

Lecture 10: The Antarctic Ozone Hole

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IV. OZONE HOLE THEORY

Strong ozone losses within the SH polar vortex in spring primarily occurs in the lower stratosphere (as discussed previously). Departures from climatological values near 300 DU were first evident in the middle 1970's (see Fig. I.B.1.1, Farman et al., 1985); dramatic changes were first noted in the middle 1980's, and the ozone hole is now a regular feature of the SH stratosphere, with a near-complete loss of ozone in the lower stratosphere (Figs. III.C.6 and III.C.7). The cause of the ozone hole has undergone very strong scrutiny and debate in the 1980's. Ground-based (NOZE I and II) and aircraft measurement campaigns (AAOE and ASHOE/MAESA) of the ozone hole chemistry and dynamics have led to a scientific consensus that chemical ozone depletion associated with chlorine and bromine are responsible for the ozone hole (WMO, 1992, 1994). Stratospheric chlorine primarily results from photochemical breakdown of chlorofluorocarbons released in the troposphere from human activities. Subsequent observations from aircraft and satellites, together with laboratory and modeling studies, have given better understanding to details of chemical ozone losses inside the ozone hole, as discussed in WMO (1995), and summarized briefly here.

In this section, we will review the processes by which this heterogeneous processes lead to catalytic ozone loss. In the first part, we will discuss the morphology of polar stratospheric clouds, and briefly touch the properties of these clouds, in the second part, we will look at the heterogeneous reactions that release chlorine into active forms. The third part will look at the direct loss process by which ozone is

destroyed, and the final part will pull all of these threads together to illustrate the temporal behavior of trace gases including ozone over the entire winter-spring period.

A. POLAR STRATOSPHERIC CLOUDS

Polar stratospheric clouds (PSCs) are fundamental to an understanding of the Antarctic ozone hole. PSCs are important because chlorine species that do not destroy ozone (HCl and ClONO₂) are converted on the surfaces of the cloud particles into forms that result in ozone destruction. As discussed earlier, observations of these clouds have a long and detailed history. Figure IV.A.1 displays a picture of a PSC in the northern hemisphere January 1989. These clouds have been visually observed since the 19th century at high latitudes.

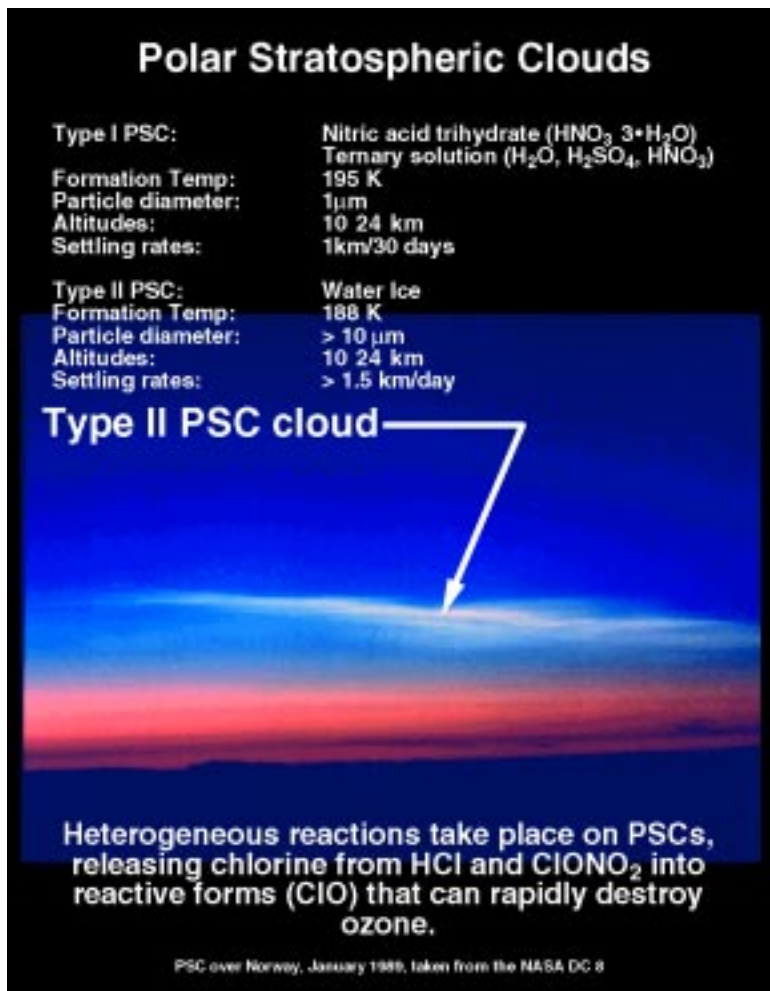


Figure IV.A.1

There are two types of PSCs, referred to as type I and type II PSCs (properties are listed on Figure IV.A.1). While the composition of type II PSCs is recognized as water ice, the composition of the type I PSCs is rather poorly understood. Originally, Crutzen and Arnold (86) and Toon et al. (86) proposed that these PSCs were formed as nitric acid hydrates. The equilibrium temperature of NAT was originally viewed as being consistent with the formation temperatures of type I PSC (McMormick ??), but recent aircraft observations using extremely precise temperature measurements have shown that the formation temperatures are inconsistent with NAT (Dye et al., 1990; Del Negro et al., 1997). Current theories suggest that the type I PSC cloud particles are composed of mixtures of HNO₃, H₂O, and H₂SO₄ (i.e., ternary solutions). These ternary solutions grow as the temperature decreases, achieving sizes providing sufficient surface areas to enable heterogeneous chemical reactions.

While the details of growth, composition, and size of type I PSCs is a subject of intense research, the presence of such particles is easily detected via both aircraft and satellite observations. Because of the small size of these type I PSCs (1 micron), they have very small sedimentation velocities (11 m/day). In the case of type II PSCs, the particles are quite large (greater than 10 microns), and can settle out of the stratosphere relatively rapidly (1 km/day) This sedimentation results in an irreversible loss of reactive nitrogen (denitrification) and water (dehydration) inside the SH vortex over the course of the very cold winter. As will be discussed, this inhibits the reformation of the reservoir ClONO₂ from active chlorine (and hence maintains high levels of active chlorine that can destroy ozone).

