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Center for  
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# **The ozone depletion problem**

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## **CICERO**

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# 1. The scientific issue

The ozone depletion issue has been on the scientific agenda almost continuously since Paul Crutzen (1971) and Harold Johnston pointed out that a projected fleet of supersonic aircraft could harm the protecting ozone shield around the Earth. At that time it was well established that ozone was present in the stratosphere in amounts sufficient to filter out harmful solar radiation. It was also known that ozone was generated in the stratosphere through the photodissociation of molecular oxygen by shortwave solar radiation, and that redistribution by transport processes taking place in the lower stratosphere (heights between approximately 15 and 30 km) played a significant role for ozone distribution. There is a large variation in the ozone distribution and in the column amount of ozone, with latitude and longitude, and with season. This was known before the ozone depletion issue was raised. It has been well recognized from the beginning that the key point for the ozone depletion issue is how the chemical loss process controls the overall ozone distribution in the stratosphere through different catalytic chemical reactions.

Our present state of knowledge of the ozone depletion problem is a result of a large and concentrated research effort over the last 25 years, where the focus has been on understanding man's impact on stratospheric ozone through the emission of certain chemical compounds (e.g. nitrogen, chlorine and bromine containing compounds). This research has consisted of laboratory studies, atmospheric measurements and model simulations of atmospheric processes. All together, the studies have advanced our understanding tremendously, both of atmospheric processes in general, and of the impact of man's activities in particular.

Issues raised regarding the ozone problem has been strongly linked to the development of our understanding of the atmospheric science behind ozone formation and distribution in the stratosphere. There are three major advancements in this process which are strongly linked to scientific discoveries:

- 1) The importance of ozone depletion by NO<sub>x</sub> emitted from high flying aircraft became an issue shortly after Paul Crutzen in a paper in 1970 showed that stratospheric NO<sub>x</sub> played a key role for the loss of stratospheric ozone. This started a concentrated international research effort that continued after the chlorine issue was raised.
- 2) The catalytic destruction of stratospheric ozone by chlorine compounds originating from the release of CFCs, originally suggested by Rowland and Molina was published shortly after Cicerone and Stolarski in 1973 had demonstrated the potential of catalytic chlorine reactions in reducing stratospheric ozone, and Lovelock through measurements had shown that CFCs were distributed throughout the troposphere.
- 3) The significance of man-made emissions for the development of the "ozone hole" has become apparent after the discoveries of large spring time ozone reductions over the Antarctica in the mid-eighties by Joe Farman and his collaborators. This has led to a highly focused research over the last 10 years.

## **2. Current status of stratospheric ozone loss**

The most recent analysis of the decrease in total ozone column densities based on satellite observations show a global average decrease of from 4 to 6 % over the last two decades. The significant winter/spring-time decreases in the two polar regions are positively shown to be a result of human activities.

The springtime (October) decrease of 50 % or more in the total ozone column over the Antarctic continent (“ozone hole”) is as large as ever (covers an area of approximately 20 million km<sup>2</sup>).

Observations performed by European scientists in the northern polar region during the last 3 - 4 winter seasons show a significant ozone loss in the lower stratosphere (at heights around 20 km) that can be traced back to enhanced chlorine levels. The ozone loss has been particularly large during the 1995 and 1996 winter seasons. In some cases chemically induced local ozone losses over 30 % have been observed.

The man induced ozone losses at northern latitudes are of particular interest since these losses occur close to or in some cases over populated areas.

### 3. Problems related to ozone layer depletion

The main consequence of ozone layer depletion which has been recognized as important for several decades is:

**a) Reduction in stratospheric ozone will lead to a reduction in the total ozone column, thereby allowing more ultraviolet (UV-B) solar radiation to penetrate to the Earth's surface.**

The solar UV-B radiation at wavelengths shorter than approximately 310 nanometer is harmful in several respects:

It has been demonstrated that the UV-B radiation is harmful for the human health. Increased UV-B radiation will lead to suppression of the immune system (possible increases in the severity of infectious diseases); adverse ocular effects (increases in cases in cataracts per year); increases in cases of non-melanoma skin cancer. In the latter case for instance, a 4 % reduction in the total ozone column world wide has been estimated to lead to an increase in cases of non-melanoma skin cancer of approximately 100.000 by the international WMO (World Meteorological Organization) panel for assessing the effect of ozone depletion.

