TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER: 2010 UPDATE

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Contents

INTRODUCTION

Ozone is present only in small amounts in Earth's atmosphere. Nevertheless, it is vital to human well-being and ecosystem health.

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.

It was discovered in the mid-1970s that some human-produced chemicals could lead to depletion of the ozone layer. The resulting increase in ultraviolet radiation at Earth's surface would likely increase the incidences of skin cancer and eye cataracts, and also adversely affect plants, crops, and ocean plankton.

Following the discovery of this environmental issue, researchers sought a better understanding of this threat to the ozone layer. Monitoring stations showed that the abundances of the ozone-depleting substances (ODSs) 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 in the atmosphere characterized the chemical reactions that were involved in ozone destruction. Computer models of the atmosphere employing this information were used to predict how much ozone depletion was occurring and how much more might 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 local-ized. A thinning of the ozone layer also has been observed over other regions of the globe, such as the Arctic and northern and southern midlatitudes.

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 indeed occurring and why. Most important, we know that if the most potent ODSs were to continue to be emitted and increase 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 an international 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 ODSs has slowed and begun to decrease. In response, global ozone depletion is no longer increasing. Now, with continued compliance, we expect substantial recovery of the ozone layer by the late 21st century. The day the Montreal Protocol was agreed upon, 16 September, is now celebrated as the International Day for the Preservation of the Ozone Layer.

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, in which continuous dialogue has been a key ingredient. A timeline of milestones associated with stratospheric ozone depletion is illustrated in Figure Q0-1. The milestones relate to stratospheric ozone science, international scientific assessments, and the Montreal Protocol.

To help maintain a broad understanding of the relationship between ozone depletion, ODSs, and the Montreal Protocol, this component of the *Scientific Assessment of Ozone Depletion: 2010* presents 20 questions and answers about the often-complex science of ozone depletion. Most questions and answers are updates of those presented in previous Ozone Assessments, while others have been added or expanded to address newly emerging issues. The questions address the nature of atmospheric ozone, the chemicals that cause ozone depletion, how global and polar ozone depletion occur, the success of the Montreal Protocol, and what could lie ahead for the ozone layer. Computer models project that the influence on global ozone of greenhouse gases and changes in climate will grow significantly in the coming decades and exceed the importance of ODSs in most atmospheric regions by the end of this century. Ozone and climate are indirectly linked because both ODSs and their substitutes contribute to climate change. 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 2010 and earlier Assessment reports as well as other international scientific assessments. These reports and the answers provided here were prepared and reviewed by a large international group of scientists[1].

Milestones in the History of Stratospheric Ozone Depletion

Scientific Milestones

Peak global emissions
of ozone-depleting
substances – 1988

1995 Nobel Prize in Chemistry
to Crutzen, Molina, and Rowland

WMO World Ozone
Data Centre – 1961

Ozone hole reported
over Antarctica – 1985

Stratospheric abundance of EESC
in midlatitudes down 10%
from 1997 peak – 2008

Global surface observations
of CFCs reported – 1973

CFC ozone-depletion
hypothesis – 1974

Stratospheric Aerosol &
Gas Experiment I (SAGE-I)
instrument launched – 1979

Peak stratospheric abundance of
EESC in midlatitudes – 1997

CFCs observed in the
stratosphere & reported as
potent greenhouse gases – 1975

Total Ozone Mapping
Spectrometer (TOMS)
instrument launched – 1978

Laboratory, field, and modeling studies
show chlorine and bromine deplete
polar stratospheric ozone – 1985–1989

International Scientific Assessments

WMO Atmospheric
Ozone – 1985

UNEP/WMO Scientific Assessments of Ozone Depletion

WMO World Plan of Action
on the Ozone Layer – 1977

1989 1991 1994   1998   2002   2006   2010

WMO The Stratosphere 1981:
Theory and Measurements

2005 – IPCC/TEAP Special
Report on Safeguarding the
Ozone Layer and the
Global Climate System

WMO Report of the International
Ozone Trends Panel – 1988

Montreal Protocol Milestones

Montreal Protocol
Amendments

→ London – 1990
→ Copenhagen – 1992
→ Vienna – 1995
→ Montreal – 1997
→ Beijing – 1999

HCFC accelerated phaseout
(Montreal – 2007 Adjustment)

Montreal Protocol on Substances
that Deplete the Ozone Layer – 1987

Vienna Convention for the
Protection of the Ozone Layer – 1985

Global production
of CFCs and halons
ends – 2010

Global consumption of ODSs
reduced by 98% – 1986 to 2008

Montreal Protocol
universal ratification
(196 nations) – 2009

Emissions of halogen source gases (ODSs + natural sources)
(Weighted by Ozone Depletion Potential (ODP))

● Based on atmospheric
observations or industry data

○ Future projections

Natural emissions

Y-axis: (Megatonnes CFC-11-equivalent per year) — 0, 0.5, 1.0, 1.5, 2.0

X-axis: Year — 1960, 1970, 1980, 1990, 2000, 2010, 2020

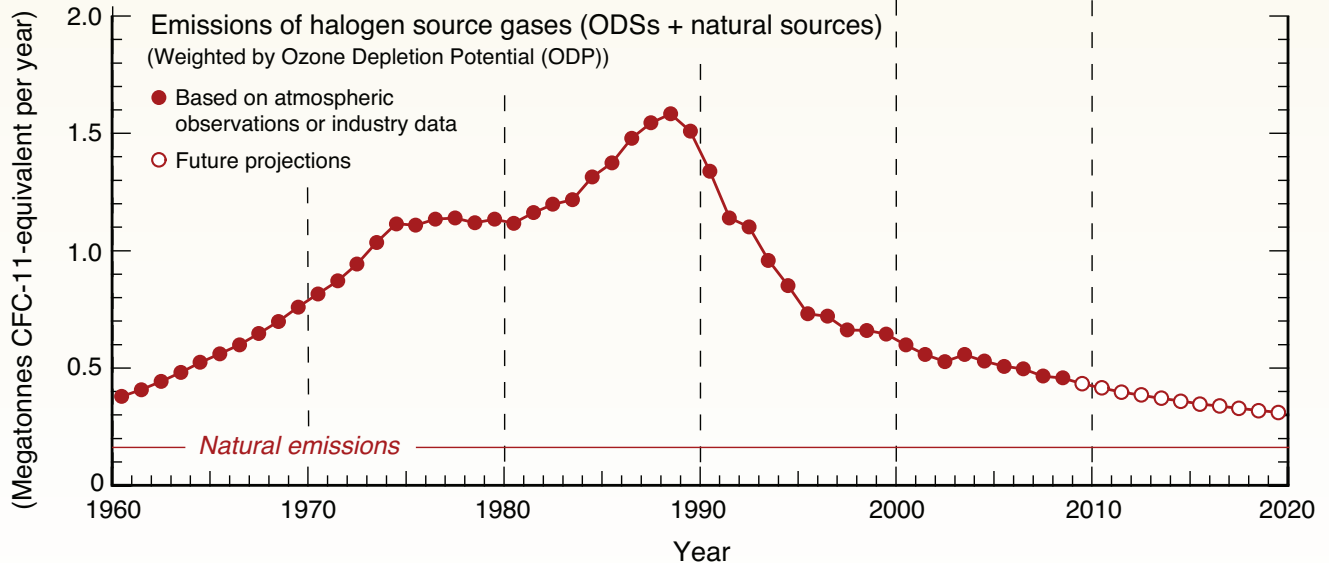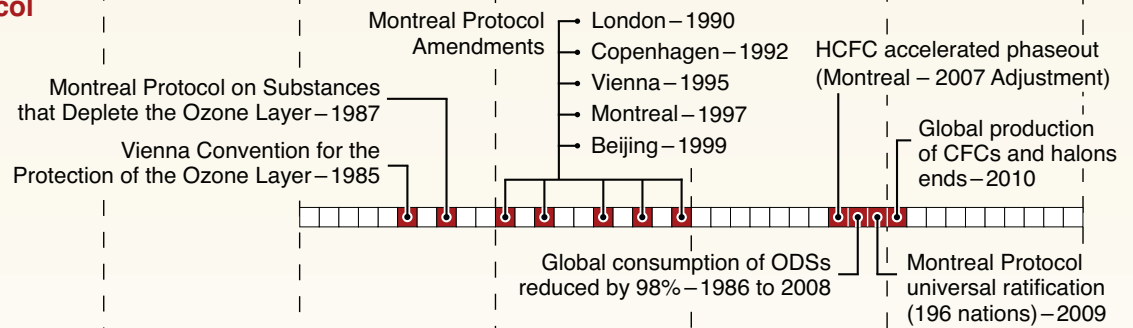**Figure Q0-1. Stratospheric ozone depletion milestones.**   This timeline highlights milestones related to the history of ozone depletion. Events represent the occurrence of important scientific findings, the completion of international scientific assessments, and highlights of the Montreal Protocol. The graph shows the history and near future of annual total emissions of ozone-depleting substances (ODSs) combined with natural emissions of halogen source gases. ODSs are halogen source gases controlled under the Montreal Protocol. The emissions, when weighted by their potential to destroy ozone, peaked near 1990 after several decades of steady increases (see Q19). Between 1990 and the present, emissions have decreased substantially as a result of the Montreal Protocol and its subsequent Amendments and Adjustments coming into force (see Q15). The Protocol began with the Vienna Convention for the Protection of the Ozone Layer in 1985. The provisions of the Protocol and its Amendments and Adjustments decisions have depended on information embodied in international scientific assessments of ozone depletion that have been produced periodically since 1989 under the auspices of UNEP and WMO. Atmospheric observations of ozone, CFCs, and other ODSs have increased substantially since the early 1970s. For example, the SAGE and TOMS satellite instruments have provided essential global views of stratospheric ozone for several decades. The Nobel Prize in Chemistry in 1995 was awarded for research that identified the threat to ozone posed by CFCs and that described key reactive processes in the stratosphere. By 2008, stratospheric chlorine abundances in the stratosphere were 10% lower than their peak values reached in the late 1990s and were continuing to decrease. January 2010 marked the end of global production of CFCs and halons under the Protocol. (A megatonne = 1 billion (10^9) kilograms.)

EESC: Equivalent effective stratospheric chlorine

ODS: Ozone-depleting substance

WMO: World Meteorological Organization

IPCC: Intergovernmental Panel on Climate Change

TEAP: Technology and Economic Assessment Panel of the Montreal Protocol

UNEP: United Nations Environment Programme

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[1] The update of this component of the Assessment was discussed by the 74 scientists who attended the Panel Review Meeting for the 2010 Ozone Assessment (Les Diablerets, Switzerland, 28 June–2 July 2010). In addition, subsequent contributions, reviews, or comments were provided by the following individuals: Ross J. Salawitch (Special Recognition), Stephen A. Montzka (Special Recognition), Stephen O. Andersen (Special Recognition), Pieter J. Aucamp, Alkiviadis F. Bais, Peter F. Bernath, Gregory E. Bodeker, Janet F. Bornman, Geir O. Braathen, Peter Braesicke, Irene Cionni, Martin Dameris, John S. Daniel, Susana B. Diaz, Ellsworth G. Dutton, James W. Elkins, Christine A. Ennis, Veronika Eyring, Vitali E. Fioletov, Marvin A. Geller, Sophie Godin-Beekmann, Malcolm K.W. Ko, Kirstin Krüger, Lambert Kuijpers, Michael J. Kurylo, Igor Larin, Gloria L. Manney, C. Thomas McElroy, Rolf Müller, Eric R. Nash, Paul A. Newman, Samuel J. Oltmans, Nigel D. Paul, Judith Perlwitz, Jean-Pierre Pommereau, Claire E. Reeves, Stefan Reimann, Alan Robock, Michelle L. Santee, Dian J. Seidel, Theodore G. Shepherd, Peter Simmonds, Anne K. Smith, Richard S. Stolarski, Matthew B. Tully, Guus J.M. Velders, Elizabeth C. Weatherhead, Ann R. Webb, Ray F. Weiss, and Durwood Zaelke.

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 (about 90%) resides in the stratosphere 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)*, meaning "to smell." Ozone has a pungent odor that allows it to be detected even at very low amounts. Ozone reacts rapidly 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 of textiles and food products.

Ozone location. Most ozone (about 90%) is found in the stratosphere, which begins about 10–16 kilometers (6–10 miles) above Earth's surface and extends up to about 50 kilometers (31 miles) altitude. The stratospheric region with the highest ozone concentration is commonly known as the "ozone layer" (see Figure Q1-2). The ozone layer extends over the entire globe with some variation in altitude and thickness. 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 low relative abundance in the atmosphere. In the stratosphere near the peak concentration of the ozone layer, there are typically a few thousand 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 result when ozone is 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 layer of gas extending over the globe. The resulting layer of pure ozone would have an average thickness of about three millimeters (about one-tenth inch) (see Q4). Nonetheless, this extremely small fraction of the atmosphere plays a vital role in protecting life on Earth (see Q3).

Ozone and Oxygen

Oxygen atom (O)

Oxygen molecule (O_2)
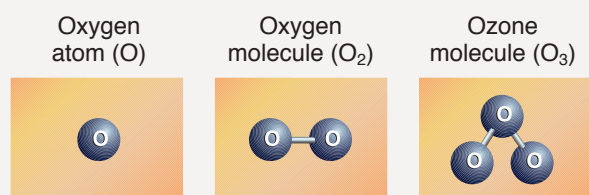
Ozone molecule (O_3)

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 the gases in Earth's atmosphere, contain two oxygen atoms bound together.

Ozone in the Atmosphere
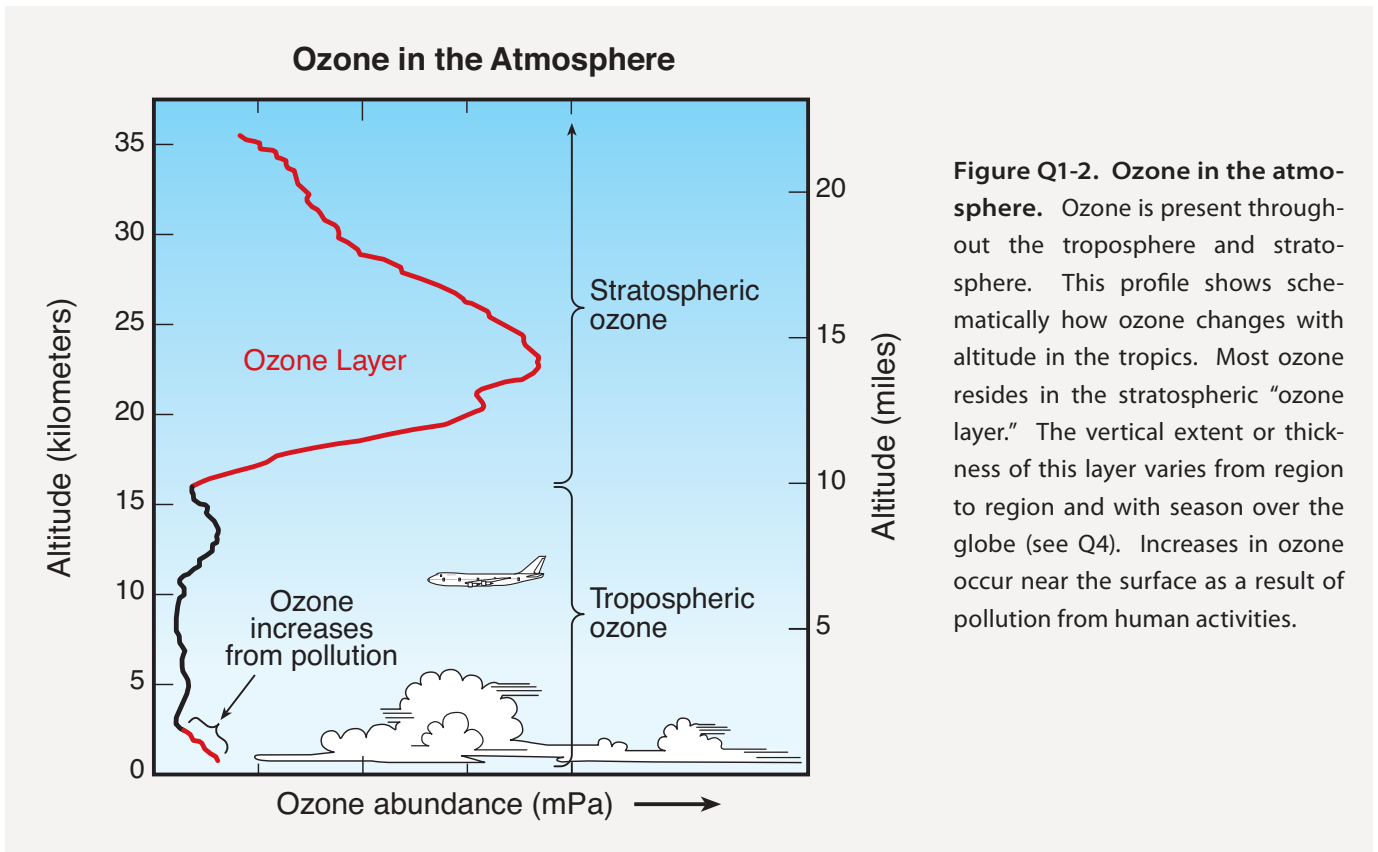
Figure Q1-2. Ozone in the atmosphere. Ozone is present throughout the troposphere and stratosphere. This profile shows schematically how ozone changes with altitude in the tropics. Most ozone resides in the stratospheric "ozone layer." The vertical extent or thickness of this layer varies from region to region and with season over the globe (see Q4). 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 by a different set of chemical reactions that involve naturally occurring gases and those from pollution sources.

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

The production of stratospheric ozone is balanced by its destruction in chemical reactions. Ozone reacts continually with sunlight and 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 hydrogen and nitrogen oxides and those containing chlorine and bromine (see Q8).

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

Tropospheric ozone. Near Earth's surface, ozone is produced by chemical reactions involving naturally occurring gases and gases from pollution sources. Ozone production reactions primarily involve hydrocarbon and nitrogen oxide gases, as well as ozone itself, and all require sunlight for completion. Fossil fuel combustion is a primary source of pollutant gases that lead to tropospheric ozone production. The production of ozone near the surface 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 by naturally occurring chemical reactions and by reactions involving human-produced chemicals. Tropospheric ozone can also be destroyed when ozone reacts with a

Stratospheric Ozone Production

Step 1

O O + Ultraviolet Sunlight → O + O

Step 2

O + O O → O O O

O + O O → O O O

Overall reaction: $3\,O_2$ —sunlight→ $2\,O_3$
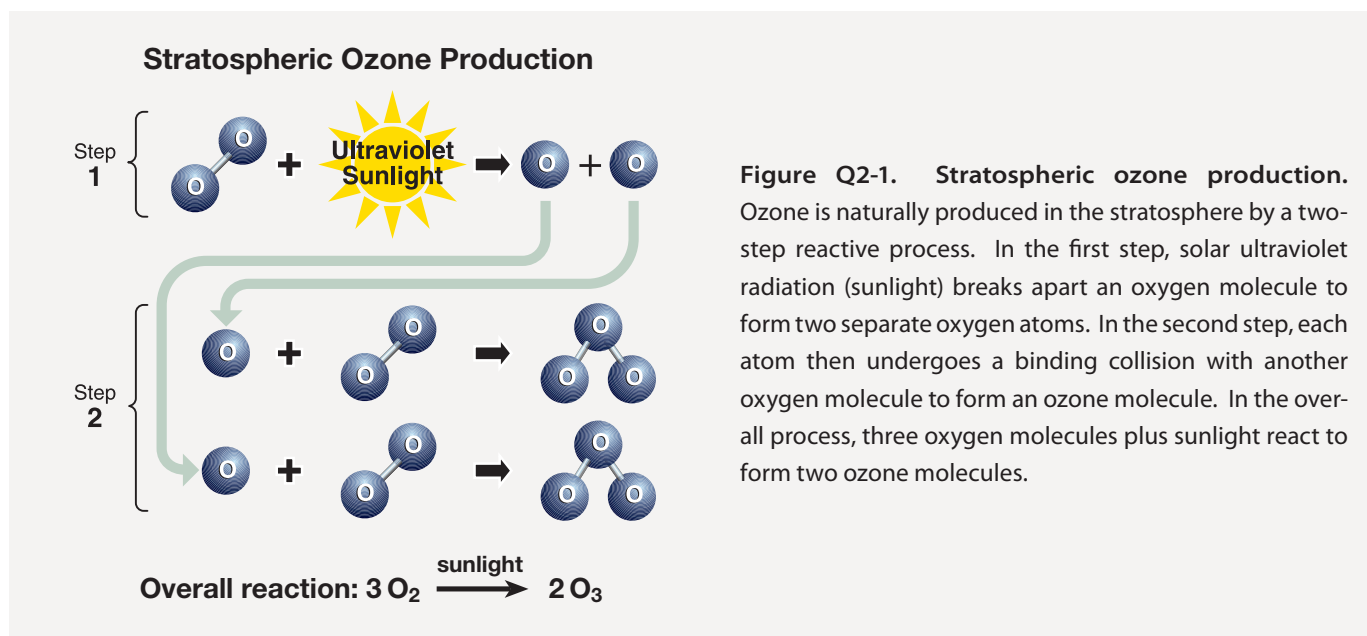
Figure Q2-1. Stratospheric ozone production. Ozone is naturally produced in the stratosphere by a two-step reactive process. In the first step, solar ultraviolet radiation (sunlight) breaks apart an oxygen molecule to form two separate oxygen atoms. In the second step, each atom then undergoes a binding 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.

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 and destroy ozone. The balance is determined by the amounts of reactive 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 loca-tion, ozone abundances increase. Similarly, if conditions change to favor other reactions that destroy ozone, abun-dances decrease. The balance of production and loss reac-tions combined with atmospheric air motions determines the global distribution of ozone on timescales of days to many months. Global ozone has decreased during the past several decades because the amounts of reactive gases containing chlorine and bromine have increased in the stratosphere (see Q13) due to human activities.

Q3   Why do we care about atmospheric ozone?

Ozone in the stratosphere absorbs a large part of the Sun's biologically harmful ultraviolet radiation. Stratospheric ozone is considered "good" ozone because of this beneficial role. In contrast, ozone formed at Earth's surface in excess of natural amounts is considered "bad" ozone because it is harmful to humans, plants, and animals. Natural ozone near the surface and in the lower atmosphere plays an important beneficial role in chemically removing pollutants from the atmosphere.

Good ozone. Stratospheric ozone is considered good for humans and other life forms because it absorbs ultraviolet-B (UV-B) radiation from the Sun (see Figure Q3-1). If not absorbed, UV-B radiation would reach Earth's surface in amounts that are harmful to a variety of life forms. In humans, increased exposure to UV-B radiation increases the risks of skin cancer, cataracts, and a suppressed immune system. UV-B radiation exposure before adulthood and cumulative exposure are both important health risk factors. 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.

Protecting good ozone. In the mid-1970s, it was discovered that gases containing chlorine and bromine atoms released by human activities could cause stratospheric ozone depletion (see Q6). These gases, referred to as halogen source gases, and as ozone-depleting substances (ODSs), chemically release their chlorine and bromine atoms after they reach the stratosphere. Ozone depletion increases surface UV-B radiation above naturally occurring amounts. International efforts have been successful in protecting the ozone layer through controls on ODS production and consumption (see Q15 and Q16).

Bad ozone. Ozone near Earth's surface in excess of natural amounts is considered bad ozone. It is formed by reactions involving human-made pollutant gases. Increasing surface ozone above natural levels is harmful to humans, plants, and other living systems because ozone reacts strongly to destroy or alter many biological molecules. High ozone exposure reduces crop yields and forest growth. In humans, expo-

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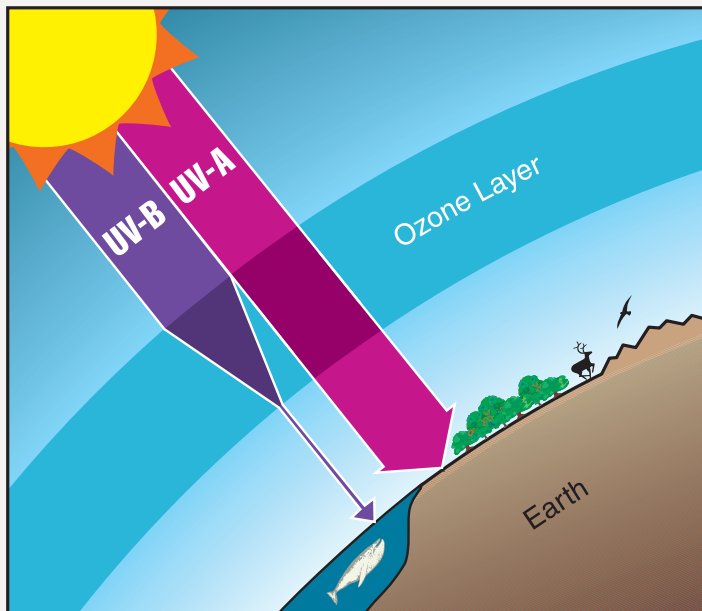
Figure Q3-1. UV protection by the ozone layer. The ozone layer resides in the stratosphere and surrounds the entire Earth. UV-B radiation (280- to 315-nanometer (nm) wavelength) from the Sun is strongly absorbed in this layer. As a result, the amount of UV-B reaching Earth's surface is greatly reduced.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

sure 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 because ozone is a greenhouse gas (see Q18). The negative effects of excess tropospheric ozone contrast sharply with the protection from harmful UV-B radiation afforded by an abundance of stratospheric ozone.

Reducing bad ozone. Limiting the emission of certain common pollutants reduces the production of excess ozone in the air surrounding humans, plants, and animals. Natural emissions from the biosphere, mainly from trees, also participate in reactions that produce ozone. 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 or limiting the emission of pollutants that cause production of excess ozone near Earth's surface.