The presence of PSCs is fundamentally different for the northern and southern hemispheres. Because of the extremely cold temperatures in the southern hemisphere, PSCs form quite early in the winter, and persist quite late into the spring. Temperatures below the frost point

form over extensive volumes for long periods of time. Hence, the southern polar vortex is both dehydrated and denitrified. This is not usually the case in the northern hemisphere, where temperatures are typically much warmer. The threshold formation and growth of PSC particles have been observed by balloon-borne measurements over Antarctica (Hofmann et al., 1989; Hofmann and Deshler, 1989), and by aircraft measurements (Dye et al., 1990; Del Negro et al., 1997). Satellite observations from the POAM II instrument shown in Figure IV.A.2 clearly provide evidence of PSC's inside the SH vortex in winter, primarily in the intensely cold lower stratosphere during the depth of winter.

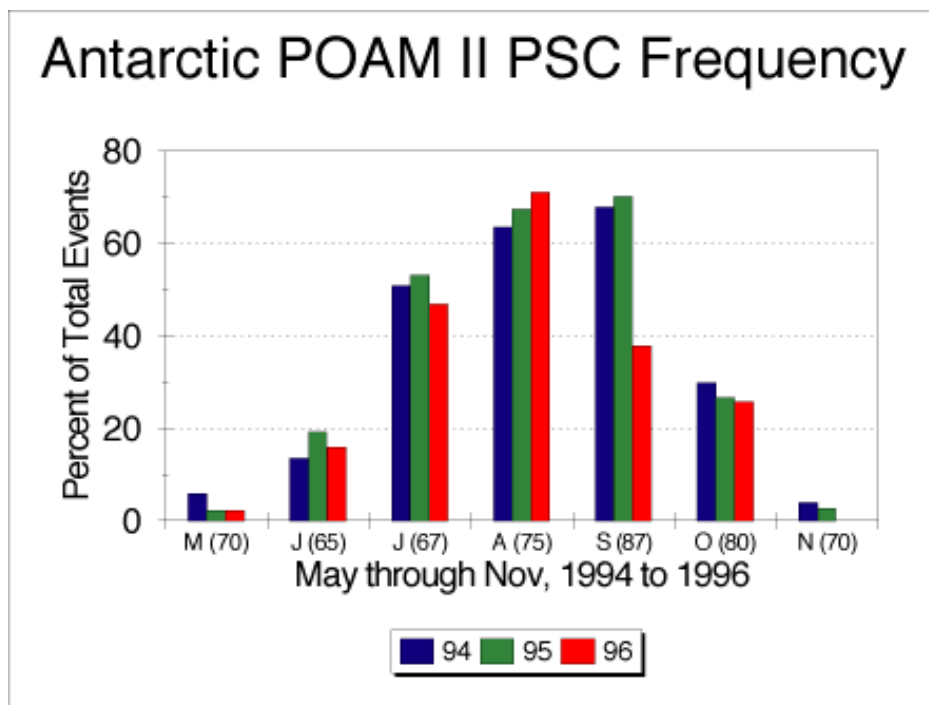


Figure IV.A.2

Note the correspondence between the PSC probability in Fig. IV.A.2 and the polar temperature evolution in Fig. II.B.2, and also the much higher frequency of PSC's in the SH than in the NH, due to the colder SH temperatures. While there are usually about 2.5 months during which temperatures are below the frost point (for nominal water vapor concentrations), the northern hemisphere typically has only a few days with temperatures below the frost point. Aircraft observations of particle surface area made just inside the polar vortex on 28

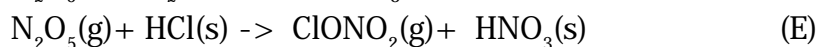
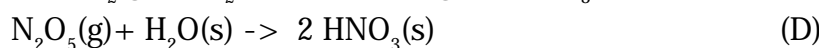
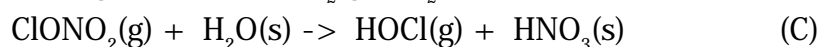
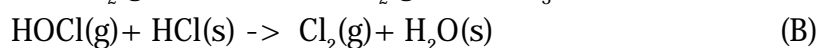
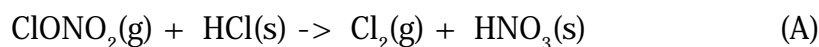
July 1994 by the NCAR MASP instrument show the strong nonlinear relationship to temperature in Figure IV.A.3 (Del Negro et al., 1997; Kawa et al., 1997).

As was shown in Fig. IV.A.2, temperatures fall below the nitric acid trihydrate limit in late July, and then fall below the frost point in June. The time period over which temperatures are below the frost point extends for 3-4 months in the southern hemisphere, whereas the frost point time period in the northern hemisphere is only a few days. Typically, air passes through these cold air masses, such that nearly the entire volume of air inside the polar vortex has been exposed to polar stratospheric clouds within a couple of weeks of the first appearance of PSCs. Since temperatures are so cool in the southern hemisphere, the period over which large particles can form is long, while this period in the northern hemisphere is quite short.

B. HETEROGENEOUS REACTIONS

Heterogeneous chemistry is fundamental to an understanding of the Antarctic ozone hole. These heterogeneous chemical processes are extremely important because they convert reservoir species such as HCl and ClONO₂ into active chlorine species such as ClO that can destroy ozone. Homogeneous chemical processes involve the reaction of chemicals in the gas phase. Stratospheric heterogeneous processes involve reactions between chemicals on the surfaces of stratospheric particles (see the section on polar stratospheric clouds).

The principal heterogeneous reactions are:



The reaction rates of these processes are measured in the lab, and are proportional to 1) gas concentration (denoted by the s), 2) particle type via the reaction probability (also known as the sticking coefficient), 3) the mean molecular velocity of the gas which is proportional to the square root of the temperature, and 4) the surface area density of the particles. Sticking coefficients for these reactions and particle types can be found in Demore et al. (1992).

