Q7

What are the reactive halogen gases that destroy stratospheric ozone?

Chlorine and bromine containing halogen source gases that enter the stratosphere arise from both human activities and natural processes (Q6). When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to other gases that also contain chlorine and bromine. Some of the gases act as chemical reservoirs, which can then be converted into ClO and BrO, the two most important reactive gases that participate in catalytic reactions that destroy ozone.

Halogen-containing gases present in the stratosphere can be divided into two groups: ***halogen source gases*** as well as ***reactive and reservoir halogen gases*** (see **Figure Q7-1**). The source gases, which include ozone-depleting substances (ODSs), are emitted at Earth's surface by natural processes and by human activities (see Q6) and are chemically inert in the lower atmosphere. Once in the stratosphere, the halogen source gases chemically convert at different rates to form the reactive and reservoir halogen gases. The conversion occurs in the stratosphere instead of the troposphere because solar ultraviolet (UV) radiation (a component of sunlight) is needed for the breakup of these compounds, and solar UV radiation is more intense in the stratosphere than the troposphere (see Q2). Reactive gases containing the halogens chlorine and bromine participate in a series of chemical reactions that remove stratospheric ozone (see Q8).

Reactive and reservoir halogen gases. The chemical conversion of halogen source gases, which involves solar ultraviolet radiation and other chemical reactions, produces a number of reactive and reservoir halogen gases. These reactive and reservoir gases contain all of the chlorine and bromine atoms originally present in the source gases. The chlorine content of all of the reactive and reservoir gases is termed ***available chlorine***, while the bromine content of similar gases is termed ***available bromine***.

