TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER

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A draft of this component of the Assessment was reviewed and discussed by the 74 scientists who attended the Panel Review Meeting for the 2002 ozone assessment (Les Diablerets, Switzerland, 24-28 June 2002). In addition, subsequent contributions, reviews, or comments were provided by the following individuals: A.-L.N. Ajavon, D.L. Albritton, S.O. Andersen, P.J. Aucamp, G. Bernhard, M.P. Chipperfield, J.S. Daniel, S.B. Diaz, E.S. Dutton, C.A. Ennis, P.J. Fraser, R.-S. Gao, R.R. Garcia, M.A. Geller, S. Godin-Beekmann, M. Graber, J.B. Kerr, M.K.W. Ko, M.J. Kurylo, G.L. Manney, K. Mauersberger, M. McFarland, G. Mégie, S.A. Montzka, R. Müller, E.R. Nash, P.A. Newman, S.J. Oltmans, M. Oppenheimer, L.R. Poole, G. Poulet, M.H. Proffitt, W.J. Randel, A.R. Ravishankara, C.E. Reeves, R.J. Salawitch, M.L. Santee, G. Seckmeyer, D.J. Siedel, K.P. Shine, C.C. Sweet, A.F. Tuck, G.J.M. Velders, R.T. Watson, and R.J. Zander.

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INTRODUCTION

Ozone is a very small part of our atmosphere, but its presence is nevertheless vital to human well-being.

Most ozone resides in the upper part of the atmosphere. This region, called the stratosphere, is more than 10 kilometers (6 miles) above Earth's surface. There, about 90% of atmospheric ozone is contained in the "ozone layer," which shields us from harmful ultraviolet light from the Sun.

However, it was discovered in the mid-1970s that some human-produced chemicals could destroy ozone and deplete the ozone layer. The resulting increase in ultraviolet radiation at Earth's surface can increase the incidences of skin cancer and eye cataracts.

Following the discovery of this environmental issue, researchers focused on a better understanding of this threat to the ozone layer. Monitoring stations showed that the abundances of the ozone-depleting chemicals were steadily increasing in the atmosphere. These trends were linked to growing production and use of chemicals like chlorofluorocarbons (CFCs) for refrigeration and air conditioning, foam blowing, and industrial cleaning. Measurements in the laboratory and the atmosphere characterized the chemical reactions that were involved in ozone destruction. Computer models employing this information could then predict how much ozone depletion was occurring and how much more could occur in the future.

Observations of the ozone layer itself showed that depletion was indeed occurring. The most severe and most surprising ozone loss was discovered to be over Antarctica. It is commonly called the "ozone hole" because the ozone depletion is so large and localized. A thinning of the ozone layer also has been observed over other regions of the globe, such as the Arctic and northern middle latitudes.

The work of many scientists throughout the world has provided a basis for building a broad and solid scientific understanding of the ozone depletion process. With this understanding, we know that ozone depletion is occurring and why. And, most important, it has become clear that, if ozone-depleting gases were to continue to accumulate in the atmosphere, the result would be more ozone layer depletion.

In response to the prospect of increasing ozone depletion, the governments of the world crafted the 1987 United Nations Montreal Protocol as a global means to address a global issue. As a result of the broad compliance with the Protocol and its Amendments and Adjustments and, importantly, the industrial development of more "ozone-friendly" substitutes for the now-controlled chemicals, the total global accumulation of ozone-depleting gases has slowed and begun to decrease. This has reduced the risk of further ozone depletion. Now, with continued compliance, we expect recovery of the ozone layer in the late 21st century. International Day for the Preservation of the Ozone Layer, 16 September, is now celebrated on the day the Montreal Protocol was agreed upon.

This is a story of notable achievements: discovery, understanding, decisions, and actions. It is a story written by many: scientists, technologists, economists, legal experts, and policymakers. And, dialogue has been a key ingredient.

To help foster a continued interaction, this component of the *Scientific Assessment of Ozone Depletion: 2002* presents 20 questions and answers about the often-complex science of ozone depletion. The questions address the nature of atmospheric ozone, the chemicals that cause ozone depletion, how global and polar ozone depletion occur, and what could lie ahead for the ozone layer. A brief answer to each question is first given in italics; an expanded answer then follows. The answers are based on the information presented in the 2002 and earlier Assessment reports. These reports and the answers provided here were all prepared and reviewed by a large international group of scientists. [1]

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I. OZONE IN OUR ATMOSPHERE

Q1: What is ozone and where is it in the atmosphere?

Ozone is a gas that is naturally present in our atmosphere. Each ozone molecule contains three atoms of oxygen and is denoted chemically as O_3. Ozone is found primarily in two regions of the atmosphere. About 10% of atmospheric ozone is in the troposphere, the region closest to Earth (from the surface to about 10-16 kilometers (6-10 miles)). The remaining ozone (90%) resides in the stratosphere, primarily between the top of the troposphere and about 50 kilometers (31 miles) altitude. The large amount of ozone in the stratosphere is often referred to as the "ozone layer."

Ozone is a gas that is naturally present in our atmosphere. Because an ozone molecule contains three oxygen atoms (see ***Figure Q1-1***), it has a chemical formula of O_3. Ozone was discovered in laboratory experiments in the mid-1800s. Ozone's presence in the atmosphere was later discovered using chemical and optical measurement methods. The word ozone is derived from the Greek word *ozein*, meaning "to smell." Ozone has a pungent odor that allows ozone to be detected even in very low amounts. Ozone will rapidly react with many chemical compounds and is explosive in concentrated amounts. Electrical discharges are generally used to make ozone for industrial processes including air and water purification and bleaching of textiles and food products.

Ozone location. Most ozone (about 90%) is found in the stratosphere, a region that begins about 10-16 kilometers (6-10 miles) above Earth's surface and extends up to about 50 kilometers (31 miles) altitude (see ***Figure Q1-2***). The stratosphere begins at higher altitudes (16 kilometers) in the tropics than in the polar regions (10 kilometers). Most ozone resides in the stratosphere in what is commonly known as the "ozone layer." The remaining ozone, about 10%, is found in the troposphere, which is the lowest region of the atmosphere between Earth's surface and the stratosphere.

Ozone abundance. Ozone molecules have a relatively low abundance in the atmosphere. In the stratosphere near the peak of the ozone layer, there are up to 12,000 ozone molecules for every *billion* air molecules (1 billion = 1000 million). Most air molecules are either oxygen (O_2) or nitrogen (N_2) molecules. In the troposphere near Earth's surface, ozone is even less abundant, with a typical range of 20 to 100 ozone molecules for each billion air molecules. The highest surface values are a result of ozone formed in air polluted by human activities.

As an illustration of the low relative abundance of ozone in our atmosphere, one can consider bringing all the ozone molecules in the troposphere and stratosphere down to Earth's surface and uniformly distributing these molecules into a gas layer over the globe. The resulting layer of pure ozone would have a thickness of less than one-half centimeter (about one-quarter inch).

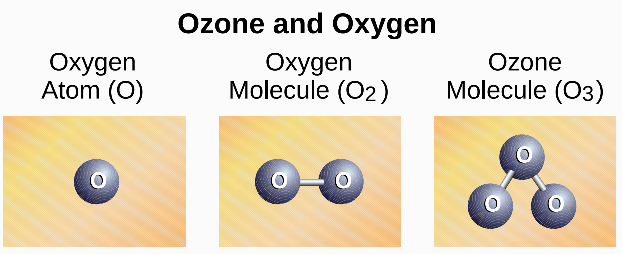


Figure Q1-1. Ozone and oxygen. A molecule of ozone (O_3) contains three oxygen (O) atoms bound together. Oxygen molecules (O_2), which constitute 21% of Earth's atmosphere, contain two oxygen atoms bound together.

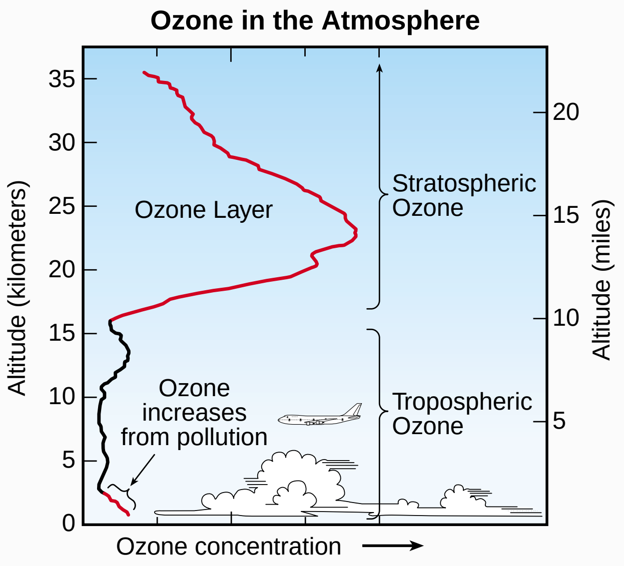


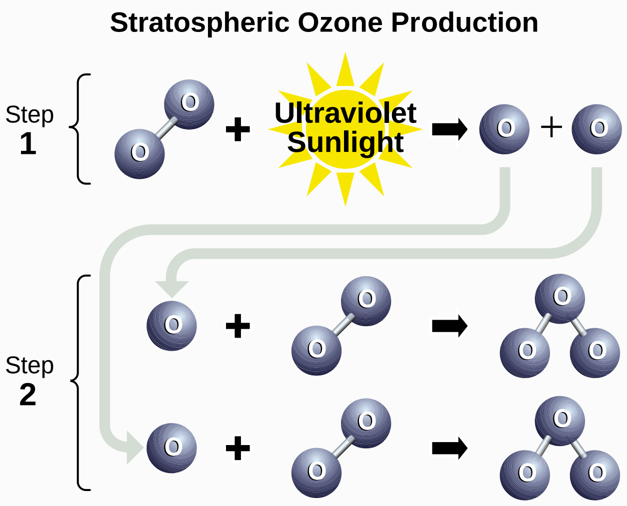
Figure Q1-2. Atmospheric ozone. Ozone is present throughout the lower atmosphere. Most ozone resides in the stratospheric "ozone layer" above Earth's surface. Increases in ozone occur near the surface as a result of pollution from human activities.

Q2: How is ozone formed in the atmosphere?

Ozone is formed throughout the atmosphere in multistep chemical processes that require sunlight. In the stratosphere, the process begins with the breaking apart of an oxygen molecule (O_2) by ultraviolet radiation from the Sun. In the lower atmosphere (troposphere), ozone is formed in a different set of chemical reactions involving hydrocarbons and nitrogen-containing gases.

Stratospheric ozone. Stratospheric ozone is naturally formed in chemical reactions involving ultraviolet sunlight and oxygen molecules, which make up 21% of the atmosphere. In the first step, sunlight breaks apart one oxygen molecule (O_2) to produce two oxygen atoms (2 O) (see ***Figure Q2-1***). In the second step, each atom combines with an oxygen molecule to produce an ozone molecule (O_3). These reactions occur continually wherever ultraviolet sunlight is present in the stratosphere. As a result, the greatest ozone production occurs in the tropical stratosphere.

The production of stratospheric ozone is balanced by its destruction in chemical reactions. Ozone reacts continually with a wide variety of natural and human-produced chemicals in the stratosphere. In each reaction, an ozone molecule is lost and other chemical compounds are produced. Important reactive gases that destroy ozone are those containing chlorine and bromine (see *Q8*).



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

Figure Q2-1. Stratospheric ozone production. 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, these atoms then undergo a binding collision with other oxygen molecules to form two ozone molecules. In the overall process, three oxygen molecules react to form two ozone molecules.

Some stratospheric ozone is transported down into the troposphere and can influence ozone amounts at Earth's surface, particularly in remote unpolluted regions of the globe.

Tropospheric ozone. Near Earth's surface, ozone is produced in chemical reactions involving naturally occurring gases and gases from pollution sources. Production reactions primarily involve hydrocarbon and nitrogen oxide gases and require sunlight. Fossil fuel combustion is a primary pollution source for tropospheric ozone production. The surface production of ozone does not significantly contribute to the abundance of stratospheric ozone. The amount of surface ozone is too small and the transport of surface air to the stratosphere is not effective enough. As in the stratosphere, ozone in the troposphere is destroyed in naturally occurring chemical reactions and in reactions involving human-produced chemicals. Tropospheric ozone can also be destroyed when ozone reacts with a variety of surfaces such as those of soils and plants.

Balance of chemical processes. Ozone abundances in the stratosphere and troposphere are determined by the *balance* between chemical processes that produce and destroy ozone. The balance is determined by the amounts of reacting gases and by how the rate or effectiveness of the various reactions varies with sunlight intensity, location in the atmosphere, temperature, and other factors. As atmospheric conditions change to favor ozone-production reactions in a certain location, ozone abundances will increase. Similarly, if conditions change to favor reactions that destroy ozone, its abundances will decrease. The balance of production and loss reactions combined with atmospheric air motions determines the global distribution of ozone on time scales of days to many months. Global ozone has decreased in the last decades because the amounts of reactive gases containing chlorine and bromine have increased in the stratosphere (see *Q13*).

Q3: Why do we care about atmospheric ozone?

Ozone in the stratosphere absorbs some of the Sun's biologically harmful ultraviolet radiation. Because of this beneficial role, stratospheric ozone is considered "good ozone." In contrast, ozone at Earth's surface that is formed from pollutants is considered "bad ozone" because it can be harmful to humans and plant and animal life. Some ozone occurs naturally in the lower atmosphere where it is beneficial because ozone helps remove pollutants from the atmosphere.

All ozone molecules are chemically identical, with each containing three oxygen atoms. However, ozone in the stratosphere has very different environmental consequences for humans and other life forms than ozone in the troposphere near Earth's surface.

Good ozone. Stratospheric ozone is considered "good" for humans and other life forms because it absorbs ultraviolet (UV)-B radiation from the Sun (see ***Figure Q3-1***). If not absorbed, UV-B would reach Earth's surface in amounts that are harmful to a variety of life forms. In humans, as their exposure to UV-B increases, so does their risk of skin cancer (see *Q17*), cataracts, and a suppressed immune system. The UV-B exposure before adulthood and cumulative exposure are both important factors in the risk. Excessive UV-B exposure also can damage terrestrial plant life, single-cell organisms, and aquatic ecosystems. Other UV radiation, UV-A, which is not absorbed significantly by ozone, causes premature aging of the skin.

The absorption of UV-B radiation by ozone is a source of heat in the stratosphere. This helps to maintain the stratosphere as a stable region of the atmosphere with temperatures increasing with altitude. As a result, ozone plays a key role in controlling the temperature structure of Earth's atmosphere.

Protecting good ozone. In the mid-1970s, it was discovered that some human-produced gases could cause stratospheric ozone depletion (see *Q6*). Ozone depletion increases harmful UV-B amounts at Earth's surface. Global efforts have been undertaken to protect the ozone layer through the regulation of ozone-depleting gases (see *Q15* and *Q16*).

Bad ozone. Ozone is also formed near Earth's surface in natural chemical reactions and in reactions caused by the presence of human-made pollutant gases. Ozone produced by pollutants is "bad" because more ozone comes in direct contact with humans, plants, and animals. Increased levels of ozone are generally harmful to living systems because ozone reacts strongly to destroy or alter many other molecules. Excessive ozone exposure reduces crop yields and forest growth. In humans, ozone exposure can reduce lung capacity; cause chest pains, throat irritation, and coughing; and worsen pre-existing health conditions related to the heart and lungs. In addition, increases in tropospheric ozone lead to a warming of Earth's surface (see *Q18*). The negative effects of increasing tropospheric ozone contrast sharply with the positive effects of stratospheric ozone as an absorber of harmful UV-B radiation from the Sun.

Reducing bad ozone. Reducing the emission of pollutants can reduce "bad" ozone in the air surrounding humans, plants, and animals. Major sources of pollutants include large cities where fossil fuel consumption and industrial activities are greatest. Many programs around the globe have already been successful in reducing the emission of pollutants that cause near-surface ozone production.

Natural ozone. Ozone is a natural component of the clean atmosphere. In the absence of human activities on Earth's surface, ozone would still be present near the surface and throughout the troposphere and stratosphere. Ozone's chemical role in the atmosphere includes helping to remove other gases, both those occurring naturally and those emitted by human activities. If all the ozone were to be removed from the lower atmosphere, other gases such as methane, carbon monoxide, and nitrogen oxides would increase in abundance.

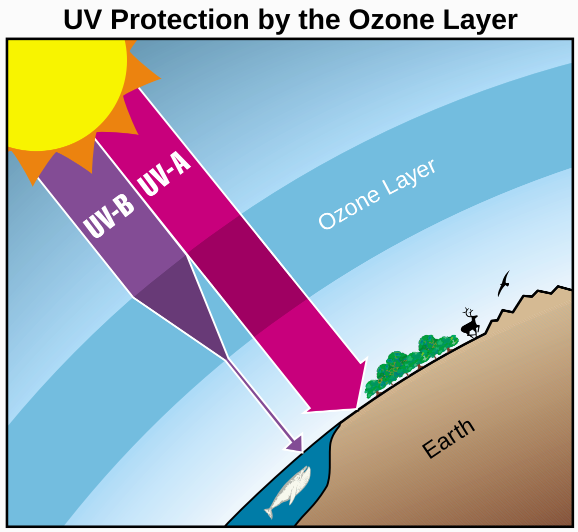

UV Protection by the Ozone Layer

Figure Q3-1. UV-B 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 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.

