The Antarctic ozone hole: An update

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Ozone ($O_3$) is of fundamental importance to our planet. It absorbs solar UV radiation at wavelengths below 320 nm that are not absorbed by any other atmospheric gases. Without ozone, that high-energy sunlight would reach the ground and destroy or damage DNA and other biologically active molecules. In humans, increased UV exposure leads to increased rates of skin cancer and of eye damage such as cataracts.

Most atmospheric ozone is found in the stratosphere, about 10–50 km above Earth’s surface. Created naturally by UV photolysis of oxygen molecules ($O_3$), ozone is destroyed by catalytic cycles (see the box on page 45) involving free radicals produced by decomposition of molecules—both naturally occurring and anthropogenic—that contain nitrogen, hydrogen, bromine, and chlorine atoms.  

In the early 1970s, Mario Molina and Sherwood Rowland identified chlorofluorocarbons (CFCs), compounds composed of carbon, fluorine, and chlorine atoms, as a growing manmade source of stratospheric chlorine. Commonly used at the time as refrigerants and aerosol propellants, the molecules are very long-lived: James Lovelock and colleagues found in 1971 that the atmospheric concentrations of the two most abundant compounds, CFCl$_3$ (also called CFC-11) and CF$_2$Cl$_2$ (CFC-12), accounted for almost all that had ever been produced. The unfettered growth of CFCs became a major concern in the scientific community because additional stratospheric chlorine would increase ozone destruction. In 1982 a National Academy of Sciences evaluation suggested that in 100 years the total global ozone would be depleted by 5–9% if CFC use continued to grow at the 1977 rate.

Only three years later, a 1985 paper by Joseph Farman, Brian Gardiner, and Jon Shanklin shook the foundations of stratospheric science: They reported drops of about 30% in October ozone levels over Antarctica (see figure 1a). Such dramatic depletion was unexpected in every sense: magnitude, year of onset, geographic region, and seasonality. The losses occurred annually and only during spring, and they took place in the Antarctic lower stratosphere, where no study had predicted sensitivity to chlorine increase. Satellite-based observations showed that the extent of depleted ozone—quickly dubbed the ozone hole—continued to grow during the 1980s; by 1992 it was about as large as North America (see figure 1b).

Within a few years, substantial research had demonstrated that CFCs did indeed pose a direct threat to the ozone layer. In response, the international community of policymakers in 1987 adopted the Montreal Protocol on Substances that Deplete the Ozone Layer, which was designed to control the production and consumption of CFCs. The cause of the ozone hole was still being debated, but dramatic losses over Antarctica provided a vivid backdrop to the negotiations.

Over subsequent decades, the Montreal Protocol has been strengthened; production of CFCs was first limited and then eliminated, and by the late 1990s and early 2000s (the date depends on the specific gas), their concentrations in the lower atmosphere (the troposphere, from the surface up to about 10 km) stopped increasing. Meanwhile, during the 1990s the October ozone at the British Antarctic Survey’s Halley Research Station hovered between 120 and 150 Dobson units, less than half the value observed during the 1960s, when stratospheric chlorine levels were close to their natural value. (Named
after George Dobson, who pioneered the study of stratospheric ozone, Dobson units measure the column density of ozone or other trace atmospheric gas: 100 DU corresponds to the amount of ozone in a vertical column that would form a layer 1 mm thick at standard temperature and pressure.)

**The explanation emerges**

The hypothesis that CFCs were the root cause of the ozone hole was puzzling: How could CFCs, mainly released in the northern latitudes, cause large depletion over Antarctica? The general features of stratospheric circulation were known, and ozone depletion was expected in the upper stratosphere, at altitudes of about 40 km. Nobody anticipated it would be the interaction of stratospheric photochemistry with Antarctica’s unique meteorological and physical processes that eventually explained the ozone observations.

