Twenty Questions and Answers About the Ozone Layer: 2010 Update

Scientific Assessment of Ozone Depletion: 2010

David W. Fahey and Michaela I. Hegglin Coordinating Lead Authors

> This document answers some of the most commonly asked questions about the ozone layer.

World Meteorological Organization United Nations Environment Programme National Oceanic and Atmospheric Administration National Aeronautics and Space Administration European Commission

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INTRODUCTION

O atmosphere. Nevertheless, it is vital to human wellbeing and ecosystem health.

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 radiation from the Sun.

It was discovered in the mid-1970s that some humanproduced chemicals could lead to depletion of the ozone layer. The resulting increase in ultraviolet radiation at Earth's surface would likely increase the incidences of skin cancer and eye cataracts, and also adversely affect plants, crops, and ocean plankton.

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

Observations of the ozone layer showed that depletion was indeed occurring. The most severe and most surprising ozone loss was discovered to be recurring in springtime over Antarctica. The loss in this region 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 and southern midlatitudes.

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 indeed occurring and why. Most important, we know that if the most potent ODSs were to continue to be emitted and increase in the atmosphere, the result would be more depletion of the ozone layer.

In response to the prospect of increasing ozone depletion,

the governments of the world crafted the 1987 United Nations Montreal Protocol as an international means to address this global issue. As a result of the broad compliance with the Protocol and its Amendments and Adjustments and, of great significance, industry's development of "ozone-friendly" substitutes for the now-controlled chemicals, the total global accumulation of ODSs has slowed and begun to decrease. In response, global ozone depletion is no longer increasing. Now, with continued compliance, we expect substantial recovery of the ozone layer by the late 21st century. The day the Montreal Protocol was agreed upon, 16 September, is now celebrated as the International Day for the Preservation of the Ozone Layer.

This is a story of notable achievements: discovery, understanding, decisions, actions, and verification. It is a story written by many: scientists, technologists, economists, legal experts, and policymakers, in which continuous dialogue has been a key ingredient. A timeline of milestones associated with stratospheric ozone depletion is illustrated in Figure Q0-1. The milestones relate to stratospheric ozone science, international scientific assessments, and the Montreal Protocol.

To help maintain a broad understanding of the relationship between ozone depletion, ODSs, and the Montreal Protocol, this component of the Scientific Assessment of Ozone Depletion: 2010 presents 20 questions and answers about the often-complex science of ozone depletion. Most questions and answers are updates of those presented in previous Ozone Assessments, while others have been added or expanded to address newly emerging issues. The questions address the nature of atmospheric ozone, the chemicals that cause ozone depletion, how global and polar ozone depletion occur, the success of the Montreal Protocol, and what could lie ahead for the ozone layer. Computer models project that the influence on global ozone of greenhouse gases and changes in climate will grow significantly in the coming decades and exceed the importance of ODSs in most atmospheric regions by the end of this century. Ozone and climate are indirectly linked because both ODSs and their substitutes contribute to climate change. 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 2010 and earlier Assessment reports as well as other international scientific assessments. These reports and the answers provided here were prepared and reviewed by a large international group of scientists¹.

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 (about 90%) resides in the stratosphere 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. Ozone has the chemical formula O_3 because an ozone molecule contains three oxygen atoms (see Figure Q1-1). 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 ó $\zeta \epsilon_{IV}$ (ozein), meaning "to smell." Ozone has a pungent odor that allows it to be detected even at very low amounts. Ozone reacts rapidly with many chemical compounds and is explosive in concentrated amounts. Electrical discharges are generally used to produce ozone for industrial processes such as air and water purification and bleaching of textiles and food products.

Ozone location. Most ozone (about 90%) is found in the stratosphere, which begins about 10–16 kilometers (6–10 miles) above Earth's surface and extends up to about 50 kilometers (31 miles) altitude. The stratospheric region with the highest ozone concentration is commonly known as the "ozone layer" (see Figure Q1-2). The ozone layer extends over the entire globe with some variation in altitude and thickness. 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 low relative abundance in the atmosphere. In the stratosphere near the peak concentration of the ozone layer, there are typically a few thousand ozone molecules for every *billion* air molecules (1 billion = 1,000 million). Most air molecules are either oxygen (O₂) or nitrogen (N₂) 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 result when ozone is formed in air polluted by human activities.

As an illustration of the low relative abundance of ozone in our atmosphere, one can imagine bringing all the ozone molecules in the troposphere and stratosphere down to Earth's surface and uniformly distributing these molecules into a layer of gas extending over the globe. The resulting layer of pure ozone would have an average thickness of about three millimeters (about one-tenth inch) (see Q4). Nonetheless, this extremely small fraction of the atmosphere plays a vital role in protecting life on Earth (see Q3).

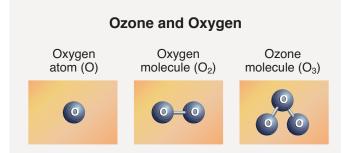


Figure Q1-1. Ozone and oxygen. A molecule of ozone (O_3) contains three oxygen (O) atoms bound together. Oxygen molecules (O_2) , which constitute 21% of the gases in Earth's atmosphere, contain two oxygen atoms bound together.

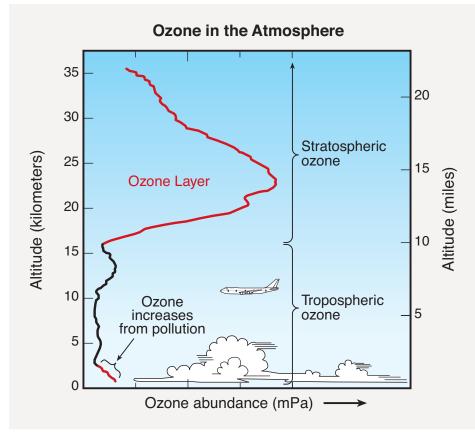


Figure Q1-2. Ozone in the atmosphere. Ozone is present throughout the troposphere and stratosphere. This profile shows schematically how ozone changes with altitude in the tropics. Most ozone resides in the stratospheric "ozone layer." The vertical extent or thickness of this layer varies from region to region and with season over the globe (see Q4). Increases in ozone occur near the surface as a result of pollution from human activities.

Q2

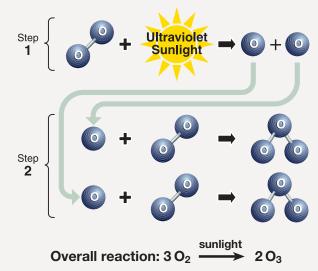
How is ozone formed in the atmosphere?

