

**Report 1994:3**

**The state of the  
ozone layer**

**A 1994 science update**

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**The State of the Ozone Layer:  
A 1994 Science Update**

by

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## Summary of recent findings

Both the ground based and satellite observation data bases have been extended since the previous international ozone assessment. There are several satellite systems in operation that provide total ozone data, which have been extensively compared with ground based data. One problem with the satellite observations is that the widely used satellite data from the TOMS instrument on the NIMBUS 7 satellite have not been available since the beginning of May 1993 due to satellite failure. A new TOMS instrument was launched on a Russian spacecraft in August 1991 and have been in continuous operation since then. Although this gives continuous TOMS observations, there are still questions about how good the trend estimates after May 1993 are using the new TOMS data. We should also bear in mind that, although, we have extended data sets by including the last years of observations, the deduced trends are strongly affected by the low values of total ozone obtained during 1992 and 1993, and there are uncertainties how representative these low values are in connection with long term ozone depletion studies.

Ozone research has to a large extent focused on ozone reductions at high northern latitudes during the last three to four years. Of particular interest has been the low ozone column densities observed at high and middle northern latitudes during the winters of 1992 and 1993. A natural question which has been raised is whether or not we here see a result of enhanced chlorine and bromine levels which in combination with special atmospheric conditions lead to enhanced ozone depletion. The June 1991 volcanic eruption of Mt. Pinatubo led to high particle concentrations in the lower stratosphere the following two years, in addition the extreme low temperatures at high northern latitudes during the winter of 1993 resulted in Polar Stratospheric Cloud (PSC) formation that was substantially higher than during a "normal year". Both these conditions led to more efficient ozone loss than we have experienced in previous years, and in 1994.

Several of the source gases of importance for the ozone depletion problem have shown reduced growth rate during the beginning of the 1990s. These changes in observed growth rate are difficult to explain for most gases. For the CFCs, however, it seems that reduced growth is a result of reduced emissions which is as a result of the control measures that have been implemented to protect the ozone layer. A further consequence of this is that we within the next few years can expect stratospheric inorganic chlorine levels to peak, whereafter a gradual decrease will occur over the next century. This shows that the Montreal agreement has been a success, which has led to substantial reductions in the emission of CFCs. Another consequence of the Montreal agreement is a significant increase in the HCFCs over the last couple of years. However, the absolute levels of the newly introduced HCFCs, like HCFC-141b and HCFC-142b, are very low.

The significant reduction in the growth rate in other source gases like CH<sub>4</sub>, N<sub>2</sub>O and CO<sub>2</sub> during the beginning of the 1990s is somewhat puzzling, as there are no good explanation why this has occurred. There are, however, indications that for some gases (e.g. CH<sub>4</sub>) the reduced growth rate could be partly due to the large column ozone reductions.

Methyl bromide and its potential role in the ozone depleting process have drawn increased attention since the previous ozone assessment. One of the largest uncertainties in the estimates of future man made impact on the ozone layer is connected to limited understanding of the role of methyl bromide. Methyl bromide is the main contributor to reactive bromine (BrO and Br) in the stratosphere. Measurements show that its concentration in the troposphere is about 10 to 15 pptv. Important uncertainties are connected to how large the man made contribution is to its sources, and to its tropospheric

lifetime. Emissions occur both from anthropogenic and biogenic sources. An important anthropogenic source is from the use of pesticides which showed marked increase during the 1980s. Other anthropogenic sources are biomass burning and automobile emissions. Large oceanic emissions have been suggested. The main sink is believed to be atmospheric oxidation by OH, but there may also be important oceanic sinks. The overall lifetime is in the range 1 to 2 years (loss through OH alone gives a lifetime of approximately 1.7 years).

There have also been made advances in modelling of ozone and ozone changes in the stratosphere. The estimates of ozone distribution and ozone changes rely heavily on 2-D model calculations. These model studies do now include the impact of heterogeneous processes occurring on aerosol particles and to some extent on PSCs. New laboratory studies have given us a better basis for estimating the impact of heterogeneous processes, and it is clear that heterogeneous chemistry in the lower stratosphere are the main cause of total ozone loss which take place as a result of enhanced ozone loss from chlorine and bromine species. Model calculations indicate that probably 2/3 or more of ozone depletion by chlorine and bromine compounds occur in the lower stratosphere as a consequence of heterogeneous reactions on particles. Inclusion of heterogeneous chemistry in the atmospheric models have made bromine reactions more important for the ozone depleting process. As a global average one bromine atom is estimated to be approximately 40 more efficient in destroying ozone than one chlorine atom. Approximately 20 % of the ozone destruction in the present day stratosphere is estimated to be due to chemical reactions involving BrO.

Estimates of Ozone Depletion Potentials (ODPs) are in agreements with previous estimates, although more emphasis is given to the shortlived compounds (HCFCs, methyl bromide). Such compounds have transient ODPs, over limited time horizons (20 to 100 years) which can be much larger than the long term steady state ODP. A typical example is the ODP for methyl bromide which has a long term ODP value of 0.71, while the value over a time horizon of 20 years is 2.3.

Increasing attention is given to the possible interaction between the ozone and the climate issues through chemical changes initiated by ozone changes in the atmosphere which affect climate gases (including ozone itself). This issue has been treated in the ozone assessment in close collaboration with the treatment of indirect chemical effects in the ongoing IPCC (Intergovernmental Panel for Climate Change) assessment of climate change (IPCC, 1994). Although this is a controversial issue, where the uncertainties are large in the estimates, it is nevertheless clear that chemical changes involving ozone will be of importance for estimates of GWPs (Global Warming Potentials) for important greenhouse gases like CH<sub>4</sub> and the CFCs. The indirect effect of CFC, through ozone reductions in the stratosphere, seems to give a negative effect which is as large as the direct effect but with opposite sign.

New model studies of the impact of a projected future fleet of supersonic transport on ozone through the emission of NO<sub>x</sub> show that it is probably small. This is a result of strong coupling between the nitrogen and chlorine compounds where reduced efficiency of chlorine reactions compensate for enhanced ozone loss through increased nitrogen oxides.

New observations of UV-B fluxes in the polar regions confirm observations that were referred to in the previous international ozone assessment that the observed ozone reductions during the last years have led to significant increases in harmful UV-B radiation during the periods of low ozone values. Model studies indicate that the increases in tropospheric UV-B radiation during the last years with low column densities significantly have affected tropospheric chemical processes involving key gases like ozone and OH.

## 1. Background

The 1994 scientific assessment of ozone depletion (WMO, 1994) discusses and summarizes the development in the area of ozone depletion after the previous assessment (WMO, 1992). Although only 3 years separate these two assessments significant developments have occurred in this time period as a result of enhanced research activities. In particular, extensive field campaigns have been launched during the last few years to study the Arctic stratosphere and the stratosphere at middle Northern Latitude and if possible identify man made impact on the ozone layer. For instance, there has been a US sponsored campaign (AASE II) which is a follow up to the earlier (1989) AASE I campaign with extensive measurements of ozone and ozone relevant gases, and there have been two European campaigns EASOE and the ongoing SESAME. The latter two campaigns include airborne measurements from balloons and ground based measurements. Observations from these campaigns are supported by new satellite observations like the UARS observations, and give a comprehensive picture of state of ozone layer, and expand our previous knowledge.

New research studies which focus on the role of bromine compounds in the ozone depleting process have been initiated during the last few years. These studies are in particular directed toward understanding the atmospheric behavior of methyl bromide and its contribution to active bromine in the stratosphere, and thereby to the ozone depleting process. Two international workshops, where the scientific issues of methyl bromide in relation to stratospheric ozone, have been held during the last two years: "The Methyl Bromide Science Workshop" in Arlington, Virginia, 2-4 June 1992, and "Methyl Bromide State of the Science Workshop" in Washington DC October 28, 1993. These workshops have provided us with an update of current knowledge on methyl bromide and the role of bromine reactions in the ozone depleting process.

Major developments have occurred in the understanding of ozone- climate relations. The focus has been directed on two areas: a) Ozone itself as a climate gas, and b) the impact imposed by ozone changes on climate gases affected by atmospheric chemistry. Methane is the most important in the latter group. The realization of the interaction between ozone and climate has led to close coordination of international assessments of ozone (WMO, 1994) and climate (IPCC, 1994). A recent workshop (NATO ARW: Ozone as a climate gas, coordinator W.-C. Wang, held at Lillehammer, Norway, June 19-23, 1994) discussed the science issues related to ozone's role as a climate gas, and problems related to the treatment of climate-chemistry interactions in modeling the impacts.

Studies of environmental impact of stratospheric ozone changes through increased UV-B radiation has been closely linked to the ozone assessments, for instance in connection with the WMO (1992) report, and the UNEP (1992) report. A similar report is under way in connection with the new WMO (1994) report. There is also a thorough discussion of the science issues in NATO (1994).

One area which is now being studied extensively is the impact of air traffic on atmospheric chemistry. A main issue is the impact on ozone. A major effort is through research coordinated by the NASA High Speed Research Program (NASA HSRP, 1993) where  $\text{NO}_x$  emission by a projected future fleet has been studied. Similar programs for studies of subsonic aircraft are recently being initiated both in the US and in Europe. The focus here is directed more toward climate issues.

Atmospheric observations have shown that the Montreal agreement on the reduction of ozone depleting substances have already had a significant influence on the growth rate of chlorine

compounds in the atmosphere. The latest renegotiation on the Montreal Protocol, which took place in Copenhagen in November 1992, resulted in a phaseout of the major chlorine compounds within 1996. A result of this is a sharp decrease in emissions, and it is probable that maximum chlorine levels in the stratosphere will be reached within the next few years. Exceptions are the decisions regarding HCFCs and methyl bromide. For HCFCs the reductions have a longer time horizon (approximately 30 to 40 years). The decision on methyl bromide is to stabilize emissions in 1995 on the 1991 level. The decision on methyl bromide, or rather lack of decision, considering its likely important role for ozone depletion, reflects the lack of knowledge concerning methyl bromide and its role in the ozone depleting process.

