. (0); Zhang (0); Dentener et al. (0)) usually compose the fine mode with diameters from  $0.001\mu m$  to  $1\mu m$ .

Different particle modes have quite different chemical/physical characteristics due to the size-dependency of the formation mechanism. These different aerosol characteristics determine the distribution of volatile species between the gas and aerosol phases. Both the gas/aerosol interaction and the formation mechanism have been important subjects in the field of air pollution modeling, atmospheric physics, and aerosol thermodynamics (Wexler et al. (0); Dentener et al. (0); Fuchs (0); Seinfeld (0); Pilinis and Seinfeld (0) and (0); Zhang et al. (0); Binkowski and Shankar (0); Lurmann et al. (0); Jacobson (0) and (0)). Even though many investigators have studied this topic, it remains a challenge to model the gas-to-particle conversions and thermodynamic processes which control the compositional size-distribution of aerosols.

In this paper we discuss the issues of modeling aerosol processes in air quality models.

## 2. Model Framework

Modeling aerosol processes is computationally intensive and challenging. Gas-to-particle conversion, coagulation and deposition are the most important dynamic processes of aerosols. Gas-to-particle conversion (or particle-to-gas conversion) is caused by four major pathways: nucleation, condensation, absorption and dissolution.

The mathematical description of aerosol dynamics can be described by the general dynamics equation (GDE),

$$\begin{aligned} \frac{\partial Q_i}{\partial t} + \nabla \bullet (uQ_i) &= \nabla \bullet (K\nabla Q_i) + \left(\frac{\partial Q_i}{\partial t}\right)_{cond/evap} + \left(\frac{\partial Q_i}{\partial t}\right)_{coag} \\ &\quad + \left(\frac{\partial Q_i}{\partial t}\right)_{react} + \left(\frac{\partial Q_i}{\partial t}\right)_{source/sink} \end{aligned} \quad (1)$$

where  $\left(\frac{\partial Q_i}{\partial t}\right)_{source/sink}$  is the rate of change of the aerosol mass of species due to nucleation, primary aerosol emission and removal, while

$\left(\frac{\partial Q_i}{\partial t}\right)_{cond/evap}$ ,  $\left(\frac{\partial Q_i}{\partial t}\right)_{coag}$  and  $\left(\frac{\partial Q_i}{\partial t}\right)_{react}$  are rates of changes due to condensation/ evaporation, coagulation and surface reaction.

There are many approaches to implement these equations in air pollution models. In this chapter we illustrate the issues related to aerosol modeling by presenting some of our efforts in this area. We are building aerosol processes into our in-house developed regional scale trace gas model, STEM (Carmichael et al. (0) and (0)). The STEM model is a three-dimensional (3D), Eulerian numerical model which accounts for the transport, chemical transformation and deposition of atmospheric pollutants (Carmichael et al. (0)). The earlier versions of the model have been used quite extensively for scientific studies and policy evaluations in the eastern United States and the Pacific Region (Chang et al. (0); Kotamarthi et Carmichael (0) and (0); Xiao et al. (0); Carmichael et al. (0)).

The current 3D version of the model includes the chemical mechanism based on Lurmann et al. (0) and Atkinson et al. (0) and modified for explicit treatment of isoprene. This version of the STEM model is a combination of the classical gas and aqueous phase chemistry calculations with an extension to treat aerosol species also. A total of 107 species (90 gas phase and 17 aerosol phase chemical species) and a total of 190 gas and aerosol phase reactions are included. The 90 gas phase species are further divided into 62 long-lived species that are transported and 28 short-lived species such as free radicals which follow a pseudo-steady-state approximation. The transport of the gaseous species is computed using a locally one dimensional (LOD) Crank Nicholson Galerkin finite element method (FEM). More details of this treatment can be found in Carmichael et al. (0) and (0). The computational structure of the model is shown in Fig. 1.

## 2.1. AEROSOL DYNAMICS

The aerosol dynamic component treats several physical aerosol processes, such as nucleation, condensation/ evaporation, coagulation, and absorption/dissolution. In order to describe each physical aerosol process, a mixture of fundamental and empirical formulas are utilized as discussed in the works of Zhang (0), Dentener et al. (0), and Saylor (0).

## 2.2. THERMODYNAMIC AND KINETIC APPROACHES

Traditionally there have been two approaches for simulating atmospheric aerosols. The first approach can be called the “kinetic approach”. Several researchers have performed atmospheric modeling studies in this way (Zhang (0); Dentener et al. (0)). They have considered the irreversible uptake characteristics from the gas to the aerosol particles using transport parameters

