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Ozone perturbations due to increases in N_2O, CH_4 and chlorocarbons: two-dimensional time-dependent calculations

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ABSTRACT

Time-dependent ozone perturbation estimates are performed in a 2-D diabatic circulation model with ozone photochemistry. Future increases in the emissions of N_2O, CH_4 and the chlorocarbons $CFCl_3$, CF_2Cl_2, $CHClF_2$, $C_2Cl_3F_3$, CH_3CCl_3 and CCl_4 are considered. The altitude variation of the calculated ozone change in the upper stratosphere is within the uncertainty limits of the observed trend reported from Umkehr data for the period 1970–1980, when the effect of temperature changes from CO_2 is included. Future ozone predictions consider only the photochemical response to source gas increases. For the integrations until the year 2030, four different emission scenarios for chlorine releases have been used. The average global ozone column has been reduced by 6·5% in the year 2030 compared to the 1960 level, when chlorine emissions are increased by 3%/year and the surface mixing ratio of N_2O and CH_4 by 0·25 and 1·0%/year, respectively. It should also be noted that in a case with low chlorocarbon emissions and a modest reduction in the total ozone column, the altitude profile is highly distorted. In addition, the latitude gradients are pronounced. When all the chlorocarbon emissions are stopped in the year 2000, a minimum in the total ozone column density is reached after about 5 years. The efficiency in the recovery of the ozone column is shown to be larger when CH_4 is assumed to increase, compared to a case when CH_4 is assumed to be constant. When the total chlorine approaches the amount of nitrogen in the stratosphere, ozone depletions begin to accelerate. This situation does not occur before the year 2030 in any of the model runs with the scenarios selected here. Ozone predictions were performed for an additional period of 50 years for the chlorocarbon scenario with the highest emissions. In this case, non-linear growth in ozone depletion was found after the middle of the next century.

1. Introduction

Possible modifications of the stratospheric ozone layer have attracted considerable interest in the last decade. Increased abundances of stratospheric chlorine from industrial emissions of chlorocarbons as well as increased levels of nitrogen species accompanying an observed increase in the concentrations of N_2O, have the potential to significantly deplete the stratospheric ozone layer. An increase in CO_2 and other radiatively active trace gases which lead to lower temperatures in the stratosphere will have the opposite effect through a decrease in ozone destruction. Enhanced ozone production is believed to take place in the troposphere due to the observed increase in CH_4.

A number of ozone perturbation experiments have been performed using two-dimensional (2-D) models (Brasseur and Bertin, 1978; Borucki et al., 1980; Pyle, 1980; Haigh and Pyle, 1982; Gidel et al., 1983; Whitten et al., 1983; Haigh, 1984; Solomon et al., 1985). In a recent study (Isaksen and Stordal, 1986), we used the 2-D diabetic circulation model of Stordal et al. (1985) for steady-state ozone perturbation studies. Perturbations due to increases in CH_4 and N_2O as well as a wide range of chlorine levels were

investigated. The main features in the distribution of ozone changes were similar to those obtained by the models of Garcia and Solomon (1983), Solomon and Garcia (1984) and Ko et al. (1985) as presented in the WMO (1986) compilation. This is not surprising, since the transport representation is similar in the models (as discussed in WMO, 1986). It deviates from most 2-D models using the Eulerian transport formulation with higher diffusion (e.g., Gidel et al., 1983) in important ways. For instance a more pronounced latitudinal gradient in the chlorine induced reductions of the total ozone columns is predicted when the diabatic circulation and slow diffusion is used for tracer transport. All the calculations mentioned above are based on steady state assumptions. Time-dependent long-time simulations have so far been confined to one dimensional (1-D) models.

In this paper, we describe a set of 2-D time dependent experiments performed with the model of Stordal et al. (1985), to our knowledge the first reported since the experiment of Vupputuri (1979). He calculated ozone changes until the year 2015 under the assumption of constant releases of chlorofluoromethanes on the 1975 level. Our understanding of the photochemistry of the stratosphere has increased considerably over the last few years, leading to ozone perturbation estimates which differ considerably from what Vupputuri obtained. 2-D models, besides offering a more realistic tracer transport than 1-D models, employ predictions of future ozone variations at various latitudes. When the time history of the future ozone distribution is considered, the difference in latitudinal response is a main concern since the predicted ozone depletion has been shown to increase significantly from lower to higher latitudes (steady state experiments, e.g. Pyle, 1980; Haigh and Pyle, 1982; Haigh, 1984; Solomon et al., 1985). As discussed in Stordal et al. (1985) the model used in the present study gives a credible description of the distributions and lifetimes of long-lived gases as O_3, N_2O, CH_4, CF_2Cl_2, $CFCl_3$ and CCl_4.

A set of scenarios of the future evolution of some source gases have been selected for the present study. It has been necessary to restrict the number of cases. Four different scenarios for the chlorocarbons have been selected in combination with increases in N_2O and CH_4. The source gas scenarios adopted are presented in Section 2. As the observed CH_4 increase is not well understood, it is far from certain that the present rate of increase ($\sim 1\%$ per year) will continue over the time period considerd in these calculations. One of the experiments has therefore been performed with future CH_4 constant at the 1980 level, making a total of five scenarios which have been selected for model simulations for the time period 1980–2030. Reference year for the model study is 1960 when the time dependent calculations are started.

The present model which extends from the surface to 50 km altitude includes the photochemistry of oxygen, hydrogen, nitrogen and chlorine compounds. The distributon of ozone loss rates due to each of these chemical families is of importance for the response in ozone to changes in the chemical composition of the stratosphere. Photochemical terms for the long lived tracers are calculated four times a year when fully diurnal computations are undertaken. The photochemical data have been updated in accordance with the latest NASA/JPL (1985) recommendations. In the discussion on ozone balance in section 3 latitudinal as well as altitudinal variations in the influence of each of the main ozone loss cycles are demonstrated.

In the middle and lower stratosphere nitrogen species are believed to contribute largely to the loss of ozone. In our previous study, we also demonstrated that nitrogen compounds have a strong influence on the efficiency of ozone depletions due to chlorine increases (Isaksen and Stordal, 1986). In light of reports that 2-D diabetic circulation models tend to underestimate the amount of odd nitrogen present in the lower stratosphere (WMO, 1986; Ko et al., 1986), we have included a discussion in section 3 of how well odd nitrogen is reproduced in the lower stratosphere in the present model.

In Section 4 we compare estimated changes in upper tropospheric ozone to the observed decadal trend in ozone in the period 1970–1980 as reported in WMO (1986). Estimated changes in ozone during that decade based on Umkehr measurments at 13 observational locations were reported.

Results describing the future evolution of the tropospheric and stratospheric ozone are described in Section 5. Figures showing the globally

and seasonally averaged total column, latitudinal and yearly variation of the ozone columns as well as altitudinal distributions are presented. For some of the scenarios the effect of a cessation or reductions in chlorine emissions is demonstrated (Section 6), which could offer useful information with respect to future emission control.

Only the study of the stratospheric depletion between 1970–1980 (Section 4) includes temperature changes. All future ozone predictions presented in this paper represent the photochemical response to source gas increases as changes in temperatures and tracer transport have not been considered.

2. Source gas scenarios

2.1. Chlorocarbons

Observations show that the concentrations of several halocarbons in the atmosphere are increasing. In an extensive measurement programme (Atmospheric Lifetime Experiment, ALE) the concentrations of $CFCl_3$, CF_2Cl_2, CCl_4 and CH_3CCl_3 have been monitored at five coastal or island stations exposed to little polluted air (Prinn et al., 1983a). A steady increase in these components have been reported at all locations during the observational period 1978–1981.

The chlorocarbons included in the present study are methyl chlorine (CH_3Cl), carbon tetrachloride (CCl_4), methyl chloroform (CH_3CCl_3) and the chlorofluorocarbons F11 = $CFCl_3$, F12 = CF_2Cl_2, F22 = $CHClF_2$ and F113 = $C_2Cl_3F_3$. These compounds are believed to be the main sources of future stratospheric chlorine. The source for these gases (except CH_3Cl) is industrial releases. As the residence times are of the order of 50-100 years (see Stordal et al., 1985) (except CH_3CCl_3 which has a residence time of about 10 years) the present increases are due to past as well as present emissions.

Table. 1. *Source gas scenarios 1960–1980*

N_2O:	1980 level 305 p.p.b., 0.2%/year increase in the period
CH_4:	1980 level 1.70 p.p.m., 1·1%/year increase in the period
CH_3Cl:	1960 level 0.6 p.p.b., constant surface boundary flux
Emissions for chlorine source gases taken from	
$CFCl_3$:	Cunnold et al. (1983a)
CF_2Cl_2:	Cunnold et al. (1983b)
CH_3CCl_3:	Prinn et al. (1983b)
CCl_4:	Simmonds et al. (1983)

Chlorocarbons release rates for the period 1960–1980 (see Table 1) are taken from Cunnold et al. (1983a, $CFCl_3$), Cunnold et al. (1983b, CF_2Cl_2), Prinn et al. (1983b, CH_3CCl_3) and Simmonds et al. (1983, CCl_4). Initially (1960) the atmosphere was assumed to contain 0·6 p.p.b. of CH_3Cl and 0·1 p.p.b. of CCl_4, resulting in a 1 p.p.b. content of stratospheric chlorine. The CH_3Cl surface flux needed to obtain the 1960 mixing ratio was kept constant in all the computations. For $CFCl_3$, CF_2Cl_2 and CH_3CCl_3 the integrations were started in 1960 with zero abundances and releases corresponding to amounts accumulated in the years prior to 1960. This can be justified since the releases were small before 1960.