Ozone is formed throughout the atmosphere in multistep chemical processes that require sunlight. In the stratosphere, the process begins with an oxygen molecule (O_2) being broken apart by ultraviolet radiation from the Sun. In the lower atmosphere (troposphere), ozone is formed by a different set of chemical reactions that involve naturally occurring gases and those from pollution sources.

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

The production of stratospheric ozone is balanced by its destruction in chemical reactions. Ozone reacts continually with sunlight and a wide variety of natural and humanproduced 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 hydrogen and nitrogen oxides and those containing chlorine and bromine (see Q8). Some stratospheric ozone is regularly transported down into the troposphere and can occasionally influence ozone amounts at Earth's surface, particularly in remote, unpolluted regions of the globe.

Tropospheric ozone. Near Earth's surface, ozone is produced by chemical reactions involving naturally occurring gases and gases from pollution sources. Ozone production reactions primarily involve hydrocarbon and nitrogen oxide gases, as well as ozone itself, and all require sunlight for completion. Fossil fuel combustion is a primary source of pollutant gases that lead to tropospheric ozone production. The production of ozone near the surface does not significantly contribute to the abundance of stratospheric ozone. The amount of surface ozone is too small in comparison and the transport of surface air to the stratosphere is not effective enough. As in the stratosphere, ozone in the troposphere is destroyed by naturally occurring chemical reactions and by reactions involving human-produced chemicals. Tropospheric ozone can also be destroyed when ozone reacts with a



Stratospheric Ozone Production

Figure Q2-1. Stratospheric ozone production. Ozone is naturally produced in the stratosphere by a two-step reactive process. In the first step, solar ultraviolet radiation (sunlight) breaks apart an oxygen molecule to form two separate oxygen atoms. In the second step, each atom then undergoes a binding collision with another oxygen molecule to form an ozone molecule. In the overall process, three oxygen molecules plus sunlight react to form two ozone molecules. 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 reactive gases and 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-producing reactions in a certain location, ozone abundances increase. Similarly, if conditions change to favor other reactions that destroy ozone, abundances decrease. The balance of production and loss reactions combined with atmospheric air motions determines the global distribution of ozone on timescales of days to many months. Global ozone has decreased during the past several decades because the amounts of reactive gases containing chlorine and bromine have increased in the stratosphere (see Q13) due to human activities.

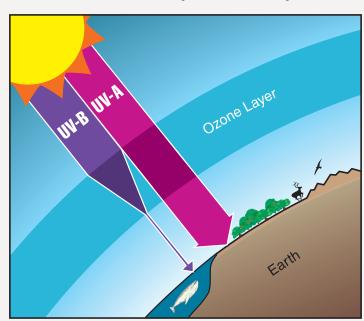
Why do we care about atmospheric ozone?

Ozone in the stratosphere absorbs a large part of the Sun's biologically harmful ultraviolet radiation. Stratospheric ozone is considered "good" ozone because of this beneficial role. In contrast, ozone formed at Earth's surface in excess of natural amounts is considered "bad" ozone because it is harmful to humans, plants, and animals. Natural ozone near the surface and in the lower atmosphere plays an important beneficial role in chemically removing pollutants from the atmosphere.

Good ozone. Stratospheric ozone is considered good for humans and other life forms because it absorbs ultraviolet-B (UV-B) radiation from the Sun (see Figure Q3-1). If not absorbed, UV-B radiation would reach Earth's surface in amounts that are harmful to a variety of life forms. In humans, increased exposure to UV-B radiation increases the risks of skin cancer, cataracts, and a suppressed immune system. UV-B radiation exposure before adulthood and cumulative exposure are both important health risk factors. 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.

Protecting good ozone. In the mid-1970s, it was discovered that gases containing chlorine and bromine atoms released by human activities could cause stratospheric ozone depletion (see Q6). These gases, referred to as halogen source gases, and as ozone-depleting substances (ODSs), chemically release their chlorine and bromine atoms after they reach the stratosphere. Ozone depletion increases surface UV-B radiation above naturally occurring amounts. International efforts have been successful in protecting the ozone layer through controls on ODS production and consumption (see Q15 and Q16).

Bad ozone. Ozone near Earth's surface in excess of natural amounts is considered bad ozone. It is formed by reactions involving human-made pollutant gases. Increasing surface ozone above natural levels is harmful to humans, plants, and other living systems because ozone reacts strongly to destroy or alter many biological molecules. High ozone exposure reduces crop yields and forest growth. In humans, expo-



UV Protection by the Ozone Layer

Figure Q3-1. UV protection by the ozone layer. The ozone layer resides in the stratosphere and surrounds the entire Earth. UV-B radiation (280- to 315-nanometer (nm) wavelength) from the Sun is strongly absorbed in this layer. As a result, the amount of UV-B reaching Earth's surface is greatly reduced. UV-A (315- to 400-nm wavelength), visible light, and other solar radiation are not strongly absorbed by the ozone layer. Human exposure to UV-B radiation increases the risks of skin cancer, cataracts, and a suppressed immune system. UV-B radiation exposure can also damage terrestrial plant life, single-cell organisms, and aquatic ecosystems. sure to high levels of ozone can reduce lung capacity; cause chest pains, throat irritation, and coughing; and worsen preexisting health conditions related to the heart and lungs. In addition, increases in tropospheric ozone lead to a warming of Earth's surface because ozone is a greenhouse gas (see Q18). The negative effects of excess tropospheric ozone contrast sharply with the protection from harmful UV-B radiation afforded by an abundance of stratospheric ozone.

Reducing bad ozone. Limiting the emission of certain common pollutants reduces the production of excess ozone in the air surrounding humans, plants, and animals. Natural emissions from the biosphere, mainly from trees, also participate in reactions that produce ozone. 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 or limiting the emission of pollutants that cause production of excess ozone near Earth's surface.

Natural ozone. In the absence of human activities, ozone would still be present near Earth's surface and throughout the troposphere and stratosphere because ozone is a natural component of the clean atmosphere. Ozone plays important roles in the atmosphere beyond absorbing UV radiation. For example, ozone initiates the chemical removal of many pollutants, such as carbon monoxide (CO) and nitrogen oxides (NO_x), as well as some greenhouse gases, such as methane (CH_4). In addition, the absorption of UV-B radiation by ozone is a natural source of heat in the stratosphere, causing temperatures to increase with altitude. Stratospheric temperatures affect the balance of ozone production and destruction processes (see Q2) and air motions that redistribute ozone throughout the stratosphere.

