The Changing Ozone Layer

MILESTONES IN THE HISTORY OF OZONE

Year	Event
1839	Discovery of the ozone by C.F. Schönbein
1860	Surface ozone started to be measured at hundreds of locations
1880	Strong absorption band of solar radiation between 200 and 320 nm attributed to upper atmosphere ozone by Hartley
1913	Proof from UV measurements that most ozone is located in the stratosphere
1920	First quantitative measurements of the total ozone content
1926	Six Dobson ozone spectrophotometers are distributed around the world for regular total ozone column measurements
1929	The Umkehr method for vertical ozone distribution is discovered and determines the ozone maximum is lower than 25 km
1930	Photochemical theory of stratospheric ozone formation and destruction based on chemistry of pure oxygen
1934	Ozone sonde on balloon shows maximum concentration at about 20 km
1955	Global network of ozone stations proposed for IGY
1957	WMO assumes responsibility for standard procedures for uniform ozone observations and the Global Ozone Observing System (GO_3OS) established
1965	Photochemical theory of ozone with destruction by HO_x radicals
1966	First ozone measurements from satellites
1971	Ozone destruction by NO_x mechanism proposed
1974	Start of consideration of ClO_x chemistry as an ozone-destroying mechanism
1974	Human-produced CFCs recognized as source of stratospheric chlorine
1975	WMO conducts first international assessment of the state of global ozone
1977	Plan of Action on Ozone Layer established by UNEP in collaboration with WMO
1981–94	Scientific assessments of the state of the ozone layer issued in 1981, 1985, 1988, 1991 and 1994 by WMO in collaboration with UNEP and national research agencies
1984	Unusually low (~200 m atm cm) total ozone at Syowa, Antarctica, in October 1982, first reported at the Ozone Commission Symposium in Halkidiki, but its significance was recognized only the next year
1985	Vienna Convention for the Protection of the Ozone Layer concluded and data from Halley station on the existence of an ozone hole during Antarctic springs since the early 1980s published by the British Antarctic Survey
1986	Analysis of Montsouris (Paris) surface ozone (1873–1910) indicates levels then were less than half of the present
1987	Montreal Protocol on Substances that Deplete the Ozone Layer concluded under UNEP auspices and basic assessment of the state of the ozone initiated by the International Ozone Trends Panel
1988	Decrease of ozone concentrations by ~10% per decade in the lower stratosphere documented; proof from NASA Antarctic Campaign that active chlorine and bromine byproducts of human activities are the cause of the Antarctic-spring ozone hole
1990	London amendment to strengthen the Montreal Protocol by phasing out all CFC production and consumption by 2000
1991	The WMO/UNEP Ozone Assessment — 1991 reveals ozone is declining not only in winter-spring but all year round and everywhere except over the tropics; very large concentrations of ClO measured in the Arctic confirms concerns for potential stronger ozone decline
1992	Copenhagen amendment further strengthened Montreal Protocol by phasing out CFCs by the end of 1995, adding controls on other compounds
1992-94	Extremely low ozone values (~100 m atm cm) during Antarctic spring and largest area ~24 m. km^2 covered; also the lowest ever ozone values measured during the northern winter-spring seasons all indicating increasing destructive capability by increasing chlorine and bromine concentrations in the stratosphere
1995	Record low ozone values (exceeding 25% below long-term average) observed January to March over Siberia and a large part of Europe

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by

Rumen D. Bojkov

NOTE

The designations employed and the presentation of material in this publication do not imply the expression of any opinion whatsoever on the part of the Secretariat of the World Meteorological Organization or the United Nations Environment Programme concerning content, the legal status of any country, territory, city or area, or of its authorities, or concerning the delimitation of its frontiers or boundaries.

FOREWORD

For millions of years the basic atmospheric composition is believed not to have changed, although some rare compounds such as carbon dioxide are known to have varied. The ozone molecules concentrated mainly between altitudes of 15 to 35 km have determined the temperature structure of the stratosphere and by absorbing the harmful ultraviolet radiation have safeguarded life on this planet. But over the past half century, humans have placed the ozone layer in jeopardy. Unwittingly we have released into the atmosphere chemicals that are destroying part of the life-protecting ozone layer and thus upsetting the delicate balance established by nature.

Isolated ozone observations were made in the 1920s, but systematic measurements began only about 40 years ago. At present nearly 60 Member countries are contributing to the World Meteorological Organization (WMO) Global Ozone Observing System (GO$_3$OS) providing data proven to be essential for understanding the state and changes of the ozone layer. These data started to be carefully analysed when, in the early 1970s, scientific findings highlighted the potential of chlorofluorocarbons (CFCs) and halons to destroy ozone with serious environmental implications.

It was not until the mid-1980s, however, that we obtained convincing evidence of ozone destruction as demonstrated by the dramatic ozone decline in the Antarctic spring. More than 25 years of extensive research by scientists from around the World has shown that compounds released into the atmosphere by humans are depleting ozone.

The atmosphere has no national boundaries, so it was immediately recognized that remedial actions should be part of an international endeavour. WMO has a continuing responsibility for working with governments to provide authoritative scientific information and advice on the state and behaviour of the Earth's atmosphere and climate. In 1975, it issued the first scientific statement "Modification of the ozone layer due to human activities and some possible geophysical consequences". Two years later, WMO joined the United Nations Environment Programme (UNEP) in preparing for an intergovernmental meeting of experts (Washington, DC, March 1977) which drew up the first international Plan of Action for the Protection of the Ozone Layer.

In the succeeding years WMO in collaboration with UNEP, coordinated preparation of a series of scientific assessments. They were based on the achievements of hundreds of scientists, from both developed and developing countries and on contributions from many national agencies. These assessments provided the basis for the UNEP-led negotiations for conclusion of the Convention on the Protection of the Ozone Layer (Vienna, 1985) and its Montreal Protocol (1987). Amendments to the Protocol (London 1990, Copenhagen 1992) required drastic cuts in the use of the CFCs, halons and other ozone-depleting substances which were implicated as the main cause of ozone destruction.

These agreements were the first global environmental risk-management treaties concluded under the United Nations umbrella. They took action to prevent an emerging problem. The story of these treaties has been both extraordinary and unprecedented, providing a model for further international action against global threats to the environment. The action to defend the ozone layer will rank as one of the great international achievements of the century. At the time

of the 50th Anniversary of the United Nations, that achievement demonstrates the spread of the spirit of cooperation among governments, industry, environmental organizations and among the peoples of the planet to ensure a prosperous and sustainable world.
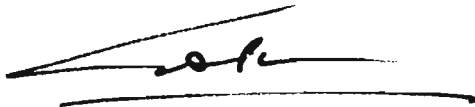
The changing ozone layer briefly tells the story of atmospheric ozone and of the actions coordinated and catalysed by WMO and UNEP to safeguard the atmosphere. It is a story stretching over the 50 years of the United Nations; a story demonstrating continuous collaboration between WMO and UNEP who have issued this booklet jointly as a contribution to the UN's 50th Anniversary commemorations.

There are still some uncertainties regarding the future of the ozone layer. But certainly its recovery depends on the ability of nations to comply with international agreements and curb emissions of substances containing chlorine and bromine that deplete stratospheric ozone. It is gratifying that the world community has made progressive steps by concluding the Vienna Convention and its Montreal Protocol. These treaties provide a dramatic example of science in the service of humankind.

This brochure concludes with a look at possible developments as we approach the next century, and considers how the nations of the world will need to collaborate to prevent future threats to the ozone layer as demanded by Agenda 21 adopted by the Earth Summit (Rio de Janeiro, June 1992).

Finally, we wish to express the gratitude of WMO and UNEP to Dr Rumen D. Bojkov for preparing this brochure.

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1. INTRODUCTION

Since the early 1970s ozone, as an atmospheric trace gas, has gone from being of interest only to a small group of scientists to an issue of global prominence. This leap occurred because those very same scientists have determined that the normal concentration of atmospheric ozone is under attack from human activities. Its decline was detected from information collected by the WMO Global Ozone Observing System (GO_3OS); since the mid-1950s from more than 150 stations and, in the last 15 years, from a few specialized satellites.Extensive laboratory studies, field measurements and theoretical investigations established a link between human-made compounds and these ozone losses. It was on the basis of this information that countries, responding to the call by the United Nations Environment Programme (UNEP), signed the first environmental Convention for the Protection of the Ozone Layer (Vienna, 1985).

Ninety-nine per cent of the air we breathe is nitrogen (78%) and oxygen (21%). Their ratio has not changed for millions of years. Rare components such as water vapour, carbon dioxide, methane, nitrous oxide, ozone and inert gases (e.g. argon, helium, neon) make up less than 1% of the volume of air. In every ten million air molecules on average only three are ozone. If all the ozone in the atmosphere was transferred to the Earth's surface, it would assume a thickness of only about 3 mm.

The total ozone in the atmospheric column at any particular place is variable and is mainly determined by large-scale atmospheric dynamics.

Although exceedingly rare, ozone molecules play a vital role in the life of our planet. They absorb harmful solar ultraviolet radiation (below about 320 nm) shielding us and all other animals and.plants from damage. Ozone also largely determines the thermal structure of the stratosphere (10-50 km) where temperature increases with height (Figure 1).

