

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.

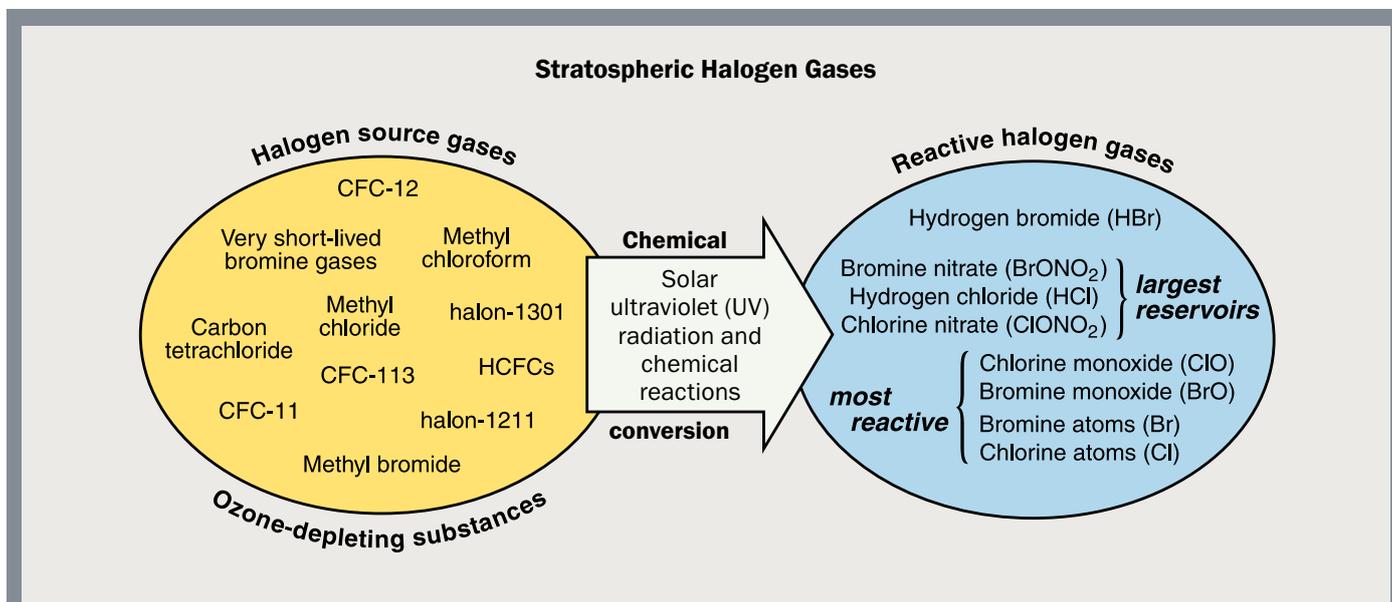


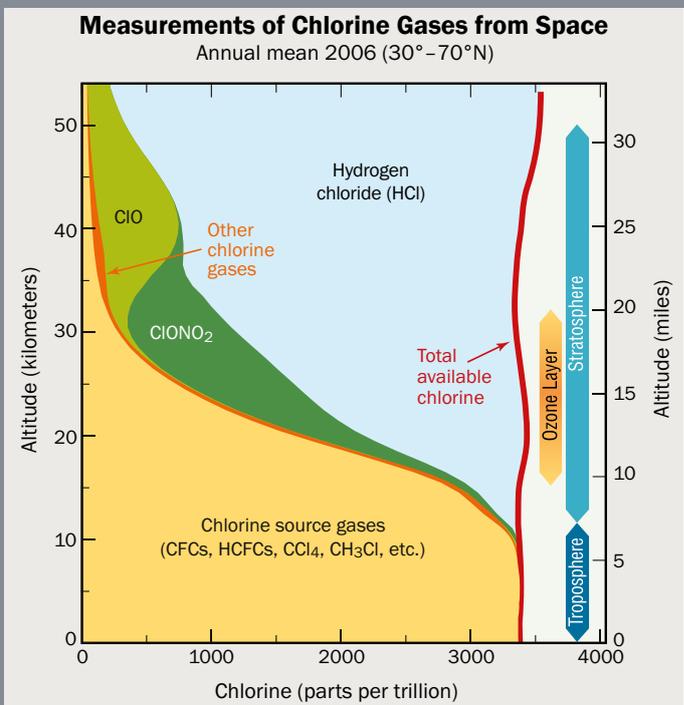
Figure Q8-1. Conversion of halogen source gases.

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 ClONO₂ that occur on the surfaces of liquid and solid polar stratospheric clouds (PSCs) (see Q10).

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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, ClONO₂, 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 ClONO₂ 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 (ClONO₂). These two gases are considered important *reservoir* gases because, while they don't react directly with ozone, they can be converted to the *most reactive* forms that 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 ClONO₂ 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, ClONO₂, 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 ClONO₂ 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

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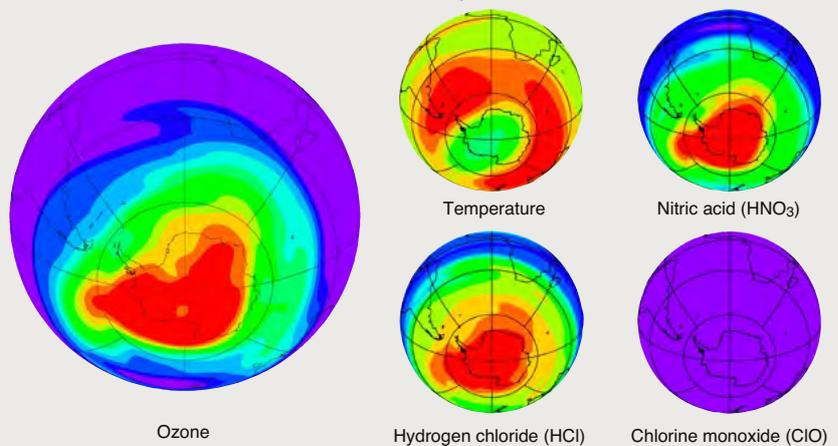
reactive chlorine gases directly into the troposphere and stratosphere. The quantities emitted by the Space Shuttle were small in comparison with halogen emissions from other human activities.

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).)

Chemical Conditions Observed in the Ozone Layer Over Antarctica

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



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

