Studies of the ozone budget using a zonal mean circulation model and linearized photochemistry

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SUMMARY

A two-dimensional, time-dependent numerical model of the atmosphere has been used to investigate the ozone budget. The photochemistry includes catalytic destruction of ozone by the oxides of hydrogen and nitrogen with the source and sink terms linearized about the equilibrium values. The behaviour of the modelled ozone is quite satisfactory especially in low and mid-latitudes. Many of the observed details have been reproduced - including hemispheric asymmetries of the total ozone amounts.

The salient features of the ozone budget are described. There is photochemical production in the mid-stratosphere in low latitudes, with destruction in the high latitudes of both hemispheres. The mean motion fluxes are the most important transport term in equatorial latitudes. Polewards, the eddies become relatively more important. A feature of the model is the near-cancellation between mean and eddy flux divergences in middle and high latitudes. The vertical eddies play only a minor role.

The hemispheric asymmetry in the total ozone amount results in part from the high-latitude mean circulation driven by the eddy fluxes of angular momentum. Tropospheric processes also are responsible for some differences between the hemispheres.

1. INTRODUCTION

In view of the recent preoccupation with the likely effects of man-made pollutants on the ozone layer, it has become increasingly important to understand the behaviour of ozone in the natural stratosphere. It was recognized by the early workers that the ozone distribution could not be explained in terms of photochemistry alone and in 1928 Dobson et al. noted that the observed distribution was consistent with a direct circulation in the stratosphere with rising motion in low latitudes and sinking motion in high. Early measurements of water vapour lent some credence to this scheme (Brewer 1949) but later workers have stressed the importance of quasi-horizontal eddy motion (e.g. Newell 1963). The measurement of mean and eddy transports, both vertical and horizontal, throughout the stratosphere over long periods of time is a formidable task and it is natural to supplement such investigations with studies in numerical models which incorporate the principal mechanisms. (See Hunt 1969; Byron-Scott 1967; Clark 1970; Rao 1973.)

In Harwood and Pyle 1975 (hereafter called HP) we described the detailed formulation of a time-dependent, two-dimensional model of the atmosphere up to mesopause levels which included dynamics, radiation and photochemistry and for which we showed the results of some preliminary integrations. Here we describe in greater detail the results of an integration with a more complete physical specification. We have investigated in particular the ozone behaviour of the model. Accordingly, we here discuss in depth the relative roles of photochemical processes and eddy and mean transports in the ozone budget.

The model extends from the ground to approximately 80 km. Dependent variables are the zonal means of temperature, of wind components and of chemical constituent concentrations. These are held as functions of time, latitude and height (log pressure) with a resolution of 6 hours, 9-47° of latitude, and half pressure scale-height (∼3-5 km). Thermal wind balance is maintained between zonal mean temperature and westerly wind; at each

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timestep the meridional circulation necessary to preserve this balance against the perturbing
effects of heating and eddy momentum and heat fluxes is calculated. Eddy transports of
heat and matter (arising from departures from the zonal mean) are computed from a
\(K\)-type diffusion theory using the \(K_s\)s given by Luther in a paper at an AIAA/AMS con-
ference in 1973. Values of horizontal eddy momentum transport are currently specified
from observations. Heating and cooling in the stratosphere are calculated explicitly in
terms of the model state but in the troposphere are specified from climatology. The solar
radiation scheme in the runs described here uses ozone concentrations determined by the
model rather than the fixed profile used in HP.

The main improvements over the formulation of the model described in HP which
are relevant to the ozone behaviour are in the treatment of the photochemistry and the eddy
momentum fluxes.

(a) Momentum fluxes

In HP horizontal momentum fluxes were specified for the stratosphere but not the
troposphere. This is rectified in the runs described here, in which values up to 50mb are
taken for each month from Oort and Rasmusson (1971), assuming seasonal symmetry
between the hemispheres. As in HP the horizontal momentum fluxes in the stratosphere are
deduced from the Nimbus V Selective Chopper Radiometer measurements. The values used
here, however, are more comprehensive, being the monthly averages of all the data available
during 1973. No symmetry has been assumed between hemispheres, a fact of some importance
to the ozone budget as discussed below.

(b) Photochemistry

Our philosophy in constructing the model has been to begin with quite simple treat-
ments for the various physical processes with some of the feedbacks suppressed. Only when
the (still quite complex) mechanisms operating in the simple scheme are fully understood
are enhancements introduced. Thus the photochemical source-sink term is linearized such
that we write

\[
\frac{\partial [O_3]}{\partial t} = \frac{([O_3]_c - [O_3])}{\tau} \quad . \quad . \quad . \quad (1)
\]

where \([\cdot]\) denotes concentration. The time constant, \(\tau\), and the photochemical equilibrium
concentration, \([O_3]_e\), are specified to the programme in the form of tables as functions of
latitude, pressure and season. Whereas in HP the Chapman photochemical scheme was
used, here \(\tau\) and \([O_3]_e\) take values appropriate to the reaction scheme of Table 1 in which
the catalytic cycles of \(NO_x\) and \(HO_x\) are included. Thus the equation to be linearized becomes

\[
\frac{\partial [O_3]}{\partial t} = 2J_2[O_2] - \frac{2k_5J_3[OH][O_3]}{k_2[O_2][M]} - \frac{2k_4J_3[O_3]^2}{k_2[O_2][M]} - \frac{2k_8k_9J_3[NO_2][O_3]^2}{k_2[O_2][M]J_{10} + [k_2[O_2][M]k_8 + k_9J_3][O_3]} \quad (2)
\]

where the assumption is made that \(NO\) and \(NO_2\) are in equilibrium through reactions
R8, 9, 10.

