Development and application of an efficient moving sectional approach for the solution of the atmospheric aerosol condensation/evaporation equations

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Abstract

Condensation of gases (H\textsubscript{2}SO\textsubscript{4}, NH\textsubscript{3}, HNO\textsubscript{3}, low vapor pressure organics, etc.) onto existing aerosols can account for a significant portion of fine particulate matter. Since aerosols affect human health, visibility, and climate change, it is important to be able to model condensation/evaporation accurately in order to predict how particle mass will change over time. (Atmos. Environ. 34 (2000) 2957) proposed adapting the trajectory-grid method, used for solving the transport equation, to solve the condensation/evaporation equation. Their preliminary results showed it to be fast and accurate in simple systems (one component, etc.). The approach of Chock and Winkler has been modified for implementation in both the Hybrid method (Atmos. Environ. 34 (2000) 3617) and the improved multicomponent aerosol dynamics model (MADM) (Aerosol Sci. Technol. 32 (2000) 482) The first improvement in MADM modifies the method for restricting the acidic flux, while the second reduces physically meaningless dry/wet oscillations in the aerosol phase by assuming the aerosol is metastable when these oscillations are present. Measurements in Claremont, CA in August of 1987 are used to evaluate the new method in a one-dimensional model and the October 1995 PM episode in the South Coast Air Basin in CA is used for evaluation in a three-dimensional chemical transport model (PMCAMx). The trajectory-grid method allows the use of a simple scheme for time step selection and provides at least a factor of two or three reduction in computational requirements compared to an ODE solver at the same level of accuracy. The improvements to MADM also have a significant effect on performance, providing over an order of magnitude reduction in computational requirements compared to the original MADM. In the three-dimensional chemical transport model, the Hybrid method of (Atmos. Environ. (2000) 3617) is applied which assumes the smallest particles are in equilibrium while the condensation/evaporation equation is solved for the larger ones. Combined with the improvements to MADM and trajectory-grid method, this Hybrid approach takes just three to four times the computational requirements of assuming bulk equilibrium for all particles, while providing more accurate predictions of the aerosol size distribution.

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1. Introduction

Atmospheric aerosols negatively affect visibility, human health, and also have an effect on global climate change. Fine and coarse particles can be emitted directly into the atmosphere, but a significant portion of aerosol mass is formed by gases partitioning into the aerosol phase. In particular, the largest contribution to fine aerosol mass in the South Coast Air Basin of California is from the condensation of ammonium nitrate onto existing particles (Kleeman and Cass, 2001). Air quality
standards are based on total PM$_{10}$ and PM$_{2.5}$ mass, so it is important to be able to predict how much new material will condense onto existing aerosols. Models must describe this process effectively so they can be used to develop strategies for reducing particulate matter, and the associated harmful effects, in the atmosphere.

In early three-dimensional air quality models, equilibrium was assumed between the gas and particle phase (Pilinis et al., 1987; Jacobson et al., 1996; Binkowski and Shankar, 1995; Lurmann et al., 1997), rather than accounting for mass transfer limitations. Although this assumption makes these models efficient and stable, several studies have shown that this equilibrium assumption can introduce errors into aerosol models, particularly for larger particles, low temperatures, and high relative humidity (Wexler and Seinfeld, 1990; Meng and Seinfeld, 1996; Lurmann et al., 1997). Most of these equilibrium methods combine the aerosols into a “bulk” particulate phase. Another approach is a size-resolved equilibrium approach, with multiple particle groups (Pilinis and Seinfeld, 1987; Jacobson et al., 1996; Jacobson, 1999; Moya et al., 2002). This method has been shown to be more accurate than the traditional “bulk” equilibrium in some cases (Jacobson, 1999), although it has not performed as well in cases where the relative humidity is <60% (Moya et al., 2002). To increase the level of accuracy, several models that treat aerosol dynamics and account for mass transfer between phases have been developed (Meng and Seinfeld, 1996; Meng et al., 1998; Jacobson et al., 1996; Jacobson, 1997a,b; Sun and Wexler, 1998a,b; Pilinis et al., 2000; Nguyen and Dabdub, 2002). A hybrid method has also been developed which solves the dynamic equations for the larger particles, which are slower to reach equilibrium, and establishes equilibrium for the smaller particles (Capaldo et al., 2000).