Even as the sun's energy produces new ozone, (see box—p.6) these gas molecules are continuously destroyed by natural compounds containing oxygen, nitrogen, hydrogen and chlorine or bromine. Such chemicals were all present in the stratosphere long before humans began

Figure 1— About 90% of the atmospheric ozone is located in the stratosphere, where it reaches its highest concentration between about 19 and 23 km above the surface of the Earth (left-hand curve). The air temperature, after a rapid decrease with height in the troposphere, increases in the stratosphere because ozone absorbs radiation (right-hand curve)
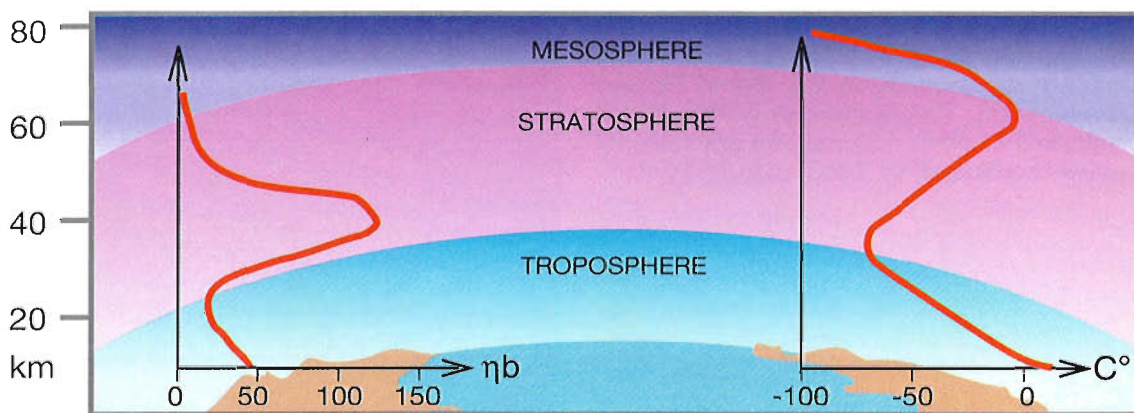
polluting the air. Nitrogen compounds come from soils and the oceans, hydrogen comes mainly from atmospheric water vapour and chlorine comes from the oceans in the form of methyl chloride and methyl bromide. Now human beings have upset the delicate balance of production and destruction. By releasing additional chlorine- and bromine- containing chemicals (e.g. chlorofluorocarbons) into the atmosphere we have enhanced the destruction of ozone leading to lower ozone concentrations in the stratosphere.

The opposite process is occurring in the lower part of the atmosphere (up to 10–12 km), called the troposphere. Here, mainly as a result of combustion processes, the local concentrations of ozone in the northern middle latitudes have more than doubled in the last 100 years. This tropospheric ozone *increase* cannot compensate for the stratospheric decline, but the changes could influence the radiative balance of the earth-atmosphere system.

This subject is being raised on the 50th Anniversary of the United Nations because it represents an environmental success story. Understanding ozone changes and the measures necessary for ozone protection require the collaboration of scientists, governments and industry worldwide. It calls for a common effort by all nations with the collaboration of specialized agencies of the United Nations, such as the United Nations Development Programme and the World Bank, and of other national and international bodies coordinated by WMO and UNEP.
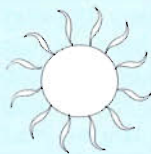
ATMOSPHERIC OZONE
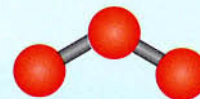
Ozone (O_3) is a form of the element oxygen (O) which has three atoms in each molecule instead of the two of normal oxygen molecules (O_2). It is formed in the stratosphere by the action of solar radiation on oxygen molecules in a process called photolysis; O_2 molecules are broken down to yield atomic oxygen, which in turn combines with molecular oxygen to produce ozone.

Ozone is destroyed naturally through a series of catalytic cycles involving oxygen, nitrogen, chlorine, bromine and hydrogen.

The stratosphere (10–50 km above the earth's surface) contains 90% of all the ozone in the atmosphere. Looking up through the atmosphere, the ozone column has its maximum partial pressure in the lower stratosphere at a level of 19–23 km above the Earth (Figure 1).

The Sun's output and the observed ozone decline

Stratospheric ozone is primarily created by ultraviolet (UV) radiation. The Sun's output affects the rate at which it is produced. The Sun's energy release in the UV part of the spectrum does vary, especially over the well-known 11-year sunspot cycle. Observations over several solar cycles since the 1950s show that total global ozone levels decrease by 1 to 2% from the maximum to the minimum of a typical solar cycle. The recently-observed long-term changes in ozone are much greater than this. They cannot be attributed to changes in solar activity.

2. OZONE MEASUREMENTS AND DISTRIBUTION

Ozone was discovered by C. F. Schönbein when observing electrical discharges in 1839 but it was not until after 1850 that it was determined to be a natural atmospheric constituent. Its name comes from the Greek word meaning "smell", a reference to ozone's distinctively pungent odour when in large concentrations. Surface ozone measurements have been made regularly since the 1860s. In 1880, experiments showed that ozone strongly absorbed radiation in the ultraviolet part of the sunlight spectrum. This led by 1913, to conclusive proof that most of the atmosphere's ozone was located in the stratosphere. It was later shown that its maximum concentration occurs between 19 and 23 km (Figure 1).

Following the first quantitative total column ozone measurements in 1920, G. M. B. Dobson, an Oxford scientist, perfected an instrument to monitor total ozone routinely. The instrument was a landmark in ozone science. It is still the backbone of the Global Ozone Observing System and is continuously in use today at almost 100 observatories around the world. Amounts of·ozone are regularly reported in thickness of the total column ozone, commonly known as Dobson Units (see box left).

Since the late 1950s, filter ozonometers at 44 stations in the former USSR have also provided valuable data. In the last decade, an automated Brewer ozone-spectrophotometer has been developed. A number of these instruments are starting to report ozone data.

Ground-based measurements are now augmented by specialized equipment on satellites, such as the Total Ozone Mapping Spectrometer (TOMS), the Stratospheric Aerosol and Gas Experiment and the Solar Backscatter Ultra Violet spectrometer.

In 1929, a method, called the Umkehr effect (see box), of determining the vertical profile of ozone concentrations was discovered. It was followed in the 1930s by the development of the photochemical theory of ozone formation by Chapman. Later, balloon ozonesondes provided ozone profile data. For more on the history of ozone see inside the front cover.

A global network of ozone observing stations formed part of the plans for the ambitious

OZONE MEASUREMENT AND UNITS

Total ozone is defined as being equal to the amount of ozone contained in a vertical column of base 1 cm^2 at standard pressure and temperature. It can be expressed in units of pressure, typically about 0.3 atmosphere centimetres. The milli-atmosphere centimetre—m atm. cm (commonly called the Dobson Unit) corresponding to an average atmospheric concentration of approximately one part per billion by volume (1 ppbv) of ozone, is most frequently used. Ozone is not distributed uniformly through the vertical column.

The world average is about 300 units, it varies geographically from about 230 to 500 Dobson Units. Total column ozone has, on average, its lowest values over the equatorial belt and increases with latitude (Figure 2).

The Umkehr effect

An optical effect is observed when the ratio of the measured intensities of scattered zenith skylight at two different wavelengths (311 and 332 nm) is plotted against the increasing zenith angle of the Sun between 60° and 90°. The ratio increases with increasing zenith angle up to about 86°, then a reversal (Umkehr) occurs.

The combination of absorption and scattering of the wavelengths produces an altitude scan from which the vertical ozone distribution in nine 5 km-thick layers can be deduced. Such calculations are carried out by a uniform method at the WMO World Ozone Data Centre which keeps more than 40 000 profiles on file.
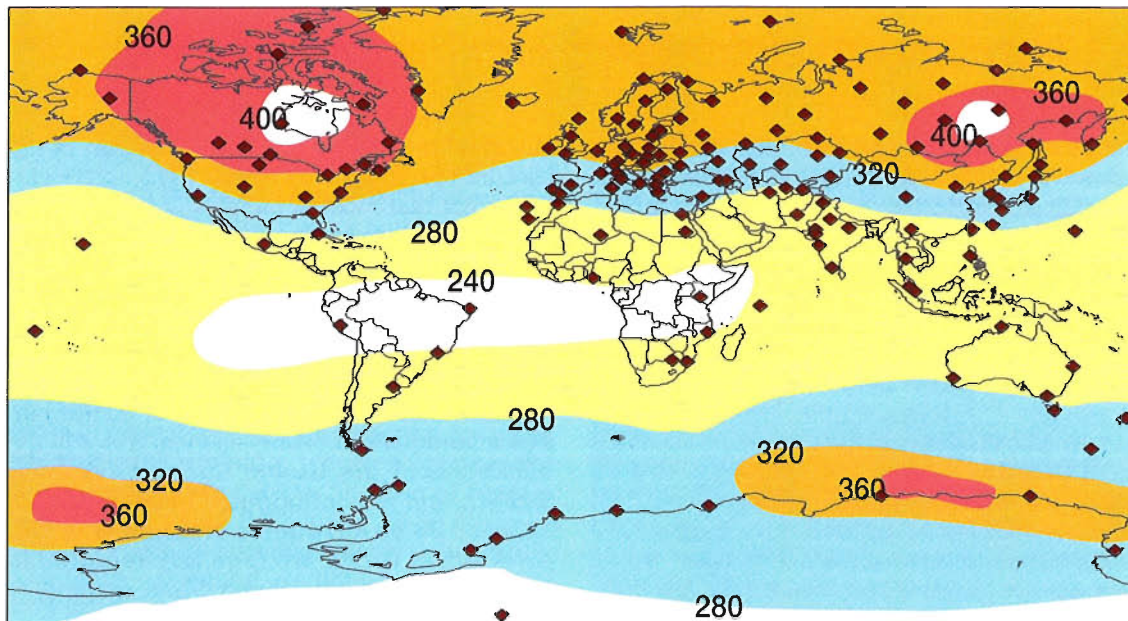
Figure 2 — Locations of active GO₃OS stations with an indication of the average ozone distribution: low in the equatorial belt, high in the middle (and northern polar latitudes)

International Geophysical Year (IGY) of 1957. During the Year, WMO assumed responsibility for the collection of ozone data from the IGY. In collaboration with the International Ozone Commission, the Organization developed standard procedures and coordination, thereby ensuring uniform high quality ozone measurements. These activities can be said to mark the launch of the WMO Global Ozone Observing System, now part of the Global Atmosphere Watch (GAW).

Up to this point, ozone studies had been undertaken solely for scientific purposes, such as determining the role of ozone in the radiative balance or its potential for being used as a tracer for atmospheric circulation. A link between increased ultraviolet radiation and skin cancer had been suspected, but the world was still *unaware* of the potential for human activities to deplete the ozone layer.

