

Ozone Conference Setting the Scene

In this Brief you will be attending a conference on ozone. You will have short talks and you may be selected to make a presentation about ground level (tropospheric) ozone and about the ozone layer (stratospheric ozone). You will also take part in discussions on how to tackle the problems associated with ozone in these two regions of the atmosphere.

Pupil Research Brief

Study Guide

Syllabus Targets Science you will learn about in this Brief

- the formation of oxygen as the Earth's atmosphere evolved resulted in the development of an ozone layer
- □ this filtered out harmful ultraviolet radiation from the Sun allowing the evolution of new living organisms
- the high temperatures produced by burning fuels can cause nitrogen and oxygen from the air to react, forming nitrogen oxides
- nitrogen oxides can harm plants and animals directly

Route through the Brief



- ultraviolet radiation can pass through the skin to deeper tissue
- high doses can cause normal cells to become cancerous
- when supplied with appropriate information you should be able to use your scientific knowledge to weigh evidence and form balanced judgements about some of the major environmental issues facing society

Outcome Checklist

You will attend a conference on ozone in the troposphere and stratosphere. You will take part in presentations and discussions about papers in each session of the conference. You will also use information from ozone monitoring stations to carry out one or more data handling investigations. You should make sure you produce the following items as you work through the Brief.

Session 1

summary notes on the papers and recommendations for action to reduce ozone levels throughout the UK

Data handling investigation

graphs showing variation in ground level ozone at one or two sites and comments on what the graphs show

Session 2

summary notes on the papers and recommendations for action to prevent the ozone layer being depleted any further

Data activity

graphs showing the variation in the ozone layer above the Antarctic during 1987 and comments on what they mean

Conference report

a brief report based on summary notes and recommendations, including relevant information from data activities

Ozone Conference Introduction to the 1st session

What is ozone?

Almost everyone has heard the term the 'ozone layer', but few people really know where it is and why it matters. Fewer still could answer the question, '*what is ozone?*' Ozone is a blue, slightly pungent gas, smelling of bleach. It is a form of oxygen, but a molecule of ozone has 3 atoms of oxygen joined together instead of the usual 2 in the oxygen molecules we breathe. This small difference is important, because ozone is poisonous. Ozone can be good for us or bad for us, depending on where in the atmosphere it is found. **Figure 1** shows the lower parts of our atmosphere.



Figure 1. The lower atmosphere

Scientists have divided the atmosphere into different layers or zones. The lowest layer is called the troposphere. This is the part of the atmosphere we live in. Above this is the stratosphere, and this is where the ozone layer occurs. Ozone here is good for us, because it stops harmful ultraviolet rays from reaching Earth. Ozone in the troposphere is bad for our health and it can also damage crops and attack a wide range of materials. The conference you are attending as part of this Brief will provide information about both tropospheric and stratospheric ozone and the problems our modern way of life are creating with respect to ozone. You will learn about the effects on health, crops and materials of ground-level ozone. You will also learn about how the widespread use of certain chemicals is destroying the ozone layer and so exposing us to the dangers of ultraviolet rays.

Ozone Conference tropospheric ozone - paper 1

The formation of ozone in the troposphere

Introduction

The focus of international attention on ozone has been the problem of the destruction of the ozone layer in the stratosphere by various chemicals. However, there is another problem with ozone that is equally as important. This is to do with the increasing levels of ground-level ozone, which could be of more immediate importance than ozone layer depletion.

Photochemical reactions

A number of pollutants in the atmosphere can cause the formation of ozone under the action of sunlight. The most important of these are oxides of nitrogen which are often given the general name of NOx gases. These gases are formed when high temperatures inside car engines and furnaces cause nitrogen and oxygen in the air to react. These NOx gases are able to react to form ozone under the action of sunlight. Such reactions are called photochemical reactions, and nitrogen dioxide (NO₂) is especially good at doing this.



Figure 1. Photochemical reactions which produce ozone

• Ozone Conference tropospheric ozone - paper 1 continued

Major causes of NOx emissions

Figure 2 shows the contribution to the levels of NOx emissions made by (a) motor vehicles and (b) power stations, throughout Great Britain.



Figure 2. Sources of NOx gases in the UK

Table 1 on the next page gives the figures for the major sources of NOx emissions in the UK from 1980 to 1991. Emissions of nitrogen oxides in the UK rose by 12% between 1986 and 1990. Road transport emissions increased by 73% in the period 1981 to 1991 and so the contribution to NOx emissions from this source reached 51% by 1990. In the same period emissions from power stations declined by 14%. Power stations caused 26% of the total UK emissions by 1991.

