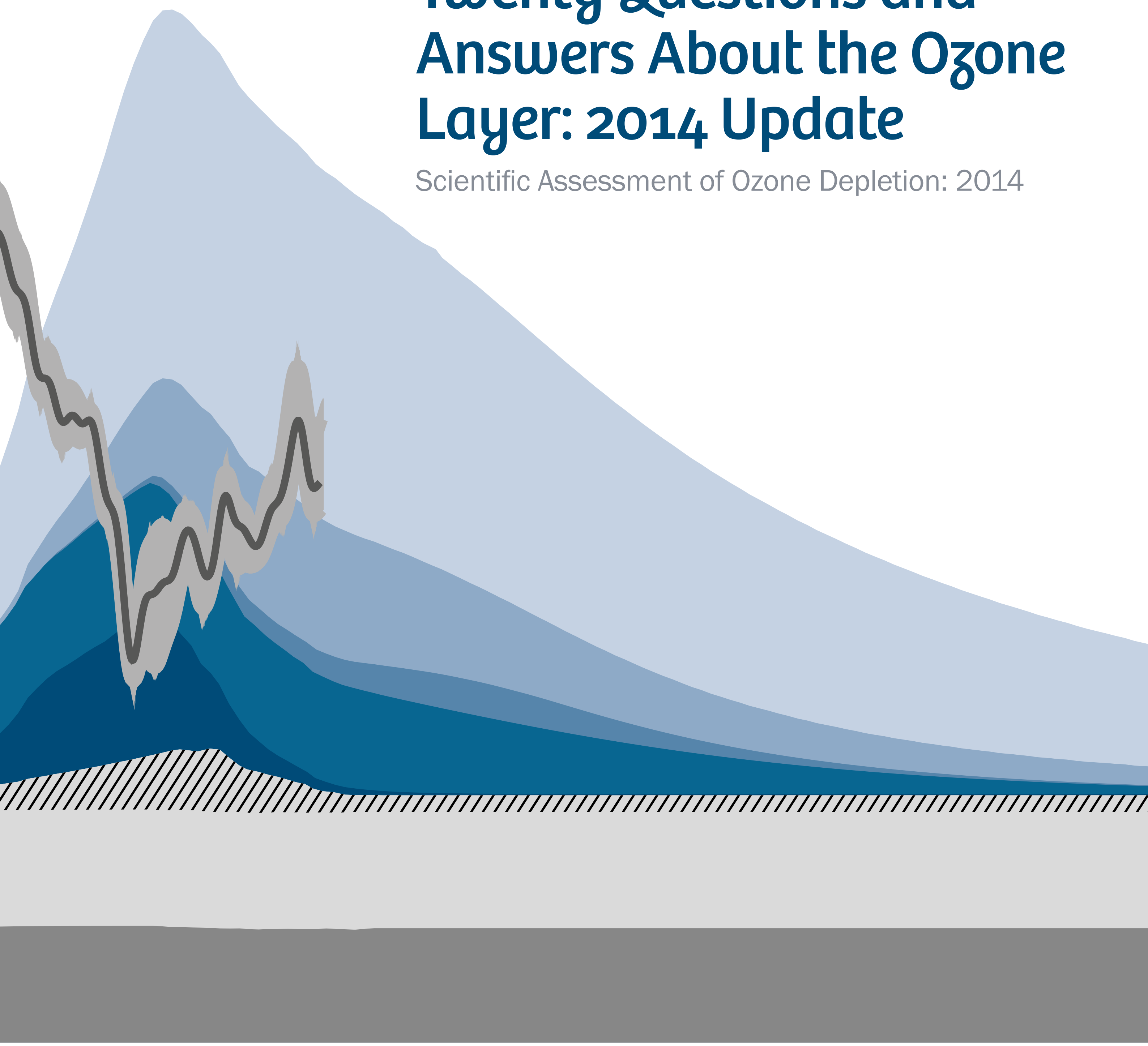
Twenty Questions and Answers About the Ozone Layer: 2014 Update

Scientific Assessment of Ozone Depletion: 2014



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

Q4

How is total ozone distributed over the globe?

The distribution of total ozone over Earth varies with location on timescales that range from daily to seasonal. The 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 polar regions.

Total ozone. Total ozone 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 values are often reported in *Dobson units* denoted as "DU." Typical values vary between 200 and 500 DU over the globe (see Figure Q4-1). The ozone molecules required for total ozone to be 500 DU around the globe would form a layer of pure ozone gas at Earth's surface having a thickness of only 5 millimeters (0.2 inches) (see Q1).

Global distribution. Total ozone varies strongly with latitude over the globe, with the largest values occurring at middle and high latitudes during all seasons (see Figure Q4-1). This 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 thickness (or vertical extent) of the ozone layer and, at the same time, total ozone. In contrast, the values of total ozone are the lowest in the tropics in all seasons (except for those within the Antarctic ozone hole) because the thickness of the ozone layer is smallest there.

Seasonal distribution. Total ozone also varies with season, as is shown in Figure Q4-1 using two-week averages of ozone taken from 2009 satellite observations. March and September plots represent the early spring and fall seasons in the Northern and Southern Hemispheres. June and December plots similarly represent the early summer and winter seasons. Total ozone shows a maximum at high latitudes during spring as a result of increased transport of ozone from its source region in the tropics toward the polar regions during late fall and winter. This ozone transport is much weaker during the summer and early fall periods and is weaker overall in the Southern Hemisphere. An important feature of seasonal ozone changes is the natural chemical destruction that occurs when daylight is continuous in the summer polar stratosphere, which causes total ozone to decrease gradually toward its lowest values in early fall.

This natural seasonal cycle can be observed clearly in the Northern Hemisphere as shown in Figure Q4-1, with increasing values in Arctic total ozone during winter, a clear maximum in spring, and decreasing values from summer to fall. In the Antarctic, however, a pronounced minimum in total ozone is observed during spring. The minimum is a consequence of the "ozone hole," which describes the widespread chemical destruction of ozone by ozone-depleting substances (see Q6 and Q11) in spring. In the late 1970s, before the ozone hole appeared each year, much higher ozone values were found in the Antarctic spring (see Q11). Now, the lowest values of total ozone across the globe and all seasons are found every late winter and spring in the Antarctic as shown in Figure Q4-1. After spring, these low values disappear from total ozone maps as polar air mixes with lower-latitude air containing much higher ozone values.

In the tropics, the total ozone changes through the progression of the seasons are much smaller than in the polar regions. This is because seasonal changes in both sunlight and ozone transport are smaller in the tropics than those in the polar regions.

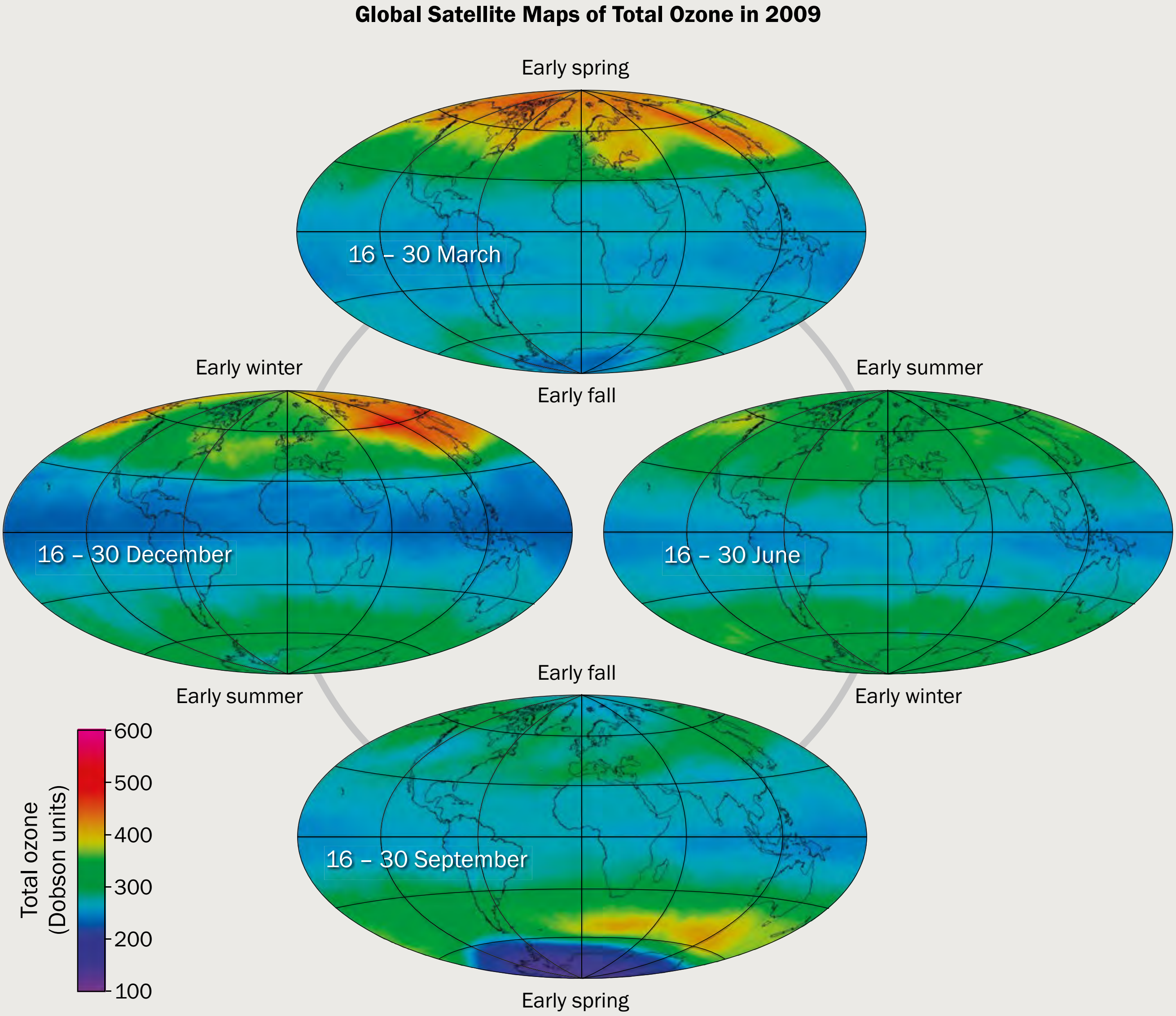


Figure Q4-1. Total ozone.
Total ozone at any location on the globe is defined as the sum of all the ozone molecules in the atmosphere directly above that location. Total ozone varies with latitude, longitude, and season, with the largest values at high latitudes and the lowest values in tropical regions. 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. The low total ozone values over Antarctica in September constitute the “ozone hole” in 2009. Since the 1980s, the ozone hole in late winter and early spring represents the lowest values of total ozone that occur over all seasons and latitudes (see Q11).

Natural variations. Total ozone varies strongly with latitude and longitude as seen within the seasonal plots in Figure Q4-1. These patterns, which change on daily to weekly timescales, come about for two reasons. First, natural air motions mix and blend air between regions of the stratosphere that have high ozone values and those that have low ozone values. Tropospheric weather systems can temporarily change the thickness of the ozone layer in a region, and thereby change total ozone. The geographical variation in these air motions in turn causes variations 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 Q4-1. Ozone changes are routinely monitored by a large group of investigators using satellite, airborne, and ground-based instruments. The continued analysis of these observations provides an important basis to quantify the contribution of human activities to ozone depletion.

