Behaviour of nitric oxide trails deposited in the mesosphere and stratosphere

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ABSTRACT

The transient behavior of a nitric oxide trail deposited in the atmosphere has been studied by numerical solution of the multidimensional diffusion equation including the effects of chemical reactions between nitric oxide and constituents of the ambient atmosphere. Starting with an initial nitric oxide concentration of 2×10^{12} molecules/cm^3 and a trail radius of 90 m, computations have been carried out for 20 km as well as 60 km. As the trail expands, atmospheric ozone interacts with nitric oxide to form nitrogen dioxide and molecular oxygen. During the day nitrogen dioxide is photodissociated to form nitric oxide, leading to a further decrease in ozone. Destruction of ozone by nitric oxide results in a depletion of ozone in the vicinity of the trail. For a quiescent atmosphere this ozone "hole" typically reaches a maximum extent in 4 to 6 hours and collapses again in 12 hours. At its maximum the 50 % or greater depletion region is one kilometer wide and 300 m thick. Trail behavior is relatively independent of altitude and background ozone but depends strongly on the magnitude of eddy diffusivity and the initial nitric oxide concentration. Wind shear stretches the trail into a thin oval, enhancing the rate of trail dissipation.

Introduction

A high density nitric oxide trail deposited in the mesosphere or stratosphere will simultaneously diffuse and react chemically with ambient atmosphereic species, most notably ozone. In this work the behavior of a trail at approximately 60 km will be explored by the solution of the appropriate multidimensional diffusion equation which includes terms representing the effects of chemistry and wind shear. A comparison will then be made with the situation in the stratosphere. The relative importance of turbulent diffusion, chemistry and wind shear have been examined carefully. It is found that no single process such as chemical kinetics can explain the temporal behavior of the trail. Both diffusion and wind shear are found to be very important.

Chemical reactions and the trail

As a nitric oxide trail expands it interacts with constituents of the ambient atmosphere. One of the most important reactions involves ozone.

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

This process enlarges the ozone hole which is created during the formation of the nitric oxide trail. The ozone distribution is normally controlled by the dissociation of O_2 involving principally the Schumann Range bands in the mesosphere with contributions from Lyman alpha and the Herzberg system which dominates in the stratosphere (Kockarts, 1971). Formation of ozone is by the three body association

$$O + O_2 + M \rightarrow O_3 + M$$

and destruction in an oxygen nitrogen atmosphere occurs by means of

$$O + O_3 \rightarrow 2\,O_2$$

photodissociation of O_3 and loss by reaction with NO.

Atomic oxygen is normally lost by the reac-

tion

$$O + O + M \rightarrow O_2 + M$$

In the presence of NO and NO_2 this loss can be increased by (Nicolet, 1965)

$$NO + O + M \rightarrow NO_2 + M$$

$$NO + O \rightarrow NO_2 + h\nu$$

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

so that odd nitrogen has an indirect effect on ozone.

It has also been proposed e.g. Crutzen (1971) that NO_2 can aid in the destruction of O_3 by means of the reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

Several reactions lead to the destruction of NO_3 including

$$NO_3 + NO \rightarrow 2\ NO_2$$

and

$$NO_3 + hv \rightarrow NO_2 + O$$
$$\rightarrow NO + O_2$$

However the rate of formation of NO_3 is 10^{-11} exp $(-3\,500/T)$ (Schofield, 1967) which at mesospheric temperatures is four orders of magnitude less than the corresponding reaction involving NO. Since the NO/NO_2 ratio is greater than unity at the edge of the trail the formation of NO_3 is of minor importance as a loss process for O_3. The quantity of NO_3 created at the edge of the trail will be proportional to $[NO_2][O_3]/[NO]$ at night. During the day there is strong photodissociation of NO_3. The reuslt of this cycle is to enhance the loss of ozone by reaction with NO.

Nitric oxide and nitrogen dioxide can be influenced by the presence of atomic nitrogen. However, it is difficult to obtain large N concentrations since the direct dissociation of molecular nitrogen is ineffective even in the presence of predissociation. Dissociation of nitric oxide in its different band systems has become of increasing interest and discussed in detail by Cieslik & Nicolet (1973). Values in the mesosphere range from a minimum of 10^{-7} sec^{-1} to 10^{-5} sec^{-1} depending on the cross sections adopted. There is no dissociation in the stratosphere. Dissociation of NO_2 to form NO and O is usually postulated. A dissociation rate of $J_{NO_2} = 10^{-2}$ sec^{-1} can be adopted (Brasseur & Nicolet, 1973) at the top of the atmosphere.

Reactions involving N include

$$N + O_2 \rightarrow NO + O$$

$$N + NO \rightarrow N_2 + O$$

$$N + O_3 \rightarrow NO + O_2$$

$$N + O + M \rightarrow NO + M$$

$$N + O \rightarrow NO + h\nu$$

$$N + NO_2 \rightarrow 2\ NO$$

All of these reactions lead to the formation and destruction of NO. However, in the ambient atmosphere the concentration of N is so small that one can neglect the effect of atomic nitrogen chemistry at the edge of the trail.

