APPENDIX A

Twenty Questions and Answers About the Ozone Layer: 2006 Update

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Repaginated for this report

TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER: 2006 UPDATE

Contents

INTRODUCTION

Ozone is a very small part of our atmosphere, but its presence is nevertheless vital to human well-being.

Most ozone resides in the upper part of the atmosphere. This region, called the stratosphere, is more than 10 kilometers (6 miles) above Earth's surface. There, about 90% of atmospheric ozone is contained in the "ozone layer," which shields us from harmful ultraviolet radiation from the Sun.

However, it was discovered in the mid-1970s that some human-produced chemicals could destroy ozone and deplete the ozone layer. The resulting increase in ultraviolet radiation at Earth's surface may increase the incidences of skin cancer and eye cataracts.

Following the discovery of this environmental issue, researchers focused on a better understanding of this threat to the ozone layer. Monitoring stations showed that the abundances of the ozone-depleting chemicals were steadily increasing in the atmosphere. These trends were linked to growing production and use of chemicals like chlorofluorocarbons (CFCs) for refrigeration and air conditioning, foam blowing, and industrial cleaning. Measurements in the laboratory and the atmosphere characterized the chemical reactions that were involved in ozone destruction. Computer models employing this information could predict how much ozone depletion was occurring and how much more could occur in the future.

Observations of the ozone layer showed that depletion was indeed occurring. The most severe and most surprising ozone loss was discovered to be recurring in springtime over Antarctica. The loss in this region is commonly called the "ozone hole" because the ozone depletion is so large and localized. A thinning of the ozone layer also has been observed over other regions of the globe, such as the Arctic and northern middle latitudes.

The work of many scientists throughout the world has provided a basis for building a broad and solid scientific understanding of the ozone depletion process. With this understanding, we know that ozone depletion is occurring and why. And, most important, we know that if ozone-depleting gases were to continue to accumulate in the atmosphere, the result would be more depletion of the ozone layer.

In response to the prospect of increasing ozone depletion, the governments of the world crafted the 1987 United Nations Montreal Protocol as a global means to address this global issue. As a result of the broad compliance with the Protocol and its Amendments and Adjustments and, of great significance, industry's development of "ozone-friendly" substitutes for the now-controlled chemicals, the total global accumulation of ozone-depleting gases has slowed and begun to decrease. This has reduced the risk of further ozone depletion. Now, with continued compliance, we expect recovery of the ozone layer by the late 21st century. The International Day for the Preservation of the Ozone Layer, 16 September, is now celebrated on the day the Montreal Protocol was agreed upon.

This is a story of notable achievements: discovery, understanding, decisions, actions, and verification. It is a story written by many: scientists, technologists, economists, legal experts, and policymakers. And, dialogue has been a key ingredient.

To help foster continued interaction, this component of the *Scientific Assessment of Ozone Depletion: 2006* presents 20 questions and answers about the often-complex science of ozone depletion. The answers are updates of those first presented in the previous ozone Assessment, *Scientific Assessment of Ozone Depletion: 2002*. The questions address the nature of atmospheric ozone, the chemicals that cause ozone depletion, how global and polar ozone depletion occur, and what could lie ahead for the ozone layer. A brief answer to each question is first given in italics; an expanded answer then follows. The answers are based on the information presented in the 2006 and earlier Assessment reports. These reports and the answers provided here were all prepared and reviewed by a large international group of scientists. [1]

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[1] The update of this component of the Assessment was discussed by the 77 scientists who attended the Panel Review Meeting for the 2006 Ozone Assessment (Les Diablerets, Switzerland, 19-23 June 2006). In addition, subsequent contributions, reviews, or comments were provided by the following individuals: S.A. Montzka (special recognition), R.J. Salawitch (special recognition), D.L. Albritton, S.O. Andersen, P.J. Aucamp, M.P. Baldwin, A.F. Bias, G. Bodeker, J.F. Bornman, G.O. Braathen, J.P. Burrows, M.-L. Chanin, C. Clerbaux, M. Dameris, J.S. Daniel, S.B. Diaz, E.G. Dutton, C.A. Ennis, V. Eyring, V.E. Fioletov, N.P. Gillet, N.R.P. Harris, M.K.W. Ko, L. Kuijpers, G.L. Manney, R.L. McKenzie, R. Müller, E.R. Nash, P.A. Newman, T. Peter, A.R. Ravishankara, A. Robock, M.L. Santee, U. Schmidt, G. Seckmeyer, T.G. Shepherd, R.S. Stolarski, W.T. Sturges, J.C. van der Leun, G.J.M. Velders, D.W. Waugh, C.S. Zerefos.

I. OZONE IN OUR ATMOSPHERE

Q1: What is ozone and where is it in the atmosphere?

Ozone is a gas that is naturally present in our atmosphere. Each ozone molecule contains three atoms of oxygen and is denoted chemically as O_3*. Ozone is found primarily in two regions of the atmosphere. About 10% of atmospheric ozone is in the troposphere, the region closest to Earth (from the surface to about 10-16 kilometers (6-10 miles)). The remaining ozone (90%) resides in the stratosphere, primarily between the top of the troposphere and about 50 kilometers (31 miles) altitude. The large amount of ozone in the stratosphere is often referred to as the "ozone layer."*

Ozone is a gas that is naturally present in our atmosphere. Ozone has the chemical formula O_3 because an ozone molecule contains three oxygen atoms (see Figure Q1-1). Ozone was discovered in laboratory experiments in the mid-1800s. Ozone's presence in the atmosphere was later discovered using chemical and optical measurement methods. The word ozone is derived from the Greek word όζειν (*ozein* in Latin), meaning "to smell." Ozone has a pungent odor that allows it to be detected even at very low amounts. Ozone will rapidly react with many chemical compounds and is explosive in concentrated amounts. Electrical discharges are generally used to produce ozone for industrial processes such as air and water purification and bleaching textiles and food products.

Ozone location. Most ozone (about 90%) is found in the stratosphere, a region that begins about 10-16 kilometers (6-10 miles) above Earth's surface and extends up to about 50 kilometers (31 miles) altitude (see Figure Q1-2). Most ozone resides in the lower stratosphere in what is commonly known as the "ozone layer." The remaining ozone, about 10%, is found in the troposphere, which is the lowest region of the atmosphere, between Earth's surface and the stratosphere.

Ozone abundance. Ozone molecules have a relatively low abundance in the atmosphere. In the stratosphere near the peak of the ozone layer, there are up to 12,000 ozone molecules for every *billion* air molecules (1 billion = 1,000 million). Most air molecules are either oxygen (O_2) or nitrogen (N_2) molecules. In the troposphere near Earth's surface, ozone is even less abundant, with a typical range of 20 to 100 ozone molecules for each billion air molecules. The highest surface values are a result of ozone formed in air polluted by human activities.

As an illustration of the low relative abundance of ozone in our atmosphere, one can imagine bringing all the ozone molecules in the troposphere and stratosphere down to Earth's surface and uniformly distributing these molecules into a gas layer over the globe. The resulting layer of pure ozone would have a thickness of less than one-half centimeter (about one-quarter inch).

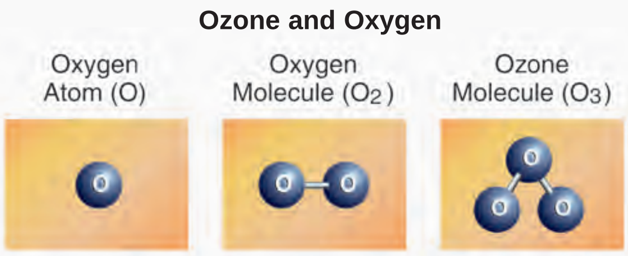

Figure Q1-1. Ozone and oxygen. A molecule of ozone (O_3) contains three oxygen (O) atoms bound together. Oxygen molecules (O_2), which constitute 21% of Earth's atmosphere, contain two oxygen atoms bound together.

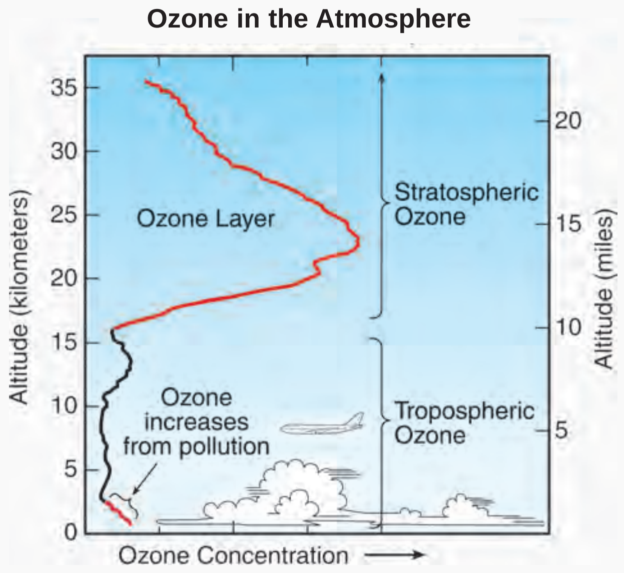

Figure Q1-2. Atmospheric ozone. Ozone is present throughout the lower atmosphere (troposphere and stratosphere). Most ozone resides in the stratospheric "ozone layer" above Earth's surface. Increases in ozone occur near the surface as a result of pollution from human activities.

Q2: How is ozone formed in the atmosphere?

Ozone is formed throughout the atmosphere in multistep chemical processes that require sunlight. In the stratosphere, the process begins with an oxygen molecule (O_2) being broken apart by ultraviolet radiation from the Sun. In the lower atmosphere (troposphere), ozone is formed in a different set of chemical reactions involving hydrocarbons and nitrogen-containing gases.

Stratospheric ozone. Stratospheric ozone is naturally formed in chemical reactions involving ultraviolet sunlight and oxygen molecules, which make up 21% of the atmosphere. In the first step, sunlight breaks apart one oxygen molecule (O_2) to produce two oxygen atoms (2 O) (see Figure Q2-1). In the second step, each atom combines with an oxygen molecule to produce an ozone molecule (O_3). These reactions occur continually wherever ultraviolet sunlight is present in the stratosphere. As a result, the greatest ozone production occurs in the tropical stratosphere.

The production of stratospheric ozone is balanced by its destruction in chemical reactions. Ozone reacts continually with a wide variety of natural and human-produced chemicals in the stratosphere. In each reaction, an ozone molecule is lost and other chemical compounds are produced. Important reactive gases that destroy ozone are those containing chlorine and bromine (see Q8).

Some stratospheric ozone is transported down into the troposphere and can influence ozone amounts at Earth's surface, particularly in remote, unpolluted regions of the globe.

Tropospheric ozone. Near Earth's surface, ozone is produced in chemical reactions involving naturally occurring gases and gases from pollution sources. Production reactions primarily involve hydrocarbon and nitrogen oxide gases and require sunlight. Fossil fuel combustion is a primary pollution source for tropospheric ozone production. The surface production of ozone does not significantly contribute to the abundance of stratospheric ozone. The amount of surface ozone is too small in comparison, and the transport of surface air to the stratosphere is not effective enough. As in the stratosphere, ozone in the troposphere is destroyed in naturally occurring chemical reactions and in reactions involving human-produced chemicals. Tropospheric ozone can also be destroyed when ozone reacts with a variety of surfaces, such as those of soils and plants.

Balance of chemical processes. Ozone abundances in the stratosphere and troposphere are determined by the *balance* between chemical processes that produce ozone and processes that destroy ozone. The balance is determined by the amounts of reacting gases and how the rate or effectiveness of the various reactions varies with sunlight intensity, location in the atmosphere, temperature, and other factors. As atmospheric conditions change to favor ozone-producing reactions in a certain location, ozone abundances will increase. Similarly, if conditions change to favor reactions that destroy ozone, abundances will decrease. The balance of production and loss reactions combined with atmospheric air motions determines the global distribution of ozone on time scales of days to many months. Global ozone has decreased in the last decades because the amounts of reactive gases containing chlorine and bromine have increased in the stratosphere (see Q13).

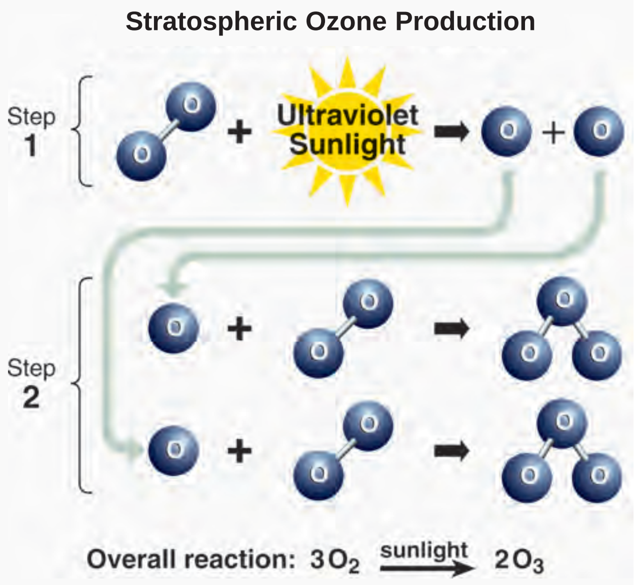

Figure Q2-1. Stratospheric ozone production. Ozone is naturally produced in the stratosphere in a two-step process. In the first step, ultraviolet sunlight breaks apart an oxygen molecule to form two separate oxygen atoms. In the second step, each atom then undergoes a binding collision with another oxygen molecule to form an ozone molecule. In the overall process, three oxygen molecules plus sunlight react to form two ozone molecules.

Q3: Why do we care about atmospheric ozone?

Ozone in the stratosphere absorbs some of the Sun's biologically harmful ultraviolet radiation. Because of this beneficial role, stratospheric ozone is considered "good" ozone. In contrast, excess ozone at Earth's surface that is formed from pollutants is considered "bad" ozone because it can be harmful to humans, plants, and animals. The ozone that occurs naturally near the surface and in the lower atmosphere is also beneficial because ozone helps remove pollutants from the atmosphere.

Natural ozone. In the absence of human activities on Earth's surface, ozone would still be present near the surface and throughout the troposphere and stratosphere because ozone is a natural component of the clean atmosphere. All ozone molecules are chemically identical, with each containing three oxygen atoms. However, ozone in the stratosphere (good ozone) has very different environmental consequences for humans and other life forms than excess ozone in the troposphere near Earth's surface (bad ozone). Natural ozone in the troposphere is also considered "good" because it initiates the chemical removal of many pollutants, such as carbon monoxide and nitrogen oxides, as well as greenhouse gases such as methane.

Good ozone. Stratospheric ozone is considered good for humans and other life forms because it absorbs ultraviolet (UV)-B radiation from the Sun (see Figure Q3-1). If not absorbed, UV-B would reach Earth's surface in amounts that are harmful to a variety of life forms. In humans, increased exposure to UV-B increases the risk of skin cancer (see Q17), cataracts, and a suppressed immune system. UV-B exposure before adulthood and cumulative exposure are both important factors in the risk. Excessive UV-B exposure also can damage terrestrial plant life, single-cell organisms, and aquatic ecosystems. Other UV radiation, UV-A, which is not absorbed significantly by ozone, causes premature aging of the skin.

The absorption of UV-B radiation by ozone is a source of heat in the stratosphere. This helps to maintain the stratosphere as a stable region of the atmosphere, with temperatures increasing with altitude. As a result, ozone plays a key role in controlling the temperature structure of Earth's atmosphere.

Protecting good ozone. In the mid-1970s, it was discovered that halogen source gases released in human activities could cause stratospheric ozone depletion (see Q6). Ozone depletion increases harmful UV-B amounts at Earth's surface. Global efforts have been undertaken to protect the ozone layer through regulation of ozone-depleting gases (see Q15 and Q16).

Bad ozone. Excess ozone formed near Earth's surface in reactions caused by the presence of human-made pollutant gases is considered bad ozone. Increased ozone amounts are harmful to humans, plants, and other living systems because ozone reacts strongly to destroy or alter many other molecules. Excessive ozone exposure reduces crop yields and forest growth. In humans, exposure to high levels of ozone can reduce lung capacity; cause chest pains, throat irritation, and coughing; and worsen pre-existing health conditions related to the heart and lungs. In addition, increases in tropospheric ozone lead to a warming of Earth's surface (see Q18). The negative effects of increasing tropospheric ozone contrast sharply with the positive effects of stratospheric ozone as an absorber of harmful UV-B radiation from the Sun.

Reducing bad ozone. Reducing the emission of pollutants can reduce bad ozone in the air surrounding humans, plants, and animals. Major sources of pollutants include large cities where fossil fuel consumption and industrial activities are greatest. Many programs around the globe have already been successful in reducing the emission of pollutants that cause excess ozone production near Earth's surface.

UV Protection by the Ozone Layer

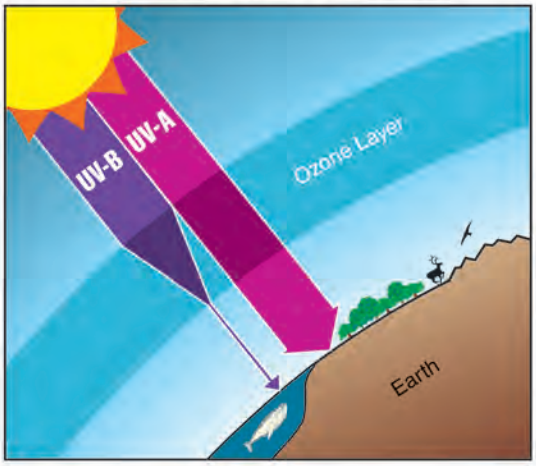

Figure Q3-1. UV-B protection by the ozone layer. The ozone layer resides in the stratosphere and surrounds the entire Earth. UV-B radiation (280- to 315-nanometer (nm) wavelength) from the Sun is partially absorbed in this layer. As a result, the amount of UV-B reaching Earth's surface is greatly reduced. UV-A (315- to 400-nm wavelength) and other solar radiation are not strongly absorbed by the ozone layer. Human exposure to UV-B increases the risk of skin cancer, cataracts, and a suppressed immune system. UV-B exposure can also damage terrestrial plant life, single-cell organisms, and aquatic ecosystems.

Q4: Is total ozone uniform over the globe?

No, the total amount of ozone above the surface of Earth varies with location on time scales that range from daily to seasonal and longer. The variations are caused by stratospheric winds and the chemical production and destruction of ozone. Total ozone is generally lowest at the equator and highest near the poles because of the seasonal wind patterns in the stratosphere.

Total ozone. Total ozone at any location on the globe is found by measuring all the ozone in the atmosphere directly above that location. Total ozone includes that present in the stratospheric ozone layer and that present throughout the troposphere (see Figure Q1-2). The contribution from the troposphere is generally only about 10% of total ozone. Total ozone values are often reported in *Dobson units,* denoted "DU." Typical values vary between 200 and 500 DU over the globe (see Figure Q4-1). A total ozone value of 500 DU, for example, is equivalent to a layer of pure ozone gas on Earth's surface having a thickness of only 0.5 centimeters (0.2 inches).

Global distribution. Total ozone varies strongly with latitude over the globe, with the largest values occurring at middle and high latitudes (see Figure Q4-1). This is a result of winds that circulate air in the stratosphere, moving tropical air rich in ozone toward the poles. Since about 1980, regions of low total ozone have occurred at polar latitudes in winter and spring as a result of the chemical destruction of ozone by chlorine and bromine gases (see Q11 and Q12). The smallest values of total ozone (other than in the Antarctic in spring) occur in the tropics in all seasons, in part because the troposphere extends to a higher altitude in the tropics, and consequently, the thickness of the ozone layer is smallest there.

Natural variations. The variations of total ozone with latitude and longitude come about for two reasons. First, natural air motions mix air between regions of the stratosphere that have high ozone values and those that have low ozone values. Air motions also increase the vertical thickness of the ozone layer near the poles, which increases the value of total ozone in those regions. Tropospheric weather systems can temporarily reduce the thickness of the stratospheric ozone layer in a region, lowering total ozone at the same time. Second, variations occur as a result of changes in the balance of chemical production and loss processes as air moves to different locations over the globe. Reductions in ultraviolet radiation from the sun in its 11-year cycle, for example, reduce the production of ozone.