Q6

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 containing chlorine and bromine. Most of these gases accumulate in the lower atmosphere because they are 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 Q6-1. The process begins with the *emission*, at Earth's surface, of source gases containing the halogens chlorine and bromine (see Q7). 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 chlorine-containing gases. 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 makes them well suited for specialized applications such as refrigeration.

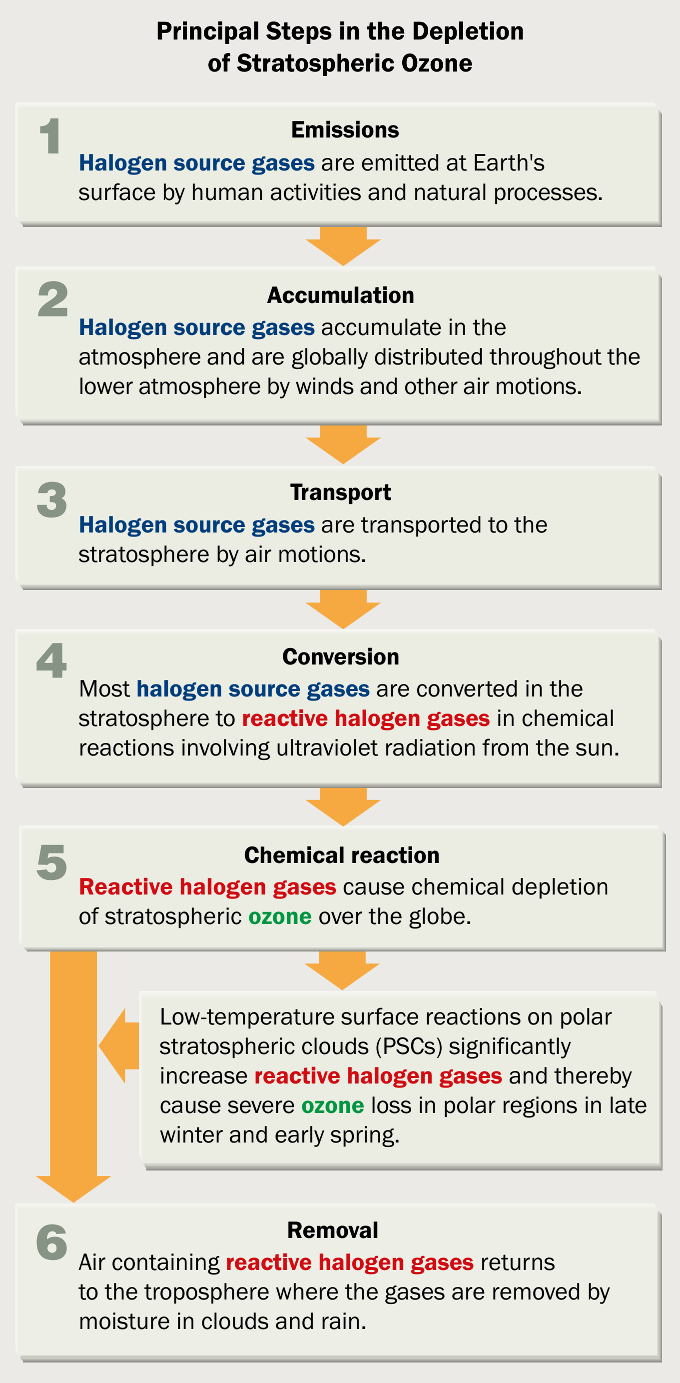
Some halogen gases are emitted in substantial quantities from natural sources (see Q7). These emissions also accumulate in the troposphere, are transported to the stratosphere, and participate in ozone destruction reactions. These naturally emitted gases are part of the natural balance of ozone production 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 Q8). The rate of conversion is related to the atmospheric lifetime of a gas (see Q7). Gases with longer lifetimes have slower conversion rates and survive longer in the atmosphere after emission. Lifetimes of the principal ODSs vary from 1 to 100 years (see Q7). 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 Q9). The average depletion of total ozone attributed to reactive gases is smallest in the tropics and largest at high latitudes (see Q13). In polar regions, surface reactions that occur at low temperatures on polar stratospheric clouds (PSCs) greatly increase the abundance of the most reactive chlorine gas, chlorine monoxide (ClO) (see Q10). This results in substantial ozone destruction in polar regions in late winter and early spring (see Q11 and Q12).

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) and methyl chloride (CH_3Cl), and gases containing iodine (see Q7).



Principal Steps in the Depletion of Stratospheric Ozone

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

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

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

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

5 Chemical reaction
Reactive halogen gases cause chemical depletion of stratospheric **ozone** over the globe.

Low-temperature surface reactions on polar stratospheric clouds (PSCs) significantly increase **reactive halogen gases** and thereby cause severe **ozone** loss in polar regions in late winter and early spring.

6 Removal
Air containing **reactive halogen gases** returns to the troposphere where the gases are removed by moisture in clouds and rain.

Figure Q6-1. Principal steps in stratospheric ozone depletion. The stratospheric ozone depletion process begins with the emission of halogen source gases by human activities and natural processes. Those emitted by human activities are also called ozone-depleting substances (ODSs). Subsequent steps are accumulation, transport, conversion, chemical reaction, and removal. Ozone depletion by halogen source gases occurs globally. Large seasonal ozone losses occur in polar regions as a result of reactions involving polar stratospheric clouds (PSCs). Ozone depletion ends when reactive halogen gases 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 studied 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 (PSCs) 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 responses 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. 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. 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 Q9). Instruments on the ground and on satellites, balloons, and aircraft now routinely detect ozone and ClO remotely using optical and microwave signals. High-altitude aircraft and balloon instruments are also used to detect both gases locally in the stratosphere (see Q5). The observations of ozone and reactive gases made in past decades are used extensively in comparisons with computer models in order to increase confidence in our understanding of stratospheric ozone depletion.

Q7

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 in fire extinguishers. Current ODS abundances in the atmosphere are known directly from air sample measurements.

Halogen source gases versus 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 now controls the global production and consumption of all ODSs (see Q15). Halogen source gases that have only 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 are shown in Figure Q7-1. Total amounts of chlorine peaked in 1993, and of bromine in 1998. The difference in the timing of the peaks is explained by the phase-out schedules, how closely emissions are tied to production, and the lifetimes of the various source gases. Also shown are the contributions to total chlorine and bromine in 2012, highlighting the reductions achieved due to the Montreal Protocol controls.

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, aerosol 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 between 1993 and 2012 (see Figure Q7-1). While the concentration of CFC-12 in 2012 was 2.4% higher than it was in 1993, it peaked in 2000 and has decreased since then (see Figure Q16-1). As substitute gases for CFCs, hydrochlorofluorocarbons (HCFCs) increased substantially between 1993 and 2012 (+157.5%). With new restrictions on global production in place since 2013, HCFCs are expected to reach peak values 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 halocarbon gases originally developed to extinguish fires. Halons were widely used to protect large computer installations, military hardware, and commercial aircraft engines. As a consequence, halons are often released directly into the atmosphere upon use. 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, but also has significant natural sources. As a result of the Montreal Protocol, the abundances of methyl bromide from human sources have substantially decreased between 1998 and 2012 (−61.8%; see Figure Q7-1). Halon-1211 reached peak values in 2005 and has been decreasing since then. Halon-1301 abundances, on the other hand, have increased by +19.9% since 1998 and are expected to increase further (although at a slower rate) because of continued small releases and a long atmospheric lifetime.

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. Natural sources of these two gases contributed about 17% to the total chlorine in the stratosphere in 2012 and about 30% of the total

Halogen Source Gases Entering the Stratosphere

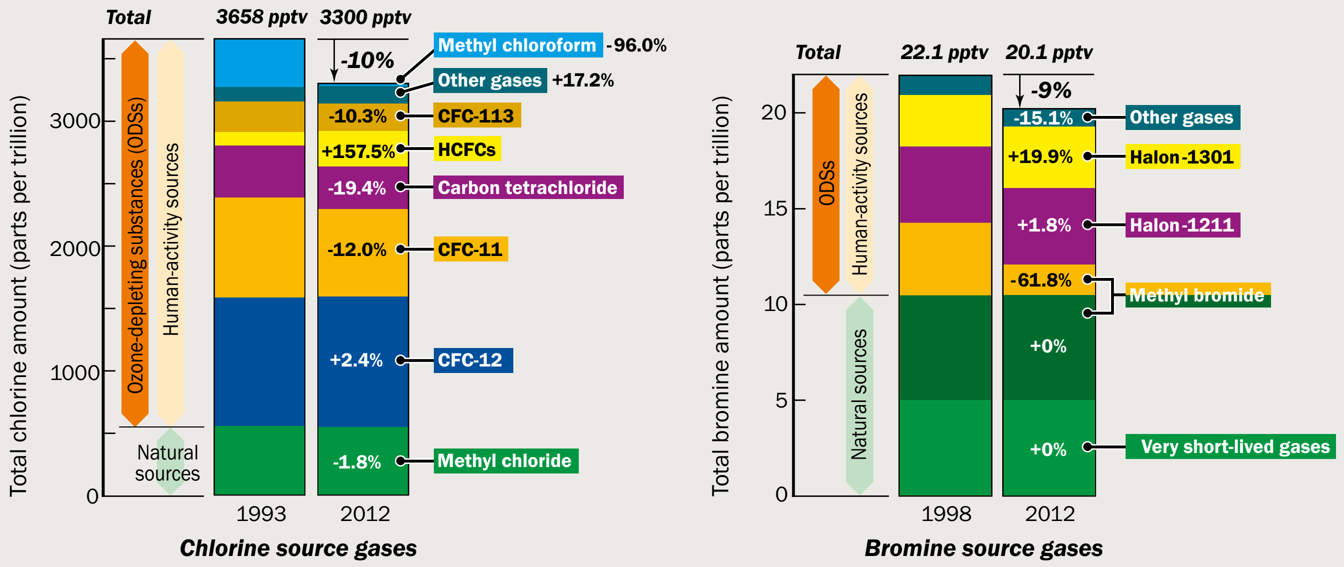


Figure Q7-1. Changes in halogen source gases entering the stratosphere.
A variety of halogen source gases emitted from natural sources and by human activities transport chlorine and bromine into the stratosphere. Ozone-depleting substances (ODSs) are the subset of these gases emitted by human activities that are controlled by the Montreal Protocol. These partitioned columns show the sources and abundances of chlorine- and bromine-containing gases entering the stratosphere in 1993 and 1998, when their total amounts peaked, respectively, and in 2012. The overall reductions in the total amounts of chlorine and bromine and the changes observed for each source gas are also indicated. The approximate amounts are derived from tropospheric observations of each gas. Note the large difference in the vertical scales: total chlorine entering the stratosphere is 150 times more abundant than total bromine. Human activities are the largest source of chlorine reaching the stratosphere and the CFCs are the most abundant chlorine-containing gases. Methyl chloride is the primary natural source of chlorine. Largest decreases between 1993 and 2012 are seen in CFC-11, carbon tetrachloride, and methyl chloroform. HCFCs, which are substitute gases for CFCs and also controlled under the Montreal Protocol, show small but still strongly increasing abundances. For bromine entering the stratosphere, halons and methyl bromide are the largest contributors. Methyl bromide has an additional, much larger, natural source. Natural sources provide a much larger contribution to total bromine entering the stratosphere than to total chlorine. Largest decreases between 1998 and 2012 are seen in methyl bromide. Halon-1211 and halon-1301 show increasing abundances. (The unit “parts per trillion” is used here as a measure of the relative abundance of a gas in air: 1 part per trillion equals the presence of one molecule of a gas per trillion (=10^{12}) total air molecules.)

bromine (Figure Q7-1). Very short-lived source gases containing bromine, such as bromoform ($CHBr_3$), are also released to the atmosphere primarily from biological activity in the oceans. Only a fraction of these emissions reaches the stratosphere, because these gases are rapidly removed in the lower atmosphere. The contribution of these very short-lived gases to the total amount of bromine in the stratosphere is estimated to be about 25% in 2012, but this number has a large uncertainty. The amounts of chlorine and bromine in the stratosphere from natural sources are believed to be fairly constant and, therefore, cannot be the cause of the ozone depletion observed since the 1980s.