Scenarios for future industrial releases will necessarily be uncertain. We have performed experiments with four different chlorocarbon scenarios. The emission rates are listed in Table 2. Our computations are partly based on the evaluation of Quinn et al. (1986) from whom we have adopted emissions for $CFCl_3$, CF_2Cl_2, $CHClF_2$, $C_2Cl_3F_3$, CCl_4 and CH_3CCl_3 in the period 1985–2030. Based on economic models, recognizing industrial usages, competitive products and economic and population growth, they have developed seven scenarios for the chlorocarbons. In our scenario C we have used emission rates between the values in their two highest scenarios (VI and VII). As can be deduced from the numbers in Table 2, the release of the largest contributors to stratospheric chlorine, CF_2Cl_2 and $CFCl_3$, increase by about 3.5 and 5% per year, respectively, until the year 2000. The increase is thereafter reduced and reaches 2% per year by the end of the period studied here for both gases. Our scenario D is chosen to be identical to their scenario II. In this scenario, the reduction in emission growth starts earlier (in the year 1990). By the end of the period in question the growth is 1% per year for CF_2Cl_2 and $CFCl_3$. We have also included one scenario with constant releases from 1980 (scenario A) as well as one with a steady 3% yearly increase in emissions after 1980 (scenario B). One of the fluorocarbons

Table. 2. *Source gas scenarios 1980–2030*

N_2O: 0.25%/year increase in the period
CH_4: either 1.0%/year increase or constant surface mixing ratio at 1980 level

Chlorinated source gas emission (10^9 g/year)

Scenario (A): Constant releases 1980 level
$CFCl_3$: 265
CF_2Cl_2: 485
CHF_2Cl: 82
CH_3CCl_3: 504
CCl_4: 60

Scenario (B): a 3%/year increase in the emissions, starting with the values of scenario A in 1980

Scenario (C): emission rates between the values of scenarios VI and VII in Quinn et al. (1986)

Year	$CFCl_3$	CF_2Cl_2	CHF_2Cl	$C_2F_3Cl_3$	CH_3CCl_3	CCl_4
1985	325.4	449.3	52.9	114.0	509.7	153.1
1990	427.6	528.5	90.8	142.0	568.6	187.7
1995	553.4	624.9	130.2	198.2	634.3	205.7
2000	716.6	745.8	176.8	277.0	707.5	225.9
2010	1024.5	994.8	284.1	334.4	854.0	272.6
2020	1332.5	1266.0	407.4	403.6	1030.9	329.2
2030	1637.0	1564.1	543.0	484.1	1235.4	382.2
2040	2006.4	1919.2	732.7	573.0	1472.9	446.8
2050	2467.6	2341.8	918.7	683.0	1743.4	523.7
2060	2936.8	2770.4	1115.5	808.4	2063.5	613.8
2070	3439.9	3226.0	1310.0	956.8	2442.4	719.4
2075	3711.1	3472.3	1408.2	1033.0	2637.6	784.1

Scenario (D): emission rates as in scenario II in Quinn et al. (1986)

Year	$CFCl_3$	CF_2Cl_2	CHF_2Cl	$C_2F_3Cl_3$	CH_3CCl_3	CCl_4
1985	323.5	446.1	57.3	114.0	509.7	41.0
1990	421.8	519.3	74.5	142.0	568.6	41.0
1995	476.2	572.7	92.4	157.0	634.3	45.0
2000	522.0	611.0	111.3	180.0	707.5	49.4
2010	594.1	683.2	139.2	217.5	854.0	58.8
2020	656.8	762.7	156.6	262.9	1030.9	70.1
2030	725.3	852.7	172.1	317.7	1235.4	83.5

($C_2Cl_3F_3$) is not explicitly represented in the model. The releases of this species is added to the releases of CF_2Cl_2 (on a Cl base) since the two gases have similar photochemical characteristics (NASA/JPL, 1985). Table 2 demonstrates that the releases of $C_2Cl_3F_3$ are modest compared to the CF_2Cl_2 releases.

The chlorocarbons are decomposed in the stratosphere where chlorine (Cl) and chlorine monoxide (ClO) radicals catalytically destroy ozone. Reductions of the stratospheric ozone layer is therefore presumed to accompany a continued growth in the chlorocarbon release rates.

2.2. N_2O

The atmospheric concentrations of nitrous oxide are increasing in the atmosphere (e.g. Weiss, 1981; Khalil and Rasmussen, 1983a). Natural sources as well as anthropogenic sources have been identified. The two main anthropogenic sources are fertilizers (Crutzen, 1974; Logan et al., 1978) and combustion processes (Weiss and Craig, 1976; Pierotti and Rasmussen, 1976).

Weiss (1981) observed an increase of about 0.2% per year in the four year period 1976–1980 and suggested that this increase was due to increasing anthropogenic releases. In the present

study this growth has been adopted for the entire period 1960–1980 (Table 1). As argued by Isaksen and Stordal (1986), the anthropogenic releases presumably constitute only a modest fraction of the total N_2O source at present (about 25%, WMO, 1986). In the future the anthropogenic fraction can be expected to increase markedly and also play a more significant role in the total N_2O budget. An accelerated growth in N_2O would then occur. Despite this speculation, a more conservative approach has been taken in the present study. A yearly growth of 0.25% is assumed for future N_2O releases in accordance with the recommendation of Environmental Protection Agency (EPA, private communication).

N_2O has a long atmospheric lifetime ($\sim$150 years, see discussion in Stordal et al., 1985) as the loss processes in the troposphere are very slow. In the stratosphere N_2O decomposes, and is partly converted to oxides of nitrogen (NO_x) which catalytically destroy ozone. Future increases in nitrous oxide will therefore be associated with ozone reductions in the stratosphere.

The efficiency of stratospheric chlorine in reducing the atmospheric ozone layer depends strongly on the level of stratospheric NO_x through various interactions between the NO_x and Cl_x chemistry. N_2O increases will therefore also influence the ozone reduction due to the presence of Cl_x in the stratosphere. The rate at which chlorocarbons and nitrous oxide are assumed to increase in combined scenario experiments are therefore essential for estimated ozone depletion.

2.3. CH_4

Atmospheric measurements have now clearly established that the concentration of methane is increasing (Rasmussen and Khalil, 1981; Blake et el., 1982; Khalil and Rasmussen, 1982; Ehhalt et al., 1983; Blake and Rowland, 1986). Since 1979 methane data have been obtained from at least six measuring sites, including the continuous record from Cape Meares, Oregon (Khalil and Rasmusssen, 1983b; 1986). After an increase of about 1.8% per year in the period 1979–1982, a temporary decline in methane was obtained at this station. This feature was associated with an El-Niño Southern Oscillation phenomenon (Khalil and Rasmussen, 1986) and reduced the average trend in the period 1979–1984 to about 1% per year. The increase in methane prior to about 1979 is more uncertain. From the period after 1965 values from 0.5% per year (Ehhalt et al., 1983) to 1.7% per year (Rasmussen and Khalil, 1981) have been reported. In this study, we used an annual increase of 1.1% for the period 1960–1980 (see Table 1).

Our understanding of the global methane budget is still insufficient. An extensive review of the present knowledge is presented in NASA (1986). The total sink is estimated to be approximately 450 Tg $year^{-1}$ (Isaksen and Hov, 1987), due to the loss through reaction with the hydroxyl radical in the troposphere. Total production of methane should be approximately the same as it is expected that there is a near balance between total production and loss of methane in the atmosphere. The relative strength of each of the sources is, however, highly uncertain (Ehhalt and Schmidt, 1978; Seiler, 1984). The latitudinal distribution of the sources is also poorly known. It is therefore difficult to explain the current rise in methane, as well as it is highly uncertain to predict future evolution of methane concentrations in the atmosphere. We have chosen here to assume a future annual increase of 1% (EPA, private communication) in most of the scenarios, but we have also included a scenario with constant level of CH_4 in the future (see Table 2).

Through its interaction with tropospheric chemistry, increases in methane releases will lead to increased ozone concentration in this region of the atmosphere. A detailed study of future changes in tropospheric ozone should also include changes in the species NO_x, NMHC (non methane hydrocarbons) and CO (Isaksen and Hov, 1987). Since release scenarios for these species are difficult to establish, changes in their emissions have not been taken into account in the present paper.

Methane also plays an important role in the partitioning between the chlorine constituents Cl, ClO and HCl in the stratosphere. Future methane changes will therefore also affect chlorine species in the stratosphere and thereby the depletion of ozone through these species.

