

# A technique for determining probability distributions for creation and destruction of ozone and other tracer particles

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## ABSTRACT

A numerical technique is presented for calculating where, on average, tracer particles at a particular place in a turbulent medium were created, and where they will be destroyed. This technique requires knowledge of creation, destruction, and transport rates, and gives as results probability distributions for creation and destruction. The technique is demonstrated on a model of stratospheric ozone, and a rough quantification is made of the statement that high latitude, low altitude ozone tends to be created in low latitude, high altitude regions.

## 1. Introduction

Consider some tracer particles located at a particular place in a turbulent medium. In this paper we show how in general it is possible to calculate where, on average, these particles were created and where they will be destroyed. The technique presented uses expressions for the rates of creation and destruction in the different parts of the region under consideration and expressions for transport of the particles within the region.

An example of tracer particles in a turbulent medium is ozone in the stratosphere. To illustrate the technique, we apply it to stratospheric ozone: we show how to calculate where the ozone at a particular place was created and where it will be destroyed. Thereby, we hope to begin to quantify the statement that stratospheric ozone at high latitudes and low altitudes tends to be created at lower latitudes and higher altitudes.

## 2. Calculating where particles are created and destroyed

Following Hewitt & Martin (1973) we divide the region of space under consideration into a set of

boxes labelled  $1, \dots, N$ , and divide time into intervals of equal duration  $\tau$ . Let  $A_{ij}$  be the probability that a particle moves from box  $i$  to box  $j$  during one such interval and  $B_i$  be the probability that a particle in box  $i$  is removed from the region during the interval  $\tau$ , by chemical transformation or by physical movement out of the region. It follows that

$$\sum_{j=1}^N A_{ij} + B_i = 1, \quad i = 1, \dots, N. \quad (1)$$

The values of  $A_{ij}$  are calculated from wind velocities, eddy diffusion coefficients and chemical sinks by a technique which will be described later.

Let  $f_{ij}$  be the probability that a particle in box  $i$  at time  $n\tau$  will be destroyed in box  $j$  at some later time. Considering that a particle in box  $i$  moves to box  $k$  during a time interval with probability  $A_{ik}$  and is destroyed in box  $j$  during the time interval with probability  $B_j$  if and only if  $i = j$ , we may write

$$f_{ij}[n] = \sum_{k=1}^N A_{ik}[n] f_{kj}[n+1] + \delta_{ij} B_j[n],$$

$$i, j = 1, \dots, N, \quad (2)$$

where  $f_{ij}[n]$ ,  $A_{ik}[n]$ ,  $B_j[n]$  represent the respective probabilities  $f_{ij}$ ,  $A_{ik}$  and  $B_j$  at time  $n\tau$ , i.e. after  $n$  time intervals have passed.

If we assume that  $f_{ij}$ ,  $A_{ik}$  and  $B_j$  are independent

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of time we may drop the time dependence in eq. (2) and write

$$f_U = \sum_{k=1}^N A_{ik} f_{kj} + \delta_{ij} B_j, \quad i, j = 1, \dots, N. \quad (3)$$

This simplification requires that we use appropriately time averaged values for wind velocities, eddy diffusion coefficients and rates of formation and destruction.

If eq. (3) is written in matrix form, the solution is given by

$$f_j = (I - A)^{-1} B_j, \quad j = 1, \dots, N, \quad (4)$$

where  $B_j$  is a column vector with  $B_j$  in the  $j$ th position and zeros elsewhere,  $A$  is the matrix of transition probabilities  $A_{ij}$ , and  $I$  is the unit matrix of order  $N$ .  $f_j$  is a column vector containing  $f_{ij}$  in the  $i$ th position. Equation (4) allows us to calculate for any box in the region under consideration the probability that a particle in this box will be destroyed in box  $j$ . Note that we do not require any knowledge of sources for this calculation. Once a particle is found in a particular box  $i$  its eventual destruction is unaffected by sources, but only affected by the transition probabilities which depend on transport properties of the medium and upon chemical and physical sinks.