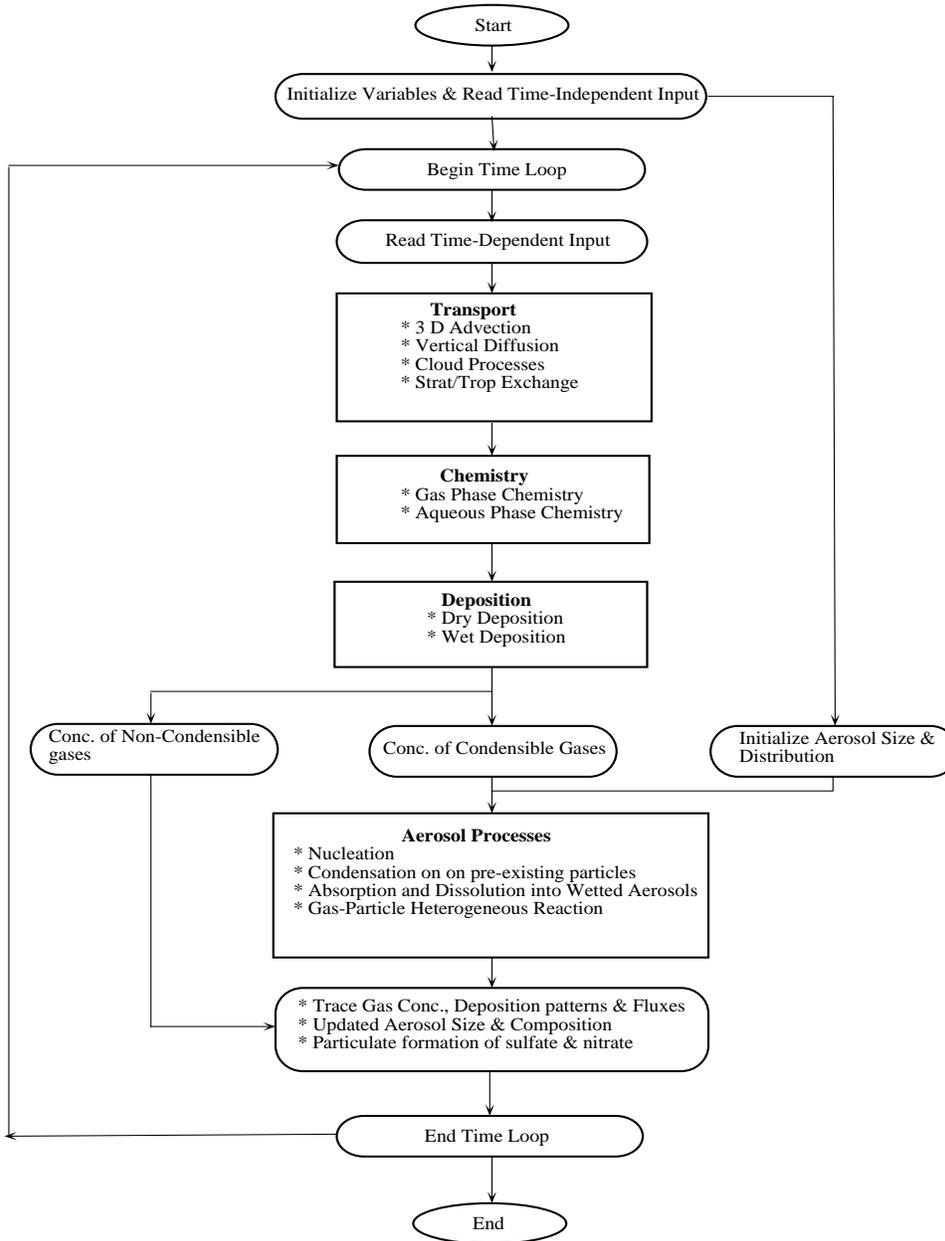


Figure 1. Schematic of the computational structure of STEM-III.

such as gas phase diffusion coefficient, accommodation coefficient and so on. In this procedure, regardless of the volatility, the species deposits irreversibly from the gas to the particles. Thus, this approach cannot take

into account the possibility that volatile species such as hydrochloric acid, nitric acid, and ammonia can be redistributed between the gas and aerosol phases. In order to better simulate the reversible distribution between the gas and the fine/coarse particles, thermodynamic approaches have been developed. Technically, this consideration is possible with the assumption that particles are charge-neutral.

Several aerosol modules have been developed to estimate the distribution of the volatile inorganic species between the gas and aerosol phases. Kim et al. (0) have compared the SCAPE (Simulating Composition of Atmospheric Particles at Equilibrium) module with other aerosol modules, such as EQUIL, KEQUIL, MARS, SEQUIL, and AIM. All of the modules other than AIM (Aerosol Inorganic Model) deal with the distribution of the volatile species in a thermodynamic manner.

In the SCAPE module, the Gibbs energy minimization scheme is employed with thermodynamic parameters, such as equilibrium constant, chemical potential, solute activity coefficient, water activity, and relative humidity of deliquescence (RHD). This module can predict the amount of volatile species distribution as well as the existing forms (ions or ion pairs) of both the volatile and non-volatile species (sulfates and mineral cations) in the aerosol particle.

### 2.3. SULFATE AND NITRATE PROCESSES

Particulate sulfate is formed by new particle formation and by chemical conversion of  $SO_2$  and  $H_2SO_4$  on aerosol surfaces. Peter and Easter (0) introduced a semi-empirical equation for binary homogeneous nucleation of  $H_2SO_4$  and  $H_2O$ ,

$$J_n = \alpha (S_s)^\beta \quad (2)$$

where,  $J_n$  is the homogeneous nucleation rate,  $cm^{-3}sec^{-1}$ , and  $S_s$  is the saturation ratio of the sulfuric acid vapor, which is defined as the ratio of the actual atmospheric vapor pressure of  $H_2SO_4$ ,  $P_a$ , to its saturation vapor,  $P_s$ , and  $\alpha$ ,  $\beta$  are empirical parameters which are dependent on relative humidity. Also, empirical relations for condensation/ evaporation processes suggested by Hanel (0) are available over three different ranges of relative humidity.

The heterogeneous production of sulfate can be modeled as a pseudo-first-order kinetic expression (Eqn. 3) based on the observation of Luria and Sievering (0),

$$\frac{dC_{sulfate}}{dt} = k_{SO_2, H_2SO_4} C_{SO_2, H_2SO_4} \quad (3)$$

where  $k_{SO_2, H_2SO_4}$  is the rate coefficient,  $cm^3 sec^{-1}$ , and  $C_{sulfate}$  and  $C_{SO_2, H_2SO_4}$  are the concentration of  $SO_4^{2-}$  in the aerosol particles and  $SO_2$  or  $H_2SO_4$  in the gas phase, respectively.

Particulate nitrate can be produced via (i) the partitioning of nitric acid between the gas and aerosol phases and (ii) heterogeneous reactions on the surface of the aerosol. One approach to modeling nitrate formation is to assume that  $HNO_3$  production in the gas phase is partitioned between the gas and aerosol phases and controlled by thermodynamic consideration. Heterogeneous production involves nighttime reactions with  $NO_3$  and  $N_2O_5$  on the surface of the aerosol. For heterogeneous production processes, the following equation can be used (Dentener et al. (0); Fuchs and Sutugin (0)):

$$k_j = \int_{r_1}^r 2k_{d,j}(r)n(r)dr \quad (4)$$

where  $n(r)dr$  is the number-concentration distribution between  $r$  and  $r+dr$ , (often assumed to be log-normal), and  $k_{d,j}(r)$  is the size-dependent mass transfer coefficient. The expression for  $k_{d,j}(r)$  is given by

$$k_{d,j} = \frac{4\pi D_j V}{1 + K_n (\lambda + 4 (1 - \frac{\alpha}{3\alpha}))} \quad (5)$$

where  $D_j$  is the gas phase diffusion coefficient in  $cm^3 sec^{-1}$ ,  $K_n$  is the dimensionless Knudsen number ( $= \frac{l}{r}$ ),  $\lambda$  is the effective free path of a gas molecule in air,  $V$  is the ventilation factor, and  $\alpha$  is the accommodation coefficient (or sticking coefficient).