Natural ozone. In the absence of human activities, ozone would still be present near Earth's surface and throughout the troposphere and stratosphere because ozone is a natural component of the clean atmosphere. Ozone plays important roles in the atmosphere beyond absorbing UV radiation. For example, ozone initiates the chemical removal of many pollutants, such as carbon monoxide (CO) and nitrogen oxides (NO_x), as well as some greenhouse gases, such as methane (CH_4). In addition, the absorption of UV-B radiation by ozone is a natural source of heat in the stratosphere, causing temperatures to increase with altitude. Stratospheric temperatures affect the balance of ozone production and destruction processes (see Q2) and air motions that redistribute ozone throughout the stratosphere.

Q4   How is total ozone distributed over the globe?

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

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

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

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

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

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

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

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

Global Satellite Maps of Total Ozone in 2009

Early spring

16 – 30 March

Early winter

Early fall

Early summer

16 – 30 December

16 – 30 June

Early summer

Early fall

Early winter

Total ozone
(Dobson units)

600

500

400

300

200

100

16 – 30 September

Early spring

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

There is 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 routinely monitored by a large group of investiga-tors using satellite, airborne, and ground-based instruments. The continued analysis of these observations provides an important basis to quantify the contribution of human activi-ties to ozone depletion.

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 instruments measure ozone locally by continuously drawing air samples into a small detection chamber. Other instruments measure ozone remotely over long distances by using ozone's unique optical absorption or emission properties.

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's detection chamber, ozone is measured by its absorption of ultraviolet (UV) light or by the electrical current or light produced in a chemical reaction involving ozone. The last 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 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. Ozone measurements are also being made routinely on some commercial aircraft flights.

Remote measurements. Remote measurements of total ozone amounts and the altitude distributions of ozone are obtained by detecting ozone at large distances 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, lasers, and starlight. For example, satellites use the absorption of solar UV radiation 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. Lasers are routinely deployed at ground

sites and on research aircraft to detect ozone over a distance of many kilometers along the laser light path. A network of ground-based detectors measures ozone by detecting small changes in the amount of the Sun's UV radiation that reaches Earth's surface. Other instruments measure ozone using its absorption of infrared or visible radiation or its emission of

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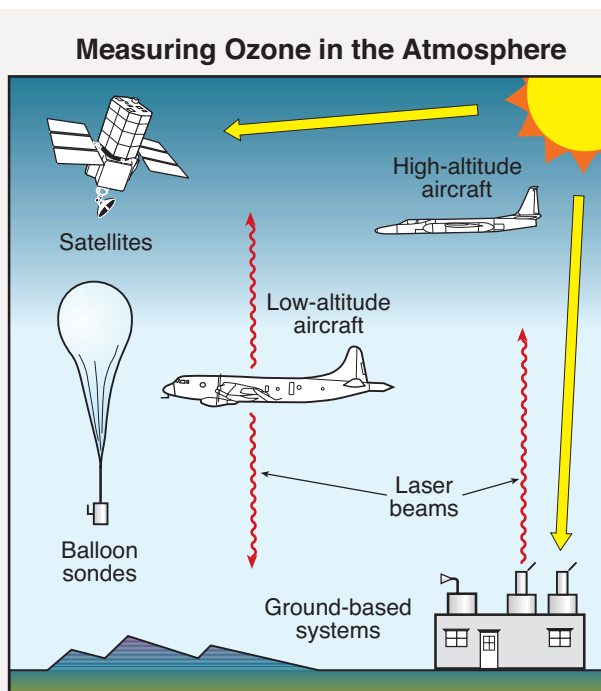
Figure Q5-1. Ozone measurements. Ozone is measured throughout the atmosphere with instruments on the ground, aircraft, high-altitude balloons, and satellites. Some instruments measure ozone locally in sampled air and others measure ozone remotely some distance away from the instrument. Instruments use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

microwave or infrared radiation. Emission measurements have the advantage of providing remote ozone measurements at night, which is particularly valuable for sampling polar regions in continuous darkness.

Global Ozone Network

The first instrument for routinely monitoring total ozone was developed by Gordon M.B. Dobson in the United Kingdom in the 1920s. The instrument, called a Féry spectrometer, made its measurements by examining the wavelength spectrum of solar ultraviolet radiation (sunlight) using a photographic plate. A small network of instruments distributed around Europe allowed Dobson to make important discoveries about how total ozone varies with location and time. In the 1930s a new instrument was developed by Dobson, now called a Dobson spectrophotometer, which precisely 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 provides a measure of total ozone above the instrument location.

A global network of total-ozone observing stations was established in 1957 as part of the International Geophysical Year. Today, there are about 100 sites located around the world ranging from South Pole, Antarctica (90°S), to Ellesmere Island, Canada (83°N), that routinely measure total ozone. The accuracy of these observations is maintained by regular instrument calibrations and intercomparisons. Data from the network have been essential for understanding the effects of chlorofluorocarbons (CFCs) and other ozone-depleting substances on the global ozone layer, starting before the launch of space-based ozone-measuring instruments and continuing to the present day. Ground-based instruments with excellent long-term stability and accuracy 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).

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

Principal Steps in the Depletion of Stratospheric Ozone

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

2 Accumulation
Halogen source gases accumulate in the atmosphere and are globally distributed throughout the lower atmosphere by winds and other air motions.

3 Transport
Halogen source gases are transported to the stratosphere by air motions.

4 Conversion
Most **halogen source gases** are converted in the stratosphere to **reactive halogen gases** in chemical reactions involving ultraviolet radiation from the Sun.

5 Chemical reaction
Reactive halogen gases cause chemical depletion of stratospheric **ozone** over the globe.

Low-temperature surface reactions on polar stratospheric clouds (PSCs) significantly increase **reactive halogen gases** and thereby cause severe **ozone** loss in polar regions in late winter and early spring.

6 Removal
Air containing **reactive halogen gases** returns to the troposphere where the gases are removed by moisture in clouds and rain.

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

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

Figure Q6-1. Principal steps in stratospheric ozone depletion. The stratospheric ozone depletion process begins with the emission of halogen source gases by human activities and natural processes. Those emitted by human activities are also called ozone-depleting substances (ODSs). Subsequent steps are accumulation, transport, conversion, chemical reaction, and removal. Ozone depletion by halogen source gases occurs globally. Large seasonal ozone losses occur in polar regions as a result of reactions involving polar stratospheric clouds (PSCs). Ozone depletion ends when reactive halogen gases are removed by rain and snow in the troposphere and deposited on Earth's surface.

Conversion, reaction, and removal. Halogen source gases do not react directly with ozone. Once in the stratosphere, halogen source gases are chemically *converted* to reactive halogen gases by ultraviolet radiation from the Sun (see Q8). The rate of conversion is related to the atmospheric lifetime of a gas (see Q7). Gases with longer lifetimes have slower conversion rates and survive longer in the atmosphere after emission. Lifetimes of the principal ODSs vary from 1 to 100 years (see Q7). Emitted gas molecules with atmospheric lifetimes greater than a few years circulate between the troposphere and stratosphere multiple times, on average, before conversion occurs.

The reactive gases formed from halogen source gases *react* chemically to destroy ozone in the stratosphere (see Q9). The average depletion of total ozone attributed to reactive gases is smallest in the tropics and largest at high latitudes (see Q13). In polar regions, surface reactions that occur at low temperatures on polar stratospheric clouds (PSCs) greatly increase the abundance of the most reactive chlorine gas, chlorine monoxide (ClO) (see Q10). This results in substantial ozone destruction in polar regions in late winter and early spring (see Q11 and Q12).

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

Tropospheric conversion. Halogen source gases with short lifetimes (less than 1 year) undergo significant chemical conversion in the troposphere, producing reactive halogen gases and other compounds. Source gas molecules that are not converted are transported to the stratosphere. Only small portions of reactive halogen gases produced in the troposphere are transported to the stratosphere because most are removed by precipitation. Important examples of halogen gases that undergo some tropospheric removal are the hydrochlorofluorocarbons (HCFCs), methyl bromide (CH_3Br), and gases containing iodine (see Q7).

Understanding Stratospheric Ozone Depletion

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

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

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

Q7   What emissions from human activities lead to ozone depletion?

Certain industrial processes and consumer products result in the emission of ozone-depleting substances (ODSs) to the atmosphere. ODSs are manufactured halogen source gases that are controlled worldwide by the Montreal Protocol. These gases bring chlorine and bromine atoms to the stratosphere, where they destroy ozone in chemical reactions. Important examples are the chlorofluorocarbons (CFCs), once used in almost all refrigeration and air conditioning systems, and the halons, which were used in fire extinguishers. Current ODS abundances in the atmosphere are known directly from air sample measurements.

Halogen source gases versus ODSs. Those halogen source gases emitted by human activities and controlled by the Montreal Protocol are referred to as ODSs within the Montreal Protocol, by the media, and in the scientific literature. The Montreal Protocol now controls the global production and consumption of ODSs (see Q15). Halogen source gases that have only natural sources are not classified as ODSs. The contributions of ODSs and natural halogen source gases to chlorine and bromine entering the stratosphere in 2008 are shown in Figure Q7-1.
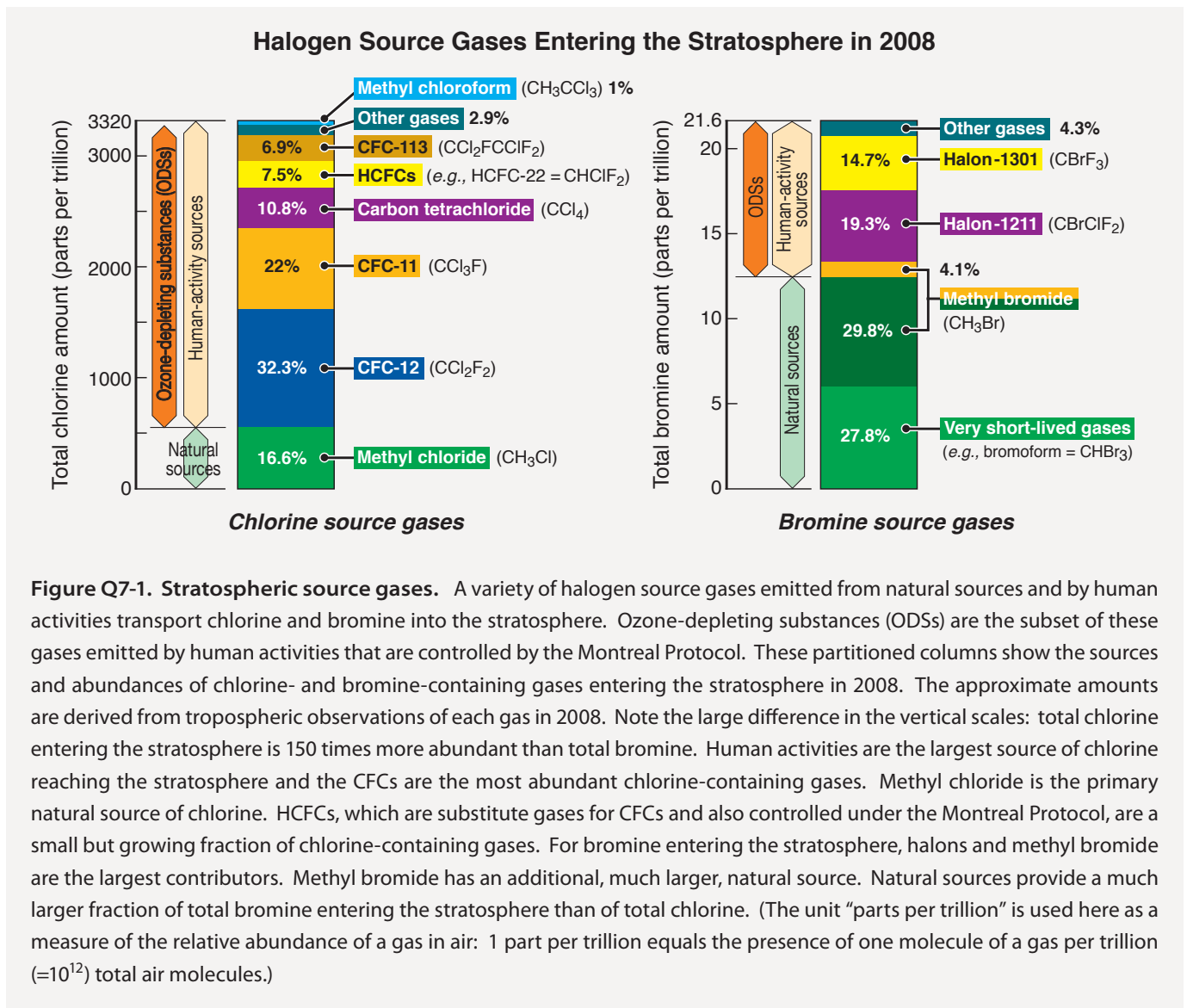
Ozone-depleting substances (ODSs). ODSs are manufactured for specific industrial uses or consumer products, most of which result in the eventual emission of these gases to the atmosphere. ODS emissions have increased substantially from the middle to the late 20th century, reached a peak in the late 1980s, and are now in decline (see Figure Q0-1). A large fraction of ODS emissions reach the stratosphere and lead to ozone depletion because chlorine and bromine atoms react to destroy ozone. ODSs that contain only carbon, chlorine, and fluorine are called *chlorofluorocarbons*, usually abbreviated as CFCs. CFCs, along with carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3), historically have been the most important chlorine-containing halogen source gases emitted by human activities. These and other chlorine-containing ODSs have been used in many applications, including refrigeration, air conditioning, foam blowing, aerosol propellants, and cleaning of metals and electronic components.

Another category of ODSs contains bromine. The most important of these gases are the halons and methyl bromide (CH_3Br). Halons are halocarbon gases originally developed to extinguish fires. Halons were widely used to protect large computer installations, military hardware, and commercial aircraft engines. As a consequence, halons are often released directly into the atmosphere upon use. Halon-1211 and halon-1301 are the most abundant halons emitted by human

activities (see Figure Q7-1). Methyl bromide is used primarily as an agricultural and pre-shipping fumigant.

Natural sources of chlorine and bromine. There are a few halogen source gases present in the stratosphere that have large natural sources. These include methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), both of which are emitted by oceanic and terrestrial ecosystems. Natural sources of these two gases contributed about 17% of the chlorine in the stratosphere in 2008 and about 30% of the bromine (see Figure Q7-1). Very short-lived source gases containing bromine, such as bromoform ($CHBr_3$), are also released to the atmosphere primarily from biological activity in the oceans. Only a fraction of these emissions reaches the stratosphere, because these gases are rapidly removed in the lower atmosphere. The contribution of these very short-lived gases to stratospheric bromine is estimated to be about 28%, but this has a large uncertainty. The contribution to stratospheric chlorine of short-lived chlorinated gases from natural and human sources is much smaller (less than 3%) and is included in *Other gases* in Figure Q7-1. The amounts of chlorine and bromine in the stratosphere from natural sources are believed to have been fairly constant since the middle of the 20th century and, therefore, cannot be the cause of ozone depletion as observed since the 1980s.

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

Halogen Source Gases Entering the Stratosphere in 2008

Chlorine source gases

Total chlorine amount (parts per trillion)

Ozone-depleting substances (ODSs) / Human-activity sources / Natural sources

- **Methyl chloroform** (CH_3CCl_3) **1%**
- **Other gases** **2.9%**
- 6.9% **CFC-113** (CCl_2FCClF_2)
- 7.5% **HCFCs** (*e.g.*, HCFC-22 = $CHClF_2$)
- 10.8% **Carbon tetrachloride** (CCl_4)
- 22% **CFC-11** (CCl_3F)
- 32.3% **CFC-12** (CCl_2F_2)
- 16.6% **Methyl chloride** (CH_3Cl)

Bromine source gases

Total bromine amount (parts per trillion)

ODSs / Human-activity sources / Natural sources

- **Other gases** **4.3%**
- 14.7% **Halon-1301** ($CBrF_3$)
- 19.3% **Halon-1211** ($CBrClF_2$)
- 4.1%
- 29.8% **Methyl bromide** (CH_3Br)
- 27.8% **Very short-lived gases** (*e.g.*, bromoform = $CHBr_3$)

Figure Q7-1. Stratospheric source gases. A variety of halogen source gases emitted from natural sources and by human activities transport chlorine and bromine into the stratosphere. Ozone-depleting substances (ODSs) are the subset of these gases emitted by human activities that are controlled by the Montreal Protocol. These partitioned columns show the sources and abundances of chlorine- and bromine-containing gases entering the stratosphere in 2008. The approximate amounts are derived from tropospheric observations of each gas in 2008. Note the large difference in the vertical scales: total chlorine entering the stratosphere is 150 times more abundant than total bromine. Human activities are the largest source of chlorine reaching the stratosphere and the CFCs are the most abundant chlorine-containing gases. Methyl chloride is the primary natural source of chlorine. HCFCs, which are substitute gases for CFCs and also controlled under the Montreal Protocol, are a small but growing fraction of chlorine-containing gases. For bromine entering the stratosphere, halons and methyl bromide are the largest contributors. Methyl bromide has an additional, much larger, natural source. Natural sources provide a much larger fraction of total bromine entering the stratosphere than of total chlorine. (The unit "parts per trillion" is used here as a measure of the relative abundance of a gas in air: 1 part per trillion equals the presence of one molecule of a gas per trillion ($=10^{12}$) total air molecules.)

Lifetimes and emissions. After emission, halogen source gases are either naturally removed from the atmosphere or undergo chemical conversion in the troposphere or stratosphere. The time to remove or convert about 60% of a gas is often called its atmospheric lifetime. Lifetimes vary from less than 1 year to 100 years for the principal chlorine- and bromine-containing gases (see Table Q7-1). The long-lived gases are primarily destroyed in the stratosphere and essentially all of the emitted halogen is available to participate in the destruction of stratospheric ozone. Gases with the short lifetimes (e.g., the HCFCs, methyl bromide, methyl chloride, and the very short-lived gases) are substantially destroyed in the troposphere and, therefore, only a fraction of the emitted halogen contributes to ozone depletion in the stratosphere.

The amount of an emitted gas that is present in the atmo-sphere represents a balance between the emission rate and the lifetime of the gas. Emission rates and atmospheric lifetimes vary greatly for the source gases, as indicated in Table Q7-1. For example, the atmospheric abundances of most of the principal CFCs and halons have decreased since 1990 while those of the leading substitute gases, the hydrochlorofluoro-carbons (HCFCs), continue to increase under the provisions of the Montreal Protocol (see Q16). In the coming decades, the emissions and atmospheric abundances of all controlled gases are expected to decrease under these provisions.

Ozone Depletion Potential (ODP). Halogen source gases are compared in their effectiveness to destroy strato-spheric ozone using the ODP, as listed in Table Q7-1 (see Q18). A gas with a larger ODP destroys more ozone over its atmo-spheric lifetime. The ODP is calculated relative to CFC-11,

Table Q7-1. Atmospheric lifetimes, global emissions, Ozone Depletion Potentials, and Global Warming Potentials of some halogen source gases and HFC substitute gases.

Gas	Atmospheric Lifetime (years)	Global Emissions in 2008 (Kt/yr) [a]	Ozone Depletion Potential (ODP) [c]	Global Warming Potential (GWP) [c]
Halogen source gases				
Chlorine gases				
CFC-11	45	52–91	1	4750
CFC-12	100	41–99	0.82	10900
CFC-113	85	3–8	0.85	6130
Carbon tetrachloride (CCl_4)	26	40–80	0.82	1400
HCFCs	1–17	385–481	0.01–0.12	77–2220
Methyl chloroform (CH_3CCl_3)	5	Less than 10	0.16	146
Methyl chloride (CH_3Cl)	1	3600–4600	0.02	13
Bromine gases				
Halon-1301	65	1–3	15.9	7140
Halon-1211	16	4–7	7.9	1890
Methyl bromide (CH_3Br)	0.8	110–150	0.66	5
Very short-lived gases (e.g., $CHBr_3$)	Less than 0.5	[b]	[b] very low	[b] very low
Hydrofluorocarbons (HFCs)				
HFC-134a	13.4	149 ± 27	0	1370
HFC-23	222	12	0	14200
HFC-143a	47.1	17	0	4180
HFC-125	28.2	22	0	3420
HFC-152a	1.5	50	0	133
HFC-32	5.2	8.9	0	716

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

[b] Estimates are very uncertain for most species.

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

which has an ODP defined to be 1. The calculations, which require the use of computer models of the atmosphere, use as the basis of comparison the ozone depletion from an equal mass of each gas emitted to the atmosphere. Halon-1211 and halon-1301 have ODPs significantly larger than CFC-11 and most other emitted gases because bromine is much more effective overall (about 60 times) on a per-atom basis than chlorine in chemical reactions that destroy ozone. The gases with small ODP values generally have short atmospheric lifetimes or contain fewer chlorine and bromine atoms.

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

tain fluorine atoms in addition to chlorine or bromine. After the source gases undergo conversion in the stratosphere (see Q6), the fluorine content of these gases is left in chemical forms that do not cause ozone depletion. As a consequence, halogen source gases that contain fluorine and no other halogens are not classified as ODSs. An important category is the hydrofluorocarbons (HFCs), which are included in Table Q7-1 because they are ODS substitute gases with ODPs of zero (see Q18).

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

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

Other non-halogen gases. Other non-halogen gases that influence stratospheric ozone abundances have also increased in the stratosphere as a result of emissions from human activities. Important examples are methane (CH_4) and nitrous oxide (N_2O), which react in the stratosphere to form water vapor and reactive hydrogen, and nitrogen oxides, respectively. These reactive products participate in the destruction of stratospheric ozone (see Q2). Increasing abundances of N_2O and CH_4, as well as CO_2, are expected to significantly affect future stratospheric ozone through combined effects on temperature, winds, and chemistry (see Q20). Although all of these gases are part of the Kyoto Protocol (see Q15) because they are climate gases, they are not classified as ODSs under the Montreal Protocol. Although past emissions of ODSs still dominate global ozone depletion, the *current* emissions of N_2O from human activities will destroy more stratospheric ozone than the *current* emissions of any ODS.

Heavier-Than-Air CFCs

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

Atmospheric measurements confirm that ozone-depleting substances with long atmospheric lifetimes are well mixed in the troposphere and are present in the stratosphere (see Figure Q8-2). The amounts found in these regions are generally consistent with the emission estimates reported by industries and governments. Measurements also show that gases that are "lighter than air," such as hydrogen (H_2) and methane (CH_4), are also well mixed in the troposphere, as expected, and not found only in the upper atmosphere. Noble gases from very light helium to very heavy xenon, which all have very long atmospheric lifetimes, are also uniformly distributed throughout the troposphere and stratosphere. Only at altitudes well above the troposphere and stratosphere (above 85 kilometers (53 miles)), where much less air is present, does the influence of winds and convection diminish to the point where heavy gases begin to separate from lighter gases as a result of gravity.

Q8

What are the reactive halogen gases that destroy stratospheric ozone?

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

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

Reactive halogen gases. The chemical conversion of halogen source gases, which involves solar ultraviolet radiation (sunlight) and other chemical reactions, produces a number of reactive halogen gases. These reactive gases contain all of the chlorine and bromine atoms originally present in the source gases. The most important reactive chlorine- and bromine-containing gases that form in the stratosphere are shown in Figure Q8-1. Throughout the stratosphere, the most abundant are typically hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$). These two gases are considered important *reservoir* gases because, while they don't react directly with ozone, they can be converted to the *most reactive* forms that
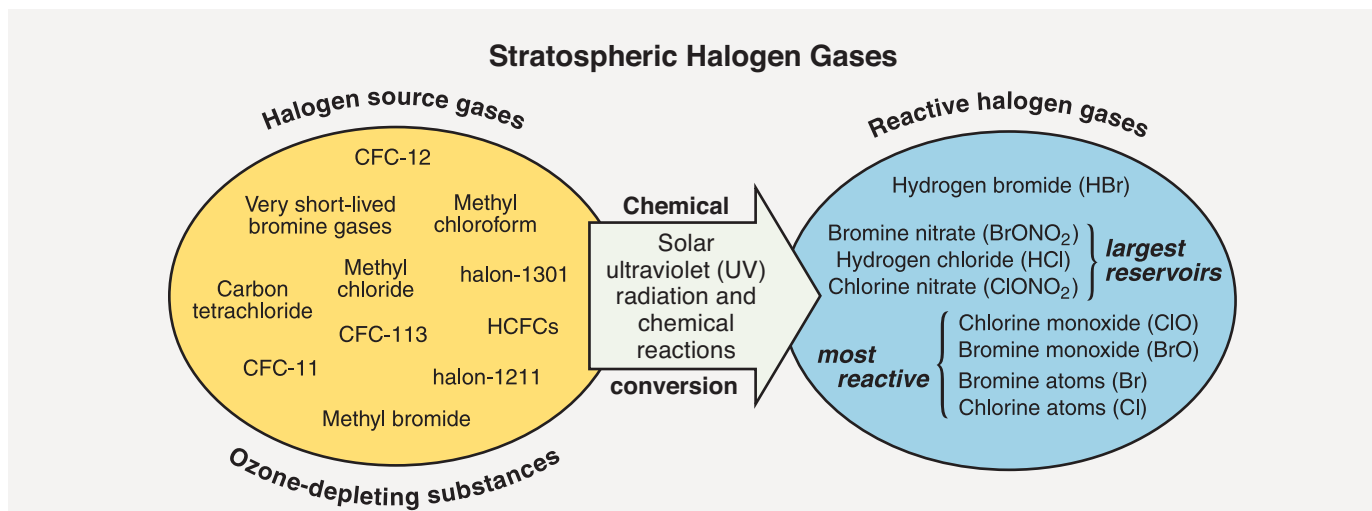

Stratospheric Halogen Gases

Figure Q8-1. Conversion of halogen source gases. Halogen source gases containing chlorine and bromine are chemically converted to reactive halogen gases primarily in the stratosphere. The conversion requires solar ultraviolet radiation and a few chemical reactions. The shorter-lived gases undergo some conversion in the troposphere. The reactive halogen gases contain all the chlorine and bromine originally present in the source gases before conversion. The reactive gases can be grouped into the reservoir gases, which do not directly destroy ozone, and the most reactive gases, which participate in ozone destruction cycles (see Q9). A principal reactive gas, ClO, is formed by reactions of the reservoir gases HCl and $ClONO_2$ that occur on the surfaces of liquid and solid polar stratospheric clouds (PSCs) (see Q10).

do chemically destroy ozone. The most reactive forms are chlorine monoxide (ClO) and bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). A large fraction of available reactive bromine is generally in the form of BrO, whereas usually only a small fraction of reactive chlorine is in the form of ClO. The special conditions that occur in the polar regions in winter cause the reservoir gases $ClONO_2$ and HCl to undergo nearly complete conversion to ClO in reactions on polar stratospheric clouds (PSCs) (see Q10).

