How is total ozone distributed over the globe?

The distribution of total ozone over the Earth varies with location on timescales that range from daily to seasonal. The variations are caused by large-scale movements of stratospheric air and the chemical production and destruction of ozone. Total ozone is generally lowest at the equator and highest in polar regions.

Total ozone. Total ozone at any location on the globe is defined as the sum of all the ozone in the atmosphere directly above that location. Most ozone resides in the stratospheric ozone layer and a small percentage (about 10%) is distributed throughout the troposphere (see Q1). Total ozone values are often reported in *Dobson units* denoted as "DU." Typical values vary between 200 and 500 DU over the globe (see Figure Q4-1). The ozone molecules required for total ozone to be 500 DU around the globe, for example, could also form a layer of pure ozone gas at Earth's surface having a thickness of only 5 millimeters (0.2 inches) (see Q1).

Global distribution. Total ozone varies strongly with latitude over the globe, with the largest values occurring at middle and high latitudes during all seasons (see Figure Q4-1). This is the result of ozone production rates from solar ultraviolet radiation that are highest on average in the tropics, and the large-scale air circulation in the stratosphere that slowly transports tropical ozone toward the poles. Ozone accumulates at middle and high latitudes, increasing the thickness (or vertical extent) of the ozone layer and, at the same time, total ozone. In contrast, the values of total ozone are the lowest in the tropics in all seasons (except in the ozone hole) because the *thickness* of the ozone layer is smallest there.

Seasonal distribution. Total ozone also varies with season, as is shown in Figure Q4-1 using two-week averages of ozone taken from 2009 satellite observations. March and September plots represent the early spring and fall seasons in the Northern and Southern Hemispheres. June and December plots similarly represent the early summer and winter seasons. Total ozone shows a maximum at high latitudes during spring as a result of increased transport of ozone from its source region in the tropics toward the polar regions during late fall and winter. This ozone transport is much weaker during the summer and early fall periods and is weaker overall in the Southern Hemisphere. An important feature of seasonal ozone changes is the natural chemical destruction that occurs when daylight is continuous in the summer polar stratosphere, which causes total ozone to decrease gradually toward its lowest values in early fall.

This natural seasonal cycle can be observed clearly in the Northern Hemisphere as shown in Figure Q4-1, with increasing values in Arctic total ozone during winter, a clear maximum in spring, and decreasing values from summer to fall. In the Antarctic, however, a pronounced minimum in total ozone is observed during spring. The minimum is a consequence of the "ozone hole," which describes the widespread chemical destruction of ozone by ozone-depleting substances (see Q6 and Q11) in spring. In the late 1970s, before the ozone hole appeared each year, much higher ozone values were found in Antarctic spring (see Q11). Now, the lowest values of total ozone across the globe and all seasons are found every spring in the Antarctic as shown in Figure Q4-1. After spring, these low values disappear from total ozone maps as polar air mixes with lower-latitude air containing much higher ozone values.

In the tropics, the total ozone changes through the springsummer-fall-winter progression of the seasons are much smaller than in the polar regions. This is because seasonal changes in both sunlight and ozone transport are smaller in the tropics than in the polar regions.

Natural variations. Total ozone varies strongly with latitude and longitude within the seasonal plots in Figure Q4-1. These patterns, which change on daily to weekly timescales, come about for two reasons. First, natural air motions mix and blend air between regions of the stratosphere that have high ozone values and those that have low ozone values. Tropospheric weather systems can temporarily change the thickness of the ozone layer in a region, and thereby change total ozone. The geographical variation in these air motions in turn causes variations in the distribution of total ozone.

Second, ozone variations occur as a result of changes in the balance of chemical production and loss processes as air moves to and from different locations over the globe. This balance, for example, is very sensitive to the amount of sunlight in a region.

There is a good understanding of how chemistry and air



Figure Q4-1. Total ozone. Total ozone at any location on the globe is defined as the sum of all the ozone molecules in the atmosphere directly above that location. Total ozone varies with latitude, longitude, and season, with the largest values at high latitudes and the lowest values in tropical regions. The variations are demonstrated here with two-week averages of total ozone in 2009 as measured with a satellite instrument. Total ozone shows little variation in the tropics (20°N–20°S latitudes) over all seasons. Total ozone outside the tropics varies more strongly with time on a daily to seasonal basis as ozone-rich air is moved from the tropics and accumulates at higher latitudes. The low total ozone values over Antarctica in September constitute the "ozone hole" in 2009. Since the 1980s, the ozone hole in late winter and early spring represents the lowest values of total ozone that occur over all seasons and latitudes (see Q11).

motions work together to cause the observed large-scale features in total ozone, such as those seen in Figure Q4-1. Ozone changes are routinely monitored by a large group of investigators using satellite, airborne, and ground-based instruments. The continued analysis of these observations provides an important basis to quantify the contribution of human activities to ozone depletion.



What are the principal steps in stratospheric ozone depletion caused by human activities?

The initial step in the depletion of stratospheric ozone by human activities is the emission, at Earth's surface, of gases containing chlorine and bromine. Most of these gases accumulate in the lower atmosphere because they are unreactive and do not dissolve readily in rain or snow. Natural air motions transport these accumulated gases to the stratosphere, where they are converted to more reactive gases. Some of these gases then participate in reactions that destroy ozone. Finally, when air returns to the lower atmosphere, these reactive chlorine and bromine gases are removed from Earth's atmosphere by rain and snow.

Principal Steps in the Depletion of Stratospheric Ozone



Halogen source gases are emitted at Earth's surface by human activities and natural processes.



Emission, accumulation, and transport. The principal steps in stratospheric ozone depletion caused by human activities are shown in Figure Q6-1. The process begins with the emission, at Earth's surface, of source gases containing the halogens chlorine and bromine (see Q7). The halogen source gases, often referred to as ozone-depleting substances (ODSs), include manufactured chemicals released to the atmosphere in a variety of applications, such as refrigeration, air conditioning, and foam blowing. Chlorofluorocarbons (CFCs) are an important example of chlorine-containing gases. Emitted source gases accumulate in the lower atmosphere (troposphere) and are *transported* to the stratosphere by natural air motions. The accumulation occurs because most source gases are highly unreactive in the lower atmosphere. Small amounts of these gases dissolve in ocean waters. The low reactivity of these manufactured halogenated gases is one property that makes them well suited for specialized applications such as refrigeration.

Some halogen gases are emitted in substantial quantities from natural sources (see Q7). These emissions also accumulate in the troposphere, are transported to the stratosphere, and participate in ozone destruction reactions. These naturally emitted gases are part of the natural balance of ozone production and destruction that predates the large release of manufactured halogenated gases.

Figure Q6-1. Principal steps in stratospheric ozone depletion. The stratospheric ozone depletion process begins with the emission of halogen source gases by human activities and natural processes. Those emitted by human activities are also called ozone-depleting substances (ODSs). Subsequent steps are accumulation, transport, conversion, chemical reaction, and removal. Ozone depletion by halogen source gases occurs globally. Large seasonal ozone losses occur in polar regions as a result of reactions involving polar stratospheric clouds (PSCs). Ozone depletion ends when reactive halogen gases are removed by rain and snow in the troposphere and deposited on Earth's surface. **Conversion, reaction, and removal.** Halogen source gases do not react directly with ozone. Once in the stratosphere, halogen source gases are chemically *converted* to reactive halogen gases by ultraviolet radiation from the Sun (see Q8). The rate of conversion is related to the atmospheric lifetime of a gas (see Q7). Gases with longer lifetimes have slower conversion rates and survive longer in the atmosphere after emission. Lifetimes of the principal ODSs vary from 1 to 100 years (see Q7). Emitted gas molecules with atmospheric lifetimes greater than a few years circulate between the troposphere and stratosphere multiple times, on average, before conversion occurs.

The reactive gases formed from halogen source gases *react* chemically to destroy ozone in the stratosphere (see Q9). The average depletion of total ozone attributed to reactive gases is smallest in the tropics and largest at high latitudes (see Q13). In polar regions, surface reactions that occur at low temperatures on polar stratospheric clouds (PSCs) greatly increase the abundance of the most reactive chlorine gas, chlorine monoxide (ClO) (see Q10). This results in substantial ozone

destruction in polar regions in late winter and early spring (see Q11 and Q12).

After a few years, air in the stratosphere returns to the troposphere, bringing along reactive halogen gases. These gases are then *removed* from the atmosphere by rain and other precipitation or deposited on Earth's land or ocean surfaces. This removal brings to an end the destruction of ozone by chlorine and bromine atoms that were first released to the atmosphere as components of halogen source gas molecules.