The Discovery of the Antarctic Ozone Hole

The first decreases in Antarctic total ozone were observed in the early 1980s over research stations located on the Antarctic continent. The measurements were made with ground-based Dobson spectrophotometers (see box in Q5). The observations showed unusually low total 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 Japan Meteorological Agency and the British Antarctic Survey. The results became widely known to the world after three scientists from the British Antarctic Survey published their observations in the scientific journal *Nature* in 1985 and speculated that CFCs were the cause. Soon after, satellite measurements confirmed the spring ozone depletion and further showed that in each late winter/early 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 as a description of the very low total ozone values that encircled the Antarctic continent in satellite images for many weeks (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.

Very early Antarctic ozone measurements. The first total ozone measurements made in Antarctica with Dobson spectrophotometers occurred in the 1950s following extensive measurements in the Northern Hemisphere and Arctic region. Total ozone values found in spring were around 300 DU, surprisingly lower than in the Arctic spring, because the assumption then was that the two polar regions would have similar values. We now know that these Antarctic values were not anomalous; indeed they are similar to those observed there in the 1970s before the ozone hole appeared (see Figure Q11-3). We also now know that Antarctic total ozone values, in comparison with Arctic values, are systematically lower in the early spring because the polar vortex is much stronger and, therefore, much more effective in reducing the transport of ozonerich air from midlatitudes to the pole (compare Figures Q11-3 and Q12-2).

In 1958, measurements of total ozone were made at the Dumont d'Urville station (66.7°S, 140°E) in Antarctica using a photographic plate method to analyze solar ultraviolet radiation after it passed through the ozone layer. The reported measurements were anomalously low, reaching 110–120 DU in September and October. These values are similar to minimum ozone hole values now routinely observed over Antarctica in the same months (see Figure Q11-2). Some have speculated that these limited observations provide evidence that an ozone hole existed before ODS emissions were large enough to cause the depletion. However, analyses of the more extensive Dobson spectrophotometer measurements made at several other Antarctic locations in 1958 did not confirm the low total ozone values. These measurements indicate that the photographic plate determinations were not a reliable source of total ozone values at the Dumont d'Urville station in 1958.

Q8

What are the reactive halogen gases that destroy stratospheric ozone?

Emissions from human activities and natural processes represent a large source of chlorine- and bromine-containing gases that enter the stratosphere. When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to more reactive gases containing chlorine and bromine. Some reactive gases act as chemical reservoirs that convert to form the most reactive gases, namely chlorine monoxide (ClO) and bromine monoxide (BrO). The most reactive gases participate in catalytic reactions that efficiently destroy ozone. Most volcanoes emit some reactive halogen gases that readily dissolve in water 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* (Figure Q8-1). The source gases, which include ozone-depleting substances (ODSs), are emitted at Earth's surface by natural processes and by human activities (see Q7). Once in the stratosphere, the halogen source gases chemically convert at different rates to form the reactive halogen gases. The conversion occurs in the stratosphere for most gases instead of the troposphere because solar ultraviolet radiation (sunlight) is more intense in the stratosphere.

Reactive halogen gases. The chemical conversion of halogen source gases, which involves solar ultraviolet radiation (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. Throughout the stratosphere, the most abundant are typically hydrogen chloride (HCl) and chlorine nitrate (ClONO₂). These two gases are considered important *reservoir* gases because, while they don't react directly with ozone, they can be converted to the *most reactive* forms that

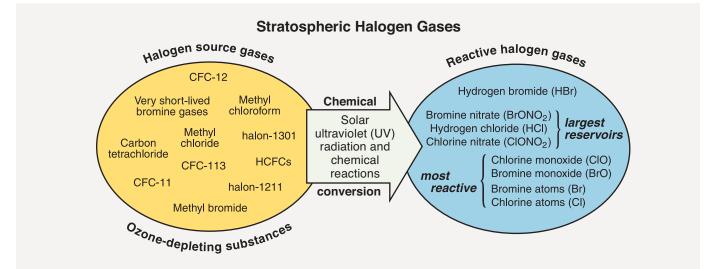


Figure Q8-1. Conversion of halogen source gases. Halogen source gases containing chlorine and bromine are chemically converted to reactive halogen gases primarily in the stratosphere. The conversion requires solar ultraviolet radiation and a few chemical reactions. The shorter-lived gases undergo some conversion in the troposphere. The reactive halogen gases contain all the chlorine and bromine originally present in the source gases before conversion. The reactive gases can be grouped into the reservoir gases, which do not directly destroy ozone, and the most reactive gases, which participate in ozone destruction cycles (see Q9). A principal reactive gas, CIO, is formed by reactions of the reservoir gases HCl and CIONO₂ that occur on the surfaces of liquid and solid polar stratospheric clouds (PSCs) (see Q10).

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 reactive bromine is generally in the form of BrO, whereas usually only a small fraction of reactive chlorine is in the form of ClO. The special conditions that occur in the polar regions in winter cause the reservoir gases $ClONO_2$ and HCl to undergo nearly complete conversion to ClO in reactions on polar stratospheric clouds (PSCs) (see Q10).

Reactive chlorine at midlatitudes. Reactive chlorine gases have been observed extensively in the stratosphere with both local and remote measurement techniques. The measurements from space displayed in Figure Q8-2 are representative of how the amounts of chlorine-containing gases change between the surface and the upper stratosphere at midlatitudes. Available chlorine (see red line in Figure Q8-2) is the sum of chlorine contained in halogen source gases and the reactive gases (e.g., HCl, ClONO₂, ClO). Available chlorine is constant to within about 15 percent from the surface to 47 kilometers (31 miles) altitude. In the troposphere, available chlorine is contained almost entirely in the source gases become a smaller fraction of available chlorine as they are converted to the reactive chlorine gases. At the highest altitudes, available chlorine is all in the form of the reactive chlorine gases.

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

Reactive chlorine in polar regions. Reactive chlorine gases in polar regions undergo large changes between the fall and late winter. Meteorological and chemical conditions in both polar regions are now routinely observed from space in all seasons. Fall and winter conditions over the Antarctic are contrasted in Figure Q8-3 using seasonal observations made near the center of the ozone layer (about 18 km (11.3 miles)) (see Figure Q12-3).