The nitric oxide and nitrogen dioxide contained in a trail can be ionized in the mesosphere by direct solar Lyman alpha radiation during the day and scattered Lyman alpha radiation at night. A starting NO density of 10^{12} cm^{-3} at 75 km will give rise to 2×10^6 electrons cm^{-3} for a zenith angle of 7.5°. This is more than three orders of magnitude above the normal background. The majority of the primary NO^+ and NO_2^+ ions formed recombine dissociatively with free electrons. However, ionic reactions do occur which modify the primary species. For instance NO_2^+ is transformed into NO^+ by the reactions

$$NO_2^+ + NO \rightarrow NO^+ + NO_2$$

The ion NO^+ can react with NO, CO_2, or N_2 to form a cluster ion which in turn is transferred into a hydrated ion of the form $H_3O^+ \cdot (H_2O)_n$. Such hydrated ions may further cluster or aid in forming aerosols under proper conditions. The dissociative recombination rate of hydrated ions is as much as a factor of 10 larger than that of NO^+ and NO_2^+. In general the electron density is great enough that NO^+ and NO_2^+ will directly recombine producing atomic nitrogen and other products. However, as the electron density decrease the percentage of hydrated ions will increase. One of the by products of hydrated

formation and loss is hydrogen compounds, which can influence the ozone distribution.

In the foregoing discussion emphasis has been placed on a nitrogen–oxygen system. Such a set of reactions overestimates the ozone concentration in the mesosphere so that it is necessary to introduce hydrogen compounds to reproduce the ambient distribution (Hunt, 1966). In particular

$$H + O_3 \rightarrow OH + O_2$$

and

$$OH + O \rightarrow H + O_2$$

are very important (Bowman et al., 1970). Hydrogen compounds can be affected by the presence of NO by reactions of the type

$$HO_2 + NO \rightarrow OH + NO_2$$

as well as the effective reaction

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

Also to be considered are reactions such as

$$NO + H + M \rightarrow HNO + M$$

The presence of large NO concentrations may create new molecules such as HNO_3.

The result of large NO concentrations in the presence of the chemistry discussed above is to reduce the ambient O_3 concentration. This is particularly true for NO concentrations greater than 10^{11} cm^{-3} as can be shown by photochemical calculations of the chemistry discussed here. Although the chemistry is important, diffusion of the nitric oxide trail and of ambient ozone, attempting to fill the depletion caused by the vehicle is the primary effect. In the following treatment the chemistry is minimized to the principle reaction, i.e., the formation of NO_2 by reaction of NO with O_3 and to the dissociation of NO_2 during the day. Two examples will be considered.

In the first an ambient ozone concentration of 2×10^{12} cm^{-3} is assumed. This corresponds to an altitude of 20 km. A computation with a starting O_3 concentration of 1×10^{10} cm^{-3} is also given. This is characteristic of the lower mesosphere under conditions of minimum seasonal temperature and diffusivity.

Solution of diffusion equations

For a homogeneous medium the dimensionless diffusion equation for the particle concentration, c, is expressed as follows:

$$\frac{\partial c}{\partial t} = \nabla^2 c \tag{1}$$

where the substitution $\partial/\partial t = (1/D)(\partial/\partial t')$ has been made to modify the time variable, t', so that it includes the diffusion coefficient D. The above equation is solved as an initial value problem.

One-dimensional diffusion gives a different time behavior than diffusion in two or three dimensions. This difference is important when estimating residence times or lifetimes of various atmospheric phenomena. A comparison of the analytical formulations of the solution is given below (Sommerfeld, 1949).

The general solution is:

$$u(x_j t) = \int_j f(\xi_j)\, U(x_j t)\, d\xi_j \tag{2}$$

for $j = 1$ the integration is for one space dimension, for $j = 2$, two dimensions, and $j = 3$ three dimensions.

The kernels U for the three situations are

$$U = (4\pi D)^{-\frac{1}{2}} \exp\left\{\frac{-(x-\zeta)^2}{4Dt}\right\} \tag{3}$$

$$U = (4\pi Dt)^{-1} \exp - \frac{(x-\zeta)^2 + (y-\eta)^2}{4Dt} \tag{4}$$

$$U = (4\pi Dt)^{-3/2} \exp - \frac{(x-\zeta)^2 + (y-\eta)^2 + (z-\zeta)^2}{4Dt} \tag{5}$$

It is seen that the pre-exponential factors show a fundamentally different time dependence, i.e.

$\frac{1}{\sqrt{t}}$ for one dimension

$\frac{1}{t}$ for two dimensions

$\frac{1}{t\sqrt{t}}$ for three dimensions

Thus one can obtain drastically different "lifetimes" depending on the number of dimensions considered.

A comparison between one dimensional and radial diffusion has been considered as an example. For a diffusion coefficient of 10^7 cm^2/sec and initial trail radius of 10 m, the time required to reduce the initial concentration from 10^{12} to 10^8 molecules cm^{-3} was 1.25×10^6 sec for one dimensional diffusion, but only 250 sec for radial diffusion.