Now, working in the opposite direction, let us see how another useful quantity may be obtained: for the particles at a particular place in the region, where, on average, the particles were created.

Let  $S_k$  represent the mass of particles formed in box  $k$  during time  $\tau$  by (say) photochemical reactions and let  $p_{ik}$  represent the probability that a particle in box  $i$  was created in box  $k$  at some earlier time. Considering that during an interval  $\tau$  the mass moving from the  $j$ th box to the  $i$ th box is  $A_{ij} m_j$  (where  $m_j$  is the mass of tracer particles in box  $j$ ) and that the mass created in the  $i$ th box is  $S_i$ , we may write

$$p_{ik} [n+1] m_j [n+1] = \sum_{j=1}^N A_{ij} [n] p_{jk} [n] m_j [n] + \delta_{ik} S_k [n], \quad i, k = 1, \dots, N. \quad (5)$$

Again we shall make the assumption that  $A_{ij}$ ,  $m_j$ ,  $S_j$  and  $p_{ik}$  are constant in time. Defining

$$q_{ik} = m_j p_{ik} \quad (6)$$

we may write

$$q_{ik} = \sum_{j=1}^N A_{ji} q_{jk} + \delta_{ik} S_k, \quad i, k = 1, \dots, N. \quad (7)$$

$q_{ik}$  is the mass of tracer particles in the  $i$ th box that originated in the  $k$ th box. Writing eq. (7) in matrix form, the solution in terms of  $q_{ik}$  is

$$q_k = S_k (I - A)^{-1}, \quad k = 1, \dots, N. \quad (8)$$

where  $S_k$  is a row vector containing  $S_k$  in the  $k$ th position and zeros elsewhere and  $q_k$  is a row vector containing the  $q_{ik}$  for  $i = 1, \dots, N$ . This solution gives us the probability that a particle in any box  $i$  originated in box  $k$ . For some purposes this may be a useful solution in its own right, but in many cases it would be preferable to get a solution of  $q_{ik}$  (or  $p_{ik}$ ) for a fixed  $i$  and for  $k$  ranging from  $1, \dots, N$ . Using eq. (8) to obtain this solution would require a calculation for each box  $k = 1, \dots, N$ , while by employing a more direct method we can get the required solution for  $q_{ik}$  with considerably reduced calculation.

At this stage we have shown how to calculate the two vectors  $f_j$  and  $q_k$ , and we may note that  $q_{ik} f_{ij}$  equals the particle mass in the  $i$ th box that was created in the  $k$ th box and that will be destroyed in the  $j$ th box. If we sum over  $i$  from 1 to  $N$ , we have, using (4) and (8),

$$\sum_{i=1}^N q_{ik} f_{ij} = q_k \cdot f_j = S_k ((I - A)^2)^{-1} B_j, \quad k, j = 1, \dots, N, \quad (9)$$

which gives us the total particle mass that was created in the  $k$ th box at some previous time, and which will be destroyed in the  $j$ th box at some future time. Now assuming that the region under consideration contains all the relevant sources and sinks for the tracer concerned, by summing the expression in (9) over  $k$  we have

$$\sum_{k=1}^N q_k \cdot f_j = S ((I - A)^2)^{-1} B_j, \quad (10)$$

which gives us the total particle mass which will be destroyed in the  $j$ th box.  $S$  is a row vector containing  $S_k$  in the  $k$ th position,  $k = 1, \dots, N$ .

Noting that the fraction of those particles destroyed in the  $j$ th box which were created in the

$k$ th box, equals the fraction of those particles now in the  $j$ th box which were created in the  $k$ th box, we have

$$p_j = \frac{S\{(I-A)^2\}^{-1} B_j}{S\{(I-A)^2\}^{-1} B_i} \quad (11)$$

where  $S$  is a square matrix of order  $N$  whose  $(i, j)$ th entry is  $\delta_{ij} S_p$  and  $p_j$  is, as required, a column vector whose  $i$ th entry is  $p_{ij}$ . Note that the quantity in the denominator of eq. (11) is simply a normalization factor whose calculation may be replaced by recalling that  $\sum_{i=1}^N p_{ji} = 1$ .