In the most thorough treatment of the ozone photochemistry it would be necessary
to evaluate Eq. (2), and hence the \(J_s\), many times during the day but this would be an
expensive computation. Since the model must be run for several simulated years the
number of costly, repetitive operations should be reduced where possible. The use of
TABLE 1. A PHOTOCHEMICAL SCHEME FOR OZONE INCLUDING CATALYTIC DESTRUCTION BY HYDROGEN AND NITROGEN COMPOUNDS

<table>
<thead>
<tr>
<th>R</th>
<th>Reaction</th>
<th>Rate Constant</th>
<th>J</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>(O_2 + h\nu \rightarrow O + O)</td>
<td>(\lambda &lt; 2424\ \text{Å} ;\ J_2)</td>
<td>Ackerman (1971), Kockarts (1971)</td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>(O + O_2 + M \rightarrow O_3 + M)</td>
<td>(k_2 = 1.05 \times 10^{-34} \exp(510/T))*</td>
<td>Ackerman (1971)</td>
<td></td>
</tr>
<tr>
<td>R3</td>
<td>(O_3 + h\nu \rightarrow O_2 + O)</td>
<td>(\lambda &lt; 11000\ \text{Å} ;\ J_5)</td>
<td>Baulch et al. (1972) review.</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>(O + O_2 \rightarrow 2O_2)</td>
<td>(k_4 = 1.9 \times 10^{-11} \exp(-2300/T))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R5</td>
<td>(O + OH \rightarrow H + O_2)</td>
<td>(k_5 = 5.8 \times 10^{-11})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R6</td>
<td>(H + O_2 + M \rightarrow H_2O + M)</td>
<td>(\lambda &lt; 4400\ \text{Å} ;\ J_{10})</td>
<td>Hall and Blacet (1952)</td>
<td></td>
</tr>
<tr>
<td>R7</td>
<td>(HO_2 + O \rightarrow OH + O_2)</td>
<td></td>
<td>Nakayama et al. (1959)</td>
<td></td>
</tr>
<tr>
<td>R8</td>
<td>(NO + O_2 \rightarrow NO_2 + O)</td>
<td>(k_8 = 9 \times 10^{-12} \exp(-1200/T))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R9</td>
<td>(NO_2 + O \rightarrow NO + O_2)</td>
<td>(k_9 = 9.4 \times 10^{-12})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R10</td>
<td>(NO_2 + h\nu \rightarrow NO + O)</td>
<td>(\lambda &lt; 4400\ \text{Å} ;\ J_{10})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* All reaction rate constants are in cm molecules units. Unless otherwise stated the rate constant used is the recommendation of Garvin and Hampson (1974). The solar flux data were taken from Ackerman (1971).

Eq. (1) represents a reasonable approximation to a more complete treatment, in keeping with our stated philosophy. Such a simple scheme must suffer from some drawbacks. For example, the ozone equilibrium concentrations and time constants should change in response to variations in the ozone path length above. We, however, use precomputed values. Similarly, the reaction rates do not respond to changes in the model temperatures. Nevertheless, the gross features of the ozone photochemistry in the atmosphere are included in Eq. (1). We intend to include the more important feedbacks in later versions.

In calculating \(\tau\) and \([O_3]_e\), latitude-independent profiles of NO, and OH were employed. The OH profile was taken from Hesstvedt (1972) as this has been shown previously to give results consistent with satellite observations using the photochemical scheme of Table 1 (Barnett et al. 1975). The NO, profile was chosen so as to make the values of \([O_3]_e\) for the equinoxes in mid-latitudes agree with the mid-latitude profile of Krueger and Minzner (1973) at heights above 2.5 pressure scale-heights \((\approx 17.5\ \text{km})\). Below this level, where the lifetime of ozone is very long, rather arbitrary low values were used. The profile is given in Table 2. The peak value of the NO, mixing ratio is a little higher than most measurements would indicate but there is still considerable discrepancy between the observations of different groups (see e.g. Ackerman 1975). The values of \([O_3]_e\) and \(\tau\) were obtained by the above procedure for the solstices and equinoxes but intermediate values were calculated at 10-day spacing by sinusoidal interpolation. Fig. 1 shows the values for 21 December.

