

COMMON QUESTIONS ABOUT OZONE

Ozone is exceedingly rare in our atmosphere, averaging about 3 molecules of ozone for every ten million air molecules. Nonetheless, atmospheric ozone plays vital roles that belie its small numbers. This Appendix to the *World Meteorological Organization/United Nations Environment Programme (WMO/UNEP) Scientific Assessment of Ozone Depletion: 1994* answers some of the questions that are most commonly asked about ozone and the changes that have been occurring in recent years. These common questions and their answers were discussed by the 80 scientists from 26 countries who participated in the Panel Review Meeting of the *Scientific Assessment of Ozone Depletion: 1994*. Therefore, this information is presented by a large group of experts from the international scientific community.

Ozone is mainly found in two regions of the Earth's atmosphere. Most ozone (about 90%) resides in a layer between approximately 10 and 50 kilometers (about 6 to 30 miles) above the Earth's surface, in the region of the atmosphere called the stratosphere. This stratospheric ozone is commonly known as the "ozone layer." The remaining ozone is in the lower region of the atmosphere, the troposphere, which extends from the Earth's surface up to about 10 kilometers. The figure below shows this distribution of ozone in the atmosphere.

While the ozone in these two regions is chemically identical (both consist of three oxygen atoms and have the chemical formula "O₃"), the ozone molecules have very different effects on humans and other living things depending upon their location.

Stratospheric ozone plays a beneficial role by absorbing most of the biologically damaging ultraviolet sunlight called UV-B, allowing only a small amount to reach the Earth's surface. The absorption of UV radiation by ozone creates a source of heat, which actually forms the stratosphere itself (a region in which the temperature rises as one goes to higher altitudes). Ozone thus plays a key role in the temperature structure of the Earth's atmosphere. Furthermore, without the filtering action of the ozone layer, more of the Sun's UV-B radiation would penetrate the atmosphere and would reach the Earth's surface in greater amounts. Many experimental studies of plants and animals, and clinical studies of humans, have shown the harmful effects of excessive exposure to UV-B radiation (these are discussed in the WMO/UNEP reports on impacts of ozone depletion, which are com-

panion documents to the WMO/UNEP scientific assessments of ozone depletion).

At the planet's surface, ozone comes into direct contact with life-forms and displays its destructive side. Because ozone reacts strongly with other molecules, high levels are toxic to living systems and can severely damage the tissues of plants and animals. Many studies have documented the harmful effects of ozone on crop production, forest growth, and human health. The substantial negative effects of surface-level tropospheric ozone from this direct toxicity contrast with the benefits of the additional filtering of UV-B radiation that it provides.

With these dual aspects of ozone come two separate environmental issues, controlled by different forces in the atmosphere. In the troposphere, there is concern about *increases* in ozone. Low-lying ozone is a key component of smog, a familiar problem in the atmosphere of many cities around the world. Higher than usual amounts of surface-level ozone are now increasingly being observed in rural areas as well. However, the ground-level ozone concentrations in the smoggiest cities are very much smaller than the concentrations routinely found in the stratosphere.

There is widespread scientific and public interest and concern about *losses* of stratospheric ozone. Ground-based and satellite instruments have measured decreases in the amount of stratospheric ozone in our atmosphere. Over some parts of Antarctica, up to 60% of the total overhead amount of ozone (known as the "column ozone") is depleted during September and October. This phenomenon has come to be known as the Antarctic "ozone hole." Smaller, but still significant, stratospheric decreases have been seen at other, more-populated regions of the Earth. Increases in surface UV-B radiation have been observed in association with decreases in stratospheric ozone.

The scientific evidence, accumulated over more than two decades of study by the international research community, has shown that human-made chemicals are responsible for the observed depletions of the ozone layer over Antarctica and likely play a major role in global ozone losses. The ozone-depleting compounds contain various combinations of the chemical elements chlorine, fluorine, bromine, carbon, and hydrogen, and are often described by the general term *halocarbons*. The com-

