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SIMULATION OF CHEMICAL KINETICS TRANSPORT IN THE STRATOSPHERE*

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INTRODUCTION

It is well known that the chemical rate equations are often very stiff and their numerical solutions must be treated quite carefully. At the present this does not present any major difficulty due to the class of special methods for stiff ordinary differential equations. However, in the simulation of chemical kinetics transport in the stratosphere and related fields we are faced with a large system of stiff partial differential equations. Abstractly we may write the equations as

$$\frac{\partial y}{\partial t} = T(y) + C(y) \quad , \tag{1}$$

where y is a vector representing the concentrations of the chemical species and t is simply time. T is a linear partial differential operator describing the mass transfer of the chemical species [Colgrove (1965A), Gudiksen (1968A)]. C is a highly nonlinear chemical kinetics operator involving not only the concentrations of these species but also some complicated integrals of these concentrations [Crutzen (1971A), Johnston (1971A)]. The physical problem is usually formulated either as an initial-boundary value problem or simply as a boundary value problem (i.e. $\frac{\partial y}{\partial t} = 0$). In the numerial solutions of Eq. (1) we must deal with a large set

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of strongly coupled partial differential equations (usually greater than ten) describing some physical processes in a nonhomogeneous medium (e.g. the atmosphere). Furthermore these processes are characterized by widely separated time constants(e.g. 10^{-6} sec to 10^{+8} sec). Following the basic concept of the method of lines [Liskovets (1965A), Walter (1970A)] by first reducing this system to a much larger system of ordinary differential equations and then utilizing a solution technique based on the method of Gear, we have successfully constructed a program for carrying out such simulations. In this report we would like to discuss the motivation, effectiveness and limitations of this solution technique. We will also present some simulation results on some physical problems of current interest.

CHEMICAL KINETICS TRANSPORT IN THE STRATOSPHERE

The conservation equation for the concentration c^i of any chemical species may be written as

$$\frac{\partial c^i}{\partial t} = \underline{\nabla}\cdot\underline{\phi}(\underline{\nabla} c^i, c^i) + P(c) - L(c) + S_i \tag{2}$$

where t = time;

$\underline{\nabla} c^i$ = gradient of c^i

$P(c)$ = photochemical production of species c^i from other species;

$L(c)$ = photochemical loss of species c^i in reactions with other species;

S_i = any other possible sources.

The dependent variables are of course functions of the spatial coordinates and t.

A typical system may be

$$\begin{aligned}
\frac{\partial y_1}{\partial t} &= \underline{\nabla}\cdot\underline{\phi}(\underline{\nabla} y_1, y_1) + S_1 + J_2 y_2 + J_3 y_4 - J_4 y_1 - k_1 y_1 y_2 \\
&\qquad - k_2 y_1 y_4 \\
\frac{\partial y_2}{\partial t} &= \underline{\nabla}\cdot\underline{\phi}(\underline{\nabla} y_2, y_2) + J_4 y_1 - J_2 y_2 - k_1 y_1 y_2 - k_3 y_2 y_3 \qquad (3) \\
\frac{\partial y_3}{\partial t} &= \underline{\nabla}\cdot\underline{\phi}(\underline{\nabla} y_3, y_3) + J_4 y_4 + k_2 y_1 y_4 - k_3 y_2 y_3 \\
\frac{\partial y_4}{\partial t} &= \underline{\nabla}\cdot\underline{\phi}(\underline{\nabla} y_4, y_4) + k_3 y_2 y_3 - J_4 y_4 - k_2 y_1 y_4 \quad .
\end{aligned}$$

The transport flux $\phi(\underline{\nabla}c^i, c^i, t)$ may be obtained either from the direct solution of the equations of motion of the earth's atmosphere or through parameterization of observed motions. Since we are interested in the distributions of the so called minor chemical species of the stratosphere we shall adopt the latter approach. A chemical species is considered to be a minor species if the ratio of its concentration to the ambient air density is less than 10^{-5}. Due to their relatively low concentrations we would like to assume that they do not affect the atmospheric motions significantly. Strictly speaking this is not quite correct, e.g. the atmospheric ozone is a major heat source in the stratosphere. From studies on atmospheric nuclear fallout [Gudiksen (1968A)] we know that the above assumption is valid at least as a first order approximation.