Tropospheric conversion. Halogen source gases with short lifetimes (less than 1 year) undergo significant chemical conversion in the troposphere, producing reactive halogen gases and other compounds. Source gas molecules that are not converted are transported to the stratosphere. Only small portions of reactive halogen gases produced in the troposphere are transported to the stratosphere because most are removed by precipitation. Important examples of halogen gases that undergo some tropospheric removal are the hydrochlorofluorocarbons (HCFCs), methyl bromide (CH₃Br), and gases containing iodine (see Q7).

Understanding Stratospheric Ozone Depletion

Our understanding of stratospheric ozone depletion has been obtained through a combination of laboratory studies, computer models, and atmospheric observations. The wide variety of chemical reactions that occur in the stratosphere have been discovered and studied in *laboratory studies*. Chemical reactions between two gases follow well-defined physical rules. Some of these reactions occur on the surfaces of polar stratospheric clouds (PSCs) formed in the winter stratosphere. Reactions have been studied that involve many different molecules containing chlorine, bromine, fluorine, and iodine and other atmospheric constituents such as carbon, oxygen, nitrogen, and hydrogen. These studies have shown that several reactions involving chlorine and bromine directly or indirectly destroy ozone in the stratosphere.

Computer models have been used to examine the combined effect of the large group of known reactions that occur in the stratosphere. These models simulate the stratosphere by including representative chemical abundances, winds, air temperatures, and the daily and seasonal changes in sunlight. These analyses show that under certain conditions chlorine and bromine react in catalytic cycles in which one chlorine or bromine atom destroys many thousands of ozone molecules. Models are also used to simulate ozone amounts observed in previous years as a strong test of our understanding of atmospheric processes and to evaluate the importance of new reactions found in laboratory studies. The responses of ozone to possible future changes in the abundances of trace gases, temperatures, and other atmospheric parameters have been extensively explored with specialized computer models (see Q20).

Atmospheric *observations* have shown what gases are present in different regions of the stratosphere and how their abundances vary. Gas and particle abundances have been monitored over time periods spanning a daily cycle to decades. Observations show that halogen source gases and reactive halogen gases are present in the stratosphere at the amounts required to cause observed ozone depletion. Ozone and chlorine monoxide (ClO), for example, have been observed extensively with a variety of instruments. ClO is a highly reactive gas that is involved in catalytic ozone destruction cycles throughout the stratosphere (see Q9). Instruments on the ground and on satellites, balloons, and aircraft now routinely detect ozone and ClO remotely using optical and microwave signals. High-altitude aircraft and balloon instruments are also used to detect both gases locally in the stratosphere (see Q5). The observations of ozone and reactive gases made in past decades are used extensively in comparisons with computer models in order to increase confidence in our understanding of stratospheric ozone depletion.

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.



Halogen Source Gases Entering the Stratosphere in 2008

Figure Q7-1. Stratospheric source gases. 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 2008. The approximate amounts are derived from tropospheric observations of each gas in 2008. 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. HCFCs, which are substitute gases for CFCs and also controlled under the Montreal Protocol, are a small but growing fraction of chlorine-containing gases. 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 fraction of total bromine entering the stratosphere than of total chlorine. (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 (=10¹²) total air molecules.)

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 hydrochlorofluoro-carbons (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 **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 = 10^9 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.

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 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 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 (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 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 (CCl₃F) and CFC-12 (CCl₂F₂) 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 (H₂) and methane (CH₄), 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.

What are the reactive halogen gases that destroy stratospheric ozone?

Emissions from human activities and natural processes represent a large source of chlorine- and bromine-containing gases that enter the stratosphere. When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to more reactive gases containing chlorine and bromine. Some reactive gases act as chemical reservoirs that convert to form the most reactive gases, namely chlorine monoxide (ClO) and bromine monoxide (BrO). The most reactive gases participate in catalytic reactions that efficiently destroy ozone. Most volcanoes emit some reactive halogen gases that readily dissolve in water and are usually washed out of the atmosphere before they can reach the stratosphere.

Reactive gases containing the halogens chlorine and bromine lead to the chemical destruction of stratospheric ozone. Halogen-containing gases present in the stratosphere can be divided into two groups: *halogen source gases* and *reactive halogen gases* (Figure Q8-1). The source gases, which include ozone-depleting substances (ODSs), are emitted at Earth's surface by natural processes and by human activities (see Q7). Once in the stratosphere, the halogen source gases chemically convert at different rates to form the reactive halogen gases. The conversion occurs in the stratosphere for most gases instead of the troposphere because solar ultraviolet radiation (sunlight) is more intense in the stratosphere.

Reactive halogen gases. The chemical conversion of halogen source gases, which involves solar ultraviolet radiation (sunlight) and other chemical reactions, produces a number of reactive halogen gases. These reactive gases contain all of the chlorine and bromine atoms originally present in the source gases. The most important reactive chlorine- and bromine-containing gases that form in the stratosphere are shown in Figure Q8-1. Throughout the stratosphere, the most abundant are typically hydrogen chloride (HCl) and chlorine nitrate (ClONO₂). These two gases are considered important *reservoir* gases because, while they don't react directly with ozone, they can be converted to the *most reactive* forms that



Figure Q8-1. Conversion of halogen source gases. Halogen source gases containing chlorine and bromine are chemically converted to reactive halogen gases primarily in the stratosphere. The conversion requires solar ultraviolet radiation and a few chemical reactions. The shorter-lived gases undergo some conversion in the troposphere. The reactive halogen gases contain all the chlorine and bromine originally present in the source gases before conversion. The reactive gases can be grouped into the reservoir gases, which do not directly destroy ozone, and the most reactive gases, which participate in ozone destruction cycles (see Q9). A principal reactive gas, CIO, is formed by reactions of the reservoir gases HCl and CIONO₂ that occur on the surfaces of liquid and solid polar stratospheric clouds (PSCs) (see Q10).

do chemically destroy ozone. The most reactive forms are chlorine monoxide (ClO) and bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). A large fraction of available reactive bromine is generally in the form of BrO, whereas usually only a small fraction of reactive chlorine is in the form of ClO. The special conditions that occur in the polar regions in winter cause the reservoir gases ClONO₂ and HCl to undergo nearly complete conversion to ClO in reactions on polar stratospheric clouds (PSCs) (see Q10).

Reactive chlorine at midlatitudes. Reactive chlorine gases have been observed extensively in the stratosphere with both local and remote measurement techniques. The measurements from space displayed in Figure Q8-2 are representative of how the amounts of chlorine-containing gases change between the surface and the upper stratosphere at midlatitudes. Available chlorine (see red line in Figure Q8-2) is the sum of chlorine contained in halogen source gases and the reactive gases (e.g., HCl, ClONO₂, ClO). Available chlorine is constant to within about 15 percent from the surface to 47 kilometers (31 miles) altitude. In the troposphere, available chlorine is contained almost entirely in the source gases become a smaller fraction of available chlorine as they are converted to the reactive chlorine gases. At the highest altitudes, available chlorine is all in the form of the reactive chlorine gases.

In the altitude range of the ozone layer at midlatitudes, as shown in Figure Q8-2, the reactive reservoir gases HCl and ClONO_2 account for most of the available chlorine. ClO, the most reactive gas in ozone depletion, is a small fraction of available chlorine. The low abundance of ClO limits the amount of ozone destruction that occurs outside of polar regions.

Reactive chlorine in polar regions. Reactive chlorine gases in polar regions undergo large changes between the fall and late winter. Meteorological and chemical conditions in both polar regions are now routinely observed from space in all seasons. Fall and winter conditions over the Antarctic are contrasted in Figure Q8-3 using seasonal observations made near the center of the ozone layer (about 18 km (11.3 miles)) (see Figure Q12-3).

In fall (May), ozone values are high over the entire Antarctic continent and beyond. Temperatures are mid-range, HCl and nitric acid (HNO₃) are high, and ClO is very low. High HCl indicates that substantial conversion of halogen source gases has occurred in the stratosphere. In the past decades, HCl and ClONO₂ reactive reservoir gases have increased substantially in the stratosphere following increased emissions of halogen source gases. HNO₃ is an abundant, naturally



Figure Q8-2. Reactive chlorine gas observations. The abundances of chlorine source gases and reactive chlorine gases as measured from space in 1994 are displayed with altitude for a midlatitude location. In the troposphere (below about 10 kilometers), all chlorine is contained in the source gases. In the stratosphere, the abundances of reactive chlorine gases increase with altitude as the amounts of chlorine source gases decline. This is a conseguence of chemical reactions initiated by solar ultraviolet radiation that convert source gases to reactive gases (see Figure Q8-1). The principal reactive chlorine gases formed are HCl, CIONO₂, and CIO. Summing the source gases with the reactive gases gives "Available chlorine," which is nearly constant with altitude up to 47 km. In the ozone layer (18-35 km), chlorine source gases are still present and HCI and CIONO₂ are the most abundant reactive chlorine gases. (The unit "parts per trillion" is defined in the caption of Figure Q7-1.)



