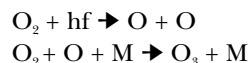


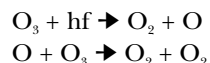


### The nature of ozone and its occurrence

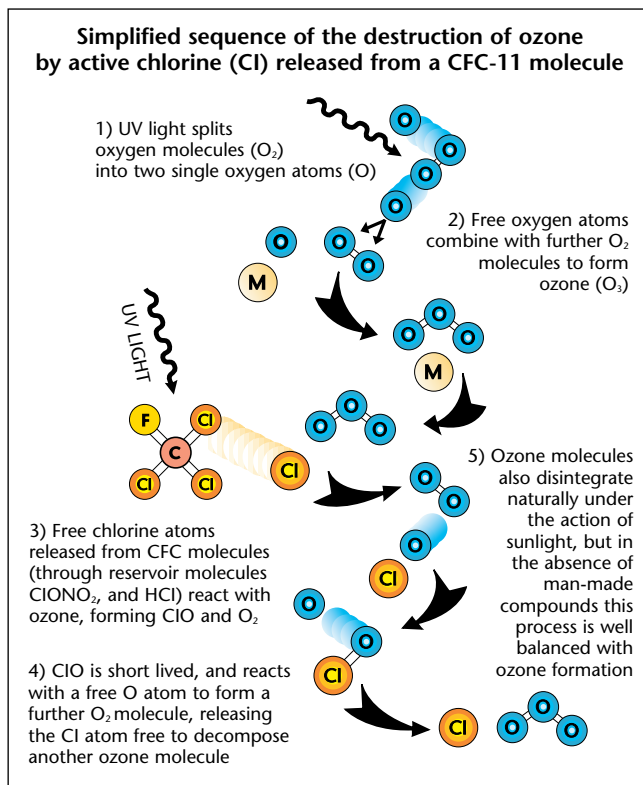
Ozone is a form of oxygen in which each molecule contains three atoms of oxygen as opposed to the normal two. It is a bluish gas and is chemically very active. When inhaled it is toxic and particularly harmful to asthmatics and others with respiratory problems. Ozone also absorbs ultraviolet radiation (UV), a property of considerable significance to life on Earth. Ozone occurs naturally in our atmosphere, which is dominated by nitrogen (78% of the total) and oxygen (21%). There are also a number of trace gases that vary in their concentration, including water vapour, carbon dioxide and ozone. Ozone's maximum concentration is only 0.001%, or one in every 100,000 molecules of air. If all the ozone were collected into a single layer it would be only 3 mm thick. The gas is formed by the action of photons (hf) of UV light with a wavelength less than 240 nm on oxygen. A third body (oxygen or nitrogen – M) carries away excess kinetic energy. The chemical reaction is:



Photons of longer wavelength can split ozone. Thus:



The balance of such reactions gives an average total ozone concentration of around 300 Dobson Units. There is a greater incidence of solar radiation in the tropics and it is there that most ozone is formed. Winds then sweep ozone towards the poles so that the thickness of the ozone layer is greater at higher latitudes. Ozone has a number of important properties. It is a greenhouse gas and it has an important role in controlling temperatures in the stratosphere. It also absorbs much of the UV radiation that reaches the outer atmosphere. The reduction in ozone could therefore affect plants and animals as well as humans.



### Destruction of the ozone layer

As the diagram above shows, CFC-11 can lead to the breakdown of ozone. However, it is chlorine and bromine that do the main damage. They are found in many chemicals which were in common use, such as carbon tetrachloride (a solvent), halons (fire extinguishers) and trichloroethane (correcting fluid) as well as CFCs (aerosols and refrigerants). Methyl bromide, used as a fumigant, also contributes to ozone depletion. One molecule of chlorine can destroy 100,000 molecules of ozone before being removed. CFCs and halons can persist in the atmosphere for more than a century.

### The impacts of ozone depletion

All living cells, whether in microbes, plants or animals, contain a complex molecule called DNA which carries the genetic code. This is the set of instructions which describes the structure and chemistry of an organism. Unfortunately, DNA readily absorbs high-energy UV-B radiation and becomes damaged so that the instructions cannot be read properly. If the amount of UV-B entering the cell increases, the risk of damage also increases and may result in malfunction or death of the organism.