The transport flux $\underline{\phi}$ consists of a term representing the mean motion and a term representing the large scale turbulent mixing commonly called eddy diffusion [Reed (1965A)],

$$\underline{\phi} = K\cdot\underline{\nabla}c^i + \underline{V}c^i \quad .$$

K is a matrix whose elements are the eddy diffusion coefficients and $\underline{V}$ is a vector describing the observed mean atmospheric motion. There are two types of terms for the photo chemical processes: the production or loss due to photolysis,

$$A_i + \text{radiation} \rightarrow A_j + A_k \quad ,$$

and that due to chemical interactions

$$A + B \rightarrow C + D \quad .$$

The former process is described by the coefficients J_ℓ in Eq. (3), where [Gelinas (1973A)]

$$J_\ell = \int d\lambda\, \sigma^i(T) Q_\ell(i \rightarrow j) I_o \exp[-\tau(\underline{x}, t)] \quad .$$

J_ℓ is commonly called the photodissocation coefficient; I_o is the radiation intensity for each wavelength λ at the top of the atmosphere; τ is an attenuation factor at point $\underline{x}$ and time t, σ^i is the total absorption cross section of molecules A_i; $Q_\ell(i \rightarrow j)$ is the quantum yield for the process in consideration; T is the temperature and $\underline{x}$ represents the spatial coordinates. The attenuation factor (optical depth) is in turn an integral over all absorptions and scattering of a given wavelength due to all chemical species present. Clearly many simplifying assumptions must be utilized in order to evaluate all the complicated integrals, however this is of no essential interest in the present context and interested readers may refer to [Gelinas (1973A)]. By comparison the chemical interactions are simply represented by temperature dependent coefficients k_ℓ for each interaction.

Physically it is known that the photochemical reaction rates span a range of time constants from about 10^{-6} sec to 10^{+5} sec. On the other hand it is also known that the atmospheric transport processes have characteristic time constants of about 10^8 or 10^9 seconds. When these processes are coupled together as in Eq. (2), the numerical solution of Eq. (2) becomes difficult. Due to the vast difference in time scales, operator splitting techniques or the method of fractional steps [Yanenko (1971A)] may seem to be quite appropriate. However, it quickly becomes evident that every time the transport operator is applied the chemical system is rudely perturbed out of equilibrium and the computing effort required to smooth the total system is again costly. Also there is the ever present question of how accurate is the time dependent solution under such artifical perturbations. On the other hand, in recognizing the diffusion operator as a smoothing operator while the chemical kinetics operators are the dominant driving force of the system, we then discretize the transport operators and solve the resulting system of ordinary differential equations with a stiff ODE solver. This approach carries with it the technical difficulties of storage and the repeated inversion of very large matrices. From the viewpoint of the numerical solution of parabolic partial differential equations this is really equivalent to using a variable order difference formula for the time operator and this by itself is an interesting numerical experiment.

NUMERICAL METHOD

We shall illustrate the details of the numerical technique by an example incorporating all the essential features of Eq. (2). Let us consider the one-dimensional equation

$$\frac{\partial c^i}{\partial t} = \frac{\partial}{\partial z} K(z) \frac{\partial c^i}{\partial z} + P^i(c) - L^i(c) \tag{4}$$

for $i = 1, \ldots, I$, with the appropriate initial and boundary conditions at $z = 0$ and $z = 1$. With J equally spaced mesh points, the semi-discrete approximating system of ordinary differential equations is

$$\frac{\partial c_j^i}{\partial t} = \frac{1}{(\Delta z)^2} \left[K_{j+\frac{1}{2}} c_{j+1}^i - \left(K_{j+\frac{1}{2}} + K_{j-\frac{1}{2}} \right) c_j^i + K_{j-\frac{1}{2}} c_{j-1}^i \right] + P^i(c_j) - L^i(c_j) \quad , \tag{5}$$