Scientists have a good understanding of how chemistry and air motions work together to cause the observed large-scale features in total ozone, such as those seen in Figure Q4-1. Ozone changes are carefully monitored by a large group of investigators using satellite, airborne, and ground-based instruments. The analysis of these observations helps scientists to estimate the contribution of human activities to ozone depletion.

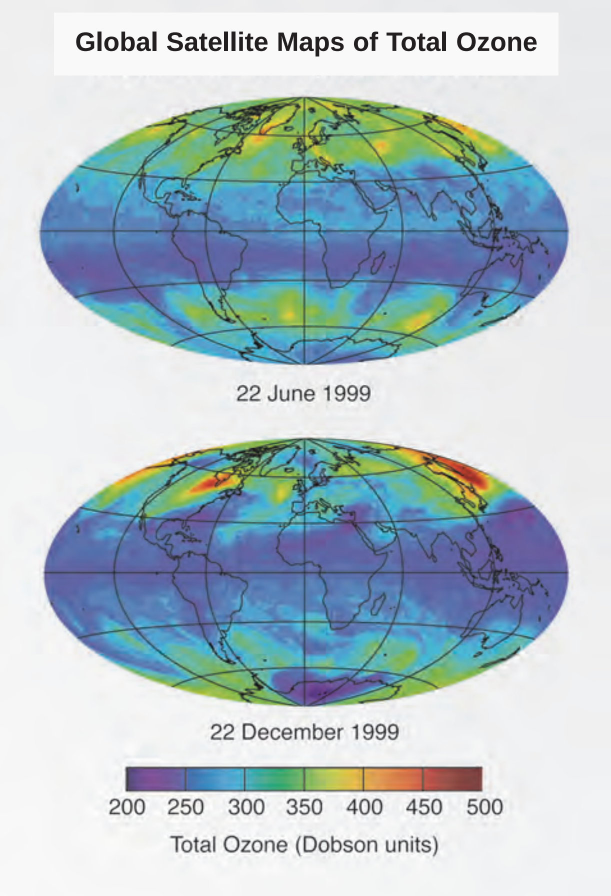

Figure Q4-1. Total ozone. A total ozone value is obtained by measuring all the ozone that resides in the atmosphere over a given location on Earth's surface. Total ozone values shown here are reported in "Dobson units" as measured by a satellite instrument from space. Total ozone varies with latitude, longitude, and season, with the largest values at high latitudes and the lowest values in tropical regions. Total ozone at most locations varies with time on a daily to seasonal basis as ozone-rich air is moved about the globe by stratospheric winds. Low total ozone values over Antarctica in the 22 December image represent the remainder of the "ozone hole" from the 1999 Antarctic winter/spring season (see Q11).

Q5: How is ozone measured in the atmosphere?

The amount of ozone in the atmosphere is measured by instruments on the ground and carried aloft on balloons, aircraft, and satellites. Some measurements involve drawing air into an instrument that contains a system for detecting ozone. Other measurements are based on ozone's unique absorption of light in the atmosphere. In that case, sunlight or laser light is carefully measured after passing through a portion of the atmosphere containing ozone.

The abundance of ozone in the atmosphere is measured by a variety of techniques (see Figure Q5-1). The techniques make use of ozone's unique optical and chemical properties. There are two principal categories of measurement techniques: *local* and *remote*. Ozone measurements by these techniques have been essential in monitoring changes in the ozone layer and in developing our understanding of the processes that control ozone abundances.

Local measurements. Local measurements of atmospheric ozone abundance are those that require air to be drawn directly into an instrument. Once inside an instrument, ozone can be measured by its absorption of ultraviolet (UV) light or by the electrical current produced in an ozone chemical reaction. The latter approach is used in the construction of "ozonesondes," which are lightweight, ozone-measuring modules suitable for launching on small balloons. The balloons ascend far enough in the atmosphere to measure ozone in the stratospheric ozone layer. Ozonesondes are launched regularly at many locations around the world. Local ozone-measuring instruments using optical or chemical detection schemes are also used routinely on board research aircraft to measure the distribution of ozone in the troposphere and lower stratosphere. High-altitude research aircraft can reach the ozone layer at most locations over the globe and can reach farthest into the layer at high latitudes in polar regions. Ozone measurements are also being made on some commercial aircraft.

Remote measurements. Remote measurements of ozone abundance are obtained by detecting the presence of ozone at large distances away from the instrument. Most remote measurements of ozone rely on its unique absorption of UV radiation. Sources of UV radiation that can be used are the Sun and lasers. For example, satellites use the absorption of UV sunlight by the atmosphere or the absorption of sunlight scattered from the surface of Earth to measure ozone over nearly the entire globe on a daily basis. A network of ground-based detectors measures ozone by the amount of the Sun's UV light that reaches Earth's surface. Other instruments measure ozone using its absorption of infrared or visible radiation or its emission of microwave or infrared radiation. Total ozone amounts and the altitude distribution of ozone can be obtained with remote measurement techniques. Lasers are routinely deployed at ground sites or on board aircraft to detect ozone over a distance of many kilometers along the laser light path.

Measuring Ozone in the Atmosphere

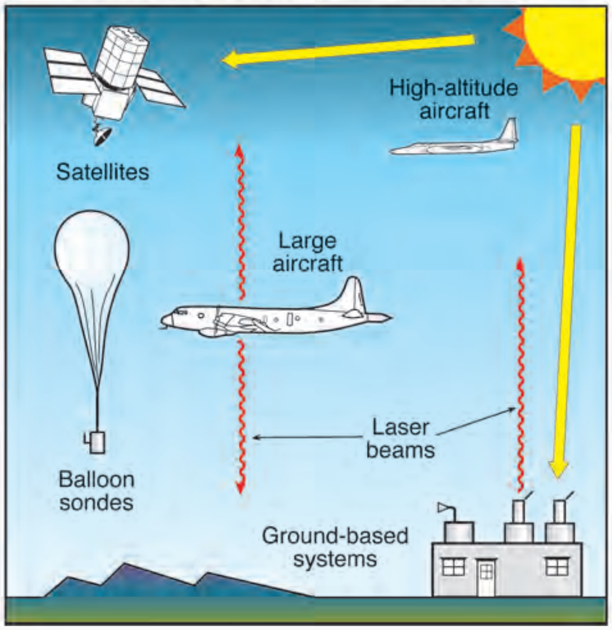

Figure Q5-1. Ozone measurements. Ozone is measured throughout the atmosphere with instruments on the ground and on board aircraft, high-altitude balloons, and satellites. Some instruments measure ozone locally in sampled air and others measure ozone remotely some distance away from the instrument. Instruments use optical techniques, with the Sun and lasers as light sources, or use chemical reactions that are unique to ozone. Measurements at many locations over the globe are made regularly to monitor total ozone amounts.

Global Ozone Dobson Network

The first instrument for routine monitoring of total ozone was developed by Gordon M. B. Dobson in the 1920s. The instrument, now called a Dobson spectrophotometer, measures the intensity of sunlight at two ultraviolet wavelengths: one that is strongly absorbed by ozone and one that is weakly absorbed. The difference in light intensity at the two wavelengths is used to provide a measurement of total ozone above the location of the instrument.

A global network of ground-based, total-ozone observing stations was established in 1957 as part of the International Geophysical Year. Today, there are about 100 sites distributed throughout the world (from South Pole, Antarctica (90°S), to Ellesmere Island, Canada (83°N)), many of which routinely measure total ozone with Dobson instruments. The accuracy of these observations is maintained by regular calibrations and intercomparisons. Data from the network have been essential for understanding the effects of chlorofluorocarbons (CFCs) and other ozone-depleting gases on the global ozone layer, starting before the launch of space-based ozone-measuring instruments and continuing to the present day. Because of their stability and accuracy, the Dobson instruments are now routinely used to help calibrate space-based observations of total ozone.

Pioneering scientists have traditionally been honored by having units of measure named after them. Accordingly, the unit of measure for total ozone is called the “Dobson unit” (see Q4).

II. THE OZONE DEPLETION PROCESS

Q6: 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 ozone-depleting 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. Eventually, these emitted source gases are transported to the stratosphere, where they are converted to more reactive gases containing chlorine and bromine. These more reactive 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.

6Emission, 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 include manufactured chemicals released to the atmosphere by a variety of human activities. Chlorofluorocarbons (CFCs) are an important example of chlorine-containing gases. Emitted source gases *accumulat*e in the lower atmosphere (troposphere) and are eventually *transported* to the stratosphere. The accumulation occurs because most source gases are unreactive in the lower atmosphere. However, small amounts of these gases dissolve or are taken up in ocean waters.

Some emissions of halogen gases come from natural sources (see Q7). These emissions also accumulate in the troposphere and are transported to the stratosphere.

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). Source gases with lifetimes greater than a few years may circulate between the troposphere and stratosphere multiple times before full conversion occurs.

The reactive gases formed in the eventual conversion of the halogen source gases react chemically to destroy ozone in the stratosphere (see Q9). The average depletion

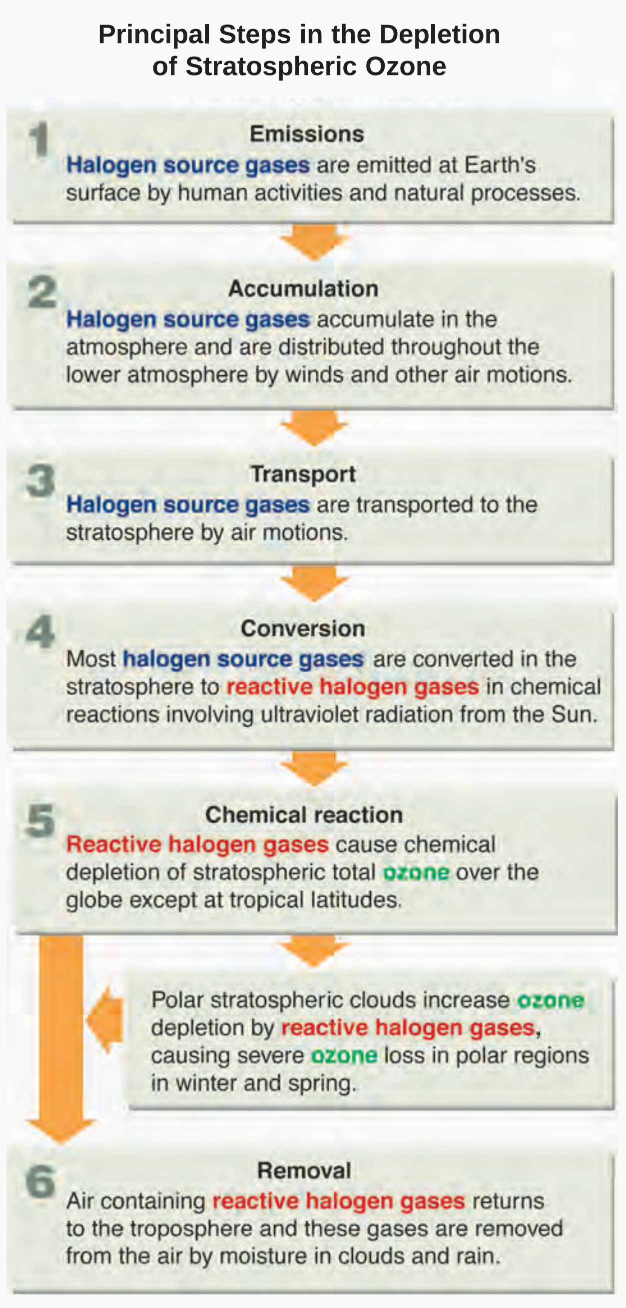

Figure Q6-1. Principal steps in stratospheric ozone depletion. The stratospheric ozone depletion process begins with the emission of halogen source gases at Earth's surface and ends when reactive halogen gases are removed by rain and snow in the troposphere and deposited on Earth's surface. In the stratosphere, the reactive halogen gases, namely chlorine monoxide (ClO) and bromine monoxide (BrO), destroy ozone.

of total ozone attributed to reactive gases is smallest in the tropics and largest at high latitudes (see Q13). In polar regions, the presence of polar stratospheric clouds greatly increases the abundance of the most reactive halogen gases (see Q10). This results in substantial ozone destruction in polar regions in winter and 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 and deposited on Earth's surface. 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 (see Q7) undergo significant chemical conversion in the troposphere, producing reactive halogen gases and other compounds. Source gas molecules that are not converted accumulate in the troposphere and are transported to the stratosphere. Because of removal by precipitation, only small portions of the reactive halogen gases produced in the troposphere are also transported to the stratosphere. Important examples of gases that undergo some tropospheric removal are the HCFCs, which are used as substitute gases for other halogen source gases (see Q15 and Q16), bromoform, and gases containing iodine (see Q7).

Understanding Stratospheric Ozone Depletion

Scientists learn about ozone destruction through a combination of laboratory studies, computer models, and stratospheric observations. In *laboratory studies* scientists are able to discover and evaluate individual chemical reactions that also occur in the stratosphere. Chemical reactions between two gases follow well-defined physical rules. Some of these reactions occur on the surfaces of particles formed in the stratosphere. Reactions have been studied that involve a wide variety of molecules containing chlorine, bromine, fluorine, and iodine and other atmospheric constituents such as oxygen, nitrogen, and hydrogen. These studies show that there exist several reactions involving chlorine and bromine that can directly or indirectly cause ozone destruction in the atmosphere.

With *computer models*, scientists can examine the overall effect of a large group of known reactions under the chemical and physical conditions found in the stratosphere. These models include winds, air temperatures, and the daily and seasonal changes in sunlight. With such analyses, scientists have shown that chlorine and bromine can react in catalytic cycles in which one chlorine or bromine atom can destroy many ozone molecules. Scientists use model results to compare with past observations as a test of our understanding of the atmosphere and to evaluate the importance of new reactions found in the laboratory. Computer models also enable scientists to explore the future by changing atmospheric conditions and other model parameters.

Scientists have conducted *observations* to find out which gases are present in various regions of the stratosphere and at what concentrations. They have monitored the change in these abundances over time periods spanning a daily cycle to decades. Observations have shown that halogen source gases and reactive halogen gases are present in the stratosphere at expected amounts. Ozone and chlorine monoxide (ClO), for example, have been observed extensively with a variety of instruments. Instruments on the ground and on board satellites, balloons, and aircraft detect ozone and ClO at a distance (remotely) using optical and microwave signals. High-altitude aircraft and balloon instruments detect both gases locally in the stratosphere (see Q5). For example, these observations show that ClO is present at elevated amounts in the Antarctic and Arctic stratospheres in the late winter/early spring season, when the most severe ozone depletion occurs (see Q8).

Q7: What emissions from human activities lead to ozone depletion?

Certain industrial processes and consumer products result in the emission of "halogen source gases" to the atmosphere. These gases bring chlorine and bromine to the stratosphere, which cause depletion of the ozone layer. For example, chlorofluorocarbons (CFCs), once used in almost all refrigeration and air conditioning systems, eventually reach the stratosphere, where they are broken apart to release ozone-depleting chlorine atoms. Other examples of human-produced ozone-depleting gases are the "halons," which are used in fire extinguishers and contain ozone-depleting bromine atoms. The production and consumption of all principal halogen source gases by human activities are regulated worldwide under the Montreal Protocol.

Principal human-produced chlorine and bromine gases. Human activities cause the emission of *halogen source gases* that contain chlorine and bromine atoms. These emissions into the atmosphere ultimately lead to stratospheric ozone depletion. The source gases that contain only carbon, chlorine, and fluorine are called "chlorofluorocarbons," usually abbreviated as CFCs. CFCs, along with carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3), historically have been the most important chlorine-containing gases that are emitted by human activities and destroy stratospheric ozone (see Figure Q7-1). These and other chlorine-containing gases have been used in many applications, including refrigeration, air conditioning, foam blowing, aerosol propellants, and cleaning of metals and electronic components. These activities have typically caused the emission of halogen-containing gases to the atmosphere.

Another category of halogen source gases contains bromine. The most important of these are the "halons" and methyl bromide (CH_3Br). Halons are halogenated hydrocarbon gases originally developed to extinguish fires. Halons are widely used to protect large computers, military hardware, and commercial aircraft engines. Because of these uses, halons are often directly released into the atmosphere. Halon-1211 and halon-1301 are the most abundant halons emitted by human activities (see Figure Q7-1). Methyl bromide, used primarily as an agricultural fumigant, is also a significant source of bromine to the atmosphere.

Human emissions of the principal chlorine- and bromine-containing gases have increased substantially since the middle of the 20th century (see Q16). The result has been global ozone depletion, with the greatest losses occurring in polar regions (see Q11 to Q13).

Other human sources of chlorine and bromine. Other chlorine- and bromine-containing gases are released regularly in human activities. Common examples are the use of chlorine gases to disinfect swimming pools and wastewater, fossil fuel burning, and various industrial processes. These activities do not contribute significantly to stratospheric amounts of chlorine and bromine because either the global source is small or the emitted gases are short-lived (very reactive or highly soluble) and, therefore, are removed from the atmosphere before they reach the stratosphere.

Natural sources of chlorine and bromine. There are a few halogen source gases present in the stratosphere that have large natural sources. These include methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), both of which are emitted by oceanic and terrestrial ecosystems. Natural sources of these two gases contribute about 17% of the chlorine currently in the stratosphere and about 30% of the bromine (see Figure Q7-1). Very short-lived source gases containing bromine, such as bromoform ($CHBr_3$), are also released to the atmosphere primarily from the oceans. Only a small 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 24%, but this has a large uncertainty. The contribution to stratospheric chlorine of short-lived chlorinated gases from natural and human sources is much smaller (< 3%) and is included in the "Other gases" category in Figure Q7-1. Changes in the natural sources of chlorine and bromine since the middle of the 20th century are not the cause of observed ozone depletion.

Lifetimes and emissions. After emission, halogen source gases are either naturally removed from the atmosphere or undergo chemical conversion. 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). Gases with the shortest 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 each emitted gas contributes to ozone depletion in the stratosphere.

The amount of a halogen source gas present in the atmosphere depends on the lifetime of the gas and the

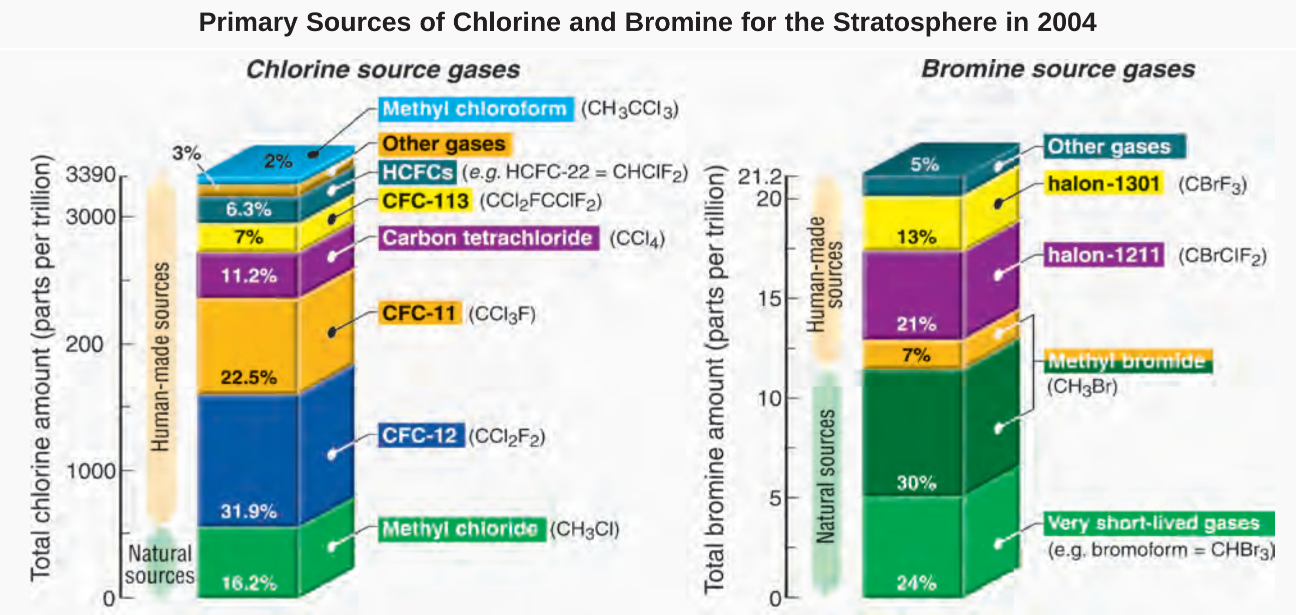

Figure Q7-1. Stratospheric source gases. A variety of gases transport chlorine and bromine into the stratosphere. These gases, called halogen source gases, are emitted from natural sources and by human activities. These partitioned columns show how the principal chlorine and bromine source gases contribute to the respective total amounts of chlorine and bromine as measured in 2004. Note the large difference in the vertical scales: total chlorine in the stratosphere is 160 times more abundant than total bromine. For chlorine, human activities account for most that reaches the stratosphere. The CFCs are the most abundant of the chlorine-containing gases released in human activities. Methyl chloride is the most important natural source of chlorine. HCFCs, which are substitute gases for CFCs and also are regulated under the Montreal Protocol, are a small but growing fraction of chlorine-containing gases. The "Other gases" category includes minor CFCs and short-lived gases. For bromine that reaches the stratosphere, halons and methyl bromide are the largest sources. Both gases are released in human activities. Methyl bromide has an additional natural source. Natural sources are a larger fraction of total bromine 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 indicates the presence of one molecule of a gas per trillion other air molecules.)

amount emitted to the atmosphere. Emissions vary greatly for the principal source gases, as indicated in Table Q7-1. Emissions of most gases regulated by the Montreal Protocol have decreased since 1990, and emissions from all regulated gases are expected to decrease in the coming decades (see Q16).