The principal effect of heterogeneous processes A, B, and C convert ClONO_2 and HCl into Cl_2 and HOCl which is degassed from the particles, while the HNO_3 is retained on the particles. All of these heterogeneous reactions act to remove nitrogen from the gas phase (N_2O_5 and ClONO_2), and sequester that odd nitrogen as HNO_3 . This process of sequestering nitrogen is known as “denoxification”. Since HNO_3 must be photolyzed by sunlight to form OH and NO_2 (ozone reactive gases), then lifetime of HNO_3 is very long during the Antarctic winter in polar night. By mid-October, the photolysis time scale for HNO_3 in the lower stratosphere is longer than 30 days, making HNO_3 a relatively inert trace gas during the ozone hole period. Further, since particles will slowly settle, the particles will carry HNO_3 to lower altitudes. This process of removing HNO_3 via particle sedimentation is called “denitrification”. The heterogeneous process A is illustrated in Figure IV.B.1 where HCl and ClONO_2 are reacting to form Cl_2 and HNO_3 .

Polar Stratospheric Cloud Surface Reaction

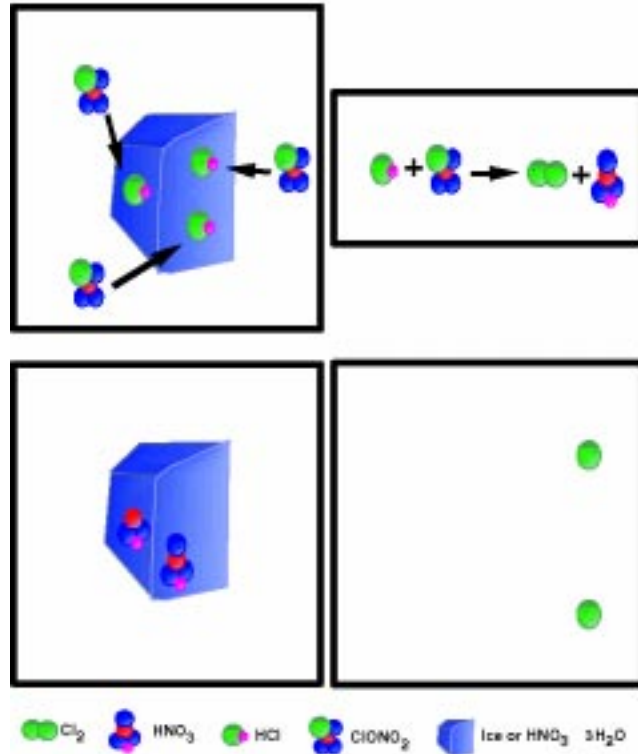


Figure IV.B.1

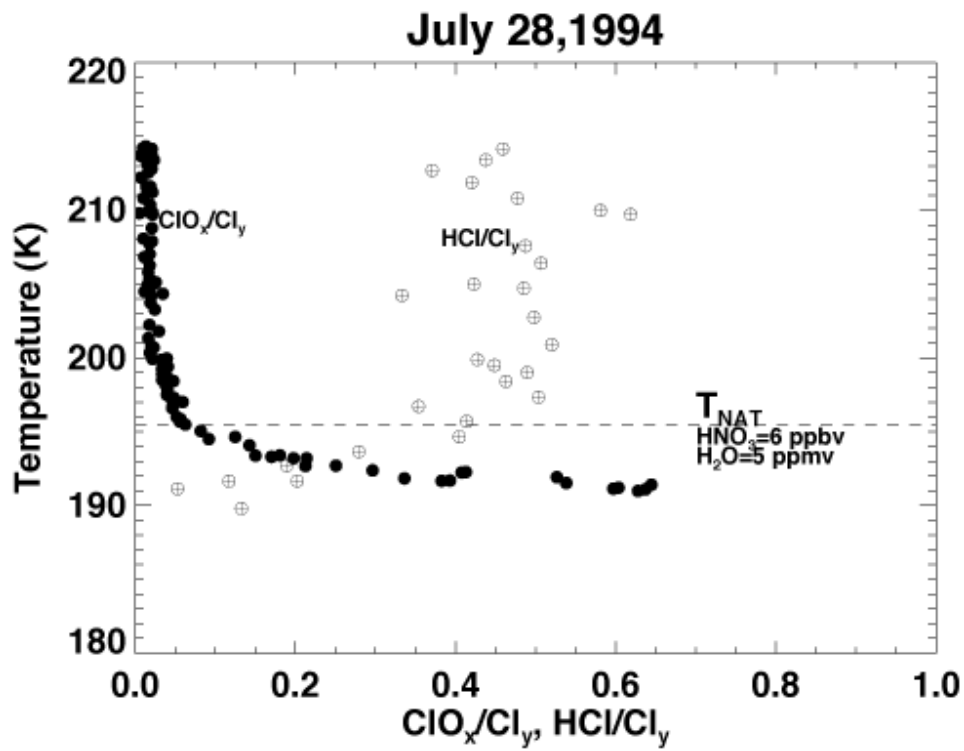
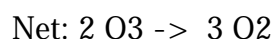
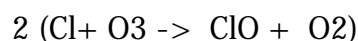
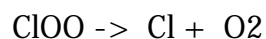
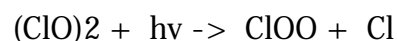
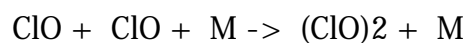


Figure IV.B.2

Figure IV.B.2 displays an example of the effect of heterogeneous processing that has been adapted from Kawa et al. (97). The plot displays the ClO_x/Cl_y and HCl/Cl_y ratios measured on a July 28, 1994 ER-2 aircraft flight into the southern hemisphere polar vortex. ClO_x is the total reactive chlorine. Note the large concentrations of ClO at temperatures below about 195 K, and the low concentrations of HCl. Kawa et al. (97) and Del Negro et al. (97) concluded that this processing was consistent with heterogeneous reactions on ternary solutions, rather than on nitric acid hydrates. These aircraft observations conclusively demonstrate the relationship of cold temperatures and PSC heterogeneous chemical effects, well before the onset of large polar loss processes.

