HANDLING THE CHEMICAL PART
IN LARGE AIR POLLUTION MODELS

JØRGEN BRANDT*, JERZY WAŚNIEWSKI**

ZAHARI ZLATEV*

Studying the transboundary transport of air pollutants is an important environmental problem. Systems of partial differential equations are normally arising when mathematical models are used in the solution of this problem. The interrelations between the different air pollutants are rather complicated. Therefore many air pollutants are to be included in the models. This leads to very large and very complicated numerical tasks. The chemical part of an air pollution model is one of the most difficult parts for the numerical algorithms. It is necessary to apply reliable and sufficiently accurate algorithms during the numerical treatment of the chemical sub-models. Moreover, it is also necessary to apply fast numerical algorithms that can be run efficiently on modern high-speed computers. These two important requirements work, as often happens in practice, in opposite directions. Therefore a good compromise is needed. Some results achieved in the efforts to find a good compromise will be described. The advantages and disadvantages of several numerical methods will be discussed. All conclusions are made for the particular situation where large air pollution models are to be treated on big modern high-speed computers. Moreover, it is also assumed that a particular air pollution model, namely the Danish Eulerian Model, is used. However, the ODE systems that arise in the chemical sub-models have at least three rather common properties, which appear again and again when large scientific and engineering problems are studied. These systems are large, stiff and badly scaled. Therefore some of the conclusions are also valid in a much more general context, i.e. in all cases where large, stiff and badly scaled systems of ODE's are to be handled numerically.

1. Long-Range Transport of Air Pollutants (LRTAP)

Air pollutants emitted by different sources can be transported, by the wind, on long distances. Several physical processes (diffusion, deposition and chemical transformations) take place during the transport. Regions that are very far from the large emission sources may also be polluted. It is well-known that the atmosphere must be kept clean (or, at least, should not be polluted too much). It is also well-known that if

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 * National Environmental Research Institute, Frederiksborgvej 399, DK-4000 Roskilde, Denmark, e-mail: {lujbr@sun4, luzz@sun2}.dmu.dk
 ** Danish Computing Centre for Research and Education, UNI• C , DTU, Bldg. 304, DK-2800 Lyngby, Denmark, e-mail: jerzy.wasniewski@uni-c.dk

the concentrations of some species exceed certain acceptable (or critical) levels, then they may become dangerous for plants, animals and humans.

The concentrations of many dangerous air pollutants have been increased during the last two-three decades. Unfortunately, this process is continuing and the concentrations of some pollutants have reached (or will soon reach) the critical (or acceptable) levels. Therefore it is important to apply some control strategies by the use of which it would be possible:

1. to reduce the air pollution to the acceptable levels,

2. to keep the air pollution under the acceptable levels.

However, it must be emphasized that both processes are normally very expensive. Therefore one *must reduce* the air pollution to the acceptable levels. Moreover, one must solve the above two tasks in an optimal way (the procedure must be as cheap as possible). This is why mathematical models are necessary in the attempt to predict the optimal way of keeping the air pollution under certain levels. It should be emphasized here that the mathematical models are the only tool by the use of which one can predict the results of many different actions and, moreover, one can attempt to choose the best solution (or, at least, a solution which is close to the best one) in the efforts to reduce the air pollution in an optimal way.

The use of a mathematical model is only a necessary condition for achieving success. In many cases it is not sufficient. Several other requirements are also to be satisfied. The reliability of the mathematical model is one of these extra requirements. The mathematical model selected should be correctly formulated and, furthermore, it should be treated numerically by sufficiently accurate numerical methods. Some results obtained in the attempts to satisfy the last requirement will be discussed in the following sections. Achieving high-speed performance in the chemical part of a large air pollution model is as a rule the most difficult task that can be solved in the attempts to ensure global efficiency during the numerical treatment of the whole model. The use of some numerical methods in the chemical sub-model will be described. Numerical results will be given to illustrate the advantages and disadvantages of the methods studied.

2. Mathematical Description of an LRTAP Model

The long range transport of air pollutants over Europe is studied by the following system of partial differential equations (PDE's):

$$
\begin{aligned}
\frac{\partial c_s}{\partial t} \; = \; & -\frac{\partial(uc_s)}{\partial x} - \frac{\partial(vc_s)}{\partial y} - \frac{\partial(wc_s)}{\partial z} \\
& + \frac{\partial}{\partial x}\left(K_x \frac{\partial c_s}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial c_s}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial c_s}{\partial z}\right) \\
& + E_s + Q_s(c_1, c_2, \ldots, c_q) - (\kappa_{1s} + \kappa_{2s})c_s, \qquad s = 1, 2, \ldots, q
\end{aligned}
\tag{1}
$$

The number of equations q is equal to the number of species that are involved in the model and varies in different studies. The largest number of equations used until now was 168 (it may be necessary to involve more species in the future). The different quantities that are involved in the mathematical model have the following meaning:

1. the concentrations are denoted by c_s;

2. u, v and w are wind velocities;

3. K_x, K_y and K_z are diffusion coefficients;

4. the emission sources in the space domain are described by the functions E_s;

5. κ_{1s} and κ_{2s} are deposition coefficients;

6. the chemical reactions are described by the non-linear functions $Q_s(c_1, c_2, \ldots, c_q)$.

The non-linear functions Q_s are of the form

$$Q_s(c_1, c_2, \ldots, c_q) = -\sum_{i=1}^{q} \alpha_{si} c_i + \sum_{i=1}^{q} \sum_{j=1}^{q} \beta_{sij} c_i c_j, \qquad s = 1, 2, \ldots, q \quad (2)$$

This is a special kind of non-linearity, but it is not clear how to exploit this fact during the numerical treatment of the model.

It is clear from the above description of the quantities involved in the mathematical model that all five physical processes (advection, diffusion, emission, deposition and chemical reactions) can be studied by using the above system of PDE's. The most important processes are the advection (the transport) and the chemical reactions. Kernels for these two parts of the model will be discussed in more detail.

2.1. Splitting the Model

It is difficult to treat the system of PDE's (1) directly. This is the reason for using different kinds of splitting. A simple splitting procedure, based on ideas proposed in (Marchuk, 1985; McRae *et al.*, 1984) can be defined, for $s = 1, 2, \ldots, q$, by the following sub-models:

$$\frac{\partial c_s^{(1)}}{\partial t} = -\frac{\partial (u c_s^{(1)})}{\partial x} - \frac{\partial (v c_s^{(1)})}{\partial y} \tag{3}$$

$$\frac{\partial c_s^{(2)}}{\partial t} = \frac{\partial}{\partial x}\left(K_x \frac{\partial c_s^{(2)}}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial c_s^{(2)}}{\partial y}\right) \tag{4}$$

$$\frac{dc_s^{(3)}}{dt} = E_s + Q_s(c_1^{(3)}, c_2^{(3)}, \ldots, c_q^{(3)}) \tag{5}$$

$$\frac{dc_s^{(4)}}{dt} = -(\kappa_{1s} + \kappa_{2s}) c_s^{(4)} \tag{6}$$

$$\frac{\partial c_s^{(5)}}{\partial t} = -\frac{\partial (w c_s^{(5)})}{\partial z} + \frac{\partial}{\partial z}\left(K_z \frac{\partial c_s^{(5)}}{\partial z}\right) \tag{7}$$

The horizontal advection, the horizontal diffusion, the chemistry, the deposition and the vertical exchange are described by the systems (3)–(7). This is not the only way to split the model defined by (1). The particular splitting procedure (3)–(7) has three advantages: (i) the physical processes involved in the big model can be studied separately, (ii) it is easier to find optimal (or good) methods for the simpler systems (3)–(7) than for the big system (1) and (iii) if the model is to be considered as a two-dimensional model (which often happens in practice), then one should just skip the system (7).

