

**MODELLING GLOBAL ATMOSPHERIC CHEMISTRY  
WITH THE FACSIMILE/CHEKMAT PACKAGE \***

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## **1. INTRODUCTION**

The increasing emission into the atmosphere of substances such as NO and hydrocarbons, combined with the observed increases in the concentrations of trace gases such as ozone, NO<sub>x</sub> and methane, necessitate the study of the chemistry of the global atmosphere. Models of the chemistry of the atmosphere such as the two-dimensional global tropospheric model described here link equations of atmospheric transport and diffusion with those describing chemical reactions. The problem of the routine solution of the resulting sets of differential equations from this type of problem has stimulated the production of a program which solves the discretised equations accurately in a routine manner.

## **2. THE CHEKMAT PROGRAM**

### **2.1 HISTORICAL BACKGROUND**

The computer program used in our modelling, CHEKMAT, has been developed at Harwell since 1968. This was when Gear [12] first popularised a method, now known as the Backward Difference Formula (BDF) method, for solving sets of ordinary differential equations (ODEs) which have a property, known as stiffness, common in ODEs arising from chemical kinetics. CHEKMAT was derived as an acronym from CHEmical Kinetics

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with MATching; the last word refers to the parameter-fitting: feature - the ability to adjust parameters (e.g. rate coefficients) for best fit between computed and experimental values of solution components (e.g. species concentrations). Although the numerical method used to solve the differential equations is an implementation of BDF, it has been refined and developed at Harwell, and incorporates many functional improvements, designed to make it more automatic and reliable, over published BDF programs. For example: all time steps, even the first one, are chosen automatically; fewer matrix recalculations are needed; convergence testing is much more rigorous; the wide range of numerical values of solution components, which occurs in this kind of problem, is properly handled. The method used follows in general that described by Curtis [5], with some further improvements.

Until 1975, CHEKMAT was limited to straightforward reaction kinetics problems, except when modified by experts. However, experience with it suggested many desirable features, and a much more powerful piece of software, called FACSIMILE and intended for easy use by nonexperts, was specified and written. This has been used and developed since 1975. It now forms the basis for two different application programs: CHEKMAT [10], which is a far more powerful and flexible ODE solver with special features for mass action kinetics and for diffusive and advective transport; and HOWGOOD [9], which is a tool for studying how the results from any continuous modelling program are affected by uncertainties in the data supplied to it.

## 2.2 GENERAL FEATURES

CHEKMAT has many features which make it suitable for use by people who are not expert in computing or mathematics, but who wish to solve modelling problems, especially in reaction kinetics. It provides a powerful special-purpose high-level programming language in which the user

describes his problem. One of its main advantages for the user is single-shot running - it reads this description as data, compiles it into an internal pseudo-code [6] for interpretive execution, and solves the problem, all in a single computer run. Although interpretative execution of the user's code carries a penalty in computer time, the saving in user's time which it makes possible greatly outweighs this, except in the largest problems (such as the current one). Work is in hand to offset this for large problems, using the fact that they do not need the full generality offered by the FACSIMILE language.

Another advantage of the FACSIMILE/CHEKMAT approach is that it enables the program to run, with unchanged user image, on an extremely wide range of computers. This is especially useful now that networks are common, since development can be done on a workstation and production runs on a more powerful server or mainframe. It is in fact available for most computers, from IBM-compatible PCs to CRAY supercomputers, although naturally the larger problems require more powerful computers.

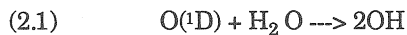
### 2.3 THE USER LANGUAGE

The CHEKMAT user language enables many kinds of problem to be specified, while containing features special to mass action kinetics and to transport by diffusion and advection. There are features for element-by-element numerical operations on scalars and on arrays of up to five dimensions; matrix operations; powerful built-in output, numerical with predefined or user-programmed formats, and graphical for plotting at coarse resolution on a character-oriented printer. There are command features for initiating and controlling the solution, describing output structures, separating the user's code into subroutines, and reading experimental data for the parameter-fitting option. For example, the solution process is controlled by statements beginning WHEN, which specify

what actions are to be taken at various stages; other run control statements, such as BEGIN, RESTART and STOP, have obvious meanings. CHEKMAT user-written calculation is organised into a series of program routines. Some of these have CHEKMAT system names, and these are executed automatically as required. For example, routine FTIME is called once per time step to calculate parameters which depend only on time, not on the solution components; routine EQUATIONS is called to compute time rates of change of solution components; routine GENERAL is called before EQUATIONS to compute parameters which do depend on the solution. Other routines are given non-system names by the user, and (for example) can be called at stages through the solution specified in a WHEN statement. In the present model, routine ANNBGT calculates annual budgets and is called at the end of each year.