Some Antarctic organisms, such as algae, lichens and mosses, contain a pigment called chlorophyll. This absorbs visible light as the energy source of photosynthesis for making organic compounds. However, it also absorbs UV-B and excessive levels can lead to the system becoming bleached and non-functional. Even enzymes and other proteins are damaged by this high-energy radiation. Living organisms, therefore, protect themselves from UV-B. Many microbes, plants and animals can synthesize protective pigments. In Antarctica, lichens and mosses have developed protective pigments and will increase pigment production in the most exposed sites. Humans have developed brown melanin to protect them from sunburn and can use protective creams and sun block.



Antarctic lichens living on rock



### Effects on human health

Although humans have natural defences against ultraviolet radiation, prolonged exposure to UV-B can have serious effects on human health. Skin, if not protected, can experience sunburn. Even BAS scientists, who usually take elaborate precautions against sunburn, have occasionally suffered burns while working under the ozone hole. Prolonged exposure can lead to the immune defences of the skin breaking down. This may lead to an increased susceptibility to infection, premature ageing of skin, skin disorders and even cancer. Many skin cancers are treatable, although a significant number can be fatal. In the UK, there has been a rise in skin cancer of 7% per year, due principally to changes in lifestyle such as holidays in the sun. An ozone hole over the UK could exacerbate this. One of the difficulties in dealing with this problem is the delay between exposure and the eventual effects, which may be 20 or 30 years later. Adult skin cancers may therefore be a result of childhood sunburn.

### Effects on plants

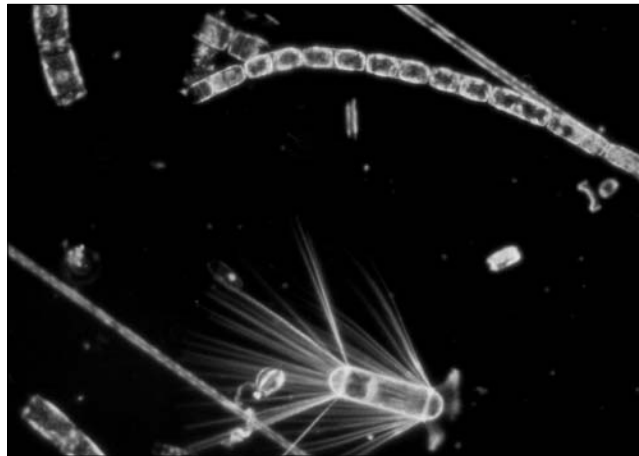
Although plants can react to UV-B by changing their pigment or growing in shaded positions, prolonged exposure may cause serious damage. Resistance to disease could be reduced and so lead to lower crop yields. Some temperate crops such as peas and cabbage are particularly sensitive. There is evidence that soya beans experience up to 25% reductions in yield when exposed to increases in UV-B. Failure of crops or even reduced cover leaves soils more prone to erosion.

### Effects on marine ecosystems

UV-B can penetrate clear water to a depth of 20 m. There is recent evidence that exposure to enhanced UV-B is harmful to phytoplankton, plankton and the larvae of fish and shrimps.

One effect of increased UV-B that could be particularly

serious in Antarctica is the possible reduction it might cause in the productivity of phytoplankton in the Southern Ocean. Phytoplankton is the basis of the marine food web and a reduction in productivity would affect dependent species such as krill, fish, penguins, seals and whales.



Phytoplankton living at the surface of the Southern Ocean could be at risk from enhanced UV-B

### Effects on the built environment

Many of the materials used in building and construction are susceptible to deterioration by UV-B. It is known to be able to break down polymers used in paints and plastics. For example, at the BAS Halley Research Station plastics quickly develop cracks and become brittle and break. Also, natural and artificial dyes, such as those used in clothing, become faded and bleached.

### Effects on climate

Marine ecosystems fix (e.g. incorporate into biologically useful material) substantial amounts of carbon from the atmosphere thus reducing level of carbon dioxide (CO<sub>2</sub>).

