Ozone perturbation experiments in a
two-dimensional circulation model

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SUMMARY

A two-dimensional circulation model is used to investigate the possible perturbation of the ozone layer by CO$_2$ and chlorofluorocarbons (CFC’s). Four experiments are described: a control run; a run including increasing levels of CO$_2$ up to 625 ppm; a run including a source of chlorine compounds from the CFCs; and a run to investigate the coupled perturbation due to both CO$_2$ and the CFC’s. The dynamical and chemical behaviour of the runs is described.

The control run reaffirms the conclusions of earlier experiments with this model (Harwood and Pyle 1980) that the summer stratopause is very close to radiative equilibrium. The strength of the polar night jet is also discussed.

The perturbations due to CO$_2$ and the CFC’s have opposite effects on ozone with increasing CO$_2$, producing an increase in column ozone which is greatest in high latitudes.

The coupled perturbation is not a linear combination of the two individual experiments. This is investigated in terms of the photochemical scheme used. The reduced temperature dependence of the ozone concentration when chlorine compounds play a significant role is shown to produce the non-linearity.

1 INTRODUCTION

The possible modification of the ozone layer as a result of man’s activities has attracted considerable interest in the last decade. The catalytic destruction of ozone by oxides of nitrogen, produced by supersonic aircraft, and by chlorine compounds following the breakdown of chlorofluorocarbons (CFC’s) has been considered in detail. The impact of changes in N$_2$O and CH$_4$ has also been discussed.

Calculations of perturbations are complex because ozone is a radiatively important stratospheric constituent and relevant chemical reaction rates are temperature dependent. Thus there is coupling between atmospheric chemistry, radiation and dynamics. For example, changes in ozone concentration in the upper stratosphere alter the temperature and hence the winds. These changes will in turn affect the ozone concentration through the temperature dependence of the chemical reactions and by influencing the transport of ozone.

It has also been suggested that stratospheric ozone will be affected by increasing levels of carbon dioxide, the concentration of which is rising (Eckdal and Keeling 1973; Bischof 1977). Calculations indicate that increases in CO$_2$ tend to warm the troposphere through the ‘greenhouse effect’ and cool the stratosphere through increased cooling to space (Manabe and Wetherald 1975). As the equilibrium concentration of ozone in the upper stratosphere is negatively correlated with temperature (Barnett et al. 1975), increased CO$_2$ levels may produce increased O$_3$ concentration in the upper atmosphere.

Calculations of perturbations to the ozone layer have been made, mainly using one-dimensional (height-only) models. Photochemical processes are considered in detail but atmospheric transport is represented poorly. Latitudinal and seasonal variations cannot be investigated properly. The feedback between ozone and temperature is often not considered while the coupling between radiatio and dynamics cannot be included.

In two-dimensional models meteorological processes can be included in more detail. Eddy transport still generally requires an empirical approach but latitudinal and seasonal variations can be considered. Furthermore, it can be argued that comparison of calculations with observations is more straightforward than with one-dimensional models, which represent some sort of global or hemispheric average.

Pyle (1980) has described experiments using the Oxford University two-dimensional model to investigate the perturbation of the ozone layer by CFC’s. Latitudinal and seasonal
variations in the perturbations were examined but the mean circulation was specified so that
the feedback between ozone, temperature, radiative heating and the mean circulation was
not included.

In experiments described in this paper the mean meridional circulation is calculated,
allowing the feedback between the ozone perturbations and the circulation to be investi-
gated. Results will be presented on the impact of CFC's and CO₂ on the ozone layer. In
particular, the importance of the feedback processes will be considered.

It is found that in many respects CFC's and CO₂ have opposite effects on ozone. For
example, in the CFC calculation the maximum ozone reductions are found in high latitudes
wheras for CO₂ maximum ozone increases are in high latitudes. It is clearly of interest to
investigate to what extent the two perturbations are additive.

For this purpose a coupled CO₂-CFC perturbation experiment has been carried out. It
is found that the two effects are not linearly additive because of changes in the tempera-
ture dependence of ozone in the upper stratosphere between runs with and without chlorine
chemistry.

In section two, the Oxford two-dimensional model is described, particularly the new
radiation scheme which is an improvement on that used previously. Subsequent sections
deal with perturbations of the ozone layer by CFC's and by CO₂ and by these two simul-
taneously. Finally the results of this coupled perturbation are discussed in detail.

2. THE MODEL

The basic formulation of the model has been given by Harwood and Pyle (1975, 1977).
The model extends from the surface to approximately 80 km. The dependent variables are
the zonal averages of temperature, wind components and chemical constituent concentra-
tions, held as functions of time, latitude and height (log pressure) with a resolution of 4 h,
9.47 degrees of latitude and 1/2 pressure scale height (about 3.5 km). Thermal wind balance
is maintained between the zonal mean temperature and westerly wind; at each 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 (arising from departures from the zonal mean) of heat and matter are
computed by a diffusion approach (Reed and German 1965) using the constants (K’s)
suggested by Luther (1973). Horizontal eddy momentum transport assumes values deduced
from satellite observations (Crane et al. 1980) above 50 mb and taken from Oort and
Rasmussen (1971) below 50 mb.

The use of the diffusion approach is open to criticism. A more acceptable approach
physically would be to deduce the transport from the properties of planetary scale waves
and the sources and sinks of trace gases (Pyle and Rogers 1980). The diffusion approach,
however, has been found to give reasonable temperature and tracer distributions as well as
the cancellation of mean and eddy transports, expected for steady waves, thereby re-
producing many of the important aspects of the behaviour of the atmosphere.