<table>
<thead>
<tr>
<th>(p (\text{mb}))</th>
<th>(\text{NO}_x (\text{v.m.r.}))</th>
<th>(p (\text{mb}))</th>
<th>(\text{NO}_x (\text{v.m.r.}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>778.8</td>
<td>(5.0 \times 10^{-11})</td>
<td>5248</td>
<td>(2.12 \times 10^{-8})</td>
</tr>
<tr>
<td>472.4</td>
<td>(5.0 \times 10^{-11})</td>
<td>3183</td>
<td>(2.1 \times 10^{-8})</td>
</tr>
<tr>
<td>286.5</td>
<td>(5.0 \times 10^{-11})</td>
<td>1930</td>
<td>(8.5 \times 10^{-9})</td>
</tr>
<tr>
<td>173.8</td>
<td>(5.0 \times 10^{-11})</td>
<td>1171</td>
<td>(1.0 \times 10^{-10})</td>
</tr>
<tr>
<td>105.4</td>
<td>(7.0 \times 10^{-11})</td>
<td>0710</td>
<td>(1.0 \times 10^{-11})</td>
</tr>
<tr>
<td>63.93</td>
<td>(9.0 \times 10^{-11})</td>
<td>0431</td>
<td>(1.0 \times 10^{-11})</td>
</tr>
<tr>
<td>38.77</td>
<td>(5.0 \times 10^{-10})</td>
<td>0261</td>
<td>(1.0 \times 10^{-11})</td>
</tr>
<tr>
<td>23.52</td>
<td>(5.0 \times 10^{-9})</td>
<td>0159</td>
<td>(1.0 \times 10^{-11})</td>
</tr>
<tr>
<td>14.26</td>
<td>(1.3 \times 10^{-8})</td>
<td>00961</td>
<td>0</td>
</tr>
<tr>
<td>8.652</td>
<td>(1.9 \times 10^{-8})</td>
<td>00583</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 1. The cross-sections of (a) ozone equilibrium partial pressure (nb) and (b) $\log_{10}$ of relaxation time constant (in seconds) for 21 December.

The use of latitude- and time-independent profiles of OH and NO$_x$ is, again, a first approximation to a more thorough treatment. Both should be expected to vary with latitude and time. The relative importance of the HO$_x$ cycle in the destruction of ozone increases with height. It is quite small around the ozone mixing ratio maximum in the middle stratosphere. Thus the influence of the variation of OH in our scheme is confined to a region of low ozone concentration (Barnett et al. 1975). Little is yet known, from observations, about the latitudinal variation of NO$_x$. It should be an aim to include the spatial and temporal variations of all the minor species in our photochemical scheme and in our more recent studies both OH and NO$_x$ do vary with the model state.

For the linearization of Eq. (2) to be a valid approximation it is required that the ozone concentration should not be too far from the equilibrium. If this is not the case

Figure 2. The dependence of the ozone relaxation time $\tau_n$ on ozone amount. The value, $\tau$, assumed in the linearization, is shown by the straight line. The values are calculations at approximately 9 mb with an overhead sun.
then second-order terms cannot be ignored. Some indication of the range of the validity of Eq. (1) is given by Fig. 2, which shows how the true nonlinear time constant, $\tau_N$, depends on the ozone concentration at approximately 30 km. $\tau_N$ is defined in Eq. (3) with $\partial [O_3]/\partial t$ calculated from Eq. (2).

$$\tau_N^{-1} = \frac{\partial [O_3]/\partial t}{([O_3]_c - [O_3])}$$

(3)

The difference between $\tau$ and $\tau_N$ depends on the departure from equilibrium. When the ozone concentration is less than the equilibrium value then $\tau < \tau_N$, and Eq. (1) will overestimate the rate of production of ozone. The situation is reversed when the concentration is greater than the equilibrium value, for then $\tau > \tau_N$ and the destruction is underestimated. Clearly, if the ozone concentration is far from equilibrium, errors are to be expected in the calculation of photochemical sources and sinks. The results of Johnston and Whitten (1973) suggest that most of the stratosphere is within 50% of equilibrium and the approximation should, therefore, be reasonable. How close the model's predicted ozone concentrations are to equilibrium is discussed in section 3(a).

To avoid computational instabilities, at heights where $\tau$ is less than twice the timestep, Eq. (1) is not used and the ozone mixing ratio is held at its equilibrium value.

There is a sink of ozone in the model troposphere. The ozone concentration at the bottom level is maintained at zero, thus resembling a rapid destruction at the ground.

2. OZONE DISTRIBUTION

(a) Total ozone

The latitude–time section of total ozone for the run is shown in Fig. 3. As in HP on the starting day (19 February) the ozone takes its spring photochemical steady-state concentration and it is nearly a year before a periodically reproducible distribution is established. At the end of the run there are small year-to-year differences.

Once the model has settled down many of the observed features of the total ozone distribution are reproduced. Unlike the results of runs in which the Chapman photochemical schemes were used, the magnitude of the total ozone amount is here satisfactory.

