

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 particular 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. Specific chemical reactions that occur on PSCs, combined with the isolation of polar stratospheric air inside the polar vortex, allow chlorine and bromine reactions to produce the ozone hole over Antarctica in springtime.

The severe depletion of stratospheric ozone in late winter and early spring in the Antarctic is known as the "ozone hole" (see Q10). 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 Q7 and Q8). The formation of the Antarctic ozone hole requires the combination of temperatures low enough to form polar strato-

spheric clouds (PSCs), isolation of polar vortex air from air in other stratospheric regions, sunlight, and sufficient amounts of available chlorine (see Q8).

Distribution of halogen gases. Halogen source gases that are emitted at Earth's surface and have lifetimes longer than about 1 year (see Table Q6-1) are present in comparable amounts through-



Figure Q9-1. Arctic and Antarctic temperatures. Air temperatures in the lower stratosphere of both polar regions reach minimum values in the lower stratosphere in their respective winter seasons. Average daily minimum values over Antarctica are as low as -92° 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 ozone layer when winter minimum temperatures fall below their formation threshold of about -78°C. This occurs on average for 1 to 4 months over the Arctic and about 5 months over Antarctica each year (see heavy orange and magenta lines). Chemical reactions within and on the surfaces of liquid and solid PSC particles cause the highly reactive chlorine gas CIO to be formed, which catalytically destroys ozone (see Q8). The range of winter minimum temperatures found in the Arctic is much greater than that 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 occurs each winter/ spring season (see Q10).

out the stratosphere in both hemispheres, even though most of the emissions occur in the Northern Hemisphere. The stratospheric abundances are comparable in both hemispheres 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 source gases 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 an extended period of time. Low temperatures are important because they allow liquid and solid PSC particles to form. Chemical reactions within and on the surfaces of these PSC particles initiate a remarkable increase in the most important reactive chlorine gas, chlorine monoxide (CIO) (see below as well as Q7 and Q8). Air is usually too warm to enable the formation of clouds in the stratosphere. Only the polar regions during winter have temperatures low enough for stratospheric clouds to form, because air cools due to lack of sunlight. In the Antarctic winter, minimum daily temperatures are generally much lower and less variable than those in the Arctic winter (see Figure Q9-1). Antarctic temperatures also remain below PSC formation temperatures for much longer periods during winter. These and other meteorological differences occur because of variations between the hemispheres in the distributions of land, ocean, and mountains at middle and high latitudes. As a consequence, winter temperatures are low enough for PSCs to form somewhere in the Antarctic for nearly the entire winter (about 5 months), and only for limited periods (about 1 to 4 months) in the Arctic for most winters.

Isolated conditions. Stratospheric air in the polar regions is relatively isolated for long periods in the winter months. This isolation results from 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. The polar vortex circulation tends to be stronger in the Southern Hemisphere (SH) than in the Northern Hemisphere (NH), because northern latitudes have more mountainous regions and adjacent areas of ocean and land with contrasting temperatures than is present at southern latitudes. This situation leads to more meteorological disturbances in the circulation of the NH, which increase the mixing in of air from lower latitudes toward the pole, warming the Arctic stratosphere. Since winter temperatures are therefore lower in the SH than in the NH polar stratosphere, the isolation of air in the polar 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 such as an increase in the abundance of CIO (see Q8). These changes persist for many weeks to months due to the isolation of stratospheric air in the Antarctic.

Polar stratospheric clouds (PSCs). Chemical reactions within and on the surfaces of liquid and solid PSC particles can substantially increase the relative abundances of reactive chlorine gases. These reactions convert the reservoir forms of chlorine gases, hydrogen chloride (HCI) and chlorine nitrate (CIONO₂), to the most important reactive form, CIO (see Figure Q7-3). The abundance of CIO increases from a small fraction of available chlorine to comprise more than half of all available chlorine (see Q7). With increased CIO, the catalytic cycles involving CIO and BrO become active in the chemical destruction of ozone whenever sunlight is available (see Q8).