The photochemical scheme (see Table 1) has been described in detail by Pyle (1980).
Continuity equations are solved for the following families: O(+D), O and O₃; N, NO, NO₂
and CINO₂; HNO₃, H₂O₂, H, OH and HO₂ (for which transport is ignored); Cl, ClO,
CINO₂ and HCl, CFCl₃, CF₂Cl₂. Within each group photochemical equilibrium is
assumed. The other species, H₂O, CH₄, H₂, N₂O and CO, are assumed to be invariant
and are specified independent of latitude. The chlorine reactions are used only in pertur-
bation studies — no naturally occurring chlorine sources are included.

Apart from the omission of the natural chlorine cycle, the scheme also excludes
HO₂NO₂, HClO, N₂O₃ and NO₃ which are sometimes treated in other models. Some of
the rate constants have now been updated with the result that the estimated ozone depletion
TABLE 1. THE PHOTOCHEMICAL SCHEME

\[
\begin{align*}
O_3 + h\nu & \rightarrow O + O \\
O + O_3 + M & \rightarrow O_3 + M \quad 1.05 \times 10^{10} \text{E}(-34) \exp(510/T) \\
O_3 + h\nu & \rightarrow O + O_3 \quad \lambda > 3077 \AA \\
& \rightarrow O^{(1D)} + O_3 \quad \lambda \leq 3077 \AA \\
O + O_3 & \rightarrow 2O_3 \quad 1.9 \times 10^{11} \exp(-2300/T) \\
O^{(1D)} + N_2 & \rightarrow O + N_2 \quad 2.0 \times 10^{11} \exp(108/T) \\
O^{(1D)} + O_2 & \rightarrow O + O_3 \quad 2.9 \times 10^{11} \exp(67/T) \\
O^{(1D)} + H_2O & \rightarrow 2OH \quad 2.3 \times 10^{-10} \\
O^{(1D)} + CH_4 & \rightarrow CH_2^+ + OH \quad 1.3 \times 10^{-10} \\
O^{(1D)} + H_2 & \rightarrow H + OH \quad 1.3 \times 10^{-10} \\
OH + O & \rightarrow H + O_2 \quad 4.2 \times 10^{-11} \\
H + O_3 + M & \rightarrow HO_3 + M \quad 2.1 \times 10^{-32} \exp(290/T) \\
HO_3 + O & \rightarrow OH + O_2 \quad 3.5 \times 10^{-11} \\
H + O_2 & \rightarrow OH + O_3 \quad 2.6 \times 10^{-11} \\
OH + O_3 & \rightarrow HO_2 + O_2 \quad 1.5 \times 10^{-12} \exp(-1000/T) \\
HO_3 + O_3 & \rightarrow OH + O_3 \quad 1.4 \times 10^{-14} \exp(-580/T) \\
CO + OH & \rightarrow CO_2 + H \quad (1 + 4.18 \times 10^{-20} \times [M]) \times \exp(-115/T) \\
HO_3 + HO_2 & \rightarrow H_2O_2 + O_2 \quad 6.4 \times 10^{13} \exp(300/T) \\
H_2O_2 + OH & \rightarrow H_2O + HO_2 \quad 1.0 \times 10^{-11} \exp(-750/T) \\
H_2O_2 + h\nu & \rightarrow 2OH \quad 5.1 \times 10^{-11} \\
OH + HO_2 & \rightarrow H_2O + O_2 \quad 2.36 \times 10^{-12} \exp(-1710/T) \\
OH + CH_4 & \rightarrow H_2O + CH_3 \quad 1.0 \times 10^{-11} \exp(-550/T) \\
OH + OH & \rightarrow H_2O + O_2 \quad 7.0 \times 10^{-11} \\
O^{(1D)} + N_2O & \rightarrow N_2 + O_2 \quad 7.0 \times 10^{-11} \\
O^{(1D)} + N_2O & \rightarrow N_2 + O_2 \quad 9.0 \times 10^{-13} \exp(-1200/T) \\
NO + O_2 & \rightarrow NO_2 + O_2 \quad 9.1 \times 10^{-12} \\
NO + O_3 & \rightarrow NO + O_3 \quad 1.2 \times 10^{-13} \exp(-2450/T) \\
NO + O_3 & \rightarrow NO + O_3 \quad 8.1 \times 10^{-12} \\
NO_2 + OH + M & \rightarrow HNO_3 + M \quad \text{Tabulation} \\
HNO_3 + h\nu & \rightarrow NO_2 + OH \\
HNO_3 + OH & \rightarrow H_2O + NO_3 \quad 8.0 \times 10^{-14} \\
NO + h\nu & \rightarrow N + O \\
N + NO & \rightarrow N_2 + O \quad 8.2 \times 10^{-11} \exp(-410/T) \\
N + O_3 & \rightarrow NO + O_2 \quad 5.5 \times 10^{-12} \exp(-320/T) \\
N + O_3 & \rightarrow NO + O_2 \quad 5.0 \times 10^{-12} \exp(-650/T) \\
CFC_13 + h\nu & \rightarrow 3Cl \\
CFC_13 + h\nu & \rightarrow 2Cl \\
CFC_13 + O^{(1D)} & \rightarrow ClO + 2Cl \quad 2.3 \times 10^{-10} \\
CFC_13 + O^{(1D)} & \rightarrow ClO + Cl \quad 2.0 \times 10^{-10} \\
Cl + O_3 & \rightarrow Cl + O_3 \quad 2.7 \times 10^{-11} \exp(-257/T) \\
Cl + O_3 & \rightarrow Cl + O_3 \quad 1.07 \times 10^{-10} \exp(-224/T) \\
ClO + NO & \rightarrow Cl + NO_2 \quad 8.0 \times 10^{-12} \exp(-250/T) \\
ClO + NO_2 + M & \rightarrow ClONO_2 + M \quad \text{Tabulation} \\
ClONO_2 + h\nu & \rightarrow ClO + NO_2 \\
ClONO_2 + O & \rightarrow ClO + NO_2 \quad 4.5 \times 10^{-12} \exp(-840/T) \\
CH_4 + Cl & \rightarrow CH_3 + HCl \quad 7.3 \times 10^{-12} \exp(-1260/T) \\
H_2 + Cl & \rightarrow H + HCl \quad 3.5 \times 10^{-11} \exp(-2290/T) \\
OH + HCl & \rightarrow H_2O + Cl \quad 2.8 \times 10^{-12} \exp(-400/T) \\
HO_2 + Cl & \rightarrow O_2 + HCl \quad 2.5 \times 10^{-11} \\
\end{align*}
\]