Ozone is being produced all year round in the stratosphere over the equatorial belt. It is trans-ported by air movements towards the polar latitudes. The bottom of the stratospheric reservoir, where most of the ozone resides, is determined by the height of the tropopause

Favoured by the extensive poleward air currents, ozone reaches its highest values over the Canadian Arctic and over Siberia. During winter in the southern hemisphere, a nearly symmetrical cold air polar vortex prevents the ozone-rich air from the tropics from reaching southernmost latitudes. Ozone concentration remains high over middle latitudes until the austral summer. As we will see later, these specific meteorological conditions over Antarctica and the presence of large amounts of reactive chlorine facilitate ozone destruction.
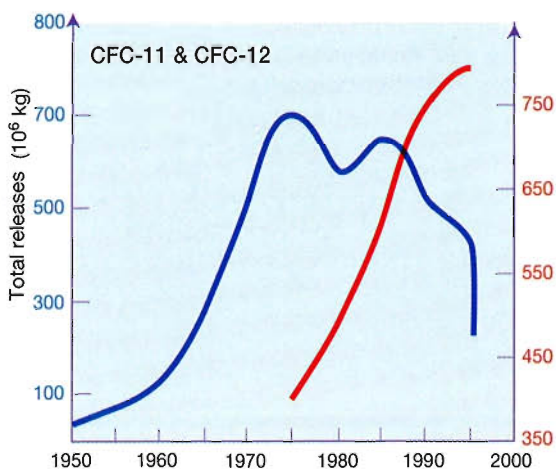
THE TROPOPAUSE

The isothermal region separating the troposphere from the stratosphere (Figure 1), the tropopause lies at an altitude of 8–10 km at polar latitudes and nearly 18 km over the equatorial belt.

3.   DEFINING THE THREAT TO THE OZONE LAYER

Until the early 1970s nobody dreamed that human activity could threaten to deplete the ozone layer. Then scientists identified two potential problems: exhausts from supersonic planes (SST) flying in the lower stratosphere, and chemicals used in refrigerators and as propellants in spray cans. In 1971, H. S. Johnston, at the University of California (Berkeley), pointed out the potential danger of a large fleet of SSTs emitting considerable amounts of nitric oxide into the lower stratosphere, possibly accelerating natural ozone destruction. Only three years later, F. S. Rowland and M. Molina showed that a widely used class of very inert chemicals known as chlorofluorocarbons were transported to the stratosphere by convective air movements. There, they could absorb high-energy photons from sunlight and release free chlorine; Once released, the chlorine could destroy stratospheric ozone through a series of catalytic reactions.

We now know that bromine from the halons used in some fire extinguishers can also be
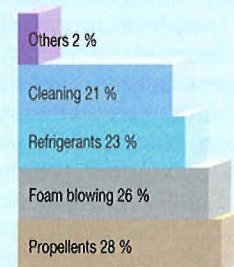
HALOCARBONS

Halocarbon is a generic term covering a number of human-produced gases all containing carbon and halogen (fluorine, chlorine or bromine) atoms. Halocarbons include chlorofluocarbons (CFCs) and halons. The first was synthesized in 1928. Since then, they have come to be widely used for a variety of purposes such as propellants in aerosol cans, in the manufacture of soft and hard foams, in refrigeration and air conditioning, and as cleaning solvents (Figure 4). Consequently, they were increasing rapidly in the atmosphere (Figure 3).

Halocarbons in the troposphere are inert, non-toxic, non-flammable, odourless and colourless. However, when they reach the stratosphere, particularly at and above the layer of maximum ozone (19–23 km), high-energy ultraviolet photons from the Sun free chlorine or bromine atoms. These atoms catalytically detach one oxygen atom from an ozone mole-cule, thus convert ozone to molecular oxygen (Figures 6 and 7).

Figure 3 — The release of of the two most widely used CFCs, CFC-11 and CFC-12, grew from insignificant amounts in the 1950s to more than 700 thousand tonnes a year in the early 1970s. It has declined in recent years as a result of measures under the Montreal Protocol. But the atmospheric concen-tration is continuing to rise (red scale) demon-strating the long lifetime of these compounds

Figure 4 — Use of CFCs in per cent of total release in 1986

Others 2 %

Cleaning 21 %

Refrigerants 23 %

Foam blowing 26 %

Propellents 28 %

released in the stratosphere, with even greater ozone-destructive effect. Some CFCs and halons can survive in the atmosphere more than a century. Moved by air currents, the halocarbons released over the past sixty years are a threat to the ozone layer for decades to come. They are carrying thousands of tons of chlorine and bromine atoms into the stratosphere. This is many times greater than the chlorine reaching the stratosphere naturally from the ocean in the form of methyl chloride and bromide.

In 1975, WMO convened a group of experts to prepare an authoritative statement entitled "Modification of the ozone layer due to human activities and some possible geophysical consequences". The statement focused on the effects of both supersonic transport and CFCs. It signalled the first international warning of the danger of substantial ozone decrease and recommended international action to provide better understanding of the issue.

The following year WMO launched the Global Ozone Research and Monitoring Project to provide advice to Members, the United Nations and other international organizations concerning:

- The extent to which anthropogenic pollutants might be responsible for reducing the quantity of ozone in the stratosphere;
- The possible impact of changes in stratospheric ozone on climate trends and on solar UV radiation at the Earth's surface;
- Identification of needs for strengthening the long-term monitoring of ozone.

Research by hundreds of scientists sponsored by government organizations from around the world has enhanced knowledge of the threat to the ozone layer. Along with increased collaboration with UNEP, this has substantially helped successful implementation of WMO's Ozone Project. It has produced 38 substantial scientific reports, including six major assessments of the ozone layer, which provided the basis for the preparation of the international ozone treaties and their amendments.

In 1984, at the Ozone Commission Symposium in Halkidiki, S. Chubachi (Japan Meteorological Agency) reported observing extremely low ozone values (about 200 m atm cm) at Syowa during many days of the 1982 Antarctic spring. The full significance of that data was recognized only after the publication in 1985 of data from a British Antarctic Survey station at Halley showing the dramatic decline of ozone—an actual "hole" in the ozone layer forming each spring since the early 1980s.

The majority of scientists thought this was the first sign that halocarbons (see box on P.9) were eroding the protective ozone layer. There was uncertainty until measurements procured by special expeditions in 1986 and 1987 documented the presence of reactive chlorine species (eg. ClO see Figure 5). These and subsequent measurements have demonstrated that human-produced CFCs are depleting the ozone and shifting the fragile chemical balance of the Antarctic stratosphere.
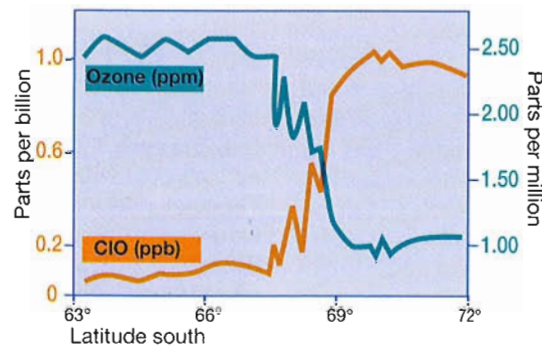

Figure 5 — Measurements of ClO concentration and ozone from aircraft (NASA, 1987). Note the rapid increase of ClO as the aircraft enters the polar vortex and the Antarctic ozone 'hole' (about 67°S) and the inverse correlation of ClO with ozone decline in mid-September when the chemically-unbalanced area in the vortex was sunlit

4. OBSERVED OZONE CHANGES

Ozone loss is especially strong over the frozen Antarctic continent because the winter circumpolar stratospheric vortex prevents extensive air exchange with mid-latitudes. This produces very low temperatures (below −80°C) which favour the generation of polar stratospheric clouds (PSC) of ice particles. Normally, chlorine and bromine are 'locked' into stable reservoir compounds (such as $ClONO_2$ $BrONO_2$ and HCL) The ice particles attract water vapour and absorb nitrogen compounds, then fall with them to lower levels of the atmosphere dehydrating and denitrifying the air in the stratosphere. With the return of sunlight in the early spring, these reservoir compounds are converted to active chlorine and bromine species on the surface of the PSCs. These substances can break apart ozone molecules with amazing efficiency (Figures 6 and 7).

In October 1987, ozone concentrations over Antarctica fell to half their normal (1957–1978) levels, and the hole spread across an area the size of Europe. Since then, the decline has accelerated and extremes reached during the past three years include:

- A record low ozone value of less than 100 m atm cm (70% deficiency) during several days;
- The greatest ozone hole ever of close to 24 million square kilometres; and
- An overall spring seasonal ozone deficiency of more than 40%.

The ozone destruction is strongest in the lower stratosphere. During late September and October of the last three years the ozone in Antarctica was practically annihilated between 13 and 20 km as shown in Figure 8. The ozone decline in spring, when the Antarctic
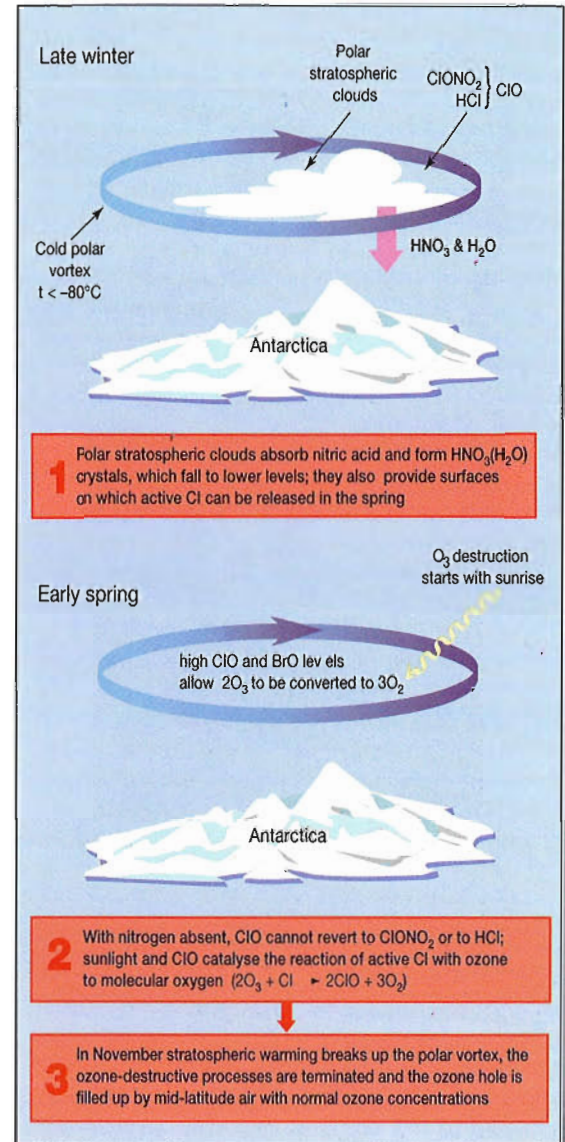
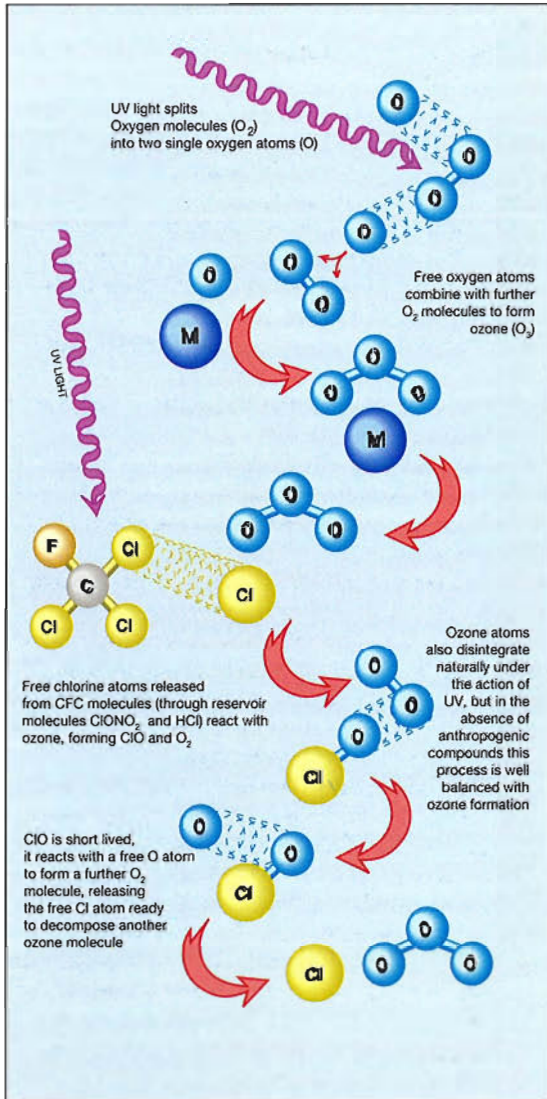*Figure 6 — schematic description of ozone destruction over Antarctica*

