Q6

What emissions from human activities lead to stratospheric ozone depletion?

Certain industrial processes and consumer products result in the emission of ozone-depleting substances (ODSs) to the atmosphere. Principal ODSs are manufactured halogen source gases that are now 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). Halogen source gases that are emitted by human activities and controlled by the Montreal Protocol are generally referred to as ODSs. 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 various ODSs and natural halogen source gases to the total amount of chlorine and bromine entering the stratosphere are shown in **Figure Q6-1**. Total chlorine and total bromine entering the stratosphere peaked in 1993 and 1999, respectively. The difference in the timing of these peaks is a result of various phaseout schedules specified by the Montreal Protocol and its amendments and adjustments, different atmospheric lifetimes of halogen source gases, and the time delays between production and emission of the numerous source gases. Also shown are the contributions to total chlorine and bromine in 2020, highlighting the reductions of 11% and 15%, respectively, achieved by the controls of the Montreal Protocol.

Ozone-depleting substances (ODSs). The principal 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). Because of their long atmospheric lifetimes, a large fraction of the emitted ODSs reach the stratosphere, where they are converted to reactive and reservoir gases containing chlorine and bromine that lead to ozone depletion.

ODSs containing only chlorine, fluorine, and carbon are called *chlorofluorocarbons*, usually abbreviated as CFCs. The principal CFCs are CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and CFC-113 (CCl_2FCClF_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 these chlorine source gases have de-creased since 1993 (see Figure Q6-1). The abundances of CFC-11 and CFC-12 in 2020 were 16% and 2.8% lower than their values in 1993, respectively.

The class of compounds known as *hydrochlorofluorocarbons* (HCFCs) contain hydrogen, in addition to chlorine, fluorine, and carbon. HCFC-22 (CHF_2Cl), developed in the 1930s, has been used as a refrigerant, primarily in residential air conditioners, since the 1940s. As detailed below, HCFCs are less harmful to the ozone layer compared to CFCs. In the 1990s, the use of HCFC-22 expanded and other HCFCs were developed as substitutes for CFCs. Consequently, the chlorine content of HCFCs entering the stratosphere increased by 185% between 1993 and 2020 (see Figure Q6-1). With restrictions on production starting in 1996, and globally in place since 2013, the atmospheric abundances of HCFCs are expected to peak between 2023 and 2030 (see Figures Q0-1 and Q15-1). Classes of compounds known as hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs) constitute the replacement for many applications of HCFCs.

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. Consequently, halons are often released directly into the atmosphere upon use or testing of these fire suppression systems. The most abundant halons emitted by human activities are halon-1211 ($CBrClF_2$) and halon-1301 ($CBrF_3$). 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 controls of the Montreal Protocol, the contribution to the atmospheric abundance of methyl bromide from human activities decreased by 71% between 1999 and 2020 (see Figure Q6-1). The concentration of halon-1211 peaked in 2005 and has been decreasing ever since, reaching an abundance in 2020 that was 22% below that measured in 1999. The abundance of halon-1301, on the other hand, increased by 19% since 1999 and is expected to slowly decline into the next decade because

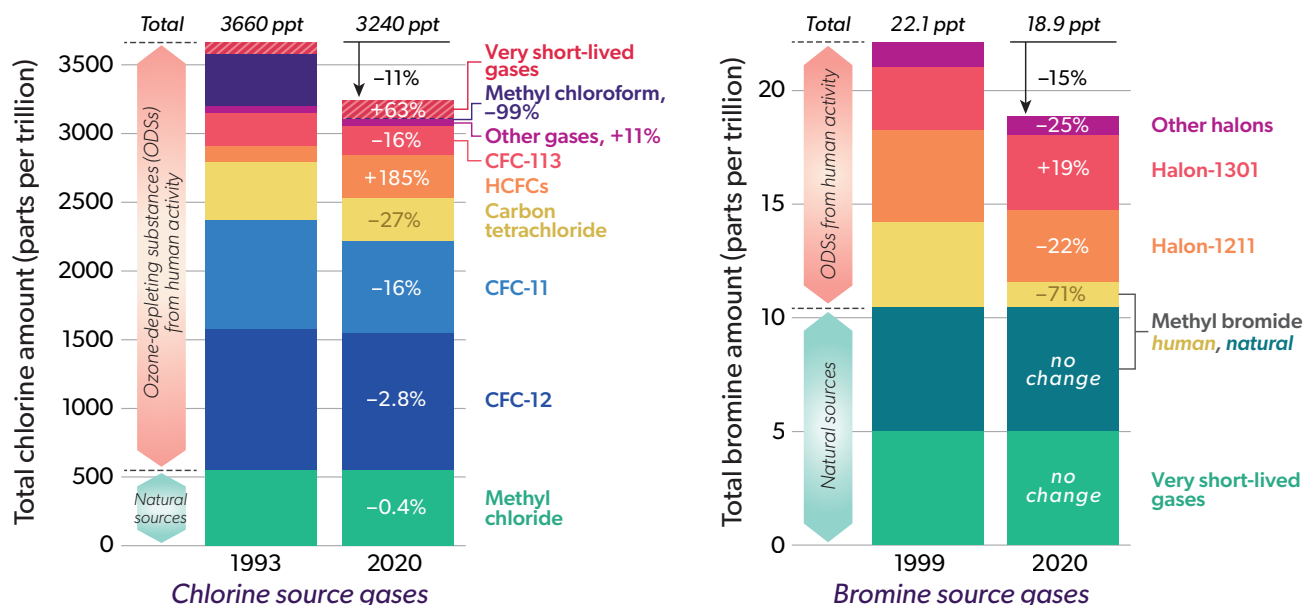## Halogen Source Gases Entering the Stratosphere

