

# Q7

## 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 in fire extinguishers. Current ODS abundances in the atmosphere are known directly from air sample measurements.

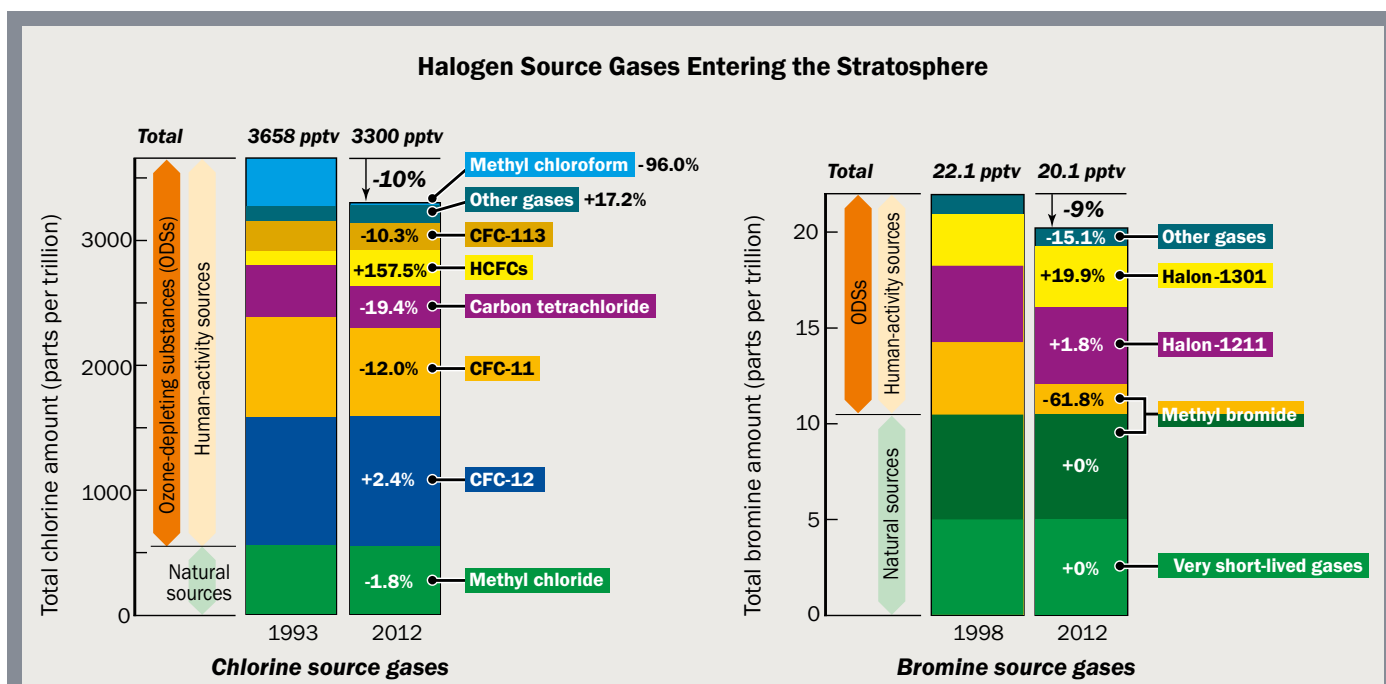
**Halogen source gases versus ODSs.** Those halogen source gases emitted by human activities and controlled by the Montreal Protocol are referred to as ODSs within the Montreal Protocol, by the media, and in the scientific literature. The Montreal Protocol now controls the global production and consumption of all ODSs (see Q15). Halogen source gases that have only 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 are shown in Figure Q7-1. Total amounts of chlorine peaked in 1993, and of bromine in 1998. The difference in the timing of the peaks is explained by the phase-out schedules, how closely emissions are tied to production, and the lifetimes of the various source gases. Also shown are the contributions to total chlorine and bromine in 2012, highlighting the reductions achieved due to the Montreal Protocol controls.

**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 20<sup>th</sup> 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 ( $\text{CCl}_3\text{F}$ ), CFC-12 ( $\text{CCl}_2\text{F}_2$ ), and CFC-113 ( $\text{CCl}_2\text{FCClF}_2$ ). CFCs, along with carbon tetrachloride ( $\text{CCl}_4$ ) and methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ), 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, aerosol 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 between 1993 and 2012 (see Figure Q7-1). While the concentration of CFC-12 in 2012 was 2.4% higher than it was in 1993, it peaked in 2000 and has decreased since then (see Figure Q16-1). As substitute gases for CFCs, hydrochlorofluorocarbons (HCFCs) increased substantially between 1993 and 2012 (+157.5%). With new restrictions on global production in place since 2013, HCFCs are expected to reach peak values between 2020 and 2030.