HNO_3, H_2O_2 and HCl are removed from the model troposphere with a time constant of 20 d.

*CH_3 \rightarrow 3 \text{HO}_2, \text{instantaneous} \\
\text{NO}_3 \rightarrow (a) \text{NO}_2 + \text{O} \text{ and } (b) \text{NO} + \text{O}_5, \text{with (a):(b) = 10:4, instantaneous.}

N.B. \text{1.0E}(-0) = 1.0 \times 10^{-10}
by CFC's is reduced (WMO 1982). In spite of these more recent evaluations of rate constants those in Table 1 are adequate for examining the feedback processes discussed earlier, the coupling between radiation, chemistry and dynamics and latitudinal and seasonal variations.

A major improvement has been made to the stratospheric radiation scheme. The cooling-to-space approximation for the calculation of radiative heating rates due to the 15 μm band of CO₂ has been replaced by the Curtis matrix method (Curtis 1956; Williams 1971; Haigh 1980). A matrix C relates local heating rates to the vertical temperature profile by \( H = CB \) where \( H, B \) are the heating rate and Planck function vectors respectively. The elements of C are transmission differences and are obtained using a modified independent line model incorporating pressure and Doppler broadening and a constant diffusivity factor of 1.7. C takes into account the radiative exchange between different levels and permits departure from local thermodynamic equilibrium in the upper mesosphere. The required collisional relaxation times are taken from Allen et al. (1979).

C depends only weakly on temperature through the temperature dependence of the linestrengths. The matrix for a standard temperature profile can, therefore, be used to calculate heating rates for any other temperature profile with the same absorber distribution to high accuracy (Williams 1971).

The cooling-to-space approximation is retained for the O₃ 9.6 μm band with cooling dependent on local temperature but not on O₃ mixing ratios.

The heating rates due to absorption of solar radiation by molecular oxygen and ozone are calculated by a simple flux depletion method using the solar fluxes and absorption cross-sections of Ackerman (1971) and Simon (1974). Both infra-red cooling and solar heating are calculated only above 25 km and scattering is neglected.

Between the tropopause and about 25 km the atmosphere is assumed to remain in radiative equilibrium owing to the great difficulty of a sufficiently accurate calculation of the heating rates when large terms of opposite sign nearly cancel (Houghton 1978; Harwood and Pyle 1975, 1980). Until these terms can be treated in detail, in particular heating in the 9.6 μm band of ozone and in the near-infra-red bands of H₂O and CO₂ and cooling in the rotation bands of H₂O, we feel that the radiative equilibrium approximation should be retained.

As in our previous work fixed heating rates are used in the troposphere.

3. THE UNPERTURBED ATMOSPHERE

In this section we describe a model run, A, which omits chlorine chemistry and assumes a CO₂ mixing ratio of 320 ppmv. Run A is taken as a control run for the perturbation experiments to be described later.

Figure 1a presents a zonal mean temperature cross section from run A for December. Compared with previous versions of the model (e.g. Harwood and Pyle 1980, hereafter HP), the simulation is improved in the upper stratosphere. The temperatures at the summer stratopause are in good agreement with observations (cf. Murgatroyd (1969)). The increase in temperature with height in the stratosphere also seems to be simulated well. The winter polar temperatures, however, are still too low with a minimum below 180 K, and at a somewhat higher altitude than observed. Thus at around 40 km there is an equator to pole temperature difference in the winter hemisphere of about 60 K compared with Murgatroyd's value of 40 K. Associated with this temperature difference the corresponding model zonal winds (Fig. 1b) are too strong. Even in the summer hemisphere there is no improvement on the zonal wind fields of HP, probably because the equatorial tropopause in run A is colder than formerly.

The improved temperature structure in the summer upper stratosphere is due both to
the modelled ozone distribution and the new radiation schemes, confirming the suggestions made in HP. The revised distribution of ozone has the effect of raising the maximum of the solar heating while the improved long wave cooling balances this heating at a somewhat lower and more realistic temperature. Two points bear emphasis. Firstly, the calculations
Here support the conclusions of HP that the summer stratopause is close to radiative equilibrium with net radiative heating rates generally less than 1 K d$^{-1}$. Secondly, this result depends critically on the self-consistency of the ozone distribution and the radiation field and temperature structure. Radiative calculations which use a fixed ozone distribution might be expected to show greater departures from equilibrium.

Although the radiation calculations appear to be satisfactory, the zonal jets are nevertheless exaggerated by a factor of between 1.5 and 2. One possible explanation for this is that the stratospheric eddy heat fluxes are too small, since the area around 30 km at the winter pole is colder than observed.