So far we have considered diffusion in a homogeneous medium. The atmosphere, however, is frequently characterized by a situation where diffusivities in the vertical and horizontal directions can differ significantly, depending on wind shear and stratification conditions. We have taken the ratio of horizontal to vertical eddy diffusion coefficients as ten to one. The trail behavior is now described by the following equation:

$$\frac{\partial c_i}{\partial t'} = D_1 \frac{\partial^2 c_i}{\partial x^2} + D_2 \frac{\partial^2 c_i}{\partial z^2} - R_i \tag{6}$$

Here D_1 and D_2 are the horizontal and vertical eddy diffusivities, and R_i is the rate of loss of species i by the relevant chemical reactions. The expression for R_i can be written in terms of the rate constant k and the concentrations, c, of different species

$$R_i = \sum_{j=1}^{N} k_{i,j} c_i c_j \tag{7}$$

In finite difference form the two-dimensional diffusion equation may be written explicitly as follows (Ames, 1969):

$$U_{i,j,k+1} - U_{i,j,k} = r_x[U_{i-1,j,k} + U_{i+1,j,k} - 2U_{i,j,k}] + r_y[U_{i,j-1,k} + U_{i,j+1,k} - 2U_{i,j,k}]$$

where

$$r_x \equiv \frac{D_1 \Delta t}{(\Delta x)^2}$$

$$r_y \equiv \frac{D_2 \Delta t}{(\Delta y)^2}$$

Using equal mesh size in the two directions, one obtains

$$r_y = r_x \left(\frac{D_2}{D_1}\right)$$

In order to solve the equations when chemistry is included, the space field can be swept for chemical reaction during a time step, Δt, followed by a sweep for diffusive relaxation for that same time step. In this way it is possible to use the explicit marching formula for diffusive relaxation, and Runge-Kutta for the solution of a set of coupled nonlinear first order equations.

Nitric oxide trail in the mesosphere

Solutions of the two-dimensional diffusion equation with chemistry are presented as three-dimensional perspective plots in Fig. 1 for a nitric oxide trail diffusing at 60 km. Only the reaction involving the destruction of ozone by NO to form NO_2 was considered. For daytime it would be necessary to include photodissociation of NO_2. It might also be necessary to consider radiactive heating of the trail due to absorption of solar energy by NO_2. One of the consequences of such heating would be boyant displacement of the trail to a higher altitude. In all cases, our boundaries should be matched to results of atmospheric solutions involving all chemical reactions.

For the above case, the horizontal diffusion coefficient was taken at 10^4 cm^2 sec^{-1}, and the vertical coefficient as 10^3 cm^2 sec^{-1}. In another example, the time behavior of the centerline nitric oxide concentration was studied for a trail of 90 meter initial nitric oxide radius, and same initial concentration as above. The diffusivity coefficients were 10^5 cm^2 sec^{-1} horizontal and 10^4 cm^2 sec^{-1} vertical.

In order to use the diffusion equations it is essential that the scales of turbulent motion be small compared with the physical dimensions of the problem. This consideration limits us to eddies less than 100 m in diameter, or roughly 1% of the scale height. At such dimensions the turbulence is almost homogeneous, but probably still contains some effects of stratification. To account for the above situation, the ratio of horizontal to vertical eddy diffusivity was taken to be ten, and the diffusion coefficients

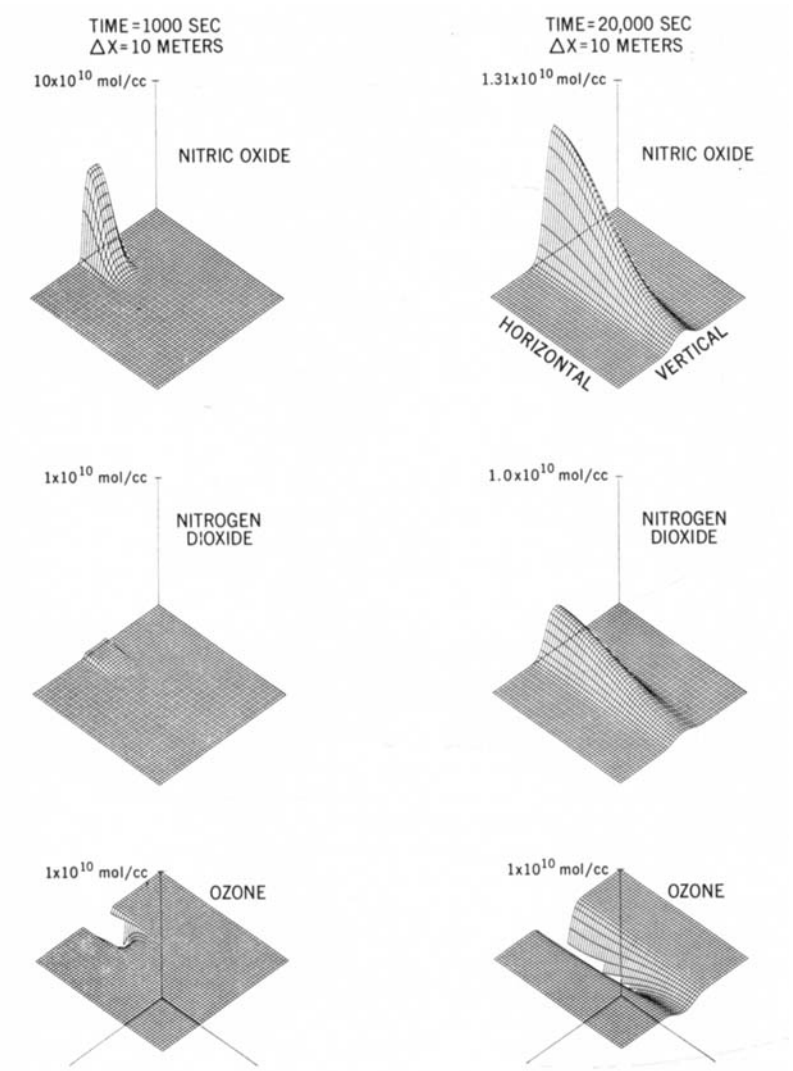

Fig. 1. Three dimensional perspective plots of NO, O_3 and NO_2 at different times.

were chosen to represent reasonable lower limits. However, large variations in eddy diffusivity are to be expected (Zimmerman & Champion, 1963).