Many previous studies have assumed that the absorbed nighttime species are very quickly converted into nitric acid via fast aqueous phase reactions with hydroxyl radicals (Heikes and Thompson (0)), and thus the overall rate is governed (limited) by mass transport processes with characteristic parameters as described by Eqns. 4 and 5.

Nitric acid may also be produced on aerosol surfaces via reactions involving surface sorbed  $NO$  and  $NO_2$ . However, the sticking coefficients for  $NO$  and  $NO_2$  are very small. The mass accommodation coefficient ( $\alpha$ ) of  $NO$  over sulfuric acid ( $H_2SO_4$   $nH_2O$ , 96 wt. %  $H_2SO_4$ ) at 298 K is less than  $1 \times 10^{-6}$  (Demore et al. (0)). Also, the mass accommodation coefficient of  $NO_2$  for the same type of surface at 273 K is of the order of  $6 \times 10^{-4}$  (Demore et al. (0)). As new experiments are conducted and more is learned about possible surface reactions, such reactions may prove to be important.

## 2.4. ORGANIC AEROSOL

While the importance of inorganic aerosols (nitrate-ammonium-sulfate mixtures) has been widely appreciated and studied, there is a growing awareness that organic aerosols are also important. Secondary organic aerosols (SOA) are a major component of urban environments (Odum et al. (0); Rogge et al. (0)), and have also been found to represent an appreciable component of the fine aerosol mass (comparable to that for sulfate) at the Grand Canyon (Mazurek et al. (0)), as well as in the marine atmosphere (Matsumoto et al. (0)). SOA are produced as a by-product of the oxidation of many organic molecules, including aromatics (Odum et al. (0)), monoterpenes (Pandis et al. (0)), and carbonyls (Grosjean et al. (0)). These reactions yield semi-volatile compounds, which along with primary semi-volatile organics, partition themselves between the gas and particle phases. Furthermore, the presence of polar organic species on the aerosol surface can make the aerosol more hygroscopic (Saxena et al. (0)), and thus increase the light scattering by particles. These organic aerosols may represent an important source of CCN (Novakov and Penner (0)).

Since aerosols and ozone share common chemical precursors and emissions sources, and are intricately linked through the photochemical oxidant cycle, it is important that they be studied in a simultaneous and coupled manner. Yet it is usual for these topics to be treated as isolated problems. A complicating factor of potentially large importance is the role of aerosols as reactive surfaces. Reactions on aerosol surfaces have been shown to play a significant role in stratospheric chemistry. However, little is known about the role of heterogeneous reactions in the lower regions of the atmosphere. However, there is a growing body of information that suggests that the photochemical oxidant cycle may be perturbed through heterogeneous uptake of volatile organic compounds, nitrogen oxides and free radicals, and subsequent reactions on the surface. Through these processes the formation rates of tropospheric ozone and secondary aerosols, and the sensitivity of  $O_3$  to  $NO_x$  and VOC emissions may be altered.

Organic aerosol formation processes can be added to the modeling approach described here. This can be done following the work of Pandis et al. (0), with aerosol production potentials/yields taken from that work and the recent work of Odum et al. (0), and partitioning between gas and aerosol phases calculated based on the approach of Pankow (0).

## 2.5. COMPUTATIONAL CONSIDERATIONS

Three-dimensional models without aerosol modules are basically composed of two parts: (i) gas-phase chemistry; and (ii) horizontal and vertical transports. Dabdub and Seinfeld (0) and (0) reported that the computation of

| Model                           | Calculation time |
|---------------------------------|------------------|
| I) Gas phase chemistry model    | 11 seconds       |
| II) Gas/aerosol model           |                  |
| Irreversible kinetic model      | 265 seconds      |
| Hybrid model ( <i>CASEI</i> )   | 6360 seconds     |
| Hybrid model ( <i>CASEII</i> )  | 331 seconds      |
| Hybrid model ( <i>CASEIII</i> ) | 8100 seconds     |

TABLE 1. Calculation time required for each simulation.

the rate of gas-phase chemical reactions is the most time-intensive calculation component. Generally, the chemistry part of the calculation takes 75-90% of the total calculation time. Thus, many efforts have been concentrated on the chemistry part for saving the computation time (Dabdub and Seinfeld (0); Carmichael et al. (0); Sandu et al. (0)). These efforts can be categorized into two groups: (i) development of more efficient implicit integrators (Sandu et al. (0)) or effective explicit solvers (Dabdub and Seinfeld (0)); and (ii) implementation of parallel computation with multiple processors (Carmichael et al. (0); Dabdub and Seinfeld (0)).

The situation is changed when an aerosol module is incorporated into three-dimensional models. Table 1 shows CPU times for coupled aerosol/chemistry calculation. The CPU times in Table 1 are obtained from an HP-UNIX A 9000/735 with 160-M RAM Machine. For the gas-phase reaction calculation, only 11 seconds are required. But, if irreversible aerosol kinetics are added into the gas-phase chemistry model, more CPU time is needed (265 seconds). (Here, the irreversible aerosol kinetics implies that the model includes aerosol dynamics such as nucleation, condensation/ evaporation, and irreversible absorption for sulfate and nitrate (Zhang (0); Dentener et al. (0); Song and Carmichael (0)).)

When the SCAPE module is incorporated into the Eulerian model and is called at every reaction time step (Hybrid model (Case I) <sup>1</sup>), the total computation time drastically increases up to 6360 seconds (Actually, the STEM-box model has two characteristic time scales: one for reaction integration (10 secons) and the other for transport-equation integration (300 seconds)). In this particular case, the number of calls to the SCAPE module is 18,680 for a two-day simulation. However, it is important to note two facts: (i) the current STEM model does not have any reaction for  $NH_3$  and

<sup>1</sup>SCAPE module is called at every reaction time step.

*HCl*; and (ii) even though the current STEM model has  $HNO_3$ -related reactions,  $HNO_3$  is a reservoir species. In other words, the level of  $HNO_3$  does not greatly affect the concentrations of other species. Hence, we can call the SCAPE module at every transport time scale (300 seconds) instead of reaction time scale (10 seconds) (Hybrid model (Case II) <sup>2</sup>). In this particular case, the SCAPE module is only called 576 times for two day simulation, and it only takes 331 seconds. This scheme was employed in the aged sea-salt particle case (Song and Carmichael (0)). (In Cases I and II, the SCAPE module employs a non-iterative scheme, which is also explained in the work of Song and Carmichael (0).) If the SCAPE module with the iterative scheme is utilized at every transport time step (300 seconds) and the two-bin SCAPE module is iterated until two modes (fine and coarse modes) share the same gas-phase concentration (hybrid model (Case III) <sup>3</sup>), the computation time drastically increases up to 8100 seconds. Of course, in this case, the computation time is dependent on the accuracy level (i.e. error tolerance).