Atmospheric transport of CFCs follows the Brewer–Dobson circulation pattern. First hypothesized by Alan Brewer to explain the extreme dryness of the stratosphere, the flow connects the tropics and polar regions: Rising air in the tropics is transported poleward and downward in the so-called extratropics at latitudes above 30°.

In the 1970s atmospheric chemistry studies established that CFCs released at the surface are broken apart by photolysis into free radicals that catalytically destroy ozone. The rate of their destruction increases exponentially with altitude. In the lower atmosphere, CFCs are protected from destruction by the ozone layer until they are lifted above it; significant losses begin at about 24 km. Their concentrations could thus be tracked to reveal the stratospheric circulation pattern.

The basic pattern soon emerged. Although anthropogenic CFCs are emitted mostly in the Northern Hemisphere, they are well mixed throughout the troposphere over the course of a couple of years, and air that enters the stratosphere in the tropics carries with it tropospheric levels of CFCs. Once the circulation lifts the air above about 24 km, now-vulnerable CFCs are photolyzed by UV radiation at wavelengths of 190–230 nm. The extratropical upper-stratospheric circulation carries CFC-depleted air poleward and downward. The tropical uplift of the Brewer–Dobson circulation is slow, only about 0.4 mm/s, and air density decreases exponentially with altitude. Hence most air that enters the stratosphere is transported poleward below 24 km. Only a small fraction (about 1%) of the mass of air in the atmosphere rises high enough each year to experience significant CFC breakdown, which accounts for atmospheric lifetimes of 52 years for CFC-11 and 102 years for CFC-12. Observations of tracers show that it takes five to seven years for air to circulate from the tropics through the stratosphere to the Antarctic lower stratosphere.

In the upper stratosphere, the chlorine concentration peaked at about 3.5 parts per billion by volume (ppbv) around 1998. Naturally occurring methyl chloride accounts for only about 0.5 ppbv of the stratospheric chlorine; nearly all the rest comes from manmade chemicals. Likewise, stratospheric bromine, another contributor to polar ozone loss, has manmade origins, primarily methyl bromide and halons—molecules composed of bromine, fluorine, and carbon.

The equivalent effective stratospheric chlorine (EESC) is a parameter that quantifies the effects of chlorine and bromine on Antarctic ozone depletion. The EESC is calculated by summing up the Cl and Br atoms in ground observations of halogen chemicals, factoring in the time it takes for those chemicals to reach the Antarctic lower stratosphere.
Ozone hole

and estimating the rate at which the CFCs and halons are destroyed. The bromine contribution is scaled by a factor of 60 to account for that atom's more efficient destruction of ozone. With those factors included, the increasing severity of ozone loss closely parallels the increase in the EESC (see figure 1a).

In late March the Sun sets at the South Pole and the long Antarctic winter begins. The dark polar stratosphere cools as IR radiation escapes to space. At southern midlatitudes, ozone continues to absorb solar radiation. Solar heating continues and thermal gradients develop. As polar temperatures fall below midlatitude temperatures, the pressure gradient forces air toward the pole. The Coriolis effect causes that air to bend to the left, producing a very strong west-to-east jet stream with speeds more than 50 m/s. That huge whirling eddy—the polar vortex—encircles the Antarctic region, extends from the troposphere to the mesosphere (at altitudes from roughly 50 km to 80 km), and prevents air from midlatitudes from mixing with air inside the vortex.

Air from the upper stratosphere and mesosphere, carried poleward by the Brewer–Dobson circulation, descends to the lower stratosphere within the core of the vortex over the course of the winter. Isolated from the midlatitudes, chlorine and bromine concentrations within the lower-stratospheric polar vortex are much greater than those at similar altitudes outside the vortex.

