

Ozone depletion

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Ozone depletion describes two distinct, but related observations: a slow, steady decline of about 4 percent per decade in the total volume of ozone in Earth's stratosphere(ozone layer) since the late 1970s, and a much larger, but seasonal, decrease in stratospheric ozone over Earth's polar regions during the same period. The latter phenomenon is commonly referred to as the **ozone hole**. In addition to this well-known stratospheric ozone depletion, there are also tropospheric ozone depletion events, which occur near the surface in polar regions during spring.

The detailed mechanism by which the polar ozone holes form is different from that for the mid-latitude thinning, but the most important process in both trends is catalytic destruction of ozone by atomic chlorine and bromine.^[1] The main source of these halogen atoms in the stratosphere is photodissociation of chlorofluorocarbon (CFC) compounds, commonly called freons, and of bromofluorocarbon compounds known as halons. These compounds are transported into the stratosphere after being emitted at the surface. Both ozone depletion mechanisms strengthened as emissions of CFCs and halons increased.

CFCs and other contributory substances are commonly referred to as **ozone-depleting substances (ODS)**. Since the ozone layer prevents most harmful UVB wavelengths (270–315 nm) of ultraviolet light (UV light) from passing through the Earth's atmosphere, observed and projected decreases in ozone have generated worldwide concern leading to adoption of the Montreal Protocol banning the production of CFCs and halons as well as related ozone depleting chemicals such as carbon tetrachloride and trichloroethane. It is suspected that a variety of biological consequences such as increases in skin cancer, damage to plants, and reduction of plankton populations in the ocean's photic zone may result from the increased UV exposure due to ozone depletion.

Pollution

Air pollution

Acid rain • Air Quality Index • Atmospheric dispersion modeling • Chlorofluorocarbon • Global dimming • Global distillation • Global warming • Indoor air quality • **Ozone depletion** • Particulate • Smog

Water pollution

Eutrophication • Hypoxia • Marine pollution • Marine debris • Ocean acidification • Oil spill • Ship pollution • Surface runoff • Thermal pollution • Wastewater • Waterborne diseases • Water quality • Water stagnation •

Soil contamination

Bioremediation • Electrical resistance heating • Herbicide • Pesticide • Soil Guideline Values (SGVs)

Radioactive contamination

Actinides in the environment • Environmental radioactivity • Fission product • Nuclear fallout • Plutonium in the environment • Radiation poisoning • Radium in the environment • Uranium in the environment

Other types of pollution

Invasive species • Light pollution • Noise pollution • Radio spectrum pollution • Visual pollution

Inter-government treaties

Montreal Protocol • Kyoto Protocol • CLRTAP • OSPAR • Stockholm Convention

Major organizations

DEFRA • EPA • Global Atmosphere Watch • EEA • Greenpeace • American Lung Association

Related topics

Environmental Science • Natural environment • Acid Rain Program

Contents

- 1 Ozone cycle overview
 - 1.1 Quantitative understanding of the chemical ozone loss process
- 2 Observations on ozone layer depletion
 - 2.1 Chemicals in the atmosphere
 - 2.1.1 CFCs in the atmosphere
 - 2.2 Verification of observations
- 3 The ozone hole and its causes
 - 3.1 Interest in ozone layer depletion
- 4 Consequences of ozone layer depletion
 - 4.1 Increased UV
 - 4.2 Biological effects of increased UV and microwave radiation from a depleted ozone layer
 - 4.2.1 Effects of ozone layer depletion on humans
 - 4.2.2 Effects on crops
 - 4.2.3 Effects on plankton
- 5 Public policy in response to the ozone hole
- 6 Current events and future prospects of ozone depletion
- 7 History of the research
 - 7.1 The Rowland-Molina hypothesis
 - 7.2 The ozone hole
- 8 Controversy regarding ozone science and policy
- 9 Ozone depletion and global warming
- 10 Misconceptions about ozone depletion
 - 10.1 CFCs are "too heavy" to reach the stratosphere
 - 10.2 Man-made chlorine is insignificant compared to natural sources
 - 10.3 An ozone hole was first observed in 1956
 - 10.4 If the theory were correct, the ozone hole should be above the sources of CFCs
 - 10.5 The "ozone hole" is a hole in the ozone layer
- 11 World Ozone Day
- 12 See also
- 13 References
 - 13.1 Nontechnical books
 - 13.2 Books on public policy issues
 - 13.3 Research articles
- 14 External links

Ozone cycle overview

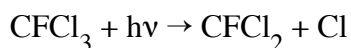
Three forms (or allotropes) of oxygen are involved in the ozone-oxygen cycle: oxygen atoms (O or

atomic oxygen), oxygen gas (O₂ or diatomic oxygen), and ozone gas (O₃ or triatomic oxygen). Ozone is formed in the stratosphere when oxygen molecules photodissociate after absorbing an ultraviolet photon whose wavelength is shorter than 240 nm. This produces two oxygen atoms. The atomic oxygen then combines with O₂ to create O₃. Ozone molecules absorb UV light between 310 and 200 nm, following which ozone splits into a molecule of O₂ and an oxygen atom. The oxygen atom then joins up with an oxygen molecule to regenerate ozone. This is a continuing process which terminates when an oxygen atom "recombines" with an ozone molecule to make two O₂ molecules: $O + O_3 \rightarrow 2 O_2$

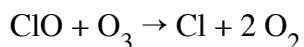
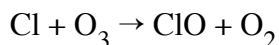
The overall amount of ozone in the stratosphere is determined by a balance between photochemical production and recombination.