Centerline nitric oxide concentrations are shown in Fig. 2. Extrapolations for three-dimensional and radial diffusion are shown, and transition to the chemically dominant regime is seen to occur after approximately one day. In the early regime, chemical reactions are important but affect eddy diffusive processes primarily through modification of the boundary conditions for the diffusion process. As the concentration gradients become shallow the rate of diffusion slows and chemical rate processes become more important. Ozone behavior for this trail is illustrated in Fig. 3, which shows development of the half width of the point of 50% ozone depletion, i.e. inside the radius shown, ozone concentration is less than 50% of the ambient value. The maximum horizontal spread of the ozone hole occurs in approximately 3 hours, and amounts to a 400 m half width for the 50% point. After approximately 5 hours, the gap begins to close, and after 9 hours the 50% point has moved to the center of the trail.

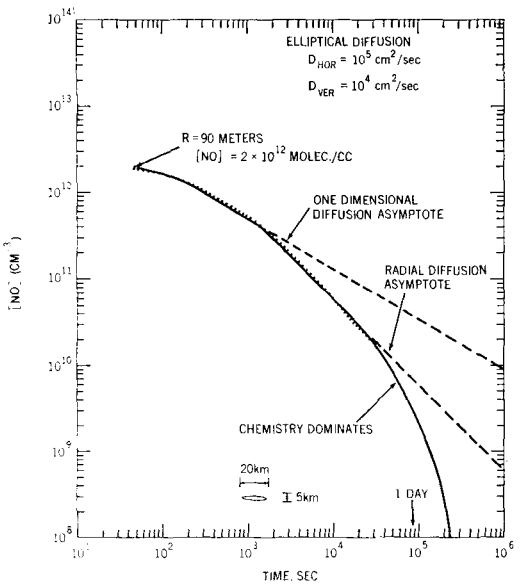

Fig. 2. Centerline nitric oxide concentrations for a trail at 60 km altitude.

At 20 hours, centerline ozone concentration is 85% of the ambient value, whereas centerline nitric oxide concentration is still 20 times as high as the natural background. The vertical extent of the ozone depletion, which is not illustrated, is less, since the vertical diffusion coefficient has been taken to be only 10% of the horizontal value. Otherwise, vertical behavior is quite similar to horizontal behavior.

Thus far, we have only discussed what may be considered a "night-time" situation, i.e. nitric oxide reacts with ozone to give nitrogen dioxide, whose further chemical activity is not considered. However, during the day nitrogen dioxide is photodissociated into products including nitric oxide, thus creating a catalytic cycle in which ozone is destroyed without any corresponding reduction in nitric oxide. This is quite true for the purely photochemical case. However, Fig. 3 shows that in the diffusive situation the recycling of nitric oxide has a relatively minor effect. The peak half width of the ozone hole is increased by only 5%, while the collapse time goes from 32 000 sec to 38 000 sec, i.e. from 9 hours to 10.5 hours. Fig. 4 shows nitric oxide decay for both night and day situations. The daytime nitric oxide does decay more slowly as expected, but the difference between daytime and nighttime cases only becomes significant for long times. For the daytime situation, nitric oxide concentration is governed primarily by diffusion, since any nitric oxide which reacts with ozone is quickly recycled by rapid photodissociation. For the corresponding day/night ozone behavior depicted in Fig. 5, the initial increase in centerline ozone concentration is very rapid, a behavior attributable to initially steep concentration gradients and small chemical influence. In half an hour a plateau region is reached which lasts for approximately four hours. The plateau is the regime of most active chemical reaction,

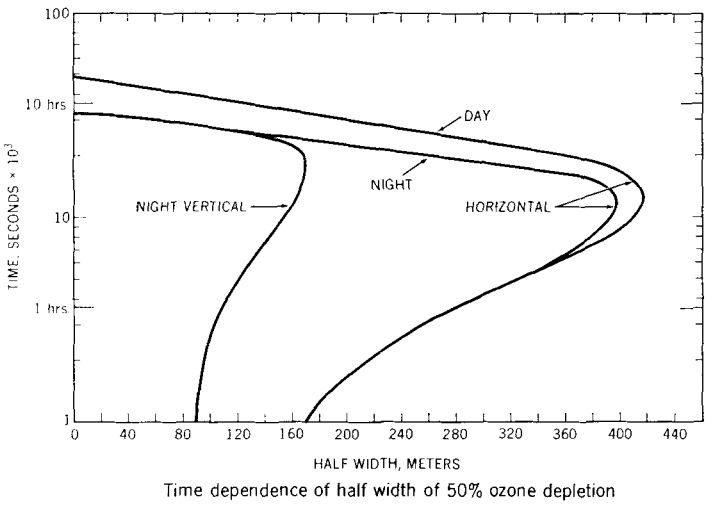

Fig. 3. Development of the half width of the point of 50% ozone depletion.