A paradigm shift

The chlorine and bromine released from source gases typically form inorganic molecules. Throughout the stratosphere, only a small fraction of inorganic chlorine resides in atomic Cl and chlorine monoxide (ClO), the reactive species participating in catalytic ozone destruction. Prior to discovery of the ozone hole, the Cl–ClO catalytic reaction (cycle 1 in the box) was considered to be the primary mechanism of ozone depletion, and most inorganic chlorine in the stratosphere was thought to be locked up in reservoirs of compounds that do not react with ozone—hydrogen chloride (HCl) and chlorine nitrate (ClONO₂).

The solution to the puzzle of the rapid decline of Antarctic ozone lay in unexpected chemical reactions—heterogeneous ones involving reactants in different phases—that liberate chlorine from its reservoirs in the extremely cold, lower-stratospheric Antarctic vortex. At 20 km, temperatures over Antarctica fall below −80 °C in mid-May; they remain below −80 °C until mid-October. In July and August, large regions of the Antarctic vortex drop below −90 °C. Polar stratospheric clouds (PSCs) form at such low temperatures (see figure 2), even though the stratosphere is extremely dry—water vapor is present at only 5 parts per million. Observations of PSCs were reported around the beginning of the 20th century during expeditions to the Antarctic continent, but the clouds’ importance to atmospheric chemistry was not understood until discovery of the ozone hole.

Heterogeneous chemical reactions on and within particles in the PSCs convert the HCl and ClONO₂ reservoir gases into Cl₂, a weakly bound molecule that is easily photolyzed into Cl free radicals. Moreover, PSCs impede chlorine deactivation into the reservoir ClONO₂ (see the box). Gas-phase nitric acid (HNO₃) condenses to form PSC particles and reduces available reactive nitrogen.

Large particles fall out of the stratosphere altogether, a process known as denitrification, so HNO₃ is not returned to the gas phase when PSCs evaporate. Still, high concentrations of CI radicals did not explain the ozone hole; the Cl–ClO catalytic reaction requires atomic oxygen, produced when ozone is photolyzed by UV light, which is nearly absent from the lower-stratospheric vortex at the very low Sun angles of the Antarctic winter.

A different catalytic cycle

A new mechanism accounts for the catalytic destruction of ozone in the absence of oxygen atoms. Rapid ozone loss begins as the first rays of sunlight illuminate the vortex in spring. In a reaction requiring only visible light, not higher-energy UV, the sunlight photolyzes the Cl₂ produced by the PSC reac-

Figure 2. Polar stratospheric clouds (PSCs) are key to the large ozone loss in the Southern Hemisphere. Heterogeneous chemical reactions within cloud particles release chlorine radicals from longer-lived reservoir gases. PSCs have long been observed at high latitudes in both hemispheres, but their major role in stratospheric photochemistry was not known until after the ozone hole was discovered. Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) images, such as this one obtained 1 August 2008, provide details on the composition, extent, and duration of PSCs in both hemispheres. As seen in this vertical profile, tropospheric weather clouds extend through the lower atmosphere to altitudes of about 10 km; PSCs are found at higher altitudes, in the stratosphere. (Image courtesy of NASA/CALIPSO/C. Trepte.)
tions in the vortex. As described in the box (cycle 2), the now-free Cl reacts with O₃ to produce ClO and O₂. Two ClO molecules combine in the presence of a third body to form Cl₂O₂, but that dimer is easily photolyzed in low light to produce Cl. A related cycle involving both ClO and BrO (cycle 3) is also important; halons and methyl bromide are the dominant anthropogenic contributors to BrO.¹⁰

The combination of inorganic chlorine and bromine from manmade compounds, extreme cold temperatures, and sunlight photochemistry accounts for the development of the Antarctic ozone hole and its seasonal dependence. Cycles 2 and 3 catalytically destroy ozone at the rate of about 1–2% per day starting in late August. By early October nearly 100% of the ozone in a layer about 16–20 km in altitude is destroyed over Antarctica.¹¹