Ozone can be destroyed by a number of free radical catalysts, the most important of which are the hydroxyl radical (OH·), the nitric oxide radical (NO·) and atomic chlorine (Cl·) and bromine (Br·). All of these have both natural and anthropogenic (manmade) sources; at the present time, most of the OH· and NO· in the stratosphere

is of natural origin, but human activity has dramatically increased the levels of chlorine and bromine. These elements are found in certain stable organic compounds, especially chlorofluorocarbons (CFCs), which may find their way to the stratosphere without being destroyed in the troposphere due to their low reactivity. Once in the stratosphere, the Cl and Br atoms are liberated from the parent compounds by the action of ultraviolet light, e.g. ('h' is Planck's constant, 'v' is frequency of electromagnetic radiation)

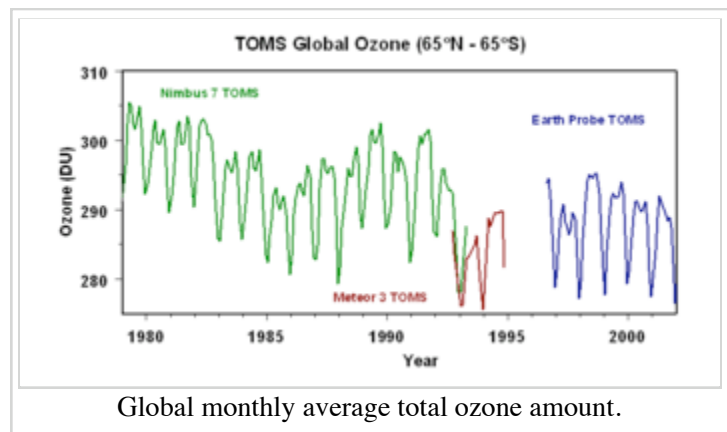


The Cl and Br atoms can then destroy ozone molecules through a variety of catalytic cycles. In the simplest example of such a cycle,^[2] a chlorine atom reacts with an ozone molecule, taking an oxygen atom with it (forming ClO) and leaving a normal oxygen molecule. The chlorine monoxide (i.e., the ClO) can react with a second molecule of ozone (i.e., O₃) to yield another chlorine atom and two molecules of oxygen. The chemical shorthand for these gas-phase reactions is:



The overall effect is a decrease in the amount of ozone. More complicated mechanisms have been discovered that lead to ozone destruction in the lower stratosphere as well.

A single chlorine atom would keep on destroying ozone (thus a catalyst) for up to two years (the time scale for transport back down to the troposphere) were it not for reactions that remove them from this



cycle by forming reservoir species such as hydrogen chloride (HCl) and chlorine nitrate (ClONO₂). On a per atom basis, bromine is even more efficient than chlorine at destroying ozone, but there is much less bromine in the atmosphere at present. As a result, both chlorine and bromine contribute significantly to the overall ozone depletion. Laboratory studies have shown that fluorine and iodine atoms participate in analogous catalytic cycles. However, in the Earth's stratosphere, fluorine atoms react rapidly with water and methane to form strongly-bound HF, while organic molecules which contain iodine react so rapidly in the lower atmosphere that they do not reach the stratosphere in significant quantities. Furthermore, a single chlorine atom is able to react with 100,000 ozone molecules. This fact plus the amount of chlorine released into the atmosphere by chlorofluorocarbons (CFCs) yearly demonstrates how dangerous CFCs are to the environment.^[3]

Quantitative understanding of the chemical ozone loss process

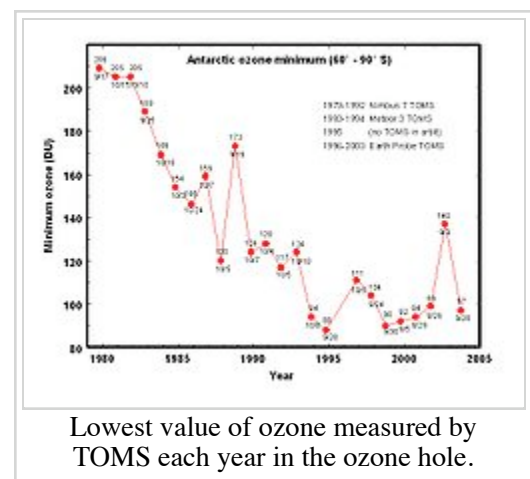
New research on the breakdown of a key molecule in these ozone-depleting chemicals, dichlorine peroxide (Cl₂O₂), calls into question the completeness of present atmospheric models of polar ozone depletion. Specifically, chemists at NASA's Jet Propulsion Laboratory in Pasadena, California, found in 2007 that the temperatures, and the spectrum and intensity of radiation present in the stratosphere created conditions insufficient to allow the rate of chemical-breakdown required to release chlorine radicals in the volume necessary to explain observed rates of ozone depletion. Instead, laboratory tests, designed to be the most accurate reflection of stratospheric conditions to date, showed the decay of the crucial molecule almost a magnitude lower than previously thought.^{[4][5][6]}

Observations on ozone layer depletion

The most pronounced decrease in ozone has been in the lower stratosphere. However, the ozone hole is most usually measured not in terms of ozone concentrations at these levels (which are typically of a few parts per million) but by reduction in the total *column ozone*, above a point on the Earth's surface, which is normally expressed in Dobson units, abbreviated as "DU". Marked decreases in column ozone in the Antarctic spring and early summer compared to the early 1970s and before have been observed using instruments such as the Total Ozone Mapping Spectrometer (TOMS).^[7]

Reductions of up to 70% in the ozone column observed in the austral (southern hemispheric) spring over Antarctica and first reported in 1985 (Farman et al 1985) are continuing.^[8] Through the 1990s, total column ozone in September and October have continued to be 40–50% lower than pre-ozone-hole values. In the Arctic the amount lost is more variable year-to-year than in the Antarctic. The greatest declines, up to 30%, are in the winter and spring, when the stratosphere is colder.

Reactions that take place on polar stratospheric clouds (PSCs) play an important role in enhancing ozone depletion.^[9] PSCs form more readily in the extreme cold of



Lowest value of ozone measured by TOMS each year in the ozone hole.

Antarctic stratosphere. This is why ozone holes first formed, and are deeper, over Antarctica. Early models failed to take PSCs into account and predicted a gradual global depletion, which is why the sudden Antarctic ozone hole was such a surprise to many scientists.

In middle latitudes it is preferable to speak of ozone depletion rather than holes. Declines are about 3% below pre-1980 values for 35–60°N and about 6% for 35–60°S. In the tropics, there are no significant trends.

Ozone depletion also explains much of the observed reduction in stratospheric and upper tropospheric temperatures.^{[10][11]} The source of the warmth of the stratosphere is the absorption of UV radiation by ozone, hence reduced ozone leads to cooling. Some stratospheric cooling is also predicted from increases in greenhouse gases such as CO₂; however the ozone-induced cooling appears to be dominant.