Late winter

Polar stratospheric clouds $ClONO_2$ HCl $\}$ ClO

Cold polar vortex t < −80°C

HNO_3 & H_2O

Antarctica

1 Polar stratospheric clouds absorb nitric acid and form $HNO_3(H_2O)$ crystals, which fall to lower levels; they also provide surfaces on which active Cl can be released in the spring

Early spring

O_3 destruction starts with sunrise

high ClO and BrO lev els allow $2O_3$ to be converted to $3O_2$

Antarctica

2 With nitrogen absent, ClO cannot revert to $ClONO_2$ or to HCl; sunlight and ClO catalyse the reaction of active Cl with ozone to molecular oxygen $(2O_3 + Cl \rightarrow 2ClO + 3O_2)$

3 In November stratospheric warming breaks up the polar vortex, the ozone-destructive processes are terminated and the ozone hole is filled up by mid-latitude air with normal ozone concentrations

Figure 7 — Schematic sequence of the destruction of ozone by active Cl released from a CFC-12 molecule

Diagram labels:
- UV light splits Oxygen molecules (O_2) into two single oxygen atoms (O)
- Free oxygen atoms combine with further O_2 molecules to form ozone (O_3)
- Ozone atoms also disintegrate naturally under the action of UV, but in the absence of anthropogenic compounds this process is well balanced with ozone formation
- Free chlorine atoms released from CFC molecules (through reservoir molecules $ClONO_2$ and HCl) react with ozone, forming ClO and O_2
- ClO is short lived, it reacts with a free O atom to form a further O_2 molecule, releasing the free Cl atom ready to decompose another ozone molecule
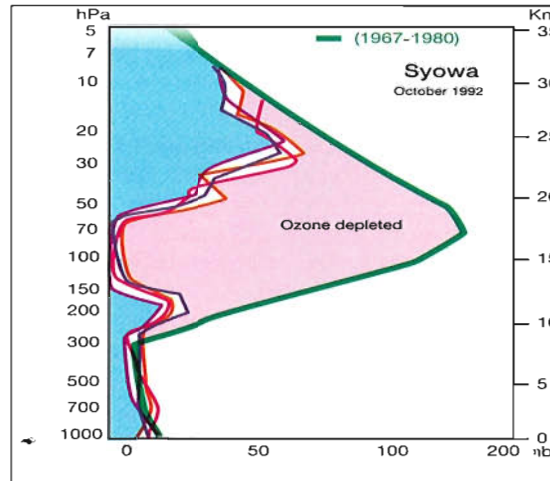

Figure 8 —Vertical ozone profiles at Syowa (69°S) during October 1992 illustrating the complete ozone destruction in the lower stratosphere. Average ozone profile from pre-ozone-hole years (1967–1980) is also shown

(Ito, JMA, Tokyo)

stratosphere is isolated and extremely cold, is many times greater than the decline in the summer season (Figure 9).

The ozone hole forms only over Antarctica because of the unique combination of weather conditions favouring ozone-destructive reactions upon the appearance of the sunlight in spring. Figure 10 shows the extent of the ozone hole on 17 October 1994 spreading over the southern tip of South America.

Since 1988, extensive measurements have been taken in the northern polar region, including many from aircraft, balloons and specialized satellites. These measurements and those from ground-based international expeditions revealed that during winter-spring the Arctic stratosphere has the same type of disturbed chemical composition, with high concentrations of destructive chlorine and bromine compounds, that causes the problems in the Antarctic. However, ozone destruction over the Arctic is not so strong for two reasons: the stratospheric temperatures are seldom below −80°C due to the frequent extensive exchange of air masses with the middle latitudes; and the Arctic vortex

QUASI-BIENNIAL OSCILLATION

QBO—Alternation of easterly and westerly wind regimes in the stratosphere in equatorial latitudes with a periodicity of roughly 24 to 30 months. The alternation has substantial effects on atmospheric transport. When the stratospheric winds are westerly, a 6-8% ozone deficiency is observed in mid-polar latitudes. When they are easterly, a similar surplus is usually recorded.

Figure 9 — Ozone seasonal deviations from pre-ozone-hole (1957–1978) averages in the Antarctic. Summary for stations Faraday, Syowa, Halley Bay, South Pole (*WMO Bulletin* 1994)
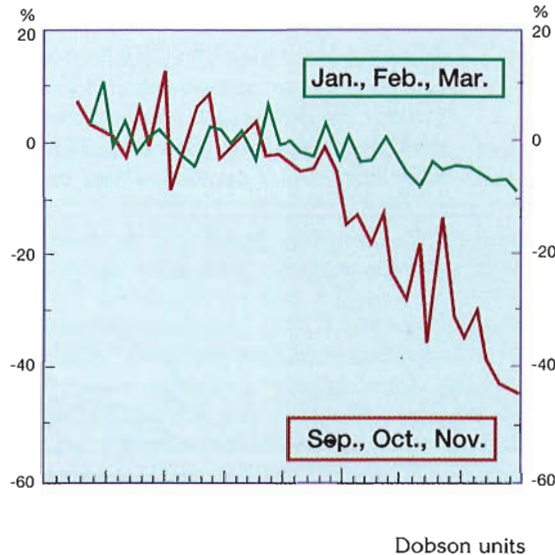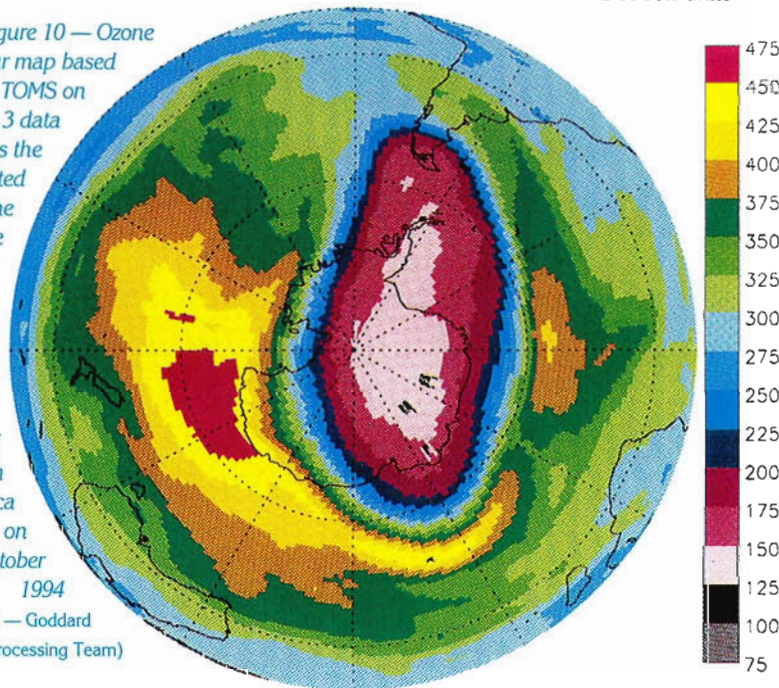

Figure 10 — Ozone contour map based on TOMS on Meteor 3 data shows the elongated ozone hole reaching over the southern cone of South America on 17 October 1994 (NASA — Goddard TOMS Processing Team)

normally dissipates in late winter *before* sunlight can cause large-scale ozone destruction

In parallel with the evidence of polar ozone decline, scientists also stepped up their search for *global* erosion of the ozone layer. During 1987-88, the International Ozone Trends Panel scrutinized recent studies and measurements made by satellites and by ground-based instruments around the world. In WMO Ozone Report No. 18 (1988) the verdict was:

- Global ozone levels had *declined* by several per cent over the past 17 years—mainly during winter-spring over middle and polar latitudes;
- Natural processes could not explain the entire ozone loss—evidence pointed towards anthropogenic halocarbons as the cause. ,

In the Ozone Assessment Report released in 1991 the news was even worse: ozone values had dropped significantly not only in winter-spring but *also in summer*. Since people spend far more time outdoors and UV-B is highest during the summer, ozone loss at that time of the year poses a much greater threat to human health.

The continuing decline in total ozone since the 1970s is statistically significant all the year round everywhere except over the equatorial belt. The GO_3OS quality-controlled data, including satellite data, show that the cumulative ozone decline over the middle and polar latitudes is close to 10%. Taking into account known natural variability the decline in both hemispheres, it is especially strong during the winter-spring (over 6–7% per decade). It is half that during the summer-autumn seasons. Detailed studies show a statistically significant *increase* in the rate of ozone decline by approximately 1.5-2.0% in the period 1981–1991, as compared to 1970–1980. Numerical expressions of ozone trends over the middle latitudes and the entire northern

ARCTIC OZONE LOSS

The greatest winter ozone declines seen in the northern hemisphere occurred in 1992–1993 and in 1995. Ozone levels between 9 and 20% below normal were recorded in middle and high latitudes. Natural long-term variability is greatest between December and March. In that period, a deviation of more than about 13% (i.e twice the standard deviation) is unlikely to occur more than once every 20 years. The decline of 20% which occurred in February and March 1993 and 1995 were, therefore, extreme cases.

