

Q7: What emissions from human activities lead to ozone depletion?

Certain industrial processes and consumer products result in the atmospheric emission of “halogen source gases.” These gases contain chlorine and bromine atoms, which are known to be harmful to the ozone layer. For example, the chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), once used in almost all refrigeration and air conditioning systems, eventually reach the stratosphere where they are broken apart to release ozone-depleting chlorine atoms. Other examples of human-produced ozone-depleting gases are the “halons,” which are used in fire extinguishers and which contain ozone-depleting bromine atoms. The production and consumption of all principal halogen source gases by human activities are regulated worldwide under the Montreal Protocol.

Human-produced chlorine and bromine gases. Human activities cause the emission of *halogen source gases* that contain chlorine and bromine atoms. These emissions into the atmosphere ultimately lead to stratospheric ozone depletion. The source gases that contain only

carbon, chlorine, and fluorine are called “chlorofluorocarbons,” usually abbreviated as CFCs. CFCs, along with carbon tetrachloride (CCl₄) and methyl chloroform (CH₃CCl₃), are the most important chlorine-containing gases that are emitted by human activities and destroy stratospheric ozone

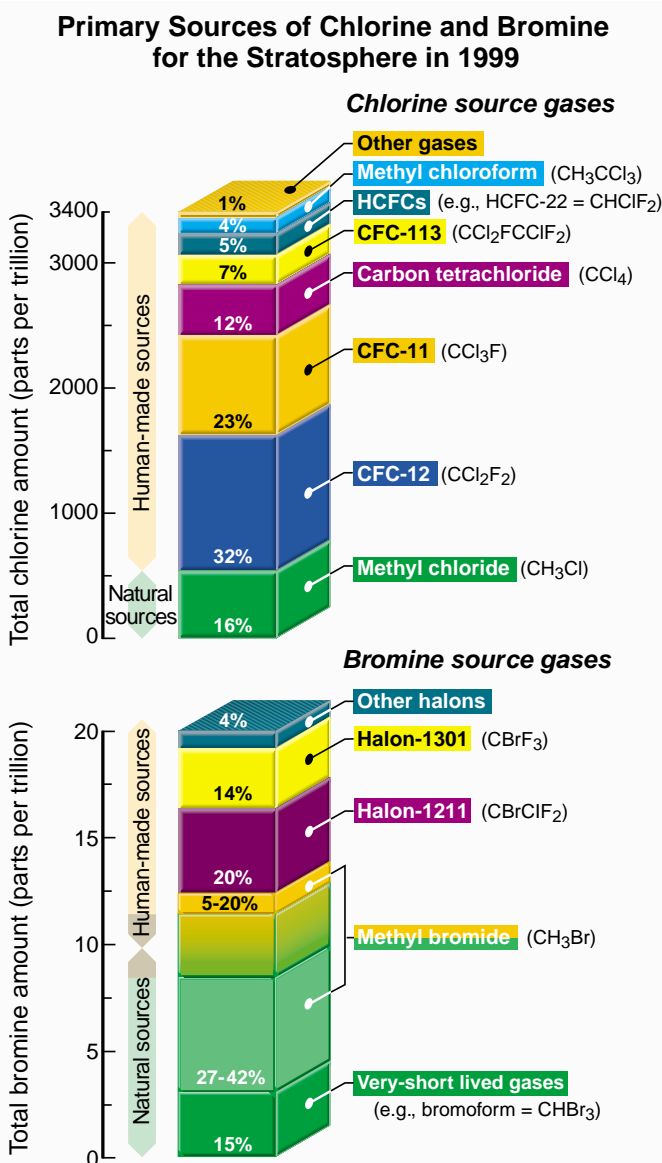


Figure Q7-1. Stratospheric source gases. A variety of gases transport chlorine and bromine into the stratosphere. These gases, called halogen source gases, are emitted from natural sources and human activities. For chlorine, human activities account for most that reaches the stratosphere. The CFCs are the most abundant of the chlorine-containing gases released in human activities. Methyl chloride is the most important natural source of chlorine. For bromine that reaches the stratosphere, halons and methyl bromide are the largest sources. Both gases are released in human activities. Methyl bromide has an additional natural source. Natural sources are a larger fraction of the total for bromine than for chlorine. HCFCs, which are substitute gases for CFCs and also are regulated under the Montreal Protocol, are a small but growing fraction of chlorine-containing gases. The abundance scale shows that the amount of chlorine in the stratosphere is greater than that of bromine by about 170 times. (The unit “parts per trillion” is a measure of the relative abundance of a gas: 1 part per trillion indicates the presence of one molecule of a gas per trillion other molecules.)

Table Q7-1. Atmospheric lifetimes, emissions, and Ozone Depletion Potentials of halogen source gases. ^a

Halogen Source Gas	Lifetime (years)	Global Emissions in 2000 (gigagrams per year) ^b	Ozone Depletion Potential (ODP)
Chlorine			
CFC-12	100	130-160	1
CFC-113	85	10-25	1
CFC-11	45	70-110	1
Carbon tetrachloride	26	70-90	0.73
HCFCs	1-26	340-370	0.02-0.12
Methyl chloroform	5	~20	0.12
Methyl chloride	1.3	3000-4000	0.02
Bromine			
Halon-1301	65	~3	12
Halon-1211	16	~10	6
Methyl bromide	0.7	160-200	0.38
Very short-lived gases	Less than 1	^c	^c

^a Includes both human activities and natural sources.

^b 1 gigagram = 10⁹ grams = 1000 metric tons.