The iterative scheme used to find the equilibrium concentrations in the two-bin gas-aerosol model (SCAPE) requires expensive computations and it is an extremely time-consuming process. The complex expressions of the activity coefficients, the wide range of the equilibrium constants and the influence of the temperature and humidity, to name only a few, make difficult the implementation of high-order methods to solve the nonlinear equilibrium equations. On the another hand, using a (safe) bisection method requires a large number of function evaluations, involving computations of the ion-pair concentrations from the ion concentrations, the activity and binary activity coefficients, and the water content. On average these computations require 70% to 80% of the CPU time, and when most of the species have non-zero ionic concentrations in the aqueous phase the time will increase to about 90% .

The performance of the code can be improved considerably in two ways:

a) By reducing the time necessary to solve the equilibrium equations inside of each bin (we will refer at this process as an internal process).

b) By reducing the number of iterations necessary to equilibrate the gaseous concentrations of the volatile species in the fine-mode with those in the coarse-mode (we will refer at this process as an external process).

The internal process can be improved by combining the safety of the bisection method with the speed of the secant method into a Brent-type algorithm. Taking advantage of the previous predicted concentrations will improve the iterative process. If the concentrations don't change signifi-

<sup>2</sup>SCAPE module is called at every transport time step (aged particle case).

<sup>3</sup>SCAPE module is called at every transport time step and employs iteration scheme (naturally emitted aerosol case).

cantly after few iterations, a fix point method combined with extrapolation is expected to converge very fast. If this fails, we return to the basic method. While the time spent is insignificant, the benefits may be considerable. In all the numerical experiments performed using these techniques in the implementation of the code will reduce the CPU time. Table 2 shows the timing results obtained with the old version of the code (SCAPE1) and Table 3 shows the results obtained with the new implementation (SCAPE2), using data from Yakushima, 3/28-31/88, with different methods for activity coefficients<sup>4</sup>. The error tolerance inside the bins was  $10^{-3}$  for the gas-liquid phase computations and  $10^{-2}$  for the solid computations, and the relative error for equilibrium between the bins was  $4 \times 10^{-3}$ . Relative differences between the predicted equilibrium concentrations of the volatile species ( $HCl$ ,  $HNO_3$ ,  $NH_3$ ) are presented in Table 4. It can be seen that the predictions remain within the required error interval, and the CPU time may be reduced up to 10 times.

Improving the external process is definitely the most important part, but also the most delicate. One possible way is to require more accuracy in the internal process. While this will increase considerable the time necessary to solve the equilibrium equations in each bin, the iteration number in the external process may be reduced dramatically. Denote by  $T_1$  and  $T_2$  the time necessary to solve the equilibrium equations in the fine, and coarse modes, by  $N_1$  the number of iterations necessary to equilibrate concentrations between bins. We may assume that the time consumed to update the results from one bin to another is negligible compared with  $\min(T_1, T_2)$ . If reducing the error tolerance will increase  $T_1$  to  $c_1T_1$  and  $T_2$  to  $c_2T_2$ , and will reduce the number of external iterations to  $N_2$ , then we obtain faster convergence whenever  $(T_1 + T_2)N_1 > (c_1T_1 + c_2T_2)N_2$ . Good results were obtained with data at Cheju and Yakushima. Further experiments should be done in order to decide for what kind of distribution of the concentrations in each bin is preferable to use smaller errors in the internal process. Once this is done, the code will automatically adjust the error to obtain the fastest convergence.

These results were obtained on a HP-UX 9000 workstation, model B180L.

## 2.6. AEROSOL CONSIDERATIONS

As discussed, the photochemical oxidant cycle is a complex system, involving interactions among ozone,  $NO_x$  ( $NO + NO_2$ ),  $HO_x$  ( $OH + HO_2$ ), various  $HC$  (hydrocarbons), solar radiation, and aerosols. While significant efforts have been directed towards understanding the photochemical

<sup>4</sup>P represents Pitzer method to compute the activity coefficients, K-M Kusil-Meissner method and B represents the Bromley method

| Temp.(K) | CPU time(sec.) |      |      | Nr. of iterations |     |    | Time(sec.)/iter |      |      |
|----------|----------------|------|------|-------------------|-----|----|-----------------|------|------|
|          | P              | K-M  | B    | P                 | K-M | B  | P               | K-M  | B    |
| 275      | 25.3           | 20.7 | 38.1 | 32                | 9   | 50 | .79             | 2.3  | .76  |
| 280      | 16.7           | 10.1 | 18.4 | 15                | 4   | 11 | 1.11            | 4.17 | 1.67 |
| 285      | 9.8            | 7.1  | 11.4 | 8                 | 4   | 6  | 1.22            | 1.77 | 1.9  |
| 290      | 6.6            | 6.6  | 9.8  | 5                 | 3   | 5  | 1.32            | 2.2  | 1.96 |
| 295      | 5.5            | 6.4  | 6.5  | 4                 | 3   | 3  | 1.37            | 2.13 | 2.16 |
| 300      | 0.39           | 2.12 | 1.88 | 3                 | 2   | 3  | 0.13            | 1.06 | .62  |

TABLE 2. SCAPE1 results for rh=0.80.

| Temp.(K) | CPU time(sec.) |      |      | Nr. of iterations |     |    | Time(sec.)/iter |      |      |
|----------|----------------|------|------|-------------------|-----|----|-----------------|------|------|
|          | P              | K-M  | B    | P                 | K-M | B  | P               | K-M  | B    |
| 275      | 3.2            | 5.0  | 2.7  | 33                | 8   | 20 | .097            | .625 | .135 |
| 280      | 1.7            | 2.5  | 1.6  | 14                | 4   | 9  | .121            | .625 | .178 |
| 285      | 1.0            | 1.3  | 1.2  | 8                 | 3   | 6  | .125            | .433 | .2   |
| 290      | 0.7            | 0.9  | 0.8  | 5                 | 3   | 4  | .14             | .3   | .2   |
| 295      | 0.6            | 0.79 | 0.67 | 4                 | 3   | 3  | .15             | .263 | .223 |
| 300      | 0.37           | 1.52 | 1.58 | 3                 | 2   | 3  | .123            | .76  | .527 |