A discussion of some of the main recent development in the ozone area is given below.

## 2. Observed trends in stratospheric ozone.

Extended series of observations of total ozone column densities, ozone profiles in the lower stratosphere, and free tropospheric ozone conform previous observations of reductions in column ozone and lower stratospheric ozone, and increases in tropospheric ozone in the Northern Hemisphere.

### 2.a Ozone reductions over Antarctica.

During the last Austral spring (October 1993) column ozone densities over the Antarctica were lower than ever measured before. At October 12, 1993 total ozone values as low as 91 DU were measured over the South Pole. Similar low values were measured throughout the region. Figure 1 shows the development of mean spring (Sept., Oct., Nov.) and summer (Jan., Feb., Mar.) values for four ground based stations in the Antarctica through 1993 (Bojkov, 1994). The significant springtime decrease in ozone which has been observed since the mid 1970s over the Antarctica

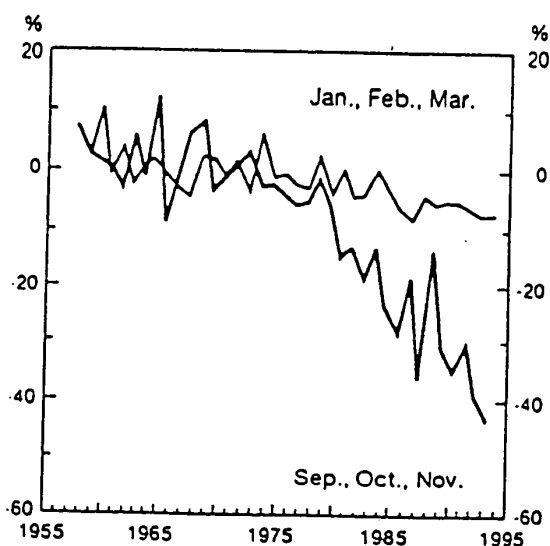


Figure 1. Observed ozone density deviations in the Antarctic from the pre-ozone hole average (1957-1978). Ref.: Bojkov (1994).

continues through 1993, with no signs of ozone recovery. Similar reductions are observed from satellites. The area where there is a significant reduction over Antarctica (less than 200 DU) has been observed to be extended during the last two years during the spring months compared to previous years. On the average the low values cover the areas south of 65 degree latitude.

There is also a downward trend during the summer months, although it is much smaller than during the spring months. Bojkov (1994a) reports that summertime values during 1994 were down by 10 % which is a further decrease from previous years.

Ozone sonde observations confirm previous observations of almost complete ozone reductions in the Antarctic stratosphere below approximately 20 km. The 1993 October observations at the station Syowa is depicted in Figure 2. The observations show decreasing values throughout the month. This is in striking contrast to observed ozone distribution in October during years prior to the development of the "ozone hole" (1967 to 1980). During these early years maxima October values were found at heights below 20 km.

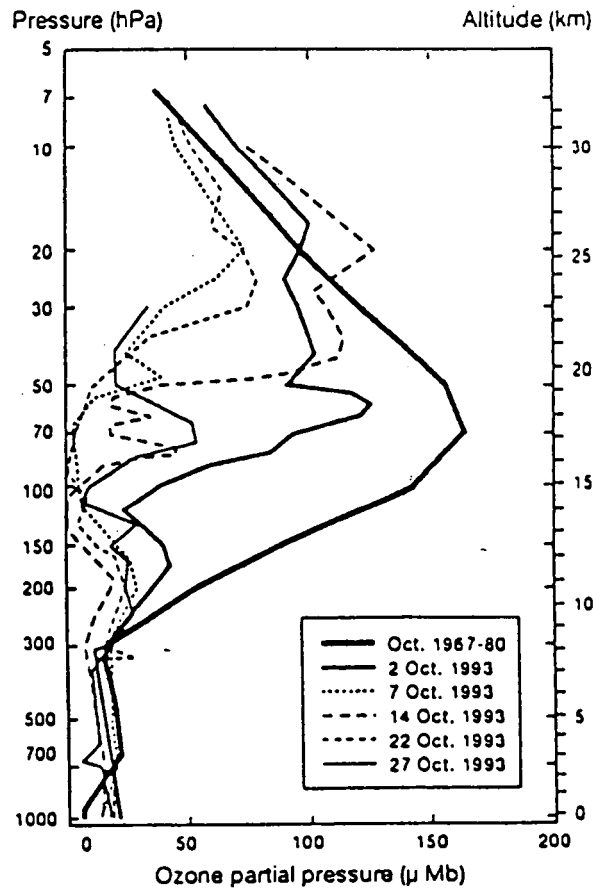


Figure 2. Vertical ozone profile at Syowa (60 degree S) for different days during the month of October 1993. The average ozone profile for the pre-ozone hole years 1967 - 1980 is included for comparison. Ref.: Bojkov, 1994.

## 2.b Ozone reductions at Northern Latitudes.

Column ozone reductions from the Dobson network in the Northern Hemisphere are most pronounced at latitudes north of 40 degree where there has been a clear trend over the last 20 years. This is illustrated in Figure 3 which shows observed column ozone densities for the latitude belt 45 to 65 degree N for the last 30 to 35 years (Bojkov et al., 1993). Observed ozone reductions for the period 1979 to 1993 significant is of the order of 5 % per decade as yearly average north of 40 degree latitude in the Northern Hemisphere, of the order of 1 to 3 % at middle and low latitudes, and no significant trend in the equatorial region. The TOMS observations on the Nimbus 7 satellite give similar but somewhat higher ozone trends. Comparisons of the TOMS data with other observations (Dobson instruments) seem to indicate that during the last couple of years of operation the TOMS instrument on NIMBUS 7 had a slight bias toward too high trends at high latitudes.

Deduced changes in the vertical profile of ozone at Northern Latitudes from satellite observations (SBUV and SAGE I & II), and from Umkehr estimates support the previous sonde measurements from a few stations of significant ozone reductions in the lower stratosphere at mid latitudes. Decadal trends during the 1980s are of the order of 5 to 10 %, and they are obtained in the lower stratosphere below about 20 km. It should also be noticed that reductions of about 5 % are deduced from observations in the 40 km region. This reduction will, however, have less impact on the ozone column density as the ozone concentrations are low in this height region.

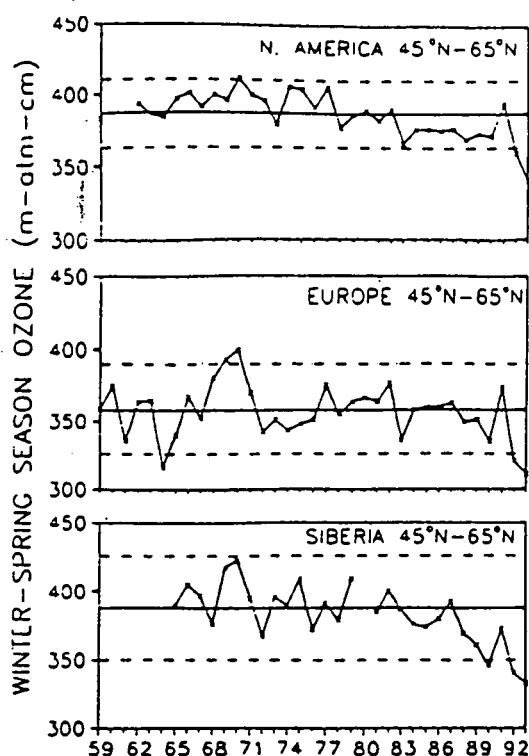


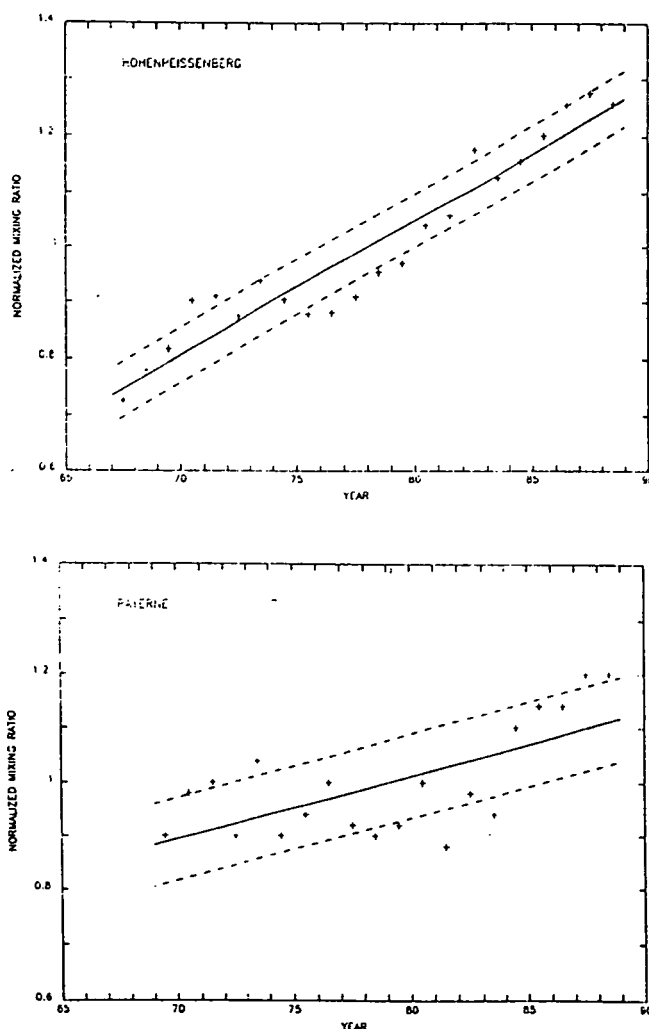
Figure 3. Seasonal mean ozone column densities for the months: December, January, February and March for mid northern latitudes. The  $2\sigma$  confidence limit is also given in the figure. Ref.: Bojkov (1994).