Another category of ODSs contains bromine. The most important of these gases are the halons and methyl bromide ( $\text{CH}_3\text{Br}$ ). Halons are halocarbon gases originally developed to extinguish fires. Halons were widely used to protect large computer installations, military hardware, and commercial aircraft engines. As a consequence, halons are often released directly into the atmosphere upon use. 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, but also has significant natural sources. As a result of the Montreal Protocol, the abundances of methyl bromide from human sources have substantially decreased between 1998 and 2012 (-61.8%; see Figure Q7-1). Halon-1211 reached peak values in 2005 and has been decreasing since then. Halon-1301 abundances, on the other hand, have increased by +19.9% since 1998 and are expected to increase further (although at a slower rate) because of continued small releases and a long atmospheric lifetime.

**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 ( $\text{CH}_3\text{Cl}$ ) and methyl bromide ( $\text{CH}_3\text{Br}$ ), both of which are emitted by oceanic and terrestrial ecosystems. Natural sources of these two gases contributed about 17% to the total chlorine in the stratosphere in 2012 and about 30% of the total



**Figure Q7-1. Changes in halogen source gases entering the stratosphere.**

A variety of halogen source gases emitted from natural sources and by human activities transport chlorine and bromine into the stratosphere. Ozone-depleting substances (ODSs) are the subset of these gases emitted by human activities that are controlled by the Montreal Protocol. These partitioned columns show the sources and abundances of chlorine- and bromine-containing gases entering the stratosphere in 1993 and 1998, when their total amounts peaked, respectively, and in 2012. The overall reductions in the total amounts of chlorine and bromine and the changes observed for each source gas are also indicated. The approximate amounts are derived from tropospheric observations of each gas. Note the large difference in the vertical scales: total chlorine entering the stratosphere is 150 times more abundant than total bromine. Human activities are the largest source of chlorine reaching the stratosphere and the CFCs are the most

abundant chlorine-containing gases. Methyl chloride is the primary natural source of chlorine. Largest decreases between 1993 and 2012 are seen in CFC-11, carbon tetrachloride, and methyl chloroform. HCFCs, which are substitute gases for CFCs and also controlled under the Montreal Protocol, show small but still strongly increasing abundances. For bromine entering the stratosphere, halons and methyl bromide are the largest contributors. Methyl bromide has an additional, much larger, natural source. Natural sources provide a much larger contribution to total bromine entering the stratosphere than to total chlorine. Largest decreases between 1998 and 2012 are seen in methyl bromide. Halon-1211 and halon-1301 show increasing abundances. (The unit “parts per trillion” is used here as a measure of the relative abundance of a gas in air: 1 part per trillion equals the presence of one molecule of a gas per trillion (=10<sup>12</sup>) total air molecules.)

bromine (Figure Q7-1). Very short-lived source gases containing bromine, such as bromoform ( $\text{CHBr}_3$ ), are also released to the atmosphere primarily from biological activity in the oceans. Only a fraction of these emissions reaches the stratosphere, because these gases are rapidly removed in the lower atmosphere. The contribution of these very short-lived gases to the total amount of bromine in the stratosphere is estimated to be about 25% in 2012, but this number has a large uncertainty. The amounts of chlorine and bromine in the stratosphere from natural sources are believed to be fairly constant and, therefore, cannot be the cause of the ozone depletion observed since the 1980s.

**Other human sources of chlorine and bromine.** 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 and human sources to total stratospheric chlorine is only about 3% and is included in *Other gases* in Figure Q7-1. The Montreal Protocol does not control the production and consumption of very short-lived substances (VSLs), although the concentrations of some (notably dichloromethane,  $\text{CH}_2\text{Cl}_2$ ) have increased substantially in recent years.

**Lifetimes and emissions.** 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 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). 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 (e.g., the HCFCs, methyl bromide, methyl chloride, and the very short-lived gases) are effectively converted to other gases in the troposphere, which are then removed by rain. Therefore, only a fraction of their halogen content potentially contributes to ozone depletion in the stratosphere.

The amount of an emitted gas that is present in the atmosphere represents a balance between its emission rate and removal rate. Emission rates and atmospheric lifetimes vary greatly for the source gases, as indicated in Table Q7-1. For example, 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 hydrochlorofluorocarbons (HCFCs), continue to increase under the provisions of the Montreal Protocol (see Q16). In the coming decades, the emissions and atmospheric abundances of all controlled gases are expected to decrease under these provisions.