The weakness of methods that describe aerosol dynamics is that they improve accuracy at the expense of a large increase in computational cost. Models that treat kinetic mass transfer explicitly typically have at least 100 times the computational requirements of equilibrium models (Seigneur, 2001). These increased computational requirements are caused by large differences in the mass transfer rates of different species or particle sizes, creating a stiff system of differential equations which needs to be solved. The hybrid method reduces these computational requirements somewhat (Koo et al., 2003), but more efficient methods of solving this system of equations still need to be developed for application to state-of-the-art three-dimensional chemical transport models, which can be used for developing emission control strategies.

Chock and Winkler (2000) proposed adapting the trajectory-grid method, used for solving the transport equation, to solve the atmospheric aerosol condensation/evaporation equation. Their preliminary results in simple systems (one component, etc.) found it to be fast and accurate. In this paper, this method is extended for use in one- and three-dimensional chemical transport models. The trajectory-grid method is a moving sectional method (Gelbard, 1990; Kim and Seinfeld, 1999), allowing the section boundaries to move as condensation/evaporation occur. Linear interpolation is applied to convert back to a fixed size grid for use with other transport processes. A brief overview of the trajectory-grid method appears below. The method is then applied to two test cases. The first involves application of a one-dimensional trajectory model to an air pollution episode in CA in August 1987. The results with the trajectory-grid method using the hybrid approach of Capaldo et al. (2000) and the fully dynamic case are compared to results using the equilibrium approach to test the efficiency of the new method and with the LSODE solver from ODEPACK (Hindmarsh, 1983) to test accuracy. The second case applies a three-dimensional chemical transport model to a PM episode in the South Coast Air Basin of California. Again, results along with the trajectory-grid method using the hybrid approach are compared with the equilibrium approach and LSODE solver to test efficiency and accuracy. Modifications to the multicomponent aerosol dynamics model (MADM) (Pilinis et al., 2000) are also implemented and their effect on accuracy and computational requirements is discussed. These modifications are discussed in the following section.

2. Modifications to MADM and HYBRID

Two modifications have been made to the original multicomponent aerosol dynamics model (hereafter referred to as MADM1). The improved version will be called MADM2. The first improvement changes the method used to limit the acidity flux. A limitation on acidity flux was first introduced by Sun and Wexler (1998a,b). They applied this constraint to near acidity conditions typical of the western United States. Under these conditions, the hydrogen ion concentration changes much faster than other important species, leading to a stiff system of differential equations requiring small time steps during integration. To avoid these numerical issues, Sun and Wexler coupled acid and base fluxes to maintain the hydrogen ion concentration at a pseudo-equilibrium. Physically, the hydrogen ion reaches its equilibrium faster than other species, so when equilibrium is temporarily broken by the condensation or evaporation of an acid or base, a compensating condensation or evaporation of an acid or base will rapidly occur to restore the hydrogen ion equilibrium (Sun and Wexler, 1998b). Pilinis et al. (2000) relaxed this constraint, allowing the hydrogen ion concentration to change at a rate as much as 10%/s.
The acidity flux is evaluated by assuming full dissociation of transferred gas species to a liquid aerosol section

\[ J_{H^+,k} = 2J_{H_2SO_4,k} + J_{HNO_3,k} + J_{HCl,k} - J_{NH_3,k}, \]

where \( J_{k} \) represents the flux of species \( i \) in section \( k \). In MADM1 (Pilinis et al., 2000), the acidity flux is restricted to a critical value, \( \gamma \) by modification of the equilibrium vapor pressure, \( c_{eq,i} \), for HNO3, HCl, and NH3 by a correction factor \( Q_k \), such that

\[ c_{eq,i} = Q_k c_{eq,i} \quad i = \text{HNO}_3, \text{HCl}, \]

\[ c_{eq,i} = \frac{J_{H(k)}}{Q_k} \quad i = \text{NH}_3. \]

