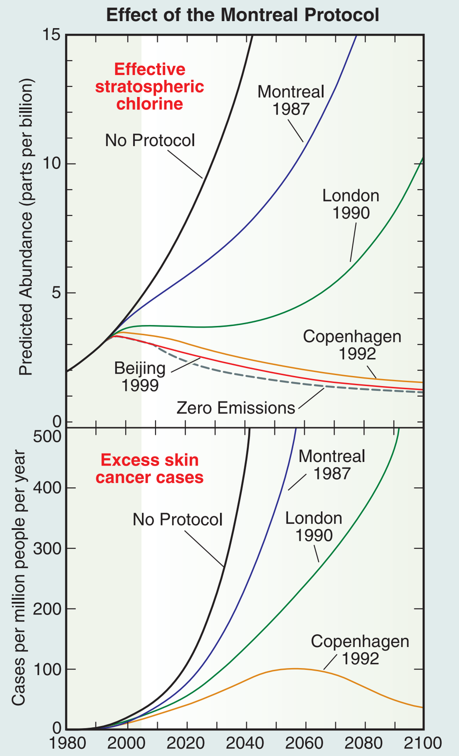
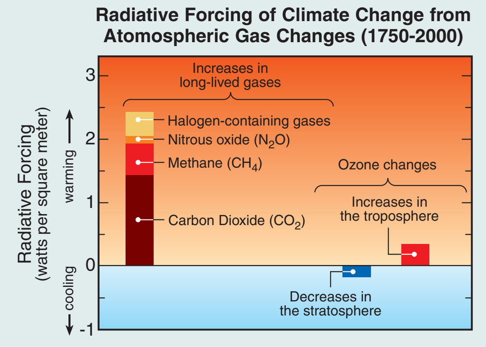
The Science of Ozone Depletion

Montreal Protocol

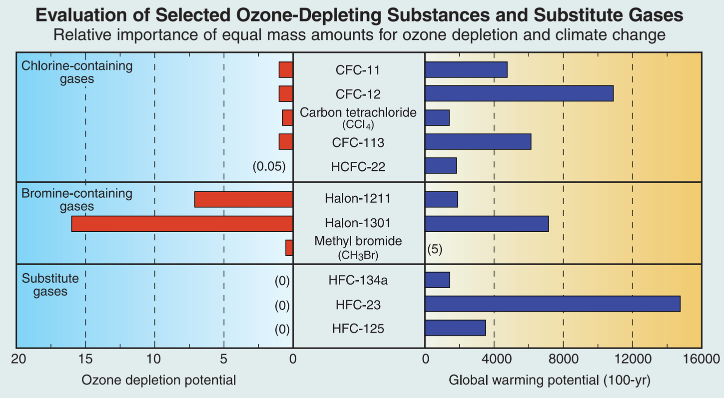


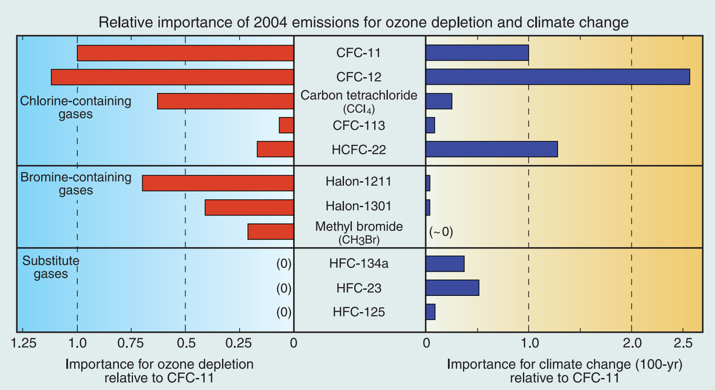
The purpose of the Montreal Protocol is to achieve reductions in stratospheric abundances of chlorine and bromine. The reductions follow from restrictions on the production and consumption of manufactured halogen source gases. Projections of the future abundance of effective stratospheric chlorine are shown in the top panel assuming *(1)* no Protocol regulations, *(2)* only the regulations in the original 1987 Montreal Protocol, and *(3)* additional regulations from the subsequent Amendments and Adjustments. The city names and years indicate where and when changes to the original 1987 Protocol provisions were agreed upon. Effective stratospheric chlorine as used here accounts for the combined effect of chlorine and bromine gases. Without the Protocol, stratospheric halogen gases are projected to increase significantly in the 21st century. The "zero emissions" line shows a hypothetical case of stratospheric abundances if all emissions were reduced to zero beginning in 2007. The lower panel shows how excess skin cancer cases might increase with no regulation and how they might be reduced under the Protocol provisions.

Ozone & Climate Change



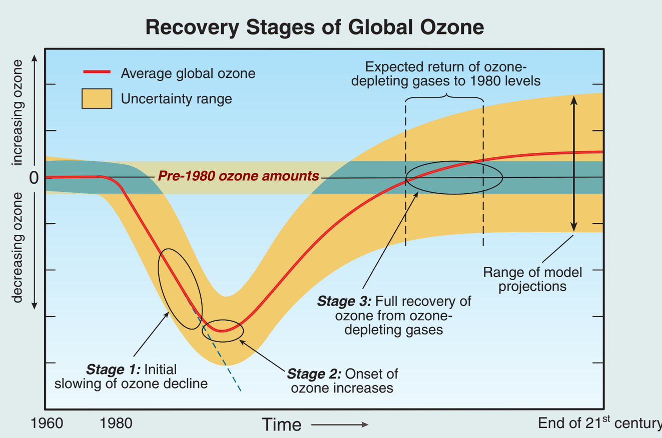
Human activities since the start of the Industrial Era *(around 1750)* have caused increases in the abundances of several longlived gases, changing the radiative balance of Earth's atmosphere. These gases, known as "greenhouse gases," result in radiative forcings, which can lead to climate change. Other international assessments have shown that the largest radiative forcings come from carbon dioxide, followed by methane, tropospheric ozone, the halogen containing gases, and nitrous oxide. Ozone increases in the troposphere result from pollution associated with human activities. All these forcings are positive, which leads to a warming of Earth's surface. In contrast, stratospheric ozone depletion represents a small negative forcing, which leads to cooling of Earth's surface. In the coming decades, halogen gas abundances and stratospheric ozone depletion are expected to be reduced along with their associated radiative forcings. The link between these two forcing terms is an important aspect of the radiative forcing of climate change.