Ozone Conference tropospheric ozone - paper 1 continued

Table 1. NOx emissions a) by source, b) by types of fuel

Nitrogen oxides (N	O _X): estir	mated ei	missions	by emissio	in source a	nd type of	fuel for the	e UK (thou:	sands of to	nnes)			
	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991 ^{Pe} to	ercentage of tal in 1991
a) by emission source													
Domestic	68	68	67	67	64	72	75	74	72	68	68	76	3
Commercial/ Public service	62	61	61	62	63	64	65	61	60	55	56	60	2
Power stations	880	839	799	787	711	775	807	826	800	769	LLL	718	26
Refineries	43	38	37	36	36	34	35	34	34	36	36	37	-
Agriculture	2	2	2	5	2	5	2	4	4	4	4	4	
Other industry Railways	279 41	268 39	258 35	250 37	237 35	243 37	242 37	243 35	247 35	236 32	231 30	224 31	8 –
Road Transport	804	810	830	868	932	026	1031	1154	1259	1376	1381	1400	51
Civil Aircraft	10	6	10	10	11	11	11	12	13	14	14	14	
Shipping	121	104	119	111	123	116	108	101	102	127	131	133	5
Offshore oil and gas		56	59	62	64	63	62	61	59	50	51	50	2
Total	2312	2297	2280	2277	2281	2392	2481	2603	2683	2764	2779	2747	100
b) by type of fuel													
Coal	980	891	824	838	574	774	852	885	854	794	786	738	27
Solid smokeless fuel	L	9	9	9	4	9	5	5	5	4	4	4	ı
Petroleum:	720	100	717	~~~	100	Б))	E71	647	002	VOL	CUO	910	00
	428	416 416	417	444	400	220	1460	042 512	550 550	707 502	579 579	584	50 21
Gas oil	174	158	168	160	170	168	157	147	147	163	161	164	. 0
Fuel oil	220	180	188	148	315	186	149	122	139	160	171	150	D
Burning oil	2	4	4	4	4	4	4	4	4	4	4	2	
Other petroleum	32	30	35	41	41	33	35	36	37	39	40	38	-
Other gas	140	139	141	144	150	160	157	166	160	156	160	175	6
Other emissions	24	24	25	25	25	25	25	25	22	21	21	71	°
Total	2312	2242	2221	2234	2216	2327	2416	2544	2626	2717	2729	2747	100

Ozone Conference tropospheric ozone - paper 1 continued

Other sources of ozone production

Other chemicals that can cause ozone to form include organic solvents used in paints, varnishes and glues, and also petrol vapour and oil industry emissions.

Ways of reducing ozone formation

Cars fitted with catalytic converters emit far lower levels of NOx gases than those without them, but there are still millions of cars that don't have them (L-registration cars and earlier are unlikely to be fitted with them). Also, the volume of motor traffic continues to increase, seemingly unchecked. Research is being conducted to find ways of improving car engines to make them less polluting, particularly of NOx gases.

Research is also being carried out to make power station furnaces produce much lower levels of nitrogen oxides by more efficient burning of fuels. Water based paints and varnishes are now widely available, but the great majority of paints and varnishes are still made with organic solvents. As yet there are no plans to introduce legislation to limit their use.

• Ozone Conference tropospheric ozone - paper 2

Monitoring Ozone in the United Kingdom

A network of ozone monitoring stations was established throughout the UK to provide detailed information about the concentrations of ozone and the changes in these concentrations on a daily and seasonal basis. Figure 1 shows where these sites are located.



Figure 1. Ozone monitoring sites

The information provided by these stations has enabled scientists to estimate the exposure of natural vegetation and to some extent, the human population to ozone in different parts of the country. A database has been built up so that trends in ozone concentration and distribution can be plotted. The data collected by the monitoring sites is freely available on the World Wide Web, and so anyone interested in air quality can download the information they require. By using a spreadsheet it is possible to plot graphs of ozone variations throughout the day, or over a week, month or year in the location they wish to study.