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Figure 3. The variation of modelled total ozone amount with time and latitude in Dobson units (m atm. cm).
The equatorial minimum is modelled well with closed minima of less than 250 Dobson units. The latitudinal variation is about two to three months out of phase with the observed behaviour, there being a minimum in the model in the northern hemisphere in December and an observed minimum at the beginning of October. This is perhaps not unreasonable since the momentum fluxes and the $K$-coefficients are obtained from one and five years data, respectively, and should not necessarily reproduce an ozone distribution averaged over a much longer period (since fluctuations from year to year are not insignificant (Dütsch 1971)).

In high latitudes the modelled hemispheres have quite different distributions of total ozone. The southern hemisphere is reproduced well. There is a closed contour of 400 Dobson units which extends polewards with time, and a south polar minimum which, like the high-latitude maximum, is delayed when compared with observations. There is more ozone in the northern hemisphere with a maximum value of 450 Dobson units which agrees quite well with observations. However, the polar maximum occurs in summer rather than in spring. There is a build-up of ozone in mid-latitudes in early spring but, unlike in the atmosphere, this does not extend rapidly to the pole. Instead there is a slow increase at high latitudes until midsummer. There is a polar minimum in December which occurs at the same time as the mid-latitude minimum. This, too, is an observed feature.

In general, the ozone pattern agrees fairly well with that found in the atmosphere, the greatest discrepancy being found in the summer northern polar region. The closed maximum in the southern hemisphere is also perhaps too long-lived. Both these differences could be due to an underestimation of ozone destruction.

(b) Ozone profile and cross-section

The cross-section of ozone partial pressure on 21 March (day 395 of the run) is shown in Fig. 4 and agrees well with observed values (Dütsch 1971). The peak ozone concentration is at a height of nearly 25 km at the equator, decreasing towards the poles. The maximum partial pressure at the spring pole agrees well with observations but is at slightly too great an altitude. In fact in spring the slope of a constant partial pressure surface below the maximum should be greater than that shown in Fig. 4. Although observations of vertical profiles in the southern hemisphere are quite scarce, it appears that the peak values at the model's south pole are too large. In the upper stratosphere and the troposphere the concentrations are similar to those found in the atmosphere. The higher tropospheric values at about 30°N and, to a lesser extent, at 30°S, are real features, occurring near the jet maxima in the vicinity of the tropopause breaks.

Profiles of the ozone partial pressure at different latitudes are plotted in Fig. 5 for day 450 (15 May). Several features which are not so evident in Fig. 4 are apparent. The profiles for all latitudes equatorwards of 50°N intersect at 28 mb. For this range of latitudes
the higher latitudes have more ozone below 28 mb while, above, ozone is more abundant in lower latitudes. In an evaluation of Umkehr observations, Dütsch (1964) found that in spring all profiles equatorwards of 60°N crossed at almost exactly 26 mb, thus giving a layer of constant concentration. Evidently the layer loosely marks a boundary between the ozone above, which is controlled by photochemistry (since photochemical theory predicts greatest concentration at low latitudes), and that below which is dynamically controlled. It appears then, that the relative importance of photochemical and dynamical processes has been modelled well in this run, certainly in low and middle latitudes.

Dütsch's observations indicate a broader maximum to the profiles with increasing latitude. While there is evidence for this in the model, the effect is not nearly so pronounced as in the atmosphere. In particular the high-latitude (76°N) profile should be much broader and extend further downwards. This is in agreement with the point made when considering Fig. 4, that the slope of the partial pressure surfaces should be steeper.

(c) Variation of ozone concentration with time

The temporal variation of ozone at different model pressure levels is presented in Fig. 6. The variation is strongly altitude-dependent. Fig. 6(a) shows the variation at 47°N which may be compared with the observed behaviour in Fig. 7, based on results from Boulder (40°N) and Zürich (47°N) (after Dütsch 1970). Although the modelled ozone concentrations are somewhat higher than observed at 39 and 64 mb the temporal variation is qualitatively correct. At 14 mb the ozone concentration is a maximum in July and a minimum in January; the ozone is photochemically controlled. At 64 mb the variation follows the variation of the total ozone amount; the maximum occurs between January and February with a minimum about six months earlier. Dynamical effects are most important. At 39 mb the ozone concentration does not show much temporal variation, the opposing influences of photochemistry and dynamics both being important. 39 mb is below the 'cross-over'
Figure 6. Time variation of modelled ozone partial pressure (a) 47°N, (b) 0°N, (c) 85°N, (d) 85°S.

Figure 7. Observed time variation of ozone partial pressure in nb after Dütsch (1970): mean of Boulder (40°N) and Zürich (47°N).
point and the slight maximum there in early winter is due to the somewhat greater influence of the dynamical processes. In the troposphere the amplitude of the variation is small.