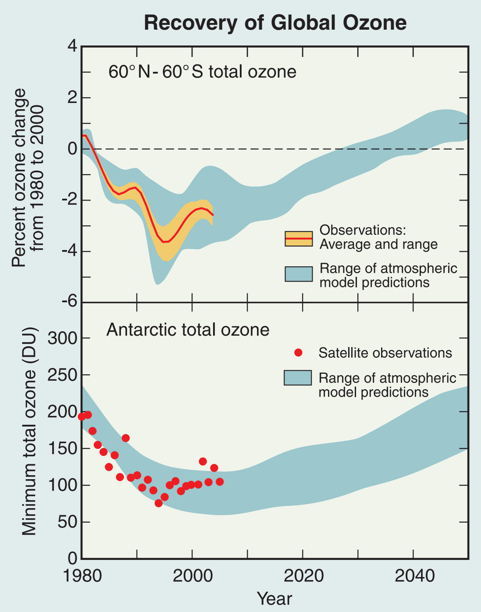
Ozone-depleting gases *(halogen source gases)* and their substitutes can be compared via their ozone depletion potentials *(ODPs)* and global warming potentials *(GWPs)*. The GWPs are evaluated for a 100-yr time interval after emission. The CFCs, halons, and HCFCs are ozone-depleting gases and HFCs, used as substitute or replacement gases, do not destroy ozone. The ODPs of CFC-11 and CFC-12, and the GWP of CO_2 have values of 1.0 by definition. Larger ODPs or GWPs indicate greater potential for ozone depletion or climate change, respectively. The top panel compares ODPs and GWPs for emissions of equal mass amounts of each gas. The ODPs of the halons far exceed those of the CFCs. HFCs have zero ODPs. All gases have non-zero GWPs that span a wide range of values. The bottom panel compares the contributions of the 2004 emissions of each gas, using CFC-11 as the reference gas. Each bar represents the product of a global emission value and the respective ODP or GWP factor. The comparison shows that 2004 emissions of ozone-depleting gases currently contribute more than substitute gas emissions to both ozone depletion and climate change. Future projections guided by Montreal Protocol provisions suggest that the contributions of ozone-depleting gases to climate change will decrease, while those of the substitute gases will increase.

Future Ozone



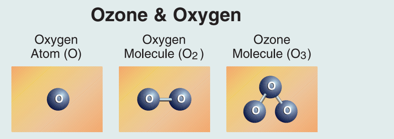
Significant ozone depletion from the release of ozone-depleting gases in human activities first became recognized in the 1980s. The Montreal Protocol provisions are expected to further reduce and eliminate these gases in the atmosphere in the coming decades, thereby leading to the return of ozone amounts to near pre-1980 values. The timeline of the recovery process is schematically illustrated with three stages identified. The large uncertainty range illustrates natural ozone variability in the past and potential uncertainties in global model projections of future ozone amounts. When ozone reaches the full recovery stage, global ozone values may be above or below pre-1980 values, depending on other changes in the atmosphere.

Observed values of midlatitude total ozone *(top panel, right)* and September-October minimum total ozone values, over Antarctica *(bottom panel, right)* have decreased beginning in the early 1980s. As halogen source gas emissions decrease in the 21st century, ozone values are expected to recover by increasing toward pre-1980 values. Atmospheric computer models that account for changes in halogen gases and other atmospheric parameters are used to predict how ozone amounts will increase. These model results show that full recovery is expected in midlatitudes by 2050, or perhaps earlier. Recovery in the Antarctic will occur somewhat later. The range of model projections comes from the use of several different models of the future atmosphere.



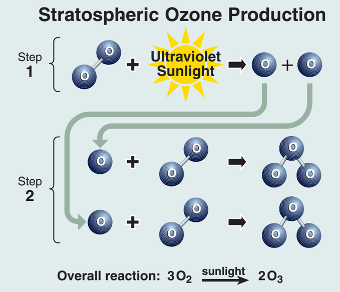
Ozone Basics

Ozone & Oxygen



A molecule of ozone *(O_3)* contains three oxygen *(O)* atoms bound together. Oxygen molecules *(O_2)*, which constitute 21% of Earth's atmosphere, contain two oxygen atoms bound together.