Figure Q6-1. Changes in halogen source gases entering the stratosphere. A variety of halogen source gases emitted by human activities and natural processes 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 abundances of chlorine- and bromine-containing gases entering the stratosphere in 1993 and 1999, when their total amounts peaked, respectively, and in 2020. The overall reductions in the total amounts of chlorine and bromine entering the stratosphere and the changes observed for each source gas are also indicated. The amounts are derived from tropospheric observations of each gas. Note the large difference in the vertical scales: total chlorine entering the stratosphere is about 150 times greater than total bromine. Both, however, are important because bromine is about 60 times more effective on a per-atom basis than chlorine at destroying ozone. Human activities are the largest source of chlorine reaching the stratosphere and CFCs are the most abundant chlorine-containing gases. Methyl chloride is the primary natural source of chlorine. The largest decreases between 1993 and 2020 are seen in methyl chloroform, carbon tetrachloride, and CFC-11. The abundance of HCFCs, which are substitute gases for CFCs and also controlled under the Montreal Protocol, have risen substantially since 1993 and have approached expected peak atmospheric abundances (see Figure Q15-1). The abundance of chlorine-containing very short-lived gases entering the stratosphere has risen substantially since 1993; these compounds originate primarily from human activity, undergo chemical loss within the troposphere, and are not controlled by the Montreal Protocol. Halons and methyl bromide are the largest contributors to bromine entering the stratosphere. The largest decrease between 1999 and 2020 is seen in the abundance of methyl bromide attributed to human activities, because of the success of the Montreal Protocol. Halon-1301 is the only brominated ODS showing an increased abundance relative to 1999. Methyl bromide also has a natural source, which is now substantially greater than the human source due to the success of the Montreal Protocol. Natural sources, which make a much larger fractional contribution to bromine entering the stratosphere than occurs for chlorine, have remained fairly constant in the recent past.

(The unit "parts per trillion" is used here as a measure of the relative abundance of a substance in dry air: 1 part per trillion equals the presence of one molecule of a gas per trillion (=10^{12}) total air molecules.)

of continued small releases and a long atmospheric lifetime (see Figure Q15-1). In 2020, the bromine content of other halons (mainly halon-1202 and halon-2402) was 25% below the amount present in 1999.

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 (defined as compounds with atmospheric lifetimes typically less

than 0.5 year) 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. However, these

reactive chemicals play no role in stratospheric ozone depletion because they readily dissolve in water and are removed in the troposphere.

In 2020, natural sources contributed about 17% of total stratospheric chlorine and about 56% of total stratospheric bromine (see Figure Q6-1). The amount of chlorine and bromine entering the stratosphere from natural sources is known to be 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 63% larger in 2020 than in 1993, and now contributes about 4% (130 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 2020 for a selected set of halogen source gases are given in **Table Q6-1**. These emissions occur from continued production of HCFCs and 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 2020 the global emission of the refrigerant HCFC-22 constituted the largest annual release, by mass, of a halocarbon from human activities. Release in 2020 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 removed from the atmosphere or undergo chemical conversion in the troposphere, stratosphere, or mesosphere. 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. Conversely, gases with short lifetimes such as methyl bromide, methyl chloride, and some HCFCs are converted to other gases in the troposphere, which are then removed from the atmosphere by rain and snow. Therefore, only a fraction of their halogen content contributes to

ozone depletion in the stratosphere. Methyl chloride, despite its large source, constituted only about 17% (540 ppt) of the halogen source gases entering the stratosphere in 2020 (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 important substitute gases, the HCFCs, continue to slowly 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 declined. In the coming decades, the emissions and atmospheric abundances of all controlled ODSs are expected to decrease under these provisions.