Ozone Depletion Potential. The halogen source gases in Figure Q7-1 are also known as "ozone-depleting substances" because they are converted in the stratosphere to reactive gases containing chlorine and bromine (see Q8). Some of these reactive gases participate in reactions that destroy ozone (see Q9). Ozone-depleting substances are compared in their effectiveness to destroy stratospheric ozone using the "Ozone Depletion Potential" (ODP), as listed in Table Q7-1 (see Q18). A gas with a larger ODP has a greater potential to destroy ozone over its lifetime in the atmosphere. The ODP is calculated on a "per mass" basis for each gas relative to CFC-11, which has an ODP defined to be 1. 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 in the stratosphere. The gases with small ODP values generally have short atmospheric lifetimes or fewer chlorine and bromine atoms. The production and consumption of all principal halogen source gases by humans are regulated under the provisions of the Montreal Protocol (see Q15).

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. 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, most are removed in the troposphere before they reach the stratosphere.

Other gases. Other gases that influence stratospheric ozone abundances also have increased in the stratosphere as a result of human activities. Important examples are methane (CH_4) and nitrous oxide (N_2O), which react in the stratosphere to form water vapor and reactive hydrogen, and nitrogen oxides, respectively. These reactive products also participate in the production and loss balance of stratospheric ozone (see Q2). The overall effect of increases in these other gases on ozone is much smaller than that caused by increases in chlorine- and bromine-containing gases from human activities (see Q18).

Table Q7-1. Atmospheric lifetimes, emissions, and Ozone Depletion Potentials of halogen source gases. [a]

Halogen Source Gas	Atmospheric Lifetime (years)	Global Emissions in 2003 [b]	Ozone Depletion Potential (ODP) [d]
Chlorine			
CFC-12	100	101-144	1
CFC-113	85	1-15	1
CFC-11	45	60-126	1
Carbon tetrachloride (CCl_4)	26	58-131	0.73
HCFCs	1-26	312-403	0.02-0.12
Methyl chloroform (CH_3CCl_3)	5	~20	0.12
Methyl chloride	1.0	1700-13600	0.02
Bromine			
Halon-1301	65	~3	16
Halon-1211	16	7-10	7.1
Methyl bromide (CH_3Br)	0.7	160-200	0.51
Very short-lived gases (e.g., $CHBr_3$)	< 0.5	[c]	[c]

[a] Includes both human activities and natural sources.

[b] Emission in gigagrams per year (1 gigagram = 10^9 grams = 1000 metric tons).

[c] Estimates are uncertain for most species.

[d] Values are calculated for emissions of equal mass for each gas.

Heavier-Than-Air CFCs

CFCs and other halogen source gases reach the stratosphere despite the fact that they are “heavier than air.” All the principal source gases are emitted and accumulate in the lower atmosphere (troposphere). The distributions of gases in the troposphere and stratosphere are not controlled by the molecular weight of the gases because air is in continual motion in these regions as a result of winds and convection. Air motions ensure that most source gases become horizontally and vertically well mixed throughout the troposphere in a matter of months. It is this well-mixed air that enters the lower stratosphere from upward air motions in tropical regions, bringing with it source gas molecules emitted from a wide variety of locations on Earth’s surface.

Atmospheric measurements confirm that halogen source gases 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 consistent with the emissions estimates reported by industries and governments. Measurements also show that gases that are “lighter than air,” such as hydrogen (H_2) and methane (CH_4), are also well mixed in the troposphere, as expected. 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.

Q8: What are the reactive halogen gases that destroy stratospheric ozone?

Emissions from human activities and natural processes include large sources of chlorine- and bromine-containing gases that eventually reach the stratosphere. When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to more reactive gases also containing chlorine and bromine. Important examples of the reactive gases that destroy stratospheric ozone are chlorine monoxide (ClO) and bromine monoxide (BrO). These reactive gases participate in "catalytic" reaction cycles that efficiently destroy ozone. Volcanoes can emit some chlorine-containing gases, but these gases are ones that readily dissolve in rainwater and ice 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*. The source gases 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 instead of the troposphere because solar UV radiation is more intense in the stratosphere.

Reactive halogen gases. The chemical conversion of halogen source gases, which involves ultraviolet 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. Away from polar regions, the most abundant are hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$). These two gases are considered *reservoir* gases because they do not react directly with ozone but can be converted to the most reactive forms that 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 stratospheric bromine is generally in the form of BrO, whereas usually only a small fraction of stratospheric chlorine is in the form of ClO. In polar regions, the reservoirs $ClONO_2$ and HCl undergo a further conversion on polar stratospheric clouds to form ClO (see Q10). In that case, ClO becomes a large fraction of available reactive chlorine.

Reactive chlorine observations. Reactive chlorine gases have been observed extensively in the stratosphere with both local and remote measurement techniques. The measurements from space at middle latitudes displayed in

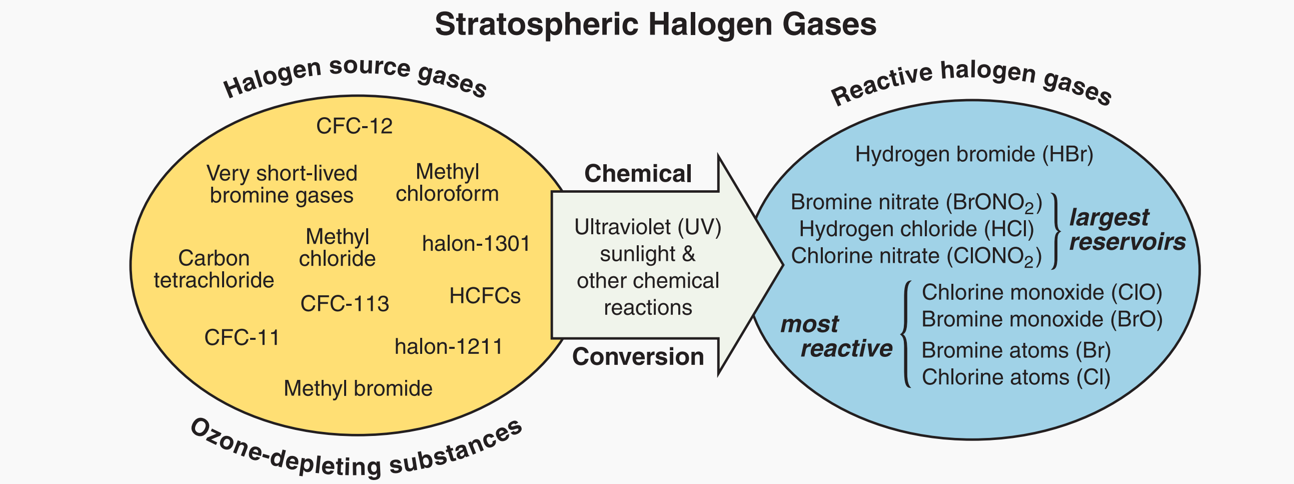

Figure Q8-1. Conversion of halogen source gases. Halogen source gases (also known as ozone-depleting substances) are chemically converted to reactive halogen gases primarily in the stratosphere. The conversion requires ultraviolet sunlight and a few other chemical reactions. The short-lived gases undergo some conversion in the troposphere. The reactive halogen gases contain all the chlorine and bromine originally present in the source gases. The reactive gases separate into reservoir gases, which do not destroy ozone, and reactive gases, which participate in ozone destruction cycles (see Q9).

Figure Q8-2 are representative of how the amounts of chlorine-containing gases change between the surface and the upper stratosphere. Available chlorine (see red line in Figure Q8-2) is the sum of chlorine contained in halogen source gases and the reactive gases HCl, $ClONO_2$, ClO, and other minor gases. Available chlorine is constant within a few percent from the surface to 47 kilometers (31 miles) altitude. In the troposphere, available chlorine is contained almost entirely in the source gases described in Figure Q7-1. At higher altitudes, the source gases become a smaller fraction of available chlorine as they are converted to reactive chlorine gases. At the highest altitudes, available chlorine is all in the form of reactive chlorine gases.

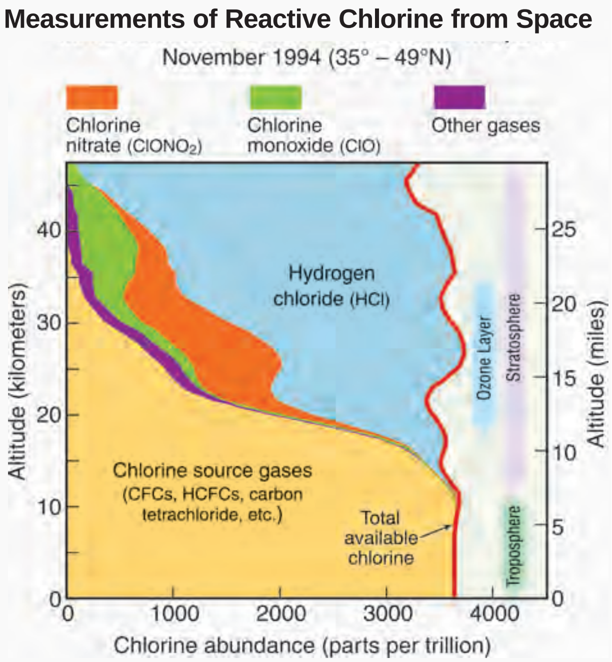

Figure Q8-2. Reactive chlorine gas observations. The abundances of chlorine source gases and reactive chlorine gases as measured from space are displayed with altitude for a midlatitude location. In the troposphere (below about 10 kilometers), all chlorine is contained in the source gases. In the stratosphere, reactive chlorine gases increase with altitude as chlorine source gases decrease. This is a consequence of chemical reactions involving ultraviolet sunlight (see Figure Q8-1). The principal reactive gases formed are HCl, $ClONO_2$, and ClO. Summing the source gases with the reactive gases gives *total available chlorine*, which is nearly constant with altitude up to 47 km. In the ozone layer, HCl and $ClONO_2$ are the most abundant reactive chlorine gases. (The unit "parts per trillion" is defined in the caption of Figure Q7-1.)

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

Reactive chlorine in polar regions. Reactive chlorine gases in polar regions in summer look similar to the altitude profiles shown in Figure Q8-2. In winter, however, the presence of polar stratospheric clouds (PSCs) causes further chemical changes (see Q10). PSCs convert HCl and $ClONO_2$ to ClO when temperatures are near minimum values in the winter Arctic and Antarctic stratosphere. In that case, ClO becomes the principal reactive chlorine species in sunlit regions and ozone loss becomes very rapid. An example of the late-winter ClO and ozone distributions is shown in Figure Q8-3 for the Antarctic stratosphere. These space-based measurements show that ClO abundances are high in the lower stratosphere over a region that exceeds the size of the Antarctic continent (greater than 13 million square kilometers or 5 million square miles). The peak abundance of ClO exceeds 1500 parts per trillion, which is much larger than typical midlatitude values shown in Figure Q8-2 and represents a large fraction of reactive chlorine in that altitude region. Because high ClO amounts cause rapid ozone loss (see Q9), ozone depletion is found in regions of elevated ClO (see Figure Q8-3).

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). Recent observations have shown that measured BrO abundances in the stratosphere are larger than expected from the conversion of the halons and methyl bromide to BrO, suggesting a significant contribution from the very short-lived bromine-containing gases.

Other sources. Some reactive halogen gases are also produced at Earth's surface by natural processes and by human activities. However, because reactive halogen gases are soluble in water, almost all become trapped in the lower atmosphere by dissolving in rainwater and ice, and ultimately are returned to Earth's surface before they can reach the stratosphere. For example, reactive chlorine is present in the atmosphere as sea salt (sodium chloride) produced by evaporation of ocean spray. Because sea salt dissolves in water, this chlorine is removed and does not reach the stratosphere in appreciable quantities. Another ground-level source is emission of chlorine gases from swimming pools, household bleach, and other uses.

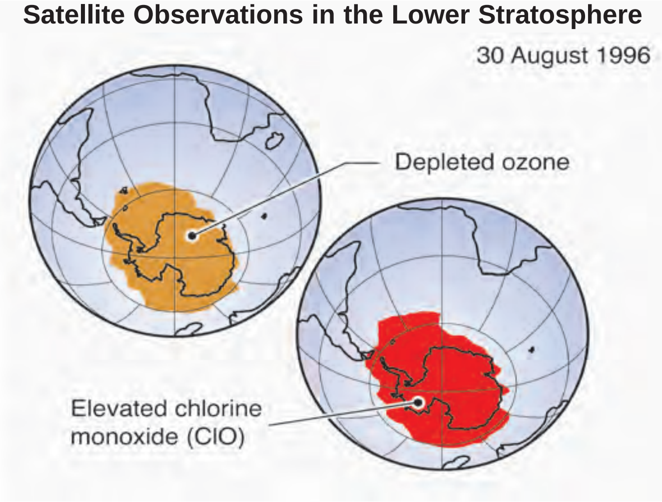

Figure Q8-3. Antarctic chlorine monoxide and ozone. Satellite instruments monitor ozone and reactive chlorine gases in the global stratosphere. Results are shown here for Antarctic winter for a narrow altitude region within the ozone layer. In winter, chlorine monoxide (ClO) reaches high values (1500 parts per trillion) in the ozone layer, much higher than observed anywhere else in the stratosphere because ClO is produced by reactions on polar stratospheric clouds (see Q10). These high ClO values in the lower stratosphere 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 values measured simultaneously within the ozone layer show very depleted values.

When released to the atmosphere, this chlorine is rapidly converted to forms that are soluble in water and removed. The Space Shuttle and other rocket motors release reactive chlorine gases directly in the stratosphere: in this case, the quantities are very small in comparison with other tropospheric sources.

Volcanoes. Volcanic plumes generally contain large quantities of chlorine in the form of hydrogen chloride (HCl). Because the plumes also contain a considerable amount of water vapor, the HCl is efficiently scavenged by rainwater and ice and removed from the atmosphere. As a result, most of the HCl in the plume does not enter the stratosphere. After large recent eruptions, the increase in HCl in the stratosphere has been small compared with the total amount of chlorine in the stratosphere from other sources.

Replacing the Loss of Ozone in the Stratosphere

The idea is sometimes put forth that humans could replace the loss of global stratospheric ozone by making ozone and transporting it to the stratosphere. Ozone amounts in the stratosphere reflect a balance between continual production and destruction by mostly naturally occurring reactions (see Q2). The addition of chlorine and bromine to the stratosphere from human activities has increased ozone destruction and lowered stratospheric ozone amounts. Adding manufactured ozone to the stratosphere would upset the existing balance. As a consequence, most added ozone would be destroyed in chemical reactions within weeks to months as the balance was restored. So, it is not practical to consider replacing the loss of global stratospheric ozone because the replacement effort would need to continue indefinitely, or as long as increased chlorine and bromine amounts remained.

Other practical 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. The replacement of the average global ozone loss of about 4% would require 120 megatons of stratospheric ozone to be distributed throughout the layer located 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 in the United States, which is now approximately 5 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 demonstrated. Concerns for a global delivery system would include further significant energy use and unforeseen environmental consequences.

Q9: 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 hundreds of ozone molecules before it reacts with another gas, breaking the cycle. In this way, a small amount of reactive chlorine or bromine has a large impact on the ozone layer. Certain ozone destruction reactions become most effective in polar regions because the reactive gas chlorine monoxide reaches very high levels there in the late winter/early spring season.

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: ClO + O and Cl + O_3. 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 reformed. 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.

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 cloud (PSC) particles (see 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 in the late winter/early spring

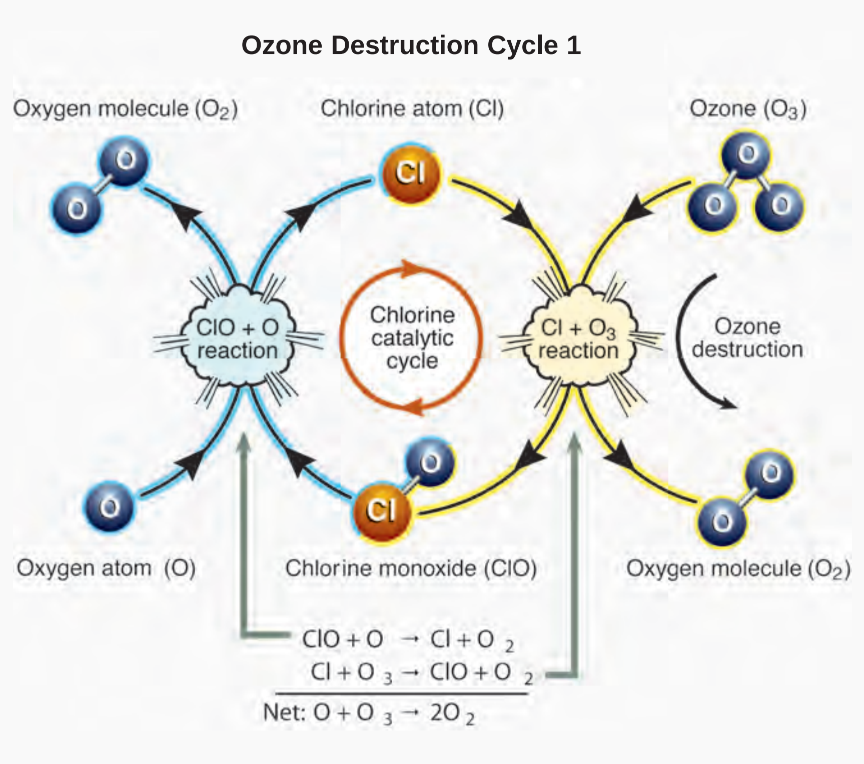

Figure Q9-1. Ozone destruction Cycle 1. The destruction of ozone in Cycle 1 involves two separate chemical reactions. The net or overall reaction is that of atomic oxygen with ozone, forming two oxygen molecules. The cycle can be considered to begin with either ClO or Cl. When starting with ClO, the first reaction is ClO with O to form Cl. Cl then reacts with (and thereby destroys) ozone and reforms ClO. The cycle then begins again with another reaction of ClO with O. Because Cl or ClO is reformed each time an ozone molecule is destroyed, chlorine is considered a catalyst for ozone destruction. Atomic oxygen (O) is formed when ultraviolet sunlight reacts with ozone and oxygen molecules. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where ultraviolet sunlight is most intense.

