

MULTI-GRID AND STEP TECHNIQUE FOR
ATMOSPHERIC CHEMICAL POLLUTANT TRANSPORT
AND DIFFUSION

by

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ABSTRACT

In order to improve efficiency and accuracy in the solution processes, multi-grid and step technique is developed for studying chemical transport and diffusion in the atmosphere. The multi-grid and step numerical method uses in the time dimension: variable order of interpolation polynomial and a variable time step and uses in the spatial dimensions: a set of different grid sizes. The capability and feasibility of the multi-grid and step technique for solving the stiff partial differential equations have been described and demonstrated.

1. INTRODUCTION

Over the years the mechanisms of oxidation of sulfur dioxide to sulfate have received considerable attention. Numerical modeling of such transformation mechanisms and rates in the atmosphere have been studied extensively, but simple linear chemical reactions have been considered primarily. In more recent years, there has been increased concern about nonlinear chemical reactions associated with a host of homogeneous and heterogeneous oxidation processes. A number of "one point" complicated kinetic models of photochemistry have been developed. The mathematical description of such a photochemical process can be reduced to a set of simultaneous coupled ordinary differential equations in which time is the only independent variable. It is known that these chemical model equations are often very stiff, which means that the individual reactions proceed with vastly different time scale. There are a few successful numerical techniques (Gear, 1971; Winslow, 1973, 1979; Hindmarsh and Byrne, 1975 and Young, 1980) for solving such stiff ordinary differential equations. However, in the simulation of chemical pollutant transport and diffusion in the ambient atmosphere, which must include calculations at many spatial grid points, the major numerical difficulty with which we are faced is to solve such a large system of stiff partial differential equations in which both time and space are independent variables. The usual approach to such problem uses multi-step implicit numerical integration method at each grid point. The stiff partial differential equations must be integrated and iterated until convergence is reached at many spatial grid points over a relatively short periods of time. Thus, computational time and storage involved in solving these sets of stiff partial differential equations describing the pollutant transport-diffusion-reaction problem increase dramatically. Therefore, a fast smoothing technique is needed in order to improve the acceleration

of the convergence within the iteration and to obtain accurate solutions in the spatial distribution. The multi-grid technique (Brandt, 1977) is the best choice for such purpose. Hence, the approach suggested in this study combines the multi-grid technique with multi-step implicit integration method into an accurate and efficient method for solving time dependent stiff partial differential equations.

2. MODEL EQUATIONS

A general mathematical description of transport, diffusion and reaction for M chemical species in the atmosphere can be written in the differential form as

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot (VC_i) + \nabla \cdot (D\nabla C_i) + Q_i + S_i - L_i(C)C_i + P_i(C) ; \tag{1}$$

$i=1, 2, \dots, M$

- where C_i is a pollutant for species i ,
- V is the wind velocity,
- D is the eddy diffusion coefficient,
- ∇C_i is the gradient of C_i ,
- Q_i is the source term for species i ,
- S_i is the sink term for species i ,
- $L_i(C)C_i$ is the chemical loss of species C_i in reactions with other species,
- and $P_i(C)$ is the chemical production of species C_i from other species.

It is noted that the variables $C_i, V, D, Q_i,$ and S_i in Eq. (1) are generally functions of time and space.

3. NUMERICAL METHOD

Given approximations for spatial derivatives [i.e., $\nabla \cdot (VC_i)$ and $\nabla \cdot (D\nabla C_i)$], one can cast Eq. (1) in the following ordinary differential form

$$\frac{dC_i}{dt} = -L_i(C)C_i + B_i(C) \tag{2}$$

where $B_i(C) = -\nabla \cdot (VC_i) + \nabla \cdot (D\nabla C_i) + P_i(C) + Q_i + S_i$ (3)

(3.a) Multi-step method

In the numerical solutions of Eq. (2) at each grid point, the method is based on the extrapolant formulation (Winslow, 1977) which is simple and efficient technique suitable for chemical kinetic problems. For the method, a Newton interpolation polynomial $P_{i,k}$ of order k for species i is constructed by passing through the unknown solution C_i^{n+1} together with the previous k solutions C_i^n , C_i^{n-1} , ..., C_i^{n-k+1} , i.e.