The behaviour at the equator is shown in Fig. 6(b). Both the 8- and 23-mb levels show a semiannual variation. At 8 mb the ozone concentration is a maximum at the equinoxes, when the sun crosses the equator, and a minimum at the solstices; dynamical effects are unimportant. At 23 mb the time at which the amplitude reaches a maximum is delayed by about a month. The time constant is a little longer there and transport cannot be entirely ignored. In the dynamically controlled region there appears to be a six-monthly wave with maxima in August and February. This arises because cross-equatorial transport and convergence of the ozone fluxes is greatest at the solstices, when the hemispheric heating gradients are largest (see Fig. 14).

Fig. 6(c) shows the change of ozone concentration with time at 85°N. The pattern differs somewhat from the other two cases. At 64 mb, the level at which for the other latitudes the ozone has been dynamically controlled, the ozone maximum occurs in midsummer at about the same time as the tropospheric maximum. Furthermore, there is a strong minimum during the polar night. This must be a transport effect since the photochemical destruction is set to zero during polar night. The 14-mb level has two maxima. The first occurs in summer and is presumably of photochemical origin. The second is during the polar night and is probably related to the minima at lower levels. At 39 mb, as at 47°N, the variation is small.

The behaviour at 85°S is shown in Fig. 6(d) where a number of differences from the 85°N results are evident. At 64 mb, the pressure level at which the high-latitude concentration profiles peak, the variation is much smoother than in the northern hemisphere. Furthermore, the minimum values are found in early summer, much later than the 85°N minimum which occurs during polar night. At 39 mb there is a greater variation in the southern hemisphere than in the northern. The maximum occurs at the onset of polar night but there is a gradual decrease during late spring and early summer. The other levels shown, 14 and 286 mb, exhibit a similar behaviour to the corresponding cases in the northern hemisphere.

3. The Ozone Budget

(a) Instantaneous rates of change

The model has reproduced many of the features of the distribution, both in time and space, of atmospheric ozone. An investigation of the ozone budget for this run serves a twofold purpose. Firstly, in those areas where the model's response has been realistic, inferences concerning the ozone budget in the atmosphere can be made with some confidence. In particular, the reasons for the hemispheric asymmetries in total O₃, namely the differences in magnitude and position of the ozone maxima, can be investigated. Secondly, in regions of disagreement some suggestions as to the causes can be proposed.

![Figure 8. Modelled ozone partial pressure (mb) for model day 671 (22 December).](image-url)
Figure 9. Rate of change of ozone number density (10^6 cm^{-3} day^{-1}) due to various processes for day 671 (22 December) (a) Total, (b) Photochemistry, (c) Convergence of horizontal eddy flux, (d) Convergence of mean motion flux, (e) Convergence of vertical component of mean motion flux, (f) Convergence of horizontal component of mean motion flux. Note the near-cancellation of (c) and (d) in the northern hemisphere.
The rate of change of ozone may be divided into: instantaneous changes due to mean motions; eddy motions; and photochemistry. The contributions in each category will be discussed in this section, illustrated by the behaviour on day 671 (22 December of the second year). Fig. 8 gives the ozone partial pressures in the model on that day. The mid-latitude, rather than polar, maxima are evident. The rates of change of ozone concentration due to photochemical effects, the large-scale eddies and the convergence of the transports by the mean meridional circulation are presented in Fig. 9. Further details of the transport terms are portrayed in Fig. 15. In general, the total rate of change (Fig. 9(a)) is a small residual of the individual components. In the winter stratosphere the largest rate of increase is in mid-latitudes, while at the pole there is a decrease. In the summer hemisphere there is a production of ozone in the polar lower stratosphere, while mid-latitudes are being depleted. These features are also evident in Fig. 3.

Below 20 km the contribution to the total rate of change of ozone by chemical reactions (Fig. 9(b)) is much less than by motions. The major ozone source region is the summer subtropical stratosphere with peak production at about 26 km. There are important sinks for ozone at the summer pole and in the upper stratosphere in the winter hemisphere.

An interesting feature is the destruction which occurs in low latitudes above the ozone source region. This has been found in all the runs we have performed, including those in which the photochemical scheme is not linearized. Ozone from the lower stratosphere is carried in the ascending branch of the Hadley cell to regions where the steady-state concentration is decreasing with height (see Fig. 15). At about 36 km, the ozone concentration is increased beyond the steady-state value by this advection and some destruction occurs. That there should be a sink of ozone in the upper stratosphere at low zenith angles was proposed by Brewer and Wilson (1968).

It is pertinent to ask how far the above results are limited by the linearization approximation. Fig. 10 shows a cross-section of the ratios of the ambient ozone mixing ratio to the equilibrium value at the same latitude and height for day 760. A large proportion of the ozone in the stratosphere is within 50% of its equilibrium value. In this region the linearization approximation should be quite satisfactory (see Fig. 2) but it will be much less satisfactory in the high-latitude lower stratosphere, especially in those regions where the ozone mixing ratio is an order of magnitude greater than its steady-state value. The ozone maximum at the northern hemisphere summer pole could well be due to the subsequent underestimation of the ozone destruction (see section 1(b)). The ozone time constant becomes very long below about 20 km. It is likely, therefore, that the most severe limitations of the photochemical scheme used will be found in its use in high latitudes between 20 and 30 km, since, as shown in Fig. 10, above 30 km the ratio becomes fairly small. Indeed, runs in which the photochemical scheme has not been linearized show much more rapid destruction of ozone (by an order of magnitude) in the summer hemisphere polar regions between 20 and 30 km. Furthermore, the use of precomputed time constants and equilibrium values,
taking no account of subsequent variations in the ozone path length, should not introduce too great an error since the departures from equilibrium are small in the region where photochemical processes are important.