^c No reliable estimate available.

(see *Figure Q7-1*). Chlorine-containing gases have been used in many applications including refrigeration, air conditioning, foam blowing, aerosol propellants, and cleaning of metals and electronic components. These activities have typically caused the emission of halogen-containing gases to the atmosphere.

Another category of halogen source gases contains bromine. The most important of these are the “halons” and methyl bromide (CH₃Br). Halons are halogenated hydrocarbon gases originally developed to extinguish fires. Halons are widely used to protect large computers, military hardware, and commercial aircraft engines. Because of these uses, halons are often directly released into the atmosphere. Halon-1211 and Halon-1301 are the most abundant halons emitted by human activities (see *Figure Q7-1*). Methyl bromide, used primarily as an agricultural fumigant, is also a significant source of bromine to the atmosphere.

Human emissions of chlorine- and bromine-containing gases have increased substantially since the middle of the 20th century (see *Q16*). The result has been global ozone depletion with the greatest losses occurring in polar regions (see *Q11* to *Q13*).

Natural sources of chlorine and bromine. There are two halogen source gases present in the stratosphere that have large natural sources. These are methyl chloride (CH₃Cl) and methyl bromide (CH₃Br), both of which are emitted by oceanic and terrestrial ecosystems. Natural sources of these two gases contribute about 16% of the chlorine currently in the stratosphere, and about 27-42% of the bromine (see *Figure Q7-1*). Very short-lived gases containing bromine, such as bromoform (CHBr₃), are also released to the atmosphere by the oceans. The estimated contribution of these gases to stratospheric bromine (about 15%) is uncertain at this time. Changes in the natural sources of chlorine and bromine since the middle of the 20th century are not the cause of observed ozone depletion.

Lifetimes and emissions. After emission, halogen source gases are either removed from the atmosphere or undergo chemical conversion. 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*). Gases with the shortest lifetimes (e.g., the HCFCs, methyl bromide, methyl chloride, and the very short-lived gases) are significantly destroyed in the troposphere, and therefore only a fraction of the emitted gas contributes to ozone depletion in the stratosphere.

The amount of a halogen source gas present in the atmosphere depends on the lifetime of the gas and the amount emitted to the atmosphere. Emissions vary greatly for the principal source gases, as indicated in *Table Q7-1*. Emissions of most gases regulated by the Montreal Protocol have decreased since 1990, and emissions from all regulated gases are expected to decrease in the coming decades (see *Q16*).

Ozone Depletion Potential. The halogen source gases in *Figure Q7-1* are also known as “ozone-depleting substances” because they are converted in the stratosphere to reactive gases containing chlorine and bromine (see *Q8*). Some of these reactive gases participate in reactions that destroy ozone (see *Q9*). Ozone-depleting substances are compared in their effectiveness to destroy stratospheric ozone using the “Ozone Depletion Potential” (ODP), as listed in *Table Q7-1*. A gas with a larger ODP has a greater potential to destroy ozone over its lifetime in the atmosphere. The ODP is calculated on a “per mass” basis for each gas relative to CFC-11, which has an ODP defined to be 1. Halon-1211 and Halon-1301 have ODPs significantly larger than CFC-11 and most other emitted gases. This results because bromine is much more effective overall (about 45 times) on a per-atom basis than chlorine in chemical reactions that destroy ozone in the stratosphere. The gases with small

TWENTY QUESTIONS

ODP values generally have short atmospheric lifetimes. The production and consumption of all principal halogen source gases by humans are regulated under the provisions of the Montreal Protocol (see *Q15*).

Fluorine and iodine. Fluorine and iodine are also halogen atoms. Most of the source gases in *Figure Q7-1* also contain fluorine atoms 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 destroy ozone. Iodine is a component of several gases that are naturally emitted from the oceans. Although iodine will participate in ozone destruction reactions, these iodine-containing

gases are largely removed in the troposphere by natural processes before the gases can reach the stratosphere.

Other gases. Other gases that influence stratospheric ozone abundances also have increased in the stratosphere as a result of human activities. Important examples are methane (CH₄) and nitrous oxide (N₂O), which react to form water vapor and reactive hydrogen and nitrogen oxides, respectively, in the stratosphere. These reactive products also participate in the production and loss balance of stratospheric ozone (see *Q2*). The overall affect of these other gases on ozone is much smaller than that caused by increases in chlorine- and bromine-containing gases from human activities.

Heavier-Than-Air CFCs

CFCs and other halogen source gases reach the stratosphere despite the fact they are “heavier than air.” All the principal source gases are emitted and accumulate in the lower atmosphere (troposphere). Air containing the emitted halogen gases is in continual motion as a result of winds and convection. Air motions ensure that the source gases are horizontally and vertically well mixed throughout the troposphere in a matter of months. It is this well-mixed air that enters the lower stratosphere from upward air motions in tropical regions, bringing with it source gas molecules emitted from a wide variety of locations on Earth’s surface.

Atmospheric measurements confirm that halogen source gases with long atmospheric lifetimes are well mixed in the troposphere and are present in the stratosphere (see *Figure Q8-2*). The amounts found in these regions are consistent with the emissions estimates reported by industry and government. Measurements also show that gases that are “lighter than air,” such as hydrogen (H₂) and methane (CH₄), are also well mixed in the troposphere, as expected. Only at altitudes well above the troposphere and stratosphere (above 85 kilometers (53 miles)), where much less air is present, do heavy gases begin to separate from lighter gases as a result of gravity.