Large ozone depletion in late winter (15 September 2008) at 18-km altitude



Figure Q8-3. Chemical conditions in the ozone layer over Antarctica. Observations of the chemical conditions in the Antarctic region highlight the changes associated with severe ozone depletion that forms the ozone hole. Satellite instruments now routinely monitor ozone, reactive chlorine gases, and temperatures in the global stratosphere. Results are shown here for fall (May) and late winter (September) seasons in Antarctic winter for a narrow altitude region near 18 kilometers (11.2 miles) within the ozone layer (see Figure Q12-3). Ozone has normal high values in fall before the onset of ozone destruction reactions causes wide spread depletion by late winter. High ozone is accompanied by moderate temperatures, normal high values of HCl and HNO₃, and normal very low CIO amounts. When CIO is not enhanced, significant ozone destruction from ozone-depleting substances does not occur. Chemical conditions are quite different in late winter when ozone undergoes severe depletion. Temperatures are much lower, HCI has been converted to CIO, the most reactive chlorine gas, and HNO₃ has been removed by the gravitational settling of PSC particles. CIO values closely surrounding the South Pole are low in September because CIO formation requires sunlight, which is still gradually returning to the highest latitudes. The high CIO values in late winter last for 1 to 2 months, cover an area that at times exceeds that of the Antarctic continent, and efficiently destroy ozone in sunlit regions in late winter/early spring. Ozone typically reaches its minimum values in early to mid-October (see Q12). Note that the first and last colors in the color bar represent values outside the indicated range of values. (The unit "parts per billion," abbreviated "ppb," is used here as a measure of the relative abundance of a gas in air: 1 part per billion equals the presence of one molecule of a gas per billion (=10⁹) total air molecules (compare to ppt in Figure Q7-1)).

occurring stratospheric compound that moderates ozone destruction chemistry and also condenses to help form polar stratospheric clouds (PSCs) (see Q10). Low ClO indicates that little conversion of the reactive reservoirs occurs in the fall, thereby limiting catalytic ozone destruction.

By late winter (September), ozone amounts reflect substantial depletion at 18-km altitude over an area larger than the Antarctic continent. Depletion throughout much of the altitude range of the ozone layer created the 2008 ozone hole shown in Figure Q11-3 (see altitude profile in Figure Q12-3). The associated meteorological and chemical conditions in late winter are very different from those found in fall: very low temperatures, very low HCl and HNO₃, and very high ClO. Low stratospheric temperatures are characteristic of winter when solar heating is reduced. Low HCl and high ClO reflect the conversion of the reactive halogen reservoir compounds, HCl and ClONO₂, to the most reactive chlorine form, ClO. This conversion occurs selectively in winter on PSCs and other stratospheric particles, which form at the very low temperatures (see Q10). Low HNO₃ is indicative of its condensation to form PSCs, some of which subsequently move to lower altitudes through gravitational settling. High ClO abundances generally cause ozone depletion to continue in the Antarctic region until mid-October (spring), when the lowest ozone values usually are observed (see Q11). As temperatures rise at the end of the winter, halting further PSC formation, ClO is converted back into the reactive reservoir species HCl and ClONO₂ (see Q10), and ozone destruction is curtailed.

Similar though less dramatic changes in meteorological and chemical conditions are also observed between fall and winter in the Arctic, where winter ozone depletion is less severe than in the Antarctic.

Reactive bromine observations. Fewer measurements are available for reactive bromine gases in the lower stratosphere than for reactive chlorine, in part because of the lower abundance of bromine. The most widely observed bromine gas is bromine monoxide (BrO), which can be observed from space. Estimates of reactive bromine abundances in the stratosphere are larger than expected from the conversion of the halons and methyl bromide source gases, suggesting that the contribution of the very short-lived bromine-containing gases to reactive bromine must also be significant (see Q7).

Other sources. Other emission sources of reactive halogen gases exist that are associated with natural processes and human activities. Most emissions become trapped in the lower atmosphere when dissolved in water, and ultimately are returned to Earth's surface before they can reach the stratosphere. Volcanoes are an important episodic source of reactive halogen gases (e.g., HCl) that do not reach the stratosphere in appreciable quantities (see Q14). Other examples include reactive chlorine produced by evaporation of ocean spray. Sea salt products dissolve in water and are removed in the lower atmosphere. Solid rocket motors, such as those used on the Space Shuttle, release reactive chlorine gases directly into the troposphere and stratosphere. At current launch rates, the emitted quantities are very small in comparison with halogen emissions from other human activities.

What are the chlorine and bromine reactions that destroy stratospheric ozone?

Reactive gases containing chlorine and bromine destroy stratospheric ozone in "catalytic" cycles made up of two or more separate reactions. As a result, a single chlorine or bromine atom can destroy many thousands of ozone molecules before it leaves the stratosphere. In this way, a small amount of reactive chlorine or bromine has a large impact on the ozone layer. A special situation develops in polar regions in the late winter/early spring season where large enhancements in the abundance of the most reactive gas, chlorine monoxide, leads to severe ozone depletion.

Stratospheric ozone is destroyed by reactions involving *reactive halogen gases*, which are produced in the chemical conversion of *halogen source gases* (see Figure Q8-1). The most reactive of these gases are chlorine monoxide (ClO), bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). These gases participate in three principal reaction cycles that destroy ozone.

Cycle 1. Ozone destruction Cycle 1 is illustrated in Figure Q9-1. The cycle is made up of two basic reactions: $Cl + O_3$ and ClO + O. The net result of Cycle 1 is to convert one ozone molecule and one oxygen atom into two oxygen molecules. In each cycle, chlorine acts as a *catalyst* because ClO and Cl react and are re-formed. In this way, one Cl atom participates in many cycles, destroying many ozone molecules. For typical stratospheric conditions at middle or low latitudes, a single chlorine atom can destroy hundreds of ozone molecules

before it happens to react with another gas, breaking the catalytic cycle, and up to tens of thousands of ozone molecules during the total time of its stay in the stratosphere.

Polar Cycles 2 and 3. The abundance of ClO is greatly increased in polar regions during winter as a result of reactions on the surfaces of polar stratospheric clouds (PSCs) (see Q8 and Q10). Cycles 2 and 3 (see Figure Q9-2) become the dominant reaction mechanisms for polar ozone loss because of the high abundances of ClO and the relatively low abundance of atomic oxygen (which limits the rate of ozone loss by Cycle 1). Cycle 2 begins with the self-reaction of ClO. Cycle 3, which begins with the reaction of ClO with BrO, has two reaction pathways to produce either Cl and Br or BrCl. The net result of both cycles is to destroy two ozone molecules and create three oxygen molecules. Cycles 2 and 3 account for most of the ozone loss observed in the Arctic and Antarctic stratospheres



Figure Q9-1. Ozone destruction Cycle 1. The destruction of ozone in Cycle 1 involves two separate chemical reactions. The net or overall reaction is that of atomic oxygen with ozone, forming two oxygen molecules. The cycle can be considered to begin with either CIO or CI. When starting with CIO, the first reaction is CIO with O to form CI. Then, Cl reacts with ozone and re-forms ClO, consuming ozone in the process. The cycle then begins again with another reaction of CIO with O. Chlorine is considered a catalyst for ozone destruction because CI and CIO are re-formed each time the reaction cycle is completed, and ozone is simply removed. Atomic oxygen (O) is formed when solar ultraviolet radiation (sunlight) reacts with ozone and oxygen molecules. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where solar ultraviolet radiation is most intense.

Ozone Destruction Cycles in Polar Regions

Ozone Destruction Cycles in Polar Regions

Cycle 3
$CIO + BrO \rightarrow CI + Br + O_2$
$\operatorname{CIO} + \operatorname{BrO} \to \operatorname{BrCI} + \operatorname{O}_2$
$\operatorname{Or} \left(\operatorname{BrCI} + \operatorname{sunlight} \rightarrow \operatorname{CI} + \operatorname{Br} \right)$
$CI + O_3 \rightarrow CIO + O_2$
$Br + O_3 \rightarrow BrO + O_2$
Net: $2O_3 \rightarrow 3O_2$

Figure Q9-2. Polar ozone destruction Cycles 2 and 3. Significant destruction of ozone occurs in polar regions because CIO abundances reach large values. In this case, the cycles initiated by the reaction of CIO with another CIO (Cycle 2) or the reaction of CIO with BrO (Cycle 3) efficiently destroy ozone. The net reaction in both cases is two ozone molecules forming three oxygen molecules. The reaction of CIO with BrO has two pathways to form the CI and Br product gases. Ozone destruction Cycles 2 and 3 are catalytic, as illustrated for Cycle 1 in Figure Q9-1, because chlorine and bromine gases react and are re-formed each time the reaction cycle is completed. Visible sunlight is required to complete each cycle and to help form and maintain CIO abundances. During polar night and other periods of darkness, ozone cannot be destroyed by these reactions.

in the late winter/early spring season (see Q11 and Q12). At high ClO abundances, the rate of polar ozone destruction can reach 2 to 3% per day in late winter/early spring.