The solution in (11) gives the probability that a particle in the  $j$ th box was introduced to the region in the  $i$ th box, for  $i = 1, \dots, N$ .

If we require the solution in terms of  $q_{ij}$  i.e. actual masses, then

$$q_j = m_j p_j \quad (12)$$

from (6). This gives for the  $j$ th box the respective particle masses that were created in other boxes.

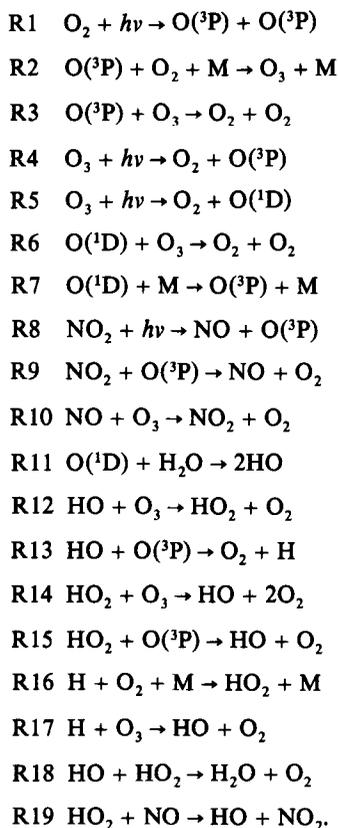
### 3. Stratospheric ozone model

We now describe the features of a stratospheric ozone model which is used to calculate, using the expressions just developed, where on average the ozone at a particular place was created and where it will be destroyed. This model is presently primarily to illustrate the technique described in the previous section, and secondarily to obtain some suggestive results about where ozone goes to and comes from in the stratosphere.

We first divide the main ozone containing regions of the atmosphere into a set of boxes. To generate the boxes a grid is assigned in the two dimensions of latitude and altitude and this is swept around the earth longitudinally. At each latitude there are 25 boxes each of 2 km height, from the surface of the earth to 50 km. At each altitude there are 25 boxes equally spaced from pole to pole. Given these 625 boxes, we need to determine the parameters  $A_{ij}$ ,  $B_j$ , and  $S_j$  for  $i, j = 1, \dots, 625$ .

The values for  $S_j$  and  $B_j$  are calculated from the expressions for photochemical creation and destruction of ozone. Given a set of fundamental reactions important for the creation and des-

truction of ozone, one approach would be to calculate theoretically the profiles of relevant atmospheric constituents such as ozone, and hence the creation and destruction rates. However, for the purposes of the present calculation it is convenient and more accurate to use observed profiles when possible, namely for those constituents that do not vary rapidly on the time scale of a day. Therefore we use constant background concentrations for air,  $O_2$ ,  $O_3$ ,  $H_2O$  and  $NO_x$  ( $=NO + NO_2$ ). In conjunction with these concentrations the following limited set of reactions is used:



Given the fixed distributions for air,  $O_2$ ,  $O_3$ ,  $H_2O$  and  $NO_x$ , we calculate the concentrations of the other atmospheric constituents by assuming them to be in equilibrium:  $O(^3P)$  through R2, R4, and R5;  $O(^1D)$  through R5 and R7;  $NO$  and  $NO_2$  through R8, R9 and R10;  $H$  through R13, R16 and R17;  $HO_x$  ( $=HO + HO_2$ ) through R11–R19. With the use of the resulting expressions we can write an expression for the time rate of change of

ozone due to the set of reactions R1–R19:

$$\frac{\partial(O_3)}{\partial t} = P - D, \quad (13)$$

$$P = 2j_1(O_2)$$

$$D = D_1 + D_2 + D_3,$$

$$D_1 = 2k_9(NO_2)(O(^3P)),$$

$$D_2 = 2\{k_{11}(O(^1D))(H_2O) + (HO_2)\{k_{14}(O_3) + k_{15}(O(^3P))\} + k_{17}(H)(O_3)\},$$

$$D_3 = 2(O_3)\{k_3(O(^3P)) + k_6(O(^1D))\}.$$

$D_1$ ,  $D_2$  and  $D_3$  account for destruction of ozone by all the reactions R1–R19 involving respectively nitrogen, hydrogen, and oxygen compounds.