A reduction in primary productivity due to ozone depletion could lower carbon fixing. This would result in higher levels of CO<sub>2</sub> and promote climate change.

Ozone is itself a greenhouse gas. Paradoxically, however, the global warming that is occurring in the troposphere may allow the stratosphere to cool. This may increase stratospheric clouds and thus increase ozone depletion. Some scientists predict a springtime ozone hole over the Arctic during the next 20 years. However, ozone depletion in the northern hemisphere is not currently a threat to human health in the UK.

Volcanic eruptions can exacerbate ozone depletion as well as cause climate change. For example, the eruption of Mount Pinatubo and Cerro Hudson in 1991 injected about 22 megatonnes of sulphur dioxide (SO<sub>2</sub>) into the stratosphere, where it persisted as sulphuric acid aerosol. Chemical reactions can take place on the surface of these aerosol particles and cause enhanced ozone depletion.

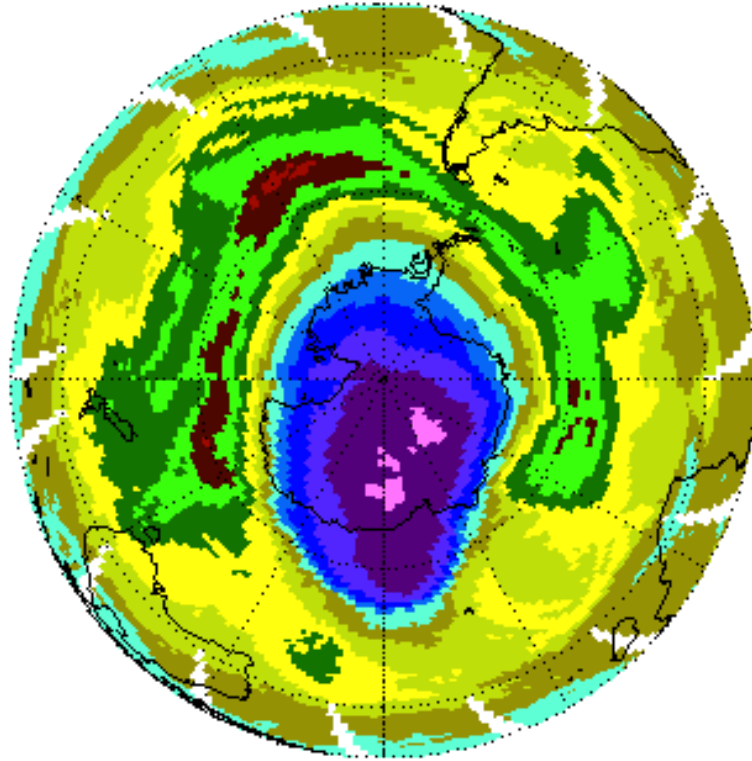


An experiment by BAS scientists using plexiglass to reduce ultraviolet light levels on Antarctic vegetation



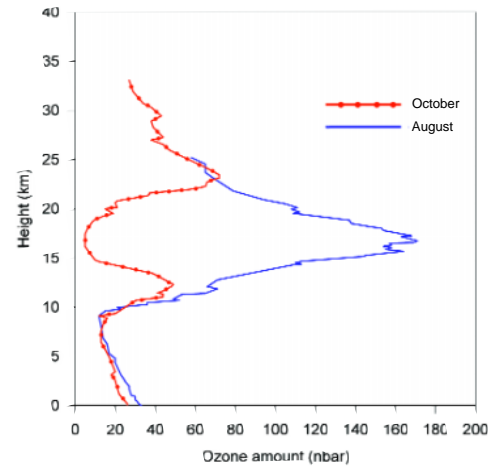
# Ozone hole data

October 1998 satellite image of the ozone hole over Antarctica. The image was taken by the NASA Total Ozone Mapping Spectrometer (TOMS).