Scientific evidence points to the fact that chlorine and bromine released by CFCs and halons are to blame for part of the ozone decline. For example, the NASA Upper Atmosphere Research Satellite measured high concentration of ClO in air masses moving southward from the Arctic into the sunlit 45°–65°N latitudes. Several other factors contributed to the extremely low ozone levels:

- The lower stratosphere was relatively cold, stimulating PSC generation and chemical ozone destruction on their surfaces;

- The quasi-biennial oscillation (see page 12) was in its westerly phase both in 1993 and in 1995, affecting stratospheric circulation, reducing ozone by 6 to 8 %;

- In 1993 the upwelling air motions of a 'blocking' anti-cyclone situated over the North Atlantic and Europe for several weeks transported ozone-deficient air from the troposphere in the sub-tropics to the polar region;

- Remnants of volcanic aerosols from the Mount Pinatubo eruption in June 1991 could have been responsible for a further reduction of 1 to 2 % (mainly on the surface of sulphates) in 1992-93.

In January–March 1995 the extremely strong ozone deficiency of 15–25% occurred over mid-latitudes from eastern Europe to the Far East. It was especially strong over Siberia (<35%) without the presence of any volcanic aerosols but with obvious abundance of ClO and a strong westerly QBO. However, researchers are not yet fully confident that they know exactly the mechanism behind the ozone drop. Because of the high natural variability in ozone over the

Figure 11 — In March 1993, total ozone deviations from the long-term mean show considerable deficiencies over northern middle latitudes. The deficiency is relatively smaller over the polar cap than over the sunnier regions. Note that 13% represents a fall of more than twice the standard deviation. Based on near-real-time information provided by GO$_3$OS. (WMO Bulletin, July1993)
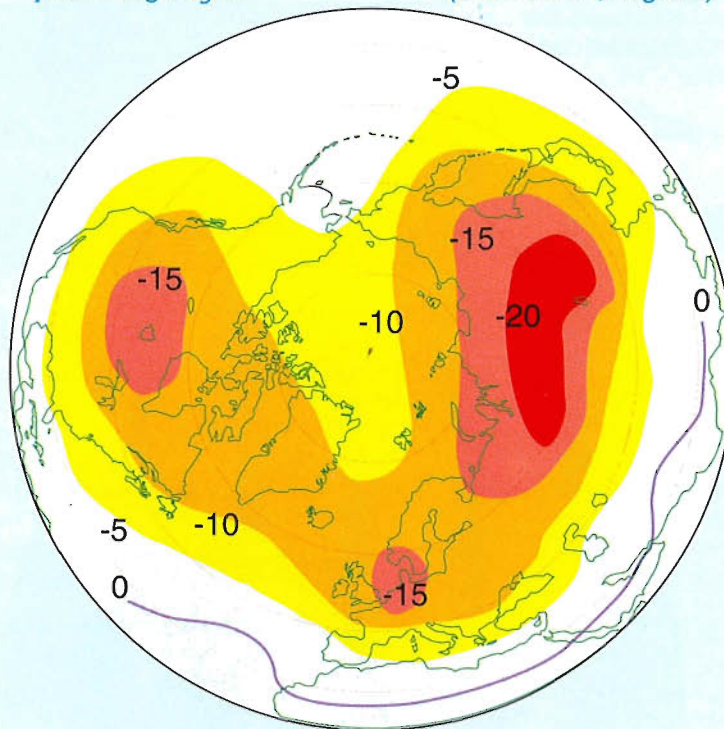
Arctic, it is difficult to determine the exact proportion of the ozone destruction attributable to human action.

Ozone decline (in per cent per decade ± 2σ) using GO_3OS data, January 1964 to March 1994, with linear trend fit for 1979–1994

Region	Dec., Jan., Feb., Mar.	May, June, July, Aug.	Sept., Oct., Nov.	Year
35°–65°N	5.8 ± 1.7	2.6 ± 1.5	2.5 ± 1.0	3.8 ± 1.2
Northern hemisphere	4.0 ± 1.1	1.9 ± 1.1	1.6 ± 0.9	2.6 ± 0.9
Southern hemisphere	2.7 ± 1.0	3.4 ± 0.8	6.6 ± 1.5	3.9 ± 0.8
35°–65°S	3.6 ± 1.2	4.9 ± 1.3	7.3 ± 2.0	5.0 ± 1.0

The estimated error limits are given as plus or minus twice the standard deviation. In fact the rates of decline are significant to more than three times the standard deviation. This means that the results would occur by chance less than once in a hundred years. Similar rates of ozone destruction are reported in the 1994 ozone assessment.

Figure 12 — Total ozone deviations from the 1964–1980 average (smoothed by 12-month running means) for Europe and North America show a major decline since the early 1970s. The quasi- biennial-oscillations are related to stratospheric dynamics
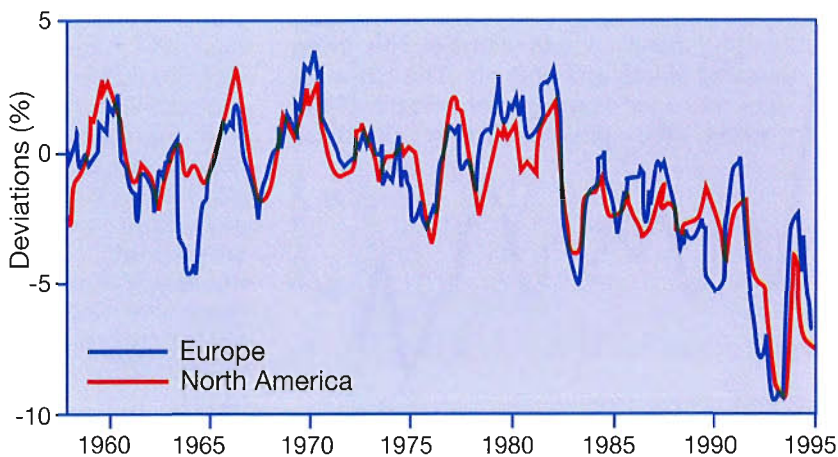
and southern hemispheres are shown in the table above. These figures provide further strong confirmation of the global decline in ozone.

An ozone decline of nearly 10% is clearly seen on the plot of long-term ozone values over Europe and North America (Figure 12). The principal *interannual* fluctuations are related mainly to stratospheric air transport variations, related to the phase changes of QBO (see box, p 12) in the equatorial stratosphere, however, the *overall decline* is in concurrence with the chlorine- and bromine-initiated ozone destruction predicted by models.

During the last ten years (1984–1993), the overall global ozone average level has fallen to 297 m atm cm from 306 in 1964–1980 (about 3%) (Figure 13). However, if the equatorial belt, where there are no significant ozone changes, is excluded, the decline over the middle and polar latitudes is more than twice as large . Some continental-scale regions have even greater cumulative deficiencies as shown in Figure 12. Figure 14 shows the differences throughout the year between mean ozone concentrations in 1964–1980 and those in the 1984–1993 period. The plot clearly shows the variation from pole to pole. It demonstrates the drastic decline (up to 35% in October) that has occurred over the southern polar region. In the northern middle and polar latitudes the major decline occurs during the winter-spring months when the difference between the 1964–1980 and 1984–1993 periods is close to 7%. There has not been any significant change in the equatorial belt.

Vertically, ozone decline is strongest in the lower stratosphere. The ozone soundings at Hohenpeissenberg show that the ozone partial

pressure in the 19–21 km layer has declined by about 30ηb representing about 20% in the past 25 years (Figure 15).

At the same time that *stratospheric* ozone is decreasing, *tropospheric* ozone—in the northern hemisphere at least—is *increasing* by about 10% per decade. An ozone increase is also noted over the savannah-fire regions in the tropics. This tropospheric ozone increase is mostly a consequence of the effect of the sun's radiation on specific air pollutants, particularly oxides of nitrogen from surface emissions, aircraft and automobile exhausts, combined with the increasing concentrations of other precursors such as methane and carbon monoxide.

Over the last one hundred years the ozone concentrations near the ground in the northern middle latitudes have more than doubled. Several sources support a lower-tropospheric ozone increase of >1% per year since the end of the nineteenth century.

They include: analytical chemical measurements at Montsouris (Paris) and a widespread network using the qualitative Schönbein method; occasional instrumented measurements from aircraft in the early 1940s; and continued monitoring in Pic du Midi (France) and in southern Germany,
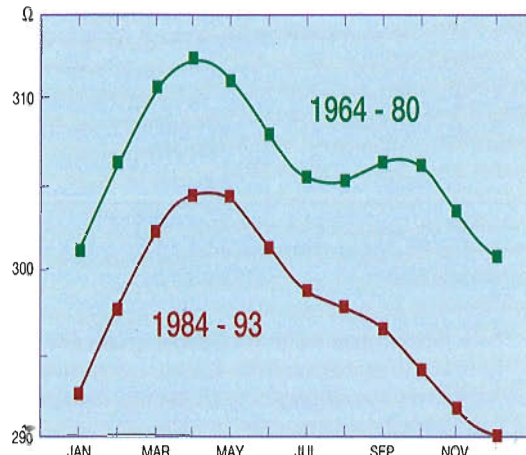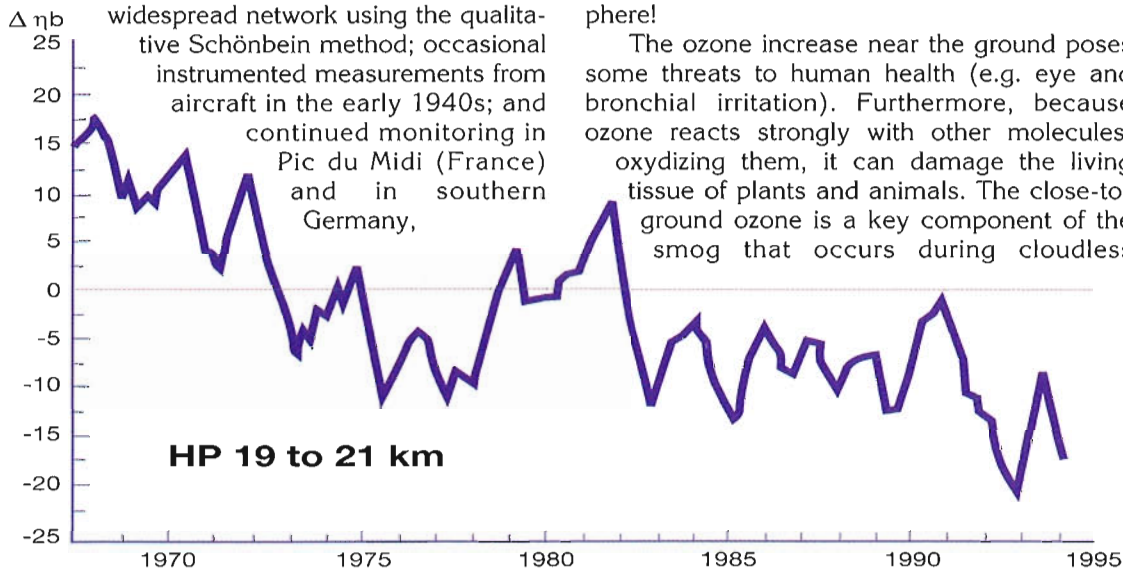