C. CATALYTIC LOSS OF OZONE

The principal loss processes for ozone during the ozone hole period involve ClO, and BrO. The ClO is formed via the photolysis of Cl₂ as the sun rises over Antarctica. Cl₂, a byproduct of the heterogeneous reactions, has a large cross section at visible wavelengths (280-420 nm), and is almost immediately broken up as the sun rises over Antarctica. This Cl is then free to engage in a catalytic reaction, where Cl can destroy an ozone molecule, and then reform itself. The ClO-ClO reaction [Molina and Molina, 1987] is:



This reaction (illustrated in Figure IV.C.1) has two key parts: 1) the reaction is limited by the amount of ClO, and proceeds as the square of the ClO concentration, 2) the reaction does not require oxygen

atoms (O) in order to destroy ozone, as do most conventional catalytic loss processes.

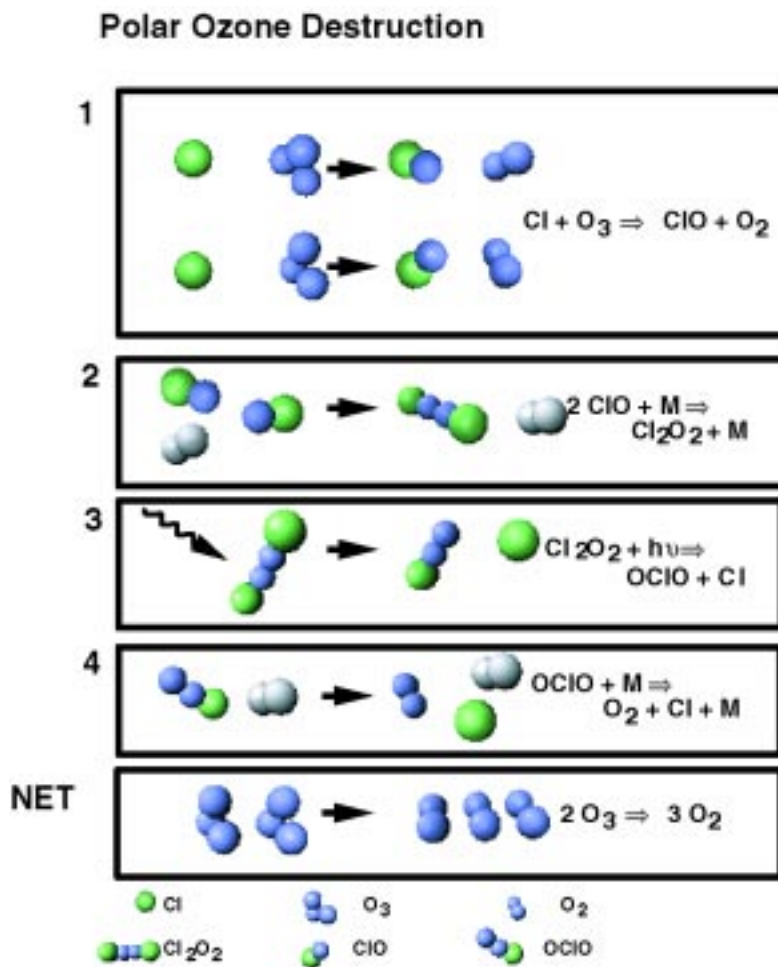


Figure IV.C.1

Mixing ratios of ClO in the Antarctic vortex have been measured from aircraft [Anderson et al., 1989], ground [Solomon et al., 1987], and from satellite [Waters et al., 1993]. The in-situ aircraft observations show ClO concentrations in excess of 1 ppbv, accounting for a substantial fraction of the inorganic chlorine.

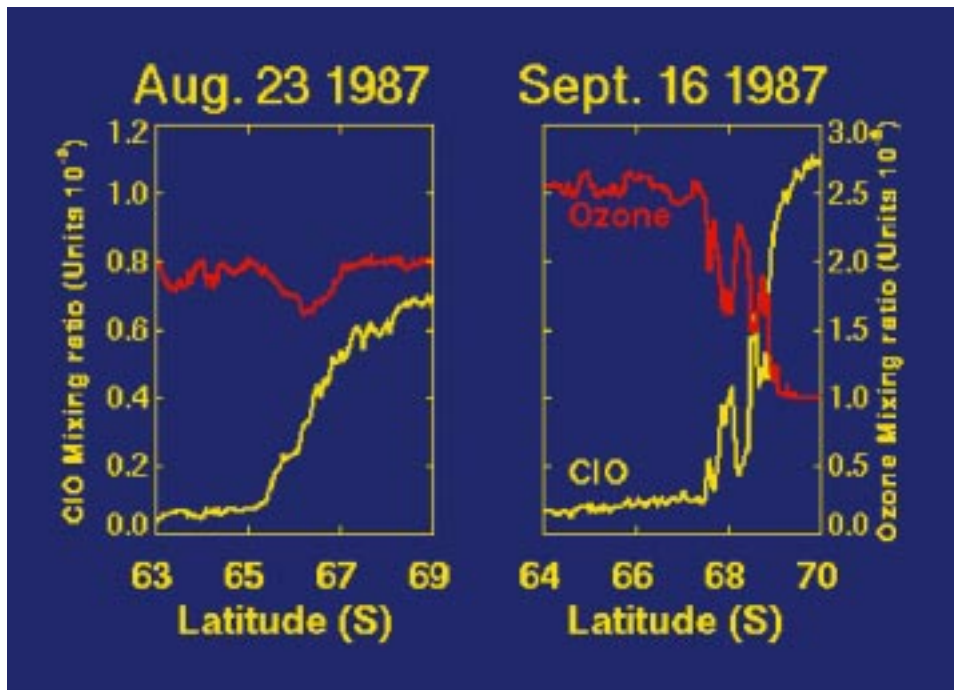
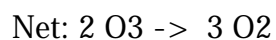
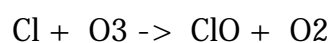
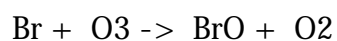
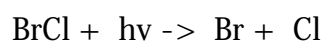
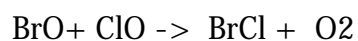
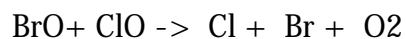


Figure IV.C.2

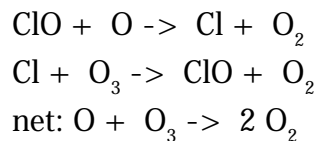
Figure IV.C.2 displays the observations of CIO from 2 aircraft flights during the AAOE mission. CIO concentrations are in excess of 1 ppbv at 70S on 16 September 1987 during the peak ozone loss period. Anderson et al. [89] calculated that the CIO-CIO reaction was responsible for approximately 40% of the ozone loss during the 1987 ozone hole period. Similar calculations by Salawitch et al. [93] show slightly more than 50% of the January 1992 northern polar ozone losses resulted from this same reaction.