Q4: Is total ozone uniform over the globe?

No, the total amount of ozone above the surface of Earth varies with location on time scales that range from daily to seasonal. The variations are caused by stratospheric winds and the chemical production and destruction of ozone. Total ozone is generally lowest at the equator and highest near the poles because of the seasonal wind patterns in the stratosphere.

Total ozone. Total ozone at any location on the globe is found by measuring all the ozone in the atmosphere directly above that location. Total ozone includes that present in the stratospheric ozone layer and that present throughout the troposphere (see ***Figure Q1-2***). The contribution from the troposphere is generally only about 10% of total ozone. Total ozone values are often reported in *Dobson units,* denoted "DU." Typical values vary between 200 and 500 DU over the globe (see ***Figure Q4-1***). A total ozone value of 500 DU, for example, is equivalent to a layer of pure ozone gas on Earth's surface having a thickness of only 0.5 centimeters (0.2 inches).

Global distribution. Total ozone varies strongly with latitude over the globe, with the largest values occurring at middle and high latitudes (see ***Figure Q4-1***). This is a result of winds that circulate air in the stratosphere, moving tropical air rich in ozone toward the poles in fall and winter. Regions of low total ozone occur at polar latitudes in winter and spring as a result of the chemical destruction of ozone by chlorine and bromine gases (see *Q11* and *Q12*). The smallest values of total ozone (other than in the Antarctic in spring) occur in the tropics in all seasons, in part because the thickness of the ozone layer is smallest in the tropics.

Natural variations. The variations of total ozone with latitude and longitude come about for two reasons. First, natural air motions mix air between regions of the stratosphere that have high ozone values and those that have low ozone values. Air motions also increase the vertical thickness of the ozone layer near the poles, which increases the value of total ozone in those regions. Tropospheric weather systems can temporarily reduce the thickness of the stratospheric ozone layer in a region, lowering total ozone at the same time. Second, variations occur as a result of changes in the balance of chemical production and loss processes as air moves to new locations over the globe. Reductions in solar ultraviolet radiation exposure, for example, will reduce the production of ozone.

Scientists have a good understanding of how chemistry and air motion work together to cause the observed large-scale features in total ozone such as those seen in ***Figure Q4-1***. Ozone changes are carefully monitored by a large group of investigators using satellite, airborne, and ground-based instruments. The analysis of these observations helps scientists to estimate the contribution of human activities to ozone depletion.

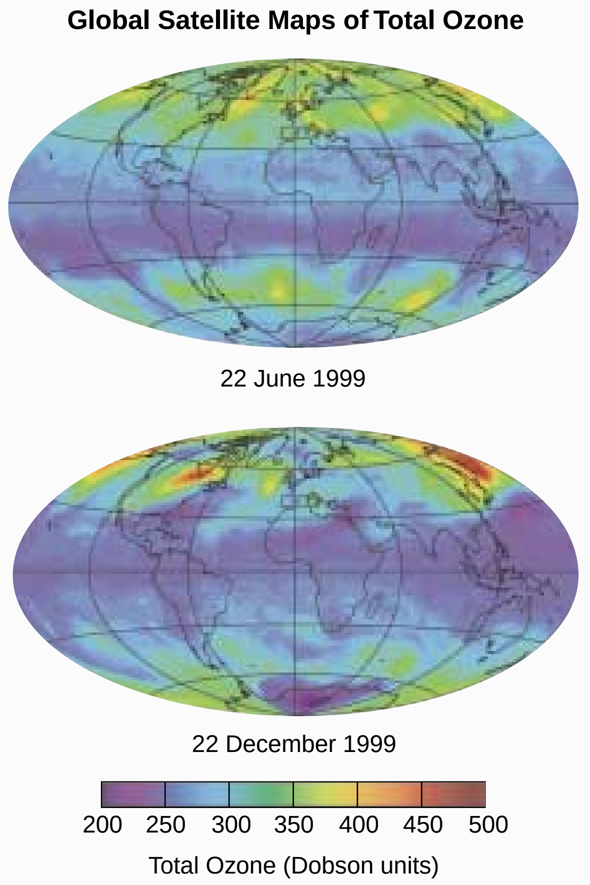


Figure Q4-1. *Total ozone.* A total ozone value is obtained by measuring all the ozone that resides in the atmosphere over a given location on Earth's surface. Total ozone values shown here are reported in "Dobson units" as measured by a satellite instrument from space. Total ozone varies with latitude, 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 (see *Q11*).

Q5: How is ozone measured in the atmosphere?

The amount of ozone in the atmosphere is measured by instruments on the ground and carried aloft in balloons, aircraft, and satellites. Some measurements involve drawing air into an instrument that contains a system for detecting ozone. Other measurements are based on ozone's unique absorption of light in the atmosphere. In that case, sunlight or laser light is carefully measured after passing through a portion of the atmosphere containing ozone.

The abundance of ozone in the atmosphere is measured by a variety of techniques (see ***Figure Q5-1***). The techniques make use of ozone's unique optical and chemical properties. There are two principal categories of measurement techniques: *direct* and *remote*. Ozone measurements by these techniques have been essential in monitoring changes in the ozone layer and in developing our understanding of the processes that control ozone abundances.

Direct measurements. Direct measurements of atmospheric ozone abundance are those that require air to be drawn directly into an instrument. Once inside an instrument, ozone can be measured by its absorption of ultraviolet (UV) light or by the electrical current produced in an ozone chemical reaction. The latter approach is used in the construction of "ozonesondes," which are lightweight ozone-measuring modules suitable for launching on small balloons. Small balloons ascend far enough in the atmosphere to measure ozone in the stratospheric ozone layer. Ozonesondes are launched weekly at many locations around the world. Direct ozone-measuring instruments using optical or chemical detection schemes are also used routinely on board research aircraft to measure the distribution of ozone in the troposphere and lower stratosphere. High-altitude research aircraft can reach the ozone layer at most locations over the globe and can reach farthest into the layer at high latitudes in polar regions. Ozone measurements are also being made on some commercial aircraft.

Remote measurements. Remote measurements of ozone abundance are obtained by detecting the presence of ozone at large distances away from the instrument. Most remote measurements of ozone rely on its unique absorption of UV radiation. Sources of UV radiation that can be used are the Sun and lasers. For example, satellites use the absorption of UV sunlight by the atmosphere or the absorption of sunlight scattered from the surface of Earth to measure ozone over the globe on a near-daily basis. A network of ground-based detectors measures ozone by the amount of the Sun's UV light that reaches Earth's surface. Other instruments measure ozone using its absorption of infrared or visible radiation or its emission of microwave or infrared radiation. Total ozone amounts and the altitude distribution of ozone can be obtained with remote measurement techniques. Lasers are routinely deployed at ground sites or on board aircraft to detect ozone over a distance of many kilometers along the laser light path.

Measuring Ozone in the Atmosphere

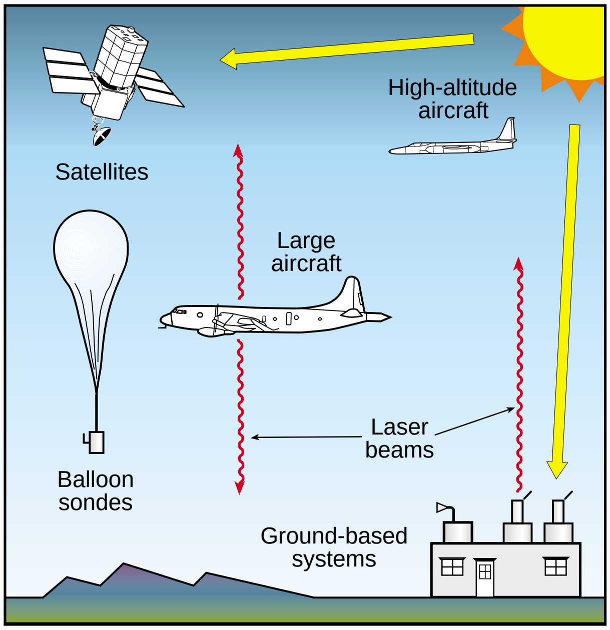


Figure Q5-1. Ozone measurements. Ozone is measured throughout the atmosphere with instruments on the ground and on board aircraft, high-altitude balloons, and satellites. Some instruments measure ozone directly in sampled air and others measure ozone remotely some distance away from the instrument. Instruments 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 weekly to monitor total ozone amounts.

II. THE OZONE DEPLETION PROCESS

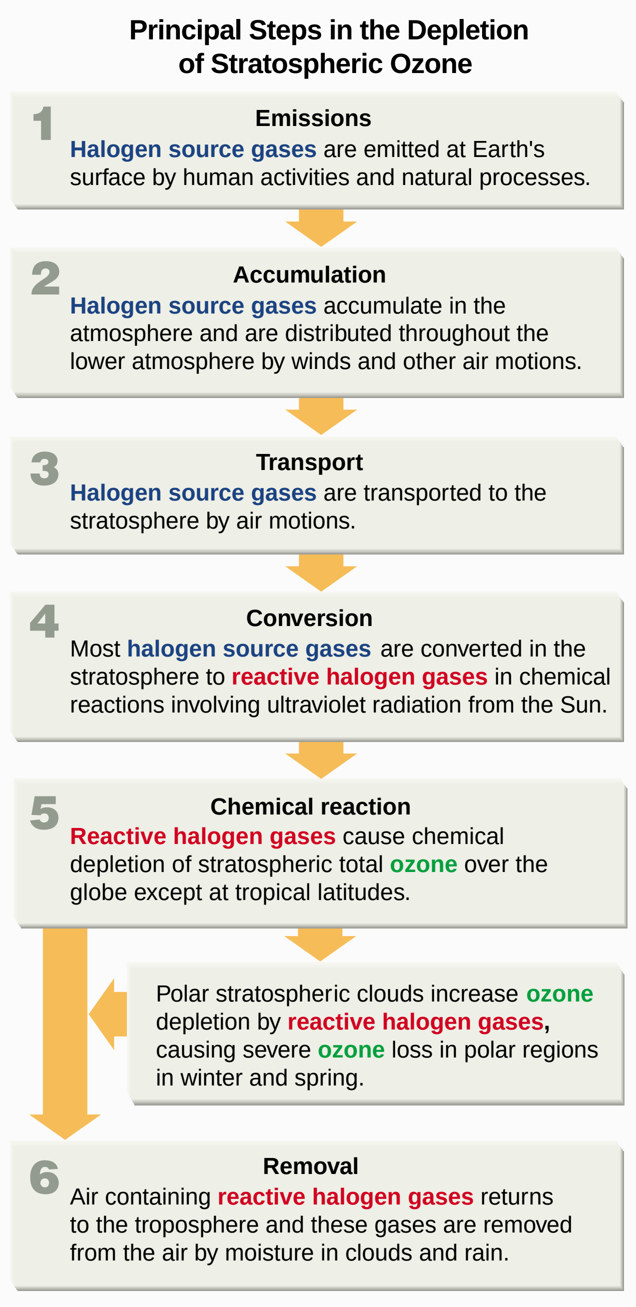
Q6: What are the principal steps in stratospheric ozone depletion caused by human activities?

The initial step in the depletion of stratospheric ozone by human activities is the emission of ozone-depleting gases containing chlorine and bromine at Earth's surface. Most of these gases accumulate in the lower atmosphere because they are unreactive and do not dissolve readily in rain or snow. Eventually, the emitted gases are transported to the stratosphere where they are converted to more reactive gases containing chlorine and bromine. These more reactive gases then participate in reactions that destroy ozone. Finally, when air returns to the lower atmosphere, these reactive chlorine and bromine gases are removed from Earth's atmosphere by rain and snow.

Emission, accumulation, and transport. The principal steps in stratospheric ozone depletion caused by human activities are shown in ***Figure Q6-1***. The process begins with the *emission* of halogen source gases at Earth's surface (see *Q7*). Halogen source gases include manufactured gases containing chlorine or bromine that are released to the atmosphere by a variety of human activities. Chlorofluorocarbons (CFCs), for example, are important chlorine-containing gases. These source gases *accumulate* in the lower atmosphere (troposphere) and are eventually *transported* to the stratosphere. The accumulation occurs because most source gases are unreactive in the lower atmosphere (troposphere). Small amounts of these gases dissolve in ocean waters.

Some emissions of halogen gases come from natural sources (see *Q7*). These emissions also accumulate in the troposphere and are transported to the stratosphere.

Conversion, reaction, and removal. Halogen source gases do not react directly with ozone. Once in the stratosphere, halogen source gases are chemically *converted* to reactive halogen gases by ultraviolet radiation from the Sun (see *Q8*). These reactive gases chemically destroy ozone in the stratosphere (see *Q9*). The average depletion of total ozone attributed to reactive gases is estimated to be small in the tropics and up to about 10% at middle latitudes (see *Q13*). In polar regions, the presence of polar stratospheric clouds greatly increases the abundance of the most reactive halogen gases (see *Q10*). This results in ozone destruction in polar regions in winter and



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.

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

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

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

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

Polar stratospheric clouds increase ozone depletion by reactive halogen gases, causing severe ozone loss in polar regions in winter and spring.

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.

Figure Q6-1. Principal steps in stratospheric ozone depletion. The stratospheric ozone depletion process begins with the emission of halogen source gases at Earth's surface and ends when reactive halogen gases are removed by rain and snow in the troposphere and deposited on Earth's surface. In the stratosphere, the reactive halogen gases, namely chlorine monoxide (ClO) and bromine monoxide (BrO), destroy ozone.

spring (see *Q11* and *Q12*). After a few years, air in the stratosphere returns to the troposphere, bringing along reactive halogen gases. These gases are then *removed* from the atmosphere by rain and other precipitation and deposited on Earth's surface. This removal brings to an end the destruction of ozone by chlorine and bromine atoms that were first released to the atmosphere as components of halogen source gas molecules.

Tropospheric conversion. Halogen source gases with short lifetimes (see *Q7*) undergo significant chemical conversion in the troposphere, producing reactive halogen gases and other compounds. Source gas molecules that are not converted accumulate in the troposphere and are transported to the stratosphere. Because of removal by precipitation, only small portions of the reactive halogen gases produced in the troposphere are also transported to the stratosphere. Important examples of gases that undergo some tropospheric removal are the HCFCs, which are used as substitute gases for other halogen source gases (see *Q15* and *Q16*), bromoform, and gases containing iodine (see *Q7*).

Understanding Stratospheric Ozone Depletion

Scientists learn about ozone destruction through a combination of laboratory studies, computer models, and stratospheric observations. In *laboratory studies* scientists are able to discover and evaluate individual chemical reactions that also occur in the stratosphere. Chemical reactions between two gases follow well-defined physical rules. Some of these reactions occur on the surfaces of particles formed in the stratosphere. Reactions have been studied that involve a wide variety of molecules containing chlorine, bromine, fluorine, and iodine and other atmospheric constituents such as oxygen, nitrogen, and hydrogen. These studies show that there exist several reactions involving chlorine and bromine that can directly or indirectly cause ozone destruction in the atmosphere.

With *computer models*, scientists can examine the overall effect of a large group of known reactions under the chemical and physical conditions found in the stratosphere. These models include winds, air temperatures, and the daily and seasonal changes in sunlight. With such analyses, scientists have shown that chlorine and bromine can react in catalytic cycles in which one chlorine or bromine atom can destroy many ozone molecules. Scientists use model results to compare with past observations as a test of our understanding of the atmosphere and to evaluate the importance of new reactions found in the laboratory. Computer models also enable scientists to explore the future by changing atmospheric conditions and other model parameters.

Scientists make *stratospheric observations* to find out what gases are present in the stratosphere and at what concentrations. Observations have shown that halogen source gases and reactive halogen gases are present in the stratosphere at expected amounts. Ozone and chlorine monoxide (ClO), for example, have been observed extensively with a variety of instruments. Instruments on the ground and on board satellites, balloons, and aircraft detect ozone and ClO at a distance using optical and microwave signals. High-altitude aircraft and balloon instruments detect both gases directly in the stratosphere. For example, these observations show that ClO is present at elevated amounts in the Antarctic and Arctic stratospheres in the winter/spring season, when the most severe ozone depletion occurs.

Q7: What emissions from human activities lead to ozone depletion?

Certain industrial processes and consumer products result in the atmospheric emission of "halogen source gases." These gases contain chlorine and bromine atoms, which are known to be harmful to the ozone layer. For example, the chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), once used in almost all refrigeration and air conditioning systems, eventually reach the stratosphere where they are broken apart to release ozone-depleting chlorine atoms. Other examples of human-produced ozone-depleting gases are the "halons," which are used in fire extinguishers and which contain ozone-depleting bromine atoms. The production and consumption of all principal halogen source gases by human activities are regulated worldwide under the Montreal Protocol.