3. Ozone loss mechanisms

Chemical loss of ozone in the stratosphere is characterized by the efficiency of chemical cycles

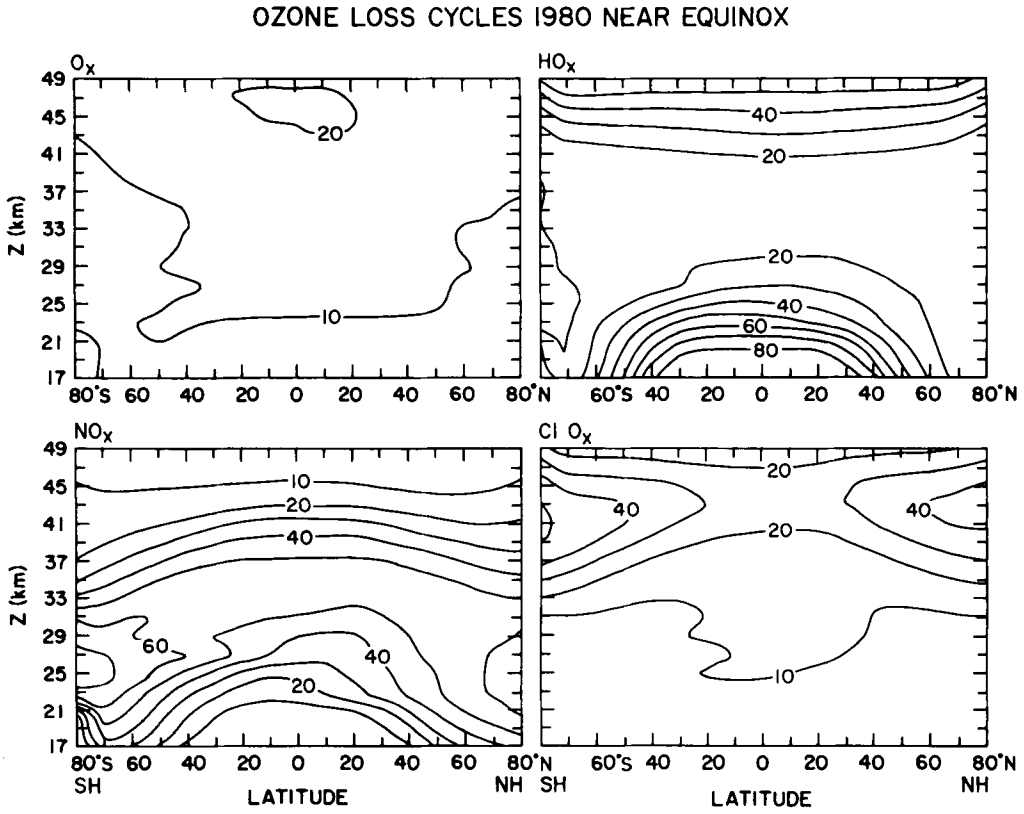

Fig. 1. % ozone loss rates due to O_x, HO_x, NO_x and ClO_x. The individual loss rates are computed from the following reactions:

O_x : $O + O_3 \rightarrow O_2 + O_2$ (times 2)
HO_x : $OH + O_3 \rightarrow HO_2 + O_2$
$HO_2 + O_3 \rightarrow OH + 2O_2$
$OH + O \rightarrow H + O_2$
$HO_2 + O \rightarrow OH + O_2$
NO_x : $NO_2 + O \rightarrow NO + O_2$ (times 2)
ClO_x : $ClO + O \rightarrow Cl + O_2$ (times 2)

involving nitrogen, hydrogen, chlorine as well as oxygen species.

We have considered the following loss reactions for odd oxygen (the parenthesized numbers to the left-hand side of the reaction denotes the number of the number of O_x molecules destroyed in the reaction; see Stordal et al. 1985 for the definition of O_x):

Oxygen:	(2) $O + O_3 \rightarrow O_2 + O_2$	R1
Hydrogen:	(1) $OH + O_3 \rightarrow HO_2 + O_2$	R2
	(1) $HO_2 + O_3 \rightarrow OH + 2O_2$	R3
	(1) $OH + O \rightarrow H + O_2$	R4
	(1) $HO_2 + O \rightarrow OH + O_2$	R5
Nitrogen:	(2) $NO_2 + O \rightarrow NO + O_2$	R6
Chlorine:	(2) $ClO + O \rightarrow Cl + O_2$	R7

Fig. 1 shows the relative loss of ozone from the oxygen, hydrogen, nitrogen and chlorine families as a function of latitude and height. The most important latitudinal differences in ozone destruction are found in the nitrogen and the chlorine cycles, particularly as the concentrations of these two families most likely will increase noticeably in the future. Fig. 1 represents the situation in 1980 when the chlorine content of the stratosphere still is low (~2.3 p.p.b.). Neverthe-

less it is seen that chlorine reactions become increasingly important going towards high latitudes, and are dominating upper stratospheric ozone loss at high latitudes in the present atmosphere. Ozone loss by nitrogen species is systematically moved to lower values as we proceed towards high latitudes. This will be of importance, not only for the response in ozone concentrations to increased levels of either NO_x or Cl_x, but also to the latitudinal response in ozone due to simultaneous changes in NO_x and Cl_x (combined scenario studies). The efficiency of the chlorine cycle at high latitudes with these moderate Cl_x levels, explains the fast high latitude response in upper stratospheric ozone, and in total ozone to chlorocarbon perturbation that will be discussed in this paper. It seems reasonable that it is in this early stage of ozone depletion, before chlorine reactions dominate the ozone loss at low latitudes, that the difference between ozone depletion at high and low latitudes is largest.

The importance of the NO_x chemistry for the ozone loss in the middle and lower stratosphere is clearly demonstrated in Fig. 1. In addition, NO_x plays a significant role for chlorine induced ozone depletion through interaction with the chlorine chemistry. Ozone perturbation studies from chlorocarbon releases do therefore rely heavily on a proper representation of NO_x levels in the model used. Unfortunately, 2-D diabatic circulation models do tend to underestimate NO_y (total odd nitrogen) levels in the lower stratosphere in equatorial regions compared to observations (WMO, 1986). At other latitudes and altitudes the agreement is better. Ko et al. (1986) suggest that the discrepancy between observed and 2-D model calculated NO_y values can be removed by taking into account NO_y production by lightening. This production is efficient in the upper troposphere in equatorial regions, where significant amounts (compared to the stratospheric NO_y produced from N_2O) can be transported up through the tropopause by the process of diabatic circulation applied in these 2-D models.

It should be pointed out that the NO_y distribution is very sensitive to the competition between the horizontal eddy diffusion and the vertical advection in the model at this low latitude region in the lower stratosphere. Our 2-D diabetic circulation model tends to give NO_y levels in better agreement with observations even without a lightening source.

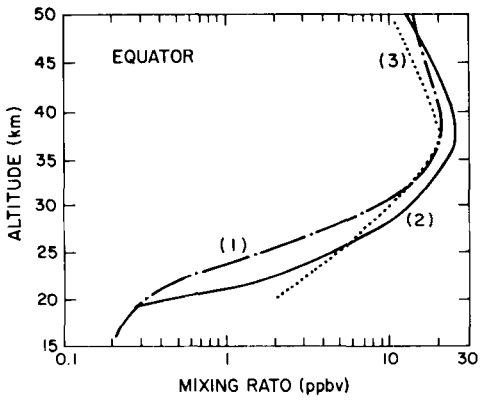

Fig. 2. Comparison of the calculated NO_y profile at the Equator in this model (curve 2) and the model of Ko et al. (1986) (curve 1; without NO_y source from lightning) with the observed nighttime concentration of $NO_2 + HNO_3$ (Callis et al., 1985; LIMS-data) (curve 3).

In Fig. 2 we have taken one of Ko et al's (1986) figures showing the NO_y profiles at Equator from their model along with observations presented by Callis et al. (1985), and included the NO_y profile from our model. In contrast to the model of Ko et al. (1986), ours underestimates NO_y only at very low altitudes. At the 25 km level (the region that holds the key to the accelerated ozone depletions at high chlorine levels, see Section 7) there is a very good agreement between our model and the measurements. Fig. 2 shows that there is in general a higher NO_y level in our model than in the model of Ko et al. (1986). The discrepancy between the models increases towards lower altitudes in the lower stratosphere. This is, at least partly, due to a balance between vertical advection and horizontal diffusion which is more in favour of the latter process in our model than in theirs.

4. Trend in ozone for the period 1970–1980

Trend estimates based on 13 Umkehr stations indicate that there has been a statistical significant reduction in ozone between 1970 and 1980 in the upper stratosphere between approximately 30 and 40 km. This reduction is estimated to be up to 0·3% per year (WMO, 1986; Reinsel et al.,

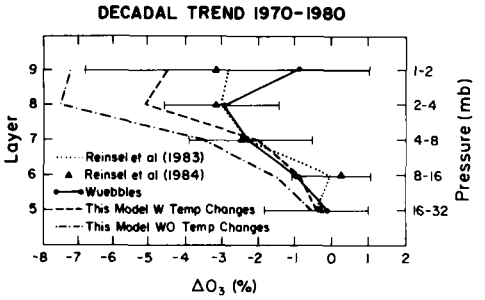

Fig. 3. Calculated ozone depletion between 1970 and 1980 with and without temperature changes from radiatively active gases in the stratosphere. The adopted temperature change is taken from a 1-D model study by Brasseur et al. (1985). Estimated global trends (Reinsel et al., 1983, 1984) are based on Umkehr data. A one-dimensional model calculation with the model of Wuebbles (1983) is included. His results (labelled Wuebbles in the figure) are published in WMO (1986).

1983; 1984) and is most pronounced in the height region where the chlorine chemistry has its strongest effect on the ozone (Fig. 1).

Although the Umkehr data are hampered by large uncertainties, the result is particularly sensitive to the corrections made for the aerosol burden in the stratosphere. Nevertheless, they represent important indications that chlorine induced perturbations can be detected in the stratosphere. For this reason it is very important to compare the estimated ozone trends based on observations with model calculated ozone depletion for the same period.