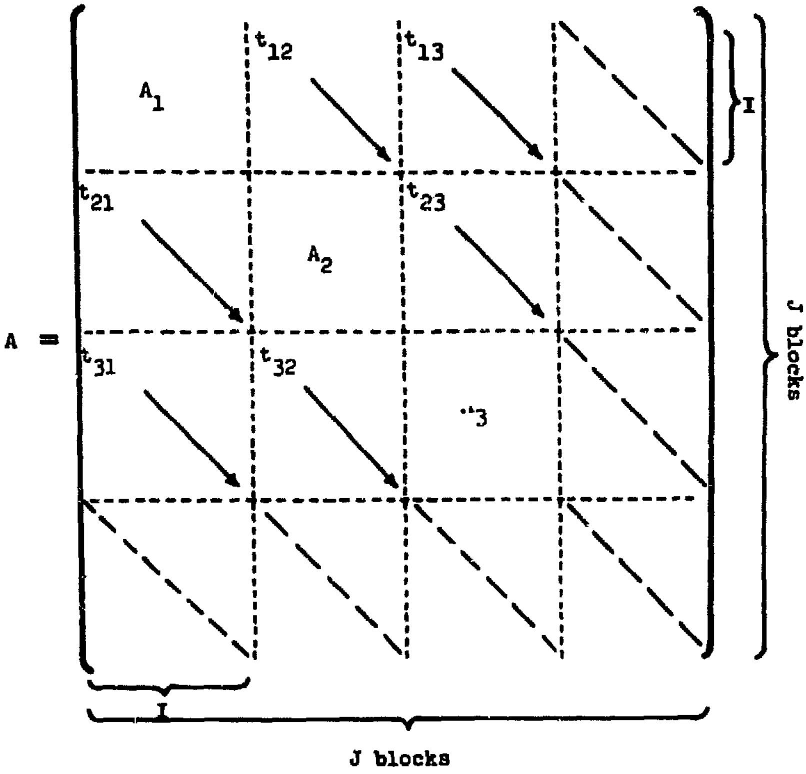
and appropriate equations at the boundary are assumed.

Since there are I chemical species and J spatial zones the size of the problem is N = IJ. The I species in any given zone interact with each other according to the system of kinetics rate equations adopted. Each given species also interacts with the same species in the neighboring zones, and the transport coefficients governing that interaction are the same for all species. Suppose that we order the variables by grouping all species in zone 1, then all species in zone 2, etc. Then the system of equations may be written

$$\frac{dy}{dt} = A(y,t)y(t) = f(y,t) \tag{6}$$

with $y = (c_1^1, \ldots, c_1^I, c_2^1, \ldots, c_2^I, \ldots, c_J^1, \ldots, c_J^I)$.

It follows from Eq. (5) that A will have the following block structure:



Here the basic blocks are I x I matrices, and there are J^2 such blocks comprising A. The diagonal blocks $A_1, \ldots, A_J$ represent the chemistry within the zones plus the diagonal element of the transport operator. The off-diagonal blocks represent the remaining portion of the transport operator, and each such block is a multiple of the I x I identity matrix. Hence A is fully described by the J matrices A_j (each I x I) and the J x J matrix $T = (t_{ij})$ of transport coefficients.

Given any initial conditons Eq. (6) is solved by a modified version of Gear's method [Gear (1968A)]. We will not discuss the details of the method here as it is well documented elsewhere [Hindmarsh (1972A), (1972B), (1972C)]. The basic nonlinear multistep formula

$$y_n = \sum_{i=1}^{q} \alpha_i y_{n-1} + \beta_0 hf(y_n, t_n)$$

is solved by a modified Newton method. This is necessitated by the complex photodissociation coefficients. The matrix to be inverted has the form $P = I - \beta_0 h \frac{\partial f}{\partial y}$ which in turn has the same structure as matrix A except that the diagonal blocks A_j are to be replaced by another set D_j. During the computation the P matrix is kept as long as possible and is reevaluated only after the failure of corrector convergence. For one-dimensional problems the storage of P is of no major concern but as we go to higher dimensional problems we will exceed the memory size of most computers in existence. For the present example storing the full P matrix require I^2J^2 locations while storing the central band requires $I^2(2J-1) - I\ (J-1)$ locations and similar estimates can be given for multi-dimensional problems. We have adopted a block iterative method for the inversion of the P matrix which reduces the storage requirements to essentially I^2 times the total number of spatial zones.