Reactive chlorine at midlatitudes. Reactive chlorine gases have been observed extensively in the stratosphere with both local and remote measurement techniques. The measurements from space displayed in Figure Q8-2 are representative of how the amounts of chlorine-containing gases change between the surface and the upper stratosphere at midlatitudes. Available chlorine (see red line in Figure Q8-2) is the sum of chlorine contained in halogen source gases and the reactive gases (e.g., HCl, $ClONO_2$, ClO). Available chlorine is constant to within about 15 percent from the surface to 47 kilometers (31 miles) altitude. In the troposphere, available chlorine is contained almost entirely in the source gases described in Figure Q7-1. At higher altitudes, the source gases become a smaller fraction of available chlorine as they are converted to

the reactive chlorine gases. At the highest altitudes, available chlorine is all in the form of the reactive chlorine gases.

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

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

In fall (May), ozone values are high over the entire Antarctic continent and beyond. Temperatures are mid-range, HCl and nitric acid (HNO_3) are high, and ClO is very low. High HCl indicates that substantial conversion of halogen source gases has occurred in the stratosphere. In the past decades, HCl and $ClONO_2$ reactive reservoir gases have increased substantially in the stratosphere following increased emissions of halogen source gases. HNO_3 is an abundant, naturally

Measurements of Reactive Chlorine from Space
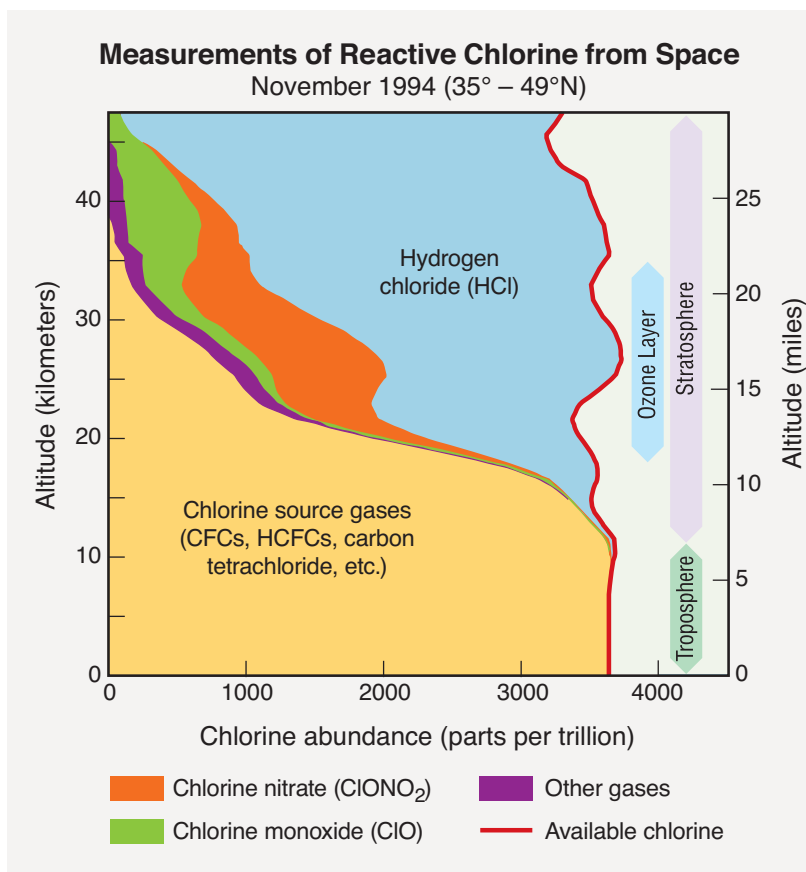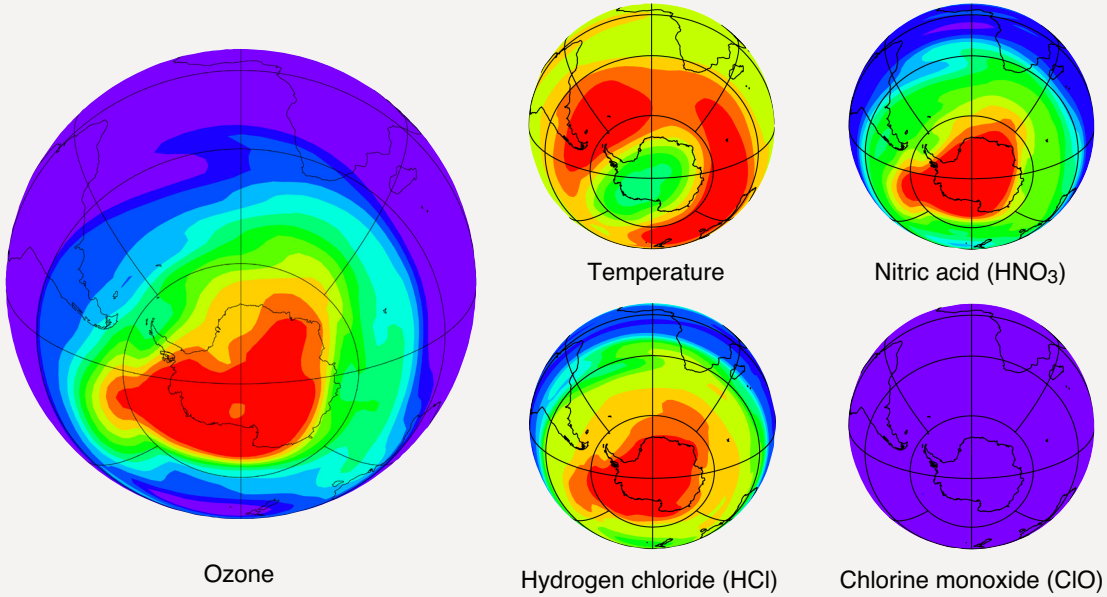November 1994 (35° – 49°N)

Figure Q8-2. **Reactive chlorine gas observations.** The abundances of chlorine source gases and reactive chlorine gases as measured from space in 1994 are displayed with altitude for a midlatitude location. In the troposphere (below about 10 kilometers), all chlorine is contained in the source gases. In the stratosphere, the abundances of reactive chlorine gases increase with altitude as the amounts of chlorine source gases decline. This is a consequence of chemical reactions initiated by solar ultraviolet radiation that convert source gases to reactive gases (see Figure Q8-1). The principal reactive chlorine gases formed are HCl, $ClONO_2$, and ClO. Summing the source gases with the reactive gases gives "Available chlorine," which is nearly constant with altitude up to 47 km. In the ozone layer (18–35 km), chlorine source gases are still present and 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.)

Chemical Conditions Observed in the Ozone Layer Over Antarctica

Normal ozone amounts in fall (1 May 2008) at 18-km altitude

Ozone

Temperature

Nitric acid (HNO₃)

Hydrogen chloride (HCl)

Chlorine monoxide (ClO)

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

Ozone

Temperature

Nitric acid (HNO₃)

Hydrogen chloride (HCl)

Chlorine monoxide (ClO)

Temperatures and chemical abundances

Low — High

1800 ——————	Ozone	—————— 2800 ppb
-85 - - - - - - -	Temperature	- - - - - - - -60°C
1.0 ——————	HNO₃	—————— 9.0 ppb
0.2 - - - - - - -	HCl	- - - - - - - 1.7 ppb
0.1 ——————	ClO	—————— 1.1 ppb
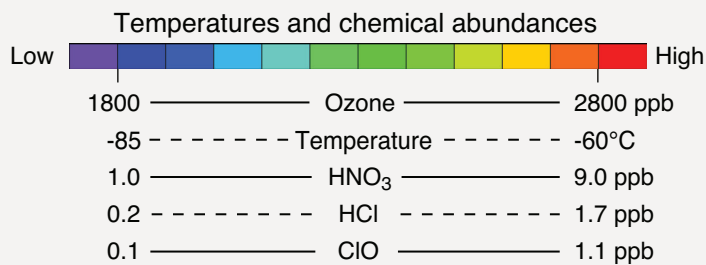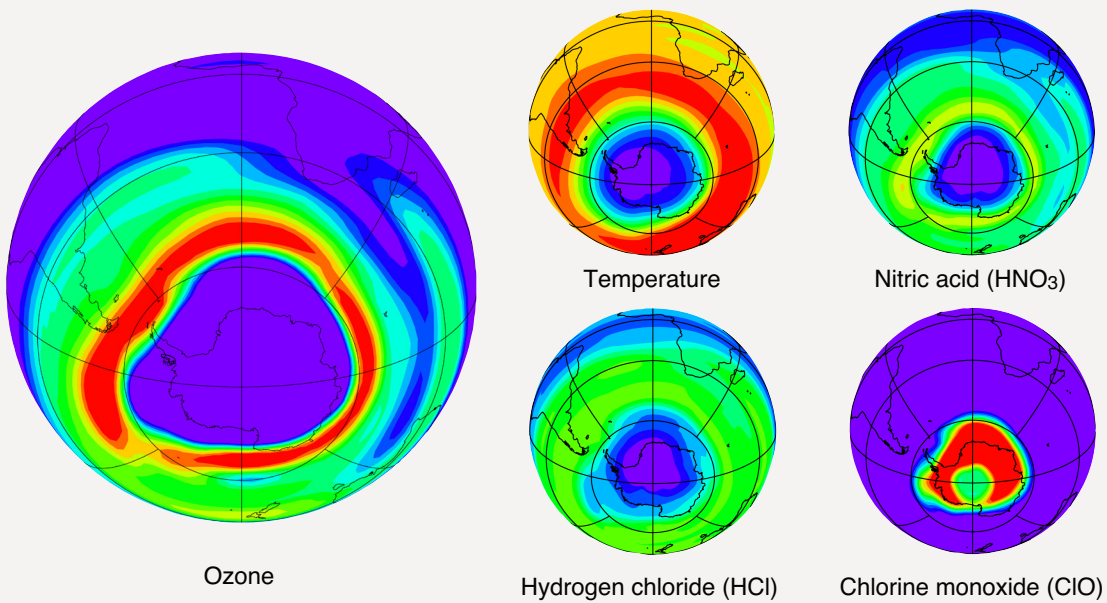
Figure Q8-3. Chemical conditions in the ozone layer over Antarctica. Observations of the chemical conditions in the Antarctic region highlight the changes associated with severe ozone depletion that forms the ozone hole. Satellite instruments now routinely monitor ozone, reactive chlorine gases, and temperatures in the global stratosphere. Results are shown here for fall (May) and late winter (September) seasons in Antarctic winter for a narrow altitude region near 18 kilometers (11.2 miles) within the ozone layer (see Figure Q12-3). Ozone has normal high values in fall before the onset of ozone destruction reactions causes wide spread depletion by late winter. High ozone is accompanied by moderate temperatures, normal high values of HCl and HNO_3, and normal very low ClO amounts. When ClO is not enhanced, significant ozone destruction from ozone-depleting substances does not occur. Chemical conditions are quite different in late winter when ozone undergoes severe depletion. Temperatures are much lower, HCl has been converted to ClO, the most reactive chlorine gas, and HNO_3 has been removed by the gravitational settling of PSC particles. ClO values closely surrounding the South Pole are low in September because ClO formation requires sunlight, which is still gradually returning to the highest latitudes. The high ClO values in late winter last for 1 to 2 months, cover an area that at times exceeds that of the Antarctic continent, and efficiently destroy ozone in sunlit regions in late winter/early spring. Ozone typically reaches its minimum values in early to mid-October (see Q12). Note that the first and last colors in the color bar represent values outside the indicated range of values. (The unit "parts per billion," abbreviated "ppb," is used here as a measure of the relative abundance of a gas in air: 1 part per billion equals the presence of one molecule of a gas per billion (=10^9) total air molecules (compare to ppt in Figure Q7-1)).

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

By late winter (September), ozone amounts reflect substantial depletion at 18-km altitude over an area larger than the Antarctic continent. Depletion throughout much of the altitude range of the ozone layer created the 2008 ozone hole shown in Figure Q11-3 (see altitude profile in Figure Q12-3). The associated meteorological and chemical conditions in late winter are very different from those found in fall: very low temperatures, very low HCl and HNO_3, and very high ClO. Low stratospheric temperatures are characteristic of winter when solar heating is reduced. Low HCl and high ClO reflect the conversion of the reactive halogen reservoir compounds, HCl and $ClONO_2$, to the most reactive chlorine form, ClO. This conversion occurs selectively in winter on PSCs and other stratospheric particles, which form at the very low temperatures (see Q10). Low HNO_3 is indicative of its condensation to form PSCs, some of which subsequently move to lower altitudes through gravitational settling. High ClO abundances generally cause ozone depletion to continue in the Antarctic region until mid-October (spring), when the lowest ozone values usually are observed (see Q11). As temperatures rise at the end of the winter, halting further PSC formation, ClO is converted back into the reactive reservoir species HCl and $ClONO_2$ (see Q10), and ozone destruction is curtailed.

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

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

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

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 thousands of ozone molecules before it leaves the stratosphere. In this way, a small amount of reactive chlorine or bromine has a large impact on the ozone layer. A special situation develops in polar regions in the late winter/early spring season where large enhancements in the abundance of the most reactive gas, chlorine monoxide, leads to severe ozone depletion.

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

Cycle 1. Ozone destruction Cycle 1 is illustrated in Figure Q9-1. The cycle is made up of two basic reactions: Cl + O$_3$ and ClO + O. The net result of Cycle 1 is to convert one ozone molecule and one oxygen atom into two oxygen molecules. In each cycle, chlorine acts as a *catalyst* because ClO and Cl react and are re-formed. In this way, one Cl atom participates in many cycles, destroying many ozone molecules. For typical stratospheric conditions at middle or low latitudes, a single chlorine atom can destroy hundreds of ozone molecules

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

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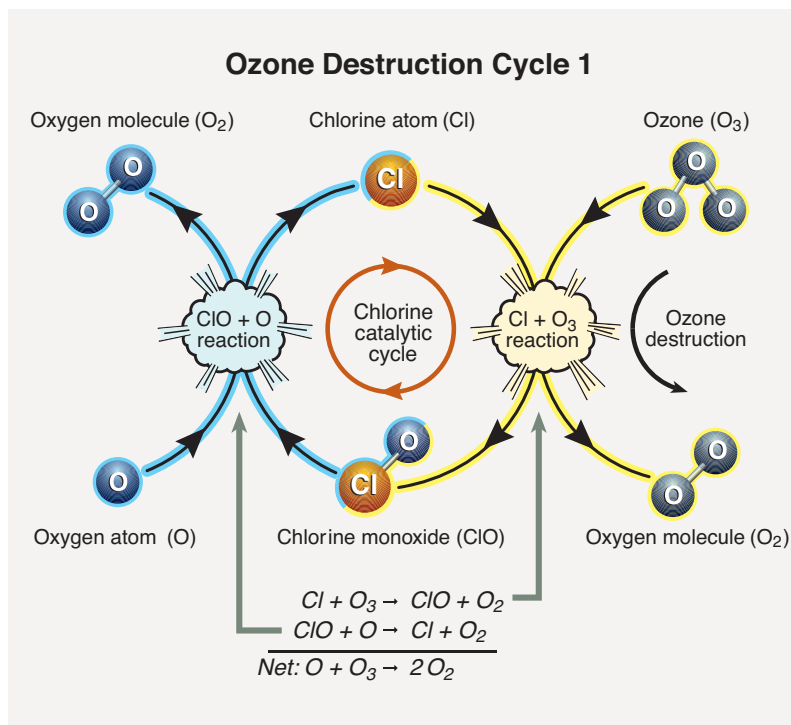

Ozone Destruction Cycle 1

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
$$Net: O + O_3 \rightarrow 2\,O_2$$

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. Then, Cl reacts with ozone and re-forms ClO, consuming ozone in the process. The cycle then begins again with another reaction of ClO with O. Chlorine is considered a catalyst for ozone destruction because Cl and ClO are re-formed each time the reaction cycle is completed, and ozone is simply removed. Atomic oxygen (O) is formed when solar ultraviolet radiation (sunlight) reacts with ozone and oxygen molecules. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where solar ultraviolet radiation is most intense.
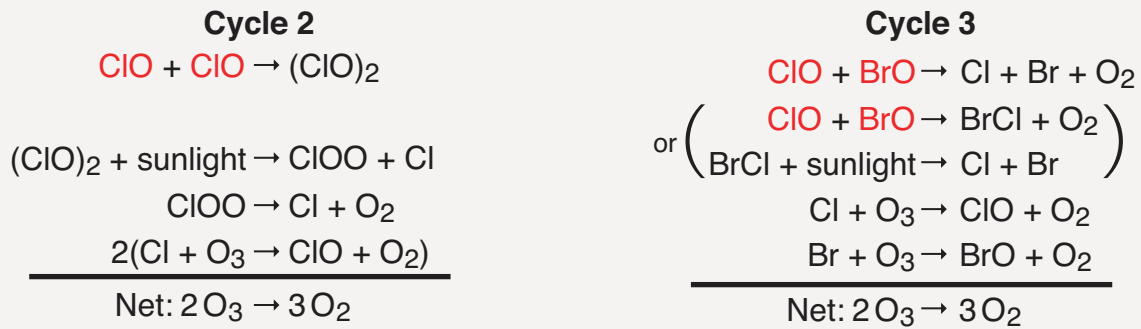
Ozone Destruction Cycles in Polar Regions

Cycle 2

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

$$(ClO)_2 + sunlight \rightarrow ClOO + Cl$$
$$ClOO \rightarrow Cl + O_2$$
$$2(Cl + O_3 \rightarrow ClO + O_2)$$

Net: $2\,O_3 \rightarrow 3\,O_2$

Cycle 3

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

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

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

Net: $2\,O_3 \rightarrow 3\,O_2$

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 re-formed each time the reaction cycle is completed. Visible sunlight is required to complete each cycle and to help form and maintain ClO abundances. During polar night and other periods of darkness, ozone cannot be destroyed by these reactions.

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

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

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

violet radiation is weak at low Sun angles. As a result, ozone destruction by Cycles 2 and 3 in the sunlit winter stratosphere greatly exceeds ozone production.

Other reactions. Global ozone abundances are controlled by many reactions that both produce and destroy ozone (see Q2). Chlorine and bromine catalytic reactions are but one group of ozone destruction reactions. Reactive hydrogen and reactive nitrogen gases, for example, are involved in other catalytic ozone-destruction cycles that also occur in the stratosphere. These reactions occur naturally in the stratosphere and their importance has not been as strongly influenced by human activities as have reactions involving halogens. The sources of reactive hydrogen and nitrogen gases are the naturally occurring gases methane (CH_4) and nitrous oxide (N_2O), respectively. The importance of reactive hydrogen and nitrogen gases relative to reactive halogen gases is expected to increase in the future, because the atmospheric abundances of the reactive halogen gases are decreasing as a result of the Montreal Protocol, while CH_4 and N_2O abundances are projected to increase substantially due to human activities.

Replacing Lost Ozone in the Stratosphere

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

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

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

Q10

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

Ozone-depleting substances 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 atmospheric and chemical conditions that exist there and nowhere else on the globe. The very low winter temperatures in the Antarctic stratosphere cause polar stratospheric clouds (PSCs) to form. Special reactions that occur on PSCs, combined with 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 late winter and early spring in the Antarctic is known as the "ozone hole" (see Q11). The ozone hole first appeared over Antarctica because atmospheric and chemical conditions unique to this region increase the effectiveness of ozone destruction by reactive halogen gases (see Q8). In addition to an abundance of these reactive gases, the formation of the Antarctic ozone hole requires temperatures low enough to form polar stratospheric clouds (PSCs), isolation from air in other stratospheric regions, and sunlight.

Distributing halogen gases. Halogen source gases emitted at Earth's surface are present in comparable abundances
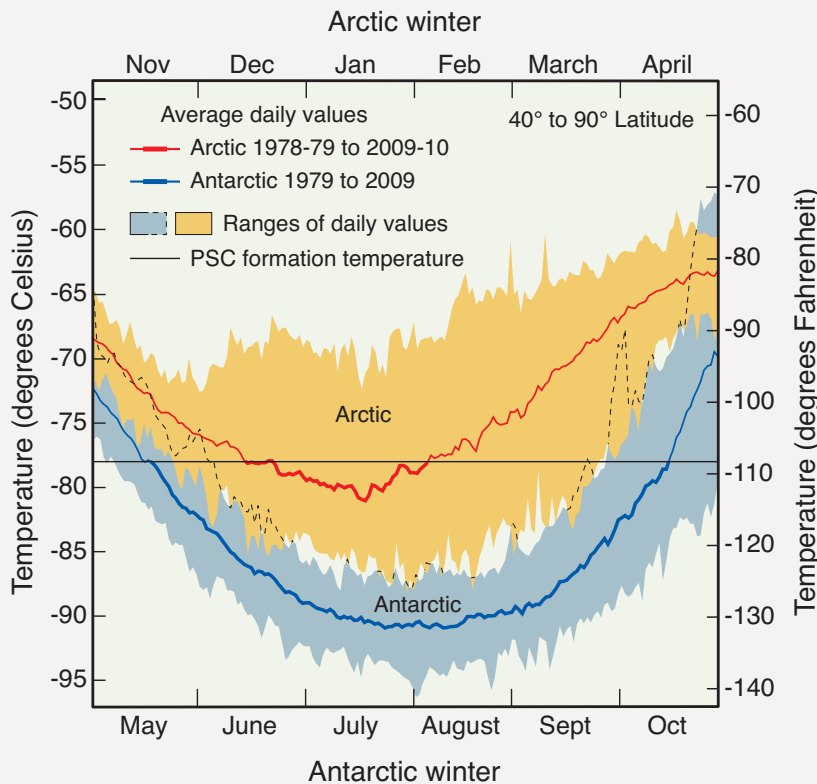

Figure Q10-1. Arctic and Antarctic temperatures. Air temperatures in both polar regions reach minimum values in the lower stratosphere in the winter season. Average daily minimum values over Antarctica are as low as −90°C in July and August in a typical year. Over the Arctic, average minimum values are near −80°C in late December and January. Polar stratospheric clouds (PSCs) are formed in the polar ozone layer when winter minimum temperatures fall below the formation temperature of 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 liquid and solid PSC particles cause the highly reactive chlorine gas ClO to be formed, which catalytically destroys 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 contrast, PSC formation temperatures are always present for many months somewhere in the Antarctic, and severe ozone depletion now occurs in each winter season (see Q11). (Note that the dashed black lines denote the upper limits of the Antarctic temperature range where they overlap with the Arctic temperature range.)

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 significant natural removal processes in the lower atmosphere and because winds and convection redistribute and mix air efficiently throughout the troposphere on the timescale of weeks to months. Halogen gases (in the form of source gases and some reactive products) enter the stratosphere primarily from the tropical upper troposphere. Stratospheric air motions then transport these gases upward and toward the pole in both hemispheres.

Low polar temperatures. The severe ozone destruction represented by the ozone hole requires that low temperatures be present over a range of stratospheric altitudes, over large geographical regions, and for extended time periods. Low temperatures are important because they allow liquid and solid PSCs to form. Reactions on the surfaces of these PSCs initiate a remarkable increase in the most reactive chlorine gas, chlorine monoxide (ClO) (see below and Q8). Stratospheric temperatures are lowest in both polar regions in winter. In the Antarctic winter, minimum daily temperatures are generally much 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. These and other meteorological differences occur because of the unequal distribution among land, ocean, and mountains between the hemispheres at middle and high latitudes. The winter temperatures are low enough for PSCs to form somewhere in the Antarctic for nearly the entire winter (about 5 months) and in the Arctic for only limited periods (10–60 days) in most winters.

Isolated conditions. Stratospheric air in the polar 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, forming a polar vortex, which prevents substantial motion of air into or out of the polar stratosphere. This circulation strengthens in winter as stratospheric temperatures decrease, with the result that the isolation of air in the vortex is much more effective in the Antarctic than the Arctic. Once chemical changes occur in polar regions from reactions on PSCs, the isolation preserves those changes for many weeks to months.

Polar stratospheric clouds (PSCs). Reactions on the surfaces of liquid and solid PSCs can substantially increase the relative abundances of the most reactive chlorine gases. These reactions convert the reservoir forms of reactive chlorine gases, chlorine nitrate ($ClONO_2$) and hydrogen chloride

(HCl), to the most reactive form, ClO (see Figure Q8-1). ClO increases from a small fraction of available reactive chlorine to comprise nearly all chlorine that is available. With increased ClO, additional catalytic cycles involving ClO and BrO become active in the chemical destruction of ozone whenever sunlight is available (see Q9).

Different types of liquid and solid PSC particles 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 significant altitude ranges. With a temperature threshold of

Arctic Polar Stratospheric Clouds (PSCs)

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 in the ozone layer during winters in the Arctic and Antarctic stratospheres wherever low temperatures occur (see Figure Q10-1). 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).

−78°C, PSCs exist in larger regions and for longer time periods in the Antarctic than the Arctic. The most common type of PSC forms from nitric acid (HNO_3) and water condensing on pre-existing liquid sulfuric acid-containing particles. Some of these particles freeze to form reactive solid particles. At even lower temperatures (−85°C or −121°F), water condenses to form ice particles. 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, which increases condensation of water and HNO_3.

When average temperatures begin increasing by late winter, PSCs form less frequently and their surface conversion reactions produce less ClO. Without continued ClO production, ClO amounts decrease and other chemical reactions re-form the reactive reservoirs, $ClONO_2$ and HCl. When PSC temperatures no longer occur, on average, either by late January to early February in the Arctic or by mid-October in the Antarctic, the most intense period of ozone depletion ends.