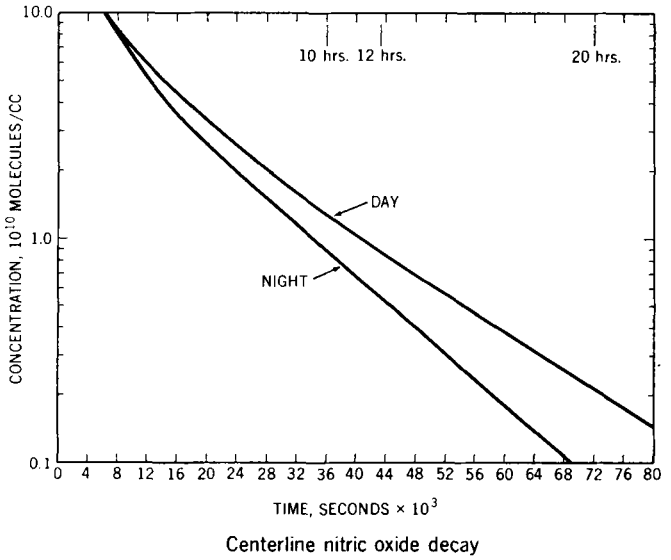

Fig. 4. Nitric oxide centerline decay for both night and day situations.

as is also evident from the nitrogen dioxide plot which reaches a maximum in this period.

It was assumed that the ozone concentration is zero in the space originally occupied by the nitric oxide. Thus, ozone increases monotonically to some asymptotic value. At the other limit, where background ozone concentration extends into the core of the initially high nitric oxide concentration regime, a rapid chemical reaction occurs, destroying ozone in the core region, and resulting in a situation very similar to the one considered.

The effect of eddy diffusivity is studied by considering cases in which the initial conditions

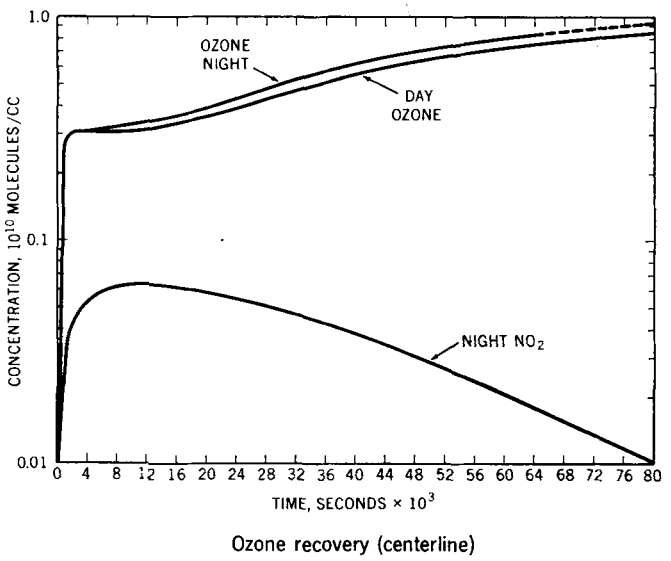

Fig. 5. Ozone and nitrogen dioxide nighttime time behavior at centerline.

Table 1. *Eddy diffusion coefficient dependence*

D, cm^2 sec^{-1}	t'(sec)	$Dt'r_0^{-2}$	[NO]	[O_3]
10^8	2×10^3	500	6×10^{10}	0.8×10^{10}
10^6	2×10^4	500	5×10^{10}	0.21×10^{10}
10^4	2×10^5	500	5×10^{10}	0.2×10^8

were identical, and the number of time steps were the same, but the eddy diffusion coefficients were varied. The situation of homogeneous radial diffusion was chosen for this comparison with an initial radius of 20 meters, and initial nitric oxide concentration of 10^{14} molecules/cm^{-3}. Results of the comparison are given in Table 1.

For the daytime situation, where the effect of chemistry on nitric oxide concentration is slight, one may expect that the time required to reach background concentration levels is inversely proportional to the diffusion coefficient. For nighttime centerline nitric oxide concentration the inverse proportionality to diffusion coefficient is no longer quite accurate. Similar behavior is observed for the centerline ozone concentration, since it is quite sensitive to chemical reactions.

The initial radius is r_0 and t' is time after 20 000 intervals. It is seen that for constant values of the quantity ($Dt'r_0^{-2}$) the centerline nitric oxide concentration is approximately the same, but that centerline ozone concentration decreases for decreasing diffusion coefficient. The reason for the above behavior is that the slower the diffusion, the longer the chemical destruction of ozone can proceed before nitric oxide concentration drops to a low value.

The effect of winds

Thus far, winds have been considered implicitly, as generators of the background turbulence which gives rise to eddy diffusivity. Winds also affect the trail in two other ways, namely advection and distortion. The former is due to a steadily blowing wind, while the latter is caused by wind shear.

First, consider the effect of advection. Berman & Goldburg (1971) quoted an annual mean zonal wind velocity of 10 m sec^{-1} for the stratosphere. The work of Smith et al. (1964) suggests higher wind speeds at higher altitudes. Taking 10 m sec^{-1} as a reasonable lower limit, one finds that in 10 000 sec (approximately 3 hours) a North–South trail will have been wafted some 100 km in the direction of the prevailing wind. A trail originally deposited in the East–West direction will have been moved along its own axis, giving little indication of wind effects. The above argument assumes a purely zonal wind, while a wind having both zonal and meridional components is probably more realistic. In that case, the corresponding effects are determined by the proper components of the wind vector relative to the trail axis.