Although this scheme helps to relieve the stiffness of the system of differential equations, it is not always efficient enough to obtain reasonable computational costs, especially in a large-scale air quality model. In some cases, for example, a \( Q_k \) value which helps to reduce the flux of ammonia can make those of HNO3 and/or HCl so big that the system may become unstable. The improved scheme in MADM2 restricts the acidity flux by modifying either the acidic or basic flux instead of both fluxes

\[ J_{+k} = \frac{J_{H(k)}}{Q_k} \quad i = \text{HNO}_3, \text{HCl} \quad \text{if} \ J_{H(k)} > \gamma, \]

\[ J_{-k} = \frac{J_{H(k)}}{Q_k} \quad i = \text{NH}_3 \quad \text{if} \ J_{H(k)} < -\gamma, \]

where \( \gamma \) represents the critical acidity flux. As in MADM, \( \gamma \) prevents the hydrogen ion concentration from changing faster than 10%/s. Allowing the hydrogen ion concentration to change by as much as 10%/s should cover all realistic physical scenarios. Thus, the limitation on acidity flux is preventing the model from simulating unrealistically high acidity fluxes (due to numerical errors). Sensitivity of the results to the value of \( \gamma \) is discussed below.

The second improvement of MADM1 is made in the step where ISORROPIA (Nenes et al., 1998), the thermodynamic module of MADM, determines the physical state of an aerosol section. Due to the difference between schemes to predict equilibrium vapor pressures for wet and dry aerosols in MADM1 it is possible for oscillations to occur between wet and dry states, which can make the numerical solution inefficient. These oscillations have no physical meaning considering the typical hysteresis phenomenon in aerosol deliquescence and crystallization. To avoid this problem in MADM2, a metastable liquid aerosol is assumed when an aerosol particle switches between the wet and dry state over 100 times at constant relative humidity. ISORROPIA then predicts the equilibrium vapor pressures for the metastable liquid aerosols. An aerosol particle is assumed to be metastable temporarily while the particle is oscillating between wet and dry states at constant relative humidity (a period of about 5–10 min). When the relative humidity subsequently changes, the metastable assumption no longer holds and the aerosol will become dry if the relative humidity is now below the deliquescence relative humidity.

3. Trajectory-grid method

The trajectory-grid method solves the condensation/evaporation equation for a multicomponent aerosol population using the method of characteristics along with equation splitting. The condensation/evaporation equation gives the change in concentration over time and can be written as

\[ \frac{\partial p_i}{\partial t} = H_p - \frac{1}{3} \frac{\partial H}{\partial \mu}. \]

where \( p_i \) is the aerosol mass concentration distribution of the \( i \)th species such that \( p_i d\mu \) is the mass concentration of \( i \) in the size range between \( \mu \) and \( \mu + d\mu \), \( \mu \) is the logarithm of the aerosol diameter, \( H = \sum_i H_i \), and \( p = \sum_i p_i \) (Chock and Winkler, 2000). \( H_i \) is the condensation rate of species \( i \) and is defined as:

\[ H_i = \frac{12D_i(c_i - c_{eq})f(Kn,z)M_i}{\rho_p D_s^2 k T}, \]

where \( D_i \) is the diffusion coefficient for species \( i \) in air, \( M_i \) is its molecular weight, \( f(Kn,z) \) is a function of the Knudsen number, \( Kn \), and the accommodation coefficient, \( z \) that gives the correction due to noncontinuum effects and imperfect accommodation (Dahneke, 1983), \( \rho_p \) is the density of the particle, \( D_p \) is the diameter of the particle, \( k \) is the Boltzmann constant, \( T \) is the temperature of the system, and \( (c_i - c_{eq}) \) is the difference between the bulk and equilibrium vapor pressure for species \( i \). Using the trajectory-grid method, Eq. (5) becomes

\[ \frac{dp_i}{dt} = H_p - \frac{1}{3} \frac{\partial H}{\partial \mu}. \]

along the characteristic curve \( d\mu/dt = H/3 \). Finally, it is split into two equations

\[ \frac{dp_i}{dt} = H_p, \]

\[ \frac{dp_i}{dt} = -\frac{1}{3} \frac{\partial H}{\partial \mu} p_i \]