Other human sources of chlorine and bromine. 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 and human sources to total stratospheric chlorine is only about 3% and is included in *Other gases* in Figure Q7-1. The Montreal Protocol does not control the production and consumption of very short-lived substances (VSLS), although the concentrations of some (notably dichloromethane, CH_2Cl_2) have increased substantially in recent years.

Lifetimes and emissions. 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 60% of a gas is often called its atmospheric lifetime. Lifetimes vary from less than 1 year to 100 years for the principal chlorine- and bromine-containing gases (see Table Q7-1). 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 (e.g., the HCFCs, methyl bromide, methyl chloride, and the very short-lived gases) are effectively converted to other gases in the troposphere, which are then removed by rain. Therefore, only a fraction of their halogen content potentially contributes to ozone depletion in the stratosphere.

The amount of an emitted gas that is present in the atmosphere represents a balance between its emission rate and removal rate. Emission rates and atmospheric lifetimes vary greatly for the source gases, as indicated in Table Q7-1. For example, 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 hydrochlorofluorocarbons (HCFCs), continue to increase under the provisions of the Montreal Protocol (see Q16). In the coming decades, the emissions and atmospheric abundances of all controlled gases are expected to decrease under these provisions.

Ozone Depletion Potential (ODP). Halogen source gases are compared in their effectiveness to destroy stratospheric ozone using the ODP, as listed in Table Q7-1 (see Q18). A gas with a larger ODP destroys more ozone over its atmospheric lifetime. The ODP is calculated relative to CFC-11, which has an ODP defined to be 1. The calculations, which require the use of atmospheric computer models, 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 small ODP values generally have short atmospheric lifetimes or contain fewer chlorine and bromine atoms.

Table Q7-1.
Atmospheric lifetimes, global emissions, Ozone Depletion Potentials, and Global Warming Potentials of some halogen source gases and HFC substitute gases.

Gas	Atmospheric Lifetime (years)	Global Emissions in 2012 (Kt/yr)[a]	Ozone Depletion Potential (ODP)[c]	Global Warming Potential (GWP)[c]
Halogen source gases				
Chlorine gases[e]				
CFC-11	52	46–68	1	5160
CFC-12	102	16–64	0.73	10300
CFC-113	93	0–7	0.81	6080
Carbon tetrachloride (CCl_4)	26	40–74	0.72	1730
HCFCs	1–18	400–528	0.01–0.10	800–2070
Methyl chloroform (CH_3CCl_3)	5	0–5	0.14	153
Methyl chloride (CH_3Cl)	0.9	2707	0.015	11
Very short-lived Cl-containing gases	less than 0.5	[b]	[b, d] very low	[b] less than 1
Bromine gases				
Halon-1301	72	1.4–2	15.2	6670
Halon-1211	16	0.3–9.3	6.9	1750
Methyl bromide (CH_3Br)	0.8	85	0.57	2
Very short-lived Br-containing gases (e.g., $CHBr_3$)	less than 0.5	[b] 260–1080	[b, d] very low	[b] very low
Hydrofluorocarbons (HFCs)				
HFC-134a	14	144–215	0	1360
HFC-23	228	11–14	0	12500
HFC-143a	51	20–25	0	5080
HFC-125	31	31–47	0	3450
HFC-152a	1.6	40–66	0	148
HFC-32	5.4	12–30	0	700

[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 gigagram = 10^9 grams).

[b] Estimates are very uncertain for most species.

[c] 100-year GWP. ODPs and GWPs are discussed in Q18. Values are calculated for emissions of an equal mass of each gas.

[d] ODP depends strongly on where the emissions occur for these gases. Emissions in the tropics have higher ODPs than emissions at midlatitudes.

[e] New measurements are now available of CFC-112a, CFC-112, CFC-113a, and HCFC-133. These gases are by-products of ODS-manufacturing and constitute only very small contributions to the total of chlorine- and bromine-containing gases.

Fluorine and iodine. Fluorine and iodine are also halogens. Many of the source gases in Figure Q7-1 also contain fluorine in addition to chlorine or bromine. After the source gases undergo conversion in the stratosphere (see Q6), the fluorine content of these gases is left in chemical forms that do not 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 hydrofluorocarbons (HFCs), which are included in Table Q7-1 because they are common ODS substitute gases. HFCs have ODPs of zero and are also strong greenhouse gases (see Q18). 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. Currently there is no evidence that any of these gases reach the stratosphere in significant amounts.

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. 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 Q2). Increasing abundances of N_2O and CH_4, as well as CO_2, are expected to significantly affect future stratospheric ozone through combined effects on temperature, winds, and chemistry (see Q20). Although all of these gases are part of the Kyoto Protocol (see Q15) because they are climate gases, they are not classified as ODSs under the Montreal Protocol. Although past emissions of ODSs still dominate global ozone depletion today, the current emissions of N_2O from human activities will destroy more stratospheric ozone in the future than the current emissions of any ODS.

Q8

What are the reactive halogen gases that destroy stratospheric ozone?

Emissions from human activities and natural processes represent a large source of chlorine- and bromine-containing gases that enter the stratosphere. When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to more reactive gases containing chlorine and bromine. Some reactive gases act as chemical reservoirs that convert to form the most reactive gases, namely chlorine monoxide (ClO) and bromine monoxide (BrO). The most reactive gases participate in catalytic reactions that efficiently destroy ozone. Most volcanoes emit some reactive halogen gases that readily dissolve in water and are usually washed out of the atmosphere before they can reach the stratosphere.

Halogen-containing gases present in the stratosphere can be divided into two groups: *halogen source gases and reactive halogen gases* (Figure Q8-1). The source gases, which include ozone-depleting substances (ODSs), are emitted at Earth's surface by natural processes and by human activities (see Q7). Once in the stratosphere, the halogen source gases chemically convert at different rates to form the reactive halogen gases. The conversion occurs in the stratosphere for most gases instead of the troposphere because solar ultraviolet radiation (a component of sunlight) is more intense in the stratosphere. Reactive gases containing the halogens chlorine and bromine lead to the chemical destruction of stratospheric ozone.

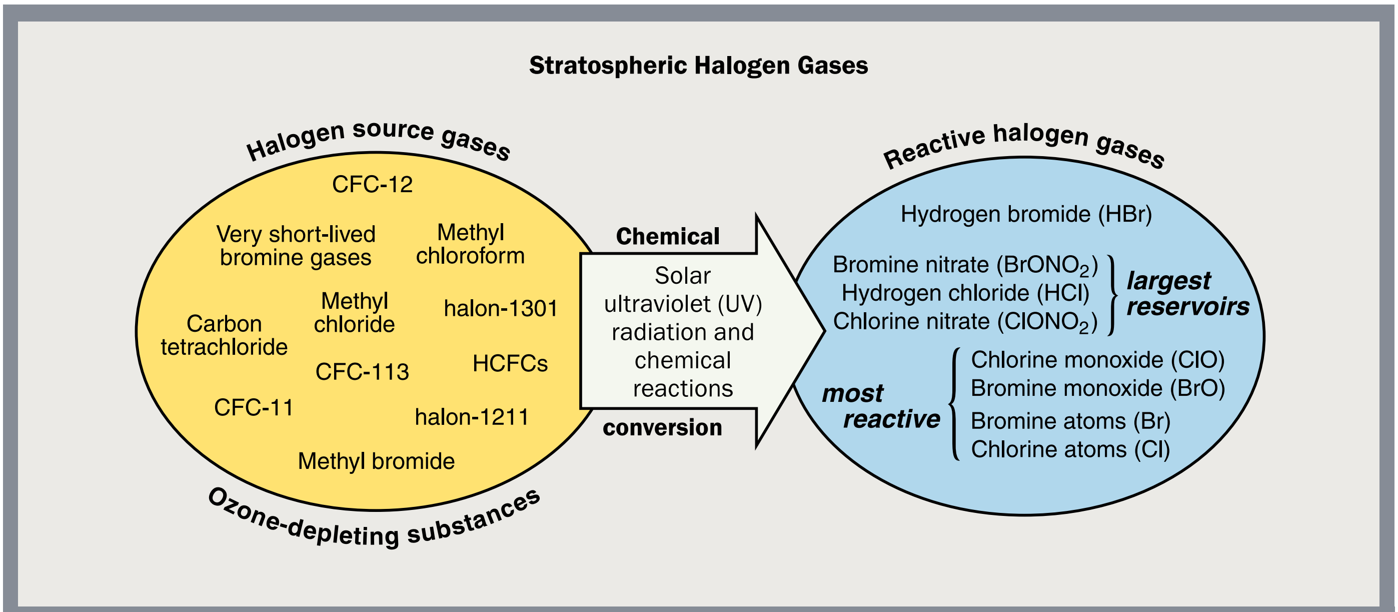


Figure Q8-1. Conversion of halogen source gases.
Halogen source gases containing chlorine and bromine are chemically converted to reactive halogen gases primarily in the stratosphere. The conversion requires solar ultraviolet radiation and a few chemical reactions. The shorter-lived gases undergo some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