Six months later the cross-section of the ratios is very similar. The long-lived closed maximum in southern mid-latitudes could also be due to an underestimation of photochemical destruction. However, the fact that the southern hemisphere high-latitude behaviour is modelled well, despite a possible breakdown of the linearization approximation, must be due to a reasonable representation of the transport processes there.

The changes produced by the total mean meridional circulation (Fig. 9(d)) and the horizontal eddies (Fig. 9(c)) are nearly balanced. The effect of the vertical eddies is small (see Fig. 15(h) and Pyle 1976) and is mainly to move ozone into the polar lower stratosphere. However, it is interesting to note that there is a discernible transfer of ozone from the stratosphere to the troposphere at about 30°N where the tropopause break would be found (Pyle 1976). Ozone is removed from the photochemical source region near the equator by the vertical component of the mean motions (Fig. 9(e) and Fig. 15(g)).

Figure 11. The latitudinal distribution of various contributions to the rate of change of ozone number density on model day 671 (22 December) (a) at 64 mb, (b) at 23 mb.
horizontal mean motions transport this ozone into mid-latitudes where it is carried downwards. There is a similar transport which moves ozone to mid-latitudes from the winter pole. The mean meridional circulation has rising motion at the pole and sinking motion in mid-latitudes. The maximum horizontal transport is at about 15 mb. Although the mean circulations in the summer hemisphere are much less intense they again tend to increase ozone in mid-latitudes.

The horizontal eddies counteract the mean circulation, moving ozone from mid-latitudes towards the poles and the equator. Thus there is a very strong eddy transport in the winter hemisphere moving ozone towards the north pole. The very near balance between the large mean and eddy terms is such that it prevents the build-up of ozone at the pole which is a feature of northern hemisphere observations.

In the summer hemisphere there is less cancellation between the individual components even though these are much smaller. Thus there is a build-up of ozone at the pole due to transport by the horizontal eddies.

Fig. 11 shows the contributions to the rate of change of ozone at two different levels on 22 December. At 64 mb photochemical changes are negligible while at 23 mb they are very important. The summer hemisphere at 64 mb is quiet with the quasi-horizontal eddy transports cancelling the mean meridional circulation. There is, however, a significant nett production at the summer pole. The most rapid increase in the winter hemisphere is at 47°N when the mean meridional circulation slightly exceeds the eddy term. Fig. 11 demonstrates the difficulty of correctly simulating the atmospheric ozone behaviour. Small errors in either the eddy or mean meridional transport will produce proportionally much larger changes in the total rate of change of ozone.

At 23 mb the most important influences are the photochemistry and the mean motions. The summer subtropics is a major photochemical source. There is production of ozone from about 65°S to 15°N. Polewards of about 50°N ozone destruction becomes small and is zero in the polar night region. It should be noted that the main ozone destruction in the high-latitude winter hemisphere occurs at pressures lower than 23 mb (Fig. 9(b)).

(b) Hemispheric differences

The near-cancellation of the eddy and mean transport terms has been pointed out above. It is clearly a difficult task to explain the main hemispheric asymmetry found in the model, namely the different distributions of total ozone in high latitudes, since we must find the cause of small changes in the difference of these two large terms.

Because the $K$-coefficients and the heating functions are symmetric about the equator for appropriate seasons, the difference between the hemispheres must be due to the eddy momentum fluxes or to tropospheric effects. In HP we showed how the mean circulation could be partitioned into those parts 'driven' by heating, eddy heat fluxes and eddy momentum fluxes. Fig. 12 shows that portion of the vertical velocities induced by the momentum fluxes on days approaching the equinoxes six months apart. The most prominent feature is the rising motion at the south pole in spring, which will tend to remove ozone, and the sinking motion at the spring north pole which will tend to increase the ozone there. Indeed, such an asymmetry does exist in the rate of change of ozone due to the mean motions at the vernal equinoxes and may be seen by comparing Fig. 15(d) with Fig. 15(j).

In the summer high latitudes of the northern hemisphere we find a circulation with horizontal flow towards the pole and sinking motion there. This is in the opposite direction to the circulation there on day 671 which removes ozone from the pole. Thus in
summer we expect a build-up of ozone in very high northern latitudes due to the mean meridional motions.

In the southern hemisphere at the summer pole the circulation is quite different from that at the north pole six months later. There is rising motion over the pole and an equatorward flow which would be expected to move ozone to lower latitudes.