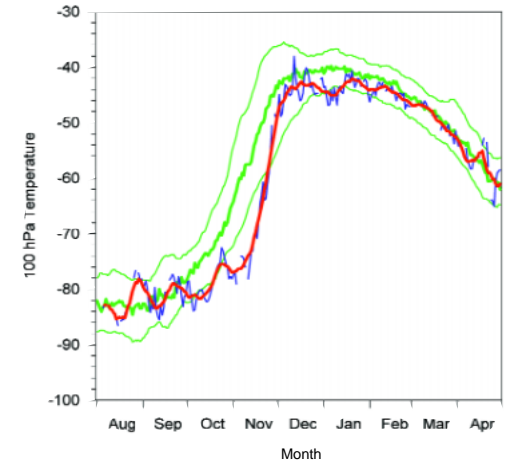


NASA

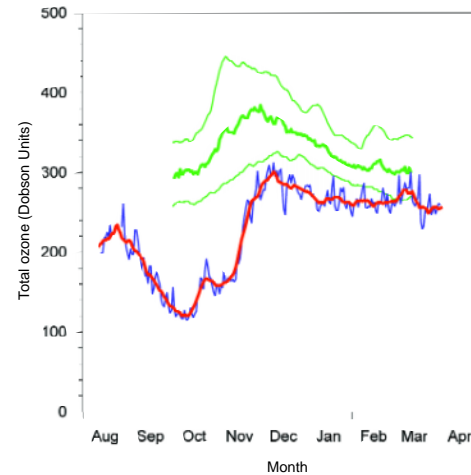
Vertical profiles of ozone at Halley, before (August 15) and during (October 13) the 1987 Antarctic ozone hole.



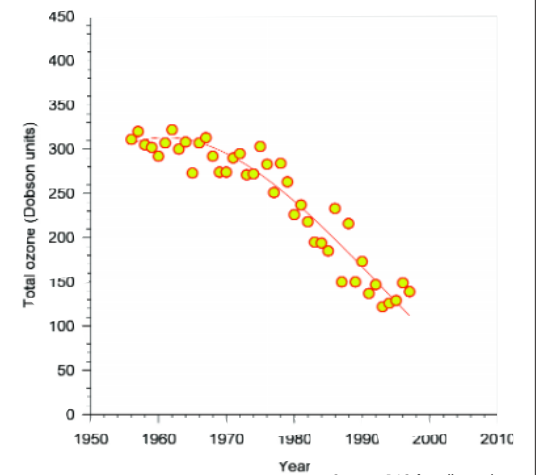
Stratospheric temperature observations at Halley for 1997/98 (red and blue lines). The upper lines (green) show the historical mean and range of values before the ozone hole was formed.



Ozone measurements at Halley 1997/98 (red and blue lines). The upper lines (green) show the historical mean and range of values before the ozone hole formed.



The decline in total ozone amount during October at Halley from 1957 to 1997.



Source: BAS for all graphs



# Measuring ozone levels

October mean total ozone levels measured at Halley Research Station and the global release of CFC-11 between 1956–92.

Year	Total ozone (Dobson Units)	CFC-11 release (kilotonnes)
1956	311	28.7
1957	320	32.2
1958	305	30.2
1959	302	30.9
1960	292	40.5
1961	307	52.1
1962	322	65.4
1963	300	80.0
1964	308	95.0
1965	273	108.3
1966	307	121.3
1967	313	137.6
1968	292	156.8
1969	274	181.9
1970	274	206.8
1971	290	226.9
1972	295	255.8
1973	271	292.4
1974	272	321.4
1975	303	310.9
1976	283	316.7
1977	251	303.9
1978	284	283.6
1979	283	263.7
1980	226	250.8
1981	237	248.2
1982	218	239.5
1983	195	252.8
1984	194	271.1
1985	185	280.8
1986	233	295.1
1987	150	310.6
1988	216	314.5
1989	150	265.2
1990	173	216.1
1991	137	188.3
1992	147	171.1



Balloon carrying a chemical radiosonde being released at Halley Research Station. Inset: A Dobson spectrophotometer in use at Halley