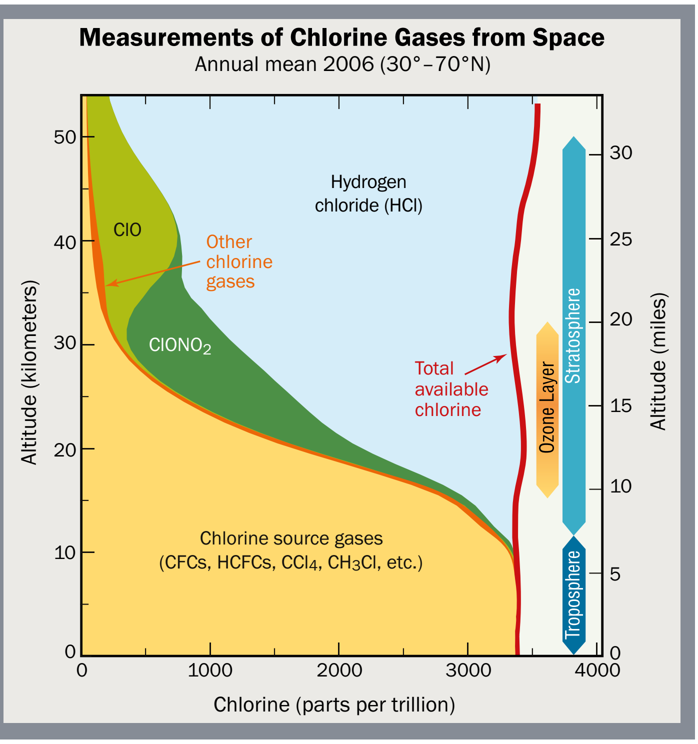


Figure Q8-2. Reactive chlorine gas observations. The abundances of chlorine source gases and reactive chlorine gases as measured from space in 2006 are displayed with altitude for a midlatitude location. In the troposphere (below about 10 kilometers), all chlorine is contained in the source gases. In the stratosphere, the abundances of reactive chlorine gases increase with altitude as the amounts of chlorine source gases decline. This is a consequence of chemical reactions initiated by solar ultraviolet radiation that convert source gases to reactive gases (see Figure Q8-1). The principal reactive chlorine gases formed are HCl, $ClONO_2$, and ClO. Summing the source gases with the reactive gases gives “Total available chlorine,” which is nearly constant with altitude throughout the stratosphere. In the ozone layer (15-25 km), chlorine source gases are still present and HCl and $ClONO_2$ are the most abundant reactive chlorine gases. (The unit “parts per trillion” is defined in the caption of Figure Q7-1.)

Reactive 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 Q8-1. 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 don’t react directly with ozone, they can be converted to the *most reactive* forms that do chemically destroy ozone. The most reactive forms are chlorine monoxide (ClO) and bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). A large fraction of available reactive bromine is generally in the form of BrO, whereas usually only a small fraction of reactive chlorine is in the form of ClO. The special conditions that occur in the polar regions in winter cause the reservoir gases $ClONO_2$ and HCl to undergo nearly complete conversion to ClO in reactions on polar stratospheric clouds (PSCs) (see Q10).

Reactive chlorine at midlatitudes. Reactive chlorine gases have been observed extensively in the stratosphere using both local and remote measurement techniques. The measurements from space displayed in Figure Q8-2 are representative of how the amounts of chlorine-containing gases change between the surface and the upper stratosphere at mid- to high latitudes. Available chlorine (see red line in Figure Q8-2) is the sum of chlorine contained in halogen source gases and in the reactive gases (e.g., CFC-11, $ClONO_2$, ClO). Available chlorine is constant to within about 10% from the surface to above 50 kilometers (31 miles) altitude. In the troposphere, available chlorine is contained almost entirely in the source gases described in Figure Q7-1. At higher altitudes, the source gases become a smaller fraction of available chlorine as they are converted to the reactive chlorine gases. At the highest altitudes, available chlorine is all in the form of the reactive chlorine gases.

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

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

In fall (May), ozone values are high over the entire Antarctic continent and beyond. Temperatures are mid-range, HCl and nitric acid (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 past decades, the reservoir gases HCl and $ClONO_2$ have increased substantially in the stratosphere following increased emissions of halogen source gases. HNO_3 is an abundant, naturally occurring stratospheric compound that plays major roles in stratospheric ozone chemistry by both moderating ozone destruction and condensing to form polar stratospheric clouds (PSCs). Low ClO indicates that little conversion of the reservoir gases occurs in the fall, thereby limiting catalytic ozone destruction.

By late winter (September), ozone amounts reflect substantial depletion at 18-km altitude over an area larger than the Antarctic continent. Antarctic ozone holes arise from similar chemical destruction throughout much of the altitude range of the ozone layer (see altitude profile in Figure Q12-3). The meteorological and chemical conditions in late winter are very different from those found in fall: very low temperatures, very low HCl and HNO_3, and very high ClO. Low stratospheric temperatures are characteristic of winter, when solar heating is reduced. Low HCl and high ClO reflect the conversion of the reactive halogen reservoir compounds, HCl and $ClONO_2$, to the most reactive chlorine form, ClO. This conversion occurs selectively in winter on PSCs, which form at the very low temperatures (see Q10). 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 Q11). 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 Q10), and ozone destruction is curtailed.

Similar though less dramatic changes in meteorological and chemical conditions are also observed between fall 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, in part because of the lower abundance of bromine. The most widely observed bromine gas is bromine monoxide (BrO), which can be observed from space. Estimates of reactive bromine abundances in the stratosphere are larger than expected from the conversion of the halons and methyl bromide source gases, suggesting that the contribution of the very short-lived bromine-containing gases to reactive bromine must also be significant (see Q7).

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

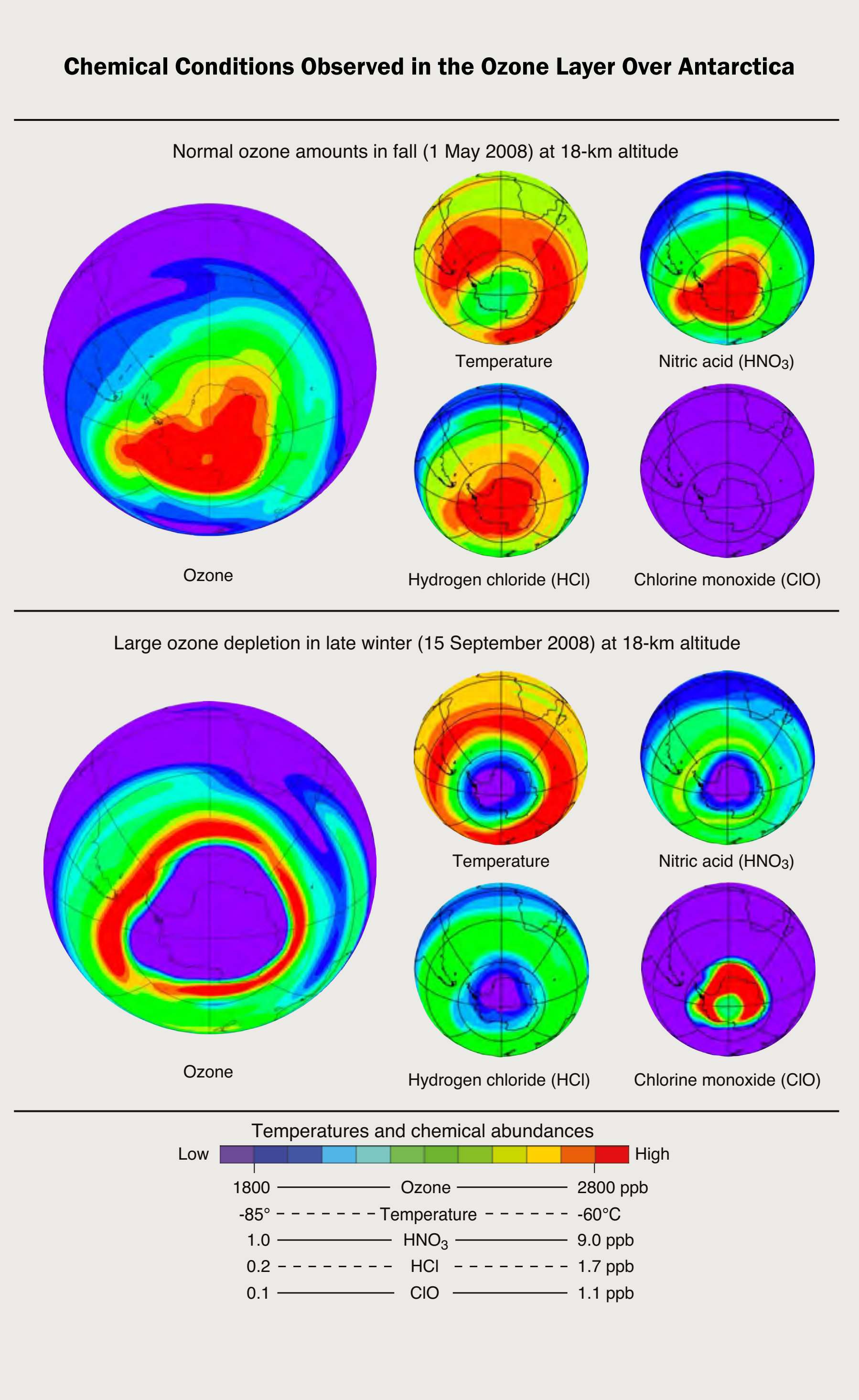


Figure Q8-3. Chemical conditions in the ozone layer over Antarctica. Observations of the chemical conditions in the Antarctic region highlight the changes associated with severe ozone depletion that forms the ozone hole. Satellite instruments now routinely monitor ozone, reactive chlorine gases, and temperatures in the global stratosphere. Results are shown here for fall (May) and late winter (September) seasons in Antarctic winter for a narrow altitude region near 18 kilometers (11.2 miles) within the ozone layer (see Figure Q12-3). Ozone has naturally high values in fall, 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 ClO amounts. When ClO is not enhanced, significant ozone destruction from ozone-depleting substances does not occur. Chemical conditions are quite different in late winter when ozone undergoes severe depletion. Temperatures are much lower, HCl has been converted to ClO (the most reactive chlorine gas), and HNO_3 has been removed by the gravitational settling of PSC particles. ClO values closely surrounding the South Pole are low in September because ClO formation requires sunlight, which is still gradually returning to the highest latitudes. The high ClO values in late winter covering an extensive area that at times exceeds that of the Antarctic continent can last for 1 to 2 months, and efficiently destroy ozone in sunlit regions in late winter/early spring. Ozone typically reaches its minimum values in early to mid-October (see Q12). Note that the first and last colors in the color bar represent values outside the indicated range of values. (The unit "parts per billion," abbreviated "ppb," is used here as a measure of the relative abundance of a gas in air: 1 part per billion equals the presence of one molecule of a gas per billion ($=10^9$) total air molecules (compare to ppt in Figure Q7-1).)

Q9

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

Reactive gases containing chlorine and bromine destroy stratospheric ozone in “catalytic” cycles made up of two or more separate reactions. As a result, a single chlorine or bromine atom can destroy many 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 Q8-1). 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 Q9-1. 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 hundreds 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 up to tens of thousands of ozone molecules.