to make it easier to find a solution. A solution for Eq. (8) can be derived (Dhaniyala and Wexler, 1996) assuming that \( H_i \) and \( H \) are constant for the time-step \( \Delta t \):

\[ p_i(\mu, t + \Delta t) = p_i(\mu, t) + H_i \frac{H_p(\mu, t)}{H_p(\mu, t)} - 1 \quad \text{for} \quad H \neq 0, \]

\[ p_i(\mu, t + \Delta t) = p_i(\mu, t) + H_p(\mu, t)\Delta t \quad \text{for} \quad H = 0. \]
The solution to Eq. (9) is

\[
p_i(\mu, t + \Delta t) = p_i(\mu, t) \exp \left[ -\frac{1}{3} \int_t^{t+\Delta t} \frac{\partial H}{\partial \mu} \, dt \right]
\]

\[
\approx p_i(\mu, t) \left( 1 - \frac{1}{3} \frac{\partial H}{\partial \mu} \Delta t \right).
\]

(12)

The value of the diameter is updated along the characteristic curve to \( \mu(t + \Delta t) = \mu(t) + (H/3)\Delta t \).

The approach of Chock and Winkler (2000) was extended in the current work to handle situations that did not arise in the original publication. Previously, the model was only used with a constant condensation rate, i.e. \( \partial H / \partial \mu = 0 \). When \( \partial H / \partial \mu \neq 0 \), additional considerations are necessary because the section size is not constant. For example, if \( \partial H / \partial \mu \) is positive, the sections will spread out over time. As this happens, the section size is no longer constant, but changes according to the relation

\[
\Delta \mu^{n+1} = \Delta \mu^n \left( 1 + \frac{1}{3} \frac{\partial H}{\partial \mu} \Delta t \right).
\]

(13)

To keep the section size constant, Eq. (12) can be combined with Eq. (14). Since the condensation gradients are small, this essentially cancels out. Consequently, the solution to Eq. (9) can be ignored and the trajectory-grid method reduces to the analytical solution of Eq. (8). As a result, the trajectory-grid reduces to a form similar to other moving sectional methods.

Finally, in order to use the solution to Eq. (8), a small enough step size must be chosen so that \( H_t \) and \( H \) do not change significantly. A simple algorithm to determine the step size \( \Delta t \) was developed. The algorithm being used calculates the change in \( H \) after each time step. If

\[
p(H_{n+1} - H_n) \Delta t \geq \varepsilon
\]

then the \( n \)th step is repeated with \( \Delta t = \Delta t/2 \), where \( \varepsilon \) is an arbitrary error tolerance. Also, if

\[
p(H_{n+1} - H_n) \Delta t \leq \delta
\]

(15)

the time step is increased by 10%, with \( \delta \) being an arbitrary lower limit. This allows the time step to increase when the system is under fairly stable conditions, but prevents it from increasing too quickly. Values of \( 10^{-4} \mu g/m^3 \) for \( \varepsilon \) and \( 10^{-3} \mu g/m^3 \) for \( \delta \) are used in this work. Using these values with the moving sectional approach gives as accurate or more accurate results than a relative tolerance of \( 10^{-3} \) and an absolute tolerance of \( 10^{-6} \) using the LSODE solver. This remains true even as the limitation on the acidity flux discussed in the previous section is varied. Either the error tolerances can be decreased or the limitation on acidity flux can be increased in an attempt to achieve more accurate results. However, for the cases presented in this paper, neither of these factors affect the results significantly, while causing an increase in the computational requirements.

4. Condensation of water

The amount of water present in the aerosol phase is calculated each step by ISORROPIA (Nenes et al., 1998). To use the analytical solution to Eq. (8), however, the condensation rate of water should be included in the total condensation rate. To include this, a scheme similar to that proposed by Meng et al. (1998), combining the condensation/evaporation rate for water given by Wexler et al. (1994) with the rate of change of water from the previous step was tested. This scheme provided little change in the solution (<1%) compared to the solution when ignoring the condensation/evaporation of water, while causing a significant increase in CPU requirements. As a result, the condensation/evaporation rate of water has been left out of the total condensation/evaporation rate. This causes a small error when the diameter is updated along the characteristic curve. Consequently, the diameter is instead updated using the relation

\[
\frac{p}{\rho_p N_p} = D_p^3
\]

(16)

where the density \( \rho_p \) and number of particles \( N_p \) remain constant while the total mass and diameter change.