Human-produced chlorine and bromine gases. Human activities cause the emission of *halogen source gases* that contain chlorine and bromine atoms. These emissions into the atmosphere ultimately lead to stratospheric ozone depletion. The source gases that contain only carbon, chlorine, and fluorine are called "chlorofluorocarbons," usually abbreviated as CFCs. CFCs, along with carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3), are the most important chlorine-containing gases that are emitted by human activities and destroy stratospheric ozone

Primary Sources of Chlorine and Bromine for the Stratosphere in 1999

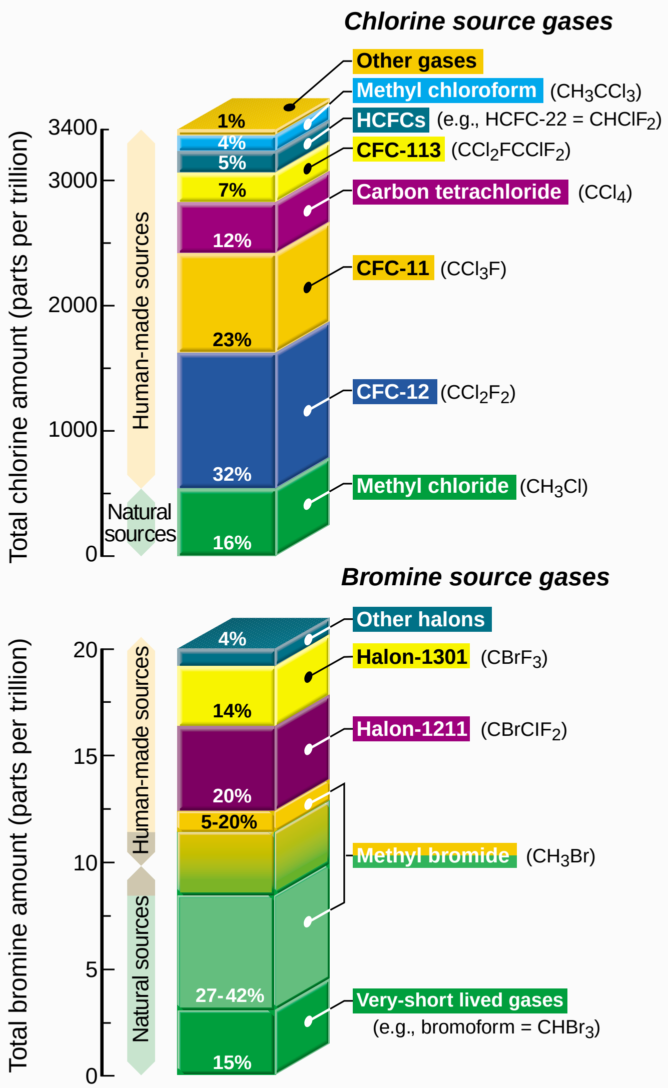


Figure Q7-1. Stratospheric source gases. A variety of gases transport chlorine and bromine into the stratosphere. These gases, called halogen source gases, are emitted from natural sources and human activities. For chlorine, human activities account for most that reaches the stratosphere. The CFCs are the most abundant of the chlorine-containing gases released in human activities. Methyl chloride is the most important natural source of chlorine. 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 the total for bromine than for 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 abundance scale shows that the amount of chlorine in the stratosphere is greater than that of bromine by about 170 times. (The unit "parts per trillion" is a measure of the relative abundance of a gas: 1 part per trillion indicates the presence of one molecule of a gas per trillion other molecules.)

Table Q7-1. Atmospheric lifetimes, emissions, and Ozone Depletion Potentials of halogen source gases. [a]

Halogen Source Gas	Lifetime (years)	Global Emissions in 2000 (gigagrams per year) [b]	Ozone Depletion Potential (ODP)
Chlorine			
CFC-12	100	130-160	1
CFC-113	85	10-25	1
CFC-11	45	70-110	1
Carbon tetrachloride	26	70-90	0.73
HCFCs	1-26	340-370	0.02-0.12
Methyl chloroform	5	~20	0.12
Methyl chloride	1.3	3000-4000	0.02
Bromine			
Halon-1301	65	~3	12
Halon-1211	16	~10	6
Methyl bromide	0.7	160-200	0.38
Very short-lived gases	Less than 1	[c]	[c]

[a] Includes both human activities and natural sources.

[b] 1 gigagram = 10^9 grams = 1000 metric tons.

[c] No reliable estimate available.

(see ***Figure Q7-1***). Chlorine-containing gases have been used in many applications including refrigeration, air conditioning, foam blowing, aerosol propellants, and cleaning of metals and electronic components. These activities have typically caused the emission of halogen-containing gases to the atmosphere.

Another category of halogen source gases contains bromine. The most important of these are the "halons" and methyl bromide (CH_3Br). Halons are halogenated hydrocarbon gases originally developed to extinguish fires. Halons are widely used to protect large computers, military hardware, and commercial aircraft engines. Because of these uses, halons are often directly released into the atmosphere. Halon-1211 and Halon-1301 are the most abundant halons emitted by human activities (see ***Figure Q7-1***). Methyl bromide, used primarily as an agricultural fumigant, is also a significant source of bromine to the atmosphere.

Human emissions of chlorine- and bromine-containing gases have increased substantially since the middle of the 20th century (see *Q16*). The result has been global ozone depletion with the greatest losses occurring in polar regions (see *Q11* to *Q13*).

Natural sources of chlorine and bromine. There are two halogen source gases present in the stratosphere that have large natural sources. These are methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), both of which are emitted by oceanic and terrestrial ecosystems. Natural sources of these two gases contribute about 16% of the chlorine currently in the stratosphere, and about 27-42% of the bromine (see ***Figure Q7-1***). Very short-lived gases containing bromine, such as bromoform ($CHBr_3$), are also released to the atmosphere by the oceans. The estimated contribution of these gases to stratospheric bromine (about 15%) is uncertain at this time. Changes in the natural sources of chlorine and bromine since the middle of the 20th century are not the cause of observed ozone depletion.

Lifetimes and emissions. After emission, halogen source gases are either removed from the atmosphere or undergo chemical conversion. The time to remove or convert about 60% of a gas is often called its atmospheric "lifetime". Lifetimes vary from less than 1 year to 100 years for the principal chlorine- and bromine-containing gases (see ***Table Q7-1***). Gases with the shortest lifetimes (e.g., the HCFCs, methyl bromide, methyl chloride, and the very short-lived gases) are significantly destroyed in the troposphere, and therefore only a fraction of the emitted gas contributes to ozone depletion in the stratosphere.

The amount of a halogen source gas present in the atmosphere depends on the lifetime of the gas and the amount emitted to the atmosphere. Emissions vary greatly for the principal source gases, as indicated in ***Table Q7-1***. Emissions of most gases regulated by the Montreal Protocol have decreased since 1990, and emissions from all regulated gases are expected to decrease in the coming decades (see *Q16*).

Ozone Depletion Potential. The halogen source gases in ***Figure Q7-1*** are also known as "ozone-depleting substances" because they are converted in the stratosphere to reactive gases containing chlorine and bromine (see *Q8*). Some of these reactive gases participate in reactions that destroy ozone (see *Q9*). Ozone-depleting substances are compared in their effectiveness to destroy stratospheric ozone using the "Ozone Depletion Potential" (ODP), as listed in ***Table Q7-1***. A gas with a larger ODP has a greater potential to destroy ozone over its lifetime in the atmosphere. The ODP is calculated on a "per mass" basis for each gas relative to CFC-11, which has an ODP defined to be 1. Halon-1211 and Halon-1301 have ODPs significantly larger than CFC-11 and most other emitted gases. This results because bromine is much more effective overall (about 45 times) on a per-atom basis than chlorine in chemical reactions that destroy ozone in the stratosphere. The gases with small

ODP values generally have short atmospheric lifetimes. The production and consumption of all principal halogen source gases by humans are regulated under the provisions of the Montreal Protocol (see *Q15*).

Fluorine and iodine. Fluorine and iodine are also halogen atoms. Most of the source gases in ***Figure Q7-1*** also contain fluorine atoms in addition to chlorine or bromine. After the source gases undergo conversion in the stratosphere (see *Q6*), the fluorine content of these gases is left in chemical forms that do not destroy ozone. Iodine is a component of several gases that are naturally emitted from the oceans. Although iodine will participate in ozone destruction reactions, these iodine-containing gases are largely removed in the troposphere by natural processes before the gases can reach the stratosphere.

Other gases. Other gases that influence stratospheric ozone abundances also have increased in the stratosphere as a result of human activities. Important examples are methane (CH_4) and nitrous oxide (N_2O), which react to form water vapor and reactive hydrogen and nitrogen oxides, respectively, in the stratosphere. These reactive products also participate in the production and loss balance of stratospheric ozone (see *Q2*). The overall affect of these other gases on ozone is much smaller than that caused by increases in chlorine- and bromine-containing gases from human activities.

Heavier-Than-Air CFCs

CFCs and other halogen source gases reach the stratosphere despite the fact they are “heavier than air.” All the principal source gases are emitted and accumulate in the lower atmosphere (troposphere). Air containing the emitted halogen gases is in continual motion as a result of winds and convection. Air motions ensure that the source gases are horizontally and vertically well mixed throughout the troposphere in a matter of months. It is this well-mixed air that enters the lower stratosphere from upward air motions in tropical regions, bringing with it source gas molecules emitted from a wide variety of locations on Earth’s surface.

Atmospheric measurements confirm that halogen source gases with long atmospheric lifetimes are well mixed in the troposphere and are present in the stratosphere (see ***Figure Q8-2***). The amounts found in these regions are consistent with the emissions estimates reported by industry and government. Measurements also show that gases that are “lighter than air,” such as hydrogen (H_2) and methane (CH_4), are also well mixed in the troposphere, as expected. Only at altitudes well above the troposphere and stratosphere (above 85 kilometers (53 miles)), where much less air is present, do heavy gases begin to separate from lighter gases as a result of gravity.

Q8: What are the reactive halogen gases that destroy stratospheric ozone?

Emissions from human activities and natural processes are large sources of chlorine- and bromine-containing gases for the stratosphere. When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to more reactive gases also containing chlorine and bromine. Important examples of the reactive gases that destroy stratospheric ozone are chlorine monoxide (ClO) and bromine monoxide (BrO). These and other reactive gases participate in "catalytic" reaction cycles that efficiently destroy ozone. Volcanoes can emit some chlorine-containing gases, but these gases are ones that readily dissolve in rainwater and ice and are usually "washed out" of the atmosphere before they can reach the stratosphere.

Reactive gases containing the halogens chlorine and bromine lead to the chemical destruction of stratospheric ozone. Halogen-containing gases present in the stratosphere can be divided into two groups: *halogen source gases* and *reactive halogen gases*. The source gases are emitted at Earth's surface by natural processes and by human activities (see *Q7*). Once they reach the stratosphere, the halogen source gases chemically convert to form the reactive halogen gases.

Reactive halogen gases. The chemical conversion of halogen source gases, which involves ultraviolet sunlight and other chemical reactions, produces a number of reactive halogen gases. These reactive gases contain all of the chlorine and bromine atoms originally present in the source gases.

The most important reactive chlorine- and bromine-containing gases that form in the stratosphere are shown in ***Figure Q8-1***. Away from polar regions, the most abundant are hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$). These two gases are considered *reservoir* gases because they do not react directly with ozone but can be converted to the most reactive forms that do chemically destroy ozone. The *most reactive* forms are chlorine monoxide (ClO) and bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). A large fraction of available stratospheric bromine is generally in the form of BrO whereas usually only a small fraction of stratospheric chlorine is in the form of ClO. In polar regions, the reservoirs $ClONO_2$ and HCl undergo a further conversion on polar stratospheric clouds (see *Q10*) to form ClO. In that case, ClO becomes a large fraction of available reactive chlorine.

Reactive chlorine observations. Reactive chlorine gases have been observed extensively in the stratosphere with both direct and remote measurement techniques. The measurements from space at middle latitudes displayed in ***Figure Q8-2*** are representative of how chlorine-containing gases change between the surface and the upper stratosphere. Available chlorine (see red line in ***Figure Q8-2***) is the sum of chlorine contained in halogen source gases and

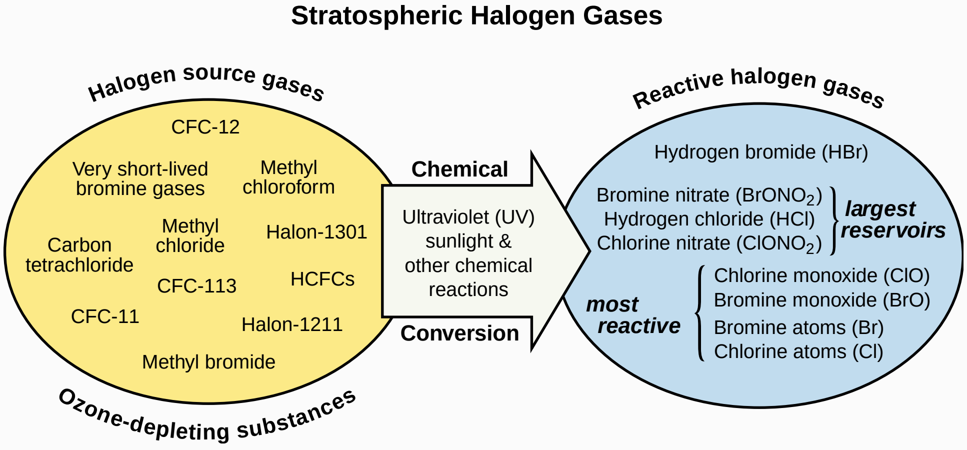


Figure Q8-1. Conversion of halogen source gases. Halogen source gases (also known as ozone-depleting substances) are chemically converted to reactive halogen gases primarily in the stratosphere. The conversion requires ultraviolet sunlight and a few other chemical reactions. The short-lived gases undergo some conversion in the troposphere. The reactive halogen gases contain all the chlorine and bromine originally present in the source gases. Some reactive gases serve as reservoirs of chlorine and bromine whereas others participate in ozone destruction cycles.

the reactive gases HCl, $ClONO_2$, ClO, and other minor gases. Available chlorine is constant within a few percent from the surface to 47 kilometers (31 miles) altitude. In the troposphere, available chlorine is contained almost entirely in the source gases described in ***Figure Q7-1***. At higher altitudes, the source gases become a smaller fraction of available chlorine as they are converted to reactive chlorine gases. At the highest altitudes, available chlorine is all in the form of reactive chlorine gases.

In the altitude range of the ozone layer, as shown in ***Figure Q8-2***, the reactive chlorine gases HCl and $ClONO_2$ account for most of available chlorine. ClO, the most reactive gas in ozone depletion, is a small fraction of available chlorine. This small value limits the amount of ozone destruction that occurs outside of polar regions.

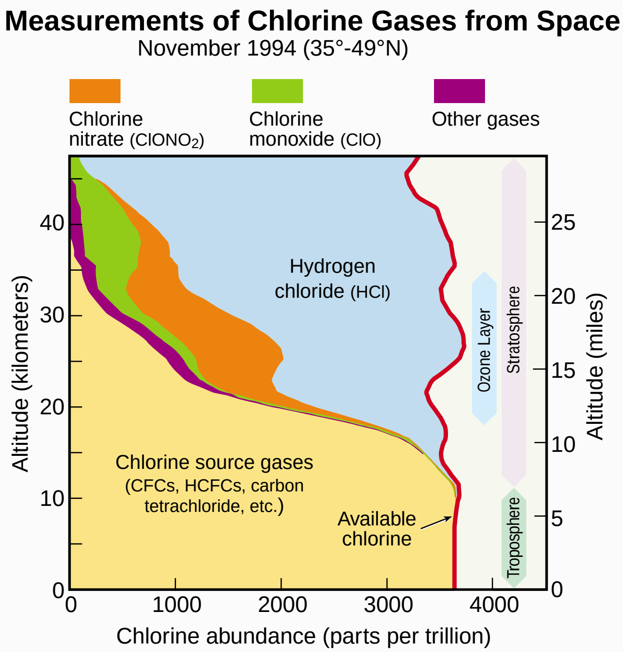


Figure Q8-2. Reactive chlorine gas observations. Reactive chlorine gases and chlorine source gases can be measured from space. These abundance measurements made over midlatitudes, for example, show that chlorine-containing source gases are present in the troposphere and that reactive chlorine gases are present in the stratosphere. In the stratosphere, reactive chlorine gases increase with altitude and chlorine source gases decrease with altitude. This results because the source gases are converted to reactive gases in chemical reactions involving ultraviolet sunlight. The principal reactive gases formed are HCl, $ClONO_2$, and ClO. The sum of reactive gases and source gases gives 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. (The unit "parts per trillion" is defined in the caption of ***Figure Q7-1***.)

Reactive chlorine in polar regions. Reactive chlorine gases in polar regions in summer look similar to the altitude profiles shown in ***Figure Q8-2***. In winter, however, the presence of polar stratospheric clouds (PSCs) causes further chemical changes (see *Q10*). PSCs convert HCl and $ClONO_2$ to ClO when temperatures are near minimum values in the winter Arctic and Antarctic stratosphere. In that case, ClO becomes the principal reactive chlorine species in sunlit regions and ozone loss becomes very rapid. An example of the late-winter ClO and ozone distributions is shown in ***Figure Q8-3*** for the Antarctic stratosphere. These space-based measurements show that ClO abundances are high in the lower stratosphere over a region that exceeds the size of the Antarctic continent (greater than 13 million square kilometers or 5 million square miles). The peak abundance of ClO exceeds 1500 parts per trillion, which is much larger than typical midlatitude values shown in ***Figure Q8-2*** and represents a large fraction of reactive chlorine in that altitude region. Because high ClO amounts cause rapid ozone loss (see *Q9*), ozone depletion is found in regions of elevated ClO (see ***Figure Q8-3***).

Reactive bromine observations. Fewer measurements are available for reactive bromine gases than for reactive chlorine, in part because of the low abundance of bromine in the stratosphere. The most widely observed bromine gas is bromine monoxide (BrO). The measured abundances are consistent with values expected from the conversion of the bromine-containing source gases such as the halons and methyl bromide.