$$P_{i,k} = C_i^{n+1} + (t - t^{n+1}) \nabla C_i^{n+1}/h + (t - t^{n+1})(t - t^n) \nabla^2 C_i^{n+1}/2!h^2 + \dots + (t - t^{n+1})(t - t^n)(t - t^{n-1}) \dots (t - t^{n-k+2}) \nabla^k C_i^{n+1}/k!h^k \quad (4)$$

$$\text{where } t^n = t^0 + nh \quad (5a)$$

$$\nabla C_i^{n+1} = C_i^{n+1} - C_i^n \quad (5b)$$

$$\nabla^2 C_i^{n+1} = \nabla C_i^{n+1} - \nabla C_i^n = C_i^{n+1} - 2C_i^n + C_i^{n-1} \quad (5c)$$

$$\vdots$$

$$\nabla^k C_i^{n+1} = \nabla^{k-1} C_i^{n+1} - \nabla^{k-1} C_i^n$$

and C_i^{n+1} is the value of C_i for species i at $(n+1)^{\text{th}}$ time step. This Newton interpolation polynomial can be written in terms of the extrapolant by defining each extrapolant $E_{i,k}^{n+1}$ for species i to be the extrapolating value from a polynomial $p_{i,k}$ of order k at $t = t^{n+1}$ over a set of previous solutions C_i^n , C_i^{n-1} , ..., C_i^{n-k+1} , i.e.

$$E_{i,k}^{n+1} = p_{i,k} = C_i^n + (t^{n+1} - t^n) \nabla C_i^n/h + (t^{n+1} - t^n)(t^{n+1} - t^{n-1}) \nabla^2 C_i^n/2!h^2 + \dots + (t^{n+1} - t^n)(t^{n+1} - t^{n-1})(t^{n+1} - t^{n-2}) \dots (t^{n+1} - t^{n-k+1}) \nabla^k C_i^n/k!h^k \quad (6)$$

The lower order extrapolant is thus

$$E_{i,0}^{n+1} = C_i^n \quad (7)$$

and the others can be easily obtained from the recursion relation

$$E_{i,k+1}^{n+1} = E_{i,k}^{n+1} + \prod_{j=0}^k \left(\frac{t^{n+1} - t^{n-j}}{t^n - t^{n-j-1}} \right) [C_i^n - E_{i,k}^n] \quad (8)$$

From Eq. (6), we have

$$\nabla C_i^n = E_{i,1}^{n+1} - C_i^n \quad (9a)$$

$$\nabla^2 C_i^n = E_{i,2}^{n+1} - E_{i,1}^{n+1} \quad (9b)$$

$$\vdots$$

$$\nabla^k C_i^n = E_{i,k}^{n+1} - E_{i,k-1}^{n+1} \quad (9c)$$

Using Eq. (7) and Eq. (9), the Eq. (5) can be rewritten as

$$\nabla C_i^{n+1} = C_i^{n+1} - E_{i,0}^{n+1} \quad (10a)$$

$$\nabla^2 C_i^{n+1} = C_i^{n+1} - E_{i,1}^{n+1} \quad (10b)$$

$$\vdots$$

$$\nabla^k C_i^{n+1} = C_i^{n+1} - E_{i,k-1}^{n+1} \quad (10c)$$

When the Newton interpolation polynomial is written in terms of the extrapolants by substituting Eq. (10) into Eq. (4) and then differentiated with respect to time, Eq. (4) takes on the simple form

$$\frac{dP_{i,k}}{dt} = \sum_{j=0}^{k-1} \frac{C_i^{n+1} - E_{i,j}^{n+1}}{t^{n+1} - t^{n-j}} \quad (11)$$

Applying Eq. (11) to system (2) and solving for C_i^{n+1} at each grid point, we finally obtain

$$C_i^{n+1} = \frac{\sum_{j=0}^{k-1} E_{i,j}^{n+1} R_j + B_i^{n+1}(C)\Delta t}{\sum_{j=0}^{k-1} R_j + L_i^{n+1}(C)\Delta t} \quad ; \quad i=1,2, \dots, M \quad (12)$$

where
$$R_j = \frac{t^{n+1} - t^n}{t^{n+1} - t^{n-j}} \tag{13}$$

Noted that B_i^{n+1} and L_i^{n+1} in Eq. (12) are functions of C_i^{n+1} . The value $E_{i,j}^{n+1}$ in Eq. (12) can be easily obtained from the recursion relation Eq. (8). Equation (12) is in a form which can be solved for C_i^{n+1} iteratively by using the last grid values of C_i^{n+1} to update B_i^{n+1} and L_i^{n+1} until convergence is reached.

The variable time step and order of interpolation polynomial for solving Eq. (12) can be adjusted through the error control. The truncational error by using the extrapolant in Eq. (6) is just $(C_i^{n+1} - E_{i,k}^{n+1})$ at $t = t^{n+1}$ which is essentially the last neglected term on the right-hand side of Eq. (6), namely $(t^{n+1} - t^n)(t^{n+1} - t^{n-1})(t^{n+1} - t^{n-2}) \dots (t^{n+1} - t^{n-k})C_i^{[k+1]}/(k+1)!$ where $C_i^{[k+1]}$ is evaluated in an interval between t^{n-k} and t^{n+1} . Then, it is easily shown that

$$[C_i^{n+1} - E_{i,k}^{n+1}]^{k+1} \propto \Delta t \tag{14}$$

Defining the relative error

$$\delta_k = \left| \frac{C_i^{n+1} - E_{i,k}^{n+1}}{C_i^{n+1}} \right| \tag{15}$$

and setting δ_0 is the desired relative error for the next new time step, we obtain by combining Eqs. (14) and (15)

$$(\Delta t)_{new} = \left(\frac{\delta_0}{\delta_k}\right)^{\frac{1}{k+1}} (\Delta t)_{old} \tag{16}$$

By computing $(\Delta t)_{new}$ for $k-1$ and $k+1$ and comparing these values of $(\Delta t)_{new}$, we have a criterion for changing the polynomial order k by ± 1 whenever it will lead to a larger time step.

