

Q6

What emissions from human activities lead to ozone depletion?

Certain industrial processes and consumer products result in the emission of ozone-depleting substances (ODSs) to the atmosphere. ODSs are manufactured halogen source gases that are controlled worldwide by the Montreal Protocol. These gases bring chlorine and bromine atoms to the stratosphere, where they destroy ozone in chemical reactions. Important examples are the chlorofluorocarbons (CFCs), once used in almost all refrigeration and air conditioning systems, and the halons, which were used as fire extinguishing agents. Current ODS abundances in the atmosphere are known directly from air sample measurements.

Halogen source gases versus ozone-depleting substances (ODSs). Those halogen source gases emitted by human activities and controlled by the Montreal Protocol are referred to as ODSs within the Montreal Protocol, by the media, and in the scientific literature. The Montreal Protocol controls the global production and consumption of ODSs (see Q14). Halogen source gases such as methyl chloride (CH_3Cl) that have predominantly natural sources are not classified as ODSs. The contributions of ODSs and natural halogen source gases to the total amount of chlorine and bromine entering the stratosphere, which peaked in 1993 and 1998, respectively, are shown in **Figure Q6-1**. The difference in the timing of the peaks is a result of different phaseout schedules specified by the Montreal Protocol, atmospheric lifetimes, and the time delays between production and emissions of the various source gases. Also shown are the contributions to total chlorine and bromine in 2016, highlighting the reductions of 10% and 11%, respectively, achieved under the controls of the Montreal Protocol.

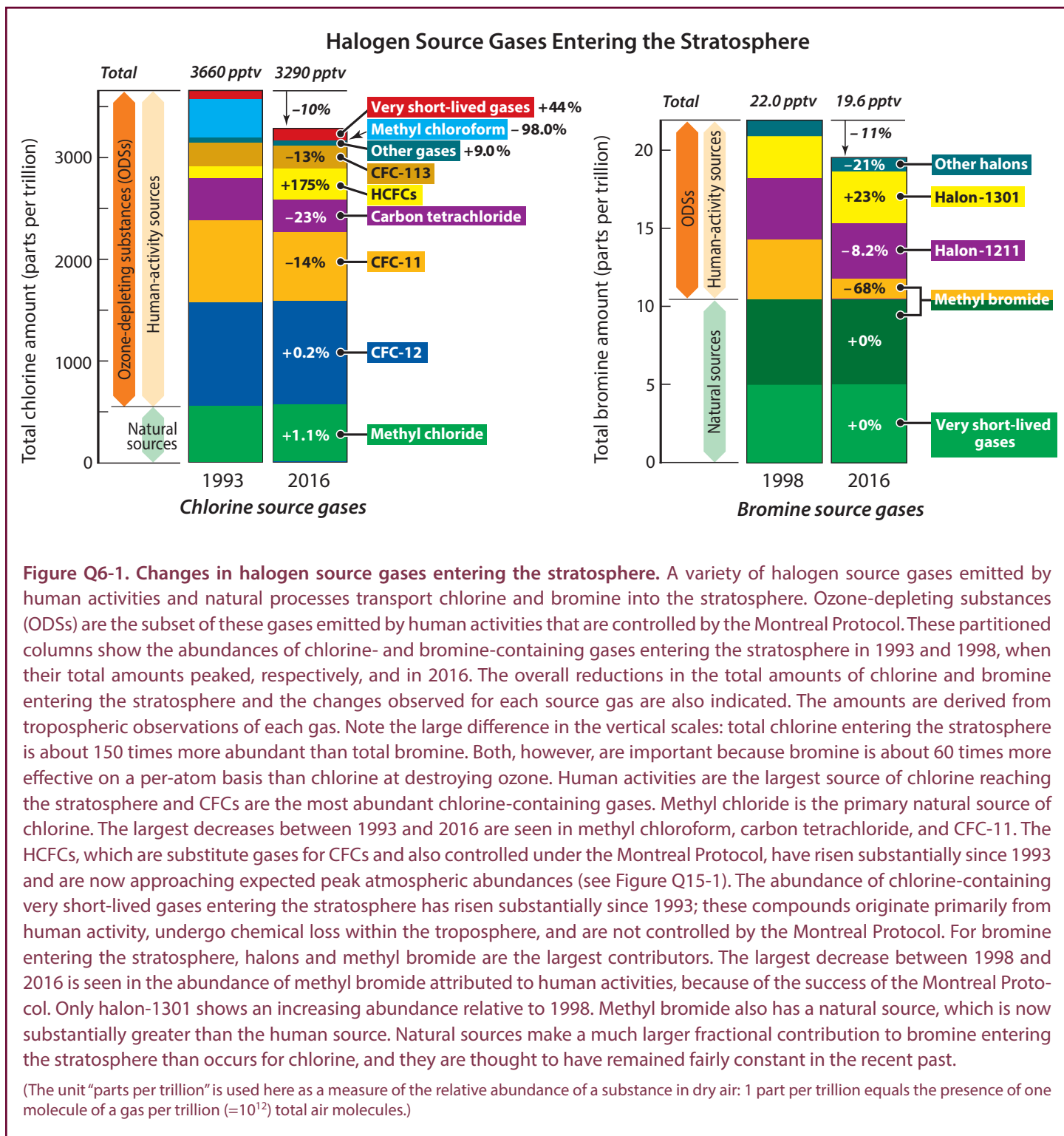
Ozone-depleting substances (ODSs). ODSs are manufactured for specific industrial uses or consumer products, most of which result in the eventual emission of these gases to the atmosphere. Total ODS emissions increased substantially from the middle to the late 20th century, reached a peak in the late 1980s, and are now in decline (see Figure Q0-1). A large fraction of the emitted ODSs reach the stratosphere, where they are converted to reactive gases containing chlorine and bromine that lead to ozone depletion.