Predictions of ozone levels remain difficult. The World Meteorological Organization Global Ozone Research and Monitoring Project - Report No. 44 (<http://www.esrl.noaa.gov/csd/assessments/1998/preface.html>) comes out strongly in favor for the Montreal Protocol, but notes that a UNEP 1994 Assessment overestimated ozone loss for the 1994–1997 period.

Chemicals in the atmosphere

CFCs in the atmosphere

Chlorofluorocarbons (CFCs) were invented by Thomas Midgley in the 1920s. They were used in air conditioning/cooling units, as aerosol spray propellants prior to the 1980s, and in the cleaning processes of delicate electronic equipment. They also occur as by-products of some chemical processes. No significant natural sources have ever been identified for these compounds — their presence in the atmosphere is due almost entirely to human manufacture. As mentioned in the *ozone cycle overview* above, when such ozone-depleting chemicals reach the stratosphere, they are dissociated by ultraviolet light to release chlorine atoms. The chlorine atoms act as a catalyst, and each can break down tens of thousands of ozone molecules before being removed from the stratosphere. Given the longevity of CFC molecules, recovery times are measured in decades. It is calculated that a CFC molecule takes an average of 15 years to go from the ground level up to the upper atmosphere, and it can stay there for about a century, destroying up to one hundred thousand ozone molecules during that time.^[12]

Verification of observations

Scientists have been increasingly able to attribute the observed ozone depletion to the increase of anthropogenic halogen compounds from CFCs by the use of complex chemistry transport models and their validation against observational data (e.g. SLIMCAT (<http://www.lec.leeds.ac.uk/~martyn/slimcat.html>), CLaMS). These models work by combining satellite measurements of chemical concentrations and meteorological fields with chemical reaction rate constants obtained in lab experiments. They are able to identify not only the key chemical reactions but also the transport processes which bring CFC photolysis products into contact with ozone.

The ozone hole and its causes

The Antarctic ozone hole is an area of the Antarctic stratosphere in which the recent ozone levels have dropped to as low as 33% of their pre-1975 values. The ozone hole occurs during the Antarctic spring, from September to early December, as strong westerly winds start to circulate around the continent and create an atmospheric container. Within this polar vortex, over 50% of the lower stratospheric ozone is destroyed during the Antarctic spring.^[13]

As explained above, the overall cause of ozone depletion is the presence of chlorine-containing source gases (primarily CFCs and related halocarbons). In the presence of UV light, these gases dissociate, releasing chlorine atoms, which then go on to catalyze ozone destruction. The Cl-catalyzed ozone depletion can take place in the gas phase, but it is dramatically enhanced in the presence of polar stratospheric clouds (PSCs).^[14]

These polar stratospheric clouds form during winter, in the extreme cold. Polar winters are dark, consisting of 3 months without solar radiation (sunlight). Not only lack of sunlight contributes to a decrease in temperature but also the polar vortex traps and chills air. Temperatures hover around or below -80 °C. These low temperatures form cloud particles and are composed of either nitric acid (Type I PSC) or ice (Type II PSC). Both types provide surfaces for chemical reactions that lead to ozone destruction.

The photochemical processes involved are complex but well understood. The key observation is that, ordinarily, most of the chlorine in the stratosphere resides in stable "reservoir" compounds, primarily hydrochloric acid (HCl) and chlorine nitrate (ClONO₂). During the Antarctic winter and spring, however, reactions on the surface of the polar stratospheric cloud particles convert these "reservoir" compounds into reactive free radicals (Cl and ClO). The clouds can also remove NO₂ from the atmosphere by converting it to nitric acid, which prevents the newly formed ClO from being converted back into ClONO₂.

The role of sunlight in ozone depletion is the reason why the Antarctic ozone depletion is greatest during spring. During winter, even though PSCs are at their most abundant, there is no light over the pole to drive the chemical reactions. During the spring, however, the sun comes out, providing energy to drive photochemical reactions, and melt the polar stratospheric clouds, releasing the trapped compounds.

Most of the ozone that is destroyed is in the lower stratosphere, in contrast to the much smaller ozone depletion through homogeneous gas phase reactions, which occurs primarily in the upper stratosphere.

Warming temperatures near the end of spring break up the vortex around mid-December. As warm, ozone-rich air flows in from lower latitudes, the PSCs are destroyed, the ozone depletion process shuts down, and the ozone hole heals.

Interest in ozone layer depletion

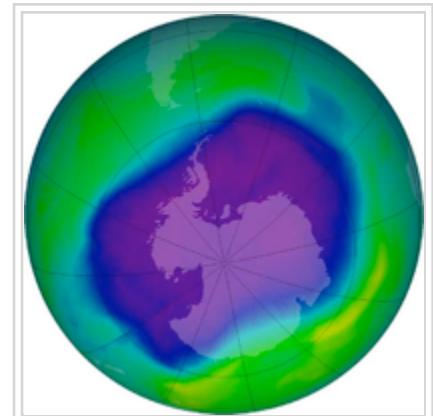


Image of the largest Antarctic ozone hole ever recorded (September 2006).

While the effect of the Antarctic ozone hole in decreasing the global ozone is relatively small, estimated at about 4% per decade, the hole has generated a great deal of interest because:

- The decrease in the ozone layer was predicted in the early 1980s to be roughly 7% over a sixty-year period.
- The sudden recognition in 1985 that there was a substantial "hole" was widely reported in the press. The especially rapid ozone depletion in Antarctica had previously been dismissed as a measurement error.
- Many were worried that ozone holes might start to appear over other areas of the globe but to date the only other large-scale depletion is a smaller ozone "dimple" observed during the Arctic spring over the North Pole. Ozone at middle latitudes has declined, but by a much smaller extent (about 4–5% decrease).
- If the conditions became more severe (cooler stratospheric temperatures, more stratospheric clouds, more active chlorine), then global ozone may decrease at a much greater pace. Standard global warming theory predicts that the stratosphere will cool.^[15]
- When the Antarctic ozone hole breaks up, the ozone-depleted air drifts out into nearby areas. Decreases in the ozone level of up to 10% have been reported in New Zealand in the month following the break-up of the Antarctic ozone hole.