Sunlight requirement. Sunlight is required to complete and maintain Cycles 1 through 3. Cycle 1 requires sunlight because atomic oxygen is formed only with solar ultraviolet radiation. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where solar ultraviolet radiation (sunlight) is most intense.

Cycles 2 and 3 require visible sunlight to complete the reaction cycles and to maintain ClO abundances. In the continuous darkness of winter in the polar stratosphere, reaction Cycles 2 and 3 cannot occur. It is only in late winter/early spring when sunlight returns to the polar regions that these cycles can occur. Therefore, the greatest destruction of ozone occurs in the partially to fully sunlit periods after midwinter in the polar stratosphere. The visible sunlight needed in Cycles 2 and 3 is not sufficient to form ozone because this process requires solar ultraviolet radiation (see Q1). In the stratosphere in the late winter/early spring period, solar ultraviolet radiation is weak at low Sun angles. As a result, ozone destruction by Cycles 2 and 3 in the sunlit winter stratosphere greatly exceeds ozone production.

Other reactions. Global ozone abundances are controlled by many reactions that both produce and destroy ozone (see Q2). Chlorine and bromine catalytic reactions are but one group of ozone destruction reactions. Reactive hydrogen and reactive nitrogen gases, for example, are involved in other catalytic ozone-destruction cycles that also occur in the stratosphere. These reactions occur naturally in the stratosphere and their importance has not been as strongly influenced by human activities as have reactions involving halogens. The sources of reactive hydrogen and nitrogen gases are the naturally occurring gases methane (CH₄) and nitrous oxide (N_2O) , respectively. The importance of reactive hydrogen and nitrogen gases relative to reactive halogen gases is expected to increase in the future, because the atmospheric abundances of the reactive halogen gases are decreasing as a result of the Montreal Protocol, while CH4 and N2O abundances are projected to increase substantially due to human activities.

Replacing Lost Ozone in the Stratosphere

The idea is sometimes put forth that humans could compensate for lost global stratospheric ozone by replacing it. Ozone could be manufactured, stored, transported to the stratosphere, and released in depleted regions. Unfortunately, the idea has substantial practical limitations.

Ozone amounts in the stratosphere reflect a continual *balance* between chemical production and destruction (see Q2). The addition of chlorine and bromine to the stratosphere from human activities has changed the natural balance by increasing ozone destruction and, thereby, lowering stratospheric ozone amounts. Chlorine and bromine destroy ozone in catalytic reactions that allow each atom to destroy many thousands of ozone molecules (see Q9). A one-time injection of manufactured ozone to the stratosphere would not restore the natural balance because the added ozone would be destroyed in the same chemical reactions with chlorine and bromine within about a year. Thus, ozone additions would need to be large and continuous as long as stratospheric chlorine and bromine amounts remained enhanced above natural amounts, a condition expected to persist for several decades (see Q16). Continuous replacement for decades would pose unprecedented technical and resource challenges that will likely be unacceptable to decision makers in the international community.

Specific technical difficulties in replacing stratospheric ozone are the large amounts of ozone required and the delivery method. The total amount of atmospheric ozone is approximately 3,000 megatons (1 megaton = 1 billion kilograms) with most residing in the stratosphere. Compensating for the average global ozone loss, currently about 3%, would require 90 megatons of ozone to be distributed regularly throughout the stratosphere many kilometers above Earth's surface. The energy required to produce this amount of ozone would be a significant fraction of the electrical power generated annually in the United States, for example, which is now approximately 4 trillion kilowatt hours. Processing and storing requirements for ozone, which is explosive and toxic in large quantities, would increase the energy requirement. In addition, methods suitable to deliver and distribute large amounts of ozone to the stratosphere have not been developed. Concerns for a global delivery system would include further significant energy use and unforeseen environmental consequences.

How large is the depletion of the global ozone layer?

Depletion of the global ozone layer began gradually in the 1980s and reached a maximum of about 5% in the early 1990s. The depletion has lessened since then and now is about 3.5% averaged over the globe. The average depletion exceeds the natural year-to-year variations of global total ozone. The ozone loss is very small near the equator and increases with latitude toward the poles. The larger polar depletion is attributed to the late winter/early spring ozone destruction that occurs there each year.

Global total ozone has decreased beginning in the 1980s (see Figure Q13-1). The decreases have occurred in the stratospheric ozone layer where most ozone resides (see Figure Q1-2). In the early 1990s, the depletion of global total ozone reached a maximum of about 5% below the 1964–1980 average. The depletion has lessened since then and now averages about 3.5% for 2006–2009. The observations shown in Figure Q13-1 have been smoothed to remove regular ozone changes that are due to natural seasonal and solar effects (see Q14). The depleted amounts are larger than the remaining natural variations in global total ozone amounts.

The observed global ozone depletion in the last three decades is attributable to increases in reactive halogen gases in the stratosphere. The lowest global total ozone values since 1980 have occurred in the years following the eruption of Mt. Pinatubo in 1991, which temporarily increased the number of sulfuric acid-containing particles throughout the stratosphere. These particles significantly increased the effective-ness of reactive halogen gases in destroying ozone (see Q14) and, thereby, increased global ozone depletion by 1–2% for several years following the eruption.

Polar regions. Observed total ozone depletion varies significantly with latitude on the globe (see Figure Q13-1). The largest reductions have occurred at high southern latitudes as a result of the severe ozone loss over Antarctica each late winter/early spring period. The next largest losses are observed in the high latitudes of the Northern Hemisphere, caused in part by winter losses over the Arctic. Although the depletion in polar regions is larger than at lower latitudes, the influence of polar regions on global ozone is limited by their small geographical area. Latitudes above 60° account for only about 13% of Earth's surface.

Midlatitude regions. Ozone depletion is also observed at the midlatitudes spanning the region between equatorial and polar latitudes. In comparison with the 1964–1980 averages, total ozone averaged for 2005–2009 is about 3.5% lower in northern midlatitudes (35°N–60°N) and about 6% lower at southern midlatitudes (35°S–60°S). Midlatitude depletion has two contributing factors. First, ozone-depleted air over both polar regions is dispersed away from the poles during and after each winter/spring period, thereby reducing average ozone at nonpolar latitudes. Second, chemical destruction occurring at midlatitudes contributes to observed depletion in these regions. This contribution is much smaller than in polar regions because the amounts of reactive halogen gases are lower and a seasonal increase of the most reactive halogen gases, such as the increase in ClO in Antarctic late winter (see Figure Q8-3), does not occur in midlatitude regions.

Tropical region. There has been little or no depletion of total ozone in the tropics (20°N–20°S latitude). In this region of the lower stratosphere, air has only recently (less than 18 months) been transported from the lower atmosphere (troposphere). As a result, the conversion of ozone-depleting substances (ODSs) to reactive halogen gases is very small. With so little reactive halogen amounts, total ozone depletion in this region is also very small. In addition, ozone production is high in the tropical stratosphere because average solar ultraviolet radiation is highest in the tropics. In contrast, stratospheric air in polar regions has been in the stratosphere for an average of 4 to 7 years, allowing time for significant conversion of ODSs to reactive halogen gases. The systematic differences in the age of stratospheric air are a well-understood consequence of the large-scale atmospheric transport: air enters the stratosphere in the tropics, moves poleward into both hemispheres, and then descends and ultimately returns to the lower atmosphere.

Recovery of global ozone. Global ozone is no longer declining as it was in the 1980s and early 1990s because ODSs are no longer increasing in the atmosphere (see Q16). During recovery from ODSs, global total ozone is expected to reach 1980 and earlier values in the coming decades. The recovery process depends on the slow removal of ODSs from



the stratosphere following emission reductions. Future changes in climate parameters will also influence ozone. The global ozone increases observed in the last 20 years cannot be attributed solely to reductions in ODSs that began in the

Figure Q13-1. Global total ozone changes. Satellite observations show depletion of global total ozone beginning in the 1980s. The top panel compares annual averages of global ozone with the average from the period 1964 to 1980 before the ozone hole appeared. Seasonal and solar effects have been removed from the observational data set. On average, global ozone decreased each year between 1980 and 1990. The depletion worsened for a few years after 1991 due to the effect of volcanic aerosol from the Mt. Pinatubo eruption. Average global ozone for 2005-2009 is about 3.5% below the 1964-to-1980 average. The bottom panel shows how the 2005-2009 depletion varies with latitude over the globe. The largest decreases have occurred at high latitudes in both hemispheres because of the large winter/spring depletion in polar regions. The losses in the Southern Hemisphere are greater than those in the Northern Hemisphere because of the Antarctic ozone hole. Long-term changes in the tropics are much smaller because reactive halogen gases are less abundant in the tropical lower stratosphere than at mid or high latitudes and ozone production rates are greater.