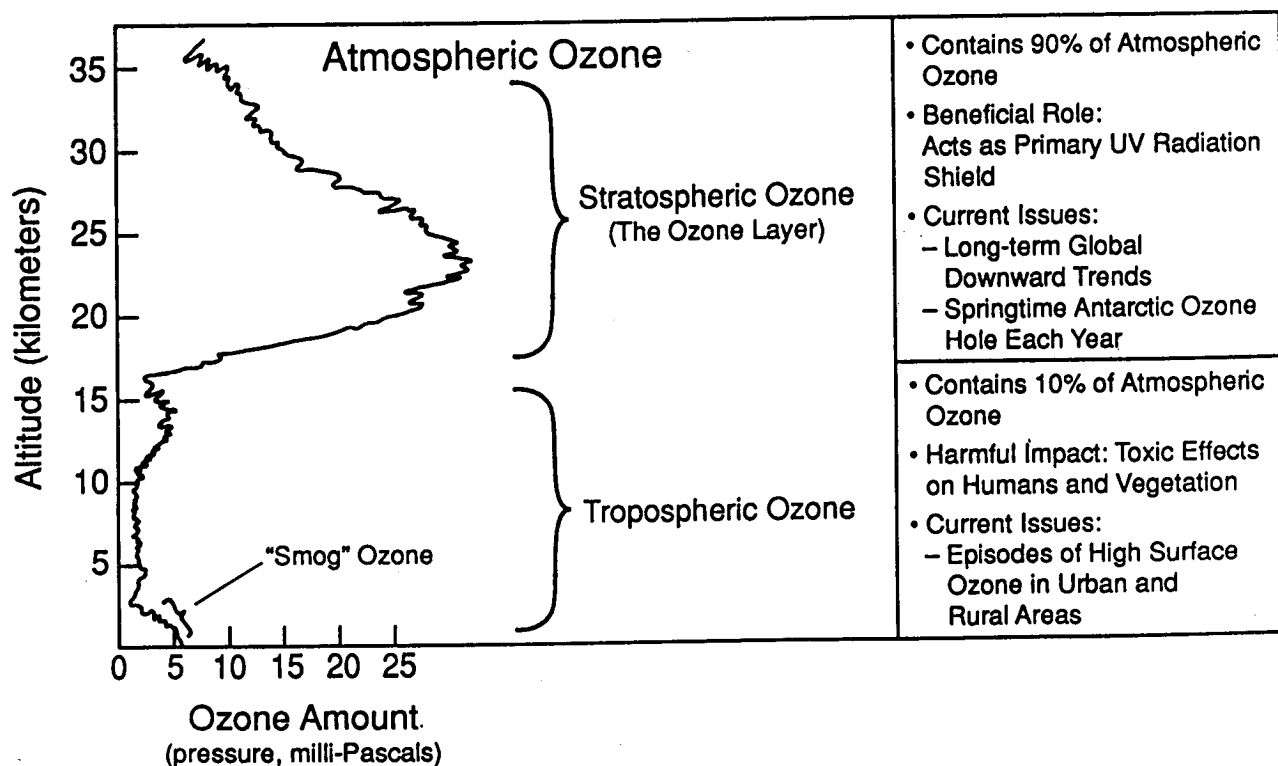
COMMON QUESTIONS

pounds that contain only carbon, chlorine, and fluorine are called *chlorofluorocarbons*, usually abbreviated as *CFCs*. CFCs, carbon tetrachloride, and methyl chloroform are important human-made ozone-depleting gases that have been used in many applications including refrigeration, air conditioning, foam blowing, cleaning of electronics components, and as solvents. Another important group of human-made halocarbons is the *halons*, which contain carbon, bromine, fluorine, and (in some cases) chlorine, and have been mainly used as fire extinguishants. Governments have decided to discontinue production of CFCs, halons, carbon tetrachloride, and methyl chloroform, and industry has developed more "ozone-friendly" substitutes.

Two responses are natural when a new problem has been identified: cure and prevention. When the problem is the destruction of the stratospheric ozone layer, the corresponding questions are: Can we repair the damage already done? How can we prevent further destruction? Remedies have been investigated that could (i) remove CFCs selectively from our atmosphere, (ii) intercept ozone-depleting chlorine before much depletion has taken place, or (iii) replace the ozone lost in the stratosphere (perhaps by shipping the ozone from cities that have too

much smog or by making new ozone). Because ozone reacts strongly with other molecules, as noted above, it is too unstable to be made elsewhere (e.g., in the smog of cities) and transported to the stratosphere. When the huge volume of the Earth's atmosphere and the magnitude of global stratospheric ozone depletion are carefully considered, approaches to cures quickly become much too expensive, impractical, and potentially damaging to the global environment. Prevention involves the internationally agreed-upon Montreal Protocol and its Amendments and Adjustments, which call for elimination of the production and use of the CFCs and other ozone-damaging compounds within the next few years. As a result, the ozone layer is expected to recover over the next fifty years or so as the atmospheric concentrations of CFCs and other ozone-depleting compounds slowly decay.

The current understanding of ozone depletion and its relation to humankind is discussed in detail by the leading scientists in the world's ozone research community in the *Scientific Assessment of Ozone Depletion: 1994*. The answers to the common questions posed below are based upon that understanding and on the information given in earlier WMO/UNEP reports.



Is the Depletion of the Ozone Layer Leading to an Increase in Ground-Level Ultraviolet Radiation?