The ozone hole has been a regular feature of the Antarctic spring since the late 1980s.¹² The Halley Station’s October mean ozone column (figure 1a), the October mean satellite map (figure 1b), and other measurements such as the annual minimum ozone column all vary year to year, but they remain well below the pre-1980 low-chlorine baseline. During the first decade of the 21st century, ground-based measurements of CFCs and satellite measurements of their breakdown products confirm that stratospheric chlorine is decreasing as expected.¹³ Yet because CFCs are long-lived, their concentrations decrease very slowly, despite near-zero global emissions resulting from the Montreal Protocol. Ozone holes are expected to occur for many years to come, with their severity dictated primarily by year-to-year variability in the Southern Hemisphere’s meteorological conditions.

Recent contrasting ozone holes illustrate some of the processes that contribute to that variability. Observations with the Ozone Monitoring Instrument on NASA’s Aura satellite revealed the largest ozone hole on record in October 2006 and one of the smallest ozone holes in the past 20 years in 2012.¹⁴ Figure 3 shows the evolution of the Antarctic ozone profiles, spatially averaged over the polar vortex, as measured with Aura’s Microwave Limb Sounder in the 2006, 2010 (a typical recent year), and 2012 spring and summer. The similarity of the profiles in August and early September suggests similar photochemical processes at the beginning of the Antarctic spring. But 2006 had an unusually cold winter, and ozone concentrations stayed low over a broader range of altitudes throughout September. In contrast, both the vertical extent and the duration of the 2012 ozone depletion were smaller; there was less photochemical ozone destruction in the warmer vortex as spring progressed. The ozone increase above 24 km in October is from transport into the region, made possible by the warmer and less stable polar vortex. The smaller-than-usual 2012 ozone hole is explained by meteorology, not by the small chlorine decrease (less than 5% since 2006) due to the Montreal Protocol. (For more on Aura and other satellites monitoring the state of the atmosphere, see the article by Tristan L’Ecuyer and Jonathan Jiang, PHYSICS TODAY, July 2010, page 36.)

### Catalytic ozone loss

Before the discovery of the Antarctic ozone hole, chlorine was already known to catalyze the conversion of ozone (O₃) to oxygen (O₂) in the stratosphere through absorption of UV radiation:

### Cycle 1

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \\
O_1 + h\nu \rightarrow \text{O}_2 + \text{O}
\]

\[
\text{Net: } 2\text{O}_3 + h\nu \rightarrow 3\text{O}_2
\]

But that reaction could not account for the unexpected extreme depletion in the Antarctic. The explanation involves previously unknown heterogeneous and photochemical interactions between stratospheric chlorine compounds and unique clouds that form in the extremely cold Antarctic winter.

### The Antarctic cycles

Reactions on and in polar stratospheric clouds (PSCs) liberate free radicals from chlorine nitrate (ClONO₂) and hydrochloric acid (HCl) reservoirs, which contain most of the atmosphere’s chlorine. The main reaction, which generates chlorine gas, is:

\[
\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3
\]

Sunlight creates free radicals:

\[
\text{Cl} + h\nu_{\text{vis}} \rightarrow 2\text{Cl}
\]

Radicals destroy ozone in two dominant classes of catalytic reactions. A third body M is needed during the reaction to conserve energy and momentum. Unlike in cycle 1, the photolysis in these cycles is driven by visible light:

#### Cycle 2

\[
\begin{align*}
2 \text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{Cl} + \text{M} & \rightarrow \text{Cl}_2 + \text{ClO}_2 + \text{M} \\
\text{Cl}_2 + \text{M} & \rightarrow \text{Cl} + \text{O}_2 + \text{M} \\
\text{Net: } 2\text{O}_3 + h\nu_{\text{vis}} & \rightarrow 3\text{O}_2
\end{align*}
\]

Cycles 2 and 3 are fast. In the Antarctic, when no ozone is left to scavenge, slower reactions with other atmospheric gases deactivate chlorine:

\[
\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3
\]