2.2. Space Discretization

Assume that the space domain is a parallellepiped which is discretized by using an equidistant grid with $N_x \times N_y \times N_z$ grid-points, where N_x, N_y and N_z are the numbers of the grid-points along the grid-lines parallel to the Ox, Oy and Oz axes, respectively. Assume also that the number of chemical species involved in the model is $q = N_s$. Finally, assume that the spatial derivatives in (1) are discretized by some numerical algorithm. Then the system of PDE's (1) will be transformed into a system of ODE's

$$\frac{\mathrm{d}g}{\mathrm{d}t} = f(t, g) \tag{8}$$

where $g(t)$ is a vector-function with $N_x \times N_y \times N_z \times N_s$ components. Moreover, the components of function $g(t)$ are the concentrations (at time t) at all grid-points and for all species. The right-hand side of (8) is also a vector function with $N_x \times N_y \times N_z \times N_s$ components which depends on the particular discretization method used and of the concentrations of the different chemical species at the grid-points. If the space-discretization method is fixed and if the concentrations are calculated (at all grid-points and for all species), then the right-hand side vector in (8) can also be calculated.

As mentioned above, the large air pollution models are not discretized directly. Some kind of splitting is always used. If the model is split into sub-models as in the previous subsection, then the application of discretization methods (normally different methods for the different sub-models) will lead to the following ODE systems:

$$\frac{\mathrm{d}g^{(1)}}{\mathrm{d}t} = f^{(1)}(t, g^{(1)}) \tag{9}$$

$$\frac{\mathrm{d}g^{(2)}}{\mathrm{d}t} = f^{(2)}(t, g^{(2)}) \tag{10}$$

$$\frac{\mathrm{d}g^{(3)}}{\mathrm{d}t} = f^{(3)}(t, g^{(3)}) \tag{11}$$

$$\frac{\mathrm{d}g^{(4)}}{\mathrm{d}t} = f^{(4)}(t, g^{(4)}) \tag{12}$$

$$\frac{\mathrm{d}g^{(5)}}{\mathrm{d}t} = f^{(5)}(t, g^{(5)}) \tag{13}$$

where $g^{(i)}$ and $f^{(i)}$, $i = 1, 2, 3, 4, 5$, are again vector-functions with $N_x \times N_y \times N_z \times N_s$ components. The functions $f^{(i)}$, $i = 1, 2, 3, 4, 5$, depend on the discretization methods used. Some particular numerical methods, that can be used in the discretization of the five sub-models (3)–(7) in order to obtain ODE systems of type (9)–(13) are listed below.

The discretization of the spatial derivatives in the sub-model describing the horizontal advection, the PDE system (3), can be carried out either by using pseudospectral expansions or by applying finite elements; (Zlatev, 1995; Zlatev *et al.*, 1994). Other numerical methods can also be applied. It is important to emphasize that the resulting system (9) contains $q = N_s$ independent ODE systems (i.e. one such a system per each chemical species). This fact could easily be exploited on parallel computers.

The discretization of the second-order spatial derivatives in the horizontal diffusion sub-model, the PDE system (4), is quite similar. Both the pseudospectral algorithm and finite elements can be used. Again, other numerical algorithms can also be applied. The number of independent systems of ODE's in the resulting system (10) is again $q = N_s$, i.e. the same as in the previous case. It may be useful to apply different numerical algorithms in the advection and diffusion parts; see again (Zlatev, 1995; Zlatev *et al.*, 1994).

The transition from (5) to (11) as well as the transition from (6) to (12) is trivial, because there are no spatial derivatives in (5) and (6). In the first case, the resulting ODE system (11) contains $N_x \times N_y \times N_z$ independent systems, each of them with N_s equations (because the chemical species at a given grid-point react with each other but not with chemical species at other grid-points). In the second case, the resulting system (12) consists of $N_x \times N_y \times N_z \times N_s$ independent ODE's (because the deposition of a given species at a given grid-point depends neither on the deposition of the other species nor on the deposition processes at the other grid-points). It is seen from the above discussion that there arise a lot of parallel tasks, in a natural way, when the ODE systems (11) and (12) are to be handled.

Finite elements can be applied in the discretization of the spatial derivatives in the vertical exchange sub-model (7). The resulting ODE system (13) consists of $N_x \times N_y \times N_s$ independent ODE systems. Each of them is defined on a vertical grid-line and, therefore, contains N_z equations.

2.3. Time Integration

It is necessary to couple the five ODE systems (9)–(13). The coupling procedure is connected with the time-integration of these systems. Assume that the values of the concentrations (for all species and at all grid-points) have been found for some

$t = t_n$. According to the notation introduced in the previous subsection, these values are components of the vector-function $g(t_n)$. The next time-step $n+1$ (at which the concentrations are found at $t_{n+1} = t_n + \Delta t$, where Δt is some increment) can be performed by integrating successively the five systems (9)–(13). The values of $g(t_n)$ are used as an initial condition in the solution of (9). The solution of each of the systems (9)–(12) is used as an initial condition in the solution of the next system. The solution of the last system (13) is used as an approximation to $g(t_{n+1})$. In this way, everything is prepared to start the calculations in the next time-step $n + 2$.

Predictor-corrector methods with several different correctors are used in the solution of the ODE systems (9) and (10). The correctors are carefully chosen so that the stability of the method is enhanced (Zlatev, 1984).

Several different methods have been tried in the solution of the ODE system (11) (Zlatev, 1995). The QSSA (quasi-steady-state approximation) is simple and relatively stable but not very accurate (therefore it has to be run with a small time-stepsize). The classical numerical methods (Backward Euler Method, the Trapezoidal Rule and a second-order Runge-Kutta algorithm) lead to the solution of non-linear systems of algebraic equations and, therefore, they are more expensive. On the other hand, these methods can be incorporated with an error control and perhaps with larger time-steps. The extrapolation methods are also promising. It is easy to achieve error estimation and to carry out the integration with large time-steps when these algorithms are used. However, it is difficult to implement such methods in an efficient way when all five systems (9)–(13) are to be treated successively. The experiments with different integration methods for the chemical sub-model (11) are continuing. The QSSA will be used in most of the experiments described here.

The next ODE system (12) contains (see the previous subsection) $N_x \times N_y \times N_z \times N_s$ independent ODE's. Moreover, all these ODE's are linear. Therefore they are solved exactly during the numerical treatment of the model.

The last ODE system, (13), can be solved by using many classical time-integration methods. The so-called θ-method (Lambert, 1991) is used in the three-dimensional version of the Danish Eulerian Model (Zlatev, 1995).