The model heat and momentum budgets exhibit a strong cancellation between the mean and eddy fluxes in high latitudes (Pyle 1976; Haigh 1980), an effect which is now well understood in terms of wave-mean flow interaction. It follows that the divergence of the Eliassen-Palm flux is small and this implies a balance between the horizontal divergence of the horizontal eddy flux of angular momentum and the vertical divergence of the horizontal eddy heat flux. Since the momentum fluxes are specified, the eddy heat fluxes in the model have to adjust to maintain this balance; this can only be achieved by changing the temperature gradients, since the diffusion constants are fixed.

If the K's for the northern hemisphere winter were greater than those tabulated by Luther (1973) an identical mid-stratospheric flux could be obtained with a smaller temperature gradient. To test this idea the northern hemisphere diffusion constants were increased by a factor of 1.5 during December. The temperature of the cold area around 30 km increased by about 10 K (but was still lower than observed). The maximum wind speed at the stratopause was correspondingly decreased from 134 to 103 m s$^{-1}$. When the K's were increased by a factor of 2.5 the area at 30 km reached a temperature of 192 K and the jet was further reduced to 68 m s$^{-1}$. The dependence of the mean zonal wind on the heat fluxes is confirmed by southern hemisphere results. The winter-time momentum fluxes are smaller than their northern hemisphere counterparts; with fixed K's, the eddy heat fluxes required to balance them imply a smaller temperature gradient, as indeed is seen in the model. Consequently the southern polar night jet is weaker with a peak wind speed of about 95 m s$^{-1}$ at the stratopause compared with the 134 m s$^{-1}$ in the northern hemisphere shown in Fig. 1b.

We note, however, that Murgatroyd (1982) shows the polar night jet, derived from SSU data, as stronger in the southern hemisphere, contrary to the model results here (see also Labitzke 1980).

The over-estimation of the polar night jet is a problem with most circulation models. It is clear that in this particular model the problem is due to too weak an eddy heat flux to the winter pole. However, the eddy momentum flux in the model is specified and our arguments are based on the balance between eddy momentum and heat flux convergences. It seems clear, however, that the problem is not associated with the radiation schemes as improved schemes produce no improvement in the simulation of the stratospheric jets.

The model ozone cross section for April from run A is shown in Fig. 2. The distribution agrees well with observations (e.g. Dütsch 1971) with a decrease in the height of the maximum concentration from equatorial to polar latitudes. There are differences of detail, however. The equatorial maximum is somewhat greater than observed while the polar maximum is too small, a value of 220 nb being perhaps appropriate.

Figure 3 shows a comparison of model profiles at 37°N with Krueger and Minzner's (1976) mid-latitude profile. Both model profiles have too little ozone below the peak concentration at about 24 km and too much up to around 40 km. This seems to be a feature of many models (see e.g. DOE 1979), Fig. 6.5 though the comparison might be somewhat improved by introducing natural chlorine sources as suggested by Groves and Tuck (1980b).

The latitude-time section of total ozone (Fig. 4) reproduces the gross features of the observed distribution, although the equatorial minimum is too high and the high latitude
maximum in the northern hemisphere is a little low. An increased poleward eddy transport (which would also reduce the mean zonal winds) might improve the simulation.

4. PERTURBATIONS BY CO$_2$

One-dimensional calculations of the effect of doubling CO$_2$ on stratospheric ozone
have been made by Luther et al. (1977), Boughner (1978), Groves and Tuck (1980a, b) and Isaksen et al. (1980). Complex photochemical schemes were included and most calculations had detailed radiation schemes. They are not, however, capable of representing latitudinal variations or dynamical feedback.

The experiment, B, described in this section was performed in order to investigate the effects of an increase in atmospheric carbon dioxide concentration. Additional Curtis matrices for the 15 $\mu$m band cooling were constructed for CO$_2$ volume mixing ratios of 400, 500 and 625 ppm appropriate to the years 2000, 2020 and 2040 A.D. (Bacastow and Keeling 1973) the same temperature profile being used in each case.

In order to reduce computing time the CO$_2$ in the model was increased at four times the estimated rate. Thus a new Curtis matrix was introduced every five model years.

As stated in Section 2, the cooling to space approximation for the 9-6 $\mu$m band of O$_3$ in the upper stratosphere and the assumption of radiative equilibrium in the lower stratosphere are both retained in run B. They might be expected to be less satisfactory in a perturbed atmosphere. However, the increased CO$_2$ cooling in the lower stratosphere would to some extent compensate the increased long wave ozone heating there, caused by enhanced emission from the warmer surface. While these assumptions may lead to errors in our estimation of the absolute change in temperature or ozone amount, they should not seriously affect our conclusions regarding the perturbations described here and in Section 6.
The net heating rates in the troposphere were unchanged but the sea surface temperatures were increased in step with the CO$_2$ mixing ratio, so as to reproduce the results of Manabe and Wetherald (1975) for doubled CO$_2$. The tropospheric temperatures could then be altered by the convective adjustment scheme.

The results for run B discussed below all refer to model day 7000 (corresponding to April in approximately 2045 A.D.). Figure 5 shows warming in the troposphere and cooling in the
stratosphere as found by other authors. The isopleth of zero temperature change follows the tropopause as in the calculations of Manabe and Wetherald (1980), suggesting that the approximations made in the heating rate calculations in the lower stratosphere are satisfactory. In the stratosphere the vertical gradient of temperature change is greater than in previously reported experiments; in low latitudes the temperature change reaches $-10\text{ K}$ at 26 km. Below this level the temperature change reflects the marked 'reverse self-healing effect' in the ozone field (see below). At the stratopause the cooling is similar to that of Luther et al. (1977) and Groves and Tuck (1980a) though larger than that of Boughner (1978).