Consequences of ozone layer depletion

Since the ozone layer absorbs UVB ultraviolet light from the Sun, ozone layer depletion is expected to increase surface UVB levels, which could lead to damage, including increases in skin cancer. This was the reason for the Montreal Protocol. Although decreases in stratospheric ozone are well-tied to CFCs and there are good theoretical reasons to believe that decreases in ozone will lead to increases in surface UVB, there is no direct observational evidence linking ozone depletion to higher incidence of skin cancer in human beings. This is partly due to the fact that UVA, which has also been implicated in some forms of skin cancer, is not absorbed by ozone, and it is nearly impossible to control statistics for lifestyle changes in the populace.

Increased UV

Ozone, while a minority constituent in the earth's atmosphere, is responsible for most of the absorption of UVB radiation. The amount of UVB radiation that penetrates through the ozone layer decreases exponentially with the slant-path thickness/density of the layer. Correspondingly, a decrease in atmospheric ozone is expected to give rise to significantly increased levels of UVB near the surface.

Increases in surface UVB due to the ozone hole can be partially inferred by radiative transfer model calculations, but cannot be calculated from direct measurements because of the lack of reliable historical (pre-ozone-hole) surface UV data, although more recent surface UV observation measurement programmes exist (e.g. at Lauder, New Zealand).^[16]

Because it is this same UV radiation that creates ozone in the ozone layer from O₂ (regular oxygen) in the first place, a reduction in stratospheric ozone would actually tend to increase photochemical production of ozone at lower levels (in the troposphere), although the overall observed trends in total

column ozone still show a decrease, largely because ozone produced lower down has a naturally shorter photochemical lifetime, so it is destroyed before the concentrations could reach a level which would compensate for the ozone reduction higher up.

Biological effects of increased UV and microwave radiation from a depleted ozone layer

The main public concern regarding the ozone hole has been the effects of surface UV on human health. So far, ozone depletion in most locations has been typically a few percent and, as noted above, no direct evidence of health damage is available in most latitudes. Were the high levels of depletion seen in the ozone hole ever to be common across the globe, the effects could be substantially more dramatic. As the ozone hole over Antarctica has in some instances grown so large as to reach southern parts of Australia and New Zealand, environmentalists have been concerned that the increase in surface UV could be significant.

Effects of ozone layer depletion on humans

UVB (the higher energy UV radiation absorbed by ozone) is generally accepted to be a contributory factor to skin cancer. In addition, increased surface UV leads to increased tropospheric ozone, which is a health risk to humans. The increased surface UV also represents an increase in the vitamin D synthetic capacity of the sunlight.^[17]

The cancer preventive effects of vitamin D represent a possible beneficial effect of ozone depletion.[8] (http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?db=pubmed&cmd=Retrieve&dopt=AbstractPlus&list_uids=17344960&query_hl=4&itool=pubmed_docsum) [9] (http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?db=pubmed&cmd=Retrieve&dopt=AbstractPlus&list_uids=17143048&query_hl=4&itool=pubmed_DocSum) In terms of health costs, the possible benefits of increased UV irradiance may outweigh the burden. [10] (http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?db=pubmed&cmd=Retrieve&dopt=AbstractPlus&list_uids=16159309&query_hl=8&itool=pubmed_DocSum)

1. Basal and Squamous Cell Carcinomas -- The most common forms of skin cancer in humans, basal and squamous cell carcinomas, have been strongly linked to UVB exposure. The mechanism by which UVB induces these cancers is well understood — absorption of UVB radiation causes the pyrimidine bases in the DNA molecule to form dimers, resulting in transcription errors when the DNA replicates. These cancers are relatively mild and rarely fatal, although the treatment of squamous cell carcinoma sometimes requires extensive reconstructive surgery. By combining epidemiological data with results of animal studies, scientists have estimated that a one percent decrease in stratospheric ozone would increase the incidence of these cancers by 2%.^[18]

2. Malignant Melanoma -- Another form of skin cancer, malignant melanoma, is much less common but far more dangerous, being lethal in about 15% - 20% of the cases diagnosed. The relationship between malignant melanoma and ultraviolet exposure is not yet well understood, but it appears that both UVB and UVA are involved. Experiments on fish suggest that 90 to 95% of malignant melanomas may be due to UVA and visible radiation^[19] whereas experiments on opossums suggest a larger role for UVB.^[18] Because of this uncertainty, it is difficult to estimate the impact of ozone depletion on

melanoma incidence. One study showed that a 10% increase in UVB radiation was associated with a 19% increase in melanomas for men and 16% for women.^[20] A study of people in Punta Arenas, at the southern tip of Chile, showed a 56% increase in melanoma and a 46% increase in nonmelanoma skin cancer over a period of seven years, along with decreased ozone and increased UVB levels.^[21]

3. Cortical Cataracts -- Studies are suggestive of an association between ocular cortical cataracts and UV-B exposure, using crude approximations of exposure and various cataract assessment techniques. A detailed assessment of ocular exposure to UV-B was carried out in a study on Chesapeake Bay Watermen, where increases in average annual ocular exposure were associated with increasing risk of cortical opacity^[22]. In this highly exposed group of predominantly white males, the evidence linking cortical opacities to sunlight exposure was the strongest to date. However, subsequent data from a population-based study in Beaver Dam, WI suggested the risk may be confined to men. In the Beaver Dam study, the exposures among women were lower than exposures among men, and no association was seen.^[23] Moreover, there were no data linking sunlight exposure to risk of cataract in African Americans, although other eye diseases have different prevalences among the different racial groups, and cortical opacity appears to be higher in African Americans compared with whites.^{[24][25]}

4. Increased Tropospheric Ozone -- Increased surface UV leads to increased tropospheric ozone. Ground-level ozone is generally recognized to be a health risk, as ozone is toxic due to its strong oxidant properties. At this time, ozone at ground level is produced mainly by the action of UV radiation on combustion gases from vehicle exhausts.

Effects on crops

An increase of UV radiation would be expected to affect crops. A number of economically important species of plants, such as rice, depend on cyanobacteria residing on their roots for the retention of nitrogen. Cyanobacteria are sensitive to UV light and they would be affected by its increase.^[26]

Effects on plankton

Research has shown a widespread extinction of plankton 2 million years ago that coincided with a nearby supernova. There is a difference in the orientation and motility of planktons when excess of UV rays reach earth. Researchers speculate that the extinction was caused by a significant weakening of the ozone layer at that time when the radiation from the supernova produced nitrogen oxides that catalyzed the destruction of ozone (plankton are particularly susceptible to effects of UV light, and are vitally important to marine food webs).^[27]

Public policy in response to the ozone hole

The full extent of the damage that CFCs have caused to the ozone layer is not known and will not be known for decades; however, marked decreases in column ozone have already been observed (as explained above).