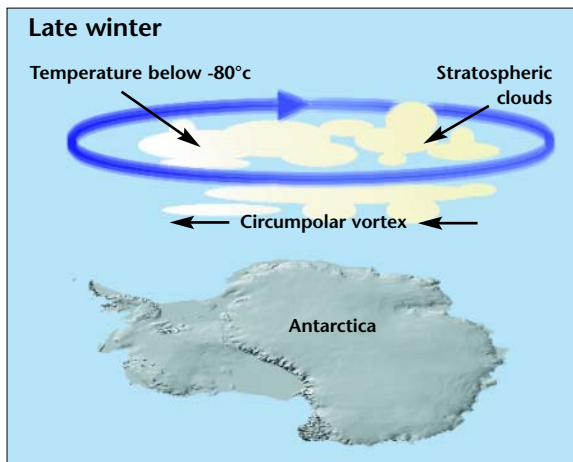
## The role of stratospheric clouds in the formation of the Antarctic ozone hole

During the Antarctic winter a strong westerly circulation around the continent, known as the circumpolar vortex, builds up in the stratosphere. This effectively cuts off the interior and allows it to cool; the temperature at 17 km above the ground falls below -80°C. Thin clouds form, which enable reactions with gases which contain chlorine to take place. When the sun returns in the spring, the chlorine is able to take part in complex catalytic chemical reactions which destroy ozone and create the ozone hole.

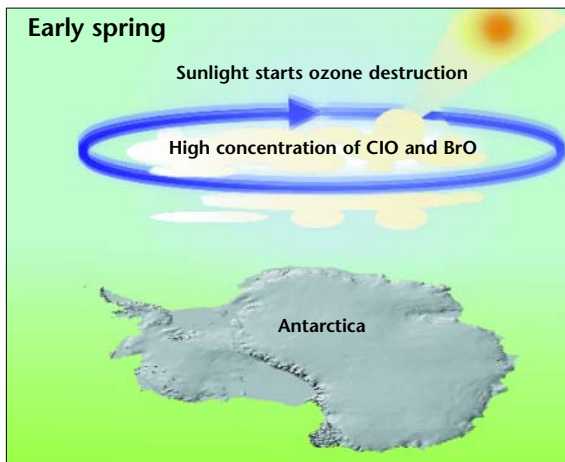
When the stratosphere warms up again during the

late spring and summer, these reactions cease, the circumpolar vortex breaks down and the ozone hole disappears as fresh ozone is brought in.

Unlike Antarctica, which is a continent surrounded by oceans, the Arctic is an ocean surrounded by mountainous continents. This means that the stratospheric circulation is much more irregular, and the temperature does not fall as low as it does in the Antarctic. Stratospheric clouds are therefore less common, which prevents the formation of a deep ozone hole over the Arctic.



Inside the circumpolar vortex, polar stratospheric clouds absorb nitric acid and form  $\text{HNO}_3 \cdot 3(\text{H}_2\text{O})$  crystals. They also provide surfaces from which active chlorine is released. Outside the vortex, chlorine is locked up in an inactive form as chlorine nitrate ( $\text{ClONO}_2$ ) or hydrogen chloride (HCl).



Sunlight and active chlorine catalyse the conversion of ozone to molecular oxygen ( $2\text{O}_3 + 2\text{ClO} \rightarrow 3\text{O}_2 + 2\text{CO}$ ). Similar reactions involving bromine instead of chlorine also take place.

In late spring (November) the stratosphere warms and the polar vortex breaks up. Rapid ozone-destroying processes come to an end, and the ozone hole is filled by mid-latitude air with higher ozone concentrations.



Mother-of-pearl clouds, a localised form of stratospheric cloud found near mountain ranges



CFCs and other ozone depleting substances were used in aerosols, solvents, foam and refrigerators