1990s, because global ozone also responded strongly to the Mt. Pinatubo eruption. The projections of long-term changes in total ozone for different regions of the globe are described in Q20.

Do changes in the Sun and volcanic eruptions affect the ozone layer?

Yes, factors such as changes in solar radiation, as well as the formation of stratospheric particles after volcanic eruptions, do influence the ozone layer. However, neither factor can explain the average decreases observed in global total ozone over the last three decades. If large volcanic eruptions occur in the coming decades, ozone depletion will increase for several years afterwards.

hanges in solar radiation and increases in stratospheric particles from volcanic eruptions both affect the abundance of stratospheric ozone. Over the last three decades, global total ozone has decreased over the globe and is now about 3.5% below pre-1980 values (see Q13). The depletion is attributed to changes in reactive halogen gases, which are represented by changes in equivalent effective stratospheric chlorine (EESC). EESC values account for stratospheric chlorine and bromine abundances and their different effectiveness in destroying ozone (see definition in Q16). A comparison of the smooth year-to-year changes in ozone and EESC shows that the quantities are inversely related to each other, with ozone first decreasing while EESC increases (see Figure Q14-1). After the mid-1990s, the annual changes in both quantities are sharply reduced. Changes in solar output and volcanic activity do not show such smooth long-term changes, as discussed below, and therefore are not considered to be the cause of long-term global ozone depletion.

Total ozone and solar changes. The formation of stratospheric ozone is initiated by ultraviolet (UV) radiation coming from the Sun (see Figure Q2-1). As a result, an increase in the Sun's radiation output increases the amount of ozone in Earth's atmosphere. The Sun's radiation output and sunspot number vary over the well-documented 11-year solar cycle. Observations over several solar cycles since the 1960s show that global total ozone levels vary by 1 to 2% between the maximum and minimum of a typical cycle. Changes in incoming solar radiation at a wavelength of 10.7 cm are often used as a surrogate for changes in solar output at UV wavelengths. The long-term changes in the 10.7-cm output in Figure Q14-1 clearly show alternating periods of maximum and minimum values in total solar output separated by about 5–6 years. If changes in solar output were the cause of global ozone depletion, a gradually decreasing output would have been observed around 1980 or earlier, slowing sharply in the mid-1990s. Since such a decrease was not observed, nor is expected based on longer-term solar observations, the longterm decreases in global ozone cannot result from changes in solar output alone. Most analyses presented in this and previous international scientific assessments quantitatively account for the influence of the 11-year solar cycle on longterm variations in ozone.

Total ozone and past volcanoes. Explosive volcanic eruptions inject sulfur gases directly into the stratosphere, causing new sulfate particles to be formed. The particles initially form in the stratosphere downwind of the volcano and then spread throughout the hemisphere or globally as air is transported by stratospheric winds. One method of detecting the presence of volcanic particles in the stratosphere uses observations of the transmission of solar radiation through the atmosphere (see Figure Q14-1). When large amounts of new particles are formed in the stratosphere over an extensive region, solar transmission is measurably reduced. The eruptions of Mt. Agung (1963), El Chichón (1982), and Mt. Pinatubo (1991) are the most recent examples of sulfur injections that temporarily reduced solar transmission.

Laboratory measurements and stratospheric observations have shown that chemical reactions on the surfaces of volcanically produced particles can increase ozone destruction by increasing the amounts of the highly reactive chlorine gas chlorine monoxide (ClO). The ozone response depends on the total abundance of EESC after the eruption (see Q16). At times of relatively low EESC, such as the early 1980s, ozone is not very sensitive to stratospheric injection of volcanic sulfate particles. At times of higher EESC amounts, such as from 1980 to the present, global ozone is expected to decrease significantly following large explosive eruptions. The most recent large eruption was that of Mt. Pinatubo, which resulted in up to a 10-fold increase in the number of particles available for surface reactions. Both El Chichón and Mt. Pinatubo increased global ozone depletion for a few years (see Figure Q14-1). EESC was too low for ozone depletion to occur after the Mt. Agung eruption in 1963. The effect on ozone diminishes during the years following an eruption as volcanic particles are gradually

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The Solar Cycle, Volcanic Eruptions, Global Ozone, and Equivalent Effective Stratospheric Chlorine

Figure Q14-1. Solar changes and volcanoes. Global total ozone values have decreased beginning in the early 1980s. Ozone values shown are the 3-month averages without corrections for solar or volcanic effects and annual averages corrected for seasonal and solar effects (from Figure Q13-1). These long-term ozone decreases are primarily attributable to equivalent effective stratospheric chlorine (EESC), which has increased over the same time period. Since the mid-1990s, changes in both quantities have slowed. Incoming solar radiation varies on a well-recognized 11-year cycle related to sunspot activity. The amount of incoming solar radiation at a wavelength of 10.7 cm is often used as a surrogate for incoming solar radiation at UV wavelengths that produce stratospheric ozone. The 10.7-cm radiation values clearly show the recent periods of solar maximum and minimum. A comparison of the solar radiation and ozone changes strongly indicates that the cyclic changes in solar output alone cannot account for the long-term decrease in total ozone. Following large volcanic eruptions, transmission of solar radiation to Earth's surface is reduced by the large number of new sulfur-containing particles formed in the stratosphere. The three large volcanic eruptions that occurred between 1960 and 2010 temporarily decreased solar transmission as measured in Hawaii. Volcanic particles increase ozone depletion only for a few years before they are removed from the stratosphere by natural processes. As a consequence, the two most recent volcanic eruptions cannot be the cause of the continuous longterm decrease found in global total ozone.

removed from the stratosphere by natural air circulation. As particles are removed, solar transmission is restored. Based on the short residence time of volcanic particles in the stratosphere, the two large eruptions in the past three decades cannot account directly for the continuous long-term decreases in global total ozone observed over the same period.

Reactive chlorine from volcanoes. Explosive volcanic plumes generally contain large quantities of reactive chlorine

in the form of hydrogen chloride (HCl). HCl is a reactive halogen gas that can be converted to ClO, which rapidly destroys ozone (see Figure Q8-3). The plumes also contain a considerable amount of water vapor, which forms rainwater and ice in the rising fresh plume. Rainwater and ice efficiently scavenge and remove HCl while it is still in the lower atmosphere (troposphere). As a result, most of the HCl in explosive volcanic plumes does not enter the stratosphere. After recent explosive eruptions, observations of HCl in the stratosphere have confirmed that increases are small compared with the total amount of chlorine in the stratosphere from other sources.

Antarctic volcanoes. Volcanoes on the Antarctic continent are of special interest due to their proximity to the Antarctic ozone hole. An explosive eruption could in principle inject volcanic aerosol and small amounts of HCl directly into the stratosphere over Antarctica, which could lead to ozone depletion. However, to be a possible cause of the annually recurring ozone hole beginning in the early 1980s, explosive Antarctic eruptions would need to have occurred at least every few years to maintain volcanic emissions in the stratosphere. This is not the case. Only the Mt. Erebus volcano is currently active in Antarctica. No explosive eruptions of Mt. Erebus or any other Antarctic volcano have occurred since 1980. Therefore, explosive volcanic eruptions in the last three decades have not caused the Antarctic ozone hole and, as noted above, have not been sufficient to cause the long-term depletion of global total ozone.

Total ozone and future volcanoes. Observations and atmospheric models indicate that the record-low ozone levels observed in 1992-1993 resulted from the large number of particles produced by the Mt. Pinatubo eruption, combined with the relatively large amounts of EESC present in the stratosphere in the early 1990s. If the Mt. Pinatubo eruption had occurred before 1980, changes to global ozone would have been much smaller than observed in 1992–1993 because EESC values were much lower. EESC values will remain substantial in the early decades of the 21st century even as ODSs decline globally, with 1980 values reached by about 2050 (see Figures Q16-1 and Q20-2). Large volcanic eruptions in the intervening years will cause more ozone depletion. If an explosive eruption larger than Mt. Pinatubo were to occur, peak ozone losses could be larger than previously observed and substantial ozone losses could persist for longer time periods. As halogen gas abundances gradually decline to 1980 values, the effect of volcanic eruptions on ozone will lessen.

Are there controls on the production of ozone-depleting substances?

Yes, the production and consumption of ozone-depleting substances are controlled under a 1987 international agreement known as the "Montreal Protocol on Substances that Deplete the Ozone Layer" and by its subsequent Amendments and Adjustments. The Protocol, now ratified by all 196 United Nations members, establishes legally binding controls on national production and consumption of ozone-depleting substances (ODSs). Production and consumption of all principal ODSs by developed and developing nations will be almost completely phased out before the middle of the 21st century.