Other sources. Some reactive halogen gases are also produced at Earth's surface by natural processes and by human activities. However, because reactive halogen gases are soluble in water, almost all become trapped in the lower atmosphere by dissolving in rainwater and ice, and ultimately are returned to Earth's surface before they can reach the stratosphere. For example, reactive chlorine is present in the atmosphere as sea salt (sodium chloride) produced by evaporation of ocean spray. Because sea salt dissolves in water, this chlorine is removed and does not reach the stratosphere in appreciable quantities. Another ground-level source is emission of chlorine gases from swimming pools, household bleach, and other uses. When released to the atmosphere, this chlorine is rapidly converted to forms that are soluble in water and removed. The Space Shuttle and other rocket motors release reactive chlorine gases directly in the stratosphere. In that case the quantities are very small in comparison with other stratospheric sources.

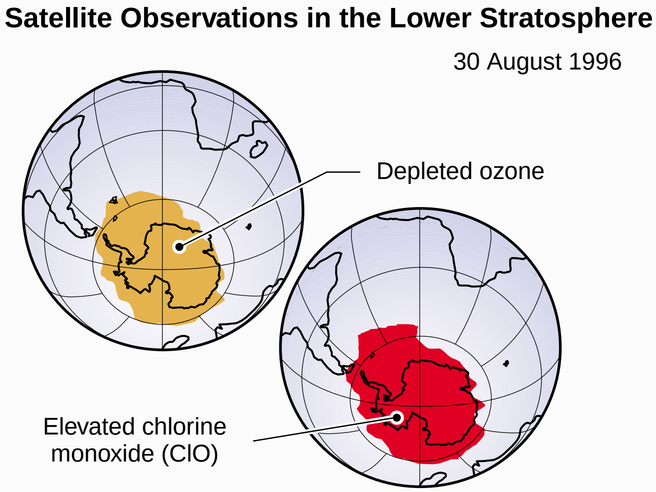


Figure Q8-3. Antarctic chlorine monoxide and ozone. Satellite instruments monitor ozone and reactive chlorine gases in the global stratosphere. Results are shown here for Antarctic winter for a narrow altitude region within the ozone layer. In winter, chlorine monoxide (ClO) reaches high values (1500 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. Ozone values measured simultaneously within the ozone layer show very depleted values.

Volcanoes. Volcanic plumes generally contain large quantities of chlorine in the form of hydrogen chloride (HCl). Because the plumes also contain a considerable amount of water vapor, the HCl is efficiently scavenged by rainwater and ice and removed from the atmosphere. As a result, most of the HCl in the plume does not enter the stratosphere. After large recent eruptions, the increase in HCl in the stratosphere has been small compared with the total amount of chlorine in the stratosphere from other sources.

Global Ozone Dobson Network

The first instrument for routine monitoring of total ozone was developed by Gordon M. B. Dobson in the 1920s. The instrument measures the intensity of sunlight at two ultraviolet wavelengths: one that is strongly absorbed by ozone and one that is weakly absorbed. The difference in light intensity at the two wavelengths is used to provide a measurement of total ozone above the instrument location.

A global network of ground-based, total ozone observing stations was established in 1957 as part of the International Geophysical Year. Today, there are about 100 sites distributed throughout the world (from South Pole, Antarctica (90°S) to Ellesmere Island, Canada (83°N)), many of which routinely measure total ozone with Dobson instruments. The accuracy of these observations is maintained by regular calibrations and intercomparisons. Data from the network have been essential for understanding the effects of chlorofluorocarbons (CFCs) and other ozone-depleting gases on the global ozone layer, starting before the launch of space-based ozone-measuring instruments and continuing to the present day. Because of their stability and accuracy, the Dobson instruments are now routinely used to help calibrate space-based observations of total ozone.

Pioneering scientists have traditionally been honored by having units of measure named after them. Accordingly, the unit of measure for total ozone is called the "Dobson unit" (see *Q4*).

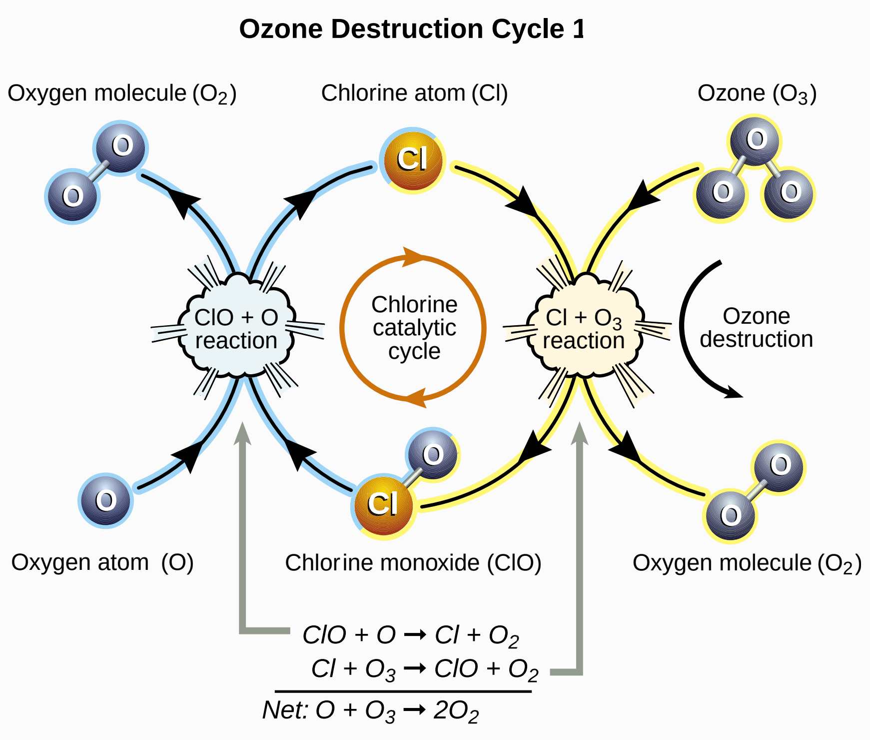
Q9: What are the chlorine and bromine reactions that destroy stratospheric ozone?

Reactive gases containing chlorine and bromine destroy stratospheric ozone in "catalytic" cycles made up of two or more separate reactions. As a result, a single chlorine or bromine atom can destroy many hundreds of ozone molecules before it reacts with another gas, breaking the cycle. In this way, a small amount of reactive chlorine or bromine has a large impact on the ozone layer. Special ozone destruction reactions occur in polar regions because the reactive gas chlorine monoxide reaches very high levels there in the winter/spring season.

Stratospheric ozone is destroyed by reactions involving *reactive halogen gases*, which are produced in the chemical conversion of *halogen source gases* (see ***Figure Q8-1***). The most reactive of these gases are chlorine monoxide (ClO) and bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). These gases participate in three principal reaction cycles that destroy ozone.

Cycle 1. Ozone destruction Cycle 1 is illustrated in ***Figure Q9-1***. The cycle is made up of two basic reactions: ClO + O and Cl + O_3. The net result of Cycle 1 is to convert one ozone molecule and one oxygen atom into two oxygen molecules. In each cycle chlorine acts as a *catalyst* because ClO and Cl react and are reformed. In this way, one Cl atom participates in many cycles, destroying many ozone molecules. For typical stratospheric conditions at middle or low latitudes, a single chlorine atom can destroy hundreds of ozone molecules before it reacts with another gas to break the catalytic cycle.

Polar Cycles 2 and 3. The abundance of ClO is greatly increased in polar regions during winter as a result of reactions on the surfaces of polar stratospheric cloud (PSC) particles (see *Q10*). Cycles 2 and 3 (see ***Figure Q9-2***) become the dominant reaction mechanisms for polar ozone loss because of the high abundances of ClO and the relatively low abundance of atomic oxygen (which limits the rate of ozone loss by Cycle 1). Cycle 2 begins with the self-reaction of ClO. Cycle 3, which begins with the reaction of ClO with BrO, has two reaction pathways to produce either Cl and Br or BrCl. The net result of both cycles is to destroy two ozone molecules and create three oxygen molecules. Cycles 2 and 3 account for most of the ozone loss observed in the Arctic and Antarctic stratospheres in the late winter/spring season (see *Q11* and *Q12*). At high ClO abundances, the rate of ozone destruction can reach 2 to 3% per day in late winter/spring.



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

Figure Q9-1. Ozone destruction Cycle 1. 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.

Ozone Destruction Cycles

Cycle 2

$$\mathrm{ClO + ClO \rightarrow (ClO)_2}$$

$$\mathrm{(ClO)_2 + sunlight \rightarrow ClOO + Cl}$$

$$\mathrm{ClOO \rightarrow Cl + O_2}$$

$$\mathrm{2(Cl + O_3 \rightarrow ClO + O_2)}$$

$$\mathrm{Net{:}\ 2O_3 \rightarrow 3O_2}$$

Cycle 3

$$\mathrm{ClO + BrO \rightarrow Cl + Br + O_2}$$

$$\text{or} \left(\begin{array}{l} \mathrm{ClO + BrO \rightarrow BrCl + O_2} \\ \mathrm{BrCl + sunlight \rightarrow Cl + Br} \end{array} \right)$$

$$\mathrm{Cl + O_3 \rightarrow ClO + O_2}$$

$$\mathrm{Br + O_3 \rightarrow BrO + O_2}$$

$$\mathrm{Net{:}\ 2O_3 \rightarrow 3O_2}$$

Figure Q9-2. Polar ozone destruction Cycles 2 and 3. Significant destruction of ozone occurs in polar regions because ClO abundances reach large values. In that 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 in ***Figure Q9-1***, because chlorine and bromine react and are reformed in each cycle. Sunlight is required to complete each cycle and to help form and maintain ClO abundances.

Sunlight requirement. Sunlight is required to complete and maintain Cycles 1 through 3. Cycle 1 requires sunlight because atomic oxygen is formed only with ultraviolet sunlight. Cycle 1 is most important in the stratosphere at tropical and middle latitudes where sunlight is most intense.

In Cycles 2 and 3, sunlight is required to complete the reaction cycles and to maintain ClO abundances. In the continuous darkness of winter in the polar stratospheres, reaction Cycles 2 and 3 cannot occur. It is only in late winter/spring when sunlight returns to the polar regions that these cycles can occur. Therefore, the greatest destruction of ozone occurs in the partially to fully sunlit periods after midwinters in the polar stratospheres. The sunlight needed in Cycles 2 and 3 is not sufficient to form ozone because ozone formation requires ultraviolet sunlight. In the stratosphere in the winter/spring period, ultraviolet sunlight is weak because Sun angles are low. As a result, ozone is destroyed in Cycles 2 and 3 in the sunlit winter stratosphere but is not produced in significant amounts.

Other reactions. Atmospheric ozone abundances are controlled by a wide variety of reactions that both produce and destroy ozone (see *Q2*). Chlorine and bromine catalytic reactions are but one group of ozone destruction reactions. Reactive hydrogen and reactive nitrogen gases, for example, are involved in other catalytic ozone-destruction cycles that also occur in the stratosphere. These reactions occur naturally in the stratosphere and their importance has not been as strongly influenced by human activities as have reactions involving halogens.

Q10: Why has an "ozone hole" appeared over Antarctica when ozone-depleting gases are present throughout the stratosphere?

Ozone-depleting gases are present throughout the stratospheric ozone layer because they are transported great distances by atmospheric air motions. The severe depletion of the Antarctic ozone layer known as the "ozone hole" forms because of the special weather conditions that exist there and nowhere else on the globe. The very cold temperatures of the Antarctic stratosphere create ice clouds called polar stratospheric clouds (PSCs). Special reactions that occur on PSCs and the relative isolation of polar stratospheric air allow chlorine and bromine reactions to produce the ozone hole in Antarctic springtime.

The severe depletion of stratospheric ozone in Antarctic winter is known as the "ozone hole" (see *Q11*). Severe depletion first appeared over Antarctica because atmospheric conditions there increase the effectiveness of ozone destruction by reactive halogen gases (see *Q8*). The formation of the Antarctic ozone hole requires abundant reactive halogen gases, temperatures low enough to form polar stratospheric clouds (PSCs), isolation of air from other stratospheric regions, and sunlight.

Distributing halogen gases. Halogen source gases emitted at Earth's surface are present in comparable abundances throughout the stratosphere in both hemispheres even though most of the emissions occur in the Northern Hemisphere. The abundances are comparable because most source gases have no important natural removal processes in the lower atmosphere and because winds and warm-air convection redistribute and mix air efficiently throughout the troposphere. Halogen gases (in the form of source gases and some reactive products) enter the stratosphere primarily from the tropical troposphere. Atmospheric air motions then transport them upward and toward the poles in both hemispheres.

Low temperatures. The severe ozone destruction represented by the ozone hole requires that low temperatures be present over a range of stratospheric altitudes, over large geographical regions, and for extended time periods. Low temperatures are important because they allow polar stratospheric clouds (PSCs) to form.

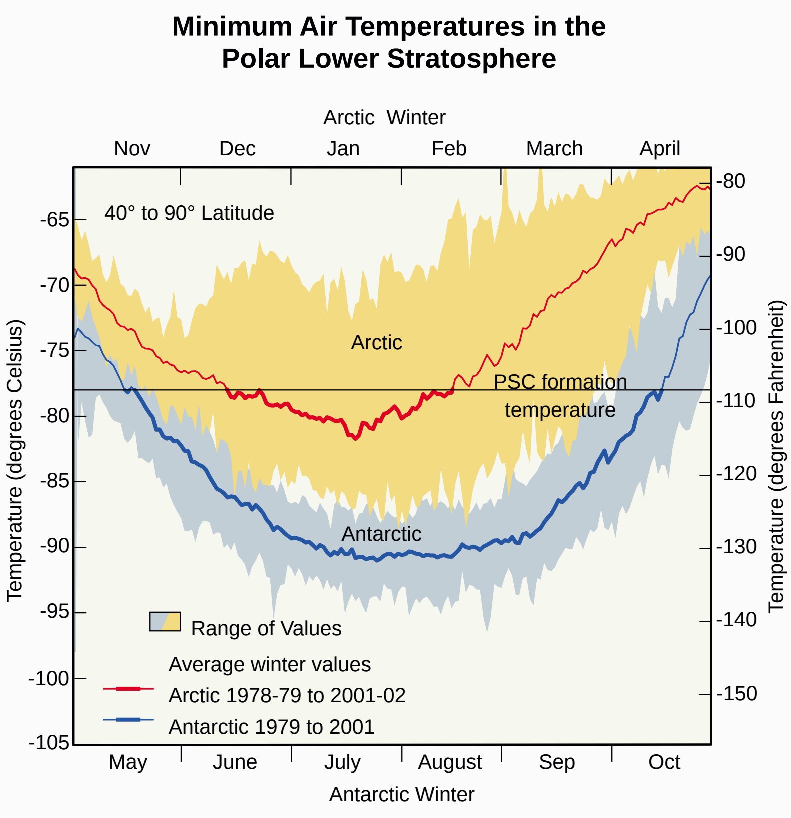


Figure Q10-1. Arctic and Antarctic temperatures. Stratospheric air temperatures in both polar regions reach minimum values in the lower stratosphere in the winter season. Minimum values over Antarctica reach –90°C in July and August in an average year. Over the Arctic, minimum average values are near –80°C in January and February. Polar stratospheric clouds (PSCs) are formed when winter temperatures fall below the formation temperature (about –78°C). This occurs on average for weeks to months over both poles (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 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 formed over many months, and severe ozone depletion now occurs in each winter season.

Reactions on the surfaces of the cloud particles initiate a remarkable increase in the most reactive halogen gases (see below and *Q8*). Temperatures are lowest in the stratosphere over both polar regions in winter. In the Antarctic winter, minimum temperatures are generally lower and less variable than in the Arctic winter (see ***Figure Q10-1***). Antarctic temperatures also remain below the PSC formation temperature for much longer periods during winter. This occurs, in part, because there are significant differences between the hemispheres in the distributions of land, ocean, and mountains at middle and high latitudes. The winter temperatures are low enough for PSCs to form for nearly the entire Antarctic winter but usually only for part of every Arctic winter.

Isolated conditions. Air in the polar stratospheric regions is relatively isolated from other stratospheric regions for long periods in the winter months. The isolation comes about because of strong winds that encircle the poles, preventing substantial motion of air in or out of the polar stratospheres. The isolation is much more effective in the Antarctic. Once chemical changes occur in the low-temperature air as a result of the presence of PSCs, the changes remain for many weeks to months.

Polar stratospheric clouds (PSCs). Polar stratospheric clouds cause changes in the abundances of reactive chlorine gases. Reactions occur on the surfaces of PSC particles that convert the reservoir forms of reactive chlorine gases, $ClONO_2$ and HCl, to the most reactive form ClO (see ***Figure Q8-1***). ClO increases from a small fraction of available reactive chlorine gases to nearly all that is available (see *Q8*). With increased ClO, additional catalytic cycles involving ClO and BrO become active in the chemical destruction of ozone when sunlight is available (see *Q9*).