Figure 13 — The monthly global average ozone values show substantial decline in the 1984–1993 period especially strong in September–January compared with the 1964–1980 level. Since the global averaging includes the huge surface of the equatorial belt where there are no significant changes, the actual decline in extra-tropical latitudes is much larger

During the last few decades also the ozone above the ground — in the middle and upper troposphere — has substantially increased as shown in Figure 16. The ozone increase in the troposphere, however, cannot compensate for the more severe ozone decline in the stratosphere!

The ozone increase near the ground poses some threats to human health (e.g. eye and bronchial irritation). Furthermore, because ozone reacts strongly with other molecules, oxydizing them, it can damage the living tissue of plants and animals. The close-to-ground ozone is a key component of the smog that occurs during cloudless

Figure 15 — Ozone in a 19-21 km layer above Hohenpeissenberg (Germany) has decreased by about 20% in the past 25 years. This 12-months running mean smoothed plot, also clearly shows the quasi-biennial oscillations at this layer. These are related to QBO fluctuations in stratospheric dynamics.

summer days over many major cities around the world. Governments are attempting to decrease its levels by regulatory measures limiting its specific sources. Some success in this direction has been noted in Europe and North America during the last few years.
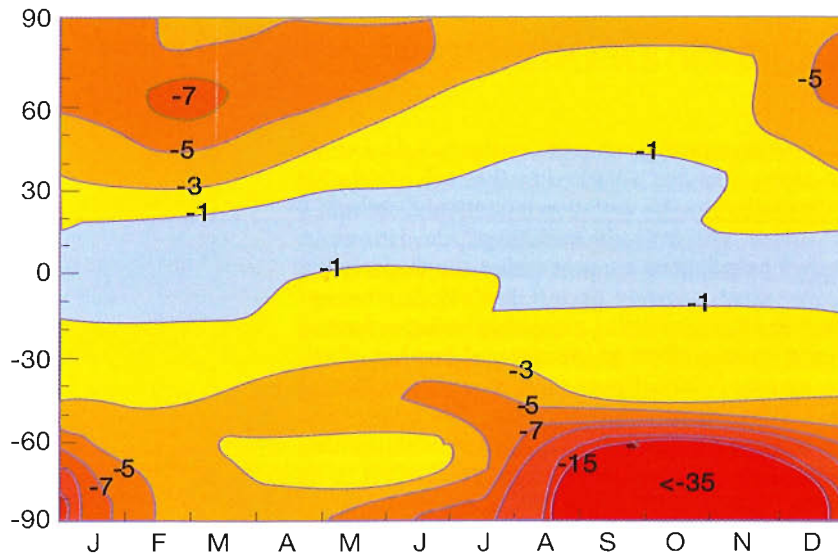
Figure 14 — Difference (per cent) between total ozone values for the two periods (1964–1980 and 1984–1993). Southward of 60°S from September through November, the difference is more than 15% with a maximum of 35% poleward of 75° in October
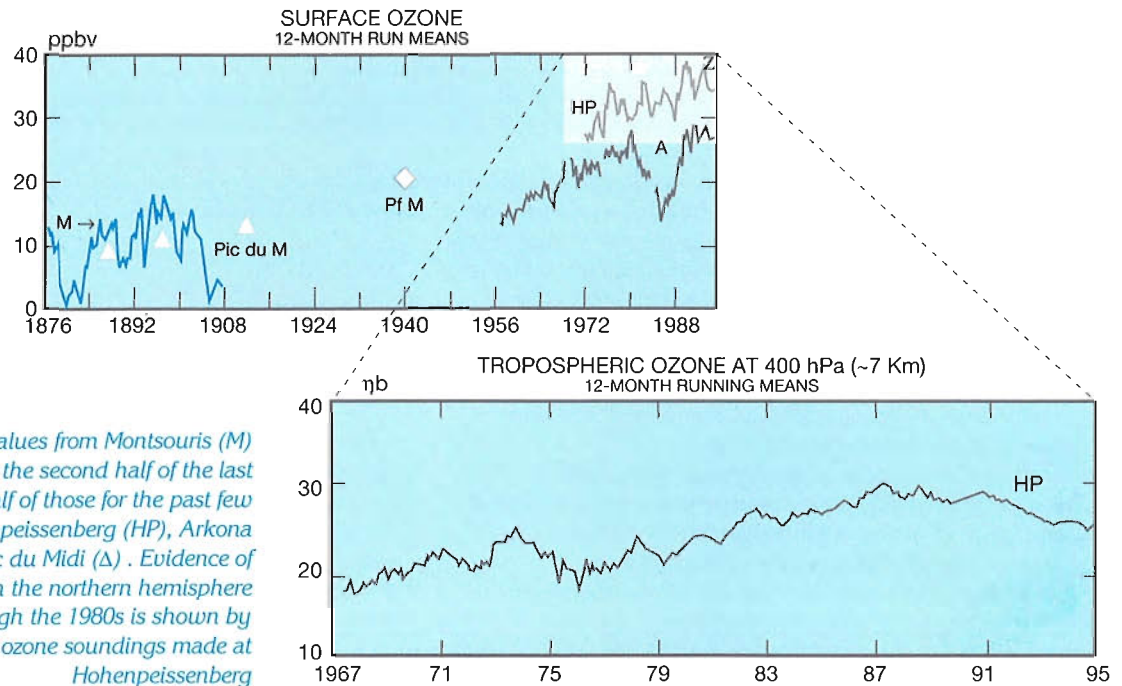

SURFACE OZONE
12-MONTH RUN MEANS

Figure 16 — Surface ozone values from Montsouris (M) and Pic du Midi (Δ) for the second half of the last century are less than half of those for the past few decades taken Hohenpeissenberg (HP), Arkona (A)Zugspitze (Z) and Pic du Midi (Δ) . Evidence of tropospheric ozone increase in the northern hemisphere at 400 hPa (~7.2 km) through the 1980s is shown by data from the ozone soundings made at Hohenpeissenberg

TROPOSPHERIC OZONE AT 400 hPa (~7 Km)
12-MONTH RUNNING MEANS

5.   RADIATIVE AND UV-B EFFECTS OF OZONE CHANGES

Greenhouse effect

Both ozone and halocarbons are "greenhouse gases". Much like carbon dioxide (CO_2), they intercept and re-radiate the Earth's outgoing infrared radiation, thereby helping to warm the lower atmosphere. However, neither ozone nor its changes are uniformly distributed, thus its radiative forcing (see box) is more complicated than those of the other principal greenhouse gases which have a long life span permitting even mixing. In general, adding ozone in the troposphere especially near the tropopause causes warming; reducing ozone in the stratosphere causes cooling. Some small temperature decline (0.6°– 0.8°) in the 12–20 km layer during the past two decades seems to be consistent with expected radiative impacts of stratospheric ozone decrease.

An accurate assessment of the radiative effect of ozone changes is limited by the lack of detailed information on the variation in vertical distribution of ozone with latitude and longitude. However, recent calculations support earlier conclusions that lower stratospheric ozone depletion in recent decades has resulted in a negative radiative forcing (i.e. a cooling effect on the climate) and has offset, by about 15–20%, the positive greenhouse forcing due to increases in other gases. The increase of tropospheric ozone since pre- industrial times may have *enhanced* the total greenhouse forcing by as much as 20%. Such changes could have an impact on the radiative balance of the earth-atmosphere system and the thermal structure of the atmosphere and thus cause as yet unpredictable changes to atmospheric circulation patterns.

OZONE AND RADIATIVE FORCING

To characterize a potential for climatic effects, "radiative forcing" (in units of Wm^{-2}) is frequently used. Its estimations are based on net solar and thermal infrared radiance at the tropopause, and are not greatly dependent on uncertainties, such as the combined interactive role of clouds, aerosols or oceans, in predicting surface climate change. A positive value signifies increased energy retention, producing warming; a negative value implies greater energy loss, ie. cooling.

- *Tropospheric ozone* has increased in the northern hemisphere since pre-industrial times. Models and deductions from observations suggest a positive radiative forcing of about 0.5 Wm^{-2}.
- *Stratospheric ozone* has decreased since the 1970s. Studies confirm that between 1980 and 1990 this has caused negative radiative forcing of about 0.1 Wm^{-2} compared with positive 0.45 Wm^{-2} forcing from an increase of other greenhouse gases in the same period.

The net global mean radiative forcing arising from ozone changes is likely to have been positive since pre-industrial time, contributing about 20% of all the greenhouse-gas-caused increase of radiative forcing in that period.
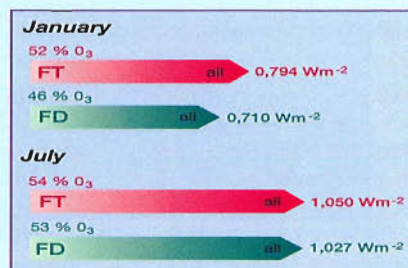

Figure 17 — See text below.

