Q8: What are the reactive halogen gases that destroy stratospheric ozone?

Emissions from human activities and natural processes are large sources of chlorine- and bromine-containing gases for the stratosphere. When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to more reactive gases also containing chlorine and bromine. Important examples of the reactive gases that destroy stratospheric ozone are chlorine monoxide (ClO) and bromine monoxide (BrO). These and other reactive gases participate in "catalytic" reaction cycles that efficiently destroy ozone. Volcanoes can emit some chlorine-containing gases, but these gases are ones that readily dissolve in rainwater and ice and are usually "washed out" of the atmosphere before they can reach the stratosphere.

Reactive gases containing the halogens chlorine and bromine lead to the chemical destruction of stratospheric ozone. Halogen-containing gases present in the stratosphere can be divided into two groups: *halogen source gases* and *reactive halogen gases*. The source gases are emitted at Earth's surface by natural processes and by human activities (see *Q7*). Once they reach the stratosphere, the halogen source gases chemically convert to form the reactive halogen gases.

Reactive halogen gases. The chemical conversion of halogen source gases, which involves ultraviolet sunlight and other chemical reactions, produces a number of reactive halogen gases. These reactive gases contain all of the chlorine and bromine atoms originally present in the source gases.

The most important reactive chlorine- and bromine-containing gases that form in the stratosphere are shown in ***Figure Q8-1***. Away from polar regions, the most abundant are hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$). These two gases are considered *reservoir* gases because they do not react directly with ozone but 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 stratospheric bromine is generally in the form of BrO whereas usually only a small fraction of stratospheric chlorine is in the form of ClO. In polar regions, the reservoirs $ClONO_2$ and HCl undergo a further conversion on polar stratospheric clouds (see *Q10*) to form ClO. In that case, ClO becomes a large fraction of available reactive chlorine.

Reactive chlorine observations. Reactive chlorine gases have been observed extensively in the stratosphere with both direct and remote measurement techniques. The measurements from space at middle latitudes displayed in ***Figure Q8-2*** are representative of how chlorine-containing gases change between the surface and the upper stratosphere. Available chlorine (see red line in ***Figure Q8-2***) is the sum of chlorine contained in halogen source gases and

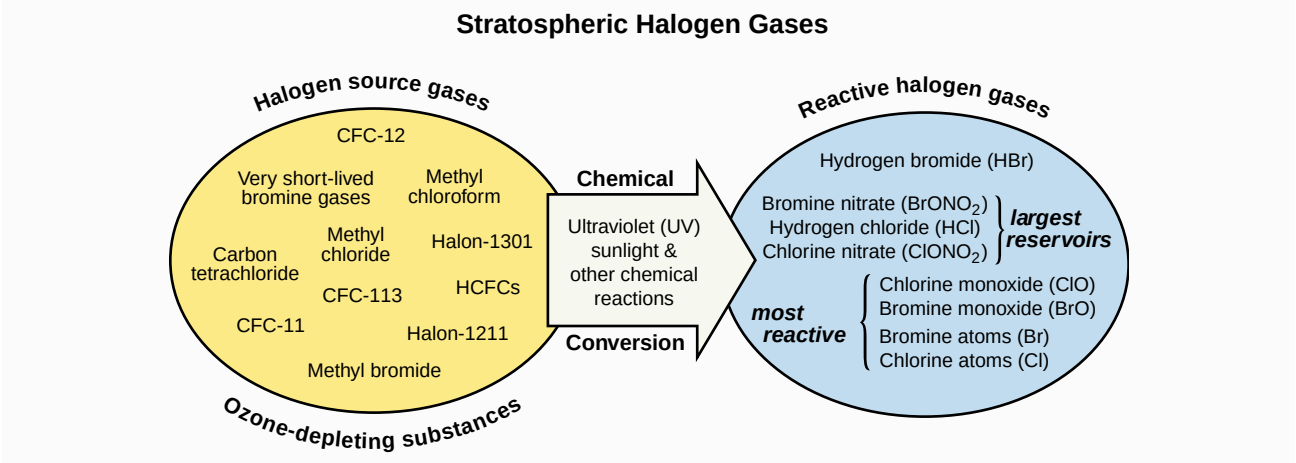

Figure Q8-1. Conversion of halogen source gases. Halogen source gases (also known as ozone-depleting substances) are chemically converted to reactive halogen gases primarily in the stratosphere. The conversion requires ultraviolet sunlight and a few other chemical reactions. The short-lived gases undergo some conversion in the troposphere. The reactive halogen gases contain all the chlorine and bromine originally present in the source gases. Some reactive gases serve as reservoirs of chlorine and bromine whereas others participate in ozone destruction cycles.