The effect on the zonal wind field is illustrated by comparing runs A and B (Fig. 6). Examination of Fig. 1b indicates that both easterly and westerly jets are weaker in run B, consistent with the reduction in the horizontal temperature gradient. For example, in Fig. 5 the equator to pole difference is reduced by more than 2 K at 10 mb. Since the model is in thermal wind balance the vertical shear of the zonal wind is also reduced.

The effect on the meridional circulation is small. The net radiative heating rate in the two runs is similar as, in general, increased absorption of solar radiation by ozone balances the cooling due to the extra CO$_2$. The eddy fluxes of heat are also little different.

The O$_3$ concentration (Fig. 7) shows an increase of 24–29% in the region of 42 km at all latitudes, in good agreement with the results of Luther et al. (1977) but somewhat larger than the 22% of Groves and Tuck (1980a). The decrease found in the lower stratosphere in some one-dimensional models is also seen here but with considerable latitudinal variation.

![Figure 7. Percentage difference in ozone concentration between runs B and A corresponding to April ~2045.](image_url)

At 24 km in low latitudes there is a decrease of nearly 10% due to the reduction in ultra-violet radiation reaching these levels because of the increased ozone concentrations above. This 'reverse self-healing effect' is not present in high latitudes because of compensation in other photochemical contributions and the dynamical transports; it occurs only in the lower stratosphere at latitudes for which the input of solar radiation is high throughout the year.
The ozone column density (Fig. 8) shows large increases of about 20% near the north pole in summer and 14% in southern hemisphere high latitudes, the difference between the hemispheres reflecting the asymmetry in the ozone distribution. In equatorial regions the increases are only 2-4% due to the 'reverse self-healing' discussed above. The global increase in total O₃ is around 9%, considerably larger than any of the values predicted by one-dimensional models. This discrepancy appears to be due to differences in the lower stratosphere. In this region ozone is predominantly dynamically controlled so a two-dimensional model should perhaps be more successful in calculating the ozone distribution. In Fig. 7, important variations in the ozone change can be seen in this region. It should be remembered, however, that our radiation scheme is least satisfactory in the lower stratosphere where ozone is very sensitive to the net heating rates (HP).

Other minor constituents also respond to the temperature changes. Figure 9a shows the percentage change in O(¹D) number density between runs A and B. O(¹D) is produced by photolysis of ozone at wavelengths less than about 310 nm. Above 35 km O(¹D) has increased with the increase in ozone, decreasing at lower levels due to the reduced flux of ultraviolet radiation.

O(¹D) in the stratosphere reacts with N₂O and H₂O to produce oxides of nitrogen and hydrogen. The percentage changes in NOₓ (NO + NO₂) and OH between runs A and B
Figure 9a. Percentage difference in the concentration of O(1D) between runs B and A for a day corresponding to April ~ 2045.

Figure 9b. As Fig. 9a but for NOx.

are shown in Figs 9b and 9c respectively. It is noted that NOx has decreased everywhere. The major source region of NOx is at around 30 km, where O(1D) is reduced. This reduction results in smaller NOx concentrations which are not compensated by any increased production of NOx above 40 km. Indeed, the time constant for NOx is so long that this increased production is cancelled by transport processes. This example demonstrates nicely the coupling
between chemistry, radiation and transport. OH, on the other hand, has a very short photochemical time constant. Its changes correspond to those of O(^1D).

5. STRATOSPHERIC PERTURBATIONS BY CFC'S

Perturbations to the ozone layer by CFCs have been investigated using the Oxford 2-D model (Pyle 1980). In order to assess the relative importance of CFC's and CO₂ on the stratosphere, calculations with CFC alone were first repeated using the present model, thus adding the feedback between ozone and the mean circulation.

The CFC source was taken as four times the average 1973-76 production rate (McCarthy et al. 1977) so that the stratospheric content of total chlorine to be expected in the year 2045, would be reached after only twenty model years, matching the doubling of CO₂ in this period.

The CFC's are destroyed in the upper stratosphere by photolysis and reaction with O(^1D) to produce Cl and ClO. These active chlorine species react in catalytic cycles to deplete ozone around 40 km and thus alter the temperature structure.

The temperature difference between run A and the CFC run, C, is shown in Fig. 10. The temperatures are reduced in run C by up to 10 K at about 40 km. In the equatorial lower stratosphere, however, increased penetration of solar radiation due to the decrease of ozone above, leads to an increase in the heating rate. The changes in the horizontal temperature gradients are associated through the thermal wind equation with modified mean zonal winds (Fig. 11) leading to a reduction in the easterly jet above 30 km. In high latitudes of the northern hemisphere the poleward temperature gradient has decreased and the westerly jet is also reduced.

As in the CO₂ calculation the meridional circulation is less affected than the zonal
Figure 10. Cross section of temperature difference (K) between runs C and A for model day 7000, April $\sim$ 2045.

Figure 11. Cross section of the difference in zonal mean zonal wind (m s$^{-1}$) between runs C and A for December $\sim$ 2045.
wind and temperature fields, the net radiative heating rates agreeing to within a few tenths \( K \cdot d^{-1} \).

Ozone changes due to the CFC’s (Fig. 12) show depletions by as much as 35\% around 40 km. This is comparable with the 27\% increase in ozone found in the CO\(_2\) runs (Fig. 7). Clearly, if the two effects are linearly additive an 8\% reduction in ozone would be found for the joint perturbation at this altitude.

The similarities of the two perturbation experiments are made yet more evident by the presence of an area of 'self-healing' in equatorial latitudes below about 25 km, increased penetration of ultraviolet leading to enhanced ozone production. As in run B, however, dynamical and chemical processes play a compensating role and, when integrated over a year, increases are only found in low latitudes.