Polar Cycles 2 and 3. The abundance of ClO is greatly increased in polar regions during winter as a result of reactions on the surfaces of polar stratospheric clouds (PSCs) (see Q8 and Q10). Cycles 2 and 3 (see Figure Q9-2) become the dominant

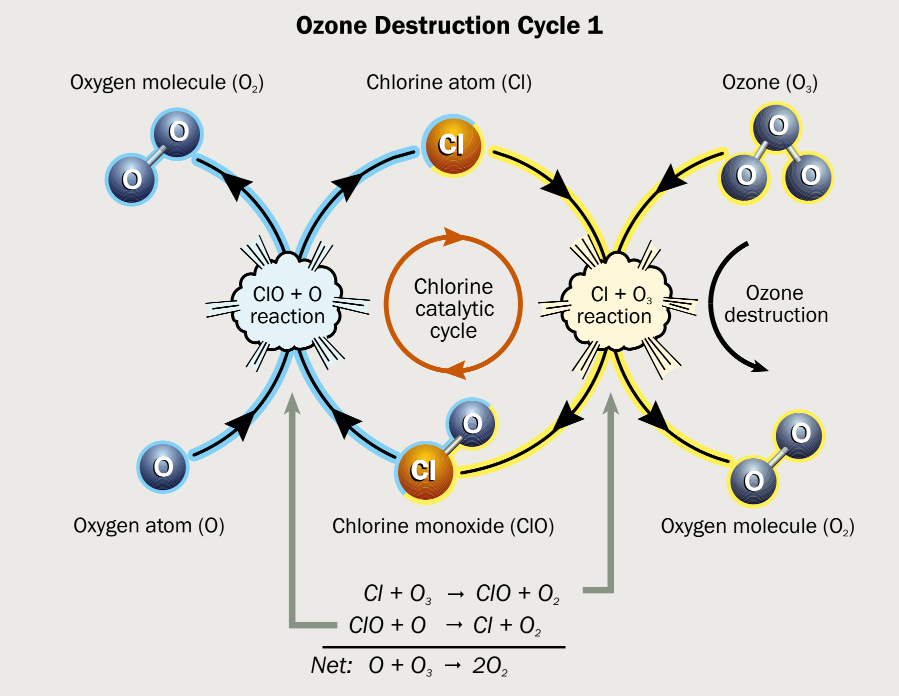


Figure Q9-1. Ozone destruction Cycle 1. The destruction of ozone in Cycle 1 involves two separate chemical reactions. The net or overall reaction is that of atomic oxygen with ozone, forming two oxygen molecules. The cycle can be considered to begin with either ClO or Cl. When starting with ClO, the first reaction is ClO with O to form Cl. Then, Cl reacts with ozone and re-forms ClO, consuming ozone in the process. 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 ozone destruction. Atomic oxygen (O) is formed when solar ultraviolet radiation (sunlight) reacts with ozone and oxygen molecules. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where solar ultraviolet radiation is most intense.

Q9

reaction mechanisms for polar ozone loss because of the high abundances of ClO and the relatively low abundance of atomic oxygen (which limits the rate of ozone loss by Cycle 1). Cycle 2 begins with the self-reaction of ClO. Cycle 3, which begins with the reaction of ClO with BrO, has two reaction pathways to produce either Cl and Br or BrCl. The net result of both cycles is to destroy two ozone molecules and create three oxygen molecules. Cycles 2 and 3 account for most of the ozone loss observed in the Arctic and Antarctic stratospheres in the late winter/early spring season (see Q11 and Q12). At high ClO abundances, the rate of polar ozone destruction can reach 2 to 3% per day in late winter/early spring.

Sunlight requirement. Sunlight is required to complete and maintain Cycles 1 through 3. Cycle 1 requires ultraviolet 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 tropical and middle latitudes, where solar ultraviolet radiation is most intense.

Cycles 2 and 3 require visible sunlight to complete the reaction cycles and to maintain ClO abundances. In the continuous darkness of winter in the polar stratosphere, reaction Cycles 2 and 3 cannot occur. It is only in late winter/early spring when sunlight returns to the polar regions that these cycles are active. Therefore, the greatest destruction of ozone occurs in the partially to fully sunlit periods after midwinter in the polar stratosphere. The visible sunlight needed in Cycles 2 and 3 is not sufficient to form ozone because this process requires solar ultraviolet radiation (see Q1). In the late winter/early spring stratosphere, solar ultraviolet radiation is weak at low Sun angles. As a result, ozone destruction by Cycles 2 and 3 in the sunlit winter stratosphere greatly exceeds ozone production.

Other reactions. Global ozone abundances are controlled by many reactions that both produce and destroy ozone (see Q2). Chlorine and bromine catalytic reactions are but one group of ozone destruction reactions. Reactive hydrogen and reactive nitrogen gases, for example, are involved in other catalytic ozone-destruction cycles that also occur in the stratosphere. These reactions occur naturally in the stratosphere and their importance has not been as strongly influenced by human activities as have reactions involving halogens. The sources of reactive hydrogen and nitrogen gases are the naturally occurring gases methane (CH_4) and nitrous oxide (N_2O), respectively. The importance of reactive hydrogen and nitrogen gases 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 CH_4 and N_2O abundances (which are not controlled under the Montreal Protocol) are projected to increase substantially due to human activities.

Ozone Destruction Cycles in Polar Regions

Cycle 2

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

Net: $2O_3 \rightarrow 3O_2$

Cycle 3

$$ClO + BrO \rightarrow Cl + Br + O_2$$

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

$$Cl + O_3 \rightarrow ClO + O_2$$
$$Br + O_3 \rightarrow BrO + O_2$$

Net: $2O_3 \rightarrow 3O_2$

Figure Q9-2. Polar ozone destruction Cycles 2 and 3.
Significant destruction of ozone occurs in polar regions where ClO abundances reach large values. In this case, the cycles initiated by the reaction of ClO with another ClO (Cycle 2) or the reaction of ClO with BrO (Cycle 3) efficiently destroy ozone. The net reaction in both cases is two ozone molecules forming three oxygen molecules. The reaction of ClO with BrO has two pathways to form the Cl and Br product gases. Ozone destruction Cycles 2 and 3 are catalytic, as illustrated for Cycle 1 in Figure Q9-1, because chlorine and bromine gases react and are re-formed each time the reaction cycle is completed. Visible sunlight is required to complete each cycle and to help form and maintain ClO abundances. During polar night and other periods of darkness, ozone cannot be destroyed by these reactions.

Q13

How large is the depletion of the global ozone layer?

Depletion of the global ozone layer increased gradually in the 1980s and reached a maximum of about 5% in the early 1990s. The depletion has lessened since then and now is about 3% averaged over the globe. The average depletion exceeds the natural year-to-year variations of global total ozone. The ozone loss is very small near the equator and increases with latitude toward the poles. The larger polar depletion is attributed to the late winter/early spring ozone destruction that occurs there each year.

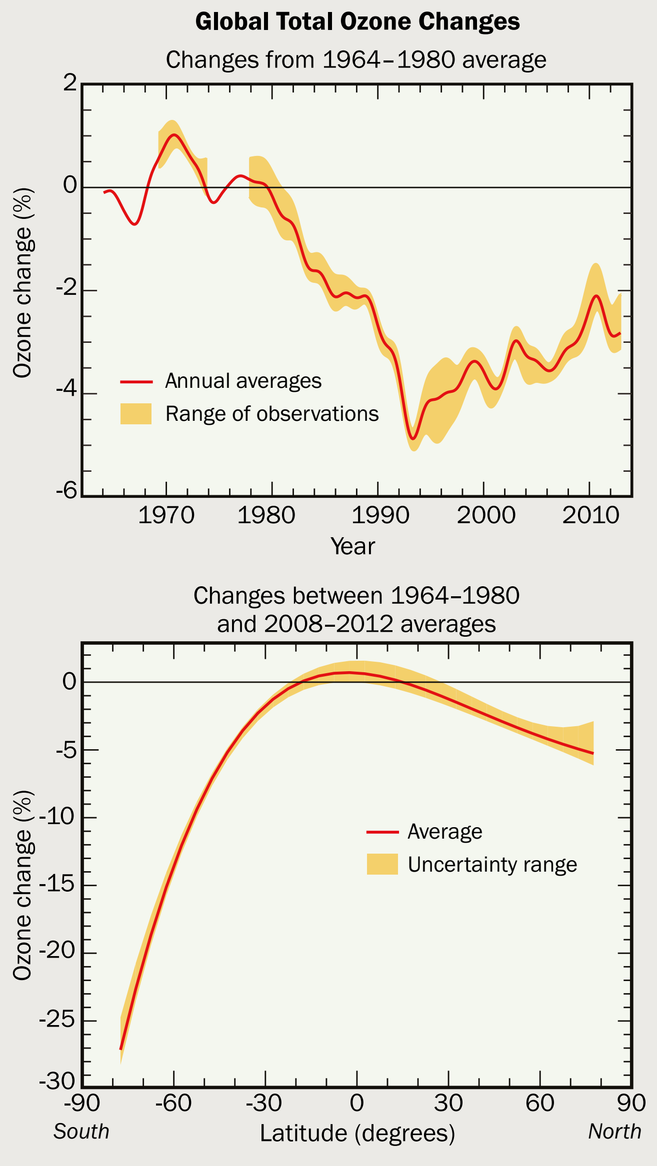
Global total ozone has decreased beginning in the 1980s (see Figure Q13-1). The decreases have occurred in the stratospheric ozone layer where most ozone resides (see Figure Q1-2). In the early 1990s, the depletion of global total ozone reached a maximum of about 5% below the 1964–1980 average. The depletion has lessened since then and during the early 2010s has averaged to about 3% below the 1964–1980 average. The observations shown in Figure Q13-1 have been smoothed to remove regular ozone changes that are due to natural seasonal and solar effects (see Q14). The depleted amounts are larger than the remaining natural variations in global total ozone amounts.

The observed global ozone depletion in the last three decades is attributable to increases in reactive halogen gases in the stratosphere. The lowest global total ozone values since 1980 have occurred in the years following the eruption of Mt. 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 Q14) and, thereby, increased global ozone depletion by 1–2% for several years following the eruption.

Polar regions. Observed total ozone depletion varies significantly with latitude on the globe (see Figure Q13-1). The largest reductions occur at high southern latitudes as a result of the severe ozone loss over Antarctica each late winter/early spring period. The next largest losses are observed in the high latitudes of the Northern Hemisphere, caused in part by winter losses over the Arctic. Although the depletion in polar regions is larger than at lower latitudes, the influence of polar regions on global ozone is limited by their small geographical area. Latitudes poleward of 60° account for only about 13% of Earth's surface.

Midlatitude regions. Ozone depletion is also observed at the midlatitudes spanning the region between equatorial and polar latitudes. In comparison with the 1964–1980 averages, total ozone averaged for 2008–2012 is about 3.5% lower in northern midlatitudes (35°N–60°N) and about 6% 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 outside polar regions. Second, chemical destruction occurring at midlatitudes contributes to observed depletion in these regions. This contribution is much smaller than in polar regions because the amounts of reactive halogen gases are lower and a seasonal increase of the most reactive halogen gases, such as the increase in ClO in the polar winter lower stratosphere (see Figure Q8-3), does not occur in midlatitude regions.

Tropical region. Total ozone in the tropics (20°N–20°S latitude) has been only weakly affected by chemical ozone depletion. In the tropical lower stratosphere, air has been transported from the lower atmosphere (troposphere) within the previous 18 months. As a result, the conversion of ozone-depleting substances (ODSs) 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, ozone production is high because average solar ultraviolet radiation is highest in the tropics. 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. The systematic differences in the age of stratospheric air are well understood and are a consequence of the 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.