The expression (13) includes all significant creation and destruction mechanisms for reactions R1 to R19, such as destruction of ozone by R12 and R13, and creation of ozone via R19, R8, and R2. It is derived in this way: the expression for  $\partial(O_3)/\partial t$  is written using *all* terms which mention  $O_3$ :  $\partial(O_3)/\partial t = -k_2(O(^3P))(O_2)(M) - k_3(O(^3P))(O_3) + \dots$ . Then expressions for  $\partial(O(^3P))/\partial t$ ,  $\partial(NO)/\partial t$ , and so forth are similarly written and set equal to zero. By substituting from the latter expressions, (13) can be achieved. Many terms cancel out or are hidden in the determination of the concentrations of atmospheric constituents: for example, R12 and R13 enter the calculation in the determination of (H) and (HO<sub>2</sub>).

Recalling that  $S_j$  is the mass of ozone produced in box  $j$  in time interval  $\tau$ ,

$$S_j = P_j V_j \tau m_{O_3}, \quad (14)$$

where  $P_j$  is  $P$  as defined in (13) at the centre of box  $j$ ,  $V_j$  is the volume of box  $j$  and  $m_{O_3}$  is the mass of an ozone molecule.

Recalling that  $B_j$  is the probability that an ozone molecule in box  $j$  will be destroyed in the interval  $\tau$ ,

$$B_j = 1 - \exp(-D_j \tau / (O_3)_j) \quad (15)$$

where  $D_j$  is  $D$  as defined in (13) at the centre of box  $j$  and  $(O_3)_j$  is the ozone concentration at the centre of box  $j$ . For the ozone concentrations we use the latitudinal cross-sections given by Dütsch (1969). The concentrations for air and molecular oxygen are taken from the U.S. Standard Atmosphere (1962), the mixing ratio for water is taken as a constant value of  $5 \times 10^{-6}$  and the constant mixing ratios

for NO<sub>x</sub> are taken from Ackerman & Muller (1972) (with the mole fraction of NO<sub>x</sub> increasing smoothly above their highest altitude to  $5 \times 10^{-8}$  at 50 km). Photodissociation rates are determined using solar flux and oxygen and ozone cross-sections of Ackerman (1971). The photodissociation rates are averaged over the daylight hours using 12 solar angles. Reaction rates and other data are the ones used by McConnell & McElroy (1973) where references for the rates are given.

The transition probabilities  $A_{ij}$  are calculated from mean winds and eddy diffusion coefficients using the general method of Martin (1975). With this numerical approach, the horizontal, vertical and anisotropic eddy diffusion coefficients, and the horizontal and vertical mean winds are incorporated in a natural manner into the numerical representation. The numerical solution to the diffusion equation gives conservation of mass, correct centre of mass motion and correct spreading (i.e. correct second moment) in all directions. Actually, the transition probabilities obtained are not greatly different from those that would be obtained using simple but appropriately chosen finite difference approximations.

The eddy diffusion coefficients of Luther (1973) and the mean winds of Louis (see Louis et al., 1974) are used in the calculation. These parameters were derived from the data of Oort & Rasmussen (1971) and are generally intermediate between those of Reed & German (1965) and those of Gudiksen et al. (1968). As boundary conditions we assume that all ozone molecules moving to the surface of the earth are absorbed there, while the box borders along the poles act as reflecting surfaces. The boundary condition at the border of the top box at 50 km is irrelevant, since for all our calculations a negligible number of trace particles approach this altitude.

