

The Ozone Layer Problem

Recent findings

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by

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1. THE URGENCY OF THE PROBLEM

The recent assessment of the ozone situation (Scientific Assessment of Stratospheric Ozone: 1991, WMO, 1992) which is based on observations and theoretical studies over several years has increased our understanding of the impact of human activities on the stratospheric ozone layer, and of the role played by CFCs and halons.

Since the last international review was performed in 1989 the studies have shown that the decrease in ozone is more widespread and more pronounced than previously found, and that the ozone decrease is more closely linked to the CFC and halon emissions than was believed earlier.

These conclusions have been strengthened by the findings this winter from two separate expeditions at high northern latitudes. One is the European campaign (EASOE), and the other (AASE II) is the follow-up of the 1989 US Arctic campaign. Nordic scientists were strongly involved in the EASOE campaign, with Kiruna in Sweden as the campaign headquarter site, and with NILU as coordination center for data collection. There was also Scandinavian participation in the AASE II expedition. The results of the expeditions support the picture that is emerging from other studies during the last few years: The significant reduction in column ozone densities which is seen over the last few years in the stratosphere at middle and high northern latitudes is likely to be linked to the human release of chlorocarbons and halons. The possibility for significantly larger ozone depletion than we have seen up to now is high.

The new findings have made it urgent to increase the effort to phase out the use of ozone depleting substances (ODS) globally.

The major findings on ozone layer depletion over the last couple of years are presented in the three sections below. Most of the material is based on the new international ozone assessment (WMO, 1992), this is given in the first section. In the following section material which has been presented after the completion of the ozone assessment (WMO, 1992), is given. The final section discusses some of the studies which have been done in the Nordic countries.

2. FINDINGS PRESENTED IN THE OZONE ASSESSMENT (WMO, 1992)

2.1 Global Ozone Reductions

Satellite and ground based observations continue to show a decrease in the total column of ozone in the Northern Hemisphere during winter. The most recent analysis show for the first time also a significant reduction in the total ozone column at mid and high latitudes in both hemispheres during spring and summer. No significant trend was found over the tropics. It is worth noticing that the decreases were larger during the 1980s than in the 1970s. Figure 1 shows the observed decrease in ozone column densities from the satellite (TOMS)

observations of total ozone as a function of latitude and season for the time period November 1978 through March 1991 (WMO, 1992). The reductions in ozone are significant at latitudes poleward of approximately 40° N and 20° S where ozone is reduced with more than 4% over this period.

2.2 Polar ozone depletion

The strong ozone hole over the Antarctic continues to occur, and contrary to earlier findings where it was observed to be deep every second year, it has been deep and extensive in the area during the latest five of six years (including 1991). Large increases in ultraviolet radiation in the Antarctic have been observed during periods with low ozone (WMO, 1992). Ozone losses comparable to the losses observed over Antarctica have not been observed in the Arctic. However, localized ozone losses have been seen in the winter concurrent with observations of elevated levels of active chlorine at high northern latitudes.

2.3 The relation between release of industrial halocarbons and ozone depletion

The most recent laboratory studies combined with re-interpretation of observations and new theoretical studies which takes into account heterogeneous reactions occurring on stratospheric particles, strengthen the evidence that the observed Antarctic ozone hole is largely a result of the increasing concentrations of chlorine- and bromine- containing chemicals in the stratosphere. There are also stronger indications that the middle- and high-latitude ozone loss in the Northern Hemisphere is largely due to chlorine and bromine compounds. It is therefore highly likely that the ozone loss at middle- and high- northern latitudes will continue to increase in the coming years as the atmospheric abundances of chlorine- and bromine- containing compounds continue to increase. Observations of the major CFC compounds show an increase in their atmospheric concentrations which is similar but slightly less than the observed increase over the past years, thus indicating that any action taken up to date to limit their atmospheric growth, so far has had only a small effect. This is in accordance with our understanding of their extremely slow breakdown in the atmosphere (lifetimes of the order of 50 to 100 years), which means that drastic reductions (approximately 75 to 90% compared to the release in 1986) in the emission of CFC-11, CFC-12, and CFC-113 have to be implemented before the concentrations in the atmosphere is stabilized or reduced.