All identifiers (names) have global scope; that is, once a scalar or array has been defined it may be referred to from any routine. The following main types of quantity may be declared: VARIABLE, for solution components of the ODE system; PARAMETER, other real-valued quantities to be manipulated by the user's program; CONSTANT, real-valued quantities which the program may not change; and INTEGER, integer-valued quantities for use in dimensions, indexing and logical decision-making. A declaration may contain array dimensions, which apply to all subsequent names in it until superseded; each name declared may be followed by initial values; the last array in a declaration may have a list of sub-arrays or scalars equivalenced to it.

As an example of the power of the language, a reaction which a chemist might write in the form



could be coded for CHEKMAT as



Here the percent sign introduces the rate coefficient (which can be an arithmetic expression if desired), the colon introduces the reaction, and the semicolon is a standard statement terminator. This equation would be the same, whether the quantities appearing in it were scalars or arrays.

The user has to code the discretisation of transport (diffusion and/or advection) partial differential operators on his chosen grid, since at present CHEKMAT does not do this. However, once this is done and coefficient and index arrays set up, the action is specified by a simple statement, in routine EQUATIONS, of the form

(2.3)            TPORT <dim.> {coeff. array} {index array} : {species list};

This causes an internal CHEKMAT subroutine to be called to add the transport terms to the rates of change of solution components.

To illustrate the value of the array features, the chemical reaction coding for a problem is often developed and tested in single-box form, each species concentration being represented by a single scalar VARIABLE. It can be converted to reaction code for a spatially nonhomogeneous problem simply by declaring these VARIABLES (and possibly some PARAMETERS used as rate coefficients) to be arrays of the grid dimensions, and enclosing sections of code in suitable ARRAY statements. Adding the transport processes consists of defining and initialising index and coefficient arrays for the partial differential operators, discretised on the chosen grid, and inserting a TPORT instruction to compute and add the transport term contributions.

Thus the whole user code for a large problem can be reasonably compact. For the present model, approximately 4,600 lines of code (including comments) were written, broken down roughly as follows:

- A. Declarations and comments, 1100 (including initial values, 390).
- B. Preliminary calculations (including interpolation of temperature, wind and eddy diffusion data to grid points, and computation of transport coefficients), 900.
- C. Calculation of time-dependent parameters such as temperatures, rate coefficients and photolysis rates, 800.
- D. Computation of time rates of change, 540.
- E. Output and budget calculation and editing (with user-defined formats), 1270.

### 3. DESCRIPTION OF THE HARWELL GLOBAL TROPOSPHERIC MODEL

The model used in this study is a two-dimensional latitudinally averaged Eulerian grid model, with a domain which extends from pole to pole and from the earth's surface to a height of 24 km. Within this domain, the model is divided into 288 grid cells, 24 in the horizontal direction and 12 in the vertical.

#### 3.1 TREATMENT OF ATMOSPHERIC DIFFUSION AND ADVECTION

Two-dimensional transport data, derived by Plumb & Mahlmann [17] from numerical experiments with a three-dimensional global circulation model, consist of a stream function for advection and eddy diffusion coefficients  $K_{xx}$ ,  $K_{yy}$ , and  $K_{xy} = K_{yx}$ . A skew-symmetrical part of the eddy diffusion tensor had been absorbed into the stream function. Curtis [7, 8] shows how to convert this information into transport coefficients of the kind needed by CHEKMAT (all the terms arising from the stream function in [8] have the wrong sign). The method achieves numerical stability by artificially increasing the diagonal terms of the diffusion tensor by just enough to ensure ellipticity of the modified total transport operator, while

retaining second order accuracy because the changes are of second order in the grid spacings.

The presence of mixed derivatives, as evidenced by the  $K_{xy}$  terms, requires a nine-point finite-difference operator, instead of the more familiar five-point operator in two space dimensions. Earlier studies [11] had shown the value of using equal volume grid cells, achieved by taking a grid equally spaced in the sine of latitude. The vertical coordinate was taken as the logarithm of pressure normalised to the surface value, and scaled with a scale height  $H_z = 7.2$  km.

Monthly transport and temperature data [2, 3] were interpolated onto the present model grid and are also interpolated with time within the model so as to provide smooth and continuous variations with time. Studies of inert tracers such as  $\text{CCl}_3\text{F}$  (CFC-11) and  $^{85}\text{Kr}$  have been used to evaluate the operation of the model [14], and the model results were in good agreement with surface observations of these species over a wide latitude range.

With the exception of the transport and temperature data referred to above, the model is driven completely by the emissions, chemistry, deposition processes and upper boundary conditions. No fixed concentration fields are maintained in the model other than those of oxygen and the total molecular number density. The concentrations of all chemical species are determined as solutions of the differential equations which define the model transport and chemistry.