Nitric acid and water removal. Once formed, PSC particles fall to lower altitudes because of gravity. The largest particles can descend several kilometers or more in the stratosphere during the low-temperature winter/spring period that lasts several months in Antarctica. Because PSCs often contain a significant fraction of available HNO_3, their descent removes HNO_3 from regions of the ozone layer. This process is called *denitrification* of the stratosphere. With less HNO_3, the highly reactive chlorine gas ClO remains chemically active for a longer period, thereby increasing chemical ozone destruction. Significant denitrification occurs each winter in the Antarctic and in some, but not all, Arctic winters, because PSC formation temperatures must be sustained over an extensive altitude region and time period to effect denitrification (see Figure Q10-1).

Ice particles form when temperatures are a few degrees lower than PSC formation temperatures. If ice temperatures persist for weeks to months over extensive altitude regions, ice particles will also fall several kilometers due to gravity. As a result, a significant fraction of water vapor can also be removed from regions of the ozone layer. This process is called *dehydration* of the stratosphere. With the low temperatures required to form ice, dehydration is common in the Antarctic and rare in the Arctic winters. The removal of water vapor does not directly affect the catalytic reactions that destroy ozone. Dehydration indirectly affects ozone destruction by suppressing PSC formation, which reduces ClO production in PSC reactions.

Discovering the role of PSCs. Ground-based observations of PSCs, and knowledge of their formation processes, were available many years before the role of PSCs in polar ozone destruction was recognized. 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 PSC particles 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 chemical role of PSC particles developed from laboratory studies of their surface reactivity, computer modeling studies of polar stratospheric chemistry, and measurements that directly sampled particles and reactive chlorine gases, such as ClO, in the polar stratosphere.

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 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 Japan Meteorological Agency and the British Antarctic Survey. The results became widely known to the world after three scientists from the British Antarctic Survey published their observations in the scientific journal *Nature* in 1985 and speculated that CFCs were the cause. 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 as a description of the very low total ozone values that encircled the Antarctic continent in satellite images for many weeks (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.

Very early Antarctic ozone measurements. The first total ozone measurements made in Antarctica with Dobson spectrophotometers occurred in the 1950s following extensive measurements in the Northern Hemisphere and Arctic region. Total ozone values found in spring were around 300 DU, surprisingly lower than in the Arctic spring, because the assumption then was that the two polar regions would have similar values. We now know that these Antarctic values were not anomalous; indeed they are similar to those observed there in the 1970s before the ozone hole appeared (see Figure Q11-3). We also now know that Antarctic total ozone values, in comparison with Arctic values, are systematically lower in the early spring because the polar vortex is much stronger and, therefore, much more effective in reducing the transport of ozone-rich air from midlatitudes to the pole (compare Figures Q11-3 and Q12-2).

In 1958, measurements of total ozone were made at the Dumont d'Urville station (66.7°S, 140°E) in Antarctica using a photographic plate method to analyze solar ultraviolet radiation after it passed through the ozone layer. The reported measurements were anomalously low, reaching 110–120 DU in September and October. These values are similar to minimum ozone hole values now routinely observed over Antarctica in the same months (see Figure Q11-2). Some have speculated that these limited observations provide evidence that an ozone hole existed before ODS emissions were large enough to cause the depletion. However, analyses of the more extensive Dobson spectrophotometer measurements made at several other Antarctic locations in 1958 did not confirm the low total ozone values. These measurements indicate that the photographic plate determinations were not a reliable source of total ozone values at the Dumont d'Urville station in 1958.

Q11

How severe is the depletion of the Antarctic ozone layer?

Severe depletion of the Antarctic ozone layer was first reported in the mid-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, thereby reducing total ozone by as much as two-thirds at some locations. This severe depletion creates the "ozone hole" apparent in images of Antarctic total ozone made using satellite observations. 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 reported in the mid-1980s. The depletion is attributable to chemical destruction by reactive halogen gases that increased in the stratosphere in the latter half of the 20th century (see Q16). Conditions in the Antarctic winter and early spring stratosphere are highly suitable for ozone depletion because of (1) the long periods of extremely low temperatures, which cause polar stratospheric clouds (PSCs) to form; (2) the large abundance of reactive halogen gases produced in reactions on PSCs; and (3) the isolation of stratospheric air, which allows time for chemical destruction processes to occur. The severity of Antarctic ozone depletion can be seen using satellite observations of total ozone, ozone altitude profiles, and long-term changes in total ozone.

Antarctic ozone hole. The most widely used images of Antarctic ozone depletion are derived from measurements of total ozone made with satellite instruments. A map of Antarctic early spring measurements shows 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 maps. The area of the ozone hole is defined here as the geographical region contained within the 220-Dobson unit (DU) contour in total ozone maps (see white line in Figure
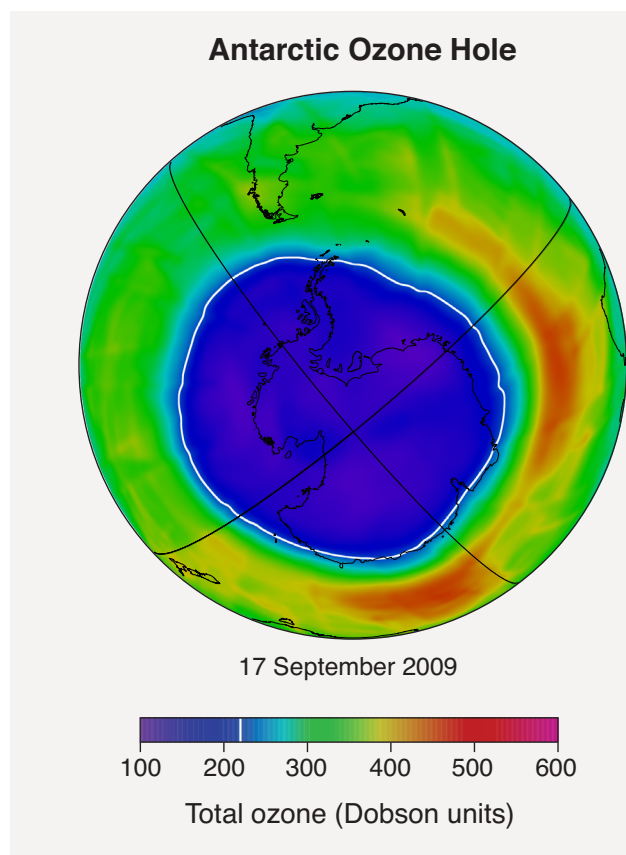

Antarctic Ozone Hole

17 September 2009

Total ozone (Dobson units)

Figure Q11-1. Antarctic ozone hole. Total ozone values are shown for high southern latitudes on 17 September 2009 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 Antarctic springtime values of about 350 DU (see Figure Q11-3). The ozone hole area is usually defined as the geographical area within the 220-DU contour (see white line) on total ozone maps. 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 toward the pole from outside the ozone hole. Note that maximum total ozone values in the Southern Hemisphere in this late winter period are generally located in a crescent-shaped region surrounding the ozone hole.
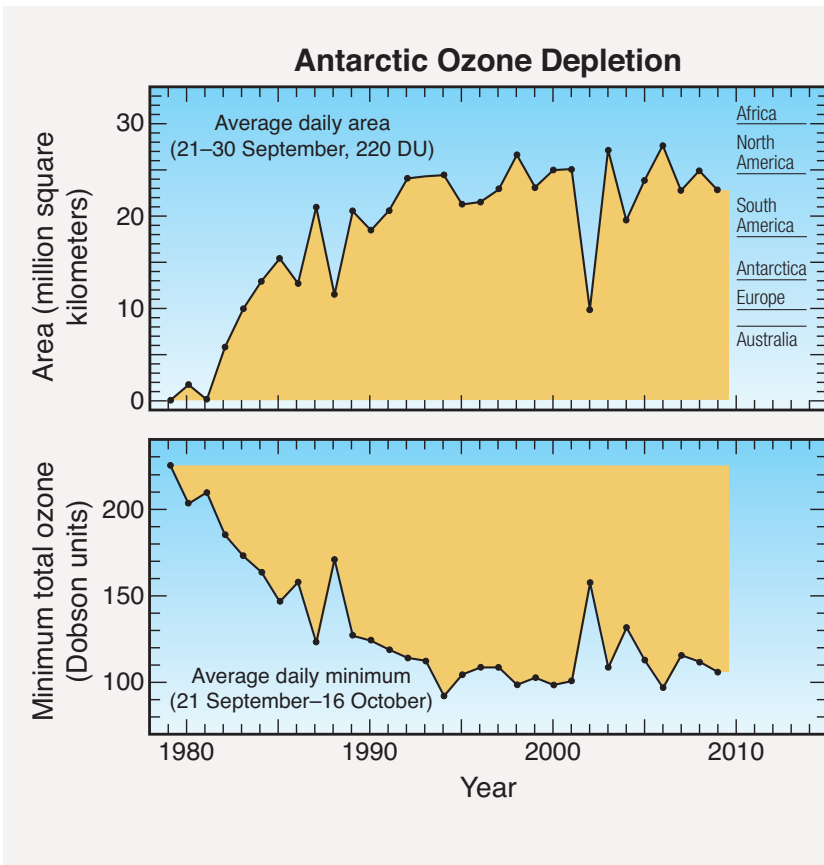
Figure Q11-2. Antarctic ozone hole features. Long-term changes are shown for key aspects of the Antarctic ozone hole: the area enclosed by the 220-DU contour on maps of total ozone (upper panel) and the minimum total ozone amount within the 220-DU contour (lower panel). The values are derived from satellite observations and averaged for each year at a time near the peak of ozone depletion, as defined by the dates shown in each panel. The areas of continents are included for reference in the upper panel. The magnitude of ozone depletion gradually increased beginning in 1980. In the 1990s, the depletion reached steady year-to-year values, except for the unusually low depletion in 2002 (see Figure Q11-4 and following box). The magnitude of Antarctic ozone depletion will decrease as ODSs are removed from the atmosphere (see Figure Q16-1). The return of Antarctic total ozone to 1980 values is not expected to occur before 2050 (see Q20).

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 to mid-October are near 100 DU, which is two-thirds below normal springtime values of about 350 DU (see Figures Q11-3 and Q12-1). Low total ozone inside the ozone hole contrasts strongly with the distribution of much larger values *outside* the ozone hole. This common feature can also be seen in Figure Q11-1, where a crescent-shaped region with maximum values of about 500 DU surrounds a large portion of the ozone hole in September 2009.

Altitude profiles of Antarctic ozone. The low total ozone values within the ozone hole are caused by nearly complete removal of ozone in the lower stratosphere. Balloonborne instruments (see Q5) demonstrate that this depletion occurs within the ozone layer, the altitude region that normally contains the highest ozone abundances. At geographic locations with the lowest total ozone values, balloon measurements show that the chemical destruction of ozone is complete over an altitude region of several kilometers. For example, in the ozone profile over South Pole, Antarctica, on 9 October 2006 (see Figure Q12-3), ozone abundances are essentially zero over

the altitude region of 14 to 21 kilometers. The lowest winter temperatures and highest reactive chlorine (ClO) abundances occur in this altitude region (see Figure Q8-3). The differences in the average South Pole ozone profiles between the decades 1962–1971 and 1990–2009 in Figure Q12-3 show how reactive halogen gases have dramatically altered the ozone layer. In the 1960s, a normal ozone layer is clearly evident in the October average profile with a peak near 16 kilometers altitude. In the 1990–2009 average profile, a broad minimum centered near 16 kilometers now occurs with ozone values reduced by up to 90% of normal values.

Long-term total ozone changes. The significant springtime ozone depletion represented by the ozone hole has only been observed since the early 1980s even though low winter temperatures and isolated conditions occur each year in the Antarctic stratosphere. Prior to 1980, the amounts of reactive halogen gases in the stratosphere were insufficient to cause significant depletion. Satellite observations can be used in multiple ways to examine how ozone depletion has changed in the Antarctic region over the last 30–40 years:
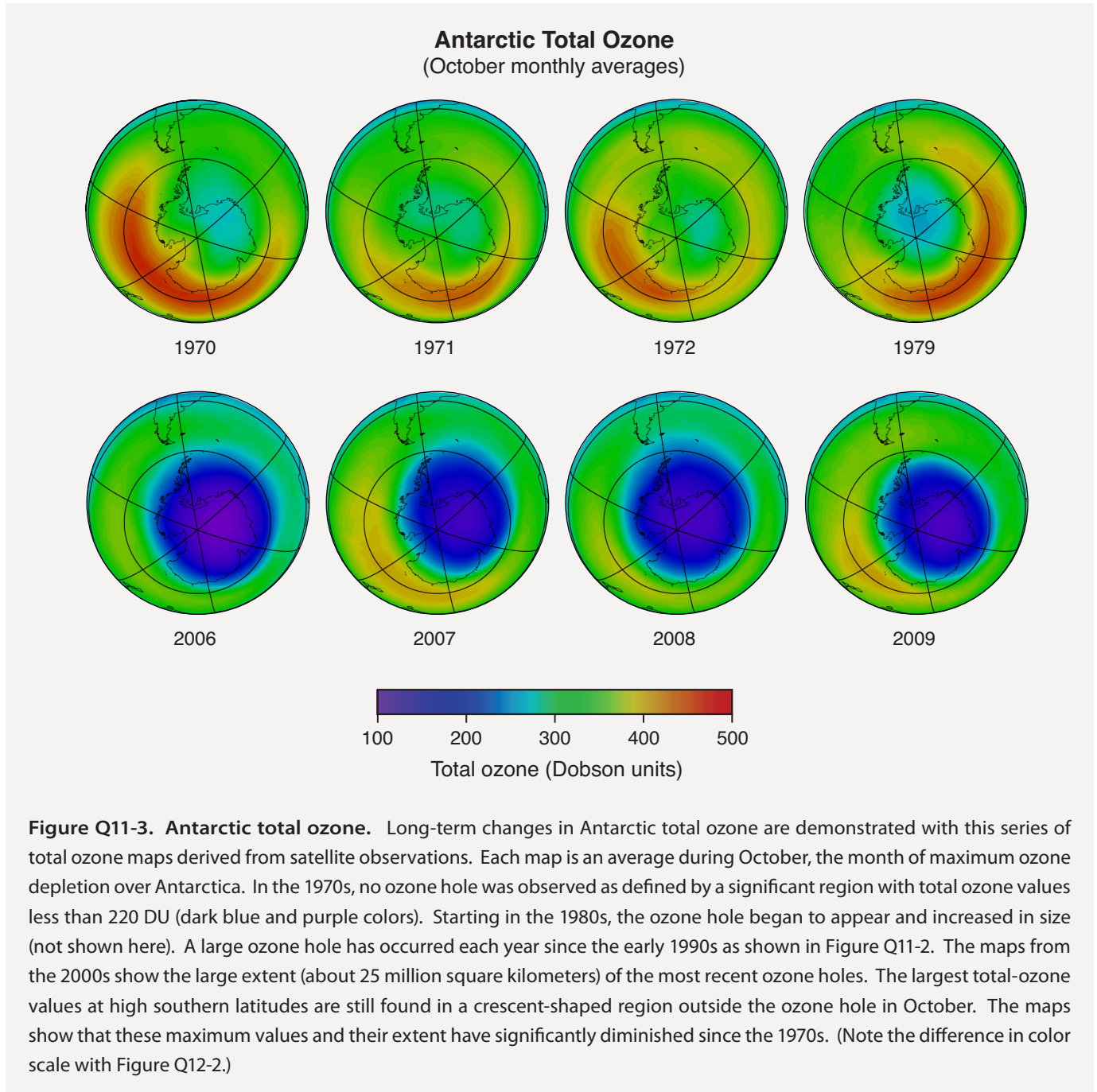
▶ First, *ozone hole areas* displayed in Figure Q11-2 show that depletion has increased since 1980 to become fairly stable in the 1990s and early 2000s near a value of 25 million

square kilometers. The exception is the unexpected low depletion in 2002, which is explained in the box at the end of this Question. The ozone-hole area is defined here as the geographical area inside the 220-DU contour on total ozone maps (see Figure Q11-1).

▶ Second, *minimum Antarctic ozone* amounts displayed in Figure Q11-2 show that the severity of the depletion has increased beginning around 1980 along with the ozone hole area. Fairly constant minimum values near 100 DU
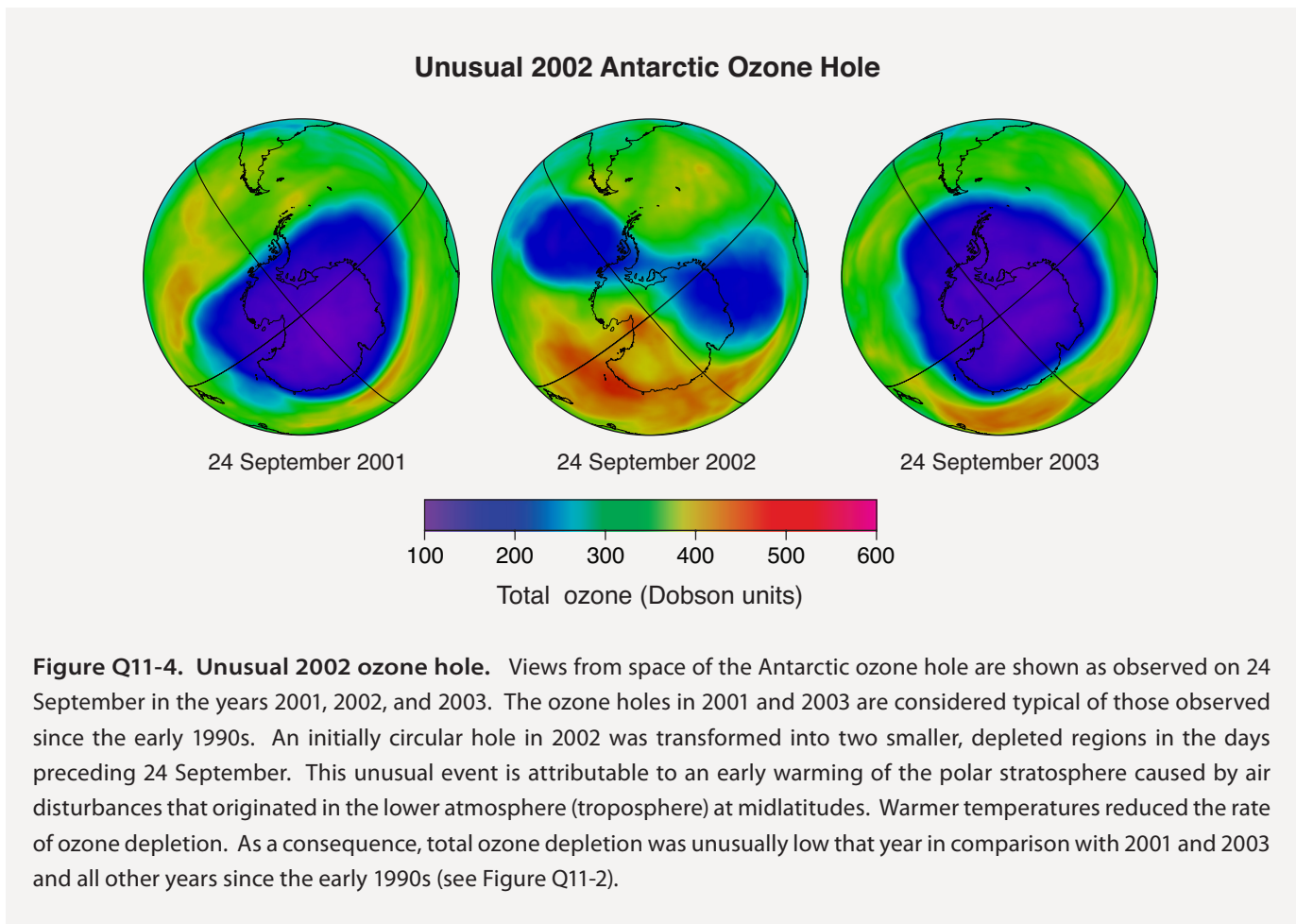
were observed in the 1990s and 2000s with 2002 being an exception.

▶ Third, *total ozone maps* over the Antarctic and surrounding regions show how the ozone hole has developed over time (see Figure Q11-3). October averages of total ozone confirm the absence of an ozone hole in the 1970s and its persistent occurrence in the late 2000s.

▶ Fourth, values of *total ozone poleward of 63°S* averaged for each October show how total ozone has changed when

Antarctic Total Ozone
(October monthly averages)

1970   1971   1972   1979

2006   2007   2008   2009

Total ozone (Dobson units)

Figure Q11-3. Antarctic total ozone. Long-term changes in Antarctic total ozone are demonstrated with this series of total ozone maps derived from satellite observations. Each map is an average during October, the month of maximum ozone depletion over Antarctica. In the 1970s, no ozone hole was observed as defined by a significant region with total ozone values less than 220 DU (dark blue and purple colors). Starting in the 1980s, the ozone hole began to appear and increased in size (not shown here). A large ozone hole has occurred each year since the early 1990s as shown in Figure Q11-2. The maps from the 2000s show the large extent (about 25 million square kilometers) of the most recent ozone holes. The largest total-ozone values at high southern latitudes are still found in a crescent-shaped region outside the ozone hole in October. The maps show that these maximum values and their extent have significantly diminished since the 1970s. (Note the difference in color scale with Figure Q12-2.)

averaged over the ozone hole and its surrounding areas (see Figure Q12-1). The values decrease strongly starting from those found in the 1970s and now are approximately 37% less than in pre-ozone-hole years (1970–1982). The average values show a larger year-to-year variability than found for the other ozone measures noted above because the average includes areas outside the ozone hole where the distribution of total ozone varies in response to meteorological conditions. The maps in Q11-3 show also how the maximum in total ozone surrounding the ozone hole each year has diminished over the last three decades, adding to the decreases noted in Figure Q12-1.

Disappearance of the ozone hole in spring. The severe depletion of Antarctic ozone occurs in the late winter/early spring season. In spring, temperatures in the polar lower stratosphere increase (see Figure Q10-1), ending PSC formation and reactions on aerosols and, consequently, the most effective chemical cycles that destroy ozone. Wintertime isolation of high-latitude air ends during this time with increasing exchange of air between the Antarctic stratosphere and lower latitudes. This allows substantial amounts of ozone-rich air to be transported poleward, where it displaces or mixes with air depleted in ozone. As a result of these large-scale transport and mixing processes, the ozone hole disappears by December.

Unusual 2002 Antarctic Ozone Hole

24 September 2001   24 September 2002   24 September 2003

100   200   300   400   500   600

Total ozone (Dobson units)

Figure Q11-4. Unusual 2002 ozone hole. Views from space of the Antarctic ozone hole are shown as observed on 24 September in the years 2001, 2002, and 2003. The ozone holes in 2001 and 2003 are considered typical of those observed since the early 1990s. An initially circular hole in 2002 was transformed into two smaller, depleted regions in the days preceding 24 September. This unusual event is attributable to an early warming of the polar stratosphere caused by air disturbances that originated in the lower atmosphere (troposphere) at midlatitudes. Warmer temperatures reduced the rate of ozone depletion. As a consequence, total ozone depletion was unusually low that year in comparison with 2001 and 2003 and all other years since the early 1990s (see Figure Q11-2).

The 2002 Antarctic Ozone Hole

The 2002 Antarctic ozone hole showed features that looked surprising at the time (see Figure Q11-4). It had much less ozone depletion as measured by the area of the ozone hole or minimum total-ozone amounts in comparison with the 2001 ozone hole. The 2002 values now stand out clearly in the year-to-year changes in these quantities displayed in Figure Q11-2. There were no forecasts of an ozone hole with unusual features in 2002 because the chemical and meteorological conditions required to deplete ozone, namely low temperatures and available reactive halogen gases, were present that year and did not differ substantially from previous years. The ozone hole initially formed as expected in August and early September 2002. Later, during the last week of September, an unexpected and surprisingly strong meteorological event occurred that dramatically reshaped the ozone hole into two separate depleted regions. As a result of this disturbance, the combined area of these two regions in late September and early October was significantly less than that observed for the previous or subsequent ozone holes.

The unexpected meteorological influence in 2002 resulted from specific atmospheric air motions that sometimes occur in polar regions. Meteorological analyses of the Antarctic stratosphere show that it was warmed by very strong, large-scale weather systems that originated in the lower atmosphere (troposphere) at midlatitudes in late September. At that time, Antarctic temperatures are generally very low (see Q10) and ozone destruction rates are near their peak values. The influence of these tropospheric systems extended poleward and upward into the stratosphere, disturbing the normal circumpolar wind flow (polar vortex) and warming the lower stratosphere where ozone depletion was ongoing. Higher temperatures reduced the rate of ozone depletion and led to the higher minimum values observed for total ozone in Figure Q11-2. 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 strong influence of the 2002 warming event is unique in the many decades of Antarctic meteorological observations. Another warming event occurred in 1988 causing smaller changes in the ozone hole features in Figure Q11-2. Large warming events are difficult to predict because of the complex conditions leading to their formation.

In 2003 through 2009, ozone hole features returned to values observed from the mid-1990s to 2001 (see Figure 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, leading to full recovery of total ozone, requires comparable, sustained reductions of ODSs in the stratosphere. Even with the source gas reductions already underway (see Q16), the return of Antarctic total ozone to 1980 values is not expected to occur before 2050.

Q12

Is there depletion of the Arctic ozone layer?

Yes, significant depletion of the Arctic ozone layer now occurs in most years in the late winter/early spring period (January–March). 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 depletion of total ozone has been observed in the Arctic stratosphere in recent decades. 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). Arctic depletion also occurs in the late winter/early spring period (January–March) over a somewhat shorter period than in the Antarctic (July–October). Similar to the Antarctic (see Q11), Arctic depletion occurs because of (1) the periods of extremely low temperatures, which cause polar stratospheric clouds (PSCs) to form; (2) the large abundance of reactive halogen gases produced in reactions on PSCs; and (3) the isolation of stratospheric air, which allows time for chemical destruction processes to occur.