2.4 The relation between ozone and climate change

It has now been established that the observed loss in column ozone densities occurs predominantly in the lower stratosphere (15-25 km) where ozone has its largest densities. This is also a region where ozone is an active greenhouse gas. Although not conclusive at the moment, the first calculations of the greenhouse effect from the observed ozone decrease during the past decade indicate a significant surface cooling at middle and high latitudes. Indeed, the cooling could

be larger in magnitude than the warming caused by the release of CFCs in the same time period. With increasing evidences of a link between lower stratospheric ozone loss and enhanced levels of chlorine and bromine in the stratosphere the climate impact of the presently used CFCs could therefore be substantially less than previously estimated. It should be stressed that the calculated climate impact of lower stratospheric ozone loss is preliminary and that more firm conclusions can only be drawn after further studies have been performed.

Observations in the troposphere have shown that ozone has increased substantially over the last two decades, also in the upper- and middle-troposphere where ozone changes are significant for the Earth's climate. In fact, sensitivity studies show that increases of the order that has been observed over Europe (about 15% per decade for more than 20 years), to a large extent could balance the cooling coming from the lower stratospheric ozone reductions if they were global or hemispheric in extent. However, at the time of writing the ozone assessment report (WMO, 1992) it was felt that there was not enough information on the large scale extent of observed free tropospheric ozone increases to draw any strong conclusions of the significance of tropospheric ozone increases for climate. As will be shown below, more recent studies show extended free tropospheric ozone increases.

2.5 Estimates of ozone depleting potentials (ODPs)

The most recent studies of the ozone layer problem, which emphasise the key role high latitude processes play for the depletion of ozone in the stratosphere, has led to a re-evaluation of the contribution of the individual ODS (Ozone Depleting Substances) to the ozone depletion. Heterogeneous processes occurring at high- and to some extent at mid- latitudes have become more significant than previously assumed. This has led to changes in ODP (which give the efficiency of a gas in depleting ozone relativ to the depletion by CFC-11) for most of the ODS. New ODPs are given in connection with the ozone assessment (WMO, 1992), and are shown in *Table 1*.

It should be noted that taking the high latitude heterogeneous processes into account in estimating ozone depletion, the impact on ozone is less uniform and the concept of a global ODP are less obvious than in previous estimates. Calculations have become more complicated and all the processes involved are not fully understood. Therefore, the estimates are connected with uncertainties, and the values could change as our understanding of the processes involved in the depletion of the ozone layer evolves further. Nevertheless, the changes in the ODPs are not drastic, as we are looking at effects relative to CFC-11. The exception here is the ODPs for the halons, which have increased as bromine reactions are becoming significantly more efficient when heterogeneous processes take place.

Table 1 below gives the new recommended ODPs from WMO (1992), which are long term values (integrated over a time period much longer than the life time of the molecules).

Table 1

Species	Best estimate of ODP
<u>CFCs</u>	
CFC-11	1.0
CFC-12	~ 1.0
CFC-113	1.07
CFC-114	~ 0.8
CFC-115	~ 0.5
<u>HFCS, HCFCs, etc.</u>	
HCFC-22	0.055
HCFC-123	0.02
HCFC-124	0.022
HCHC-141b	0.11
HCFC-142b	0.065
HCFC-225ca	0.025
HCFC-225cb	0.033
CCl ₄	1.08
CH ₃ CCl ₃	0.12
<u>Brominated Compounds</u>	
H-1301	~ 16
H-1211	~ 4
H-1202	1.3
H-2402	~ 7
H-1201	~ 1.4
H-2401	~ 0.25
H-2311	~ 0.14
CH ₃ Br	~ 0.6

In addition to be sensitive to the heterogeneous chemistry, the ODPs for the brominated compounds will depend on the chlorine level in the stratosphere. At high chlorine levels ODPs for bromine compounds are more efficient.