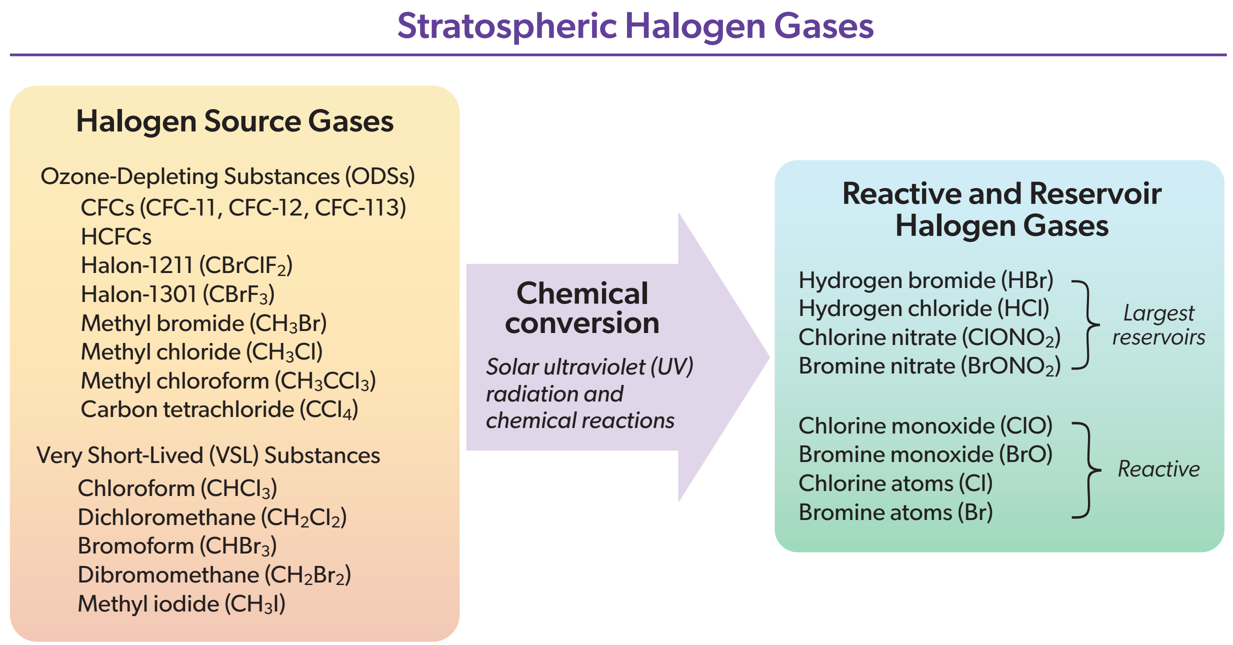


Figure Q7-1. Conversion of halogen source gases. Halogen source gases containing chlorine and bromine are chemically converted to reactive and reservoir halogen gases, primarily in the stratosphere. The conversion requires solar ultraviolet radiation and a few chemical reactions. The very short-lived substances undergo partial loss in the troposphere, so a smaller fraction of these gases reach the stratosphere compared to the other source gases. The gases produced by this chemical conversion can be grouped into the reservoir gases, which do not directly destroy ozone, and the reactive gases, which participate in ozone destruction cycles (see Q8). A principal reactive gas, ClO, is formed from the reservoir gases HCl and $ClONO_2$ by reactions that occur on the surfaces of liquid and solid polar stratospheric clouds (PSCs) (see Q9).

The most important reactive and reservoir chlorine and bromine containing gases that form in the stratosphere are shown in Figure Q7-1. Throughout the stratosphere, the most abundant are typically hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$). These two gases are considered ***reservoir*** gases because, while they do not react directly with ozone, they can be converted to the most reactive forms that do chemically destroy ozone. The halogens most reactive with ozone are chlorine monoxide (ClO) and bromine monoxide (BrO) molecules, as well as chlorine and bromine (Cl and Br) atoms. A large fraction of available bromine is generally in the form of BrO, whereas usually only a small fraction of available chlorine is in the form of ClO. The unusually cold conditions that occur in the polar regions during winter cause the reservoir gases HCl and $ClONO_2$ to undergo nearly complete conversion to ClO and related reactive gases. This conversion occurs through chemical reactions that take place on the surface or within polar stratospheric cloud (PSC) particles (see Q9).

Chlorine at midlatitudes. Reactive and reservoir chlorine gases have been observed extensively in the stratosphere using both local and remote measurement techniques, including observations from satellite instruments. The measurements from space displayed in **Figure Q7-2** are representative of how the amounts of chlorine-containing gases change between the surface and the upper stratosphere at middle to high latitudes. Total chlorine (see red line in Figure Q7-2) is the sum of chlorine contained in halogen source gases (e.g., CFC-11, CFC-12) and in the reservoir and reactive gases (e.g., HCl, $ClONO_2$, and ClO). Total chlorine is constant to within about 10% from the surface to above 50 km (31 miles) altitude. In the troposphere, total chlorine is contained almost entirely in the source gases described in Figure Q6-1. At higher altitudes, the source gases become a smaller fraction of total chlorine as they are converted to the reactive and reservoir chlorine gases. At the highest altitudes, total chlorine is all in the form of reactive and reservoir chlorine gases.

In the altitude range of the ozone layer at midlatitudes, as shown in Figure Q7-2, the reservoir gases HCl and $ClONO_2$ account for most of the available chlorine. The abundance of ClO, the most important reactive gas in ozone depletion, is a small fraction of total chlorine. The abundance of ClO peaks in the upper stratosphere about 40 km (24.9 miles) above the surface. In this region of the atmosphere the abundance of ozone reached a minimum in the late 1990s, at about the time the abundance of ClO in the upper stratosphere maximized. In the lower and middle stratosphere (altitudes below about 30 km, or 18.6 miles above the surface), the low abundance of ClO tends to limit the amount of ozone destruction that occurs outside of polar regions.

Chlorine in polar regions. Chlorine gases in polar regions undergo large changes between autumn and late winter. Meteorological and chemical conditions in both polar regions are now routinely observed from space in all seasons. Maps of autumn and late winter conditions at an altitude of 18 km (11.2 miles), near the center of the ozone layer (see Figure Q11-3) over the Antarctic are contrasted in **Figure Q7-3**. These observations document dramatic differences in chemistry and temperature for these two seasons.

