Twenty Questions and Answers About the Ozone Layer: 2018 Update

Scientific Assessment of Ozone Depletion: 2018

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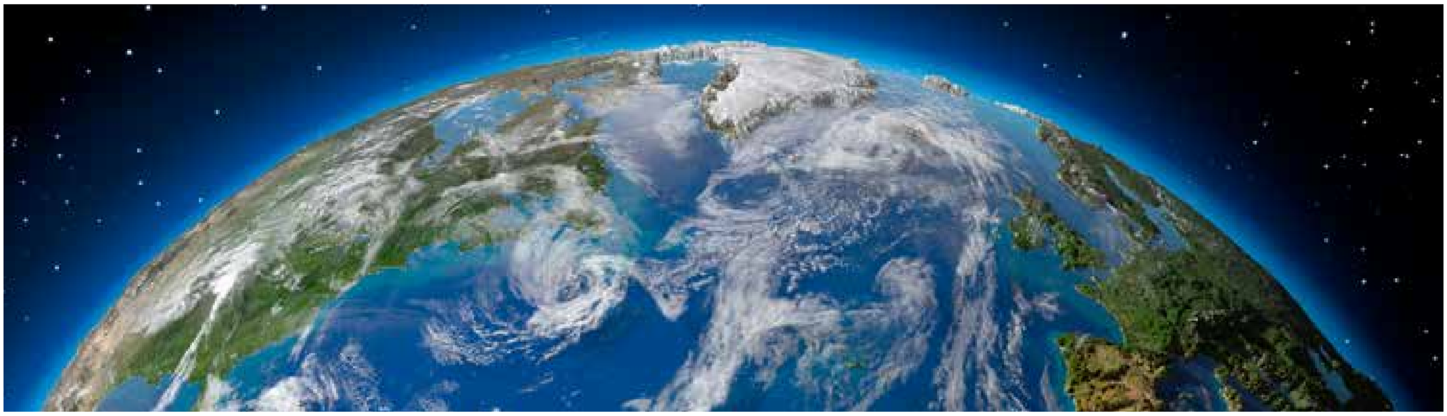


World Meteorological Organization
United Nations Environment Programme
National Oceanic and Atmospheric Administration
National Aeronautics and Space Administration
European Commission

Q3 How is total ozone distributed over the globe?

The distribution of total ozone over Earth varies with geographic location and on daily to seasonal timescales. These variations are caused by large-scale movements of stratospheric air and the chemical production and destruction of ozone. Total ozone is generally lowest at the equator and highest in midlatitude and polar regions.

Total ozone. The total ozone column at any location on the globe is defined as the sum of all the ozone in the atmosphere directly above that location. Most ozone resides in the stratospheric ozone layer and a small percentage (about 10%) is distributed throughout the troposphere (see Q1). Total ozone column values are often reported in *Dobson units* denoted as "DU." Typical values vary between 200 and 500 DU over the globe, with a global average abundance of about 300 DU (see **Figure Q3-1**). The quantity of ozone molecules required for total ozone to be 300 DU could form a layer of pure ozone gas at Earth's surface having a thickness of only 3 millimeters (0.12 inches) (see Q1), which is about the height of a stack of 2 common coins. It is remarkable that a layer of pure ozone only 3 millimeters thick protects life on Earth's surface from harmful UV radiation emitted by the Sun (see Q2).

Global distribution. Total ozone varies strongly with latitude over the globe, with the largest values occurring at middle and high latitudes during most of the year (see Figure Q3-1). This distribution is the result of the large-scale circulation of air in the stratosphere that slowly transports ozone from the tropics, where ozone production from solar ultraviolet radiation is highest, toward the poles. Ozone accumulates at middle and high latitudes, increasing the vertical extent of the ozone layer and, at the same time, total ozone. Values of total ozone are generally smallest in the tropics for all seasons. An exception in recent decades is the region of low values of ozone over Antarctica during spring in the Southern Hemisphere, a phenomenon known as the Antarctic ozone hole (dark blue, Figure Q3-1; also see Q10 and Q11).

Seasonal distribution. Total ozone also varies with season, as shown in Figure Q3-1 using two-week averages of ozone taken from 2009 satellite observations. March and September plots represent the early spring and autumn seasons in the Northern and Southern Hemispheres. June and December plots similarly represent the early summer and winter seasons. During spring, total ozone exhibits maximums at latitudes poleward of about 45°N in the Northern Hemisphere and between 45° and 60°S in the Southern Hemisphere. These spring maximums are a result of increased transport of ozone from its source region in the tropics toward high latitudes during late autumn and winter. This poleward ozone transport is much weaker during the summer and early autumn periods and is weaker overall in the Southern Hemisphere.

This natural seasonal cycle can be observed clearly in the Northern Hemisphere as shown in Figure Q3-1, with increasing values in Arctic total ozone during winter, a clear maximum in spring, and decreasing values from summer to autumn. In the Antarctic, however, a pronounced minimum in total ozone is observed during spring. The minimum is known as the "ozone hole", which is caused by the widespread chemical depletion of ozone in spring by pollutants known as ozone-depleting substances (see Q5 and Q10). In the late 1970s, before the ozone hole appeared each year, much higher ozone values than those currently observed were found in the Antarctic spring (see Q10). Now, the lowest values of total ozone across the globe and all seasons are found every late winter/early spring in the Antarctic as shown in Figure Q3-1. After spring, these low values disappear from total ozone maps as polar air mixes with lower-latitude air containing much higher amounts of ozone.

In the tropics, the change in total ozone through the progression of the seasons is much smaller than in the polar regions. This feature is due to seasonal changes in both sunlight and ozone transport being much smaller in the tropics compared to polar regions.

Natural variations. Total ozone varies strongly with latitude and longitude as seen within the seasonal plots in Figure Q3-1. These patterns come about for two reasons. First, atmospheric winds transport air between regions of the stratosphere that have high ozone values and those that have low ozone values. Tropospheric weather systems can temporarily alter the vertical extent of the ozone layer in a region, and thereby change total ozone. The regular nature of these air motions, in some cases associated with geographical features (oceans and mountains), in turn causes recurring patterns in the distribution of total ozone.

Second, ozone variations occur as a result of changes in the balance of chemical production and loss processes as air moves to and from different locations over the globe. This balance, for example, is very sensitive to the amount of sunlight in a region.

There is a good understanding of how chemistry and air motions work together to cause the observed large-scale features in total ozone, such as those seen in Figure Q3-1. Ozone changes are routinely monitored by a large group of investigators using satellite, airborne, and ground-based instruments. The continued analyses of these observations provide an important basis to quantify the contribution of human activities to ozone depletion.

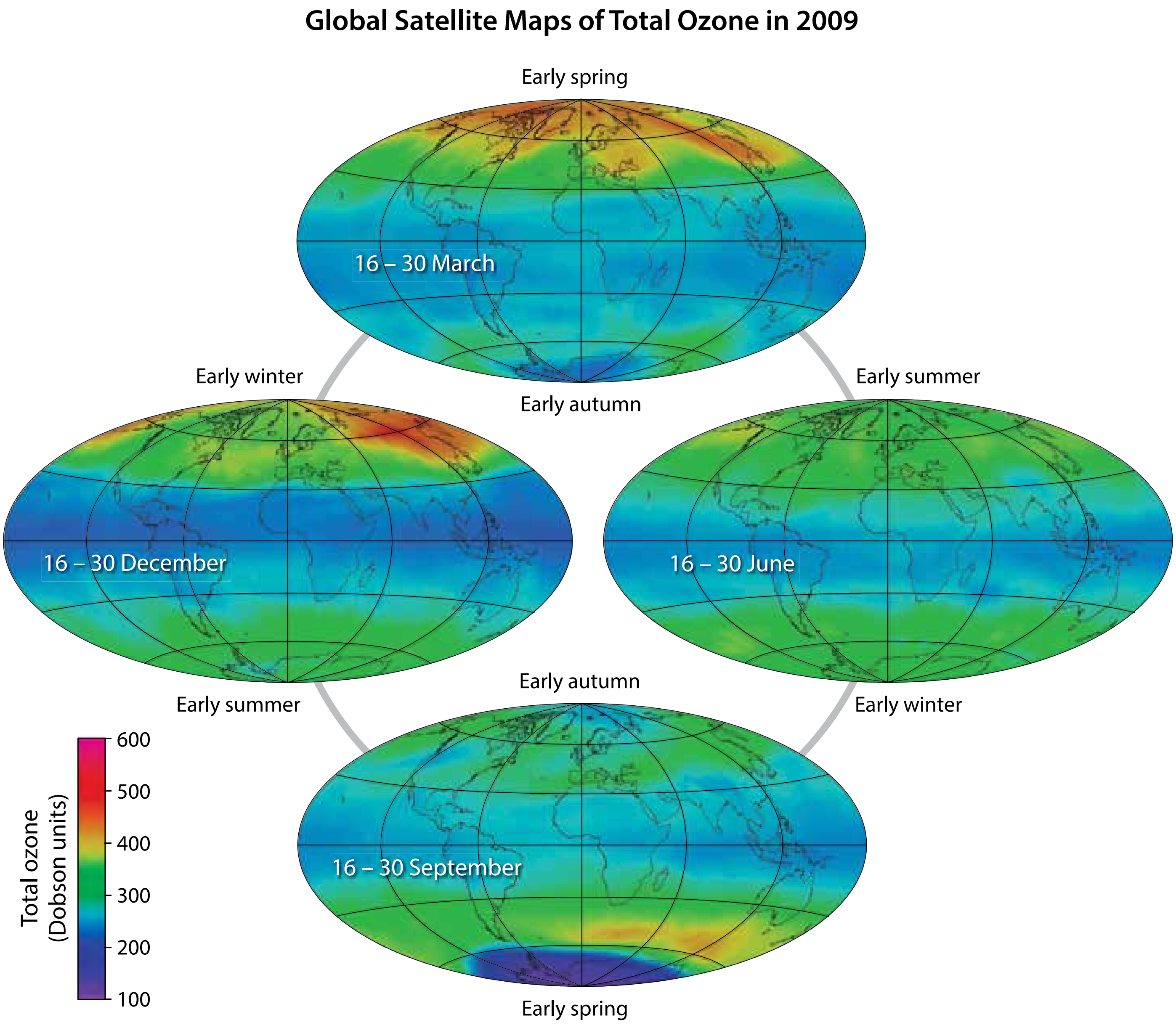


Figure Q3-1. Total ozone. Total ozone at any location on the globe is defined as the sum of all the ozone molecules in the atmosphere directly above that location. Total ozone varies with latitude, longitude, and season, with the largest values at high latitudes and the lowest values in tropical regions. The variations are demonstrated here with two-week averages of total ozone in 2009 as measured with a satellite instrument. Total ozone shows little variation in the tropics (20°N–20°S latitudes) over all seasons. Total ozone outside the tropics varies more strongly with time on a daily to seasonal basis as ozone-rich air is moved from the tropics and accumulates at higher latitudes, with more being transported in winter. The low total ozone values over Antarctica in September constitute the "ozone hole" in 2009. Since the 1980s, the ozone hole in late winter/early spring represents the lowest values of total ozone that occur over all seasons and latitudes (see Q10).

Q5

How do emissions of halogen source gases lead to stratospheric ozone depletion?

The initial step in the depletion of stratospheric ozone by human activities is the emission, at Earth's surface, of gases that contain chlorine and bromine and have long atmospheric lifetimes. Most of these gases accumulate in the lower atmosphere because they are relatively unreactive and do not dissolve readily in rain or snow. Natural air motions transport these accumulated gases to the stratosphere, where they are converted to more reactive gases. Some of these 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 Q5-1**. The process begins with the *emission*, at Earth's surface, of long-lived source gases containing the halogens chlorine and bromine (see Q6). The halogen source gases, often referred to as ozone-depleting substances (ODSs), include manufactured chemicals released to the atmosphere in a variety of applications, such as refrigeration, air conditioning, and foam blowing. Chlorofluorocarbons (CFCs) are an important example of a chlorine-containing source gas. Emitted source gases *accumulate* in the lower atmosphere (troposphere) and are *transported* to the stratosphere by natural air motions. The accumulation occurs because most source gases are highly unreactive in the lower atmosphere. Small amounts of these gases dissolve in ocean waters. The low reactivity of these manufactured halogenated gases is one property that made them well suited for specialized applications such as refrigeration.

Some halogen gases are emitted in substantial quantities from natural sources (see Q6). These emissions also accumulate in the troposphere, are transported to the stratosphere, and participate in ozone destruction reactions. These naturally emitted gases are part of the natural balance of ozone production and destruction that predates the large release of manufactured halogenated gases.

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 Q7). The rate of conversion is related to the atmospheric lifetime of a gas (see Q6). Gases with longer lifetimes have slower conversion rates and survive longer in the atmosphere after emission. Lifetimes of the principal ODSs vary from about 1 to 100 years (see Table Q6-1). Emitted gas molecules with atmospheric lifetimes greater than a few years circulate between the troposphere and stratosphere multiple times, on average, before conversion occurs.

The reactive gases formed from halogen source gases *react* chemically to destroy ozone in the stratosphere (see Q8). The average depletion of total ozone attributed to reactive gases is smallest in the tropics and largest at high latitudes (see Q12). In polar regions, surface reactions that occur at low temperatures on polar stratospheric clouds greatly increase the abundance of the most reactive chlorine gas, chlorine monoxide (ClO) (see Q9). This process results in substantial ozone destruction in polar regions in late winter/early spring (see Q10 and Q11).

After a few years, air in the stratosphere returns to the troposphere, bringing along reactive halogen gases. These reactive halogen gases are then *removed* from the atmosphere by rain and other precipitation or deposited on Earth's land or ocean surfaces. 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 (less than 1 year) undergo significant chemical conversion in the troposphere, producing reactive halogen gases and other compounds. Source gas molecules that are not converted are transported to the stratosphere. Only small portions of reactive halogen gases produced in the troposphere are transported to the stratosphere because most are removed by precipitation. Important examples of halogen gases that undergo some tropospheric removal are the hydrochlorofluorocarbons (HCFCs), methyl bromide (CH_3Br), methyl chloride (CH_3Cl), and gases containing iodine (see Q6).