Ozone Destruction Cycles

Cycle 2

$$ClO + ClO \rightarrow (ClO)_2$$

$$(ClO)_2 + \text{sunlight} \rightarrow ClOO + Cl$$

$$ClOO \rightarrow Cl + O_2$$

$$2(Cl + O_3 \rightarrow ClO + O_2)$$

$$\text{Net: } 2O_3 \rightarrow 3O_2$$

Cycle 3

$$ClO + BrO \rightarrow Cl + Br + O_2$$

$$\text{or} \left(\begin{array}{c} ClO + BrO \rightarrow BrCl + O_2 \\ BrCl + \text{sunlight} \rightarrow Cl + Br \end{array} \right)$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$Br + O_3 \rightarrow BrO + O_2$$

$$\text{Net: } 2O_3 \rightarrow 3O_2$$

Figure Q9-2. Polar ozone destruction Cycles 2 and 3. Significant destruction of ozone occurs in polar regions because ClO abundances reach large values. In this case, the cycles initiated by the reaction of ClO with another ClO (Cycle 2) or the reaction of ClO with BrO (Cycle 3) efficiently destroy ozone. The net reaction in both cases is two ozone molecules forming three oxygen molecules. The reaction of ClO with BrO has two pathways to form the Cl 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 reformed in each cycle. Sunlight is required to complete each cycle and to help form and maintain ClO abundances.

season (see Q11 and Q12). At high ClO abundances, the rate of 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 ultraviolet sunlight. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where ultraviolet 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 stratospheres, 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 stratospheres. The visible sunlight needed in Cycles 2 and 3 is not sufficient to form ozone because this process requires ultraviolet sunlight. In the stratosphere in the late winter/early spring period, ultraviolet sunlight is weak because Sun angles are low. As a result, ozone is destroyed by Cycles 2 and 3 in the sunlit winter stratosphere but is not produced in significant amounts.

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.

Q10: Why has an "ozone hole" appeared over Antarctica when ozone-depleting gases are present throughout the stratosphere?

Ozone-depleting gases are present throughout the stratospheric ozone layer because they are transported great distances by atmospheric air motions. The severe depletion of the Antarctic ozone layer known as the "ozone hole" occurs because of the special weather conditions that exist there and nowhere else on the globe. The very low temperatures of the Antarctic stratosphere create ice clouds called polar stratospheric clouds (PSCs). Special reactions that occur on PSCs and the relative isolation of polar stratospheric air allow chlorine and bromine reactions to produce the ozone hole in Antarctic springtime.

The severe depletion of stratospheric ozone in Antarctic winter is known as the "ozone hole" (see Q11). Severe depletion first appeared over Antarctica because atmospheric conditions there increase the effectiveness of ozone destruction by reactive halogen gases (see Q8). The formation of the Antarctic ozone hole requires abundant reactive halogen gases, temperatures low enough to form polar stratospheric clouds (PSCs), isolation of air from other stratospheric regions, and sunlight.

Distributing halogen gases. Halogen source gases emitted at Earth's surface are present in comparable abundances throughout the stratosphere in both hemispheres even though most of the emissions occur in the Northern Hemisphere. The abundances are comparable because most source gases have no important natural removal processes in the lower atmosphere and because winds and warm-air convection redistribute and mix air efficiently throughout the troposphere. Halogen gases (in the form of source gases and some reactive products) enter the stratosphere primarily from the tropical upper troposphere. Atmospheric air motions then transport them upward and toward the poles in both hemispheres.

Low temperatures. The severe ozone destruction represented by the ozone hole requires that low tempera-

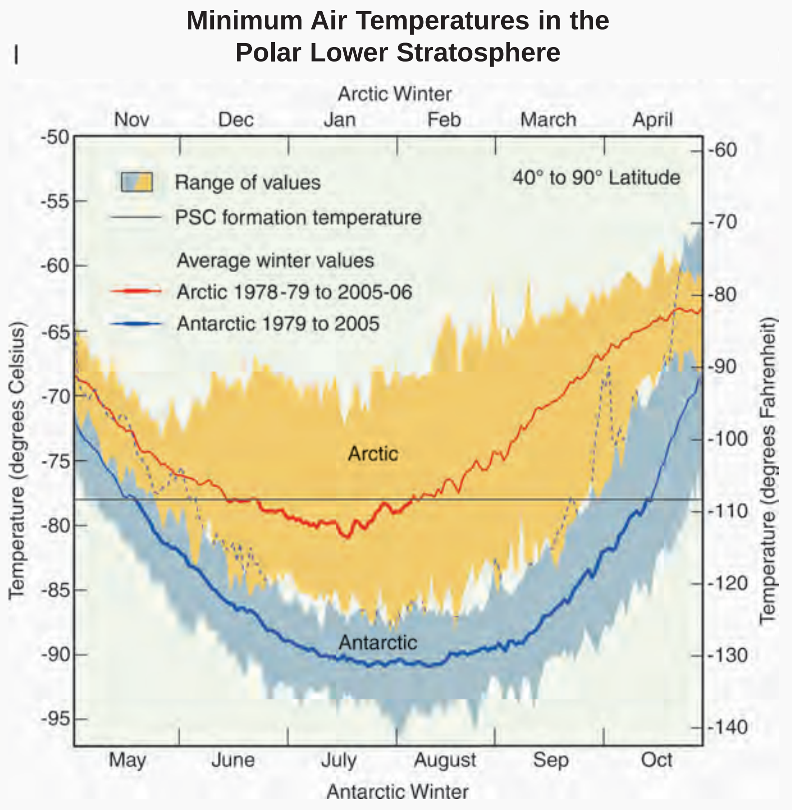

Figure Q10-1. Arctic and Antarctic temperatures. Stratospheric air temperatures in both polar regions reach minimum values in the lower stratosphere in the winter season. Average minimum values over Antarctica are as low as –90°C in July and August in a typical year. Over the Arctic, average minimum values are near –80°C in January and February. Polar stratospheric clouds (PSCs) are formed when winter minimum temperatures fall below the formation temperature (about –78°C). This occurs on average for 1 to 2 months over the Arctic and 5 to 6 months over Antarctica (see heavy red and blue lines). Reactions on PSCs cause the highly reactive chlorine gas ClO to be formed, which increases the destruction of ozone (see Q9). The range of winter minimum temperatures found in the Arctic is much greater than in the Antarctic. In some years, PSC formation temperatures are not reached in the Arctic, and significant ozone depletion does not occur. In the Antarctic, PSCs are present for many months, and severe ozone depletion now occurs in each winter season.

tures be present over a range of stratospheric altitudes, over large geographical regions, and for extended time periods. Low temperatures are important because they allow polar stratospheric clouds (PSCs) to form. Reactions on the surfaces of the cloud particles initiate a remarkable increase in the most reactive halogen gases (see below and Q8). Temperatures are lowest in the stratosphere over both polar regions in winter. In the Antarctic winter, minimum temperatures are generally lower and less variable than in the Arctic winter (see Figure Q10-1). Antarctic temperatures also remain below the PSC formation temperature for much longer periods during winter. This occurs, in part, because there are significant meteorological differences between the hemispheres, resulting from the differences in the distributions of land, ocean, and mountains at middle and high latitudes. The winter temperatures are low enough for PSCs to form for nearly the entire Antarctic winter but usually only for part of every Arctic winter.

Isolated conditions. Air in the polar stratospheric regions is relatively isolated from other stratospheric regions for long periods in the winter months. The isolation comes about because of strong winds that encircle the poles, preventing substantial motion of air in or out of the polar stratospheres. The isolation is much more effective in the Antarctic than the Arctic. Once chemical changes occur in the cold air as a result of the presence of PSCs, the changes remain for many weeks to months.

Polar stratospheric clouds (PSCs). Polar stratospheric clouds cause changes in the relative abundances of reactive chlorine gases. Reactions occur on the surfaces of PSC particles that convert the reservoir forms of reactive chlorine gases, $ClONO_2$ and HCl, to the most reactive form, ClO (see Figure Q8-1). ClO increases from a small fraction of available reactive chlorine gases to nearly all that is available (see Q8). With increased ClO, additional catalytic cycles involving ClO and BrO become active in the chemical destruction of ozone when sunlight is available (see Q9).

PSCs form when stratospheric temperatures fall below about –78°C (–108°F) in polar regions (see Figure Q10-1). As a result, PSCs are often found over large areas of the winter polar regions and over a significant altitude range. At low polar temperatures, nitric acid (HNO_3) and water condense on preexisting sulfur-containing particles to form solid and liquid PSC particles. At even lower temperatures, ice particles also form. PSC particles grow large enough and are numerous enough that cloud-like features can be observed from the ground under certain conditions, particularly when the Sun is near the horizon (see Figure Q10-2). PSCs are often found near mountain ranges in polar regions because the motion of air over the mountains can cause local cooling of stratospheric air.

When temperatures increase by early spring, PSCs no longer form and the production of ClO ends. Without continued ClO production, ClO amounts decrease as other chemical reactions reform $ClONO_2$ and HCl. As a result, the intense period of ozone depletion ends.

PSC removal. Once formed, PSC particles move downward because of gravity. The largest particles move down several kilometers or more in the stratosphere during the low-temperature winter/spring period. Because most PSCs contain nitric acid, their downward motion removes nitric acid from regions of the ozone layer. That process is called *denitrification*. With less nitric acid, the

Arctic Polar Stratospheric Clouds

Figure Q10-2. Polar stratospheric clouds. This photograph of an Arctic polar stratospheric cloud (PSC) was taken from the ground at Kiruna, Sweden (67°N), on 27 January 2000. PSCs form during winters in the Arctic and Antarctic stratospheres. The particles grow from the condensation of water and nitric acid (HNO_3). The clouds often can be seen with the human eye when the Sun is near the horizon. Reactions on PSCs cause the highly reactive chlorine gas ClO to be formed, which is very effective in the chemical destruction of ozone (see Q9).

highly reactive chlorine gas ClO remains chemically active for a longer period, thereby increasing chemical ozone destruction. Denitrification occurs each winter in the Antarctic and in some, but not all, Arctic winters, because PSC formation temperatures are required over an extensive time period.

Discovering the role of PSCs. The formation of PSCs has been recognized for many years from ground-based observations. However, the geographical and altitude extent of PSCs in both polar regions was not known fully until PSCs were observed by a satellite instrument in the late 1970s. The role of PSCs in converting reactive chlorine gases to ClO was not understood until after the discovery of the Antarctic ozone hole in 1985. Our understanding of the PSC role developed from laboratory studies of their surface reactivity, computer modeling studies of polar stratospheric chemistry, and sampling of PSC particles and reactive chlorine gases, such as ClO, in the polar stratospheric regions.

The Discovery of the Antarctic Ozone Hole

The first decreases in Antarctic total ozone were observed in the early 1980s over research stations located on the Antarctic continent. The measurements were made with ground-based Dobson spectrophotometers (see box in Q5). The observations showed unusually low total overhead ozone during the late winter/early spring months of September, October, and November. Total ozone was lower in these months compared with previous observations made as early as 1957. The early published reports came from the British Antarctic Survey and the Japan Meteorological Agency. The results became more widely known in the international community after three scientists from the British Antarctic Survey published them in the journal *Nature* in 1985. Soon after, satellite measurements confirmed the spring ozone depletion and further showed that in each late winter/early spring season starting in the early 1980s, the depletion extended over a large region centered near the South Pole. The term “ozone hole” came about from satellite images of total ozone that showed very low values encircling the Antarctic continent each spring (see Q11). Currently, the formation and severity of the Antarctic “ozone hole” are documented each year by a combination of satellite, ground-based, and balloon observations of ozone.

III. STRATOSPHERIC OZONE DEPLETION

Q11: How severe is the depletion of the Antarctic ozone layer?

Severe depletion of the Antarctic ozone layer was first observed in the early 1980s. Antarctic ozone depletion is seasonal, occurring primarily in late winter and early spring (August-November). Peak depletion occurs in early October when ozone is often completely destroyed over a range of altitudes, reducing overhead total ozone by as much as two-thirds at some locations. This severe depletion creates the "ozone hole" in images of Antarctic total ozone made from space. In most years the maximum area of the ozone hole far exceeds the size of the Antarctic continent.

The severe depletion of Antarctic ozone, known as the "ozone hole," was first observed in the early 1980s. The depletion is attributable to chemical destruction by reactive halogen gases, which increased in the stratosphere in the latter half of the 20th century (see Q16). Conditions in the Antarctic winter stratosphere are highly suitable for ozone depletion because of (1) the long periods of extremely low temperatures, which promote polar stratospheric cloud (PSC) formation; (2) the abundance of reactive halogen gases, which chemically destroy ozone; and (3) the isolation of stratospheric air during the winter, which allows time for chemical destruction to occur (see Q10). The severity of Antarctic ozone depletion can be seen using satellite observations of total ozone, ozone altitude profiles, and long-term average values of polar total ozone.

Antarctic ozone hole. The most widely used images of Antarctic ozone depletion are those from space-based measurements of total ozone. Satellite images made during Antarctic winter and spring show a large region centered near the South Pole in which total ozone is highly depleted (see Figure Q11-1). This region has come to be called the "ozone hole" because of the near-circular contours of low ozone values in the images. The area of the ozone hole is defined here as the area contained within the 220-Dobson unit (DU) contour in total ozone maps (light blue color in Figure Q11-1). The maximum area has reached 25 million square kilometers (about 10 million square miles) in recent years, which is nearly twice the area of the Antarctic continent (see Figure Q11-2). Minimum values of total ozone inside the ozone hole averaged in late September have reached below 100 DU, which is well below normal springtime values of about 200 DU (see Figure Q11-2).

Altitude profiles of Antarctic ozone. Ozone within the "ozone hole" is also measured using balloonborne instruments (see Q5). Balloon measurements show changes within the ozone layer, the vertical region that contains the highest ozone abundances in the stratosphere. At geographic locations where the lowest total ozone values occur in ozone hole images, balloon measurements show that the chemical destruction of ozone is complete over a vertical region of several kilometers. Balloon measurements shown in Figure Q11-3 give an example of such depletion over South Pole, Antarctica, on 2 October 2001. The altitude region of total depletion (14-20 kilometers) in the profile corresponds to the region of lowest

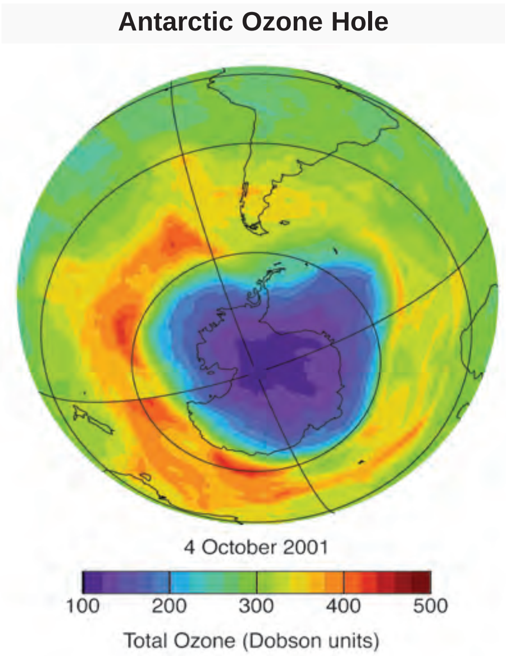

Figure Q11-1. Antarctic "ozone hole." Total ozone values are shown for high southern latitudes as measured by a satellite instrument. The dark blue and purple regions over the Antarctic continent show the severe ozone depletion or "ozone hole" now found during every spring. Minimum values of total ozone inside the ozone hole are close to 100 Dobson units (DU) compared with normal springtime values of about 200 DU (see Q4). In late spring or early summer (November-December) the ozone hole disappears in satellite images as ozone-depleted air is displaced and mixed with ozone-rich air transported poleward from outside the ozone hole.

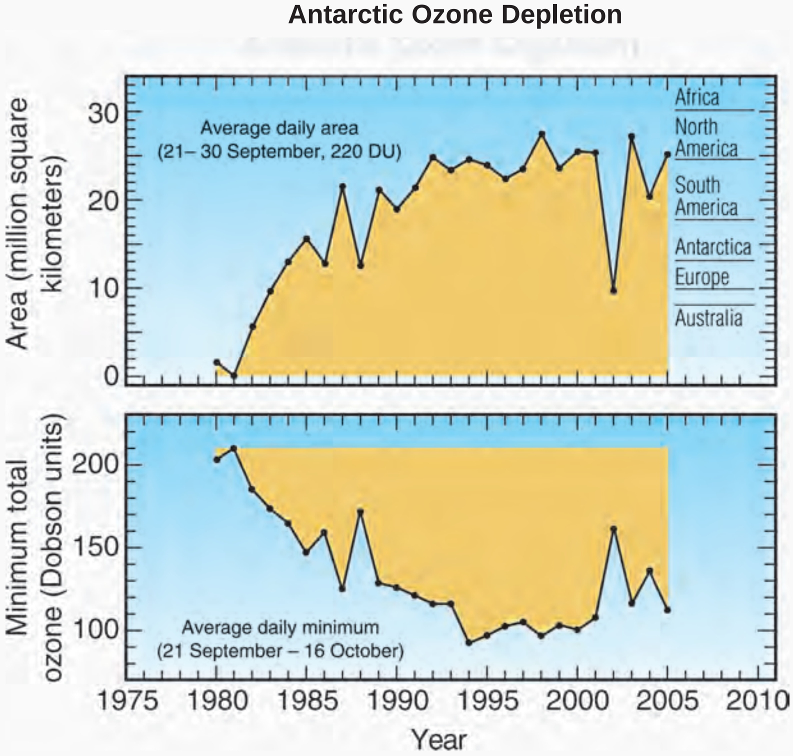

Figure Q11-2. Antarctic ozone hole features. Values are shown for key parameters of the Antarctic ozone hole: the area enclosed by the 220-DU total ozone contour and the minimum total ozone amount, as determined from space-based observations. The values are averaged for each year near the peak of ozone depletion, as defined by the dates shown in each panel. The ozone hole areas are contrasted to the areas of continents in the upper panel. The intensity of ozone depletion gradually increased beginning in 1980. In the 1990s, the depletion reached fairly steady values, except for the anomalously low depletion in 2002 (see Figure Q11-box). The intensity of Antarctic ozone depletion will decrease as part of the ozone recovery process (see Q19 and Q20).

winter temperatures and highest chlorine monoxide (ClO) abundances. The average South Pole ozone profiles for the decades 1962-1971 and 1992-2001 (see Figure Q11-3) show how reactive halogen gases have dramatically altered the ozone layer. For the 1960s, the ozone layer is clearly evident in the October average profile and has a peak near 16 kilometers. For the 1990s, minimum average values in the center of the layer have fallen by 90% from the earlier values.

Long-term total ozone changes. Low winter temperatures and isolated conditions occur each year in the Antarctic stratosphere, but significant spring ozone depletion has been observed every year only since the early 1980s. In prior years, the amounts of reactive halogen gases in the stratosphere were insufficient to cause significant depletion. Satellite observations can be used to examine how ozone depletion has changed with time in both polar regions for the last three decades. Changes in ozone hole areas and minimum Antarctic ozone amounts are shown in Figure Q11-2. Depletion has increased since 1980 to become fairly stable in the 1990s and early 2000s, with the exception of 2002 (see Q11-box). Total ozone averaged over the Antarctic region in late winter/early spring shows similar features (Figure Q12-1). Average values decreased steadily through the 1980s and 1990s, reaching minimum values that were 37% less than in pre-ozone-hole years (1970-1982). The year-to-year changes in the average values reflect variations in the meteorological conditions, which affect the extent of low polar temperatures and the transport of air into and out of the Antarctic winter stratosphere (see Figure Q11-box). However, essentially all of the ozone depletion in the Antarctic in most years is attributable to chemical loss from reactive halogen gases.

Restoring ozone in spring. The depletion of Antarctic ozone occurs primarily in the late winter/early spring season. In spring, temperatures in the lower polar stratosphere eventually warm, thereby ending PSC formation as well as the most effective chemical cycles that destroy ozone (see Q10). The transport of air between the polar stratosphere and lower latitudes also increases during this time, ending winter isolation. This allows ozone-rich air to be transported to polar regions, displacing air in which ozone has been severely depleted. This displaced air is mixed at lower latitudes with more abundant ozone-rich air. As a result, the ozone hole disappears by December and Antarctic ozone amounts remain near normal until the next winter season.