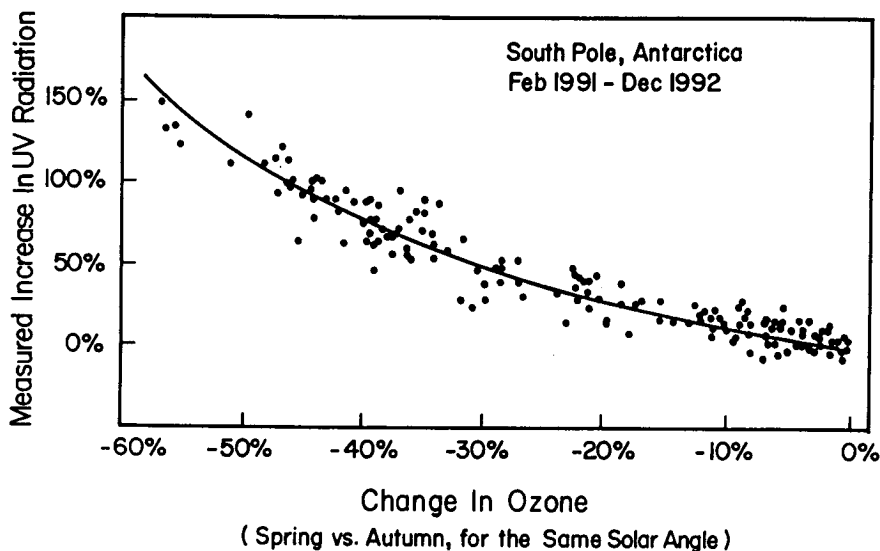
The Sun emits light over a wide range of energies, with about two percent given off in the form of high-energy, ultraviolet (UV) radiation. Some of this UV radiation (UV-B) is especially effective in causing damage to living things, including sunburn, skin cancer, and eye damage for humans. The amount of solar UV radiation received at any particular location on the Earth's surface depends upon the position of the Sun above the horizon, on the amount of ozone in the atmosphere, and upon local cloudiness and pollution. Scientists agree that in the absence of changes in clouds or pollution, decreases in atmospheric ozone will increase ground-level UV radiation.

The largest decreases in ozone during the last decade have been observed over Antarctica, especially during each September and October when the "ozone hole" forms. During the last several years, simultaneous measurements of UV radiation and total ozone have been made at several Antarctic stations. As shown in the figure below, when the ozone amounts decrease, UV-B increases. Because of the ozone hole, the UV-B intensity at Palmer Station, Antarctica, in late October, 1993, was

more intense than found at San Diego, California, at any time during all of 1993.

In areas where small ozone depletion has been observed, UV-B increases are more difficult to detect. Detection of UV trends associated with ozone decreases can also be complicated by changes in cloudiness or by local pollution, as well as by difficulties in keeping the detection instrument in precisely the same condition over many years. Prior to the late 1980s, instruments with the necessary accuracy and stability for measurement of small long-term trends in ground-level UV-B were not employed. Recently, however, such instruments have been used in the Antarctic because of the very large changes in ozone being observed there. When high-quality measurements have been made in other areas far from major cities and their associated air pollution, decreases in ozone have regularly been accompanied by increases in UV-B. The data from urban locations with older, less specialized instruments provide much less reliable information, especially because good simultaneous measurements are not available for any changes in cloudiness or local pollution.

Increases in Erythemal (Sunburning) UV Radiation Due to Ozone Reductions



How Severe Is the Ozone Depletion Now, and Is It Expected to Get Worse?

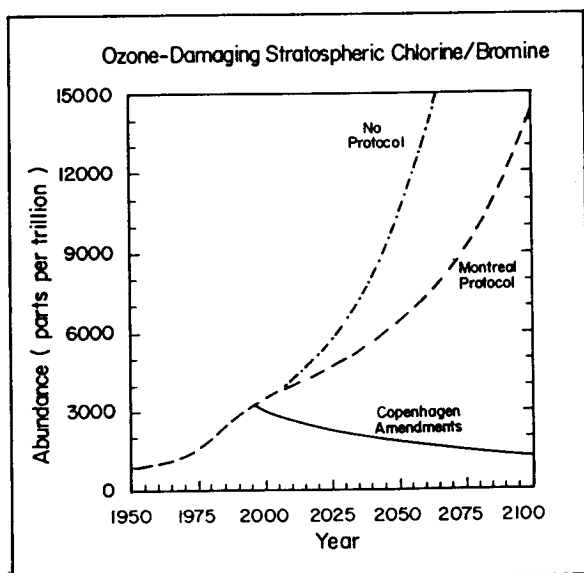
Scientific evidence shows that ozone depletion caused by human-made chemicals is continuing and is expected to persist until chlorine and bromine levels are reduced. Worldwide monitoring has shown that stratospheric ozone has been decreasing for the past two decades or more. Globally averaged losses have totaled about 5% since the mid-1960s, with cumulative losses of about 10% in the winter and spring and 5% in the summer and autumn over locations such as Europe, North America, and Australia. Since the late-1970s, an ozone "hole" has formed in Antarctica each Southern Hemisphere spring (September / October), in which up to 60% of the total ozone is depleted. The large increase in atmospheric concentrations of human-made chlorine and bromine compounds is responsible for the formation of the Antarctic ozone hole, and the weight of evidence indicates that it also plays a major role in midlatitude ozone depletion.