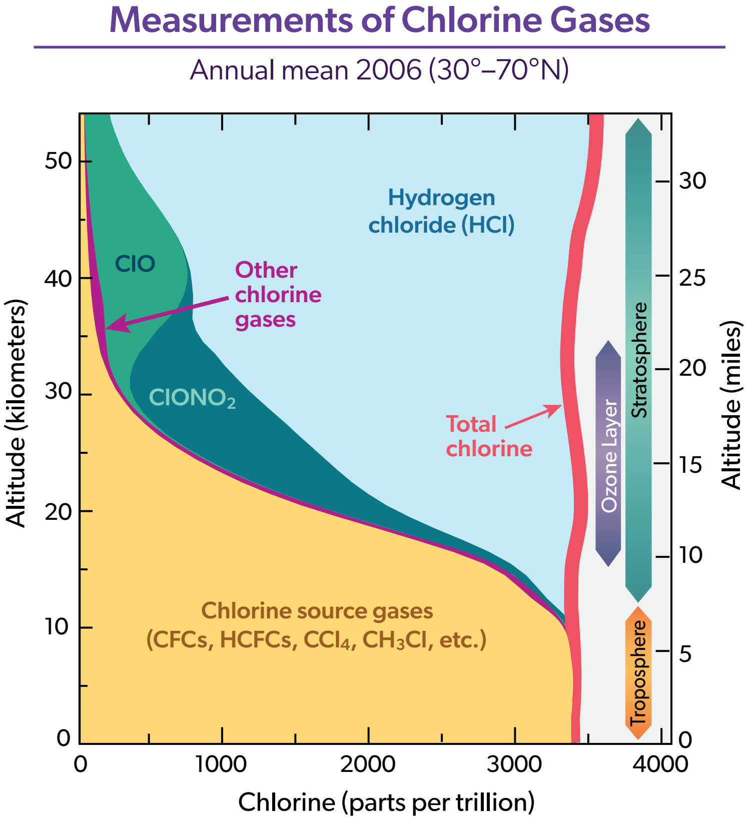


Figure Q7-2. Chlorine gas observations. The abundances of chlorine source gases as well as reactive and reservoir chlorine gases as measured in 2006, averaged over 30° to 70°N latitude, are displayed as a function of altitude. In the troposphere (below about 12 km), all of the measured chlorine is contained in the source gases. In the stratosphere, the total chlorine content of reactive and reservoir gases (termed available chlorine) increases with altitude as the amount of chlorine source gases declines. This transition is a consequence of chemical reactions initiated by solar ultraviolet radiation that convert source gases to available chlorine (see Figure Q7-1). The principal reactive and reservoir chlorine gases formed are HCl, $ClONO_2$, and ClO. Adding up the source gases with available chlorine gives "Total chlorine", which is nearly constant with altitude throughout the atmosphere. In the midlatitude ozone layer (15–35 km), chlorine source gases are still present and HCl and $ClONO_2$ constitute the most abundant forms of available chlorine.

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

Ozone values are high over the entire Antarctic continent during autumn in the Southern Hemisphere. Temperatures are mid-range, HCl and nitric acid (HNO_3) are high, and ClO is very low. High HCl indicates that substantial conversion of halogen source gases to this reservoir gas has occurred in the stratosphere. In the 1980s and early 1990s, the abundances of the reservoir gases HCl and $ClONO_2$ increased substantially in the stratosphere following increased emissions of halogen source gases. HNO_3 is an abundant, primarily naturally-occurring stratospheric compound that plays a major role in stratospheric ozone chemistry by both moderating ozone destruction and condensing to form polar stratospheric clouds (PSCs), thereby enabling conversion of chlorine reservoirs gases to ozone-destroying forms (see Q9). The low abundance of ClO indicates that little conversion of the reservoir to reactive gases occurs in autumn, thereby limiting chemical ozone destruction.