Polar Ozone Depletion

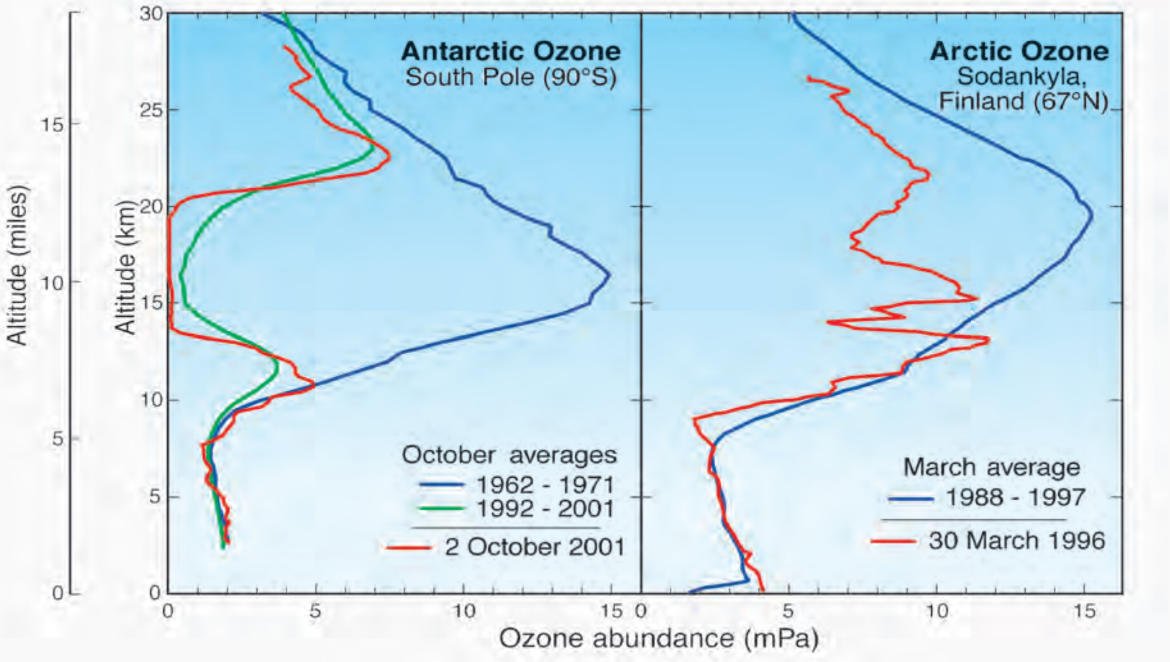

Figure Q11-3. Arctic and Antarctic ozone distribution. The stratospheric ozone layer resides between about 10 and 50 kilometers (6 to 31 miles) above Earth's surface over the globe. Long-term observations of the ozone layer with balloonborne instruments allow the winter Antarctic and Arctic regions to be compared. In the Antarctic at the South Pole, halogen gases have destroyed ozone in the ozone layer beginning in the 1980s. Before that period, the ozone layer was clearly present, as shown here using average ozone values from balloon observations made between 1962 and 1971. In more recent years, as shown here for 2 October 2001, ozone is destroyed completely between 14 and 20 kilometers (8 to 12 miles) in the Antarctic in spring. Average October values in the ozone layer now are reduced by 90% from pre-1980 values. The Arctic ozone layer is still present in spring as shown by the average March profile obtained over Finland between 1988 and 1997. However, March Arctic ozone values in some years are often below normal average values as shown here for 30 March 1996. In such years, winter minimum temperatures are generally below PSC formation temperatures for long periods. Ozone abundances are shown here with the unit "milli-Pascals" (mPa), which is a measure of absolute pressure (100 million mPa = atmospheric sea-level pressure).

The Anomalous 2002 Antarctic Ozone Hole

The 2002 Antarctic ozone hole showed features that surprised scientists. They considered it anomalous at the time because the hole had much less area as viewed from space and much less ozone depletion as measured by minimum column ozone amounts when compared with values in several preceding years (see Figure Q11-box). The 2002 ozone hole area and minimum ozone values stand out clearly in displays of the year-to-year changes in these quantities (see Figure Q11-2). The smaller area was unexpected because the conditions required to deplete ozone, namely low temperatures and available reactive halogen gases, are not expected to have large year-to-year variations. Ozone was being depleted in August and early September 2002, but the hole *broke apart* into two separate depleted regions during the last week of September. The depletion in these two regions was significantly less than was observed inside either the 2001 or 2003 ozone holes, but still substantially greater than was observed in the early 1980s.

The anomalous behavior in 2002 occurred because of specific atmospheric air motions that sometimes occur in polar regions, not large decreases in reactive chlorine and bromine amounts in the Antarctic stratosphere. The Antarctic stratosphere was warmed by very strong, large-scale weather systems in 2002 that originated in the lower atmosphere (troposphere) at midlatitudes in late September. In late September, Antarctic temperatures are generally very low (see Q10) and ozone destruction rates are near their peak values. These tropospheric systems traveled poleward and upward into the stratosphere, upsetting the circumpolar wind flow and warming the lower stratosphere where ozone depletion was ongoing. The higher-than-normal impact of these weather disturbances during the critical time period for ozone loss reduced the total loss of ozone in 2002.

The warming in 2002 was unprecedented in Antarctic meteorological observations. Warming events are difficult to predict because of their complex formation conditions.

Large Antarctic ozone depletion returned in 2003 through 2005, in a manner similar to that observed from the mid-1990s to 2001 (see Figures Q11-box and Q11-2). The high ozone depletion found since the mid-1990s, with the exception of 2002, is expected to be typical of coming years. A significant, sustained reduction of Antarctic ozone depletion, defined as ozone recovery, requires the removal of halogen source gases from the stratosphere (see Q19 and Q20).

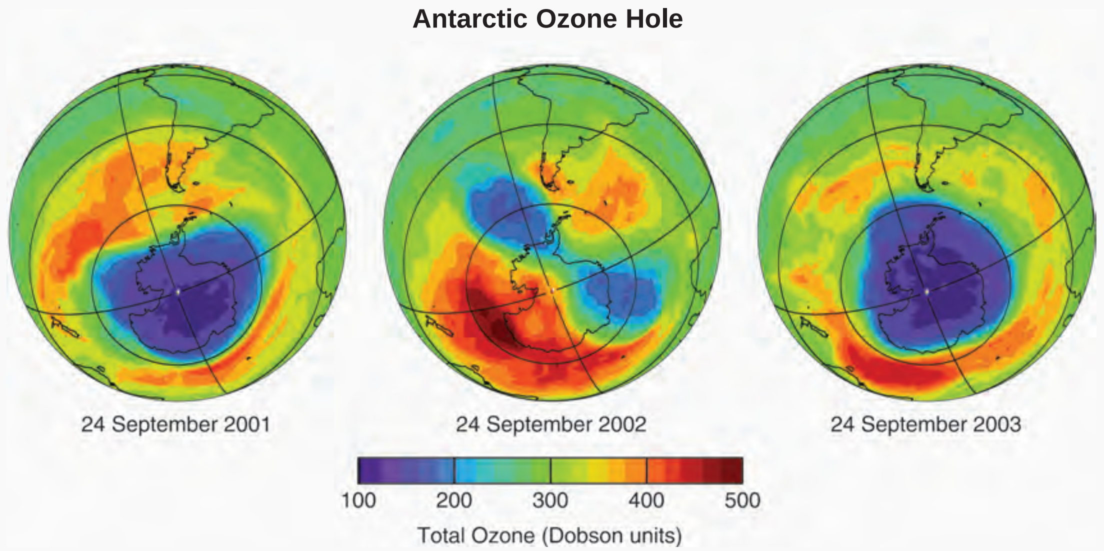

Figure Q11-Box. Anomalous 2002 ozone hole. Views from space of the Antarctic ozone hole as observed on 24 September in each of three consecutive years. The hole split and elongated in 2002, reducing the total depletion of ozone observed that year in comparison with 2001 and 2003. The anomalous depletion in 2002 is attributable to an early warming of the polar stratosphere caused by air disturbances originating in midlatitudes, rather than to large changes in the amounts of reactive chlorine and bromine in the Antarctic stratosphere.

Q12: Is there depletion of the Arctic ozone layer?

> *Yes, significant depletion of the Arctic ozone layer now occurs in some years in the late winter/early spring period (January-April). However, the maximum depletion is less severe than that observed in the Antarctic and is more variable from year to year. A large and recurrent "ozone hole," as found in the Antarctic stratosphere, does not occur in the Arctic.*

Significant ozone depletion in the Arctic stratosphere occurs in cold winters because of reactive halogen gases. The depletion, however, is much less than the depletion that now occurs in every Antarctic winter and spring. Although Arctic depletion does not generally create persistent "ozone hole"-like features in Arctic total ozone maps, depletion is observed in altitude profiles of ozone and in long-term average values of polar ozone.

Altitude profiles of Arctic ozone. Arctic ozone is measured using a variety of instruments (see Q5), as for the Antarctic (see Q11). These measurements show changes within the ozone layer, the vertical region that contains the highest ozone abundances in the stratosphere. Figure Q11-2 shows an example of balloonborne measurements of a depleted ozone profile in the Arctic region on 30 March 1996, and contrasts the depletion with that found in the Antarctic. The 30 March spring profile shows much less depletion than the 2 October spring profile in the Antarctic. In general, some reduction in the Arctic ozone layer occurs each late winter/early spring season. However, complete depletion each year over a broad vertical layer, as is now common in the Antarctic stratosphere, is not found in the Arctic.

Long-term total ozone changes. Satellite and ground-based observations can be used to examine the average total ozone abundances in the Arctic region for the last three decades and to contrast them with Antarctic abundances (see Figure Q12-1). Decreases from the pre-ozone-hole average values (1970-1982) were observed in the Arctic beginning in the 1980s, when similar changes were occurring in the Antarctic. The decreases have reached a maximum of about 30% but have remained smaller than those found in the Antarctic since the mid-1980s. The year-to-year changes in the Arctic and Antarctic average ozone values reflect annual variations in meteorological conditions that affect the extent of low polar temperatures and the transport of air into and out of the polar stratosphere. The effect of these variations is generally greater for the Arctic than the Antarctic.

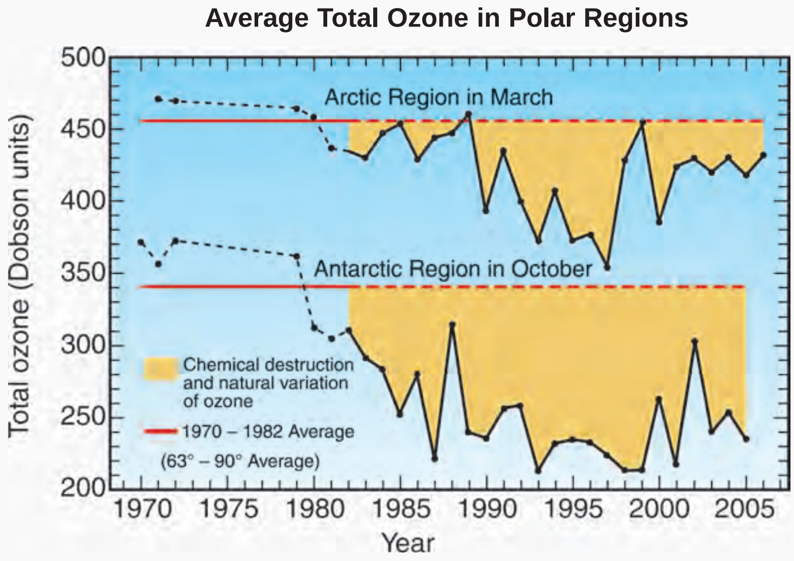

Figure Q12-1. Average polar ozone. Total ozone in polar regions is measured by well-calibrated satellite instruments. Shown here is a comparison of average springtime total ozone values found between 1970 and 1982 (solid and dashed red lines) with those in later years. Each point represents a monthly average in October in the Antarctic or in March in the Arctic. After 1982, significant ozone depletion is found in most years in the Arctic and all years in the Antarctic. The largest average depletions have occurred in the Antarctic since 1990. The ozone changes are the combination of chemical destruction and natural variations. Variations in meteorological conditions influence the year-to-year changes in depletion, particularly in the Arctic. Essentially all of the decrease in the Antarctic and usually most of the decrease in the Arctic each year are attributable to chemical destruction by reactive halogen gases. Average total ozone values over the Arctic are naturally larger at the beginning of each winter season because more ozone is transported poleward each season in the Northern Hemisphere than in the Southern Hemisphere.

Arctic vs. Antarctic. The Arctic winter stratosphere is generally warmer than its Antarctic counterpart (see Figure Q10-1). Higher temperatures reduce polar stratospheric cloud (PSC) formation, which slows the conversion of reactive chlorine gases to form ClO and, as a consequence, reduces the amount of ozone depletion (see Q10). Furthermore, the temperature and wind conditions are much more variable in the Arctic from winter to winter and within a winter season than in the Antarctic. Large year-to-year differences occur in Arctic minimum temperatures and the duration of PSC-forming temperatures into early spring. In a few Arctic winters, minimum temperatures are not low enough for PSCs to form. These factors combine to cause ozone depletion to be variable in the Arctic from year to year, with some years having little to no ozone depletion.

As in the Antarctic, depletion of ozone in the Arctic is confined to the late winter/early spring season. In spring, temperatures in the lower stratosphere eventually warm, thereby ending PSC formation as well as the most effective chemical cycles that destroy ozone. The subsequent transport of ozone-rich air into the Arctic stratosphere displaces ozone-depleted air. As a result, ozone layer abundances are restored to near-normal values until the following winter.

High Arctic total ozone. A significant difference exists between the Northern and Southern Hemispheres in how ozone-rich stratospheric air is transported into the polar regions from lower latitudes during fall and winter. In the northern stratosphere, the poleward and downward transport of ozone-rich air is stronger. As a result, total ozone values in the Arctic are considerably higher than in the Antarctic at the beginning of each winter season (see Figure Q12-1).

Q13: How large is the depletion of the global ozone layer?

The ozone layer has been depleted gradually since 1980 and now is about an average of 4% lower over the globe. The average depletion exceeds the natural variability of the ozone layer. The ozone loss is very small near the equator and increases with latitude toward the poles. The larger polar depletion is primarily a result of the late winter/early spring ozone destruction that occurs there each year.

Stratospheric ozone has decreased over the globe since the 1980s. The depletion, which in the period 1997-2005 averaged about 4% (see Figure Q13-1), is larger than natural variations in ozone. The observations shown in Figure Q13-1 have been smoothed to remove regular ozone changes that are due to seasonal and solar effects (see Q14). The increase in reactive halogen gases in the stratosphere is considered to be the primary cause of the average depletion. The lowest ozone values in recent years occurred following the 1991 eruption of Mt. Pinatubo, which increased the number of sulfur-containing particles in the stratosphere. The particles remain in the stratosphere for several years, increasing the effectiveness of reactive halogen gases in destroying ozone (see Q14).

Observed ozone depletion varies significantly with latitude on the globe (see Figure Q13-1). The largest losses occur at the highest 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 Northern Hemisphere, caused in part by late winter/early spring losses over the Arctic. Ozone-depleted air over both polar regions is dispersed away from the poles during and after each winter/spring period. Ozone depletion also occurs directly at latitudes between the equator and polar regions but is smaller because of the presence of lower amounts of reactive halogen gases (see Q8).

Tropical regions. There has been little or no depletion of total ozone in the tropics (between about 20° latitude north and south of the equator in Figure Q13-1*)*. In

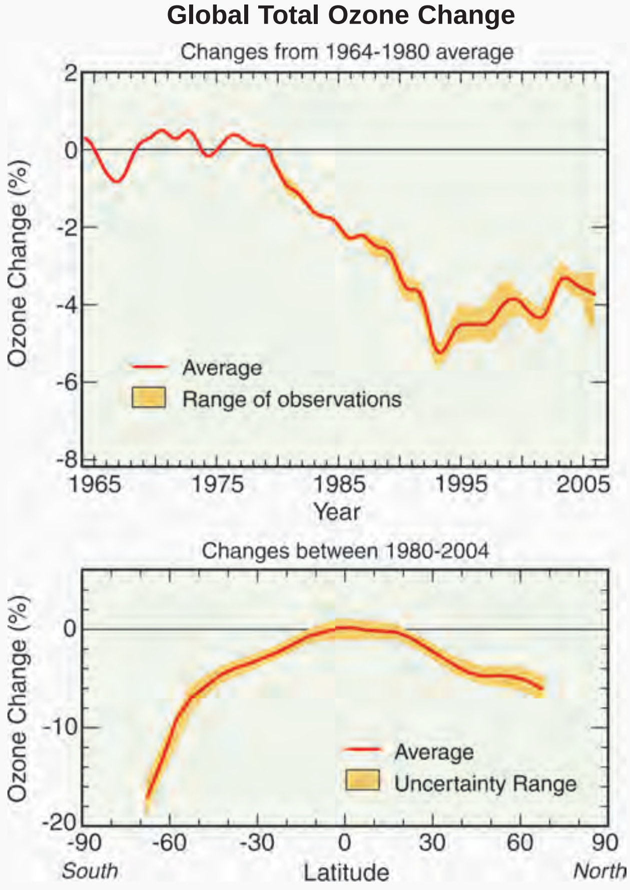

Figure Q13-1. Global total ozone changes. Satellite observations show a decrease in global total ozone values over more than two decades. The top panel compares global ozone values (annual averages) with the average from the period 1964 to 1980. Seasonal and solar effects have been removed from the data. On average, global ozone decreased each year between 1980 and the early 1990s. The decrease worsened during the few years when volcanic aerosol from the Mt. Pinatubo eruption in 1991 remained in the stratosphere. Now global ozone is about 4% below the 1964-to-1980 average. The bottom panel compares ozone changes between 1980 and 2004 for different latitudes. The largest decreases have occurred at the highest 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.

this region of the lower stratosphere, air has only recently (less than 18 months) been transported from the lower atmosphere. As a result, the conversion of halogen source gases to reactive halogen gases is very small. Because of the low abundance of reactive gases, total ozone depletion in this region is very small. In contrast, stratospheric air in polar regions has been in the stratosphere for an average of 4 to 7 years; therefore, the abundance of reactive halogen gases is much larger.

Seasonal changes. The magnitude of global ozone depletion also depends on the season of the year. In comparison with the 1964-1980 averages, total ozone averaged for 2002-2005 is about 3% lower in northern middle latitudes (35°N-60°N) and about 6% lower at southern middle latitudes (35°S-60°S). The seasonality of these changes is also somewhat different in the two hemispheres. In the summer/autumn periods, the decline in total ozone is about 2% in the Northern Hemisphere and 5% in the Southern Hemisphere. In winter/spring, the decline is about 5-6% in both hemispheres.

Q14: 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 two decades. If large volcanic eruptions occur in the coming decades, ozone depletion will increase for several years after the eruption.

Changes in solar radiation and increases in stratospheric particles from volcanic eruptions both affect the abundance of stratospheric ozone, but they have not caused the long-term decreases observed in total ozone.

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-known 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 solar output at a wavelength of 10.7 cm, although much larger than changes in total solar output, are often used to show when periods of maximum and minimum total output occur (see Figure Q14-1). The Sun's output has gone through maximum values around 1969, 1980, 1991, and 2002. In 2006, the solar output was decreasing towards a minimum.