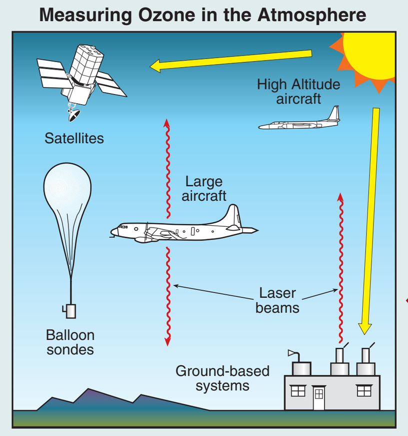
Stratospheric Ozone Production



Overall reaction: $3O_2 \xrightarrow{\text{sunlight}} 2O_3$

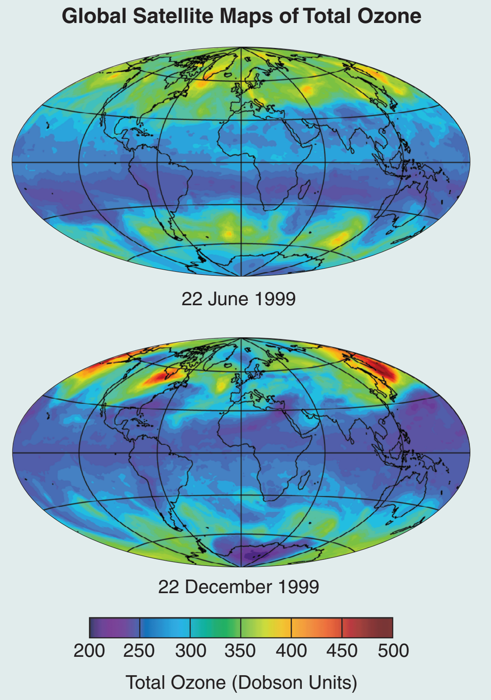
Ozone is naturally produced in the stratosphere in a two-step process. In the first step, ultraviolet sunlight breaks apart an oxygen molecule to form two separate oxygen atoms. In the second step, each atom then undergoes a binding collision with another oxygen molecule to form an ozone molecule. In the overall process, three oxygen molecules plus sunlight react to form two ozone molecules.

Measuring Ozone in the Atmosphere



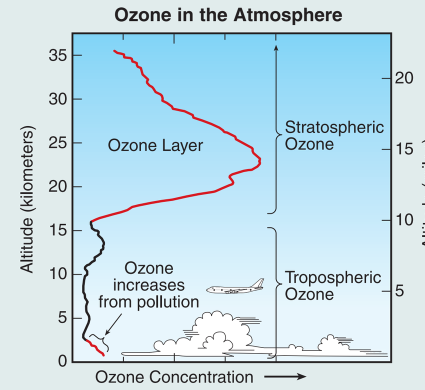
Ozone is measured throughout the atmosphere with instruments on the ground and on board aircraft, high-altitude balloons, and satellites. Some instruments measure ozone locally in sampled air and others measure ozone remotely some distance away from the instrument. Instruments use optical techniques, with the Sun and lasers as light sources, or use chemical reactions that are unique to ozone. Measurements at many locations over the globe are made regularly to monitor total ozone amounts.

Global Satellite Maps of Total Ozone



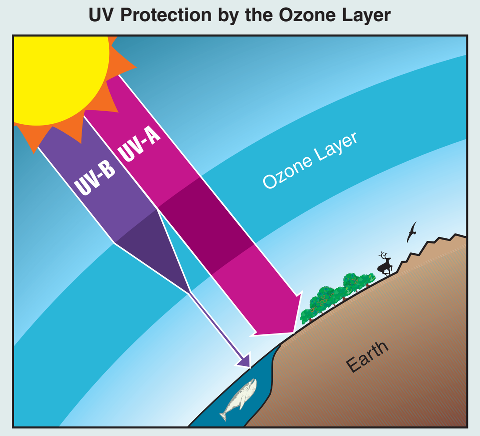
A total ozone value is obtained by measuring all the ozone that resides in the atmosphere over a given location on Earth's surface. Total ozone values shown here are reported in "Dobson units" as measured by a satellite instrument from space. Total ozone varies with latitude, longitude, and season, with the largest values at high latitudes and the lowest values in tropical regions. Total ozone at most locations varies with time on a daily to seasonal basis as ozone-rich air is moved about the globe by stratospheric winds. Low total ozone values over Antarctica in the 22 December image represent the remainder of the "ozone hole" from the 1999 Antarctic winter/spring season.

Ozone in the Atmosphere



Ozone is present throughout the lower atmosphere *(troposphere and stratosphere)*. Most ozone resides in the stratospheric "ozone layer" above Earth's surface. Increases in ozone occur near the surface as a result of pollution from human activities.

UV Protection by the Ozone Layer

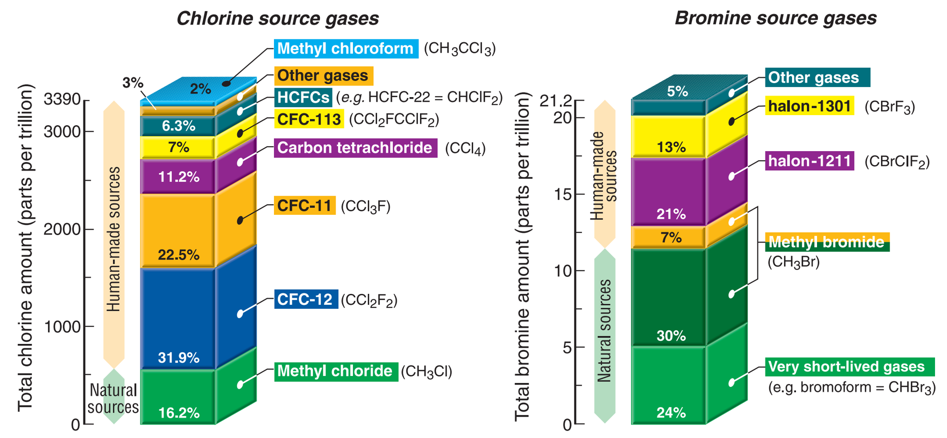


The ozone layer resides in the stratosphere and surrounds the entire Earth. UV-B radiation *(280- to 315- nanometer (nm) wavelength)* from the Sun is partially absorbed in this layer. As a result, the amount of UV-B reaching Earth's surface is greatly reduced. UV-A *(315- to 400-nm wavelength)* and other solar radiation are not strongly absorbed by the ozone layer. Human exposure to UV-B increases the risk of skin cancer, cataracts, and a suppressed immune system. UV-B exposure can also damage terrestrial plant life, single cell organisms, and aquatic ecosystems.