After a 1976 report by the U.S. National Academy of Sciences concluded that credible scientific

evidence supported the ozone depletion hypothesis, a few countries, including the United States, Canada, Sweden, and Norway, moved to eliminate the use of CFCs in aerosol spray cans. At the time this was widely regarded as a first step towards a more comprehensive regulation policy, but progress in this direction slowed in subsequent years, due to a combination of political factors (continued resistance from the halocarbon industry and a general change in attitude towards environmental regulation during the first two years of the Reagan administration) and scientific developments (subsequent National Academy assessments which indicated that the first estimates of the magnitude of ozone depletion had been overly large). The European Community rejected proposals to ban CFCs in aerosol sprays while even in the U.S., CFCs continued to be used as refrigerants and for cleaning circuit boards. Worldwide CFC production fell sharply after the U.S. aerosol ban, but by 1986 had returned nearly to its 1976 level. In 1980, DuPont closed down its research program into halocarbon alternatives.

The US Government's attitude began to change again in 1983, when William Ruckelshaus replaced Anne M. Burford as Administrator of the United States Environmental Protection Agency. Under Ruckelshaus and his successor, Lee Thomas, the EPA pushed for an international approach to halocarbon regulations. In 1985 20 nations, including most of the major CFC producers, signed the Vienna Convention which established a framework for negotiating international regulations on ozone-depleting substances. That same year, the discovery of the Antarctic ozone hole was announced, causing a revival in public attention to the issue. In 1987, representatives from 43 nations signed the Montreal Protocol. Meanwhile, the halocarbon industry shifted its position and started supporting a protocol to limit CFC production. The reasons for this were in part explained by "Dr. Mostafa Tolba, former head of the UN Environment Programme, who was quoted in the June 30, 1990 edition of *The New Scientist*, '...the chemical industry supported the Montreal Protocol in 1987 because it set up a worldwide schedule for phasing out CFCs, which [were] no longer protected by patents. This provided companies with an equal opportunity to market new, more profitable compounds.'"^[28]

At Montreal, the participants agreed to freeze production of CFCs at 1986 levels and to reduce production by 50% by 1999. After a series of scientific expeditions to the Antarctic produced convincing evidence that the ozone hole was indeed caused by chlorine and bromine from manmade organohalogens, the Montreal Protocol was strengthened at a 1990 meeting in London. The participants agreed to phase out CFCs and halons entirely (aside from a very small amount marked for certain "essential" uses, such as asthma inhalers) by 2000. At a 1992 meeting in Copenhagen, the phase out date was moved up to 1996.

To some extent, CFCs have been replaced by the less damaging hydro-chloro-fluoro-carbons (HCFCs), although concerns remain regarding HCFCs also. In some applications, hydro-fluoro-carbons (HFCs) have been used to replace CFCs. HFCs, which contain no chlorine or bromine, do not contribute at all to ozone depletion although they are potent greenhouse gases. The best known of these compounds is probably HFC-134a (R-134a), which in the United States has largely replaced CFC-12 (R-12) in automobile air conditioners. In laboratory analytics (a former "essential" use) the ozone depleting substances can be replaced with various other solvents.^[29]

Ozone Diplomacy, by Richard Benedick (Harvard University Press, 1991) gives a detailed account of the negotiation process that led to the Montreal Protocol. Pielke and Betsill (http://sciencepolicy.colorado.edu/admin/publication_files/1997.11.pdf) provide an extensive review of early US government responses to the emerging science of ozone depletion by CFCs.

Current events and future prospects of ozone depletion

Since the adoption and strengthening of the Montreal Protocol has led to reductions in the emissions of CFCs, atmospheric concentrations of the most significant compounds have been declining. These substances are being gradually removed from the atmosphere. By 2015, the Antarctic ozone hole would have reduced by only 1 million km² out of 25 (Newman *et al.*, 2004); complete recovery of the Antarctic ozone layer will not occur until the year 2050 or later. Work has suggested that a detectable (and statistically significant) recovery will not occur until around 2024, with ozone levels recovering to 1980 levels by around 2068.^[30]

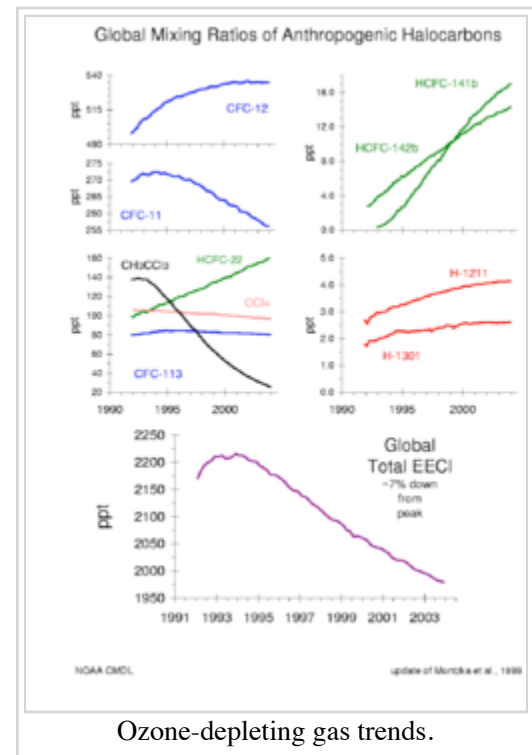
The decrease in ozone-depleting chemicals has also been significantly affected by a decrease in bromine-containing chemicals. The data suggest that substantial natural sources exist for atmospheric methyl bromide (CH₃Br).^[31]

The 2004 ozone hole ended in November 2004, daily minimum stratospheric temperatures in the Antarctic lower stratosphere increased to levels that are too warm for the formation of polar stratospheric clouds (PSCs) about 2 to 3 weeks earlier than in most recent years.^[32]

The Arctic winter of 2005 was extremely cold in the stratosphere; PSCs were abundant over many high-latitude areas until dissipated by a big warming event, which started in the upper stratosphere during February and spread throughout the Arctic stratosphere in March. The size of the Arctic area of anomalously low total ozone in 2004-2005 was larger than in any year since 1997. The predominance of anomalously low total ozone values in the Arctic region in the winter of 2004-2005 is attributed to the very low stratospheric temperatures and meteorological conditions favorable for ozone destruction along with the continued presence of ozone destroying chemicals in the stratosphere.^[33]