5. Test cases

The first test case involves a one-dimensional trajectory framework. Twenty-four trajectories were modeled, each reaching Claremont, CA on a different hour on 28 August 1987. The secondary organic aerosol model (SOAM) is the host one-dimensional trajectory model (Koo et al., 2003; Pandis et al., 1992). Eight size sections are used to represent the aerosol distribution, with 25 organic and inorganic species in the aerosol phase. The vertical air column following the trajectory is divided into five separate cells. Nine different approaches were used to model these trajectories: four fully dynamic methods (MADM1/LSODE, MADM2/LSODE, MADM1/T-G, and MADM2/T-G), four hybrid methods (HYBR1/LSODE, HYBR2/LSODE, HYBR1/T-G, and HYBR2/T-G), and a bulk equilibrium method (EQUI). MADM1/LSODE uses MADM1 (Pilinis et al., 2000) to simulate aerosol dynamics and solves the resulting system of equations using the LSODE solver from ODEPACK (Hindmarsh, 1983). The LSODE solver here uses the Adams-Moulton formula (Shampine, 1994) for solving the system of ODEs. MADM2/LSODE combines the improved MADM2 with the LSODE solver. MADM1/T-G and MADM2/T-G use the corresponding version of MADM to solve aerosol dynamics, while using the trajectory-grid method to solve the system of equations. The four hybrid methods
assume that particles <0.625 μm in diameter are in equilibrium with the gas phase, while using either MADM1 or MADM2 for aerosol dynamics, and either the LSODE solver or trajectory-grid method for solving the resulting system of equations.

The second test case uses a three-dimensional framework for modeling the October 1995 PM episode in the South Coast Air Basin of California. The host model in this case is the chemical transport model PMCAMx, using the framework of CAMx (ENVIRON, 2002) and adding the size-resolved aerosol module. The model inputs are setup for a 325 × 200 km² region with 5 × 5 km² grid resolution and ten vertical layers (65 × 40 grid squares). The modeling region is shown in Fig. 1, including the five sites where PM_{10} and PM_{2.5} daily average concentrations were measured during this episode. The region extends from central Santa Barbara County to northern San Diego County from north to south and from the Pacific Ocean to Coachella Valley from west to east. The aerosol distribution is split into 10 moving size sections, with 13 inorganic and organic species in the aerosol phase.

6. Results—computational requirements

6.1. One-dimensional model

The computational requirements of the nine different methods for the one-dimensional case are shown in Fig. 2. MADM1/LSODE and MADM1/T-G are significantly slower than the other methods, taking over 100 CPU s/cell/simulation hour and 50 s/cell/h, respectively, on a 1.2 GHz AMD CPU with 1 Gb RAM. The improvements to MADM make the fully dynamic models much more efficient, reducing these times to 4.2 s/cell/h for MADM2/LSODE and just 1.5 s/cell/h for MADM2/T-G, well over an order of magnitude decrease. For the hybrid methods using the ODE solver, the improvements to MADM again make a big difference, reducing the computational requirements from 5.0 s/cell/h for HYBR1/LSODE to 0.8 s/cell/h for HYBR2/LSODE. A difference is also seen in the computational requirements for HYBR1/T-G and HYBR2/T-G, with the improvements to MADM reducing the computational requirements by a factor of two from 0.49 to 0.25 s/cell/h. HYBR1/T-G and HYBR2/T-G both outperform HYBR2/LSODE. The most efficient method is the full equilibrium method, with EQUI taking just 0.083 s/cell/h, although this method is only about three times faster than HYBR2/T-G.

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**Fig. 1.** The modeling domain for the three-dimensional chemical transport model. The domain surrounds the South Coast Air Basin of California. The five sites where PM_{10} and PM_{2.5} measurements were taken are also shown.