Principal Steps in the Depletion of Stratospheric Ozone

1 Emissions

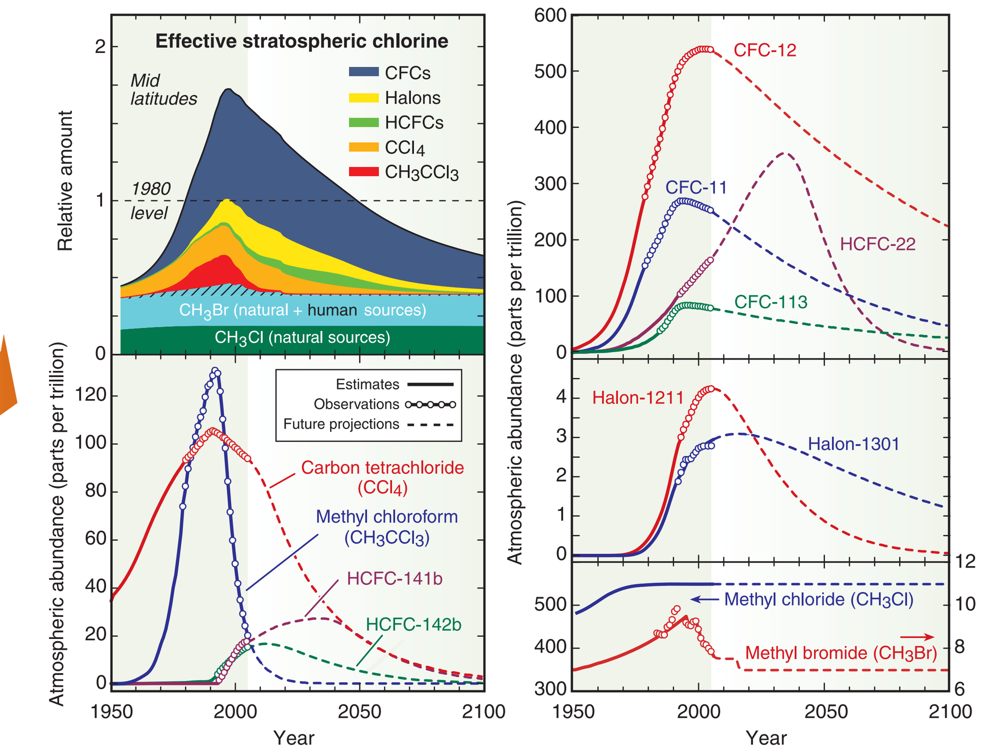
Halogen source gases are emitted at Earth's surface by human activities and natural processes.



A variety of gases transport chlorine and bromine into the stratosphere. These gases, called halogen source gases, are emitted from natural sources and by human activities. These partitioned columns show how the principal chlorine and bromine source gases contribute to the respective total amounts of chlorine and bromine as measured in 2004. Note the large difference in the vertical scales: total chlorine in the stratosphere is 160 times more abundant than total bromine. For chlorine, human activities account for most that reaches the stratosphere. The CFCs are the most abundant of the chlorine-containing gases released in human activities. Methyl chloride is the most important natural source of chlorine. HCFCs, which are substitute gases for CFCs and also are regulated under the Montreal Protocol, are a small but growing fraction of chlorine-containing gases. The "Other gases" category includes minor CFCs and short-lived gases. For bromine that reaches the stratosphere, halons and methyl bromide are the largest sources. Both gases are released in human activities. Methyl bromide has an additional natural source. Natural sources are a larger fraction of total bromine than of total chlorine. *(The unit "parts per trillion" is used here as a measure of the relative abundance of a gas in air: 1 part per trillion indicates the presence of one molecule of a gas per trillion other air molecules.)*

2 Accumulation

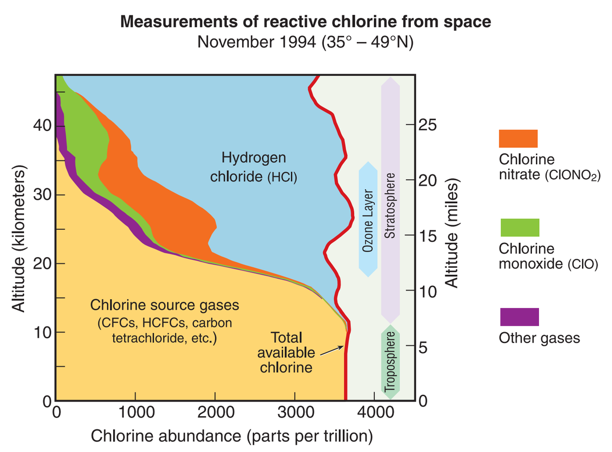
Halogen source gases accumulate in the atmosphere and are distributed throughout the lower atmosphere by winds and other air motions.



The rise in effective stratospheric chlorine values in the 20th century has slowed and reversed in the last decade *(top left panel)*. Effective stratospheric chlorine values are a measure of the potential for ozone depletion in the stratosphere, obtained by summing over adjusted amounts of all chlorine and bromine gases. Effective stratospheric chlorine levels as shown here for midlatitudes will return to 1980 values around 2050. The return to 1980 values will occur around 2065 in polar regions. In 1980, ozone was not significantly depleted by the chlorine and bromine then present in the stratosphere. A decrease in effective stratospheric chlorine abundance follows reductions in emissions of individual halogen source gases. Overall emissions and atmospheric concentrations have decreased and will continue to decrease given international compliance with the Montreal Protocol provisions. The changes in the atmospheric abundance of individual gases at Earth's surface shown in the panels were obtained using a combination of direct atmospheric measurements, estimates of historical abundance, and future projections of abundance. The past increases of CFCs, along with those of CCl_4 and CH_3CCl_3, have slowed significantly and most have reversed in the last decade. HCFCs, which are used as CFC substitutes, will continue to increase in the coming decades. Some halon abundances will also continue to grow in the future while current halon reserves are depleted. Smaller relative decreases are expected for CH_3Br in response to production and use restrictions because it has substantial natural sources. CH_3Cl has large natural sources and is not regulated under the Montreal Protocol.