All species occurring in the model are subjected individually to the transport operator. The alternative of transporting only "family groups" (e.g. the  $\text{NO}_x$  species), as is done in some other models, has been considered. In the latter method, after the transport contribution to the rate of change of the total group concentration has been computed, it must be shared out among the species making up the group. To do this properly requires the solution at each integration step of a large system of equations, which is generally nonlinear because (a) species (e.g. nitric acid) may belong to more

than one family group, and (b) species in a group may react with each other or themselves. The most efficient way of solving these equations to reasonable accuracy seems to be our choice, to include both transport and chemistry for each species, taking special action to avoid excessive computation due to the interaction between them. This could arise because of excessive "fill-in" of initially zero elements in the (very sparse) iteration matrix used, when it is decomposed for equation solving. We avoid this at present by omitting the transport terms from the iteration matrix, and accepting a consequent limit on the size of time step (typically to a few hours, in the present model). In the longer term, we plan to partly use transport terms in the iteration, while avoiding the resulting fill-in.

### 3.2 THE CHEMICAL MECHANISM

In the model it is necessary to restrict the number of species and the complexity of the mechanism in order to produce a tractable problem. However, sufficient detail must be retained so as to represent the chemical processes in a realistic manner. Residual uncertainties in our knowledge of tropospheric chemistry complicate the selection of the chemical scheme.

The mechanism used in the present work contains 56 chemical species, including water vapour, 12 hydrocarbons, 8 carbonyl compounds and 5 organic peroxides. There are 91 thermal reactions and 27 photolytic processes. Diurnal average calculations are made throughout, but night-time  $\text{NO}_3$  chemistry is modelled with a further 7 reactions. The rate coefficients for the thermal reactions were taken from recent reviews such as that of Atkinson et al. [1]. The photolysis rates are calculated for each grid cell as diurnal averages for each month, and are interpolated to intermediate times [13].

The model emissions inventory contains 17 species thought to be important in controlling tropospheric chemistry on a global scale. These include  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CH}_4$ , together with 12 hydrocarbons



including isoprene and terpene. The distribution of the emissions in the model is described by ten separate source categories, each having a separate dependence on latitude and time of year. The derivation of these functions of latitude and time of year is discussed by Hough [15], who also describes the full chemical mechanism.

### 3.3 WATER VAPOUR AND CLOUDS

The model treats evaporation from the surface using local values of the vertical diffusion coefficient. In each grid cell, the local precipitation rate into the grid cell immediately below is parameterised as a smooth function of the relative humidity. The water vapour pattern produced is similar to that observed, including the observed minimum in the region of the tropical tropopause [14]. The predicted rainfall pattern is similar to a latitude average of the observed annual rainfall. The cloud cover in each grid cell in the lowest few kilometres of the model is calculated using the algorithm of Buriez et al. [4] based on relative humidity and atmospheric pressure. 3.4

### 3.4 REMOVAL AND BOUNDARY PROCESSES

The model includes both wet and dry deposition. Dry deposition velocities for each species removed are used, taking into account the fraction of land, sea and ice in each latitude range. The species removed by dry deposition are:  $O_3$ ,  $NO_2$ , PAN,  $H_2O_2$ ,  $H_2$ , CO and organic peroxides. Wet deposition is parameterised as a function of the local liquid water content, the rainfall rate, and the solubility of the species concerned. Species transported and removed by wet processes are:  $HNO_3$ ,  $H_2O_2$ , HCHO, organic peroxides, and  $\alpha$ -dicarbonyl compounds.

Transport across the upper boundary of species with very low mixing ratios in this region can be ignored. However, this is not the case for ozone,  $NO_x$  and methane, and the exchange of these species across this boundary needs to be modelled. This exchange is represented as diffusion, using the

local value of the vertical diffusion coefficient. The required mixing ratios of the species above the model domain were taken from observations, including satellite observations for ozone [16].

#### 4. RESULTS

A complete description of the model results for a simulation of present-day conditions is given by Hough [15]. The model has also been used to simulate future atmospheric concentrations of trace gases from estimates of emission changes. The assumption made in this approach is that the other model input parameters, including atmospheric temperatures, remain constant during each simulation. However, the change in tropospheric chemistry with temperature is one of the feedbacks between climate and the chemistry of the atmosphere [19], and the resultant change in the radiatively active gases in the model ( $O_3$ ,  $CH_4$  and  $N_2O$ ) is clearly of interest, and the effects of altering the temperature globally are investigated here.