(3.b) Multi-grid and step formulations

The spatial solutions for Eq. (12) can be obtained by applying the method described above at each grid point in the spatial domain. The common approach in the spatial calculation is to use a mesh with constant grid size for the solution processes, i.e. without considering adaptive grid size as time step presented

earlier. Therefore, much computational time can be wasted in solving an unnecessarily large system of algebraic equation (12) by iteration. Hence, a multi-grid technique based on the structure of multi-level adaptive technique (Brandt, 1977), which employs a set of different grid sizes to approximate the same domain in the solution processes, combines with the multi-step method presented in the previous section to be used in this study. Preliminary results using this multi-grid technique on the time-dependent problems have been presented elsewhere (Lee and Meyers, 1980).

First, the problem is discretized in space at each specified time step by numerical approximations on a sequence of grids G^1, G^2, \dots, G^m , where G^1 is the coarsest grid. Typically, the grids have mesh size $h_K = 2h_{K+1}$ where h_K represents the grid size of the grid G^K . We assume the exact discrete solutions $C_i^{n+1,f}$ where f denotes the fine grid, to be the sum of approximate solutions and residual error functions, such as

$$C_i^{n+1,f} = \chi_i^{n+1,f} + \epsilon_i^{n+1,f} \quad (17)$$

where $\chi_i^{n+1,f}$ are approximate solutions of $C_i^{n+1,f}$ from the iteration procedure, and $\epsilon_i^{n+1,f}$ are the residual errors on the fine grid domain at $(n+1)^{th}$ time step for species i . After substituting Eq. (17) into Eq. (12), we have the residual equation for Eq. (12) on the fine grid domain.

$$\begin{aligned} & \left[\sum_{j=0}^{k-1} R_j + L_i^{n+1}(C)\Delta t \right] \epsilon_i^{n+1,f} + [L_i^{n+1,f}(C) - L_i^{n+1,f}(\chi)] \chi_i^{n+1,f} \\ & - [B_i^{n+1,f}(C) - B_i^{n+1,f}(\chi)] \Delta t \\ & = F_i^{n+1,f} - \left\{ \left[\sum_{j=0}^{k-1} R_j + L_i^{n+1,f}(\chi)\Delta t \right] \chi_i^{n+1,f} - B_i^{n+1,f}(\chi)\Delta t \right\} \end{aligned}$$

$$\text{where } F_i^{n+1,f} = \sum_{j=0}^{k-1} E_{i,j}^{n+1} R_j$$

(18)

Before solving Eq. (18), let $S_i^{n+1,f}$ represent the terms in the right-hand side of Eq. (18). If $S_i^{n+1,f}$ for each species fluctuates with a wavelength larger than $4 h_f$ over the fine grid, the residual equation (18) can be solved on the coarse grid. Therefore, any fluctuations of $S_i^{n+1,f}$ with a wavelength less than $4 h_f$ should be smoothed out through a relaxation technique. Once the $S_i^{n+1,f}$ are smoothed, the residual equations then can be interpolated into the coarse grid and solved for $e_i^{n+1,c}$, which are the approximate solutions of $\epsilon_i^{n+1,c}$ on the coarse grid. By doing that, the computational time is reduced tremendously by solving the residual equation (18) on the coarse grid instead of the fine grid. For this purpose, the residual equation on the coarse grid domain can be constructed as follow:

$$\begin{aligned}
& \left[\sum_{j=0}^{k-1} R_j + I_f^c (L_i^{n+1,f}(C))\Delta t \right] \chi_i^{n+1,c} - I_f^c (B_i^{n+1,f}(C))\Delta t \\
& = I_f^c \{ F_i^{n+1,f} - \left[\sum_{j=0}^{k-1} R_j + L_i^{n+1,f}(X)\Delta t \right] \chi_i^{n+1,f} - B_i^{n+1,f}(X)\Delta t \} \\
& + \left[\sum_{j=0}^{k-1} R_j + I_f^c (L_i^{n+1}(X))\Delta t \right] (I_f^c \chi_i^{n+1,f}) - I_f^c (B_i^{n+1,f}(X))\Delta t
\end{aligned} \tag{19}$$

where $\chi_i^{n+1,c} = e_i^{n+1,c} + I_f^c \chi_i^{n+1,f}$ and I_f^c represents an interpolation operator from the fine grid to the coarse grid.