Different types of liquid and solid PSC particles form when stratospheric temperatures fall below about -78° C (-108° F) in polar regions (see Figure Q9-1). As a result, PSCs are often found over large areas of the winter polar regions and over extensive altitude ranges in both hemispheres, with substantially larger regions and for longer time periods in the Antarctic than in the Arctic. The most common type of PSC forms from nitric acid (HNO₃) and water

Arctic Polar Stratospheric Clouds (PSCs)



Figure Q9-2. Polar stratospheric clouds. This photograph of an Arctic polar stratospheric cloud (PSC) was taken in Kiruna, Sweden (67°N), on 27 January 2000. PSCs form in the ozone layer during winters in the Arctic and Antarctic, wherever sufficiently low temperatures occur (see Figure Q9-1). The particles grow from the condensation of water, nitric acid (HNO₃), and sulfuric acid (H₂SO₄). The clouds often can be seen with the human eye when the Sun is near the horizon. Reactions within and on PSC surfaces lead to the formation of the highly reactive gas chlorine monoxide (CIO), which is very effective in the chemical destruction of ozone (see Q7 and Q8).

condensing on pre-existing liquid sulfuric acid (H_2SO_4)-containing particles. Some of these particles freeze to form 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 Q9-2**). 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 HNO₃.

When average temperatures begin increasing in late winter, PSCs form less frequently, which slows down the conversion of chlorine from reservoir to reactive forms throughout the polar region. Without continued production, the abundance of ClO decreases as other chemical reactions re-form the reservoir gases, $CIONO_2$ and HCI. When temperatures rise above PSC formation thresholds, usually sometime between late January and early March in the Arctic and by mid-October in the Antarctic (see Figure Q9-1), the most intense period of ozone depletion ends.

Nitric acid and water removal. Once formed, the largest PSC particles fall to lower altitudes because of gravity. The largest particles can descend several kilometers in the stratosphere within a few days during the low-temperature winter/spring period. 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. Because HNO_3 is a source for nitrogen oxides (NO_x) in the stratosphere, denitrification removes the NO_x available for converting the highly reactive chlorine gas CIO back into the reservoir gas CIONO₂. As a result, CIO

remains chemically active for a longer period, thereby increasing chemical ozone destruction. Significant denitrification occurs each winter in the Antarctic and only for 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 Q9-1).

Ice particles form at temperatures that are a few degrees lower than those required for PSC formation from HNO_3 . If these water ice particles grow large enough, their gravitational settling can remove a significant fraction of water vapor 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 the Antarctic and rare in the Arctic. 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 the production of CIO by reactions on PSCs.

Discovering the role of PSCs. Ground-based observations of PSCs were available many decades before the role of PSCs in polar ozone destruction was recognized. The geographical and altitudinal extent of PSCs in both polar regions was not fully known until PSCs were observed by satellite instruments starting in the late 1970s. The role of PSC particles in converting reservoir chlorine gases to CIO 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 sampled particles and reactive chlorine gases, such as CIO, 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 Q4) installed as part of the effort to increase observations of Earth's atmosphere during the International Geophysical Year that began in 1957 (see Figure Q0-1). The observations showed unusually low total ozone during the austral late winter/early spring months of September, October, and November. Total ozone was lower in these months in the early 1980s 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 prestigious scientific journal *Nature* in 1985. They suggested that rising abundances of atmospheric CFCs were the cause of the steady decline in total ozone over the Halley Bay research station (76°S) observed during successive Octobers starting in the early 1970s. Soon after, satellite measurements confirmed the spring ozone depletion and further showed that for each late winter/early spring season starting in the early 1980s, the depletion of ozone extended over a large region centered near the South Pole. The term "ozone hole" came about as a description of the very low values of total ozone, apparent in satellite images, that extend over the Antarctic continent for many weeks each October (spring in the Southern Hemisphere) (see Q10). 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 observed in the Antarctic spring were found to be around 300 Dobson units (DU), lower than those in the Arctic spring. The Antarctic values were surprising because the assumption at the time was that the two polar regions would have similar values. We now know that these 1950s Antarctic values were not anomalous; in fact, similar values were observed near the South Pole in the early 1970s, before the ozone hole appeared (see Figure Q10-3). Antarctic total ozone values in early spring are systematically lower than those in the Arctic early spring because the Southern Hemisphere polar vortex is much stronger and colder and, therefore, much more effective in reducing the transport of ozone-rich air from midlatitudes to the pole (compare Figures Q10-3 and Q11-2).