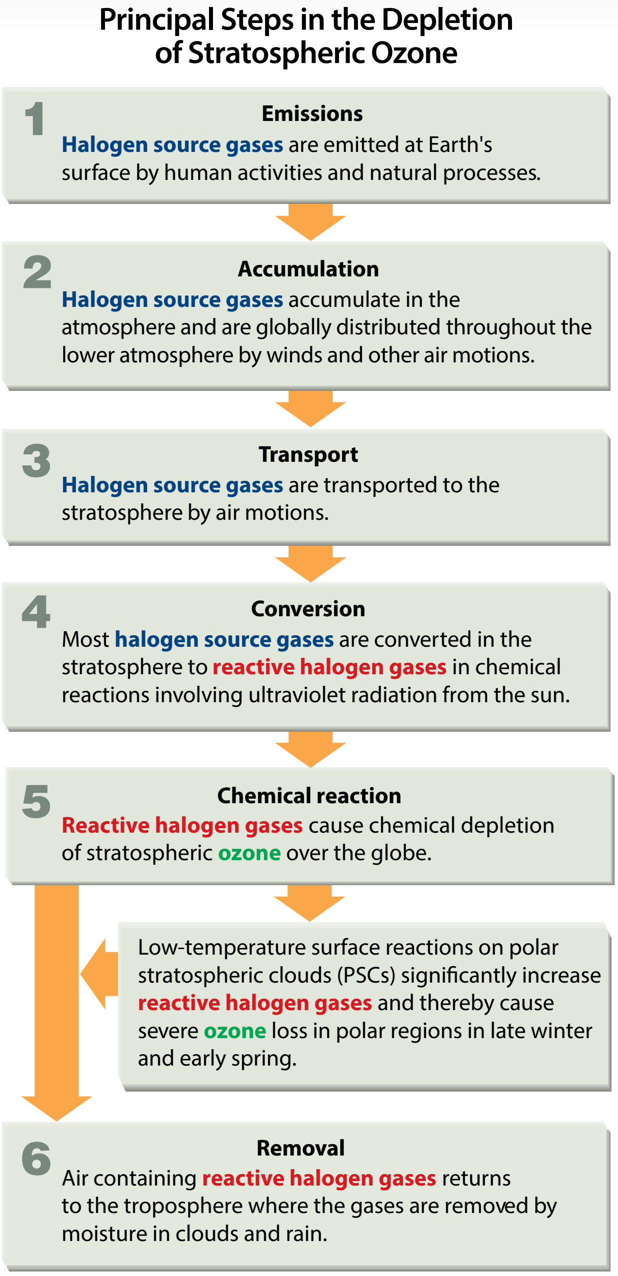


Figure Q5-1. Principal steps in stratospheric ozone depletion. The stratospheric ozone depletion process begins with the emission of halogen source gases by human activities and natural processes. These compounds have at least one carbon and one halogen atom, causing them to be chemically stable and leading to common use of the term halocarbon, an abbreviation for halogen and carbon. Many halocarbon gases emitted by human activities are also called ozone-depleting substances (ODSs); all ODSs contain at least one chlorine or bromine atom (see Q7). These compounds undergo little or no chemical loss within the troposphere, the lowest region of the atmosphere, and accumulate until transported to the stratosphere. Subsequent steps are conversion of ODSs to reactive halogen gases (see Q8), chemical reactions that remove ozone (see Q8), and eventual removal of the reactive halogen gases. Ozone depletion by halogen source gases occurs globally (see Q12). Large seasonal ozone losses occur in the polar regions as a result of reactions involving polar stratospheric clouds (see Q7 and Q9). Ozone depletion by reactive halogen gases ends when they are removed by rain and snow in the troposphere and deposited on Earth's surface.

Understanding Stratospheric Ozone Depletion

Our understanding of stratospheric ozone depletion has been obtained through a combination of laboratory studies, computer models, and atmospheric observations. The wide variety of chemical reactions that occur in the stratosphere have been discovered and investigated in *laboratory studies*. Chemical reactions between two gases follow well-defined physical rules. Some of these reactions occur on the surfaces of polar stratospheric clouds formed in the winter stratosphere. Reactions have been studied that involve many different molecules containing chlorine, bromine, fluorine, and iodine and other atmospheric constituents such as carbon, oxygen, nitrogen, and hydrogen. These studies have shown that several reactions involving chlorine and bromine directly or indirectly destroy ozone in the stratosphere.

Computer models have been used to examine the combined effect of the large group of known reactions that occur in the stratosphere. These models simulate the stratosphere by including representative chemical abundances, winds, air temperatures, and the daily and seasonal changes in sunlight. These analyses show that under certain conditions chlorine and bromine react in catalytic cycles in which one chlorine or bromine atom destroys many thousands of ozone molecules. Models are also used to simulate ozone amounts observed in previous years as a strong test of our understanding of atmospheric processes and to evaluate the importance of new reactions found in laboratory studies. The response of ozone to possible future changes in the abundances of trace gases, temperatures, and other atmospheric parameters have been extensively explored with specialized computer models (see Q20).

Atmospheric *observations* have shown what gases are present in different regions of the stratosphere and how their abundances vary with respect to time and location. Gas and particle abundances have been monitored over time periods spanning a daily cycle to decades. Observations show that halogen source gases and reactive halogen gases are present in the stratosphere at the amounts required to cause observed ozone depletion (see Q7). Ozone and chlorine monoxide (ClO), for example, have been observed extensively with a variety of instruments. ClO is a highly reactive gas that is involved in catalytic ozone destruction cycles throughout the stratosphere (see Q8). Instruments on the ground and on satellites, balloons, and aircraft now routinely measure the abundance of ozone and ClO remotely using optical and microwave signals. High-altitude aircraft and balloon instruments are also used to measure both gases locally in the stratosphere (see Q4). Observations of ozone and reactive gases made in past decades are used extensively in comparisons with computer models to increase confidence in our understanding of stratospheric ozone depletion.

Q6

What emissions from human activities lead to ozone depletion?

Certain industrial processes and consumer products result in the emission of ozone-depleting substances (ODSs) to the atmosphere. ODSs are manufactured halogen source gases that are controlled worldwide by the Montreal Protocol. These gases bring chlorine and bromine atoms to the stratosphere, where they destroy ozone in chemical reactions. Important examples are the chlorofluorocarbons (CFCs), once used in almost all refrigeration and air conditioning systems, and the halons, which were used as fire extinguishing agents. Current ODS abundances in the atmosphere are known directly from air sample measurements.

Halogen source gases versus ozone-depleting substances (ODSs). Those halogen source gases emitted by human activities and controlled by the Montreal Protocol are referred to as ODSs within the Montreal Protocol, by the media, and in the scientific literature. The Montreal Protocol controls the global production and consumption of ODSs (see Q14). Halogen source gases such as methyl chloride (CH_3Cl) that have predominantly natural sources are not classified as ODSs. The contributions of ODSs and natural halogen source gases to the total amount of chlorine and bromine entering the stratosphere, which peaked in 1993 and 1998, respectively, are shown in **Figure Q6-1**. The difference in the timing of the peaks is a result of different phaseout schedules specified by the Montreal Protocol, atmospheric lifetimes, and the time delays between production and emissions of the various source gases. Also shown are the contributions to total chlorine and bromine in 2016, highlighting the reductions of 10% and 11%, respectively, achieved under the controls of the Montreal Protocol.

Ozone-depleting substances (ODSs). ODSs are manufactured for specific industrial uses or consumer products, most of which result in the eventual emission of these gases to the atmosphere. Total ODS emissions increased substantially from the middle to the late 20th century, reached a peak in the late 1980s, and are now in decline (see Figure Q0-1). A large fraction of the emitted ODSs reach the stratosphere, where they are converted to reactive gases containing chlorine and bromine that lead to ozone depletion.

ODSs containing only carbon, chlorine, and fluorine are called *chlorofluorocarbons*, usually abbreviated as CFCs. The principal CFCs are CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and CFC-113 (CCl_2FCClF_2). CFCs, along with carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3), historically have been the most important chlorine-containing halogen source gases emitted by human activities. These and other chlorine-containing ODSs have been used in many applications, including refrigeration, air conditioning, foam blowing, spray can propellants, and cleaning of metals and electronic components. As a result of the Montreal Protocol controls, the abundances of most of these chlorine source gases have decreased since 1993 (see Figure Q6-1). The concentrations of CFC-11 and CFC-12 peaked in 1994 and 2002, respectively, and have since decreased (see Figure Q15-1). The abundance of CFC-11 in 2016 was 14% lower than its peak value, while that of CFC-12 in 2016 was 5% lower than its peak (see Figure Q15-1). As substitute gases for CFCs, the atmospheric abundances of hydrochlorofluorocarbons (HCFCs) increased substantially between 1993 and 2016 (+175%). With restrictions on global production in place since 2013, the atmospheric abundances of HCFCs are expected to peak between 2020 and 2030.

Another category of ODSs contains bromine. The most important of these gases are the halons and methyl bromide (CH_3Br). Halons are a group of industrial compounds that contain at least one bromine and one carbon atom; halons may or may not contain a chlorine atom. Halons were originally developed to extinguish fires and were widely used to protect large computer installations, military hardware, and commercial aircraft engines. As a consequence, upon use halons are released directly into the atmosphere. Halon-1211 and halon-1301 are the most abundant halons emitted by human activities.

Methyl bromide is used primarily as a fumigant for pest control in agriculture and disinfection of export shipping goods, and also has significant natural sources. As a result of the Montreal Protocol, the contribution to the atmospheric abundance of methyl bromide from human activities has substantially decreased between 1998 and 2016 (–68%; see Figure Q6-1). Halon-1211 reached peak concentration in 2005 and has been decreasing ever since, reaching an abundance in 2016 that was 8.2% below that measured in 1998. The abundance of halon-1301, on the other hand, has increased by 23% since 1998 and is expected to continue to increase very slightly into the next decade because of continued small releases and a long atmospheric

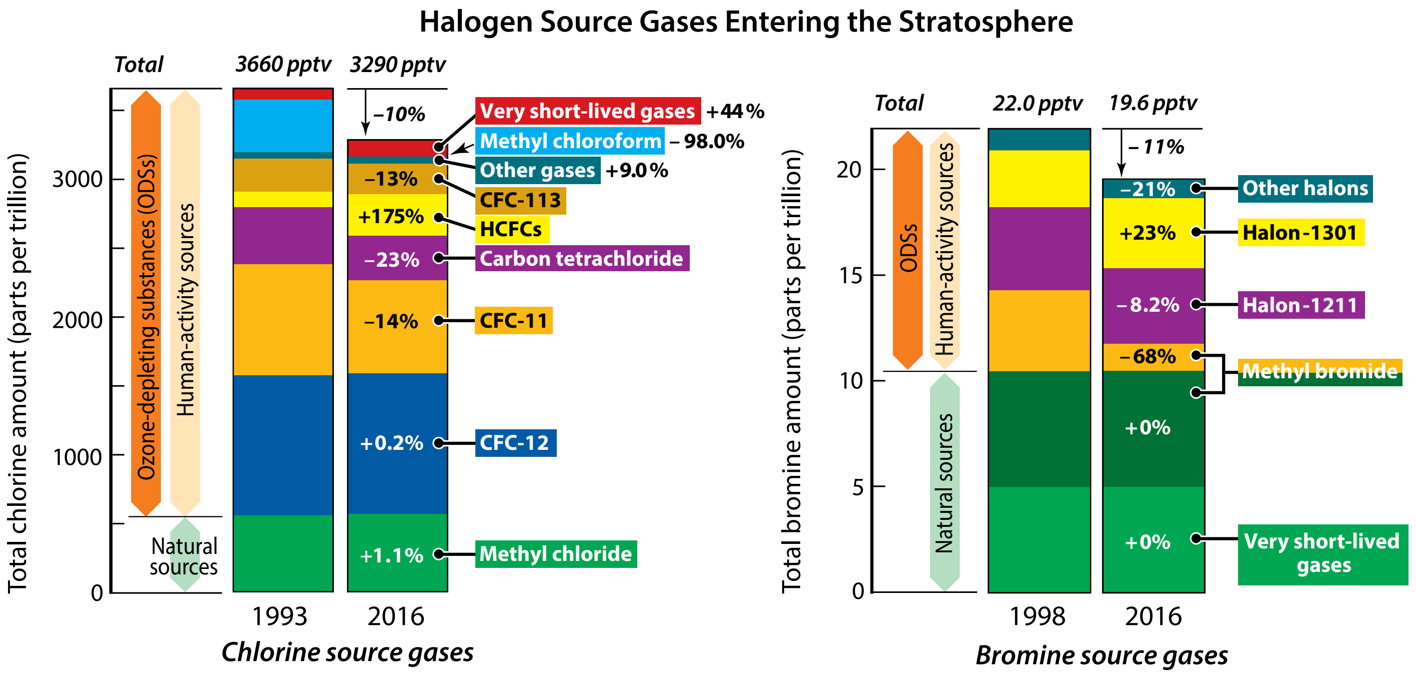


Figure Q6-1. Changes in halogen source gases entering the stratosphere. A variety of halogen source gases emitted by human activities and natural processes transport chlorine and bromine into the stratosphere. Ozone-depleting substances (ODSs) are the subset of these gases emitted by human activities that are controlled by the Montreal Protocol. These partitioned columns show the abundances of chlorine- and bromine-containing gases entering the stratosphere in 1993 and 1998, when their total amounts peaked, respectively, and in 2016. The overall reductions in the total amounts of chlorine and bromine entering the stratosphere and the changes observed for each source gas are also indicated. The amounts are derived from tropospheric observations of each gas. Note the large difference in the vertical scales: total chlorine entering the stratosphere is about 150 times more abundant than total bromine. Both, however, are important because bromine is about 60 times more effective on a per-atom basis than chlorine at destroying ozone. Human activities are the largest source of chlorine reaching the stratosphere and CFCs are the most abundant chlorine-containing gases. Methyl chloride is the primary natural source of chlorine. The largest decreases between 1993 and 2016 are seen in methyl chloroform, carbon tetrachloride, and CFC-11. The HCFCs, which are substitute gases for CFCs and also controlled under the Montreal Protocol, have risen substantially since 1993 and are now approaching expected peak atmospheric abundances (see Figure Q15-1). The abundance of chlorine-containing very short-lived gases entering the stratosphere has risen substantially since 1993; these compounds originate primarily from human activity, undergo chemical loss within the troposphere, and are not controlled by the Montreal Protocol. For bromine entering the stratosphere, halons and methyl bromide are the largest contributors. The largest decrease between 1998 and 2016 is seen in the abundance of methyl bromide attributed to human activities, because of the success of the Montreal Protocol. Only halon-1301 shows an increasing abundance relative to 1998. Methyl bromide also has a natural source, which is now substantially greater than the human source. Natural sources make a much larger fractional contribution to bromine entering the stratosphere than occurs for chlorine, and they are thought to have remained fairly constant in the recent past.

(The unit "parts per trillion" is used here as a measure of the relative abundance of a substance in dry air: 1 part per trillion equals the presence of one molecule of a gas per trillion ($=10^{12}$) total air molecules.)

lifetime (see Figure Q15-1). The bromine content of other halons (mainly halon-1202 and halon-2402) in 2016 was 21% below the amount present in 1998.

Natural sources of chlorine and bromine. There are a few halogen source gases present in the stratosphere that have large natural sources. These include methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), both of which are emitted by oceanic and terrestrial ecosystems. In addition, very short-lived source gases containing bromine such as bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) are also released to the atmosphere, primarily from biological activity in the oceans. Only a fraction of the emissions of very short-lived source gases reaches the stratosphere because these gases are efficiently removed in the lower atmosphere. Volcanoes provide an episodic source of reactive halogen gases that sometimes reach the stratosphere in appreciable quantities. Other natural sources of halogens include reactive chlorine and bromine produced by evaporation of ocean spray.

These reactive chemicals readily dissolve in water and are removed in the troposphere. In 2016, natural sources contributed about 16% of total stratospheric chlorine and about 50% of total stratospheric bromine (see Figure Q6-1). The amount of chlorine and bromine entering the stratosphere from natural sources is fairly constant over time and, therefore, cannot be the cause of the ozone depletion observed since the 1980s.