the reactive gases HCl, $ClONO_2$, ClO, and other minor gases. Available chlorine is constant within a few percent from the surface to 47 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 reactive chlorine gases. At the highest altitudes, available chlorine is all in the form of reactive chlorine gases.

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

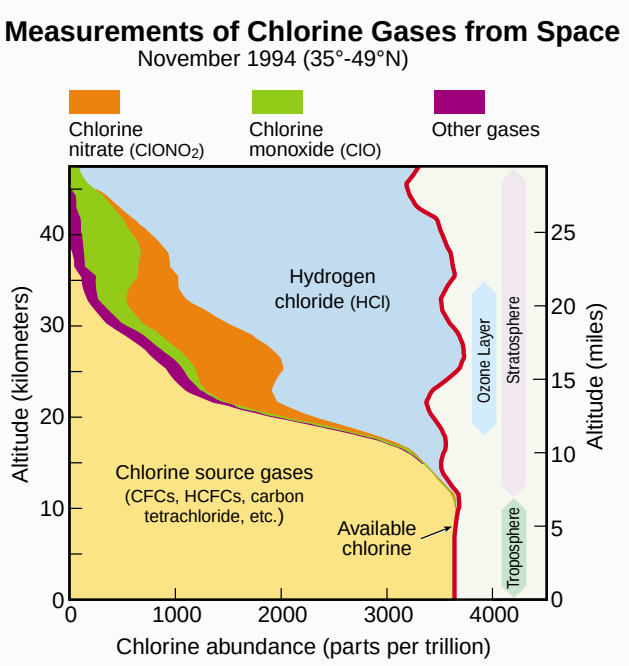

Figure Q8-2. Reactive chlorine gas observations. Reactive chlorine gases and chlorine source gases can be measured from space. These abundance measurements made over midlatitudes, for example, show that chlorine-containing source gases are present in the troposphere and that reactive chlorine gases are present in the stratosphere. In the stratosphere, reactive chlorine gases increase with altitude and chlorine source gases decrease with altitude. This results because the source gases are converted to reactive gases in chemical reactions involving ultraviolet sunlight. The principal reactive gases formed are HCl, $ClONO_2$, and ClO. The sum of reactive gases and source gases gives available chlorine, which is nearly constant with altitude up to 47 km. In the ozone layer, 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 chlorine in polar regions. Reactive chlorine gases in polar regions in summer look similar to the altitude profiles shown in ***Figure Q8-2***. In winter, however, the presence of polar stratospheric clouds (PSCs) causes further chemical changes (see *Q10*). PSCs convert HCl and $ClONO_2$ to ClO when temperatures are near minimum values in the winter Arctic and Antarctic stratosphere. In that case, ClO becomes the principal reactive chlorine species in sunlit regions and ozone loss becomes very rapid. An example of the late-winter ClO and ozone distributions is shown in ***Figure Q8-3*** for the Antarctic stratosphere. These space-based measurements show that ClO abundances are high in the lower stratosphere over a region that exceeds the size of the Antarctic continent (greater than 13 million square kilometers or 5 million square miles). The peak abundance of ClO exceeds 1500 parts per trillion, which is much larger than typical midlatitude values shown in ***Figure Q8-2*** and represents a large fraction of reactive chlorine in that altitude region. Because high ClO amounts cause rapid ozone loss (see *Q9*), ozone depletion is found in regions of elevated ClO (see ***Figure Q8-3***).

Reactive bromine observations. Fewer measurements are available for reactive bromine gases than for reactive chlorine, in part because of the low abundance of bromine in the stratosphere. The most widely observed bromine gas is bromine monoxide (BrO). The measured abundances are consistent with values expected from the conversion of the bromine-containing source gases such as the halons and methyl bromide.