A second reaction of nearly comparable effect to the CIO-CIO reaction is the BrO-CIO reaction [McElroy et al., 1986]. This catalytic reaction is:



Again, as with the ClO-ClO reaction, this BrO-ClO reaction does not require oxygen atoms. Anderson et al. [90] calculated that this reaction accounts for a loss rate that is about 50% smaller than the ClO-ClO reaction. Similar ozone loss rates are calculated by Salawitch et al. [1992] for the northern polar winter of 1992. While the BrO concentrations (nearly 2 orders of magnitude less than ClO) are much smaller than ClO concentrations, the BrO-ClO reaction rate is very large, yielding only slightly smaller ozone loss rates.

A third loss process is the conventional catalytic loss process of ClO with oxygen atoms via:



Calculations by Salawitch et al. [92] indicate that this process accounts for less than 15% of the total loss. Anderson et al. [1989] indicates that the ClO-O reaction is much less important than the ClO-ClO and ClO-BrO reactions, accounting for only 3% of the observed ozone loss.

D. TEMPORAL EVOLUTION OF OZONE AND OTHER TRACE GASES

Photochemical loss of ozone by catalytic reactions involving chlorine (discussed in section IV.C) involves two important components: 1) a change of chlorine from inactive so-called “reservoir” species (namely ClONO₂ and HCl) into active chlorine (Cl₂, ClO and its dimer Cl₂O₂) via heterogeneous processes (discussed in section IV.B), and 2) exposure to sunlight. These processes, which determine the location and timing of the ozone hole, are illustrated schematically in Fig. IV.D.1 (adapted from Webster et al., (1993)).

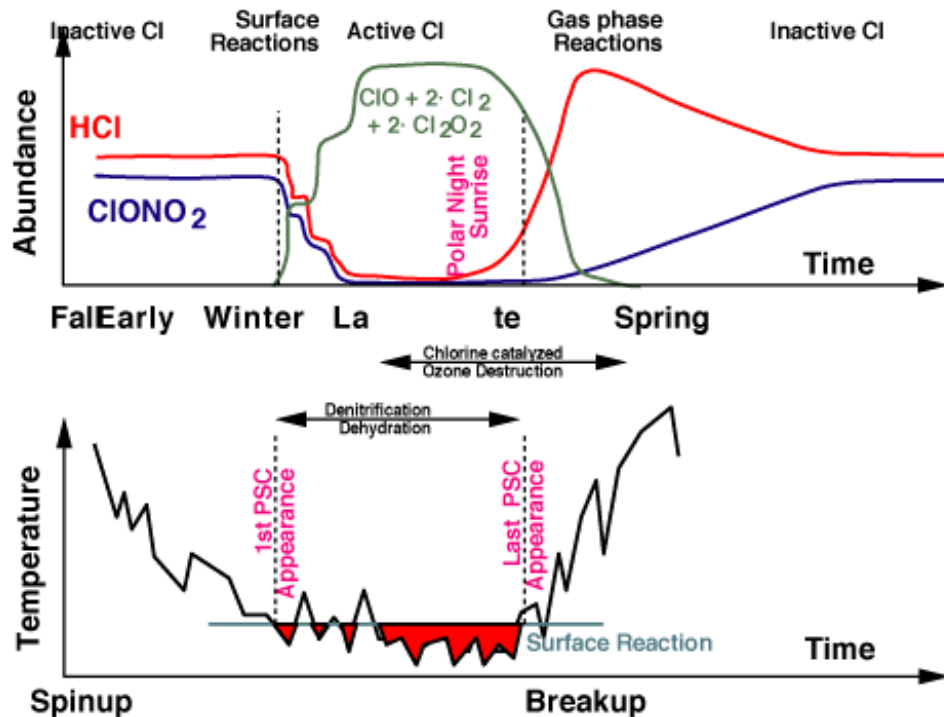
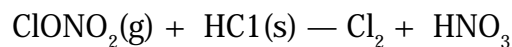


Figure IV.D.1

The key factor which occurs inside the SH polar vortex is the transformation from reservoir to reactive chlorine species via the heterogeneous processes. The principal heterogeneous reaction:



converts the relatively benign reservoir species ClONO₂ and HCl into Cl₂, which can then be photolyzed by visible wavelengths. The particles on which the heterogeneous reactions occur are sulfate aerosols or polar stratospheric clouds (discussed in section IV.A), which in turn form only at the very cold temperatures of the vortex interior (typically at temperatures below 195 K). By middle winter, most of the chlorine inside the vortex in the SH lower stratosphere is in the form of Cl₂, requiring only weak sunlight to initiate catalytic ozone loss.