Other human activities that are sources of chlorine and bromine gases. Other chlorine- and bromine-containing gases are released to the atmosphere from human activities. Common examples are the use of chlorine-containing solvents and industrial chemicals, and the use of chlorine gases in paper production and disinfection of potable and industrial water supplies (including swimming pools). Most of these gases are very short-lived and only a small fraction of their emissions reaches the stratosphere. The contribution of very short-lived chlorinated gases from natural sources and human activities to total stratospheric chlorine was 44% larger in 2016 compared to 1993, and now contributes about 3.5% (115 ppt) of the total chlorine entering the stratosphere (see Figure Q6-1). The Montreal Protocol does not control the production and consumption of very short-lived chlorine source gases, although the atmospheric abundances of some (notably dichloromethane, CH_2Cl_2) have increased substantially in recent years. Solid rocket engines, such as those used to propel payloads into orbit, release reactive chlorine gases directly into the troposphere and stratosphere. The quantities of chlorine emitted globally by rockets is currently small in comparison with halogen emissions from other human activities.

Lifetimes and emissions. Estimates of global emissions in 2016 for a selected set of halogen source gases are given in Table Q6-1. These emissions occur from continued production of HCFCs and hydrofluorocarbons (HFCs) as well as the release of gases from banks. Emission from *banks* refers to the atmospheric release of halocarbons from existing equipment, chemical stockpiles, foams, and other products. In 2016 the global emission of the refrigerant HCFC-22 (CHF_2Cl) constituted the largest annual release, by mass, of a halocarbon from human activities. Release in 2016 of HFC-134a (CH_2FCF_3), another refrigerant, was second largest. The emission of methyl chloride (CH_3Cl) is primarily from natural sources such as the ocean biosphere, terrestrial plants, salt marshes and fungi. The human source of methyl chloride is small relative to the total natural source (see Q15).

After emission, halogen source gases are either naturally removed from the atmosphere or undergo chemical conversion in the troposphere or stratosphere. The time to remove or convert about 63% 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 Q6-1). The long-lived gases are converted to other gases primarily in the stratosphere and essentially all of their original halogen content becomes available to participate in the destruction of stratospheric ozone. Gases with short lifetimes such as HCFCs, methyl bromide, and methyl chloride are effectively converted to other gases in the troposphere, which are then removed by rain and snow. Therefore, only a fraction of their halogen content potentially contributes to ozone depletion in the stratosphere. Methyl chloride, despite its large source, constituted only about 17% (555 ppt) of the halogen source gases entering the stratosphere in 2016 (see Figure Q6-1).

The amount of an emitted gas that is present in the atmosphere represents a balance between its emission and removal rates. A wide range of current emission rates and atmospheric lifetimes are derived for the various source gases (see Table Q6-1). The atmospheric abundances of most of the principal CFCs and halons have decreased since 1990 in response to smaller emission rates, while those of the leading substitute gases, the HCFCs, continue to increase under the provisions of the Montreal Protocol (see Q15). In the past few years, the rate of the increase of the atmospheric abundance of HCFCs has slowed down. In the coming decades, the emissions and atmospheric abundances of all controlled gases are expected to decrease under these provisions.

Ozone Depletion Potential (ODP). Emissions of halogen source gases are compared in their effectiveness to destroy stratospheric ozone based upon their ODPs, as listed in Table Q6-1 (see Q17). Once in the atmosphere, a gas with a larger ODP destroys more ozone than a gas with a smaller ODP. The ODP is calculated relative to CFC-11, which has an ODP defined to be 1. The calculations, which require the use of computer models that simulate the atmosphere, use as the basis of comparison the ozone depletion from an equal mass of each gas emitted to the atmosphere. Halon-1211 and halon-1301 have ODPs significantly larger than that of CFC-11 and most other chlorinated gases because bromine is much more effective (about 60 times) on a per-atom basis than chlorine in chemical reactions that destroy ozone. The gases with smaller values of ODP generally have shorter atmospheric lifetimes or contain fewer chlorine and bromine atoms.

Fluorine and iodine. Fluorine and iodine are also halogens. Many of the source gases in Figure Q6-1 also contain fluorine in addition to chlorine or bromine. After the source gases undergo conversion in the stratosphere (see Q5), the fluorine content of these gases is left in chemical forms that do not cause ozone depletion. As a consequence, halogen source gases that contain fluorine and no other halogens are not classified as ODSs. An important example of these are the HFCs, which are included in Table Q6-1 because they are common ODS substitute gases. HFCs have ODPs of zero and are also strong greenhouse gases, as quantified by a metric termed the Global Warming Potential (GWP) (see Q17). The Kigali Amendment to the Montreal Protocol now controls the production and consumption of some HFCs (see Q19), especially those HFCs with higher GWPs.

Iodine is a component of several gases that are naturally emitted from the oceans and some human activities. Although iodine can participate in ozone destruction reactions, iodine-containing source gases all have very short lifetimes. The importance for stratospheric ozone of very short-lived iodine containing source gases is an area of active research.

Other non-halogen gases. Other non-halogen gases that influence stratospheric ozone abundances have also increased in the stratosphere as a result of emissions from human activities (see Q20). Important examples are methane (CH_4) and nitrous oxide (N_2O), which react in the stratosphere to form water vapor and reactive hydrogen, and nitrogen oxides, respectively. These reactive products participate in the destruction of stratospheric ozone (see Q1). Increased levels of atmospheric carbon dioxide (CO_2) alter stratospheric temperature and winds, which also affect the abundance of stratospheric ozone. Should future atmospheric abundances of CO_2, CH_4 and N_2O increase significantly relative to present day values, these increases will affect future levels of stratospheric ozone through combined effects on temperature, winds, and chemistry (see Figure Q20-3). Efforts are underway to reduce the emissions of these gases under the Paris Agreement of the United Nations Framework Convention on Climate Change because they cause surface warming (see Q18 and Q19). Although past emissions of ODSs still dominate global ozone depletion today, future emissions of N_2O from human activities are expected to become relatively more important for ozone depletion as future abundances of ODSs decline (see Q20).

Table Q6-1. Atmospheric lifetimes, global emissions, Ozone Deletion Potentials, and Global Warming Potentials of some halogen source gases and HFC substitute gases.

Gas	Atmospheric Lifetime (years)	Global Emissions in 2016 (kt/yr)[a]	Ozone Depletion Potential (ODP)[b]	Global Warming Potential (GWP)[b]
Halogen Source Gases				
Chlorine Gases				
CFC-11 (CCl_3F)	52	61 – 84	1	5160
Carbon tetrachloride (CCl_4)	32	23 – 50	0.87	2110
CFC-113 (CCl_2FCClF_2)	93	2 – 13	0.81	6080
CFC-12 (CCl_2F_2)	102	13 – 57	0.73	10300
Methyl chloroform (CH_3CCl_3)	5.0	0 – 4	0.14	153
HCFC-141b (CH_3CCl_2F)	9.4	52 – 68	0.102	800
HCFC-142b (CH_3CClF_2)	18	20 – 29	0.057	2070
HCFC-22 (CHF_2Cl)	12	321 – 424	0.034	1780
Methyl chloride (CH_3Cl)	0.9	4526 – 6873	0.015	4.3
Bromine Gases				
Halon-1301 ($CBrF_3$)	65	1 – 2	15.2	6670
Halon-1211 ($CBrClF_2$)	16	1 – 5	6.9	1750
Methyl bromide (CH_3Br)	0.8	121 – 182	0.57	2
Hydrofluorocarbons (HFCs)				
HFC-23 (CHF_3)	228	12 – 13	0	12690
HFC-143a (CH_3CF_3)	51	26 – 30	0	5080
HFC-125 (CHF_2CF_3)	30	58 – 67	0	3450
HFC-134a (CH_2FCF_3)	14	202 – 245	0	1360
HFC-32 (CH_2F_2)	5.4	31 – 39	0	705
HFC-152a (CH_3CHF_2)	1.6	45 – 62	0	148
HFO-1234yf ($CF_3CF{=}CH_2$)	0.03	not available	0	less than 1

[a] Includes both human activities (production and banks) and natural sources. Emissions are in units of kilotonnes per year (1 kilotonne = 1000 metric tons = 1 million (10^6) kilograms). These emission estimates are based on analysis of atmospheric observations and hence, for CFC-11, the unreported emissions recently noted (see Q15) are represented by the given range. The range of values for each emission estimate reflects the uncertainty in estimating emissions from atmospheric observations.

[b] 100-year GWP. ODPs and GWPs are discussed in Q17. Values are calculated for emissions of an equal mass of each gas. ODPs given here reflect current scientific values and in some cases differ from those used in the Montreal Protocol.

Q7

What are the reactive halogen gases that destroy stratospheric ozone?

The chlorine- and bromine-containing gases that enter the stratosphere arise from both human activities and natural processes. When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to more reactive gases that also contain chlorine and bromine. Some reactive gases act as chemical reservoirs which can then be converted into the most reactive gases, namely ClO and BrO. These most reactive gases participate in catalytic reactions that efficiently destroy ozone.

Halogen-containing gases present in the stratosphere can be divided into two groups: *halogen source gases and reactive halogen gases* (see **Figure Q7-1**). The source gases, which include ozone-depleting substances (ODSs), are emitted at Earth's surface by natural processes and by human activities (see Q6). 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 instead of the troposphere for most gases because solar ultraviolet radiation (a component of sunlight) is more intense in the stratosphere (see Q2). Reactive gases containing the halogens chlorine and bromine lead to the chemical destruction of stratospheric ozone.

Reactive halogen gases. The chemical conversion of halogen source gases, which involves solar ultraviolet radiation 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 Q7-1. Throughout the stratosphere, the most abundant are typically hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$). These two gases are considered important *reservoir* gases because, while they do not react directly with ozone, they can be converted to the *most reactive* forms that do chemically destroy ozone. The most

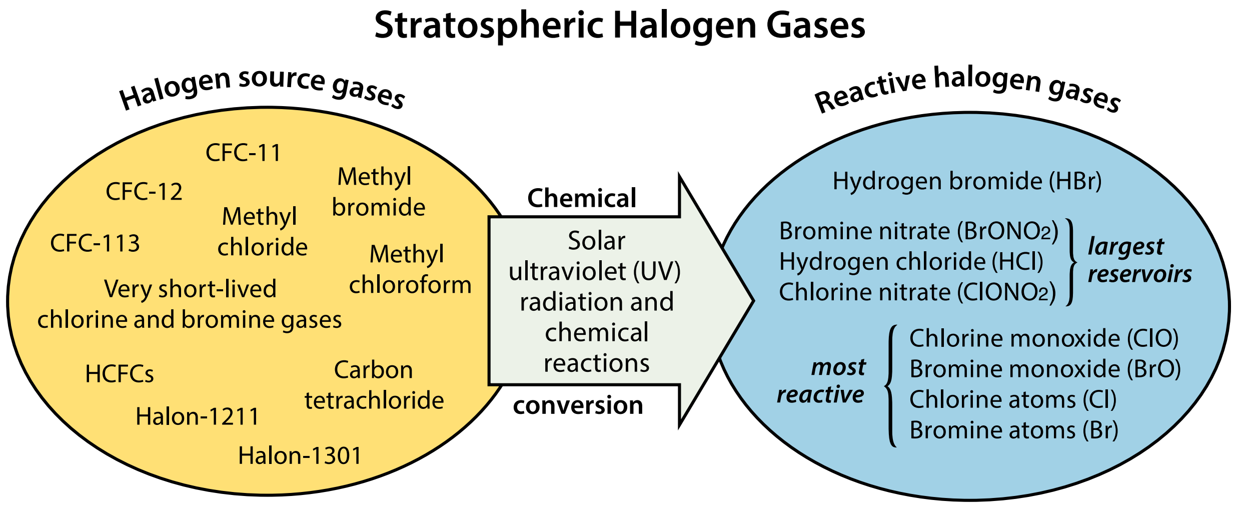


Figure Q7-1. Conversion of halogen source gases. Halogen source gases containing chlorine and bromine are chemically converted to reactive halogen gases, primarily in the stratosphere. Most of the halogen source gases are ozone-depleting substances. The conversion requires solar ultraviolet radiation and a few chemical reactions. The shorter-lived gases undergo partial 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 Q8). A principal reactive gas, ClO, is formed by reactions of the reservoir gases HCl and $ClONO_2$ that occur on the surfaces of liquid and solid polar stratospheric clouds (PSCs) (see Q9).

reactive forms are chlorine monoxide (ClO) and bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). A large fraction of total reactive bromine is generally in the form of BrO, whereas usually only a small fraction of total reactive chlorine is in the form of ClO. The special conditions that occur in the polar regions during winter cause the reservoir gases HCl and $ClONO_2$ to undergo nearly complete conversion to ClO in reactions on polar stratospheric clouds (PSCs) (see Q9).

Reactive chlorine at midlatitudes. Reactive chlorine gases have been observed extensively in the stratosphere using both local and remote measurement techniques. The measurements from space displayed in **Figure Q7-2** are representative of how the amounts of chlorine-containing gases change between the surface and the upper stratosphere at middle to high latitudes. Total available chlorine (see red line in Figure Q7-2) is the sum of chlorine contained in halogen source gases (e.g., CFC-11, CFC-12) and in the reactive gases (e.g., HCl, $ClONO_2$, and ClO). Available chlorine is constant to within about 10% from the surface to above 50 km (31 miles) altitude. In the troposphere, total chlorine is contained almost entirely in the source gases described in Figure Q6-1. At higher altitudes, the source gases become a smaller fraction of total available chlorine as they are converted to the 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 at midlatitudes, as shown in Figure Q7-2, the reservoir gases HCl and $ClONO_2$ account for most of the available chlorine. The abundance of 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 autumn and late winter. Meteorological and chemical conditions in both polar regions are now routinely observed from space in all seasons. Autumn and winter conditions over the Antarctic are contrasted in **Figure Q7-3** using seasonal observations made near the center of the ozone layer (about 18 km (11.2 miles) altitude; see Figure Q11-3).

Ozone values are high over the entire Antarctic continent during autumn in the Southern Hemisphere. Temperatures are mid-range, HCl and nitric acid (HNO_3) are high, and ClO is very low. High HCl indicates that substantial conversion of halogen source gases has occurred in the stratosphere. In the 1980s and early 1990s, the abundance of reservoir gases HCl and $ClONO_2$ increased substantially in the stratosphere following increased emissions of halogen source gases. HNO_3 is an abundant, primarily naturally-occurring stratospheric compound that plays a major role in stratospheric ozone chemistry by both moderating ozone destruction and condensing to form PSCs, thereby enabling conversion of chlorine reservoirs gases to ozone-destroying forms. The low abundance of ClO indicates that little conversion of the reservoir gases occurs in the autumn, thereby limiting catalytic ozone destruction.

