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

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

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

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

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

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



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

#### **Ozone Destruction Cycles in Polar Regions**

#### **Ozone Destruction Cycles in Polar Regions**

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

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

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

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

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

Other reactions. Global ozone abundances are controlled by many reactions that both produce and destroy ozone (see Q2). Chlorine and bromine catalytic reactions are but one group of ozone destruction reactions. Reactive hydrogen and reactive nitrogen gases, for example, are involved in other catalytic ozone-destruction cycles that also occur in the stratosphere. These reactions occur naturally in the stratosphere and their importance has not been as strongly influenced by human activities as have reactions involving halogens. The sources of reactive hydrogen and nitrogen gases are the naturally occurring gases methane (CH<sub>4</sub>) and nitrous oxide  $(N_2O)$ , respectively. The importance of reactive hydrogen and nitrogen gases relative to reactive halogen gases is expected to increase in the future, because the atmospheric abundances of the reactive halogen gases are decreasing as a result of the Montreal Protocol, while CH4 and N2O abundances are projected to increase substantially due to human activities.

#### Replacing Lost Ozone in the Stratosphere

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

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

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

### Why has an "ozone hole" appeared over Antarctica when ozonedepleting 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 CIO 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.)

### Minimum Air Temperatures in the Polar Stratosphere

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 (CIONO<sub>2</sub>) 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<sub>3</sub>). 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 CIO 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<sub>3</sub>) 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 ( $-85^{\circ}$ C or  $-121^{\circ}$ 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<sub>3</sub>.

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<sub>2</sub> 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<sub>3</sub>, their descent removes HNO<sub>3</sub> from regions of the ozone layer. This process is called *denitrification* of the stratosphere. With less HNO<sub>3</sub>, 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 CIO 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 ozonerich 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.

### 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 20<sup>th</sup> 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



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 (CIO) 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



**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.



**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.

### 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 20<sup>th</sup> 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 stronger 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-toyear 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.



**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).