It is interesting that there are significant differences between this calculation and that of Pyle (1980) in the high latitude lower stratosphere. Larger depletions in this region are found in the present work due to the use of the newer HO\(_2\) rate constants, which play their most significant role in the lower stratosphere.

The integrated ozone column depletion is shown in Fig. 13. As in Pyle (1980), the pronounced latitudinal and seasonal variations would strongly influence the penetration of ultraviolet radiation to the surface.

The similarities between the two perturbation runs are intriguing. Both runs produce a significant temperature reduction in the upper stratosphere but their effects on ozone are opposite. It is germane to ask to what extent the two perturbations are additive. This question is investigated in the next section where the combined perturbation is considered.

6. The simultaneous perturbations

Both Groves and Tuck (1980b) and Isaksen et al. (1980) have found that simultaneous
Figure 13. Latitude-time section of the percentage difference in total ozone between runs C and A, corresponding roughly to the year 2045.

**TABLE 2. RESULTS OF SIMULTANEOUS PERTURBATIONS**

Percentage change in total O₃ for various CO₂ and ClX contents. Groves and Tuck (1980b):

<table>
<thead>
<tr>
<th>CO₂ content (ppm)</th>
<th>ClX content predicted for year 2020</th>
<th>ClX content predicted for year 2060</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>natural</td>
<td>2020</td>
</tr>
<tr>
<td>275</td>
<td>0</td>
<td>-2.6</td>
</tr>
<tr>
<td>600</td>
<td>+3.2</td>
<td>-4.3</td>
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</table>

Isaksen et al. (1980):

<table>
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<th></th>
<th>natural</th>
<th>2000</th>
<th>2020</th>
<th>2040</th>
</tr>
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<tbody>
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<td>300</td>
<td>0</td>
<td>-7.4</td>
<td>-11.1</td>
<td>-13.9</td>
</tr>
<tr>
<td>600</td>
<td>+4.3</td>
<td>-4.1</td>
<td>-8.1</td>
<td>-11.1</td>
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</tbody>
</table>

Present work:

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<th></th>
<th>zero ClX</th>
<th>2000</th>
<th>2020</th>
<th>2040</th>
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<tbody>
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<td>320</td>
<td>0</td>
<td>-3.2</td>
<td>-8.3</td>
<td>-12.8</td>
</tr>
<tr>
<td>400</td>
<td>+3.0</td>
<td>-0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>+5.9</td>
<td></td>
<td>-4.1</td>
<td></td>
</tr>
<tr>
<td>625</td>
<td>+8.8</td>
<td></td>
<td></td>
<td>-8.1</td>
</tr>
</tbody>
</table>
perturbations in one-dimensional models are not linearly additive, as shown in Table 2. In Isaksen et al. the CO₂ effect makes only a small adjustment to the CFC perturbation, whereas Groves and Tuck find a larger cancellation between the two. Since Isaksen et al. base their temperature changes on Groves and Tuck's work, the differences between the two calculations must lie in the photo-chemical schemes.

In a simultaneous perturbation, run D, carried out in our model, the CO₂ content was increased in steps as for run B and the CFC's introduced as in run C. The changes in global O₃ predicted for various CO₂ and CIX contents (Table 2) show marked deviation from linearity; by 2040 the net decrease is 8.1% compared with the 4.0% expected from summing the two individual perturbations. The corresponding percentage changes in ozone concentration as a function of height at the equator are shown in Fig. 14. At nearly all altitudes,

![Figure 14](image)

**Figure 14.** Percentage change in ozone concentration between runs B and A (-----), runs C and A (-----) and runs D and A (.....) as a function of height at the equator. April ~ 2045.

and especially at around 40 km where the depletion is greatest, the changes in the coupled run are more negative than the sum of runs B and C and this is reflected in the changes in column density at all latitudes shown in Fig. 15. There are large changes in temperature between runs D and A with a decrease of more than 20 K in the upper stratosphere (see Fig. 16). Associated with this are changes in the zonal wind; the polar night jet is reduced by 16 m s⁻¹ (~ 10%) near 60 km and the summer easterly jet is also reduced in strength. The mid-latitude westerly jets in the lower stratosphere have strengthened slightly.

In the following section it will be shown that the temperature changes, combined with the temperature dependence of the chemical reactions can account for the non-additive behaviour.
Figure 15. Percentage change in column density versus latitude between runs B and A (--), runs C and A (--.--.--.) and runs D and A (--.--.--.). April ~ 2045.

Figure 16. Cross section of the temperature difference (K) between runs D and A. April ~ 2045.

7. The Temperature Dependence of Ozone in the Upper Stratosphere

Table 3 shows the major production and destruction mechanisms for ozone. Many reactions have been omitted; we restrict the discussion to these few for the purpose of illustration. There are four main cycles: the Chapman (odd oxygen) reactions and the HO_4,
TABLE 3

\[
\begin{array}{ccc}
\text{O}_2 + h\nu & \rightarrow & \text{O} + \text{O} & J_8 \\
\text{O} + \text{O}_3 + \text{M} & \rightarrow & \text{O}_3 + \text{M} & k_3 \\
\text{O}_2 + h\nu & \rightarrow & \text{O} + \text{O}_3 & J_5 \\
\text{O}_2 + \text{O} & \rightarrow & 2\text{O}_2 & k_{23} \\
\text{O} + \text{OH} & \rightarrow & \text{H} + \text{O}_2 & k_{1} \\
\text{H} + \text{O}_3 + \text{M} & \rightarrow & \text{HO}_2 + \text{M} & k_{9} \\
\text{HO}_2 + \text{O} & \rightarrow & \text{OH} + \text{O}_2 & k_{10} \\
\text{H} + \text{O}_3 & \rightarrow & \text{HO}_2 + \text{O}_2 & k_{11} \\
\text{NO} + \text{O}_3 & \rightarrow & \text{NO}_2 + \text{O}_2 & k_{17} \\
\text{NO}_2 + \text{O} & \rightarrow & \text{NO} + \text{O}_2 & k_{10} \\
\text{Cl} + \text{O}_3 & \rightarrow & \text{ClO} + \text{O}_2 & k_{9} \\
\text{ClO} + \text{O} & \rightarrow & \text{Cl} + \text{O}_2 & k_{44}
\end{array}
\]