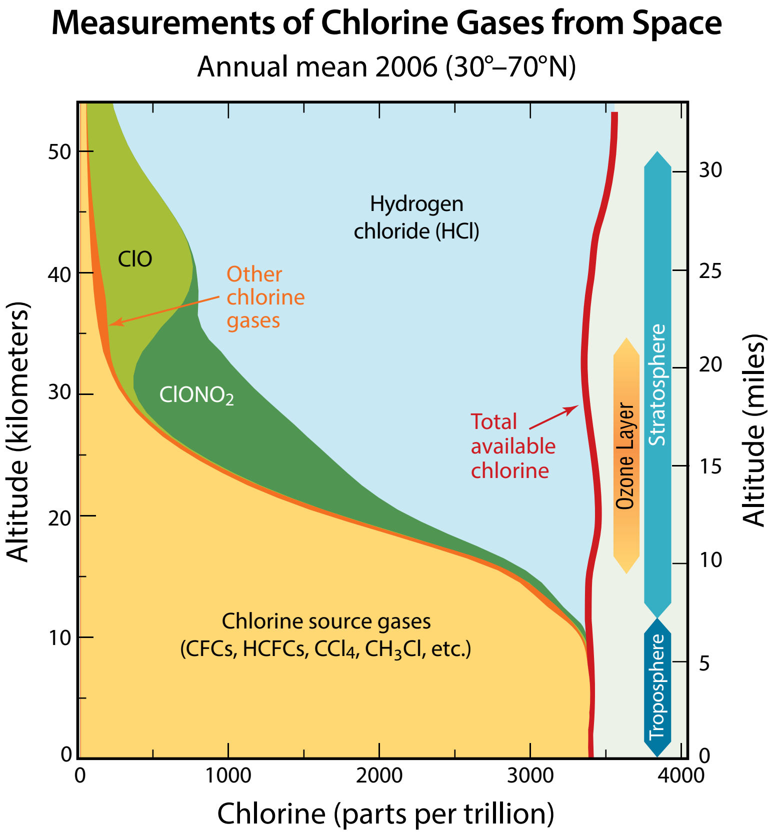


Figure Q7-2. Reactive chlorine gas observations. The abundances of chlorine source gases and reactive chlorine gases as measured from space in 2006 are displayed as a function of altitude for a range of latitudes. In the troposphere (below about 12 km), all of the measured chlorine is contained in the source gases. In the stratosphere, the total chlorine content of reactive gases increases with altitude as the amount of chlorine source gases declines. This is a consequence of chemical reactions initiated by solar ultraviolet radiation that convert source gases to reactive gases (see Figure Q7-1). The principal reactive chlorine gases formed are HCl, $ClONO_2$, and ClO. Adding up the source gases with the reactive gases gives "Total available chlorine", which is nearly constant with altitude throughout the stratosphere. In the ozone layer (15–35 km), chlorine source gases are still present and HCl and $ClONO_2$ are the most abundant reactive chlorine gases at midlatitudes.

(The unit "parts per trillion" is defined in the caption of Figure Q6-1.)

By late winter (September), a remarkable change in the composition of the Antarctic stratosphere has taken place. Low amounts of ozone reflect substantial depletion at 18 km altitude over an area larger than the Antarctic continent. Antarctic ozone holes arise from similar chemical destruction throughout much of the altitude range of the ozone layer (see altitude profile in Figure Q11-3). The meteorological and chemical conditions in late winter, characterized by very low temperatures, very low HCl and HNO_3, and very high ClO, are distinctly different from those found in autumn. Low stratospheric temperatures occur during winter, when solar heating is reduced. Low HCl and high ClO reflect the conversion of the reactive halogen reservoir compounds, HCl and $ClONO_2$, to the most reactive form of chlorine, ClO. This conversion occurs selectively in winter on PSCs, which form at very low temperatures (see Q9). Low HNO_3 is indicative of its condensation to form PSCs, some of which subsequently descend 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 Q10).

As temperatures rise at the end of the winter, PSC formation is halted, ClO is converted back into the reservoir species HCl and $ClONO_2$ (see Q9), and ozone destruction is curtailed.

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

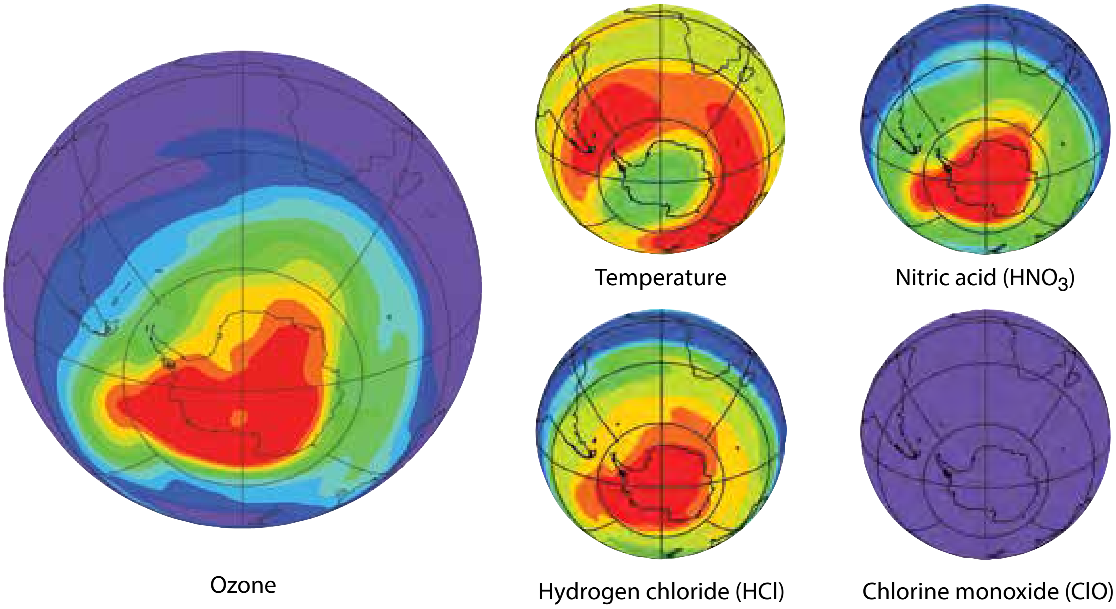
Reactive bromine observations. Fewer measurements are available for reactive bromine gases in the lower stratosphere than for reactive chlorine. This difference arises is in part because of the lower abundance of bromine, which makes quantification of its atmospheric abundance more challenging. The most widely observed bromine gas is 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 Q6).

Figure Q7-3. Chemical conditions in the ozone layer over Antarctica. Observations of the chemical conditions in the Antarctic region highlight the changes associated with the formation of the ozone hole. Satellite instruments have been routinely monitoring ozone, reactive chlorine gases, and temperatures in the global stratosphere. Results are shown here for autumn (May) and late winter (September) seasons in the Antarctic region, for a narrow altitude region near 18 km (11.2 miles) within the ozone layer (see Figure Q11-3). Ozone has naturally high values in autumn, before the onset of ozone destruction reactions that cause widespread depletion. The high ozone is accompanied by moderate temperatures, high values of HCl and HNO_3, and very low amounts of ClO. When the abundance of ClO is low, significant ozone destruction from halogens does not occur. Chemical conditions are quite different in late winter when ozone undergoes severe depletion. Temperatures are much lower, HCl has been converted to ClO (the most reactive chlorine gas), and HNO_3 has been removed by the gravitational settling of polar stratospheric cloud particles. The abundance of ClO closely surrounding the South Pole is low in September because formation of ClO requires sunlight, which is still gradually returning to the most southerly latitudes. The high values of ClO in late winter cover an extensive area that at times exceeds that of the Antarctic continent and can last for several months, leading to efficient destruction of ozone in sunlit regions in late winter/early spring. Ozone typically reaches its minimum values in early to mid-October (see Q11). Note that the first and last colors in the color bar represent values outside the indicated range of values.

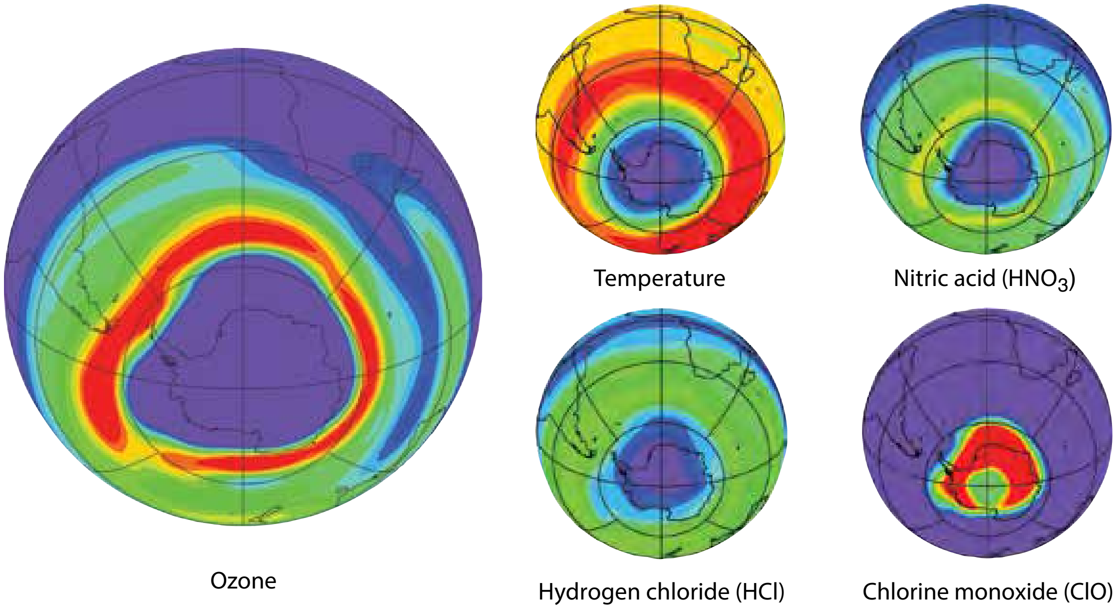
(The unit "parts per billion," abbreviated "ppb," is used here as a measure of the relative abundance of a substance in dry air: 1 part per billion equals the presence of one molecule of a gas per billion (=10^9) total air molecules (compare to ppt in Figure Q6-1).)

Chemical Conditions Observed in the Ozone Layer Over Antarctica

Normal ozone amounts in autumn (1 May 2008) at 18 km altitude



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



Temperatures and chemical abundances

1800	Ozone	2800 ppb
−85°	Temperature	−60°C
1.0	HNO_3	9.0 ppb
0.2	HCl	1.7 ppb
0.1	ClO	1.1 ppb

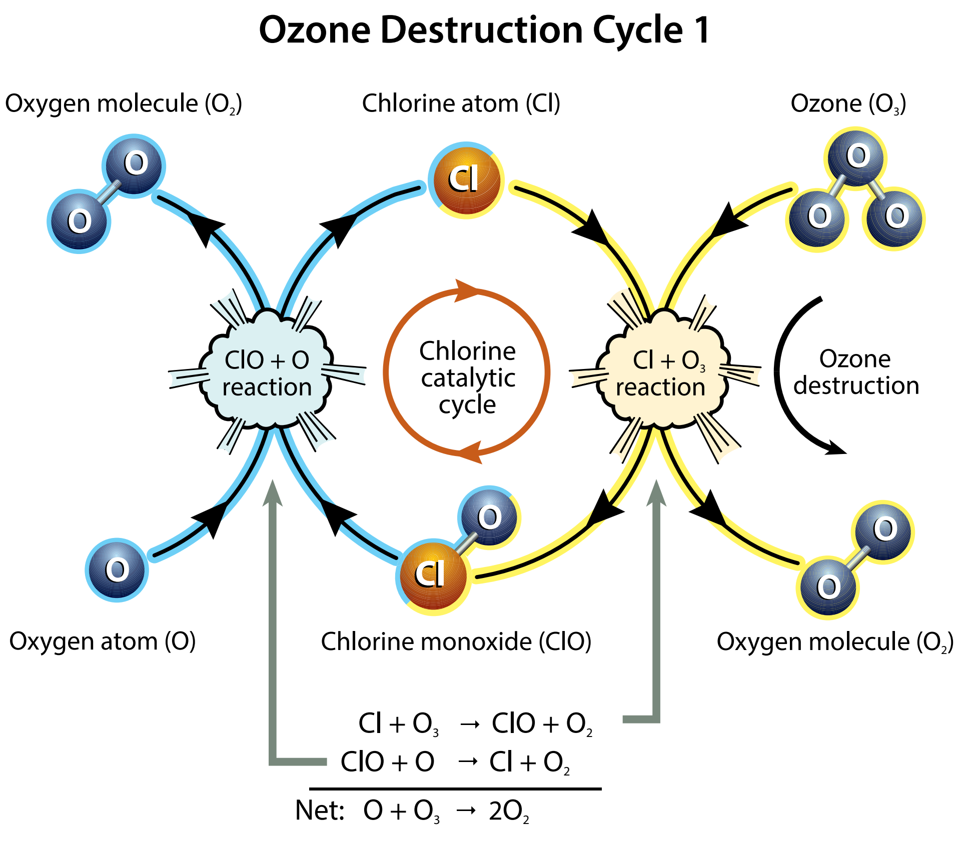
Q8 What are the chlorine and bromine reactions that destroy stratospheric ozone?

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 thousands of ozone molecules before it leaves the stratosphere. In this way, a small amount of reactive chlorine or bromine has a large impact on the ozone layer. A special situation develops in polar regions in the late winter/early spring season, where large enhancements in the abundance of the most reactive gas, chlorine monoxide, lead to severe ozone depletion.

Stratospheric ozone is destroyed by reactions involving *reactive halogen gases*, which are produced in the chemical conversion of *halogen source gases* (see Figure Q7-1). The most reactive of these gases are chlorine monoxide (ClO), 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 Q8-1**. The cycle is made up of two basic reactions: Cl + O_3 and ClO + O. 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 re-formed. 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 thousands of ozone molecules before it happens to react with another gas, breaking the catalytic cycle. During the total time of its stay in the stratosphere, a chlorine atom can thus destroy many thousands of ozone molecules.

Polar Cycles 2 and 3. The abundance of ClO is greatly increased in polar regions during late winter and early spring, relative to



$$\begin{aligned} Cl + O_3 &\rightarrow ClO + O_2 \\ ClO + O &\rightarrow Cl + O_2 \\ \hline \text{Net: } O + O_3 &\rightarrow 2O_2 \end{aligned}$$

Figure Q8-1. Ozone destruction Cycle 1. The destruction of ozone in Cycle 1 involves two separate chemical reactions. 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 and O_2. Then, Cl reacts with O_3 and re-forms ClO, consuming O_3 in the process and forming another O_2. The net or overall reaction is that of atomic oxygen (O) with ozone (O_3), forming two oxygen molecules (O_2). The cycle then begins again with another reaction of ClO with O. Chlorine is considered a catalyst for ozone destruction because Cl and ClO are re-formed each time the reaction cycle is completed, and hence available for further destruction of ozone. Atomic oxygen is formed when solar ultraviolet (UV) radiation reacts with O_3 and O_2 molecules. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where solar UV radiation is most intense.

other seasons, as a result of reactions on the surfaces of polar stratospheric clouds (see Q7 and Q9). Cycles 2 and 3 (see **Figure Q8-2)** 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 that 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 stratosphere over the Arctic and Antarctic regions in the late winter/early spring season (see Q10 and Q11). At high ClO abundances, the rate of polar ozone destruction can reach 2 to 3% per day.

Sunlight requirement. Sunlight is required to complete and maintain these reaction cycles. Cycle 1 requires ultraviolet (UV) radiation (a component of sunlight) that is strong enough to break apart molecular oxygen into atomic oxygen. Cycle 1 is most important in the stratosphere at altitudes above about 30 km (18.6 miles), where solar UV-C radiation (100 to 280 nanometer (nm) wavelengths) is most intense (see Figure Q2-1).