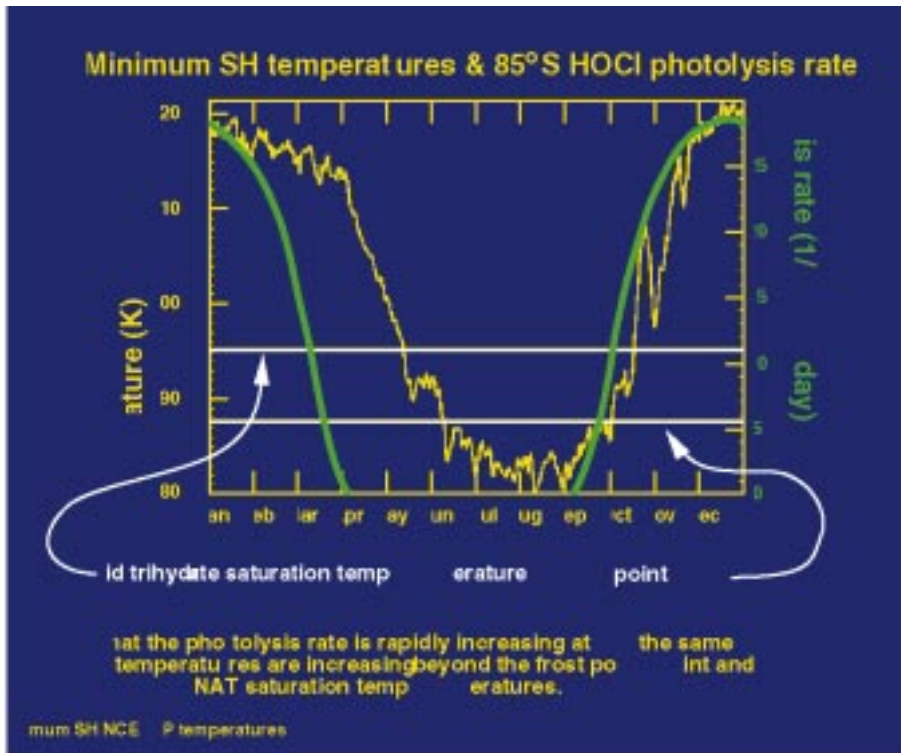


Figure IV.D.2

Figure IV.D.2 illustrates the return of sunlight which photolyzes HOCl and the disappearance of the cold temperatures. The cold temperatures over Antarctica result in the formation of PSCs, which in turn convert HCl and ClONO₂ into Cl₂ and HOCl. As the sun rises, the HOCl and Cl₂ are photolyzed, and initiate the catalytic reactions that destroy ozone.

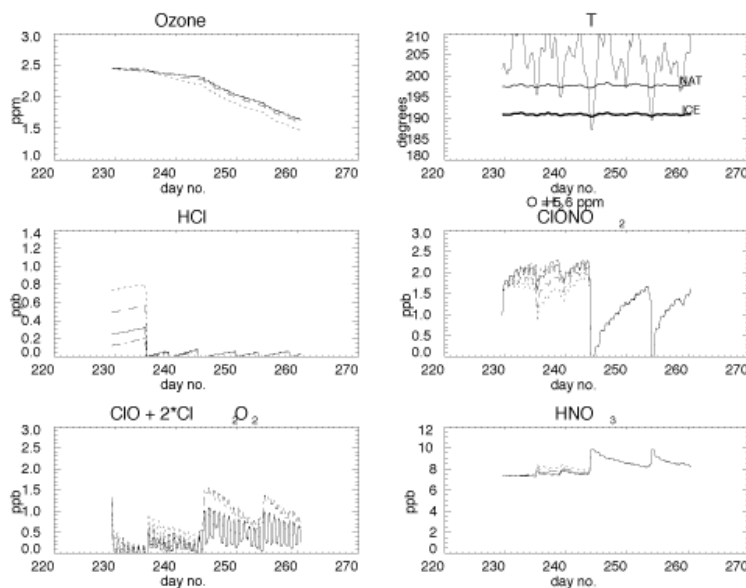


Figure IV.D.3

Figure IV.D.3 displays the chemical evolution of an air parcel just inside the Antarctic polar vortex from August 17 to September 17, 1992 as computed from a chemical trajectory model (adapted from Schoeberl et al., 1996). Over this 30 day period, the parcel loses approximately 30% of its ozone (top left panel). The parcel initially encounters temperatures below the nitric acid trihydrate equilibrium temperature (top right panel), leading to the formation of a PSC, and initiating the $\text{HCl} + \text{ClONO}_2$ heterogeneous reaction. Both HCl (middle left) rapidly decrease as this heterogeneous reactions convert HCl into Cl_x ($\text{ClO} + 2 \cdot \text{Cl}_2\text{O}_2$, bottom left). While HNO_3 (bottom right panel) is formed in this reaction, it is photolyzed into OH and NO_2 , and the NO_2 reacts with ClO to reform ClONO_2 . The $\text{ClONO}_2 + \text{H}_2\text{O}$ heterogeneous reaction is initiated on day 244 as the temperature falls below the frost point. This heterogeneous reaction converts all of the ClONO_2 into nitric acid, increasing the Cl_x dramatically, and accelerating the ozone loss process. This parcel evolution is generally consistent with observations of chlorine partitioning near the edge of the polar vortex. The differences between this parcel evolution and the evolution of a parcel deep within the vortex are: 1) most of the HNO_3 has been removed through denitrification as large PSCs settle out of the stratosphere, 2) most of the chlorine is in the form of Cl_x , since there is no HNO_3 to photolyze to reform ClONO_2 , and 3) ozone losses are larger, since Cl_x is quite large (more than 1ppb).