Ozone Conference tropospheric ozone paper 2 continued

Information on ozone levels is also available to the general public on CEEFAX and TELETEXT as well as the *Air Quality Helpline* (free phone 0800 55 66 77). The air quality is described in these services in the following terms:

Air Quality	Hourly average ozone concentration (ppb)
Very Good	0-49
Good	50-89
Poor	90-179
Very poor	above 180

(ppb = parts per billion)

These are the concentrations of ozone above the *natural background level*. Ozone is present all the time in low concentrations. This is the background level and will be explained later in the second session of the conference. Air quality information is useful, for example, to asthma sufferers, since high ozone levels can bring on attacks.



Figure 2. Maximum hourly mean ozone concentrations recorded each month over all sites from 1972 - 1990

Ozone Conference tropospheric ozone - paper 2 continued

Sunlight is needed for NOx gases and organic solvents to react with air to make ozone, and so the ozone level always rises in the summer months, as can be seen in Figure 2. Ozone levels also vary during the day. Figure 3 shows the variation at one monitoring station, Harwell.



Figure 3. The variations in ozone levels at the Harwell monitoring station

Since it can be carried along by air currents, some of the ozone in the atmosphere can come from elsewhere in the world. **Figure 4** shows the concentrations of ozone of 4 monitoring stations both from UK and European sources.

The ozone generated in Britain can in turn be carried away to other parts of the world. Thus, it is evident that any measures that are introduced to curb pollutants that cause ozone to form must be enforced internationally, and not just in one or two countries, if they are to be effective.



Figure 4. UK and continental European sources for ozone (May to December 1989)

Ozone Conference tropospheric ozone - paper 3

The effects of ozone on humans, plants and animals

Effects on humans

It has been known for a long time that exposure to high concentrations of ozone can produce significant damage to the lungs. In recent years more attention has been given to the effects of low levels of ozone, similar to those found outdoors in some parts of the UK during summer weather. Research has shown that exposure to the levels of ozone experienced during summertime, or during *photochemical smog* can cause inflammation of the airways inside the lungs and damage to the lining of the lungs. The inflammation of the airways causes some resistance to airflow and reduction in lung volume. It is likely that such damage will be fully repaired if the 'photochemical episode' is short. In places such as Mexico City, Athens and Los Angeles, where such smogs are much more frequent than in the UK and ozone concentrations far higher, lung damage could be permanent.The effect of any given concentration of ozone is considerably increased by exercise, which increases the volume of air inhaled. So people should not take vigorous exercise when ozone levels are high.



Figure 1. The effects of ozone on Forced Expiratory Volume (FEV)

Figure 1 above shows the results of an experiment in which people were exposed to different concentrations of ozone for 6 hours while exercising. They were required to expel as much air from their lungs as possible in one go by blowing into a bag - before and after exposure to the ozone. The amount of air expelled is called the *Forced Expiratory Volume* (FEV). The reduction in the FEV after exposure shows how much the capacity of the lungs has decreased.

• Ozone Conference tropospheric ozone paper 3 continued

These changes in lung capacity could be a real problem for people with asthma. There are indications that the amount of people suffering from asthma, and the severity of their asthma, has increased over recent decades. The amount of traffic has also increased rapidly at the same time, producing increased vehicle emissions, which leads to an increase in ozone levels. This has led to the suggestion that the two are connected. As there is a lack of data about this, no conclusions can be drawn as yet about the possible link. It is possible that exposure to high levels of ozone in early childhood might increase the likelihood of those with 'asthma genes' becoming more sensitive to certain chemicals that trigger the onset of asthma. At present there is little scientific evidence to support this theory or any others that have been put forward.

There is, however, some evidence to suggest that ozone can increase the sensitivity of hay fever sufferers to pollen. A small scale study showed that symptoms of hay fever (sneezing, sore eyes, etc.) were more severe when ozone levels were above 40 ppb. The study was too small to be conclusive and more work is needed to prove beyond doubt the link between ozone and increase in hay fever severity.

The lack of conclusive statistics to prove that ozone has a damaging effect on health does *not* mean that it definitely *doesn't* have an effect. The World Health Organisation and the European Community have drawn up guidelines on ozone levels. These include providing information to the public if ozone rises above 90 ppb, and giving health advice if it goes above 180 pp. In Los Angeles there are set courses of action if ozone gets above 3 different levels:

- 1 above 200 ppb
- 2 above 300 ppb
- 3 above 500 ppb

At level 1 schools and colleges restrict the outdoor activities of students, and at level 3 the general public, schools, commercial, industrial and government activities operate as though the day is a major national holiday. Ozone levels in the UK have not so far exceeded 180 ppb, but they do go above 90 ppb. **Figure 2** on the next page is a map of the UK showing the number of hours when the ozone level exceeded 90 ppb between April and September, 1993.