An example of the major contribution of ozone change to the total radiative forcing by all major greenhouse gases (CO_2, CH_4, N_2O, CFCs, O_3) from 1971–1980 to 1981–1990 over the northern mid-latitudes, using ozone soundings at Hohenpeissenberg, is shown above. Calculations for two different modelling assumptions, fixed temperature (FT) and fixed dynamical heating (FD), . show that ozone changes were responsible for nearly half of the radiative forcing under the given modelling treatment. (Wang *et al.*, GRL 1993)

Ultra-violet radiation

Figure 18 — Between September and November 1994, the Antarctic ozone hole extended to reach Ushuaia (55°S). Measurements of UV–B reaching the ground correlate inversely with ozone levels overhead. In mid-October, when the ozone hole spread over Ushuaia producing a 60% deficiency (only 151 m atm cm) on 17th, the rise in UV-B at both 300 and 305 nm was dramatic.

The life-protecting role of atmospheric ozone stems from its ability to absorb dangerous ultra-violet radiation with wavelengths shorter than 320 nm. The small amount of UV-B that does manage to penetrate through the ozone shield could cause considerable harm to human health, including eye cataracts, an increase of non-melanoma skin cancers, damage to genetic DNA, and suppression of the efficiency of the immune system.

Under cloudless conditions, each 1% reduction in ozone results in an increase of about 1.3% in the UV-B which affects skin tissue reaching the surface of the earth. The total ozone decline so far has resulted in a small increase in UV-B (280 to 320 nm) reaching the ground except over the tropical belt. Further ozone decline could have considerable harmful consequences, not only to humans but to other life forms and tropospheric chemistry. Crops and the aquatic ecosystem, including ocean plankton, could be damaged with yet unforeseen consequences. Some effects are largely a function of overall dose, while others depend upon reaching a given cumulative threshold. The Impact Assessment Panel is estimating that a *sustained* 1% decrease in total ozone will result in an increase in non-melanoma skin cancers of approximately 2 %.
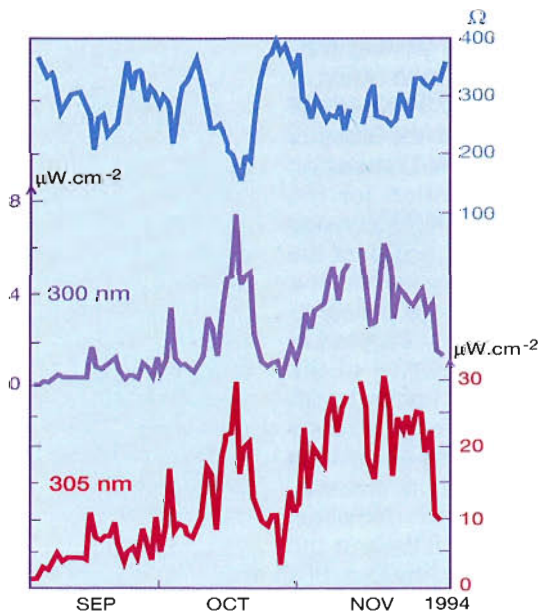
In addition, marine phytoplankton are a major sink for CO_2 and any UV-B effect on them could have a role in future CO_2 trends and consequently on climate. The UV-B increase will result in higher photodissociation rates of key trace gases that control the chemical processes in the troposphere.

Given that long-term, precise UV-B measurements are insufficient, and that the intensity of the radiation measured at the ground depends on the cloud cover, albedo, aerosol and the presence of SO_2, the inverse correlation between UV-B intensity and the total ozone amount is well established.

Over those parts of the globe where the ozone changes are most severe, i.e. under the ozone hole, the increase of the UV-B is well documented. The maximum UV-B levels at the South Pole are reached in October — well before the summer solstice, and DNA-damaging radiation at Palmer station (64°S) during October can exceed the maximum summer values measured at San Diego (32°N). At mid-latitudes the UV-B increase is smaller but well evident during low ozone periods.For example, the ozone decline of about 15% observed at the most southern tip of South America during October of the past 15 years has caused an average increase of UV-B reaching the ground of 85% at around 300 nm and 35% at around 305 nm wavelengths. During the ozone hole expansion over Ushuaia in mid-October 1994 the intensity of the short UV-B wavelengths, around 300 nm, increased five times and the 305nm twice compared to "normal' ozone conditions(Figure18). It was, to a great extent, the prospects of continuous increase of UV-B which prompted the international community to take regulatory action in the 1980s as described in the next chapter.

6. PLAN OF ACTION ON THE OZONE LAYER

The first WMO intergovernmental scientific statement warning of the danger to the ozone layer, distributed in 1975, prepared the ground for legal action. In 1976, UNEP called for "an examination of the need and justification for recommending any national and international controls over the release of man-made chemicals". In the same year the UNEP Governing Council authorized convening a meeting of experts designated by governments, intergovernmental and non-governmental organizations (NGOs). WMO joined UNEP in the preparation and conduct of the meeting, held in Washington, DC, from 1 to 9 March 1977. WMO provided an 80-page "Survey of the state of knowledge of the ozone layer" with a series of proposals covering the monitoring of ozone and relevant rare species, data analysis, modelling and laboratory photochemistry, and UV-B measurements. UNEP laid the foundation for international action.

The representatives of 32 countries adopted the "World Plan of Action on the Ozone Layer". This 21-point research plan covered the monitoring of ozone and solar radiation, the assessment of the effect of ozone depletion on human health, ecosystems and climate, and the development of ways of assessing the costs and benefits of control measures. WMO took responsibility for the atmospheric research plan. UNEP was given "a broad coordinating and catalytic role". By adopting the Action Plan, governmental experts accepted that there was a potential problem, though its extent had yet to be determined, and recommended actions to get to grips with it. In the same spirit, some countries soon took action to control CFCs; the USA, Canada, Norway and Sweden began phasing out their use in aerosol cans apart from essential medical and other uses. In 1980 the Commission of European Community agreed not to increase its capacity to produce CFCs 11 and 12 and called for a 30% cut in their use in spray cans by 1982.

To review implementation of the Action Plan, UNEP set up a Coordinating Committee on the Ozone Layer. It comprised representatives of countries with major scientific programmes involved in the Action Plan, WMO, the World Health Organization and NGOs. The committee met regularly until the mid-1980s and became the focal point for international action. Hypothesis were debated by scientists and challenged by industry until the requirement for control of CFCs became accepted.

Figure 19 — The contributions to the overall chlorine loading of the atmosphere are mostly anthropogenic (82%) and only 18% from natural sources

The Vienna Convention

Over the years, continued concern and and increased scientific information led to growing international acceptance of the need to take action to protect the ozone layer. In January 1982, UNEP convened the first meeting of an *Ad hoc* Group of Legal and Technical Experts for the Elaboration of a Global Framework Convention for the Protection of the Ozone Layer. WMO facilitated preparation of a detailed scientific review of the issue. The meeting identified the framework for a convention. After three years of extensive negotiations coordinated by UNEP, it was adopted in Vienna, March 1985. The 21 articles of the Convention pledge parties to protect human health and the environment from the effects of ozone depletion. Two annexes provide for participating states to co-operate in atmospheric ozone research, observations, and data and information exchange. In Vienna it was also agreed to work towards the preparation of concrete measures in the form of a protocol to the Convention.
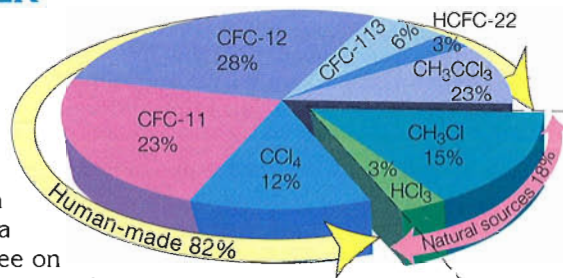
The Montreal Protocol

The landmark Protocol on Substances that Deplete the Ozone Layer, which was adopted in Montreal (September 1987), called for 50% reduction of CFCs by the year 2000 (see box).

The Protocol contains a comprehensive schedule for phasing out the production and consumption as well as control measures on manufacturing, export and import of ozone depleting chemicals. The Parties to the Protocol also established panels of experts on scientific issues, environmental effects and on technical and economic assessments.

The Vienna Convention and its Montreal Protocol provide a dramatic example of science in the service of humankind. Atmospheric scientists had revealed the risk of halocarbons, allowing world leaders to take decisive action to protect the ozone layer.

Through active collaboration between WMO and UNEP, it became possible to achieve an important first in environmental management: to identify a threat and to take action to limit the extent of damage at an early stage before its effects were felt. The negotiations and agreements on the ozone issue signified that, for the first time, the nations of the world had joined forces under the United Nations umbrella to protect the Earth for future generations.

In the years following the Convention, more scientific evidence emerged on the harmful effects of chlorine and bromine compounds. As observations confirmed the increasing damage to the ozone layer, the Parties to the Montreal Protocol decided to strengthen the requirements and to include new substances. They adopted relevant amendments and adjustments (London, 1990 and Copenhagen, 1992). Achieving the goals of the Protocol depends critically on widespread cooperation among all nations. Recognizing the importance of participation of developing countries an initiative in the form of a ten-year grace period for implementation of the requirements was agreed upon.

Furthermore, in order to make the earlier phase-out fair for developing countries, the revised Protocol established an environmental fund paid for by developed nations. The fund helps developing countries with technical assistance and transfer of technology to switch over to more "ozone friendly" replacement compounds.

PHASE-OUT SCHEDULE

1. CHEMICALS COVERED BY 1987 MONTREAL PROTOCOL

CFCs (11, 12, 113, 114, 115) Phase down 1986 levels by: 20% by the end of 1994
50% by the end of 1999

2. THE MONTREAL PROTOCOL (LONDON AMENDMENT-1990)

CFCs (13, 111, 112, 211, 212, 213, 214, 215, 216, 217) Phase down 1989 levels by:
20% 1993
85% 1997
100% 2000

Halons (1211, 1301, 2402) Freeze in 1992 at 1986 levels, then
Phase down by: 50% 1995
100% 2000

Carbon tetrachloride Phase down 1989 levels by: 85% 1995
100% 2000

Methyl chloroform Freeze in 1993
Phase down 1989 levels by: 30% 1995
70% 2000
100% 2005

3. FURTHER STRENGTHENING OF THE MONTREAL PROTOCOL (COPENHAGEN AMENDMENT-1992)

CFCs	phase out	100%	by the end of 1995
Halons	phase out	100%	by the end of 1993
Carbon tetrachloride	phase out	100%	by the end of 1995
Methyl chloroform	phase out	100%	by the end of 1995
Methyl bromide	freeze at 1991 levels		by the end of 1994
HCFCs	Phase down 1989 levels by:	35%	by the end of 2004
		90%	by the end of 2014
		99.5%	by the end of 2019
	100%		by the end of 2029

7. THE FUTURE

As can be seen, WMO has played a major role in identifying and communicating the problem of ozone depletion. It has coordinated assessments of the authoritative scientific evidence to support the UNEP-led international discussions which led to the Vienna Convention, its Montreal Protocol and subsequent amendments. Even with full international compliance with the existing agreements, it is estimated that chlorine and bromine concentrations will continue to increase in the stratosphere until the turn of the century. Peak global ozone losses are expected to occur during the next ten years, when another 3–4% of the ozone will be destroyed (in some years more), before the rates of decline ozone level off and start to diminish (see last line of Figure 20).