2.6 Time dependent ODPs

Several of the compounds with low ODP have short chemical lifetimes compared to CFC-11 (HCFC-22, HCFC-123, HCFC-141b, HCFC-142b). The ODP for such compounds over a time horizon which are shorter than the lifetime of CFC-11 (CFC-11 is used as reference gas for calculations of ODP) will be larger than the values given in *Table 1*. This point has been discussed thoroughly in WMO (1989). Since the lifetime of CFC-11 is approximately 60 years, ODPs for the short lived gases over time horizons up to 30 years could be substantially larger than the values given in *Table 1*. *Table 2* gives a few examples of calculated time dependent ODPs for time horizons of 10, 20 and 50 years (C.Brühl, private communications).

Table 2. Time dependent ODPs

	τ yrs	α	Time horizons (yrs)		
			10	20	50
CFC-11	69	1	1	1	1
HCHC-22	16	0.06	0.16	0.15	0.11
HCFC-123	1.5	0.012	0.12	0.06	0.02
HCFC-141b	8.5	0.075	0.40	0.29	0.16
HCFC-142b	24.2	0.05	0.12	0.12	0.10

Time horizons of 10 to 20 years are of particular importance, as this is the period over which chlorine levels in the stratosphere are expected to increase, despite the strong regulations on CFCs that will be implemented over the next years. It will be important to limit chlorine growth in this time period. The largest change in ODP when we consider a limited time horizon of 10 or 20 years as compared to an infinite time horizon is found for the compound with the shortest lifetime, e.g. HCFC-123. The increase is approximately a factor 10 on a time horizon of 10 years, and a factor 5 on a time horizon of 5 years.

Compounds with lifetimes longer than the lifetime of CFC-11 (CFC-12, CFC-115) have ODPs over a short time horizon that is smaller than the values given in *Table 1*.

Methyl chloroform is of particular interest as it is a gas which is produced in large quantities, and which has a short lifetime (6 to 7 years). Estimates of its short term impact on ozone (WMO, 1989) indicate that it is comparable to CFC-11 on a 10 years time horizon, and approximately half as efficient as CFC-11 on a 20 years time horizon. Both numbers are substantially larger than the long term value of 0.12 given in *Table 1*.

2.7 Estimates of Global Warming Potentials (GWPs) for chlorine and bromine compounds

In connection with the update of the 1990 IPCC report, the IPCC Supplement Report (IPCC,1992), which has recently been completed, GWPs have been re-evaluated. GWPs for chlorine and bromine containing compounds are given in Table 3, and they are relativ to CO₂. Values are given for a 100 years time horizon. Indirect chemical effects are included only qualitatively.

Table 3.

Global Warming Potentials (GWPs) for chlorine and bromine compounds from the 1992 IPCC supplement (IPCC, 1992).

Gas	Lifetime (years)	Direct GWP*	Sign of indir. effect
CFC-11	55	3400	negative
CFC-12	116	7100	negative
CFC-113	110	4500	negative
CFC-114	400	7000	negative
CFC-115	500	7000	negative
HCFC-22	16	1600	negative
HCFC-123	1.8	95	negative
HCFC-124	7	440	negative
HCFC-141b	11	580	negative
HCFC-142b	22	1800	negative
HFC-125	41	3400	none
HFC-134a	16	1200	none
HFC-143a	64	3800	none
HFC-152a	1.8	150	none
CCl ₄	47	1300	negative
CH ₃ CCl ₃	6.1	100	negative
CF ₃ Br	77	4900	negative

* Time horizon 100 years

The direct GWPs for some of the compounds are slightly higher than in the previous report. This is a result of new measurements of their loss reactions, which give slower oxidation than previously assumed. The indirect effect, through ozone reduction in the stratosphere, is substantial, although no values are given. The sign of the indirect effect is negative for all chlorine- and bromine- containing compounds. Preliminary calculations of the indirect effects based on observed ozone loss give values which are comparable to the direct effects. Thus, if we take both direct and indirect effects into account, the GWPs for CFCs and HCFCs are likely to be strongly reduced. The overall role of CFCs and HCFCs as greenhouse gases is likely much smaller than previously assumed.