By late winter (September), a remarkable change in the composition of the Antarctic stratosphere has taken place. Low amounts of ozone reflect substantial depletion at 18 km altitude over an area larger than the Antarctic continent. Antarctic ozone holes arise from similar chemical destruction throughout much of the altitude range of the ozone layer (see altitude profile in Figure Q11-3). The meteorological and chemical conditions in late winter, characterized by very low temperatures, very low HCl and HNO_3, and very high ClO, are distinctly different from those found in autumn. Low stratospheric temperatures occur during winter, when solar heating is reduced. Low HCl and high ClO reflect the conversion of the halogen reservoir compounds, HCl and $ClONO_2$, to the most important reactive form of chlorine, ClO. This conversion occurs selectively in winter on PSCs, which form at very low temperatures (see Q9). Low HNO_3 is indicative of its condensation to form these PSCs, some of which subsequently fall to lower altitudes through gravitational settling. High abundances of ClO generally cause ozone depletion to continue in the Antarctic region until mid-October (spring), when the lowest ozone values usually are observed (see Q10). As temperatures rise at the end of the winter, PSC formation is halted, ClO is converted back into the reservoir species HCl and $ClONO_2$ (see Q9), and ozone destruction is curtailed.

Similar changes in meteorological and chemical conditions are also observed between autumn and late winter for some years in the Arctic, leading to substantial ozone loss. In spring of 2020, Arctic ozone reached exceptionally low values. A very stable, cold, and long-lived stratospheric Arctic vortex enabled halogen-catalyzed chemical ozone loss that exceeded the previous record-breaking loss observed in spring 2011 (see Q11). Substantial chemical loss of Arctic ozone will continue to occur in cold winters/springs, as long as the concentrations of ODSs are well above natural levels.

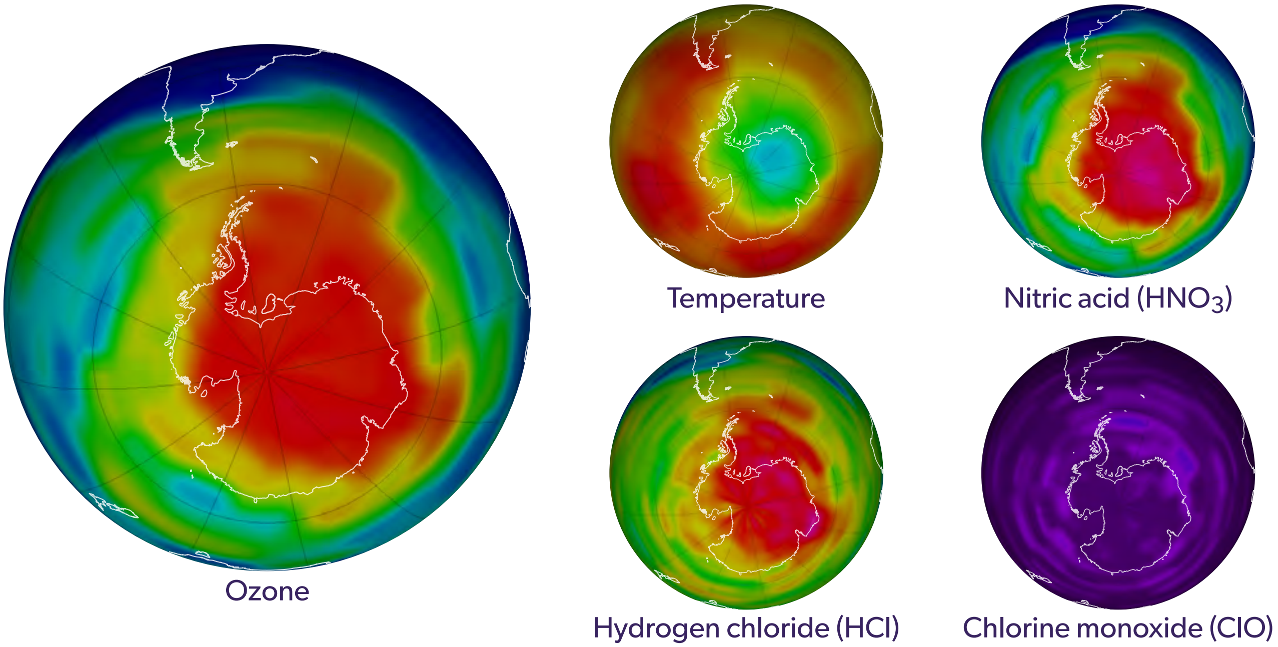
Bromine observations. Fewer measurements are available for reactive and reservoir bromine gases in the lower stratosphere than for chlorine gases. This difference arises in part because of the lower abundance of bromine, which makes quantification of its atmospheric abundance more challenging. The most widely observed bromine gas is BrO, which can be observed from space. Estimates of the concentration of available bromine in the stratosphere are higher than expected from the decomposition of halons and methyl bromide, the most important bromine source gases that are produced by human activities. This difference was the first direct evidence that very short-lived (VSL) bromine-containing source gases reach the stratosphere. Subsequently, direct observations of VSL source gases have confirmed their importance. In 2020, slightly more than one-quarter of the total stratospheric bromine is supplied by these naturally occurring, VSL source gases (see Q6).