Heuristically, we know that the diagonal matrices D_j contain not only all the nonlinear chemistry terms but also the diagonal elements of the transport operator. Therefore, when considered in its block form, the matrix P should be diagonally dominant. Consequently we may be fairly confident that successive overrelaxation (SOR) method will converge. Let $x_j = (c_j^1, c_j^2, \ldots, c_j^I)$ be the j<u>th</u> block of y, then the system

$$Py = b$$

is iteratively solved using the SOR formula

$$D_j x_j^{(\upsilon+1)} + w \sum_{i<j} t_{ji} x_i^{(\upsilon+1)} = (1-w)\, D_j x_i^{(\upsilon)} - w \sum_{i>j} t_{ji} x_j^{(\upsilon)} + w b_j \quad , \tag{7}$$

b_j being the $j^{\underline{th}}$ block of b. The over-relaxation parameter w is determined by an algorithm similar to the one first suggested by Carré [Carré (1961A)]. There are two advantages in using SOR Eq. (7). The first is the relatively small storage required for P. Now we need only to store J matrices of dimension I x I or I^2J total locations, or I^2 times the total number of spatial zones in general (plus a small matrix $T=(t_{ij})$). The second advantage is that by retaining the LU decompositions of each D_j then the overrelaxation iterations (Eq. (7)) become computationally inexpensive. Furthermore the same LU decomposition is used as long as the modified Newton iterations converge. It also should be noted that each time a new LU decomposition is required the total computational cost is much less than for the full P matrix. We shall call the SOR iterations Eq. (7) the inner iteration as compared to the basic modified Newton's iteration in the original ODE solver. The convergence criteria for the relative error of the inner iteration is set to be ε. By varying the parameter ε over a range of .1 to .00001, no significant differences were found in the entire solutions of various problems. By this we mean that the relative error of the solutions has always remained less than the preset relative error constant of the ODE solver. This indicates that only a very modest accuracy of the SOR solution is required for the ODE solver to perform adequately. We have found that the higher order implicit formula for the time operator indeed limits the truncation error to be purely due to the spatial difference formula. The available numerical data suggests that this solution technique may prove to be applicable to broad classes of parabolic problems. At the present we are studying this in more detail but we already have some interesting evidence. For example, if we use the familiar factor $\frac{\alpha\Delta t}{(\Delta x)^2}$ as a heuristic guide, the present method at times can use time steps so large that $\frac{\alpha\Delta t}{(\Delta x)^2} \sim 10^5$ while preserving the prescribe accuracy.

While applying this method to a wide class of physical problems we noticed an instability which is somewhat puzzling. This is illustrated in Fig. 1. This is a graph of the time step size history. The crosses indicate when the program actually decided on an

