

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 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 chlorine and bromine entering the stratosphere in 2008 are shown in Figure Q7-1.

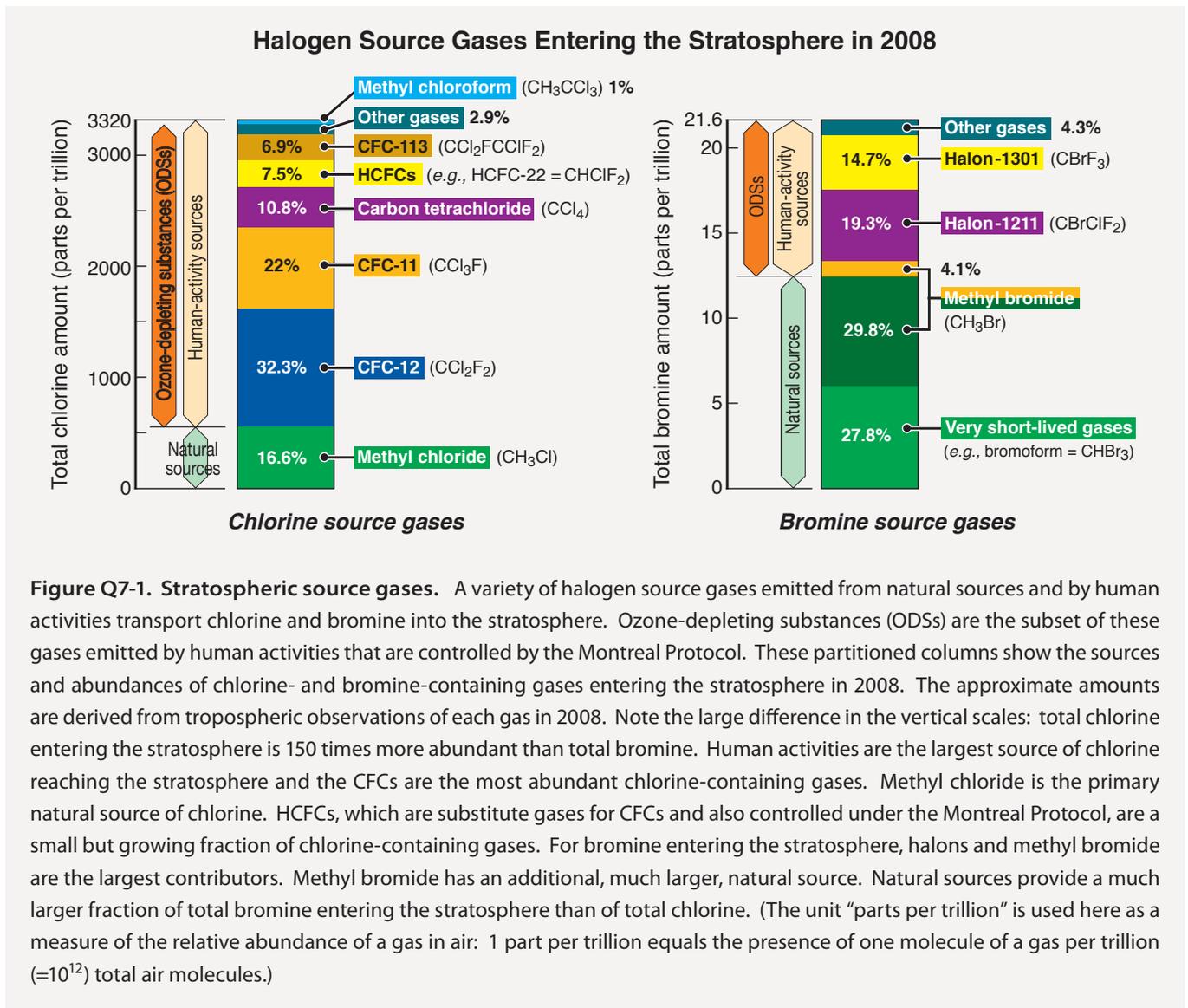
Ozone-depleting substances (ODSs). ODSs are manufactured for specific industrial uses or consumer products, most of which result in the eventual emission of these gases to the atmosphere. ODS emissions have increased substantially from the middle to the late 20th century, reached a peak in the late 1980s, and are now in decline (see Figure Q0-1). A large fraction of ODS emissions reach the stratosphere and lead to ozone depletion because chlorine and bromine atoms react to destroy ozone. ODSs that contain only carbon, chlorine, and fluorine are called *chlorofluorocarbons*, usually abbreviated as CFCs. CFCs, along with carbon tetrachloride (CCl₄) and methyl chloroform (CH₃CCl₃), 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.

Another category of ODSs contains bromine. The most important of these gases are the halons and methyl bromide (CH₃Br). 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 (see Figure Q7-1). Methyl bromide is used primarily as an agricultural and pre-shipping fumigant.

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 (CH₃Cl) and methyl bromide (CH₃Br), both of which are emitted by oceanic and terrestrial ecosystems. Natural sources of these two gases contributed about 17% of the chlorine in the stratosphere in 2008 and about 30% of the bromine (see Figure Q7-1). Very short-lived source gases containing bromine, such as bromoform (CHBr₃), 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 stratospheric bromine is estimated to be about 28%, but this has a large uncertainty. The contribution to stratospheric chlorine of short-lived chlorinated gases from natural and human sources is much smaller (less than 3%) and is included in *Other gases* in Figure Q7-1. The amounts of chlorine and bromine in the stratosphere from natural sources are believed to have been fairly constant since the middle of the 20th century and, therefore, cannot be the cause of ozone depletion as observed since the 1980s.