### 3. Increases in tropospheric ozone

Observations have shown that there have been long term increases in the free troposphere and in surface ozone in the Northern Hemisphere on a decadal time scale (Bojkov, 1988; Kley et al., 1988).

Free tropospheric ozone in the Northern Hemisphere, as deduced from ozone sondes, show significant increase since the beginning of the 1970s and through the 1980s (London and Liu, 1992). Data from european stations (Hohenpeissenberg in Germany and Payerne in Switzerland in particular; Figure 4, London and Liu, 1992) indicate increases in free tropospheric ozone up to 50 %, while US and Japanese stations indicate increases of 10 to 20 %. Analysis of ozone data show average increases in the Northern Hemisphere of approximately 10 % per decade in free tropospheric ozone since 1970 (WMO, 1994). Recent studies referred to in WMO (1994) indicate that the strong upward trend over Europe has been levelling off during the first years of the 1990s.



**Figure 4.** Observed changes in the free tropospheric ozone over the two european stations: Hohenpeissenberg in Germany and Payerne in Switzerland. The  $1\sigma$  is indicated on the figure. Ref.: London and Liu (1992).

All studies of the ozone increases show strong regional variations in the ozone trends. Although there are strong indications of human influences on free tropospheric ozone through the observed increases, there is, however, a clear limitation in establishing a long term trend in free tropospheric ozone, since the spatial coverage is poor, and the quality of the data is variable. This puts severe limitations on our possibility to use observations to estimate the human influence on free tropospheric ozone.

Ground based measurements of ozone show a positive long term trend in the Northern Hemisphere, and a negative trend in the Southern Hemisphere. The most pronounced changes are found at high latitudes in both hemispheres (WMO, 1994). Analysis of ozone measurements made during the last part of the last century indicate that ozone was approximately 10 ppt. This is as much as a factor 4 smaller than what is typically found over industrial areas in Europe and North America today. A large part of this increase seems to have occurred since 1950. In a recent review reported in WMO (1994) it was concluded that ozone measurements at a number of European sites gave increases by approximately a factor 2.

High altitude mountain stations like Zugspitze in Germany (3000 m ASL) and Maunu Loa on Hawaii (3400 m ASL), which should indicate free tropospheric ozone changes show ozone increases over the last two decades. Observations do, however, indicate reduced increases at these surface stations as indicated by the measurements from Zugspitze (Figure 5). Increasing ozone trends is found at remote surface stations in the Northern Hemisphere.

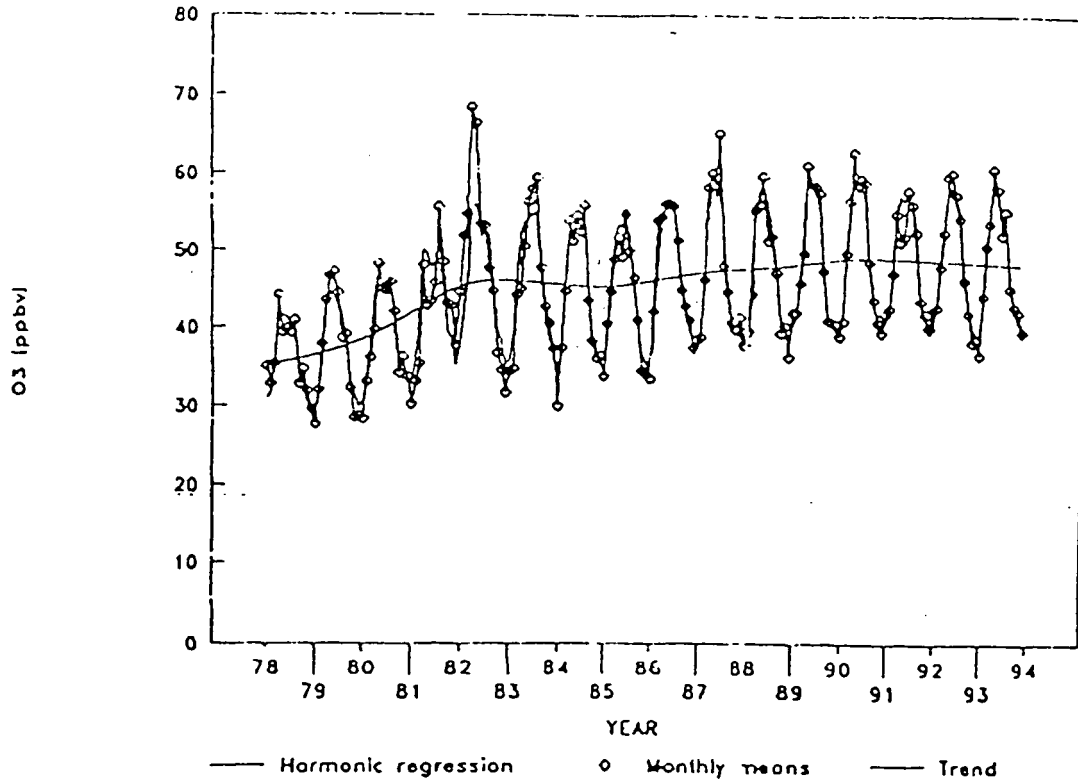


Figure 5. Observed surface ozone concentrations at the mountain station Zugspitze in Germany. Ref.: WMO (1994).

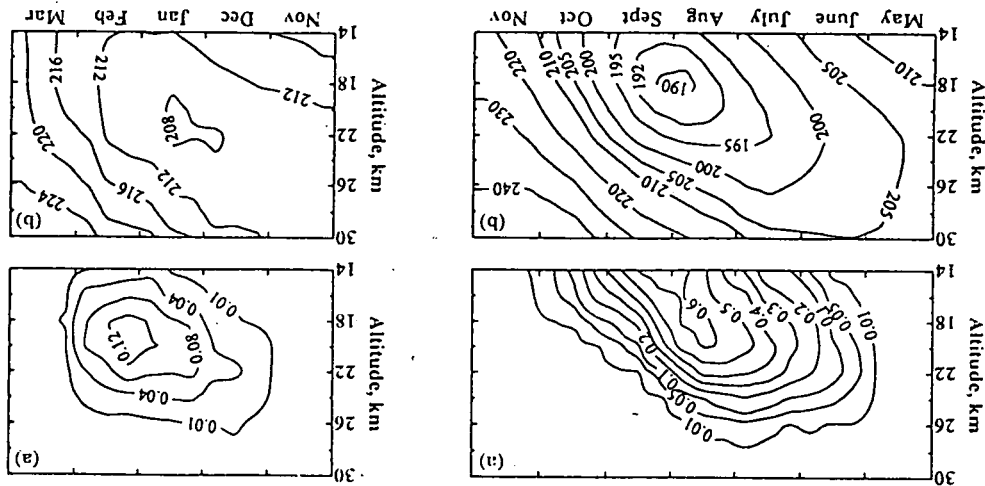
This increasing long term ozone trend found in observations throughout the Northern Hemisphere during the last decades, is a strong indication of human influence on the hemispheric ozone levels. The observed negative trend in the Southern Hemisphere, during the last few years, is probably due to the combined effect of small anthropogenic emissions of ozone precursors, which lead to a net *in situ* ozone destruction in most of the hemisphere, and enhanced UV fluxes, due to reduced stratospheric ozone (Fuglestedt et al., 1994).

**4. Increased ozone loss in the lower stratosphere due to heterogeneous reactions.**

Two types of heterogeneous processes initiate enhanced ozone loss in the lower stratosphere: Reactions occurring on Polar Stratospheric Clouds (PSCs) in the wintertime polar stratosphere when temperatures are low, and on sulfate aerosols at all latitudes and seasons. Both the PSC and the sulfate aerosol loadings in the stratosphere can vary strongly from year to year, providing large variations in the impact on ozone. The significance of these processes is that they occur mainly at heights between 15 and 25 km where ozone concentrations are highest.

**4.2 Observations of the long term occurrence of PSCs.**

Observations have shown that the formation of PSC particles is a continuous occurring phenomenon each winter in the lower stratosphere in the two polar regions, with higher probability in the Antarctica than in the Arctic due to lower temperatures. 10 years zonal average sighting probabilities for PSCs in the two polar regions are shown in Figure 6 along with zonal average temperatures (Poole and Pitts, 1994).



**Figure 6. 10 years zonal average of PSC sighting probabilities from SAM II, for the Antarctic (upper left) and for the Arctic (upper right), and temperatures for the Antarctic (lower left) and for the Arctic (lower right). Ref.: Poole and Pitts (1994).**

#### 4.b Heterogeneous chemistry on stratospheric sulfate particles and on Polar Stratospheric Clouds (PSCs).

The impact on ozone by sulfate particles is initiated through the heterogeneous reactions given in Table 1:

$\text{ClONO}_2$	+	$\text{HCl}$	$\rightarrow$	$\text{Cl}_2$	+	$\text{HNO}_3$
$\text{ClONO}_2$	+	$\text{H}_2\text{O}$	$\rightarrow$	$\text{HOCl}$	+	$\text{HNO}_3$
$\text{N}_2\text{O}_5$	+	$\text{HCl}$	$\rightarrow$	$\text{ClNO}_2$	+	$\text{HNO}_3$
$\text{N}_2\text{O}_5$	+	$\text{H}_2\text{O}$	$\rightarrow$	$\text{HNO}_3$	+	$\text{HNO}_3$
$\text{HOCl}$	+	$\text{HCl}$	$\rightarrow$	$\text{Cl}_2$	+	$\text{H}_2\text{O}$

Table 1. Heterogeneous reactions occurring on PSCs and aerosol particles.

In the above reactions the HCl molecules are attached to the particles while  $\text{ClONO}_2$  and  $\text{N}_2\text{O}_5$  are in gaseous form.