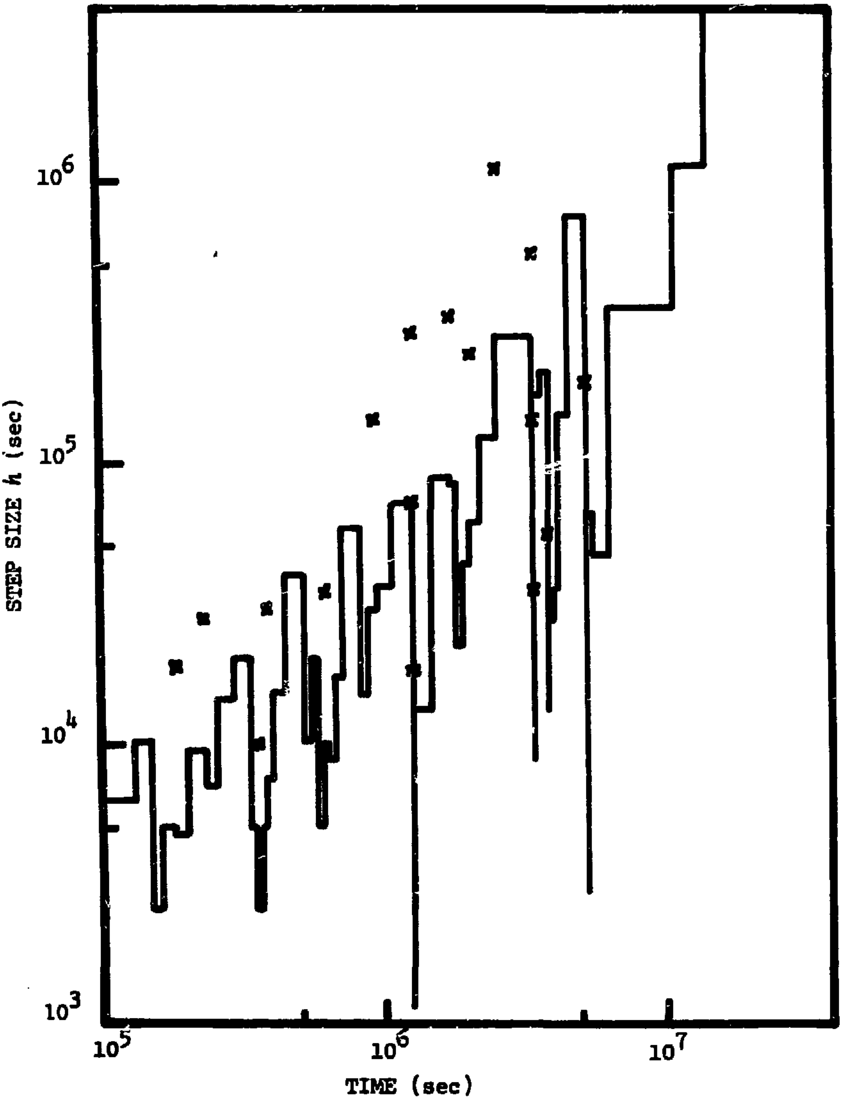


Figure 1. An example of the time history of step size h exhibiting certain instabilities in the error and step size control algorithms.

increase in step size and then failed to converge in the corrector stage. In fact there exist multiple failures even though at the later failures the time step size has already gone below the original time step size prior to the attempted increase. By modifying the step size changing algorithm to include some memory of previous failures and limiting the allowable increases accordingly, we are able to eliminate multiple failures but still observe over estimation. We should note that during all the multiple failures the solutions have hardly changed at all. Prior to and after this interval of instability the step size behaves very well and increases monotonically. This kind of instability may warrant further study in the near future.

The same solution technique has been applied to several two-dimensional problems with completely satisfactory results. For example the largest set of equations that we have solved involves 9 chemical species, 44 vertical zones, and 20 horizontal zones. This means that we have applied this solution technique to a system of 8316 ordinary differential equations. The solution was obtained over a time interval from 0.0 to 10^{10} sec. and it took 50 minutes on the CDC 7600.

SST AND THE POLLUTION OF THE STRATOSPHERE

The stratosphere is by definition a relatively calm region of the atmosphere. Consequently, the residence time of any material brought into the stratosphere is quite large (order of a year or more). With the advent of supersonic transports, which will be flying at the stratospheric altitudes, the environmental impact of the engine exhaust has become a major concern. A principal concern has been the the possible catalytic destruction of ozone (O_3) by nitric oxide (NO). The hot engine exhaust contains a significant amount of NO which will be deposited in the stratosphere. Given a fleet of SST's the injected NO concentration could exceed many times the ambient [SCEP (1970A)]. Furthermore, the enhanced NO concentrations will greatly increase the destruction of O_3 through the so called NO_x catalytic cycle [Crutzen (1971A), Johnston (1971A)]

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2 \quad .$$

The net effect of these two reactions is to convert O_3 and O to two O_2's. It has been estimated that based on certain estimates of NO production rate from SST there could be a world wide reduction in ozone of from 3% to 50% [Johnston (1971A)]. Unfortunately ozone

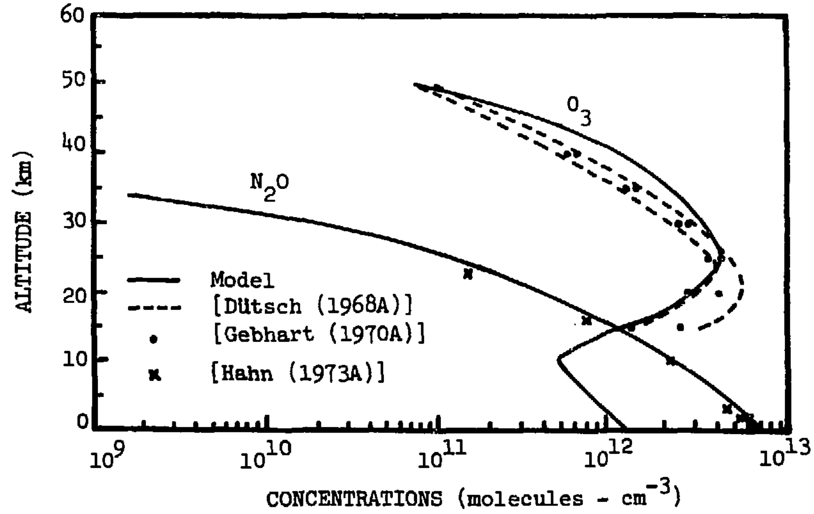


Figure 2. Examples of model computed ambient concentrations and some comparable measurements.

