

# Q10

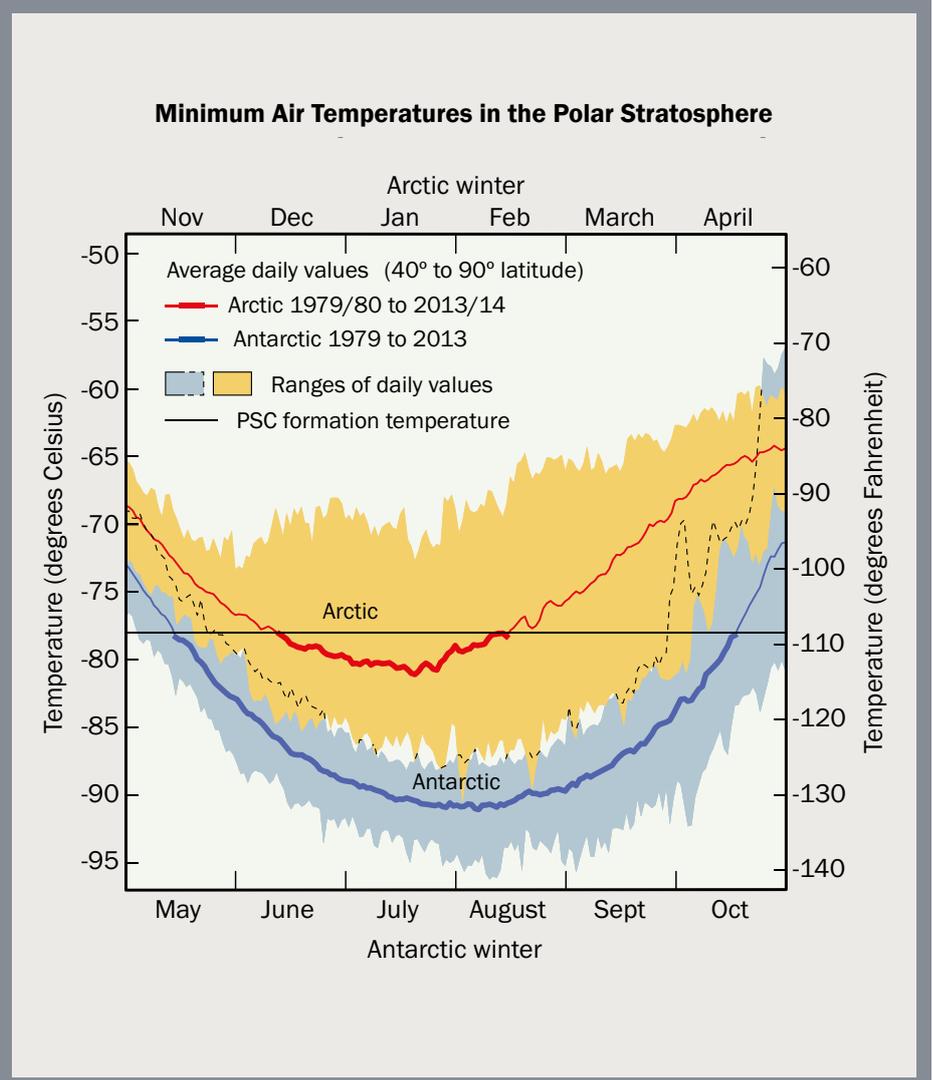
## Why has an “ozone hole” appeared over Antarctica when ozone-depleting substances are present throughout the stratosphere?

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 meteorological 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 isolation of polar stratospheric air in the polar vortex, 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 appears over Antarctica because meteorological 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

**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  $-90^{\circ}\text{C}$  in July and August in a typical year. Over the Arctic, average minimum values are near  $-80^{\circ}\text{C}$  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  $-78^{\circ}\text{C}$ . 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  $\text{ClO}$  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.)



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ozone hole requires temperatures low enough to form polar stratospheric clouds (PSCs), isolation from air in other stratospheric regions, and sunlight.

**Distribution of halogen gases.** Halogen source gases that are emitted at Earth's surface and have lifetimes longer than about 1 year are present in comparable abundances throughout the stratosphere in both hemispheres, even though most of the emissions occur in the Northern Hemisphere. The abundances are comparable because most long-lived 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 that leads to the ozone hole requires low temperatures to 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 the polar regions in winter. In the Antarctic winter, minimum daily temperatures are generally much lower and less variable than those in the Arctic winter (see Figure Q10-1). Antarctic temperatures also remain below PSC formation temperatures for much longer periods during winter. These and other meteorological differences occur because of the differences in the distribution of land, ocean, and mountains between the hemispheres at middle and high latitudes. Winter temperatures are low enough for PSCs to form somewhere in the Antarctic for nearly the entire winter (about 5 months), but only for limited periods (10–60 days) in the Arctic in most winters.

**Isolated conditions.** Stratospheric air in the polar regions is relatively isolated for long periods in the winter months. The isolation is provided by strong winds that encircle the poles during winter, forming a *polar vortex*, which prevents substantial transport and mixing of air into or out of the polar stratosphere. This circulation strengthens in winter as stratospheric temperatures decrease. Since winter temperatures are lower in the Southern than in the Northern Hemisphere polar stratosphere, the isolation of air in the vortex is much more effective in the Antarctic than in the Arctic. Once temperatures drop low enough, PSCs form within the polar vortex and induce chemical changes that are preserved by the isolation 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<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, the 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  $-78^{\circ}\text{C}$  ( $-108^{\circ}\text{F}$ ) 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 larger regions and for longer time periods in the Antarctic than in 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 solid particles. At even lower temperatures

### 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 ( $\text{HNO}_3$ ). 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).

( $-85^\circ\text{C}$  or  $-121^\circ\text{F}$ ), 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 localized cooling in the stratosphere, which increases condensation of water and  $\text{HNO}_3$ .

When average temperatures begin increasing by late winter, PSCs form less frequently and conversion reactions on their surfaces produce less ClO. Without continued ClO production, ClO amounts decrease and other chemical reactions re-form the reservoir gases,  $\text{ClONO}_2$  and HCl. When temperatures rise above PSC formation thresholds, which typically occurs 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 within a few days during the low-temperature winter/spring period. Because PSCs often contain a significant fraction of available  $\text{HNO}_3$ , their descent removes  $\text{HNO}_3$  from regions of the ozone layer. This process is called *denitrification* of the stratosphere. Because  $\text{HNO}_3$  is a source for nitrogen oxides ( $\text{NO}_x$ ) in the stratosphere, denitrification removes the  $\text{NO}_x$  available for converting the highly reactive chlorine gas ClO back into the reservoir gas  $\text{ClONO}_2$ . As a result, ClO remains chemically active for a longer period, thereby increasing chemical ozone destruction. Significant denitrification occurs each winter in the Antarctic but only in occasional winters in the Arctic, because PSC formation temperatures must be sustained over an extensive altitude region and time period to lead to denitrification (see Figure Q10-1).

Ice particles form at temperatures that are a few degrees lower than those required for PSC formation from  $\text{HNO}_3$ . If ice particles grow large enough, they can fall several kilometers due to gravity. As a result, a significant fraction of water vapor can be removed from regions of the ozone layer over the course of a winter. This process is called *dehydration* of the stratosphere. Because of the very low temperatures required to form ice, dehydration is common in Antarctic but rare in 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 later in winter, which reduces ClO production in PSC reactions.

**Discovering the role of PSCs.** Ground-based observations of PSCs 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 Dobson units (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.