During 1992 and 1993 ozone in many locations dropped to record low values: springtime depletions exceeded 20% in some populated northern midlatitude regions, and the levels in the Antarctic ozone hole fell to the lowest values ever recorded. The unusually large ozone decreases of 1992 and 1993 are believed to be related, in part, to the volcanic eruption of Mount Pinatubo in the Philippines during 1991. This eruption produced large

amounts of stratospheric sulfate aerosols that temporarily increased the ozone depletion caused by human-made chlorine and bromine compounds. Recent observations have shown that as those aerosols have been swept out of the stratosphere, ozone concentrations have returned to the depleted levels consistent with the downward trend observed before the Mount Pinatubo eruption.

In 1987 the recognition of the potential for chlorine and bromine to destroy stratospheric ozone led to an international agreement (The United Nations Montreal Protocol on Substances that Deplete the Ozone Layer) to reduce the global production of ozone-depleting substances. Since then, new global observations of significant ozone depletion have prompted amendments to strengthen the treaty. The 1992 Copenhagen Amendments call for a ban on production of the most damaging compounds by 1996. The figure shows past and projected future stratospheric abundances of chlorine and bromine: (a) without the Protocol; (b) under the Protocol's original provisions; and (c) under the Copenhagen Amendments now in force. Without the Montreal Protocol and its Amendments, continuing human use of CFCs and other compounds would have tripled the stratospheric abundances of chlorine and bromine by about the year 2050. Current scientific understanding indicates that such increases would have led to global ozone depletion very much larger than observed today. In contrast, under current international agreements, which are now reducing and will eventually eliminate human emissions of ozone-depleting gases, the stratospheric abundances of chlorine and bromine are expected to reach their maximum within a few years and then slowly decline. All other things being equal, the ozone layer is expected to return to normal by the middle of the next century.

In summary, record low ozone levels have been observed in recent years, and substantially larger future global depletions in ozone would have been highly likely without reductions in human emissions of ozone-depleting gases. However, worldwide compliance with current international agreements is rapidly reducing the yearly emissions of these compounds. As these emissions cease, the ozone layer will gradually improve over the next several decades. The recovery of the ozone layer will be gradual because of the long times required for CFCs to be removed from the atmosphere.



When Did the Antarctic Ozone Hole First Appear?

The Antarctic ozone hole is a new phenomenon. The figure shows that observed ozone over the British Antarctic Survey station at Halley Bay, Antarctica first revealed obvious decreases in the early 1980s compared to data obtained since 1957. The ozone hole is formed each year when there is a sharp decline (currently up to 60%) in the total ozone over most of Antarctica for a period of about two months during Southern Hemisphere spring (September and October). Observations from three other stations in Antarctica, also covering several decades, reveal similar progressive, recent decreases in springtime ozone. The ozone hole has been shown to result from destruction of stratospheric ozone by gases containing chlorine and bromine, whose sources are mainly human-made halocarbon gases.

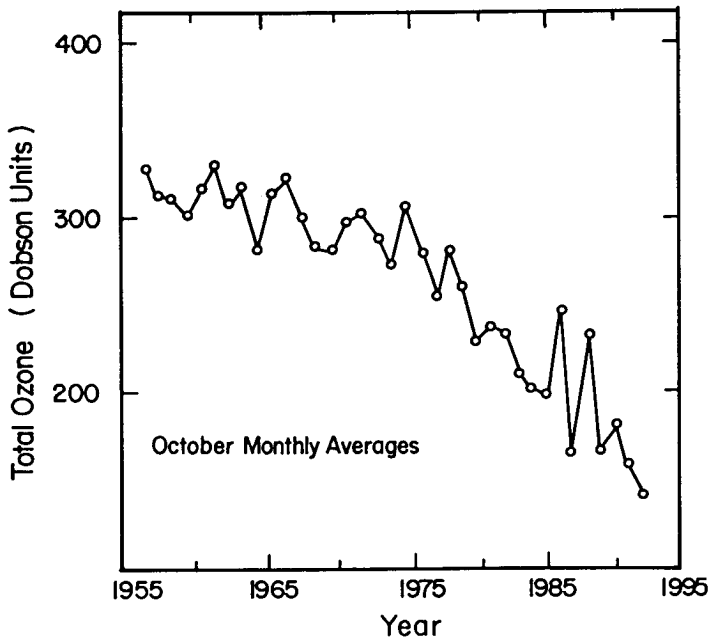
Before the stratosphere was affected by human-made chlorine and bromine, the naturally occurring springtime ozone levels over Antarctica were about 30-40% lower than springtime ozone levels over the Arctic. This natural difference between Antarctic and Arctic conditions was first observed in the late 1950s by Dobson. It stems