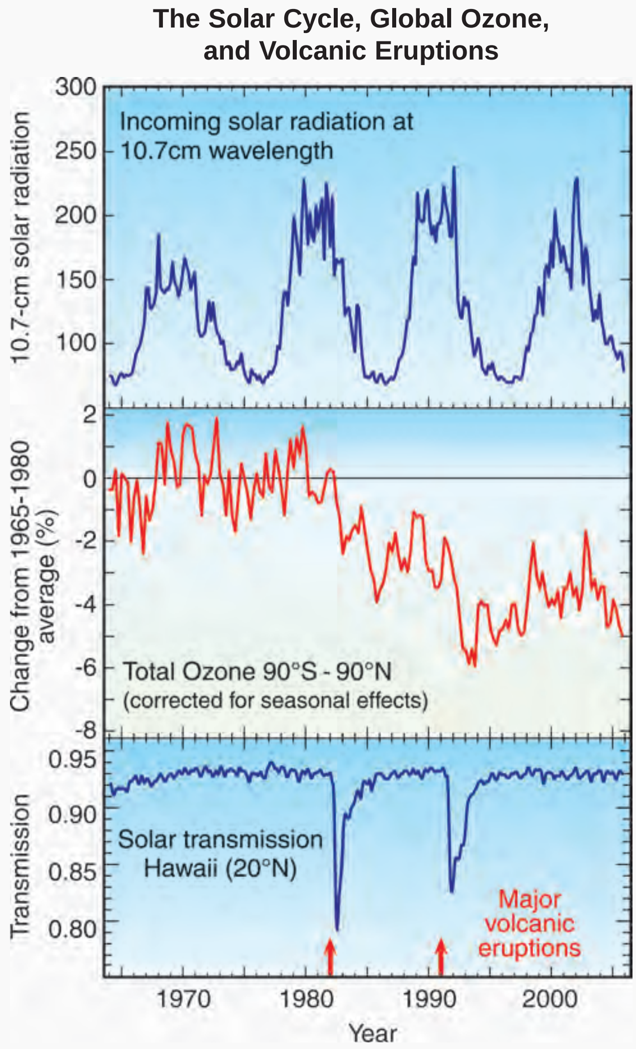
The Solar Cycle, Global Ozone, and Volcanic Eruptions

Figure Q14-1. Solar changes and volcanoes. Total ozone values have decreased beginning in the early 1980s (see middle panel). The ozone values shown are 3-month averages corrected for seasonal effects. Incoming solar radiation, which produces ozone in the stratosphere, changes on a well-recognized 11-year cycle. The amount of solar radiation at a wavelength of 10.7-cm is often used to document the 11-year cycle (see top panel). A comparison of the top and middle panels indicates that the cyclic changes in solar output cannot account for the long-term decreases in ozone. Volcanic eruptions occurred frequently in the 1965 to 2005 period. The largest recent eruptions are El Chichón (1982) and Mt. Pinatubo (1991) (see red arrows in bottom panel). Large volcanic eruptions are monitored by the decreases in solar transmission to Earth's surface that occur because new particles are formed in the stratosphere from volcanic sulfur emissions (see bottom panel). These particles increase ozone depletion only temporarily because they do not remain in the stratosphere for more than a few years. A comparison of the middle and bottom panels indicates that large volcanic eruptions also cannot account for the long-term decreases found in global total ozone.

Over the last two decades, average total ozone has decreased over the globe. Average values in recent years show about 4% depletion from pre-1980 values (see Figure Q14-1). The ozone values shown are 3-month averages corrected for seasonal effects but not for solar effects. Over the same period, changes in solar output show the expected 11-year cycle but do not show a decrease with time. For this reason, the long-term decreases in global ozone cannot result from changes in solar output alone. Most examinations of long-term ozone changes presented in this and previous international scientific assessments quantitatively account for the influence of the 11-year solar cycle.

Past volcanoes. Large volcanic eruptions inject sulfur gases directly into the stratosphere, causing new sulfate particles to be formed. The particles initially form in the stratosphere above and downwind of the volcano location and then often spread throughout the hemisphere or globally as air is transported by stratospheric winds. The presence of volcanic particles in the stratosphere is shown in observations of solar transmission through the atmosphere. When large amounts of particles are present in the stratosphere, transmission of solar radiation is significantly reduced. The large eruptions of El Chichón (1982) and Mt. Pinatubo (1991) are recent examples of events that temporarily reduced solar transmission (see Figure Q14-1).

Laboratory measurements and stratospheric observations have shown that chemical reactions on the surface of volcanically produced particles increase ozone destruction by increasing the amounts of the highly reactive chlorine gas, chlorine monoxide (ClO). The amount of ClO produced is proportional to the total abundance of reactive chlorine in the stratosphere (see Figure Q16-1). Ozone depletion increases as a consequence of increased ClO. 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). After a few years, however, the effect of volcanic particles on ozone is diminished by their gradual removal from the stratosphere by natural air circulation. Because of particle removal, the two large volcanic eruptions of the last two decades cannot account for the long-term decreases observed in ozone over the same period.

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 reactive halogen gases present in the stratosphere in the 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 the abundances of reactive halogen gases in the stratosphere were smaller. In the early decades of the 21st century, the abundance of halogen source gases will still be substantial in the global atmosphere (see Figure Q16-1). If large volcanic eruptions occur in these early decades, ozone depletion will increase for several years. If an eruption larger than Mt. Pinatubo occurs, ozone losses could be larger than previously observed and persist longer. Only later in the 21st century when halogen gas abundances have declined close to pre-1980 values will the effect of volcanic eruptions on ozone be lessened.

IV. CONTROLLING OZONE-DEPLETING GASES

Q15: Are there regulations on the production of ozone-depleting gases?

Yes, the production of ozone-depleting gases is regulated under a 1987 international agreement known as the "Montreal Protocol on Substances that Deplete the Ozone Layer" and its subsequent Amendments and Adjustments. The Protocol, now ratified by over 190 nations, establishes legally binding controls on the national production and consumption of ozone-depleting gases. Production and consumption of all principal halogen-containing gases by developed and developing nations will be significantly phased out before the middle of the 21^{st} 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 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 country ratification, entered into force in 1989. The Protocol established legally binding controls for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion. National consumption of a halogen gas is defined as the amount that production and imports of a gas exceed its export to other nations.

Amendments and Adjustments. As the scientific basis of ozone depletion became more certain after 1987 and substitutes and alternatives became available to replace the principal halogen source gases, the Montreal Protocol was strengthened with Amendments and Adjustments. These revisions put additional substances under regulation, accelerated existing control measures, and prescribed phaseout dates for the production and con-

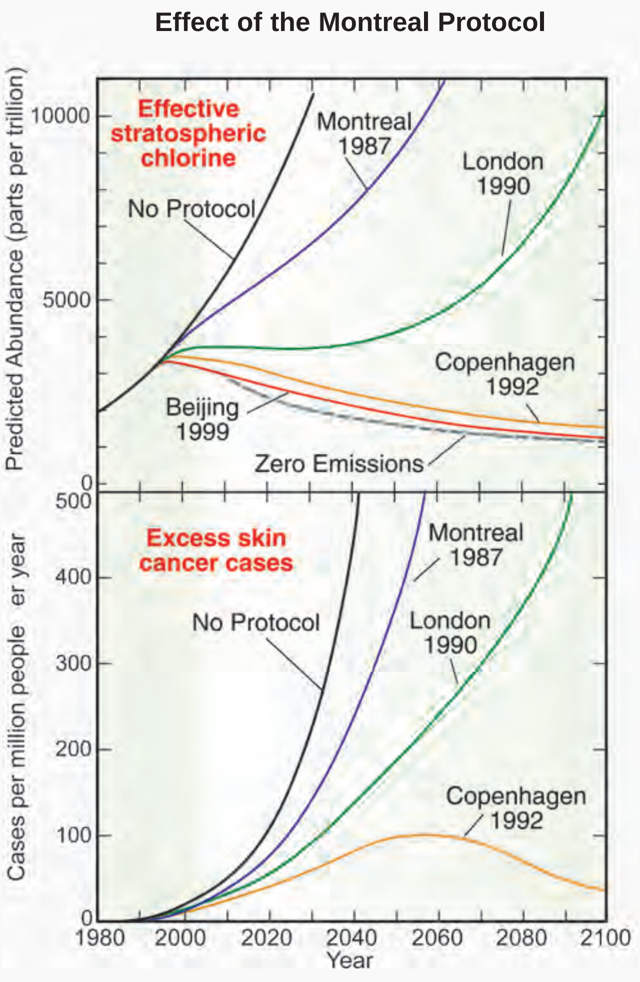

Figure Q15-1. Effect of the Montreal Protocol. The purpose of the Montreal Protocol is to achieve reductions in stratospheric abundances of chlorine and bromine. The reductions follow from restrictions on the production and consumption of manufactured halogen source gases. Projections of the future abundance of *effective stratospheric chlorine* (see Q16) are shown in the top panel assuming (1) no Protocol regulations, (2) only the regulations in the original 1987 Montreal Protocol, and (3) additional regulations from the subsequent Amendments and Adjustments. The city names and years indicate where and when changes to the original 1987 Protocol provisions were agreed upon. Effective stratospheric chlorine as used here accounts for the combined effect of chlorine and bromine gases. Without the Protocol, stratospheric halogen gases are projected to increase significantly in the 21^{st} century. The "zero emissions" line shows a hypothetical case of stratospheric abundances if all emissions were reduced to zero beginning in 2007. The lower panel shows how excess skin cancer cases (see Q17) might increase with no regulation and how they might be reduced under the Protocol provisions. (The unit "parts per trillion" is defined in the caption of Figure Q7-1.)

sumption of certain gases. The initial Protocol called for only a slowing of chlorofluorocarbon (CFC) and halon production. The 1990 London Amendments to the Protocol called for a phaseout of the production and consumption of the most damaging ozone-depleting substances in developed nations by 2000 and in developing nations by 2010. The 1992 Copenhagen Amendments accelerated the date of the phaseout to 1996 in developed nations. Further controls on ozone-depleting substances were agreed upon in later meetings in Vienna (1995), Montreal (1997), and Beijing (1999).

Montreal Protocol projections. Future stratospheric abundances of effective stratospheric chlorine (see Q16) can be calculated based on the provisions of the Montreal Protocol. The concept of *effective stratospheric chlorine* accounts for the combined effect on ozone of chlorine- and bromine-containing gases. The results are shown in Figure Q15-1 for the following cases:

- No Protocol and continued production increases of 3% per year (business-as-usual scenario).
- Continued production and consumption as allowed by the Protocol's original provisions agreed upon in Montreal in 1987.
- Restricted production and consumption as outlined in the subsequent Amendments and Adjustments as decided in London in 1990, Copenhagen in 1992, and Beijing in 1999.
- Zero emissions of ozone-depleting gases starting in 2007.

In each case, production of a gas is assumed to result in its eventual emission to the atmosphere. Without the Montreal Protocol and with continued production and use of CFCs and other ozone-depleting gases, effective stratospheric chlorine is projected to have increased tenfold by the mid-2050s compared with the 1980 value. Such high values likely would have increased global ozone depletion far beyond that currently observed. As a result, harmful UV-B radiation would have also increased substantially at Earth's surface, causing a rise in excess skin cancer cases (see Q17 and lower panel of Figure Q15-1).

The 1987 provisions of the Montreal Protocol alone would have only slowed the approach to high effective chlorine values by one or more decades in the 21st century. Not until the 1992 Copenhagen Amendments and Adjustments did the Protocol projections show a *decrease* in future effective stratospheric chlorine values. Now, with full compliance to the Montreal Protocol and its Amendments and Adjustments, use of the major human-produced ozone-depleting gases will ultimately be phased out and effective stratospheric chlorine will slowly decay, reaching pre-1980 values in the mid-21st century (see Q16).

Zero emissions. Effective chlorine values in the coming decades will be influenced by emissions of halogen source gases produced in those decades, as well as the emission of currently existing gases that are now being used or stored in various ways. Examples of long-term storage are CFCs in refrigeration equipment and foams, and halons in fire-fighting equipment. Some continued production and consumption of ozone-depleting gases is allowed, particularly in developing nations, under the agreements. As a measure of the contribution of these continued emissions to the effective chlorine value, the "zero emissions" case is included in Figure Q15-1. In this hypothetical case, all emissions of ozone-depleting gases are set to zero beginning in 2007. The reductions in effective stratospheric chlorine below the values expected with the 1999 Beijing agreement would be relatively small.

HCFC substitute gases. The Montreal Protocol provides for the transitional use of hydrochlorofluorocarbons (HCFCs) as substitute compounds for principal halogen source gases such as CFC-12. HCFCs differ chemically from most other halogen source gases in that they contain hydrogen (H) atoms in addition to chlorine and fluorine atoms. HCFCs are used for refrigeration, for blowing foams, and as solvents, which were primary uses of CFCs. HCFCs are 88 to 98% less effective than CFC-12 in depleting stratospheric ozone because they are chemically removed primarily in the troposphere (see Q18). This removal partially protects stratospheric ozone from the halogens contained in HCFCs. In contrast, CFCs and many other halogen source gases are chemically inert in the troposphere and, hence, reach the stratosphere without being significantly removed. Because HCFCs still contribute to the chlorine abundance in the stratosphere, the Montreal Protocol requires a gradual phaseout of HCFC consumption in developed and developing nations that will be complete in 2040.

HFC substitute gases. Hydrofluorocarbons (HFCs) are also used as substitute compounds for CFCs and other halogen source gases. HFCs contain only hydrogen, fluorine, and carbon atoms. Because HFCs contain no chlorine or bromine, they do not contribute to ozone depletion (see Q18). As a consequence, the Montreal Protocol does not regulate the HFCs. However, HFCs (as well as all halogen source gases) are radiatively active gases that contribute to human-induced climate change as they accumulate in the atmosphere (see Q18). HFCs are included in the group of gases listed in the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC).

Q16: Has the Montreal Protocol been successful in reducing ozone-depleting gases in the atmosphere?

Yes, as a result of the Montreal Protocol, the total abundance of ozone-depleting gases in the atmosphere has begun to decrease in recent years. If the nations of the world continue to follow the provisions of the Montreal Protocol, the decrease will continue throughout the 21st century. Some individual gases, such as halons and hydrochlorofluorocarbons (HCFCs), are still increasing in the atmosphere but will begin to decrease in the next decades if compliance with the Protocol continues. Around midcentury, the effective abundance of ozone-depleting gases should fall to values that were present before the Antarctic "ozone hole" began to form in the early 1980s.

Effective stratospheric chlorine. The Montreal Protocol has been successful in slowing and reversing the increase of ozone-depleting gases (halogen source gases) in the atmosphere. An important measure of its success is the change in the value of *effective stratospheric chlorine.* Effective stratospheric chlorine values are a measure of the potential for ozone depletion in the stratosphere, obtained by summing over adjusted amounts of all chlorine and bromine gases. The adjustments account for the different rates of decomposition of the gases and the greater per-atom effectiveness of bromine in depleting ozone (see Q7). Although chlorine is much more abundant in the stratosphere than bromine (160 times) (see Figure Q7-1), bromine atoms are about 60 times more effective than chlorine atoms in chemically destroying ozone molecules. Increases in effective stratospheric chlorine in the past decades have caused ozone depletion. Accordingly, ozone is expected to recover in the future as effective stratospheric chlorine values decrease.

Effective stratospheric chlorine changes. In the latter half of the 20th century up until the 1990s, effective stratospheric chlorine values steadily increased (see Figure Q16-1). Values are derived from individual halogen source gas abundances obtained from measurements, historical estimates of abundance, and projections of future abundance. As a result of the Montreal Protocol regulations, the long-term increase in effective stratospheric chlorine slowed, reached a peak, and began to decrease in the 1990s. This initial decrease means that the potential for stratospheric ozone depletion has begun to lessen as a result of the Montreal Protocol. The decrease in effective chlorine is 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 become small, natural destruction processes gradually remove halogen-containing gases from the global atmosphere. Reduction of effective stratospheric chlorine amounts to 1980 values or lower will require many decades because the lifetimes of halogen source gas molecules in the atmosphere range up to 100 years (see Figure Q16-1 and Table Q7-1).

Individual halogen source gas reductions. The reduction in the atmospheric abundance of a gas in response to regulation depends on a number of factors that include (1) how rapidly gas reserves are used and released to the atmosphere, (2) the lifetime for the removal of the gas from the atmosphere, and (3) the total amount of the gas that has already accumulated in the atmosphere.

The regulation of human-produced halogen source gases under the Montreal Protocol is considered separately for each class of one or more gases and is based on several factors. The factors include (1) the effectiveness of each class in depleting ozone in comparison with other halogen source gases, (2) the availability of suitable substitute gases for domestic and industrial use, and (3) the impact of regulation on developing nations.

Methyl chloroform and CFCs. The largest reduction in the abundance of a halogen source gas has occurred for methyl chloroform (CH_3CCl_3) (see Figure Q16-1). The implementation of the Montreal Protocol caused global production of methyl chloroform to be reduced to near zero. Atmospheric abundances subsequently dropped rapidly 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. The reduction in effective chlorine in the 1990s came primarily from the reduction in methyl chloroform abundance in the atmosphere. Significant emissions reductions have also occurred for the chlorofluorocarbons CFC-11, CFC-12, and CFC-113 starting in the 1990s. As a result, the atmospheric amounts of these gases have all peaked, and CFC-11 and CFC-113 abundances have decreased slightly (see Figure Q16-1). As emissions of CFCs are reduced, their atmospheric abundances will decrease more slowly than methyl chloroform because of longer CFC atmospheric lifetimes (see Table Q7-1) and because CFCs escape very slowly to the atmosphere from their use in refrigeration

Past and Expected Future Abundances of Atmospheric Halogen Source Gases

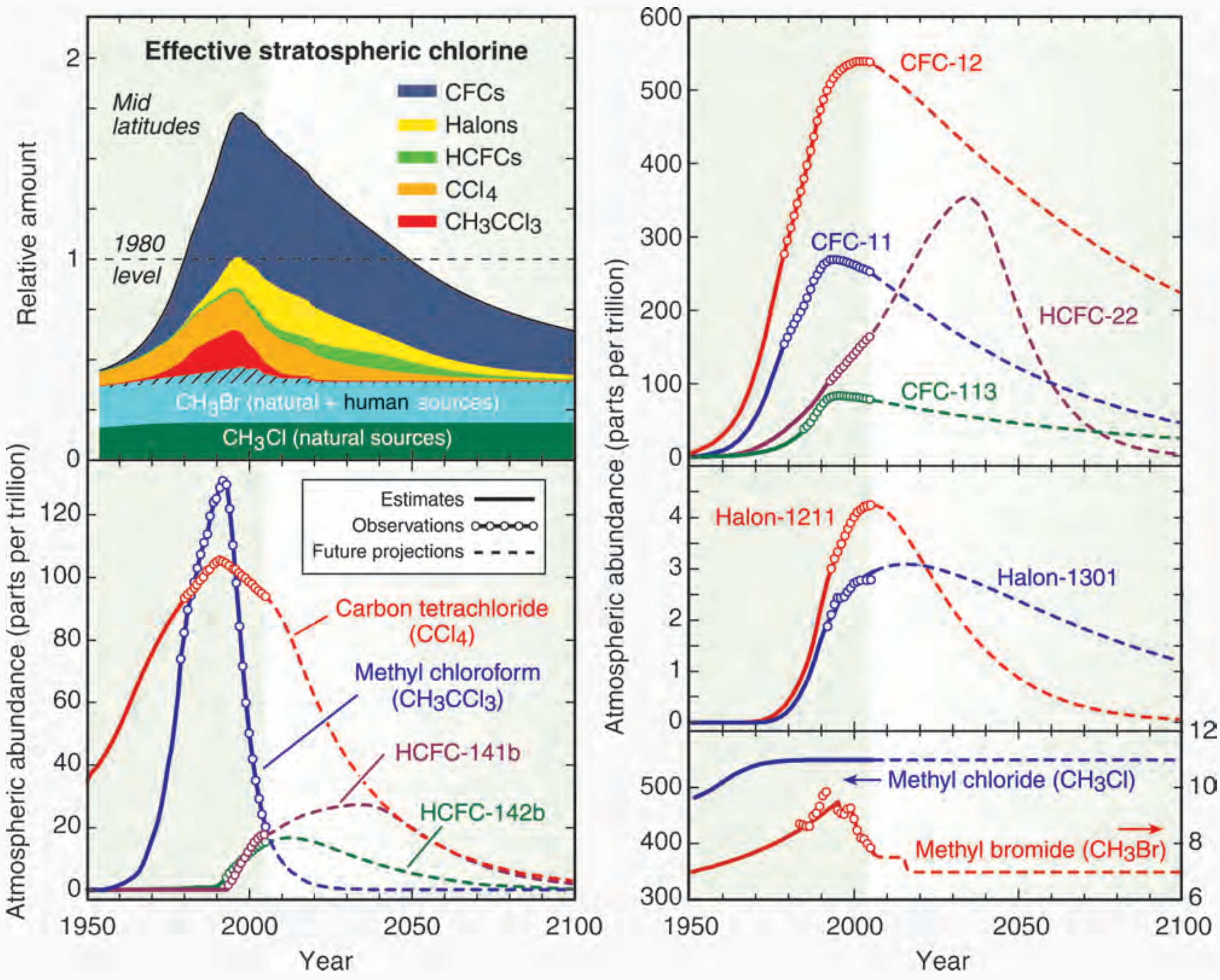

Figure Q16-1. Halogen source gas changes. The rise in effective stratospheric chlorine values in the 20th century has slowed and reversed in the last decade (top left panel). Effective stratospheric chlorine values are a measure of the potential for ozone depletion in the stratosphere, obtained by summing over adjusted amounts of all chlorine and bromine gases. Effective stratospheric chlorine levels as shown here for midlatitudes will return to 1980 values around 2050. The return to 1980 values will occur around 2065 in polar regions. In 1980, ozone was not significantly depleted by the chlorine and bromine then present in the stratosphere. A decrease in effective stratospheric chlorine abundance follows reductions in emissions of individual halogen source gases. Overall emissions and atmospheric concentrations have decreased and will continue to decrease given international compliance with the Montreal Protocol provisions (see Q15). The changes in the atmospheric abundance of individual gases at Earth's surface shown in the panels were obtained using a combination of direct atmospheric measurements, estimates of historical abundance, and future projections of abundance. The past increases of CFCs, along with those of CCl_4 and CH_3CCl_3, have slowed significantly and most have reversed in the last decade. HCFCs, which are used as CFC substitutes, will continue to increase in the coming decades. Some halon abundances will also continue to grow in the future while current halon reserves are depleted. Smaller relative decreases are expected for CH_3Br in response to production and use restrictions because it has substantial natural sources. CH_3Cl has large natural sources and is not regulated under the Montreal Protocol. (See Figure Q7-1 for chemical names and formulas. The unit "parts per trillion" is defined in the caption of Figure Q7-1.)

and foam products.