In fall (May), ozone values are high over the entire Antarctic continent and beyond. Temperatures are mid-range, HCl and nitric acid (HNO₃) are high, and ClO is very low. High HCl indicates that substantial conversion of halogen source gases has occurred in the stratosphere. In the past decades, HCl and ClONO₂ reactive reservoir gases have increased substantially in the stratosphere following increased emissions of halogen source gases. HNO₃ is an abundant, naturally

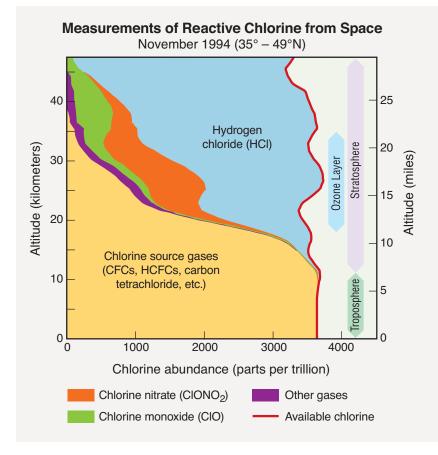
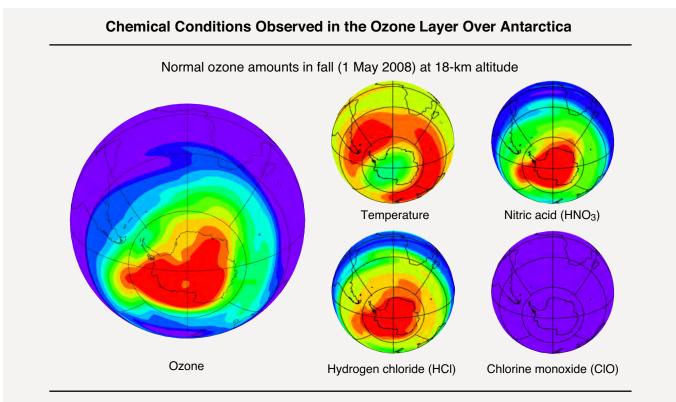


Figure Q8-2. Reactive chlorine gas observations. The abundances of chlorine source gases and reactive chlorine gases as measured from space in 1994 are displayed with altitude for a midlatitude location. In the troposphere (below about 10 kilometers), all chlorine is contained in the source gases. In the stratosphere, the abundances of reactive chlorine gases increase with altitude as the amounts of chlorine source gases decline. This is a conseguence of chemical reactions initiated by solar ultraviolet radiation that convert source gases to reactive gases (see Figure Q8-1). The principal reactive chlorine gases formed are HCl, CIONO₂, and CIO. Summing the source gases with the reactive gases gives "Available chlorine," which is nearly constant with altitude up to 47 km. In the ozone layer (18-35 km), chlorine source gases are still present and HCI and CIONO₂ are the most abundant reactive chlorine gases. (The unit "parts per trillion" is defined in the caption of Figure Q7-1.)



Large ozone depletion in late winter (15 September 2008) at 18-km altitude

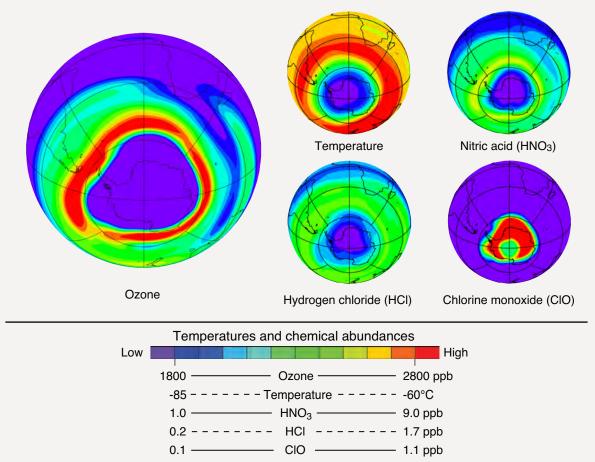


Figure Q8-3. Chemical conditions in the ozone layer over Antarctica. Observations of the chemical conditions in the Antarctic region highlight the changes associated with severe ozone depletion that forms the ozone hole. Satellite instruments now routinely monitor ozone, reactive chlorine gases, and temperatures in the global stratosphere. Results are shown here for fall (May) and late winter (September) seasons in Antarctic winter for a narrow altitude region near 18 kilometers (11.2 miles) within the ozone layer (see Figure Q12-3). Ozone has normal high values in fall before the onset of ozone destruction reactions causes wide spread depletion by late winter. High ozone is accompanied by moderate temperatures, normal high values of HCl and HNO₃, and normal very low CIO amounts. When CIO is not enhanced, significant ozone destruction from ozone-depleting substances does not occur. Chemical conditions are quite different in late winter when ozone undergoes severe depletion. Temperatures are much lower, HCI has been converted to CIO, the most reactive chlorine gas, and HNO₃ has been removed by the gravitational settling of PSC particles. CIO values closely surrounding the South Pole are low in September because CIO formation requires sunlight, which is still gradually returning to the highest latitudes. The high CIO values in late winter last for 1 to 2 months, cover an area that at times exceeds that of the Antarctic continent, and efficiently destroy ozone in sunlit regions in late winter/early spring. Ozone typically reaches its minimum values in early to mid-October (see Q12). Note that the first and last colors in the color bar represent values outside the indicated range of values. (The unit "parts per billion," abbreviated "ppb," is used here as a measure of the relative abundance of a gas in air: 1 part per billion equals the presence of one molecule of a gas per billion (=10⁹) total air molecules (compare to ppt in Figure Q7-1)).

occurring stratospheric compound that moderates ozone destruction chemistry and also condenses to help form polar stratospheric clouds (PSCs) (see Q10). Low ClO indicates that little conversion of the reactive reservoirs occurs in the fall, thereby limiting catalytic ozone destruction.

By late winter (September), ozone amounts reflect substantial depletion at 18-km altitude over an area larger than the Antarctic continent. Depletion throughout much of the altitude range of the ozone layer created the 2008 ozone hole shown in Figure Q11-3 (see altitude profile in Figure Q12-3). The associated meteorological and chemical conditions in late winter are very different from those found in fall: very low temperatures, very low HCl and HNO₃, and very high ClO. Low stratospheric temperatures are characteristic of winter when solar heating is reduced. Low HCl and high ClO reflect the conversion of the reactive halogen reservoir compounds, HCl and ClONO₂, to the most reactive chlorine form, ClO. This conversion occurs selectively in winter on PSCs and other stratospheric particles, which form at the very low temperatures (see Q10). Low HNO₃ is indicative of its condensation to form PSCs, some of which subsequently move to lower altitudes through gravitational settling. High ClO abundances generally cause ozone depletion to continue in the Antarctic region until mid-October (spring), when the lowest ozone values usually are observed (see Q11). As temperatures rise at the end of the winter, halting further PSC formation, ClO is converted back into the reactive reservoir species HCl and ClONO₂ (see Q10), and ozone destruction is curtailed.