PSCs form when stratospheric temperatures fall below about –78°C (–108°F) in polar regions. As a result, PSCs are often found over vast areas of the winter polar regions and over a significant altitude range. At low polar temperatures, nitric acid (HNO_3) and sulfur-containing gases condense with water vapor to form solid and liquid PSC particles. At even lower temperatures, ice particles also form. PSC particles grow large enough and are numerous enough that cloud-like features can be observed from the ground under certain conditions, particularly when the Sun is near the horizon (see ***Figure Q10-2***). PSCs are often found near mountain ranges in polar regions because the motion of air over the mountains can cause local cooling of stratospheric air.

When temperatures warm in spring, PSCs no longer form and the production of ClO ends. Without continued ClO production, ClO amounts decrease as other chemical reactions reform $ClONO_2$ and HCl. As a result, the intense period of ozone depletion ends.

PSC removal. Once formed, PSC particles move downward because of gravity. The largest particles move down several kilometers or more in the stratosphere during the low-temperature winter/spring period. Because most PSCs contain nitric acid, their downward motion removes nitric acid from regions of the ozone layer. That process is called *denitrification*. With less nitric acid, the highly reactive chlorine gas ClO remains chemically active for a longer period, thereby increasing chemical ozone destruction. Because PSC formation temperatures are required (see ***Figure Q10-1***), denitrification occurs each winter in the Antarctic and in some, but not all, Arctic winters.

Arctic Polar Stratospheric Clouds

Figure Q10-2. 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 along with nitrogen and sulfur gases. Because the particles are large and numerous, 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.

Discovering the role of PSCs. The formation of PSCs has been recognized for many years from ground-based observations. However, the geographical and altitude extent of PSCs in both polar regions was not known fully until PSCs were observed by a satellite instrument in the late 1970s. The role of PSCs in converting reactive chlorine gases to ClO was not understood until after the discovery of the Antarctic ozone hole in 1985. Our understanding of the PSC role developed from laboratory studies of their surface reactivity, computer modeling studies of polar stratospheric chemistry, and direct sampling of PSC particles and reactive chlorine gases, such as ClO, in the polar stratospheric regions.

The Discovery of the Antarctic Ozone Hole

The first decreases in Antarctic ozone were observed in the early 1980s over research stations located on the Antarctic continent. The observations showed unusually low total overhead ozone during the late winter/early spring months of September, October, and November. Total ozone was lower in these months compared with previous observations made as early as 1957. The early-published reports came from the British Antarctic Survey and the Japan Meteorological Agency. The results became more widely known in the international community after they were published in the journal *Nature* in 1985 by three scientists from the British Antarctic Survey. Soon after, satellite measurements confirmed the spring ozone depletion and further showed that in each late winter/spring season starting in the early 1980s, the depletion extended over a large region centered near the South Pole. The term “ozone hole” came about from satellite images of total ozone that showed very low values encircling the Antarctic continent each spring (see *Q11*). Currently, the formation and severity of the Antarctic “ozone hole” are documented each year by a combination of satellite, ground-based, and balloon observations of ozone.

III. STRATOSPHERIC OZONE DEPLETION

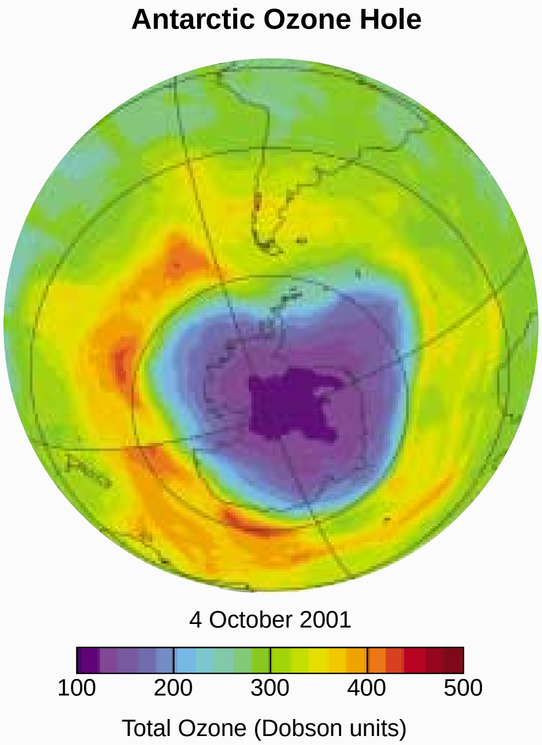
Q11: How severe is the depletion of the Antarctic ozone layer?

Severe depletion of the Antarctic ozone layer was first observed in the early 1980s. Antarctic ozone depletion is seasonal, occurring primarily in late winter and spring (August-November). Peak depletion occurs in October when ozone is often completely destroyed over a range of altitudes, reducing overhead total ozone by as much as two-thirds at some locations. This severe depletion creates the "ozone hole" in images of Antarctic total ozone made from space. In most years the maximum area of the ozone hole usually exceeds the size of the Antarctic continent.

The severe depletion of Antarctic ozone known as the "ozone hole" was first observed in the early 1980s. The depletion is attributable to chemical destruction by reactive halogen gases, which increased in the stratosphere in the latter half of the 20th century (see *Q16*). Conditions in the Antarctic winter stratosphere are highly suitable for ozone depletion because of (1) the long periods of extremely low temperatures, which promote PSC formation and removal; (2) the abundance of reactive halogen gases, which chemically destroy ozone; and (3) the isolation of stratospheric air during the winter, which allows time for chemical destruction to occur (see *Q10*). The severity of Antarctic ozone depletion can be seen using images of total ozone from space, ozone altitude profiles, and long-term average values of polar total ozone.

Antarctic ozone hole. The most widely used images of Antarctic ozone depletion are those from space-based measurements of total ozone. Satellite images made during Antarctic winter and spring show a large region centered near the South Pole in which total ozone is highly depleted (see ***Figure Q11-1***). This region has come to be called the "ozone hole" because of the near-circular contours of low ozone values in the images. The area of the ozone hole has reached 25 million square kilometers (about 10 million square miles) in recent years, which is nearly twice the area of the Antarctic continent. Minimum values of total ozone inside the ozone hole have fallen as low as 100 Dobson units (DU) compared with normal springtime values of about 300 DU (see *Q4*). The mass of ozone destroyed over the Antarctic each season has reached an estimated 80 megatons, which is about 3% of the global ozone mass (1 megaton = 1 billion kilograms = 2.2 billion pounds).

Altitude profiles of Antarctic ozone. Ozone within the "ozone hole" is also measured using balloonborne instruments (see *Q5*). Balloon measurements show changes within the ozone layer, the vertical region that contains the highest ozone abundances in the stratosphere. At geographic locations where the lowest total ozone values occur in ozone hole images, balloon measurements show that the chemical destruction of ozone is complete over a vertical region of several kilometers. ***Figure Q11-2*** shows an example of such depletion with balloon measurements


Antarctic Ozone Hole

4 October 2001

Figure Q11-1. Antarctic "ozone hole." Total ozone values are shown for high southern latitudes as measured by a satellite instrument. The dark regions over the Antarctic continent show the severe ozone depletion now found in 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 300 DU (see *Q4*). In late spring or early summer (November-December) the ozone hole disappears as ozone-depleted air is displaced and diluted by ozone-rich air from outside the ozone hole.

made over South Pole, Antarctica, on 2 October 2001. The altitude region of total depletion (14-20 kilometers) in the profile corresponds to the region of lowest winter temperatures and highest ClO abundances. The average South Pole ozone profiles for the decades 1962-1971 and 1992-2001 (see ***Figure Q11-2***) show how reactive halogen gases have changed the ozone layer. In the 1960s, the ozone layer is clearly evident in the October average profile. In the 1990s, minimum average values in the center of the layer have fallen by 90% from the earlier values.

Long-term total ozone changes. Low winter temperatures and isolated conditions occur each year in the Antarctic stratosphere. As a result, significant spring ozone depletion has been observed every year since the early 1980s. In prior years, the amounts of reactive halogen gases in the stratosphere were insufficient to cause significant depletion. Satellite observations can be used to examine the average total ozone abundances in both polar regions for the last three decades (see ***Figure Q12-1***). In the Antarctic, average values decreased steadily through the 1980s and 1990s, reaching minimum values that were 37% less than in pre-ozone-hole years (1970-1982). The year-to-year changes in the average values reflect variations in the meteorological conditions, which affect the extent of low polar temperatures and the transport of air into and out of the Antarctic winter stratosphere. However, essentially all of the ozone depletion in the Antarctic in most years is attributable to chemical loss from reactive halogen gases.

Restoring ozone in spring. The depletion of Antarctic ozone occurs primarily in the late winter/spring season. In spring, temperatures in the lower polar stratosphere eventually warm, thereby ending PSC formation and the most effective chemical cycles that destroy ozone (see *Q10*). The transport of air between the polar stratosphere and lower latitudes also increases during this time, ending winter isolation. This allows ozone-rich air to be transported to polar regions, displacing air in which ozone has been severely depleted. This displaced air is diluted at lower latitudes with more abundant ozone-rich air. As a result, the ozone hole disappears by December and Antarctic ozone amounts remain near normal until the next winter season.

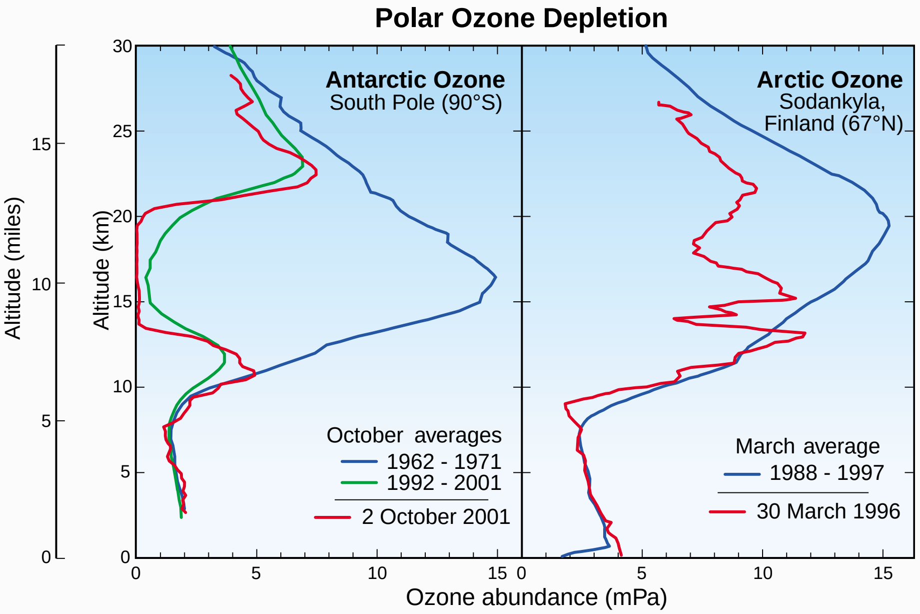


Figure Q11-2. Arctic and Antarctic ozone distribution. The stratospheric ozone layer resides between about 10 and 50 kilometers (6 to 31 miles) above Earth's surface over the globe. Long-term observations of the ozone layer from small balloons allow the winter Antarctic and Arctic regions to be compared. 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).)

Q12: Is there depletion of the Arctic ozone layer?

Yes, significant depletion of the Arctic ozone layer now occurs in some years in the late winter/spring period (January-April). However, the maximum depletion is generally less severe than that observed in the Antarctic and is more variable from year to year. A large and recurrent "ozone hole," as found in the Antarctic stratosphere, does not occur in the Arctic.

Significant ozone depletion in the Arctic stratosphere occurs in cold winters because of reactive halogen gases. The depletion, however, is much less than occurs in every Antarctic winter and spring. Although Arctic depletion does not generally create persistent "ozone hole"-like features in Arctic total ozone maps, depletion is observed in altitude profiles of ozone and in long-term average values of polar ozone.

Altitude profiles of Arctic ozone. Arctic ozone is measured using balloonborne instruments (see *Q5*), as in the Antarctic (see *Q11*). Balloon measurements show changes within the ozone layer, the vertical region that contains the highest ozone abundances in the stratosphere. ***Figure Q11-2*** shows an example of a depleted ozone profile in the Arctic region on 30 March 1996, and contrasts the depletion with that found in the Antarctic. The 30 March spring profile shows much less depletion than the 2 October spring profile in the Antarctic. In general, some reduction in the Arctic ozone layer occurs each winter/spring season. However, complete depletion each year over a broad vertical layer, as is now common in the Antarctic stratosphere, is not found in the Arctic.

Long-term total ozone changes. Satellite observations can be used to examine the average total ozone abundances in the Arctic region for the last three decades and to contrast them with results from the Antarctic (see ***Figure Q12-1***). Decreases from the pre-ozone-hole average values (1970-1982) were observed in the Arctic beginning in the 1980s, when similar changes were occurring in the Antarctic. The decreases have reached a maximum of 22%, but have remained smaller than those found in the Antarctic since the mid-1980s. The year-to-year changes in the average Arctic and Antarctic average ozone values reflect annual variations in meteorological conditions that affect the extent of low polar temperatures and the transport of air into and out of the polar stratosphere. The effect of these variations is generally greater for the Arctic than the Antarctic. In almost all years, most of the Arctic ozone decrease (about 75%) is attributable to chemical destruction by reactive halogen gases.

Arctic vs. Antarctic. The Arctic winter stratosphere is generally warmer than its Antarctic counterpart (see ***Figure Q10-1***). Higher temperatures reduce polar stratospheric cloud (PSC) formation, the conversion of reac-

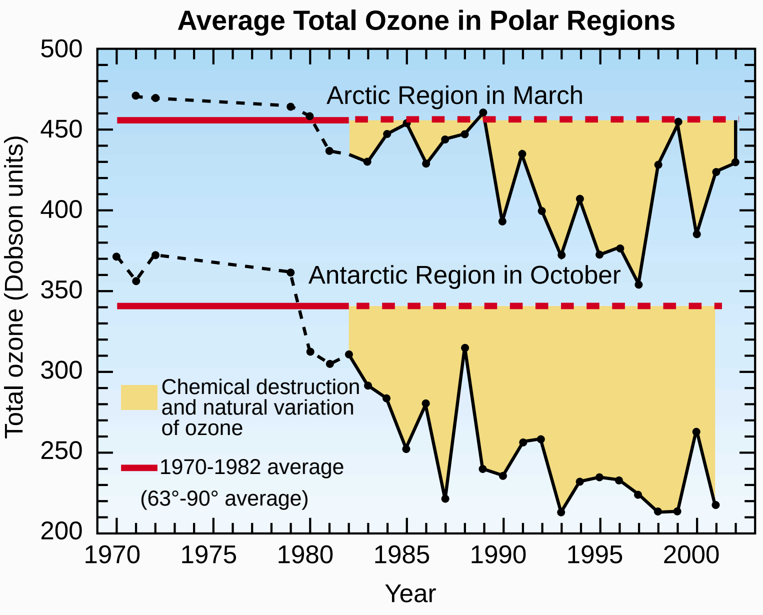


Figure Q12-1. Average polar ozone. Total ozone in polar regions is measured by well-calibrated satellite instruments. Shown here is a comparison of average springtime total-ozone values found between 1970 and 1982 (solid red line) with those in later years. Each point represents a monthly average in 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 in the last decade. Natural 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 initially larger each winter/spring season because more ozone is transported poleward in the Northern Hemisphere each season than in the Southern Hemisphere.

tive chlorine gases to form ClO, and, as a consequence, the amount of ozone depletion (see *Q10*). Furthermore, the temperature and wind conditions are much more variable in the Arctic from winter to winter and within a winter season than in the Antarctic. Large year-to-year differences occur in Arctic minimum temperatures and the duration of PSC-forming temperatures into early spring. In a few Arctic winters, minimum temperatures are not low enough for PSCs to form. These factors combine to cause ozone depletion to be variable in the Arctic from year to year, with some years having little to no ozone depletion.

As in the Antarctic, depletion of ozone in the Arctic is confined to the late winter/spring season. In spring, temperatures in the lower stratosphere eventually warm, thereby ending PSC formation and the most effective chemical cycles that destroy ozone. The subsequent transport of ozone-rich air into the Arctic stratosphere displaces ozone-depleted air. As a result, ozone layer abundances are restored to near-normal values until the following winter.

High Arctic total ozone. A significant difference exists between the Northern and Southern Hemispheres in how ozone-rich stratospheric air is transported into the polar regions from lower latitudes during fall and winter. In the northern stratosphere, the poleward and downward transport of ozone-rich air is stronger. As a result, before the onset of ozone depletion in the 1980s, total ozone values in the Arctic were considerably higher than in the Antarctic in winter and spring (see ***Figure Q12-1***). The Arctic values have remained higher to the present day because of the greater depletion of Antarctic ozone.

Replacing the Loss of “Good” Ozone in the Stratosphere

The idea is sometimes put forth that humans could replace the loss of global stratospheric ozone, called “good” ozone, by making ozone and transporting it to the stratosphere. Ozone amounts reflect a balance in the stratosphere between continual production and destruction by mostly naturally occurring reactions (see *Q2*). The addition of chlorine and bromine to the stratosphere from human activities has increased ozone destruction and lowered “good” ozone amounts. Adding manufactured ozone to the stratosphere would upset the existing balance. As a consequence, most added ozone would be destroyed in chemical reactions within weeks to months as the balance was restored. So, it is not practical to consider replacing the loss of global stratospheric ozone because the replacement effort would need to continue indefinitely, or as long as increased chlorine and bromine amounts remained.