3. Need for High-Speed Computers

The size of the systems that arise after the space discretization and the splitting procedures used to treat numerically (1) is enormous. Consider the case where the model is two-dimensional. Let us assume that the model is discretized on a (96×96) grid (such a grid has been used in the Danish Eulerian Model since 1993) and that $q = 35$. Then the number of equations in each of the four systems of ODE's (9)–(12) is 322560. The time-stepsize used in the advection step is 15 min. The chemical sub-model (11) cannot be treated with such a large time-stepsize (because it is very stiff; especially when photochemical reactions are involved). Therefore six small time-steps are carried out for each advection time-step (this means that the chemical time-stepsize is 2.5 min). From this description it is clear that in fact nine systems of ODE's (each of them containing 322560 equations) are to be treated per advection

step. Assume that a one-month run is to be carried with the model. This will result in 3456 advection time-steps (taking here into account that it is necessary to use five extra days in order to start up the model).

Consider now the case where the model is three-dimensional. Assume that ten layers are used in the vertical direction. Then the number of equations in each system of ODE's is 3225600 (i.e. ten times greater than in the previous case). The number of systems to be treated at each time-step is increased from four to five. The number of time-steps remains the same, i.e. 3456. The chemical sub-model must again be integrated by using smaller time-steps.

It is clear that such large problems can be solved *only* if new and modern high-speed computers are used. Moreover, it is necessary to select right numerical algorithms (which are most suitable for the high-speed computers available) and to perform the programming work very carefully in order to exploit fully the great potential power of the vector and/or parallel computers.

4. The Chemical Part of the Model

It has been mentioned several times that the chemical sub-model is the most time-consuming part during the numerical treatment of a large air-pollution model. There are a lot of open questions when the chemical part is handled. The basic question is: What is the optimal chemical scheme? The answer will, of course, depend on the requirements that are stated, and for different requirements different chemical schemes will provide the best choice. However, even if the requirements are well-defined, it is still difficult to select the chemical scheme which will satisfy these requirements with minimal computational efforts. In an attempt to answer this question, experiments with four chemical schemes are carried out (some other chemical schemes can be found in (Borrell *et al.*, 1990)).

The first of them contains only ten species. It has been tested in (Hov *et al.*, 1988). This scheme is rather good when different numerical algorithms are to be tested (it is rather small, but contains all difficult reactions, including photochemical ones).

The second chemical scheme contains 35 species. It has been proposed by (Gery *et al.*, 1989). This scheme is well-known under the name the CBM IV scheme and has been used in several large air pollution models. In fact, the scheme actually used here is an enhanced version of the CBM IV scheme; the enhancements have been obtained by adding several reactions for handling the ammonia-ammonium transformations in the atmosphere (Zlatev, 1995).

The third chemical scheme contains 56 species. It is very similar to the scheme used by (Simpson, 1992; 1993).

The fourth chemical scheme contains 168 species. This scheme is similar to one of the schemes developed by Derwent and Hov (1979).

The experiments with these schemes are continuing. The main conclusion from the results obtained until now is that not only is the size of the systems (9)–(13) increased quickly when the number of species in the scheme grows, but also these

systems become very stiff and very badly scaled. This causes great difficulties when the systems (9)–(13) are treated numerically.

It should be emphasized that the ODE systems (9)–(13) are very badly scaled also for the first scheme with ten species. This is illustrated in Table 1. It is seen that the initial values of the different species vary in the range $[10^{-3}, 10^{11}]$, while the concentrations of nitrogen oxide, NO, vary in the range $[10^{-24}, 10^{11}]$. The effect of badly scaling is even more pronounced for larger chemical schemes.

Tab. 1. The initial values, the minimal values and the maximal values of the concentrations (measured in molecules per cubic centimeter) obtained in a short run of the chemical scheme with ten species (the run starts at 6:00 and ends at 24:00 the next day).

Pollutant	Initial condition	Minimal value	Maximal value
NO	1.0×10^{11}	7.1×10^{-24}	1.0×10^{11}
NO_2	1.0×10^{11}	7.6×10^7	1.0×10^{11}
HC	1.0×10^{11}	8.4×10^8	1.0×10^{11}
ALD	5.0×10^{10}	5.0×10^{10}	5.1×10^{11}
O_3	5.0×10^{11}	5.0×10^{11}	1.6×10^{12}
HNO_3	1.0×10^{10}	1.0×10^{10}	2.1×10^{11}
HO_2	1.0×10^6	1.0×10^6	1.3×10^{12}
RO_2	1.0×10^6	1.0×10^6	4.3×10^{10}
OH	1.0×10^5	1.9×10^{-19}	7.3×10^7
$O(^1D)$	1.0×10^{-3}	3.4×10^{-28}	2.6×10^{-2}

The fact that the chemical schemes are very badly scaled is not the only problem for the numerical algorithms. The sun-rise and sun-set periods also cause troubles. The photochemical reactions are switched on after sun-rise and switched off after sun-set. This causes rapid changes of some of the concentrations. The changes around sun-rises and sun-sets are clearly seen in Fig. 1.

5. The Quasi-Steady-State-Approximation (QSSA)

Consider the ODE system (11). This system reduces to small ODE systems; their number is equal to the number of grid-points, and the size of each of them is equal to the number of species (see Subsection 2.2). It is clear that one can consider the ODE system at any of the grid-point in order to explain how a numerical method can be chosen. It is worthwhile to simplify the notation. Let us select an arbitrary grid-point and denote by y_s the concentration of the s-th chemical species, $s = 1, 2, ..., q$. Furthermore, let us denote the corresponding right-hand side by f_s. Then the small ODE system corresponding to the grid-point chosen can be written as:

$$\frac{dy_s}{dt} = f_s(t, y_1, y_2, ..., y_q), \qquad s = 1, 2, ..., q \tag{14}$$

This notation is commonly used in the field of numerical methods for ordinary differential equations. However, the chemists prefer to rewrite (14) in the following form:

$$\frac{dy_s}{dt} = P_s(t, y_1, y_2, ..., y_q) - L_s(t, y_1, y_2, ..., y_q)c_s, \qquad s = 1, 2, ..., q \quad (15)$$

where $P_s = P_s(t, y_1, y_2, ..., y_q)$ and $L_s = L_s(t, y_1, y_2, ..., y_q)$ are non-negative functions which are called production terms and loss terms, respectively.
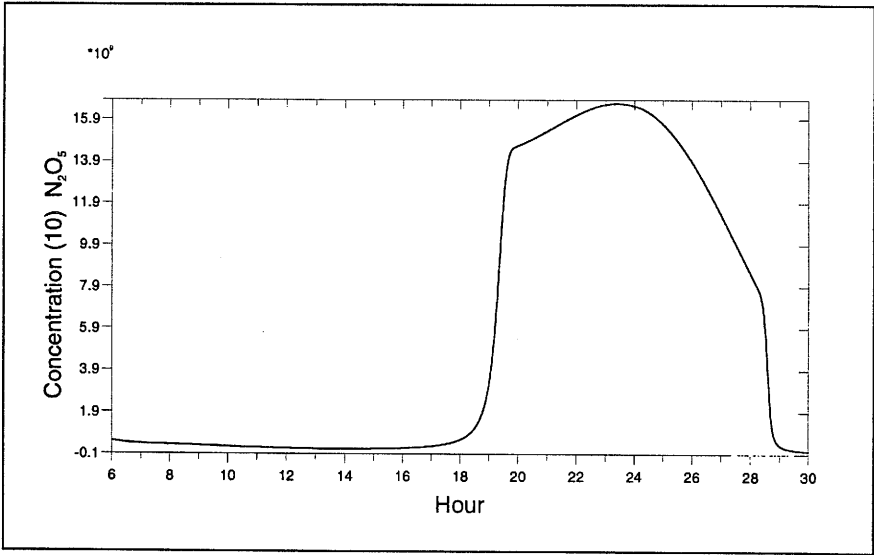

Fig. 1. The variation of the N_2O_5 concentrations from the scheme with 56 species (the concentrations are measured in molecules/cm^3).