Montreal Protocol. In 1985, a treaty called the Vienna Convention for the Protection of the Ozone Layer was signed by 20 nations in Vienna. The signing nations agreed to take appropriate measures to protect the ozone layer from human activities. The Vienna Convention was a framework agreement that supported research, exchange of information, and future protocols. In response to growing concern, the Montreal Protocol on Substances that Deplete the Ozone Layer was signed in 1987 and, following sufficient country ratification, entered into force in 1989. The Protocol has been successful in establishing legally binding controls for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion. Halogen source gases containing chlorine and bromine controlled under the Montreal Protocol are referred to as ozonedepleting substances (ODSs). National consumption of an ODS is defined as the amount that production and imports of the substance exceed its export to other nations. The Protocol provisions are structured for developed countries to act first and for developing countries to follow with some financial assistance. In 2010, the Montreal Protocol became the first international treaty to achieve universal ratification by all 196 United Nations members.

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Amendments and Adjustments. As the scientific basis of ozone depletion became more certain after 1987 and substitutes and alternatives became available to replace ODSs, the Montreal Protocol was strengthened with Amendments and Adjustments. Each Amendment is named after the city in which the meeting of the Parties to the Montreal Protocol took place and by the year of the meeting. The timeline in Figure Q0-1 shows some of the major decisions that have been adopted in the last two decades. These decisions have put additional ODSs under control, accelerated existing control measures, and prescribed phase-out dates for the production and consumption of certain gases. The initial Protocol called for a 50% reduction in chlorofluorocarbon (CFC) production and a freeze on halon production. The 1990 London Amendment called for a phase-out of the production and consumption of the most damaging ODSs in developed nations by 2000 and in developing nations by 2010. The 1992 Copenhagen Amendment accelerated the phase-out date to 1996 in developed nations. Further controls on ODSs were agreed upon in later meetings in Vienna (1995), Montreal (1997, 2007), and Beijing (1999).

Influence of the Montreal Protocol. Montreal Protocol controls are based on several factors that are considered separately for each ODS. The factors include (1) the effectiveness in depleting ozone in comparison with other substances (see Ozone Depletion Potential (ODP) in Q18), (2) the availability of suitable substitutes for domestic and industrial use, and (3) the potential impact of controls on developing nations. The influence of Montreal Protocol provisions on stratospheric ODS abundances can be demonstrated with long-term changes in equivalent effective stratospheric chlorine (EESC). Calculations of EESC combine the amounts of chlorine and bromine present in surface air to form a measure of the potential for ozone destruction in a particular stratospheric region on an annual basis (see definition in Q16). The long-term changes in EESC at midlatitudes are shown in Figure Q15-1 for several cases:

▶ No Protocol. Without the Montreal Protocol the production, use, and emissions of CFCs and other ozone-depleting substances is expected to have increased after 1987 with an annual growth rate of about 3% (business-as-usual scenario). As a result, EESC is projected to have increased nearly 10-fold by the mid-2050s compared with the 1980 value. Computer models of the atmosphere indicate that such high EESC values would have at least doubled global total ozone depletion between 1990 and 2010 and increased it far beyond that by midcentury. As a result, harm-



ful UV-B radiation would have increased substantially at Earth's surface, causing a global rise in skin cancer and cataract cases (see Q17).

► Montreal Protocol provisions. International compliance with only the 1987 provisions of the Montreal Protocol and the later 1990 London Amendment would have substantially slowed the projected growth of EESC. Not until the 1992 Copenhagen Amendments and Adjustments did the Protocol projections show a *decrease* in future EESC values. The provisions became more stringent with the Amendments and Adjustments adopted in Beijing in 1999 and Montreal in 1997 and 2007. Now, with full compliance to the Protocol, most ODSs will be almost completely phased out, with some exemptions for critical uses (see Q16). Global EESC is slowly decaying from its peak value in the late 1990s and is expected to reach 1980 values in the mid-21st century. The success of the Montreal Protocol to date is demonstrated by the decline in ODP-weighted emissions of ODSs shown in Figure Q0-1. Total emissions peaked in 1988 at values about 10-fold higher than natural Figure Q15-1. Effect of the Montreal Protocol. The objective of the Montreal Protocol is the protection of the ozone layer through control of the global production and consumption of ODSs. Projections of the future abundances of ODSs expressed as equivalent effective stratospheric chlorine (EESC) values (see Q16) are shown separately for the midlatitude stratosphere for (1) no Protocol provisions, (2) the provisions of the original 1987 Montreal Protocol and some of its subsequent Amendments and Adjustments, and (3) zero emissions of ODSs starting in 2011. The city names and years indicate where and when changes to the original 1987 Protocol provisions were agreed upon (see Figure Q0-1). EESC is a relative measure of the potential for stratospheric ozone depletion that combines the contributions of chlorine and bromine from ODS surface observations (see Q16). Without the Protocol, EESC values are projected to have increased significantly in the 21st century. Only with the Copenhagen (1992) and subsequent Amendments and Adjustments did projected EESC values show a long-term decrease.

emissions. Between 1988 and 2010, ODS emissions from human activities have decreased by over 80%.

► Zero emissions. EESC values in the coming decades will be influenced by (1) the slow natural removal of ODSs still present in the atmosphere, (2) emissions from continued production and use of ODSs, and (3) emissions from currently existing *banks* containing a variety of ODSs. ODS banks are associated with applications that involve longterm containment of halogen gases. Examples are CFCs in refrigeration equipment and insulating foams, and halons in fire-fighting equipment. New emissions are projected based on continued production and consumption of ODSs, particularly in developing nations, under existing Protocol provisions.

The zero-emissions case demonstrates the EESC values that would occur if it were possible to set all ODS emissions to zero beginning in 2011. This would eliminate the contributions from new production and bank emissions. Significant differences from the Montreal 2007 projections are evident in the first decades following 2011 because the phase-out of all ODS production under the Protocol is not yet complete and bank emissions are substantial. Zero emissions would bring forward the return of EESC to 1980 levels by about 13 years.

HCFC substitute gases. The Montreal Protocol provides for the use of hydrochlorofluorocarbons (HCFCs) as transitional, short-term substitute compounds for ODSs with higher ODPs, such as CFC-12. HCFCs are used for refrigeration, in making insulating foams, and as solvents, all of which were primary uses of CFCs. HCFCs are generally more reactive in the troposphere than other ODSs because they contain hydrogen (H) in addition to chlorine, fluorine, and carbon. HCFCs are 88 to 98% less effective than CFC-12 in depleting stratospheric ozone because their chemical removal occurs primarily in the troposphere (see ODPs in Table Q7-1). This removal protects stratospheric ozone from most of the halogen content of HCFC emissions. In contrast, CFCs and many other ODSs release all of their halogen content in the stratosphere because they are chemically inert in the troposphere (see Q6).

Under the provisions of the Montreal Protocol, developed and developing countries may continue to use HCFCs as ODS substitutes in the coming decades before they are ultimately phased out. In the most recent Adjustment to the Protocol (Montreal 2007), the phase-out of HCFCs for all Parties was accelerated so that it will be complete in 2030, a decade earlier than in previous provisions. In adopting this decision, the Parties reduced the contribution of HCFC emissions to both long-term ozone depletion and future climate forcing (see Q18 and Q19).

HFC substitute gases. Hydrofluorocarbons (HFCs) are used as long-term substitute compounds for CFCs, HCFCs, and other ODSs. HFCs contain hydrogen, fluorine, and carbon. HFCs do not contribute to ozone depletion because they contain no chlorine, bromine, or iodine. As a consequence, HFCs are not ODSs and are not subject to the provisions of the Montreal Protocol. HFCs and all ODSs are radiatively active gases that contribute to human-induced climate change based on their accumulation in the atmosphere (see Q18). HFCs are included in the basket of gases being controlled by the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC). The Kyoto Protocol is an international treaty designed to protect climate by controlling emissions of HFCs, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆). HFC emissions are expected to grow substantially in coming decades as the demand for their use as substitute gases and in new applications increases in developed and developing countries. The climate change contribution from future HFC emissions will be minimized if HFCs with very low Global Warming Potentials (GWPs) (less than 100) are chosen to meet the growing demand (see Q18).

Has the Montreal Protocol been successful in reducing ozone-depleting substances in the atmosphere?

Yes, as a result of the Montreal Protocol, the overall abundance of ozone-depleting substances (ODSs) in the atmosphere has been decreasing for about a decade. If the nations of the world continue to comply with the provisions of the Montreal Protocol, the decrease will continue throughout the 21st century. Those gases that are still increasing in the atmosphere, such as halon-1301 and HCFC-22, will begin to decrease in the coming decades if compliance with the Protocol continues. Only after midcentury will the effective abundance of ODSs fall to values that were present before the Antarctic ozone hole was observed in the early 1980s.

The Montreal Protocol and its Amendments and Adjustments have been very successful in reducing the atmospheric abundance of ozone-depleting substances (ODSs). ODSs are halogen source gases released by human activities. Under the Protocol, the production and consumption of individual ODSs are now controlled in all 196 nations that are Parties to the Protocol (see Q15). The success of the Montreal Protocol controls is documented by (1) observed changes and future projections of the atmospheric abundance of the principal ODSs and (2) long-term values of *equivalent effective stratospheric chlorine* (EESC).