There are now a number of laboratory studies who confirm that these reactions occur on PSCs and on sulfate aerosol particles. The chlorine compounds formed through the above reactions are rapidly broken up in the sunlit atmosphere to give the ozone destructing compounds Cl and ClO. In this way chlorine reservoir gases are converted to active (ozone destructing) compounds. The conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$  is of importance for the ozone loss process, in that it leads to a reduction of NO and  $\text{NO}_2$  concentrations.

#### 4c. Significance of heterogeneous processes for ozone loss.

Through the chemical processes given in Table 1 chlorine reservoir gases are converted to compounds like HOCl,  $\text{ClNO}_2$  and  $\text{Cl}_2$  which are rapidly converted to ozone destructing compounds (e.g. ClO). As a result of this ClO is strongly enhanced in the lower stratosphere, leading to major ozone loss (particularly in the presence of CFCs) through the reaction sequence given in Table 2:

Through this loss sequence two ozone molecules are lost each time. Due to its quadratic dependence on ClO, this reaction is particularly efficient under PSC conditions when ClO is strongly enhanced. At moderately enhanced ClO levels like, conditions when sulfate particles are present, the ClO reaction with BrO (see section 9) is also important.

	ClO	+	ClO	+	M	→	(ClO) <sub>2</sub>	+	M		
	(ClO) <sub>2</sub>	+	hν			→	Cl	+	ClOO		
	ClOO	+	M			→	Cl	+	O <sub>2</sub>	+	M
	2(Cl	+	O <sub>3</sub>			→	ClO	+	O <sub>2</sub> )		
NET	O <sub>3</sub>	+	O <sub>3</sub>			→	O <sub>2</sub>	+	O <sub>2</sub>	+	O <sub>2</sub>

**Table 2. Stratospheric ozone loss by chlorine in the lower stratosphere, initiated by heterogeneous reactions (mainly on PSCs).**

**5. The observed large Northern Hemispheric reductions in total ozone column densities in 1992-1993.**

The June 1991 volcanic eruption of Mt. Pinatubo led to high particle concentrations in the lower stratosphere the following two years, in addition the extreme low temperatures at high northern latitudes during the winter of 1993 resulted in Polar Stratospheric Cloud (PSC) formation that was substantially higher than during a "normal year" shown in Figure 6. A combination of these conditions led to more efficient ozone loss than we have experienced in previous years, and what was observed during the winter of 1994.

The increased loading of particles in the stratosphere after the volcanic eruption at Mt. Pinatubo in June 1991 provided a good opportunity to study possible effects of enhanced particle levels in the stratosphere in combination with enhanced levels of chlorine and bromine species from man made sources. In addition, low temperatures in the northern stratospheric polar region, led to enhanced PSCs (Polar Stratospheric Clouds) during the winter of 1993. The observed values of ozone during the winter and spring of 1993 were lower than in any previous years. There have been speculations that the low ozone values during 1992 and 1993 were a result of enhanced chlorine and bromine levels which in combination with high sulfate particle and PSC levels lead to enhanced ozone depletion.

TOMS observations show global reductions in ozone column densities (polar regions exclude) during the winter of 1993 of about 5 % compared to the 1979 to 1993 average (ref.: WMO, 1994). The reductions were particularly large at high and middle northern latitudes, where reductions of about 10 % were recorded during March of 1993 (Figure 7, Bojkov et al., 1993). The extreme low ozone column densities at northern latitudes were observed throughout most of the first half of 1993 as shown in Figure 8 from the observations by the Brewer instrument located at Edmonton, Canada (McElroy et al., 1994). During the second half of 1993 and the first half of 1994 ozone column densities were closer to normal at middle and high northern latitude stations. This suggests that the years 1992 and 1993 were anomalous years, probably with enhanced ozone destruction compared to a "normal" year.

Deviations (%) for March 1, 1993 - March 31, 1993.

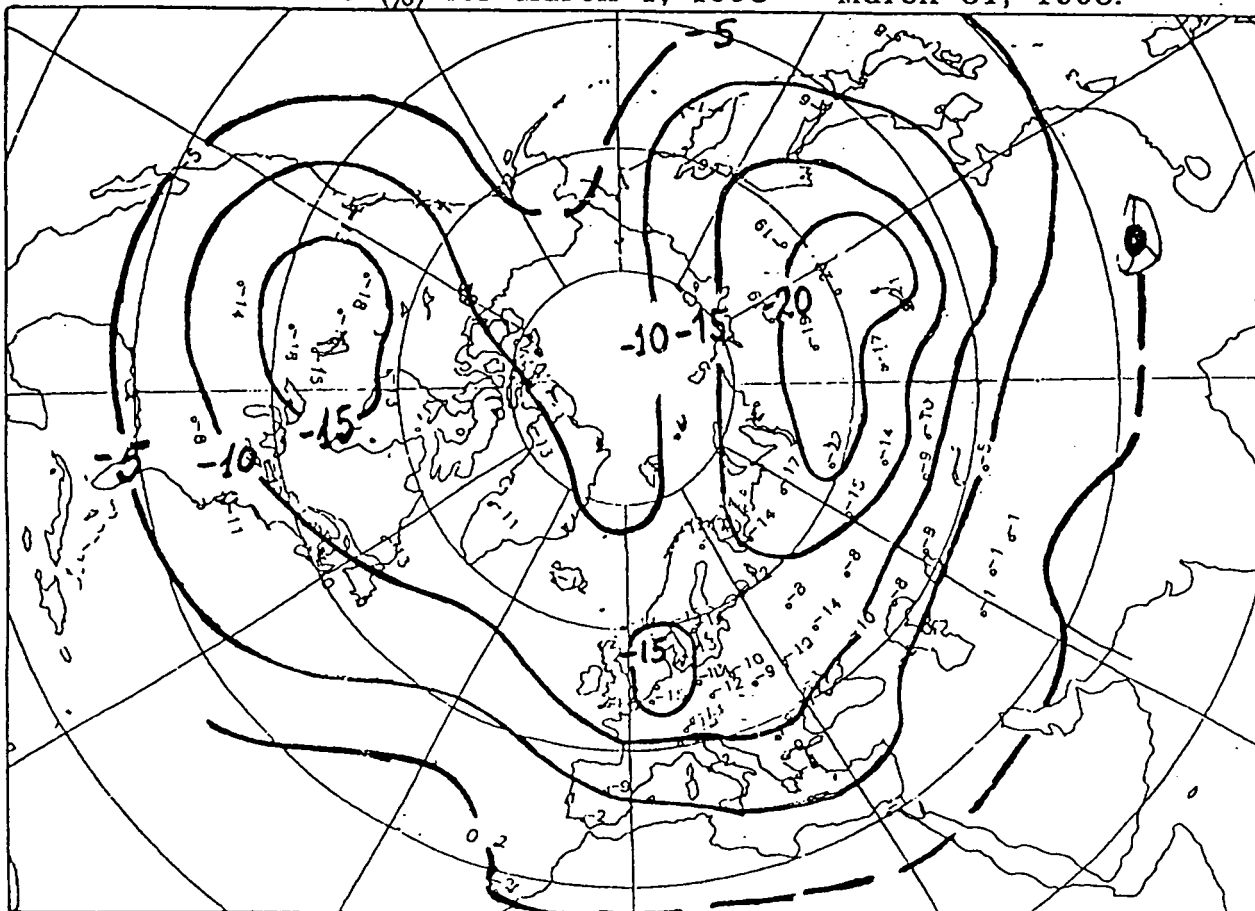


Figure 7. Reductions in ozone column densities over the Northern Hemisphere during March of 1993 as compared to the long term values for the same month. Ref.: Zerefos (1993, private communications).

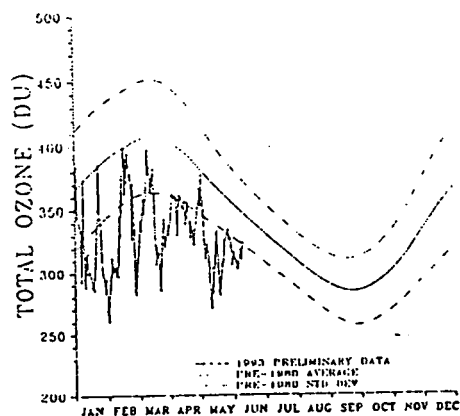
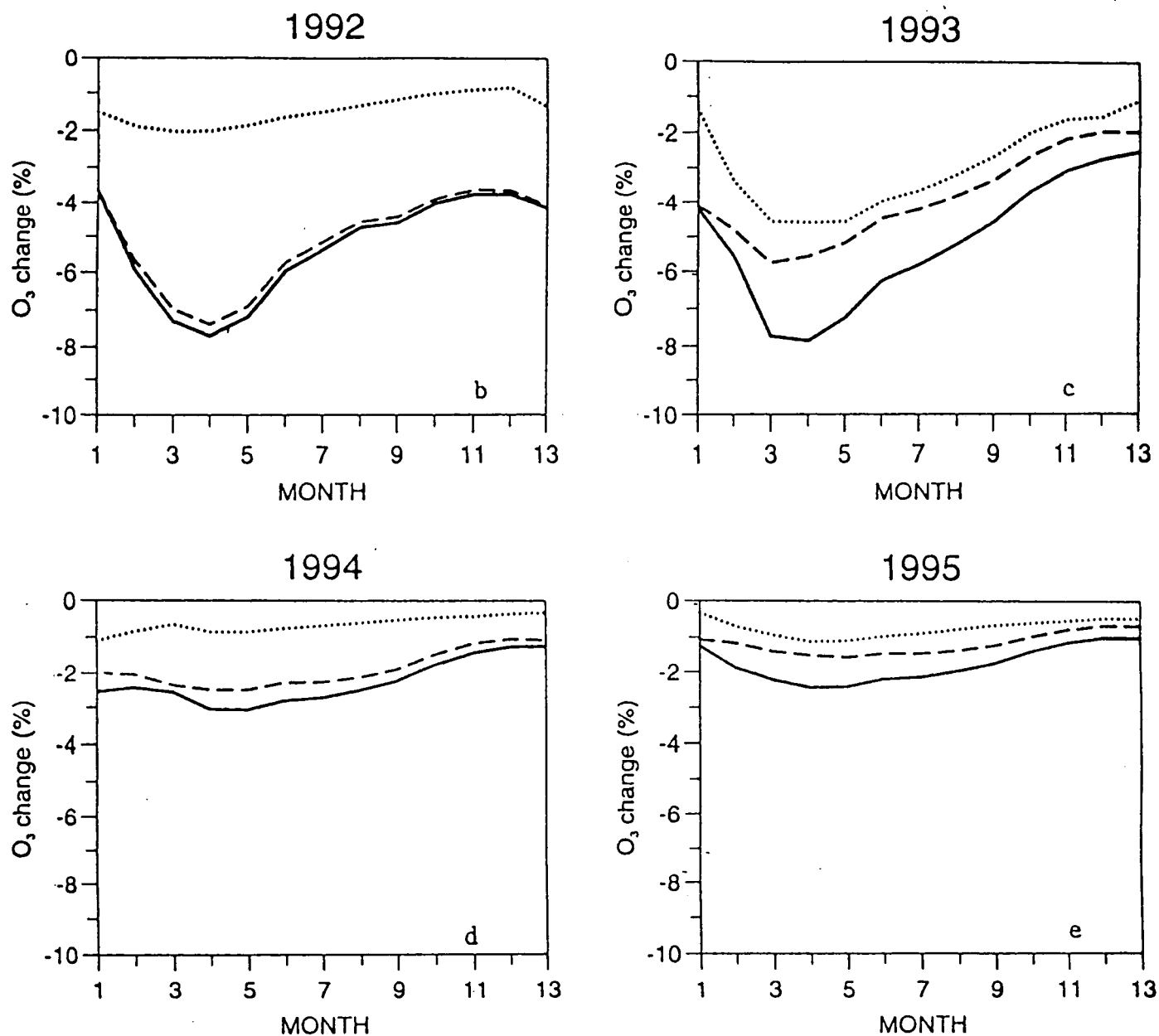