Other human sources of chlorine and bromine. Other chlorine- and bromine-containing gases are released regularly from human activities. Common examples are the use of chlorine gases to disinfect swimming pools and wastewater, fossil fuel burning, biomass burning, and various industrial processes. These emissions do not contribute significantly to stratospheric amounts of chlorine and bromine because either the global source is small, or the emitted gases and their degradation products are short-lived (very reactive or highly soluble). As a consequence, the chlorine and bromine content of these gases is prevented from reaching the stratosphere in significant amounts.



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 primarily destroyed in the stratosphere and essentially all of the emitted halogen is available to participate in the destruction of stratospheric ozone. Gases with the short lifetimes (e.g., the HCFCs, methyl bromide, methyl chloride, and the very short-lived gases) are substantially destroyed in the troposphere and, therefore, only a fraction of the emitted halogen contributes to ozone depletion in the stratosphere.

The amount of an emitted gas that is present in the atmo-

sphere represents a balance between the emission rate and the lifetime of the gas. 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 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,

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 2008 (Kt/yr) ^a	Ozone Depletion Potential (ODP) ^c	Global Warming Potential (GWP) ^c
Halogen source gases				
Chlorine gases				
CFC-11	45	52–91	1	4750
CFC-12	100	41–99	0.82	10900
CFC-113	85	3–8	0.85	6130
Carbon tetrachloride (CCl ₄)	26	40–80	0.82	1400
HCFCs	1–17	385–481	0.01–0.12	77–2220
Methyl chloroform (CH ₃ CCl ₃)	5	Less than 10	0.16	146
Methyl chloride (CH ₃ Cl)	1	3600–4600	0.02	13
Bromine gases				
Halon-1301	65	1–3	15.9	7140
Halon-1211	16	4–7	7.9	1890
Methyl bromide (CH ₃ Br)	0.8	110–150	0.66	5
Very short-lived gases (e.g., CHBr ₃)	Less than 0.5	^b	^b very low	^b very low
Hydrofluorocarbons (HFCs)				
HFC-134a	13.4	149 ± 27	0	1370
HFC-23	222	12	0	14200
HFC-143a	47.1	17	0	4180
HFC-125	28.2	22	0	3420
HFC-152a	1.5	50	0	133
HFC-32	5.2	8.9	0	716

^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 = 10⁹ grams).

^b Estimates are very uncertain for most species.

^c 100-year GWPs. ODPs and GWPs are discussed in Q18. Values are calculated for emissions of an equal mass of each gas.

which has an ODP defined to be 1. The calculations, which require the use of computer models of 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 CFC-11 and most other emitted gases because bromine is much more effective overall (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.

Fluorine and iodine. Fluorine and iodine are also halogen atoms. Many of the source gases in Figure Q7-1 also con-

tain 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 cause ozone depletion. As a consequence, halogen source gases that contain fluorine and no other halogens are not classified as ODSs. An important category is the hydrofluorocarbons (HFCs), which are included in Table Q7-1 because they are ODS substitute gases with ODPs of zero (see Q18).

Iodine is a component of several gases that are naturally emitted from the oceans. Although iodine can participate in ozone destruction reactions, these iodine-containing source gases generally have very short lifetimes and, as a result, only

a very small fraction reaches the stratosphere. There are large uncertainties in how these emissions vary with season and geographical region.

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 (CH_4) and nitrous oxide (N_2O), 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 N_2O and CH_4 , as well as 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, the *current* emissions of N_2O from human activities will destroy more stratospheric ozone than the *current* emissions of any ODS.

Heavier-Than-Air CFCs

CFCs and other ozone-depleting substances reach the stratosphere despite the fact that they are “heavier than air.” For example, molecules of CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) are approximately 4–5 times heavier than the average molecule of air, since air is composed primarily of oxygen and nitrogen. The emissions of long-lived gases accumulate in the lower atmosphere (troposphere). The distribution of these gases in the troposphere and stratosphere is not controlled by the molecular weight of each gas because air is in continual motion in these regions as a result of winds and convection. Continual air motions ensure that new emissions of long-lived gases are horizontally and vertically well mixed throughout the troposphere within a few months. It is this well-mixed air that enters the lower stratosphere from upward air motions in tropical regions, bringing with it ozone-depleting substances emitted from any location on Earth’s surface.

Atmospheric measurements confirm that ozone-depleting substances 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 generally consistent with the emission estimates reported by industries and governments. Measurements also show that gases that are “lighter than air,” such as hydrogen (H_2) and methane (CH_4), are also well mixed in the troposphere, as expected, and not found only in the upper atmosphere. Noble gases from very light helium to very heavy xenon, which all have very long atmospheric lifetimes, are also uniformly distributed throughout the troposphere and stratosphere. Only at altitudes well above the troposphere and stratosphere (above 85 kilometers (53 miles)), where much less air is present, does the influence of winds and convection diminish to the point where heavy gases begin to separate from lighter gases as a result of gravity.