Similar though less dramatic changes in meteorological and chemical conditions are also observed between fall and winter in the Arctic, where winter ozone depletion is less severe than in the Antarctic.

Reactive bromine observations. Fewer measurements are available for reactive bromine gases in the lower stratosphere than for reactive chlorine, in part because of the lower abundance of bromine. The most widely observed bromine gas is bromine monoxide (BrO), which can be observed from space. Estimates of reactive bromine abundances in the stratosphere are larger than expected from the conversion of the halons and methyl bromide source gases, suggesting that the contribution of the very short-lived bromine-containing gases to reactive bromine must also be significant (see Q7).

Other sources. Other emission sources of reactive halogen gases exist that are associated with natural processes and human activities. Most emissions become trapped in the lower atmosphere when dissolved in water, and ultimately are returned to Earth's surface before they can reach the stratosphere. Volcanoes are an important episodic source of reactive halogen gases (e.g., HCl) that do not reach the stratosphere in appreciable quantities (see Q14). Other examples include reactive chlorine produced by evaporation of ocean spray. Sea salt products dissolve in water and are removed in the lower atmosphere. Solid rocket motors, such as those used on the Space Shuttle, release reactive chlorine gases directly into the troposphere and stratosphere. At current launch rates, the emitted quantities are very small in comparison with halogen emissions from other human activities.

Are there controls on the production of ozone-depleting substances?

Yes, the production and consumption of ozone-depleting substances are controlled under a 1987 international agreement known as the "Montreal Protocol on Substances that Deplete the Ozone Layer" and by its subsequent Amendments and Adjustments. The Protocol, now ratified by all 196 United Nations members, establishes legally binding controls on national production and consumption of ozone-depleting substances (ODSs). Production and consumption of all principal ODSs by developed and developing nations will be almost completely phased out before the middle of the 21st century.

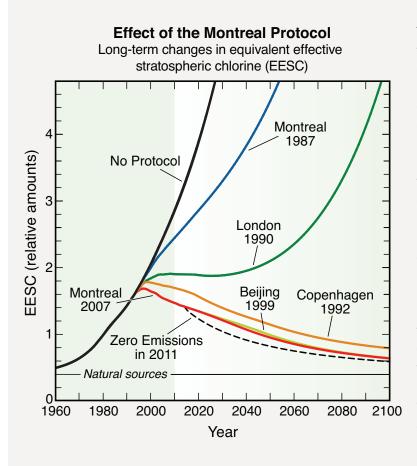
Montreal Protocol. In 1985, a treaty called the Vienna Convention for the Protection of the Ozone Layer was signed by 20 nations in Vienna. The signing nations agreed to take appropriate measures to protect the ozone layer from human activities. The Vienna Convention was a framework agreement that supported 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, following sufficient country ratification, entered into force in 1989. The Protocol has been successful in establishing legally binding controls for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion. Halogen source gases containing chlorine and bromine controlled under the Montreal Protocol are referred to as ozonedepleting substances (ODSs). National consumption of an ODS is defined as the amount that production and imports of the substance exceed its export to other nations. The Protocol provisions are structured for developed countries to act first and for developing countries to follow with some financial assistance. In 2010, the Montreal Protocol became the first international treaty to achieve universal ratification by all 196 United Nations members.

U15

Amendments and Adjustments. As the scientific basis of ozone depletion became more certain after 1987 and substitutes and alternatives became available to replace ODSs, the Montreal Protocol was strengthened with Amendments and Adjustments. Each Amendment is named after the city in which the meeting of the Parties to the Montreal Protocol took place and by the year of the meeting. The timeline in Figure Q0-1 shows some of the major decisions that have been adopted in the last two decades. These decisions have put additional ODSs under control, accelerated existing control measures, and prescribed phase-out dates for the production and consumption of certain gases. The initial Protocol called for a 50% reduction in chlorofluorocarbon (CFC) production and a freeze on halon production. The 1990 London Amendment called for a phase-out of the production and consumption of the most damaging ODSs in developed nations by 2000 and in developing nations by 2010. The 1992 Copenhagen Amendment accelerated the phase-out date to 1996 in developed nations. Further controls on ODSs were agreed upon in later meetings in Vienna (1995), Montreal (1997, 2007), and Beijing (1999).

Influence of the Montreal Protocol. Montreal Protocol controls are based on several factors that are considered separately for each ODS. The factors include (1) the effectiveness in depleting ozone in comparison with other substances (see Ozone Depletion Potential (ODP) in Q18), (2) the availability of suitable substitutes for domestic and industrial use, and (3) the potential impact of controls on developing nations. The influence of Montreal Protocol provisions on stratospheric ODS abundances can be demonstrated with long-term changes in equivalent effective stratospheric chlorine (EESC). Calculations of EESC combine the amounts of chlorine and bromine present in surface air to form a measure of the potential for ozone destruction in a particular stratospheric region on an annual basis (see definition in Q16). The long-term changes in EESC at midlatitudes are shown in Figure Q15-1 for several cases:

▶ No Protocol. Without the Montreal Protocol the production, use, and emissions of CFCs and other ozone-depleting substances is expected to have increased after 1987 with an annual growth rate of about 3% (business-as-usual scenario). As a result, EESC is projected to have increased nearly 10-fold by the mid-2050s compared with the 1980 value. Computer models of the atmosphere indicate that such high EESC values would have at least doubled global total ozone depletion between 1990 and 2010 and increased it far beyond that by midcentury. As a result, harm-



ful UV-B radiation would have increased substantially at Earth's surface, causing a global rise in skin cancer and cataract cases (see Q17).