In the Arctic, PSCs evaporate and return HNO₃ to the gas phase. Nitrogen dioxide (NO₂) produced from HNO₃ then deactivates ClO:

\[
\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}
\]
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The ozone hole also affects the Southern Hemisphere’s surface climate. As the Sun returns to Antarctica, ozone should be present, absorbing radiation and thereby warming the polar vortex. There is less heating because of ozone depletion, Antarctic lower-stratospheric temperatures are below their pre-ozone-hole average during spring and summer, and the polar vortex persists one to two weeks longer. Because the circumpolar flow around Antarctica extends to the surface, the tropospheric jet is strengthened during the southern summer, which increases the surface wind stress and thereby modifies the ocean circulation. Increased greenhouse gas levels lead to surface warming in the Arctic and might be expected to have the same effect in the Antarctic. However, observations and models show that the ozone depletion has caused the interior of Antarctica to cool. The wind and temperature changes driven by ozone depletion also change Southern Hemisphere precipitation patterns.

Important lessons, promising future

The story of the Antarctic ozone hole is a remarkable one. The ozone depletion was unexpected, rapid, and large: Continental-scale losses of 50% developed in about 15 years. The worldwide response was even quicker. The scientific community amassed additional meteorological and atmospheric-constituent information in the Antarctic and established the cause of the phenomenon within a few years.

Figure 5. Simulations of the Antarctic ozone hole contrast the “expected future” (blue lines at left and top images at right) resulting from curtailing chlorofluorocarbons and a “world avoided” scenario (red lines and bottom images) in which CFC use increases annually by 3%. In the top left, the equivalent effective stratospheric chlorine (EESC) accounts for the influence of chlorine and the more-destructive bromine, both products of anthropogenic gases. The plotted EESC, in parts per billion by volume, is the average over 75°–90° S at 20 km. The bottom left plots the October ozone column density averaged over the same region. By 2014 the EESC in the “world avoided” is almost twice that in the “expected future,” and total ozone is about 80 Dobson units less. By 2060 the EESC is 17 times as high, Antarctic total ozone is 260 DU less, and large ozone depletions cover the entire globe.

Figure 4. A tale of two poles. Measurements of the Arctic’s total column ozone (left) from various ground stations show less ozone during winter and spring in recent years compared with the late 1960s, but the shape of the seasonal cycle—low values in the fall, high values in the spring—is largely unchanged. In the Antarctic (right), however, the springtime increases of the late 1960s have been replaced by large losses in September and October. The Arctic plot has been displaced by 180 days to align with the seasons in the Antarctic.
Policymakers acted to implement the Montreal Protocol. Subsequent amendments to the protocol have followed detailed discoveries about the processes that produce the ozone hole and have largely eliminated anthropogenic emissions of CFCs and halons; left unrestrained, the growth of those emissions would have been disastrous for the ozone layer.

The Antarctic ozone hole teaches important lessons. Models synthesize knowledge and provide projections for the future, but if processes such as heterogeneous chemical reactions are missing, then projections are hopelessly flawed. Nothing can replace a foundation of observations that predates environmental change. Long-term Antarctic observations of the stratospheric ozone column were thought to be unimportant. The persistence of Farman and other scientists led to the long series of Halley measurements that ultimately revealed the ozone depletion. Laboratory studies, focused observational campaigns, and modeling were essential in testing the various hypotheses to explain the ozone hole. Those research efforts broadened understanding of the interplay among dynamic, radiative, and photochemical processes of the stratosphere and established the connection to CFCs.

The future of Antarctic ozone is promising. Ground and satellite observations show that chlorine levels in the troposphere and stratosphere are decreasing. Model projections suggest that ozone will return to 1980 levels between 2050 and 2070. The ozone hole has been an iconic feature, a testament to the possibility of unexpected and large impacts of anthropogenic actions on the environment. Its disappearance will symbolize the possibility of protecting Earth through cooperative actions.

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