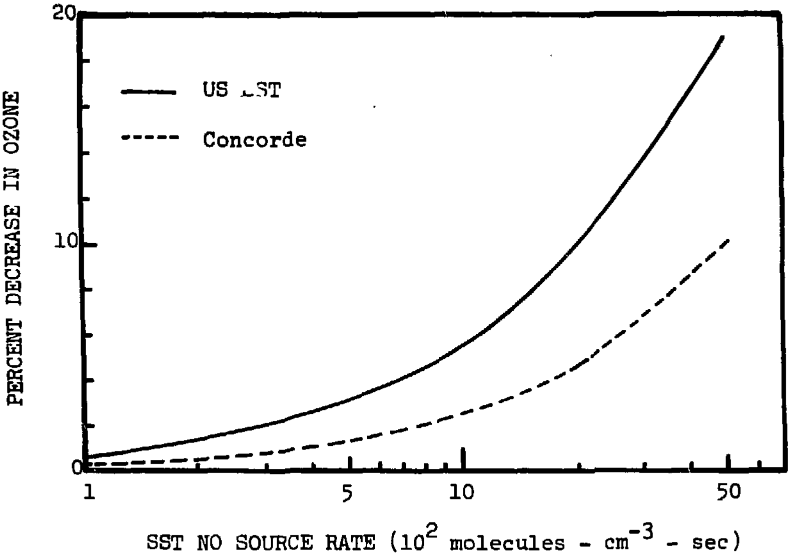


Figure 3. The model predicted decreases in average ozone density due to fleets of US SST flying between 19.5 and 20.5 km and Concorde flying between 16.5 and 17.5 km.

not only is a major source of heat in the stratosphere but it is also the shield of ultraviolet (UV) radiation. Due to the large optical depth of UV radiation even a few percent change in ozone will cause up to many folds of changes in UV radiation depending on the frequency. Of course, UV radiation is directly related to many forms of skin cancer in man and the delicate balance of the biosphere in general.

In view of this and in recognition of the limitations of the early studies, a large effort is currently being devoted to studying this question of possible SST pollution in the stratosphere. As a part of this effort we have developed and are developing several theoretical models to study the governing physical processes in the stratosphere.

We have used equations of the form Eq. (2) to simulate the globally averaged distribution of minor chemical species in the stratosphere. Some examples of the computed distributions are shown in Fig. 2 along with some measurements. Given estimates on the size of the proposed SST fleet, the flight frequency, the fuel consumption rates and the engine emission index, we can estimate the NO source rate, S_{NO}, and use Eq. (2) to obtain the range of probable perturbations in the global ozone content. Fig. 3 gives some of the theoretical estimates based on a one dimensional model. A distinction is made between the American SST and the Concorde because they not only have different engines with different emission rates but also different flight altitudes. The latter is especially important since the lower the flight altitude: the shorter the residence time for the pollutant. This will significantly affect the extent of the perturbations as is evident in Fig. 3. It is clear that the predicted perturbations are much smaller than the previously published estimates. At the present it is not clear how we may use these results and other similar predictions to be obtained from more elaborate models in projecting the environmental consequences. Hopefully this will be possible in the near future.

ATMOSPHERIC NUCLEAR TESTS AND OZONE

In the study of chemical kinetics transport in the stratosphere, validation of the simulation results through comparison with observations is most essential. Unfortunately it is impossible to carry out global scale experiments involving chemical releases. We are forced to search the past for possible means of validation. It has been pointed out [Foley (1973A)] that the atmospheric nuclear tests in the 1950's and early 1960's injected substantial amounts of NO_x into the stratosphere. It would follow that an examination of the ozone measurements of that period could possibly be used

