Q5 How do emissions of halogen source gases lead to stratospheric ozone depletion?

The initial step in the depletion of stratospheric ozone by human activities is the emission, at Earth's surface, of gases that contain chlorine and bromine and have long atmospheric lifetimes. Most of these gases accumulate in the lower atmosphere because they are relatively unreactive and do not dissolve readily in rain or snow. Natural air motions eventually 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 stratospheric large-scale circulation patterns return this air to the lower atmosphere, these reactive chlorine and bromine gases are removed from Earth's atmosphere by rain and snow.

The principal steps in stratospheric ozone depletion caused by human activities are shown in **Figure Q5-1**.

Emission, accumulation, and transport. The process begins with the ***emission***, at Earth's surface, of long-lived source gases containing the halogens chlorine and bromine (see Q6). The halogen source gases, often referred to as ozone-depleting substances (ODSs), include manufactured chemicals released to the atmosphere when used in a variety of applications, such as refrigeration, air conditioning, and foam blowing. Chlorofluorocarbons (CFCs) are an important example of chlorine-containing source gases. Emitted source gases ***accumulate*** in the lower atmosphere (troposphere) and are slowly ***transported*** to the stratosphere by natural air motions. The accumulation occurs because most source gases are highly unreactive in the lower atmosphere. Furthermore, only a small amount of halogen source gases dissolve in ocean waters. The low reactivity of these manufactured halogenated gases within the lower atmosphere is one property that made them well suited for specialized applications such as refrigeration.

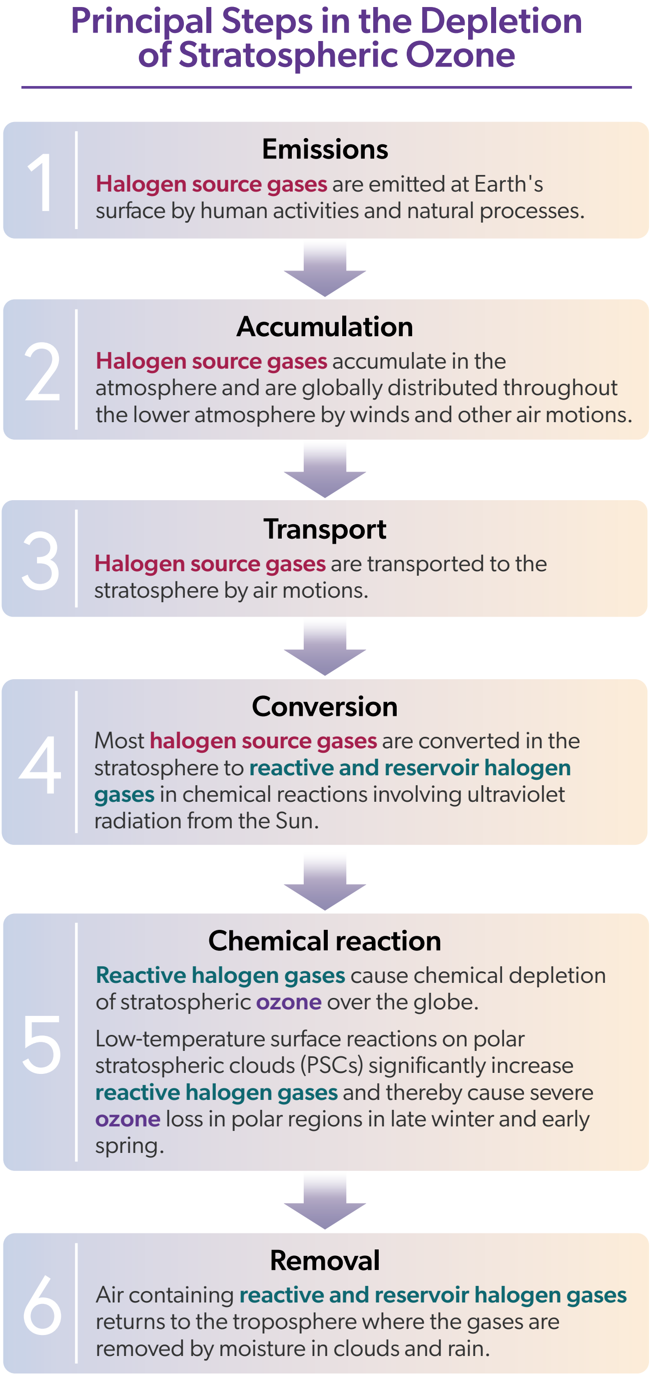
Some halogen gases are emitted in substantial quantities from natural sources (see Q6). These emissions also accumulate in the troposphere, are transported to the stratosphere, and participate in ozone destruction reactions. These naturally emitted gases are part of the natural balance of ozone production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

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

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

Air in the stratosphere is generally isolated from the troposphere. A small portion of stratospheric air returns to the troposphere every day, bringing along reactive and reservoir halogen gases. On average, it takes several years for air throughout the global stratosphere to return to the troposphere. Reactive halogen gases that are transported back to the troposphere are ***removed*** from the atmosphere by rain and other precipitation or deposited by wind onto Earth's land or ocean surfaces. These removal processes bring 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 and reservoir halogen gases. Source gas molecules that are not converted are transported to the stratosphere. Only small portions of reactive and reservoir 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, prior to transport to the stratosphere, are the hydrochlorofluorocarbons (HCFCs), methyl bromide (CH_3Br), methyl chloride (CH_3Cl), and gases containing iodine (see Q6).



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 and reservoir 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 and reservoir halogen gases** returns to the troposphere where the gases are removed by moisture in clouds and rain.

Figure Q5-1. Principal steps in stratospheric ozone depletion. The stratospheric ozone depletion process begins with the emission of halogen source gases by human activities and natural processes. These compounds have at least one carbon and one halogen atom, causing them to be chemically stable and leading to common use of the term halocarbon, an abbreviation for halogen and carbon. Many halocarbon gases emitted by human activities are also ozone-depleting substances (ODSs); all ODSs contain at least one chlorine or bromine atom (see Q7). Most of these compounds undergo little or no chemical loss within the troposphere, the lowest region of the atmosphere, and accumulate until transported to the stratosphere. Subsequent steps are the conversion of ODSs to reactive and reservoir halogen gases and chemical reactions that remove ozone (see Q8). Ozone depletion by halogen gases occurs throughout the globe (see Q12), with the largest losses occurring in the polar regions during late winter and early spring (see Q9 to Q11). Ozone depletion ends when reactive and reservoir 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 investigated in *laboratory studies*. Chemical reactions between two gases follow well-defined physical rules. Some of these reactions occur on the surfaces of polar stratospheric clouds formed in the winter stratosphere. Reactions have been studied that involve many different molecules containing chlorine, bromine, fluorine, and iodine and other atmospheric constituents such as carbon, oxygen, nitrogen, and hydrogen. These studies have shown that several reactions involving chlorine and bromine directly or indirectly destroy ozone in the stratosphere.

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

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