3 Transport

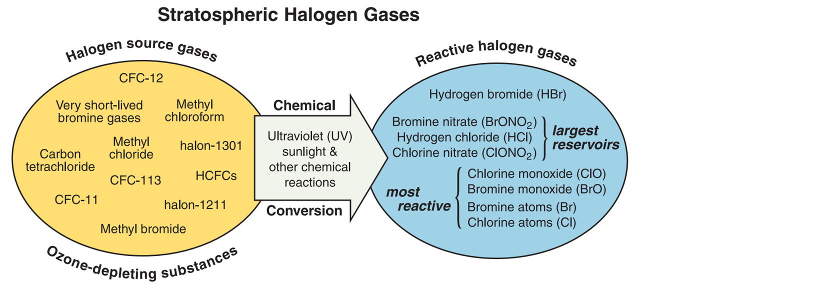
Halogen source gases are transported to the stratosphere by air motions.



The abundances of chlorine source gases and reactive chlorine gases as measured from space are displayed with altitude for a midlatitude location. In the troposphere *(below about 10 kilometers)*, all chlorine is contained in the source gases. In the stratosphere, reactive chlorine gases increase with altitude as chlorine source gases decrease. This is a consequence of chemical reactions involving ultraviolet sunlight. The principal reactive gases formed are HCl, $ClONO_2$, and ClO. Summing the source gases with the reactive gases gives total available chlorine, which is nearly constant with altitude up to 47 km. In the ozone layer, HCl and $ClONO_2$ are the most abundant reactive chlorine gases.

4 Conversion

Most **halogen source gases** are converted in the stratosphere to **reactive halogen gases** in chemical reactions involving ultraviolet radiation from the sun.



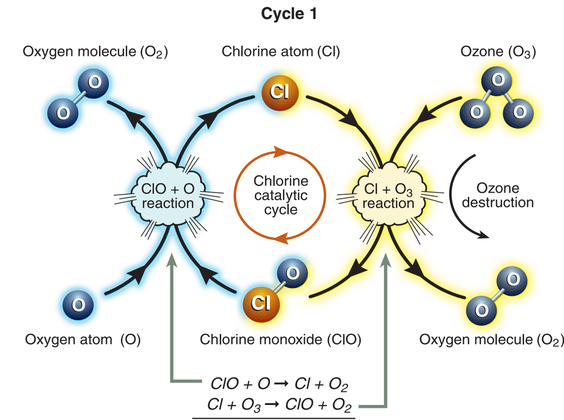
Halogen source gases *(also known as ozone-depleting substances)* are chemically converted to reactive halogen gases primarily in the stratosphere. The conversion requires ultraviolet sunlight and a few other chemical reactions. The short-lived gases undergo some conversion in the troposphere. The reactive halogen gases contain all the chlorine and bromine originally present in the source gases. The reactive gases separate into reservoir gases, which do not destroy ozone, and reactive gases, which participate in ozone destruction cycles.

5a Chemical reaction

Reactive halogen gases cause chemical depletion of stratospheric total **ozone** over the globe except at tropical latitudes.

Ozone Destruction Cycles

Cycle 1



$ClO + O \rightarrow Cl + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
Net: $O + O_3 \rightarrow 2O_2$

Cycle 2

$ClO + ClO \rightarrow (ClO)_2$
$(ClO)_2 + \text{sunlight} \rightarrow ClOO + Cl$
$ClOO \rightarrow Cl + O_2$
$2(Cl + O_3 \rightarrow ClO + O_2)$
Net: $2O_3 \rightarrow 3O_2$

Cycle 3

$ClO + BrO \rightarrow Cl + Br + O_2$
or ($ClO + BrO \rightarrow BrCl + O_2$; $BrCl + \text{sunlight} \rightarrow Cl + Br$)
$Cl + O_3 \rightarrow ClO + O_2$
$Br + O_3 \rightarrow BrO + O_2$
Net: $2O_3 \rightarrow 3O_2$

The destruction of ozone in Cycle 1 involves two separate chemical reactions. The net or overall reaction is that of atomic oxygen with ozone, forming two oxygen molecules. The cycle can be considered to begin with either ClO or Cl. When starting with ClO, the first reaction is ClO with O to form Cl. Cl then reacts with *(and thereby destroys)* ozone and reforms ClO. The cycle then begins again with another reaction of ClO with O. Because Cl or ClO is reformed each time an ozone molecule is destroyed, chlorine is considered a catalyst for ozone destruction. Atomic oxygen *(O)* is formed when ultraviolet sunlight reacts with ozone and oxygen molecules. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where ultraviolet sunlight is most intense.

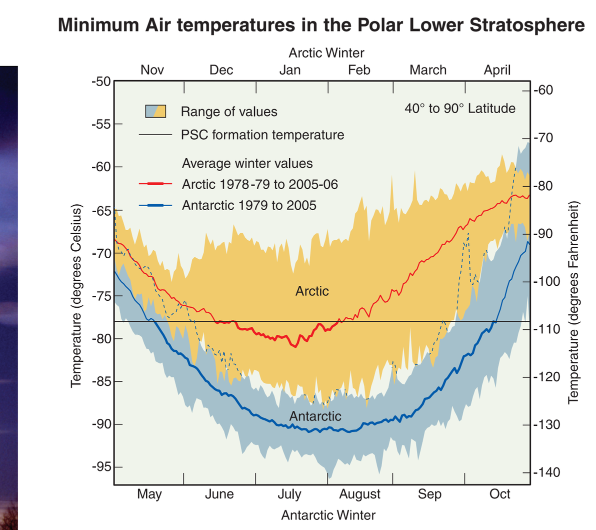
Significant destruction of ozone occurs in polar regions because ClO abundances reach large values. In this case, the cycles initiated by the reaction of ClO with another ClO *(Cycle 2)* or the reaction of ClO with BrO *(Cycle 3)* efficiently destroy ozone. The net reaction in both cases is two ozone molecules forming three oxygen molecules. The reaction of ClO with BrO has two pathways to form the Cl and Br product gases. Ozone destruction Cycles 2 and 3 are catalytic, as illustrated for Cycle 1, because chlorine and bromine gases react and are reformed in each cycle. Sunlight is required to complete each cycle and to help form and maintain ClO abundances.