Cycles 2 and 3 also require sunlight. In the continuous darkness of winter in the polar stratosphere, reaction Cycles 2 and 3 cannot occur. Sunlight is needed to break apart $(ClO)_2$ and BrCl, resulting in abundances of ClO and BrO large enough to drive rapid ozone loss by Cycles 2 and 3. These cycles are most active when sunlight returns to the polar regions in late winter/early spring. Therefore, the greatest destruction of ozone occurs in the partially to fully sunlit periods after midwinter in the polar stratosphere.

Sunlight in the UV-A (315 to 400 nm wavelengths) and visible (400 to 700 nm wavelengths) parts of the spectrum needed in Cycles 2 and 3 is not sufficient to form ozone because this process requires more energetic solar UV-C solar radiation (see Q1 and Q2). In the late winter/early spring, only UV-A and visible solar radiation is present in the polar stratosphere, due to low Sun angles. As a result, ozone destruction by Cycles 2 and 3 in the sunlit polar stratosphere during springtime greatly exceeds ozone production.

Other reactions. Global abundances of ozone are controlled by many other reactions (see Q1). Reactive hydrogen and reactive nitrogen gases, for example, are involved in catalytic ozone-destruction cycles, similar to those described above, that also take place in the stratosphere. Reactive hydrogen is supplied by the stratospheric decomposition of water (H_2O) and methane (CH_4). Methane emissions result from both natural sources and human activities. The abundance of stratospheric H_2O is controlled by the temperature of the upper tropical troposphere as well as the decomposition of stratospheric CH_4. Reactive nitrogen is supplied by the stratospheric decomposition of nitrous oxide (N_2O), also emitted by natural sources and human activities. The importance of reactive hydrogen and nitrogen gases in ozone depletion relative to reactive halogen gases is expected to increase in the future because the atmospheric abundances of the reactive halogen gases are decreasing as a result of the Montreal Protocol, while abundances of CH_4 and N_2O are projected to increase due to various human activities (see Q20).

Ozone Destruction Cycles
in Polar Regions

Cycle 2

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

Cycle 3

$$\begin{aligned} ClO + BrO &\rightarrow Cl + Br + O_2 \\ \text{or} \left(\begin{aligned} ClO + BrO &\rightarrow BrCl + O_2 \\ BrCl + \text{sunlight} &\rightarrow Cl + Br \end{aligned} \right) & \\ Cl + O_3 &\rightarrow ClO + O_2 \\ Br + O_3 &\rightarrow BrO + O_2 \\ \hline \text{Net: } 2O_3 &\rightarrow 3O_2 \end{aligned}$$

Figure Q8-2. Polar ozone destruction Cycles 2 and 3. Significant destruction of ozone occurs during late winter and early spring in the polar regions when abundances of ClO reach large values. In this case, the cycles initiated by the reaction of ClO with another ClO (Cycle 2) or the reaction of ClO with BrO (Cycle 3) efficiently destroy ozone. The net reaction in both cases is two ozone (O_3) molecules forming three oxygen (O_2) molecules. The reaction of ClO with BrO has two pathways to form the Cl and Br product gases that lead to loss of ozone. The destruction of ozone by Cycles 2 and 3 is catalytic, as illustrated for Cycle 1 in Figure Q8-1, because chlorine and bromine gases react and are re-formed each time the reaction cycle is completed. Sunlight is required to complete each cycle and to help form and maintain elevated abundances of ClO. During polar night and other periods of darkness, ozone cannot be destroyed by these reactions.

Q12 How large is the depletion of the global ozone layer?

The abundance of globally averaged total ozone is now about 2–3% below the amount present during 1964–1980. The abundance of global total ozone declined steadily throughout the 1980s due to the increases in reactive halogen gases in the stratosphere resulting from human activities. In the early 1990s, global total ozone was depleted by 5% relative to the 1964–1980 average, the maximum depletion observed during the modern instrument era. In both hemispheres, total ozone depletion is small near the equator and increases toward the poles. The larger depletion at higher latitudes is due, in part, to the late winter/early spring destruction of ozone that occurs in polar regions, particularly in Antarctica.

Global total ozone started decreasing in the 1980s (see **Figure Q12-1**) due to the rise in stratospheric halogens that result from human activities (see Figure Q15-1). Most of the depletion has occurred in the stratospheric ozone layer, where most ozone resides (see Figure Q1-2). By the early 1990s, total ozone was 5% lower than the 1964–1980 average. Ozone depletion subsequently diminished, so that by 2010 globally averaged ozone was 2-3% less than the 1964–1980 average. The observations shown in Figure Q12-1 have been smoothed to remove regular variations in ozone due to natural seasonal effects and year-to-year changes in atmospheric circulation (see Q13). Over the past few years, observed global ozone has been about 2.2% lower than the 1964-1980 average.

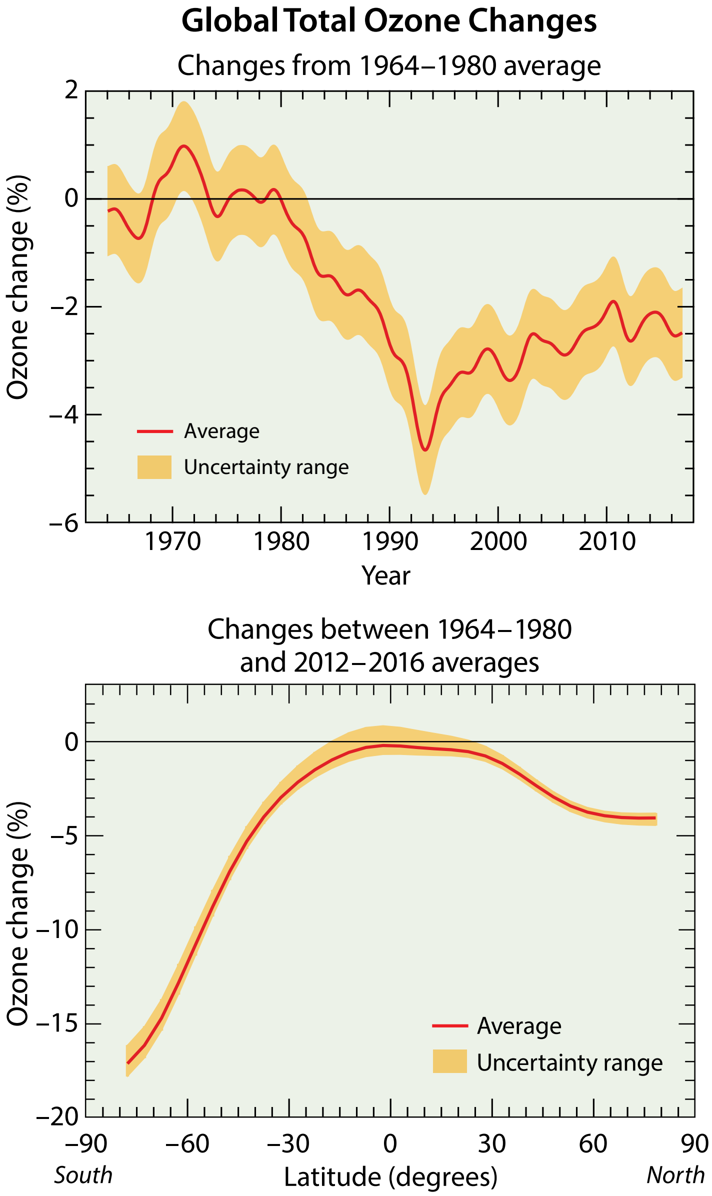
The observed global ozone depletion in the past four decades is attributable to increases in reactive halogen gases in the stratosphere (see Q13). The lowest global total ozone values since 1980 have occurred in the years following the volcanic eruption of Mount Pinatubo in 1991, which temporarily increased the number of sulfuric acid-containing particles throughout the stratosphere. These particles significantly increased the effectiveness of reactive halogen gases in destroying ozone (see Q13) and, thereby, increased global ozone depletion by about 2% for several years following the eruption.

Polar regions. Observed total ozone depletion varies significantly with latitude across the globe (see Figure Q12-1). The largest reductions occur at high southern latitudes as a result of the severe ozone loss over Antarctica each late winter/early spring period (see Q9 and Q10). The next largest losses are observed in the high latitudes of the Northern Hemisphere, caused in part by winter losses over the Arctic in some years (see Q11). Although the depletion of ozone in polar regions is larger than at lower latitudes, the contribution of polar ozone loss to globally averaged depletion is limited by the smaller geographical area of high-latitude regions. Latitudes poleward of 60° account for only about 13% of Earth's surface.

Midlatitude regions. Ozone depletion is also observed at midlatitudes. In comparison with the 1964–1980 average amounts, total ozone averaged for 2012–2016 is about 3% lower in northern midlatitudes (35°N–60°N) and about 5.5% lower at southern midlatitudes (35°S–60°S). Midlatitude depletion has two contributing factors. First, ozone-depleted air over both polar regions is dispersed away from the poles during and after each winter/spring period, thereby reducing average ozone at midlatitudes. Second, chemical destruction occurring at midlatitudes contributes to observed depletion in these regions. Ozone depletion at midlatitudes is much smaller than in polar regions (see Q20) because the amount of reactive halogen gases is lower and the seasonal increase of ClO, the most reactive halogen gas, does not occur.

Tropical region. Total ozone in the tropics (20°N–20°S latitude) has been only weakly affected by chemical depletion. In the tropical lower stratosphere, air is transported from the lower atmosphere (troposphere) over about an 18-month period. As a result, the fraction of ozone-depleting substances (ODSs) converted to reactive halogen gases is still very small. With little reactive halogen available, total ozone depletion in this region is also very small. In addition, net ozone production occurs in the tropics because of high average amounts of solar ultraviolet radiation. In contrast, stratospheric air in polar regions has been in the stratosphere for an average of 4 to 7 years, allowing time for significant conversion of ODSs to reactive halogen gases (see Figure Q5-1). These systematic differences in stratospheric air are a consequence of large-scale atmospheric transport: air enters the stratosphere in the tropics, moves poleward in both hemispheres, and then descends and ultimately returns to the troposphere in the middle to high latitudes.

Figure Q12-1. Global total ozone changes. Ground-based and satellite observations show depletion of global total ozone beginning in the 1980s. The top panel compares the difference between annual averages of total ozone averaged over 60°S to 60°N latitude, relative to the amount of ozone that was present during the period 1964–1980. Seasonal effects have been removed from the observational data set. A 1964–1980 baseline is used because large amounts of ozone depletion had not occurred during these years (see Figure Q10-3). On average, global ozone decreased each year between 1980 and 1990. The depletion worsened for a few years after 1991 due to the effect of volcanic aerosol from the eruption of Mount Pinatubo (see Q13). Since 2010, global ozone has been about 2-3% less than the 1964–1980 average. The bottom panel shows how the 2012–2016 depletion varies with latitude over the globe. The largest decreases have occurred at high latitudes in both hemispheres because of the large winter/spring depletion in polar regions. The losses in the Southern Hemisphere are greater than those in the Northern Hemisphere because of the Antarctic ozone hole. Long-term changes in the tropics are much smaller because reactive halogen gases are less abundant in the tropical lower stratosphere than at mid or high latitudes, and ozone production rates are greater.



Initial Signs of Ozone Recovery

The Montreal Protocol, strengthened by its Amendments and Adjustments, has successfully controlled the production and consumption of ozone-depleting substances (ODSs), which act to destroy the ozone layer (see Q14). As a result, atmospheric abundances of ODSs have peaked and are now decreasing (see Q6 and Q15). By 2018, equivalent effective stratospheric chlorine (EESC; the total chlorine and bromine abundances in the stratosphere) had declined by 18% at midlatitudes from peak values that occurred in 1997. This raises the question, is global ozone increasing in response to the observed decrease in EESC?

Identifying an ozone increase that is attributable to the observed decrease in the amount of ODSs is challenging because halogen levels are not the only factor that determines the abundance of stratospheric ozone. For example, the global ozone minimum was observed half a decade before the EESC maximum was reached. This difference in timing resulted from the strong global ozone response to enhanced amounts of stratospheric aerosol after the volcanic eruption of Mount Pinatubo in 1991, which led to increased ozone depletion for several years. Observed global ozone increases in the mid-1990s were caused by the steady removal of volcanic aerosol from the stratosphere, which occurred at the time EESC was approaching its maximum (see Q13).

Another factor complicating the identification of ozone recovery in different regions of the atmosphere is the year-to-year variations of the stratospheric circulation. These variations lead to ozone variability in most regions of the atmosphere that is currently still larger than the increases in ozone expected from the observed decrease in EESC. Finally, increases in greenhouse gases (GHGs) such as carbon dioxide (CO_2), which warm the lower atmosphere, affect ozone by decreasing stratospheric temperatures and by strengthening the stratospheric circulation. A warmer atmosphere slows down the rate of ozone loss reactions and a stronger circulation enhances the transport of ozone from the tropics to middle and high latitudes.

Midlatitude observations show an ozone increase of about 2% per decade in the upper stratosphere (between 35 and 45 km altitude) over the period 2000–2016. Model simulations that allow for separation of the various factors that affect ozone suggest that about half of this increase results from a cooling in this region due to rising amounts of atmospheric CO_2, while the other half results from decreases in EESC. Variations in upper stratospheric ozone are mainly controlled by changes in chemistry and temperature in this region of the atmosphere, rather than stratospheric circulation. The increase in upper stratospheric ozone coincident with the decline in EESC constitutes an initial sign of ozone recovery. However, ozone in the upper stratosphere makes only a small contribution to total ozone.

Total ozone declined over most of the globe (60°S–60°N) during the 1980s and early 1990s, reaching a minimum in 1993 due to the combined effects of ODSs and the eruption of Mount Pinatubo (see Figure Q12-1). The value of EESC peaked in the midlatitude stratosphere in 1997 (see Figure Q13-1). Since 1997, total ozone has increased in the range of 0.3-1.2% per decade. A significant component of the year-to-year fluctuations in total ozone is caused by natural variation in the stratospheric circulation. Consequently, attribution of the observed increase in global total ozone since 1997 to declining levels of EESC is not yet definitive. The decline in EESC since 1997 is expected to have caused an increase in total ozone of about 1% per decade, which is small compared to the natural year-to-year variability in total ozone that has been observed (see Figure Q13-1).

There are emerging indications that the size and maximum ozone depletion (depth) of the Antarctic ozone hole has diminished since 2000 (see Figure Q10-2). This recovery is clearest during September, which is early spring in the Southern Hemisphere. Although accounting for the effect of natural variability on the size and depth of the ozone hole is challenging, the weight of evidence suggests that the decline in EESC made a substantial contribution to these observed trends.

The impact on stratospheric ozone from accumulated emissions of the most prominent ODSs, CFC-11 and CFC-12, will continue for several decades because of the long atmospheric lifetime of these ODSs. Assuming compliance with the Montreal Protocol, EESC will continue to decline over the coming decades and will return to pre-1980 levels around midcentury (see Figures Q15-1 and Q20-2). Increases in GHG abundances are expected to accelerate the return of the global ozone layer to pre-1980 levels (see Q20). However, as long as atmospheric abundances of ODSs remain elevated, the possibility of substantial reductions in total ozone following major volcanic eruptions (see Q13) will persist.

Q13 Do changes in the Sun and volcanic eruptions affect the ozone layer?