Extrapolation of higher altitude wind shear data of Bedinger & Constantinides (1969) to 60 km indicates an average vertical shear of 7 m sec^{-1}/km, or 0.7 m sec^{-1}/100 m. Thus, two horizontal layers, separated in altitude by 100 m would move at an average rate of 0.7 m sec^{-1} relative to each other. In three hours, the displacement would therefore be as large as 7 km. If the wind shear is perpendicular to the trail axis, then the trail cross section will be stretched into a thin oval shape, decreasing the thickness of the ozone hole, and increasing the rate of dissipation of nitric oxide. Such behavior is illustrated by the stretched contour profiles shown later in this paper. On the other hand, a trail whose axis is parallel to the axis of shear will suffer only a slight distortion in the concentration profile.

Fig. 6 gives a comparison of centerline nitric oxide concentration with and without wind shear. It is readily seen that wind shear plays quite an important role.

Nitric oxide trails in the stratosphere

The background ozone concentration at 20 km is two orders of magnitude greater than at 60 km. The temperature at 20 km is slightly higher, resulting in somewhat larger rate coefficients at the lower altitude. There are also differences in the overall photochemistry of the atmosphere, but no significant difference in the predominant interaction of nitric oxide and ozone. Atmospheric structure at 20 km is characterized by a temperature inversion, while the distribution at 60 km approaches an adiabatic profile. Thus, the atmosphere at 20 km tends to be highly stratified, though not neces-

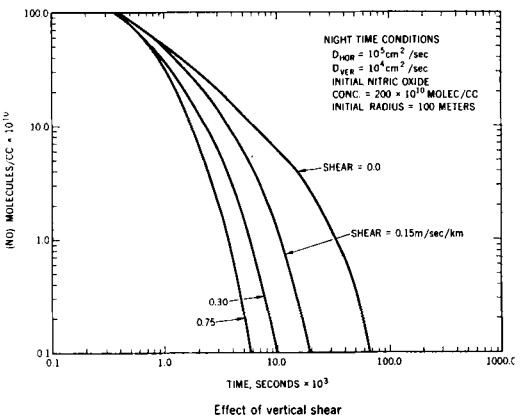

Fig. 6. Comparison of centerline nitric oxide concentrations with and without wind shear.

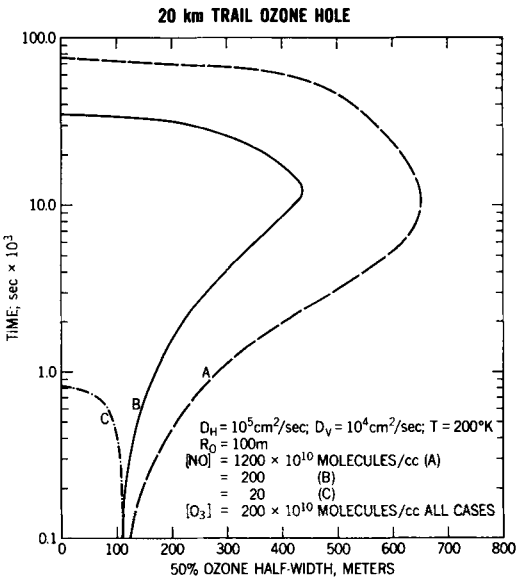

Fig. 7. Development of ozone hole at 20 km for different initial nitric oxide concentrations.

sarily quiescent. Long (1959) has studied the motion of fluids with density stratification both theoretically, and experimentally. One of Long's important findings is that stratification tends to produce very sharp vertical variations in horizontal velocity.

The initial trail characteristics are the same as in the 60 km example and the diffusivities are 10^4 cm^2 sec^{-1} vertical, and 10^5 cm^2 sec^{-1} horizontal. The vertical value is typical (Dyer, 1970), but the horizontal diffusivity does not include wind transport, and is thus considerably less than that generally quoted. Wind transport at 20 km is represented as a step wind rather than the steady shear assumed for the 60 km example. For comparison purposes, the temperature at 20 km is assumed to be the same as at 60 km. This results in about a 30% underestimate of the rate constant for ozone and nitrogen dioxide conversion at 20 km.

Fig. 7 gives the 20 km case, corresponding to the 60 km study shown in Fig. 3. Development of the ozone hole, centerline nitric oxide decay, and centerline ozone recovery were all identical for the daytime case chosen for comparison. Centerline ozone recovery was measured in terms of percentage of background ozone concentration. The only difference between the two cases was in the final collapse of the 50% ozone half width between 100 meters and zero. Here, the 20 km case collapsed in 34.5×10^3 sec, as compared with 38×10^3 for sec the 60 km case. The above behavior is quite surprising, considering that background ozone concentration at 20 km is 200 times greater than at 60 km. We must conclude that the process is essentially diffusion controlled, until a time of 2×10^4 sec is reached, when chemistry becomes dominant. This confirms the observation made in Fig. 2 that chemistry begins to dominate at about 2×10^4 sec for the initial nitric oxide conditions considered.

The time at which chemical rates become important is sensitive to initial nitric oxide concentration but not to background ozone concentration. Fig. 7 shows what happens when the initial nitric oxide concentration is varied. Curve B represents the case discussed above.