5b

Polar Stratospheric Clouds increase **ozone** depletion by **reactive halogen gases** causing severe **ozone** loss in polar regions in winter and spring.

Arctic Polar Stratospheric Clouds

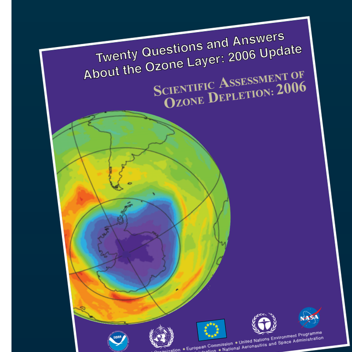
This photograph of an Arctic polar stratospheric cloud *(PSC)* was taken from the ground at Kiruna, Sweden *(67°N)*, on 27 January 2000. PSCs form during winters in the Arctic and Antarctic stratospheres. The particles grow from the condensation of water and nitric acid *(HNO_3)*. The clouds often can be seen with the human eye when the Sun is near the horizon. Reactions on PSCs cause the highly reactive chlorine gas ClO to be formed, which is very effective in the chemical destruction of ozone.



Stratospheric air temperatures in both polar regions reach minimum values in the lower stratosphere in the winter season. Average minimum values over Antarctica are as low as –90°C in July and August in a typical year. Over the Arctic, average minimum values are near –80°C in January and February. Polar stratospheric clouds *(PSCs)* are formed when winter minimum temperatures fall below the formation temperature *(about –78°C)*. This occurs on average for 1 to 2 months over the Arctic and 5 to 6 months over Antarctica *(see heavy red and blue lines)*. Reactions on PSCs cause the highly reactive chlorine gas ClO to be formed, which increases the destruction of ozone. The range of winter minimum temperatures found in the Arctic is much greater than in the Antarctic. In some years, PSC formation temperatures are not reached in the Arctic, and significant ozone depletion does not occur. In the Antarctic, PSCs are present for many months, and severe ozone depletion now occurs in each winter season.

6 Removal

Air containing **reactive halogen gases** returns to the troposphere and these gases are removed from the air by moisture in clouds and rain.



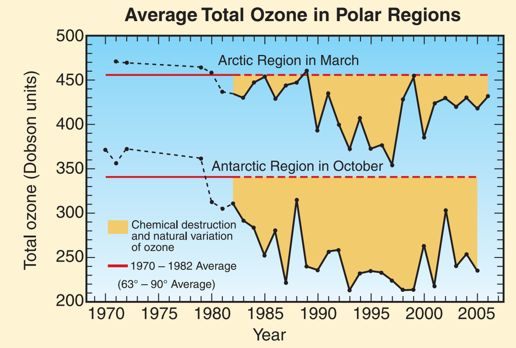
Twenty Questions and Answers About the Ozone Layer: 2006 Update

Scientific Assessment of Ozone Depletion: 2006

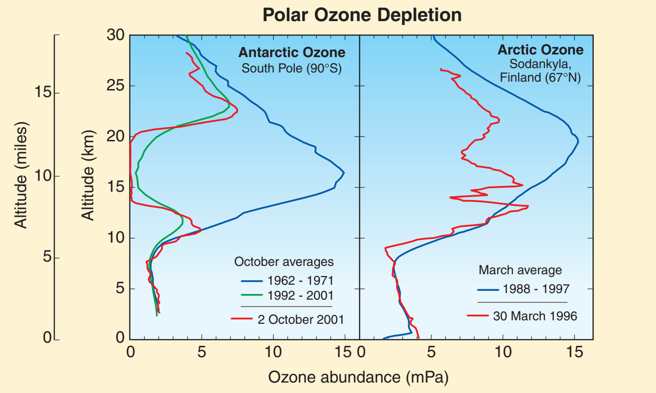
United Nations Environment Programme
World Meteorological Organization

WMO UNEP NOAA NASA

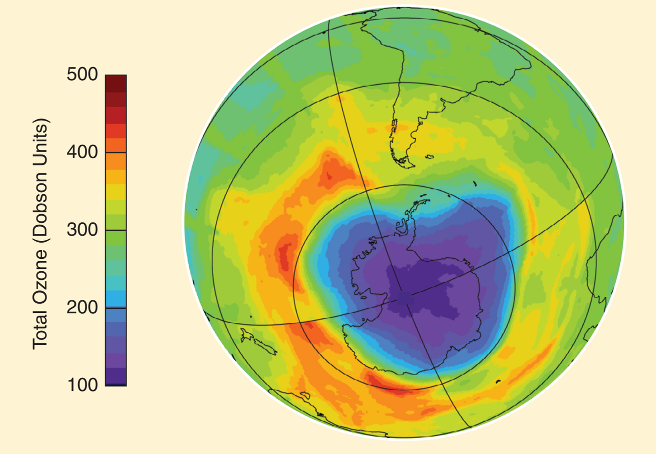
Polar Ozone Depletion



Total ozone in polar regions is measured by well-calibrated satellite instruments. Shown here is a comparison of average springtime total ozone values found between 1970 and 1982 *(solid and dashed red lines)* with those in later years. Each point represents a monthly average in October in the Antarctic or in March in the Arctic. After 1982, significant ozone depletion is found in most years in the Arctic and all years in the Antarctic. The largest average depletions have occurred in the Antarctic since 1990. The ozone changes are the combination of chemical destruction and natural variations. Variations in meteorological conditions influence the year-to-year changes in depletion, particularly in the Arctic. Essentially all of the decrease in the Antarctic and usually most of the decrease in the Arctic each year are attributable to chemical destruction by reactive halogen gases. Average total ozone values over the Arctic are naturally larger at the beginning of each winter season because more ozone is transported poleward each season in the Northern Hemisphere than in the Southern Hemisphere.