► Montreal Protocol provisions. International compliance with only the 1987 provisions of the Montreal Protocol and the later 1990 London Amendment would have substantially slowed the projected growth of EESC. Not until the 1992 Copenhagen Amendments and Adjustments did the Protocol projections show a *decrease* in future EESC values. The provisions became more stringent with the Amendments and Adjustments adopted in Beijing in 1999 and Montreal in 1997 and 2007. Now, with full compliance to the Protocol, most ODSs will be almost completely phased out, with some exemptions for critical uses (see Q16). Global EESC is slowly decaying from its peak value in the late 1990s and is expected to reach 1980 values in the mid-21st century. The success of the Montreal Protocol to date is demonstrated by the decline in ODP-weighted emissions of ODSs shown in Figure Q0-1. Total emissions peaked in 1988 at values about 10-fold higher than natural Figure Q15-1. Effect of the Montreal Protocol. The objective of the Montreal Protocol is the protection of the ozone layer through control of the global production and consumption of ODSs. Projections of the future abundances of ODSs expressed as equivalent effective stratospheric chlorine (EESC) values (see Q16) are shown separately for the midlatitude stratosphere for (1) no Protocol provisions, (2) the provisions of the original 1987 Montreal Protocol and some of its subsequent Amendments and Adjustments, and (3) zero emissions of ODSs starting in 2011. The city names and years indicate where and when changes to the original 1987 Protocol provisions were agreed upon (see Figure Q0-1). EESC is a relative measure of the potential for stratospheric ozone depletion that combines the contributions of chlorine and bromine from ODS surface observations (see Q16). Without the Protocol, EESC values are projected to have increased significantly in the 21st century. Only with the Copenhagen (1992) and subsequent Amendments and Adjustments did projected EESC values show a long-term decrease.

emissions. Between 1988 and 2010, ODS emissions from human activities have decreased by over 80%.

► Zero emissions. EESC values in the coming decades will be influenced by (1) the slow natural removal of ODSs still present in the atmosphere, (2) emissions from continued production and use of ODSs, and (3) emissions from currently existing *banks* containing a variety of ODSs. ODS banks are associated with applications that involve longterm containment of halogen gases. Examples are CFCs in refrigeration equipment and insulating foams, and halons in fire-fighting equipment. New emissions are projected based on continued production and consumption of ODSs, particularly in developing nations, under existing Protocol provisions.

The zero-emissions case demonstrates the EESC values that would occur if it were possible to set all ODS emissions to zero beginning in 2011. This would eliminate the contributions from new production and bank emissions. Significant differences from the Montreal 2007 projections are evident in the first decades following 2011 because the phase-out of all ODS production under the Protocol is not yet complete and bank emissions are substantial. Zero emissions would bring forward the return of EESC to 1980 levels by about 13 years.

HCFC substitute gases. The Montreal Protocol provides for the use of hydrochlorofluorocarbons (HCFCs) as transitional, short-term substitute compounds for ODSs with higher ODPs, such as CFC-12. HCFCs are used for refrigeration, in making insulating foams, and as solvents, all of which were primary uses of CFCs. HCFCs are generally more reactive in the troposphere than other ODSs because they contain hydrogen (H) in addition to chlorine, fluorine, and carbon. HCFCs are 88 to 98% less effective than CFC-12 in depleting stratospheric ozone because their chemical removal occurs primarily in the troposphere (see ODPs in Table Q7-1). This removal protects stratospheric ozone from most of the halogen content of HCFC emissions. In contrast, CFCs and many other ODSs release all of their halogen content in the stratosphere because they are chemically inert in the troposphere (see Q6).

Under the provisions of the Montreal Protocol, developed and developing countries may continue to use HCFCs as ODS substitutes in the coming decades before they are ultimately phased out. In the most recent Adjustment to the Protocol (Montreal 2007), the phase-out of HCFCs for all Parties was accelerated so that it will be complete in 2030, a decade earlier than in previous provisions. In adopting this decision, the Parties reduced the contribution of HCFC emissions to both long-term ozone depletion and future climate forcing (see Q18 and Q19).

HFC substitute gases. Hydrofluorocarbons (HFCs) are used as long-term substitute compounds for CFCs, HCFCs, and other ODSs. HFCs contain hydrogen, fluorine, and carbon. HFCs do not contribute to ozone depletion because they contain no chlorine, bromine, or iodine. As a consequence, HFCs are not ODSs and are not subject to the provisions of the Montreal Protocol. HFCs and all ODSs are radiatively active gases that contribute to human-induced climate change based on their accumulation in the atmosphere (see Q18). HFCs are included in the basket of gases being controlled by the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC). The Kyoto Protocol is an international treaty designed to protect climate by controlling emissions of HFCs, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆). HFC emissions are expected to grow substantially in coming decades as the demand for their use as substitute gases and in new applications increases in developed and developing countries. The climate change contribution from future HFC emissions will be minimized if HFCs with very low Global Warming Potentials (GWPs) (less than 100) are chosen to meet the growing demand (see Q18).

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. Changes in ozone and climate are directly linked because ozone absorbs solar radiation and is also a greenhouse gas. Stratospheric ozone depletion and increases in global tropospheric ozone that have occurred in recent decades have opposing contributions to climate change. The ozone-depletion contribution, while leading to surface cooling, is small compared with the contribution from all other greenhouse gas increases, which leads to surface warming. The total forcing from these other greenhouse gases is the principal cause of observed and projected climate change. Ozone depletion and climate change are indirectly linked because both ozone-depleting substances and their substitutes are greenhouse gases.

While stratospheric ozone depletion is not the principal cause of climate change, aspects of ozone depletion and climate change are closely linked. Both processes involve gases released to the atmosphere by human activities. The links are best understood by examining the contribution to climate change of the gases involved: ozone; ozone-depleting substances (ODSs) (or halogen source gases) and their substitutes; and other leading greenhouse gases.

Greenhouse gases and the radiative forcing of climate. The warming of the Earth by the Sun is enhanced by the presence of natural *greenhouse gases*, of which water vapor is an important example. Without this natural greenhouse effect, the Earth's surface would be much colder. Human activities since the preindustrial era have led to long-term increases in the atmospheric abundances of a number of long-lived and shortlived greenhouse gases. This group includes stratospheric

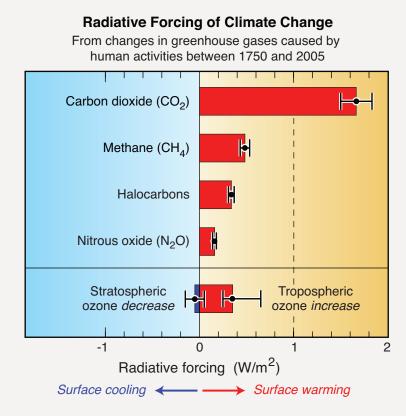


Figure Q18-1. Radiative forcing of greenhouse gases. Human activities since the start of the Industrial Era (around 1750) have caused increases in the abundances of several shortlived and long-lived gases, known as greenhouse gases, that all contribute to the radiative forcing of climate, also known as climate forcing. Radiative forcing is expressed in units of watts per square meter (W/m^2) . As shown in the figure, the largest forcings are those of carbon dioxide (CO₂), followed by methane (CH₄), tropospheric ozone, halocarbon gases, and nitrous oxide (N₂O). The black whiskers on each bar show uncertainties in the values. Tropospheric ozone increases result from the emission of pollutant gases and create a positive ozone forcing. Positive forcings lead 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. Halocarbons include all ODSs, their substitutes, and a few other gases

(see Figure Q18-2). In the coming decades, ODS abundances and stratospheric ozone depletion are expected to be reduced, along with their associated radiative forcings.