Figure 8. Ozone column densities at Edmonton, Canada for the first months of 1993, compared with pre 1980 values. Ref.: McElroy et al. (1994).

## 6. Model calculated ozone decrease.

Model studies have shown that heterogeneous reactions are effective in initiating ozone reductions when PSCs are present in the stratosphere (Hoffman and Solomon, 1989; Isaksen et al., 1990). Furthermore, model studies performed in connection with the two latest international ozone



b) - e) Differences (%) in total ozone for particular years for latitudes  $50^\circ$  and  $60^\circ$  N between a reference time dependent run with gas phase and heterogeneous chemistry on background aerosols (quiet periods) and time dependent runs with heterogeneous chemistry on PSCs (.....) separately, Pinatubo particles (-----) separately and PSCs and Pinatubo particles (—) combined.

Figure 9. Calculated ozone depletion due to heterogenous reactions at northern latitudes during the years 1992 to 1995. Ref.: Isaksen and Rognerud (1994, submitted for publication).

assessments (WMO, 1992; WMO,1994) have demonstrated that sulfate particles could also initiate enhanced ozone loss in the stratosphere.

An indication that enhanced conversion from chlorine reservoir gases (HCl, ClONO<sub>2</sub>) to active chlorine compounds (Cl and ClO) probably took place through heterogeneous processes, is given by the observations of high wintertime ClO values in the Northern Stratosphere during the winter of 1992/1993 (Waters et al., 1993). Such high values are difficult to explain if only gas phase reactions were responsible for Cl and ClO formation.

#### 6.a Calculated ozone reductions during the 1990s.

Model calculations with special emphasis on the impact of particles and PSCs on the ozone chemistry in the post Mt. Pinatubo stratosphere (1992, 1993 and 1994) has been performed by different modelling groups. As an example, the calculated column ozone depletion by the enhanced sulfate particle and PSC concentrations in the Northern Stratosphere (40 to 50 degree N latitude), for the years 1992, 1993, and 1994 is shown in Figure 9 (Isaksen and Rognerud, 1994; submitted for publication). 1995 is also included in the calculations, assuming average pre 1992 conditions for particles and PSCs. The calculations demonstrate that it is likely that 1992 and 1993 were exceptional years where special atmospheric conditions (high particle and PSC concentrations) made the chlorine and bromine gases particularly effective in the ozone depletion process. It is also likely that under more "normal" conditions like the situation in 1994 will see less impact on the ozone. Nevertheless, as long as chlorine and bromine levels in the stratosphere are increasing, as we have seen up to now, there will be a continuous longterm downward trend in ozone.

#### 6.b Calculated future ozone depletion from chlorine and bromine compounds.

Future ozone depletions will depend critically on the chlorine and bromine emission scenarios. It is clear that with the rapid reductions in CFC emissions, which have been observed, chlorine levels in the stratosphere will reach maximum values within the next few years, and the same will be the

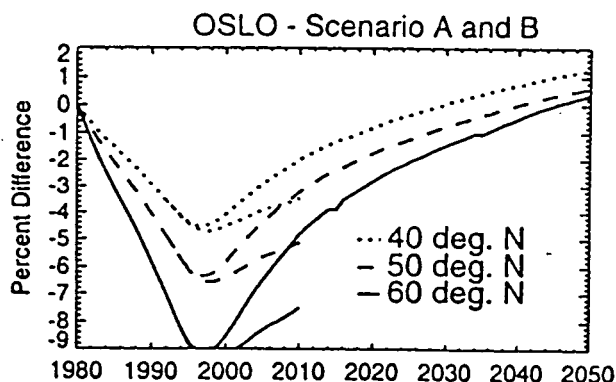
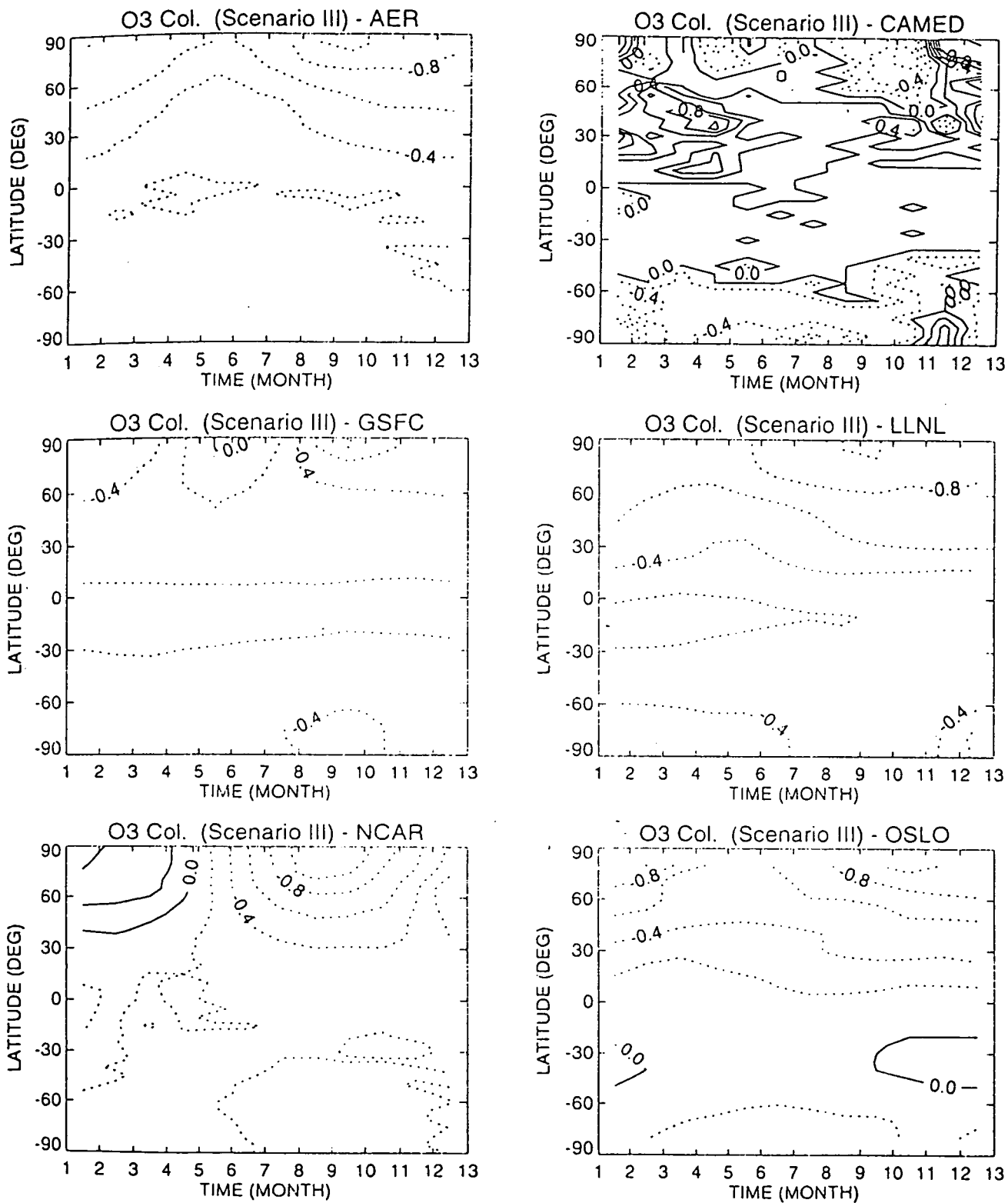


Figure 10. Model calculated global average ozone depletion with the Oslo 2-D model for two different scenarios in accordance with the present Montreal Protocol regulations. A: full compliance, calculations until 2050. B: Non-compliance, calculations until 2010. Ref.: WMO (1994).