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**Fig. 2.** Comparison of the computational requirements for each method for solving the one-dimensional-trajectory model. Times are for a 1.2 GHz AMD CPU with 1 Gb RAM.
6.2. Three-dimensional model

The hybrid approaches (particularly HYBR2/T-G) show great promise for use in computationally intensive three-dimensional chemical transport models. The three fastest hybrid approaches (HYBR2/T-G, HYBR1/T-G, and HYBR2/LSODE) were implemented into the three-dimensional model to examine their accuracy and computational efficiency. The computational requirements for these three hybrid approaches are shown in Fig. 3 along with the results of the bulk equilibrium approach. HYBR1/T-G takes on average 0.2 CPU s/cell/simulation hour over the three-day episode on the same 1.2 GHz AMD CPU with 1 Gb RAM. This translates into 32 h of CPU time per day of simulation. This was faster than HYBR2/LSODE, which took 0.36 s/cell/h (or 57 CPU hours/day of simulation). HYBR2/T-G was more efficient than either of these two methods, taking just 0.076 s/cell/h (12 h/day of simulation). Again, the most efficient method was the equilibrium method, requiring just 0.02 s/cell/h over the three-day period (3 h per day of simulation). While HYBR1/T-G and HYBR2/LSODE are over an order of magnitude slower than EQUI, HYBR2/T-G took only four times as long, representing a significant improvement over previous methods.

7. Results—accuracy

7.1. One-dimensional model

For the one-dimensional study, predicted results can be compared to PM$_{10}$ and PM$_{2.5}$ measurements taken at Claremont on 28 August 1987 with a filter-based sampler (Fitz et al., 1989). Fig. 4 compares the predictions of MADM2/T-G, MADM2/LSODE, HYBR2/T-G and HYBR2/LSODE to the measured PM$_{10}$ and PM$_{2.5}$ mass of various aerosol species over five sampling periods on 28 August (0:00–5:00, 5:00–9:00, 9:00–13:00, 13:00–17:00 and 17:00–24:00 PST). Little difference is seen between the predicted values using the trajectory-grid method and the LSODE solver, indicating that the trajectory-grid method increases the efficiency of the dynamic and hybrid methods without sacrificing accuracy. In addition, both methods satisfactorily predict the measured concentrations, with only one point having an error greater than 30% (PM$_{2.5}$ ammonia from 17:00 to 24:00 PST). Predictions using MADM1 and HYBR1 are not shown, but these results are also similar to the respective MADM2 and HYBR2 predictions (see Koo et al., 2003).

It is also useful to compare the dynamic and hybrid methods with the equilibrium method, to determine whether the accuracy increases enough using these methods to justify the increased computational expense. Koo et al. (2003) showed that the hybrid and dynamic methods gave better size distribution predictions than the equilibrium method, particularly for ammonia and nitrate. This trend can be seen by viewing the PM$_{10}$ and PM$_{2.5}$ mass and nitrate predictions at Claremont, shown in Figs. 5 and 6. Since all the fully dynamic methods and all the hybrid methods gave similar results, the most efficient versions, MADM2/T-G and HYBR2/T-G were chosen for comparing hybrid and dynamic methods with the equilibrium method. Compared to the MADM2/T-G, EQUI overpredicts PM$_{2.5}$ mass by as much as 10.8%. This problem with the equilibrium method is even more evident looking at the nitrate concentration plots in Fig. 6. Compared to the dynamic method, the PM$_{2.5}$ nitrate is overpredicted by as much as 30%, while the PM$_{10}$ nitrate is always underpredicted, by as much as 23%. In fact, an average of 93% of the nitrate aerosol mass is predicted to be in the smallest four size sections ($<0.625$ µm) using the equilibrium method, compared to 51% and 54% for the hybrid and dynamic methods, respectively.

7.2. Three-dimensional model

The hybrid and equilibrium predictions can be compared. The daily average predicted PM$_{10}$ and PM$_{2.5}$ concentrations for HYBR2/T-G on 18 October over the entire modeling region are shown in Fig. 7. The highest concentrations are seen in Riverside and Fontana and eastward. The concentrations are highest here because of farms to the west of these two cities which release heavy ammonia emissions. Little difference is seen between the three hybrid methods, HYBR1/T-G, HYBR2/T-G, and HYBR2/LSODE, so HYBR2/T-G was chosen as representative of all three-hybrid models.
The results from the EQUI and HYBR2/T-G models are compared to measurements at Anaheim, Los Angeles, Diamond Bar, Fontana, and Riverside. The predicted vs. measured daily average PM$_{10}$ and PM$_{2.5}$ mass and nitrate concentrations are seen in Fig. 8.