Fig. 3 shows height profiles at 40°N for the decadal depletion from our 2-D model studies. Global trend estimates reported in WMO (1986) are also given in the figure. Estimates with no temperature feedback give upper stratospheric ozone depletion larger than what is deduced from Umkehr observations. We have, however, also done one model study where we included temperature changes between 1970 and 1980. The stratospheric temperature decreases adopted for this period are taken from the one-dimensional model study by Brasseur et al. (1985). Their calculations are based on a combined scenario, where temperature decreases in the 1970–1980 period result from increases in CO_2 and other trace species. We have assumed that approximately $\frac{1}{3}$ of the estimated change from the preindustrial era up to 1983 given by Brasseur et al. (1985) takes place between 1970 and 1980. This gives temperature decreases of approximately 2K in the 45–50 km region and less than 1 K below 35 km. (Their 1-D temperature change profile has been used at all latitudes and all seasons in our 2-D calculations, introducing inaccuracies, mainly at high latitudes). It is seen that ozone depletion when the temperature feedback is considered (Fig. 3) becomes approximately $\frac{2}{3}$ of the estimated depletion when no temperature effect is considered, bringing the calculations in better agreement with the observed trends.

The temperature effect from CO_2 is found to be more pronounced at low latitudes than at high latitudes, thus increasing the latitudinal differences in ozone depletion when temperature feedback is included. The reason for this is that nitrogen reactions which dominate ozone loss at low latitudes becomes less efficient at lower temperatures (Isaksen et al., 1980), while this is not the case for chlorine reactions which dominate at high latitudes (see Fig. 1).

Temperature changes will have a pronounced effect on the trend in total ozone as shown in Table 3. Global ozone decrease between 1970 and 1980 is reduced from 0.62% to 0.21% when temperature feedback is included. If a faster methane increase is assumed (2.0%/year), ozone loss is decreased since the ozone production increases in the troposphere and since the chlorine chemistry becomes less active with respect to ozone destruction (see reaction R18, Section 7). There is then even a slight increase (+0·03%) in the total column of ozone. At high latitudes

Table. 3. *Time-dependent 2-D model calculations of ozone column depletion between 1970 and 1980; the numbers are for March and are given in %*

	1	2	3
global	−0.62	−0.21	+0.03
60°N	−1.84	−1.13	−0.88

Case 1. Without temperature feedback and with 1.1% annual increase in CH_4 releases.
Case 2. With temperature feedback and 1.1% annual increase in CH_4 releases
Case 3. With temperature feedback and 2% annual increase in CH_4 releases.

(60°N) similar changes in ozone reductions occur, although the depletion is pronounced in all three model studies discussed above.

5. Time-dependent future ozone experiments

The distribution of ozone at three different points of time, the years 1980, 2000 and 2020 will be used to illustrate some main features in the development of ozone changes. Fig. 4 shows the change in the total ozone column as a function of latitude and time of the year. The depicted changes result from a model run with a chlorine increase as assumed in scenario C. Simultaneous increases in N_2O and CH_4 (see Tables 1, 2) are assumed. Fig. 4 also shows latitude-altitude cross sections for the solstices (Northern Hemisphere

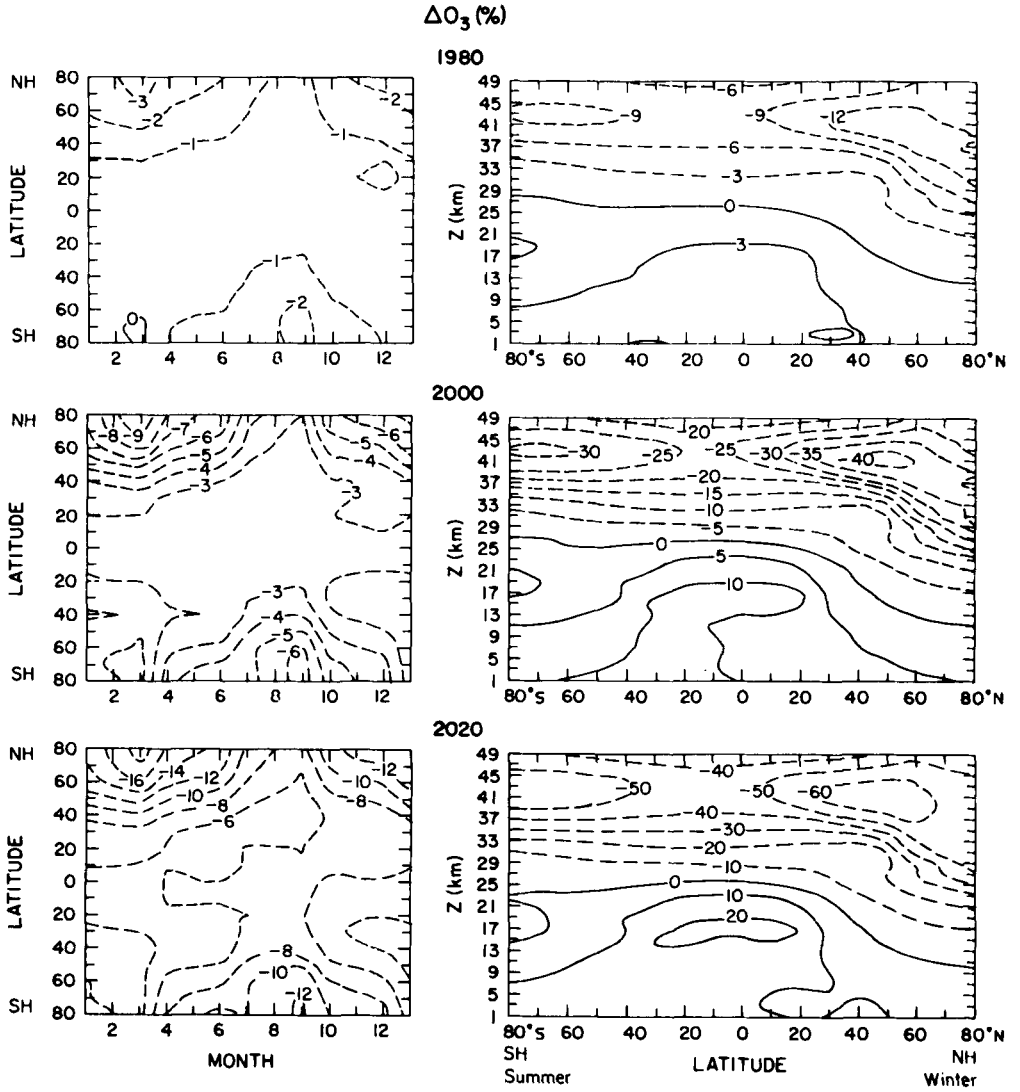

Fig. 4. % ozone changes in the year 1980 (see scenario Table 1) and the years 2000 and 2020 in the chlorine emission case C with simultaneous increases in N_2O and CH_4 (see Table 2). The left-hand side panels depict changes in the total ozone columns as a function of latitude and time of the year. The right-hand side panels show altitude-latitude cross sections of local ozone changes for solstice conditions.

winter) in the same years. The latitudinal, altitudinal and yearly patterns are similar to those obtained in the steady state ozone calculations reported earlier with this (Isaksen and Stordal, 1986) and other 2-D models (especially the diabatic type models; WMO, 1986): ozone reductions take place in the middle and upper stratosphere, with most pronounced depletions at high latitudes in the upper stratosphere as a result of chlorine chemistry. The balance between active chlorine compounds (Cl and ClO), and the inactive compound HCl is shifted towards higher values of Cl and ClO. This is due to low CH_4 mixing ratios resulting from downward transport ($Cl + CH_4 \rightarrow HCl + CH_3$ is main reaction converting active chlorine to HCl; see Solomon and Garcia, 1984; Solomon et al., 1985). The maximum reductions are about 15, 40 and 65% in the years 1980, 2000 and 2020, respectively. In the lower stratosphere at low and mid latitudes increased penetration of UV radiation, resulting in the so-called self healing effect, leads to increased levels of ozone. The growth in methane leads to increases in ozone in the entire troposphere, with maximum increases in the upper tropical troposphere. The model predicts a steady increase from 5% to 20% between the years 1980 to 2020.

In the lower stratosphere, where ozone is mainly transport dependent, the isolines for constant percentage change slope poleward and downward due to the prevailing circulation pattern (see discussion in Solomon et al., 1985). This transport feature is the main cause for the marked latitudinal gradient in changes of the total ozone columns due to increased levels of chlorine and nitrogen in the stratosphere. Maximum depletions occur at high latitudes during winter and spring when the poleward and downward transport is most pronounced.

As pointed out by Isaksen and Stordal (1986) the latitudinal gradient in total ozone depletion caused by increase of stratospheric chlorine and nitrogen is enhanced by the effect of CH_4 increase. However, even if the low latitude ozone columns are only modestly changed, the height distribution of ozone is highly distorted. These changes are believed to have the potential for large climatological effects (WMO, 1986). In the present (1986) atmosphere, the estimated ozone changes are modest, as discussed in Section 4. The situation may, however, be quite different already at the turn of the century, when large depletions in the upper stratosphere are estimated to take place. By that time depletion in ozone column densities may exceed 5% at middle and high latitudes. Towards the year 2020 ozone depletion will continue to grow strongly, as a result of the pronounced increase in release rates of the chlorocarbons.