As a final step in the calculation of  $A_{ij}$  it is necessary to remove from consideration those particles chemically destroyed during the time  $\tau$ ; the row sums of  $A$  calculated as indicated above are therefore normalized by eq. (1) so that

$$\sum_{j=1}^N A_{ij} = 1 - B_i, \quad i = 1, \dots, N.$$

To obtain the time-independent parameters necessary for the use of the solutions (8) and (11), all parameters, including eddy diffusion coeffi-

icients, mean winds, and photodissociation rates (averaged over the daylight hours as indicated earlier) were evaluated for conditions at the March equinox.

To make sure that the ozone model was reasonably self-consistent, starting with Dütsch's ozone profiles, the model was used to obtain the ozone distribution from the generalization of (8),

$$\mathbf{m} = \mathbf{S}(\mathbf{I} - \mathbf{A})^{-1}, \tag{16}$$

where  $\mathbf{m}$  is a row vector of the ozone masses in each box. This revised ozone distribution  $\mathbf{m}$  was reasonably consistent with the original ozone distribution considering the lack of seasonal variation in the model.

#### 4. Results

Results based on the ozone model just described are presented in Figs. 1-6. In Figs. 1, 3, and 5 are presented distributions of the probability that ozone, anywhere in the stratosphere, will be destroyed in regions about three given points. In Figs. 2, 4, and 6 are presented probability distributions describing where, on average, ozone at these same three given points was created.

If the initial point is say 35 km altitude at the equator (not shown), only regions near to the point are found to contain ozone that is eventually destroyed in the region of the point. This result is,

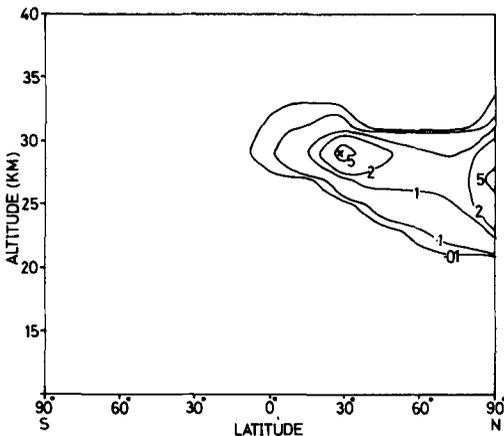


Fig. 1. Contours of the probability, multiplied by  $10^{18}$ , that an ozone molecule at a given location will be destroyed in a volume of  $1 \text{ m}^3$  located at 29 km altitude,  $28.8^\circ \text{ N}$ . This latter location is marked by an "x".

as expected, given the short time required to obtain photochemical equilibrium at high altitudes, and serves mainly to verify that the calculational procedure is working properly.

Figs. 1-6 show results for 3 points of progressively higher latitudes and lower altitudes. Here can be seen a suggestion of the extent of the validity of the idea that ozone at high latitudes and low altitudes was created at lower latitudes and higher altitudes. It is easy to see that the effect becomes more dramatic at high latitudes, so that in Fig. 6 almost all the ozone at the point in question was created at a lower latitude and a higher altitude. Summarizing the results in Figs. 1-6, we may say

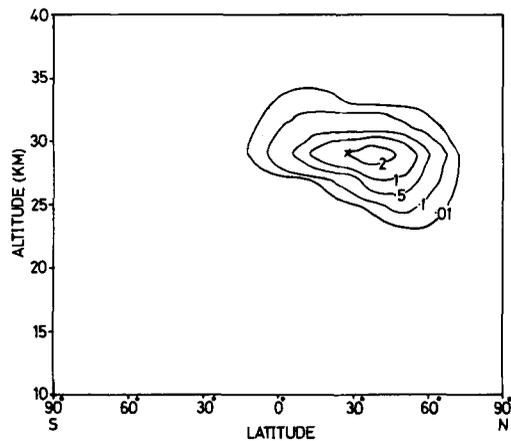


Fig. 2. Contours of the probability, multiplied by  $10^{18}$ , that an ozone molecule at 29 km altitude,  $28.8^\circ \text{ N}$  (this location is marked by an "x"), was created in a volume of  $1 \text{ m}^3$  at a given location.