Ozone Conference tropospheric ozone - paper 3 continued

Effects on vegetation

Controlled experiments have shown that there is a clear reduction in the yield of some crops when ozone levels are only slightly higher than normal, i.e. about 20-30 ppb. These crops include wheat, barley, spinach, peas, beans and clover. It is estimated that in the United States 4 billion dollars-worth of damage is done to crops by ozone each year. Trees can also be damaged by ozone. Research on young trees has shown that levels of ozone found in Southern Britain can affect the growth of certain types of tree, especially conifers. Ozone could also make trees less tolerant of the cold or of drought.

Effects on materials

Ozone is very reactive and its effect on polymers is well known. Cracks can develop, for example, in rubber when a little stress is applied in the presence of very small amounts of ozone. The annual economic loss to the United States due to damage to polymers by ozone is estimated to be 1757 million dollars. Ozone also attacks cellulose in textiles, reducing their strength as well as fading the fabrics. The damage ozone causes to paints is estimated to amount to 731 million dollars in the USA. No figures for the cost of damage to materials due to ozone are available for the UK.



Figure 2. Hours above 90 ppb between April and September 1993

Ozone Conference Introduction to the 2nd session

How the ozone layer cuts down on the amount of ultraviolet radiation reaching the surface of the earth

Oxygen normally exists as molecules of 2 atoms, O_2 . This is sometimes called *dioxygen*. Ozone is another form of oxygen, but with molecules of 3 atoms, O_3 .



The free oxygen that is released will quickly combine with an O_2 molecule to re-form ozone. In this way ozone is continually being made and destroyed, and all the time ultraviolet radiation is being used up. This cuts down drastically the amount of UV that reaches the Earth's surface. There are about 5 billion tonnes of ozone in the stratosphere, which may seem like a vast quantity, but if all the ozone could be brought down to sea level and spread evenly over the Earth's surface it would be squeezed by air pressure into a layer just 3mm thick!

Ozone can also be formed by passing an electrical spark through air. So, some ozone is made every time lightning strikes during a thunderstorm. This and some of the ozone formed in the stratosphere reaching the Earth's surface means that there is a small amount of ozone in the air we breathe all the time. This 'background' ozone is present in concentrations of 20-30 parts per billion (ppb) by volume.

absorbed

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Ozone Conference stratospheric ozone - paper A

Monitoring ozone layer depletion

Concern that stratospheric ozone could be destroyed by certain commonly-used chemicals was raised in the mid 1970's, but it was not until 1985 that evidence of ozone loss was published in the scientific journal *Nature*. In that year scientists from the British Antarctic Survey reported the results of work they had done the previous year at Halley Bay in the Antarctic. They had measured ozone levels using instruments sent up into the stratosphere on board weather balloons. These instruments showed that the ozone concentration had fallen below half the levels previously measured. At altitudes between 12 and 22 km in September and October 1984 (the Antarctic spring), the ozone had virtually disappeared. In fact, the NASA weather satellite *Nimbus* 7 had also detected the ozone layer hole, but the computer that processed its information was programmed to discount data that fell below 180 D.U., which stands for Dobson Units. Dobson was an Oxford professor who developed the monitoring technique used for ozone. A Dobson Unit measures the thickness of the ozone layer if it were brought down to sea-level and was at a temperature of 0°C. One D.U. is the same as one-thousandth of a centimetre. The British Antarctic Survey had measured ozone concentrations of at least 200 D.U. up until 1984.



Figure 1. The hole in the ozone layer above Antarctica, October 1987

Figure 1 shows the hole as it was in 1987, when its area was roughly the same as the size of the U.S.A. The ozone layer hole forms over Antarctica because of its unique weather system. The air above the continent is cut off from the rest of the atmosphere by strong winds which swirl round the pole during the Antarctic winter. The conditions created are ideal for the ozone-destroying chemical reactions to occur. The hole heals when the Antarctic summer occurs (our wintertime) and opens up again each October. **Figure 2** on the next page shows 'contour' maps of the distribution of ozone above Antarctica for (a) October 1981 and (b) October 1989. The maps show the drastic depletion of ozone over the whole of the South Pole in a timespan of 8 years.