It is clear that a difference in the mean motions is responsible, at least in part, for the different behaviour of the total ozone amount in the two hemispheres and that, in turn, this difference is strongly connected with the different convergences of the horizontal eddy momentum flux to the north and south of the equator.

A further difference between the two hemispheres lies in their total ozone content. In run A of HP and in all subsequent runs there is more ozone to the north of the equator than to the south, as observed. The only asymmetry in the driving forces in the early runs came from the climatological latent heat release and the sea-surface temperatures, both of which were time-independent. The latent heat release employed was stronger in the southern hemisphere. This displaced the upward branch of the Hadley circulation into the southern hemisphere (see Fig. 6(a) of HP), and induced a meridional flow from the southern to the northern hemisphere in the upper troposphere and lower stratosphere throughout the year. Moreover, the induced downward motion is stronger in the northern hemisphere. These features account for the greater ozone concentrations in the northern hemisphere.

Evidently, the tropospheric circulation is of importance to the ozone budget of the stratosphere. Models in which the lower boundary is taken to be the tropopause are
omitting an important effect. Indeed, it should be an aim to include tropospheric processes in a model-dependent fashion.

(c) Temporal variations

The development of some of the driving forces with time can be seen in Fig. 13. All the rates of change are small during the summer at 64 mb, 47°N (Fig. 13(a)). The very strong cancellation between the horizontal eddy transports and the mean motions is again evident. The vertical and horizontal convergences of the mean motion transports are greater, by at least an order of magnitude except in winter, than the rest of the influences. They oppose one another (and this is true almost everywhere), with the vertical component increasing the ozone concentration, carrying ozone down the mixing ratio profile. With the onset of winter there is a large increase in both eddy activity and the mean motion transport. The wintertime increase in ozone at 64 mb, 47° (see Fig. 6(a)) is due to the slightly stronger mean motions.

In Fig. 13(b) the ozone rate of change at the same latitude as above but at 14 mb is shown. The vertical flux convergence in the downward branch of the Hadley cell, which increases the mixing ratio at 64 mb, decreases it at this level. The total rate of change of ozone in the figure follows closely the rate of change due to photochemistry which at this level is a most important component of the ozone budget, in agreement with the earlier conclusions. The correspondence between the two is most noticeable in summer. Although the total effect of the mean motions is small, the two components are still large.

Fig. 13(c) shows the contributions at 64 mb, 85°N and should be compared with Fig. 6(c). The decrease in ozone concentration which begins with the advent of polar night is clearly because the effect of the large increase in the vertical transport is greater than the opposing effect of horizontal eddies. The increase in ozone at 14 mb in the polar night region shown in Fig. 6(c) is caused by a convergence of mean vertical ozone flux. Ozone is being moved from the lower to the upper atmosphere by the strong vertical velocities (see HP and Fig. 15). (This transport is partly responsible for the mid-latitude ozone trough observed near the stratopause (Finger et al. 1975), since the mixing ratios in the polar night region are increased beyond the photochemical equilibrium values of the neighbouring latitudes.)

During spring the circulation reverses and the mean motions now transport ozone to the pole while the horizontal eddies tend to remove it. There is, however, a nett transport to the pole during spring and early summer.

The behaviour near the south pole, shown in Fig. 13(d), is quite different. At the start of winter, ozone is removed from the pole at 64 mb by the mean circulation transport which is larger than the increase caused by the eddies. This is similar to the northern hemisphere case. During spring, however, the eddies still cause the ozone at the pole to increase.

(d) Ozone fluxes

Latitude–time sections of the vertically-integrated horizontal fluxes, both mean and eddy, are given in Fig. 14. A number of features are evident. The equatorial fluxes are stronger at the solstices than at the equinoxes with the flux of ozone due to the mean motions, from the summer to the winter hemisphere, being more important than that due to the eddies in these low latitudes. The calculated variation of ozone at the equator (Fig. 6(b)) can be explained in terms of the change in horizontal fluxes. At high latitudes the behaviour is quite different in the two hemispheres. At the north pole throughout
Figure 13. The time variation of the various contributions to the rate of change of ozone number density. (a) at 64 mb, 47°N; (b) at 14 mb, 47°N; (c) at 64 mb, 85°N; (d) at 64 mb, 85°S.
almost all the year the mean motion flux is positive and is opposed by the eddy transports. In the southern hemisphere the mean motions move ozone northwards for more than six months of the year.

The mean meridional motion and eddy fluxes of ozone, and their sum, are shown in Fig. 15 for the four different seasons. A number of interesting features are apparent, emphasizing the points already made. The cross-equatorial flux due to the mean motions is much stronger at the solstices than at the equinoxes. While the flow is generally from the summer to the winter hemisphere there is a small region in the lower stratosphere where the flux is in the opposite direction. The downward mean flux is strongest in mid-latitudes with the eddy fluxes being away from the area of convergence. There is a significant mean
flux into the troposphere. The difference between the polar latitudes in spring is evident, with a nett downward flux in the northern hemisphere and an upward flux in the southern hemisphere. The high-latitude fluxes in summer and autumn are small and photochemical changes will be relatively more important there.