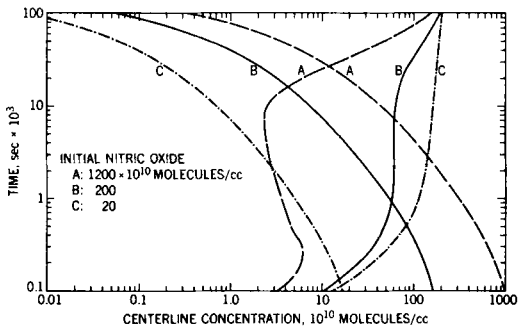

Fig. 8. Centerline nitric oxide and ozone concentrations at 20 km.

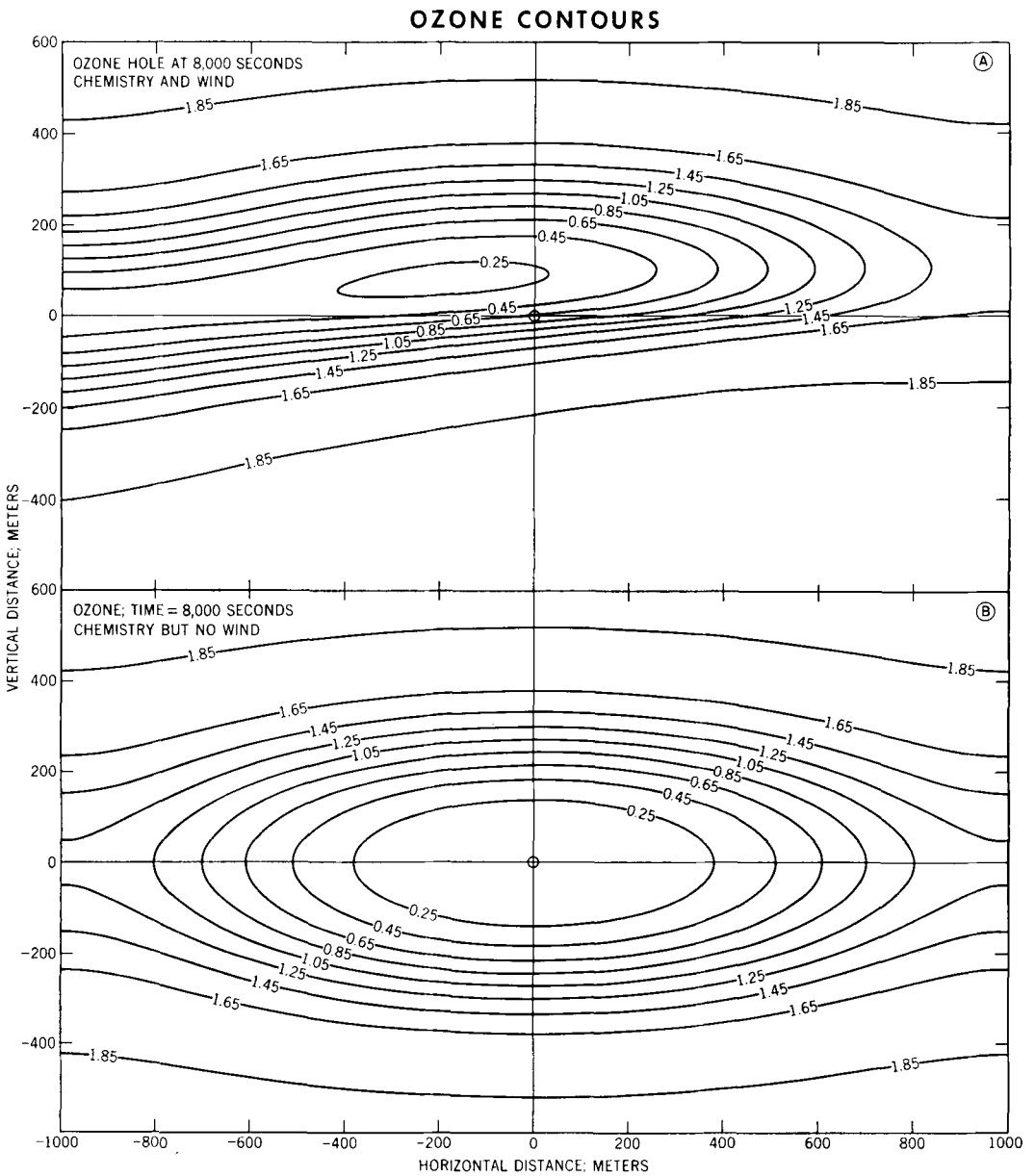

Fig. 9. Concentration contour behavior at 20 km (*A*) with and (*B*) without wind.

Curve A represents an initial nitric oxide concentration of 1.2×10^{13} molecules cm^{-3}. Here the ozone hole grows more rapidly, reaching a larger maximum size, and takes longer to collapse. However, the time at which maximum size is reached is not very different from the previous case. Curve C shows a situation where the initial nitric oxide concentration is 2.0×10^{11} molecules cm^{-3}, i.e. only 10% of the background ozone concentration. In this instance there is no growth of the ozone hole, and the initial hole collapses rapidly. Essentially, the nitric oxide concentration diffusing into the ozone is so low that destruction of ozone is slow

compared with diffusion. Fig. 8 shows centerline nitric oxide concentration, and centerline ozone concentration as functions of time. There is nothing surprising about the nitric oxide curves, but the ozone curves are interesting as they illustrate the varying relative importance of diffusion and chemical kinetics. For case C, which had the lowest initial nitric oxide concentration, the centerline ozone displays essentially diffusive behavior, its concentration increasing monotonically with time. Case B shows initially increasing concentration, to a plateau region, after which there is a monotonic increase. The two regions of increase are essentially dominated by diffusion, while the plateau indicates a "steady state" where ozone destruction by nitric oxide is balanced by diffusive replenishment. Case A, with the highest initial nitric oxide, shows centerline ozone increasing to a maximum, then decreasing to a minimum value, then again increasing toward the background value. Initially diffusion dominates, until the product $[NO][O_3]$ (integrated over the reaction regime, rather than just the value at the center) reaches a sufficient value to enable chemical kinetics to become important.