from the exceptionally cold temperatures and different winter wind patterns within the Antarctic stratosphere as compared to the Arctic. This is not at all the same phenomenon as the marked downward trend in total ozone in recent years referred to as the ozone hole and shown in the figure below.

Changes in stratospheric meteorology cannot explain the ozone hole. Measurements show that wintertime Antarctic stratospheric temperatures of past decades have not changed prior to the development of the hole each September. Ground, aircraft, and satellite measurements have provided, in contrast, clear evidence of the importance of the chemistry of chlorine and bromine originating from human-made compounds in depleting Antarctic ozone in recent years.

A single report of extremely low Antarctic winter ozone in one location in 1958 by an unproven technique has been shown to be completely inconsistent with the measurements depicted here and with all credible measurements of total ozone.

**Historical Springtime Total Ozone Record
for Halley Bay, Antarctica (76°S)**



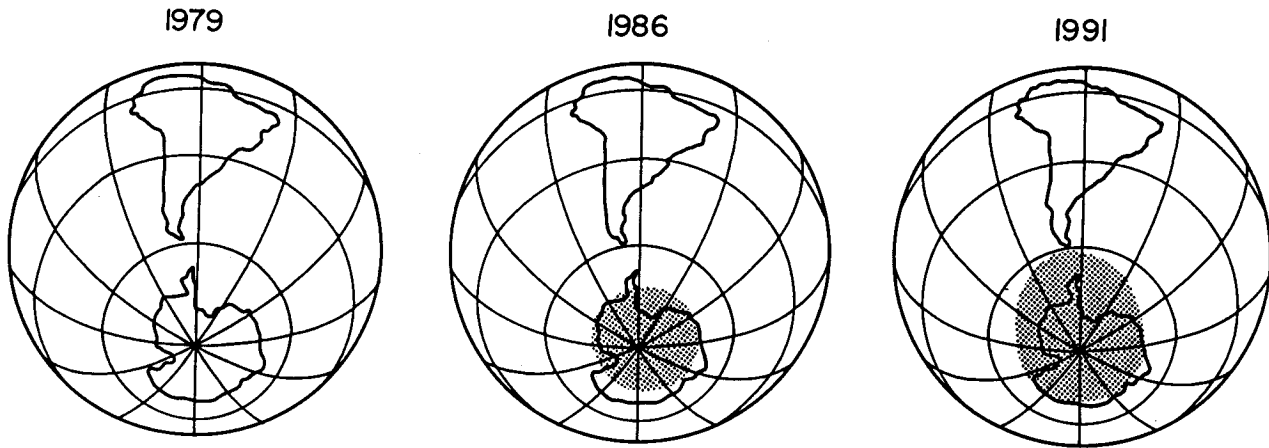
Why is the Ozone Hole Observed over Antarctica When CFCs Are Released Mainly in the Northern Hemisphere?

Human emissions of CFCs do occur mainly in the Northern Hemisphere, with about 90% released in the latitudes corresponding to Europe, Russia, Japan, and North America. Gases such as CFCs that are insoluble in water and relatively unreactive are mixed within a year or two throughout the lower atmosphere (below about 10 km). The CFCs in this well-mixed air rise from the lower atmosphere into the stratosphere mainly in tropical latitudes. Winds then move this air poleward – both north and south – from the tropics, so that air throughout the stratosphere contains nearly the same amount of chlorine. However, the meteorologies of the two polar regions are very different from each other because of major differences at the Earth's surface. The South Pole is part of a very large land mass (Antarctica) that is com-

pletely surrounded by ocean. These conditions produce very low stratospheric temperatures which in turn lead to formation of clouds (polar stratospheric clouds). The clouds that form at low temperatures lead to chemical changes that promote rapid ozone loss during September and October of each year, resulting in the ozone hole.