UV-B radiation will have an impact on terrestrial plants: Growth and photosynthesis can be inhibited; UV-B radiation interact with other environmental factors, making it difficult to predict the effect.

The aquatic ecosystem is affected: It is already under UV-B stress, and increased UV-B radiation will cause further detrimental effects; could have impact on the uptake on CO<sub>2</sub>, thereby affecting climate; will lead to reduced biomass production.

The problems with the enhanced UV-B radiation as a result of decreased ozone column densities have been recognized for several decades. This is a problem that does not discriminate between changes in ozone in the different height region, whether it occurs in the stratosphere (at height above approximately 15 km and below 55 km) or in the troposphere (at height below approximately 15 km); it is the column amount of ozone above the surface that filter out the harmful solar radiation that is of importance. However, since 90 % of the ozone in a column above the surface is located in the stratosphere, changes in stratospheric ozone is first of all what matters for the UV-B fluxes.

Apart from industrial regions, where low level pollution (ozone and particles) partly have masked the effect of ozone depletion, there are now clear evidences that stratospheric ozone depletion leads to enhances in the UV-B radiation.

For instance: Solar flux observations over the Antarctica show that the intensity of the shortwave solar radiation are more enhanced during the period of the "ozone hole" in the spring months (October) than at mid-summer (end of December) when the ozone distribution is back to normal for that time of the year. These particular observations are a clear result of the observed behavior of the ozone layer. There are also studies that indicate that the enhanced UV-B radiation has led to enhanced levels of mortality of organisms in the surface levels of the ocean along the ice sheets. This is probably a first indication of a link between reduced

stratospheric ozone from man made chemicals and environmental effects caused by enhanced intensity of harmful solar radiations.

The relation between ozone depletion and enhanced UV-B radiation has not been as clearly demonstrated at Northern latitudes as we have seen in the Southern hemisphere, although there are evidences of ozone depletion in the northern polar latitudes. However, it has been shown that the significant ozone reductions which has been observed over Europe during the last 5 years has led to enhanced UV-B fluxes. This is for instance very evident from solar flux observations observed over Thessaloniki in Greece since 1991. (Zcrefos et. al., 1995).

The current situation is therefore that there are available data which link the observed ozone decreases during the last years to enhanced harmful solar radiation.

**b) There are also links from ozone depletion to climate change: Changes in the height profile of ozone, particularly in the lower stratosphere and in the upper troposphere, are of relevance for the Earth's climate.**

Ozone is an efficient greenhouse gas that contribute to the heating of the Earth's surface. The observed stratospheric ozone depletion is largest in the lower stratosphere (15 to 25 km). Since this is a region were temperatures are much lower than at the surface, changes in this region will have the largest effect on surface temperatures. The result of the observed ozone decreases is according to model studies that there will be a cooling effect, particularly at high latitudes in the two hemispheres where the largest ozone reductions have been observed. Since it now has been clearly demonstrated that the ozone loss to a large extent is a result enhanced CFC levels, the secondary effect of ozone cooling should be taken into account when the radiative heating from the very potent climate gases CFCs are considered. The result of this is that the CFCs are becoming less important as climate gases than previously assumed when chemical effect on gases like ozone was not considered.

Another area of research of the impact of ozone layer changes which has drawn considerable attention is the:

**c) Increases in the oxidation capacity of the troposphere.**

Recent model studies of the tropospheric chemistry have shown that the enhanced UV-B radiation that has followed the reduction in stratospheric ozone the last few years, is likely to have enhanced the oxidation process (oxidation capacity) in the troposphere significantly. This in turn have affected environmental processes like surface ozone generation, acid rain and the oxidation of climate gases like methane.

The issues under points b) and c) represent new area of research where the environmental impact of changes in the ozone layer is only partly understood.

## 4. The need for coordinated action

The ozone depletion problem is a global problem which acts on a decadal time scale rather than annual or shorter time scales. This has to do with the very long lifetime of the CFCs, the primary sources of ozone, and with the time it takes for man-emitted source gases at the Earth's surface to reach the stratosphere. This delay is estimated to be approximately 5 years. Gases emitted at different locations at the Earth's surface will be completely mixed before they reach the stratosphere. The CFC gases emitted in one country will have the same global impact as CFC gases emitted in other countries. There is another consideration which is of importance: Due to the very long lifetimes of the CFCs, the atmospheric concentrations respond very slowly to changes in emissions, and it takes decades to reduce their atmospheric concentrations to acceptable levels once the emissions have taken place. The long lifetime and the time history of previous emissions also means that reductions need to be significant before we will have significant chlorine reductions in the stratosphere. As an example: In order to *stabilize* the CFC concentrations at the 1990 levels it has been shown that *emissions of the major compounds* needed to be reduced by 70 to 80 % compared to the 1986 emissions.