Yes, factors such as changes in solar radiation and the formation of stratospheric aerosol particles after explosive volcanic eruptions do influence the ozone layer. Global ozone abundances vary by 1–2% between the maximum and minimum of the 11-year solar cycle. The abundance of global ozone decreased by about 2% for a few years after the June 1991 eruption of Mount Pinatubo, due to volcanic enhancement of stratospheric sulfate aerosols. However, neither factor can explain the observed decrease in global total ozone or the severe ozone depletion observed in polar regions over the past half century. The primary influence on long-term changes in total global ozone is the abundance of stratospheric halogens.

Changes in solar radiation and increases in stratospheric aerosols (small particles) from volcanic eruptions both affect the abundance of stratospheric ozone. Global total ozone in the early 1990s decreased by about 5% when compared to pre-1980 values, and is now about 2-3% below the 1964–1980 average value (see Q12). The long-term depletion of ozone is primarily attributed to increases in reactive halogen gases, with additional depletion in the early 1990s associated with the volcanic eruption of Mount Pinatubo. Equivalent effective stratospheric chlorine (EESC) is often used as a measure of the potential of reactive halogen gases to deplete ozone (see definition in Q15). Comparisons of the long-term changes in solar radiation, stratospheric volcanic aerosol, and EESC are useful in evaluating the contribution of these factors to long-term changes in total ozone.

Total ozone and solar changes. The formation of stratospheric ozone is initiated by ultraviolet (UV) radiation emitted by the Sun (see Q1). As a result, an increase in the Sun's UV radiation output increases the amount of ozone in Earth's atmosphere. Since the 1960s, ground-based and satellite instruments have recorded variations in the total energy emitted by the Sun, which is well correlated with changes in solar UV radiation. The Sun's radiation output varies over the well-documented 11-year solar cycle, as shown in **Figure Q13-1**. The long-term solar record exhibits alternating maximum and minimum values of total output, with maximum values separated by about 11 years. Global total ozone is relatively high compared to surrounding years during times of solar maxima and is relatively low during solar minima due to the sensitivity of ozone production to UV radiation, which increases during solar maxima. Analysis of measurements of ozone and solar output shown in Figure Q13-1 shows that ozone levels vary by 1 to 2% between the maximum and minimum of a typical solar cycle. In addition to this 11-year variation, the total ozone record exhibits a long-term downward trend. If a decline in solar output were the primary cause of the long-term decline in global total ozone, then the solar output would exhibit a similar long-term decrease. Instead, the solar output varies about a stable baseline over the modern instrument record. This comparison demonstrates that the observed long-term decline in global total ozone does not result from changes in the Sun's UV radiation output.

Total ozone and past volcanoes. Explosive volcanic eruptions inject sulfur gases directly into the stratosphere, causing new sulfate aerosol particles to be produced. These particles initially form downwind of the volcano and then disperse over large regions, as air is transported by stratospheric winds. The largest impact on global ozone usually takes place after explosive volcanic eruptions in the tropics, because the stratospheric circulation efficiently spreads tropical volcanic plumes to both hemispheres. A principal method of detecting the presence of volcanic particles in the stratosphere is to measure the transmission of solar radiation through the stratosphere to the ground, which is termed stratospheric aerosol optical depth (SAOD). When large amounts of new particles form over an extensive region of the stratosphere, solar transmission is measurably reduced and SAOD increases. Figure Q13-1 shows the long-term record of SAOD averaged over the entire stratosphere, based on measurements from ground-based and satellite instruments. Large increases in SAOD (reductions in solar transmission) are apparent after the explosive eruptions of Mount Agung (1963), Volcán de Fuego (1974), El Chichón (1982), and Mount Pinatubo (1991), all of which occurred in the tropics. Reduced transmission of solar radiation persists for a few years after each of these eruptions, until the stratospheric circulation and gravitational settling bring the volcanic sulfate aerosol particles back to the lower atmosphere, where they are removed by precipitation.

Volcanic aerosol is primarily composed of sulfur compounds (sulfate). Chemical reactions on the surface of sulfate aerosol particles destroy stratospheric ozone by increasing the abundance of chlorine monoxide (ClO), a highly reactive chlorine gas

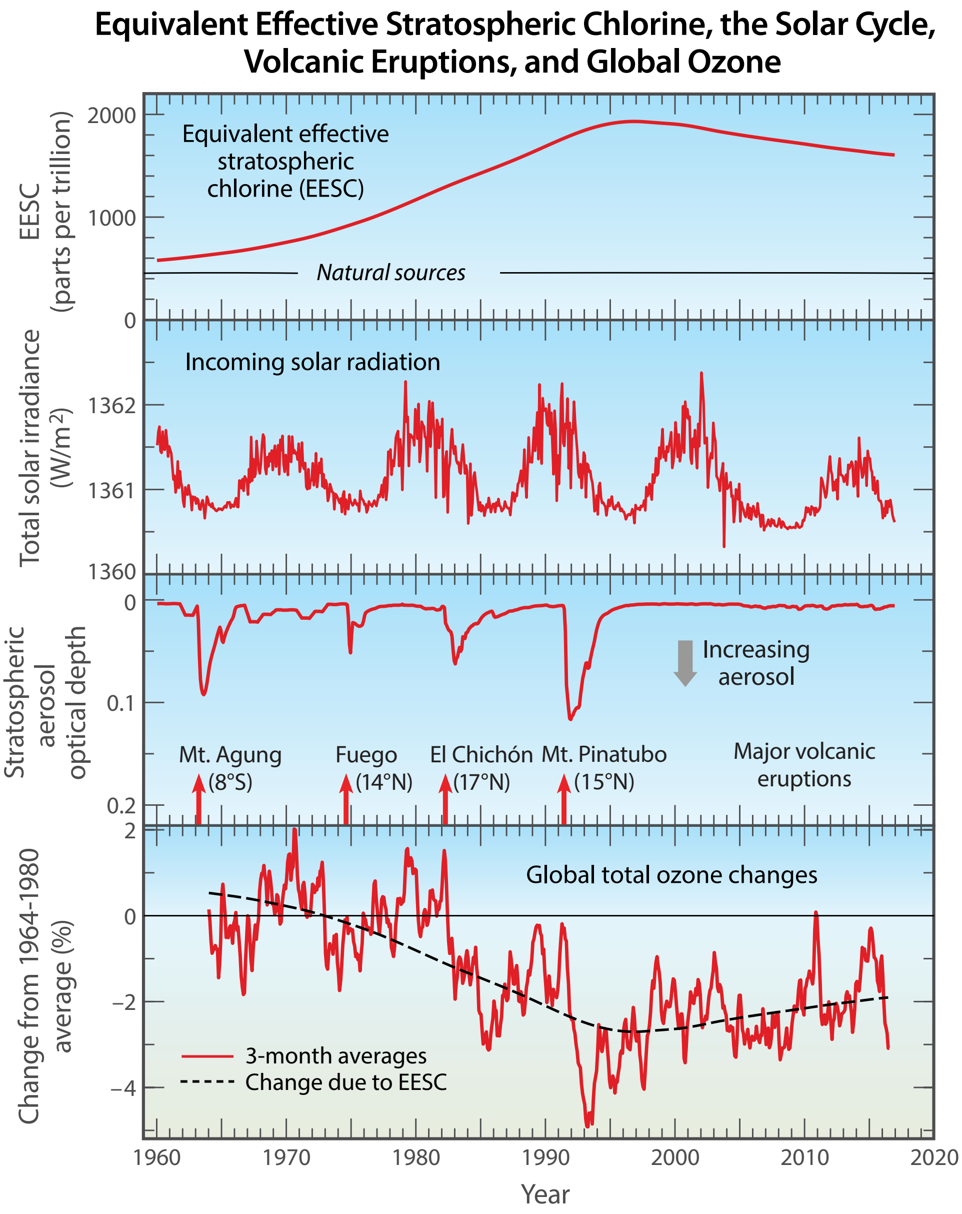


Figure Q13-1. The effects on ozone of EESC, solar changes, and volcanic eruptions. A comparison of the long-term variation in total solar radiation, a measure of the abundance of stratospheric sulfate particles, and EESC with global total ozone provides a basis to evaluate the primary influences on ozone over the past half century. The top panel shows the record of equivalent effective stratospheric chlorine (EESC) for the midlatitude, lower stratosphere (about 19 km altitude). EESC represents the potential for stratospheric ozone depletion by halogens, which result primarily from human activities (see Q15). The second panel shows the total energy of incoming solar radiation, with peaks and valleys defining the maxima and minima of the 11-year solar cycle. Following the explosive volcanic eruptions marked on the third panel, the number of sulfur-containing particles in the stratosphere exhibits a dramatic rise. These particles decrease the transmission of solar radiation through the stratosphere, which is recorded by an increase in the quantity termed stratospheric aerosol optical depth. The bottom panel shows differences in global total ozone, averaged over 60°S to 60°N latitude, from the 1964–1980 average value. Global total ozone is 1-2% higher at solar maxima than solar minima due to enhanced formation of ozone by solar ultraviolet radiation (see Q1). Reactions on sulfate particles enhance the abundance of highly reactive chlorine compounds, increasing the depletion of stratospheric ozone after major volcanic eruptions. The maximum depletion of ozone occurs in mid-1993, after the eruption of Mount Pinatubo. The bottom panel also shows the change in global total ozone attributed to EESC, found using an analysis that considers the effects on ozone of numerous natural and human-related factors. The long-term changes in ozone are consistent with the variation of EESC: prior to the mid-1990s EESC steadily rose while global ozone declined, and since the late 1990s EESC has declined and global ozone has risen. If solar output were the primary cause of the long-term variation in global total ozone in recent decades, then solar output would exhibit a similar pattern of decline followed by an increase. If volcanic activity were the primary cause of the long-term ozone decline, then stratospheric optical depth would exhibit a slow, gradual rise in recent decades. This figure illustrates that the primary influence on changes in global total ozone over the past half century is the abundance of stratospheric halogens.

(see Q7). The amount of ozone depletion depends on both the mass of sulfate aerosol produced following the eruption and the value of EESC (see Q15). Global ozone decreased for a few years following the eruptions of Mount Agung, Volcán de Fuego, El Chichón and Mount Pinatubo. The ozone reduction from the eruption of Mount Pinatubo stands out in the global ozone record because it occurred at a time when EESC was near its peak and the perturbation to stratospheric sulfate aerosol was especially large (see Figures Q12-1 and Q13-1). Analysis of ozone observations shows that global total ozone declined by about 2% following the eruption of Mount Pinatubo in June 1991, and that this effect persisted for 2 to 3 years after the eruption. At times of relatively low EESC, such as the early 1960s, total ozone is not as sensitive to a volcanically induced increase in stratospheric aerosol as during current times, when values of EESC are much higher than background levels.

If changes in the abundance of volcanic aerosol in the stratosphere were the primary cause of the long-term decline in global total ozone, then the record of stratospheric aerosol optical depth (marker of volcanic sulfate particles) would exhibit a slow, gradual rise. Instead, stratospheric volcanic aerosol has been quite low since 1995, a period of time over which global total ozone has been about 2-3% below the pre-1980 value. The data record shown in Figure Q13-1 provides evidence that the long-term decrease in global total ozone does not result from changes in volcanic aerosol.

Total ozone and EESC. Values of EESC are derived from surface observations of ozone-depleting substances (ODSs) and represent the potential for ozone depletion from halogens at particular times and locations of the stratosphere (see Q15). The EESC record for the midlatitude, lower stratosphere rose well above the natural background level in the 1980s, peaked in 1997, and in 2018 was 18% below the peak value. The bottom panel of Figure Q13-1 compares the observed long-term record of global total ozone (red line) to the variation in ozone attributed to the changes in EESC (black dashed line). This attribution curve is computed by a statistical model that considers the effects on ozone of EESC, stratospheric sulfur containing particles, variations in the total energy of incoming solar radiation, as well as a few factors related to changes in stratospheric circulation. The observed record of global total ozone follows the same general tendencies of the EESC attribution curve over the past half century, providing strong evidence that changes in stratospheric halogens in response to human activities are the primary factor responsible for the long-term variation of ozone depletion. Further evidence linking ODSs and long-term variations in total column ozone is provided by the climate-chemistry model simulations highlighted in Q20.

Reactive halogen source gases from volcanic eruptions. Explosive volcanic eruptions have the potential to inject halogens directly into the stratosphere, in the form of gases such as hydrogen chloride (HCl), bromine monoxide (BrO), and iodine monoxide (IO). Although HCl does not react directly with ozone, stratospheric injections of HCl and other chlorine-containing gases following explosive volcanic eruptions can lead, through chemical reactions, to elevated chlorine monoxide (ClO) that destroys ozone (see Figure Q7-3). Eruption plumes also contain a considerable amount of water vapor, which forms rainwater and ice in the rising fresh plume. Rainwater and ice efficiently scavenge and remove HCl while the plume is still in the lower atmosphere (troposphere). Most of the HCl in the explosive plume of Mount Pinatubo did not enter the stratosphere because of this scavenging by precipitation. The amount of injected halogens depends on the chemical composition of the magma, conditions of the eruption such as its explosivity and the local meteorology. Recent analyses of several historic, extremely large volcanic eruptions show the potential for quite large ozone loss from the stratospheric injection of halogens. A volcanic eruption of this nature has not occurred during the time period of the modern observational record.

Antarctic volcanoes. Volcanoes on the Antarctic continent are of special interest due to their proximity to the Antarctic ozone hole. An explosive eruption could in principle inject volcanic aerosol or halogens directly into the stratosphere over Antarctica and contribute to ozone depletion. To be a possible cause of the annually recurring ozone hole beginning in the early 1980s, explosive eruptions of Antarctic volcanoes large enough to inject material into the stratosphere would need to have occurred at least every few years. This is not the case. Mount Erebus and Deception Island are the only two currently active volcanoes in Antarctica. No explosive eruptions of these volcanoes, or any other Antarctic volcano, have occurred since 1980. Explosive volcanic eruptions in the last three decades have not caused the Antarctic ozone hole and, as noted above, have not been sufficient to cause the long-term depletion of global total ozone.

Total ozone and future volcanoes. The abundance of EESC will remain high for much of the 21st century due to the long atmospheric lifetime of ODSs (see Q15-1). With its slow decline, EESC will remain above the 1960 value throughout this century. Consequently, throughout the rest of this century, increases in the abundance of stratospheric sulfate aerosol particles caused by large volcanic eruptions similar to Mount Pinatubo have the potential to reduce global total ozone values for a few years. The ozone layer will be most vulnerable to such an eruption until midcentury, since EESC is projected to return to the 1980 value around 2050. Following an explosive eruption much larger than Mount Pinatubo, or an eruption that injects halogens into the stratosphere, peak ozone losses could both be greater than previously observed and persist for longer periods of time.

Q14 Are there controls on the production of ozone-depleting substances?

Yes, the production and consumption of ozone-depleting substances (ODSs) are controlled 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 198 parties, establishes legally binding controls on national production and consumption of ODSs. Production and consumption of all principal ODSs by developed and developing nations will be almost completely phased out by 2030.

The Vienna Convention and the Montreal Protocol. In 1985, a treaty called the *Vienna Convention for the Protection of the Ozone Layer* was signed by 28 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 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 ozone-depleting substances (ODSs). National consumption of an ODS is defined as production plus imports of the controlled substance, minus exports of the substance. The Protocol provisions are structured for developed countries to act first and for developing countries to follow with some financial assistance. In 2009, the Montreal Protocol became the first multilateral environmental agreement to achieve universal ratification.