A 2005 IPCC summary of ozone issues observed that observations and model calculations suggest that the global average amount of ozone depletion has now approximately stabilized. Although considerable variability in ozone is expected from year to year, including in polar regions where depletion is largest, the ozone layer is expected to begin to recover in coming decades due to declining ozone-depleting substance concentrations, assuming full compliance with the Montreal Protocol.^[34]

Temperatures during the Arctic winter of 2006 stayed fairly close to the long-term average until late January, with minimum readings frequently cold enough to produce PSCs. During the last week of January, however, a major warming event sent temperatures well above normal — much too warm to support PSCs. By the time temperatures dropped back to near normal in March, the seasonal norm was well above the PSC threshold.^[35] Preliminary satellite instrument-generated ozone maps show seasonal ozone buildup slightly below the long-term means for the Northern Hemisphere as a whole, although



some high ozone events have occurred.^[36] During March 2006, the Arctic stratosphere poleward of 60 degrees North Latitude was free of anomalously low ozone areas except during the three-day period from March 17 to 19 when the total ozone cover fell below 300 DU over part of the North Atlantic region from Greenland to Scandinavia.^[37]

The area where total column ozone is less than 220 DU (the accepted definition of the boundary of the ozone hole) was relatively small until around 20 August 2006. Since then the ozone hole area increased rapidly, peaking at 29 million km² September 24. In October 2006, NASA reported that the year's ozone hole set a new area record with a daily average of 26 million km² between 7 September and 13 October 2006; total ozone thicknesses fell as low as 85 DU on October 8. The two factors combined, 2006 sees the worst level of depletion in recorded ozone history. The depletion is attributed to the temperatures above the Antarctic reaching the lowest recording since comprehensive records began in 1979.^{[38][39]}

The Antarctic ozone hole is expected to continue for decades. Ozone concentrations in the lower stratosphere over Antarctica will increase by 5%–10% by 2020 and return to pre-1980 levels by about 2060–2075, 10–25 years later than predicted in earlier assessments. This is because of revised estimates of atmospheric concentrations of Ozone Depleting Substances — and a larger predicted future usage in developing countries. Another factor which may aggravate ozone depletion is the draw-down of nitrogen oxides from above the stratosphere due to changing wind patterns.^[40]

History of the research

The basic physical and chemical processes that lead to the formation of an ozone layer in the earth's stratosphere were discovered by Sydney Chapman in 1930. These are discussed in the article Ozone-oxygen cycle — briefly, short-wavelength UV radiation splits an oxygen (O₂) molecule into two oxygen (O) atoms, which then combine with other oxygen molecules to form ozone. Ozone is removed when an oxygen atom and an ozone molecule "recombine" to form two oxygen molecules, i.e. $O + O_3 \rightarrow 2O_2$. In the 1950s, David Bates and Marcel Nicolet presented evidence that various free radicals, in particular hydroxyl (OH) and nitric oxide (NO), could catalyze this recombination reaction, reducing the overall amount of ozone. These free radicals were known to be present in the stratosphere, and so were regarded as part of the natural balance – it was estimated that in their absence, the ozone layer would be about twice as thick as it currently is.

In 1970 Prof. Paul Crutzen pointed out that emissions of *nitrous* oxide (N₂O), a stable, long-lived gas produced by soil bacteria, from the earth's surface could affect the amount of *nitric* oxide (NO) in the stratosphere. Crutzen showed that nitrous oxide lives long enough to reach the stratosphere, where it is converted into NO. Crutzen then noted that increasing use of fertilizers might have led to an increase in nitrous oxide emissions over the natural background, which would in turn result in an increase in the amount of NO in the stratosphere. Thus human activity could have an impact on the stratospheric ozone layer. In the following year, Crutzen and (independently) Harold Johnston suggested that NO emissions from supersonic aircraft, which fly in the lower stratosphere, could also deplete the ozone layer.

The Rowland-Molina hypothesis

In 1974 Frank Sherwood Rowland, Chemistry Professor at the University of California at Irvine, and his postdoctoral associate Mario J. Molina suggested that long-lived organic halogen compounds, such as CFCs, might behave in a similar fashion as Crutzen had proposed for nitrous oxide. James Lovelock (most popularly known as the creator of the Gaia hypothesis) had recently discovered, during a cruise in the South Atlantic in 1971, that almost all of the CFC compounds manufactured since their invention in 1930 were still present in the atmosphere. Molina and Rowland concluded that, like N_2O , the CFCs would reach the stratosphere where they would be dissociated by UV light, releasing Cl atoms. (A year earlier, Richard Stolarski and Ralph Cicerone at the University of Michigan had shown that Cl is even more efficient than NO at catalyzing the destruction of ozone. Similar conclusions were reached by Michael McElroy and Steven Wofsy at Harvard University. Neither group, however, had realized that CFC's were a potentially large source of stratospheric chlorine — instead, they had been investigating the possible effects of HCl emissions from the Space Shuttle, which are very much smaller.)

The Rowland-Molina hypothesis was strongly disputed by representatives of the aerosol and halocarbon industries. The Chair of the Board of DuPont was quoted as saying that ozone depletion theory is "a science fiction tale...a load of rubbish...utter nonsense".^[28] Robert Abplanalp, the President of Precision Valve Corporation (and inventor of the first practical aerosol spray can valve), wrote to the Chancellor of UC Irvine to complain about Rowland's public statements (Roan, p 56.) Nevertheless, within three years most of the basic assumptions made by Rowland and Molina were confirmed by laboratory measurements and by direct observation in the stratosphere. The concentrations of the source gases (CFCs and related compounds) and the chlorine reservoir species (HCl and $ClONO_2$) were measured throughout the stratosphere, and demonstrated that CFCs were indeed the major source of stratospheric chlorine, and that nearly all of the CFCs emitted would eventually reach the stratosphere. Even more convincing was the measurement, by James G. Anderson and collaborators, of chlorine monoxide (ClO) in the stratosphere. ClO is produced by the reaction of Cl with ozone — its observation thus demonstrated that Cl radicals not only were present in the stratosphere but also were actually involved in destroying ozone. McElroy and Wofsy extended the work of Rowland and Molina by showing that bromine atoms were even more effective catalysts for ozone loss than chlorine atoms and argued that the brominated organic compounds known as halons, widely used in fire extinguishers, were a potentially large source of stratospheric bromine. In 1976 the U.S. National Academy of Sciences released a report which concluded that the ozone depletion hypothesis was strongly supported by the scientific evidence. Scientists calculated that if CFC production continued to increase at the going rate of 10% per year until 1990 and then remain steady, CFCs would cause a global ozone loss of 5 to 7% by 1995, and a 30 to 50% loss by 2050. In response the United States, Canada, Sweden and Norway banned the use of CFCs in aerosol spray cans in 1978. However, subsequent research, summarized by the National Academy in reports issued between 1979 and 1984, appeared to show that the earlier estimates of global ozone loss had been too large.