To compare the equilibrium and hybrid models, the mean normalized bias

$$N_{\text{BIAS}} = \frac{100}{N} \sum_{i=1}^{N} \left( \frac{\text{Pred}_i - \text{Obs}_i}{\text{Obs}_i} \right)$$

(17)

and mean normalized error

$$N_{\text{ERROR}} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{\text{Pred}_i - \text{Obs}_i}{\text{Obs}_i} \right|$$

(18)

are calculated, where $N$ represents the measurements at all five sites for 17, 18, and 19 October. The results are shown in Table 1. The results for the HYBR2/LSODE model are similar to the results for the HYBR2/T-G method. For the two hybrid methods, the mean normalized bias is within ±15% for all four variables, while the mean normalized error ranges from 15.7% to 26.6%. The results are similar for the equilibrium method, with the exception of PM$_{2.5}$ nitrate, which has a mean normalized bias of 25.5% and a mean normalized error of 33.0%. Although no guidelines are available for particulate matter concentrations, the statistical goals of ozone performance given by the ARB and EPA are a mean normalized bias within
±15% and a mean normalized error <35%. The hybrid methods satisfy these performance requirements for all four variables, while the equilibrium fails to meet the normalized bias requirement for PM$_{2.5}$ nitrate.

The equilibrium method has the same problem it did with the one-dimensional test case, providing a poor size distribution, particularly with ammonia and nitrate. To illustrate this point, the PM$_{10}$ and PM$_{2.5}$ mass and nitrate predicted hourly concentrations on 18 October are shown in Figs. 9 and 10 for each measurement site. Again, HYBR2/T-G is chosen as representative of all three-hybrid methods. The three measurement sites with the highest daily averages, Los Angeles, Riverside, and Fontana, all show good agreement between the equilibrium and hybrid methods for PM$_{10}$ and PM$_{2.5}$ mass. For the other two sites, Anaheim and Diamond Bar, excellent agreement is seen for the first half of the day, but small deviations in the aerosol mass predictions are seen in the afternoon when the predicted PM$_{10}$ mass drops below 50 $\mu$g/m$^3$. For the predicted nitrate aerosol mass, the agreement is not as good between the equilibrium and hybrid methods. Although the total nitrate mass predicted by the equilibrium method is not unreasonable and closely follows the trend of the hybrid methods, the predicted PM$_{10}$ and PM$_{2.5}$ nitrate concentrations of the equilibrium method are nearly identical to each other, and tend to be in between the predicted PM$_{10}$ and PM$_{2.5}$ nitrate concentrations of the hybrid method. This indicates that the bulk equilibrium method is shifting some nitrate from the coarse to the fine PM. The agreement is again the worst for the less polluted Diamond Bar and Anaheim sites.
7.3. Sensitivity to changes in critical acidity flux

The sensitivity of the results to changes in the critical acidity flux was analyzed for the one-dimensional model. In each size section $k$, the critical acidity flux $\gamma_k$ is proportional to the aerosol hydrogen ion concentration $c_{H^+}k$ according to the relation

$$\gamma_k = Ac_{H^+}k,$$

where $A$ is an arbitrary constant. The base case uses a value of 0.1 s$^{-1}$ for $A$, allowing the hydrogen ion concentration to vary by as much as 10% in each section. As in the original publication of MADM (Pilinis et al., 2000), little change in accuracy was seen when the value of $A$ was varied between 0.01 and 1 s$^{-1}$. The computational requirements increase by a factor of two as $\gamma$ was increased in this range using the hybrid approach, and by a factor of four for the dynamic case. The sensitivity beyond this range was also tested for both approaches. In the hybrid case, the error introduced by restricting the acidity flux is less than a few percent, even while $A$ varies from 0 to 10.0 s$^{-1}$. The computational requirements increase by a factor of four over this range. For the dynamic approach, the critical acidity flux has a more significant effect. For values of $A$ below 0.01 s$^{-1}$, the results are significantly affected and do not reflect the results obtained when the critical acidity flux is increased. With a value of $A$ ranging from 0.01 to 10.0 s$^{-1}$, however, the results do not change by more than a few percent, while the computational requirements increase by over an order of magnitude.