•Ozone Conference stratospheric ozone - paper A continued



Figure 2. The distribution of ozone above Antarctica for a) October 1981, and b) October 1989

Ozone Conference stratospheric ozone - paper A continued

The graphs in Figure 3 show the total ozone measurements from 1957 to 1995 over Halley Bay in October, when the ozone layer appears, and February, when the ozone concentration is greatest. In both cases, the trend is downwards, showing that there is a general thinning of the ozone layer all year round. In fact, the total ozone values in early October are now about one third those observed in the 1960's. Total ozone in February has also decreased by over 20% since the 1960's. Monitoring of the ozone layer all over the world has shown a steady loss of ozone. There is clear evidence that there is widespread ozone losses in the Arctic in winter, similar to the beginning of the Antarctic ozone layer hole.



Figure 4. Ozone measurements over Lerwick



Figure 3. Monthly mean total ozone observed over Halley Bay from 1957 - 1995

Thinning of the ozone layer has several consequences. The effects of the increased amount of ultraviolet radiation reaching the ground will be explained in a later paper, but there is another important effect that should be pointed out. There is strong evidence to suggest that reduced levels of ozone in the stratosphere tends to cool the climate. We haven't noticed this because carbon dioxide and other gases have produced

the Greenhouse effect, which causes the climate to warm up! Calculations have indicated that ozone layer depletion has offset global warming by at least 30% for the period since 1979.

Clearly the consequences of the thinning of the ozone layer are very serious and there is now no doubt about the causes of the depletion. These causes will be explained in another paper to be presented in this session.

Figure 4 shows the results of measurements taken over Lerwick in Scotland (latitude 60°N). The measurement on March 5th 1996 was 195 D.U., the first time that a value below 200 has ever been recorded above the U.K. The graph also shows the average daily values of total ozone from 1981 to 1995 (solid line). Similar low results were reported elsewhere in Northern Europe. In fact, the total ozone in high Northern latitudes was about 20% below the average for 1979 to 1986.

•Ozone Conference stratospheric ozone - paper B

The causes of ozone layer depletion

In 1974 Dr F Sherwood Rowland and Dr Mario Molina of the University of California published a paper which showed that a common family of chemicals called *chlorofluorocarbons*, or CFCs, could cause ozone depletion. These CFCs had been used since the Second World War in ever increasing amounts in a wide variety of applications. One of these was as a propellant in aerosols. Propellants are added to, say, deodorant to 'push' it out of the can when the button is depressed. CFCs were chosen for this task because they do not react chemically with almost anything they touch and they are not flammable. Because they are chemically inert they were thought to be safe.

CFCs are also used to make both soft foam for furniture and hard expanded polymers such as styrofoam. Styrofoam is used extensively as packing material and disposable cups, egg boxes and fast food containers. One particular CFC, known as CFC-12 or *Freon*, was widely used as a refrigerator coolant, and others were used to remove grease from computer chips and as dry cleaning solvents. The work published by Rowland and Molina caused an initial shock, not least because the manufacture of CFCs was a multi-million dollar industry, but little or no action was taken because of lack of evidence that the ozone layer was being destroyed. The findings of the British Antarctic Survey in 1984 altered all that.

The problem with CFCs is the very chemical inertness that caused them to be used in aerosols in the first place. Once expelled into the air CFC molecules can linger in the lower atmosphere for years before they reach the ozone layer. Once there, they will eventually be broken down under the action of ultraviolet radiation. As their name suggests chlorofluorocarbon molecules are made up of differing proportions of chlorine, fluorine and carbon atoms. To illustrate what happens, let us look at a CFC molecule with 1 carbon atom, 3 chlorine atoms and a fluorine atom.



(2) The free chlorine 'grabs' an oxygen atom from ozone

Figure 2. CFCs and ozone depletion (part 1)

Ozone Conference stratospheric ozone - paper B continued

Ozone is constantly being broken up and re-formed by ultraviolet radiation in the ozone layer.



(4) The free oxygen combines with chlorine monoxide to release free chlorine

Figure 2. CFCs and ozone depletion (part 2)

The free chlorine can go on to break up another ozone molecule. In fact it can carry on doing this for perhaps a hundred years before it leaves the stratosphere, breaking up around one hundred thousand molecules of ozone in the meantime.