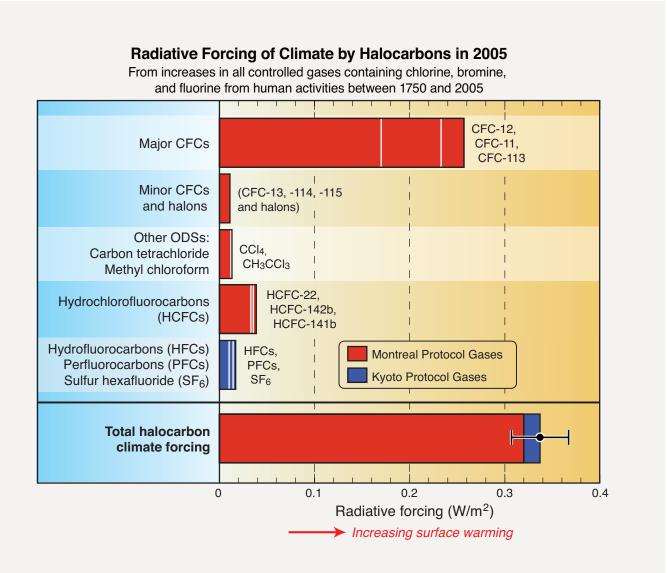


Figure Q18-2. Halocarbons and radiative forcing of climate change. Halocarbon gases in the atmosphere represent an important contribution to the radiative forcing of climate between 2005 and the preindustrial era (see Figure Q18-1). Halocarbons are all gases containing chlorine, bromine, or fluorine atoms that are now controlled as ozone-depleting substances (ODSs) by the Montreal Protocol or as climate change gases by the Kyoto Protocol (see color shading). Shown in the figure are the separate contributions of each gas or group of gases, as estimated using atmospheric abundance histories and Global Warming Potentials (GWPs) (see Figure Q18-3). The gases listed in the right hand labels begin with the largest contribution in each group, except for CFC-13, CFC-114, CFC-115, and halons, which are shown as one total value. The individual forcing terms add together to form the bottom bar representing the total halocarbon forcing. The forcings of CFC-11 and CFC-12, the largest halocarbon contributions, are already decreasing and will continue to decrease as CFCs are gradually removed from the atmosphere (see Figure Q16-1). In contrast, the contributions of the intermediate-term ODS substitute gases, HCFCs, are projected to grow for another two decades before decreasing. The future contributions of the long-term ODS substitute gases, HFCs, are also expected to increase. In this case, the total contribution will depend strongly on which HFCs are used because the GWPs of individual HFCs vary widely (see Figure Q18-3).

and tropospheric ozone, halocarbons, carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). ODSs and their substitutes make up a large fraction of the halocarbons in today's atmosphere. The natural abundances of these gases in Earth's atmosphere change the balance between incoming solar radiation and outgoing infrared radiation, warming the atmosphere and surface. Increases in the abundance of these gases from human activities cause more outgoing radiation to be absorbed, which further warms the atmosphere and surface. This change in Earth's radiative balance caused by human activities is called a *radiative forcing of climate* or, more simply, a *climate forcing*. The magnitude of this *energy* imbalance is usually evaluated at the top of the troposphere (tropopause) and is expressed using units of watts per square *meter* (W/m^2) . The potential for climate change increases as this radiative forcing increases.

A summary of radiative forcings in 2005 resulting from the increases in the principal long-lived and short-lived greenhouse gases during the Industrial Era is shown in Figure Q18-1. All forcings shown relate to human activities. Positive forcings generally lead to *warming* and negative forcings lead to *cooling* of Earth's surface. Climate forcings also lead to other changes, such as in precipitation patterns and extreme weather events. International climate assessments conclude that much of the observed surface warming and changes in other climate parameters over the last decades is due to increases in the abundance of carbon dioxide and other greenhouse gases caused by human activities.

Stratospheric and tropospheric ozone. Stratospheric and tropospheric ozone both absorb infrared radiation emitted by Earth's surface, trapping heat in the atmosphere. Stratospheric ozone also significantly absorbs solar radiation. As a result, increases or decreases in stratospheric or tropospheric ozone induce a climate forcing and, therefore, represent direct links between ozone and climate. In recent decades, global stratospheric ozone has decreased due to rising reactive chlorine and bromine amounts in the atmosphere, while global tropospheric ozone in the Industrial Era has increased due to pollution from human activities (see Q3). Stratospheric ozone depletion has caused a small negative radiative forcing since preindustrial times, while increases in tropospheric ozone have caused a positive radiative forcing (see Figure Q18-1). Summing the positive forcing due to tropospheric ozone increases with the smaller negative forcing from stratospheric ozone depletion yields a net positive radiative forcing. The large uncertainty in tropospheric ozone forcing reflects the difficulty in quantifying tropospheric ozone trends and in

modeling the complex production and loss processes that control its abundance. The negative radiative forcing from stratospheric ozone depletion will diminish in the coming decades as ODSs are gradually removed from the atmosphere.

Stratospheric ozone depletion cannot be a principal cause of present-day global climate change for two reasons: first, the climate forcing from ozone depletion is negative, which leads to surface cooling. Second, the total forcing from other longlived and short-lived gases in Figure Q18-1 is positive and far larger. The total forcing from these other gases is the principal cause of observed and projected climate change.

Carbon dioxide, methane, and nitrous oxide. The accumulation of carbon dioxide during the Industrial Era represents the largest climate forcing related to human activities. Carbon dioxide concentrations continue to increase in the atmosphere primarily as the result of burning fossil fuels (coal, oil, and natural gas) for energy and transportation, as well as from cement manufacturing. The atmospheric abundance of carbon dioxide in 2005 was about 36% above what it was 260 years ago in preindustrial times. Carbon dioxide is considered a *long-lived* gas, since a significant fraction remains in the atmosphere 100–1000 years after emission.