Global Total Ozone Changes

Changes from 1964–1980 average

Changes between 1964–1980 and 2008–2012 averages

Figure Q13-1. Global total ozone changes.
Satellite observations show depletion of global total ozone beginning in the 1980s. The top panel compares annual averages of global ozone with the average from the period 1964 to 1980 before the ozone hole appeared. Seasonal and solar effects have been removed from the observational data set. 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 Mt. Pinatubo eruption (see Q14). Average global ozone for 2008–2012 is about 2.5% below the 1964–1980 average. The bottom panel shows how the 2008–2012 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.

Q13

Initial Signs of Ozone Recovery

The Montreal Protocol, strengthened by its Amendments and adjustments, has successfully controlled the production and consumption of ODSs that act to destroy the ozone layer (Q15). As a result, atmospheric abundances of ODSs have peaked and are now decreasing (Q7 and Q16). By 2012, equivalent effective stratospheric chlorine (EESC; the total chlorine and bromine abundances in the stratosphere) had declined by 15% at midlatitudes from peak values of around 15 years ago. This raises the question, is global ozone increasing in response to the observed EESC decreases?

Identifying an ozone increase is not easy, because ODS levels are not the only factor that determines global ozone levels. For example, the global ozone minimum was observed half a decade before the EESC maximum was reached. The difference in the timing resulted from the strong global ozone response to enhanced stratospheric aerosol loading after the Mount Pinatubo eruption in 1991, which led to increased ozone depletion for several years. Observed global ozone increases through the 1990s were therefore a result of the steady removal of the aerosol from the stratosphere, and not a sign of decreasing ODSs (see Q14). 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 signal expected from the observed EESC decreases. Finally, greenhouse gas increases (such as carbon dioxide, CO_2) affect ozone by decreasing stratospheric temperatures (which slows down ozone depletion rates) and by strengthening the stratospheric circulation (which enhances the transport of ozone from the tropics to higher latitudes). It is therefore difficult to attribute observed ozone changes to these different factors.

Observations now show a clear 5% increase of ozone in the upper stratosphere (42 km) over the 2000-2013 period. Model simulations that allow for separation of the different factors suggest that about half of this increase results from a cooling in this region due to CO_2 increases, while the other half results from EESC decreases. Also, total column ozone declined over most of the globe during the 1980s and early 1990s (by about 2.5% averaged over 60°S to 60°N). It has remained relatively unchanged since 2000, with indications of a small increase in total column ozone in recent years. Models suggest that this small increase is likely due to EESC decreases. These findings based on both models and observations suggest that there are initial signs of ozone recovery.

Because of their long lifetime, the impact on stratospheric ozone of the most prominent ODSs (CFC-11 and CFC-12) will continue for many decades after emissions have ceased. Assuming continued compliance with the Montreal Protocol, EESC will continue to decline over the coming decades and will return to pre-1980 levels around midcentury. With the exception of the tropics (see Q20), climate change is expected to accelerate the return of the ozone layer to pre-1980 levels. However, as long as ODS levels remain elevated in the atmosphere, the possibility of extreme low-ozone events due to volcanic eruptions or cold winter conditions persists into the second half of the 21st century.

Q14

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

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

Changes in solar radiation and increases in stratospheric particles from volcanic eruptions both affect the abundance of stratospheric ozone. Global total ozone in the early 1990s had decreased by about 5% when compared to pre-1980 values, and is now about 3% below pre-1980 values (see Q13). The depletion is primarily attributed to increases in reactive halogen gases, with additional depletion in the early 1990s associated with the volcanic eruption of Mt. Pinatubo. Reactive halogen gases are represented by changes in *equivalent effective stratospheric chlorine* (EESC). EESC values account for stratospheric chlorine and bromine abundances and their different effectiveness in destroying ozone (see definition in Q16). A comparison of the smooth year-to-year changes in ozone and EESC shows that the quantities are inversely related to each other, with ozone first decreasing while EESC increased (see Figure Q14-1). After the mid-1990s, the annual changes in both quantities remained constant and then slowly reversed sign. Changes in solar output and volcanic activity do not show such smooth long-term changes, as discussed below, and therefore cannot be the cause of long-term global ozone depletion.

Total ozone and solar changes. The formation of stratospheric ozone is initiated by ultraviolet (UV) radiation coming from the Sun (see Figure Q2-1). As a result, an increase in the Sun's radiation output increases the amount of ozone in Earth's atmosphere. The Sun's radiation output and sunspot number vary over the well-documented 11-year solar cycle. Observations over several solar cycles since the 1960s show that global total ozone levels vary by 1 to 2% between the maximum and minimum of a typical cycle. Changes in incoming solar radiation at a wavelength of 10.7 cm are often used as a surrogate for changes in solar output at UV wavelengths. The long-term changes in the 10.7-cm output in Figure Q14-1 clearly show alternating periods of maximum and minimum values in total solar output separated by about 5 to 6 years. If changes in solar output were the cause of global ozone depletion, a gradually decreasing output would have been observed around 1980 or earlier, slowing sharply in the mid-1990s. Since such a decrease was not observed, nor is expected based on longer-term solar observations, the long-term decreases in global ozone cannot result from changes in solar output alone. Most analyses presented in this and previous international scientific assessments quantitatively account for the influence of the 11-year solar cycle on long-term variations in ozone.

Total ozone and past volcanoes. Explosive volcanic eruptions inject sulfur gases directly into the stratosphere, causing new sulfate particles to be formed. The particles initially form in the stratosphere downwind of the volcano and then spread throughout the hemisphere or globally as air is transported by stratospheric winds. One method of detecting the presence of volcanic particles in the stratosphere uses observations of the transmission of solar radiation through the atmosphere (see Figure Q14-1). When large amounts of new particles are formed in the stratosphere over an extensive region, solar transmission is measurably reduced. The eruptions of Mt. Agung (1963), El Chichón (1982), and Mt. Pinatubo (1991) are the most recent examples of sulfur injections that temporarily reduced solar transmission.

Laboratory measurements and stratospheric observations have shown that chemical reactions on the surfaces of volcanically produced particles can increase ozone destruction by increasing the amounts of the highly reactive chlorine gas, chlorine monoxide (ClO). The ozone response depends on the total abundance of EESC after the eruption (see Q16). At times of relatively low EESC, such as the early 1960s, ozone is not very sensitive to stratospheric injection of volcanic sulfate particles. At times of higher EESC amounts, such as from 1980 to the present, global ozone is expected to decrease significantly following large explosive eruptions. The most recent large eruption was that of Mt. Pinatubo, which resulted in as much as a 10-fold increase in the number of particles available for surface reactions. Both El Chichón and Mt. Pinatubo increased global ozone depletion for a few years (see Figure Q14-1). EESC was too low for ozone depletion to occur after the Mt. Agung eruption in 1963. The effect on ozone diminishes during the years following an eruption as volcanic particles are gradually removed from the stratosphere by gravitational settling and large-scale atmospheric transport. As particles are removed, solar transmission is restored. Based on the short residence time of volcanic particles in the stratosphere, the two large eruptions in the past three decades cannot account directly for the continuous long-term decreases in global total ozone observed over the same period.

Reactive chlorine from volcanoes. Explosive volcanic plumes generally contain large quantities of reactive chlorine in the form of hydrogen chloride (HCl). HCl is a reactive halogen gas that can be converted to ClO, which rapidly destroys ozone (see Figure Q8-3). The 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 it is still in the lower atmosphere (troposphere). As a result, most of the HCl in explosive volcanic plumes does not enter the stratosphere. After recent explosive eruptions, observations of HCl in the stratosphere have confirmed that increases are small compared with the total amount of chlorine in the stratosphere from other sources.

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 and small amounts of HCl directly into the stratosphere over Antarctica, which could lead to ozone depletion. However, to be a possible cause of the annually recurring ozone hole beginning in the early 1980s, explosive Antarctic eruptions would need to have occurred at least every few years to maintain volcanic emissions in the stratosphere. This is not the case. Only the Mt. Erebus volcano is currently active in Antarctica. No explosive eruptions of Mt. Erebus or any other Antarctic volcano have occurred since 1980. Therefore, 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. Observations and atmospheric models indicate that the record-low ozone levels observed in 1992–1993 resulted from the large number of particles produced by the Mt. Pinatubo eruption, combined with the relatively large amounts of EESC present in the stratosphere in the early 1990s. If the Mt. Pinatubo eruption had occurred before 1980, changes to global ozone would have been much smaller than observed in 1992–1993 because EESC values were much lower. EESC values will remain substantial in the early decades of the 21st century even as ODSs decline globally, with 1980 values not reached until about 2050 (see Figures Q16-1 and Q20-2). Large volcanic eruptions in the intervening years will cause more ozone depletion. If an explosive eruption larger than Mt. Pinatubo were to occur, peak ozone losses could be larger than previously observed and substantial ozone losses could persist for longer time periods. As halogen gas abundances gradually decline, the effect of volcanic eruptions on ozone will lessen.

The Solar Cycle, Volcanic Eruptions, Global Ozone, and Equivalent Effective Stratospheric Chlorine