Individual ODS reductions. The reduction in the atmospheric abundance of an ODS in response to controls on production and consumption depends principally on two factors: (1) how rapidly an ODS is used and released to the atmosphere after being produced and (2) the lifetime for the removal of the ODS from the atmosphere (see Table Q7-1). For example, the abundances of ODSs with short lifetimes respond quickly to emission reductions. Long-term changes in ODS abundances are constructed from (1) estimates of historical emissions and bank quantities using industry reports, (2) abundances measured in air trapped for years in accumulated snow (firn) in polar regions, (3) observed atmospheric abundances using ground-based measurements, and (4) projections of future abundances based on compliance with Montreal Protocol provisions and patterns of use in developed and developing countries. The results for individual ODSs and the natural chlorine source gas, methyl chloride (CH₃Cl), are shown in Figure Q16-1 and described as follows:

► CFCs. Chlorofluorocarbons (CFCs) include some of the most destructive chlorine-containing ODSs. CFC-11 and CFC-12, each with an Ozone Depletion Potential (ODP) near 1, are the most abundant ODSs in the atmosphere owing to large historical emissions and long atmospheric lifetimes (45–100 years). Production and consumption of

CFCs in developed countries ended in 1996 and that in developing countries ended by January 2010. As a consequence, CFC-11 and CFC-113 abundances have peaked in the atmosphere and have been declining for more than a decade. In contrast, CFC-12 abundances have only recently shown a decrease, owing to its longer lifetime (100 years) and continuing emissions from CFC-12 banks, namely, refrigeration and air conditioning equipment and thermal insulating foams. With no further global production of the principal CFCs allowed except for limited exempted uses and with some continuing emissions from banks, CFC abundances are projected to decline steadily throughout this century.

- ► Halons. Halons are the most destructive brominecontaining ODSs. The most abundant in the atmosphere, halon-1211 and halon-1301, have abundances about 100 times less than CFC-11 and CFC-12 and account for a significant fraction of bromine from all ODSs (see Figure Q7-1). Production and consumption of halons in developed countries ended in 1994 and that in developing countries ended by January 2010. In the 2005-2008 period, atmospheric abundances of halon-1211 showed a significant decrease for the first time. Halon-2402 abundances have been decreasing for a few years while those of halon-1301 continue to increase. The increase is likely due to substantial banks in fire-extinguishing and other equipment that gradually release halon-1301 to the atmosphere. The abundance of halon-1301 is expected to remain high well into the 21st century because of its long lifetime (65 years) and continued release.
- ► Methyl chloroform. The largest reduction to date in the abundance of an ODS (about 90% from its peak value) has been observed for methyl chloroform. Production and consumption of methyl chloroform in developed countries ended in January 1996 and that in developing countries



Past and Projected Atmospheric Abundances of Halogen Source Gases

Figure Q16-1. Halogen source gas changes. The atmospheric abundances of individual ozone-depleting substances (ODSs) at Earth's surface were obtained using a combination of direct atmospheric measurements, estimates of historical abundance, and future projections of abundance. The gases shown are all ODSs except for methyl chloride. The past increases of CFCs, along with those of carbon tetrachloride, methyl chloroform, and halon-1211, have slowed and reversed in the last two decades. HCFCs, which are used as transitional substances to replace CFCs, will likely continue to increase in the coming decades before a complete phase-out. Halon-1301 abundances will also likely continue to grow in the next decade while current halon banks are depleted. Future decreases in methyl bromide are expected to be small. Abundances of methyl chloride, which is not controlled under the Montreal Protocol and has large natural sources, are projected to be constant in the future.

The rise in equivalent effective stratospheric chlorine (EESC) values in the 20th century has slowed and reversed in the last decade (top left panel). EESC is a measure of the potential for ozone depletion in the stratosphere derived from surface measurements of chlorine and bromine gases (see Q16). EESC values are reduced as ODS emissions decrease. EESC, as shown here for the stratosphere at midlatitudes, returns to 1980 values around 2050. In polar regions, the return to 1980 values occurs almost 10 years later. International compliance with the Montreal Protocol provisions will ensure that EESC values will continue to decrease as projected (see Q15). (The unit "parts per trillion" is defined in the caption of Figure Q7-1.)

is scheduled to end by January 2015. Atmospheric abundances responded rapidly to the reduced emissions starting in the mid-1990s because methyl chloroform has a short atmospheric lifetime (about 5 years). Methyl chloroform is used mainly as a solvent and has no significant long-term storage following production. It will approach complete removal from the atmosphere after the phase-out in developing countries is complete.

- ► **HCFC substitute gases.** The Montreal Protocol allows for the use of hydrochlorofluorocarbons (HCFCs) as shortterm, transitional substitutes for CFCs and in other specific applications. As a result, the abundances of HCFC-22, HCFC-141b, and HCFC-142b continue to grow in the atmosphere with rates that have remained constant or increased in recent years in response to greater application demand. HCFCs pose a lesser threat to the ozone layer than CFCs because they have low ODP values (less than 0.12). The most recent Adjustment to the Montreal Protocol (Montreal 2007) accelerated the phase-out of HCFCs by a decade for both developed (2020) and developing countries (2030) (see Q15). Even with the accelerated phase-out, future projections show HCFC abundances that continue to increase, reach peak values before the mid-21st century, and steadily decrease thereafter. The response of atmospheric abundances to decreasing emissions will be relatively rapid because of short atmospheric lifetimes of HCFCs (less than 20 years).
- ► Carbon tetrachloride. Carbon tetrachloride has been phased out in both developed countries (January 1996) and developing countries (January 2010). As a result, atmospheric abundances of carbon tetrachloride have been decreasing for two decades. The decline is somewhat less rapid than expected, suggesting that actual emissions are larger than reported or the atmospheric lifetime is greater than current estimates. Production of carbon tetrachloride for use as raw material (feedstock) to make other chemicals is exempted under the Protocol because emission to the atmosphere does not occur in this case.
- ▶ Methyl chloride and methyl bromide. Both methyl chloride and methyl bromide are distinct among halogen source gases because substantial fractions of their emissions are associated with natural processes (see Q7). Methyl chloride is not an ODS under the Montreal Protocol because it is not manufactured or used in appreciable quantities. Its abundance in the atmosphere has remained fairly constant throughout the last 60 years and will remain constant if the balance of its natural production and loss processes

remains unchanged. Methyl bromide is controlled under the Protocol because it is manufactured for use as a fumigant. Developed country production and consumption of methyl bromide ended in January 2005 and that in developing countries is scheduled to end by January 2015. The Protocol currently provides exemptions for some methyl bromide production and use as an agricultural and preshipment fumigant. Atmospheric abundances of methyl bromide responded rapidly to the reduced emissions starting in 1999 because its atmospheric removal lifetime is less than 1 year. Future projections show only small changes in methyl bromide abundances based on the assumptions of unchanged contributions from natural sources and small use in developing countries. An important uncertainty in these projections is the future amounts that will be produced and emitted under Montreal Protocol use exemptions.

Equivalent effective stratospheric chlorine (EESC). Important measures of the success of the Montreal Protocol are the past and projected changes in the values of equivalent effective stratospheric chlorine (EESC), which was introduced in Figures Q14-1 and Q15-1. EESC is designed as one measure of the potential for ozone depletion in the stratosphere that can be calculated from atmospheric *surface abundances* of ODSs and natural chlorine and bromine gases. All gases used in the calculation are shown in Figure Q7-1. For both past and future EESC values, the required atmospheric abundances are derived from measurements, historical estimates, or future projections based on compliance with Montreal Protocol provisions.

EESC is expressed as a hypothetical amount of chlorine available in the stratosphere to deplete ozone. The term *equivalent* indicates that bromine gases, scaled by their greater peratom effectiveness in depleting ozone, are included in EESC. The term *effective* indicates that only the estimated fraction of ODSs that are currently in the form of reactive halogen gases in the stratosphere is included in an EESC value (see Q8). Although chlorine is much more abundant in the stratosphere than bromine (about 150-fold) (see Figure Q7-1), bromine atoms are about 60 times more effective than chlorine atoms in chemically destroying ozone in the lower stratosphere. EESC generally depends on the year and latitude region in the stratosphere being considered.

Another quantitative measure of the potential for ozone depletion in the stratosphere that is highly related to EESC is *effective stratospheric chlorine* (ESC). ESC, as defined in Q20, is calculated with chemistry-climate models rather than directly from ODS observations.