Arctic ozone depletion is much less than that observed each Antarctic winter/spring season. Large and recurrent ozone holes as found in the Antarctic stratosphere do not occur in the Arctic. Depletion is limited because, in comparison to Antarctic conditions, Arctic average temperatures are always significantly higher (see Figure Q10-1) and the isolation of stratospheric air is less effective. Temperature and other meteorological differences occur because northern polar latitudes have more land and mountainous regions than southern polar latitudes (compare Figures Q11-3 and Q12-2). In a few Arctic winters, for example, PSCs did not form because temperatures never reached low enough values. These differences cause the extent and timing of Arctic ozone depletion to vary considerably from year to year. Depletion in some winter/spring seasons occurs over many weeks; in others only for brief early or late periods; and in some not at all.

Long-term total ozone changes. Satellite observations can be used in two important ways to examine the average total ozone abundances in the Arctic region for the last 30–40 years and to contrast these values with Antarctic abundances:

▶ First, *total ozone poleward of 63°N* averaged for each March shows quantitatively how total ozone has changed in the Arctic (see Figure Q12-1). The seasonal poleward and downward transport of ozone-rich air is naturally stron-

ger in the Northern Hemisphere. As a result, total ozone values at the *beginning* of each winter season in the Arctic are considerably higher than in the Antarctic. Before depletion sets in, normal Arctic values are close to 450 DU and Antarctic values near 330 DU. Decreases from pre-ozone-hole average values (1970–1982) were observed in the Arctic by the mid-1980s, when larger changes were already occurring in the Antarctic. The decreases in total ozone have reached a maximum of about 30% and generally remain smaller than those found in the Antarctic. The low value of Arctic total ozone in March 1997 relative to 1970–1982 observations is the most comparable to Antarctic depletion. In the 1996/1997 Arctic winter, low temperatures facilitated large amounts of chemical depletion, while meteorological conditions kept ozone transport to high latitudes below average values.

Overall, the Arctic values tend to show larger year-to-year variability than in the Antarctic. Ozone differences from the 1970-to-1982 average value are due to a combination of chemical destruction by ODSs and meteorological (natural) variations. In the last two decades, these two aspects have contributed about equally to observed ozone changes. The amount of chemical destruction depends in large part on stratospheric temperatures. Meteorological conditions determine how well Arctic stratospheric air is isolated from ozone-rich air at lower latitudes and influence the extent of low temperatures.

▶ Second, *total ozone maps* over the Arctic and surrounding regions (see Figure Q12-2) show year-to-year changes in March total ozone. In the 1970s, total ozone values were near 450 DU when averaged over the Arctic region in March. Beginning in the 1990s and continuing into the late 2000s, values above 450 DU were increasingly absent from the March average maps. A comparison of the 1971 and 2009 maps, for example, shows a striking reduction of total ozone throughout the Arctic region. The large geographical extent of low total ozone in the map of March 1997 is rare in
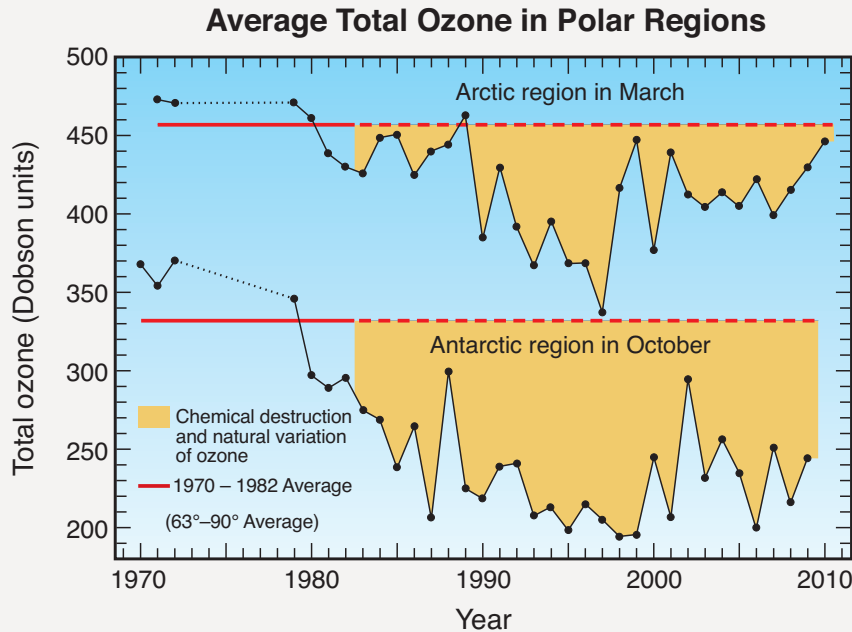
Figure Q12-1.   Average total ozone in polar regions. Long-term changes in average total ozone are shown for the Antarctic and Arctic for the respective regions defined by latitudes between 63° and 90°. Total ozone is measured with satellite instruments.   The reference values (red lines) are averages of springtime total ozone values available from observations between 1970 and 1982. Each point represents a monthly average for October in the Antarctic or 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 ozone, particularly in the Arctic. Essentially all of the decrease in the Antarctic and usually about 50% of the decrease in the Arctic each year are attributable to chemical destruction by reactive halogen gases. In the Arctic, the other 50% is attributable to natural variations in the amounts of ozone transported to polar regions before and during winter. Average total ozone values over the Arctic are naturally larger at the beginning of each winter season because, in the preceding months, more ozone is transported poleward in the Northern Hemisphere than in the Southern Hemisphere.

the Arctic observational record of the last three decades as noted above in the discussion of Figure Q12-1.

Altitude profiles of Arctic ozone.   Arctic ozone is measured using a variety of instruments (see Q5), as in the Antarctic, to document daily to seasonal changes within the ozone layer. Spring Arctic and Antarctic balloonborne measurements are contrasted in Figure Q12-3 using Arctic profiles from the Ny-Ålesund research station at 79°N. For 1991–2009, the March average reveals a substantial ozone layer and total ozone of 382 DU, contrasting sharply with the severely depleted Antarctic ozone layer in the October average for these years. This further demonstrates how higher stratospheric temperatures and meteorological variability have protected the Arctic ozone layer from the greater ozone losses that occur in the Antarctic, despite similar reactive halogen abundances in the two regions.

The separate Arctic profile shown for 29 March 1996 is one of the most severely depleted in the two-decade record from Ny-Ålesund. Although significant, this depletion is modest in

comparison to that routinely observed in the Antarctic, such as in the profile from 9 October 2006. The near-complete depletion of ozone over many kilometers in altitude, as is now common in the Antarctic stratosphere, has never been observed in the Arctic.

Restoring ozone in spring.   As in the Antarctic, ozone depletion in the Arctic is confined to the late winter/early spring season. In spring, temperatures in the polar lower stratosphere increase (see Figure Q10-1), ending PSC formation and reactions on aerosols, as well as the most effective chemical cycles that destroy ozone. Wintertime isolation of high-latitude air ends during this time with increasing exchange of air between the Arctic stratosphere and lower latitudes. This allows more ozone-rich air to be transported poleward, where it displaces or mixes with air in which ozone may have been depleted. As a result of this large-scale transport and mixing processes, any ozone depletion disappears by April or earlier.
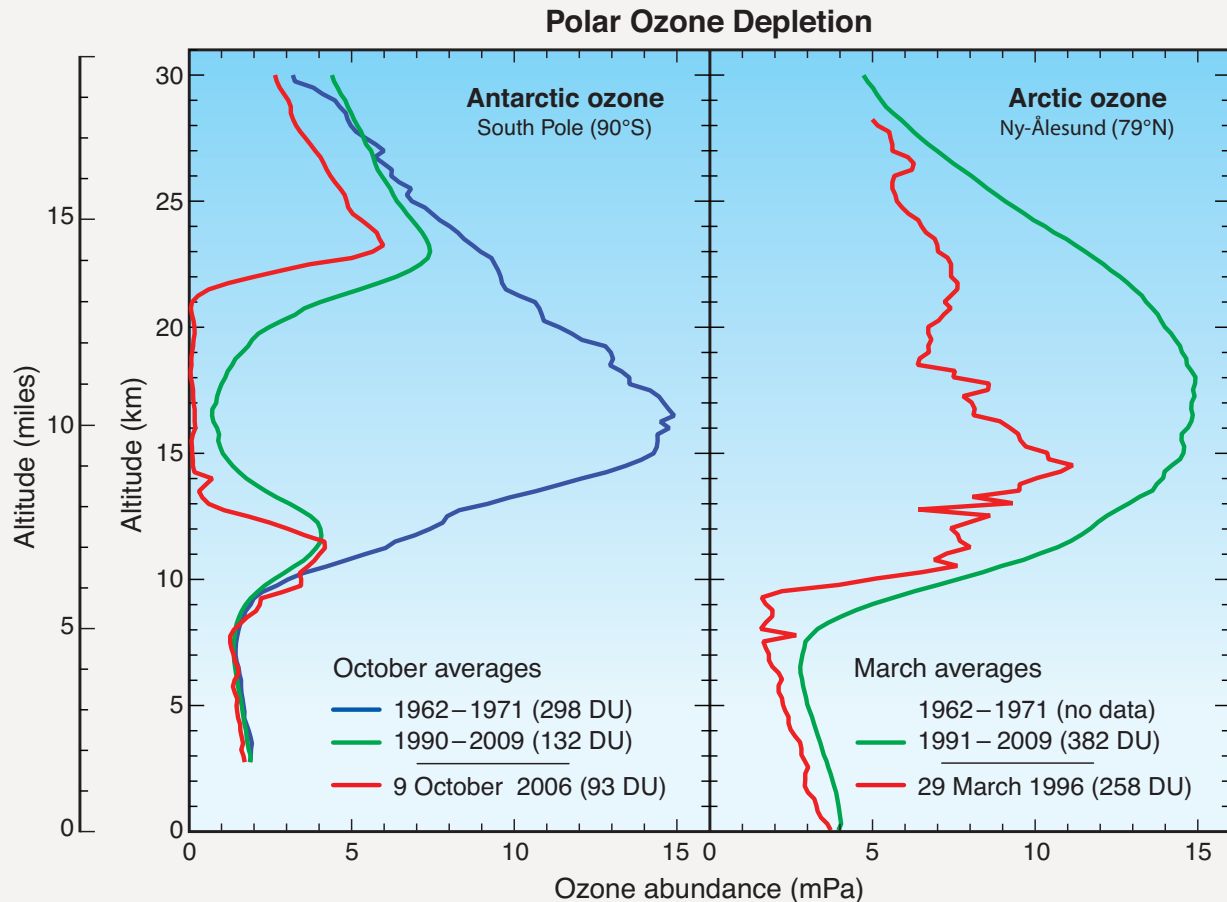
Arctic Total Ozone
(March monthly averages)

Figure Q12-2. Arctic total ozone. Long-term changes in Arctic total ozone are evident in this series of total ozone maps derived from satellite observations. Each map is an average during March, the month when some ozone depletion is usually observed in the Arctic. In the 1970s, the Arctic region had normal ozone values in March, with values of 450 DU and above (orange and red colors). Ozone depletion on the scale of the Antarctic ozone hole does not occur in the Arctic. Instead, late winter/early spring ozone depletion has eroded the normal high values of total ozone. On the maps from the late 2000s, the extent of values of 450 DU and above is greatly reduced in comparison with the 1970s maps. The large region of low total ozone in 1997 is unusual in the Arctic record and is attributable to meteorological conditions that led to below-average stratospheric temperatures and a strong polar vortex that winter. (Note the difference in color scale with Figure Q11-3.)

Figure Q12-3. Vertical distribution of Arctic and Antarctic ozone. Most stratospheric ozone resides between about 10 and 30 kilometers (6 to 19 miles) above Earth's surface. Long-term observations of the ozone layer with balloonborne instruments allow winter ozone altitude profiles to be compared between the Antarctic and Arctic regions. In the Antarctic at the South Pole (left panel), a normal ozone layer was observed to be present between 1962 and 1971. In more recent years, as shown here for 9 October 2006, ozone is almost completely destroyed between 14 and 21 kilometers (9 to 13 miles) in the Antarctic in spring. Average October values in the last decades (1990–2009) are 90% lower than pre-1980 values at the peak altitude of the ozone layer (16 kilometers). In contrast, the Arctic ozone layer is still present in spring as shown by the average March profile for 1991–2009 obtained over the Ny-Ålesund site (right panel). No Ny-Ålesund data are available for the 1962–1971 period before significant ODS destruction began. Some March profiles do reveal significant depletion, as shown here for 29 March 1996. In such years, winter minimum temperatures are generally lower than normal, allowing PSC formation for longer periods. Arctic profiles with depletion similar to that shown for 9 October 2006 at the South Pole have never been observed. The number in parentheses for each profile is the total ozone value in Dobson units (DU). Ozone abundances are shown here as the pressure of ozone at each altitude using the unit "milli-Pascals" (mPa) (100 million mPa = atmospheric sea-level pressure).

Q13

How large is the depletion of the global ozone layer?

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

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

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

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

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

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

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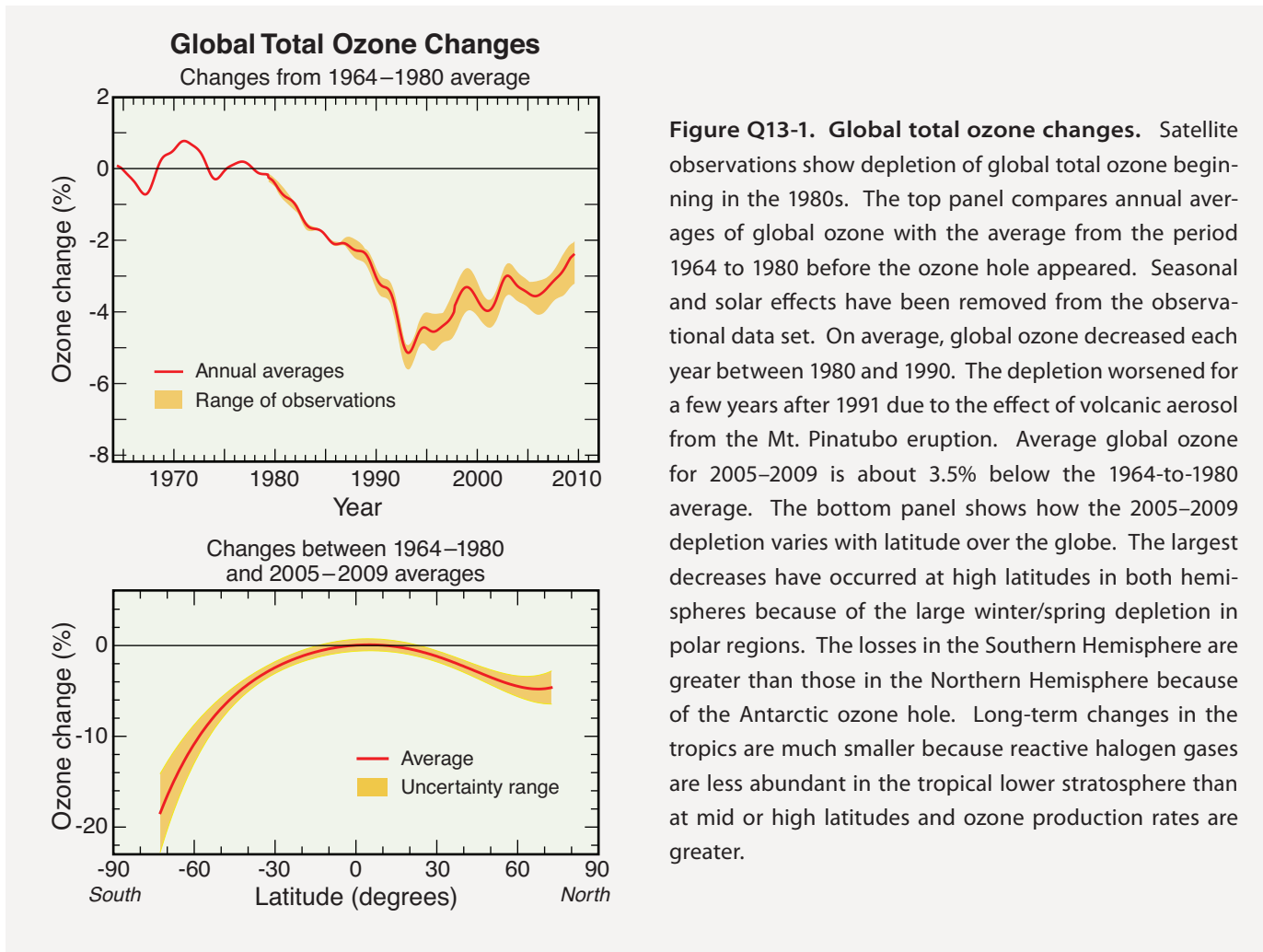
Global Total Ozone Changes

Changes from 1964−1980 average

Changes between 1964−1980 and 2005−2009 averages

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

the stratosphere following emission reductions. Future changes in climate parameters will also influence ozone. The global ozone increases observed in the last 20 years cannot be attributed solely to reductions in ODSs that began in the 1990s, because global ozone also responded strongly to the Mt. Pinatubo eruption. The projections of long-term changes in total ozone for different regions of the globe are described in Q20.

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 three decades. If large volcanic eruptions occur in the coming decades, ozone depletion will increase for several years afterwards.

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

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

term decreases in global ozone cannot result from changes in solar output alone. Most analyses presented in this and previous international scientific assessments quantitatively account for the influence of the 11-year solar cycle on long-term variations in ozone.

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

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

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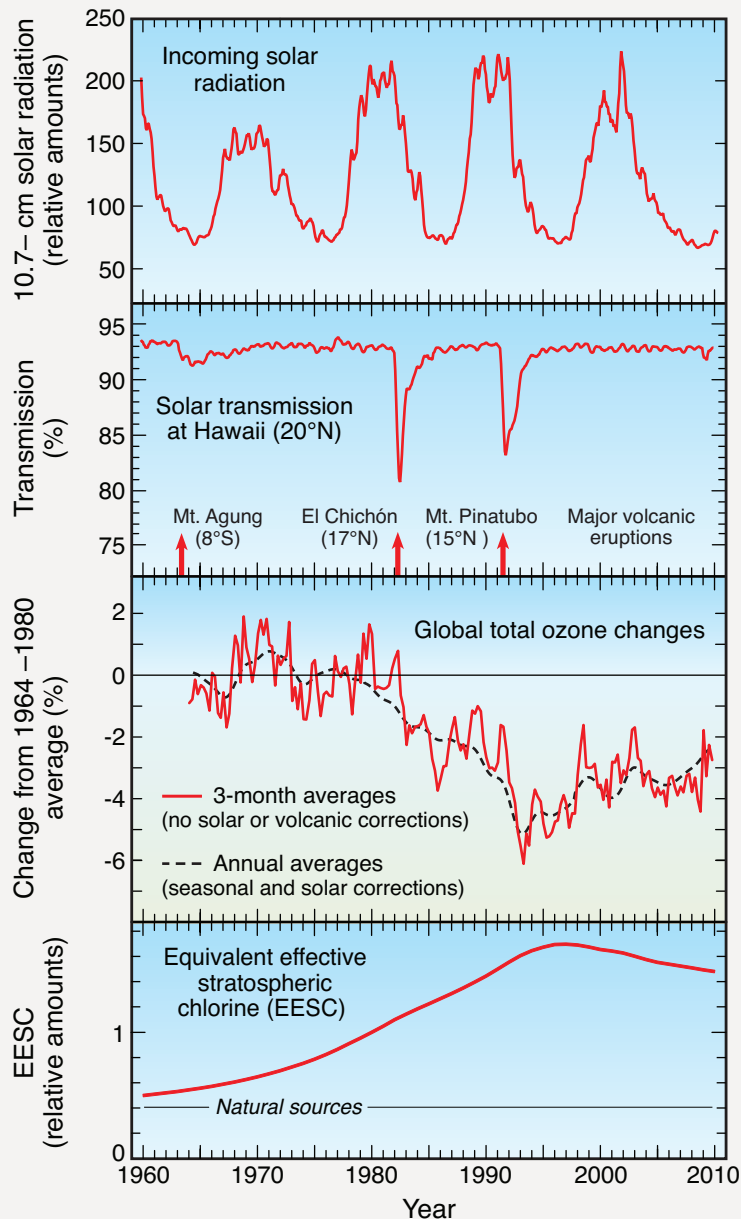

Figure Q14-1. Solar changes and volcanoes. Global total ozone values have decreased beginning in the early 1980s. Ozone values shown are the 3-month averages without corrections for solar or volcanic effects and annual averages corrected for seasonal and solar effects (from Figure Q13-1). These long-term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

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

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

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

eruptions, observations of HCl in the stratosphere have confirmed that increases are small compared with the total amount of chlorine in the stratosphere from other sources.

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

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

Q15

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

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

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

Amendments and Adjustments. As the scientific basis of ozone depletion became more certain after 1987 and substitutes and alternatives became available to replace ODSs, the Montreal Protocol was strengthened with Amendments and Adjustments. Each Amendment is named after the city in which the meeting of the Parties to the Montreal Protocol took place and by the year of the meeting. The timeline in Figure Q0-1 shows some of the major decisions that have been adopted in the last two decades. These decisions have put additional ODSs under control, accelerated existing control measures, and prescribed phase-out dates for the production and consumption of certain gases. The initial Protocol called

for a 50% reduction in chlorofluorocarbon (CFC) production and a freeze on halon production. The 1990 London Amendment called for a phase-out of the production and consumption of the most damaging ODSs in developed nations by 2000 and in developing nations by 2010. The 1992 Copenhagen Amendment accelerated the phase-out date to 1996 in developed nations. Further controls on ODSs were agreed upon in later meetings in Vienna (1995), Montreal (1997, 2007), and Beijing (1999).

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

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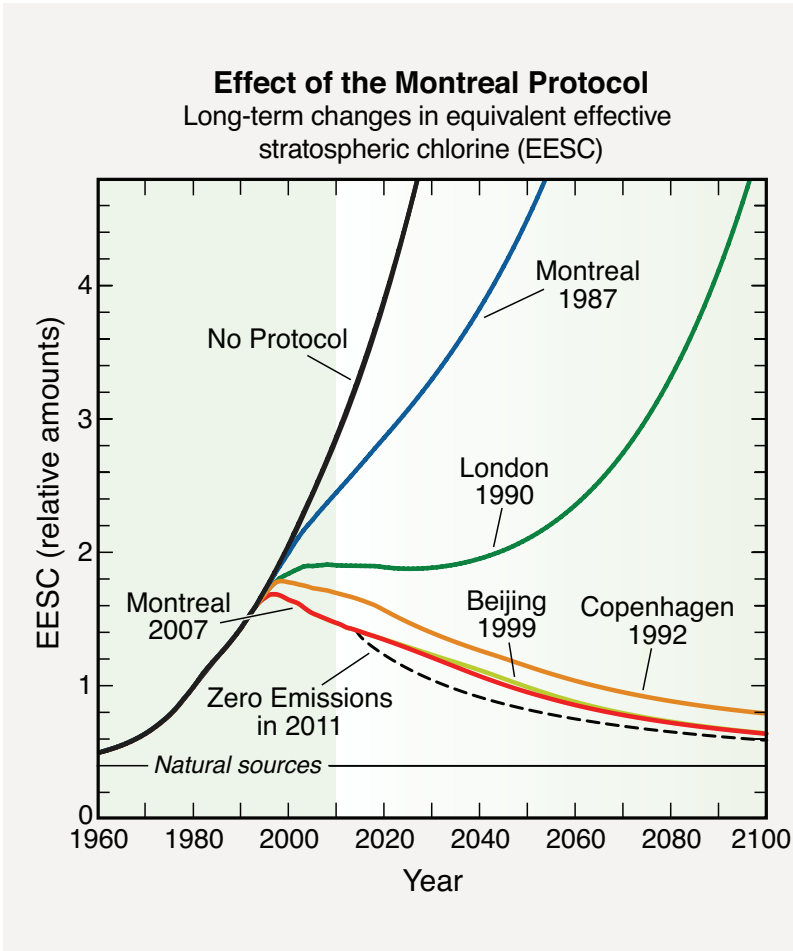
Effect of the Montreal Protocol
Long-term changes in equivalent effective stratospheric chlorine (EESC)

Figure Q15-1. Effect of the Montreal Protocol. The objective of the Montreal Protocol is the protection of the ozone layer through control of the global production and consumption of ODSs. Projections of the future abundances of ODSs expressed as equivalent effective stratospheric chlorine (EESC) values (see Q16) are shown separately for the midlatitude stratosphere for (1) no Protocol provisions, (2) the provisions of the original 1987 Montreal Protocol and some of its subsequent Amendments and Adjustments, and (3) zero emissions of ODSs starting in 2011. The city names and years indicate where and when changes to the original 1987 Protocol provisions were agreed upon (see Figure Q0-1). EESC is a relative measure of the potential for stratospheric ozone depletion that combines the contributions of chlorine and bromine from ODS surface observations (see Q16). Without the Protocol, EESC values are projected to have increased significantly in the 21st century. Only with the Copenhagen (1992) and subsequent Amendments and Adjustments did projected EESC values show a long-term decrease.

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

▶ **Montreal Protocol provisions.** International compliance with only the 1987 provisions of the Montreal Protocol and the later 1990 London Amendment would have substantially slowed the projected growth of EESC. Not until the 1992 Copenhagen Amendments and Adjustments did the Protocol projections show a *decrease* in future EESC values. The provisions became more stringent with the Amendments and Adjustments adopted in Beijing in 1999 and Montreal in 1997 and 2007. Now, with full compliance to the Protocol, most ODSs will be almost completely phased out, with some exemptions for critical uses (see Q16). Global EESC is slowly decaying from its peak value in the late 1990s and is expected to reach 1980 values in the mid-21st century. The success of the Montreal Protocol to date is demonstrated by the decline in ODP-weighted *emissions* of ODSs shown in Figure Q0-1. Total emissions peaked in 1988 at values about 10-fold higher than natural

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

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

The zero-emissions case demonstrates the EESC values that would occur if it were possible to set all ODS emissions to zero beginning in 2011. This would eliminate the contributions from new production and bank emissions. Significant differences from the Montreal 2007 projections are evident in the first decades following 2011 because the

phase-out of all ODS production under the Protocol is not yet complete and bank emissions are substantial. Zero emissions would bring forward the return of EESC to 1980 levels by about 13 years.