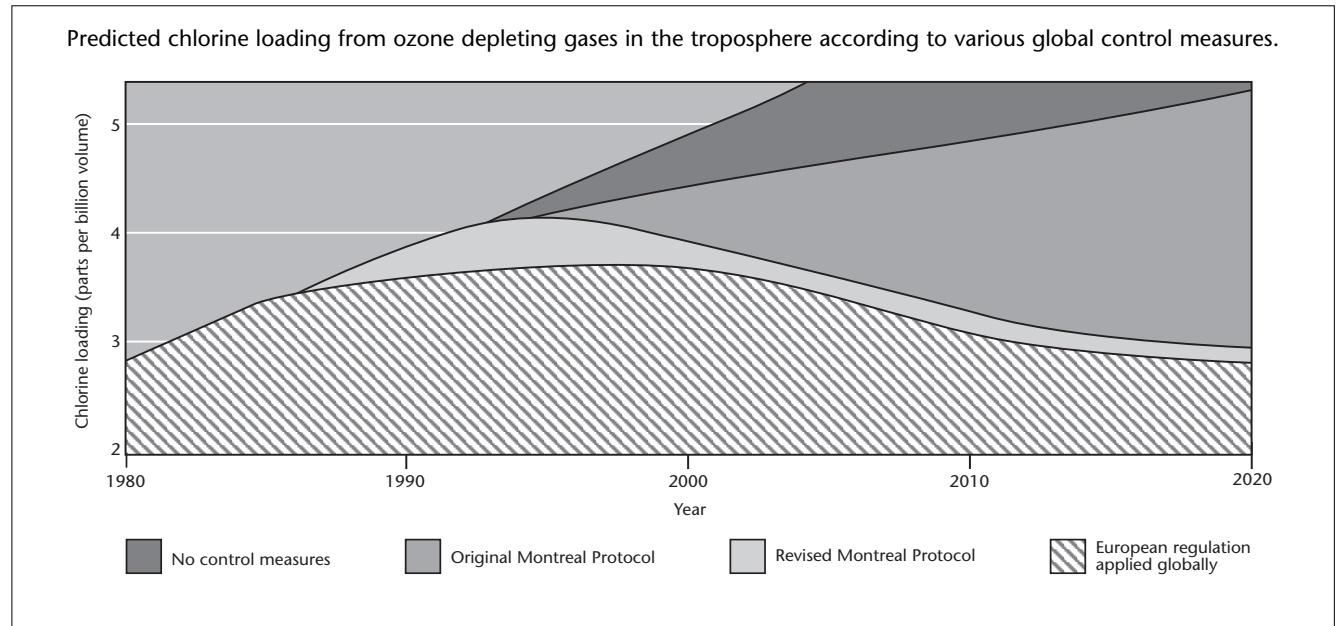
In 1974, US scientists suggested that the growing use of CFCs was likely to cause ozone depletion. Some countries, including the US, took action in the early 1980s to ban the non-essential use of ozone depleting substances. However, decision-makers realised that only coordinated international action could counteract this global threat. This resulted in the signing of the Vienna Convention for the Protection of the Ozone Layer in 1985, which established cooperation on monitoring and research, and set up a framework for international response to the problem.

Following the publication in 1985 by BAS scientists of the discovery of the ozone hole in Antarctica concern greatly increased. This led to the signing of the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987, which came into force in 1989. It controls the production and consumption of ozone depleting substances and originally aimed to halve the use of CFCs by 1999. It is a historic agreement, as it was the first international treaty designed on the basis of scientific evidence to prevent, rather than to cure, a global environmental problem.

In 1990, a further meeting of the 80 countries who had ratified the Protocol agreed to phase out the production and consumption of CFCs, halons and carbon tetrachloride by 2000, and trichloroethane by 2005 in developed countries. Less developed countries (LDCs) have been given until 2010 to phase out these substances and have been provided with a multi-lateral fund worth about \$1 billion to assist them.

In March 1991, the European Community (EC) implemented tougher measures requiring member states to phase out CFCs and carbon tetrachloride by the beginning of 1995.

In November 1992, a further meeting of the Montreal Protocol countries occurred in Copenhagen. This brought forward the phasing out of CFCs, as well as carbon



tetrachloride and trichloroethane to 1996. Halons were to be eliminated by 1994. Additional measures were introduced controlling the production and use of hydrochlorofluorocarbons (HCFCs) and methyl bromide.

In December 1994, the EC decided to phase out HCFCs by 2015 with a 25% cut in methyl bromide by January 1998.

In November 1995, the Montreal Protocol nations met for the seventh time. They agreed to phase out methyl bromide by 2010. They also met in September 1997 and brought forward the phasing out of methyl bromide to 2005 for developed countries and to 2010 for LDCs. Additionally, a licensing system was agreed to control imports and exports.