Other chemicals can also do this. They include carbon tetrachloride, an industrial solvent; 1.1.1 trichloroethane, also a solvent used in adhesives and in correction fluid; methyl bromide, a powerful fumigant used to kill pests in soil, flour mills and cereal stockpiles; and halons. Halons are another family of carbon-based chemicals, but these contain bromine, which is a much more powerful ozone depletion agent. At least one scientist has suggested that a quarter of the chlorine in the stratosphere could have been released by wood-rotting fungi. Major volcanic eruptions can have a noticeable effect on ozone depletion and there is evidence that sunspot activity could also play a major role in the development of the ozone layer hole in the Antarctic. Scientists at NASA have shown that the ozone concentration in the stratosphere is at its lowest there when sunspot activity is at a maximum.

It is possible that the increase in particles streaming out from the Sun in the solar wind has some effect on the formation of ozone. However, the majority of scientists believe that CFCs, halons and other chemicals are the main culprits in destroying ozone in the ozone layer.

• Ozone Conference stratospheric zone - paper C

The consequences of ozone layer depletion

When the ozone layer was formed millions of years ago, life was able to evolve on land for the first time. This is because the layer reduced the amount of ultraviolet radiation from the Sun that reached the ground. Ultraviolet radiation has a range of wavelengths from 4 nm to 400 nm (nm = nanometer, one billionth of a metre), between x-rays and visible light in the electromagnetic spectrum. Ultraviolet radiation is responsible for the formation of vitamin D and it gives us a suntan. It is very effective at killing bacteria and so UV lamps are sometimes used in food storage rooms for this purpose. UV can also be very harmful to humans and animals, especially in the 290 to 320 nm range. This is the waveband known as UV-B. It can cause skin cancers and cataracts. It can also damage DNA, causing mutations to occur, and it can suppress the immune system, impairing the ability of our bodies to fight off infectious diseases. UV-B can penetrate the ocean to depths of up to 20 metres, where it can kill plankton (the base of the food chain in the sea) and harm the larvae of fish, shrimp and crab.

Tests on some 300 plants have shown that two thirds are affected by ultraviolet radiation. Among those particularly vulnerable are peas, melons, mustard and cabbage. UV-B is also known to break down polymers used in buildings, paints, packaging and many other products.

The ozone layer drastically reduces the amount of UV-B that reaches us, and prevents any ultraviolet radiation with wavelengths below 290 nm getting to ground level. So, any damage to this layer could have devastating consequences to the whole world. CFCs and halons are widely blamed for causing ozone layer depletion, and the effects we have seen so far are probably going to get worse. These chemicals take years to get into the stratosphere and then stay around destroying ozone for decades. So, although the use of ozone depleting chemicals has declined sharply in the last decade, the chemicals that were discharged into the atmosphere before then have yet to do their worst damage.

Action on ozone depletion

In 1987 representatives from 24 countries met in Montreal, Canada, to discuss the problem of ozone layer depletion. At the end of the conference the delegates signed a document called *The Montreal Protocol on Substances that deplete the ozone layer*, which was an action plan to control the use of CFCs and other chemicals. The idea was to freeze the level of CFC and halon production and then begin to cut down use of CFCs, halons, etc. The document allowed developing countries a longer period to cut their use of ozone depleters.

Ozone Conference stratospheric ozone - paper C continued

These countries, in an effort to catch up with the richer countries, have relied more and more on CFCs to improve their prosperity. It was stated that developing countries did not cause the ozone layer to be damaged and so they should not be expected to bear the burden of stopping the use of CFCs without international help. As a result a mechanism was put in place to provide financial and technical help to developing countries to assist them to phase out the use of ozone depleting chemicals.

The Protocol has been toughened up since, notably in London in 1990 and in Copenhagen in 1992, when the phase-out of the chemicals already controlled by the Protocol was speeded up. The Copenhagen agreement also introduced control on methyl bromide as well as HCFCs and HBFCs. These last two are groups of chemicals that have largely replaced CFCs as a short term measure. HCFCs are between one-fiftieth and onetenth as harmful to the ozone layer as CFCs.

Many more countries have signed the Protocol and real progress has been made. Some countries such as Canada as well as the European Community have introduced even stricter controls than the Montreal Protocol, and much research is being carried out to find safe alternatives to the chemicals we still use that are ozone depleters. The maximum effect of ozone depletion will not be seen until the first quarter of the 21st century, and the ozone layer is not likely to be repaired until the third quarter of the 21st century at the earliest.