We are now discussing significant chlorine reductions over the next decades as a result of the agreement obtained in the Montreal Protocol and in later amendments. Such reductions can only be fulfilled with nearly full compliance of the Montreal agreement. It is therefore important that there is full international agreement about the phaseout of ozone depleting substances, and that this agreement is followed up by the all countries.

## 5. Action taken to reduce ozone depleting substances (ODS)

A large number of chemical compounds, which are emitted due to human activity, has been identified as ozone depleting substances, and their ozone depletion potential (ODP) has been estimated based on global atmospheric model studies. These are first of all organic chlorine and bromine compounds. The ODP for a gas is given as the global reduction of ozone for a certain emission (1 kg) of the gas, compared to the reduction of ozone for a similar emission of a reference gas over an indefinite time horizon. CFC-11 (CFCl<sub>3</sub>) has been adopted as reference gas. Table 1 shows ODP for different man made chlorine and bromine compounds presented in the most recent ozone assessment which was published in 1995 (Scientific Assessment of Ozone Depletion: 1994).

Trace gas	Lifetime (year)	ODP
CFC-11	50	1
CFC-12	102	0.82
CFC-113	85	0.90
CFC-114	300	0.84
CFC-115	1700	0.40
CCl <sub>4</sub>	42	1.20
CH <sub>3</sub> CCl <sub>3</sub>	5.4	0.12
HCFC-22	13.3	0.04
HCFC-123	1.4	0.014
HCFC-124	5.9	0.03
HCFC-141b	9.4	0.10
HCFC-142b	19.5	0.05
CH <sub>3</sub> Br	1.3	0.64
H-1301	65	12
H-1211	20	5.1

**Table 1. The main ozone depleting substances (ODS) which are regulated through the Montreal Protocol, their atmospheric lifetime and ozone depletion potential (ODP). Source: (WMO, 1995)**

The large variation in ozone depletion due to the presence of the chlorine and bromine source gases reflects the difference in the efficiency of the gases in depleting stratospheric ozone over their respective atmospheric lifetimes. The first group of compounds are the chlorinated source gases originally identified as ODS which in general have high ODPs. The second group (the HCFCs) consists of CFC substitutes which for most of the gases have substantially smaller ODPs than the CFCs. The last group in the table represent the main bromine source gases, which in general are much more efficient in depleting stratospheric ozone than chlorine compounds, therefore the high ODPs.

The difference in ODPs between the compounds are first of all a result of the difference in atmospheric lifetimes of the gases. Longlived compounds (e.g. CFCs) will build up larger concentrations than the shortlived before they are removed from the atmosphere, thereby making them more efficient ODS.

The emissions and the time horizons for the phase out of the ODS are determined by the agreements obtained through the Montreal Protocol in 1987 and the later amendments to the protocol obtained in London in 1990 and in Copenhagen in 1992, and the Vienna adjustment in 1995. According to these agreements the use of the major chlorine sources in the stratosphere: CFCs (like CFC-11 and CFC-12), methyl chloroform, carbon tetrachloride and the halons, should be phased out by now (1997) For the less efficient HCFCs, there is an agreement for phase out over the next 2 to 3 decades.

All major emitting CFC countries (industrialized and developing) have signed the agreement. It seems clear that the Montreal Agreement has had a significant impact on the global emissions of ODS over the last 6 to 8 years. Reported changes in the emission of key ODS after 1988, when changes in emissions started to become significant for most of the gases affected by the Montreal Protocol, is shown in Table 2.