For the three-dimensional case, the value of $A$ was varied from 0.01 to 10.0 s$^{-1}$ using the hybrid approach. Over this range, the results changed by only a few percent throughout the modeling domain with the smallest errors seen in the area of interest surrounding...
the measurement sites, indicating that a value of 0.1 s/C0 for A is reasonable. The computational requirements were also not affected significantly over this range, increasing by \(\approx 10\%\) as A increased from 0.01 to 0.1 s/C0, and then by about a factor of two as A was increased to 10.0 s/C0.

### 8. Conclusions

Applied to the trajectory-grid method, the improvements to MADM and simple time step selection scheme are shown to effectively solve the condensation/evaporation equation in chemical transport models. 

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**Table 1**  
Statistical comparison of hybrid (using both the trajectory-grid method and an ODE solver) and equilibrium method predictions with measurements at five locations from 17 October to 19 October 1995

<table>
<thead>
<tr>
<th>Method</th>
<th>Equilibrium</th>
<th>HYBR2/T-G</th>
<th>HYBR2/LSODE</th>
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<tr>
<td></td>
<td>N_{BIAS}</td>
<td>N_{ERROR}</td>
<td>N_{BIAS}</td>
</tr>
<tr>
<td>PM10 mass</td>
<td>−12.8</td>
<td>22.5</td>
<td>−13.3</td>
</tr>
<tr>
<td>PM10 nitrate</td>
<td>−14.8</td>
<td>25.1</td>
<td>−11.3</td>
</tr>
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<td>PM2.5 mass</td>
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<td>15.2</td>
<td>−4.4</td>
</tr>
<tr>
<td>PM2.5 nitrate</td>
<td>25.5</td>
<td>33.0</td>
<td>14.0</td>
</tr>
</tbody>
</table>

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Fig. 8. Predicted vs. measured PM\(_{10}\) and PM\(_{2.5}\) aerosol mass and aerosol nitrate concentrations at five different monitoring sites in the South Coast Air Basin of California from 17 October to 19 October 1995. Concentrations predicted by the equilibrium and hybrid method are shown. The 1:1 and 30% error lines are also shown.
Fig. 9. Comparison of hourly aerosol mass concentrations on 18 October 1995 at five locations predicted by the equilibrium and hybrid method in a three-dimensional chemical transport model.
Fig. 10. Comparison of hourly nitrate aerosol mass concentrations on 18 October 1995 at five locations predicted by the equilibrium and hybrid method in a three-dimensional chemical transport model.
approach is shown to be an efficient method of accounting for kinetic mass transfer, while maintaining good accuracy. Combined with the hybrid method, which uses an equilibrium assumption for the smaller particles, this moving sectional method requires just three to four times the computation requirements of using the bulk equilibrium assumption for all particles in both a one-dimensional trajectory model and a three-dimensional chemical transport model.

The results using the efficient moving sectional method are virtually identical to results obtained using the same framework and using an ODE solver to solve the condensation/evaporation equation, both in one- and three-dimensional chemical transport models. The performance is also satisfactory compared to measured concentrations using both the one- and three-dimensional models. Predicted concentrations using the hybrid and dynamic trajectory-grid methods were also compared to predictions of the more efficient bulk equilibrium method. The equilibrium method predictions for PM$_{10}$ and PM$_{2.5}$ mass were found to be similar to the other methods. The size distribution of individual species, particularly for ammonia and nitrate, does not compare as well to measurements, however, indicating problems with the accuracy of the equilibrium method. Nearly all the nitrate is predicted to be in the smallest size sections by the equilibrium method, causing the predicted PM$_{2.5}$ nitrate concentrations to be too high even while the PM$_{10}$ nitrate concentrations are often underpredicted by the equilibrium method.

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References