Crutzen, Molina, and Rowland were awarded the 1995 Nobel Prize in Chemistry for their work on stratospheric ozone.

The ozone hole

The discovery of the Antarctic "ozone hole" by British Antarctic Survey scientists Farman, Gardiner and Shanklin (announced in a paper in *Nature* in May 1985) came as a shock to the scientific community,

because the observed decline in polar ozone was far larger than anyone had anticipated. Satellite measurements showing massive depletion of ozone around the south pole were becoming available at the same time. However, these were initially rejected as unreasonable by data quality control algorithms (they were filtered out as errors since the values were unexpectedly low); the ozone hole was detected only in satellite data when the raw data was reprocessed following evidence of ozone depletion in *in situ* observations. When the software was rerun without the flags, the ozone hole was seen as far back as 1976.^[41]

Susan Solomon, an atmospheric chemist at the National Oceanic and Atmospheric Administration (NOAA), proposed that chemical reactions on polar stratospheric clouds (PSCs) in the cold Antarctic stratosphere caused a massive, though localized and seasonal, increase in the amount of chlorine present in active, ozone-destroying forms. The polar stratospheric clouds in Antarctica are only formed when there are very low temperatures, as low as -80 degrees C, and early spring conditions. In such conditions the ice crystals of the cloud provide a suitable surface for conversion of unreactive chlorine compounds into reactive chlorine compounds which can deplete ozone easily.

Moreover the polar vortex formed over Antarctica is very tight and the reaction which occurs on the surface of the cloud crystals is far different from when it occurs in atmosphere. These conditions have led to ozone hole formation in Antarctica. This hypothesis was decisively confirmed, first by laboratory measurements and subsequently by direct measurements, from the ground and from high-altitude airplanes, of very high concentrations of chlorine monoxide (ClO) in the Antarctic stratosphere.

Alternative hypotheses, which had attributed the ozone hole to variations in solar UV radiation or to changes in atmospheric circulation patterns, were also tested and shown to be untenable.

Meanwhile, analysis of ozone measurements from the worldwide network of ground-based Dobson spectrophotometers led an international panel to conclude that the ozone layer was in fact being depleted, at all latitudes outside of the tropics. These trends were confirmed by satellite measurements. As a consequence, the major halocarbon producing nations agreed to phase out production of CFCs, halons, and related compounds, a process that was completed in 1996.

Since 1981 the United Nations Environment Programme has sponsored a series of reports on scientific assessment of ozone depletion. The most recent is from 2007 where satellite measurements have shown the hole in the ozone layer is recovering and is now the smallest it has been for about a decade^[11] (<http://abc.net.au/news/stories/2007/11/16/2092527.htm>).

Controversy regarding ozone science and policy

That ozone depletion takes place is not seriously disputed in the scientific community.^[42] There is a consensus among atmospheric physicists and chemists that the scientific understanding has now reached a level where countermeasures to control CFC emissions are justified, although the decision is ultimately one for policy-makers.

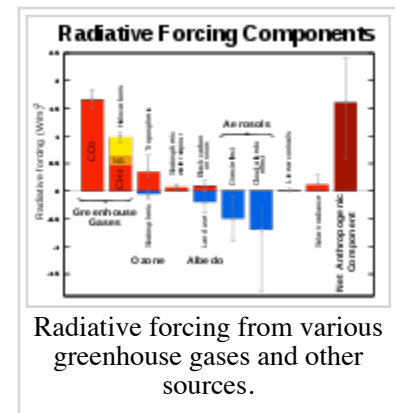
Despite this consensus, the science behind ozone depletion remains complex, and some who oppose the enforcement of countermeasures point to some of the uncertainties. For example, although increased UVB has been shown to constitute a melanoma risk, it has been difficult for statistical studies to

establish a direct link between ozone depletion and increased rates of melanoma. Although melanomas did increase significantly during the period 1970–1990, it is difficult to separate reliably the effect of ozone depletion from the effect of changes in lifestyle factors (e.g., increasing rates of air travel).

Ozone depletion and global warming

Although they are often interlinked in the mass media, the connection between global warming and ozone depletion is not strong. There are five areas of linkage:

- The same CO₂ radiative forcing that produces near-surface global warming is expected to cool the stratosphere.^[43] This cooling, in turn, is expected to produce a relative *increase* in polar ozone (O₃) depletion and the frequency of ozone holes.
- Conversely, ozone depletion represents a radiative forcing of the climate system. There are two opposing effects: Reduced ozone causes the stratosphere to absorb less solar radiation, thus cooling the stratosphere while warming the troposphere; the resulting colder stratosphere emits less long-wave radiation downward, thus cooling the troposphere. Overall, the cooling dominates; the IPCC concludes that "*observed stratospheric O₃ losses over the past two decades have caused a negative forcing of the surface-troposphere system*"^[44] of about -0.15 ± 0.10 watts per square meter (W/m²).^[45]
- One of the strongest predictions of the greenhouse effect is that the stratosphere will cool.^[43] Although this cooling has been observed, it is not trivial to separate the effects of changes in the concentration of greenhouse gases and ozone depletion since both will lead to cooling. However, this can be done by numerical stratospheric modeling. Results from the National Oceanic and Atmospheric Administration's Geophysical Fluid Dynamics Laboratory show that above 20 km (12.4 miles), the greenhouse gases dominate the cooling.^[46]
- Ozone depleting chemicals are also greenhouse gases. The increases in concentrations of these chemicals have produced 0.34 ± 0.03 W/m² of radiative forcing, corresponding to about 14% of the total radiative forcing from increases in the concentrations of well-mixed greenhouse gases.^[45]
- The long term modeling of the process, its measurement, study, design of theories and testing take decades to both document, gain wide acceptance, and ultimately become the dominant paradigm. Several theories about the destruction of ozone, were hypothesized in the 1980s, published in the late 1990s, and are currently being proven. Dr Drew Schindell, and Dr Paul Newman, NASA Goddard, proposed a theory in the late 1990s, using a SGI Origin 2000 supercomputer, that modeled ozone destruction, accounted for 78% of the ozone destroyed. Further refinement of that model, accounted for 89% of the ozone destroyed, but pushed back the estimated recovery of the ozone hole from 75 years to 150 years. (An important part of that model is the lack of stratospheric flight due to depletion of fossil fuels.)