Fig. 5 shows the time-dependent depletion in globally and seasonally averaged total ozone column densities. The curves represent the four chlorine scenarios (see Table 2). N_2O and CH_4 increases are assumed in all the results depicted in Fig. 5. An ozone reduction of 1% compared to the 1960 level was reached some time between 1980 and 1985. Note that the effect of temperature changes is not included in the results presented in this and the forthcoming sections. In the scenario where the chlorine releases are kept constant at 1980 levels, the ozone reduction continues to increase to about 2% in 2010. For the rest of the time period considered the global ozone is practically unchanged. In the three remaining scenarios with increasing chlorine releases, ozone columns in the entire time period in question decrease. At the year 2030 the ozone reductions are 8.5% in the scenario C case, 5.0% in the scenario D case and 6.5% in the case (B) with 3% increases in chlorine emissions. All values refer to average global reductions. These values can be compared to results obtained by the

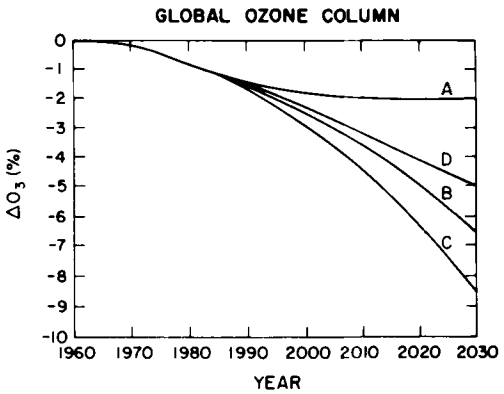

Fig. 5. Calculated changes in globally and seasonally-averaged ozone column as a function of time for the four chlorine scenarios (Table 2). Increases in N_2O (0·25%/year) and CH_4 (1%/year) have been included.

1-D model of Wuebbles (1983) which has been run for our scenario C (Wuebbles, 1986; private communication) with as well as without temperature changes. In the latter case the reductions are slightly less in his model as compared to ours. The time evolution is, however, very similar in the 1-D and 2-D model runs.

Fig. 4 showed a pronounced latitudinal gradient in the ozone changes. At high latitudes we also find marked seasonal variations. In order to illustrate the latitudinal effect we show time variations of ozone column densities at different latitudes in the constant chlorine release case (Fig. 6). The spring values have been chosen since the latitudinal gradient is largest at that time of the year (see Fig. 4). Even if the globally and seasonally averaged ozone column densities show small changes towards the year 2030, the column densities are still decreasing markedly at high latitudes. For instance, the reduction in the year 2030 is 8.3% at 60°N latitude, 3.8% at 40°N, while the global average reduction is only 2.0%.

The ozone reductions at 60°N latitude during spring are presented in Fig. 7 for the four chlorine scenarios. In all cases N_2O and CH_4 increases are assumed. Ozone reductions are more than twice as large as the globally and seasonally averaged reductions showed in Fig. 5. Particularly in the scenario C case the springtime ozone reduction is pronounced at 60°N. At this latitude the ozone column density decreases at a rate of approximately 0.4% per year in the year 2030. Note that high latitude depletion show little dependence on the scenarios chosen up to year 2000. The depletion is pronounced in all four cases, contrary to what is seen for the global average reductions (Fig. 5).

The most dramatic ozone reduction takes place at high latitudes in the upper stratosphere (see Fig. 4). Fig. 8 compares local ozone changes with time at the 43 km level at 60°N during the winter for different scenarios. In all cases the ozone reduction is more than 30% by the turn of the century, and the depletion continues towards the year 2030. The reductions range from 45% in scenario A to 72% in scenario C.

Based on what has been shown in Figs. 7 and 8, it can be concluded that the ozone depletion at high latitudes, total column depletion as well as local depletion in the upper stratosphere, will be pronounced towards the beginning of the next century, independent of which of the four chlorine scenarios that is adopted.

The temperature is believed to change in the future as a result of an altered distribution of radiatively active gases. Ozone reductions, as predicted in the results presented here for the

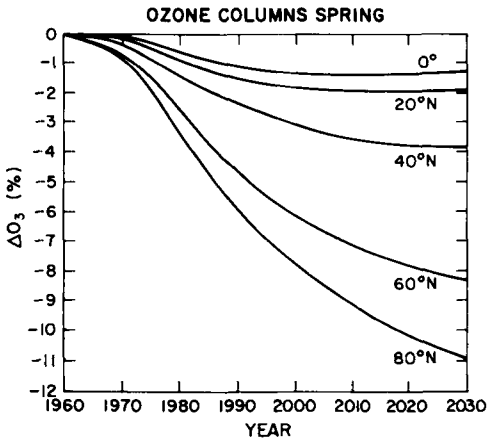

Fig. 6. Changes in total ozone colomn with time for various latitudes. The results are for the spring in the case of 1980 level constant chlorine emission (scenario A) and growth in N_2O and CH_4.

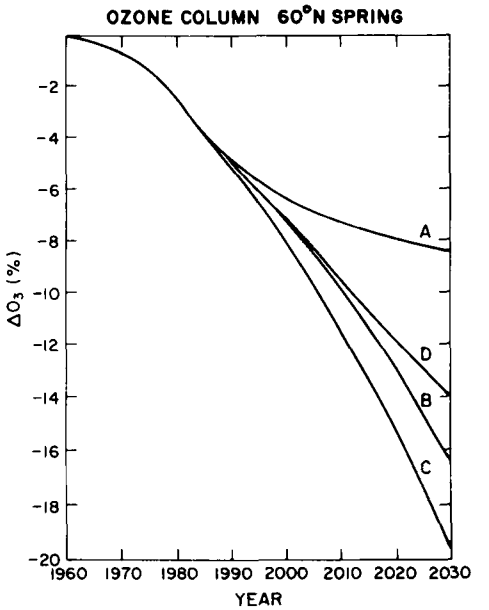

Fig. 7. As Fig. 5, but for the ozone column at 60° during spring.

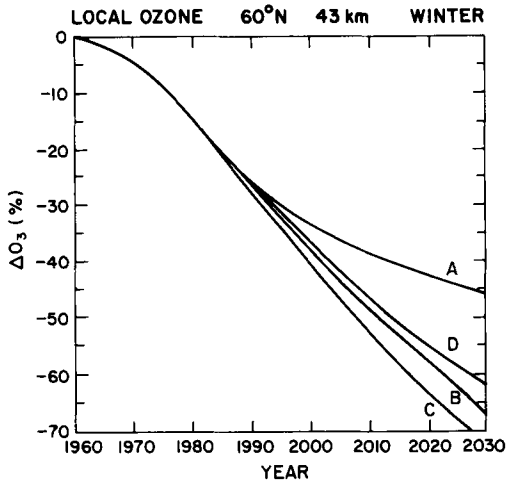

Fig. 8. As Fig. 5, but for local ozone densities at 60°N at the 43 km level during winter.

middle and upper stratosphere, will lead to temperature reductions. In addition CO_2 and other radiatively active gases which are increasing in the atmosphere at present, and also leading to reductions in the stratospheric temperatures (see, e.g., Ramanathan et al., 1985; WMO, 1986). These temperature changes will influence the ozone distribution as we have seen in Fig. 3, leading to smaller ozone reductions from increases in stratospheric chlorine and nitrogen, at least in the upper stratosphere.

It is also likely that when the stratospheric temperature distribution is altered changes in the circulation will take place. This in turn will influence the calculated ozone distribution. Ozone is jointly controlled by dynamical and photochemical processes. Even in regions where the ozone chemistry is fast, the dynamics can be of importance through the distribution of other longlived species. The works of Fels et al. (1980) and Schoeberl and Strobel (1978), however, indicate a thermal rather than dynamical response to O_3 and CO_2 temperature perturbations. Their finding supports the approach taken in this study, where we have used fixed dynamics in all the calculations. In their study Fels et al. (1980) assumed uniform perturbations in O_3 and CO_2 making the application of their results somewhat uncertain for the O_3 perturbations presented in this paper.

6. Response in ozone to future regulations in chlorine releases

The results presented in this and other studies show that large ozone depletions, especially at high latitudes (see Section 5) wil take place early in the next century if the chlorine emissions continue to grow. Extended emission control could then be imposed. In some experiments we have therefore studied the effect of reductions in chlorine releases. In Fig. 9 the effect of a cease in chlorine releases is demonstrated. In two of the cases, the constant 1980 level release case (scenario A) and the 3% yearly emission increase case (scenario B), the emissions are assumed to come to a halt in the year 2000. N_2O and CH_4 have still, however, been assumed to continue their increases. In both cases the globally and seasonally averaged ozone column density continues to decrease for a period after the cease of the emissions; about 3 and 5 years in the scenarios A and B, respectively. The relatively efficient recovery of the ozone layer after chlorine releases are stopped, is a result of the continued increase in CH_4 releases after the year 2000.

Due to considerable uncertainties in the CH_4 scenario one experiment was performed with constant CH_4 surface mixing ratios (see section 2). In this case ozone is depleted substantially in the years after 1980 even in the chlorine scenario

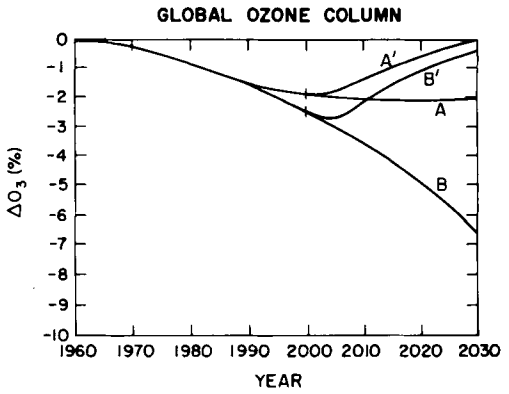

Fig. 9. Calculated changes in globally and seasonally averaged ozone column as a function of time for the chlorine scenarios A and B. Also included is the change in ozone column after a cease in the chlorine emissions after the year 2000 (A' and B'). Growth in N_2O and CH_4 is included.