HCFC substitute gases. The Montreal Protocol allows for the use of hydrochlorofluorocarbons (HCFCs) as short-term substitutes for CFCs. As a result, the abundances of HCFC-22, HCFC-141b, and HCFC-142b continue to grow in the atmosphere (see Figure Q16-1). HCFCs pose a lesser threat to the ozone layer than CFCs because they are partially destroyed in the troposphere by chemical processes, thus reducing the overall effectiveness of their emissions in destroying stratospheric ozone. Under the Montreal Protocol, HCFC consumption will reach zero in developed nations by 2030 and in developing nations by 2040 (see Q15). Thus, the future projections in Figure Q16-1 show HCFC abundances reaching a peak in the first decades of the 21st century and steadily decreasing thereafter.

Halons. The atmospheric abundances of halon-1211 and halon-1301 account for a significant fraction of bromine from all source gases (see Figure Q7-1) and continue to grow despite the elimination of production in developed nations in 1994 (see Figure Q16-1). The growth in abundance continues because substantial reserves are held in fire-extinguishing equipment and are gradually being released, and production and consumption are still allowed in developing nations. Atmospheric halon abundances can be expected to remain high well into the 21st century because of their long lifetimes and continued release.

Methyl chloride and methyl bromide. Both methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) are distinct among principal halogen source gases because a substantial fraction of their emissions is associated with natural processes (see Q7). The average atmospheric abundance of methyl chloride, which is not regulated under the Montreal Protocol, will remain fairly constant throughout this century if natural sources remain unchanged. At century's end, methyl chloride is expected to account for a large fraction of remaining effective stratospheric chlorine because the abundances of other gases, such as the CFCs, are expected to be greatly reduced (see Figure Q16-1). The abundance of methyl bromide, which is regulated under the Protocol, has already decreased in recent years and is projected to decrease further as a result of production phaseouts in developed and developing countries. For the later decades of the century, methyl bromide abundances are shown as nearly constant in Figure Q16-1. However, these abundances are uncertain because the amounts of exempted uses of methyl bromide under the Montreal Protocol are not known for future years.

V. IMPLICATIONS OF OZONE DEPLETION

Q17: 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 have confirmed that surface ultraviolet radiation has increased in regions where ozone depletion is observed.

The depletion of stratospheric ozone leads to an increase in surface ultraviolet radiation. 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. Changes in UV-B at the surface have been observed directly and can be estimated from ozone changes.

Surface UV-B radiation. The amount of ultraviolet radiation reaching Earth's surface depends in large part on the amount of ozone in the atmosphere. Ozone molecules in the stratosphere absorb UV-B radiation, thereby significantly reducing the amount of this radiation that reaches Earth's surface (see Q3). If total ozone amounts are reduced in the stratosphere, then the amount of UV radiation reaching Earth's surface generally increases. This relationship between total ozone and surface UV radiation has been studied at a variety of locations with direct measurements of both ozone and UV. The actual amount of UV reaching a location depends on a large number of additional factors, including the position of the Sun in the sky, cloudiness, and air pollution. In general, surface UV at a particular location on Earth changes throughout the day and with season as the Sun's position in the sky changes.

Long-term surface UV changes. Satellite observations of long-term global ozone changes can be used to estimate changes in global surface UV that have occurred over the past two decades. These changes are of interest because UV radiation can cause harm to humans, other life forms, and materials (see Q3). The amount of UV that produces an "erythemal" or sunburning response in humans is often separately evaluated. Long-term changes in sunburning UV at a particular location have been estimated from the changes in total ozone at that location. The results show that average erythemal UV has increased due to ozone reduction by up to a few percent per decade between 1979 and 1998 over a wide range of latitudes (see Figure Q17-1). The largest increases are found at high polar latitudes in both hemispheres. As expected, the increases occur where decreases in total ozone are observed to be the largest (see Figure Q13-1). The smallest changes in erythemal UV are in the tropics, where long-term total ozone changes are smallest.

Changes in Surface Ultraviolet Radiation

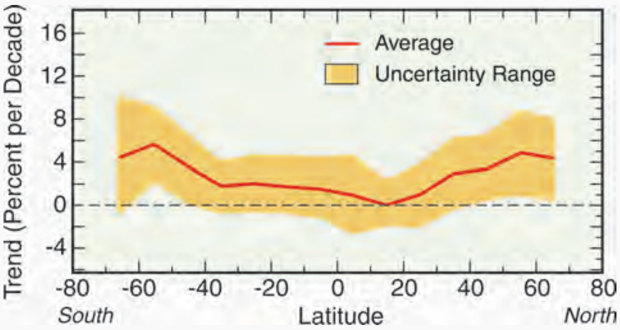

Figure Q17-1. Changes in surface UV radiation. Ultraviolet (UV) radiation at Earth's surface has increased over much of the globe since 1979. Also known as "erythemal radiation," sunburning UV is harmful to humans and other life forms. The increases shown here for 1979-1998 are estimated from observed decreases in ozone and the relationship between ozone and surface UV established at some surface locations. The estimates are based on the assumption that all other factors that influence the amount of UV radiation reaching the Earth's surface, such as aerosol abundances and cloudiness, are unchanged. The estimated changes in ultraviolet radiation in the tropics are the smallest because observed ozone changes are the smallest there.

UV Index changes. The "UV Index" is a measure of daily surface UV levels that is relevant to the effects of UV on human skin. The UV Index is used internationally to increase public awareness about the detrimental effects of UV on human health and to guide the need for protective measures. The UV Index is essentially the amount of erythemal irradiance as measured on a horizontal surface. The daily maximum UV Index varies with location and season, as shown for three locations in

Figure Q17-2. The highest daily values generally occur at the lowest latitudes (tropics) and in summer when the midday Sun is closest to overhead. Values in San Diego, California, for example, normally are larger year round than those found in Barrow, Alaska, which is at higher latitude. At a given latitude, UV Index values increase in mountainous regions. The UV Index becomes zero in periods of continuous darkness found during winter at high-latitude locations.

An illustrative example of how polar ozone depletion increases the maximum daily UV Index is shown in Figure Q17-2. Normal UV Index values for Palmer, Antarctica, in spring were estimated from satellite measurements made during the period 1978-1983, before the appearance of the "ozone hole" over Antarctica (see red dotted line). In the last decade (1991-2001), severe and persistent ozone depletion in spring has increased the UV Index well above normal values for several months (see thick red line). Now, spring UV Index values in Palmer, Antarctica (64°S), sometimes equal or exceed even the peak summer values measured in San Diego, California (32°N).

Other causes of long-term UV changes. The surface UV values may also change as a result of other human activities or climate change. Long-term changes in cloudiness, aerosols, pollution, and snow or ice cover will cause long-term changes in surface UV. At some ground sites, measurements indicate that long-term changes in UV have resulted from changes in one or more of these factors. The impact of some of the changes can be complex. For example, an increase in cloud cover usually results in a reduction of UV radiation below the clouds, but can increase radiation above the clouds (in mountainous regions).

UV changes and skin cancer. Skin cancer cases in humans are expected to increase with the amount of UV reaching Earth's surface. Atmospheric scientists working together with health professionals can estimate how skin cancer cases will change in the future. The estimates are based on knowing how UV increases as total ozone is depleted and how total ozone depletion changes with effective stratospheric chlorine (see Q16). Estimates of future excess skin cancer cases are shown in Figure Q15-1 using future estimates of effective stratospheric chlorine based on the 1992 and earlier Montreal Protocol provisions and assuming that other factors (besides

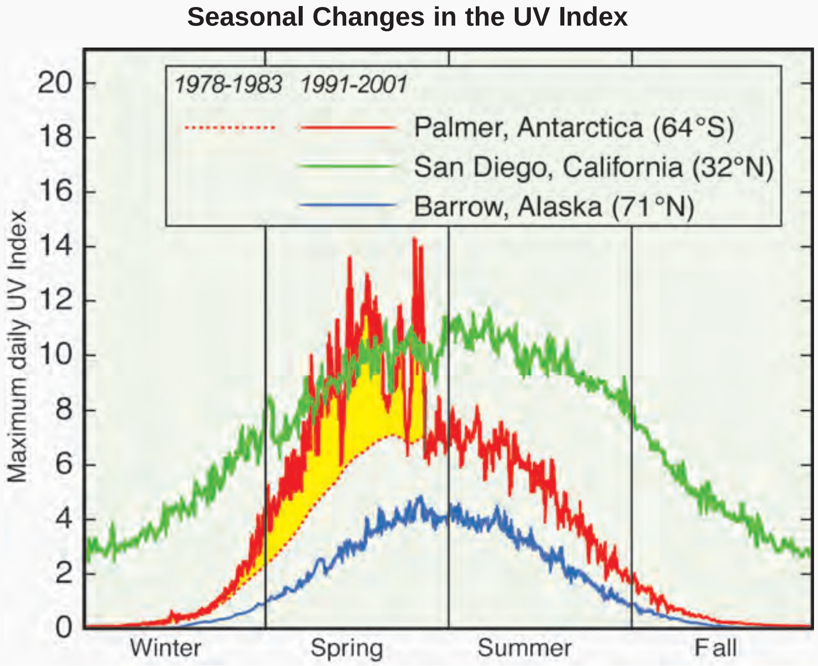

Figure Q17-2. Changes in UV Index. The maximum daily UV Index is a measure of peak sunburning UV that occurs during the day at a particular location. UV-B, which is absorbed by ozone, is an important component of sunburning UV. The UV Index varies with latitude and season, and with the Sun's elevation in the local sky. The highest values of the maximum daily UV Index occur in the tropics, where the midday Sun is highest throughout the year and where total ozone values are lowest. The lowest average UV Index values occur at high latitudes. As an example, the figure compares the seasonal UV Index at three locations. The UV Index is higher throughout the year in San Diego, a low-latitude location, than in Barrow, a high-latitude location. Index values are zero at high latitudes in winter when darkness is continuous. The effect of Antarctic ozone depletion is demonstrated by comparing the Palmer and San Diego data in the figure. Normal values estimated for Palmer are shown for the 1978-1983 period before the "ozone hole" occurred each season (see red dotted line). In the decade 1991-2001, Antarctic ozone depletion has increased the maximum UV Index value at Palmer throughout spring (see yellow shaded region). Values at Palmer now sometimes equal or exceed those measured in spring and even in the summer in San Diego, which is located at much lower latitude.

ozone) affecting surface UV are unchanged in the future. The cases are those that would occur in a population with the UV sensitivity and age distribution such as that of the United States. The cases counted are those in *excess* of the number that occurred in 1980 before ozone depletion was observed (about 2000 per million population), with the assumption that the population's sun exposure remains unchanged. The case estimates include the fact that skin cancer in humans occurs long after the exposure to sunburning UV. The results illustrate that, with current Protocol provisions, excess skin cancer cases are predicted to increase in the early to middle decades of the 21st century. By century's end, with the expected decreases in halogen source gas emissions, the number of excess cases is predicted to return close to 1980 values. Without the provisions of the Protocol, excess skin cancer cases would have been expected to increase substantially throughout the century.

Q18: Is depletion of the ozone layer the principal cause of climate change?

No, ozone depletion itself is not the principal cause of climate change. However, because ozone absorbs solar radiation and is a greenhouse gas, ozone changes and climate change are linked in important ways. Stratospheric ozone depletion and increases in global tropospheric ozone that have occurred in recent decades both contribute to climate change. These contributions to climate change are significant but small compared with the total contribution from all other greenhouse gases. Ozone and climate change are indirectly linked because both ozone-depleting gases and substitute gases contribute to climate change.

Radiative forcing of climate change. Human activities and natural processes have led to the accumulation in the atmosphere of several long-lived and radiatively active gases known as "greenhouse gases." Ozone is a greenhouse gas, along with carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and halogen source gases. The accumulation of these gases in Earth's atmosphere changes the balance between incoming solar radiation and outgoing infrared radiation. Greenhouse gases generally change the balance by absorbing outgoing radiation, leading to a warming at Earth's surface. This change in Earth's radiative balance is called a *radiative forcing of climate change*.

A summary of radiative forcings resulting from the increases in long-lived greenhouse gases in the industrial era is shown in Figure Q18-1. All forcings shown relate to human activities. Positive forcings generally lead to *warming* and negative forcings lead to *cooling* of Earth's surface. The accumulation of carbon dioxide represents the largest forcing term. Carbon dioxide concentrations are increasing in the atmosphere primarily as the result of burning coal, oil, and natural gas for energy and transportation; and from cement manufacturing. The atmospheric abundance of carbon dioxide is currently about 35% above what it was 250 years ago, in preindustrial times. In other international assessments, much of the observed surface warming over the last 50 years has been linked to increases in carbon dioxide and other greenhouse gas concentrations caused by human activities.

Stratospheric and tropospheric ozone. Stratospheric and tropospheric ozone both absorb infrared radiation emitted by Earth's surface, effectively trapping heat in the atmosphere. Stratospheric ozone also significantly absorbs solar radiation. As a result, increases or decreases

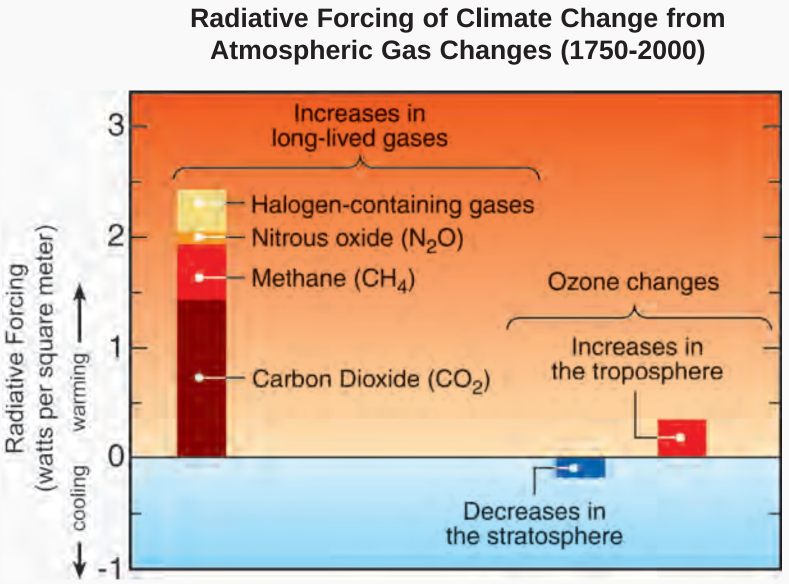

Figure Q18-1. Radiative forcing of climate change from atmospheric gas changes. Human activities since the start of the Industrial Era (around 1750) have caused increases in the abundances of several long-lived gases, changing the radiative balance of Earth's atmosphere. These gases, known as "greenhouse gases," result in radiative forcings, which can lead to climate change. Other international assessments have shown that the largest radiative forcings come from carbon dioxide, followed by methane, tropospheric ozone, the halogen-containing gases (see Figure Q7-1), and nitrous oxide. Ozone increases in the troposphere result from pollution associated with human activities. All these forcings are positive, which leads to a warming of Earth's surface. In contrast, stratospheric ozone depletion represents a small negative forcing, which leads to cooling of Earth's surface. In the coming decades, halogen gas abundances and stratospheric ozone depletion are expected to be reduced along with their associated radiative forcings. The link between these two forcing terms is an important aspect of the radiative forcing of climate change.

in stratospheric or tropospheric ozone cause radiative forcings and represent direct links of ozone to climate change. In recent decades, stratospheric ozone has decreased due to rising chlorine and bromine amounts in the atmosphere, while troposphere ozone in the industrial era has increased due to pollution from human activities (see Q3). Stratospheric ozone depletion causes a negative radiative forcing, while increases in tropospheric ozone cause a positive radiative forcing (see Figure Q18-1). The radiative forcing due to tropospheric ozone increases is currently larger than that associated with stratospheric ozone depletion. The negative forcing from ozone depletion represents an offset to the positive forcing from the halogen source gases, which cause ozone depletion.

Halogen source gases and HFCs. An important link between ozone depletion and climate change is the radiative forcing from halogen source gases and hydrofluorocarbons (HFCs). Halogen source gases are the cause of ozone depletion (see Q7) and HFCs are substitute gases (see Q15). Both groups of gases cause radiative forcing in the atmosphere, but with a wide range of effectiveness. The principal gases in each group are intercompared in Figure Q18-2 (top panel) using their "*ozone depletion potentials*" (ODPs) and "*global warming potentials*" (GWPs), which indicate the effectiveness of each gas in causing ozone depletion and climate change, respectively. The ODPs of CFC-11 and CFC-12, and the GWP of CO_2 all are assigned a value of 1.0. For ozone depletion, the halons are the most effective gases (for equal mass amounts) and HFCs cause no ozone depletion (see Q7). For climate change, all gases make a contribution, with CFC-12 and HFC-23 having the largest effect (for equal mass amounts). Montreal Protocol actions (see Q15) that have led to reductions in CFC concentrations and increases in HCFC and HFC concentrations have also reduced the total radiative forcing from these gases. It is important to note that, despite a GWP that is small in comparison to many other greenhouse gases, CO_2 is the most important greenhouse gas related to human activities because its atmospheric abundance is so much greater than the abundance of other gases.

The relative importance of total emissions of halogen source gases and HFCs to ozone depletion and climate change is illustrated for a single year (2004) of emissions in the bottom panel of Figure Q18-2. The values displayed are proportional to the product of 2004 annual global emissions and the ODP or GWP. The results in the lower panel are shown relative to CFC-11, because it is often used as a reference gas. The comparison shows that the importance of CFC emissions in 2004 to future ozone depletion exceeds that of the halons, despite the higher halon ODP values, because CFC emissions are larger. Similarly, the contributions of CFC and HCFC-22 emissions in 2004 to climate change are currently larger than the halon or HFC contributions. These 2004 results represent only incremental contributions of these gases to either ozone depletion or climate change. The overall contribution of a gas depends on its total accumulation in the atmosphere, which in turn depends on its long-term emission history and atmospheric lifetime (see Q7 and Q16). In the case of ozone depletion, the relative contributions of the halogen source gases can be compared through their respective contributions to effective stratospheric chlorine (see Q16).