Ozone Depletion Potential (ODP). The effectiveness of halogen source gases at destroying stratospheric ozone is given by the ODP (see Table Q6-1 and Q17). A gas with a larger ODP destroys more stratospheric ozone than a gas with a smaller ODP. The calculation of ODP requires the use of computer models that simulate atmospheric ozone and is found relative to CFC-11, which has an ODP defined to be 1. The ODP of a gas is based upon a comparison of the amount of ozone depletion caused by the continuous emission to the atmosphere of a certain mass of that gas, relative to the amount of ozone depletion following emission of the same mass of CFC-11. Halogen source gases controlled by the Montreal Protocol have a wide range of ODPs. 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 compared to gases with larger ODPs.

HFCs & other fluorine-containing gases. Many of the source gases in Figure Q6-1 also contain fluorine, another halogen, 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 do not contain chlorine or bromine and, consequently, all HFCs have an ODP of zero.

Many HFCs are 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 HFCs (see Q19), especially those HFCs with high GWPs. As a result, industry has transitioned in part to production and use of a subset of HFCs with very low GWPs known as hydrofluoroolefins (HFOs), which are also composed of hydrogen, fluorine, and carbon atoms. Here, the "O" stands for olefin, a term used by chemists to refer to the double carbon bond of these compounds that results in small tropospheric lifetimes and GWPs for HFOs. One such HFO, HFO-1234yf (CF_3CFCH_2), has a GWP of less than 1 due to its 12 day lifetime.

Iodine containing gases. Iodine is a component of several gases that are naturally emitted from the oceans and from some human activities. Research on the importance of iodine for stratospheric ozone is being conducted, in part, because trifluoroiodomethane (CF_3I) is a possible replacement for halons in fire extinguishers and also because CF_3I has been proposed as an ingredient of low-GWP refrigerant blends. Although iodine can participate in ozone destruction reactions, iodine-containing source gases all have very short lifetimes, with most of the removal occurring in the lower atmosphere within a few days. Since the last assessment, there has been an upward revision to the upper limit on the amount of iodine reaching the stratosphere, which is now estimated to be about 1 ppt. The importance for stratospheric ozone of very short-lived iodine containing source gases, including a possible enhancement of polar ozone depletion, remains an active area of investigation.

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 (CH_4), which reacts in the stratosphere to form water vapor and reactive hydrogen, and nitrous oxide (N_2O), which reacts in the stratosphere to form nitrogen oxides. These reactive products participate in the destruction of stratospheric ozone. Increased levels of atmospheric carbon dioxide (CO_2) alter stratospheric temperature and winds, which also affect the abundance of stratospheric ozone. Should future atmospheric abundances of CO_2, CH_4, and N_2O 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 Q20-2). 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 N_2O from human activities are expected to become relatively more important for ozone depletion as the atmospheric 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 2020 (kt/yr)[a]	Ozone Depletion Potential (ODP)[b]	Global Warming Potential (GWP)[b]
Halogen Source Gases				
Chlorine Gases				
CFC-11 (CCl_3F)	52	36 – 58	1	6410
Carbon tetrachloride (CCl_4)	30	27 – 60	0.87	2150
CFC-113 (CCl_2FCClF_2)	93	1 – 13	0.82	6530
CFC-12 (CCl_2F_2)	102	3 – 48	0.75	12,500
Methyl chloroform (CH_3CCl_3)	5.0	1 – 3	0.12	164
HCFC-141b (CH_3CCl_2F)	8.8	48 – 67	0.102	808
HCFC-142b (CH_3CClF_2)	17	15 – 23	0.057	2190
HCFC-22 (CHF_2Cl)	12	284 – 403	0.038	1910
Methyl chloride (CH_3Cl)	0.9	3759 – 5677	0.015	6
Bromine Gases				
Halon-1301 ($CBrF_3$)	72	1 – 2	17	7430
Halon-1211 ($CBrClF_2$)	16	1 – 5	7.1	1990
Methyl bromide (CH_3Br)	0.8	111 – 154	0.57	2
Hydrofluorocarbons (HFCs)				
HFC-23 (CHF_3)	228	16 – 18	0	14,700
HFC-143a (CH_3CF_3)	52	27 – 33	0	5900
HFC-125 (CHF_2CF_3)	31	78 – 98	0	3820
HFC-134a (CH_2FCF_3)	14	216 – 275	0	1470
HFC-32 (CH_2F_2)	5.3	56 – 77	0	749
HFC-152a (CH_3CHF_2)	1.5	41 – 63	0	153
HFO-1234yf (CF_3CFCH_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 gigagram = 10^9 grams). These emission estimates are based on analysis of atmospheric observations. 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.