Assume that some approximations y_s^n to the solutions $y_s(t_n)$ of (15) at $t = t_n$ have been found. Let Δt be a given increment such that $t_{n+1} = t_n + \Delta t$. Then the QSSA (the quasi-steady-state-approximation) can be applied to calculate approximations y_s^{n+1} to the solutions $y_s(t_{n+1})$ of (15) at $t = t_{n+1}$. In (Hesstvedt *et al.*, 1978) the QSSA is defined by using (for $s = 1, 2, ..., q$) the following three formulae:

$$y_s^{n+1} = \frac{P_s}{L_s} \qquad \text{for} \quad \Delta t L_s > 10 \qquad (16)$$

$$y_s^{n+1} = \frac{P_s}{L_s} + (y_s^n - \frac{P_s}{L_s})e^{-\Delta t L_s} \qquad \text{for} \quad 0.01 < \Delta t L_s \leq 10 \qquad (17)$$

$$y_s^{n+1} = y_s^n + \Delta t(P_s - L_s y_s^n) \qquad \text{for} \quad \Delta t L_s \leq 0.01 \qquad (18)$$

where it is assumed that the functions P_s and L_s are calculated for $t = t_n$. This means that all the three formulae are considered as explicit ones. However, this

algorithm is normally combined with some iterative process. The following actions are to be carried out at each iteration (until certain stopping criteria are satisfied) when an iterative procedure is used:

1. Calculate approximations y_s^{n+1} for $s = 1, 2, ..., q$.

2. Update the values of P_s and L_s or $s = 1, 2, ..., q$.

3. Check the stoping criteria.

Such an iterative process is often used in practice (it is called either the functional iteration or the simple iteration), but there is no guarantee that it will converge. Moreover, very often no stopping criteria are specified (i.e. the third task in the algorithm given above is simply omitted, and the iteration is stopped after some prescribed number of iterations). Nevertheless, many experiments which were carried out in (Hesstvedt *et al.*, 1978) indicate that the QSSA gives good results when the time-steps are small ($\Delta t \leq 30$ seconds).

The straight forward application of the QSSA on modern high-speed computers (especially on vector processors) may result in slow performance. Indeed, three questions are to be asked at each grid-point and for each species (i.e. up to 10^6 times at each time-step). Moreover, the calculation of the exponential function is expensive on some computers. This is why some simplifications of this scheme has been proposed in (Verwer and van Loon, 1996; Verwer and Simpson, 1996). Two main ideas are used in these references: (i) only formula (17) is applied in the numerical integration and (ii) the exponential function with the approximation is replaced by

$$e^{-\Delta t L_s} = \frac{1}{1 + \Delta t L_s + 0.5(\Delta t L_s)^2} \tag{19}$$

Then it can easily be seen that the following formula can be used to calculate approximations to y_s^{n+1}, where $s = 1, 2, ..., q$ and $n = 1, 2, ...$ (assuming here that some starting approximations y_s^0 for $s = 1, 2, ..., q$ are given):

$$y_s^{n+1} = \frac{y_s^n + [1 + 0.5\Delta t L_s]\Delta t P_s}{1 + \Delta t L_s + 0.5(\Delta t L_s)^2} \tag{20}$$

The use of the last formula can be combined with all devices that are usually used together with the QSSA algorithm (one can e.g. apply the lumped mass principle and/or separate the chemical species into two groups, namely slowly varying species and quickly varying species). One can apply this formula both as an explicit formula (inserting in P_s and L_s the values of the concentrations obtained at step n) or as an implicit formula (inserting in P_s and L_s the values of the concentrations obtained at step $n + 1$). The simple functional iterative procedure may be applied in the former case (as for the classical QSSA algorithm). In the latter case an iterative method must be used. One can use again the functional iteration, but a more advanced iterative method (some modification of the classical Newton method, methods based on the use of a Krylov subspace or the Gauss-Seidel iteration) can also be applied in this case.

6. Use of Some Classical ODE Methods

Let us consider formula (14). Introduce the abbreviations $f_s = f_s(t, y_1, y_2, ..., y_q)$ for $s = 1, 2, ..., q$. Several classical numerical methods can be formulated by using this notation:

$$y_s^{n+1} = y_s^n + \Delta t f_s^{n+1}, \qquad \text{for} \quad s = 1, 2, ..., q \qquad (21)$$

$$y_s^{n+1} = y_s^n + 0.5\Delta t(f_s^{n+1} + f_s^n), \qquad \text{for} \quad s = 1, 2, ..., q \qquad (22)$$

$$y_s^{n+1} = y_s^n + 0.5\Delta t(k_{1s}^{n+1} + k_{2s}^{n+1}), \qquad \text{for} \quad s = 1, 2, ..., q \qquad (23)$$

where

$$k_{1s}^{n+1} = f_s(t + 0.5\Delta t, y_1^n + \Delta t\gamma k_{11}^{n+1}, y_2^n + \Delta t\gamma k_{12}^{n+1}, ..., y_q^n + \Delta t\gamma k_{1q}^{n+1}) \qquad (24)$$

and

$$k_{2s}^{n+1} = f_s(t + 0.5\Delta t, y_1^n + \Delta t(\beta k_{11}^{n+1} + \gamma k_{21}^{n+1}), y_2^n + \Delta t(\beta k_{12}^{n+1} + \gamma k_{22}^{n+1}), \qquad (25)$$

$$..., y_q^n + \Delta t(\beta k_{1q}^{n+1} + \gamma k_{2q}^{n+1}))$$

the constants β and γ being defined by

$$\beta = \sqrt{2} - 1, \qquad \gamma = 1 - 0.5\sqrt{2} \qquad (26)$$

The Backward Euler Method is defined by (21). Another implementation of this method can be found in (Hertel *et al.*, 1993). In the latter implementation the chemical scheme is divided into blocks; the properties of the particular chemical scheme, which is attached to the model, are exploited in order to determine proper blocks (thus, the blocked method is tuned to the particular chemical scheme used). The Trapezoidal Rule is defined by (22). Finally, the second-order Runge-Kutta method from (Zlatev, 1981) is defined by the remaining formulae (23)–(26).

Each of these methods has both some advantages and some disadvantages. The Backward Euler Method is computationally very simple. It has very nice stability properties (it is L-stable, see e.g. (Hairer and Wanner, 1991) for the concept of L-stability). However, this method is not very accurate; its order of accuracy is one.