Long-term changes in EESC. In the latter half of the 20th century up until the 1990s, EESC values steadily increased (see Figure Q16-1), causing global ozone depletion. As a result of the Montreal Protocol regulations, the long-term increase in EESC slowed, values reached a peak, and EESC began to decrease in the 1990s. The initial decrease came primarily from the substantial, rapid reductions in emissions of methyl chloroform, which has a lifetime of only 5 years. The decrease is continuing with declining emissions of CFCs and other long-lived ODSs. Decreasing EESC means that the potential

for stratospheric ozone depletion is now lessening each year as a result of the Montreal Protocol. Decreases in EESC are projected to continue throughout the 21st century if all nations continue to comply with the provisions of the Protocol. The decrease will continue because as emissions are reduced, natural processes continue to gradually remove halogencontaining gases from the global atmosphere. Reduction of EESC values to 1980 values or lower will require several more decades because the most abundant ODS molecules now in the atmosphere have lifetimes ranging from 10 to 100 years.

Does depletion of the ozone layer increase ground-level ultraviolet radiation?

Yes, ultraviolet radiation at Earth's surface increases as the amount of overhead total ozone decreases, because ozone absorbs ultraviolet radiation from the Sun. Measurements by ground-based instruments and estimates made using satellite data provide evidence that surface ultraviolet radiation has increased in large geographic regions in response to ozone depletion.

The depletion of stratospheric ozone leads to an increase in solar ultraviolet radiation at Earth's surface. The increase occurs primarily in the ultraviolet-B (UV-B) component of the Sun's radiation. UV-B is defined as radiation in the wavelength range of 280 to 315 nanometers, which is invisible to the human eye. Long-term changes in UV-B radiation reaching the surface have been measured directly and can be estimated from total ozone changes.

UV-B radiation can harm humans, other life forms, and materials (see Q3). Most of the effects of sunlight on the human body are caused by UV-B exposure. A principal effect is skin erythema, which leads to sunburning. Excess exposure may lead to skin cancers. Erythemal radiation is regularly reported to the public in many countries in the form of the "UV Index." The long-term changes in surface UV-B radiation are important to study because of its potential harmful effects and relationship to ozone depletion.

Surface UV-B radiation. The amount of UV-B radiation reaching Earth's surface at a particular location depends in large part on total ozone at that location. Ozone molecules in the stratosphere and in the troposphere absorb UV-B radiation, thereby significantly reducing the amount that reaches Earth's surface (see Q3). If conditions occur that reduce the abundance of ozone molecules somewhere in the troposphere or stratosphere, total ozone is reduced and the amount of UV-B radiation reaching Earth's surface below is increased proportionately. This relationship between total ozone and surface UV-B radiation has been confirmed at a variety of locations with direct measurements of both quantities.

Additional causes of UV changes. The actual amount of UV-B radiation reaching the Earth's surface at a specific location and time depends on a number of factors in addition to total ozone. The primary additional factor is the position of the Sun in the sky, which changes with daily and seasonal cycles. Other factors include local cloudiness, the altitude of the location, the amount of ice or snow cover, and the amounts of atmospheric particles (aerosols) in the atmosphere above the location. Changes in clouds and aerosols are partially related to air pollution and greenhouse gas emissions from human activities. Measurements indicate that both increases and decreases in UV radiation at certain locations have resulted from changes in one or more of these factors. Estimating the impact of changes in these factors is complex. For example, an increase in cloud cover usually results in a reduction of UV radiation below the clouds and could at the same time increase surface radiation in any nearby mountainous regions above the clouds.

Long-term surface UV changes. Long-term changes in UV-B radiation have been estimated from measurements made with special UV monitoring instruments at several surface locations since about 1990. For example, as a consequence of Antarctic ozone depletion, the average UV-B measured at the South Pole during spring between 1991 and 2006 was 55-85% larger than estimated for the years 1963-1980. In addition, satellite observations of ozone changes have been used to estimate changes in surface UV-B radiation that have occurred over the past three decades. With satellite observations, the UV-B radiation changes can be separately attributed to changes in ozone and clouds. The results show that erythemal radiation has increased by up to 6% between 1979 and 2008 over a wide range of latitudes outside the tropics (see lower panel of Figure Q17-1). The largest percentage increases have occurred at high polar latitudes in both hemispheres, where the largest annual decreases in total ozone are observed (see Figure Q13-1). Over this time period the UV increases due to ozone depletion are partially offset by changes in cloudiness, primarily in the high latitudes of the Southern Hemisphere (see top panel in Figure Q17-1). Without changes in cloudiness, the increases in erythemal radiation at these latitudes would have reached a maximum close to 9%. The smallest changes in erythemal UV have been in the tropics, where long-term changes in total ozone are smallest (see Q13). In the tropics and in the Northern Hemisphere the average changes in clouds during this period were very small. As a result, the net increases in erythemal radiation in these regions are determined primarily by ozone depletion.

UV Index changes. The UV Index is a measure of the erythemal radiation that occurs at a particular surface location and time. The index is used internationally to increase public awareness about the detrimental effects of UV on human health and to guide the need for personal protective measures. The maximum daily UV Index varies with location and season, as shown for three sites in Figure Q17-2. The UV Index increases when moving from high to low latitudes and is highest in summer when the midday Sun is closest to overhead. UV Index values in San Diego, California, at 32°N, for example, are generally higher than those in Barrow, Alaska, at 71°N. At all latitudes, UV Index values increase in mountainous regions and over snow- or ice-covered regions. The UV Index is zero during periods of continuous darkness in winter at high-latitude locations.

The UV Index over Antarctica has increased dramatically due to ozone depletion, as illustrated in Figure Q17-2. Normal index values for Palmer, Antarctica, at 64°S in spring were estimated from satellite measurements made during the period 1978–1980, before the appearance of the ozone hole over Antarctica. In the period from 1991 to 2006, the severe and persistent ozone depletion that occurred in late winter and early spring over Antarctica increased the average UV Index well above normal values for several months. Now, the spring UV Index measured in Palmer, Antarctica, routinely equals or exceeds spring and summer values measured in San Diego, California, located at a much lower latitude (32°N).

UV changes and human health. Over the past several decades, depletion of the stratospheric ozone layer together with societal changes in lifestyle have increased UV-B radiation exposure for many people. Increased exposure has adverse health effects, primarily associated with eye and skin disorders. UV radiation is a recognized risk factor for some types of cataracts. For the skin, the most common threat is



Figure Q17-1. Long-term changes in surface erythemal radiation. Solar ultraviolet (UV) radiation at Earth's surface has increased over much of the globe since 1979. Erythemal radiation, which can lead to sunburning, is a component of surface UV radiation that is harmful to humans and other life forms. Surface erythemal radiation responds to changes in total ozone as well as clouds and aerosols. Satellite observations have been used to estimate the long-term changes of erythemal radiation due to changes in ozone, clouds, and aerosols. These estimates show that erythemal radiation at Earth's surface has increased over much of the globe over the period 1979 to 2008, particularly at midlatitudes in both hemispheres (bottom panel). The increases in the Southern Hemisphere would have been larger without the offsetting changes due to clouds and aerosols (upper panel). The smallest estimated changes in erythemal radiation are in the tropics because observed total ozone changes over this period are smallest there (see Figure Q13-1). The shaded areas surrounding the figure lines represent the uncertainties in the estimated changes.

skin cancer. Over the past decades, the incidence of several types of skin tumors has risen significantly among people of all skin types. Skin cancer in humans occurs long after exposure to sunburning UV. With current Montreal Protocol provisions, projections of additional skin cancer cases associated with ozone depletion are largest in the early to middle decades of the 21st century and represent a significant global health

issue. An important human health benefit of UV-B radiation exposure is the production of vitamin D, which plays a significant role in bone metabolism and the immune system. Human exposure to solar UV-B radiation requires a careful balance to maintain adequate vitamin D levels while minimizing long-term risks of skin and eye disorders.



Figure Q17-2. Long-term changes in the UV Index. The UV Index is a measure of the erythemal radiation that reaches the surface at a particular location and time. Sunburning in humans is caused by erythemal radiation. The UV Index varies with total ozone above a location, as well as the Sun's midday position in the local sky, which depends on latitude and season. The highest values of the UV Index occur in the tropics, where the midday Sun is highest throughout the year and where total ozone values are low. The lowest average UV Index values occur at high latitudes. The figure shows daily maximum UV Index values at several locations. Values are higher throughout the year in San Diego, a low-latitude location, than in Barrow, a high-latitude location. UV Index values are zero at high latitudes in winter when darkness is continuous. Measurements at Palmer, Antarctica, demonstrate the effect of Antarctic ozone depletion. Normal values estimated for Palmer are shown for 1978–1980, a period before the appearance of the "ozone hole" (see red dashed line). In the period 1990-2006, Antarctic ozone depletion increased

the UV Index at Palmer throughout spring and into summer (see yellow shaded region). Springtime values at Palmer now routinely equal or exceed those measured in spring and summer in San Diego, which is located at much lower latitude.