After solving Eq. (19) for $\chi_i^{n+1,c}$ on the coarse grid, we interpolate $\chi_i^{n+1,c}$ back into fine grid, and therefore, form improved approximations to $\chi_i^{n+1,f}$, i.e.,

$$(\chi_i^{n+1,f})_{\text{new}} = (\chi_i^{n+1,f})_{\text{old}} + I_c^f (\chi_i^{n+1,c} - I_f^c \chi_i^{n+1,f}) \tag{20}$$

The advantage of the multi-grid process is that by a further application of the same technique until the coarsest grid is reached, Eq. (19) need be solved only on the coarsest grid.

(3.c.) Pseudospectral approximations for spatial derivatives.

It has been mentioned earlier that approximations of spatial derivatives in $B_i(C)$ are required for the computation of Eq. (12). When the finite difference method is used for evaluating spatial derivatives, computational dispersion is often a serious problem. Thus, an approximation of a high order of accuracy is demanded. Such an approximation can be constructed by using a finite Fourier transform in which the spatial derivatives are computed with high accuracy. In this section, a brief summary of the pseudospectral approximations for spatial derivatives in a nonperiodic problem is given. Detailed derivations and applications may be found in the work of Lee (1981 a,b).

For simplicity, assuming the atmosphere is incompressible, Eq. (3) can be written as

$$B_i(C) = - (V \cdot \nabla D) \cdot \nabla C_i + D \nabla^2 C_i + P_i(C) + Q_i + S_i \tag{21}$$

The spatial derivative terms in Eq. (21) are calculated through the pseudospectral technique. The idea is to express the solution as the sum of periodic function and a polynomial function in one direction at a time. The pseudospectral technique is applied only to the periodic function to obtain its derivatives while the polynomial function can be calculated by obtaining the polynomial coefficients which can be computed by using periodic polynomial spline satisfying the boundary conditions (Lee, 1981 b). Thus, Eq. (21) can be rewritten as

$$B_i(C) = - \sum_{j=1}^3 (V_j - \frac{\partial D}{\partial X_j}) (\frac{\partial C_{P_i}}{\partial X_j} + \sum_{\ell=1}^{N_j} b_{j,\ell} X_j^{\ell-1}) + D \sum_{j=1}^3 (\frac{\partial^2 C_{P_i}}{\partial X_j^2} + \sum_{\ell=2}^{N_j} \ell(\ell-1) b_{j,\ell} X_j^{\ell-2}) + P_i(C) + Q_i + S_i \tag{22}$$

where $X_j = (x, y, z)$ and $V_j = (u, v, w)$ are the dimensions of the uniform mesh in x, y and z , respectively. C_{P_i} denotes a periodic function for species i and

and $b_{j,\lambda}$ are the coefficients of polynomial function with degree N_j in X_j -direction. As mentioned earlier, the derivatives ($\partial C_p / \partial X_j$ and $\partial^2 C_p / \partial X_j^2$) can be obtained through pseudospectral technique by applying a finite Fourier transform and the coefficients $b_{j,\lambda}$ can be obtained by solving a system of algebraic equations formulated from the idea of periodic polynomial spline. The $\partial D / \partial X_j$ can be calculated in the same manner as $\partial C / \partial X_j$.

With the use of Eqs. (12), (18), (19), (20) and (22), a system of stiff partial differential equation (1) describing the atmospheric chemical pollutant transport and diffusion can be solved accurately and efficiently by using the multi-grid and step numerical technique presented in this paper.

4. NUMERICAL EXAMPLES

In order to implement and test the application of the multi-grid and step technique, we first performed the calculation of the two-dimensional advection equation [i.e. the right-hand side of Eq. (2) contains only $B(C) = -\nabla \cdot (VC)$]. The exact solution to the advection equation should keep C unchanged after a time of one revolution. In this test, the term of $B(C)$ is a function of C^{n+1} , which is known as implicit method. In our experiment, the coarsest grid has 9×9 mesh points and the finest grid has 17×17 mesh points. The Jacobi relaxation technique is used in the calculation of the multi-grid algorithm. Fig. 1 shows the three-dimensional perspective plots. The shape of cone is kept very well after one revolution.

In the second test, a stiff problem containing fast and slow reactants is chosen to demonstrate the feasibility of the technique. In Fig. 2, solid lines are numerical solutions and symbols (square for fast reactant and triangle for slow reactant) represent analytical solutions. It is seen that the numerical solutions agree well with this analytical solutions. The upper ordinate of Fig. 2

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shows the calculations in the beginning time period in which there are very sharp stiffnesses. Therefore, the initial time step $\Delta t = 10^{-5}$ was reduced automatically by the program to $\Delta t = 10^{-7}$ for accuracy. In order to illustrate the stability and efficiency of the method, the time step Δt and the order of polynomial k are plotted versus time in Fig. 3. In the beginning of simulation, the time step increases steadily while the order, necessarily an integer, increases in a step-like fashion. Upon reaching equilibrium state, the order remains at the maximum order allowed and the time step remains between 0.25 and 0.30. There are no instabilities occurring.