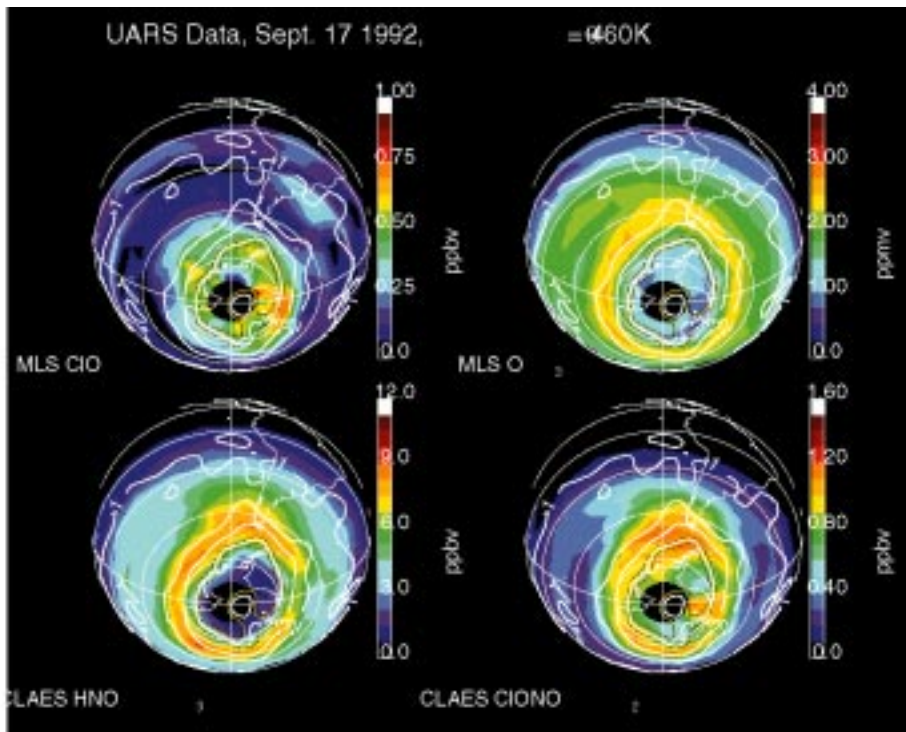


Figure IV.D.4

Figure IV.D.4 shows simultaneous UARS satellite observations of CIO (MLS), O_3 (MLS), HNO_3 (CLAES), and $ClONO_2$ (CLAES) on 17 September 1992 (xxxx).. These show strongly enhanced levels of CIO inside the SH polar vortex with concomitant levels of low $ClONO_2$. The spatial patterns of CIO are also clearly mirrored in the low ozone values. The SH polar vortex is also strongly denitrified, with virtually no HNO_3 (Douglass et al., 1995).

The evolution of chemical constituents in the ozone hole is illustrated using the global observations of the UARS satellite. As discussed in section II, downward transport of air from the upper and mid stratosphere will tend to increase values of ozone, HNO_3 , and $ClONO_2$ inside the polar vortex. Figure III.C.9 shows the increase of ozone inside the polar vortex which begins during the southern fall and into winter. Loss of ozone is apparent by late August, and has significantly reduced ozone by late September. Figure IV.D.5 shows the evolution of MLS observations of CIO over the same period.

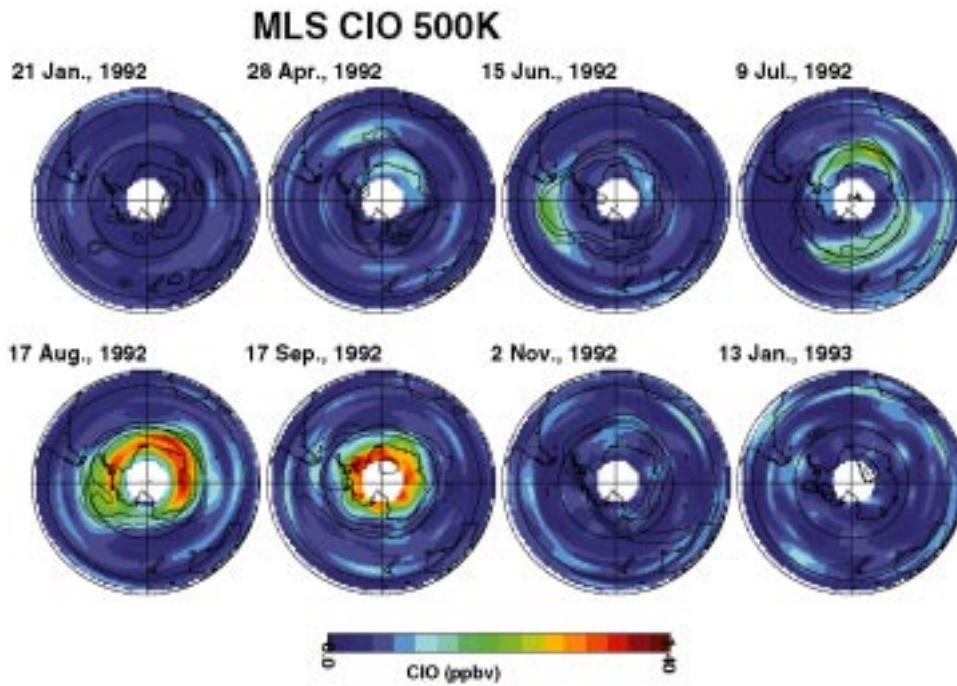


Figure IV.D.5

Peak values of CIO occur in the August-September period during the period of rapid ozone loss. These CIO values have decreased to background levels by early November. Midwinter values of CIO are reasonably large, but do not achieve the very large values since most of the chlorine is found in species such as Cl_2 , HCl, and Cl_2O_2 .