In contrast, the Earth's surface in the northern polar region lacks the land/ocean symmetry characteristic of the southern polar area. As a consequence, Arctic stratospheric air is generally much warmer than in the Antarctic, and fewer clouds form there. Therefore, the ozone depletion in the Arctic is much less than in the Antarctic.

Schematic of Antarctic Ozone Hole

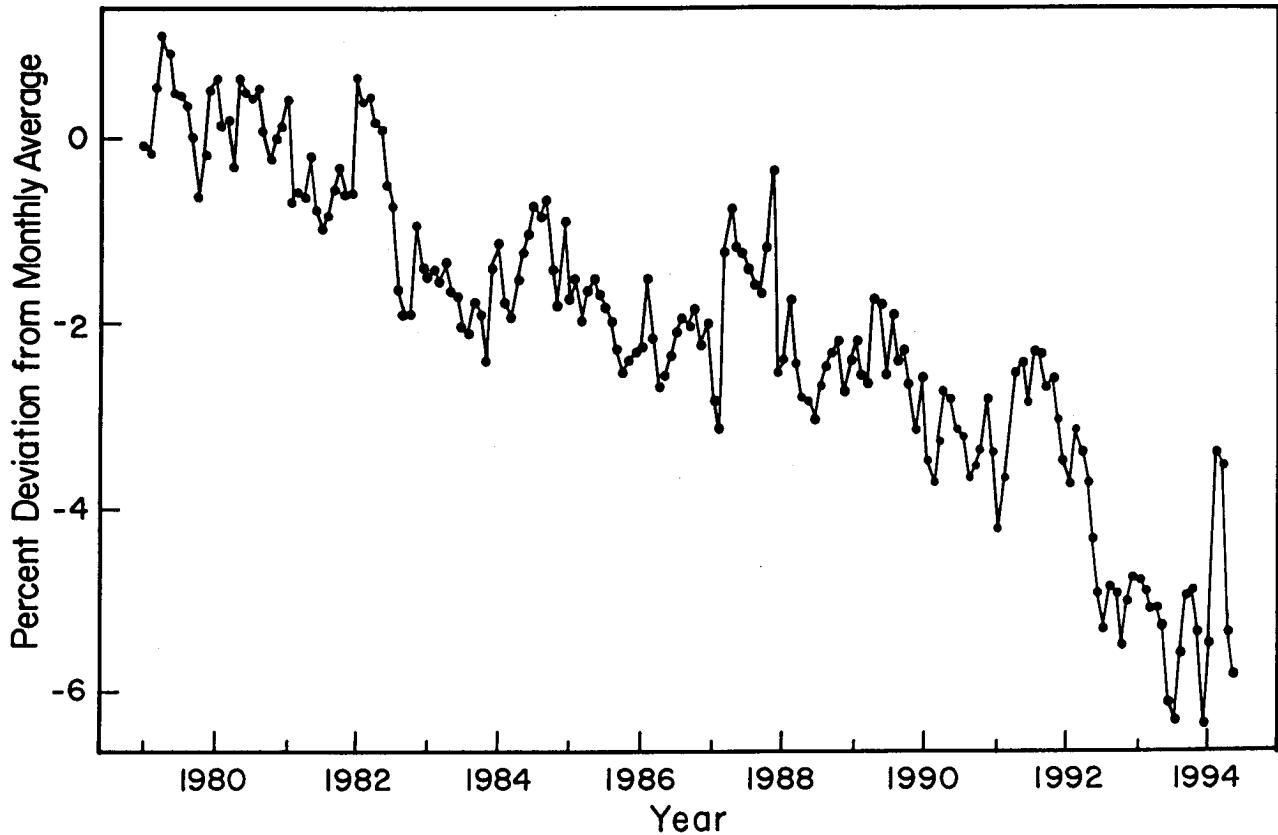


Can Changes in the Sun's Output Be Responsible for the Observed Changes in Ozone?

Stratospheric ozone is primarily created by ultraviolet (UV) light coming from the Sun, so the Sun's output affects the rate at which ozone is produced. The Sun's energy release (both as UV light and as charged particles such as electrons and protons) does vary, especially over the well-known 11-year sunspot cycle. Observations over several solar cycles (since the 1960s) show that total global ozone levels decrease by 1-2% from the maximum to the minimum of a typical cycle. Changes in the Sun's output cannot be responsible for the observed long-term changes in ozone, because these downward

trends are much larger than 1-2%. Further, during the period since 1979, the Sun's energy output has gone from a maximum to a minimum in 1985 and back through another maximum in 1991, but the trend in ozone was downward throughout that time. The ozone trends presented in this and previous international scientific assessments have been obtained by evaluating the long-term changes in ozone concentrations after accounting for the solar influence (as has been done in the figure below).