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

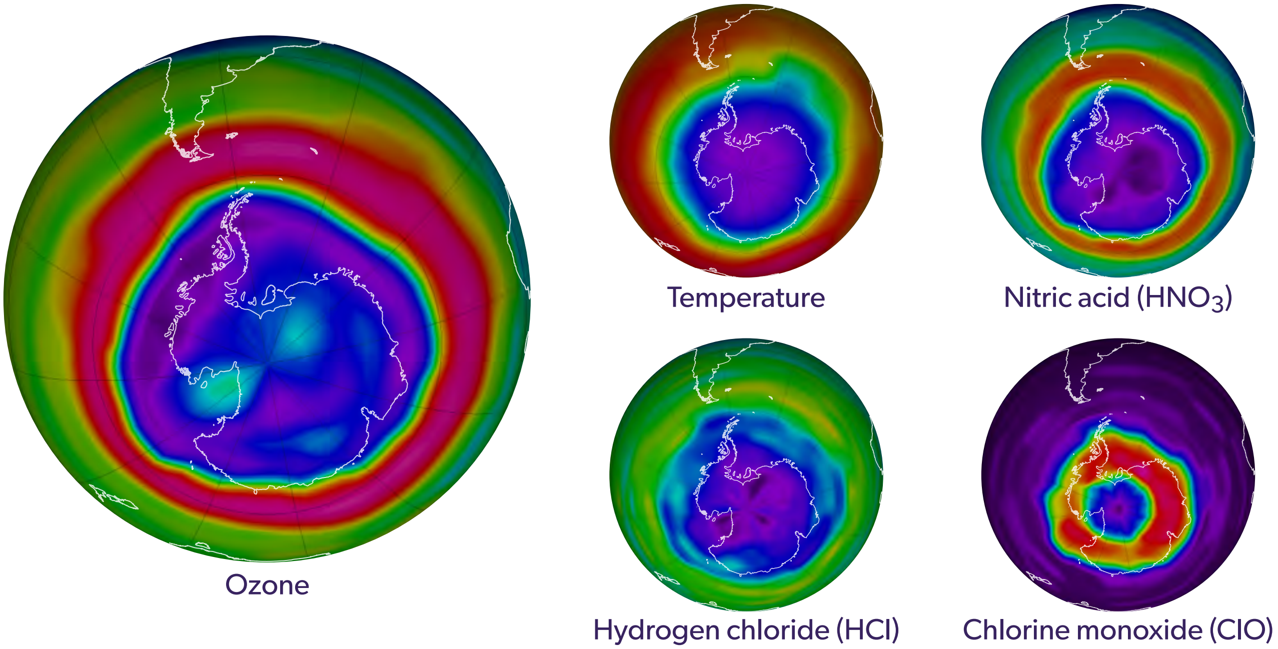
(The unit "parts per billion," abbreviated "ppb," is used here as a measure of the relative abundance of a substance in dry air: 1 part per billion equals the presence of one molecule of a gas per billion ($=10^9$) total air molecules (compare to ppt in Figure Q6-1).)

Chemical Conditions Observed in the Ozone Layer Over Antarctica

Normal ozone amounts in autumn (1 May 2021) at 18 km altitude



Large ozone depletion in late winter (15 September 2021) at 18 km altitude



Temperatures and chemical abundances

Low — High

Low		High
750	Ozone	3600 ppb
−95°	Temperature	−50° C
0.0	HNO_3	12.0 ppb
0.0	HCl	2.2 ppb
0.0	ClO	2.2 ppb