Trade in illegally produced CFCs is becoming an increasing problem with a vigorous black market developing. It has been suggested that illegal shipments of

CFCs now amount to some 20% of former production levels. China has been identified as one source, and 150 tonnes originating from there were confiscated in the Netherlands in 1997. Illegal CFC trading could undermine the attempts of the Montreal Protocol nations to attain pre-1970 ozone levels by the year 2050 and thus cause a delay to 2100 or beyond.

Although much has been done by the international community to combat the threat of ozone depletion, the problem is by no means solved. All ozone depleting substances need to be phased out as quickly as possible. Even if the world stopped using these substances tomorrow, it will still take until about 2050 before the ozone hole disappears. This is because CFCs and halons are such stable gases that they will remain in the atmosphere for decades after release.



The hole in the ozone layer has attracted much publicity in recent years following its discovery by BAS scientists in the early 1980s. Much of this publicity has been speculative if not sensational. This worksheet examines the nature of ozone, the circumstances that led to the discovery of the ozone hole in Antarctica, the environmental effects of ozone depletion and the international steps taken to counter the threat.

### What is ozone and where is it found?

Ozone exists naturally in the atmosphere as the result of a set of complex reactions involving the action of ultraviolet (UV) radiation on oxygen. These involve not only the creation of ozone but also its destruction. Its concentration in the atmosphere is at a very low level, and until 25 years ago was in a natural balance.

#### Task 1

Resource OZ1 provides information about nature of ozone and its formation in the atmosphere. Resource OZ2 shows data on the occurrence of ozone in the atmosphere above Antarctica. Look at both these resources. Briefly note the characteristics of ozone and how it is formed. Comment on the distribution of the gas over the Earth by explaining the differences between the regions of maximum ozone generation and maximum occurrence. With the aid of a diagram show the heights at which ozone is concentrated and comment on the temperatures found at these heights.

What is the name of the atmospheric layer in which most ozone is found?

With reference to a suitable text, contrast the formation of ozone with that of carbon dioxide.

### How is ozone measured?

Atmospheric ozone has been measured at the British Antarctic Survey (BAS) Halley Research Station (see the



The BAS Halley Research Station

map in Resource N1 to find its location) for over 40 years using a Dobson spectrophotometer. This instrument compares the intensities of two wavelengths of ultraviolet light from the sun. One wavelength is strongly absorbed by ozone and the other is only weakly absorbed. Once the instrument has been calibrated, the ratio of the intensities indicates how much ozone there is in the atmosphere. However, as the sun is the normal source of UV light it is not possible to make regular measurements of ozone during the dark Antarctic winter. Ozone is measured vertically with the use of chemical radiosondes carried aloft by balloons. It is also possible to measure ozone concentrations using satellite sensors. The monitoring techniques used at Halley are illustrated in Resource OZ3. The total level of ozone in the atmosphere is measured in Dobson Units (DU), which are equivalent to milli-atmosphere-centimetres. A typical measurement is about 300 DU (e.g. 3 mm at Standard Temperature and Pressure).

### What is the ozone hole and how was it discovered?

The first sign of damage to the ozone layer was reported in 1985 by scientists at BAS who had been measuring ozone levels over Halley since 1957. Their daily recordings enabled them to establish a long historical record that

showed daily, weekly, monthly and annual variations in ozone concentrations. Some of these records can be seen in Resource OZ2. In the early 1980s the scientists began to collect some surprising and unusual data.

#### Task 2

Study the graphs shown in Resource OZ2. Compare the ozone measurements over the year at Halley for 1997/98 and for the years 1957–72 (both mean and range).

- At what time of year were ozone levels the lowest?
- When were they highest?
- How much variation was there during the course of the year in the two different periods?
- How do the ozone measurements vary with temperature in the two different periods?

With reference to the diagram showing vertical variations in ozone, describe the differences in the vertical distribution for October and August.

Between which heights are the differences greatest?

What changes in climate occur in Antarctica between August and October (remember the hemisphere!)?

The BAS scientists found that during the month of October each year ozone was almost completely destroyed over Antarctica. They had discovered the ozone hole. This did not correspond to satellite measurements by US scientists, but a review of their data showed a software error which had rejected all the ozone measurements below the normal levels.