TABLE 3. SCAPE2 results for rh=0.80.

ozone formation and the nonlinear interactions between  $NO_x$  and  $HC$ , the impact of aerosol on tropospheric ozone production has received less attention because their impacts were thought to be small [EPA, 1991; SAI, 1995]. However, aerosols perturb the radiation balance, and thus affect photodissociation reactions. For example,  $NO_2$  photolysis is the only primary source for tropospheric ozone production. Thus aerosol effects on  $NO_2$  photodissociation could lead to significant impact on ozone levels. This effect has recently been studied and the presence of aerosol was found to increase or decrease the ground level ozone concentration by more than 20ppbv, depending on the single scattering albedo of particle [Dickerson, et al. 1997 (0)]. The significant role of aerosol in the photochemical oxidant cycle has

| Temp.(K) | HCl |     |     | $NH_3$ |     |     | $HNO_3$ |      |     |
|----------|-----|-----|-----|--------|-----|-----|---------|------|-----|
|          | P   | K-M | B   | P      | K-M | B   | P       | K-M  | B   |
| 275      | 4.4 | 3.0 | 4.8 | 5.2    | 3.9 | 1.0 | 4.7     | 1.9  | 4.7 |
| 280      | 1.0 | 1.3 | 3.9 | 2.8    | 6.6 | 5.4 | 0.9     | 1.5  | 4.3 |
| 285      | 2.9 | 0.9 | 7.2 | 1.4    | 2.8 | 8.7 | 2.9     | 8.3  | 7.7 |
| 290      | 5.9 | 3.7 | 4.8 | 9.7    | 0.3 | 6.3 | 6.2     | 3.7  | 5.4 |
| 295      | 0.2 | 0.7 | 4.1 | 1.8    | 1.1 | 1.0 | 0.3     | 0.5  | 4.4 |
| 300      | 0.3 | 8.4 | 3.5 | 3.0    | 0.3 | 4.3 | 0.4     | 10.2 | 3.9 |

TABLE 4. Relative differences between the predicted results ( $\times 10^{-3}$ ).

not been fully exploited yet due to the large number of parameters and complicated interactions among aerosol, radiation, ozone and  $NO_x$ . ADIFOR is a powerful tool for sensitivity analysis, and can help in studying the role of aerosol-radiation interactions in the photochemical oxidant cycle.

To demonstrate this ADIFOR is applied to a coupled chemistry/ transport/ radiative transfer model, and is based on the STEM-III model (Crist, 1994 (0)).

## 2.7. ADIFOR APPLICATION ON STEM

In order to study the role of aerosol-radiation interactions in the photochemical oxidant cycle, ADIFOR is applied on a 1D STEM model. While the STEM 1D model simulates the tropospheric chemistry from the Earth's surface up to 8km altitude with 400km resolution, the radiative transfer model estimates perturbation of solar radiation from the Earth's surface up to 60km altitude. The radiation wavelength covers from 203nm to 435nm within 80 intervals. The modeling site studied is located at Bridgeport Connecticut, a typical urban region, 73.3 degrees W in longitude, 41.5 degrees N in latitude. The model is driven by local meteorological data. Relative humidity (RH) is at 70% for a June period. Typical aerosol mass concentrations in boundary layer vary from 10 to  $70\mu g/m^3$  on the East Coast of US [Novakov, et al., 1997 (0)]. For the base simulation, urban aerosol optical properties are used with concentration of  $50\mu g/m^3$  within the boundary layer (0~2km altitude). The physical and optical properties of urban aerosols are obtained from d'Almeida [1995] (0). At  $\lambda=550nm$ , aerosol extinction coefficient  $\sigma_{ex} = 6.985E^{-6}/m$ , single scattering albedo  $\omega = 0.9383$ , asymmetric factor  $g = 0.647$ . Simulations start at 7:00 pm local time and

continually run with a 15 minutes interval for 3 days.

The top graph in Fig. 2 shows the calculated diurnal cycle of ground level ozone,  $NO_x$ , and NMHC for these conditions. As the sun rises, photodissociation begins with  $NO_2$  photolysis providing atomic oxygen for ozone formation. The concentration of ozone rapidly builds up, while  $NO_x$  and NMHC are consumed and their concentrations decrease. The ozone curve reaches its peak and  $NO_x$  and NMHC curves reach their minimum in the early afternoon. As the sun sets, the ozone production decreases due to the inactive photodissociation, and  $NO_x$  and NMHC accumulate due to the continuous  $NO_x$  and NMHC emissions. The input temperature and eddy diffusion show a diurnal variation with high value at day time and low value at night, which cause chemical reactions and vertical transport more active in day time than at night. These facts can also contribute to the diurnal cycling of ozone,  $NO_x$  and NMHC.

The first-order sensitivities of ozone concentration to the independent variables TOMS, NMHC and  $NO_x$  emissions are also shown in Fig. 2. These sensitivities also show a diurnal cycle with peaks at sun rise. TOMS and NMHC emissions have positive impacts on ozone, but  $NO_x$  emissions have a negative influence on ozone concentration. Comparing the results from aerosol-free condition and with  $50\mu g/m^3$  urban aerosol loading in the boundary layer, one finds a significant reduction of ozone (up to 31% at local noon after 3 days) when aerosols are present. Also, the presence of aerosol in the air enhances the impact of NMHC and  $NO_x$  on ozone, and weakens the influence of TOMS on ozone concentration.

### 3. Kinetic PreProcessor

The issues raised above regarding aerosol equilibrium, solution of stiff ODE's, sensitivity analysis, place great demands on the software. We have been developing software tools to assist model development and testing. The KPP preprocessor is shown in figure 3. This tool facilitates change chemical mechanisms, evaluating ODE solvers, assisting sensitivity analysis, etc. Further details can be found in (0) and at <http://www.cgrer.uiowa.edu/people/vdamian>.