ODSs containing only carbon, chlorine, and fluorine are called *chlorofluorocarbons*, usually abbreviated as CFCs. The principal CFCs are CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and CFC-113 ($\text{CCl}_2\text{FCClF}_2$). CFCs, along with carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3), historically have been the most important chlorine-containing halogen source gases emitted by human activities. These and other chlorine-containing ODSs have been used in many applications, including refrigeration, air

conditioning, foam blowing, spray can propellants, and cleaning of metals and electronic components. As a result of the Montreal Protocol controls, the abundances of most of these chlorine source gases have decreased since 1993 (see Figure Q6-1). The concentrations of CFC-11 and CFC-12 peaked in 1994 and 2002, respectively, and have since decreased (see Figure Q15-1). The abundance of CFC-11 in 2016 was 14% lower than its peak value, while that of CFC-12 in 2016 was 5% lower than its peak (see Figure Q15-1). As substitute gases for CFCs, the atmospheric abundances of hydrochlorofluorocarbons (HCFCs) increased substantially between 1993 and 2016 (+175%). With restrictions on global production in place since 2013, the atmospheric abundances of HCFCs are expected to peak between 2020 and 2030.

Another category of ODSs contains bromine. The most important of these gases are the halons and methyl bromide (CH_3Br). Halons are a group of industrial compounds that contain at least one bromine and one carbon atom; halons may or may not contain a chlorine atom. Halons were originally developed to extinguish fires and were widely used to protect large computer installations, military hardware, and commercial aircraft engines. As a consequence, upon use halons are released directly into the atmosphere. Halon-1211 and halon-1301 are the most abundant halons emitted by human activities.

Methyl bromide is used primarily as a fumigant for pest control in agriculture and disinfection of export shipping goods, and also has significant natural sources. As a result of the Montreal Protocol, the contribution to the atmospheric abundance of methyl bromide from human activities has substantially decreased between 1998 and 2016 (–68%; see Figure Q6-1). Halon-1211 reached peak concentration in 2005 and has been decreasing ever since, reaching an abundance in 2016 that was 8.2% below that measured in 1998. The abundance of halon-1301, on the other hand, has increased by 23% since 1998 and is expected to continue to increase very slightly into the next decade because of continued small releases and a long atmospheric



lifetime (see Figure Q15-1). The bromine content of other halons (mainly halon-1202 and halon-2402) in 2016 was 21% below the amount present in 1998.

Natural sources of chlorine and bromine. There are a few halogen source gases present in the stratosphere that have large natural sources. These include methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), both of which are emitted by oceanic and terrestrial ecosystems. In addition, very short-lived source gases

containing bromine such as bromoform (CHBr_3) and dibromomethane (CH_2Br_2) are also released to the atmosphere, primarily from biological activity in the oceans. Only a fraction of the emissions of very short-lived source gases reaches the stratosphere because these gases are efficiently removed in the lower atmosphere. Volcanoes provide an episodic source of reactive halogen gases that sometimes reach the stratosphere in appreciable quantities. Other natural sources of halogens include reactive chlorine and bromine produced by evaporation of ocean spray.