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

Under the provisions of the Montreal Protocol, developed and developing countries may continue to use HCFCs as ODS substitutes in the coming decades before they are ultimately phased out. In the most recent Adjustment to the Protocol (Montreal 2007), the phase-out of HCFCs for all Parties was accelerated so that it will be complete in 2030, a decade earlier than in previous provisions. In adopting this decision, the

Parties reduced the contribution of HCFC emissions to both long-term ozone depletion and future climate forcing (see Q18 and Q19).

HFC substitute gases. Hydrofluorocarbons (HFCs) are used as long-term substitute compounds for CFCs, HCFCs, and other ODSs. HFCs contain hydrogen, fluorine, and carbon. HFCs do not contribute to ozone depletion because they contain no chlorine, bromine, or iodine. As a consequence, HFCs are not ODSs and are not subject to the provisions of the Montreal Protocol. HFCs and all ODSs are radiatively active gases that contribute to human-induced climate change based on their accumulation in the atmosphere (see Q18). HFCs are included in the *basket of gases* being controlled by the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC). The Kyoto Protocol is an international treaty designed to protect climate by controlling *emissions* of HFCs, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6). HFC emissions are expected to grow substantially in coming decades as the demand for their use as substitute gases and in new applications increases in developed and developing countries. The climate change contribution from future HFC emissions will be minimized if HFCs with very low Global Warming Potentials (GWPs) (less than 100) are chosen to meet the growing demand (see Q18).

Q16

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

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

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

Individual ODS reductions. The reduction in the atmospheric abundance of an ODS in response to controls on production and consumption depends principally on two factors: (1) how rapidly an ODS is used and released to the atmosphere after being produced and (2) the lifetime for the removal of the ODS from the atmosphere (see Table Q7-1). For example, the abundances of ODSs with short lifetimes respond quickly to emission reductions. Long-term changes in ODS abundances are constructed from (1) estimates of historical emissions and bank quantities using industry reports, (2) abundances measured in air trapped for years in accumulated snow (firn) in polar regions, (3) observed atmospheric abundances using ground-based measurements, and (4) projections of future abundances based on compliance with Montreal Protocol provisions and patterns of use in developed and developing countries. The results for individual ODSs and the natural chlorine source gas, methyl chloride (CH_3Cl), are shown in Figure Q16-1 and described as follows:

▶ **CFCs.** Chlorofluorocarbons (CFCs) include some of the most destructive chlorine-containing ODSs. CFC-11 and CFC-12, each with an Ozone Depletion Potential (ODP) near 1, are the most abundant ODSs in the atmosphere owing to large historical emissions and long atmospheric lifetimes (45–100 years). Production and consumption of CFCs in developed countries ended in 1996 and that in developing countries ended by January 2010. As a consequence, CFC-11 and CFC-113 abundances have peaked in the atmosphere and have been declining for more than a decade. In contrast, CFC-12 abundances have only recently shown a decrease, owing to its longer lifetime (100 years) and continuing emissions from CFC-12 banks, namely, refrigeration and air conditioning equipment and thermal insulating foams. With no further global production of the principal CFCs allowed except for limited exempted uses and with some continuing emissions from banks, CFC abundances are projected to decline steadily throughout this century.

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

▶ **Methyl chloroform.** The largest reduction to date in the abundance of an ODS (about 90% from its peak value) has been observed for methyl chloroform. Production and consumption of methyl chloroform in developed countries ended in January 1996 and that in developing countries
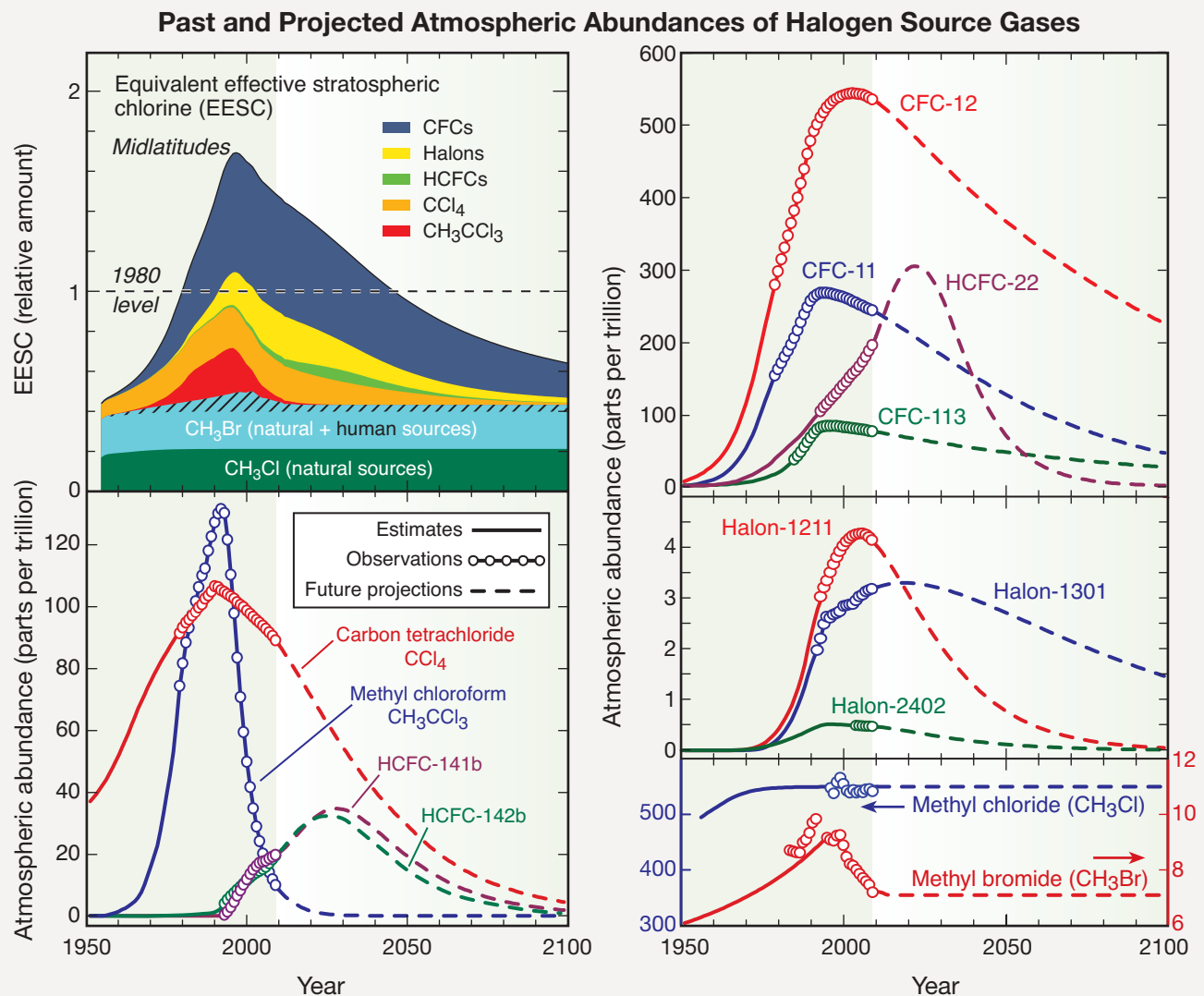
Figure Q16-1. Halogen source gas changes. The atmospheric abundances of individual ozone-depleting substances (ODSs) at Earth's surface were obtained using a combination of direct atmospheric measurements, estimates of historical abundance, and future projections of abundance. The gases shown are all ODSs except for methyl chloride. The past increases of CFCs, along with those of carbon tetrachloride, methyl chloroform, and halon-1211, have slowed and reversed in the last two decades. HCFCs, which are used as transitional substances to replace CFCs, will likely continue to increase in the coming decades before a complete phase-out. Halon-1301 abundances will also likely continue to grow in the next decade while current halon banks are depleted. Future decreases in methyl bromide are expected to be small. Abundances of methyl chloride, which is not controlled under the Montreal Protocol and has large natural sources, are projected to be constant in the future.

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

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

► **HCFC substitute gases.** The Montreal Protocol allows for the use of hydrochlorofluorocarbons (HCFCs) as short-term, transitional substitutes for CFCs and in other specific applications. As a result, the abundances of HCFC-22, HCFC-141b, and HCFC-142b continue to grow in the atmosphere with rates that have remained constant or increased in recent years in response to greater application demand. HCFCs pose a lesser threat to the ozone layer than CFCs because they have low ODP values (less than 0.12). The most recent Adjustment to the Montreal Protocol (Montreal 2007) accelerated the phase-out of HCFCs by a decade for both developed (2020) and developing countries (2030) (see Q15). Even with the accelerated phase-out, future projections show HCFC abundances that continue to increase, reach peak values before the mid-21st century, and steadily decrease thereafter. The response of atmospheric abundances to decreasing emissions will be relatively rapid because of short atmospheric lifetimes of HCFCs (less than 20 years).

► **Carbon tetrachloride.** Carbon tetrachloride has been phased out in both developed countries (January 1996) and developing countries (January 2010). As a result, atmospheric abundances of carbon tetrachloride have been decreasing for two decades. The decline is somewhat less rapid than expected, suggesting that actual emissions are larger than reported or the atmospheric lifetime is greater than current estimates. Production of carbon tetrachloride for use as raw material (feedstock) to make other chemicals is exempted under the Protocol because emission to the atmosphere does not occur in this case.

► **Methyl chloride and methyl bromide.** Both methyl chloride and methyl bromide are distinct among halogen source gases because substantial fractions of their emissions are associated with natural processes (see Q7). Methyl chloride is not an ODS under the Montreal Protocol because it is not manufactured or used in appreciable quantities. Its abundance in the atmosphere has remained fairly constant throughout the last 60 years and will remain constant if the balance of its natural production and loss processes remains unchanged. Methyl bromide is controlled under the Protocol because it is manufactured for use as a fumigant. Developed country production and consumption of methyl bromide ended in January 2005 and that in developing countries is scheduled to end by January 2015. The Protocol currently provides exemptions for some methyl bromide production and use as an agricultural and pre-shipment fumigant. Atmospheric abundances of methyl bromide responded rapidly to the reduced emissions starting in 1999 because its atmospheric removal lifetime is less than 1 year. Future projections show only small changes in methyl bromide abundances based on the assumptions of unchanged contributions from natural sources and small use in developing countries. An important uncertainty in these projections is the future amounts that will be produced and emitted under Montreal Protocol use exemptions.

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

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

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

Long-term changes in EESC. In the latter half of the 20th century up until the 1990s, EESC values steadily increased (see Figure Q16-1), causing global ozone depletion. As a result of the Montreal Protocol regulations, the long-term increase in EESC slowed, values reached a peak, and EESC began to decrease in the 1990s. The initial decrease came primarily from the substantial, rapid reductions in emissions of methyl chloroform, which has a lifetime of only 5 years. The decrease is continuing with declining emissions of CFCs and other long-lived ODSs. Decreasing EESC means that the potential for stratospheric ozone depletion is now lessening each year as a result of the Montreal Protocol. Decreases in EESC are projected to continue throughout the 21st century if all nations continue to comply with the provisions of the Protocol. The decrease will continue because as emissions are reduced, natural processes continue to gradually remove halogen-containing gases from the global atmosphere. Reduction of EESC values to 1980 values or lower will require several more decades because the most abundant ODS molecules now in the atmosphere have lifetimes ranging from 10 to 100 years.

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 provide evidence that surface ultraviolet radiation has increased in large geographic regions in response to ozone depletion.

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

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

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

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

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

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

The UV Index over Antarctica has increased dramatically due to ozone depletion, as illustrated in Figure Q17-2.

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

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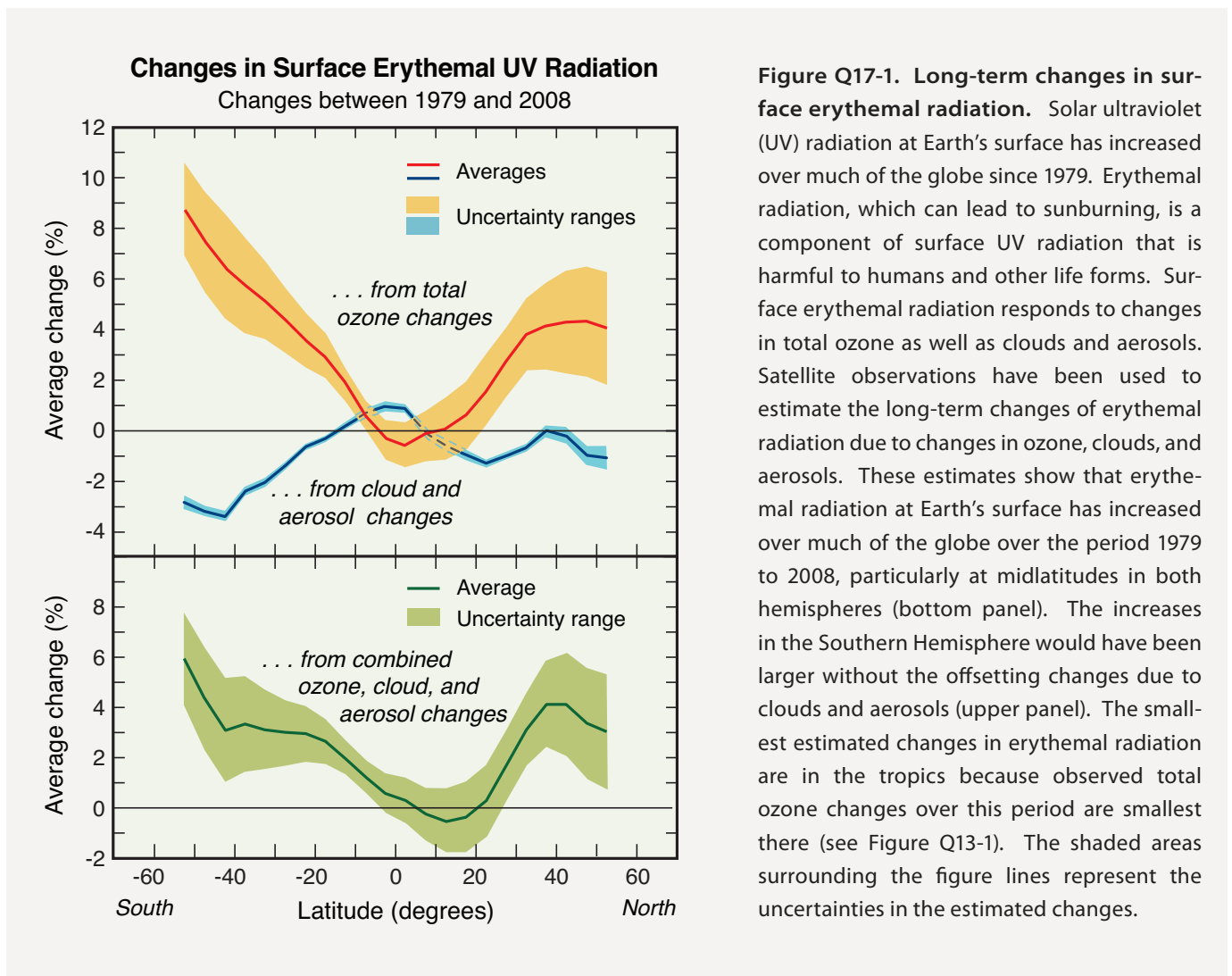

Figure Q17-1. Long-term changes in surface erythemal radiation. Solar ultraviolet (UV) radiation at Earth's surface has increased over much of the globe since 1979. Erythemal radiation, which can lead to sunburning, is a component of surface UV radiation that is harmful to humans and other life forms.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

skin cancer. Over the past decades, the incidence of several types of skin tumors has risen significantly among people of all skin types. Skin cancer in humans occurs long after exposure to sunburning UV. With current Montreal Protocol provisions, projections of additional skin cancer cases associated with ozone depletion are largest in the early to middle decades of the 21st century and represent a significant global health issue. An important human health benefit of UV-B radiation exposure is the production of vitamin D, which plays a significant role in bone metabolism and the immune system. Human exposure to solar UV-B radiation requires a careful balance to maintain adequate vitamin D levels while minimizing long-term risks of skin and eye disorders.

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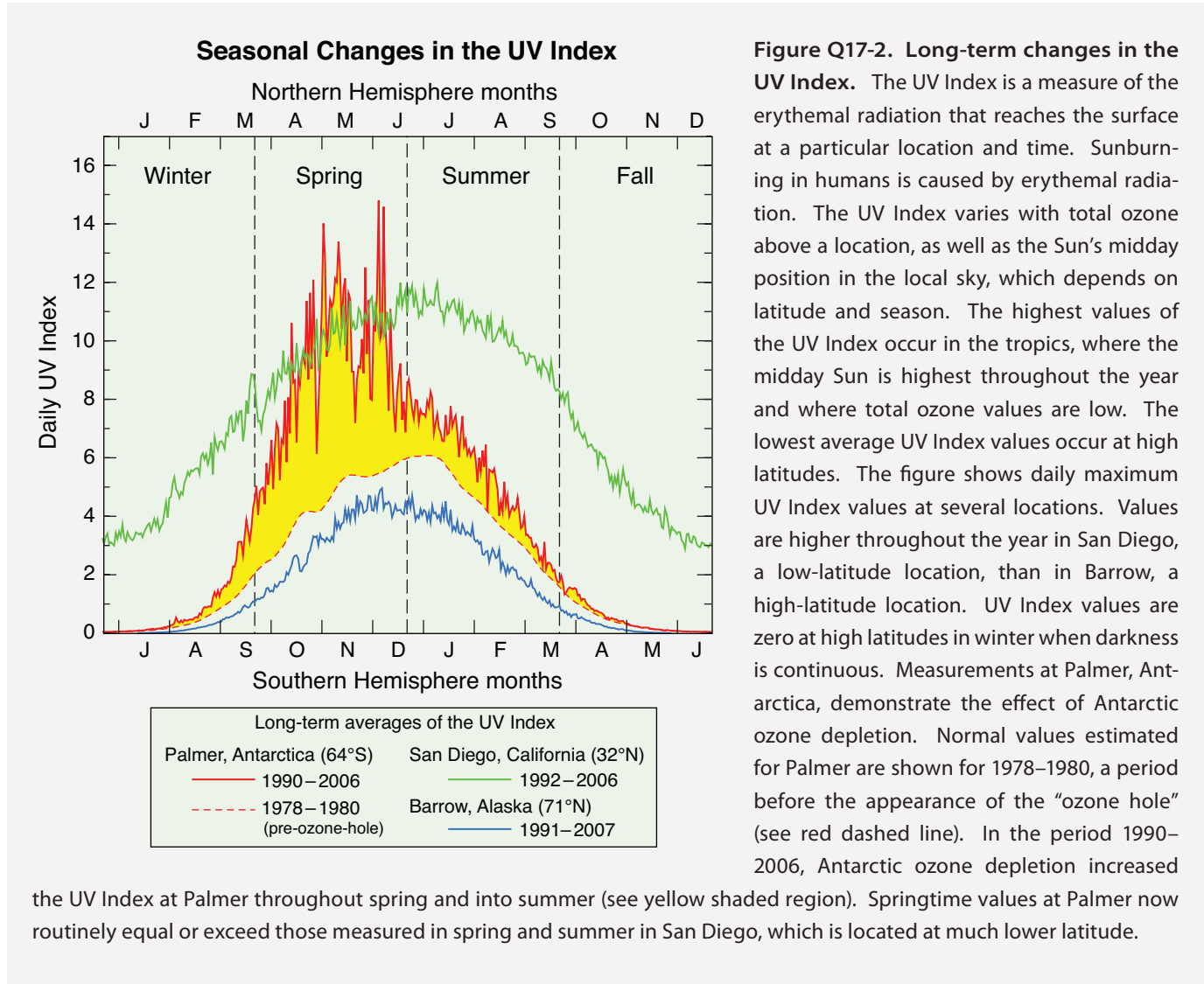
Figure Q17-2. Long-term changes in the UV Index. The UV Index is a measure of the erythemal radiation that reaches the surface at a particular location and time. Sunburning in humans is caused by erythemal radiation. The UV Index varies with total ozone above a location, as well as the Sun's midday position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

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. Changes in ozone and climate are directly linked because ozone absorbs solar radiation and is also a greenhouse gas. Stratospheric ozone depletion and increases in global tropospheric ozone that have occurred in recent decades have opposing contributions to climate change. The ozone-depletion contribution, while leading to surface cooling, is small compared with the contribution from all other greenhouse gas increases, which leads to surface warming. The total forcing from these other greenhouse gases is the principal cause of observed and projected climate change. Ozone depletion and climate change are indirectly linked because both ozone-depleting substances and their substitutes are greenhouse gases.

While stratospheric ozone depletion is not the principal cause of climate change, aspects of ozone depletion and climate change are closely linked. Both processes involve gases released to the atmosphere by human activities. The links are best understood by examining the contribution to climate change of the gases involved: ozone; ozone-depleting substances (ODSs) (or halogen source gases) and their substitutes; and other leading greenhouse gases.

Greenhouse gases and the radiative forcing of climate. The warming of the Earth by the Sun is enhanced by the presence of natural *greenhouse gases*, of which water vapor is an important example. Without this natural greenhouse effect, the Earth's surface would be much colder. Human activities since the preindustrial era have led to long-term increases in the atmospheric abundances of a number of long-lived and short-lived greenhouse gases. This group
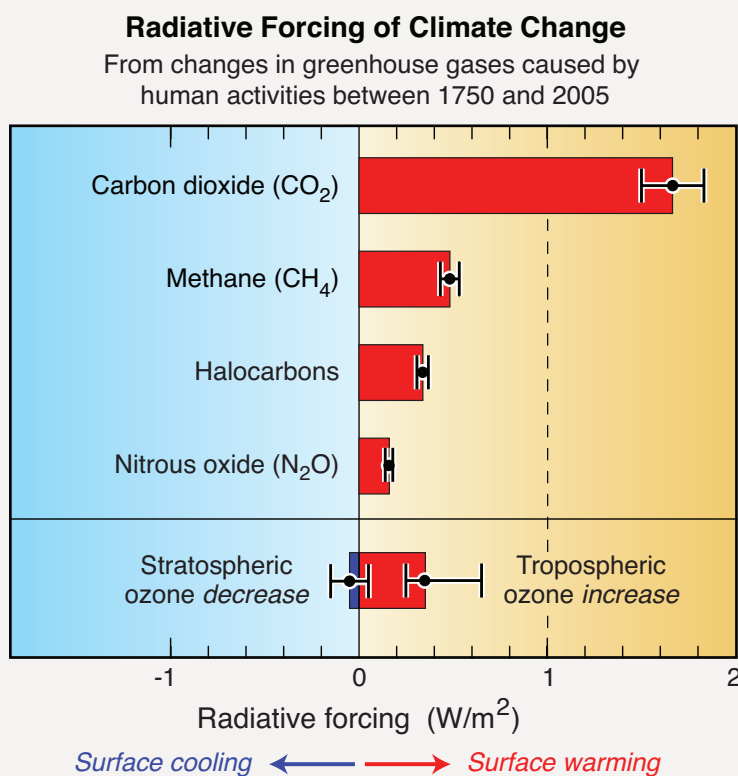

Radiative Forcing of Climate Change
From changes in greenhouse gases caused by human activities between 1750 and 2005

Radiative forcing (W/m^2)