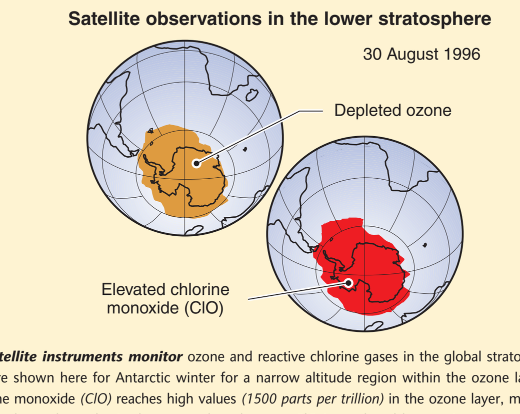
The stratospheric ozone layer resides between about 10 and 50 kilometers *(6 to 31 miles)* above Earth's surface over the globe. Long-term observations of the ozone layer with balloonborne instruments allow the winter Antarctic and Arctic regions to be compared. In the Antarctic at the South Pole, halogen gases have destroyed ozone in the ozone layer beginning in the 1980s. Before that period, the ozone layer was clearly present, as shown here using average ozone values from balloon observations made between 1962 and 1971. In more recent years, as shown here for 2 October 2001, ozone is destroyed completely between 14 and 20 kilometers *(8 to 12 miles)* in the Antarctic in spring. Average October values in the ozone layer now are reduced by 90% from pre-1980 values. The Arctic ozone layer is still present in spring as shown by the average March profile obtained over Finland between 1988 and 1997. However, March Arctic ozone values in some years are often below normal average values as shown here for 30 March 1996. In such years, winter minimum temperatures are generally below PSC formation temperatures for long periods. Ozone abundances are shown here with the unit "milli-Pascals" *(mPa)*, which is a measure of absolute pressure *(100 million mPa = atmospheric sea-level pressure)*.



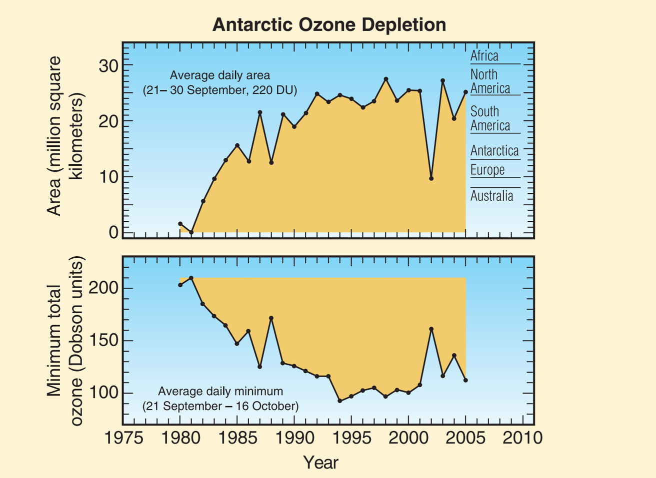
Antarctic Ozone Hole

4 October 2001

Total ozone values are shown for high southern latitudes as measured by a satellite instrument. The dark blue and purple regions over the Antarctic continent show the severe ozone depletion or "ozone hole" now found during every spring. Minimum values of total ozone inside the ozone hole are close to 100 Dobson units *(DU)* compared with normal springtime values of about 200 DU. In late spring or early summer *(November-December)* the ozone hole disappears in satellite images as ozone depleted air is displaced and mixed with ozone-rich air transported poleward from outside the ozone hole.



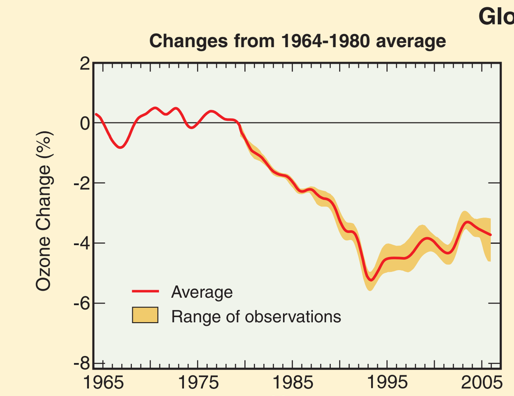
Satellite instruments monitor ozone and reactive chlorine gases in the global stratosphere. Results are shown here for Antarctic winter for a narrow altitude region within the ozone layer. In winter, chlorine monoxide *(ClO)* reaches high values *(1500 parts per trillion)* in the ozone layer, much higher than observed anywhere else in the stratosphere because ClO is produced by reactions on polar stratospheric clouds. These high ClO values in the lower stratosphere last for 1 to 2 months, cover an area that at times exceeds that of the Antarctic continent, and efficiently destroy ozone in sunlit regions in late winter/early spring. Ozone values measured simultaneously within the ozone layer show very depleted values.

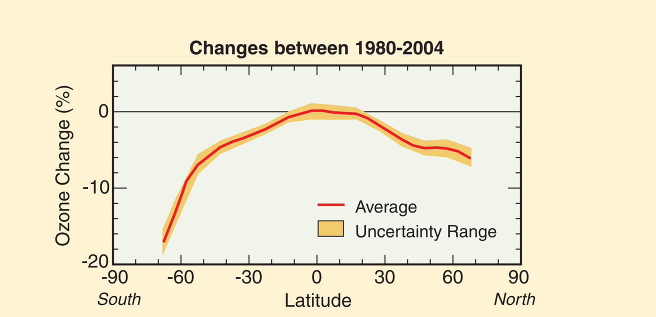


Values are shown for key parameters of the Antarctic ozone hole: the area enclosed by the 220-DU total ozone contour and the minimum total ozone amount, as determined from space-based observations. The values are averaged for each year near the peak of ozone depletion, as defined by the dates shown in each panel. The ozone hole areas are contrasted to the areas of continents in the upper panel. The intensity of ozone depletion gradually increased beginning in 1980. In the 1990s, the depletion reached fairly steady values, except for the anomalously low depletion in 2002. The intensity of Antarctic ozone depletion will decrease as part of the ozone recovery process.