Global Ozone Trend (60°S–60°N)



Does Most of the Chlorine in the Stratosphere Come from Human or Natural Sources?

Most of the chlorine in the stratosphere is there as a result of human activities.

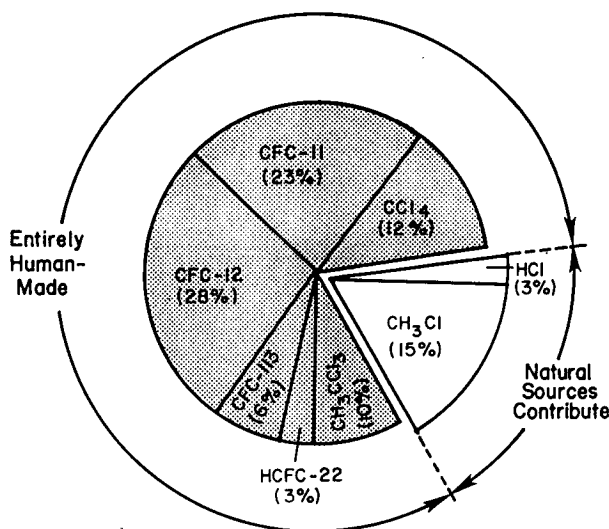
Many compounds containing chlorine are released at the ground, but those that dissolve in water cannot reach stratospheric altitudes. Large quantities of chlorine are released from evaporated ocean spray as sea salt (sodium chloride) aerosol. However, because sea salt dissolves in water, this chlorine quickly is taken up in clouds or in ice, snow, or rain droplets and does not reach the stratosphere. Another ground-level source of chlorine is its use in swimming pools and as household bleach. When released, this chlorine is rapidly converted to forms that dissolve in water and therefore are removed from the lower atmosphere, never reaching the stratosphere in significant amounts. Volcanoes can emit large quantities of hydrogen chloride, but this gas is rapidly converted to hydrochloric acid in rain water, ice, and snow and does not reach the stratosphere. Even in explosive volcanic plumes that rise high in the atmosphere, nearly all of the hydrogen chloride is scrubbed out in precipitation before reaching stratospheric altitudes.

In contrast, human-made halocarbons – such as CFCs, carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3) – are not soluble in water, do not react with snow or other natural surfaces, and are not broken down chemically in the lower atmosphere. While the exhaust

from the Space Shuttle and from some rockets does inject some chlorine directly into the stratosphere, this input is very small (less than one percent of the annual input from halocarbons in the present stratosphere, assuming nine Space Shuttle and six Titan IV rocket launches per year).

Several pieces of evidence combine to establish human-made halocarbons as the primary source of stratospheric chlorine. First, measurements (see the figure below) have shown that the chlorinated species that rise to the stratosphere are primarily manufactured compounds (mainly CFCs, carbon tetrachloride, methyl chloroform, and the HCFC substitutes for CFCs), together with small amounts of hydrochloric acid (HCl) and methyl chloride (CH_3Cl) which are partly natural in origin. The natural contribution now is much smaller than that from human activities, as shown in the figure below. Second, in 1985 and 1992 researchers measured nearly all known gases containing chlorine in the stratosphere. They found that human emissions of halocarbons plus the much smaller contribution from natural sources could account for all of the stratospheric chlorine compounds. Third, the *increase* in total stratospheric chlorine measured between 1985 and 1992 corresponds with the known increases in concentrations of human-made halocarbons during that time.

Primary Sources of Chlorine Entering the Stratosphere



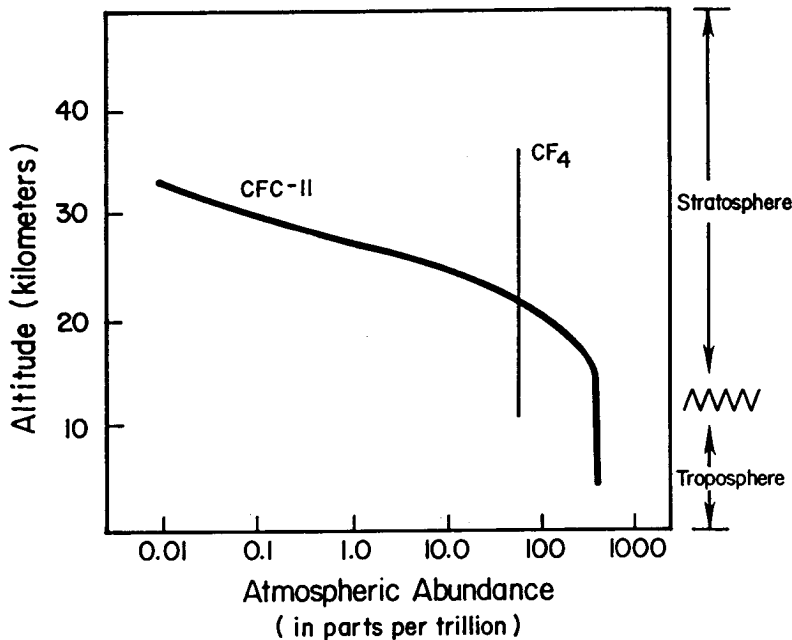
How Can Chlorofluorocarbons (CFCs) Get to the Stratosphere If They're Heavier than Air?