The next problem to be considered is the effect of a step wind. In this case we did not need to do a comparison with 60 km calculations, so the temperature was taken as 230°K, which is more characteristic of the stratosphere than the 200°K considered previously. The background ozone and initial nitric oxide concentration were assumed to be 1.85×10^{12} molecules cm^{-3}. Diffusivities were kept constant, and a comparison made between a windless situation with a case having a very weak step wind, i.e. 0.25 m sec^{-1}. However, the average shear across the step is 7.5 m sec^{-1} km^{-1}, which is a relatively high value.

Fig. 9 A illustrates the effect of the step wind. The no wind situation is illustrated in Fig. 9 B. Examination of Fig. 9 A shows that wind modification is most noticeable on the innermost contour where the ozone depletion is greatest. This contour is decreased by more than a factor of four in height, and by almost a factor of two in length. Similar decreases in height are shown by other contours, though not to the same extent. Note the non-symmetric shape of the wind distorted contours.

Conclusions

Behavior of a nitric oxide trail deposited in the mesosphere or stratosphere is determined by several factors including eddy diffusivity and the presence of winds. It is also a strong function of the initial nitric oxide trail content. The nitric oxide trail reacts with ambient ozone to form nitrogen dioxide. For a trail of 100 m initial radius, an ozone hole will form to a maximum size in 4 to 6 hours and then decay. The overall recovery time of the atmosphere following the creation of the trail is less than 12 hours. However, this time can be shortened by the presence of a wind shear.

REFERENCES

Ames, W. F. 1969. *Numerical methods for partial differential equations.* Barnes and Noble, New York.

Bedinger, J. F. & Constantinides, E. 1969. Investigation of temporal variations of winds, GCA-TR-69-3-N, GCA Corporation, Bedford, Mass.

Berman, C. & Goldburg, A. 1971. Global dispersion of supersonic transport exhaust in the stratosphere. D180-12981-1, Boeing, Seattle, 1971.

Bowman, M. R., Thomas, L. & Geisler, J. E. 1970. *J. Atm. and Terr. Phys. 32*, 1661.

Brasseur, G. & Nicolet, M. 1973. *Planet. Space. Sci. 21*, 939.

Cieslik, S. & Nicolet, M. 1973. *Planet. Space Sci. 21*, 9.

Crutzen, P. J. 1971. *J. Geophys. Res. 76*, 7311.

Dyer, A. J. 1970. *J. Geophys. Res. 75*, 3007.

Hunt, B. G. 1966. *J. Geophys. Res. 71*, 1385.

Kockarts, G. 1971. *Mesospheric models and related experiments.* D. Reidel Publishing Co., Dordrecht.

Long, R. R. 1959. *J. Geophys. Res. 64*, 2151.

Nicolet, M. 1965. *J. Geophys. Res. 70*, 679.

Schofield, K. 1967. *Planet. Space Sci. 15*, 643.

Smith, W. L., Katchen, L., Sacher, P., Swartz, P. & Theon, J. 1964. Temperature, Pressure, and Wind Measurements with the Rocket Grenade Experiment, 1960–1963, NASA TR R-211.

Sommerfeld, A. 1949. *Partial differential equations in physics.* Academic Press, New York.

Zimmerman, S. P. & Champion, K. S. W. 1963. *J. Geophys. Res. 68*, 3049.

ПОВЕДЕНИЕ СЛЕДА ОКИСИ АЗОТА, ЗАНЕСЕННОГО В МЕЗОСФЕРУ И СТРАТОСФЕРУ

Эволюция следа окиси азота, занесенного в атмосферу, изучена путем численного решения многомерного уравнения диффузии с учетом эффектов химических реакций между окисью азота и составляющими окружающей атмосферы. В начальный момент концентрация окиси азота бралась равной $2 \cdot 10^{12}$ молекул на $см^{-3}$ и радиус следа 90 метров и вычисления проводились для высот 20 и 60 *км*. По мере расширения следа атмосферный озон взаимодействует с окисью азота с образованием двуокиси азота и молекулярного кислорода. В течение дня двуокись азота подвергается фотодиссоциации и образуется окись азота, что ведет к дальнейшему уменьшению количества озона в окрестности следа. Для спокойной атмосферы эта «дыра» в поле озона обычно достигает максимальной протяженности за время от 4 до 6 часов и снова схлопывается через 12 часов. Во время своего максимума область 50 %-ной недостачи озона имеет ширину порядка 1 *км* и толщину около 300 *м*. Поведение следа сравнительно не зависит от высоты и концентрации озона в окружающей атмосфере, но сильно зависит от величины коэффициента турбулентного перемешивания и начальной концентрации окиси азота. Поперечный сдвиг скорости ветра растягивает след в тонкий овал, увеличивая скорость диссипации следа.