These reactive chemicals readily dissolve in water and are removed in the troposphere. In 2016, natural sources contributed about 16% of total stratospheric chlorine and about 50% of total stratospheric bromine (see Figure Q6-1). The amount of chlorine and bromine entering the stratosphere from natural sources is fairly constant over time and, therefore, cannot be the cause of the ozone depletion observed since the 1980s.

Other human activities that are sources of chlorine and bromine gases. Other chlorine- and bromine-containing gases are released to the atmosphere from human activities. Common examples are the use of chlorine-containing solvents and industrial chemicals, and the use of chlorine gases in paper production and disinfection of potable and industrial water supplies (including swimming pools). Most of these gases are very short-lived and only a small fraction of their emissions reaches the stratosphere. The contribution of very short-lived chlorinated gases from natural sources and human activities to total stratospheric chlorine was 44% larger in 2016 compared to 1993, and now contributes about 3.5% (115 ppt) of the total chlorine entering the stratosphere (see Figure Q6-1). The Montreal Protocol does not control the production and consumption of very short-lived chlorine source gases, although the atmospheric abundances of some (notably dichloromethane, CH_2Cl_2) have increased substantially in recent years. Solid rocket engines, such as those used to propel payloads into orbit, release reactive chlorine gases directly into the troposphere and stratosphere. The quantities of chlorine emitted globally by rockets is currently small in comparison with halogen emissions from other human activities.

Lifetimes and emissions. Estimates of global emissions in 2016 for a selected set of halogen source gases are given in Table Q6-1. These emissions occur from continued production of HCFCs and hydrofluorocarbons (HFCs) as well as the release of gases from banks. Emission from *banks* refers to the atmospheric release of halocarbons from existing equipment, chemical stockpiles, foams, and other products. In 2016 the global emission of the refrigerant HCFC-22 (CHF_2Cl) constituted the largest annual release, by mass, of a halocarbon from human activities. Release in 2016 of HFC-134a (CH_2FCF_3), another refrigerant, was second largest. The emission of methyl chloride (CH_3Cl) is primarily from natural sources such as the ocean biosphere, terrestrial plants, salt marshes and fungi. The human source of methyl chloride is small relative to the total natural source (see Q15).

After emission, halogen source gases are either naturally removed from the atmosphere or undergo chemical conversion in the troposphere or stratosphere. The time to remove or convert about 63% 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 Q6-1). The long-lived gases are converted to other gases primarily in the stratosphere and essentially all of their original halogen content becomes available to participate in the destruction of stratospheric ozone. Gases with short lifetimes such as HCFCs, methyl bromide, and methyl chloride are effectively converted to other

gases in the troposphere, which are then removed by rain and snow. Therefore, only a fraction of their halogen content potentially contributes to ozone depletion in the stratosphere. Methyl chloride, despite its large source, constituted only about 17% (555 ppt) of the halogen source gases entering the stratosphere in 2016 (see Figure Q6-1).

The amount of an emitted gas that is present in the atmosphere represents a balance between its emission and removal rates. A wide range of current emission rates and atmospheric lifetimes are derived for the various source gases (see Table Q6-1). The atmospheric abundances of most of the principal CFCs and halons have decreased since 1990 in response to smaller emission rates, while those of the leading substitute gases, the HCFCs, continue to increase under the provisions of the Montreal Protocol (see Q15). In the past few years, the rate of the increase of the atmospheric abundance of HCFCs has slowed down. In the coming decades, the emissions and atmospheric abundances of all controlled gases are expected to decrease under these provisions.

Ozone Depletion Potential (ODP). Emissions of halogen source gases are compared in their effectiveness to destroy stratospheric ozone based upon their ODPs, as listed in Table Q6-1 (see Q17). Once in the atmosphere, a gas with a larger ODP destroys more ozone than a gas with a smaller ODP. The ODP is calculated relative to CFC-11, which has an ODP defined to be 1. The calculations, which require the use of computer models that simulate the atmosphere, use as the basis of comparison the ozone depletion from an equal mass of each gas emitted to the atmosphere. Halon-1211 and halon-1301 have ODPs significantly larger than that of CFC-11 and most other chlorinated gases because bromine is much more effective (about 60 times) on a per-atom basis than chlorine in chemical reactions that destroy ozone. The gases with smaller values of ODP generally have shorter atmospheric lifetimes or contain fewer chlorine and bromine atoms.