Global Ozone Depletion

Global Total Ozone Change

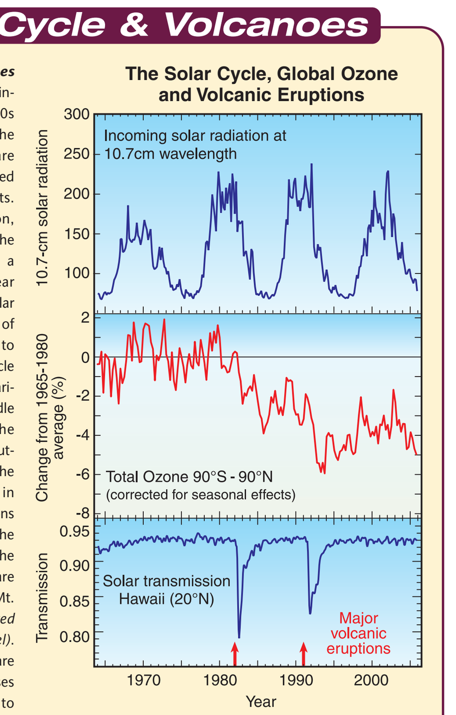




Satellite observations show a decrease in global total ozone values over more than two decades. The left panel compares global ozone values *(annual averages)* with the average from the period 1964 to 1980. Seasonal and solar effects have been removed from the data. On average, global ozone decreased each year between 1980 and the early 1990s. The decrease worsened during the few years when volcanic aerosol from the Mt. Pinatubo eruption in 1991 remained in the stratosphere. Now global ozone is about 4% below the 1964- to-1980 average.

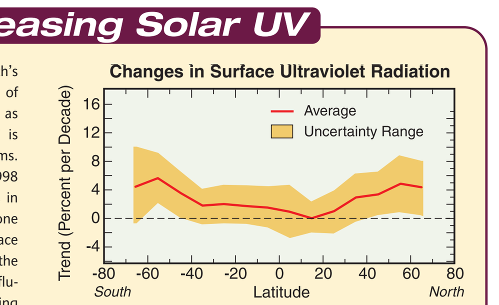
The right panel compares ozone changes between 1980 and 2004 for different latitudes. The largest decreases have occurred at the highest latitudes in both hemispheres because of the large winter/spring depletion in polar regions. The losses in the Southern Hemisphere are greater than those in the Northern Hemisphere because of the Antarctic ozone hole. Long-term changes in the tropics are much smaller because reactive halogen gases are less abundant in the tropical lower stratosphere.

Solar Cycle & Volcanoes

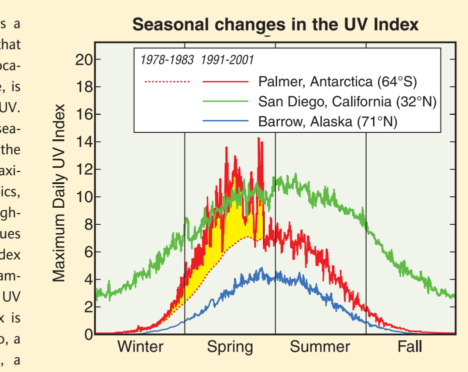


Total ozone values have decreased beginning in the early 1980s *(see middle panel)*. The ozone values shown are 3-month averages corrected for seasonal effects. Incoming solar radiation, which produces ozone in the stratosphere, changes on a well-recognized 11-year cycle. The amount of solar radiation at a wavelength of 10.7-cm is often used to document the 11-year cycle *(see top panel)*. A comparison of the top and middle panels indicates that the cyclic changes in solar output cannot account for the long-term decreases in ozone. Volcanic eruptions occurred frequently in the 1965 to 2005 period. The largest recent eruptions are El Chichón *(1982)* and Mt. Pinatubo *(1991) (see red arrows in bottom panel)*. Large volcanic eruptions are monitored by the decreases in solar transmission to Earth's surface that occur because new particles are formed in the stratosphere from volcanic sulfur emissions *(see bottom panel)*. These particles increase ozone depletion only temporarily because they do not remain in the stratosphere for more than a few years. A comparison of the middle and bottom panels indicates that large volcanic eruptions also cannot account for the long-term decreases found in global total ozone.

Increasing Solar UV



Ultraviolet (UV) radiation at Earth's surface has increased over much of the globe since 1979. Also known as "erythemal radiation," sunburning UV is harmful to humans and other life forms. The increases shown here for 1979-1998 are estimated from observed decreases in ozone and the relationship between ozone and surface UV established at some surface locations. The estimates are based on the assumption that all other factors that influence the amount of UV radiation reaching the Earth's surface, such as aerosol abundances and cloudiness, are unchanged. The estimated changes in ultraviolet radiation in the tropics are the smallest because observed ozone changes are the smallest there.



The maximum daily UV Index is a measure of peak sunburning UV that occurs during the day at a particular location. UV-B, which is absorbed by ozone, is an important component of sunburning UV. The UV Index varies with latitude and season, and with the Sun's elevation in the local sky. The highest values of the maximum daily UV Index occur in the tropics, where the midday Sun is highest throughout the year and where total ozone values are lowest. The lowest average UV Index values occur at high latitudes. As an example, the figure compares the seasonal UV Index at three locations. The UV Index is higher throughout the year in San Diego, a low-latitude location, than in Barrow, a high-latitude location. Index values are zero at high latitudes in winter when darkness is continuous. The effect of Antarctic ozone depletion is demonstrated by comparing the Palmer and San Diego data in the figure. Normal values estimated for Palmer are shown for the 1978-1983 period before the "ozone hole" occurred each season *(see red dotted line)*. In the decade 1991-2001, Antarctic ozone depletion has increased the maximum UV Index value at Palmer throughout spring *(see yellow shaded region)*. Values at Palmer now sometimes equal or exceed those measured in spring and even in the summer in San Diego, which is located at much lower latitude.

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