NO\textsubscript{3} and ClO\textsubscript{3} cycles which catalytically destroy odd oxygen (i.e. O + O\textsubscript{3}). The equilibrium equation for ozone may be written approximately

\[
J_2[\text{O}_3] = \frac{k_3 J_5[\text{O}_3]^2}{k_2[\text{O}_2][\text{M}]} + \frac{k_5 J_3[\text{OH}][\text{O}_3]}{k_2[\text{O}_2][\text{M}]} + k_{17}[\text{NO}][\text{O}_3] + k_{50}[\text{Cl}][\text{O}_3].
\]  

(1)

We use Eq. (1) to obtain an estimate of the ozone temperature dependence. Eq. (1) can only be written in this form if we assume that equilibrium between the species in each cycle in Table 3 is rapidly established. If we had chosen to write Eq. (1) in terms of the rate-limiting steps its form would have been somewhat different. For example, a term \(k_{10}[\text{NO}_2]\) [O], which has no explicit temperature-dependence, would replace \(k_{17}[\text{NO}][\text{O}_3]\). However, \([\text{NO}_2]\) and \([\text{O}]\) are both temperature dependent because of the rapid partitioning between \([\text{NO}]\) and \([\text{NO}_2]\) (which depends on \(k_{17}\) and between \([\text{O}]\) and \([\text{O}_3]\). Hence the temperature dependencies obtained from Eq. (1) and the complete model are broadly similar. Eq. (1) does permit an analytic insight into the ozone temperature dependence for the various perturbations.

Following Barnett et al. (1975) the equation may be rewritten:

\[
S = \alpha A e^{-aT}[\text{O}_3]^2 + \alpha B e^{-bT}[\text{O}_3] + C e^{-cT}[\text{O}_3] + D e^{-dT}[\text{O}_3]
\]

(2)

where \(S\), \(A\), \(B\), \(C\) and \(D\) are independent of temperature, the exponential terms are the temperature-dependent contributions of the reaction rates and \(\alpha = J_3/J_2\) [OH] and [NO] have been assumed independent of temperature (a fair assumption for present purposes); [Cl] will be discussed shortly.

Differentiating with respect to \(T^{-1}\), neglecting the temperature dependence of \(\alpha\) (this may introduce errors of the order of 15%, Pyle 1976) and rearranging

\[
\frac{d\ln[\text{O}_3]}{dT^{-1}} = \frac{a + b f_1 + c f_2 + d f_3}{2 + f_1 + f_2 + f_3}
\]

(3)

where \(f_1\), \(f_2\) and \(f_3\) are the rates of the rate of destruction of ozone by the HO\textsubscript{2}, NO\textsubscript{3} and ClO\textsubscript{3} cycles, respectively, to the pure oxygen scheme. We see that the temperature dependence of ozone is an average of the four schemes, weighted according to their relative strengths.

From the reaction rates in Table 1, \(a = 2810\) K, \(b = 510\) K and \(c = 1200\) K. Contributions to \(d\) come from \(k_{50}\) and from the temperature dependence of [Cl]. Considering \(k_{50}\) alone gives \(d = 257\) K·Cl, however, is strongly, and inversely, dependent on temperature through the reaction

\[
\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3.
\]

\[k = 7.3 \times 10^{-12} \exp(-1260/T) \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1},
\]
so that $d$ may be smaller than 257 K or even negative. For the present we take $d = 0$; this assumption will not affect the conclusions made later but serves as illustration that the CIX destruction cycle is far less dependent on temperature than any of the other catalytic destruction cycles. Notice that Isaksen et al. (1980) attribute the non-linearity of the coupled perturbation to the temperature dependence of $[\text{Cl}]$. This, however, is only one contributing factor.

The relative importance of each cycle at the equator near 40 km is shown for the four runs in Table 4 with the corresponding values of $f_1$, $f_2$, and $f_3$ given in brackets. For runs A and B the oxygen and HOx cycles are of similar importance while the NOX cycle is about twice as significant. In runs C and D the destruction by ClOx is clearly the most effective with the NOX cycle contributing about half as much and the HOx and oxygen cycles less than 10% of the total.

**Table 4. Percentage of total ozone destruction due to the various cycles at 40 km, equator, April, 2045**

<table>
<thead>
<tr>
<th>Cycle</th>
<th>A (%)</th>
<th>B (%)</th>
<th>C (%)</th>
<th>D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure oxygen</td>
<td>26.3</td>
<td>24.4</td>
<td>6.6</td>
<td>4.5</td>
</tr>
<tr>
<td>HOX ($f_2$)</td>
<td>17.9 (0.68)</td>
<td>19.6 (0.80)</td>
<td>9.5 (1.44)</td>
<td>8.7 (1.95)</td>
</tr>
<tr>
<td>NOX ($f_3$)</td>
<td>55.8 (2.13)</td>
<td>56.0 (2.29)</td>
<td>30.0 (4.54)</td>
<td>25.9 (5.79)</td>
</tr>
<tr>
<td>ClOx ($f_3$)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>53.9 (8.17)</td>
<td>60.9 (13.59)</td>
</tr>
</tbody>
</table>

Using the temperature factors derived above and the $f$-factors in Table 4 gives the temperature dependences of ozone at 40 km in Table 5.