The next example involves a set of atmospheric chemical kinetic reactions, based on the mechanisms of the SCHEME model for atmospheric photochemical systems (Levine and Schwartz, 1978), as shown here in Table I. The numerical results using present technique are compared with the one using EPISODE code (Hindmarch and Byrne, 1975). Comparisons are shown in Table II for three and six hours simulation, respectively, for 12 chemical species with 30 chemical reactions. It is seen that the multi-grid and step method has about the same order of accuracy as EPISODE. However in this test run for six hours simulation, it takes 5.4 minutes for the present technique and 18.7 minutes for EPISODE code on a CDC 7600. For the present code, it requires 3776 time steps for six hours simulation while it needs 3600 time steps for EPISODE code because small time steps are necessary for accuracy in the present code during the first minute of simulation.

5. SUMMARY AND CONCLUSION

A multi-grid and step technique for solving the problem of chemical transport and diffusion in the atmosphere has been described. The basic steps for numerical techniques presented in this study are (1) to write a system of stiff ordinary differential equation in a form of extrapolant based on backward differentiation method, (2) to discretize the stiff partial differential equation on a

suitable grid domain by using a pseudospectral technique and (3) to solve the algebraic system by using a multi-grid method.

The present paper has demonstrated the capability and feasibility of the multi-grid and step technique for solving the stiff partial differential equations. The accuracy and efficiency have been shown in the test examples. The method of multi-grid and step has emerged as a potentially useful numerical techniques for atmospheric chemical problems.

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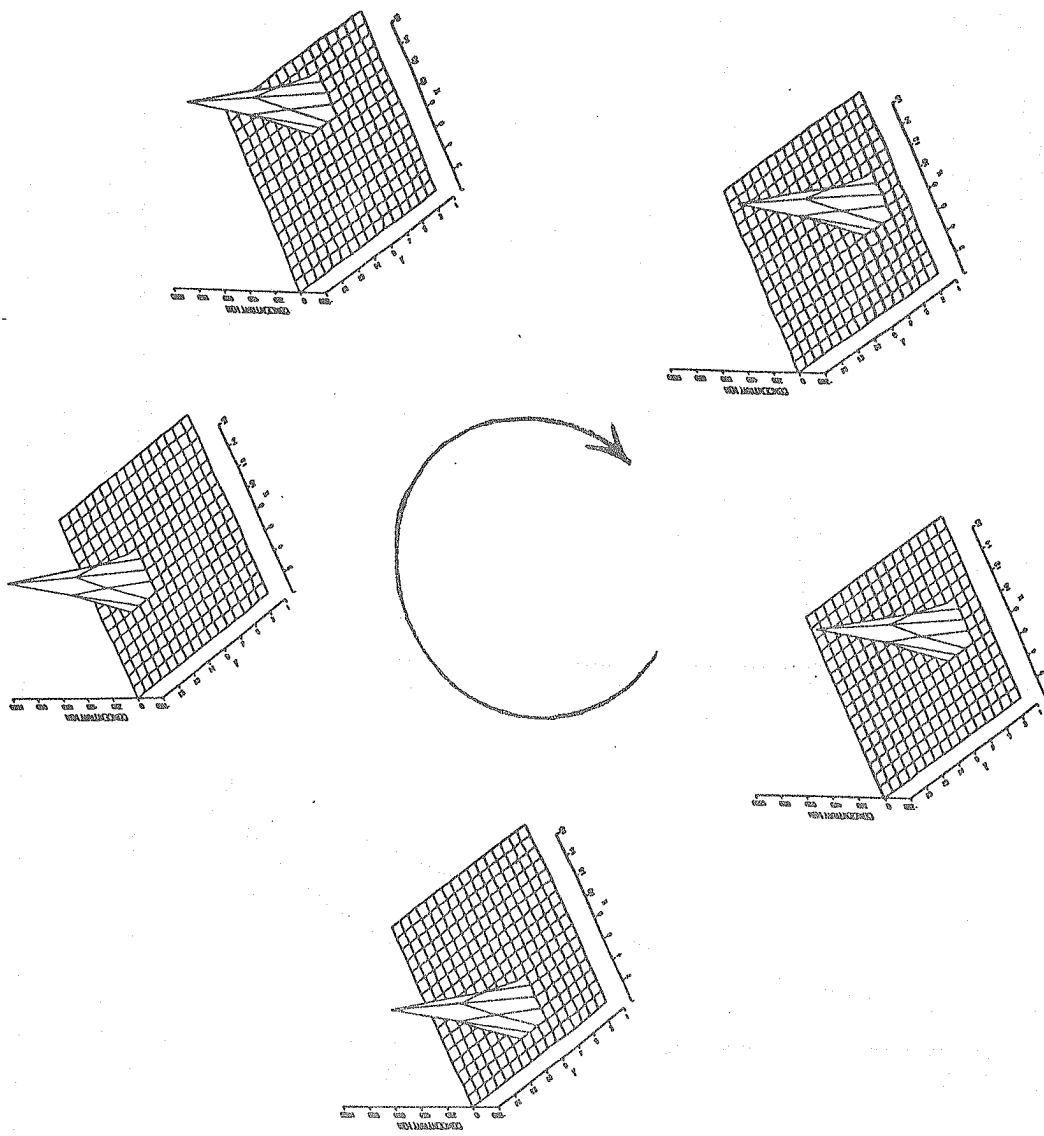