Methane is a *short-lived* climate gas (atmospheric lifetime of about 10 years) that has both human and natural sources. Human sources include livestock, rice agriculture, and landfills. Natural sources include wetlands, oceans, and forests.

Nitrous oxide is a *long-lived* climate gas (atmospheric lifetime of about 110 years) that also has both human and natural sources. The largest human source is agricultural activities, especially related to fertilization. Microbial processes in soils that are part of natural biogeochemical cycles represent the largest natural source. In the stratosphere, nitrous oxide is the principal source of reactive nitrogen species, which participate in ozone destruction cycles (see Q2 and Q7).

Halocarbons. Halocarbons in the atmosphere contribute to both ozone depletion and climate change. As used here, halocarbons represent those gases containing chlorine, bromine, or fluorine atoms that are now controlled substances under the Montreal Protocol or the Kyoto Protocol. ODSs are the halocarbons controlled under the Montreal Protocol. HFC substitute gases, perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆) are controlled under the Kyoto Protocol. In 2005, the halocarbon contribution to climate forcing was 0.34 W/m^2 , which is the third or fourth largest following carbon dioxide and methane (see Figure Q18-1). The contributions of individual halocarbon gases are highlighted in Figure Q18-2. Within the halocarbons, CFCs contribute the largest percentage (80%) to the 2005 climate

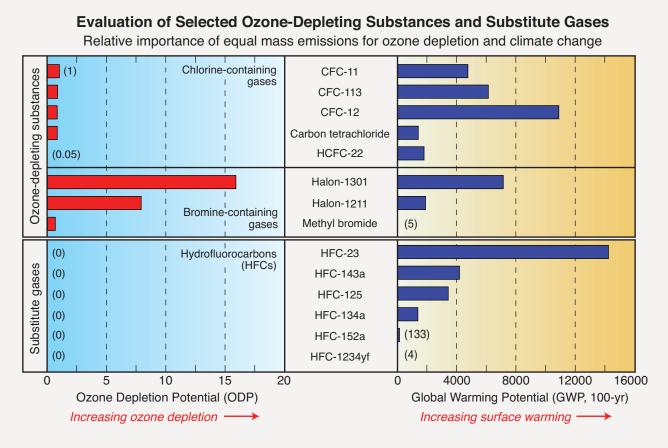


Figure Q18-3. ODPs and GWPs. ODSs and their substitutes can be compared via their Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) (see Table Q7-1). Larger ODPs or GWPs indicate greater potential for ozone depletion or climate warming, respectively, when a gas is emitted to the atmosphere. The ODP and GWP values are derived assuming an equal mass of each gas is emitted. The GWPs shown here are evaluated for a 100-year time interval after emission. The ODP of CFC-11 and the GWP of CO₂ are assigned reference values of 1.0. The CFCs, halons, and HCFCs are ozone-depleting substances (see Q7) while HFCs, used as ODS substitutes, do not destroy ozone (ODPs equal 0). The ODPs of the halons far exceed those of the CFCs. All ODSs and their substitutes shown here have a non-zero GWP, with values spanning the wide range of 4 to 14,000.

forcing. HCFCs, the intermediate-term ODS substitutes, make the next largest contribution (12%). The atmospheric abundance of HFCs, the longer-term ODS substitutes, contributes only 3% to the 2005 halocarbon climate forcing.

The large contribution of the CFCs is expected to gradually decrease following the projected decline in their atmospheric abundance (see Figure Q16-1). Based on their long lifetimes, CFCs will still make a significant contribution, and most likely the largest ODS contribution, to halocarbon climate forcing at the end of the 21^{st} century. Halocarbons controlled under the Kyoto Protocol (HFCs, PFCs, and SF₆) represent about 5% of halocarbon climate forcing in 2005. With the projected growth of HFC production and consumption in

developing nations, this percentage contribution is expected to increase substantially in the coming decades.

Ozone Depletion Potentials and Global Warming Potentials. An important way of comparing the influence of individual halocarbons on ozone depletion and climate change is to use Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs). The ODP and GWP of a gas quantify its effectiveness in causing ozone depletion and climate forcing, respectively (see Table Q7-1). The principal halocarbon gases are contrasted with each other in Figure Q18-3. The ODP of CFC-11 and the GWP of carbon dioxide are assigned reference values of 1. The CFCs and carbon tetrachloride all have ODPs near 1, indicating comparable effectiveness in causing ozone depletion. The principal halons have ODPs greater than 7, making them the most effective ozone-depleting substances. HFCs have ODPs of zero since they cause no ozone depletion (see Q7).

All halocarbons have non-zero GWPs and, therefore, contribute to climate forcing. The GWP does not correspond strongly with the ODP of a gas because these quantities depend on different chemical and physical properties. For example, while HFC-134a does not destroy ozone (ODP equal 0), each gram emitted is 1,370 times more effective than a gram of carbon dioxide in causing climate forcing. The future selection of specific HFCs as ODS substitutes or for use in new global applications will have important consequences for climate forcing. When these HFCs are eventually released to the atmosphere, the contribution to climate forcing will depend on their GWPs, which could vary over a wide range (4 to 14,000).

Montreal Protocol regulations have led to reductions in CFC emissions and increases in HCFC emissions (see Q16). As a result of these actions, the total radiative forcing from ODSs is slowly decreasing (see Q19). Overall halocarbon radiative forcing, however, is slowly increasing because of growing contributions from HFCs, PFCs, and SF₆. It is important to note that, despite having a GWP that is small in

comparison to many other halocarbons and other greenhouse gases, carbon dioxide is the most important greenhouse gas related to human activities because its emissions are large and its atmospheric abundance is far greater than the abundances of other emitted gases.

Impact of climate change on ozone. 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, lower temperatures and stronger polar winds could both increase the extent and severity of winter polar ozone depletion. While the Earth's surface is expected to continue warming in response to the net positive radiative forcing from greenhouse gas increases, the stratosphere is expected to continue cooling. A cooler stratosphere would extend the time period over which polar stratospheric clouds (PSCs) are present in winter and early spring and, as a result, might increase polar ozone depletion. In the upper stratosphere at altitudes above PSC formation regions, a cooler stratosphere is expected to increase ozone amounts because lower temperatures decrease the effectiveness of ozone loss reactions. Furthermore, climate change may alter the strength of the stratospheric circulation and with it the distribution of ozone in the stratosphere (see Q20).