As a group, the principal halogen source gases represent a positive direct radiative forcing in the Industrial Era that is comparable to the forcing from methane, the second most important greenhouse gas. In the coming decades, the abundances of these ozone-depleting gases and their associated positive radiative forcings are expected to decrease (see Q16). Future growth in HFC emissions, while uncertain, will contribute a positive forcing that will counter the decrease from ozone-depleting gases. Finally, reductions in ozone-depleting gases will be followed by reductions in stratospheric ozone depletion and its associated *negative* radiative forcing.

Impact of climate change on ozone. Certain changes in Earth's climate could affect the future of the ozone layer. Stratospheric ozone is influenced by changes in temperatures and winds in the stratosphere. For example, lower temperatures and stronger polar winds could both affect the extent and severity of winter polar ozone depletion. While the Earth's surface is expected to warm in response to the net positive radiative forcing from greenhouse gas increases, the stratosphere is expected to cool. A cooler stratosphere would extend the time period over which polar stratospheric clouds (PSCs) are present in polar regions and, as a result, might increase winter ozone depletion. In the upper stratosphere at altitudes above PSC formation regions, a cooler stratosphere is expected to increase ozone amounts and, hence, hasten recovery, because lower temperatures favor ozone production over loss (see Q2). Similarly, changes in atmospheric composition that lead to a warmer climate may also alter ozone amounts (see Q20).

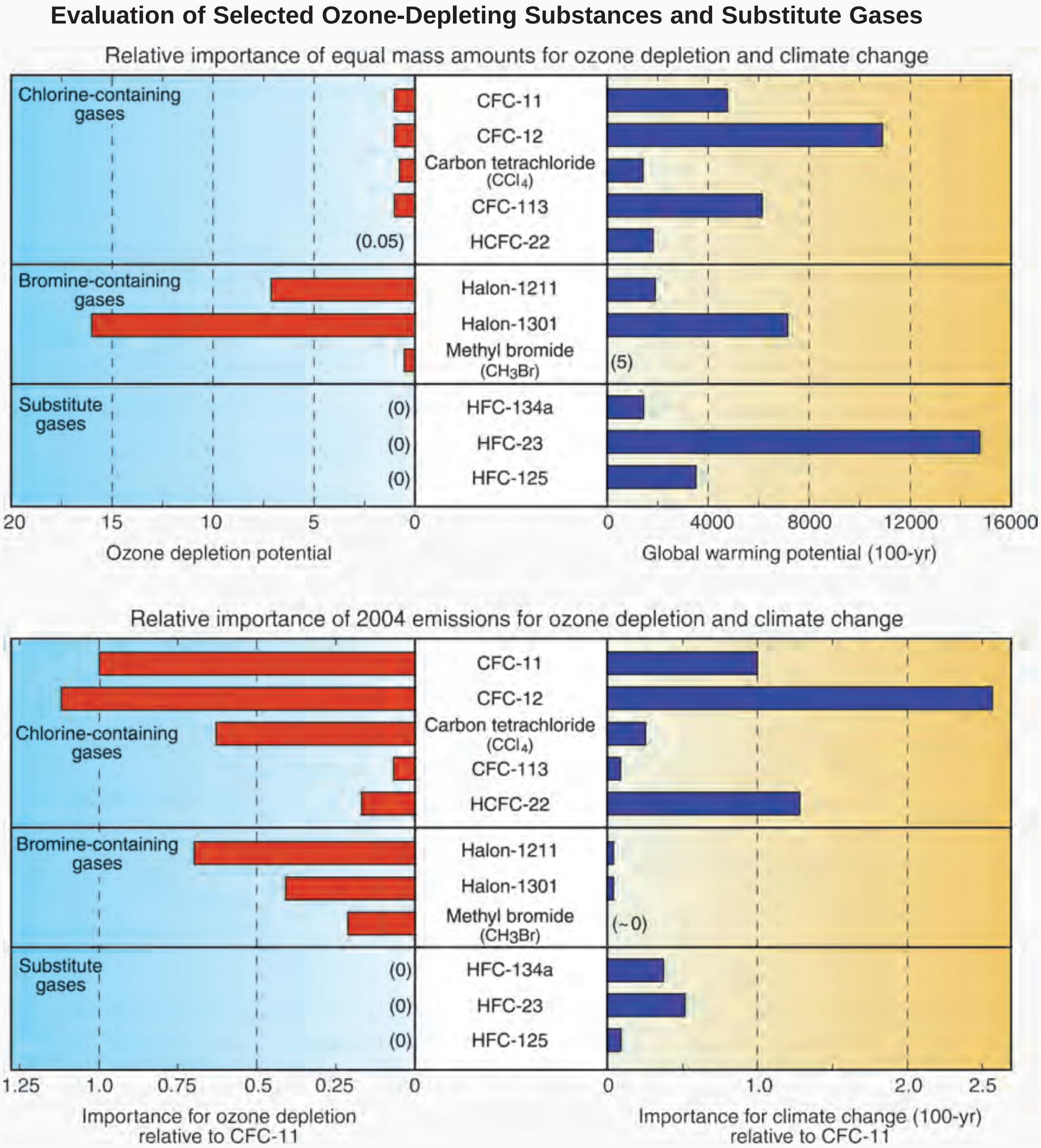

Figure Q18-2. Evaluation of ozone-depleting gases and their substitutes. Ozone-depleting gases (halogen source gases) and their substitutes can be compared via their ozone depletion potentials (ODPs) and global warming potentials (GWPs). The GWPs are evaluated for a 100-yr time interval after emission. The CFCs, halons, and HCFCs are ozone-depleting gases (see Q7) and HFCs, used as substitute or replacement gases, do not destroy ozone. The ODPs of CFC-11 and CFC-12, and the GWP of CO_2 have values of 1.0 by definition. Larger ODPs or GWPs indicate greater potential for ozone depletion or climate change, respectively. The top panel compares ODPs and GWPs for emissions of equal mass amounts of each gas. The ODPs of the halons far exceed those of the CFCs. HFCs have zero ODPs. All gases have non-zero GWPs that span a wide range of values. The bottom panel compares the contributions of the 2004 emissions of each gas, using CFC-11 as the reference gas. Each bar represents the product of a global emission value and the respective ODP or GWP factor. The comparison shows that 2004 emissions of ozone-depleting gases currently contribute more than substitute gas emissions to both ozone depletion and climate change. Future projections guided by Montreal Protocol provisions suggest that the contributions of ozone-depleting gases to climate change will decrease, while those of the substitute gases will increase.

VI. STRATOSPHERIC OZONE IN THE FUTURE

Q19: How will recovery of the ozone layer be identified?

Scientists expect to identify the recovery of the ozone layer with detailed ozone measurements in the atmosphere and with global models of ozone amounts. Increases in global ozone and reductions in the extent and severity of the Antarctic "ozone hole" will be important factors in gauging ozone recovery. Natural variations in ozone amounts will limit how soon recovery can be detected with future ozone measurements.

Recovery process. Identifying the recovery of the ozone layer from depletion associated with halogen gases will rely on comparisons of the latest ozone values with values measured in the past. Because of its importance, ozone will likely be measured continuously in the future using a variety of techniques and measurement platforms (see Q5). Atmospheric computer models will be used to predict future abundances of ozone and attribute observed changes to ozone-depleting gases and other factors.

The recovery process is schematically shown for *global* ozone in Figure Q19-1. Ozone has declined from pre-1980 amounts due to past increases in halogen gases in the stratosphere (see Q16). In the future, as the overall decline in these gases continues in response to Montreal Protocol provisions, global ozone is expected to recover, approaching or exceeding pre-1980 values (see Q20). Ozone recovery attributable to decreases in ozone-depleting gases can be described, in general, as a process

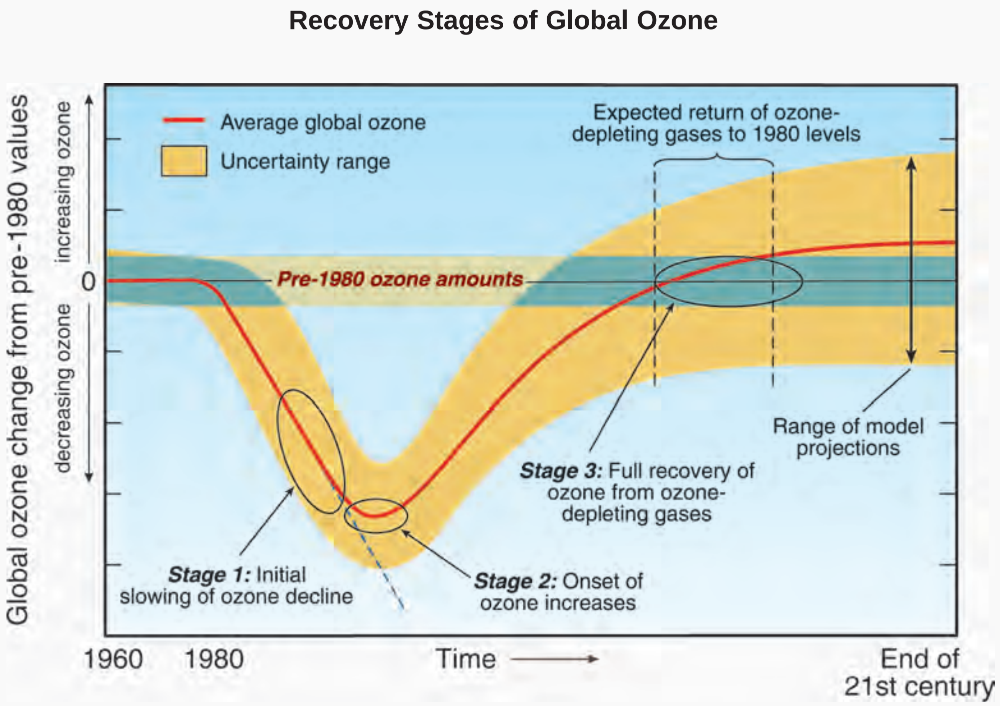

Figure Q19-1. Recovery stages of global ozone. Significant ozone depletion from the release of ozone-depleting gases in human activities first became recognized in the 1980s. The Montreal Protocol provisions are expected to further reduce and eliminate these gases in the atmosphere in the coming decades, thereby leading to the return of ozone amounts to near pre-1980 values. The timeline of the recovery process is schematically illustrated with three stages identified. The large uncertainty range illustrates natural ozone variability in the past and potential uncertainties in global model projections of future ozone amounts. When ozone reaches the full recovery stage, global ozone values may be above or below pre-1980 values, depending on other changes in the atmosphere (see Q20).

involving three stages:

(1) The **initial slowing of ozone decline,** identified as the occurrence of a statistically significant reduction in the rate of decline in ozone.

(2) The **onset of ozone increases (turnaround),** identified as the occurrence of statistically significant increases in ozone above previous minimum values.

(3) The **full recovery of ozone from ozone-depleting gases,** identified as when ozone is no longer significantly affected by ozone-depleting gases from human activities.

Each recovery stage is noted in Figure Q19-1. The red line and shaded region in the figure indicate the expected average value and the uncertainty range, respectively, in global ozone amounts. The large uncertainty range illustrates natural ozone variability in the past and potential uncertainties in global model projections of future ozone amounts.

In the full recovery of global ozone, the milestone of the return of ozone to pre-1980 levels is considered important because prior to 1980 ozone was not significantly affected by human activities. As a consequence, this milestone is useful, for example, to gauge when the adverse impacts of enhanced surface ultraviolet (UV) radiation on human health and ecosystems caused by ozone-depleting substances are likely to become negligible. The uncertainty range in model results indicates that ozone amounts may be below or above pre-1980 values when ozone has fully recovered from the effects of ozone-depleting gases from human activities (see Q20). The wide range of uncertainty for global ozone in the final stage of recovery represents, in part, the difficulty in accurately forecasting the effects of future changes in climate and atmospheric composition on the abundance of ozone (see Q20).

Natural factors. Stratospheric ozone is influenced by two important natural factors, namely, changes in the output of the Sun and volcanic eruptions (see Q14). Evaluations of ozone recovery include the effects of these natural factors. The solar effect on ozone is expected to be predictable based on the well-established 11-year cycle of solar output. The uncertainty range in Figure Q19-1 includes solar changes. Volcanic eruptions are particularly important because they enhance ozone depletion caused by reactive halogen gases, but cannot be predicted. The occurrence of a large volcanic eruption in the next decades when effective stratospheric chlorine levels are still high (see Figure Q16-1) may obscure progress in overall ozone recovery by temporarily increasing ozone depletion. The natural variation of ozone amounts also limits how easily small improvements in ozone abundances can be detected.

Q20: When is the ozone layer expected to recover?

Substantial recovery of the ozone layer is expected near the middle of the 21st century, assuming global compliance with the Montreal Protocol. Recovery will occur as chlorine- and bromine-containing gases that cause ozone depletion decrease in the coming decades under the provisions of the Protocol. However, the influence of changes in climate and other atmospheric parameters could accelerate or delay ozone recovery, and volcanic eruptions in the next decades could temporarily reduce ozone amounts for several years.

Halogen source gas reductions. Ozone depletion caused by human-produced chlorine and bromine gases is expected to gradually disappear by about the middle of the 21st century as the abundances of these gases decline in the stratosphere. The decline in *effective stratospheric chlorine* will follow the reductions in emissions that are expected to continue under the provisions of the Montreal Protocol and its Adjustments and Amendments (see Figure Q16-1). The emission reductions are based on the assumption of full compliance by the developed and developing nations of the world. The slowing of increases in atmospheric abundances and the initial decline of several halogen gases have already been observed (see Figure Q16-1). One gas, methyl chloroform, has already decreased by about 90% from its peak value. Natural chemical and transport processes limit the rate at which halogen gases are removed from the stratosphere. The atmospheric lifetimes of the halogen source gases range up to 100 years (see Table Q7-1). Chlorofluorocarbon-12 (CFC-12), with its 100-year lifetime, will require about 200 to 300 years before it is removed (less than 5% remaining) from the atmosphere (see Figure Q16-1). At midlatitudes, effective stratospheric chlorine is not expected to reach pre-1980 values until about 2050.

Ozone projections. Computer models of the atmosphere are used to assess past changes in the global ozone distribution and to project future changes. Two important measures of ozone considered by scientists are global total ozone averaged between 60°N and 60°S latitudes, and minimum ozone values in the Antarctic "ozone hole." Both measures show ongoing ozone depletion that began in the 1980s (see Figure Q20-1). The model projections indicate that for 60°N-60°S total ozone, the first two stages of recovery (slowing of the decline and turnaround

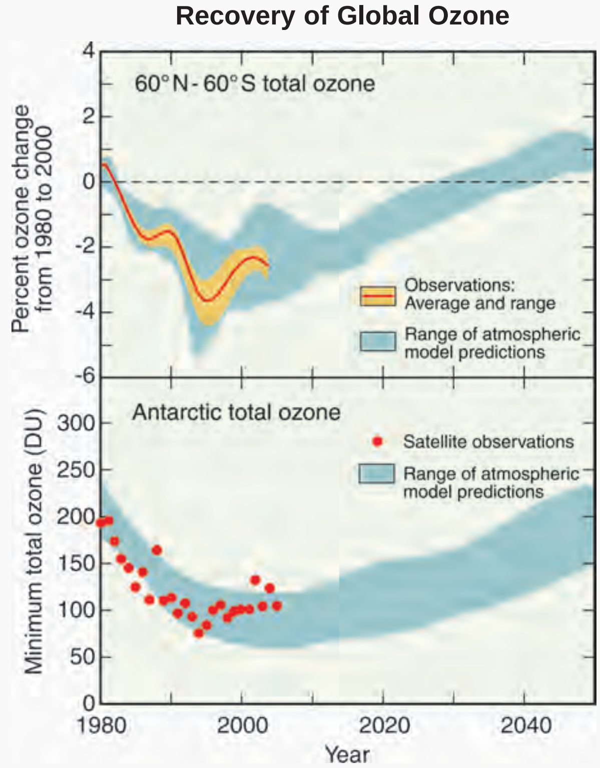

Figure Q20-1. Global ozone recovery predictions. Observed values of midlatitude total ozone (top panel) and September-October minimum total ozone values, over Antarctica (bottom panel) have decreased beginning in the early 1980s. As halogen source gas emissions decrease in the 21st century, ozone values are expected to recover by increasing toward pre-1980 values. Atmospheric computer models that account for changes in halogen gases and other atmospheric parameters are used to predict how ozone amounts will increase. These model results show that full recovery is expected in midlatitudes by 2050, or perhaps earlier. Recovery in the Antarctic will occur somewhat later. The range of model projections comes from the use of several different models of the future atmosphere.

(see Q19)) will be reached before 2020. Full recovery, with ozone reaching or exceeding pre-1980 values, is expected to occur by the middle of the 21st century. The range of projections comes from several computer models of the atmosphere. Some of these models indicate that recovery of 60°N-60°S total ozone may come well before midcentury.

Models predict that Antarctic ozone depletion will also reach the first two stages of recovery by 2020, but somewhat more slowly than 60°N-60°S total ozone. Full recovery could occur by mid-century but some models show later recovery, between 2060 and 2070. Declines in effective stratospheric chlorine amounts will occur later over the Antarctic than at lower latitudes because air in the Antarctic stratosphere is older than air found at lower latitudes. As a result, reductions in halogen loading to pre-1980 values will occur 10-15 years later in the Antarctic stratosphere than in the mid-latitude stratosphere.

A different atmosphere in 2050. By the middle of the 21st century, halogen amounts in the stratosphere are expected to be similar to those present in 1980 before the onset of significant ozone depletion (see Figure Q16-1). However, climate and other atmospheric factors will not be the same in 2050 as in 1980, and this could cause ozone abundances in 2050 to be somewhat different from those observed in 1980. Stratospheric ozone abundances are affected by a number of natural and human-caused factors in addition to the atmospheric abundance of halogen gases. Important examples are stratospheric temperatures and air motions, volcanic eruptions, solar activity, and changes in atmospheric composition. Separating the effects of these factors is challenging because of the complexity of atmospheric processes affecting ozone.

The ozone recovery projections in Figures Q19-1 and Q20-1 attempt to take these various factors into account. For example, since 1980 human activities have increased the atmospheric abundance of important greenhouse gases, including carbon dioxide, methane, and nitrous oxide. Other international assessments have shown that the accumulation of these gases is linked to the warmer surface temperatures and lower stratospheric temperatures observed within recent decades. Warmer surface temperatures could change the emission rates of naturally occurring halogen source gases. Lower temperatures in the upper stratosphere (at about 40 kilometers (25 miles) altitude) accelerate ozone recovery because ozone destruction reactions proceed at a slower rate. In contrast, reduced temperatures in the polar lower stratosphere during winter might increase the occurrence of polar stratospheric clouds (PSCs) and, therefore, enhance chemical ozone destruction (see Q10). Further increases of stratospheric water vapor, such as those that have occurred over the last two decades, could also increase PSC occurrences and associated ozone destruction. Therefore, a cooler, wetter polar stratosphere could delay polar ozone recovery beyond what would be predicted for the 1980 atmosphere. Increased abundances of methane and nitrous oxide due to human activities also cause some change in the overall balance of the chemical production and destruction of global stratospheric ozone. Finally, one outcome that cannot be included precisely in models is the occurrence of one or more large volcanic eruptions in the coming decades. Large eruptions would increase stratospheric sulfate particles for several years, temporarily reducing global ozone amounts (see Q14).

As a consequence of these potential changes, the return of effective stratospheric chlorine and ozone to pre-1980 levels may not occur at the same time. In some regions of the stratosphere, ozone may remain below pre-1980 values after effective chlorine has declined to pre-1980 levels.