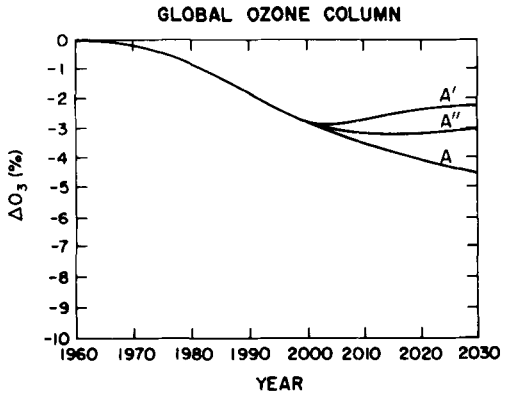

Fig. 10. Calculated changes in the globally and seasonally averaged ozone column for the chlorine scenario A when CH_4 is assumed to be constant after 1980. Also included are cases when the chlorine emissions are ceased in the year 2000 (A') or reduced by 7% annually after the year 2000 (A').

A case. In the year 2030 the reduction in the global ozone column density reaches 4·5% (see Fig. 10).

The future CH_4 evolution will also have a pronounced influence on the recovery of the ozone column after a potential stop in chlorine releases. One of the experiments described in Fig. 10 repeats the experiment with chlorine releases stopped in the year 2000 (chlorine scenario A) assuming now constant future CH_4. In this case the recovery of the ozone layer is slower. In the period 2020–2030 in this experiment ozone continues to recover in the upper stratosphere due to decreases in stratospheric chlorine. In the middle and lower stratosphere there is a weak ozone reduction, mainly attributed to the N_2O growth, compensating for the production in the upper stratosphere such that the globally averaged total column is almost constant throughout the period.

So far, results of a total removal of chlorine emissions have been demonstrated. A prompt cease in the emissions at a certain time, as we have assumed in the year 2000, must be considered unlikely. A gradual reduction of the emissions could be more conceivable. A scenario with a 7% yearly decrease in CFC emissions starting in the year 2000 (after constant releases from 1980, scenario (A)) is therefore included in Fig. 10 in the constant CH_4 case. This case is identical to scenario IX in the OECD (1981) report. In this particular case it takes about 15 years to reach a minimum in ozone column densities and the increase thereafter is extremely slow in agreement with the 1-D calculations of Wuebbles (1983). 30 years after the implementation of an emission reduction the global ozone depletion is 3.1%, compared to 4.5% in the case without emission reductions.

As discussed in Section 5 (Fig. 6), the ozone column decays more rapidly at higher than at lower latitudes. Correspondingly, when chlorine releases are ceased, the increase will be faster. This is demonstrated in Fig. 11, which shows results from 60° latitude in the experiments where chlorine releases were ceased in the year 2000 in the scenario A and B cases (Fig. 9). The local behaviour of ozone at 60° northern latitude at the 43 km level is similar to the behaviour of total ozone. Minimum ozone is obtained about 5 years after the emissions are ceased, and ozone recovery is fast thereafter. When emissions are reduced by 7% per year instead of being ceased, the period of decreasing ozone is prolonged to 13 years.

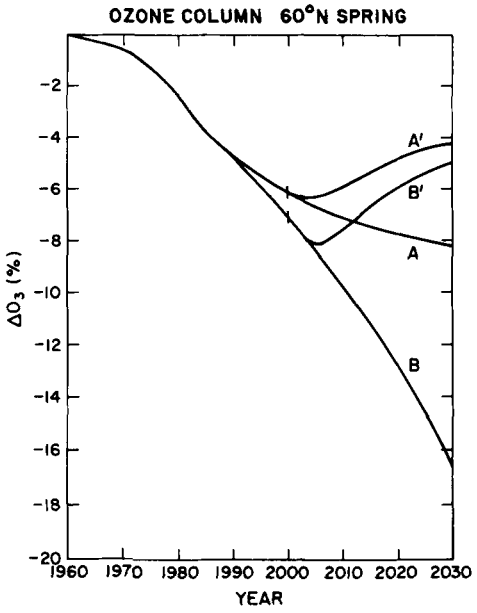

Fig. 11. As Fig. 9, but for the ozone column at 60° northern latitude during spring.

7. Non-linear ozone reductions at very high chlorine levels

Since Cicerone et al. (1983) reported a pronounced non-linear relationship between ozone reductions and increases in stratospheric chlorine, this relation has been subject to extensive studies. Cicerone et al. (1983) found a more rapid growth in ozone reductions than in stratospheric chlorine for Cl_x mixing ratios up to about 10 p.p.b. Prather et al. (1984), Hermann and McQuillan (1985) and Isaksen and Stordal (1986) found the relationship to be almost linear in this Cl_x range. They found, however, a faster growth in ozone reductions than in Cl_x mixing ratios from the point where Cl_x becomes larger than the amount of statospheric NO_y (total odd nitrogen). It was therefore of interest to see if this situation occurred in the time dependent experiments described in this paper. The values for Cl_x and NO_y in case C, the scenario with the largest chlorine emissions, are shown in Fig. 12. The Cl_x abundancy increases rapidly after the turn of the century and reaches 12 p.p.b. in the year 2030, well below the predicted 25 p.p.b. of NO_y. The point of increasingly growing ozone reductions is therefore reached much later than the year 2030 in all the calculations presented here. As discussed in Isaksen and Stordal (1986) there is still a considerable uncertainty in the modelled NO_y (as well as in NO_y measurements). The lower the values of NO_y, the earlier the accelerated ozone depletion will start. The NO_y results presented include an increase in N_2O of 0·25% per year, a growth rate which is somewhat uncertain. The accompanying increase in NO_y values is much slower than the growth in Cl_x. In the 50 years time period from 1980 to 2030 the stratospheric level of NO_y has incrased by 16.5%.

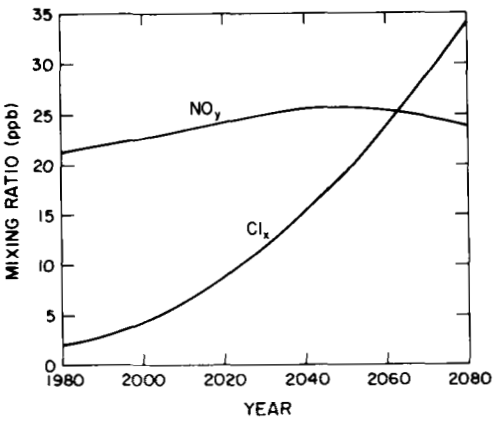

Fig. 12. Maximum stratospheric levels of Cl_x and NO_y as function of time, in the chlorine scenario C case (see Table 2) with simultaneous increases in N_2O and CH_4 until the year 2030.

To study the alterations in the ozone chemistry when Cl_x reaches the level of NO_y, we have run the scenario (C) case for an additional period of 50 years. The chlorine release rates for this period are also contained in Table 2. The yearly growth in emissions for CF_2Cl_2 and $CFCl_3$ decrease from about 2% in the year 2030 to less than 1% 50 years later. Since the predicted increases in CH_4 and N_2O are based on presently observed trends, we find their scenarios to be highly uncertain in the middle of the next century. We have therefore assumed constant surface mixing ratios for CH_4 and N_2O in the period 2030–2080. This assumtion is also convenient for the present study since Cl_x levels then will exceed the level of NO_y earlier. With the adopted scenario Cl_x catches up with NO_y between 2060 and 2070 and reaches 34 p.p.b. in the year 2080.

As pointed out by Isaksen and Stordal (1986), their steady state experiments showed that for high levels of stratospheric chlorine the most significant ozone reduction will be in the lower stratosphere. Fig. 13 illustrates that the time-dependent calculations confirm this behaviour. The absolute changes in ozone concentrations in 3 different 10-year periods are given as altitude-latitude contour plots. In the first period, 1980–1990, the poleward and downward transport results in maximum ozone depletions at high latitudes in the lower stratosphere. At mid and low latitudes the largest depletions are confined to the middle stratosphere. Forty years later, in the period 2020–2030, the depletions in the middle stratosphere as well as the self healing effect at middle and low latitudes have been intensified. The zero line separating the two regions has descended 2-3 km. As in the former period, the maximum decrease in the upper region (at mid and low latitudes) is similar in magnitude to the maximum increase in the lower region. This is no longer the case in the period 2060–2070 when the nonlinear growth in ozone depletions at low and middle latitudes have started. Maximum deple-

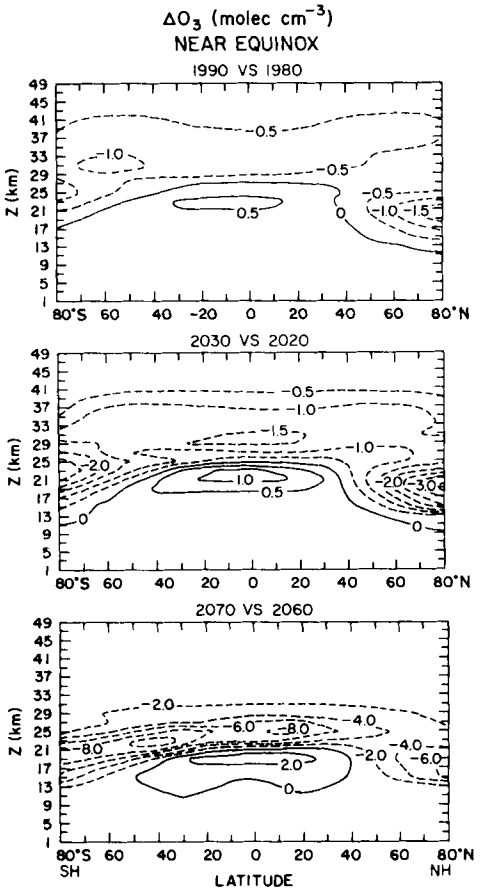

Fig. 13. Changes in ozone densities (10^{11} molec cm^{-3}) as a function of altitude and latitude in the experiment discussed in Section 6. The changes are given for the 10-year intervals 1980–1990, 2020–2030 and 2060–2070 for near equinox conditions.

tions are found (as in Isaksen and Stordal, 1986) in the 25 km region where the zero line was located 80 years earlier. The large ozone depletions are due to increase in stratospheric chlorine, which is shown to influence the loss rate of ozone increasingly, even in the lower stratosphere.