Other practical difficulties in replacing stratospheric ozone are the large amounts of ozone required and the delivery method. The total amount of atmospheric ozone is approximately *3000 megatons* (1 megaton = 1 billion kilograms) with most residing in the stratosphere. The replacement of the average global ozone loss of 3% would require 90 megatons of stratospheric ozone to be distributed throughout the layer located many kilometers above Earth’s surface. The energy required to produce this amount of ozone would be a significant fraction of the electrical power generated in the United States, which is now approximately 5 trillion kilowatt hours. Processing and storing requirements for ozone, which is explosive and toxic in large quantities, would increase the energy requirement. In addition, methods suitable to deliver and distribute large amounts of ozone to the stratosphere have not been demonstrated yet. Concerns for a global delivery system would include further significant energy use and unforeseen environmental consequences.

Q13: How large is the depletion of the global ozone layer?

The ozone layer has been depleted gradually since 1980 and now is about an average of 3% lower over the globe. The depletion, which exceeds the natural variations of the ozone layer, is very small near the equator and increases with latitude toward the poles. The large average depletion in polar regions is primarily a result of the late winter/spring ozone destruction that occurs there annually.

Stratospheric ozone has decreased over the globe since the 1980s. The depletion, which in the period 1997-2001 averaged about 3% (see ***Figure Q13-1***), is larger than natural variations in ozone. The observations shown in ***Figure Q13-1*** have been smoothed to remove regular ozone changes that are due to seasonal and solar effects (see *Q14*). The increase in reactive halogen gases in the stratosphere is considered to be the primary cause of the average depletion. The lowest ozone values in recent years occurred following the 1991 eruption of Mt. Pinatubo, which increased the number of sulfur-containing particles in the stratosphere. The particles remain in the stratosphere for several years, increasing the effectiveness of reactive halogen gases in destroying ozone (see *Q14*).

Observed ozone depletion varies significantly with latitude on the globe (see ***Figure Q13-1***). The largest losses occur at the highest southern latitudes as a result of the severe ozone loss over Antarctica each winter/spring period. The next largest losses are observed in the Northern Hemisphere, caused in part by winter/spring losses over the Arctic. Air depleted in ozone over both polar regions spreads away from the poles during and after each winter/spring period. Ozone depletion also occurs directly at latitudes between the equator and polar regions, but is smaller because of smaller amounts of reactive halogen gases present there.

Tropical regions. There has been little or no depletion of total ozone in the tropics (between about 20° latitude north and south of the equator in ***Figure Q13-1****)*. In this region of the lower stratosphere, air has only recently (less than 18 months) been transported from the lower atmosphere. As a result, the conversion of halogen source gases to reactive halogen gases is very small. Because of the low abundance of reactive gases, total ozone depletion in this region is also very small. In contrast, stratospheric air in polar regions has been in the stratosphere for an average of 4 to 7 years, and the abundance of reactive halogen gases is much larger.

Seasonal changes. The magnitude of global ozone depletion also depends on season of the year. In the period pre-1980 to 1997-2001, average total ozone decreased by about 3% in northern middle latitudes (35°N-60°N) and about 6% at southern middle latitudes (35°S-60°S). The seasonality of these changes is different in the two hemispheres. In the Northern Hemisphere, larger decreases are observed in winter/spring (4%) than in summer/autumn (2%). In the Southern Hemisphere, the decreases are about the same (6%) during all seasons.

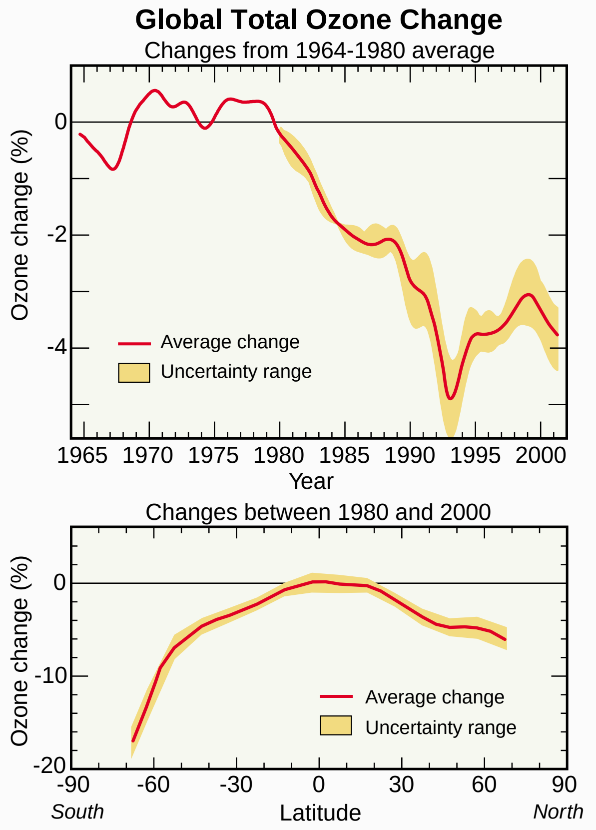


Figure Q13-1. Global total ozone changes. Global total ozone values decreased by an average of a few percent in the last two decades, as measured by satellite instruments. In the top panel, global ozone changes are compared with average global ozone found in the period of 1964 to 1980. Between 1980 and 2000, the largest decreases occurred following the volcanic eruption of Mt. Pinatubo in 1991. In the 1997 to 2001 period global ozone was reduced by about 3% from the 1964-1980 average. In the bottom panel, ozone changes between 1980 and 2000 are compared 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 greater losses that occur each year in the Antarctic stratosphere. Long-term changes in the tropics are much smaller because reactive halogen gases are not abundant in the tropical lower stratosphere.

Q14: Do changes in the Sun and volcanic eruptions affect the ozone layer?

Yes, factors such as changes in solar radiation, as well as the formation of stratospheric particles after volcanic eruptions, do influence the ozone layer. However, neither factor can explain the average decreases observed in global total ozone over the last two decades. If large volcanic eruptions occur in the coming decades, ozone depletion will increase for several years after the eruption.

Changes in solar radiation and increases in stratospheric particles from volcanic eruptions both affect the abundance of stratospheric ozone, but they have not caused the long-term decreases observed in total ozone.

Solar changes. The formation of stratospheric ozone is initiated by ultraviolet (UV) radiation coming from the Sun (see ***Figure Q2-1***). As a result, an increase in the Sun's radiation output increases the amount of ozone in Earth's atmosphere. The Sun's radiation output and sunspot number vary over the well-known 11-year solar cycle. Observations over several solar cycles (since the 1960s) show that global total ozone levels vary by 1 to 2% between the maximum and minimum of a typical cycle. Changes in solar output at a wavelength of 10.7 cm, although much larger than changes in total solar output, are often used to show when periods of maximum and minimum total output occur (see ***Figure Q14-1***). Since 1978, the Sun's output has gone through maximum values around 1969, 1980, and 1991, and is currently near a maximum value in 2002.

Over the last two decades, average total ozone has decreased over the globe. Average values in recent years

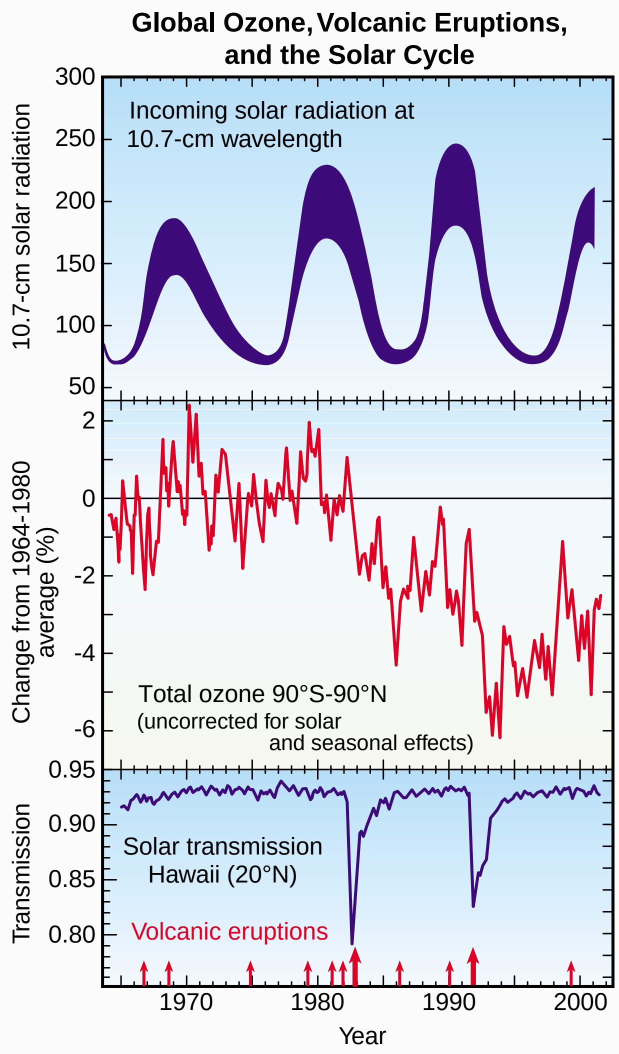


Figure Q14-1. Solar changes and volcanoes. Total ozone values have decreased beginning in the early 1980s (see middle panel). The ozone values shown have not been smoothed for solar and seasonal effects as they were in ***Figure Q13-1***. Incoming solar radiation, which produces ozone in the stratosphere, changes on a well-recognized 11-year cycle. Solar radiation at 10.7-cm wavelength is often used to show the times of maximum and minimum solar output (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 2002 period. The largest recent eruptions are El Chichón (1982) and Mt. Pinatubo (1991) (see large red arrows). 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 but 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.

show a 3-4% depletion from pre-1980 values (see ***Figure Q14-1***). The ozone values shown have not been smoothed for solar and seasonal effects as they were for ***Figure Q13-1***. Over the same period, changes in solar output show the expected 11-year cycle but do not show a decrease with time. For this reason, the long-term decreases in global ozone cannot result from changes in solar output alone. Most discussions of long-term ozone changes presented in this and previous international scientific assessments account for the influence of the 11-year solar cycle.

Past volcanoes. Large volcanic eruptions inject sulfur gases directly into the ozone layer, causing new sulfate particles to be formed. The particles initially form in the stratosphere above the volcano location and then spread globally as air is transported within the stratosphere. The presence of volcanic particles in the stratosphere is shown by observations of solar transmission through the atmosphere. When large amounts of particles are present in the stratosphere, transmission of solar radiation is reduced. The large eruptions of El Chichón (1982) and Mt. Pinatubo (1991) are recent examples of events that temporarily reduced transmission (see ***Figure Q14-1***).

Laboratory measurements and stratospheric observations have shown that chemical reactions on the surface of volcanically produced particles increase ozone destruction by increasing the amounts of the highly reactive chlorine gas, chlorine monoxide (ClO). Ozone depletion increases as a consequence of increased ClO. The most recent large eruption was that of Mt. Pinatubo, which resulted in up to a 10-fold increase in the number of particles available for surface reactions. Both El Chichón and Mt. Pinatubo reduced global ozone for a few years (see ***Figure Q14-1***). After a few years, the effect of volcanic particles diminishes as volcanically produced particles are gradually removed from the stratosphere by natural air circulation. Because of particle removal, the few large volcanic eruptions of the last two decades cannot account for the long-term decreases observed in ozone over the same period.

Future volcanoes. Observations and atmospheric models indicate that the record-low ozone levels observed in 1992-1993 resulted from the relatively large number of particles produced by the Mt. Pinatubo eruption, combined with the relatively large amounts of halogen gases present in the stratosphere in the 1990s. If the Mt. Pinatubo eruption had occurred before 1980, changes to global ozone would have been much smaller than observed in 1992-1993 because the abundance of halogen gases in the stratosphere was smaller. In the early decades of the 21st century, the abundance of halogen gases will still be substantial in the global atmosphere (see ***Figure Q16-1***). If large volcanic eruptions occur in these early decades, ozone depletion will increase for several years. If an eruption larger than Mt. Pinatubo occurs then ozone losses could be larger than previously observed and persist longer. Only later in the 21st century when halogen gas abundances have declined will the effect of volcanic eruptions on ozone be lessened.

IV. CONTROLLING OZONE-DEPLETING GASES

Q15: Are there regulations on the production of ozone-depleting gases?

Yes, the production of ozone-depleting gases is regulated under a 1987 international agreement known as the "Montreal Protocol on Substances that Deplete the Ozone Layer" and its subsequent Amendments and Adjustments. The Protocol, now ratified by over 180 nations, establishes legally binding controls on the national production and consumption of ozone-depleting gases. Production and consumption of all principal halogen-containing gases by developed and developing nations will be significantly reduced or phased out before the middle of the 21st century.

Montreal Protocol. In 1985, a treaty called the *Convention for the Protection of the Ozone Layer* was signed by 20 nations in Vienna. The signing nations agreed to take appropriate measures to protect the ozone layer from human activities. The Vienna Convention supported research, exchange of information, and future protocols. In response to growing concern, the *Montreal Protocol on Substances that Deplete the Ozone Layer* was signed in 1987 and ratified in 1989. The Protocol established legally binding controls for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion. National consumption of a halogen gas is defined as the amount that production and imports of a gas exceed its export to other nations.

Amendments and Adjustments. As the scientific basis of ozone depletion became more certain after 1987 and substitutes and alternatives became available for the principal halogen source gases, the Montreal Protocol was strengthened with Amendments and Adjustments. These revisions added new controlled substances, accelerated existing control measures, and scheduled phaseouts of the production of certain gases. The initial Protocol called for only a slowing of chlorofluorocarbon (CFC) and halon production. The 1990 London Amendments to the Protocol called for a phaseout of the production of the most damaging ozone-depleting substances in developed nations by 2000 and in developing nations by 2010. The 1992 Copenhagen Amendments accelerated the date of the phaseout to 1996 in developed nations. Further controls on ozone-depleting substances were agreed upon in later meetings in Vienna (1995), Montreal (1997), and Beijing (1999).

Montreal Protocol projections. The future stratospheric abundances of effective stratospheric chlorine can be projected based on the provisions of the Montreal Protocol. The concept of effective stratospheric chlorine accounts for the combined effect on ozone of chlorine- and bromine-containing gases. The results are shown in ***Figure Q15-1*** for the following cases:

- No Protocol and continued production increases of 3% per year (business-as-usual scenario).
- Continued production as allowed by the Protocol's original provisions agreed upon in Montreal in 1987.
- Restricted production as outlined in the subsequent Amendments and Adjustments: London, 1990; Copenhagen, 1992; and Beijing, 1999. (The city names and years signify where and when the agreements were made.)
- Zero emissions of ozone-depleting gases starting in 2003.

In each case, production of a gas is assumed to result in its eventual emission to the atmosphere. Without the Montreal Protocol, continued production and use of CFCs and other ozone-depleting gases are projected to have increased effective stratospheric chlorine tenfold by the mid-2050s compared with the 1980 value. Such high values likely would have increased global ozone depletion far beyond that currently observed. As a result, harmful UV-B radiation would have increased substantially at Earth's surface, causing a rise in excess skin cancer cases (see lower panel of ***Figure Q15-1*** and *Q17*).

The 1987 provisions of the Montreal Protocol would have only slowed the approach to high effective chlorine values by one or more decades in the 21st century. Not until the 1992 Copenhagen Amendments and Adjustments did the Protocol projections show a *decrease* in future effective stratospheric chlorine values. Now, with full compliance to the Montreal Protocol and its Amendments and Adjustments, use of the major human-produced ozone-depleting gases will ultimately be phased out and effective stratospheric chlorine will slowly decay, reaching pre-ozone-hole values in the mid-21st century.

Zero emissions. Effective chlorine values in the coming decades will be influenced by emissions of halogen source gases produced in those decades as well as the emission of currently existing gases that are now being used or stored in various ways. Some continued production and consumption of ozone-depleting gases is allowed, particularly in developing nations, under the 1999 Beijing agreements. As a measure of the contribution of these continued emissions to the effective chlorine value, the "zero emissions" case is included in ***Figure Q15-1***. In this hypothetical case, all emissions of ozone-depleting gases are set to zero beginning in 2003. The reductions in effective stratospheric chlorine beyond the values expected for the 1999 Beijing agreement would be significantly smaller than most earlier changes, as shown.

HCFC substitute gases. The Montreal Protocol provides for the transitional use of hydrochlorofluorocarbons (HCFCs) as substitute compounds for principal halogen source gases such as CFC-12. HCFCs differ chemically from most other halogen source gases in that they contain hydrogen (H) atoms in addition to chlorine and fluorine atoms. HCFCs are used for refrigeration, for blowing foams, and as solvents, which were primary uses of CFCs. HCFCs are 1 to 15% as effective as CFC-12 in depleting stratospheric ozone because they are chemically removed primarily in the troposphere. This removal partially protects stratospheric ozone from the halogens contained in HCFCs. In contrast, CFCs and many other halogen source gases are chemically inert in the troposphere and, hence, reach the stratosphere without being significantly removed. Because HCFCs still contribute to the halogen abundance in the stratosphere, the Montreal Protocol requires the production and consumption of HCFCs to end in developed and developing nations by 2040.

HFC substitute gases. Hydrofluorocarbons (HFCs) are also used as substitute compounds for CFCs and other halogen source gases. HFCs contain only hydrogen, fluorine, and carbon atoms. Because HFCs contain no chlorine or bromine, they do not contribute to ozone depletion. As a consequence, the HFCs are not regulated by the Montreal Protocol. However, HFCs (as well as all halogen source gases) are radiatively active gases that contribute to human-induced global warming and climate change as they accumulate in the atmosphere (see *Q18*). HFCs are included in the group of gases listed in the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCC).