Figure 1. Three-dimensional perspective plots of a two-dimensional rotation cone.

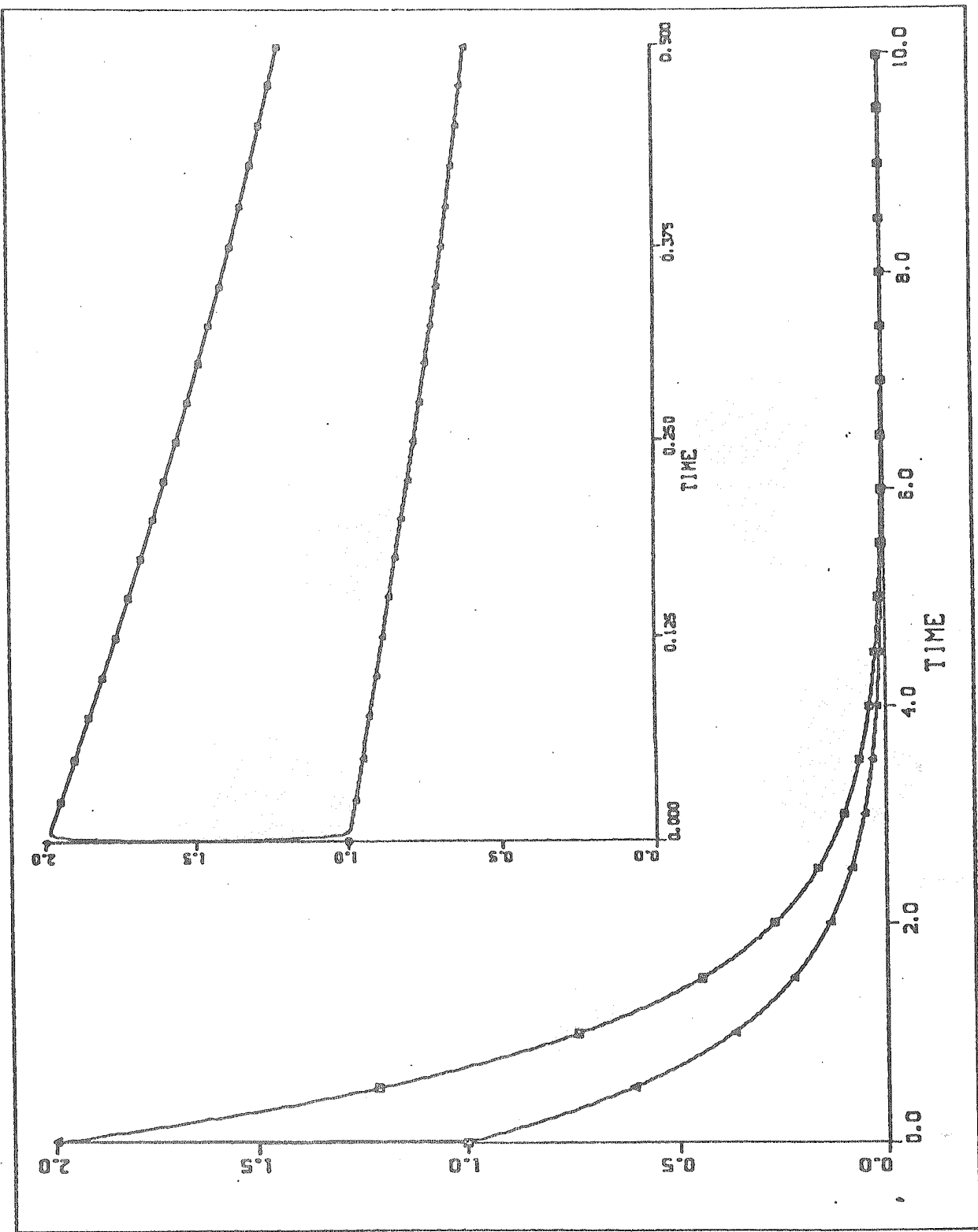


Figure 2. Numerical and analytical solutions for fast and slow reactants. The solutions in the beginning of time period are shown expanded in the upper ordinate.