Surface cooling ← → Surface warming

Figure Q18-1. Radiative forcing of greenhouse gases. Human activities since the start of the Industrial Era (around 1750) have caused increases in the abundances of several short-lived and long-lived gases, known as greenhouse gases, that all contribute to the radiative forcing of climate, also known as climate forcing. Radiative forcing is expressed in units of *watts per square meter (W/m^2)*. As shown in the figure, the largest forcings are those of carbon dioxide (CO_2), followed by methane (CH_4), tropospheric ozone, halocarbon gases, and nitrous oxide (N_2O). The black whiskers on each bar show uncertainties in the values. Tropospheric ozone increases result from the emission of pollutant gases and create a positive ozone forcing. Positive forcings lead 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. Halocarbons include all ODSs, their substitutes, and a few

other gases (see Figure Q18-2). In the coming decades, ODS abundances and stratospheric ozone depletion are expected to be reduced, along with their associated radiative forcings.
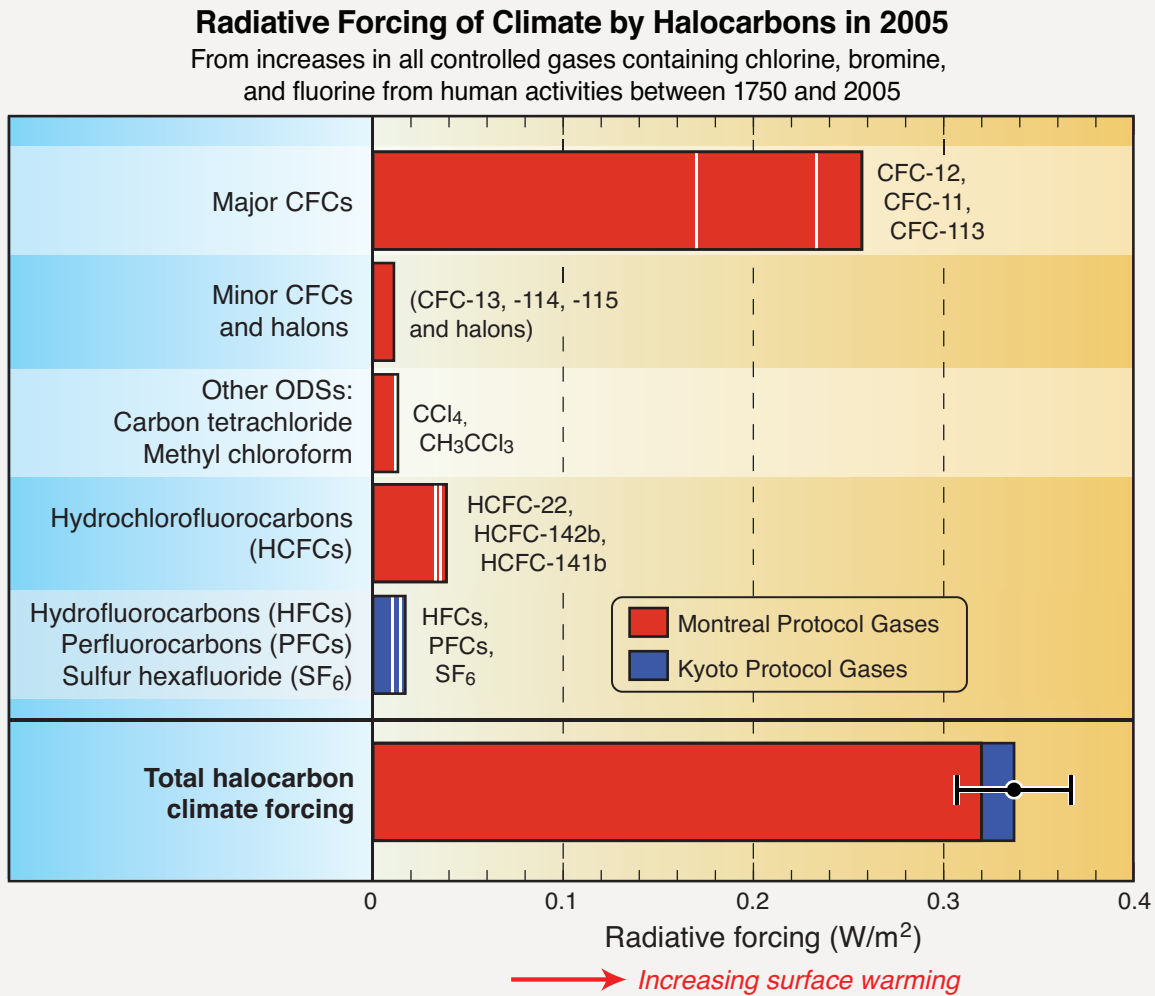
Figure Q18-2. Halocarbons and radiative forcing of climate change.   Halocarbon gases in the atmosphere represent an important contribution to the radiative forcing of climate between 2005 and the preindustrial era (see Figure Q18-1). Halocarbons are all gases containing chlorine, bromine, or fluorine atoms that are now controlled as ozone-depleting substances (ODSs) by the Montreal Protocol or as climate change gases by the Kyoto Protocol (see color shading). Shown in the figure are the separate contributions of each gas or group of gases, as estimated using atmospheric abundance histories and Global Warming Potentials (GWPs) (see Figure Q18-3). The gases listed in the right hand labels begin with the largest contribution in each group, except for CFC-13, CFC-114, CFC-115, and halons, which are shown as one total value. The individual forcing terms add together to form the bottom bar representing the total halocarbon forcing. The forcings of CFC-11 and CFC-12, the largest halocarbon contributions, are already decreasing and will continue to decrease as CFCs are gradually removed from the atmosphere (see Figure Q16-1). In contrast, the contributions of the intermediate-term ODS substitute gases, HCFCs, are projected to grow for another two decades before decreasing. The future contributions of the long-term ODS substitute gases, HFCs, are also expected to increase. In this case, the total contribution will depend strongly on which HFCs are used because the GWPs of individual HFCs vary widely (see Figure Q18-3).

includes stratospheric and tropospheric ozone, halocarbons, carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). ODSs and their substitutes make up a large fraction of the halocarbons in today's atmosphere. The natural abundances of these gases in Earth's atmosphere change the balance between incoming solar radiation and outgoing infrared radiation, warming the atmosphere and surface. Increases in the abundance of these gases from human activities cause more outgoing radiation to be absorbed, which further warms the atmosphere and surface. This change in Earth's radiative balance caused by human activities is called a *radiative forcing of climate* or, more simply, a *climate forcing*. The magnitude of this *energy* imbalance is usually evaluated at the top of the troposphere (tropopause) and is expressed using units of *watts per square meter* (W/m^2). The potential for climate change increases as this radiative forcing increases.

A summary of radiative forcings in 2005 resulting from the increases in the principal long-lived and short-lived greenhouse gases during 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. Climate forcings also lead to other changes, such as in precipitation patterns and extreme weather events. International climate assessments conclude that much of the observed surface warming and changes in other climate parameters over the last decades is due to increases in the abundance of carbon dioxide and other greenhouse gases caused by human activities.

Stratospheric and tropospheric ozone. Stratospheric and tropospheric ozone both absorb infrared radiation emitted by Earth's surface, trapping heat in the atmosphere. Stratospheric ozone also significantly absorbs solar radiation. As a result, increases or decreases in stratospheric or tropospheric ozone induce a climate forcing and, therefore, represent direct links between ozone and climate. In recent decades, global stratospheric ozone has *decreased* due to rising reactive chlorine and bromine amounts in the atmosphere, while global tropospheric ozone in the Industrial Era has *increased* due to pollution from human activities (see Q3). Stratospheric ozone depletion has caused a small *negative* radiative forcing since preindustrial times, while increases in tropospheric ozone have caused a *positive* radiative forcing (see Figure Q18-1). Summing the positive forcing due to tropospheric ozone increases with the smaller negative forcing from stratospheric ozone depletion yields a net positive radiative forcing. The large uncertainty in tropospheric ozone forcing reflects the difficulty in quantifying tropospheric ozone trends and in

modeling the complex production and loss processes that control its abundance. The negative radiative forcing from stratospheric ozone depletion will diminish in the coming decades as ODSs are gradually removed from the atmosphere.

Stratospheric ozone depletion cannot be a principal cause of present-day global climate change for two reasons: first, the climate forcing from ozone depletion is negative, which leads to surface cooling. Second, the total forcing from other long-lived and short-lived gases in Figure Q18-1 is positive and far larger. The total forcing from these other gases is the principal cause of observed and projected climate change.

Carbon dioxide, methane, and nitrous oxide. The accumulation of carbon dioxide during the Industrial Era represents the largest climate forcing related to human activities. Carbon dioxide concentrations continue to increase in the atmosphere primarily as the result of burning fossil fuels (coal, oil, and natural gas) for energy and transportation, as well as from cement manufacturing. The atmospheric abundance of carbon dioxide in 2005 was about 36% above what it was 260 years ago in preindustrial times. Carbon dioxide is considered a *long-lived* gas, since a significant fraction remains in the atmosphere 100–1000 years after emission.

Methane is a *short-lived* climate gas (atmospheric lifetime of about 10 years) that has both human and natural sources. Human sources include livestock, rice agriculture, and landfills. Natural sources include wetlands, oceans, and forests.

Nitrous oxide is a *long-lived* climate gas (atmospheric lifetime of about 110 years) that also has both human and natural sources. The largest human source is agricultural activities, especially related to fertilization. Microbial processes in soils that are part of natural biogeochemical cycles represent the largest natural source. In the stratosphere, nitrous oxide is the principal source of reactive nitrogen species, which participate in ozone destruction cycles (see Q2 and Q7).

Halocarbons. Halocarbons in the atmosphere contribute to both ozone depletion and climate change. As used here, halocarbons represent those gases containing chlorine, bromine, or fluorine atoms that are now controlled substances under the Montreal Protocol or the Kyoto Protocol. ODSs are the halocarbons controlled under the Montreal Protocol. HFC substitute gases, perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6) are controlled under the Kyoto Protocol. In 2005, the halocarbon contribution to climate forcing was 0.34 W/m^2, which is the third or fourth largest following carbon dioxide and methane (see Figure Q18-1). The contributions of individual halocarbon gases are highlighted in Figure Q18-2. Within the halocarbons, CFCs contribute the largest percentage (80%) to the 2005 climate

Evaluation of Selected Ozone-Depleting Substances and Substitute Gases
Relative importance of equal mass emissions for ozone depletion and climate change
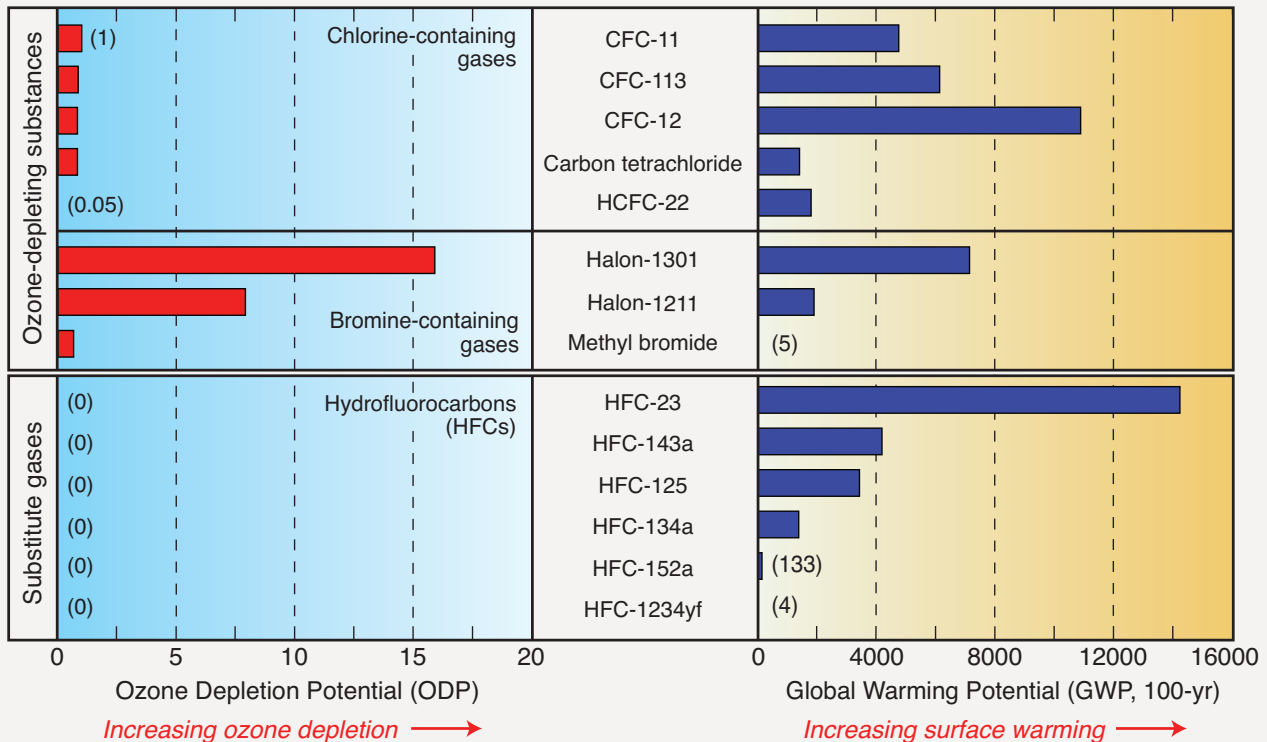

Figure Q18-3. ODPs and GWPs. ODSs and their substitutes can be compared via their Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) (see Table Q7-1). Larger ODPs or GWPs indicate greater potential for ozone depletion or climate warming, respectively, when a gas is emitted to the atmosphere. The ODP and GWP values are derived assuming an equal mass of each gas is emitted. The GWPs shown here are evaluated for a 100-year time interval after emission. The ODP of CFC-11 and the GWP of CO_2 are assigned reference values of 1.0. The CFCs, halons, and HCFCs are ozone-depleting substances (see Q7) while HFCs, used as ODS substitutes, do not destroy ozone (ODPs equal 0). The ODPs of the halons far exceed those of the CFCs. All ODSs and their substitutes shown here have a non-zero GWP, with values spanning the wide range of 4 to 14,000.

forcing. HCFCs, the intermediate-term ODS substitutes, make the next largest contribution (12%). The atmospheric abundance of HFCs, the longer-term ODS substitutes, contributes only 3% to the 2005 halocarbon climate forcing.

The large contribution of the CFCs is expected to gradually decrease following the projected decline in their atmospheric abundance (see Figure Q16-1). Based on their long lifetimes, CFCs will still make a significant contribution, and most likely the largest ODS contribution, to halocarbon climate forcing at the end of the 21st century. Halocarbons controlled under the Kyoto Protocol (HFCs, PFCs, and SF_6) represent about 5% of halocarbon climate forcing in 2005. With the projected growth of HFC production and consumption in

developing nations, this percentage contribution is expected to increase substantially in the coming decades.

Ozone Depletion Potentials and Global Warming Potentials. An important way of comparing the influence of individual halocarbons on ozone depletion and climate change is to use Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs). The ODP and GWP of a gas quantify its effectiveness in causing ozone depletion and climate forcing, respectively (see Table Q7-1). The principal halocarbon gases are contrasted with each other in Figure Q18-3. The ODP of CFC-11 and the GWP of carbon dioxide are assigned reference values of 1. The CFCs and carbon tetrachloride all have ODPs near 1, indicating comparable

effectiveness in causing ozone depletion. The principal halons have ODPs greater than 7, making them the most effective ozone-depleting substances. HFCs have ODPs of zero since they cause no ozone depletion (see Q7).

All halocarbons have non-zero GWPs and, therefore, contribute to climate forcing. The GWP does not correspond strongly with the ODP of a gas because these quantities depend on different chemical and physical properties. For example, while HFC-134a does not destroy ozone (ODP equal 0), each gram emitted is 1,370 times more effective than a gram of carbon dioxide in causing climate forcing. The future selection of specific HFCs as ODS substitutes or for use in new global applications will have important consequences for climate forcing. When these HFCs are eventually released to the atmosphere, the contribution to climate forcing will depend on their GWPs, which could vary over a wide range (4 to 14,000).

Montreal Protocol regulations have led to reductions in CFC emissions and increases in HCFC emissions (see Q16). As a result of these actions, the total radiative forcing from ODSs is slowly decreasing (see Q19). Overall halocarbon radiative forcing, however, is slowly increasing because of growing contributions from HFCs, PFCs, and SF_6. It is important to note that, despite having a GWP that is small in comparison to many other halocarbons and other greenhouse gases, carbon dioxide is the most important greenhouse gas related to human activities because its emissions are large and its atmospheric abundance is far greater than the abundances of other emitted gases.

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 increase the extent and severity of winter polar ozone depletion. While the Earth's surface is expected to continue warming in response to the net positive radiative forcing from greenhouse gas increases, the stratosphere is expected to continue cooling. A cooler stratosphere would extend the time period over which polar stratospheric clouds (PSCs) are present in winter and early spring and, as a result, might increase polar ozone depletion. In the upper stratosphere at altitudes above PSC formation regions, a cooler stratosphere is expected to increase ozone amounts because lower temperatures decrease the effectiveness of ozone loss reactions. Furthermore, climate change may alter the strength of the stratospheric circulation and with it the distribution of ozone in the stratosphere (see Q20).

Q19

Have reductions of ozone-depleting substances under the Montreal Protocol also protected Earth's climate?

Yes. All ozone-depleting substances are also greenhouse gases that contribute to climate forcing when they accumulate in the atmosphere. Montreal Protocol controls have led to a substantial reduction in the emissions of ozone-depleting substances (ODSs) over the last two decades. These reductions have provided the added benefit of reducing the human contribution to climate change while protecting the ozone layer. Without Montreal Protocol controls, the climate forcing contribution from annual ODS emissions could now be 10-fold larger than its present value, which would be a significant fraction of the climate forcing from current carbon dioxide (CO_2) emissions.

The success of the Montreal Protocol in controlling the production and consumption of ozone-depleting substances (ODSs) has protected the ozone layer (see Q15). The resulting reductions in atmospheric abundances of ODSs also reduced the human influence on climate because all ODSs are greenhouse gases (see Q18). By protecting both ozone and climate, the Montreal Protocol has provided a *dual benefit* to society and Earth's ecosystems. In the following, the dual benefit of the Montreal Protocol is highlighted by considering long-term baseline and world-avoided scenarios of ODS emissions that use Ozone Depletion Potentials (ODPs), Global Warming Potentials (GWPs), equivalent effective stratospheric chlorine (EESC), and the radiative forcing of climate change.

Baseline ODS scenarios. The baseline scenarios of past and future ODS emissions presented here include the emissions of principal halogen source gases. They are constructed from (1) historical annual production and consumption of individual ODSs reported to the Montreal Protocol, (2) projected annual production and consumption of ODSs
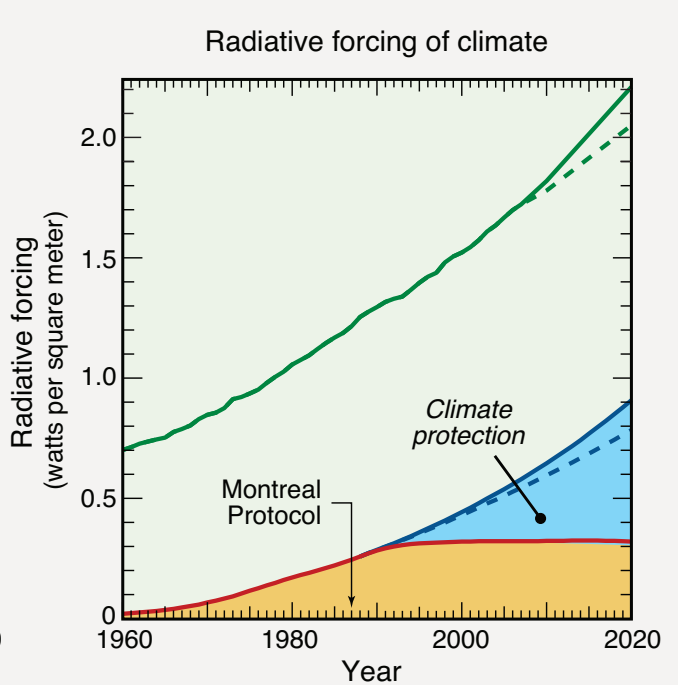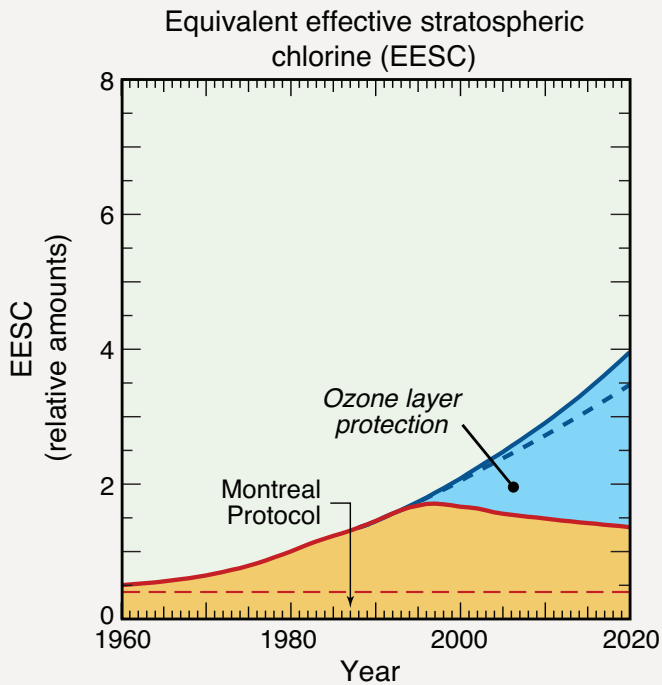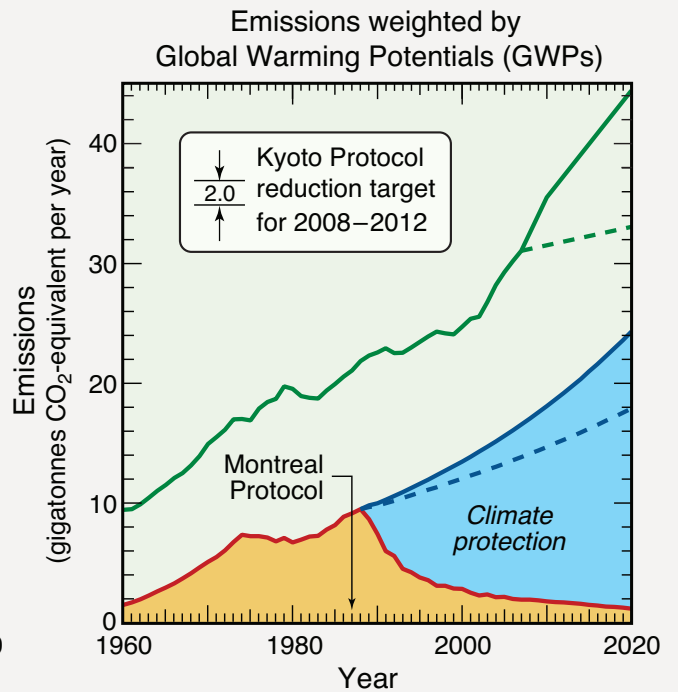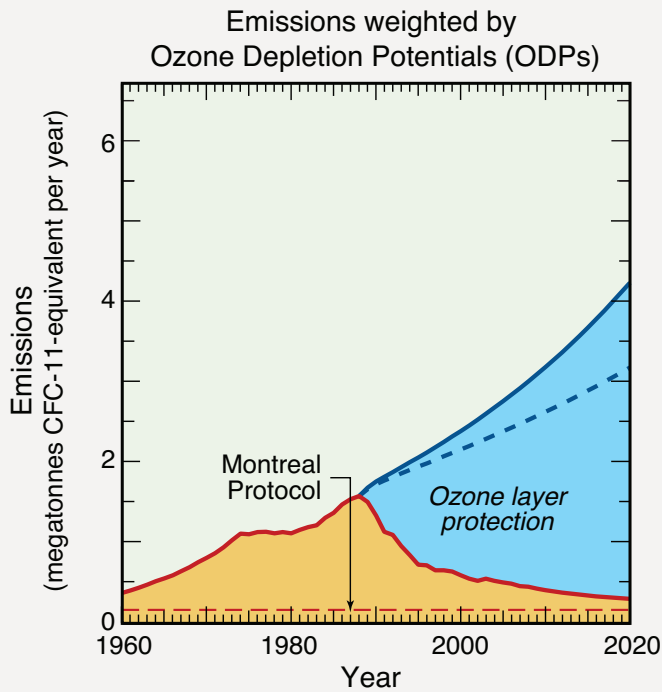
for future years based on provisions of the Protocol, (3) estimates of ODS banks, (4) atmospheric observations of ODSs and some naturally occurring halogen source gases, such as methyl chloride (CH_3Cl), and (5) weighting factors related to ozone depletion and climate change.

In forming two of the baseline scenarios shown in Figure Q19-1 (upper panels), the emissions of each gas are added together after being *weighted* (multiplied) by the Ozone Depletion Potential (ODP) or the Global Warming Potential (GWP) of the respective gas (see Q18 and Table Q7-1). In the ODP-weighted scenario, the emission sum is expressed as *CFC-11-equivalent* emissions because CFC-11 is the reference gas with an assigned ODP value of 1. For example, in the sum, 1 kg of halon-1211 emissions is added as 7.9 kg of CFC-11-equivalent emissions because the ODP of halon-1211 is 7.9. Similarly, the GWP-weighted sum is expressed as CO_2-*equivalent* emissions because CO_2 is the reference gas with an assigned GWP of 1. For example, in the sum, 1 kg of carbon tetrachloride emissions is added as 1400 kg of CO_2-equivalent emissions

Figure Q19-1. Montreal Protocol protection of ozone and climate. The provisions of the Montreal Protocol have substantially reduced ozone-depleting substances (ODSs) in the atmosphere. This has protected the ozone layer and also reduced the potential for climate change because ODSs are greenhouse gases. The scenarios and comparisons shown here demonstrate this dual benefit of the Montreal Protocol. Baseline scenarios for ODS emissions include all principal gases weighted by their Ozone Depletion Potentials (ODPs) or Global Warming Potentials (GWPs) (top panels). With these weightings, emissions are expressed as CFC-11-equivalent or CO_2-equivalent mass per year. The lower panels show EESC and radiative forcing of climate as derived from the respective ODP- and GWP-weighted scenarios. The world-avoided emission scenarios assume ODS emission growth of 2 or 3% per year beyond 1987 abundances. Shown for reference are the emissions and radiative forcing of CO_2, and the emissions reduction target of the first commitment period of the Kyoto Protocol. The contributions of natural halogen source gases are shown in the ODP-weighted and EESC scenarios (red dashed lines) and are negligible in the GWP-weighted and radiative forcing scenarios. The magnitude of the dual benefit has increased since about 1987 as shown by differences between the world-avoided and baseline scenarios (blue shaded regions in each panel). For completeness, these differences can be adjusted by offsets due to additional ozone depletion and HFC emissions (see text). (A megatonne = 1 billion (10^9) kilograms. A gigatonne = 1 trillion (10^{12}) kilograms.)

The Montreal Protocol Protection of Ozone and Climate
From global emissions of all ozone-depleting substances (ODSs) and CO_2

Emissions weighted by Ozone Depletion Potentials (ODPs)

Emissions weighted by Global Warming Potentials (GWPs)

Equivalent effective stratospheric chlorine (EESC)

Radiative forcing of climate

Legend:
- Baseline ODS scenarios
- Natural halogen sources
- World-avoided scenarios
- 3% / 2% Annual growth from 1987 without the Montreal Protocol
- CO_2 scenarios
- Lower limits in CO_2 scenarios

because the GWP of carbon tetrachloride is 1400.

World-avoided ODS scenarios. The baseline scenario of ODS emissions can be contrasted with a scenario of ODS emissions that the world has *avoided* by agreeing to the Montreal Protocol (see Figure Q19-1). These world-avoided emissions are estimated by assuming that emissions of ODSs in the baseline scenario increase beyond 1987 values with a 2 or 3% annual growth rate. These growth rates are consistent with the strong market for ODSs in the late 1980s that included a wide variety of current and potential applications and that had potential for substantial new growth in developing countries.

CO$_2$ emission scenarios. Long-term CO$_2$ emission scenarios are also shown for comparison, as derived from past and projected CO$_2$ emissions, because CO$_2$ is the principal greenhouse gas related to human activities. The projected CO$_2$ emissions have high and low scenarios that are derived using different basic assumptions about future economies, technical progress, and societal decisions.