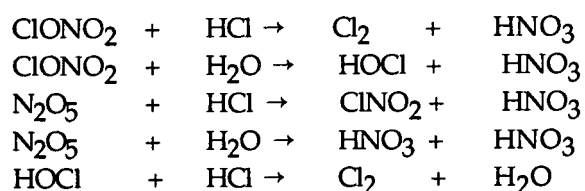
It is interesting to notice that some of the HFCs (e.g. HFC-125, HFC-134a, and HFC-143a), which have no effect on the ozone and thereby are not affected by the uncertainties in the calculations of the indirect effect from ozone changes, could have appreciable climate effects. HFC-152 has also no indirect chemical effect on climate, its direct effect is, however, small compared with the other HFCs (see *Table 3*).

The impact of nitrogen oxides (NO_x) on stratospheric ozone depends strongly on the height of NO_x release. In the lowest part (below about 20 km) NO_x produces ozone, while above it breaks down ozone. Furthermore, NO_x interacts strongly with chlorine through the formation of chlorine nitrate. Increases in NO_x will reduce the chlorine effect of ozone. Therefore, the impact on ozone of N_2O , which produces NO_x in the stratosphere, will depend on the chlorine level. The more chlorine is present in the stratosphere, the less efficient will the ozone loss by N_2O be. Model calculations of ozone depletion show that the interaction between chlorine and nitrogen compounds in the stratosphere becomes stronger when heterogeneous reactions in the stratosphere are included in the calculations. ODP for N_2O at different chlorine levels should be estimated.

2.8 Estimates of ozone depletion

Since it is now recognized that heterogeneous chemistry will enhance the ozone depletion by chlorine compounds in the stratosphere significantly, and affect the chlorine nitrogen interaction in the lower stratosphere, special emphasis has been given to parameterize heterogeneous chemical processes in the lower stratosphere. Several model groups participated in the ozone assessment (WMO, 1992) of ozone depletion which considered chemical reactions on PSCs (Polar Stratospheric Clouds) and on background sulfate aerosols.

Figures 2 and 3 show the ozone loss calculated with the University of Oslo 2-D model as a function of latitude and month for the period 1970 to 1991 and 1970 to 2000, respectively, from anthropogenic releases of CFCs and halons when the following heterogeneous chemistry reactions are included in the model:



These reactions are assumed to occur on PSCs and on background aerosol particles.

Calculations with new and updated heterogeneous chemistry in the stratosphere give ozone reductions from CFC and halon emissions over the past decade (approximately 2/3 of the reduction given in *Figure 2*) which are in agreement

with the pronounced ozone reductions which are observed at mid and high northern latitudes. The observed reduction between 1980 and 1990 at mid and high northern latitudes is in the range 4-8%.

The adopted scenario for CFC and halon emissions, which has been considered most likely, gives increases in the chlorine loading of the stratosphere until the turn of the century, whereafter there is a slow decrease. This leads to total ozone decreases which have their largest values in approximately 8 to 10 years from now. *Figure 3* shows the calculated ozone depletion from anthropogenic chlorine and bromine in year 2000. When the ozone layer is at its minimum, global average column densities are approximately 2% lower than today and about 7% lower than in 1970. The largest reductions will occur at high latitudes in winter, where column densities are up to 20% lower than in 1970. The global average column density of ozone will in 2050 be slightly less than it was in 1970, prior to ozone reductions by CFCs. The recovery of the ozone layer will first occur at low latitudes, and later at high latitudes. Therefore; although it is estimated to be full recovery of the ozone layer at low latitudes in 2050, and even a slight increase compared to 1970, there will still be a significant reduction in the ozone column density at high latitudes.

It is believed that with the adopted parameterization of the heterogeneous chemistry, and with the updated chemistry the model gives a reasonable description of the present ozone depletion and also of future ozone depletion from releases of CFCs and halons for the emission scenario that is adopted, although we cannot rule out surprises as we have seen in the past.