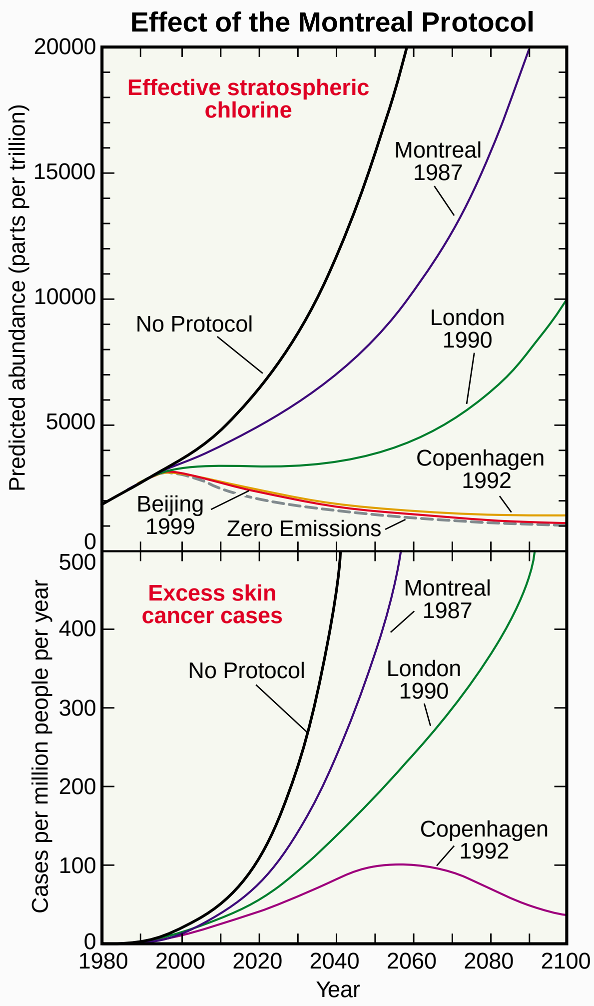


Figure Q15-1. Effect of the Montreal Protocol. The purpose of the Montreal Protocol is to achieve reductions in stratospheric abundances of chlorine and bromine. The reductions follow from restrictions on the production and consumption of manufactured halogen source gases. Predictions for the future 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 a Protocol, stratospheric halogen gases are projected to have increased significantly in the 21st century. The "zero emissions" line shows stratospheric abundances if all emissions were reduced to zero beginning in 2003. The lower panel shows how excess skin cancer cases (see *Q17*) would increase with no regulations and how they will be reduced under the Protocol provisions. (The unit "parts per trillion" is defined in the caption of ***Figure Q7-1***.)

Q16: Has the Montreal Protocol been successful in reducing ozone-depleting gases in the atmosphere?

Yes, as a result of the Montreal Protocol, the total abundance of ozone-depleting gases in the atmosphere has begun to decrease in recent years. If the nations of the world continue to follow the provisions of the Montreal Protocol, the decrease will continue throughout the 21st century. Some individual gases such as halons and hydrochlorofluorocarbons (HCFCs) are still increasing in the atmosphere, but will begin to decrease in the next decades if compliance with the Protocol continues. By midcentury, the effective abundance of ozone-depleting gases should fall to values present before the Antarctic "ozone hole" began to form in the early 1980s.

Effective stratospheric chlorine. The Montreal Protocol has been successful in slowing and reversing the increase of ozone-depleting gases in the atmosphere. An important measure of its success is the change in the value of *effective stratospheric chlorine*. Effective chlorine is based on measured or estimated abundances of both chlorine- and bromine-containing gases in the stratosphere. The two groups of gases are not simply added together, because bromine gases are much more effective on a per-atom basis than chlorine in depleting ozone (see *Q7*). Instead, the amounts for bromine gases are multiplied by a factor that accounts for their greater effectiveness and then added to the total amount of chlorine. Bromine atoms are much less abundant in the stratosphere than chlorine (see ***Figure Q7-1***), but are about 45 times more effective than chlorine in chemically destroying ozone molecules. Increases in effective chlorine in the past decades have caused stratospheric ozone depletion. Accordingly, ozone is expected to recover in the future as effective chlorine values decrease.

Effective stratospheric chlorine changes. In the latter half of the 20th century up until the 1990s, effective chlorine values steadily increased (see ***Figure Q16-1***). The values shown were calculated using halogen source gas abundances obtained from measurements, historical estimates of abundance, and future projections of abundance. As a result of the Montreal Protocol regulations, the long-term increase in effective chlorine slowed, reached a peak, and began to decrease in the 1990s. This small and continuing decrease means that the potential for stratospheric ozone depletion has begun to lessen as a result of the Montreal Protocol. The decrease in effective chlorine is projected to continue throughout the 21st century if all nations continue to comply with the provisions of the Protocol. Once halogen gas emissions from human activities have ceased, the decrease in effective chlorine will continue as natural destruction processes gradually reduce halogen gas abundances in the global atmosphere. Significant reduction requires decades because the lifetimes of halogen source gas molecules in the atmosphere range up to 100 years (see ***Table Q7-1***).

Individual halogen source gases. Reductions in effective chlorine follow directly from decreases in the emission of individual halogen source gases. The regulation of human-produced halogen source gases under the Montreal Protocol is considered separately for each class of one or more gases and is based on several factors. The factors include (1) the effectiveness of each class in depleting ozone in comparison to other halogen source gases; (2) the availability of suitable substitute gases for domestic and industrial use; and (3) the impact of regulation on developing nations.

The change in atmospheric abundance of a gas in response to regulation also depends on a number of factors that include (1) how the gas is used and released to the atmosphere; (2) how rapidly the gas is chemically destroyed in the atmosphere; and (3) the total amount of the gas that has accumulated in the atmosphere.

Methyl chloroform and CFCs. The largest reduction in the abundance of a halogen source gas has occurred for methyl chloroform (CH_3CCl_3). As shown in ***Figure Q16-1***, atmospheric methyl chloroform values dropped abruptly as a result of the provisions of the Montreal Protocol that reduced global production to near zero. Atmospheric abundances subsequently dropped rapidly because methyl chloroform has a short atmospheric lifetime (about 5 years). In addition, methyl chloroform is used mainly as a solvent and therefore has no significant long-term storage reservoir, as do refrigerants, for example. The reduction in effective chlorine in the 1990s came primarily from the reduction in methyl chloroform abundance in the atmosphere. Significant emissions reductions have also occurred for the chlorofluorocarbons CFC-11, CFC-12, and CFC-113 starting in the 1990s. As a result, the atmospheric increases of these gases have slowed, and CFC-11 and CFC-113 abundances have decreased slightly (see ***Figure Q16-1***). Because of longer lifetimes in the atmosphere (see ***Table Q7-1***), CFC abundances decrease more slowly than methyl chloroform as their emissions are reduced.

HCFC substitute gases. The Montreal Protocol allows for the use of hydrochlorofluorocarbons (HCFCs) as short-term substitutes for CFCs. As a result, the abundances of HCFC-22, HCFC-141b, and HCFC-142b continue to grow in the atmosphere (see ***Figure Q16-1***). HCFCs are desirable as CFC substitutes because they are partially destroyed in the troposphere by chemical processes, thus reducing the overall effectiveness of their emissions in destroying stratospheric ozone. Under the Montreal Protocol, HCFC production will reach zero in developed nations by 2030 and in developing nations by 2040. Thus, the future projections in ***Figure Q16-1*** show HCFC abundances reaching a peak in the first decades of the 21st century and steadily decreasing thereafter.

Halons. The atmospheric abundances of Halon-1211 and Halon-1301 are significant fractions of all bromine-containing source gases (see ***Figure Q7-1***) and continue to grow despite the elimination of production in developed nations in 1994 (see ***Figure Q16-1***). The growth in abundance continues because substantial reserves are held in fire-extinguishing equipment and are gradually being released, and production and consumption are still allowed in developing nations. Release of stored halons could keep atmospheric halon abundances high well into the 21st century.

Methyl chloride and methyl bromide. Both methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) are unique among halogen source gases because a substantial fraction of their sources are associated with natural processes (see *Q7*). The average atmospheric abundance of methyl chloride, which is not regulated under the Montreal Protocol, is expected to remain nearly constant throughout this century. At century's end, methyl chloride is expected to account for a large fraction of remaining effective stratospheric chlorine because the abundances of other gases, such as the CFCs, are expected to be greatly reduced (see ***Figure Q16-1***). The abundance of methyl bromine, which is regulated under the Protocol, is projected to decrease in the first decades of this century as a result of production phaseouts in developed and developing countries. In the remaining decades of the century, methyl bromide abundances are expected to be nearly constant.

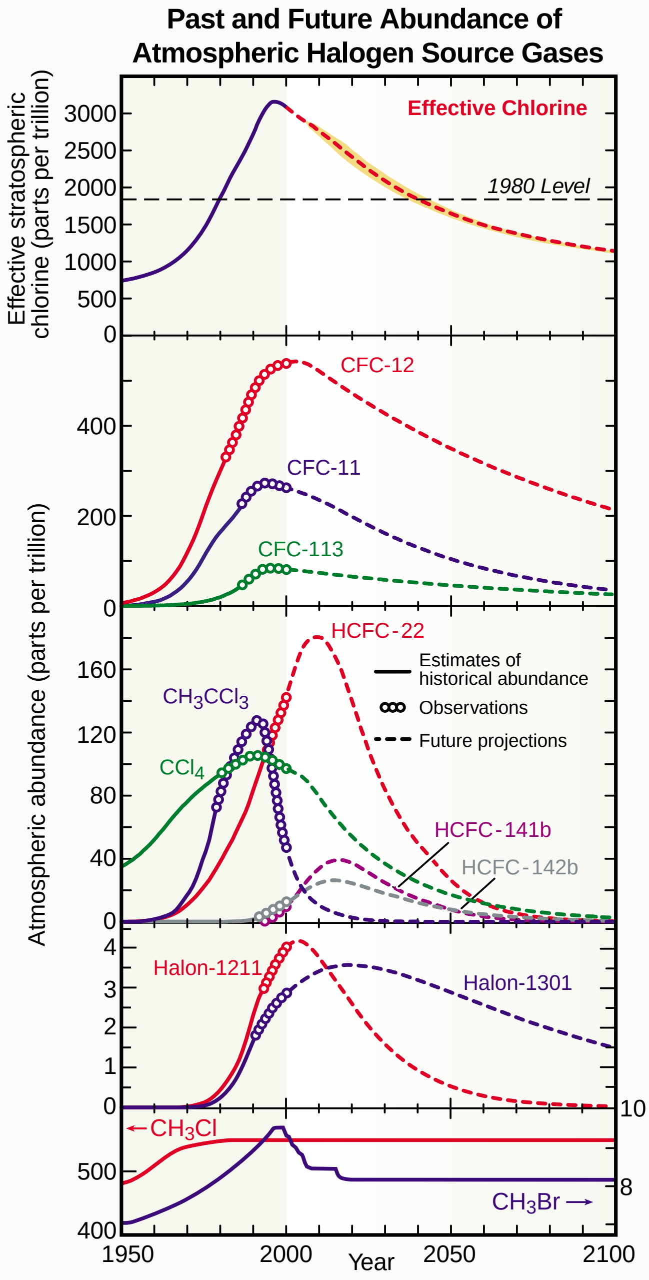


Figure Q16-1. Halogen source gas changes. The rise in effective stratospheric chlorine values in the 20th century has slowed and reversed in the last decade (top panel). Effective chlorine values combine the measured or projected abundances of chlorine-containing gases with those of bromine-containing gases in a way that properly accounts for the greater effectiveness of bromine in depleting stratospheric ozone. As effective chlorine decreases in the 21st century, the potential for ozone depletion from halogen gases will also decrease. The decrease in effective chlorine values is a result of reductions in individual halogen source gas emissions. The emissions decreased because of the Montreal Protocol, which restricts production and consumption of manufactured halogen gases. The changes in the atmospheric abundance of individual gases are shown in the lower panels using a combination of direct atmospheric measurements, estimates of historical abundance, and future projections of abundance. The increases of CFCs, along with those of CCl_4 and CH_3CCl_3, have either slowed significantly or reversed in the last decade. HCFCs, which are being used as CFC substitutes, will continue to increase in the coming decades. Some halon abundances will also grow in the future while current halon reserves are being depleted. Smaller relative decreases are expected for CH_3Br in response to restrictions because it has substantial natural sources. CH_3Cl has large natural sources and is not regulated under the Montreal Protocol. (See ***Figure Q7-1*** for chemical names and formulas. The unit "parts per trillion" is defined in the caption of ***Figure Q7-1***.)

V. IMPLICATIONS OF OZONE DEPLETION

Q17: Does depletion of the ozone layer increase ground-level ultraviolet radiation?

Yes, ultraviolet radiation at Earth's surface increases as the amount of overhead total ozone decreases, because ozone absorbs ultraviolet radiation from the Sun. Measurements by ground-based instruments and estimates made using satellite data have confirmed that surface ultraviolet radiation has increased in regions where ozone depletion is observed.

The depletion of stratospheric ozone leads to an increase in surface ultraviolet radiation. The increase occurs primarily in the ultraviolet-B (UV-B) component of the Sun's radiation. UV-B is defined as radiation in the wavelength range of 280 to 315 nanometers. Changes in UV-B at the surface have been observed directly and can be estimated from ozone changes.

Surface UV-B radiation. The amount of ultraviolet radiation reaching Earth's surface depends in large part on the amount of ozone in the atmosphere. Ozone molecules in the stratosphere absorb UV-B radiation, thereby significantly reducing the amount of this radiation that reaches Earth's surface (see *Q3*). If total ozone amounts are reduced in the stratosphere, then the amount of UV radiation reaching Earth's surface generally increases. This relationship between total ozone and surface UV radiation has been studied at a variety of locations with direct measurements of both ozone and UV. The actual amount of UV reaching a location depends on a large number of additional factors, including the position of the Sun in the sky, cloudiness, and air pollution. In general, surface UV at a particular location on Earth changes throughout the day and with season as the Sun's position in the sky changes.

Long-term surface UV changes. Satellite observations of long-term global ozone changes can be used to estimate changes in global surface UV that have occurred over the past two decades. These changes are of interest because UV radiation can cause harm to humans and other life forms (see *Q3*). The amount of UV that produces an "erythemal" or sunburning response in humans is often separately evaluated. UV-B radiation is a large component of sunburning UV. Long-term changes in sunburning UV at a location can be estimated from the changes in total ozone at that location. The results show that average sunburning UV has increased by up to a few percent per decade between 1979 and 1992 over a wide range of latitudes (see ***Figure Q17-1***). The largest increases are found at high polar latitudes in both hemispheres. As expected, the increases occur where decreases in total ozone are observed to be the largest (see ***Figure Q13-1***). The smallest changes in sunburning UV are in the tropics, where long-term total ozone changes are smallest.

UV Index changes. The "UV Index" is a measure of daily surface UV levels that is relevant to the effects of UV on human skin. The UV Index is used internationally to increase public awareness about the detrimental effects of UV on human health and to guide the need for protective measures. The Index is essentially a measure of erythemal radiation, of which UV-B is a principal component. The daily maximum UV Index varies with location and season, as shown for three locations in ***Figure Q17-2***. The highest daily values generally occur at the lowest latitudes (tropics) and in summer when the midday Sun is closest to overhead. Values in San Diego, California, for example, normally are larger year round than those found in Barrow, Alaska, which is at a higher latitude. At a given latitude, UV Index values increase in mountainous regions. Winter and fall values become zero in periods of continuous darkness at high-latitude locations.

An illustrative example of how polar ozone depletion increases the maximum daily UV Index is shown in ***Figure Q17-2***. Normal UV Index values for Palmer, Antarctica, in spring were estimated from satellite measurements made during the period 1978-1983, before the appearance of the "ozone hole" over Antarctica (see red dotted line). In the last decade (1991-2001) severe and persistent ozone depletion in spring has increased the UV Index well above normal values for several months (see thick red line). Now spring UV Index values in Palmer (64°S) sometimes equal or exceed normal values measured in San Diego (32°N) in spring.

Other causes of long-term UV changes. The intensity of surface UV-B may also change as a result of other human activities or climate change. Long-term changes in cloudiness, aerosols, pollution, and snow or ice cover will cause long-term changes in surface UV-B. At some ground sites, measurements indicate that long-term changes in UV-B have resulted from changes in one or more of these factors. The impact of some of the changes can be complex. For example, a change in cloud cover usually results in a reduction of UV-B radiation below the cloud layer, but can increase radiation above the layer (in mountainous regions).