### 4. Closing Comments

Most of the recent attention regarding tropospheric aerosols has focused on their radiative properties. Secondary aerosols formed via the photochemical oxidant cycle play a significant role in radiative transfer by absorption and scattering of solar and terrestrial radiation, and by changing the optical properties of clouds through modification of the distribution of cloud condensation nuclei (CCN) (Charlson et al.(0)). Current estimates suggest

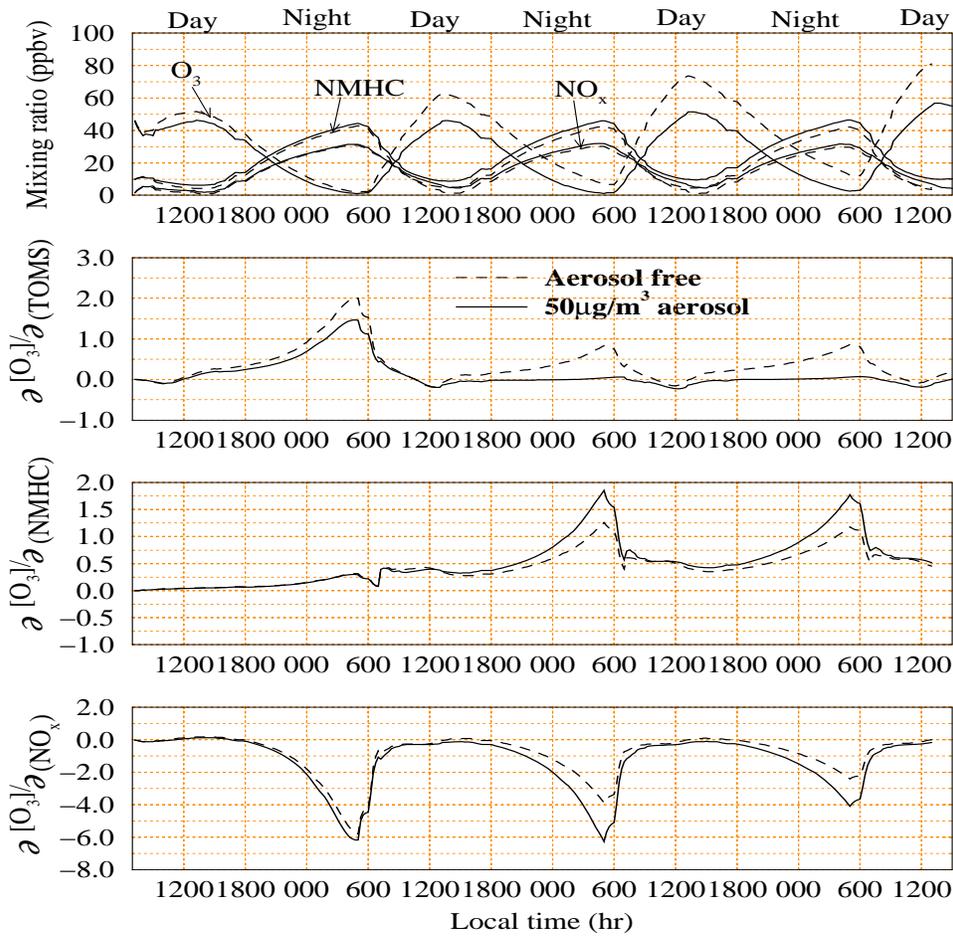


Figure 2. Diurnal Cycle of  $O_3$ ,  $NO_x$ , and NMHC, and Sensitivity of  $O_3$  concentration to TOMS, Emissions of NMHC, and  $NO_x$ .

that the climate forcing due to aerosols linked to fossil fuel combustion and biomass burning largely offset that due to greenhouse gases in vast portions of the tropics and industrialized areas (Kiehl and Briegleb (0)). However, large uncertainties remain in assessing the role of aerosols in climate and atmospheric dynamics due to the lack of detailed information on size distribution, chemical composition, surface properties, source strengths, and atmospheric transport and removal processes. Secondary aerosols also have a major impact on ambient visibility (Mazurek et al. (0)), and have significant adverse impacts on human health (Dockery et al. (0)).

While the importance of inorganic aerosols (nitrate-ammonium-sulfate

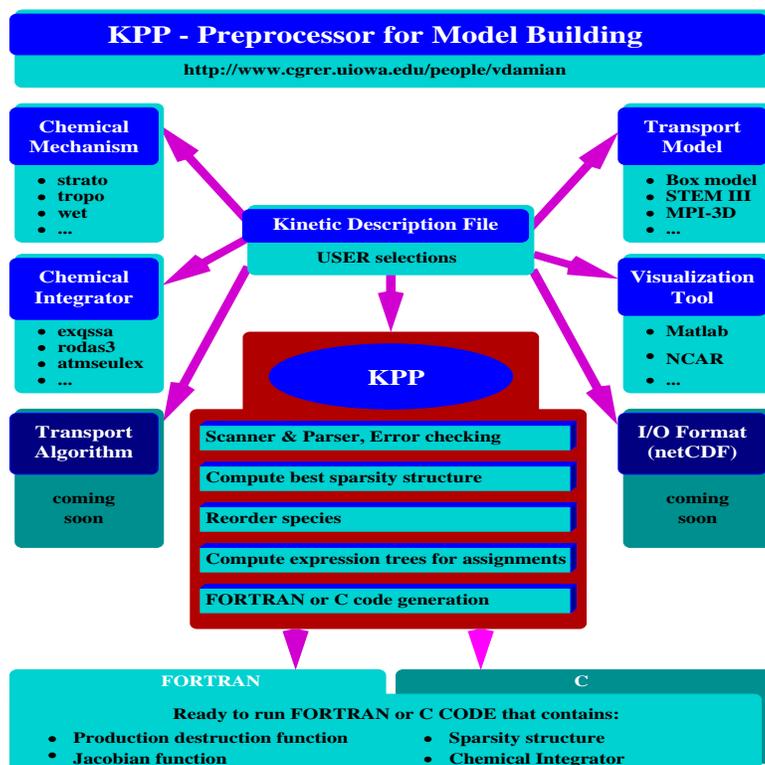


Figure 3. Schematic of the KPP Software Tool for Model Building.

mixtures) has been widely appreciated and studied, there is growing awareness that organic aerosols are also important. Secondary organic aerosols (SOA) are a major component of urban environments (Odum et al. (0); Rogge, et al. (0)), and have also been found to represent an appreciable component of the fine aerosol mass (comparable to that for sulfate) at the Grand Canyon (Mazurek et al. (0)), as well as in the marine atmosphere (Matsumoto et al. (0)). SOA are produced as a by-product of the oxidation of many organic molecules, including aromatics (Odum et al. (0)), monoterpenes (Pandis et al. (0)), and carbonyls (Grosjean et al. (0)). These reactions yield semi-volatile compounds, which along with primary semi-volatile organics, partition themselves between the gas and particle phases.