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 three decades. These decisions listed additional ODSs under control, accelerated the timing of existing control measures, and prescribed phaseout dates for the production and consumption of certain gases. The initial Protocol measures were a 50% reduction in chlorofluorocarbon (CFC) production and a freeze on halon production. The 1990 London Amendment called for a phaseout 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 phaseout date for CFCs, halons, carbon tetrachloride, and methyl chloroform to 1996 in developed nations and also initiated controls on future production of hydrochlorofluorocarbons (HCFCs) in developed nations. Further controls on ODSs were agreed upon in later meetings in Vienna (1995), Montreal (1997, 2007), and Beijing (1999). The latest development is the 2016 Kigali Amendment (see Q19), which expanded the Montreal Protocol to control production and consumption of certain hydrofluorocarbons (HFCs). As explained below, HFCs are greenhouses gases (GHGs) which warm climate and do not cause ozone depletion.

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 Q17), (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 Q15). 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 existing ODS banks containing a variety of compounds. The phrase ODS banks refers to long-term containment of ODSs in various applications. Examples are CFCs in refrigeration equipment and insulating foams, and halons in fire-extinguishing equipment. Annual emissions are projected based on release from existing banks and any new production and consumption of ODSs allowed under the Montreal Protocol. The long-term changes in EESC at midlatitudes are shown in **Figure Q14-1** for several cases:

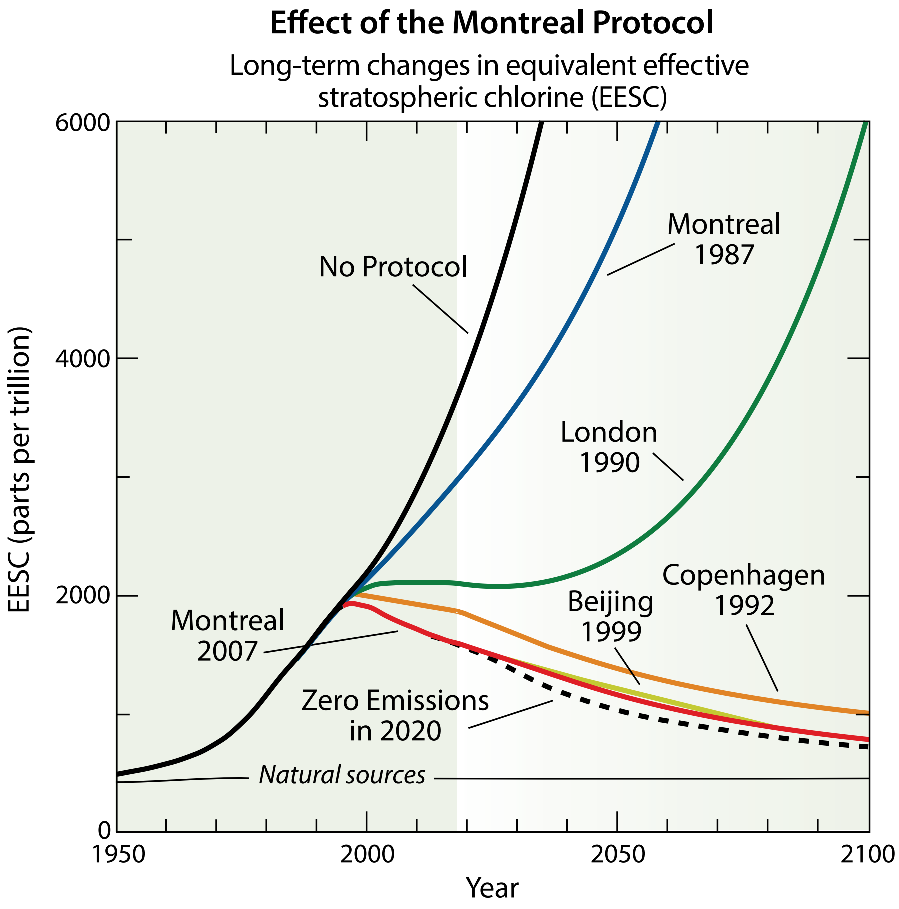


Figure Q14-1. Effect of the Montreal Protocol. The Montreal Protocol protects the ozone layer through control of the global production and consumption of ozone-depleting substances (ODSs). Equivalent effective stratospheric chlorine (EESC) is a quantity that represents the abundance of halogens available for ozone depletion in the stratosphere. Values of EESC are based upon either analysis of surface observations of ODSs (see Q15) or projections of future abundances of ODSs. Projections of EESC for the midlatitude lower stratosphere (about 19 km altitude) are shown separately for: no Protocol provisions; the provisions of the original 1987 Montreal Protocol and some of its subsequent Amendments and Adjustments; and zero emissions of ODSs starting in 2020. The city names and years indicate where and when changes to the original 1987 Protocol provisions were agreed upon (see Figure Q0-1). Without the Protocol, EESC values would have increased significantly in the 21st century, leading to large amounts of ozone depletion throughout the world, including over highly populated regions. Only with the Copenhagen (1992) and subsequent Amendments and Adjustments did projected EESC values show a long-term decrease. The EESC values from observations shown in Figure Q15-1 agree well with the Montreal 2007 curve shown in this figure. The contributions from very short-lived gases (see Figure Q6-1), which have been minor to this point, are not included in any of these EESC time series.

- **No Protocol.** In a scenario without the Montreal Protocol, the production, use and emissions of CFCs and other ODSs continue to increase after 1987 at a rate faster than what actually occurred. This No Protocol scenario is illustrated using an annual growth rate of 3% for the emissions of all ODSs. As a result, EESC increases nearly 10-fold by the mid-2050s compared with the 1980 value. Computer models of the atmosphere show that EESC under the No Protocol scenario doubles global total ozone depletion between 1990 and 2010 relative to what actually occurred, and increases ozone depletion much more by midcentury. As a result, harmful UV-B radiation increases substantially at Earth's surface by the middle of the 21st century, causing damage to ecosystem health, and a global rise in skin cancer and cataract cases (see Q16). Since ODSs are powerful GHGs, the climate forcing from ODSs would have increased substantially without the Montreal Protocol (see Q18).
- **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. The projections showed a decrease in future EESC values for the first time with the 1992 Copenhagen Amendments and Adjustments. 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, ODSs will ultimately be phased out, with some exemptions for critical uses (see Q15). 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 1987 at values about 10-fold higher than natural emissions. Between 1987 and 2018, ODS emissions from human activities have decreased by almost 80%.

- **Zero emissions.** The zero emissions scenario demonstrates the reduction in EESC that occurs if emissions of all ODSs are set to zero beginning in 2020. This assumption eliminates the emissions from new production as well as banks. Significant differences from the Montreal 2007 projections are evident in the first decades following 2020 because the phaseout of all ODS production under the Protocol will not be complete in 2020 and continued bank emissions are substantial. In the zero-emissions scenario, EESC returns to the 1980 value about a decade earlier than currently projected (solid red and dashed black lines, Figure Q14-1).

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-11 in depleting stratospheric ozone because their chemical removal occurs primarily in the troposphere (see ODPs in Table Q6-1). This removal protects stratospheric ozone from most of the halogen content of HCFC emissions. In contrast, CFCs and some other ODSs release all of their halogen content in the stratosphere because they are chemically inert in the troposphere (see Q5).

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 2007 Adjustment to the Protocol, the phaseout of HCFCs was accelerated so that production ceases by 2020 for developed countries and by 2030 for developing countries, about 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 Q17 and Q18).

HFC substitute gases. Hydrofluorocarbons (HFCs) are used as transitional, short-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 or bromine. However, HFCs and all ODSs are also GHGs with long atmosphere lifetimes, so they contribute to human-induced climate change (see Q18 and Q19). Under the auspices of the United Nations Framework Convention on Climate Change (UNFCCC), HFCs are included in the basket of controlled GHGs. The Paris Agreement of the UNFCCC is an international accord designed to reduce the emissions of GHGs in order to limit global warming to well below 2.0°C relative to the start of the Industrial Era and pursue efforts to limit global warming to 1.5°C warming. Future growth in the emissions of HFCs with high Global Warming Potentials (GWPs) is limited by the 2016 Kigali Amendment to the Montreal Protocol (see Q19).

Very short-lived chlorine source gases. Very short-lived halogenated source gases, defined as compounds with atmospheric lifetimes shorter than 0.5 years, are primarily converted to reactive halogen gases in the lower atmosphere (troposphere). Atmospheric release of most very short-lived chlorine source gases, such as dichloromethane (CH_2Cl_2), result primarily from human activities. This class of compounds is not regulated by the Montreal Protocol. The atmospheric abundance of very-short lived chlorine source gases has increased substantially since the early 1990s and these gases presently contribute about 3.5% (115 ppt) to the total chlorine entering the stratosphere (see Figure Q6-1). Nonetheless, the estimates of EESC shown in Figure Q14-1 do not include contributions from very short-lived chlorine source gases because prior abundances of key gases such as CH_2Cl_2 exhibit large variability with respect to time and place of observation. Furthermore, projection of future abundances of very short-lived chlorine source gases are highly uncertain due to the lack of information on industrial sources. Should this class of compounds ever pose a threat to the ozone layer, future controls would be effective almost immediately because these compounds are removed from the stratosphere within a few years.

Q15

Has the Montreal Protocol been successful in reducing ozone-depleting substances in the atmosphere?

Yes, as a result of the Montreal Protocol, the overall abundance of ozone-depleting substances (ODSs) in the atmosphere has been decreasing for the past two decades. If the nations of the world continue to comply with the provisions of the Montreal Protocol, the decrease will continue throughout the 21st century. Those gases that are still increasing in the atmosphere, such as halon-1301 and hydrochlorofluorocarbons (HCFCs), will begin to decrease in the coming decades if compliance with the Protocol continues. However, it is only after midcentury that the abundance of ODSs is expected to fall to values that were present before the Antarctic ozone hole was first observed in the early 1980s, due to the long atmospheric lifetime of these gases.

The Montreal Protocol and its Amendments and Adjustments have been very successful in reducing the atmospheric abundance of ozone-depleting substances (ODSs). ODSs are halogen source gases released by human activities whose production and consumption are now controlled by all of the parties to the Montreal Protocol (see Q14). The success of the Montreal Protocol controls is documented by (1) observed changes and future projections of the atmospheric abundances of the principal ODSs and (2) the long-term decrease in *equivalent effective stratospheric chlorine* (EESC).

Individual ODS reductions. The reduction in the atmospheric abundance of an ODS in response to controls on production and consumption depends principally on how rapidly this ODS is used and released to the atmosphere after being produced, as well as the atmospheric lifetime of the ODS (see Table Q6-1). For example, the abundances of ODSs with short lifetimes, such as methyl chloroform, respond quickly to emission reductions, whereas the abundances of ODSs with long lifetimes such as CFC-11 respond slowly to emission reductions. Estimates of long-term changes in the atmospheric abundances of ODSs are based upon: (1) their measured abundances in air trapped for years within accumulated snow in polar regions, (2) observed atmospheric abundances using ground-based measurements, (3) projections of future abundances based on estimated future demand and compliance with Montreal Protocol provisions for the production and consumption of ODSs, and (4) emissions from ODS banks. The term *bank* refers to the total amount of ODSs contained in existing equipment, chemical stockpiles, foams, and other products that have not yet been released to the atmosphere. The destruction of ODSs in banks prevents the eventual release of these compounds into the atmosphere. The long-term changes of the atmospheric abundances of individual ODSs and the natural chlorine and bromine source gases, methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), assuming compliance with the Montreal Protocol, are shown in **Figure Q15-1**. Key aspects of families of ODSs shown in this figure are:

- **CFCs.** Chlorofluorocarbons (CFCs) include some of the most destructive chlorine-containing ODSs. CFC-11 and CFC-12, with Ozone Depletion Potentials (ODP) of 1 and 0.73, are the most abundant ODSs in the atmosphere owing to large historical emissions and long atmospheric lifetimes of about 50 and 100 years, respectively (see Table Q6-1). Under the Montreal Protocol, allowed production and consumption of CFCs ended in 1996 for developed countries and in January 2010 for developing countries. As a consequence, the atmospheric abundances of CFC-11 and CFC-113 peaked in 1994 and 1996, respectively, and have been declining for more than a decade. In contrast, the abundance of CFC-12 peaked in 2002 and has only recently shown a decrease, owing to its longer lifetime (102 years) and continuing emissions from CFC-12 banks, namely, refrigeration and air conditioning equipment and thermal insulating foams. With no further global production of the principal CFCs, except for some limited exempted uses, and with some continuing emissions from banks, CFC abundances are projected to decline steadily throughout this century. In recent years, the annual decline in CFC-11 has slowed measurably compared to the expected decline due to unreported production outside the provisions of the Montreal Protocol.
- **Halons.** Halons are the most destructive bromine-containing ODSs. Halon-1211 and halon-1301, the most abundant halons in the atmosphere, have concentrations that are about 100 times less than CFC-11 and CFC-12. Together, halon-1211 and halon-1301 account for a significant fraction of bromine from all ODSs (see Figure Q6-1). Under the Montreal Protocol, production and consumption of halons for controlled uses ended in January 1994 for developed countries and in January 2010 for developing