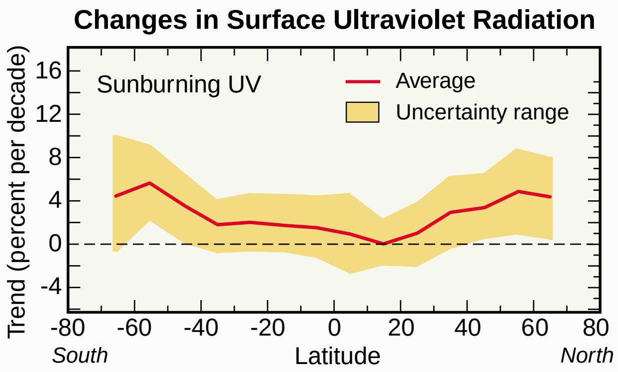
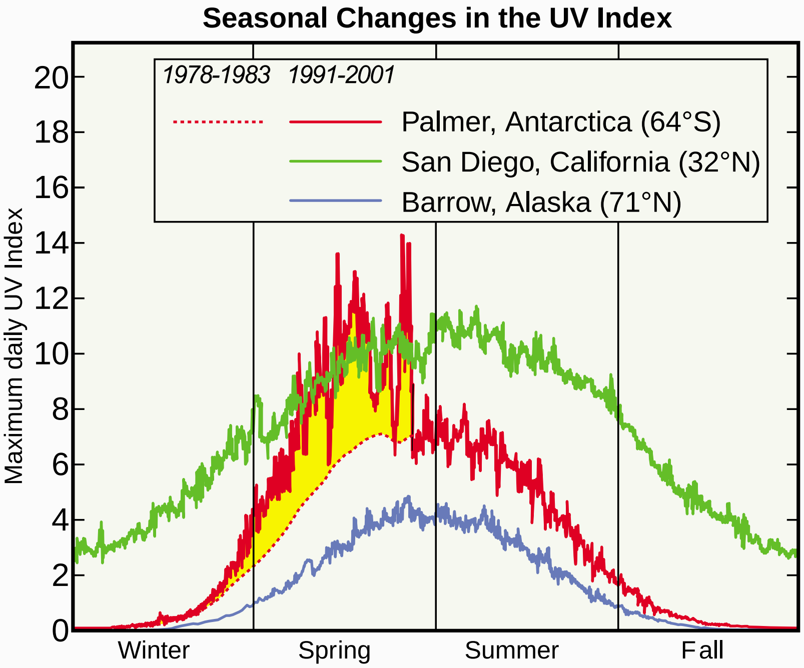


Figure Q17-1. Changes in surface UV radiation. Ultraviolet (UV) radiation at Earth's surface that causes sunburning has increased over the globe between 1979 and 1992. Also known as "erythemal radiation," sunburning UV is harmful to humans and other life forms. The increase shown here is estimated from observed decreases in ozone and the relationship between ozone and surface UV established at some surface locations. The changes in ultraviolet radiation in the tropics are estimated to be the smallest because observed changes in tropical ozone have been the smallest.

UV changes and skin cancer. Skin cancer cases in humans increase with the amount of sunburning UV reaching Earth's surface. Atmospheric scientists working together with health professionals can estimate how skin cancer cases will change in the future. The estimates are based on knowing how sunburning UV increases as total ozone is depleted and how total ozone depletion changes with effective stratospheric chlorine (see *Q16*). Estimates of future excess skin cancer cases are shown in ***Figure Q15-1*** using future estimates of effective chlorine based on the 1992 Montreal Protocol provisions. The cases are those that would occur in a population with the UV sensitivity and age distribution such as that of the United States. The cases counted are those in *excess* of the number that occurred in 1980 before ozone depletion was observed (about 2000 per million population). The case estimates include the fact that skin cancer in humans occurs long after the exposure to sunburning UV. The results show that, with current Protocol provisions, excess skin cancer cases are predicted to increase in the early to middle decades of the 21st century. By century's end, with the expected decreases in halogen source gas emissions, the number of excess cases is predicted to return close to 1980 values. Without the provisions of the Protocol, excess skin cancer cases would be expected to increase unchecked throughout the century.

Figure Q17-2. Changes in UV Index. 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 as the Sun's path through the local sky changes. 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. For comparison, the figure shows that the UV Index is higher in San Diego than in Barrow throughout the year. Index values are zero at high latitudes when darkness is continuous. The effect of ozone depletion on the Index 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 last decade (1991-2001), Antarctic ozone depletion has led to an increase in 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 in San Diego, which is located at a much lower latitude.



Q18: Is depletion of the ozone layer the principal cause of climate change?

No, ozone depletion itself is not the principal cause of climate change. However, because ozone is a greenhouse gas, ozone changes and climate change are linked in important ways. Stratospheric ozone depletion and increases in global tropospheric ozone that have occurred in recent decades both contribute to climate change. These contributions to climate change are significant but small compared with the total contribution from all other greenhouse gases. Ozone and climate change are indirectly linked because ozone-depleting gases, such as the chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and halons, also contribute to climate change.

Ozone depletion is not the major cause of climate change, but ozone changes are linked to climate change in important ways.

Radiative forcing of climate change. Human activities have led to the accumulation in the atmosphere of several long-lived and radiatively active gases known as "greenhouse gases." Ozone is a greenhouse gas, along with carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and halogen source gases. The accumulation of these gases changes the radiative balance of Earth's atmosphere. The balance is between incoming solar radiation and outgoing infrared radiation. Greenhouse gases generally change the balance by absorbing outgoing radiation, leading to a warming at Earth's surface. This change in Earth's radiative balance is called a *radiative forcing of climate change*. If the total forcing from all gases becomes large enough, climate could change in significant ways. A summary of radiative forcings resulting from the increase in long-lived greenhouse gases is shown in ***Figure Q18-1***. All forcings shown relate to human activities. Positive forcings lead to *warming* and negative forcings lead to *cooling* of Earth's surface. The accumulation of carbon dioxide is the largest forcing term. Carbon dioxide concentrations are increasing in the atmosphere primarily as the result of the burning of coal, oil, and natural gas for energy and transportation. The atmospheric abundance of carbon dioxide is currently about 30% above what it was 150 years ago in preindustrial times.

Stratospheric and tropospheric ozone. Changes in stratospheric and tropospheric ozone both represent radiative forcings of climate change. Stratospheric ozone absorbs solar radiation, which heats the stratosphere and affects air motions and chemical reactions. Stratospheric and tropospheric ozone both absorb infrared radiation emitted by Earth's surface, effectively trapping heat in the atmosphere below. Overall, the depletion of stratospheric ozone represents a negative radiative forcing. In contrast,

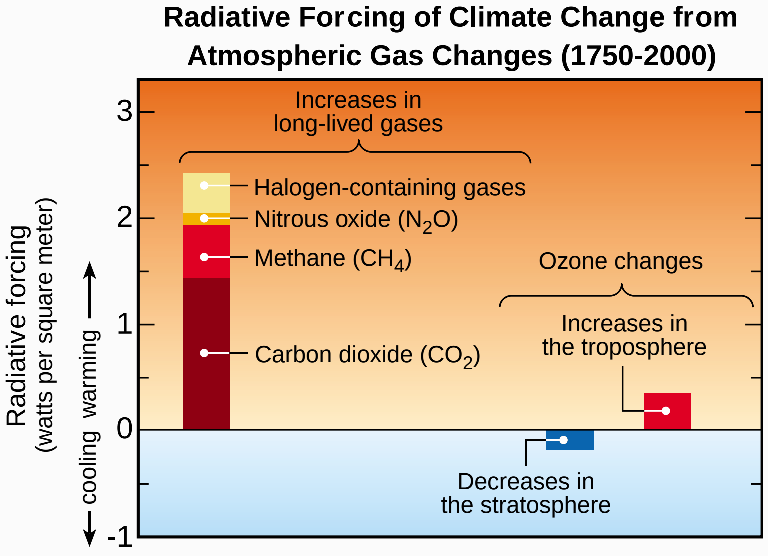


Figure Q18-1. Climate change from atmospheric gas changes. Human activities since 1750 have caused increases in the abundances of several long-lived gases, changing the radiative balance of Earth's atmosphere. These gases, known as "greenhouse gases," result in *radiative forcings*, which can lead to climate change. The largest radiative forcings come from carbon dioxide, followed by methane, tropospheric ozone, the halogen-containing gases (see ***Figure Q7-1***), 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.

increases in tropospheric ozone due to surface pollution represent a positive radiative forcing. The radiative forcing due to tropospheric ozone increases is larger than that associated with stratospheric ozone depletion. Both forcing terms are significant, but are small in comparison with the total forcing from all other greenhouse gases.

Halogen source gases. An indirect link between ozone depletion and climate change is the radiative forcing from halogen source gases. These gases, which include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and halons (see ***Figure Q7-1***), are radiatively active in the atmosphere before they are chemically converted in the stratosphere. As a group, they represent a significant positive radiative forcing. Once converted, they form reactive halogen gases, which chemically destroy ozone. In the coming decades, halogen gas abundances and their associated positive radiative forcings are expected to decrease (see *Q16*). With reduced halogen gases, stratospheric ozone depletion and its associated negative radiative forcing will also be reduced. This link between these two forcing terms is an important aspect of the radiative forcing of climate change.

HFCs. The radiative forcing of halogen-containing gases in ***Figure Q18-1*** also includes that of the HFCs, which do not cause ozone depletion. The HFCs are increasing in the atmosphere because of their use as substitute gases for the CFCs and other halogen gases. HFCs are not regulated under the Montreal Protocol, but are included in the group of gases listed in the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCC).

Climate change. Certain changes in Earth's climate could affect the future of the ozone layer. Stratospheric ozone is influenced by changes in temperatures and winds in the stratosphere. For example, low temperatures and strong polar winds both affect the extent and severity of winter polar ozone depletion. While Earth's surface is expected to warm in response to the positive radiative forcing from carbon dioxide increases, the stratosphere is expected to cool. Indeed, a small cooling of the lower stratosphere has occurred since the 1970s. A cooler stratosphere would extend the time period over which polar stratospheric clouds (PSCs) are present in polar regions and, as a result, might increase winter ozone depletion. These changes could delay the recovery of the ozone layer. In the upper stratosphere at altitudes above PSC formation regions, a cooler stratosphere is expected to increase ozone amounts. Changes in atmospheric composition that lead to a warmer climate may also affect the balance of production and loss processes of stratospheric ozone (see *Q20*).

VI. STRATOSPHERIC OZONE IN THE FUTURE

Q19: How will recovery of the ozone layer be detected?

Scientists expect to detect the recovery of the ozone layer with careful comparisons of the latest ozone measurements with past values. Changes in total overhead ozone at various locations and in the extent and severity of the Antarctic "ozone hole" will be important factors in gauging ozone recovery. Natural variations in ozone amounts will limit how soon recovery can be detected with future ozone measurements.

Recovery factors. Detecting the recovery of the ozone layer will rely on comparisons of the latest ozone values with values measured in the past. Because of its importance, ozone likely will be measured continuously in the future using a variety of techniques and measurement platforms (see *Q5*). In the ozone comparisons, scientists will look for improvements in certain factors related to the distribution of ozone. These factors include the following:

- A lessening of the decline in global ozone, either in total ozone or ozone at specific altitudes in the stratosphere.
- An increase in global total ozone amounts toward values found before 1980 when halogen source gas abundances in the atmosphere were much lower than today.
- A sustained reduction in the maximum size of the Antarctic "ozone hole."
- A sustained increase in the minimum value of ozone found in the Antarctic ozone hole.
- Less ozone depletion in Arctic winters during which temperatures are below polar stratospheric cloud (PSC) formation temperatures.

As the ozone layer approaches full recovery, scientists expect to observe improvements in all these factors.

Natural factors. Global total ozone is influenced by two important natural factors, namely, changes in the output of the Sun and volcanic eruptions (see *Q14*). The evaluation of ozone recovery must include the effects of these natural factors. The solar effect on ozone is expected to be predictable based on the well-established 11-year cycle of solar output. Volcanic eruptions are particularly important because they increase ozone depletion caused by reactive halogen gases, but cannot be predicted. The occurrence of a large volcanic eruption in the next decades when effective stratospheric chlorine levels are still high (see ***Figure Q16-1***) may obscure progress in overall ozone recovery by temporarily increasing ozone depletion. The natural variation of ozone amounts will also limit how easily small improvements in ozone abundances can be detected.

Q20: When is the ozone layer expected to recover?

The ozone layer is expected to recover by the middle of the 21st century, assuming global compliance with the Montreal Protocol. Chlorine- and bromine-containing gases that cause ozone depletion will decrease in the coming decades under the provisions of the Protocol. However, volcanic eruptions in the next decades could delay ozone recovery by several years and the influence of climate change could accelerate or delay ozone recovery.

Halogen source gas reductions. Ozone depletion caused by human-produced chlorine and bromine gases is expected to gradually disappear by about the middle of the 21st century as the abundances of these gases decline in the stratosphere. The decline will follow the reductions in emissions that are expected to occur under the provisions of the Montreal Protocol and its Adjustments and Amendments (see ***Figure Q16-1***). The emission reductions are based on the assumption of full compliance by the developed and developing nations of the world. The slowing of the increases in the atmospheric abundances of several halogen gases and the substantial reduction of one principal halogen gas, methyl chloroform, has already occurred. Natural chemical and transport processes limit the rate at which halogen gases can be removed from the stratosphere. The atmospheric chemical lifetimes of the halogen source gases range up to 100 years (see ***Table Q7-1***). Chlorofluorocarbon-12 (CFC-12), with a lifetime of 100 years, will require about 200 to 300 years before it is removed (less than 5% remaining) from the atmosphere (see ***Figure Q16-1***).

Ozone predictions. Computer models of the atmosphere are used to assess past changes in global ozone and predict future changes. Two important measures of ozone considered by scientists are global total ozone averaged between 60°N and 60°S latitudes, and minimum ozone values in the Antarctic "ozone hole." Both measures show ongoing ozone depletion that began in the 1980s (see ***Figure Q20-1***). The range of model predictions shows that the lowest ozone values are expected to occur before 2020 and that substantial recovery of ozone is expected by the middle of the 21st century. The range of predic-

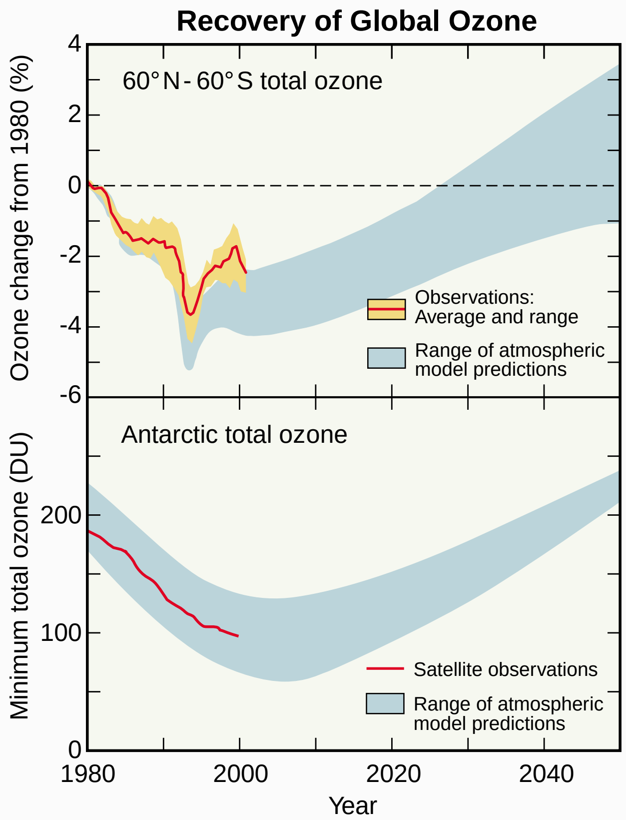


Figure Q20-1. Global ozone recovery predictions. Observed values of global total ozone (top panel) and minimum total ozone over Antarctica (bottom panel) have decreased beginning in the early 1980s. As halogen source gas emissions decrease in the early 21st century, ozone values are expected to increase and recover toward pre-1980 values. Atmospheric computer models that account for changes in halogen gases and other atmospheric parameters can be used to predict how ozone amounts will increase. These model results show that recovery is expected to be significant by 2050, or perhaps earlier. The range of model predictions comes from the use of several different models that have different assumptions about the future climate and composition of the atmosphere. These assumptions are an attempt to account for estimated differences in atmospheric composition and other parameters between 1980, before the "ozone hole" began, and 2050.

tions comes from several computer models of the atmosphere that have different assumptions concerning the future climate and composition of the atmosphere. Some of these models indicate that recovery of total ozone may possibly come well before midcentury.

A different atmosphere in 2050. By the middle of the 21st century, halogen amounts in the stratosphere are expected to be similar to those present in 1980 before the onset of the ozone hole (see ***Figure Q16-1)***. However, other aspects of the global atmosphere will not be the same in 2050 as in 1980. The ozone recovery evaluations in ***Figure Q20-1*** attempt to take these differences into account. For example, since 1980 human activities have increased the abundance of important greenhouse gases, including carbon dioxide, methane, and nitrous oxide. The accumulation of these gases is expected to cause warmer surface temperatures and colder stratospheric temperatures. Colder temperatures may accelerate ozone recovery in the upper stratosphere (about 40 kilometers (25 miles) altitude). Colder winter temperatures over polar regions will increase the occurrences of polar stratospheric clouds (PSCs) and chemical ozone destruction (see *Q10*). Water vapor increases that have occurred in the stratosphere over the last two decades also will lead to increased PSC occurrences and associated ozone destruction. A cooler, wetter polar stratosphere could delay ozone recovery beyond what would be predicted for the 1980 atmosphere. Increased methane and nitrous oxide abundances due to human activities also cause some change in the overall balance of the chemical production and destruction of global stratospheric ozone. Finally, an outcome not included in models is the occurrence of one or more large volcanic eruptions in the coming decades. In that case, stratospheric particles may increase for several years, temporarily reducing global ozone amounts (see *Q14*) and delaying the recovery of the ozone layer.