It is very difficult to predict with any certainty when the ozone layer might recover. Figure 20 shows the calculated stratospheric chlorine-equivalent concentrations resulting from the predicted manufacture and consumption levels of halocarbons with full compliance to the original Protocol, its London amendment and the more stringent measures for phase out by January 1996 as accepted at the Copenhagen Conference (November 1992). Scientific evidence points to the stratospheric chlorine-equivalent concentration of 2 parts per billion volume (ppbv), reached at the end of the 1970s, as being a dangerous threshold for ozone depletion.

At the present time, chlorine-equivalent concentrations exceed 3.7 ppbv, and are expected to increase for another 3–5 years. Without the Montreal Protocol, continuing use of CFCs and other ozone destructive compounds would have tripled the present stratospheric abundance of chlorine and bromine by the middle of the next century. Such increases would have led to ozone depletion very much larger than that observed today.

Only full compliance with the Montreal Protocol, strengthened by the London and Copenhagen amendments, will prevent chlorine levels exceeding 4 ppbv and ensure that they begin to decline to reach the 2 ppbv level some time in the middle of the next century. All things being equal, only then would the ozone layer return to normal pre-ozone-hole levels. It should be emphasized that the expected recovery of the ozone layer would have been impossible without the Montreal Protocol and its amendments.

Decision-makers must have authoritative information on the state of the ozone layer when they review existing
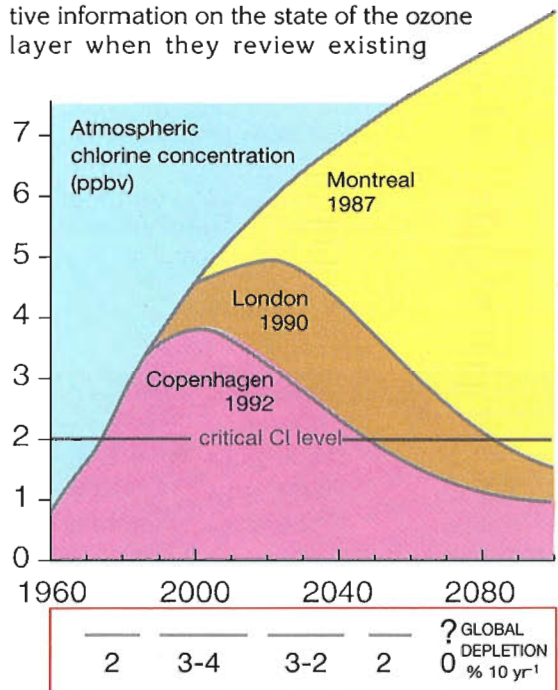
Figure 20 — The measured chlorine-equivalent concentrations in the atmosphere (since 1960) and projections according to the various measures to phase out CFCs and other ozone-depleting substances. The numbers on the bottom line indicate the predicted global ozone depletion per decade if the conditions of the strengthened Montreal Protocol are observed

international agreements. To provide this information, the GO_3OS must be maintained and improved well into the next century. As must the entire Global Atmosphere Watch (GAW) that monitors other chemical constituents of the atmosphere, from both ground and space. Only the common efforts of national Meteorological Services and environmental authorities, encouraged and coordinated by WMO and UNEP, can provide scientists with the necessary data. Then they can make more accurate assessments and predictions needed by governments to protect the global environment for future generations.

As UNEP is called upon to coordinate environmental protection treaties, so WMO is being called upon to meet increasing obligations regarding the monitoring and study of ozone and other atmospheric pollutants. To meet these challenges, WMO and UNEP will have to collaborate even more closely with one another and with their Members and other international and national institutions. Through such collaboration it will be possible for WMO and UNEP to fulfil their responsibilities and provide the basis for concentrated international action to safeguard the atmosphere. By assessing and predicting the extent of harmful human influences, they will be able to issue warnings of danger. As mentioned in the Foreword, a spirit of cooperation among scientists, governments and industry has been evident in negotiations to protect the ozone layer. On the occasion of its 50th Anniversary, and in the decades to follow, the United Nations can be proud of this achievement which will help ensure a prosperous and sustainable planet for the peoples of the world.

METHYL BROMIDE

Another widely-used chemical which poses a threat to the ozone layer is methyl bromide CH_3Br. This can release bromine, which is 30 to 60 times as destructive to ozone as is chlorine.

Methyl Bromide is used as a fumigant for soils and commodities, including the quarantine treatment of some products for international trade, and as a transport fuel additive. Total annual anthropogenic release is now estimated to be more than double the 40 000 tonnes released annually in the early 1980s. In addition, natural sources such as burning biomass contribute a further 30 000 to 50 000 tonnes a year. More than half of all the CH_3Br produced is released into the atmosphere, where concentrations are currently between 8 and 15 parts per thousand. million by volume.No single alternative chemical is at present available to replace all methyl bromide applications.

OZONE ISSUES AT A GLANCE — 1995

- Ozone decreases continue in all latitudes, except over the equatorial belt (20°S–20°N); the ozone decline during winter-spring in the last 25 years is twice as strong as during the summer season, both being statistically significant;

- The global average ozone decline during the last 15 years is estimated at about 5%; however, the overall ozone loss in the extratropics for the same time was between 6.5% in the northern and 9.5% in the southern hemisphere; the downward trend during the 1980s and 1990s was significantly larger than during the 1970s;

- The main ozone decline observed in the vertical plane is in the lower stratosphere (below 23 km) ~10% per decade;

- The change in skin-reddening ultraviolet radiation at ground-level resulting from changes in column ozone has been observed and quantified for cloudless days as increasing by about 1.3% for each per cent of total ozone decline;

- The Antarctic-spring ozone hole in 1994 was as deep and extensive in the area covered as were the extremes so far observed in 1992 and 1993. At the end of September and early October the ozone loss over Antarctica was about 60% of the pre-ozone-hole averages and during a few days reached 70%;

- Evidence suggests that the cause for the Antarctic-spring ozone hole is primarily heterogeneous processes on the surfaces of polar stratospheric clouds and sulphate aerosols involving man-made chlorine and bromine;

- Greater ozone losses at polar and mid-latitudes are expected as long as the atmospheric levels of chlorine and bromine compounds continue to increase. The concentrations of these compounds is expected to start declining about the turn of the, century providing all countries strictly adhere to the requirements of the strengthened Montreal Protocol;

- A frequent meridional exchange of air in the lower stratosphere of the northern hemisphere precludes the possibility of an isolated circumpolar vortex with extremely low stratospheric temperatures as occurs over the Antarctic. The available observations do not indicate an extensive ozone reduction like the Antarctic "ozone hole", although analogous disturbed atmospheric chemistry was found in 1989, and very high ClO concentrations were confirmed during the 1991–1992 and the following Arctic winters. These make it increasingly likely that substantial Arctic ozone losses may occur, for short times, during particularly cold stratospheric outbreaks in sun-lit upper-middle latitudes as in some of the episodes with extremely low ozone (over 20% deficiency) observed in 1992, 1993 and early 1995;

- It is necessary to reduce further stratospheric halogen abundances in order to bring chlorine loading back to 2 ppbv (the abundance in the late 1970s, which is when the Antarctic ozone hole-type of destruction started and when the accelerated trends in total-column ozone losses in the northern hemisphere began). Full compliance with a strengthened Montreal Protocol by all nations would allow chlorine levels to return to <2 ppbv by 2060–2070;

- Anything other than modest substitution of HCFCs for CFCs could both increase the peak chlorine loading and sustain for decades unprecedented levels of stratospheric chlorine (currently phase down by 90% by 2015 was agreed in Copenhagen, 1992);

- Although there is some decline in the growth rates of several major ozone-depleting substances, demonstrating the expected impact of the strengthened Montreal Protocol, the continuous use of methyl bromide is being viewed as a significant supplement to the ozone-depleting compounds;

- The observed lower-stratospheric ozone depletions have been used to calculate the changes in the radiative balance of the atmosphere and indicate that, over the last 25 years, they have tended to cool the lower stratosphere at middle and high latitudes by close to 1°C with possible effects on the surface-troposphere system which could be answered only after interactive chemical and dynamic calculations for the entire atmosphere;

- Model simulations and limited observations suggest that tropospheric ozone has increased in the northern middle latitudes since pre-industrial times. Such changes would augment by about 20% the radiative forcing from all other greenhouse gases over the same time span;

- The ozone levels in the troposphere up to 10–12 km above the few existing balloonsonde stations at northern middle latitudes have increased by about 10% per decade from the mid 1960s until the end of the 1980s. Although the database is sparse, some preliminary studies project a significant positive contribution to the global surface warming close to that of the other greenhouse gases;

- Present models containing only gas-phase chemistry cannot simulate the observed ozone depletion at middle and high latitudes, however, if heterogeneous processes on sulphate aerosols are incorporated, the predicted ozone depletion will increase but still will not explain the entire middle latitude decline;

- It is apparent that strong volcanic eruptions able to inject a large amount of volcanic-sulphate aerosol in the lower stratosphere facilitate the occurrence of heterogeneous processes on sulphate aerosols causing some additional ozone destruction within the aerosol layer lasting usually a year after the eruption;

- A previous assessment of the impact of a projected large fleet of supersonic aircraft on stratospheric ozone estimated that the ozone loss increases with the amount of nitrogen oxides emitted. However, recent studies have shown that reactions on sulphate aerosols can change the partitioning of nitrogen oxides and thus reduce the intensity of ozone depletion. Nitrogen oxide emissions from aircraft in the 8–11 km corridor could enhance the tropospheric ozone.