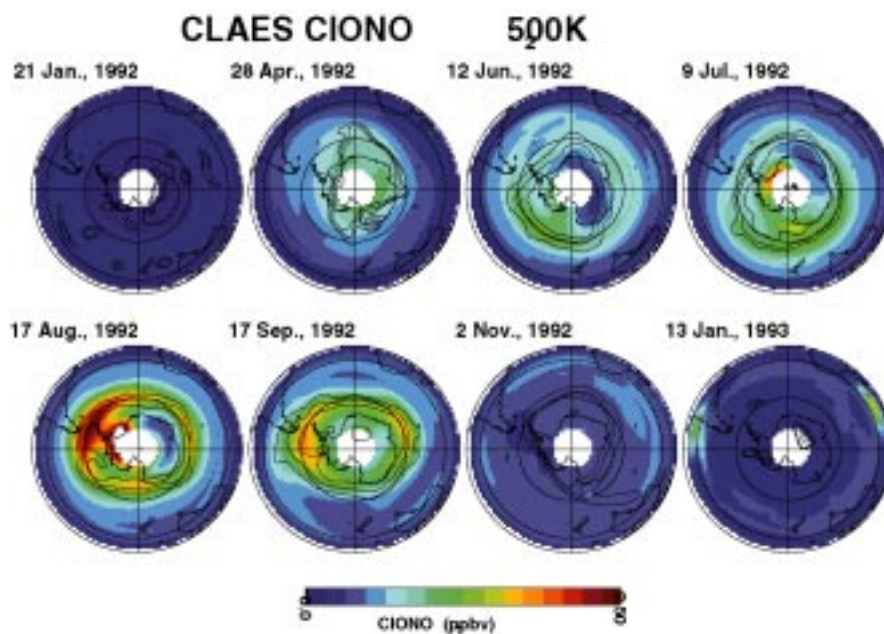


Figure IV.D.6

As discussed, the source of the ClO is from the reservoir species such as HCl and ClONO₂. Figure IV.D.6 displays the evolution of CLAES ClONO₂ observations over the course of 1992. Values of ClONO₂ are small in midsummer, and begin to increase in the fall. As temperatures decrease inside the polar vortex, PSCs form, and convert the chlorine in ClONO₂ into the reactive forms. Thus, large ClONO₂ deficits are observed inside the polar vortex during the July, August, and September periods. The ClONO₂ distributions also display large variability inside the polar vortex. An example of such variability is the large maximum of ClONO₂ near the Antarctic peninsula on 17 August 1992 in Figure IV. D.6. This maximum results from the reformation of ClONO₂ as HNO₃ is photolyzed and the photolysis product NO₂ reacts with the high values of ClO inside the polar vortex. Such behavior is evident in the trajectory calculation of Figure IV.D.3.

Heterogeneous reactions convert nitrogen from the reservoir species such as N₂O₅ and ClONO₂ into nitric acid, which remains on the PSCs, and subsequently sediments out of the stratosphere. Figure IV.D.7 displays the evolution of CLAES HNO₃ observations over the course of 1992.

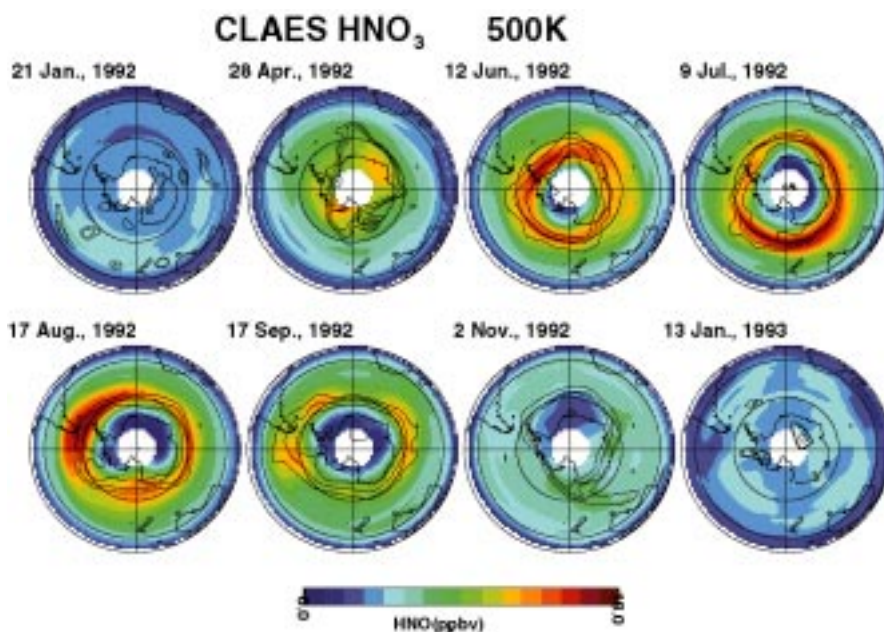


Figure IV.D.7

Values of HNO_3 are small in midsummer, and begin to increase in the fall because of the downward transport of higher concentrations of HNO_3 into the lower stratosphere. As temperatures decrease inside the polar vortex, PSCs form, and convert the nitrogen in ClONO_2 and N_2O_5 into HNO_3 , which remains on the PSC. As the temperatures continue to cool, large ice particles form and fall, removing the HNO_3 . By midwinter, a substantial fraction of the HNO_3 has been removed from the polar vortex, with relatively higher concentrations in the vortex collar. As noted in the previous paragraph, the photolysis of HNO_3 into OH and NO_2 will decrease the concentrations of ClO . The maximum of ClONO_2 near the Antarctic peninsula on 17 August 1992 in Figure IV. D.6 is related to the maximum of HNO_3 in Figure IV.D.7. The HNO_3 photolysis product NO_2 reacts with the high values of ClO inside the polar vortex creating the ClONO_2 maximum in Fig. IV.D.6. The values of HNO_3 inside the polar vortex remain low into November.

The necessary conditions for the formation of the ozone hole are: 1) temperatures cold enough to form PSCs, 2) vortex isolation, 3) persistence of cold temperatures late into spring, or complete denitrification, and 4) sufficient levels of chlorine. Figure IV.D.8 summarizes the main elements of the theory.



Figure IV.D.8

The main elements are: a) HCl and ClONO₂ react on PSCs to form Cl₂, b) the Cl₂ is degassed from the PSC while HNO₃ remains on the PSC, c) the Cl₂ is photolyzed, d) the Cl then destroys ozone primarily via the ClO-ClO and ClO-BrO reactions. Without the first necessary condition, the reservoir chlorine species cannot be converted to reactive forms. Because midlatitude air contains high concentrations of NO and NO₂, the vortex isolation prevents this nitrogen from reacting with the ClO, interfering with the catalytic loss process. The third condition is that there must be a small amount of sunlight to drive the catalytic loss process. Finally, without sufficient chlorine, the ozone loss is too small.

The ozone hole is a clear example of how observations, laboratory work, and theory can interact to determine the causes of a phenomena. Initially, observations defined the issue of the ozone hole. A large amount of time and effort was expended determining the precision and accuracy of observations conducted from the 1940's to the present. Hypotheses of the cause were quickly put together, which were tested via continued observational programs, and via ground-based, aircraft, and satellite measurements. The laboratory work determined key reactions, and established probabilities of gas reactions with particles. These lab observations were then combined with meteorological observations to produce simulations of the ozone hole.

The ozone hole conditions over Antarctica are now well understood. Both historical observations and current observations give atmospheric scientists exceptional confidence in descriptions and evaluation of Antarctic stratospheric conditions. Details of transport, kinetics, chemistry, and particle physics continue to refine our understanding of the ozone hole. The future holds the promise that the ozone hole will disappear sometime in the middle of the next century as chlorine concentrations decrease.