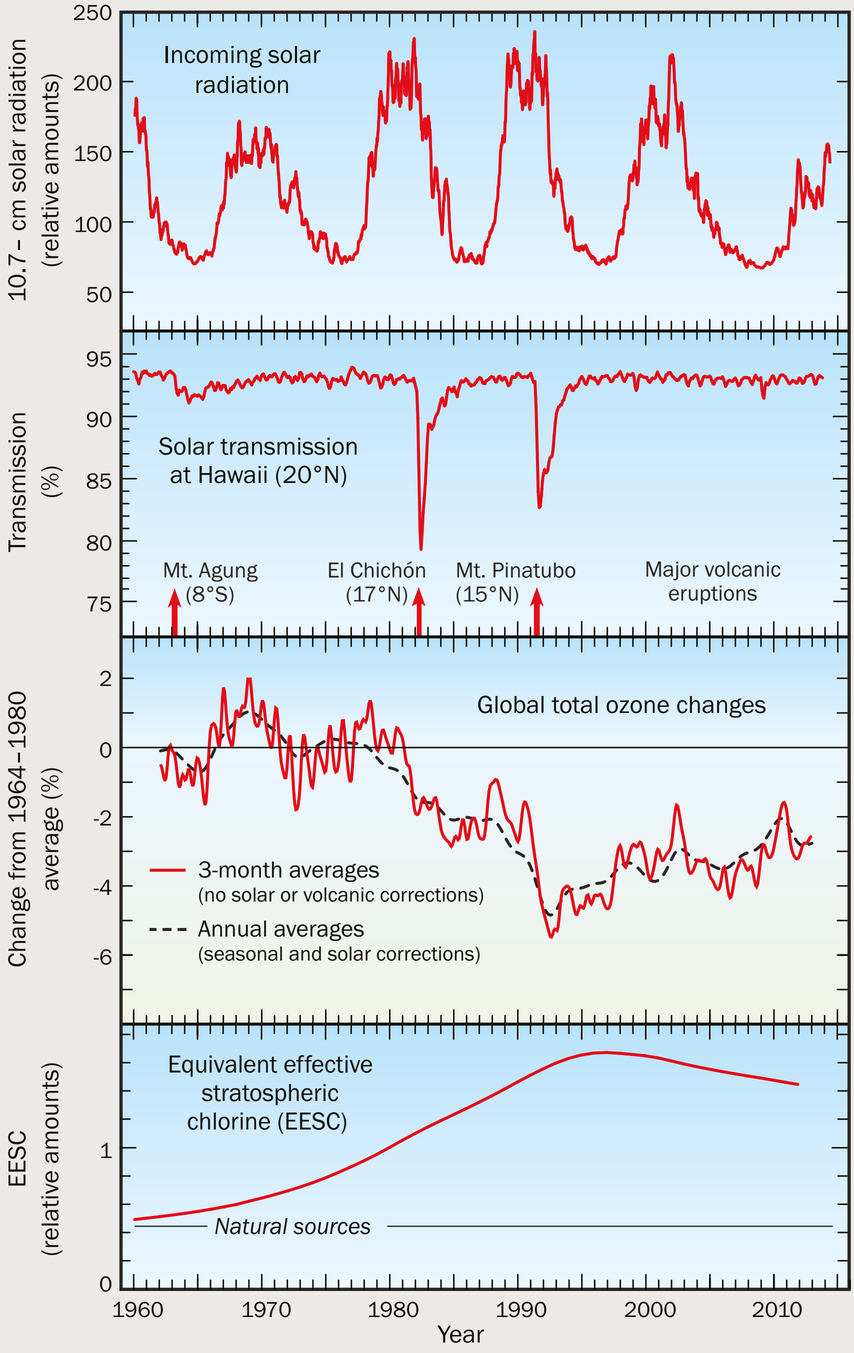


Figure Q14-1. Solar changes and volcanoes.
Global total ozone values have decreased beginning in the early 1980s. Ozone values shown are the 3-month averages without corrections for solar or volcanic effects and annual averages corrected for seasonal and solar effects (from Figure Q13-1). These long-term ozone decreases are primarily attributable to equivalent effective stratospheric chlorine (EESC), which has increased over the same time period. Since the mid-1990s, changes in both quantities have slowed and reversed sign. Incoming solar radiation varies on a well-recognized 11-year cycle related to sunspot activity. The amount of incoming solar radiation at a wavelength of 10.7 cm is often used as a surrogate for incoming solar radiation at UV wavelengths that produce stratospheric ozone. The 10.7-cm radiation values clearly show the recent periods of solar maximum and minimum. A comparison of the solar radiation and ozone changes strongly indicates that the cyclic changes in solar output alone cannot account for the long-term decrease in total ozone. Following large volcanic eruptions, transmission of solar radiation to Earth's surface is reduced by the large number of new sulfur-containing particles formed in the stratosphere. The three large volcanic eruptions that occurred between 1960 and 2010 temporarily decreased solar transmission as measured in Hawaii. Volcanic particles increase ozone depletion only for a few years before they are removed from the stratosphere by natural processes. As a consequence, the two most recent volcanic eruptions cannot be the cause of the continuous long-term decrease found in global total ozone.

Q15

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

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

Montreal Protocol. In 1985, a treaty called the *Vienna Convention for the Protection of the Ozone Layer* was signed by 20 nations in Vienna. The signing nations agreed to take appropriate measures to protect the ozone layer from human activities. The Vienna Convention was a framework agreement that supported research, exchange of information, and future protocols. In response to growing concern, the *Montreal Protocol on Substances that Deplete the Ozone Layer* was signed in 1987 and, following sufficient country ratification, entered into force in 1989. The Protocol has been successful in establishing legally binding controls for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion. Halogen source gases containing chlorine and bromine controlled under the Montreal Protocol are referred to as ozone-depleting substances (ODSs). National consumption of an ODS is defined as the amount that production and imports of the substance exceed its export to other nations. The Protocol provisions are structured for developed countries to act first and for developing countries to follow with some financial assistance. In 2009, the Montreal Protocol became the first international treaty to achieve universal ratification by all 196 United Nations members.

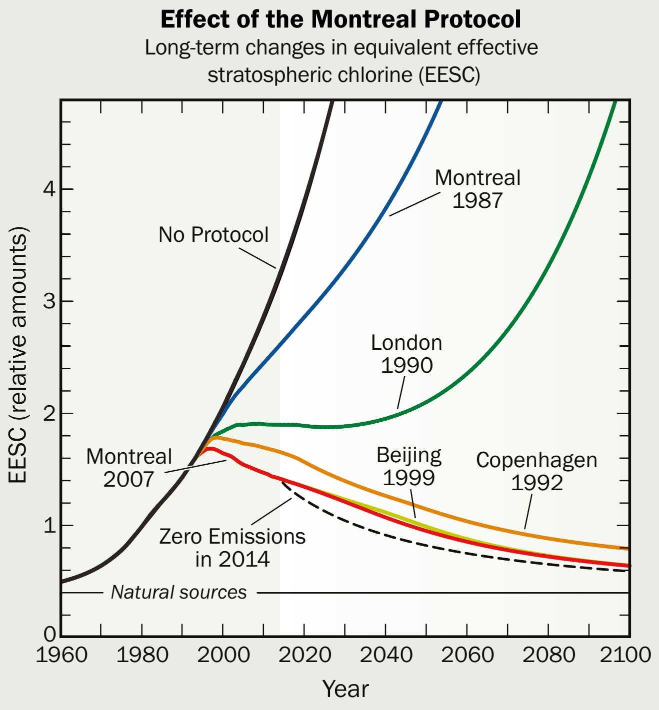


Figure Q15-1. Effect of the Montreal Protocol. The objective of the Montreal Protocol is the protection of the ozone layer through control of the global production and consumption of ODSs. Projections of the future abundances of ODSs expressed as equivalent effective stratospheric chlorine (EESC) values (see Q16) are shown separately for the midlatitude stratosphere for (1) no Protocol provisions, (2) the provisions of the original 1987 Montreal Protocol and some of its subsequent Amendments and adjustments, and (3) zero emissions of ODSs starting in 2014. The city names and years indicate where and when changes to the original 1987 Protocol provisions were agreed upon (see Figure Q0-1). EESC is a relative measure of the potential for stratospheric ozone depletion that combines the contributions of chlorine and bromine from ODS surface observations (see Q16). Without the Protocol, EESC values are projected to have increased significantly in the 21st century. Only with the Copenhagen (1992) and subsequent Amendments and adjustments did projected EESC values show a long-term decrease.

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 have put additional ODSs under control, accelerated the timing of existing control measures, and prescribed phase-out dates for the production and consumption of certain gases. The initial Protocol called for a 50% reduction in chlorofluorocarbon (CFC) production and a freeze on halon production. The 1990 London Amendment called for a phase-out of the production and consumption of the most damaging ODSs in developed nations by 2000 and in developing nations by 2010. The 1992 Copenhagen Amendment accelerated the phase-out date to 1996 in developed nations. Further controls on ODSs were agreed upon in later meetings in Vienna (1995), Montreal (1997, 2007), and Beijing (1999).

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

- **No Protocol.** Without the Montreal Protocol the production, use, and emissions of CFCs and other ozone-depleting substances is expected to have increased after 1987 with an annual growth rate of about 3% (business-as-usual scenario). As a result, EESC is projected to have increased nearly 10-fold by the mid-2050s compared with the 1980 value. Computer models of the atmosphere indicate that such high EESC values would have at least doubled global total ozone depletion between 1990 and 2010 and increased it far beyond that by midcentury. As a result, harmful UV-B radiation would have increased substantially at Earth's surface, causing damage to ecosystem health and a global rise in skin cancer and cataract cases (see Q17).
- **Montreal Protocol provisions.** International compliance with only the 1987 provisions of the Montreal Protocol and the later 1990 London Amendment would have substantially slowed the projected growth of EESC. Not until the 1992 Copenhagen Amendments and adjustments did the Protocol projections show a decrease in future EESC values. The provisions became more stringent with the Amendments and adjustments adopted in Beijing in 1999 and Montreal in 1997 and 2007. Now, with full compliance to the Protocol, most ODSs will be almost completely phased out, with some exemptions for critical uses (see Q16). Global EESC is slowly decaying from its peak value in the late 1990s and is expected to reach 1980 values in the mid-21st century. The success of the Montreal Protocol to date is demonstrated by the decline in ODP-weighted emissions of ODSs shown in Figure Q0-1. Total emissions peaked in 1987 at values about 10-fold higher than natural emissions. Between 1987 and 2014, ODS emissions from human activities have decreased by almost 80%.

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

  The zero-emissions case demonstrates the EESC values that would occur if it were possible to set all ODS emissions to zero beginning in 2014. This would eliminate the contributions from new production and bank emissions. Significant differences from the Montreal 2007 projections are evident in the first decades following 2014 because the phase-out of all ODS production under the Protocol is not yet complete and bank emissions are substantial. Zero emissions would bring forward the return of EESC to 1980 levels by about 13 years.

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

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

HFC substitute gases. Hydrofluorocarbons (HFCs) are used as substitute compounds for CFCs, HCFCs, and other ODSs. HFCs contain hydrogen, fluorine, and carbon. HFCs do not contribute to ozone depletion because they contain no chlorine, bromine, or iodine. As a consequence, HFCs are not ODSs and are not subject to the provisions of the Montreal Protocol. HFCs and all ODSs are radiatively active gases that contribute to human-induced climate change based on their accumulation in the atmosphere (see Q18). HFCs are included in the basket of gases controlled by the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC). The Kyoto Protocol is an international treaty designed to protect climate by controlling emissions of carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), HFCs, perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6). HFC emissions are expected to grow substantially in coming decades as the demand for their use as substitute gases and in new applications increases in developed and developing countries. The climate change contribution from future HFC emissions would be minimized if HFCs with very low Global Warming Potentials (GWPs) (less than 100) were chosen to meet the growing demand (see Q18 and Q19).

Q16

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 more than a decade. 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 HCFCs, will begin to decrease in the coming decades if compliance with the Protocol continues. However, it is only after midcentury that the effective abundance of ODSs is expected to fall to values that were present before the Antarctic ozone hole was first observed in the early 1980s.

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. Under the Protocol, the production and consumption of individual ODSs are now controlled in all 196 nations that are Parties to the Protocol (see Q15). 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) long-term changes 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 two factors: (1) how rapidly an ODS is used and released to the atmosphere after being produced and (2) the lifetime for the removal of the ODS from the atmosphere (see Table Q7-1). For example, the abundances of ODSs with short lifetimes respond quickly to emission reductions. Long-term changes in ODS abundances are constructed from (1) estimates of historical emissions and bank quantities using industry reports, (2) abundances measured in air trapped for years in accumulated snow (firn) in polar regions, (3) observed atmospheric abundances using ground-based measurements, and (4) projections of future abundances based on compliance with Montreal Protocol provisions and patterns of use in developed and developing countries. The results for individual ODSs and the natural chlorine and bromine source gases, methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), are shown in Figure Q16-1 and described as follows:

- **CFCs.** Chlorofluorocarbons (CFCs) include some of the most destructive chlorine-containing ODSs. CFC-11 and CFC-12, each with an Ozone Depletion Potential (ODP) near 1, are the most abundant ODSs in the atmosphere owing to large historical emissions and long atmospheric lifetimes (50–100 years). Production and consumption of CFCs in developed countries ended in 1996 and that in developing countries ended by January 2010. As a consequence, CFC-11 and CFC-113 abundances have peaked in the atmosphere and have been declining for more than a decade. In contrast, CFC-12 abundances have only recently shown a decrease, owing to its longer lifetime (100 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 allowed except for limited exempted uses and with some continuing emissions from banks, CFC abundances are projected to decline steadily throughout this century.