The Trapezoidal Rule is more accurate (it is a second-order method). It is also computationally simple (but it is slightly more expensive than the Backard Euler Method). It is only A-stable, which indicates that one can have some stability problems when the ODE system solved is very stiff.

The Runge-Kutta method defined by formulae (23)–(26) is both an accurate and very stable. Its order of accuracy is two and it is L-stable. However, this method is computationally much more expensive than the other two methods. The implementation of this method which has been used in the experiments requires about two or three times more computing time than the other two methods. The computing time is a very important factor when large air pollution problems are to be

treated numerically. Therefore this method (or, more precisely, the implementation of this method used in the experiments) has been judged as unsuitable. However, it should be mentioned here that either a better implementation of this method or another Runge-Kutta method may be useful if it allows us to carry out the numerical integration with large time-stepsizes. Further efforts in this direction are necessary.

The above discussion indicates that a combination of the Trapezoidal Rule and the Backward Euler Method might work well if such a combination results in a numerical method which has the advantages of the two underlining methods: the good stability properties of the Backward Euler Method and the good accuracy of the Trapezoidal Rule. An attempt to obtain a combination that preserves the good properties of the two underlining methods has been carried out by using the following two major rules:

1. If the Trapezoidal Rule is in use and if the time-stepsize has been reduced successively three times, then switch from the Trapezoidal Rule to the Backward Euler Method.

2. If the Backward Euler Method is in use and if the time-stepsize has successfully been increased three times, then switch from the Backward Euler Method to the Trapezoidal Rule.

Some other rules are also to be used. For example, some rules for the treatment of negative concentrations are necessary (negative concentrations will normally cause great problems when chemical modules are to be handled). However, the above two rules are the most important for the combined method. The procedure can perhaps be refined. It will be shown here that even in such a simple form it produces rather satisfactory results (see Table 2 to Table 4).

The combined method has been tested in a chemical module based on the reaction scheme proposed in (Gery *et al.*, 1989). The module has been run as a box-model. This means that only the small ODE system (14) is treated; if the chemical scheme contains 35 species, then (14) contains 35 equations. The difficulties which may arise when the chemical module is inserted in a large air pollution model will be discussed in the next section.

The combined method performs considerably better than the second-order Runge-Kutta method. The same is true when the combined method is compared with the method based on the Trapezoidal Rule only. Therefore the performance of the combined method is compared with the performance of the QSSA and with the performance achieved when only the Backward Euler is used in the calculations. The computing times achieved when the methods selected were run over a time-interval of 42 hours are shown in Table 2; some accuracy results are given in Table 3 and Table 4. The accuracy of the results is checked by using a reference run performed with a very small stepsize ($\Delta t = 0.01\,\text{s}$).

6.1. Comparing the Computational Efficiency

The computing times for QSSA, which are given in Table 2, were obtained by using a constant stepsize and a fixed number of iterations (with no attempt to control the

errror). In the other two methods the time-stepsize shown is an upper bound of the time-stepsize that can be selected during the calculations. Moreover, an error control (based on simple local truncation error estimates) is carried out with these two methods; in an attempt to keep, at every time-step, the relative local truncation error (for every compound) less than 0.01. The results in Table 2 show that:

- The combined method is faster than the Backward Euler Method for all stepsizes.
- For small stepsizes (5 s and 10 s) the combined method is faster than QSSA, but QSSA is faster when the stepsizes are larger than 10 s (and much faster when the stepsize is very large; say, $\Delta t = 900$ s)

The choice of a good stepsize may be a problem for QSSA. Different values of the stepsize are used in the literature. Hesstvedt *et al.* (1978) recommend the use of $\Delta t = 30$ s this recommendation is based on many experiments. The same choice of the stepsize for QSSA has been made in (Chock *et al.*, 1994) where several solvers are compared. Shieh *et al.* (1988) have used $\Delta t = 30$ s during daytime, $\Delta t = 60$ s during nighttime, but $\Delta t = 12$ s during sunrise and sunset. Odman *et al.* (1992) move up used $\Delta t = 5$ s in photochemical simulations in order to improve the accuracy. On the other hand, Simpson (1992; 1993) is permanently using $\Delta t = 900$ s in the numerical treatement of his photooxidant model.

Tab. 2. Computing times, measured in seconds, obtained on a SUN work-station by using three numerical algorithms (the run starts at 6:00 and ends at 24:00 the next day).

Time-stepsize	QSSA	Backward Euler	Combined Method
5 s	85.8	82.3	80.7
10 s	43.7	44.3	39.6
30 s	14.9	19.9	16.4
150 s	3.1	10.9	6.2
900 s	0.6	11.3	4.7

Tab. 3. The largest relative errors found during the calculation of nitrogen dioxide by using three numerical algorithms (the run starts at 6:00 and ends at 24:00 the next day).

Time-stepsize	QSSA	Backward Euler	Combined Method
5 s	2.3×10^{-2}	1.4×10^{-3}	1.4×10^{-4}
10 s	2.3×10^{-2}	2.9×10^{-3}	2.9×10^{-4}
30 s	2.0×10^{-2}	8.6×10^{-3}	8.8×10^{-4}
150 s	2.9×10^{-2}	4.4×10^{-2}	4.3×10^{-3}
900 s	2.3×10^{-1}	8.9×10^{-2}	6.4×10^{-2}

Tab. 4. The largest relative errors found during the calculation of the hydroxyl radical
by using three numerical algorithms (the run starts at 6:00 and ends at 24:00
the next day).

Time-stepsize	QSSA	Backward Euler	Combined Method
5 s	3.5×10^{-1}	2.1×10^{-3}	2.1×10^{-3}
10 s	3.5×10^{-1}	3.3×10^{-3}	3.3×10^{-3}
30 s	3.5×10^{-1}	1.1×10^{-2}	1.1×10^{-2}
150 s	6.0×10^{-1}	5.3×10^{-2}	5.3×10^{-2}
900 s	1.1×10^{-0}	7.9×10^{-1}	9.8×10^{-2}

In general, the choice $\Delta t = 30$ s seems to be the best for the QSSA (taking into
account both the computational efficiency and accuracy). The results on the SUN
work-station indicate that for such a computer the combined method is much more
efficient than the QSSA when the fact that this method achieves the same degree
of accuracy with a stepsize $\Delta t = 900$ s is taken into account. However, if a large
air pollution model is to be treated numerically, then a modern high-speed computer
(with vector and/or parallel capabilities) is to be used. The QSSA, used in the form
given by (20), can be run very efficiently on such computers (due to its simplicity).
Some careful programming work is needed in order to answer the question: Is the
combined method competitive with QSSA (when it is run with $\Delta t = 30$ s) on the
modern high-speed computers? If the answer to this question is positive, then the
combined method should be preferred because it also tries to control the errors during
the computations. There are plans to optimize the combined method on several high-
speed computers. Some standard building blocks, templates (see e.g. Barrett *et al.*,
1994), can be applied during the optimization process.