Fluorine and iodine. Fluorine and iodine are also halogens. Many of the source gases in Figure Q6-1 also contain fluorine in addition to chlorine or bromine. After the source gases undergo conversion in the stratosphere (see Q5), the fluorine content of these gases is left in chemical forms that do not cause ozone depletion. As a consequence, halogen source gases that contain fluorine and no other halogens are not classified as ODSs. An important example of these are the HFCs, which are included in Table Q6-1 because they are common ODS substitute gases. HFCs have ODPs of zero and are also strong greenhouse gases, as quantified by a metric termed the Global Warming Potential (GWP) (see Q17). The Kigali Amendment to the Montreal Protocol now controls the production and consumption of some HFCs (see Q19), especially those HFCs with higher GWPs.

Iodine is a component of several gases that are naturally emitted from the oceans and some human activities. Although iodine can participate in ozone destruction reactions, iodine-containing source gases all have very short lifetimes. The importance for stratospheric ozone of very short-lived iodine containing source gases is an area of active research.

Other non-halogen gases. Other non-halogen gases that influence stratospheric ozone abundances have also increased in the stratosphere as a result of emissions from human activities (see Q20). Important examples are methane (CH₄) and nitrous oxide (N₂O), which react in the stratosphere to form water vapor and reactive hydrogen, and nitrogen oxides, respectively. These reactive products participate in the destruction of stratospheric ozone (see Q1). Increased levels of atmospheric carbon dioxide (CO₂) alter stratospheric temperature and winds, which also affect the abundance of stratospheric ozone. Should future atmospheric abundances of CO₂, CH₄ and N₂O increase significantly

relative to present day values, these increases will affect future levels of stratospheric ozone through combined effects on temperature, winds, and chemistry (see Figure Q20-3). Efforts are underway to reduce the emissions of these gases under the Paris Agreement of the United Nations Framework Convention on Climate Change because they cause surface warming (see Q18 and Q19). Although past emissions of ODSs still dominate global ozone depletion today, future emissions of N₂O from human activities are expected to become relatively more important for ozone depletion as future abundances of ODSs decline (see Q20).

Table Q6-1. Atmospheric lifetimes, global emissions, Ozone Deletion Potentials, and Global Warming Potentials of some halogen source gases and HFC substitute gases.

Gas	Atmospheric Lifetime (years)	Global Emissions in 2016 (kt/yr) ^a	Ozone Depletion Potential (ODP) ^b	Global Warming Potential (GWP) ^b
Halogen Source Gases				
Chlorine Gases				
CFC-11 (CCl ₃ F)	52	61 – 84	1	5160
Carbon tetrachloride (CCl ₄)	32	23 – 50	0.87	2110
CFC-113 (CCl ₂ FCClF ₂)	93	2 – 13	0.81	6080
CFC-12 (CCl ₂ F ₂)	102	13 – 57	0.73	10300
Methyl chloroform (CH ₃ CCl ₃)	5.0	0 – 4	0.14	153
HCFC-141b (CH ₃ CCl ₂ F)	9.4	52 – 68	0.102	800
HCFC-142b (CH ₃ CClF ₂)	18	20 – 29	0.057	2070
HCFC-22 (CHF ₂ Cl)	12	321 – 424	0.034	1780
Methyl chloride (CH ₃ Cl)	0.9	4526 – 6873	0.015	4.3
Bromine Gases				
Halon-1301 (CBrF ₃)	65	1 – 2	15.2	6670
Halon-1211 (CBrClF ₂)	16	1 – 5	6.9	1750
Methyl bromide (CH ₃ Br)	0.8	121 – 182	0.57	2
Hydrofluorocarbons (HFCs)				
HFC-23 (CHF ₃)	228	12 – 13	0	12690
HFC-143a (CH ₃ CF ₃)	51	26 – 30	0	5080
HFC-125 (CHF ₂ CF ₃)	30	58 – 67	0	3450
HFC-134a (CH ₂ F ₂ CF ₃)	14	202 – 245	0	1360
HFC-32 (CH ₂ F ₂)	5.4	31 – 39	0	705
HFC-152a (CH ₃ CHF ₂)	1.6	45 – 62	0	148
HFO-1234yf (CF ₃ CF=CH ₂)	0.03	not available	0	less than 1

^a Includes both human activities (production and banks) and natural sources. Emissions are in units of kilotonnes per year (1 kilotonne = 1000 metric tons = 1 million (10⁶) kilograms). These emission estimates are based on analysis of atmospheric observations and hence, for CFC-11, the unreported emissions recently noted (see Q15) are represented by the given range. The range of values for each emission estimate reflects the uncertainty in estimating emissions from atmospheric observations.

^b 100-year GWP. ODPs and GWPs are discussed in Q17. Values are calculated for emissions of an equal mass of each gas. ODPs given here reflect current scientific values and in some cases differ from those used in the Montreal Protocol.