Q16

Past and Projected Atmospheric Abundances of Halogen Source Gases

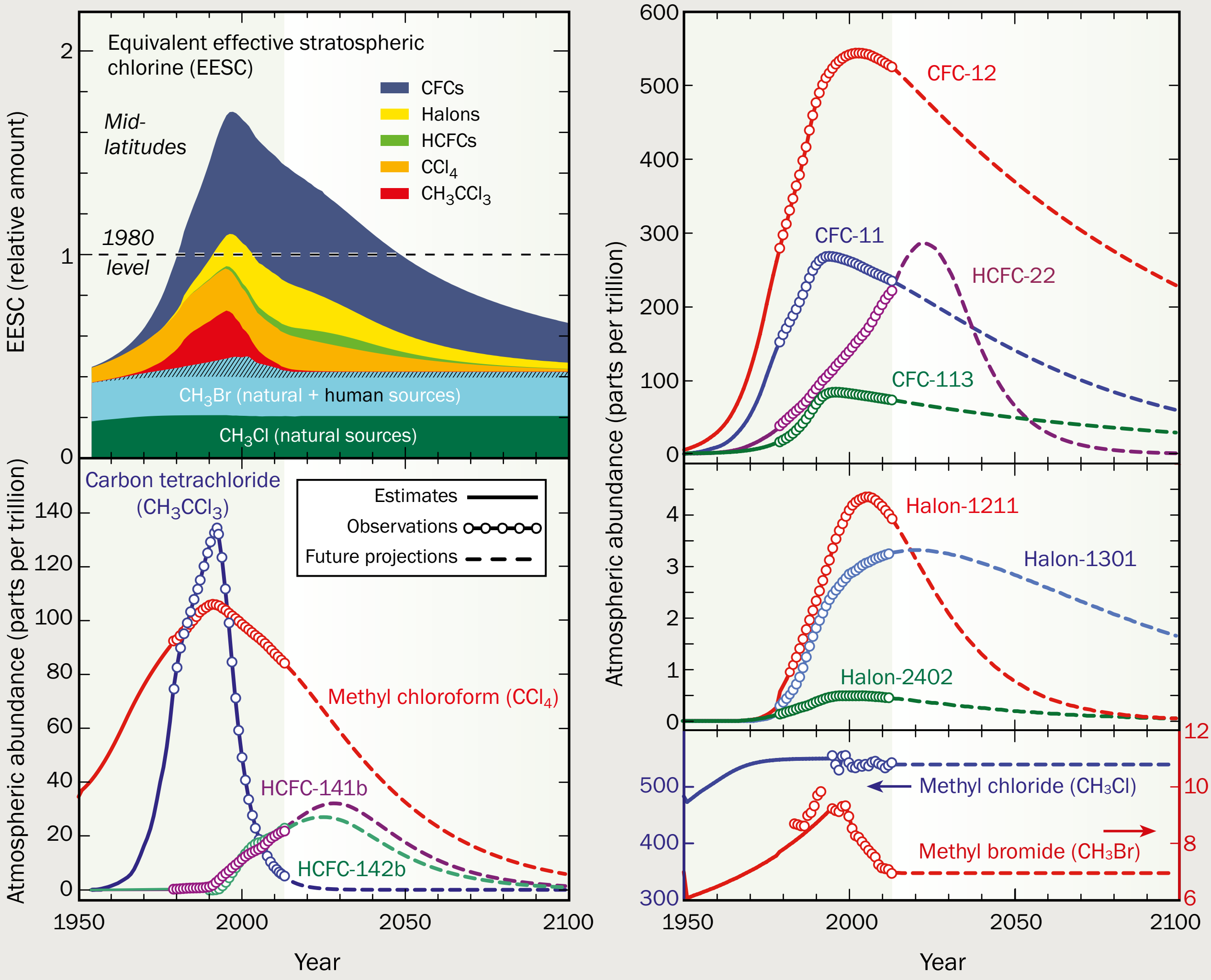


Figure Q16-1. Halogen source gas changes.
The atmospheric abundances of individual ozone-depleting substances (ODSs) at Earth's surface were obtained using a combination of direct atmospheric measurements, estimates of historical abundance, and future projections of abundance. The gases shown are all ODSs except for methyl chloride. The past increases of CFCs, along with those of carbon tetrachloride, methyl chloroform, and halon-1211, have slowed and reversed in the last two decades. HCFCs, which are used as transitional substances to replace CFCs, will likely continue to increase in the coming decades before a complete phase-out. Halon-1301 abundances will also likely continue to grow in the next decade while current halon banks are depleted. Future decreases in methyl bromide are expected to be small. Abundances of methyl chloride, which is not controlled under the Montreal Protocol and has large natural sources, are projected to be constant in the future. The very short-lived gases are not included here.
The rise in equivalent effective stratospheric chlorine (EESC) values in the 20th century has slowed and reversed in the last decade (top left panel). EESC is a measure of the potential for ozone depletion in the stratosphere derived from surface measurements of chlorine and bromine gases (see Q16). EESC values are reduced as ODS emissions decrease. EESC, as shown here for the stratosphere at midlatitudes, returns to 1980 values around 2050. In polar regions, the return to 1980 values occurs more than two decades later. International compliance with the Montreal Protocol provisions will ensure that EESC values will continue to decrease as projected (see Q15). (The unit "parts per trillion" is defined in the caption of Figure Q7-1.)

- **Halons.** Halons are the most destructive bromine-containing ODSs. The most abundant in the atmosphere, halon-1211 and halon-1301, have abundances about 100 times less than CFC-11 and CFC-12 and account for a significant fraction of bromine from all ODSs (see Figure Q7-1). Production and consumption of halons in developed countries ended in 1994 and that in developing countries ended by January 2010. Atmospheric abundances of halon-1211 show significant decreases since peak concentrations were measured in the early 2000s. Halon-2402 abundances have been decreasing slowly for a few years while those of halon-1301 continue to increase. The increase is likely due to substantial banks in fire-extinguishing and other equipment that gradually release halon-1301 to the atmosphere. The abundance of halon-1301 is expected to remain high well into the 21^{st} century because of its long lifetime (65 years) and continued release.
- **Methyl chloroform.** The largest reduction to date in the abundance of an ODS (96% from its peak value) has been observed for methyl chloroform. Production and consumption of methyl chloroform in developed countries ended in January 1996 and that in developing countries is scheduled to end by January 2015. Atmospheric abundances responded rapidly to the reduced emissions starting in the mid-1990s because methyl chloroform has a short atmospheric lifetime (about 5 years). Methyl chloroform is used mainly as a solvent and has no significant long-term storage following production. It will approach complete removal from the atmosphere after the phase-out in developing countries is complete.
- **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 abundances of HCFC-22, HCFC-141b, and HCFC-142b continue to grow in the atmosphere in response to greater application demand. HCFCs pose a lesser threat to the ozone layer than CFCs because they have low ODP values (less than 0.12). The most recent adjustment to the Montreal Protocol (Montreal 2007) accelerated the phase-out of HCFCs by a decade for both developed countries (2020) and developing countries (2030) (see Q15). Even with the accelerated phase-out, future projections show HCFC abundances that continue to increase, reach peak values around 2030, and steadily decrease thereafter. The response of atmospheric abundances to decreasing emissions will be relatively rapid because of the short atmospheric lifetimes of HCFCs (less than 20 years).
- **Carbon tetrachloride.** Carbon tetrachloride has been phased out in both developed countries (January 1996) and developing countries (January 2010). As a result, atmospheric abundances of carbon tetrachloride have been decreasing for two decades. The decline is somewhat less rapid than expected, suggesting that actual emissions are larger than reported or the atmospheric lifetime is greater than current estimates. Production of carbon tetrachloride for use as raw material (feedstock) to make other chemicals is exempted under the Protocol because emission to the atmosphere from this use is believed to be minimal.
- **Methyl chloride and methyl bromide.** Both methyl chloride and methyl bromide are distinct among halogen source gases because substantial fractions of their emissions are associated with natural processes (see Q7). Methyl chloride is not an ODS under the Montreal Protocol because it is not manufactured or used in appreciable quantities. Its abundance in the atmosphere has remained fairly constant throughout the last 60 years and will remain constant if the balance of total sources and loss processes remains unchanged. Methyl bromide is controlled under the Protocol because it is manufactured for use as a fumigant. Developed country production and consumption of methyl bromide ended in January 2005 and that in developing countries is scheduled to end by January 2015. The Protocol

currently provides exemptions for some methyl bromide production and use as an agricultural and pre-shipment fumigant. Atmospheric abundances of methyl bromide responded rapidly to the reduced emissions starting in 1999 because its atmospheric removal lifetime is less than 1 year. Future projections show only small changes in methyl bromide abundances based on the assumptions of unchanged contributions from natural sources and small use in developing countries. An important uncertainty in these projections is the future amounts that will be produced and emitted under Montreal Protocol use 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 (EESC), which was introduced in Figures Q14-1 and Q15-1. 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. All gases used in the calculation are shown in Figure Q7-1. For both past and future EESC values, the required atmospheric abundances are derived from measurements, historical estimates, or future projections based on compliance with Montreal Protocol provisions.

EESC is expressed as a hypothetical amount of chlorine 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. The term *effective* indicates that only the estimated fraction of ODSs that are currently in the form of reactive halogen gases in the stratosphere is included in an EESC value (see Q8). Although chlorine is much more abundant in the stratosphere than bromine (about 150-fold) (see Figure Q7-1), bromine atoms are about 60 times more effective than chlorine atoms in chemically destroying ozone in the lower stratosphere. EESC values generally depend on the year and latitude region in the stratosphere being considered.

Another quantitative measure of the potential for ozone depletion in the stratosphere that is highly related to EESC is *effective stratospheric chlorine* (ESC). ESC, as defined in Q20, is calculated with chemistry-climate models rather than inferred from tropospheric ODS observations.

Long-term changes in EESC. In the latter half of the 20th century up until the 1990s, EESC values steadily increased (see Figure Q16-1), causing global ozone depletion. As a result of the Montreal Protocol regulations, the long-term increase in EESC slowed, values reached a peak, and EESC began to decrease in the late 1990s. By 2012, EESC at midlatitudes had declined by about 15% from its peak value in 1997. The initial decrease came primarily from the substantial, rapid reductions in emissions of methyl chloroform, which has a lifetime of only 5 years. The decrease is continuing with declining emissions of CFCs and other long-lived ODSs. Decreasing EESC means that the potential for stratospheric ozone depletion is now lessening each year as a result of the Montreal Protocol. Decreases in EESC are projected to continue throughout the 21st century if all nations continue to comply with the provisions of the Protocol. The decrease will continue because as emissions are reduced, natural processes continue to gradually remove halogen-containing gases from the global atmosphere. 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.