We will now focus on the rather dramatic changes in the chemistry of the lower stratosphere that is asssumed to take place by the year 2080 when the stratospheric chlorine level becomes very large. Other chlorine reactions than reaction R7 below must then be considered. Wuebbles and Chang (1981) listed four different chlorine cyles resulting in O_x destruction (the number in brackets to the left-hand side of each equation represent the number of O_x molecules lost in the reaction, as described in Section 3):

cycle 1

(2) $ClO + O \rightarrow Cl + O_2$		R7
(0) $Cl + O_3 \rightarrow ClO + O_2$		R8
net: $O + O_3 \rightarrow 2\,O_2$		

cycle 2

(0) $Cl + O_3$	$\rightarrow ClO + O_2$	R8
(0) $NO + O_3$	$\rightarrow NO_2 + O_2$	R9
(0) $ClO + NO_2 + M$	$\rightarrow ClONO_2 + M$	R10
(1) $ClONO_2 + h\upsilon$	$\rightarrow Cl + NO_3$	R11
(1) $NO_3 + h\upsilon$	$\rightarrow NO + O_2$	R12
net: $2\,O_3$	$\rightarrow 3\,O_2$	

The dissociation of NO_3 has an alternative pathway to reaction (R12). Only the fraction of the dissociation forming NO ($\frac{1}{9}$, see NASA/JPL, 1985) leads to O_x destruction. The net loss term for cycle (2) is then $\frac{2}{9}\,J_{11}\,ClONO_2$ since the $ClONO_2$ dissociation is the rate limiting step (see e.g. Wuebbles and Chang, 1981; Cicerone et al., 1983).

cycle 3

(0) $Cl + O_3$	$\rightarrow ClO + O_2$	R8
(0) $ClO + NO$	$\rightarrow Cl + NO_2$	R13
(2) $NO_2 + O$	$\rightarrow NO + O_2$	R6
net: $O + O_3$	$\rightarrow 2\,O_2$	

cycle 4

(0) $Cl + O_3$	$\rightarrow ClO + O_2$	R8
(0) $ClO + HO_2$	$\rightarrow HOCl + O_2$	R14
(1) $HOCl + h\upsilon$	$\rightarrow OH + Cl$	R15
(1) $OH + O_3$	$\rightarrow HO_2 + O_2$	R2
net: $2\,O_3$	$\rightarrow 3\,O_2$	

At very high chlorine levels, HOCl dissociation (R15) becomes faster than the rate of the reaction $OH + O_3$ (R2). Another reaction is then converting OH to HO_2, namely OH + ClO, constituting a 5th O_x loss cycle:

cycle 5

$Cl + O_3$	$\rightarrow ClO + O_2$	R8
$ClO + HO_2$	$\rightarrow HOCl + O_2$	R14
(1) $HOCl + h\upsilon$	$\rightarrow OH + Cl$	R15
(1) $OH + ClO$	$\rightarrow HO_2 + Cl$	R16
$Cl + O_3$	$\rightarrow ClO + O_2$	R8
net: $2\,O_3$	$\rightarrow 3\,O_2$	

Cycle 1 is the only pure chlorine cycle, while the 4 remaining cycles involve nitrogen (2 and 3) and hydrogen (4 and 5) compounds. As noted in Wuebbles and Chang (1981) the distribution of the ozone loss between the individual families is then not obvious. We have taken the following approach in this study:

Cycle 3 has the O_x loss reaction (R6) in common with the pure nitrogen catalytic cycle

$$NO_2 + O \rightarrow NO + O_2 \qquad R6$$
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad R17$$

We distribute the O_x loss between the two cycles so that T17/(T13 + T17) is attributed to the pure nitrogen chain and the remaining T13/(T13 + T17) to chlorine cycle (3). Here T_n represents the rate k_nXY of reaction R_n with X and Y as reactants.

The rate limiting process in cycle 5 is reaction (R16). The loss rate of cycle (5) is therefore set to the rate of R16 times two, since two O_x are lost in each cycling. The HOCl dissociation (R15) is common for cycles 4 and 5. the part of the rate of this reaction which exceeds the rate of R16 is attributed to cycle 4. This cycle has reaction R2 common with the pure hydrogen loss chain

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad R2$$
$$HO_2 + O_3 \rightarrow OH + 2\,O_2 \qquad R3$$

Only the part of the rate of R2 which has not been involved in the chlorine cycles 4 and 5 is attributed to the pure hydrogen caused O_x loss.

Fig. 14 shows the fraction of the O_x loss attributed to the various chlorine cycles in the year 2080. Altitude-latitude cross sections are given for the season March-May. In the region of chemical control chlorine cycles stand for at least 80% of the total loss. The contribution of the pure hydrogen cycle is reduced to less than 10% except around the stratosphere where a 10% influence remains. The influence of the pure nitrogen cycle as well as the oxygen cycle is also less than 10%. Chlorine cycle (1) is dominating, even in the lower stratosphere. At low latitudes this cycle stands for 70% of the total loss at the 25 km level. In the middle stratosphere cycle (3) is the second largest depletion cycle, attaining a maximum of more than 30%. The chlorine cycle (2) involving chlorine nitrate is effective only at very low altitudes at high latitudes where contributions of 10-20% are obtained. Below the 25 km level the two cycles involving HOCl, cycles 4 and 5, gradually increase their influence. Each of these cycles contribute to the O_x loss with about 10-20% in the transition region. Since the ozone chemistry has become faster in the lower stratosphere the transition region has lowered. For instance, the contour line representing a chemical lifetime of 40 days has descended 5 km during the period 1980-2080 (most of it the last 50 years). The descent of the transition region will significantly influence the poleward and downward transport to high latitudes, since the source regions of largest influence are moved downward to locations with lower ozone mixing ratios.

Since the chemistry of O_x in the year 2080 is dominated by the chlorine cycles, as demonstrated in Fig. 14, the explanation to the accelerated growth in ozone depletion must be sought in the chlorine chemistry. At all altitudes above the 30 km level more than half of the ozone has vanished in the year 2080, leading to a slower growth in ozone depletions there. Accelerated depletion of the total column can only take place due to the highly non-linear increase in ozone reductions in the lower stratosphere which was demonstrated in Fig. 13.

The explanation for the accelerated chlorine influence can be found in the changes in the balance between ozone depleting components and passive reservoirs in the chlorine chemistry in the lower stratosphere (Cicerone et al., 1983; Prather et al., 1984). The calculations show that HCl has effectively been converted mainly to ClO but also $ClONO_2$ in this region in the period 2030-2080.

The explanation for the increase in the fraction of ClO must be sought in changes in components determining the balance between the chlorine components. Fig. 15 shows the change in the period 2030-2080 in some key components as well as in the ratio between ClO and HCl. The increase in the ratio ClO/HCl is large in the lower stratosphere. At the 25 km level at low latitudes this ratio has increased by a factor 3-4 in the 50 year period in question. The ratio can be expressed as a product of the ratios ClO/Cl and Cl/HCl. The first of these ratios, ClO/Cl, increases by a factor of about 2 since the NO concentrations drop (Fig. 15), lowering the rate of reaction R13. The Cl/HCl ratio increases by a factor 1.5-2 in the lower stratosphere at low latitudes, since CH_4 decreases and OH increases