**Figure 11.** Model calculated changes in ozone column densities resulting from  $\text{NO}_x$  emissions of a projected future fleet of supersonic aircraft flying in the lower stratosphere at approximately 21 km, with low  $\text{NO}_x$  emission. The result are from 6 different 2-D models which participate in NASA HSRP. Ref.: NASA (1993).

ozone depletion. **Figure 10** shows calculated global average ozone depletion between 1980 and 2050 for the most likely emission scenario. The calculations are done using a two dimensional model which took part in the ozone assessment (WMO, 1994). Maximum ozone depletion is reached within the next four years, with global average reductions of the order of up to 10 %.

### 6.c Calculated impact of future supersonic air traffic.

The impact on ozone from supersonic aircraft flying in the lower stratosphere has been studied for more than two decades, since the Climate Impact Assessment Programme (CIAP), sponsored by the US Department of Transportation was started in 1972 (CIAP, 1972). Earlier estimates of significant ozone reductions from  $\text{NO}_x$  emitted from airplanes is not supported by the recent studies. Model studies performed through the NASA HSRP (NASA, 1993) give small changes in ozone column densities for a projected future fleet of supersonic aircraft. **Figure 11** gives model calculated (time dependent 2-D models) changes with latitude and month in ozone column densities due to  $\text{NO}_x$  from supersonic aircraft flying at approximately 21 km. height in 2015. Low  $\text{NO}_x$  Emission Index (EI=5, g  $\text{NO}_x/\text{kg}$ ) is assumed. Ozone changes are less than 1 % through the whole area. The main reason why ozone depletion is less than in previous studies is due to the introduction of heterogeneous chemistry in the models which leads to enhanced ozone depletion in the lower stratosphere. Ozone loss by increased  $\text{NO}_x$  at these heights is compensated for by less loss through chlorine reactions involving ClO due to enhanced conversion of ClO to  $\text{ClONO}_2$  when  $\text{NO}_x$  levels are increased. It should be noticed that aircraft emissions may affect stratospheric ozone through other processes like impact on the temperature, and on the enhanced formation of particles.

## 7. Changes in CFCs and HCFCs as a result of implementation of the Montreal Protocol

The implementation of the Montreal protocol has had two distinct results, firstly the total amount of man made organic chlorine which is emitted into the atmosphere is reduced, due to the reduction in the emissions of the main CFCs (e.g. CFC-11, CFC-12, CFC-113), and secondly to significant increases in the CFC substitutes, the HCFCs (e.g. HCFC-22, HCFC-141b, HCFC-142b), although the concentrations of most of these compounds are very low (often in the low ppt range).

### 7.a Reduced emissions and atmospheric growth rate of CFCs.

Reported emissions to the atmosphere of the CFCs since 1990 show significant decreases (**Figure 12**, WMO, 1994). These decreases are in agreement with calculated reductions based on observed changes in the CFCs. The increases in CFC-11 concentrations in the atmosphere have levelled off during the last few years at most baseline stations, and globally on the average there are no significant increases. CFC-12 shows reduced increases although it is less significant than in the case of CFC-11. This can be explained by the longer lifetime of CFC-12 compared to CFC-11 (102 years compared to 50 years, WMO, 1994) which require larger reductions in the emissions of CFC-12 before atmospheric concentrations are stabilized. The impact of reduced emissions of CFC-11 and CFC-12 during the last years is shown in **Figure 13**, which shows the last two decades development of CFC-11 and CFC-12 for different baseline stations on the Earth's surface.

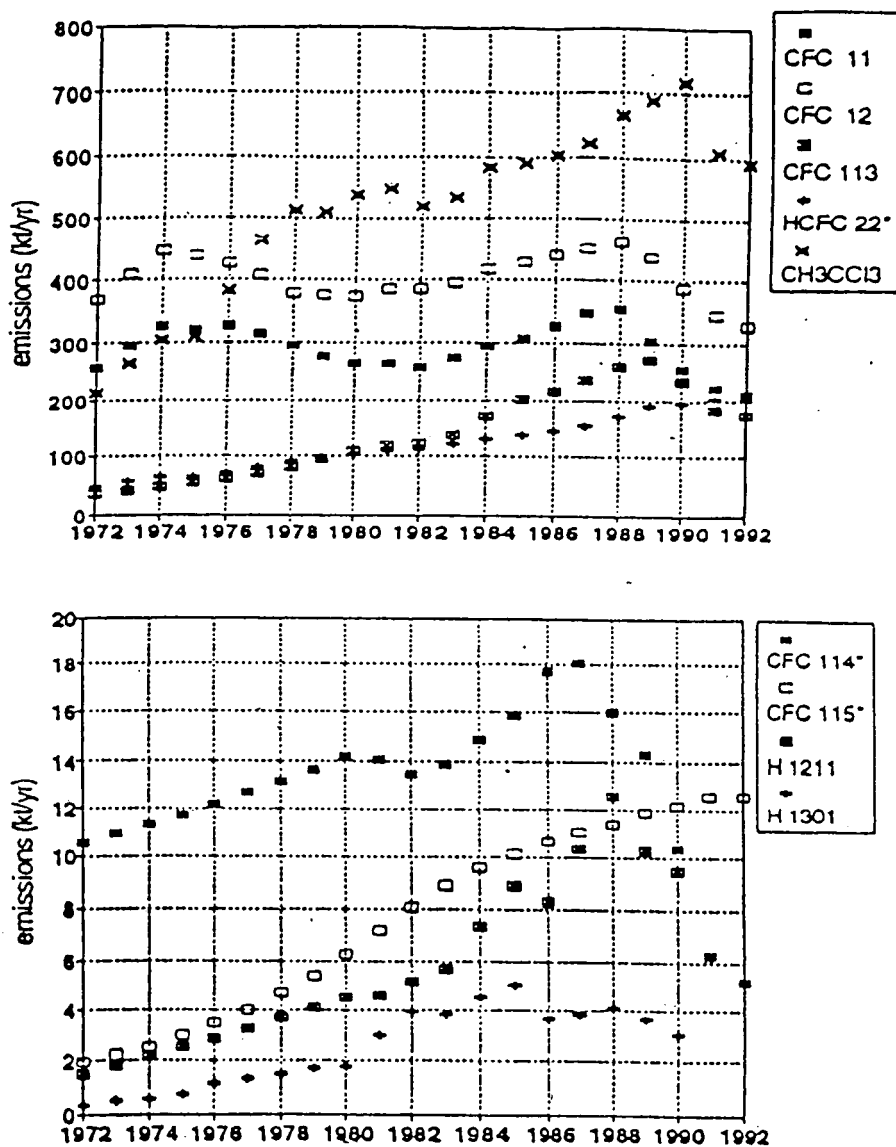


Figure 12. Reported yearly emissions of some of the key chlorine and bromine compounds. Ref.: WMO (1994).

### 7.b Increases in the atmospheric concentrations of HCFCs.

As a consequence of the implementation of the Montreal Protocol, the HCFCs show a developments that are different from the CFCs. The emission of the most abundant substitute, HCFC-22, has not decreased during the last few years, as shown in Figure 12 and its atmospheric concentration has therefore continued to increase significantly. The last measurements indicate increases in the range 6 to 7 % per year (WMO, 1994). Other substitutes are seen to increase

sharply. Recent measurements have identified HCFC-141b and HCFC-142b in air samples. Their concentrations are extremely low (Penkett, 1994; private communications), in the low ppt and sub ppt range, but their concentrations are increasing rapidly, in accordance with increasing use.