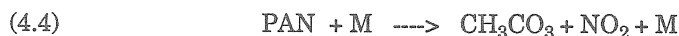
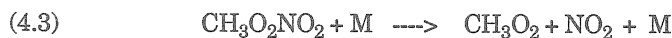
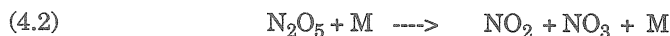
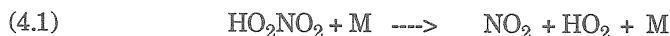
Several changes to the model conditions are caused by changes in temperatures. The increase in the saturated water vapour pressure with temperature results in increased water vapour concentrations throughout the domain, as the rainfall amount is controlled by an algorithm which tends to maintain the relative humidity at the same values. The increase in the global inventory of water vapour is  $6.7\% K^{-1}$ , slightly higher than the increase in water vapour content per unit surface area of  $5.5\% K^{-1}$  found by Ravel and Ramanathan [18] from a regression of water content with sea surface temperature. This increase has a direct radiative feedback to global climate, but also influences tropospheric chemistry, mainly through the reaction (2.1).

The global inventory of the hydroxyl radical (OH) was found to increase by  $3.7\% K^{-1}$ , which has important implications for many other species due to the reactivity of OH. Many species which react with this

radical, such as methane and the non-methane hydrocarbons, decrease by 1.3 % K<sup>-1</sup> . Other radicals interdependent on OH have also increased: HO by 2.2 % K<sup>-1</sup> and CH<sub>3</sub>O<sub>2</sub> by 4 % K<sup>-1</sup>.

The increased evaporation rate results in higher rainfall amounting to about 5 % K<sup>-1</sup> . This has the effect of increasing the washout of species which are soluble, but this is compensated by the reduced solubility at higher temperatures and by the change in concentrations, as well as the fact that highly soluble species are already efficiently removed in lower levels of the atmosphere. The net effect is that the washout remains the same for HNO<sub>3</sub> , decreases slightly for HCHO, CH<sub>3</sub>COO<sub>2</sub>H, HCOCHO and CH<sub>3</sub>COCHO, and increases slightly for H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH.

Many of the thermal rate coefficients used in these calculations are temperature dependent [1], and four of these have much greater temperature coefficients than any others, in the range 16 to 22 % K<sup>-1</sup> . These refer to the thermal decomposition reactions:



The high decomposition rate of PAN at high temperature is well known, and limits its distribution in the atmosphere, and also creates large seasonal changes. The rate of change in the global inventory for PAN is -8 % K<sup>-1</sup> in January and -13 % K<sup>-1</sup> in July. This change reduces the proportion of the total reactive nitrogen in the form of PAN, though the seasonal change is greater. The dry deposition of PAN to the surface is also reduced, but this represents only a small term in the NO<sub>x</sub> budget. In addition to changes in the thermal rate coefficients, small increases were observed in the photolysis rates due to temperature sensitive cross sections and to reductions in the concentrations of the absorbing gases.

The amount of ozone in the model decreased with increasing temperature at a rate of about  $1.5 \% K^{-1}$ . This is largely due to the reaction (2.1) proceeding more rapidly due to the increased water vapour concentrations, but changes due to increased radical concentrations also increase the rate of loss of ozone. The loss is partially compensated by increases in photochemical production caused by increases in the radicals  $HO_2$  and  $CH_3 O_2$ . The increased reactivity of the model reduces the turnover time for ozone in the model from 57 days to 54 days when an increase of 2 K is applied. Of the other radiatively active gases in the model, nitrous oxide has a long lifetime in the atmosphere and is not studied here. The final change in the methane concentrations due to the temperature rise has not been determined because its lifetime is several times longer than the model run time. However the loss of methane proceeds mainly through its reaction with OH, and an increase of around 1.2 K is sufficient to change the model from having an increasing inventory of around 0.6 % per year to one with a stable inventory. Further increases in temperature will result in a net loss of tropospheric methane assuming that emission remains constant.

The treatment adopted here has been idealistic, as global temperature rise has been applied uniformly throughout the model domain. Only the changes in atmospheric chemistry have been modelled here, ignoring changes in emissions with increasing temperature and also treating the atmospheric transport as invariant. The maintenance of relative humidity in the model applies two constraints to its behaviour: the increase in water vapour concentration is restricted to that indicated by the saturated vapour pressure curve, and the cloud amounts remain constant because they are also linked to relative humidity. Changes in cloud amounts may also need to be considered, as these influence the photolysis rates used in the model.

## 5. CONCLUSIONS

The FACSIMILE/CHEKMAT program for solving sets of ordinary differential equations is briefly described. Many features of this program make it easy to use by scientists who are not expert mathematicians, including a user language with special features for reaction kinetics and diffusive and advective transport. As an example of its use, a large Eulerian grid model of the global troposphere is briefly described, together with an example of its use to show the sensitivity of tropospheric chemistry to temperature.

The increase in atmospheric water vapour with increasing temperature is well known, and forms a positive feedback to the greenhouse effect. The increased water vapour concentrations also influence the tropospheric chemistry, notably on the radical concentrations in the troposphere. This has the effect of decreasing the concentrations of two radiatively active gases in the model, ozone and methane, and thus forms an additional negative feedback to global temperature change.

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