**Table 5**

<table>
<thead>
<tr>
<th>Run</th>
<th>$d \ln[O_3]/dT^{-1}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1188</td>
</tr>
<tr>
<td>B</td>
<td>1172</td>
</tr>
<tr>
<td>C</td>
<td>557</td>
</tr>
<tr>
<td>D</td>
<td>461</td>
</tr>
</tbody>
</table>

We see that in the runs in which the ClOx destruction cycle plays the leading role the temperature dependence of ozone is correspondingly low. Thus, reductions in temperature produced by, for example, an increase in CO2 will have a smaller effect on O3. The non-linearity of the coupled perturbation is due to this change in temperature dependence.

Note that differences are found between the value obtained for runs A and B and between runs C and D, although these pairs contain identical photochemical schemes. This can be ascribed to the fact that the upper stratospheric temperatures appropriate to each run are different and that the temperature dependence of O3 itself depends slightly on temperature through the changing emphasis of the destruction cycles, i.e. the $f$-factors. Thus, the ClOx cycle is responsible for 61% of the O3 destruction in run D and 54% in run C.

In Fig. 17 is shown a plot of $\log_{10} [O_3]$ versus $T^{-1}$ using values obtained from the model. The slope is much steeper for runs A and B than for runs C and D as expected from the simple photochemistry discussed above. The temperatures at the equator near 40 km on Day 7000 (April - 2045) for runs A and B were 253 and 242 K respectively and $d \ln[O_3]/dT^{-1}$ at an intermediate temperature is, from Fig. 17, about 1550 K. At the same point and date the temperatures in runs C and D were 242 and 230 K, the slope of the appropriate graph gives $d \ln[O_3]/dT^{-1} \approx 800$ K. Both these values are higher than those obtained by the simplified calculations based on Eq. (1). The difference is due to the various approxi-
Figure 17. Log$_{10}$ (ozone concentration (molec$^{-3}$)) versus reciprocal temperature (K$^{-1}$) for model runs A, B, C and D.

mations in Eqs. (1) and (3): the simplified photochemical scheme, the neglect of $\delta x/dT^{-1}$ (in fact negative) and of the temperature dependence of [O$_2$], [M], [NO] and [OH] and the use of an approximate value for $d$.

Notice that the small variation of the temperature dependence with temperature, discussed above, can be seen for all four runs in Fig. 17.

The decrease in temperature of run B relative to run A at the equator near 40 km on Day 7000 will cause an increase in ozone concentration:

$$\frac{\Delta\text{[O}_3\text{]}}{\text{[O}_3\text{]}} = 1550 \Delta(T^{-1}) = \frac{(1550)(11)}{(253)(242)} = 0.28$$

A 28% increase may indeed be observed in Figs. 7 and 13.

The difference between runs C and D due to the decrease in temperature will be

$$\frac{\Delta\text{[O}_3\text{]}}{\text{[O}_3\text{]}} = 800 \Delta(T^{-1}) = \frac{(800)(12)}{(242)(230)} = 0.17$$

From Fig. 14 the ozone concentration at 40 km in run C is 63% of that in run A so the concentration of run D should be $1.17 \times 63\% = 74\%$ of run A. This is in good agreement with the 73% shown in Fig. 14.

Thus the non-linearity of the effects of CO$_2$ and CFC's on ozone can be explained by the reduction in the temperature-dependence of the ozone concentration associated with the presence of the chlorine compounds.
8. CONCLUSIONS

Four experiments have been described using a two-dimensional circulation model. The improvements in the radiation calculations and in the photochemical scheme over earlier versions of the model have led to an improved stratopause structure. Earlier conclusions that the summer stratopause is very close to radiative equilibrium (HP) appear to be confirmed. Despite the improvements in the radiation schemes the zonal jets are too strong. This is probably associated with the eddy transport of heat in the model.

The three perturbation experiments confirm the importance of considering radiative, photochemical and dynamical feedback processes. The perturbations due to CFC's and CO\textsubscript{2} have quite a similar effect on the temperature and wind structure of the stratosphere but opposite effect on ozone. The temperature is reduced by around 10 K at 40 km with a reduction in the strength of the jets. A most important feedback, not considered here, is the change in eddy transport associated with these changes in the zonal mean structure. In the CFC calculation ozone is reduced in the upper stratosphere, with an area of 'self-healing' in the equatorial lower stratosphere. For the CO\textsubscript{2} perturbation, the ozone increases around 40 km, but there is some reduction below, again in the equatorial lower stratosphere. The greatest column changes for both perturbations occur in high latitudes.

The coupled perturbation does not behave like a linear combination of the two effects. In the coupled calculation, the presence of chlorine in the upper stratosphere reduces the temperature dependence of the ozone concentration and thus the temperature changes due to increasing CO\textsubscript{2} have less effect.

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REFERENCES


D.O.E. 1979 Chlorofluorocarbons and their effect on stratosphere ozone. Pollution Paper No. 15, H.M.S.O.


Pyle, J. A. and Rogers, C. F.

1980 'Stratospheric transport by stationary planetary waves—
the importance of chemical processes'. Quart. J. R. 

Reed, R. J. and German, K. E.

1965 'A contribution to the problems of stratospheric diffusion by 

Simon, P. C.

1974 'Balloon measurements of solar fluxes between 1960Å and 
2300 Å'. Proceedings of the third CIAP conference, 
137–142, U.S. Dept. of Transportation.

Williams, A. P.


W.M.O.

W.M.O. global ozone research and monitoring project. 
Report No. 11