Trace gas	Estimated changes in emission (%) 1988 - 1992
CFC-11	- 45
CFC-12	- 30
CFC-113	- 30
CFC-114	- 65
CFC-115	10
CH <sub>3</sub> CCl <sub>3</sub>	- 15
HCFC-22	30
HCFC-142b	450
H-1301	- 25(*)
H-1211	- 25(*)

**Table 2: Estimated changes (%) in the emissions of some of the ODS which are regulated by the Montreal Protocol over the time period 1988 to 1992, except for gases which are marked with (\*), for which the changes is between 1988 and 1990 estimates based on figures given in the 1995 WMO ozone assessment.**

The reported emission of CFCs (except CFC-115) and the halons have been reduced significantly, and this trend has continued after 1992. For the HCFCs the situation is different, since they partly are substitutes for CFCs. The increase have been particularly large for the higher HCFCs, here represented by HCFC-142b. However, we should bear in mind that their concentrations are low compared to the major CFCs. For instance: The HCFC-142b mixing ratio in 1992 is 3.5 pptv compared to the mixing ratio of CFC-12 of 500 pptv. The observed rapid increase of the HCFCs will therefore have a moderate impact on the stratospheric

chlorine burden. It is clear that the total emission of chlorine containing compounds contributing to the stratospheric burden of ODS has decreased significantly since the late 1980s.

Observations of the atmospheric concentrations of the major man emitted chlorine compounds have shown reduced growth rate during the last few years, undoubtedly a result of reduced emissions. All major CFCs, methyl chloroform, carbon tetrachloride and the halons were reported in the recent WMO ozone assessment report (1995) to show significant slower growth in the time period from 1990 to 1992 than what was reported in the previous report for the time period prior to 1990.

One of the gases which show the most clearly reduction in growth rate is CFC-11. During the last couple of years its growth has leveled off. In fact, recent observations of the tropospheric burden of total man emitted chlorine compounds indicate that the chlorine peak has been reached in the troposphere. It is therefore likely that we can expect a gradual decline in the tropospheric burden in the future. There is a delay of approximately 5 years for the chlorine peak to reach the stratosphere due to the slow transport processes. It therefore looks like we can expect maximum chlorine levels in the stratosphere to be reached around the turn of the century, and see declining levels in the next century.

The conclusions to be drawn from these studies must be that we see a distinct effect on the ODS in the stratosphere as a result of the agreement reached in the Montreal Protocol. This agreement has already resulted in reduced chlorine levels compared to what we would have had without the Montreal Agreement. The effect will be more apparent on the chlorine level and on ozone reduction in the coming decades as the total chlorine burden in the stratosphere starts to decrease as a result of the reduced emissions.

## 6. Future actions

A future reduction in the chlorine levels as outlined above, require that there are nearly full compliance with the Montreal Agreement. It has been shown that only moderate deviations in certain sectors of ODS use could, particularly in the long run, give marked deviations from the expected decline in the total ODS loading. There are several complicating factors in determining future requirements for ODS regulations. Since the Montreal Protocol was agreed upon in 1987, we have seen more or less continuous strengthening of the agreement, which has first of all been a result of development in our scientific understanding of the problem over the last 10 years. Even if we, as it looks at present, will be able to control the chlorine increases, we are most of all interested in the impact on ozone, where there are uncertainties to be solved. The bromine chemistry is less well known, and the importance of the interaction with stratospheric particles needs to be better understood. In particular, changes which are connected to temperature changes could be significant. For instance, the enhanced ozone loss in the lower stratosphere in the Northern Hemisphere during the last winters seems to be linked to a colder winter stratosphere, which enhances particles and particle induced ozone loss. There is a possibility that this is linked to climate changes (there is a general decrease in lower stratospheric temperatures over the last two decades), and that we could have enhanced ozone loss in the future due to a colder stratosphere. In that case it is possible that we will not see an ozone recovery as would be the case if ozone levels were dictated by the changes in chlorine levels alone.

It will therefore be important to follow closely the development in the ozone layer and in the chemical composition of ozone depleting gases over the next decades to better understand the interaction between the ozone depleting gases and the ozone layer. It will also be of importance to follow the development in the global distribution of ozone depleting substances through observations and global modeling, particularly the substituting gases which will be phased out over an extended time period, and which have shown a rapid increase in global distribution over the last few years. Such studies will give valuable information on the global emissions of ODS.

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# ***This is CICERO***

CICERO was established by the Norwegian government in April 1990 as a non-profit organization associated with the University of Oslo.

The research concentrates on:

- International negotiations on climate agreements. The themes of the negotiations are distribution of costs and benefits, information and institutions.
- Global climate and regional environment effects in developing and industrialized countries. Integrated assessments include sustainable energy use and production, and optimal environmental and resource management.
- Indirect effects of emissions and feedback mechanisms in the climate system as a result of chemical processes in the atmosphere.

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