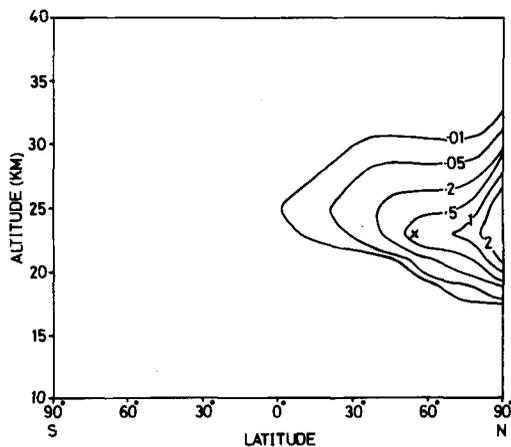


Fig. 3. As Fig. 1, for the location 23 km,  $57.6^\circ \text{ N}$ .

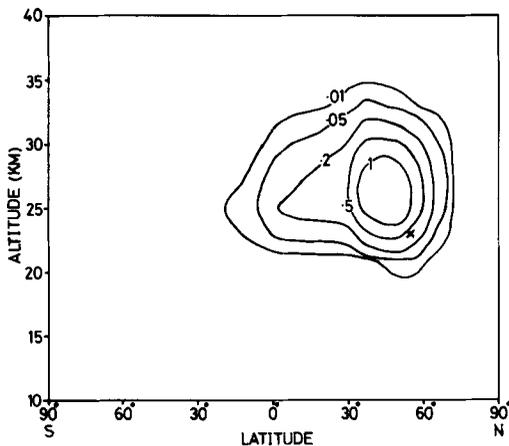


Fig. 4. As Fig. 2, for the location 23 km, 57.6° N.

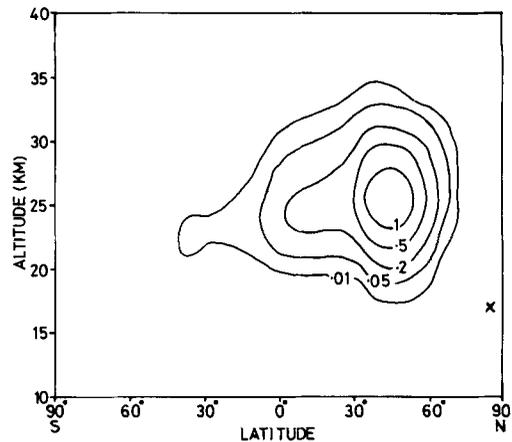


Fig. 6. As Fig. 2, for the location 17 km, 86.4° N.

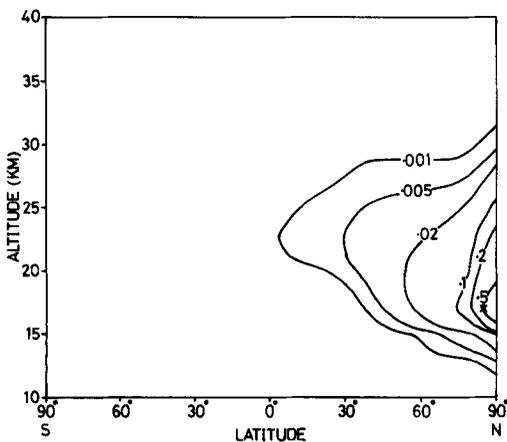


Fig. 5. As Fig. 1, for the location 17 km, 86.4° N.

that at low latitude, high altitude points most ozone is destroyed relatively near its source, but that the ozone which is not so destroyed makes up an important part of the ozone at higher latitude, lower altitude points; and that at source points at higher latitudes and lower altitudes, less of the ozone is destroyed near its source, and the same effect becomes exaggerated.