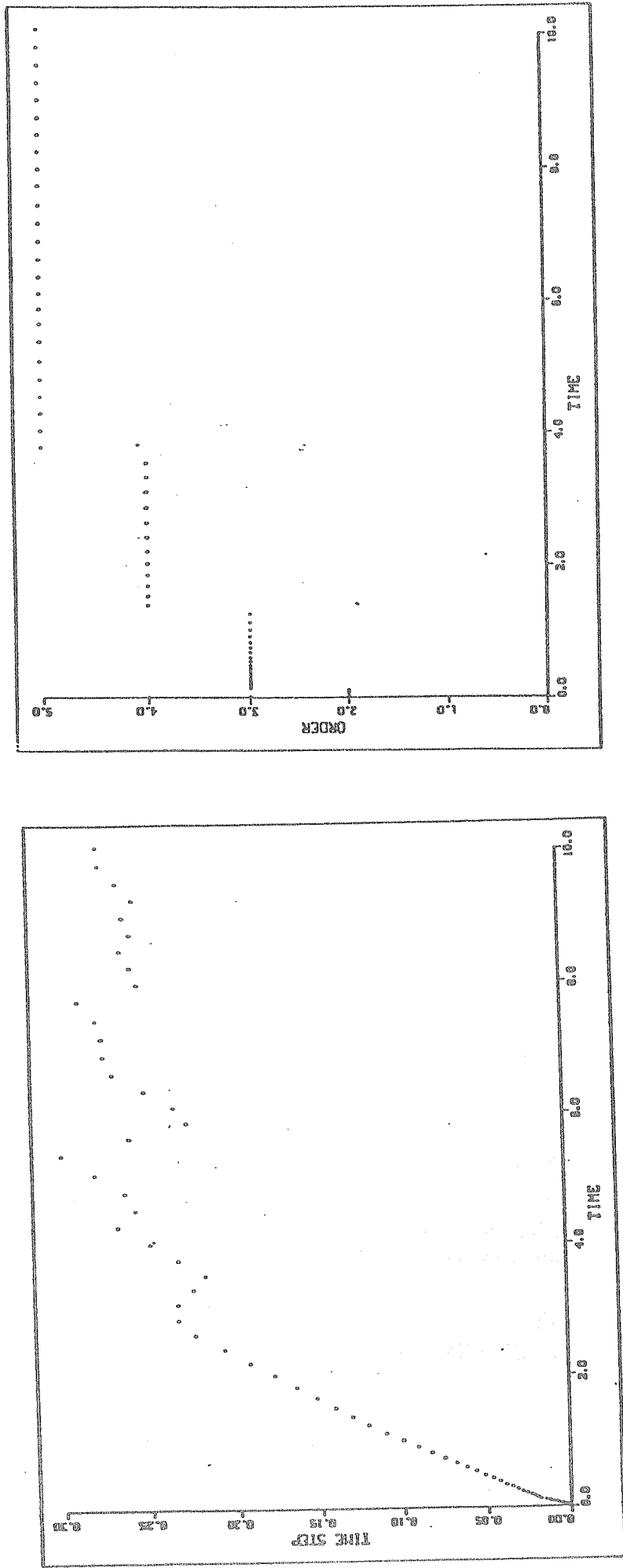


Figure 3. (a) Time step Δt versus time and (b) order of polynomial k versus time.

Table I. Reaction mechanisms in SCHEME model for atmospheric photochemical systems.