BAS staff take every precaution to avoid getting sunburnt

**Task 3** Look at the October 1998 satellite image of ozone levels over Antarctica (Resource OZ2). Draw a map overlay of Antarctica using the image as a base. Draw on the ozone hole (blue/white areas). Estimate the size of the hole (in million km<sup>2</sup>). Why is the hole not circular? Why is the size and shape of the hole a worry to people living in Tierra del Fuego (southern South America), the Falkland Islands and South Island (New Zealand)?

Look at the change in October mean ozone at Halley between 1950 and 1997 (Resource OZ2). How much of a decline in ozone has there been in absolute terms? Calculate the percentage fall. If there was to be no change in the decline, estimate the October mean ozone at Halley in 2050.

Over the past fifteen years there has been a significant decline in the amount of ozone over Antarctica in the austral spring. In 1998, 40% of the ozone was lost at heights between 14 and 22 km, virtually all of it for a six week period. The hole has also grown in size each year. In October 1998, it covered most of Antarctica and reached an area twice the size of Europe (24 million km<sup>2</sup>).

### What causes ozone depletion?

Destruction of ozone occurs naturally in the atmosphere. Indeed until the 20th century a natural balance had evolved between creation and loss, both due to the action of solar radiation. Although there have been natural variations due, for example, to volcanic eruptions, the losses identified in the 1980s were too great to be explained by natural cycles. Scientists suspected that a range of man-made chlorine and bromine based gases, such as chlorofluorocarbons (CFCs), might be responsible for ozone depletion. CFCs were used in fridges, air-conditioning units, plastic foams and aerosol sprays.

**Task 4** Examine the table showing the global release of CFC-11 and mean October ozone levels at Halley in Resource OZ3. ➤

➤ Carry out a Spearman Rank correlation test to establish whether there is a relationship between the two sets of data. Is the result significant at the 90% level and is the relationship positive or negative? Explain your results. If you found a relationship it was only indicative of an association.

Scientists have found that CFCs are very stable compounds and can remain in the atmosphere for over a century. These gases do not break down in the lower atmosphere and are transported high into the stratosphere where they are eventually broken down by UV radiation. This reaction releases free chlorine, which acts as a catalyst in the destruction of ozone.

**Task 5** Resource OZ1 describes how ozone is destroyed in the stratosphere. Create a series of bullet points that summarises the processes involved and the role played by CFCs and other ozone depleting gases.

### Why did the hole appear first over Antarctica?

The explanation for the development of the ozone hole over Antarctica lies in the unique climatic conditions that prevail there.

**Task 6** Study an atlas map of global wind circulation and the annotated diagram and photograph in Resource OZ4. How do the winds circulate around Antarctica? How much insolation occurs at the South Pole in winter? What therefore happens to temperatures? Although moisture is scarce in the Antarctic stratosphere in winter, what is likely to happen to it as it is cooled to as low as -80°C? Describe the role of stratospheric clouds, in conjunction with chlorine and bromine, in ozone destruction.

### What effects does ozone depletion have?


The ozone layer plays an important role in the atmosphere. It protects us from the harmful effects of certain wavelengths of UV radiation, particularly UV-B radiation (radiation between the wavelengths 280-320 nanometres).

**Task 7** Study Resource OZ1 which discusses the effects of ozone depletion. Create a table that summarises the potential impacts of ozone loss on humans, plants, marine ecosystems, the built environment and climate. Identify the possible effects in Antarctica and the Southern Ocean.

**What has been done to combat ozone depletion and is it enough?**

**Task 8** Read the summary of steps that have been taken to combat ozone depletion (Resource OZ5). Create a time sequence in boxes showing the progress made. The box below will start you off:

**1974 Role of CFCs identified**



Comment on the trends shown in the graph in Resource OZ5. When should the level of ozone depleting gases in the atmosphere start to drop? How might the black market in ozone depleting substances affect the meeting of internationally agreed targets?

**What can we learn from the ozone hole?**

**Task 9** In pairs identify five key messages that have emerged from your study of the ozone hole. Share your five points with the class. What were the most popular messages overall? Why?