6.2. Comparison of the Accuracy of Different Methods

The accuracy achieved by different methods is measured in the following way. The
combined method has been run with a very small stepsize $\Delta t = 0.01$ s. The results
obtained at the end of every interval of 15 min (these are called reference concen-
trations) have been saved. The calculated concentrations $CALC$ and the reference
concentrations REF are available (for each compound) at the end of every interval of
15 min. Some background concentrations $BACK$ are also available (again for each
compound); these are some typical concentrations for the rural regions. By using
these three quantities, the error made can be estimated (at the end of every interval
of 15 min) by

$$ERR = \frac{|CALC - REF|}{\max(REF, 10^{-5}BACK)} \tag{27}$$

This estimation is calculated (at the end of every period of 15 min) for each
compound and for every method. At the end of calculations the maximal values are
computed (over the whole time interval of 42 hours) again for every compound and

for each method. Some of these values (for the three methods chosen and for two of the compounds: nitrogen dioxide and the hydroxyl radical) are given in Table 3 and Table 4.

It is seen that the combined method is rather accurate. For some species and for large stepsizes the Backward Euler Method has difficulties; see the results for the hydroxyl radical in Table 4. The QSSA may have severe problems with accuracy; see again Table 4. It should be mentioned that if the modified form of the QSSA, given by (20), is used, then an error estimator can be incorporated in the QSSA. However, if this is done, then this method will loose a lot of its computational efficiency, which is the most important advantage of the QSSA.

7. Coupling Advection with Chemistry

Let us consider now the coupling of the chemical module with the other modules in a large air pollution model. To simplify the discussion only the coupling of chemistry and advection will be considered. Similar discussion can be carried out when the other modules (the diffusion and deposition ones) are added to the advection-chemistry combination.

It is relatively easy to test the advection module of an air pollution model. One can construct test examples (whose analytical solution is known) and use them in the verification process. The rotation test, proposed simultaneously in (Crowley, 1968; Molenkampf, 1968) is commonly used. Other test examples can also be constructed; see (Zlatev, 1995).

It is more difficult to test the chemical modules. The commonly used procedure is to calculate a reference solution by running the chemical module with a sufficiently small time-stepsize (this approach has been used in the previous section).

Assume that both the advection module and the chemistry module have been carefully tested. Assume also that the tests indicate that both modules perform satisfactorily well. Then the question is: Will also the combination of these two modules perform well? It will be shown in this section that, unfortunately, the answer to this question is in some cases negative.

The following simple test example (consisting of two modules: horizontal advection and chemistry) can be used in order to show why the above statement is true:

$$\frac{\partial c_s}{\partial t} = -(1-y)\frac{\partial c_s}{\partial x} - (x-1)\frac{\partial c_s}{\partial y}$$
$$+ Q_s(c_1, c_2, \ldots, c_q), \qquad s = 1, 2, \ldots, q \qquad (28)$$

where

$$0 \le x \le 2 \quad \text{and} \quad 0 \le y \le 2 \qquad (29)$$

If the chemical terms are removed and if it is assumed that $q = 1$, then this test example is reduced to the classical Molenkampf-Crowley rotation test (Crowley, 1986;

Molenkampf, 1968). Note that the wind velocities are defined in a special way, so that the wind trajectories will be concentric circles whose common centre is the point with coordinates $x = 1$ and $y = 1$. Moreover, the motion is with a constant angular velocity. This means that if we have some given distribution of the concentrations at the starting time t_{start}, then at some time t_{end} a full rotation of the concentration field around the point $x = 1$, $y = 1$ will be accomplished and, thus, at t_{end} the concentrations must be distributed in the same way as at the beginning (at t_{start}).

If the horizontal advection is removed, and if the space domain is discretized, then the concentrations at each grid-point will vary (due to the chemical reactions), but the variations are only caused by chemical transformations at each grid-point (there is no motion of particles from one grid-point to another).

One can study separately the two physical processes (either the horizontal advection or only chemistry) by using this test example. Moreover, one can also study the coupling of advection and chemistry (by treating at each time step first the horizontal advection and then the chemistry). This generalization of the rotation test has been proposed and used in (Hov et al., 1988); see also (Zlatev, 1995).

Some numerical results with the generalized test are given in Fig. 2 and in Fig. 3. Four plots are shown in each of these two figures.

The upper-left plot represents the initial distribution of the concentrations. The distribution forms a cone if the pollutant is a primary one (i.e. if it is emitted in the atmosphere). All concentrations at the beginning are constant, at all grid-points, for the secondary pollutants (the pollutants which are created in the atmosphere by the chemical transformations; these are set to the background values at the beginning of the computations).

The upper-right plot represents the distribution of the concentrations after a full rotation in the case when a pure advection test is carried out (i.e. when the chemical reactions are decoupled). This means that in the ideal case, when there are no errors, both upper plots must be identical.

The lower-left plot represents the case where only a pure chemical test is run over the time-interval needed to perform a full rotation (the transport part, i.e. the advection, is decoupled).

The lower-right plot represents the distribution of the concentrations after one rotation for the most general case that can be treated by this test, i.e. the case where both the transport and the chemical reactions are activated. In the ideal case, when there are no errors, both lower two plots must be identical.

The results shown in Fig. 2 are very good. However, the results shown in Fig. 3 indicate that problems could appear. In this particular case the difficulties are due to the sharp gradients caused by the chemical reactions.

Similar difficulties have also been observed for some other chemical species. By animation of the rotation, it could be seen that the problems arise mainly at sun-rises and sun-sets (because the chemical subroutines produce sharp gradients in these periods, which cannot be resolved by the advection subroutines). These experiments tell us, once again, that one should be very careful during the periods when the photochemical reactions are activated and desactivated. One should probably try to run the code with smaller time-stepsizes in these critical periods.
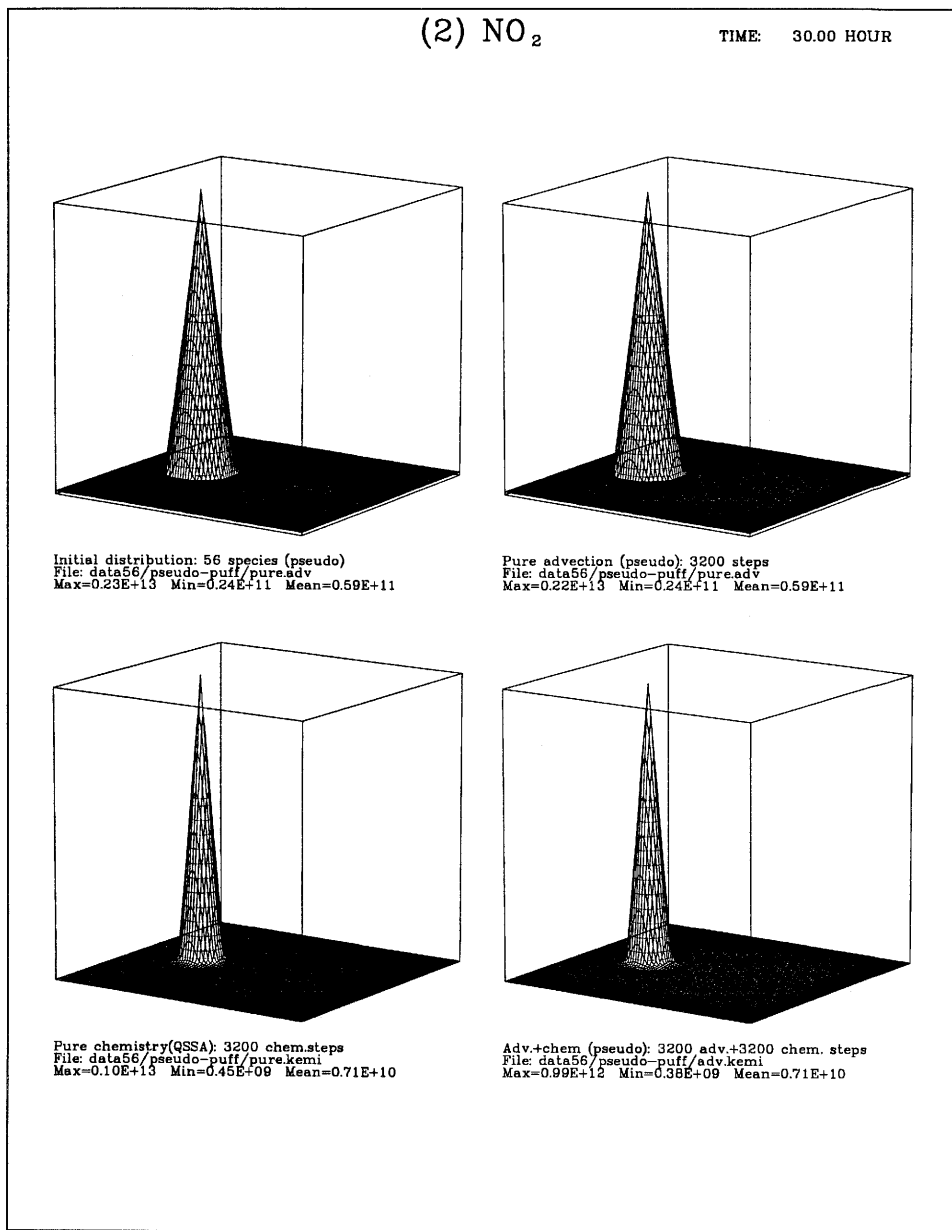
Fig. 2. Distribution of the nitrogen di-oxide concentrations:
(a) at the beginning (upper, left),
(b) at the end of the pure advection test (upper, right),
(c) at the end of the pure chemistry test (lower, left) and
(d) at the end of the advection-chemistry test (lower, right).