Past and Projected Atmospheric Abundances of Halogen Source Gases

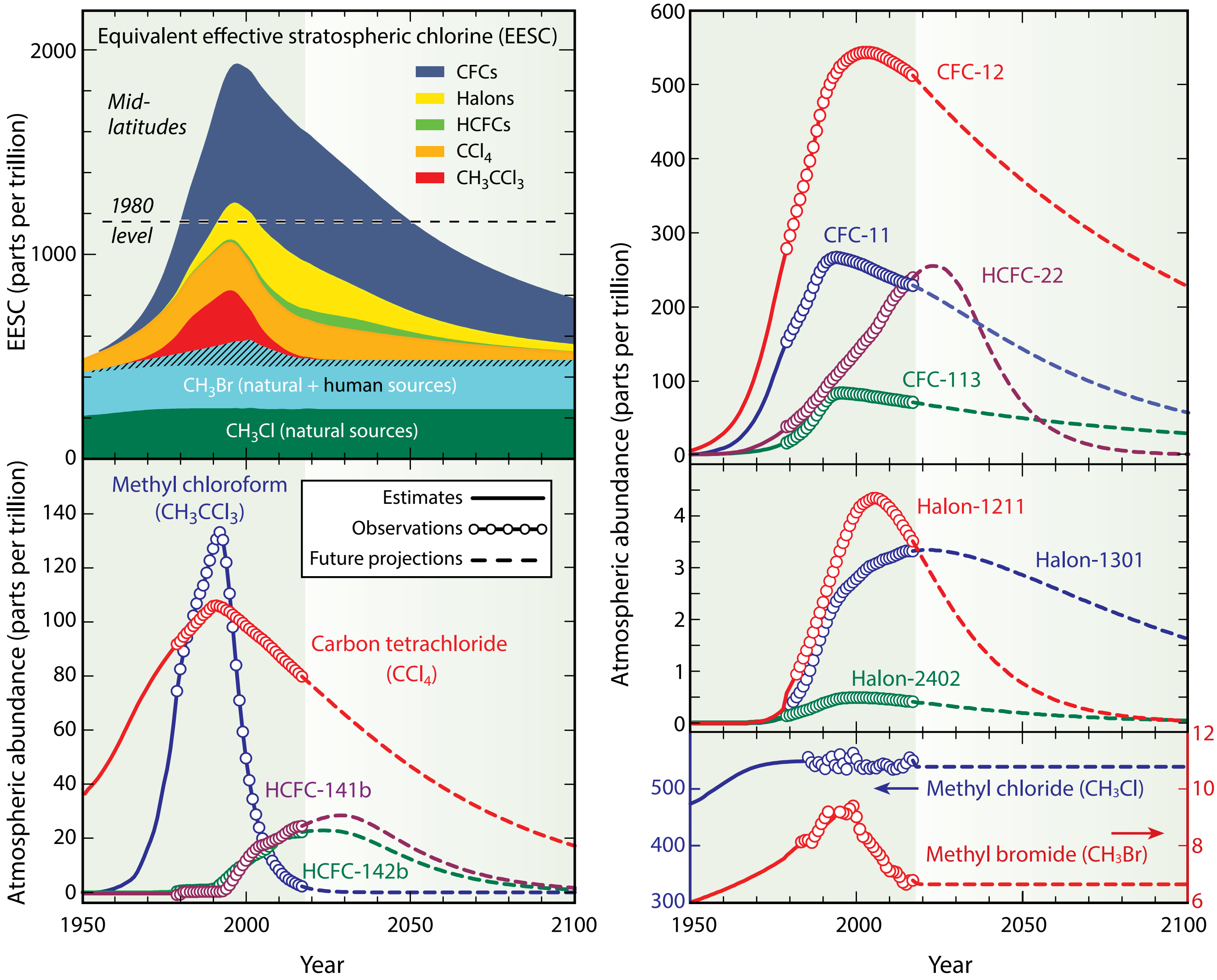


Figure Q15-1. Halogen source gas changes. The surface abundances of individual gases shown here were obtained using a combination of direct atmospheric measurements, estimates of historical abundances, and future projections of abundances assuming compliance with the Montreal Protocol. The gases are all ODSs except for methyl chloride, which is produced by natural processes. The past increases of CFCs, along with those of carbon tetrachloride, methyl chloroform, halon-1211, and halon-2402, have slowed and reversed in the last three decades. The abundances of most HCFCs, which are used as transitional substances to replace CFCs, will likely continue to increase in the next one to two decades before production and consumption are completely phased out. The abundance of halon-1301 has nearly peaked and is expected to decline in coming decades. Future decreases in methyl bromide are expected to be modest, since industrial production is now much smaller than occurred in the 1990s. The abundance of methyl chloride, which is not controlled under the Montreal Protocol, is projected to be constant in the future. Values of EESC shown here for the midlatitude lower stratosphere (about 19 km altitude) are based on observations and projections (see Q14-1). EESC rose rapidly during the latter half of the prior century, peaking in the late 1990s. Since the late 1990s, the trend in EESC has reversed due to the effectiveness of the Montreal Protocol in reducing the production and consumption of ODSs. In the midlatitude stratosphere EESC is projected to return to its 1980 value around year 2050. In polar regions EESC is projected to return to 1980 values about a decade later (see Figure Q20-2). International compliance with the provisions of the Montreal Protocol is required to ensure that EESC will continue to decrease as projected (see Q14). In recent years, the decline in CFC-11 has slowed measurably compared to the expected decline due to unreported production. The contributions from very short-lived gases (see Figure Q6-1) are not included in this EESC time series.

(The unit "parts per trillion" is defined in the caption of Figure Q6-1.)

countries, with some essential use exemptions for both developed and developing countries. Atmospheric abundances of halon-1211 show significant decreases since peak concentrations were measured in the mid-2000s. Halon-2402 abundances have been decreasing slowly for the past two decades while those of halon-1301 have nearly peaked and are expected to decline in coming decades. The slow decline for halon-1301 is likely due to substantial banks in fire-extinguishing and other equipment that gradually release this compound to the atmosphere years after production. The abundance of halon-1301 is expected to remain high well into the 21st century because of its long lifetime (65 years) and continued release.

- **Methyl chloroform.** The largest reduction to date in the abundance of an ODS (98% from its peak value) has been observed for methyl chloroform (CH_3CCl_3). Production and consumption of methyl chloroform in developed countries ended in January 1996 and that in developing countries ended in January 2015, with limited essential use exemptions. Atmospheric abundances responded rapidly to the reduced emissions starting in the mid-1990s because methyl chloroform has a short atmospheric lifetime of about 5 years. Methyl chloroform is used mainly as a solvent and is typically emitted soon after production. This compound is now approaching complete removal from the atmosphere due to the success of the Montreal Protocol.
- **HCFC substitute gases.** The Montreal Protocol allows for the use of hydrochlorofluorocarbons (HCFCs) as short-term, transitional substitutes for CFCs and in other specific applications. As a result, the atmospheric abundances of HCFC-22, HCFC-141b, and HCFC-142b continue to grow in response to continued production, mainly in the developing world. HCFCs pose a lesser threat to the ozone layer than CFCs, because HCFCs have lower ODP values (less than about 0.12; see Table Q6-1). The 2007 Montreal Adjustment to the Protocol accelerated the phaseout of HCFCs by a decade for both developed countries (2020) and developing countries (2030) (see Q14). Even with the accelerated phaseout, future projections show that HCFC abundances continue to increase, reach peak values between 2020 and 2030, and steadily decrease thereafter. The response of atmospheric abundances to decreasing emissions (due to gradual releases from existing banks such as insulating foams) will be relatively rapid because of the short atmospheric lifetimes of HCFCs (less than 18 years).
- **Carbon tetrachloride.** Production and consumption of carbon tetrachloride (CCl_4) for controlled uses in developed countries was phased out in 1996 and that in developing countries in 2010, with some essential use exemptions. As a result, atmospheric abundances of carbon tetrachloride have been decreasing for two decades. The decline is considerably less rapid than expected, suggesting that actual emissions are larger than the emissions derived from the reported consumption. Carbon tetrachloride that is used as raw material (feedstock) to make other chemicals is exempted when calculating the controlled levels of production and consumption under the Montreal Protocol, and some residual emissions do occur. However, current understanding of global sources suggests emissions of carbon tetrachloride are presently dominated by inadvertent production and subsequent release during the chemical manufacturing processes of other compounds, as well as release from landfills and contaminated soils.
- **Methyl chloride and methyl bromide.** Both methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) are distinct among halogen source gases because substantial fractions of their emissions are associated with natural processes (see Q6). Methyl chloride is not controlled under the Montreal Protocol. The abundance of CH_3Cl in the atmosphere has remained fairly constant throughout the last 60 years (see Figure Q15-1). Current sources of methyl chloride from human activities are thought to be small relative to its natural source, and to be dominated by the combustion of coal and chemical manufacturing.

  In contrast, methyl bromide is controlled under the Montreal Protocol. Methyl bromide is primarily used as a fumigant. Nearly all developed country production and consumption of methyl bromide ended in January 2005 and that in developing countries ended in January 2015. The Protocol currently provides limited exemptions for methyl bromide production and use as a fumigant in agriculture as well as for quarantine and pre-shipment applications. Atmospheric abundances of methyl bromide declined rapidly in response to the reduced emissions starting in 1999, because its atmospheric lifetime is less than 1 year (see Figure Q15-1). Future projections show only small changes in methyl bromide abundances based on the assumptions of unchanged contributions from natural sources and small continued critical use exemptions. An important uncertainty in these projections is the future amount that will be produced and emitted under Montreal Protocol critical use, quarantine and pre-shipment exemptions.

Equivalent effective stratospheric chlorine (EESC). Important measures of the success of the Montreal Protocol are the past and projected changes in the values of *equivalent effective stratospheric chlorine,* which was introduced in Figures Q13-1 and Q14-1. EESC is designed as one measure of the potential for ozone depletion in the stratosphere that can be calculated from atmospheric surface abundances of ODSs and natural chlorine and bromine gases. The calculation considers CFCs, HCFCs, methyl chloroform, carbon tetrachloride, halons, as well as methyl chloride and methyl bromide. For both past and future EESC values, the required atmospheric abundances are derived from measurements, historical estimates, or future projections based on compliance with the provisions of the Montreal Protocol.

EESC is derived from the amount of chlorine and bromine available in the stratosphere to deplete ozone. The term *equivalent* indicates that bromine gases, scaled by their greater per-atom effectiveness in depleting ozone, are included in EESC. Although chlorine is much more abundant in the stratosphere than bromine (about 150-fold) (see Figure Q6-1), bromine atoms are about 60 times more efficient than chlorine atoms in chemically destroying ozone in the lower stratosphere. The term *effective* indicates that only the estimated fractions of ODSs that have been converted to reactive halogen gases, for a particular region of the stratosphere at a specified time, are included in the computed value of EESC value (see Q5 and Q7). Long-term changes of EESC generally depend on the altitude and latitude region in the stratosphere under consideration. The value shown in Figure Q15-1 is for the midlatitude, lower stratosphere (about 19 km altitude).

Long-term changes in EESC. In the latter half of the 20th century up until the 1990s, EESC values steadily increased (see Figure Q15-1), causing global ozone depletion. As a result of the Montreal Protocol regulations, the long-term increase in EESC slowed, values reached a peak near the end of 1996, and EESC then began to decrease. By 2018, EESC at midlatitudes had declined by about 18% from the peak value. The initial decrease came primarily from the substantial, rapid reductions in the atmospheric abundance of methyl chloroform, which has a lifetime of only 5 years. The decrease is continuing with declining abundances of CFCs, carbon tetrachloride, and methyl bromide. Decreases depend on natural processes that gradually decompose and remove halogen-containing gases from the global atmosphere (see Q5). Reduction of EESC to 1980 values or lower will require several more decades because the most abundant ODS gases now in the atmosphere have lifetimes ranging from 10 to 100 years (see Table Q6-1).

Terminology

CCM	chemistry-climate model
CFC	chlorofluorocarbon, a group of industrial compounds that contains at least one chlorine, fluorine, and carbon atom
CFC-11-equivalent	a unit for the measure of the mass of emission of an ODS, equal to the product of the actual mass emission of the ODS times its ODP
CO_2-equivalent	a unit for the measure of the mass of emission of a GHG, equal to the product of the actual mass emission of the GHG times its GWP
DU	Dobson unit, a measure of total column ozone; $1\ \text{DU} = 2.687 \times 10^{16}$ molecules/cm^2
EESC	equivalent effective stratospheric chlorine, a measure of the total amount of reactive chlorine and bromine gases in the stratosphere that is available to deplete stratospheric ozone
GHG	greenhouse gas
gigatonne	1 billion (10^9) metric tons = 1 trillion (10^{12}) kilograms
GWP	global warming potential, a measure of the effectiveness of the emission of a gas to cause an increase in the radiative forcing of climate, relative to the radiative forcing caused by the emission of the same mass of CO_2; all GWPs used here are for a 100-year time interval
halon	a group of industrial compounds that contain at least one bromine and carbon atom; may or may not contain a chlorine atom
HCFC	hydrochlorofluorocarbon, a group of industrial compounds that contain at least one hydrogen, chlorine, fluorine, and carbon atom
HFC	hydrofluorocarbon, a group of industrial compounds that contain at least one hydrogen, fluorine, and carbon atom and no chlorine or bromine atoms
HFO	hydrofluoroolefin, a group of industrial compounds that contain at least one hydrogen, fluorine, and carbon atom and no chlorine or bromine atoms, and also include a double carbon bond that causes these gases to be more reactive in the troposphere than other HFCs
IPCC	Intergovernmental Panel on Climate Change
kilotonne	1000 metric tons = 1 million (10^6) kilograms
megatonne	1 million (10^6) metric tons = 1 billion (10^9) kilograms
mPa	millipascal; 100 million mPa = atmospheric sea-level pressure
nm	nanometer, one billionth of a meter (10^{-9} m)
ODP	ozone-depletion potential, a measure of the effectiveness of the emission of a gas to deplete the ozone layer, relative to the ozone depletion caused by the emission of the same mass of CFC-11
ODS	ozone-depleting substance
ozone layer	the region in the stratosphere with the highest concentration of ozone, between about 15 and 35 km altitude
ppb	parts per billion; 1 part per billion equals the presence of one molecule of a gas per billion (10^9) total air molecules
ppm	parts per million; 1 part per million equals the presence of one molecule of a gas per million (10^6) total air molecules
ppt	parts per trillion; 1 part per trillion equals the presence of one molecule of a gas per trillion (10^{12}) total air molecules
PFC	perfluorocarbon, a group of industrial compounds that contain only carbon and fluorine atoms
PSC	polar stratospheric cloud
RCP	Representative Concentration Pathway
RF	radiative forcing of climate
SAOD	stratospheric aerosol optical depth
stratosphere	layer of the atmosphere above the troposphere that extends up to around 50 km altitude, and that includes the ozone layer
TEAP	Technology and Economic Assessment Panel of the Montreal Protocol
troposphere	lower layer of the atmosphere that extends from the surface to about 10-15 km (6-9 miles) altitude
UNEP	United Nations Environment Programme
UNFCCC	United Nations Framework Convention on Climate Change

UV	ultraviolet radiation
UV-A	ultraviolet radiation between wavelengths of 315 and 400 nm
UV-B	ultraviolet radiation between wavelengths of 280 and 315 nm
UV-C	ultraviolet radiation between wavelengths of 100 and 280 nm
WMO	World Meteorological Organization

Chemical Formulae

Bromine Compounds:

$CBrClF_2$	halon-1211
$CBrF_3$	halon-1301
$CBrF_2CBrF_2$	halon-2402
CH_2Br_2	dibromomethane
$CHBr_3$	bromoform
CH_3Br	methyl bromide
Br	atomic bromine
BrO	bromine monoxide
BrCl	bromine monochloride

Chlorine Compounds:

CCl_3F	CFC-11
CCl_2F_2	CFC-12
CCl_2FCClF_2	CFC-113
CCl_4	carbon tetrachloride
CH_2Cl_2	dichloromethane
CH_3CCl_3	methyl chloroform
CH_3Cl	methyl chloride
CHF_2Cl	HCFC-22
CH_3CCl_2F	HCFC-141b
CH_3CClF_2	HCFC-142b
Cl	atomic chlorine
ClO	chlorine monoxide
$(ClO)_2$	chlorine monoxide dimer, chemical structure ClOOCl
$ClONO_2$	chlorine nitrate
HCl	hydrogen chloride

Other Halogens:

CHF_3	HFC-23
CH_2F_2	HFC-32
CHF_2CF_3	HFC-125
CH_2FCF_3	HFC-134a
CH_3CF_3	HFC-143a
CH_3CHF_2	HFC-152a
$CF_3CF{=}CH_2$	HFO-1234yf
CF_4	carbon tetrafluoride
C_2F_6	perfluoroethane
IO	iodine monoxide
SF_6	sulfur hexafluoride

Other gases:

CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
H	atomic hydrogen
H_2O	water vapor
HNO_3	nitric acid
H_2SO_4	sulfuric acid
N_2	molecular nitrogen
N_2O	nitrous oxide
NO_x	nitrogen oxides
O	atomic oxygen
O_2	molecular oxygen
O_3	ozone