4. DISCUSSION

The success of the model, particularly in low and middle latitudes, gives confidence that the ozone budget, at least in these latitudes, has been reproduced well. It is thus possible to construct a tentative model of ozone behaviour. The main features at the December solstice are photochemical production at low zenith angles in the mid-stratosphere with some destruction above and in higher latitudes. Ozone is transported from the source region to the northern middle latitudes by the mean circulation. The eddies move ozone to both poles from mid-latitudes, but more strongly in the winter hemisphere. The mean circulation counteracts the eddies, transporting ozone back to mid-latitudes. There is significant transport into the troposphere in the northern subtropics by both mean and eddy motions.

During spring in the model's northern hemisphere the circulation changes and the mean motions move ozone to polar latitudes throughout most of the year. The eddies again counteract the mean meridional circulation.

The southern hemisphere behaviour in high latitudes differs from the model presented above. Throughout much of the year the eddies transport ozone to the pole with the mean circulation opposing this. The nett ozone flux away from the pole is such that the maximum values occur around 60°S.

The near-cancellation between eddy and mean transports is a feature of the model. That such a balance must exist for momentum and heat has been known since the study of Charney and Drazin (1961) (see also the discussion by Holton 1975). That a similar balance should exist for ozone is probably a result of the shortness of the eddy diffusion time scale compared with variations in the mean circulation. A typical value of $K_{yy}$ is $1 \times 10^6$ m$^2$s$^{-1}$ giving a time scale of 10 days for diffusion over distances of 1000 km. The eddies will thus rapidly adjust the ozone distribution to damp out transient disturbances and leave only the slow seasonal variations. The near-balance accounts for the fact that steady-state calculations are capable of obtaining a reasonable degree of agreement with observations for a particular season.

The model reproduced the two important hemispheric asymmetries of total ozone: (a) the larger amounts in the model's northern hemisphere are partially attributable to the tropospheric circulation, thus indicating the need for a reasonable treatment of the tropospheric processes in a stratospheric model of this kind; and (b) the major differences in the total ozone patterns between the hemispheres are brought about as a result of asymmetries in the mean meridional circulation which are themselves due, in large part, to the asymmetric eddy fluxes of angular momentum. In HP we stressed the role of the eddy momentum fluxes, particularly in low latitudes. Here we have stressed their importance to the ozone budget in high latitudes also. It should clearly be an aim to include these eddy fluxes in a model-dependent fashion.

Although a polar maximum was obtained in the northern hemisphere this was delayed when compared with observations. That the maximum persists into summer is probably due to a limitation of the linearization approximation. Certainly the rate of destruction in summer high latitudes was underestimated when compared with results using a non-linear mathematical treatment. However, the maximum should be established at the pole
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(d)

(e)

(f)
Figure 15. The latitude–height distribution of longitudinally-integrated ozone flux. The arrow vector is proportional to the number of ozone molecules crossing per unit time a hypothetical ring at the latitude and height of the arrow's tail.

(a), (d), (g), (j), contribution by mean motion advection.
(b), (e), (h), (k), contribution by eddy motion.
(c), (f), (i), (l), total.
Fine shading: photochemical source $> 3 \times 10^9 \text{cm}^{-2} \text{day}^{-1}$.
Coarse shading: photochemical sink $> 3 \times 10^9 \text{cm}^{-2} \text{day}^{-1}$. 
in late winter. The failure to reproduce this must be due to dynamical rather than photochemical processes.

It should be remembered that the momentum fluxes are representative of one year only. Using them, one should not necessarily expect to reproduce the behaviour of the atmosphere averaged over a much longer period of time. An interesting test of the sensitivity of the model would be to use eddy momentum fluxes appropriate to a different year. The high-latitude eddy coefficients could be at fault. Fabian and Libby (1974), in a number of experiments with different eddy coefficients and mean circulations, consistently predicted peaks in the concentration profiles of radioactive fallout which were at a height of one or two kilometres above the observed peaks when they used Luther's eddy coefficients. If the discrepancy was caused by incorrect representations of eddy transports then it is likely that the slope of the mixing paths (i.e. the ratio $K_{zz}$ to $K_{yy}$) should be steeper in high latitudes.

Various experiments are proposed to investigate the effect of the variation of model parameters (e.g. the eddy momentum fluxes and the $K$-coefficients) on ozone behaviour. Runs have been performed in which the photochemical scheme is no longer linearized and in which gases other than $O_3$ are allowed to vary with the model state. These will be discussed in later papers.

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REFERENCES


Byron-Scott, R. 1967 A stratospheric general circulation experiment incorporating diabatic heating and ozone photochemistry, Publication in Meteorology No. 87, Arctic Meteorology Research Group, Dept. of Meteorology, McGill University, Montreal, Quebec.


Newell, R. E. 1963 Transfer through the tropopause and within the stratosphere, Quart. J. R. Met. Soc., 89, 167–204.