3. RECENT FINDINGS

3.1 Ozone depletion at mid- and high- northern latitudes

The first results from the two 1991/1992 Arctic campaigns (EASOE and AASE II) show that the stratosphere was highly perturbed this winter. ClO levels were enhanced, also outside the polar region. NO_x levels were reduced in several areas. Both of these observations strengthen earlier suspicions of enhanced ozone depletion in northern areas from anthropogenic releases of CFCs and halons. It is possible that the observed perturbations could be partly due to the aerosol particles from the volcanic eruption from Mount Pinatubo in the Philippines in June 1991. Increased levels of particles are expected to enhance the possibility of ozone depletion in the stratosphere through anthropogenic releases of CFCs and halons. Measurements have shown that ozone levels were low during winter and spring 1992 over high northern latitudes. For instance, Bojkov (1992, private communications) reports that the ozone column densities were particularly low at latitudes 50 to 60 degree over Europe and Asia during January (up to 20% lower as normal), and that the values were also lower than normal over Canada. It should, however, be noted that the data are not yet fully analyzed with regard to ozone depletions, and conclusions drawn about pronounced anthropogenic impact on the 1992 stratospheric ozone is therefore

premature. In connection with the EASOE campaign earlier this year, it was pointed out that the low ozone values observed over Europe this winter could partly be explained by unusual weather patterns.

3.2 Tropospheric ozone increases

After the completion of the ozone assessment (WMO,1992) ozone sonde observations for several stations over an extended area in the Northern Hemisphere have been presented in two papers. Bojkov (Paper presented at the ozone symposium in Charlottesville, USA in June 1992) reported that ozone sonde measurements from Canada and Japan show similar increases in tropospheric ozone as found at European stations. London and Liu (1992) have performed similar analysis of ozone sonde data covering a period up to 25 year for 10 stations. All northern hemispheric stations showed a long term trend on the average of 1.2% pr year in the middle troposphere (500 hPa). Aspendale in Australia showed a very small trend. It looks therefore like there is a broader base of support for the assumption that free tropospheric ozone is increasing on a large scale in the Northern Hemisphere. The data do, however, show that there are large regional variations; the increase being more pronounced over industrial areas than over remote locations.

3.3 Ozone depletion by methyl bromide

During the past six months particular attention has been given to the possible role of methyl bromide (CH_3Br) for ozone depletion. A recent assessment (June,1992) of methyl bromides role for ozone depletion was held in Washington, D.C., and the discussion below is based on that assessment (UNEP, 1992).

Methyl bromide is the main bromine compound which is transported to the stratosphere even if its atmospheric lifetime is less than two years. Its concentration is about 10 to 12 pptv. It is now recognized that a large fraction of the emission of methyl bromide is from man made activities and that its concentration is increasing. The main area of usage is as a pre-planting fumigant. Other usage is as post-harvesting fumigant and as a structural fumigant. Probably around 50% of the methyl bromide used in this way escapes to the atmosphere (around 30.000 tonnes in 1990). This source is estimated to represent about 30% of the total methyl bromide emitted to the atmosphere.

The significance of bromine compounds for the ozone depletion is that bromine is 40 times or more efficient in reducing the ozone layer than chlorine. The very short lifetime of methyl bromide compared to that of CFC-11, means that the short term effect compared to the effect of F-11 is much larger than the long term steady state value given by its ODP (Table 1). It is therefore of interest to estimate the short term effect of methyl bromide over the next 20 years when chlorine and bromine compounds are likely to have their maximum impact on ozone. In *Table 4* we have used the University of Oslo 2-D model (Isaksen, 1992) to

calculate the time dependent effect relative to CFC-11 of an enhanced emission of methyl bromide on ozone for the next 35 years. The numbers give the efficiency of 1 kg of methyl bromide released relative to 1 kg of CFC-11 for different time horizons.

Table 4. Time dependent ozone depletion by CH₃Br relative to CFC-11.

	1995	2000	2005	2010	2015	2020	2025
Rel.eff.	11.2	3.60	2.21	1.93	1.52	1.27	1.11

The University of Oslo 2-D model and the AER model (USA) (UNEP, 1992) were used to estimate the additional ozone depletion that an increase of 10 pptv of CH₃Br would cause. In both calculations the ozone depletion between 1990 and 2000 would increase by a factor of 1.3.