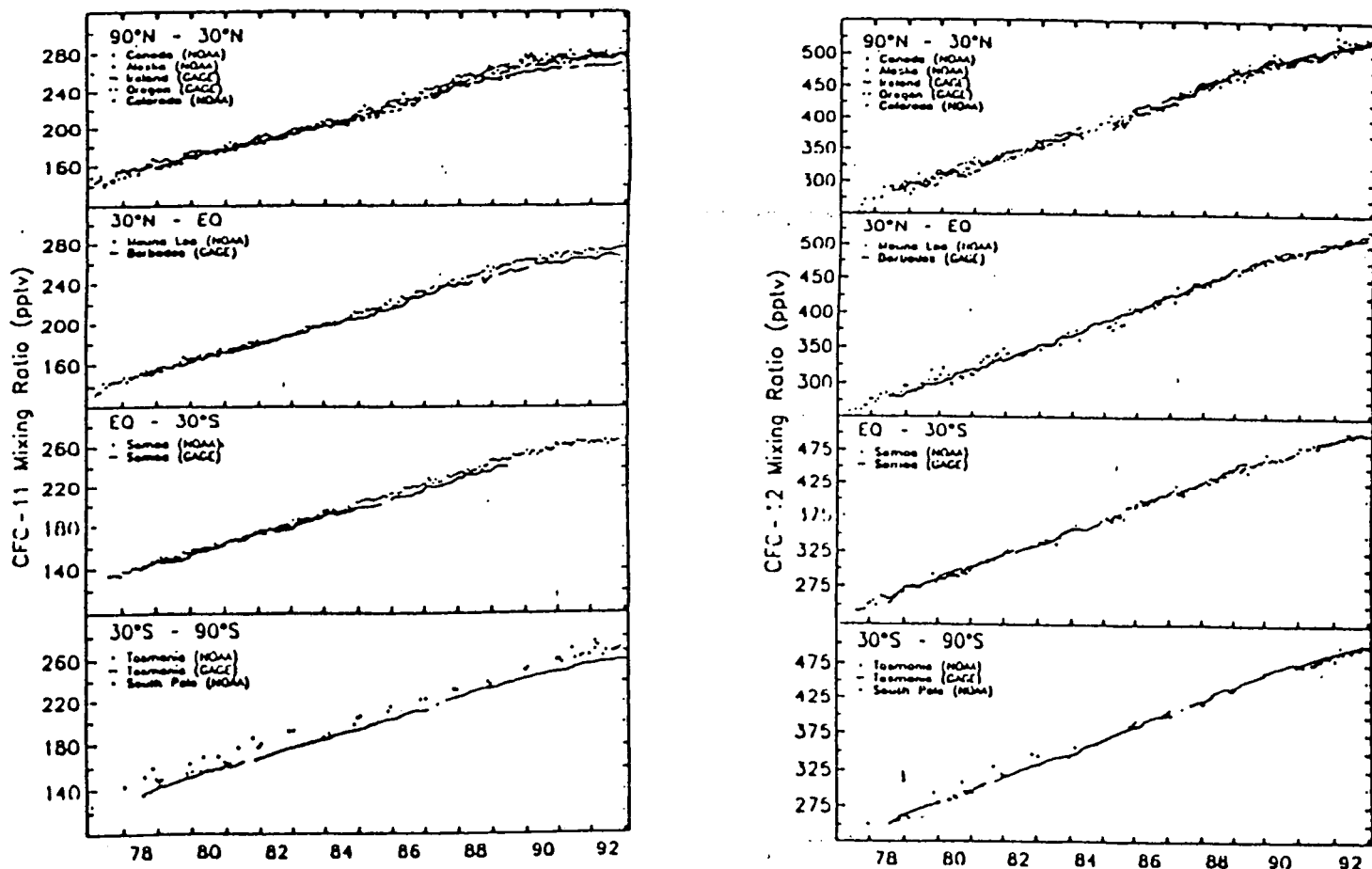


Figure 13. Observed growth in CFC-11 and CFC-12 at different baseline stations during the time period 1977 to 1993. Ref.: WMO (1994).

## 8. Changes in other source gases of relevance to the ozone and the climate issues.

During the anomalous years 1992 and 1993, most of the source gases of importance for the ozone and the climate issues showed reduced growth rates. This is the case for  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . The methane growth rate has been approximately halved over the last 10 years as shown in Figure 14. Since methane is strongly part of the tropospheric ozone chemistry, and is sensitive to changes in UV-B radiation, and thereby to the thickness of the ozone column, it is likely that its growth rate is affected by decreasing ozone column densities during this time period. The impact

of increased UV-B radiation on methane is to increase tropospheric OH and thereby reduce chemical lifetime of methane, and thereby its growth rate. In a recent study, Fuglested et al. (1994) suggest that approximately 1/3 of the observed reduction in the growth rate is due to reduced stratospheric ozone.

The reduced growth rates of  $N_2O$  and  $CO_2$  is difficult to explain, however, recent observations of  $CO_2$  indicate that the growth rate has started to increase again. It is therefore likely that the observed reduced growth rates of different gases lately are short term phenomena caused by some hitherto unknown atmospheric processes, and that the longterm trend of the gases is not affected to the same degree.

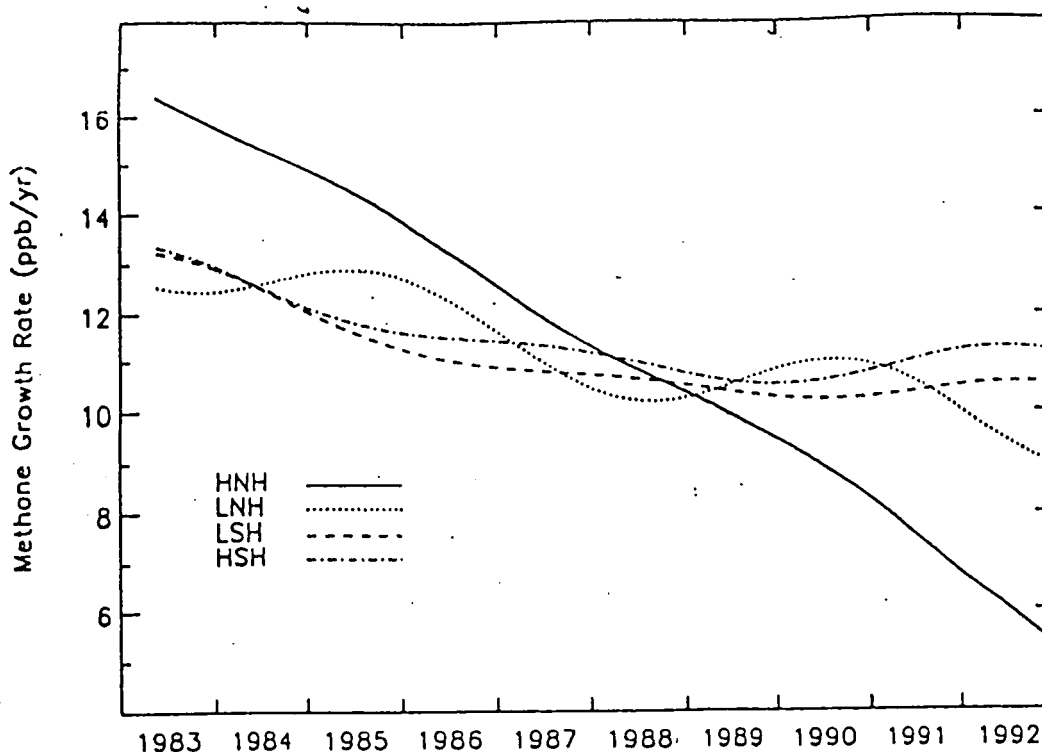


Figure 14. Observed changes in  $CH_4$  growth rate over the last 10 years at different latitudes (high and low latitudes in the two hemispheres). Ref.: WMO (1994).

## 9. The role of bromine compounds in the ozone depletion process

Although the concentrations of inorganic bromine compounds in the stratosphere are significantly less than the concentrations of inorganic chlorine compounds (the ratio is approximately 1 to 200 in the stratosphere), it is partly compensated for by a larger fraction of bromine being in the form of ozone destructing compounds (Br and BrO) than their chlorine counterparts (Cl and ClO) in the lower stratosphere. Both groups contribute efficiently to ozone destruction in this part of the stratosphere. There is, however, a considerable uncertainty connected to the role of bromine in the ozone destructing process.

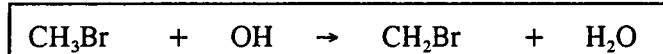
### 9.a Distribution and change in atmospheric concentration of methyl bromine.

The role of methyl bromide for stratospheric ozone depletion is of particular concern. Its presence in the atmosphere is well established. Measurements give mixing ratios in the range 10 to 15 ppt (MBGC, 1994). Rowland (1992, paper presented at MBGC, 1992) reports nearly constant mixing ratios from the surface and up to the top of the troposphere, with a gradual decrease the first few km above the tropopause. The measurements reported by MBGC (1994) give a marked gradient between the two hemispheres, corresponding to a ratio of approximately 1.2. This difference indicates an uneven distribution in the source strength between the two hemispheres, and a relatively short atmospheric lifetime (probably in the range 1,3 to 2 years).

The current growth rate in atmospheric concentrations of methyl bromide is uncertain, but the observed rate is consistent with a significant anthropogenic source.

Global emissions of methyl bromide is believed to originate both from natural and anthropogenic sources. A major fraction of man's use of methyl bromide is as fumigant in agricultural practices in certain sectors. Biomass burning and emission from automobiles are other anthropogenic sources. It is also likely that there is a significant net natural production from the oceans. The fraction released from anthropogenic sources are uncertain; some studies indicate that it is 30 % of the total release. However, the studies are not inconsistent with values in the range 30 to 70 %. The reported anthropogenic use (excluding biomass burning and automobile emissions) has increased over the years 1984 to 1990 with 6 to 7 % per year on average in this period. Since the natural emission is not known, but likely to be the dominant source, changes in total source strength is difficult to estimate. Assuming that the increases in emissions follow the increases in sale, increases from man's activity in total source strength is probably in the range 2 to 5 % per year.

The loss processes of methyl bromide have not fully been established. A main loss path is through the reaction with the hydroxyl radical in the troposphere:



and in the stratosphere through photodissociation:



While most of the atmospheric loss occurs through the former of these two reactions, the latter reaction contributes to stratospheric bromine. This means that only a minor part of methyl bromine emitted into the atmosphere is transported to the stratosphere. Nevertheless, methyl bromide constitutes the main source of ozone-depleting bromine in the stratosphere.

Based on the rate constant for the OH reaction, and the calculated distribution of OH in the troposphere a lifetime of 1.7 to 2.0 years is obtained for methyl bromide. Recent studies indicate that methyl bromide could also be absorbed in surface water. This would lead to a smaller atmospheric lifetime and reduce the significance of man-made emissions. A lifetime in the range 1.0 to 2.0 years seems most likely.

### 9.b Ozone loss through bromine reactions

Recent development in stratospheric chemistry has shown that the bromine reactions are more significant for ozone destruction than previously assumed. Several chemical cycles involving bromine compounds have been identified as ozone destructing mechanisms in the stratosphere (WMO, 1992; WMO, 1994). The main catalytical bromine cycles responsible for the ozone destruction in the lower stratosphere are (McElroy et al., 1986):

	BrO	+	ClO	→	Br	+	Cl	+	O <sub>2</sub>
	Cl	+	O <sub>3</sub>	→	ClO	+	O <sub>2</sub>		
	Br	+	O <sub>3</sub>	→	BrO	+	O <sub>2</sub>		
Net	O <sub>3</sub>	+	O <sub>3</sub>	→	O <sub>2</sub>	+	O <sub>2</sub>	+	O <sub>2</sub>

Table 3. Ozone loss through the BrO + ClO reaction.

and (Solomon et al., 1986):

	BrO	+	HO <sub>2</sub>	→	HOBr	+	O <sub>2</sub>		
	HOBr	+	hν	→	Br	+	OH		
	Br	+	O <sub>3</sub>	→	BrO	+	O <sub>2</sub>		
	OH	+	O <sub>3</sub>	→	HO <sub>2</sub>	+	O <sub>2</sub>		
Net	O <sub>3</sub>	+	O <sub>3</sub>	→	O <sub>2</sub>	+	O <sub>2</sub>	+	O <sub>2</sub>

Table 4. Ozone loss through the BrO + HO<sub>2</sub> reaction.