(47) C_5H_8 TIME: 30.00 HOUR

Initial distribution: 56 species (pseudo)
File: data56/pseudo−puff/pure.adv
Max=0.91E+02 Min=0.78E+00 Mean=0.20E+01

Pure advection (pseudo): 3200 steps
File: data56/pseudo−puff/pure.adv
Max=0.90E+02 Min=0.78E+00 Mean=0.20E+01

Pure chemistry(QSSA): 3200 chem.steps
File: data56/pseudo−puff/pure.kemi
Max=0.29E−04 Min=0.28E−35 Mean=0.66E−08

Adv.+chem (pseudo): 3200 adv.+3200 chem. steps
File: data56/pseudo−puff/adv.kemi
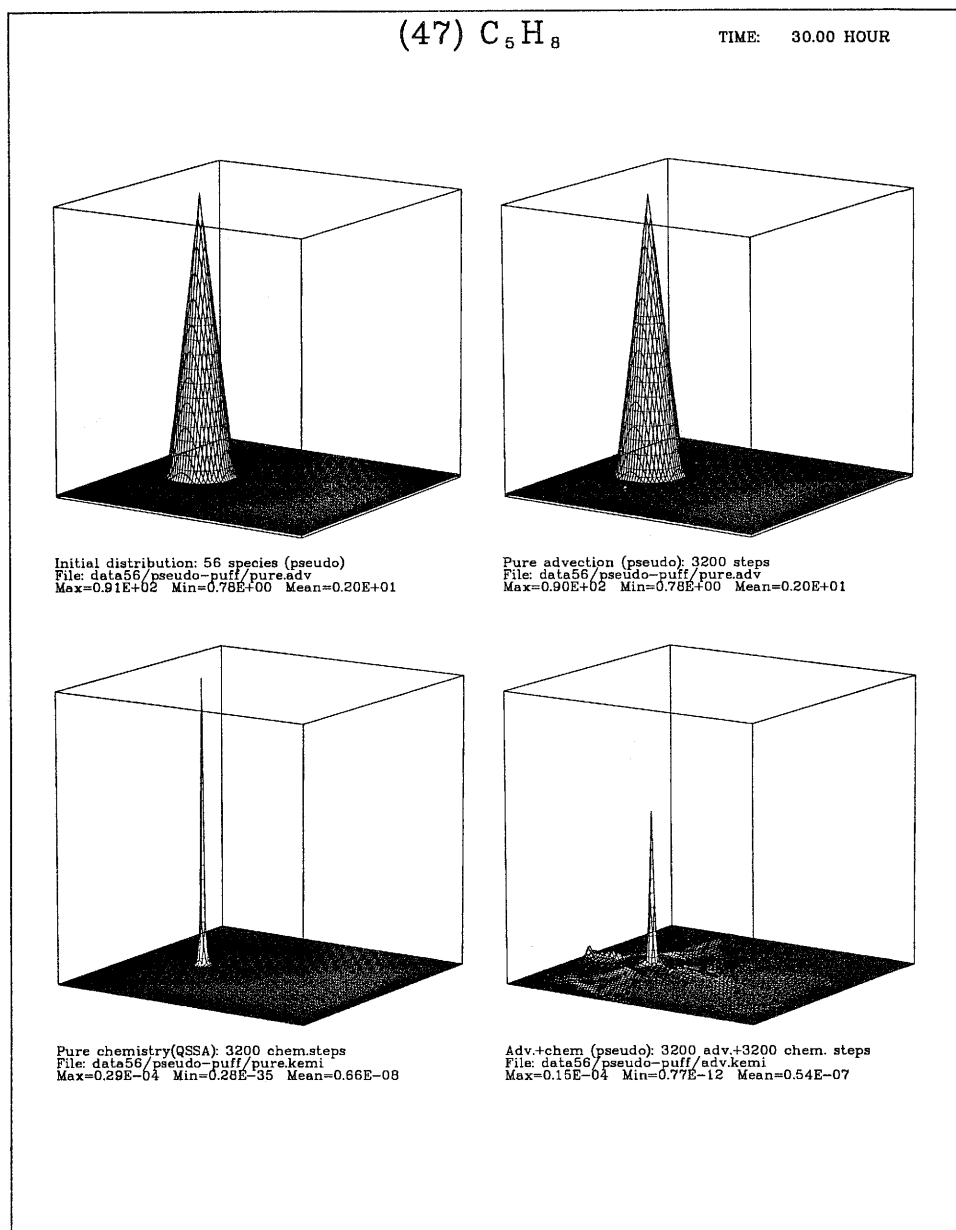Max=0.15E−04 Min=0.77E−12 Mean=0.54E−07

Fig. 3. Distribution of the isoprene concentrations:
          (a) at the beginning (upper, left),
          (b) at the end of the pure advection test (upper, right),
          (c) at the end of the pure chemistry test (lower, left) and
          (d) at the end of the advection-chemistry test (lower,
              right).