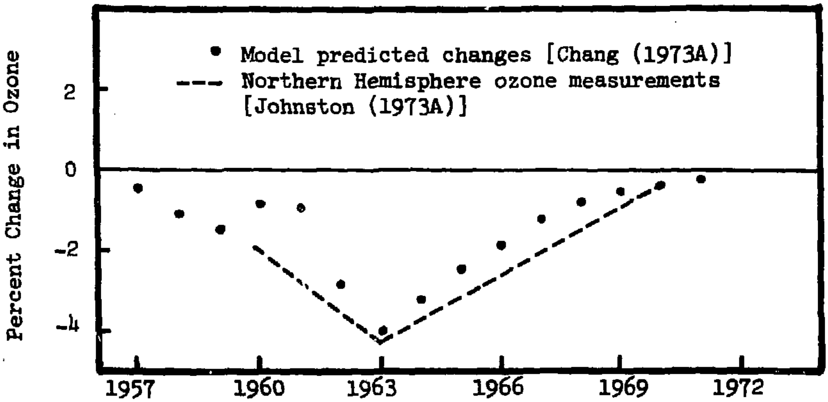


Figure 4. The model predicted decreases in yearly averaged ozone density due to atmospheric nuclear tests in the 1950's and early 1960's and a trend analysis of ozone measurements.

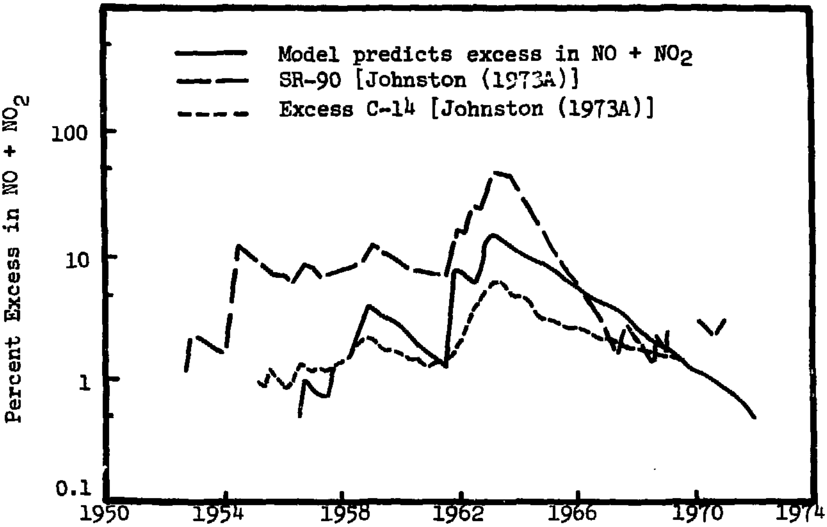


Figure 5. A comparison of the computed and measured deviations from normal of some representative traces from 1952 to 1970.

to estimate the significance of NO_x catalytic destruction of ozone in the stratosphere. This past inadvertent NO injection experiment is of great interest provided that we can properly estimate the expected perturbation and the available data. In order to carry out such a study one must use a time dependent model and compute the time history of perturbations from 1956 to 1970 starting with the ambient atmosphere as determined by the model. Based on our solution technique we are able to carry out such a simulation [Chang (1973A)].

By parameterizing the processes of production and injection of NO into the stratosphere during each atmospheric nuclear test, we have constructed a highly discontinuous source function,

$$S_{NO}(t,z) = \sum_{m=1}^{M} S_m \delta(t-t_m)\ H(z-z_m^B)\ H(z_m^T-z)$$

where $\delta(\cdot)$ is the delta function and $H(\cdot)$ is the unit step function. S_m is the total NO produced per unit volume. t_m is the time of the $m^{\underline{th}}$ test. z_m^B and z_m^T are the bottom and top of the nuclear cloud for the $m^{\underline{th}}$ test. In the one-dimensional simulation, S_m has been averaged over the surface of the earth. This will introduce significant error locally but negligable error in the global averaged model [Chang (1973A)].

Figure 5 gives the predicted changes in the yearly averaged ozone measurement and a trend analysis of the ozone data in the literature. The data is normalized to the simulation result at 1970. The apparent agreement is still being discussed in the literature since there exists other data analyses which may or may not show the same trend. However, we have another source of unexpected support in the time history of the predicted total excess NO + NO_2 in the stratosphere from the nuclear test. From chemical kinetics theory NO + NO_2 can serve as a tracer in the stratosphere. Figure 6 is a graph of the excess NO + NO_2 and the concentrations of two observed tracers, namely strontium 90 and excess carbon 14 [Johnston (1973A)]. All data are normalized at 1969 but all the curves are plotted on the same semi-log scale. We feel that the agreement is a validation not only of this study but also of the success of the numerical method.

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