The first of these two cycles also involve ClO, thereby linking the stratospheric chlorine and bromine chemistry together. In this way future ozone loss by the bromine will depend on the development in chlorine levels.

Since ClO is strongly affected by heterogeneous chemistry, the BrO + ClO reaction will also be affected, but less than chlorine reactions (the reaction ClO + ClO). Observations show that BrO is only moderately enhanced by PSCs. The catalytic cycle involving the reaction BrO + HO<sub>2</sub> will not depend directly on the ClO enhancement in PSCs, and operates efficiently as will be shown, also outside the polar regions. De to the large uncertainty in the rate constant, and the potential importance of the reaction, the reaction HO<sub>2</sub> + ClO has been given particular attention in recent studies.

Model calculations indicate that approximately 20 % the total ozone loss in the stratosphere is occurring by the above bromine reactions, with larger contributions at mid and high latitudes. The

efficiency of bromine reactions in the stratosphere is approximately 40 times that of chlorine as a global average. This underline the importance played by methyl bromide in stratospheric ozone chemistry.

#### 10. Calculated ODPs.

Calculated ODPs are not significantly different from previous calculations. More emphasis compared to previous assessment have been given to the transient effect (transient ODP) over a limited time horizon of the shortlived chlorine and bromine source gases. This is particularly true for methyl bromide.

Trace Gas	Model Derived ODP
CFC-11	1.0
CFC-12	0.82
CFC-113	0.90
CFC-114	0.85
CFC-115	0.40
CCl <sub>4</sub>	1.20
CH <sub>3</sub> CCl <sub>3</sub>	0.12
HCFC-22	0.04
HCFC-123	0.014
HCFC-124	0.03
HCFC-141b	0.10
HCFC-142b	0.05
HCFC-225ca	0.02
HCFC-225cb	0.02
CH <sub>3</sub> Br (2 yr lifetime)	0.96
CH <sub>3</sub> Br (1.3 yr lifetime)	0.64
CF <sub>3</sub> Br (H1301)	12
CF <sub>2</sub> ClBr (H1211)	5.1
CF <sub>3</sub> I	< 0.01
CH <sub>3</sub> Cl	0.02

**Table 5. Steady state ODP values derived from 2-D model calculations and from semi-empirical approach (WMO, 1994). The values are normalized, based on lifetimes recommended in the last ozone assessment WMO (1994).**



### 10.a Steady state ODPs.

The updated values for ODP from WMO (1994) is given in **Table 5** for different chlorine and bromine compounds derived from 2-D model calculations and from a semi-empirical approach (Solomon et al., 1992). There are still considerable uncertainties connected to the ODP for the bromine source gases ( $\text{CH}_3\text{Br}$ , H-1211, H-1301) due to uncertainties connected to the bromine chemistry.

### 10.b Time dependent ODP for methyl bromide.

Time dependent ODPs for methyl bromide are calculated using a 2-D model (Isaksen and Rognerud, 1994; submitted for publication) by first running the time dependant model with perturbed  $\text{CFCl}_3$ , followed by a similar calculation where, in addition, a perturbation to methyl bromide is added. The resulting ODPs are given in **Table 6**. In the calculations, a lifetime of 1.7 years is used for methyl bromide. As we have discussed earlier, there are substantial uncertainty connected to the calculation of the lifetime of methyl bromide, which is reflected in the range that is given in **Table 5** for the steady state value.

The time dependent values for  $\text{CH}_3\text{Br}$  are for a model run with perturbation starting in 1990. The full impact of methyl bromide on ozone is rapidly established due to its short lifetime. However, since the time dependent numbers are given relative to the effect of  $\text{CFCl}_3$ , and the impact of the latter compound is gradually increasing, the relative numbers for  $\text{CH}_3\text{Br}$  will decrease.

Year	2000	2005	2010	2015	2020	2025	2030
Rel. eff.	5.56	3.25	2.28	1.83	1.53	1.33	1.21

**Table 6.** Time dependant ODPs for methyl bromide over different time horizons (10 to 40 years). Starting year for the calculations is 1990.

## 11. Tropospheric UV-B changes.

The stratospheric ozone reductions we have experienced over the last decade is estimated to have led to significant enhancements in the UV-B flux entering the lower atmosphere. Observations have shown strong anti-correlation between ozone column densities and UV-B fluxes during the last few years when column ozone densities are small. This is clearly demonstrated in **Figure 15** which shows column ozone densities and UV irradiance at 300 nanometer (nm) for the the three last months of 1991 over the South Pole (WMO, 1994). Peak UV-B radiation clearly occurs during periods with minimum ozone column densities. Comparisons of Antarctic data with data from the Arctic where ozone reductions are less significant clearly demonstrate that Antarctic ozone depletion enhances harmful UV-B radiation (WMO, 1994). For instance, the DNA-weighted UV radiation is several fold larger at the South Pole than in the Arctic, while visible radiation, which is not affected by ozone is similar at the two sites.

Model studies indicate that the change in ozone column densities we have seen over the last decade has led to a perturbation in tropospheric chemistry that is significant for ozone and other key compounds. In particular, it is likely that OH levels are enhanced significantly (Madronich and Granier, 1994; Fuglestedt et al., 1994).

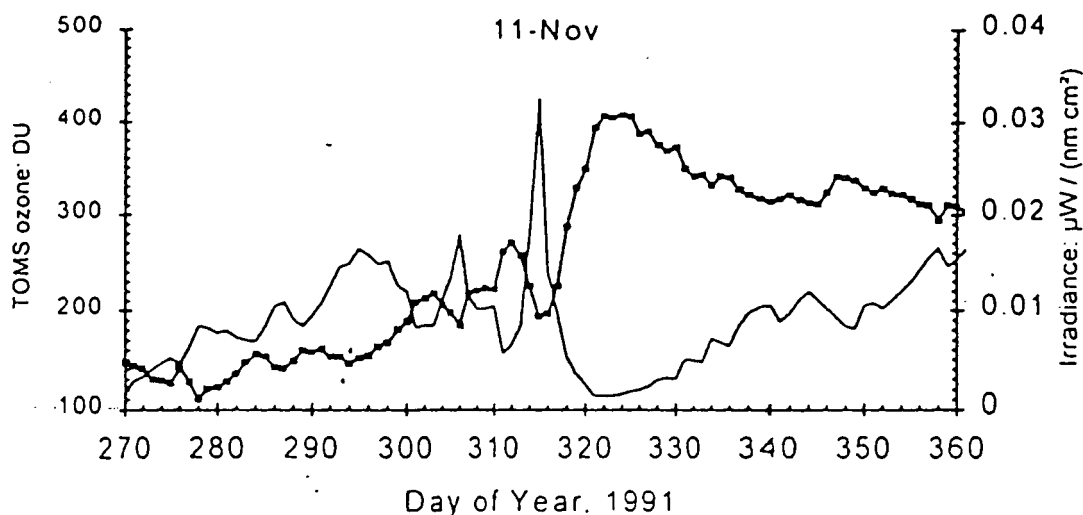


Figure 15. Observed ozone column densities and UV-B radiation at the South Pole during the three last months of 1991. Ref.: WMO (1994).

## 12. The relation between chemistry and climate change.

Increasing attention has been given to the impact of chemical changes induced by stratospheric ozone changes on the climate gases. Firstly, ozone by itself is a climate gas; changes in its distribution can therefore be of importance to the Earth's climate. From a climate point of view, ozone changes in the lower stratosphere and upper troposphere will have the largest impact on surface temperatures. Secondly, changes in the atmospheric chemistry will affect other climate gases, first of all methane, which are controlled by OH in the troposphere. They will give indirect climate effects through changes in atmospheric chemistry. Two areas have been studied in connection with the latest ozone and climate assessments: Climate effects from CFC induced ozone changes, and indirect effects from methane through its impact on tropospheric ozone and on its own concentrations through changes in the chemical composition (e.g. changes in OH).

### 12.a Impact on stratospheric ozone from enhanced levels of CFCs.

In the case of CFCs the impact on ozone will give a negative climate effect through ozone reductions in the lower stratosphere. Estimates of the overall effect is that the indirect ozone effect nearly cancels the direct greenhouse effect from CFC taken as a global average value. The negative indirect effect at high latitudes is, however, found to be substantially larger than the positive direct effect from CFCs.

### **12.b Chemical impact on methane in the troposphere.**

Increased emission of methane will on a global scale lead to enhanced ozone formation. It will also lead to reduced levels of OH increasing its lifetime. Both these indirect effects are positive which will add to the direct climate effect from enhanced methane emissions. Estimates of the indirect effects from methane gives values similar to the direct effect (WMO, 1994). This conclusion is similar to the conclusion drawn in the previous international climate assessment (IPCC, 1992), and it means that when we add indirect chemical effects, methane becomes twice as efficient as a climate gas as it is when only the direct effect is considered.

### **12.c The significance of climate-chemistry interactions.**

The important conclusion of these studies are that if indirect effects are taken into account CFCs role as greenhouse gases are strongly reduced, while methane becomes more important.

These two types of studies are in good agreement with the suggestions of the indirect effects that was given in the previous ozone assessment. There are, however, two points that should be kept in mind when indirect effects involving ozone are considered:

There are large spatial and temporal variations in the ozone changes, and there are substantial uncertainties connected to calculations of chemical effects. This means that there are large uncertainties connected with indirect effects.

It should be pointed out that there are several other indirect effects of potential importance that have not yet been considered. More attention should therefore be given to this type of studies in the future.

## **13. Concluding remarks**

Although large amounts of new information about the state of the ozone layer has been gathered during the last few years, the main conclusions are the same as were drawn in the previous assessment: There are growing evidences that the increased emissions of CFCs and bromine compounds are effecting the stratospheric ozone on a global basis, which, unless emissions are continued to be strongly regulated will lead to substantial future ozone reductions.

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