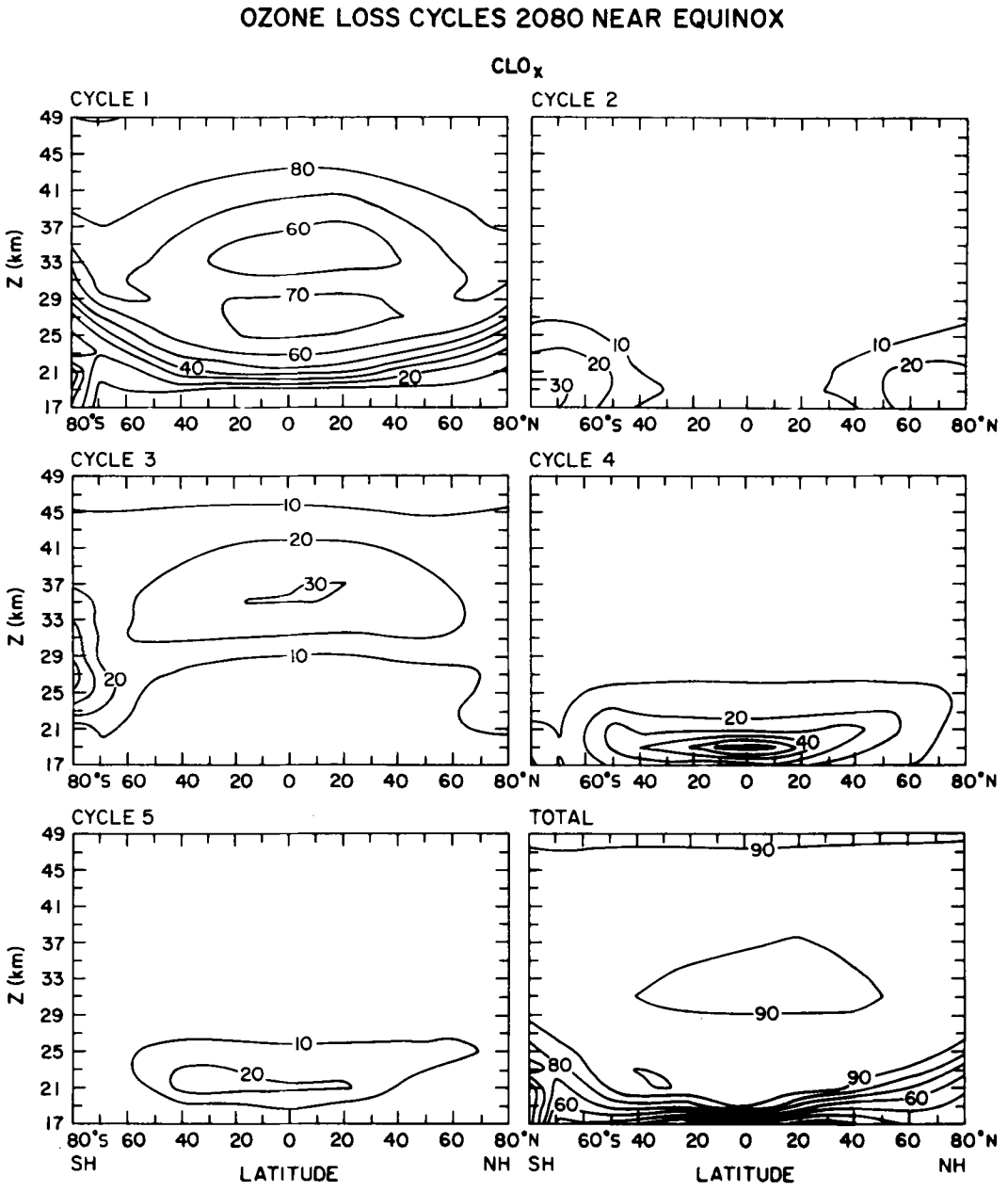

Fig. 14. Percentage ozone loss rates due to ClO_x cycles (see text, Section 7).

(Fig. 15), both favour an increase in the Cl/HCl ratio. As discussed by Isaksen and Stordal (1986) CH_4 decreases since OH increases and since the reaction

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad R18$$

becomes a significant loss reaction for CH_4 in the upper stratosphere. OH increases due to lowered levels of HNO_3 and HO_2NO_2 (Prather et al., 1984) as well as an efficient transformation from HO_2 via HOCl (see detailed discussion in Isaksen and Stordal, 1986).

The time-dependent experiments described

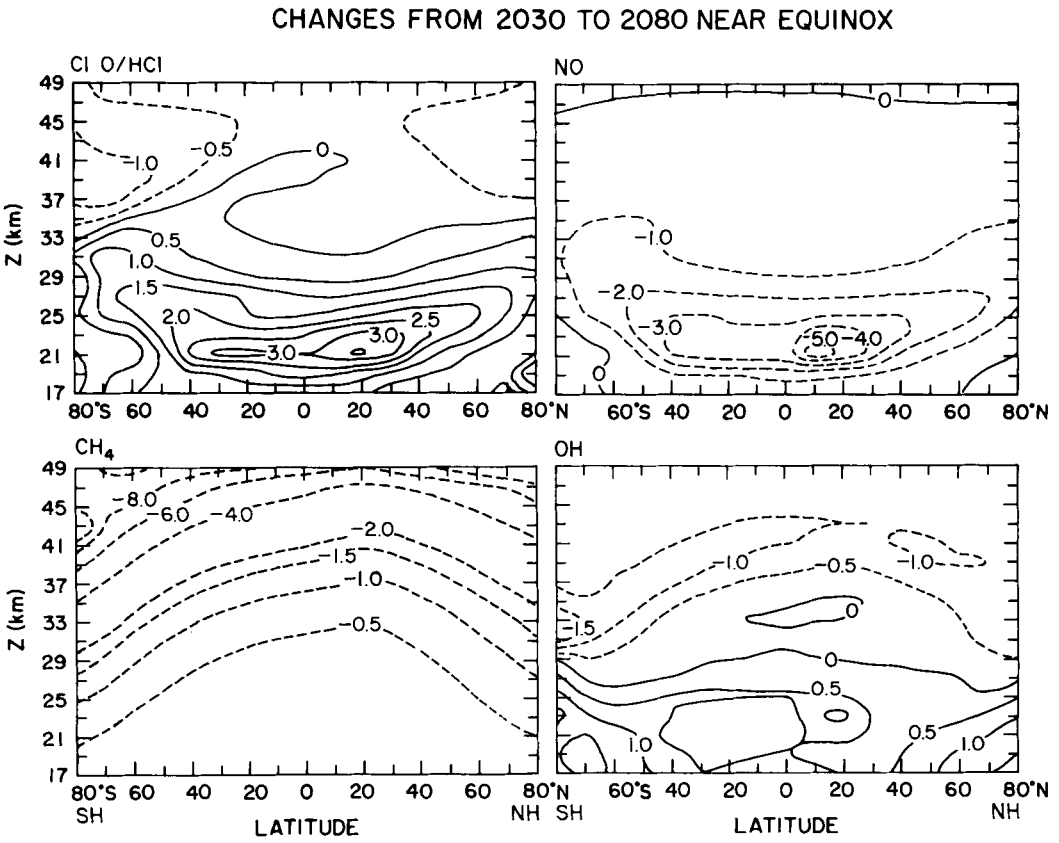

Fig. 15. Changes in one ratio and three components in the period 2030–2080 in the experiment considered in Section 7. Altitude-latitude cross sections are given for the quantities $\log_2 (\mu_{2080}/\mu_{2030})$ where μ represent, firstly the ratio ClO/HCl, secondly the mixing ratios of NO, CH_4 and OH.

here confirm the point made by Prather et al. (1984) and Isaksen and Stordal (1986) that accelerated ozone depletion at high chlorine levels occurs as a result of the fractional ClO increase. HOCl and to some extent $ClONO_2$ contribute to the non-linearity.

According to the present understanding of the chemistry of the stratosphere (NASA/JPL, 1985) the transformation of the active components Cl and ClO to the main reservoir HCl takes place through Cl reactions. At high chlorine levels, when the Cl-ClO balance is shifted towards the latter component the loss mechanisms for Cl + ClO are less efficient. Isaksen and Stordal (1986) demonstrated, however, that only small yields of reactions like ClO + OH and HOCl + hυ for pathways leading to HCl formation could decrease the non-linear ozone depletion significantly.

8. Conclusions

Two different scenarios for future release rates (Quinn et al., 1986) of several chlorocarbons have been used in the present work to study the time evolution of ozone in a 2-D diabatic circulation model. Even with the most conservative assumptions substantial decrease in the global ozone column is predicted early in the next century. This depletion will take place despite ozone increases in the troposphere due to increases in CH_4. Large latitudinal gradients in the ozone depletion are found, demonstrating the need for 2-D models in studies of stratospheric perturbations. The model estimates show that reductions in the total column will first take place at high latitudes, especially during winter and spring, and that the largest depletions occur in the upper stratosphere. The latter estimates are in agree-

ment with observed trends in the period 1970-1980 (Reinsel et al., 1984).

The work of Quinn et al. (1986) suggests increases in CFC releases in coming decades, making time dependent, as opposed to steady state, calculations necessary for the evaluation of future ozone. Due to the long lifetimes of several chlorocarbons, the ozone response to chlorine releases is highly delayed. It is therefore important to notice that the releases of the first decades to come will lay the ground for the ozone depletions in a large part of the next century.

The accelerated ozone depletion that has been predicted when the level of stratospheric chlorine approaches the level of odd nitrogen compounds (NO_y) (see, e.g., Prather et al., 1984; Isaksen and Stordal, 1986) will, according to the present study, not take place until after the middle of the next century, even in the highest chlorine scenario case of this study. As the amount of NO_y present in the stratosphere today is connected with uncertainties, better knowledge of NO_y is needed before we can determine the time when possible non-linear growth in stratospheric ozone can be expected. This question is of great importance, since rather dramatic ozone depletions can be expected from that time. The reason for this accelerated depletion is diagnosed to be changes in the partitioning between chlorine species in the lower stratosphere.

The future ozone depletions presented in this paper represent the purely photochemical response to increases in CH_4, N_2O and the chlorocarbons. Preliminary results from the same model indicate that when the temperature changes are taken into account (from O_3 and CO_2 changes) the predictions for the total ozone columns are changed only moderately. The accompanying changes in the dynamics of the stratosphere and its feedback to the ozone are still uncertain. The work of Fels et al. (1980) and Schoeberl and Strobel (1978) indicate that the response to changes in temperatures will be thermal rather than dynamical.

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