Furthermore, the presence of polar organic species on the aerosol surface can make the aerosol more hygroscopic (Saxena et al. (0)), and thus increase the light scattering by particles. These organic aerosols may represent an important source of CCN (Novakov and Penner (0)).

Since aerosols and ozone share common chemical precursors and emissions sources, and are intricately linked through the photochemical oxidant cycle, it is important that they be studied in a simultaneous and coupled manner. The need to analyze ozone and aerosols together, and the lack of fundamental information on potentially important chemical processes, provide the motivation for the continued development of aerosol models.

## References

- R.D. Atkinson, D.L. Baulch, R.A. Cox, R.F.Jr. Hampson, J.A. Kerr, and J. Troe. Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry. *J. of Chemical Kinetics*, 21:115–190, 1989.
- F.S. Binkowski and U. Shankar. The Regional Particle Matter Model 1. Model Description and Preliminary Results. *J. Geophys. Res.*, 100:26191–26209, 1995.
- G.R. Carmichael and L.K. Peters. An Eulerian Transport/ Transformation/ Removal Model for  $SO_2$  and Sulfate - I. Model Development. *Atmos. Environ.*, 18:937–951, 1984.
- G.R. Carmichael, L.K. Peters, and T. Kitada. A Second Generation Model for Regional-Scale Transport/Chemistry/Deposition. *Atmos. Environ.*, 20:173–188, 1986.
- G.R. Carmichael, L.K. Peters, and R.D. Saylor. The STEM-II Regional Scale Acid Deposition and Photochemical Oxidant Model - I. An Overview of Model Development and Applications. *Atmos. Environ.*, 25:2077–2090, 1991.
- G.R. Carmichael, A. Sandu, F.A. Potra, V. Damian, and M. Damian. The Current State and the Future Directions in Air Quality Modeling. *SAMS*, 25:75–105, 1996.
- G.R. Carmichael, I. Uno, M.J. Phadnis, Y. Zhang, and Y. Sunwoo. Tropospheric Ozone Production and Transport in the Springtime in East Asia. *J. Geophys. Res.*, 1997 (submitted).
- T.S. Chang, G.R. Carmichael, H. Kurita, and H. Ueda. The Transport and Formation of Photochemical Oxidants in Central Japan. *Atmos. Environ.*, 23:363–393, 1989.
- R.J. Charlson, S.E. Schwartz, J.M. Hales, R.D. Cess, J.A.Jr. Coakley, J.M. Hansen, and D.J. Hofmann. Climate Forcing by Anthropogenic Aerosols. *Science*, pages 423–430, 1992.
- K. Crist. Comprehensive Regional Scale Air Pollution/Radiative Modeling. *PhD. Thesis. Dept. of Chemical Engineering, The University of Iowa, Iowa City*, 1994.
- D. Dabdub and J.H. Seinfeld. Air Quality Modeling on Massively Parallel Computers. *Atmos. Environ.*, 28:1679–1689, 1994.
- D. Dabdub and J.H. Seinfeld. Numerical Advective Schemes Used in Air Quality Models - Sequential and Parallel Implementation. *Atmos. Environ.*, 28:3369–3385, 1994.
- D. Dabdub and J.H. Seinfeld. Extrapolation Techniques Used in the Solution of Stiff ODEs Associated with Chemical Kinetics of Air Quality Models. *Atmos. Environ.*, 29:403–410, 1995.
- A.G. d'Almeida, P. Koepke, and E.P.Shettle. *Atmospheric Aerosols Global Climatology and Radiative Characteristics*. A. Deepak Publishing, Hampton, Virginia, USA., 1991.
- V. Damian. Tools for Air Quality Modeling. *PhD. Thesis, Dept. of Compute Science, The University of Iowa, Iowa City*, 1998.
- W.B. Demore, C.J. Howard, D.M. Golden, C.E. Kolb, R.F. Hampson, M.J. Kurylo, and