1. $\text{NO}_2 \rightarrow \text{NO} + \text{O}_3$	• k_1
2. $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2$	k_3
3. $\text{NO} + \text{NO}_2 + \text{O}_3 \rightarrow 2\text{NO}_2$	$k_4 k_5 \tau$
4. $2\text{NO}_2 + \text{O}_3 \rightarrow (2\text{HONO}_2)^\dagger$	$k_4 \gamma' \tau$
5. $\text{NO}_2 + \text{NO} \rightarrow 2\text{NO}_2$	• $k_1 k_9 / k_2 [\text{O}_2]$
6. $2\text{NO}_2 \rightarrow \text{NO} + \text{NO}_2$	• $k_1 k_{10} / k_2 [\text{O}_2]$
7. $2\text{NO}_2 + \text{NO} \rightarrow 3\text{NO}_2$	• $k_1 k_5 k_{11} \tau / k_2 [\text{O}_2]$
8. $3\text{NO}_2 \rightarrow \text{NO}_2 (+ 2\text{HONO}_2)$	• $k_1 k_{11} \gamma' \tau / k_2 [\text{O}_2]$
9. $\text{HONO} \rightarrow \text{NO} + \text{HO}$	• k_{14}
10. $\text{NO}_2 + \text{HO} \rightarrow (\text{HONO}_2)$	k_{15}
11. $\text{NO} + \text{HO} \rightarrow \text{HONO}$	k_{16}
12. $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{HO}$	k_{17}
13. $\text{H}_2\text{O}_2 \rightarrow 2\text{HO}$	• k_{18}
14. $\text{NO}_2 + \text{OLEF} \rightarrow \text{NO}_2 + \text{RO}_2 + .5\text{HO}_2 + .5\text{RCOO}_2$	• $k_1 k_{19} / k_2 [\text{O}_2]$
15. $\text{OLEF} + \text{HO} \rightarrow \text{ALD} + \text{RO}_2$	k_{20}
16. $\text{OLEF} + \text{O}_3 \rightarrow \text{ALD} + \text{RCOO}_2 + \text{HO}$	k_{21}
17. $\text{ALD} \rightarrow .25\text{RO}_2 + .75\text{HO}_2$	• k_{22}
18. $\text{ALD} + \text{HO} \rightarrow .5\text{RCOO}_2 + .5\text{HO}_2$	k_{23}
19. $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{ALD} + \text{HO}_2$	k_{24}
20. $\text{NO} + \text{RCOO}_2 \rightarrow \text{NO}_2 + \text{RO}_2$	k_{25}
21. $\text{NO}_2 + \text{RCOO}_2 \rightarrow (\text{PAN})$	k_{26}
22. $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	k_{30}
23. $\text{RO}_2 + \text{HO}_2 \rightarrow \text{ALD} + \text{HO}_2 + \text{HO}$	k_{31}
24. $2\text{RO}_2 \rightarrow 2\text{ALD} + 2\text{HO}_2$	k_{32}
25. $\text{HO} \rightarrow \text{HO}_2$	$k_{33} [\text{CO}]$
26. $\text{NO}_2 + \text{HO}_2 \rightarrow \text{HONO}$	k_{34}
27. $\text{SO}_2 + \text{HO}_2 \rightarrow \text{HO} (+ \text{H}_2\text{SO}_4)$	k_{38}
28. $\text{SO}_2 + \text{RO}_2 \rightarrow \text{ALD} + \text{HO}_2 (+ \text{H}_2\text{SO}_4)$	k_{39}
29. $\text{SO}_2 + \text{HO} \rightarrow \text{HO}_2 (+ \text{H}_2\text{SO}_4)$	k_{40}
30. $\text{SO}_2 + \text{NO}_2 \rightarrow \text{NO}_2 (+ \text{H}_2\text{SO}_4)$	• $k_1 k_{41} / k_2 [\text{O}_2]$

• Rate coefficient depends upon solar intensity.

† Compounds shown in parentheses are sink species not otherwise included in SCHEME.

$$\tau = \{k_5[\text{NO}] + \gamma'[\text{NO}_2]\}^{-1}$$

$$\gamma' = \{k_7 k_6 / (k_7 + k_8 [\text{H}_2\text{O}])\} - k_6$$

Table II. Comparison of EPISODE solutions with present model results for three and six hours simulation time, respectively, for 12 pollutant species.

	TIME = 180 (MIN)		TIME = 360 (MIN)	
	PRESENT MODEL	EPISODE	PRESENT MODEL	EPISODE
HO ₂	0.149125 x 10 ⁻³	0.148320 x 10 ⁻³	0.126569 x 10 ⁻³	0.125744 x 10 ⁻³
RO ₂	0.114785 x 10 ⁻⁴	0.115225 x 10 ⁻⁴	0.193062 x 10 ⁻⁴	0.195619 x 10 ⁻⁴
R _{COO} 2	0.849568 x 10 ⁻⁵	0.850495 x 10 ⁻⁵	0.596217 x 10 ⁻⁵	0.610356 x 10 ⁻⁵
H ₂ O ₂	0.230666 x 10 ⁻¹	0.229652 x 10 ⁻¹	0.420635 x 10 ⁻¹	0.417969 x 10 ⁻¹
OLEF	0.134814 x 10 ⁻²	0.127868 x 10 ⁻²	0.281587 x 10 ⁻⁴	0.257370 x 10 ⁻⁴
ALD	0.718058 x 10 ⁻¹	0.709588 x 10 ⁻¹	0.307491 x 10 ⁻¹	0.300513 x 10 ⁻¹
NO ₂	0.174122 x 10 ⁻¹	0.170503 x 10 ⁻¹	0.402571 x 10 ⁻²	0.386798 x 10 ⁻²
NO	0.994564 x 10 ⁻³	0.975217 x 10 ⁻³	0.203494 x 10 ⁻³	0.196072 x 10 ⁻³
SO ₂	0.908958 x 10 ⁻²	0.908088 x 10 ⁻²	0.848759 x 10 ⁻²	0.847311 x 10 ⁻²
HONO	0.171523 x 10 ⁻³	0.167171 x 10 ⁻³	0.315560 x 10 ⁻⁴	0.301587 x 10 ⁻⁴
O ₃	0.321381	0.321000	0.364480	0.363400
HO	0.837048 x 10 ⁻⁷	0.839357 x 10 ⁻⁷	0.393690 x 10 ⁻⁷	0.397520 x 10 ⁻⁷