The main intrinsic limitation of the method as applied to ozone is the requirement that creation and destruction rates are constant in time. We judge that our results are fairly representative of results including time variations. Naturally our results are no better than the data on which they are based. The most serious deficiency in these is perhaps the eddy diffusion coefficients. Whatever the error caused by errors in the data, we suggest that our results give more of an indication of where ozone goes than a simple statement that low altitude, high latitude ozone tends to be created in high altitude, low latitude regions. However, our major aim has been to show *how* certain implications of a specific ozone model may be determined—e.g. for ozone at a particular place, where it was created and where it will be destroyed—in the hope that a means of obtaining such information can be used to gain a better understanding of other models.

## 5. Acknowledgments

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## REFERENCES

- Ackerman, M. 1971. Ultraviolet solar radiation related to mesospheric processes. In *Mesospheric Models and Related Experiments* (ed. G. Fiocco), Dordrecht, D. Reidel, 149–159.
- Ackerman, M. & Muller, C. 1972. Stratospheric nitrogen dioxide from infrared absorption spectra. *Nature* 240, 300–301.
- Dütsch, H. U. 1969. Atmospheric ozone and ultraviolet radiation. In *Climate of the Free Atmosphere* (ed. D. F. Rex), pp. 383–432, Vol. 4 of H. E. Landsberg (ed. in chief), *World Survey of Climatology*, Amsterdam, Elsevier.
- Gudiksen, P. H., Fairhall, A. W. & Reed, R. J. 1968. Roles of mean meridional circulation and eddy dif-

- fusion in the transport of trace substances in the lower stratosphere. *J. Geophys. Res.* 73, 4461–4473.
- Hewitt, R. G. & Martin, B. 1973. A method for calculating residence times. *J. Geophys. Res.* 78, 6212–6217.
- Louis, J. F., London, J. and Danielsen, E. F. 1974. The interaction of radiation and the meridional circulation in the stratosphere. *Proceedings of the international conference on structure, composition and general circulation of the upper and lower atmospheres and possible anthropogenic perturbations*, January 14–25, Melbourne, Australia, 1205–1214.
- Luther, F. M. 1973. Monthly mean values of eddy diffusion coefficients in the lower stratosphere, presented at the *AIAA/AMS International conference on the environmental impact of aerospace operations in the high atmosphere*, June 11–13, Denver, Colorado.
- Martin, B. 1975. Numerical representations which model properties of the solution to the diffusion equation. *J. Comput. Phys.* 17, 358–383.
- McConnell, J. C. & McElroy, M. B. 1973. Odd nitrogen in the atmosphere. *J. Atmos. Sci.* 30, 1465–1480.
- Oort, A. H. & Rasmusson, E. M. 1971. *Atmospheric Circulation Statistics*. Washington, D.C., U.S. Government Printing Office.
- Reed, R. J. & German, K. E. 1965. A contribution to the problem of stratospheric diffusion by large-scale mixing. *Mon. Weather Rev.* 93, 313–321.
- U.S. Standard Atmosphere, 1962. Washington, D.C., U.S. Government Printing Office.

#### МЕТОД ДЛЯ ОПРЕДЕЛЕНИЯ РАСПРЕДЕЛЕНИЙ ВЕРОЯТНОСТЕЙ ДЛЯ ОБРАЗОВАНИЯ И РАЗРУШЕНИЯ ОЗОНА И ДРУГИХ ЧАСТИЦ—ТРАССЕРОВ.

Представлен численный метод для расчетов, где в среднем частицы-трассеры образуются в турбулентном потоке и где они разрушаются. Этот метод требует знания скоростей образования, разрушения и переноса и позволяет находить распределения вероятностей для образования и

разрушения частиц. Метод демонстрируется на модели стратосферного озона и делается грубая проверка утверждения, что высокоширотный озон на низких высотах имеет тенденцию к образованию в низких широтах на больших высотах.