- M.J. Molina. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. *JPL Publication 92-20*, 1992.
- F.J. Dentener, G.R. Carmichael, Y. Zhang, J. Lelieveld, and P.J. Crutzen. Role of Mineral Aerosol as a Reactive Surface in the Global Troposphere. *J. Geophys. Res.*, 101:22869–22889, 1996.
- R. Dentener and P. Crutzen. Reaction of  $N_2O_5$  on Tropospheric Aerosols: Impact of the Global Distributions of  $NO_x$ ,  $O_3$  and  $OH$ . *J. of Geophys. Res.*, 98:7149–7163, 1993.
- R.R. Dickerson, S. Kondragunta, G. Stenchikov, K.L. Civerolo, B.G. Doddridge, and B.N. Holben. The Impact of Aerosols on Solar Ultraviolet Radiation and Photochemical Smog. *Science*, 278:827–830, 1997.
- D. Dockery, A. Pope, X. Xu, J. Spengler, J. Ware, M. Fay, B. Ferris, and F. Speizer. An Association between Air Pollution and Mortality in Six U.S. Cities. *The New England J. of Medicine*, 329:1733–1759, 1993.
- N.A. Fuchs. *The Mechanics of Aerosols*. Pergamon Press, 1964.
- N.A. Fuchs and A.G. Sutugin. *Highly Dispersed Aerosols*. Ann Arbor Science, 1970.
- E. Grosjean, D. Grosjean, M. Frazer, and G. Cass. Air Quality Model Evaluation Data for Organics. 2. C1 - C14 Carbonyls in Los Angeles Air. *Environ. Sci. Technol.*, 30:2687–2703, 1996.
- G. Hanel. The Properties of Atmospheric Aerosol Particles as a Function of the Relative Humidity at Thermodynamic Equilibrium with the Surrounding Moist Air. *Advance Geophysics*, 19:73–188, 1976.
- B. Heikes and A.M. Thompson. Effects of Heterogeneous Processes on  $NO_3$ ,  $HONO$ , and  $HNO_3$  Chemistry in the Troposphere. *J. Geophys. Res.*, 88:10883–10895, 1983.
- D.J. Jacob, J.A. Logan, G.M. Gardner, C.M. Spivakovsky R.M. Yevich, S.C. Wofsy, S. Sillman, and M.J. Prather. Factors Regulating Ozone over the United States and its Export to the Global Atmosphere. *J. Geophys. Res.*, 98:14817–14826, 1993.
- M.Z. Jacobson. Development and Application of a New Air Pollution Modeling System - II. Aerosol Module Structure and Design. *Atmos. Environ*, 31:131–144, 1997.
- M.Z. Jacobson. Development and Application of a New Air Pollution Modeling System - III. Aerosol-Phase Simulations. *Atmos. Environ*, 31:587–608, 1997.
- J. Kiehl and B. Briegleb. The Relative Roles of Sulfate Aerosols and Green House Gases in Climate Forcing. *Science*, 260:311–314, 1993.
- Y.P. Kim, J.H. Seinfeld, and P. Saxena. Atmospheric Gas-Aerosol Equilibrium I. Thermodynamic Model. *Aerosol Sci. Technol.*, 19:157–181, 1993.
- V.R. Kotamarthi and G.R. Carmichael. The Long Range Transport of Pollutants in the Pacific Rim Region. *Atmos. Environ.*, 24:1521–1534, 1990.
- V.R. Kotamarthi and G.R. Carmichael. A Modeling Study of the Long-Range Transport of Kosa Using Particle Trajectory Methods. *Tellus*, 45:426–441, 1993.
- M. Luria and H. Sievering. Heterogeneous and Homogeneous Oxidation of  $SO_2$  in the Remote Maritime Atmosphere. *Atmos. Environ*, 25:1489–1496, 1991.
- F.W. Lurmann, A.C. Loyd, and R. Atkinson. A Chemical Mechanism for Use in Long-Range Transport/Acid Deposition Computer Modeling. *J. of Geophys. Res.*, 91:10905–10936, 1986.
- F.W. Lurmann, A.S. Wexler, S.N. Candis, S. Musarra, N. Kumar, and J.H. Seinfeld. Modeling Urban and Regional Aerosols: II. Application to California's South Coast Air Basin. *Atmos. Environ.*, 1997 (submitted).
- K. Matsumoto, H. Tanaka, I. Nagao, and Y. Ishizaka. Contribution of Particulate Sulfate and Organic Carbon to Cloud Condensation Nuclei in the Marine Atmosphere. *Geophys. Res. Lett.*, 24:655–658, 1997.
- M. Mazurek, M. Masonjones, H. Masonjones, L. Salmon, G. Cass, K. Hallock, and M. Leach. Visibility-Reducing Organic Aerosols in the Vicinity of Grand Canyon National Park: Properties Observed by High Resolution Gas Chromatography. *J. Geophys. Res.*, 102:3779–3793, 1997.
- T. Novakov, D. Hegg, and P. Hobbs. Airborne Measurements of Carbonaceous Aerosols on the East Coast of the United States. *J. Geophys. Res.*, 102:30023–30030, 1997.

- T. Novakov and P. Penner. Large Contribution of Organic Aerosols to Cloud-Condensation Nuclei Concentrations. *Nature*, 365:823–826, 1993.
- J. Odum, T. Jungkamp, R. Griffin, R. Flagan, and J. Seinfeld. The Atmospheric Aerosol Forming Potential of Whole Gasoline Vapor. *Science*, 276:96–99, 1997.
- S. Pandis, H. Harley, G. Cass, and J. Seinfeld. Secondary Organic Aerosol Formation and Transport. *Atmos. Environ.*, 26:2269–2282, 1992.
- J. Pankow. An Absorption Model of Gas/Particle Partitioning of Organic Compounds in the Atmosphere. *Atmos. Environ.*, 28:185–188, 1994.
- L.K. Peters and D. Easter. Binary Homogeneous Nucleation as a Mechanism for New Particle Formation in the Atmosphere. *Monthly Update*, 3:1–5.
- C. Pilinis and J.H. Seinfeld. Continuous Development of a General Equilibrium Model for Inorganic Multi-Component Atmospheric Aerosols. *Atmos. Environ.*, 21:2453–2466, 1987.
- C. Pilinis and J.H. Seinfeld. Development and Evaluation of an Eulerian Photochemical Gas-Aerosol Model. *Atmos. Environ.*, 22:1985–2001, 1988.
- W.F. Rogge, M.A. Mazurek, L.M. Hildemann, G.R. Cass, and B.R.T. Simoneit. Quantification of Urban Organic Aerosols at a Molecular Level: Identification, Abundance and Seasonal Variation. *Atmos. Environ.*, 27:1309–1330, 1993.
- A. Sandu, F.A. Potra, G.R. Carmichael, and V. Damian. Efficient Implementation of Fully Implicit Methods for Atmospheric Chemical Kinetics. *J. Computational Physics*, 129:101–110, 1996.
- P. Saxena, L. Hildemann, P. McMurry, and J. Seinfeld. Organics Alter Hygroscopic Behavior of Atmospheric Particles. *J. Geophys. Res.*, 100:18755–18770, 1995.
- R.D. Saylor. An Estimation of the Potential Significance of Heterogeneous Loss to Aerosols as an Additional Sink for Hydroperoxy Radicals in the Troposphere. *Atmos. Environ.*, 31:3653–3658, 1997.
- J.H. Seinfeld. *Atmospheric Chemistry and Physics of Air Pollution*. John Wiley and Sons, 1986.
- C.H. Song and G.R. Carmichael. Gas-to-Particle Conversion and Thermodynamic Distribution of Sulfuric Acid and Volatile Inorganic Species in the Marine Boundary Layer. *Atmos. Environ.*, 1998 (submitted).
- A.P. Waggoner, R.E. Weiss, N. Ahlquist, P. Voert, S. Will, and R.J. Charson. *Atmos. Environ.*, 15:1891, 1981.
- A.S. Wexler, F.W. Lurmann, and J.H. Seinfeld. Modeling Urban and Regional Aerosols - I. Model Developments. *Atmos. Environ.*, 28:531–546, 1994.
- H. Xiao, G.R. Carmichael, J.N. Durchenwald, D. Thornton, and A. Brady. Long Range Transport of  $SO_x$  and Dust in East Asia During the PEM West - B Experiment. *J. Geophys. Res.*, 102:28589–28612, 1997.
- Y. Zhang, Y. Sunwoo, V. Kothamarthi, and G.R. Carmichael. Photochemical Oxidant Processes in the Presence of Dust: An Evaluation of the Impact of Dust on Particulate Nitrate and Ozone Formation. *J. Appl. Meteorol.*, 33:813–824, 1994.
- Y. Zhang. The Chemical Role of Mineral Aerosols in the Troposphere in East Asia. *PhD. Thesis, University of Iowa, Iowa City*, 1994.