The above calculations show that due to the large short term ozone depletion efficiency of methyl bromide, a reduction in the anthropogenic emission of this gas could lead to a substantial gain in ozone depletion over the first few years. In the 1991 ozone assessment (WMO, 1992) it was estimated that a reduction of 10% in the global yearly emission (10 000 tonnes) of methyl bromide would be the equivalent of advancing the CFC phaseout by up to three years. This conclusion is confirmed by the new methyl bromide assessment.

The assessment has identified two main areas of uncertainties. The first one is the fraction which escapes to the atmosphere when it is used as a preplant fumigant, and the second is surface removal processes.

4. OZONE MEASUREMENTS IN THE NORDIC COUNTRIES

Ozone measurements are performed in all nordic countries, with measurements of total ozone on a continuous basis. Some of the ongoing activities in the area is presented below.

Island has the longest unbroken series in the Nordic countries. Total ozone has been measured on a regular basis in Reykjavik since 1957. Trend analysis of the revised data give a statistical significant linear reduction in the period 1957 to 1977 of $0.11 \pm 0.07\%$ pr year in the annual average total ozone, and in the period 1977 to 1990 of $0.30 \pm 0.11\%$ pr year. The decline is caused by a pronounced summertime decline, with no significant reduction during winter or fall (Bjarnason et al., 1992).

Observations of total ozone in Sweden (Norrköping) is shown in *Figure 4* (W. Josefsson, SMHI, personal communication) for the 6 first months of 1992. All months show monthly mean values which are below the longterm mean values. The deviation from the longterm mean is most pronounced during the winter months, but the values are also lower during May and June. This is in accordance with the analysis discussed earlier.

The Norwegian Dobson measurements from Oslo have been reanalysed during the last year. The result of this new analysis, is that the continuous observations, which has been recorded over the last 12 to 14 years, now show a significant decrease in total ozone (S. Larssen, 1992, paper presented at the quadrennial ozone symposium in Charlotteville, USA).

5. IMPLICATIONS OF THE RECENT STUDIES

The new findings have led several governments to consider a faster phaseout of CFCs and halons. It will probably also lead to a discussion of including several of the proposed HCFCs in the Montreal Protocol.

One important finding which has been apparent for some time in connection with the development of the Antarctic ozone hole, and which also seems to emerge from the more recent ozone observations at mid- and high- northern latitudes, is the non-linearity in the decrease in the lower stratospheric ozone. The loss occurs predominantly at heights between 15 and 25 km and it has been linked to enhanced chemical activities in the presence of stratospheric particles.

Ozone observations show that the decrease in a region is much more rapid after a certain time than it was earlier. This happened during the development of the Antarctic ozone hole, and seem to be happening in connection with the slower but still significant ozone reductions in the Northern Hemisphere. It is possible that this occurs when the chlorine content in the stratosphere exceeds a certain level. This level could be different in the two hemispheres, due to different efficiencies of the ozone depleting chemistry during the spring months. In the Antarctic region high chlorine levels persists for a long time period during the spring months with efficient ozone depletion chemistry, while in the Arctic region conditions with high chlorine levels are broken up much earlier, resulting in less efficient ozone depletion.

Model calculations of future ozone changes points to substantial ozone loss over the next 10 years due to continued chlorine and bromine increases in the stratosphere. These increases will be only moderately affected by actions taken to limit CFC emission. This is due to the extremely long lifetimes of the major CFC compounds (CFC-11, CFC-12, CFC-113) which react very slowly to changes in emissions. Changes over the next 10 years will therefore to a large extent be determined by previous emissions. We can therefore expect continued decreases in ozone until the turn of the century, regardless of actions taken to reduce CFC emissions.

However, chlorine and bromine levels in the stratosphere, and thereby the ozone depletion beyond a 10 year time horizon will depend critically on the measures taken over the next few years to reduce emission of chlorine and bromine containing compounds.

The conclusion of the newly completed assessment is that the ozone problem is more severe than previously believed, and that action should be taken to reduce the release of ODS more efficient than previously agreed upon.

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