ODP-weighted emissions scenarios. The ODP-weighted emissions in the ODS baseline scenario are a measure of the overall threat to stratospheric ozone from ODSs (see Figure Q19-1, upper left panel). When ODP-weighted emissions increase (decrease) in a given year, more (less) ozone will be destroyed in future years. ODP-weighted emissions increased substantially in the baseline scenario between 1960 and 1987, the year the Montreal Protocol was signed (see Figure Q19-1 and Q0-1). After 1987, ODP-weighted emissions began a long and steady decline to present-day values. The decline in emissions is expected to continue, causing the atmospheric abundances of individual ODSs to decrease (see Figure Q16-1). The reduction in ODP-weighted emissions from the 1987 value is a conservative measure of the annual emissions avoided by the Montreal Protocol since 1987 and, hence, of the success of the Montreal Protocol in protecting the ozone layer.

Annual ODP-weighted emissions in the world-avoided scenario are about double the 1987 values by 2020. The annual differences between the world-avoided emissions and the baseline scenario (blue shaded region in Figure Q19-1) provide reasonable upper-limits to the ODP-weighted emissions avoided by the Montreal Protocol each year since 1987.

GWP-weighted emissions scenarios. The GWP-weighted emissions in the ODS baseline scenario are a measure of the overall threat to climate from ODSs (see Figure Q19-1, upper right panel). As ODS emissions accumulate in the atmosphere, their climate forcing contribution increases. The long-term changes in the GWP-weighted scenario are

very similar to those in the ODP-weighted scenario. Both show an increase before 1987 and decrease afterwards. The similarity follows from the predominant role that CFC-11 and CFC-12 emissions play in ozone depletion and climate forcing from ODSs. The reduction in GWP-weighted emissions since 1987 is a conservative measure of the substantial success of the Montreal Protocol in reducing the potential for climate change from human activities. The annual differences since 1987 between the world-avoided emissions and the baseline scenario (blue shaded region in Figure Q19-1) provide reasonable upper-limits to the GWP-weighted emissions avoided by the Montreal Protocol each year since 1987.

The climate protection calculated using differences between world-avoided emissions and the baseline scenario has two offsetting effects. The first is the additional ozone depletion that would be caused by world-avoided ODS emissions. Ozone depletion offsets ODS climate forcing because a greenhouse gas (ozone) is being removed from the atmosphere in response to ODS emissions (see Q18). The second effect is the increase in emissions of HFC substitute gases that occurred in response to ODS reductions from Montreal Protocol controls. More HFCs in the atmosphere offset the gain in climate protection from ODS reductions because HFCs are also greenhouse gases (see Q18).

The combined magnitude of these offsets in 2010, for example, is about 30% of the difference between the baseline and world-avoided scenarios. The resulting net GWP-weighted emission reduction in 2010 is about 9.7–12.5 gigatonnes CO$_2$-equivalent per year. In contrast, the annual emissions reduction target adopted by the Kyoto Protocol during its first commitment period (2008–2012) is estimated as 2 gigatonnes CO$_2$-equivalent per year (see Figure Q19-1). The reductions are expected to result from controlling the Kyoto Protocol basket of gases that includes HFCs and does not include ODSs (see Q18). As a result, the upper limit for the net reduction in annual GWP-weighted emissions achieved by the Montreal Protocol in 2010 is *5- to 6-fold larger* than the Kyoto Protocol target.

Annual GWP-weighted emissions of ODSs were a large percentage (about 20–40%) of CO$_2$-baseline emissions between 1960 and 1989 (see Figure Q19-1). Thereafter, this percentage has steadily decreased and is projected to reach 2–3% by 2020. This projection stands in sharp contrast to the world-avoided scenario, in which the percentage increases to 40–75% of CO$_2$-baseline emissions by 2020.

EESC scenarios. The EESC scenario in Figure Q19-1 (lower left panel) provides a measure of the year-to-year potential of the atmospheric abundances of ODSs to destroy

stratospheric ozone. Changes in historical and projected atmospheric *emissions* of ODSs cause changes in their atmospheric *abundances*. The derivation of EESC from ODS atmospheric abundances is discussed in Q16 and similar EESC baseline scenarios are shown in Figures Q14-1, Q15-1, and Q16-1 for different time intervals. An *increase* in ODP-weighted emissions always leads to some increase in EESC in the years following the emissions. When ODS-weighted emissions *decreased* after 1987, EESC did not proportionally decrease because of the long atmospheric lifetimes of the principal ODSs. In Figure Q19-1, for example, EESC reached its peak nearly a decade after the peak in ODP-weighted emissions, and by 2010 the decrease in EESC from its peak value was only about 10%, compared to the 70% decrease in ODP-weighted emissions achieved by 2010.

Radiative forcing of climate change scenarios. The radiative forcing derived for the ODS baseline scenario in Figure Q19-1 (lower right panel) provides a measure of the year-to-year contribution to climate forcing from atmospheric ODS abundances. The radiative forcing of an ODS is proportional to its radiative efficiency and the net increase in its atmospheric abundance during the Industrial Era. Increases in abundance up to the present are derived from atmospheric observations. Future abundances rely on projected emissions and atmospheric lifetimes of each gas. In Figure Q19-1, radiative forcing due to ODSs increases smoothly from 1960 onward, peaks in 2003 and decreases very gradually in subsequent years. Radiative forcing responds to ODS emission reductions in a manner similar to EESC, with the current slow decline attributable to the two principal contributing gases, CFC-11 and CFC-12, and their long atmospheric lifetimes (45–100 years).

The differences in ODS climate forcing between the world-avoided and baseline scenarios are offset by additional ozone depletion and HFC emissions in a manner similar to that noted above for differences in GWP-weighted emissions. After accounting for these two offsets, the climate forcing due to ODSs in the world-avoided scenario is approximately 70% higher than that in the baseline scenario in 2010 and approximately 30% of that due to CO_2.

The considerable contributions that ODSs could have made to climate forcing, if not controlled by the Montreal Proto-col, attests to their potency as greenhouse gases. ODSs had negligible atmospheric abundances 50–60 years ago and, as a group, represent chlorine amounts that currently are about 100,000 times less abundant in the atmosphere than CO_2.

The future. Fewer control options are available to increase the dual benefit of the Montreal Protocol beyond 2020 because the most effective and abundant ODSs have already been phased out under Montreal Protocol provisions (see Q16). The most recent Montreal Protocol action increased ozone and climate protection by accelerating the phase-out of HCFCs (Montreal in 2007) (see Q15). This provision is expected to reduce total GWP-weighted emissions of HCFCs by about 50% between 2010 and 2050, corresponding to about 18 gigatonnes of CO_2-equivalent emissions. The accelerated HCFC phase-out protects ozone by advancing the date that EESC returns to 1980 values by 4–5 years.

Ozone and climate protection could be further enhanced with Montreal Protocol provisions that increase the effectiveness of capturing and destroying ODSs contained in banks, namely, those ODSs currently being used in refrigeration, air conditioning, and fire protection equipment, or stockpiled for servicing long-term applications.

Future projections suggest that growth in HFC production and consumption could result in GWP-weighted emissions of up to 8.8 gigatonnes CO_2-equivalent per year by 2050, primarily in developing nations. The 2050 value is comparable to the peak in GWP-weighted ODS emissions in 1988 (see Figure Q19-1). The estimate assumes that HFC application demand would be met using the same suite of HFCs currently used in developed countries. If future HFC demand is met instead with lower-GWP substances, the 2050 estimate would be substantially reduced. International proposals have been put forth for the Montreal Protocol to expand its production and consumption controls to include HFCs. The expansion would occur in collaboration with the Kyoto Protocol, which currently includes HFCs in its basket of gases. If the proposals are successful, the Montreal Protocol would have the opportunity to guide the transition from ODSs to HFCs in a manner that would optimize the protection of the ozone layer and climate while minimizing the burden on participating nations.

Q20

How is ozone expected to change in the coming decades?

Substantial recovery of the ozone layer from the effects of ozone-depleting substances (ODSs) is expected near the middle of the 21st century, assuming global compliance with the Montreal Protocol. Recovery will occur as ODSs and reactive halogen gases in the stratosphere decrease in the coming decades. In addition to responding to ODSs, future ozone amounts will increasingly be influenced by expected changes in climate. The resulting changes in stratospheric ozone will depend strongly on the geographic region. During the long recovery period, large volcanic eruptions could temporarily reduce global ozone amounts for several years.

Substantial recovery from the depletion of global and polar ozone caused by ODSs is expected in the later decades of this century. The recovery follows on the success of the Montreal Protocol in reducing the global production and consumption of ODSs. Now, the atmospheric abundances of most major ODSs and the associated values of equivalent effective stratospheric chlorine (EESC) are in decline (see Q16). In contrast to the diminishing role of ODSs, changes in climate are expected to have an increasing influence on future ozone. Important aspects are the projected growth of greenhouse gas abundances and the resulting changes in stratospheric temperatures and the stratospheric circulation. Chemistry-climate models can be used to project how ozone is expected to respond to changes in ODSs and climate in different geographical regions during the recovery period. Global events, such as major volcanic eruptions and geoengineering actions, may also influence future total ozone amounts.

Using chemistry-climate models. Projections of total ozone presented here are based on the results from a group of chemistry-climate models that take into account the influences of changes in ODSs and climate. These models show how changes in ozone are expected to vary across global regions by evaluating the complex interaction of the processes that control ozone and climate involving radiation, chemistry, and transport. Required model inputs include, for example, historical and projected emissions of ODSs, carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), and changes in sea surface temperatures. The results from chemistry-climate model simulations are used to identify aspects of the models that are particularly important for future ozone abundances. For example, model projections for the coming decades show a strengthening in the atmospheric circulation that brings air to the stratosphere in the tropics, moves air poleward into both hemispheres, and then returns it to the troposphere at middle to high latitudes. These circu-

lation changes will significantly alter the global distribution of ozone and the atmospheric lifetimes of ODSs and other long-lived gases.

Simulating recent ozone changes. Comparisons of model results with observations help confirm the causes of ozone depletion and increase confidence in model projections of future ozone amounts. Two important measures of ozone, global total ozone and minimum total ozone values in the Antarctic, are compared to the group of chemistry-climate model simulations in Figure Q20-1. Both ozone measures show substantial depletion since 1980. The average model value follows the observed decline in both ozone measures, indicating that the main processes involved in ozone depletion are reasonably well represented by the models. Some differences between the simulations and observations can be explained by unusual meteorological conditions, volcanic eruptions, changes in solar activity, or other natural influences, which are not all fully accounted for in the various models used here. In Figure Q20-1, global total ozone has increased in the last 20 years, while Antarctic minimum ozone values have been relatively constant. The global total ozone increases cannot be attributed solely to reductions in ODSs that began in the 1990s, because total ozone has also recovered from additional depletion caused by the 1991 Mt. Pinatubo eruption (see Q14).

Equivalent stratospheric chlorine (ESC) projections. Equivalent stratospheric chlorine (ESC) values are also projected in chemistry-climate models to represent how the potential for reactive halogen gases (see Q8) to destroy ozone varies over time. ESC is similar to equivalent effective stratospheric chlorine (EESC) (see Q16) in that both represent a weighted sum of reactive chlorine and bromine gases in the stratosphere. The weighting in each accounts for the greater effectiveness of bromine atoms in destroying ozone. ESC can be calculated more precisely and comprehensively

than EESC because the chemistry-climate models can derive ESC as a function of altitude, latitude, longitude, and time. The ESC calculations are based on the history and projections of ODS surface abundances and the chemical and transport processes that control (1) the conversion of ODSs to reactive halogen gases, (2) the distribution of reactive halogen gases in the global stratosphere and (3) their ultimate removal from the stratosphere.

The long-term changes in ESC in the global and regional analyses shown in Figure Q20-2 are highly similar. In all regions, changes in ESC from 1960 values increase smoothly with time, reach a peak near the end of the 20th century, and decrease gradually until the end of the 21st century. Values at the end of the 21st century are approaching those in 1960, indicating that ODSs are largely removed from the stratosphere by that time. ESC returns to 1980 values several decades sooner than to 1960 values because of the slow rate of decline.

Peak ESC values around the year 2000 are highest in polar regions and lowest in the tropics. In the tropics, stratospheric air has only recently been transported from the troposphere, with the result that only a small fraction of ODSs has undergone conversion to reactive halogen gases (see Q8). In polar regions, the fraction is much larger because stratospheric air requires several years on average to journey from its entry point in the tropics to the polar lower stratosphere. During this time, a much larger fraction of ODSs undergoes conversion to reactive halogen gases.

Long-term total ozone projections.   Total ozone changes derived from chemistry-climate models, as referenced to 1960 values, are shown in Figure Q20-2. The range of values from the group of models is included in the figure as one measure of the uncertainty in the model projections. Total ozone changes in the different regions are described as follows:

▶ **Antarctic.** Total ozone changes are largest in the Antarctic region in springtime (October). Chemistry-climate models show that ODSs are the predominant factor in Antarctic ozone depletion in the past and in the coming decades. Changes in climate parameters have a smaller role. As a result, total ozone changes closely *mirror* changes in ESC: as ESC increases, ozone proportionately decreases; as ESC decreases, ozone proportionately increases. Antarctic total ozone is projected to return to 1980 levels after midcentury and later than in any other region. Meteorological variability in polar regions in late
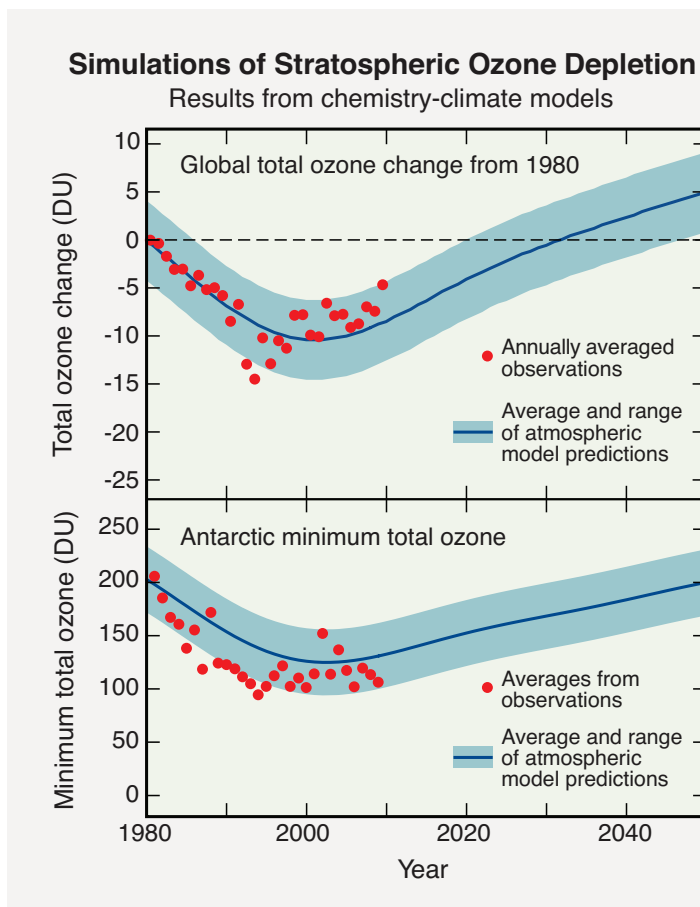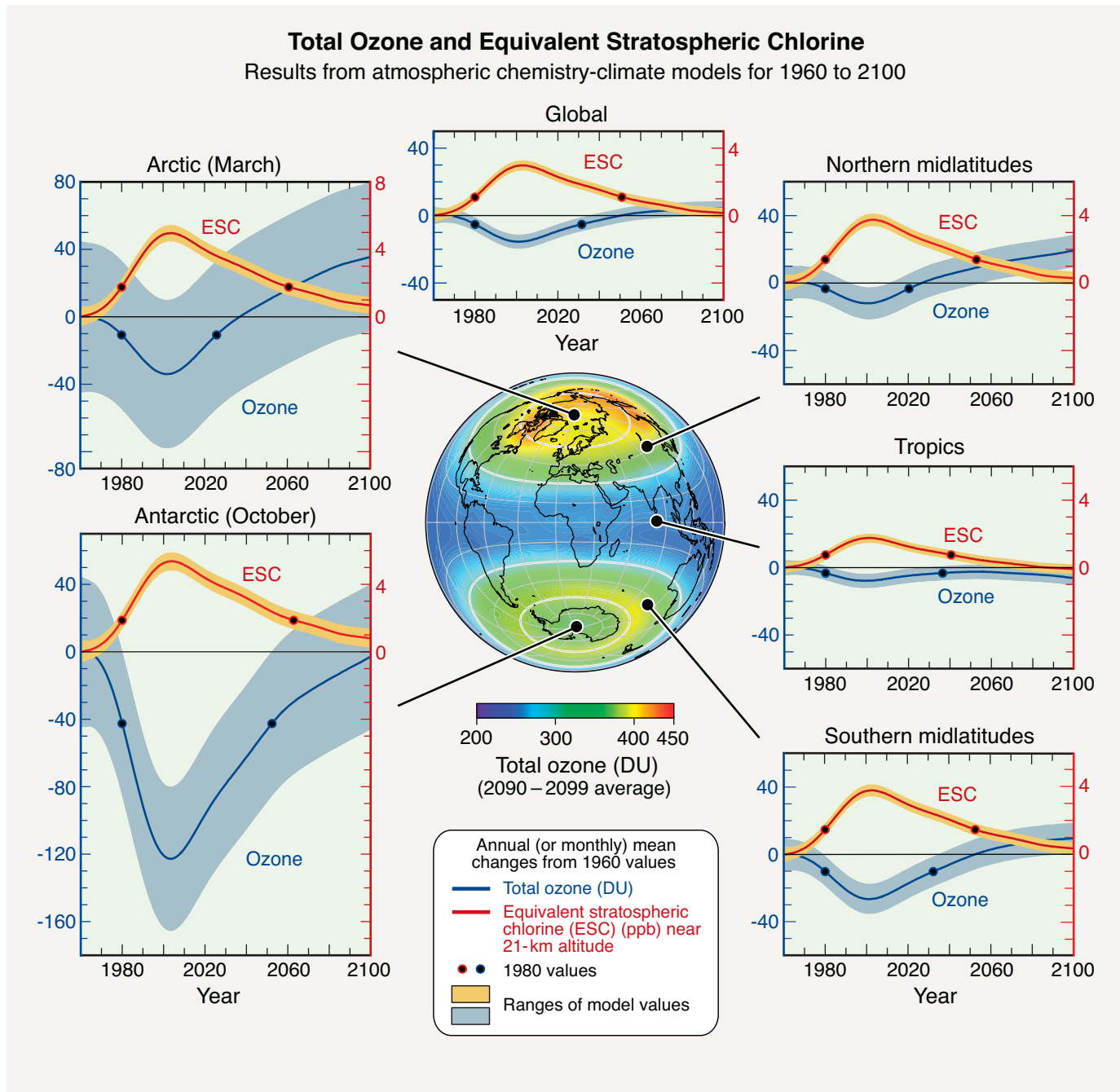

Simulations of Stratospheric Ozone Depletion
Results from chemistry-climate models

Figure Q20-1. Simulations of ozone depletion. Chemistry-climate models of the atmosphere that account for changes in ozone-depleting substances (ODSs) and climate parameters are widely used to assess past ozone changes and project future ozone. Agreement in comparisons of model results with observations increases confidence in the model projections and our understanding of the processes leading to ozone depletion. Observed values of global total ozone (top panel) and minimum total ozone values over Antarctica (bottom panel) decreased beginning in the early 1980s (red points). Ozone is no longer decreasing in either region. The observations lie mostly within the range of projections derived from a group of chemistry-climate models (blue shading). Differences between models and observations can occur due to unusual meteorological conditions, volcanic eruptions, changes in solar activity, or other influences, which are not fully accounted for in the different models. As ODS abundances decrease in the 21st century, chemistry-climate models project global total ozone to increase steadily and exceed 1980 values, and Antarctic minimum ozone to return to 1980 values.

Total Ozone and Equivalent Stratospheric Chlorine
Results from atmospheric chemistry-climate models for 1960 to 2100

winter/early spring when ozone depletion occurs causes a large range in the model projections.

▶ **Arctic.** Total ozone changes in the Arctic region in springtime (March) are considerably smaller than in the Antarctic. In contrast to the Antarctic, ozone changes do not closely mirror changes in ESC. After midcentury, Arctic total ozone increases to values above those that would be expected from ESC reductions alone because of the strengthening of the atmospheric circulation and the enhanced stratospheric cooling associated with increases

in CO_2. By 2100 Arctic total ozone is projected to be well above both 1960 and 1980 values. The large range in projections compared to other nonpolar regions is due to greater meteorological variability as noted for the Antarctic. Arctic total ozone is projected to return to 1980 levels between 2020 and 2035, which is two to three decades before ESC returns to 1980 levels, and to continue to increase until the end of the century.

▶ **Northern and southern midlatitudes.** The annual averages of total ozone changes in midlatitudes are much

Figure Q20-2. Long-term changes in ozone and equivalent stratospheric chlorine (ESC). Chemistry-climate models are used to make projections of total ozone amounts that account for the effects of ozone-depleting substances (ODSs) and climate change. Regional and global projections are shown for total ozone and ESC for the period 1960–2100, referenced to 1960 values. The globe in the center shows average total ozone projections for the last decade of the 21st century. Total ozone depletion increased after 1960 as ESC values steadily increased throughout the stratosphere. ESC values have peaked and are now in a slow decline. All the projections show maximum total ozone depletion around 2000, coincident with the highest abundances of ESC. Thereafter, total ozone increases, except in the tropics, as ESC slowly declines. In all the projections except the Antarctic and the tropics, total ozone returns to 1960 values by midcentury, which is earlier than expected from the decrease in ESC alone. The earlier returns are attributable to climate change, which influences total ozone through changes in stratospheric transport and temperatures. In the tropics, in contrast, climate change causes total ozone to remain below 1960 values throughout the century. In the Antarctic, the effect of climate change is smaller than in other regions. As a result, Antarctic total ozone in springtime mirrors the changes in ESC, with both closely approaching 1960 values at century's end. The dots on each curve mark the occurrences of 1980 values of total ozone and ESC. Note that the equal vertical scales in each panel allow direct comparisons of ozone and ESC changes between regions.

smaller than the springtime losses in polar regions. Both midlatitude regions resemble the Arctic with total ozone returning to 1960 and 1980 values much sooner than ESC. In the northern midlatitudes, the models predict a return to 1960 values in 2030 whereas ESC requires the full century to return close to 1960 values. Total ozone in southern midlatitudes changes in a manner similar to the northern midlatitudes. Differences are that in southern midlatitudes the 1960 return date for total ozone is somewhat later (2055) and the maximum ozone depletion observed near 2000 is greater. Both aspects reflect the influence of Antarctic stratospheric air, depleted in ozone, being routinely transported to southern midlatitudes in spring (see Q11). The more rapid return of total ozone in both regions compared with ESC derives again from the influence of climate-induced changes in transport and upper stratospheric temperatures in the model projections. The model range is significantly less in midlatitude annual averages than in the polar springtime averages. After returning to either 1960 or 1980 values, total ozone continues to increase in both hemispheres and significantly exceeds those values by 2100.

► **Tropics.** Total ozone changes in the tropics are smaller than in any other region. Ozone is less sensitive to ESC in the tropical stratosphere because of the dominant roles of production and transport in controlling ozone. In contrast to other regions, chemistry-climate models project total ozone to remain below 1960 values throughout the 21st century. Total ozone gradually returns to 1980 values in 2040, peaks around 2060 and decreases again until the end of the century. The different total ozone behavior in the tropics

is due to the changing balance between ozone increases in the upper stratosphere and decreases in the lower stratosphere. The ozone increases in the upper stratosphere occur from declining ODS abundances and decreases in temperatures caused by increasing greenhouse gases, primarily CO_2. In the lower stratosphere, ozone is reduced because the strengthening of the stratospheric circulation reduces the time for ozone production before air leaves the tropics. These circulation changes also influence the Arctic and midlatitude regions as noted above.

► **The globe.** The annual averages of global total ozone are projected to return to 1960 levels around the middle of the century (2040 to 2080) while ESC returns to 1960 values near century's end. The comparable return dates for 1980 values are substantially earlier. Chemistry-climate model analysis suggests that this early return of total ozone is primarily a result of upper stratosphere cooling and a strengthened circulation as noted for midlatitude ozone. The larger total ozone changes shown for polar regions in springtime do not significantly influence global total ozone values because these values are annual averages and polar regions are a small geographical fraction of the globe.

Future ultraviolet radiation. Projections of long-term changes in total ozone can be used to estimate long-term changes in solar ultraviolet radiation reaching Earth's surface (see Q17). The UV-B component of ultraviolet radiation increases as total ozone decreases. Based on the global total ozone projections, clear-sky UV-B radiation is expected to *decrease* below 1960 values by the end of the century because ozone is above 1960 values in the later decades. The latitude

regions likely to have some *increase* in ultraviolet radiation are the Antarctic and the tropics, where total ozone remains lower than 1960 values until the end of the century. Large increases or decreases in surface erythemal radiation away from 1960 values are expected to lead to adverse effects on human and ecosystem health.

Volcanoes and geoengineering. Other factors not included in chemistry-climate models can potentially affect future total ozone amounts. Explosive volcanic eruptions have temporarily reduced global total ozone in the past (see Q14). Similar eruptions, especially in the early decades of this century when ESC values are highest, are also expected to reduce total ozone for a few years. Volcanic eruptions are an additional source of uncertainty not included in the ozone projections in Figure Q20-2.

Several *geoengineering* methods have been proposed to reduce climate forcing from human activities. A widely discussed proposal is the enhancement of sulfate aerosols in the stratosphere from direct injections of sulfur or sulfuric acid. The expected response is a cooling of the climate system from increased aerosol scattering of sunlight, similar to that observed after some explosive volcanic eruptions. The required injections, if sustained over many years, are likely to have unintended consequences such as reductions in total ozone amounts and changes in stratospheric temperatures and circulation.