**Ozone Depletion Potential (ODP).** Halogen source gases are compared in their effectiveness to destroy stratospheric ozone using the ODP, as listed in Table Q7-1 (see Q18). A gas with a larger ODP destroys more ozone over its atmospheric lifetime. The ODP is calculated relative to CFC-11, which has an ODP defined to be 1. The calculations, which require the use of atmospheric computer models, 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 small ODP values generally have short atmospheric lifetimes or contain fewer chlorine and bromine atoms.

**Table Q7-1.**

Atmospheric lifetimes, global emissions, Ozone Depletion Potentials, and Global Warming Potentials of some halogen source gases and HFC substitute gases.

| Gas   | Atmospheric Lifetime (years) | Global Emissions in 2012 (Kt/yr) <sup>a</sup> | Ozone Depletion Potential (ODP) <sup>c</sup> | Global Warming Potential (GWP) <sup>c</sup> |
|---|------------------------------|---|--|---|
| <b>Halogen source gases</b>                                     |                              |   |  |   |
| <b>Chlorine gases<sup>e</sup></b>                               |                              |   |  |   |
| CFC-11  | 52                           | 46–68   | 1  | 5160  |
| CFC-12  | 102                          | 16–64   | 0.73   | 10300                                       |
| CFC-113   | 93                           | 0–7   | 0.81   | 6080  |
| Carbon tetrachloride (CCl <sub>4</sub> )                        | 26                           | 40–74   | 0.72   | 1730  |
| HCFCs   | 1–18                         | 400–528                                       | 0.01–0.10                                    | 800–2070                                    |
| Methyl chloroform (CH <sub>3</sub> CCl <sub>3</sub> )           | 5                            | 0–5   | 0.14   | 153   |
| Methyl chloride (CH <sub>3</sub> Cl)                            | 0.9                          | 2707  | 0.015  | 11  |
| Very short-lived Cl-containing gases                            | less than 0.5                | <sup>b</sup>                                  | <sup>b, d</sup> very low                     | <sup>b</sup> less than 1                    |
| <b>Bromine gases</b>  |                              |   |  |   |
| Halon-1301  | 72                           | 1.4–2   | 15.2   | 6670  |
| Halon-1211  | 16                           | 0.3–9.3                                       | 6.9  | 1750  |
| Methyl bromide (CH <sub>3</sub> Br)                             | 0.8                          | 85  | 0.57   | 2   |
| Very short-lived Br-containing gases (e.g., CHBr <sub>3</sub> ) | less than 0.5                | <sup>b</sup> 260–1080                         | <sup>b, d</sup> very low                     | <sup>b</sup> very low                       |
| <b>Hydrofluorocarbons (HFCs)</b>                                |                              |   |  |   |
| HFC-134a  | 14                           | 144–215                                       | 0  | 1360  |
| HFC-23  | 228                          | 11–14   | 0  | 12500                                       |
| HFC-143a  | 51                           | 20–25   | 0  | 5080  |
| HFC-125   | 31                           | 31–47   | 0  | 3450  |
| HFC-152a  | 1.6                          | 40–66   | 0  | 148   |
| HFC-32  | 5.4                          | 12–30   | 0  | 700   |

<sup>a</sup> Includes both human activities (production and banks) and natural sources. Emissions are in units of kilotonnes per year (1 kilotonne = 1000 metric tons = 1 gigagram = 10<sup>9</sup> grams).

<sup>b</sup> Estimates are very uncertain for most species.

<sup>c</sup> 100-year GWP. ODPs and GWPs are discussed in Q18. Values are calculated for emissions of an equal mass of each gas.

<sup>d</sup> ODP depends strongly on where the emissions occur for these gases. Emissions in the tropics have higher ODPs than emissions at midlatitudes.

<sup>e</sup> New measurements are now available of CFC-112a, CFC-112, CFC-113a, and HCFC-133. These gases are by-products of ODS-manufacturing and constitute only very small contributions to the total of chlorine- and bromine-containing gases.

# Q7

**Fluorine and iodine.** Fluorine and iodine are also halogens. Many of the source gases in Figure Q7-1 also contain fluorine 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 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 hydrofluorocarbons (HFCs), which are included in Table Q7-1 because they are common ODS substitute gases. HFCs have ODPs of zero and are also strong greenhouse gases (see Q18). 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. Currently there is no evidence that any of these gases reach the stratosphere in significant amounts.

**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. Important examples are methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ), 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 Q2). Increasing abundances of  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , as well as  $\text{CO}_2$ , are expected to significantly affect future stratospheric ozone through combined effects on temperature, winds, and chemistry (see Q20). Although all of these gases are part of the Kyoto Protocol (see Q15) because they are climate gases, they are not classified as ODSs under the Montreal Protocol. Although past emissions of ODSs still dominate global ozone depletion today, the current emissions of  $\text{N}_2\text{O}$  from human activities will destroy more stratospheric ozone in the future than the current emissions of any ODS.