Misconceptions about ozone depletion

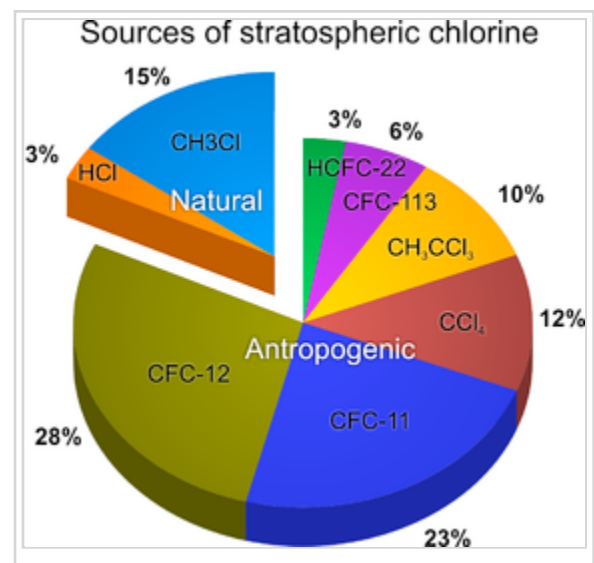
A few of the more common misunderstandings about ozone depletion are addressed briefly here; more detailed discussions can be found in the ozone-depletion FAQ (<http://www.faqs.org/faqs/ozone-depletion>) .

CFCs are "too heavy" to reach the stratosphere

It is sometimes stated that since CFC molecules are much heavier than nitrogen or oxygen, they cannot reach the stratosphere in significant quantities.^[47] But atmospheric gases are not sorted by weight; the forces of wind (turbulence) are strong enough to fully intermix gases in the atmosphere. CFCs are heavier than air, but just like argon, krypton and other heavy gases with a long lifetime, they are uniformly distributed throughout the turbosphere and reach the upper atmosphere.^[48]

Man-made chlorine is insignificant compared to natural sources

Another objection occasionally voiced is that *It is generally agreed that natural sources of tropospheric chlorine (volcanoes, ocean spray, etc.) are four to five orders of magnitude larger than man-made sources.* While strictly true, *tropospheric* chlorine is irrelevant; it is *stratospheric* chlorine that affects ozone depletion. Chlorine from ocean spray is soluble and thus is washed out by rainfall before it reaches the stratosphere. CFCs, in contrast, are insoluble and long-lived, which allows them to reach the stratosphere. Even in the lower atmosphere there is more chlorine present in the form of CFCs and related haloalkanes than there is in HCl from salt spray, and in the stratosphere halocarbons dominate overwhelmingly.^[49] Only one of these halocarbons, methyl chloride, has a predominantly natural source, and it is responsible for about 20 percent of the chlorine in the stratosphere; the remaining 80% comes from manmade compounds.



Very large volcanic eruptions can inject HCl directly into the stratosphere, but direct measurements^[50] have shown that their contribution is small compared to that of chlorine from CFCs. A similar erroneous assertion is that soluble halogen compounds from the volcanic plume of Mount Erebus on Ross Island, Antarctica are a major contributor to the Antarctic ozone hole.

An ozone hole was first observed in 1956

G.M.B. Dobson (Exploring the Atmosphere, 2nd Edition, Oxford, 1968) mentioned that when springtime ozone levels over Halley Bay were first measured, he was surprised to find that they were ~320 DU, about 150 DU below spring levels, ~450 DU, in the Arctic. These, however, were the pre-ozone hole normal climatological values. What Dobson describes is essentially the *baseline* from which the ozone hole is measured: actual ozone hole values are in the 150–100 DU range.

The discrepancy between the Arctic and Antarctic noted by Dobson was primarily a matter of timing: during the Arctic spring ozone levels rose smoothly, peaking in April, whereas in the Antarctic they stayed approximately constant during early spring, rising abruptly in November when the polar vortex broke down.

The behavior seen in the Antarctic ozone hole is completely different. Instead of staying constant, early springtime ozone levels suddenly drop from their already low winter values, by as much as 50%, and normal values are not reached again until December.^[51]

If the theory were correct, the ozone hole should be above the sources of CFCs

CFCs are well mixed in the troposphere and the stratosphere. The reason the ozone hole occurs above Antarctica is not because there are more CFCs there but because the low temperatures allow polar stratospheric clouds to form.^[52] There have been anomalous discoveries of significant, serious, localized "holes" above other parts of the globe.^[42]

The "ozone hole" is a hole in the ozone layer

When the "ozone hole" forms, essentially all of the ozone in the lower stratosphere is destroyed. The upper stratosphere is much less affected, however, so that the overall amount of ozone over the continent declines by 50 percent or more. The ozone hole does not go all the way through the layer; on the other hand, it is not a uniform 'thinning' of the layer either. It's a "hole" in the sense of "a hole in the ground", a depression, not in the sense of "a hole in the windshield."

World Ozone Day

In 1994, the United Nations General Assembly voted to designate September 16 as "World Ozone Day", to commemorate the signing of the Montreal Protocol on that date in 1987.

See also

- Ozone-oxygen cycle
- Montreal Protocol
- "Scientific Assessment of Ozone Depletion", a series of technical reports compiled under the auspices of the World Meteorological Organization and the United Nations Environmental Program.
- CFCs
- Melanoma, skin cancer
- Greenhouse gas
- Ultraviolet
- CLaMS Chemical Lagrangian Model of the Stratosphere
- Global Warming, ice shelves
- Atmospheric window

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