8. Concluding Remarks and Future Plans

The general conclusion is that there are still a lot of unresolved problems when chemical modules are to be treated numerically. It is necessary to develop fast, rubust and sufficiently accurate algorithms for these modules. This is not an easy task, because

1. the chemical modules lead to the solution of extremely stiff ODE's,

2. the systems of ODE's are very badly scaled,

3. some chemical species vary very quickly in certain short intervals (sun-rises and sun-sets).

4. even when the chemical module itself works satisfactorily well, its performance can be degraded in the process of coupling the chemistry with the other physical processes.

If some splitting procedure is used in the treatment of the air pollution model under consideration (and this is the case for all known large models), then it is perhaps necessary to use one-step integration methods.

It seems to be necessary to apply some reliable error estimators. This is why the use of extrapolation techniques, where the error estimators are naturally built in the procedures, may be useful. The basic requirement is to select fast extrapolation methods. Some of the methods developed by Deuflhard and his co-workers, (Deuflhard, 1983; 1985; Deuflhard and Nowak, 1986; Deuflhard *et al.*, 1987; 1990) may be applicable in large air pollution models

Some of the chemical reactions are very fast. Therefore it is not uncommon to assume that such reactions are performed instantaneously. This assumption leads in a natural way to the solution of differential-algebraic systems in the chemical sub-models. Therefore fast solvers for such systems are also necessary. It must be emphasized here that if some splitting procedure is used, then the differential-algebraic systems solvers should be based on the application of one-step methods. Some of the methods studied by Petzold (1983; 1986) or in (Deuflhard *et al.*, 1987) could be useful (perhaps after some adjustment) in the treatment of chemical modules in large air pollution models.

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References

Barrett R., Berry M., Chan T.F., Demmel J., Donato J., Dongarra J., Eijkhout V., Pozo R., Romine C. and van der Vorst H. (1994): *Templates for the Solution of Linear Systems: Building Blocks for Iterative Methods.* — Philadelphia: SIAM.

Borrell P., Borrell P.M. and Seiler W. (1990): *Transport and Transformation of Pollutants in the Troposphere.* — The Hague: SPB Academic Publishing bv.

Chock D.P., Winkler S.L. and Sun P. (1994): *Comparison of stiff chemistry solvers for air quality models.* — Environ. Sci. Technol., v.28, pp.1882–1892.

Crowley W.P. (1968): *Numerical advection experiments.* — Mon. Weath. Rev., v.96, pp.1–11.

Deuflhard P. (1983): *Order and stepsize control in extrapolation methods.* — Numer. Math., v.41, pp.399–422.

Deuflhard P. (1985): *Recent progress in extrapolation methods for ordinary differential equations.* — SIAM Rev., v.27, pp.505–535.

Deuflhard P., Hairer E. and Zugch M. (1987): *One step and extrapolation methods for differential-algebraic equations.* — Numer. Math., v.51, pp.501–516.

Deuflhard P. and Nowak U. (1986): *Efficient numerical simulation and identification of large reaction systems.* — Ber. Bensendes Phys. Chem., v.90, pp.940–946.

Deuflhard P., Nowak U. and Wulkow M. (1990): *Recent development in chemical computing.* — Computers Chem. Engng., v.14, pp.1249–1258.

Derwent R.G. and Hov Ø. (1979): *Computer modelling studies of photochemical air pollution in North-West Europe.* — Report No. R–9434. Environmental and Medical Sciences Division, Harwell Laboratory, Oxfordshire, OX11 0RA, England.

Gery M.W., Whitten G.Z., Killus J.P. and Dodge M.C. (1989): *A photochemical kinetics mechanism for urban and regional modeling.* — J. Geophys. Res., v.94, pp.12925–12956.

Hairer E. and Wanner G. (1991): *Solving Ordinary Differential Equations, II: Stiff and Differential-Algebraic Problems.* — Berlin, Heidelberg, New York, London: Springer.

Hertel O., Berkowicz R., Christensen J. and Hov Ø. (1993): *Test of two numerical schemes for use in atmospheric transport-chemistry models.* — Atmospheric Environment, v.27A, pp.2591–2611.

Hesstvedt E., Hov Ø. and Isaksen I.A. (1978): *Quasi-steady-state approximations in air pollution modelling: comparison of two numerical schemes for oxidant prediction.* — Int. J. Chemical Kinetics, v.10, pp.971–994.

Hov Ø., Zlatev Z., Berkowicz R., Eliassen A. and Prahm L.P. (1988): *Comparison of numerical techniques for use in air pollution models with non-linear chemical reactions.* — Atmospheric Environment, v.23, pp.967–983.

Lambert J.D. (1991): *Numerical Methods for Ordinary Differential Equations.* — Chichester, New York, Brisbane, Toronto, Singapore: Wiley.

Marchuk G.I. (1985): *Mathematical Modeling for the Problem of the Environment.* — Studies in Mathematics and Applications, No.16, Amsterdam: North-Holland.

McRae G.J., Goodin W.R. and Seinfeld J.H. (1984): *Numerical solution of the atmospheric diffusion equations for chemically reacting flows.* — J. Comp. Phys., v.45, pp.1–42.

Molenkampf C.R. (1968): *Accuracy of finite-difference methods applied to the advection equation.* — J. Appl. Meteor., v.7, pp.160–167.

Odman M.T., Kumar N. and Russell A.G. (1992): *A comparison of fast chemical kinetic solvers for air quality modeling.* — Atmospheric Environment, v.26A, pp.1783–1789.

Petzold L.R. (1983): *Automatic selection of methods for solving stiff and nonstiff systems of ordinary differential equations.* — SIAM J. Sci. Statist. Comput., v.4, pp.136–148.

Petzold L.R. (1986): *Order results for implicit Runge-Kutta methods applied to differential-algebraic systems.* — SIAM J. Numer. Anal., v.23, pp.837–852.

Shieh D.S., Chang Y. and Carmichael G.R. (1988): *The evaluation of numerical techniques for solution of stiff ordinary differential equations arising from chemical kinetic problems.* — Environ. Software, v.3, pp.28–38.

Simpson D. (1992): *Long-period modelling of photochemical oxidants in Europe. Model calculations for July 1985.* — Atmospheric Environment, v.26A, pp.1609–1634.

Simpson D. (1993): *Photochemical model calculations over Europe for two extended summer periods, 1985 and 1989. Model results and comparisons with observations.* — Atmospheric Environment, v.27A, pp.921–943.

Verwer J.G. and van Loon M. (1996): *An evaluation of explicit pseudo-steady state approximation for stiff ODE systems from chemical kinetics.* — J. Comput. Phys., (to appear).

Verwer J.G. and Simpson D. (1996): *Explicit methods for stiff ODE's from atmospheric chemistry.* — Appl. Numer. Math., (to appear).

Zlatev Z. (1981): *Modified diagonally implicit Runge-Kutta methods.* — SIAM J. Sci. Statist. Comput., v.2, pp.157–166.

Zlatev Z. (1984): *Application of predictor-corrector schemes with several correctors in solving air pollution problems.* — BIT, v.24, pp.700–715.

Zlatev Z. (1995): *Computer treatment of large air pollution models.* — Dordrecht, Boston, London: Kluwer Academic Publishers.

Zlatev Z., Dimov I. and Georgiev K. (1994): *Studying long-range transport of air pollutants.* — Computational Science and Engineering, v.1, No.3, pp.45–52.