Although the CFC molecules are indeed several times heavier than air, thousands of measurements have been made from balloons, aircraft, and satellites demonstrating that the CFCs are actually present in the stratosphere. The atmosphere is not stagnant. Winds mix the atmosphere to altitudes far above the top of the stratosphere much faster than molecules can settle according to their weight. Gases such as CFCs that are insoluble in water and relatively unreactive in the lower atmosphere (below about 10 km) are quickly mixed and therefore reach the stratosphere regardless of their weight.

Much can be learned about the atmospheric fate of compounds from the measured changes in concentration versus altitude. For example, the two gases carbon tetrafluoride (CF_4 , produced mainly as a by-product of the manufacture of aluminum) and CFC-11 (CCl_3F , used in a variety of human activities) are both much heavier than

air. Carbon tetrafluoride is completely unreactive in the lower 99.9% of the atmosphere, and measurements show it to be nearly uniformly distributed throughout the atmosphere as shown in the figure. There have also been measurements over the past two decades of several other completely unreactive gases, one lighter than air (neon) and some heavier than air (argon, krypton), which show that they also mix upward uniformly through the stratosphere regardless of their weight, just as observed with carbon tetrafluoride. CFC-11 is unreactive in the lower atmosphere (below about 15 km) and is similarly uniformly mixed there, as shown. The abundance of CFC-11 decreases as the gas reaches higher altitudes, where it is broken down by high energy solar ultraviolet radiation. Chlorine released from this breakdown of CFC-11 and other CFCs remains in the stratosphere for several years, where it destroys many thousands of molecules of ozone.

Measurements of CFC-11 and CF_4



What is the Evidence that Stratospheric Ozone is Destroyed by Chlorine and Bromine?

Laboratory studies show that chlorine (Cl) reacts very rapidly with ozone. They also show that the reactive chemical chlorine oxide (ClO) formed in that reaction can undergo further processes which regenerate the original chlorine, allowing the sequence to be repeated very many times (a "chain reaction"). Similar reactions also take place between bromine and ozone.

But do these ozone-destroying reactions occur in the real world? All of our accumulated scientific experience demonstrates that if the conditions of temperature and pressure are like those in the laboratory studies, the same chemical reactions will take place in nature. However, many other reactions including those of other chemical species are often also taking place simultaneously in the stratosphere, making the connections among the changes difficult to untangle. Nevertheless, whenever chlorine (or bromine) and ozone are found together in the stratosphere, the ozone-destroying reactions must be taking place.

Sometimes a small number of chemical reactions is so important in the natural circumstance that the connections are almost as clear as in laboratory experiments. Such a situation occurs in the Antarctic stratosphere during the springtime formation of the ozone hole. During August and September 1987 – the end of winter and beginning of spring in the Southern Hemisphere – aircraft equipped with many different instruments for measuring a large number of chemical species were flown repeated-

ly over Antarctica. Among the chemicals measured were ozone and chlorine oxide, the reactive chemical identified in the laboratory as one of the participants in the ozone-destroying chain reactions. On the first flights southward from the southern tip of South America, relatively high concentrations of ozone were measured everywhere over Antarctica. By mid-September, however, the instruments recorded low concentrations of ozone in regions where there were high concentrations of chlorine oxide and vice versa, as shown in the figure. Flights later in September showed even less ozone over Antarctica, as the chlorine continued to react with the stratospheric ozone.

Independent measurements made by these and other instruments on this and other airplanes, from the ground, from balloons, and from satellites have provided a detailed understanding of the chemical reactions going on in the Antarctic stratosphere. Regions with high concentrations of reactive chlorine reach temperatures so cold (less than approximately -80°C , or -112°F) that stratospheric clouds form, a rare occurrence except during the polar winters. These clouds facilitate other chemical reactions that allow the release of chlorine in sunlight. The chemical reactions related to the clouds are now well understood through study under laboratory conditions mimicking those found naturally. Scientists are working to understand the role of such reactions of chlorine and bromine at other latitudes, and the involvement of particles of sulfuric acid from volcanoes or other sources.

Measurements of Ozone and Reactive Chlorine from a Flight into the Antarctic Ozone Hole