Other sources. Some reactive halogen gases are also produced at Earth's surface by natural processes and by human activities. However, because reactive halogen gases are soluble in water, almost all become trapped in the lower atmosphere by dissolving in rainwater and ice, and ultimately are returned to Earth's surface before they can reach the stratosphere. For example, reactive chlorine is present in the atmosphere as sea salt (sodium chloride) produced by evaporation of ocean spray. Because sea salt dissolves in water, this chlorine is removed and does not reach the stratosphere in appreciable quantities. Another ground-level source is emission of chlorine gases from swimming pools, household bleach, and other uses. When released to the atmosphere, this chlorine is rapidly converted to forms that are soluble in water and removed. The Space Shuttle and other rocket motors release reactive chlorine gases directly in the stratosphere. In that case the quantities are very small in comparison with other stratospheric sources.

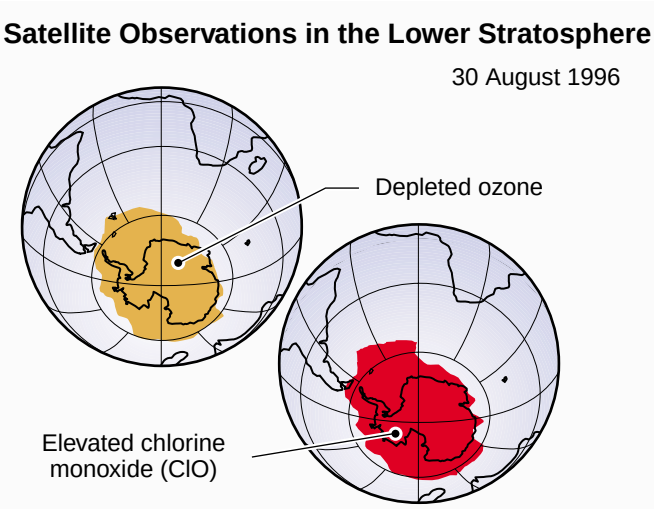

Figure Q8-3. Antarctic chlorine monoxide and ozone. Satellite instruments monitor ozone and reactive chlorine gases in the global stratosphere. Results are shown here for Antarctic winter for a narrow altitude region within the ozone layer. In winter, chlorine monoxide (ClO) reaches high values (1500 parts per trillion) in the ozone layer, much higher than observed anywhere else in the stratosphere because ClO is produced by reactions on polar stratospheric clouds. These high ClO values in the lower stratosphere last for 1 to 2 months, cover an area that at times exceeds that of the Antarctic continent, and efficiently destroy ozone in sunlit regions. Ozone values measured simultaneously within the ozone layer show very depleted values.

Volcanoes. Volcanic plumes generally contain large quantities of chlorine in the form of hydrogen chloride (HCl). Because the plumes also contain a considerable amount of water vapor, the HCl is efficiently scavenged by rainwater and ice and removed from the atmosphere. As a result, most of the HCl in the plume does not enter the stratosphere. After large recent eruptions, the increase in HCl in the stratosphere has been small compared with the total amount of chlorine in the stratosphere from other sources.

Global Ozone Dobson Network

The first instrument for routine monitoring of total ozone was developed by Gordon M. B. Dobson in the 1920s. The instrument measures the intensity of sunlight at two ultraviolet wavelengths: one that is strongly absorbed by ozone and one that is weakly absorbed. The difference in light intensity at the two wavelengths is used to provide a measurement of total ozone above the instrument location.

A global network of ground-based, total ozone observing stations was established in 1957 as part of the International Geophysical Year. Today, there are about 100 sites distributed throughout the world (from South Pole, Antarctica (90°S) to Ellesmere Island, Canada (83°N)), many of which routinely measure total ozone with Dobson instruments. The accuracy of these observations is maintained by regular calibrations and intercomparisons. Data from the network have been essential for understanding the effects of chlorofluorocarbons (CFCs) and other ozone-depleting gases on the global ozone layer, starting before the launch of space-based ozone-measuring instruments and continuing to the present day. Because of their stability and accuracy, the Dobson instruments are now routinely used to help calibrate space-based observations of total ozone.

Pioneering scientists have traditionally been honored by having units of measure named after them. Accordingly, the unit of measure for total ozone is called the “Dobson unit” (see *Q4*).