# Stratospheric ozone depletion (Solomon 1999)

**CHAPMAN REACTIONS**

$O_2 + h\nu \rightarrow O + O$;   $O + O_2 \rightarrow O_3$;   $O_3 + h\nu \rightarrow O_2 + O$;   $O + O_2 \rightarrow O_3$
$O + O_3 \rightarrow O_2 + O_2$

**CFC REACTIONS**

1) CFC + $h\nu \rightarrow Cl + ClO$
2) $Cl + H \rightarrow HCl$
   $ClO + NO_2 \rightarrow ClONO_2$  (2 & 3)
3) $HCl + ClONO_2 \rightarrow HNO_3 + Cl_2$ (reaction happens on PSCs)
4) $Cl_2 + h\nu \rightarrow 2Cl$

**CATALYTIC (CHAIN) REACTIONS**

$Cl + O_3 \rightarrow ClO + O_2$;   $O_3 + h\nu \rightarrow O_2 + O$;   $ClO + O \rightarrow Cl + O_2$
Net result: $2O_3 + h\nu \rightarrow 3O_2$
$ClO + ClO + M \rightarrow Cl_2O_2 + M$
$Cl_2O_2 + h\nu \rightarrow Cl + ClO_2$
$ClO_2 + M \rightarrow Cl + O_2 + M$
Net cycle: $2O_3 \rightarrow 3O_2$

**GAS PHASE CHEMISTRY**

CFCs:
- inert; insoluble => can't be washed out by precip.
- Entry point s thie tropics:  go from troposphere to strat
- Eventually, they wash out as HCl, which is solluble

**Chlorine partioning**

| Active | Reservoir |
|---|---|
| Cl | HCl |
| ClO | $ClONO_2$ |

⇒ Without PSCs - Active = ~ 1%;)     (Most chlorine is in res. )
⇒ With PSCs, potentially 'active' chlorine increased by a factor of 100, almost all of the chlorine from the inert reservoirs, HCl & $ClONO_2$, has been preactivated into $CL_2$ gas. With the first sunlight in spring, the $CL_2$ is fully activated into CL and ClO by means of solar dissociation.  {See graph from 1 page summary}                          .

**Vertical distribution**
- greatest amount of Cl is found ~ 40km
- Greatest $O_3$ depl occurs ~ 20km

**Heterogenous Chemistry**

Chemistry takes place on surfaces.  Stratospheric Aerosols: Liquid particles – 75% Sulfuric Acid ($H_2SO_4$), 25% H20 Sources: Volcanic eruptions, Aircraft emittance: $NO_x$, $CO_2$, $H_2O$ vapor, sulfur compounds, soot.

Res species will react on sfc, molec chlorine (Cl2) will be released.  It will only get decomposed later from UV, then get chain reaction.
Requirements for rapid $O_3$ loss:
1) Heterogeneous 'activation' of chlorine from HCl & ClO $NO_2$ reservoirs
2) Suppression of $NO_2$ (essential element in keeping the chlorine active.

**POLAR VORTEX/JET**
- unique winter circulation, compl isolated from mid-lats
- results from polar cooling & coriolis; edge is ~ 64°S
- When sun goes behind the horizon in the polar regions (fall), solar radiation does not exist.
- LW rad comes from $CO_2$ & $H_2O$, (Stratosphere has little $H_2O$, so most from $CO_2$)
- Result: lose heat, strat *T* decr, as winter comes.
- Strong *T* & *p* gradients
- When vortex breaks, $O_3$ replenishes

Arctic:
- Rossby waves (from mountains etc) penetrate & disturbs the vortex ⇒ vortex is not as well developed or stable.
- ~ 10° warmer than Antarctic

Antarctic
- Colder than NH
- Vortex is more stable, colder

**POLAR STRATOSPHERIC CLOUDS (PSCs)**
- PSCs are the medium on which reservoir chlorine compounds are converted into ozone-destroying chlorine radicals.
- Temp plays a major role in their development; form:12–25km
- Type 1: (195K) mixture of $H_2O$, $H_2SO_4$ , $HNO_3$
  NAT – Nitirc Acid Trihydrate $HNO_3$ + $3(H_2O)$
  - 1a non-spherical & crystalline particles (reflect highly depolarized signal)
  - 1b Spherical & liquid (reflect a virtually unchanged polarization)
- Type 2 (188K) water ice crystals

If the crystals are big, they will leave the atm ⇒ denitrification & dehydration.
- The normally inert reservoir chlorine compounds ($ClONO_2$ and Hcl) can react on the surfaces of the PSC ice particles:

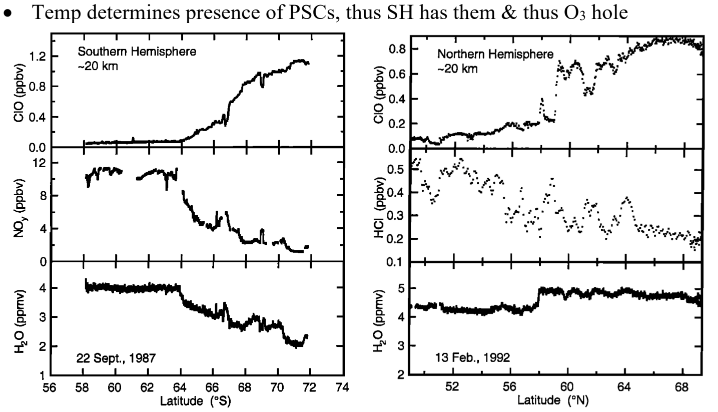
**Denoxification**
- Removal of various N species (gaseous Nitrogen Oxides Nox) to $HNO_3$ ($HNO_3$ is a component of type 1 PSC).  This occurs on PSCs.  It is removing N which would otherwise form the inert reservoir.  Imp in $O_3$ depl. Upsetting the balance
- N can be released when PSCs evaporate.
- The overall effect is a net removal of $NO_2$.  This is significant because ClO is an important catalyst in the destruction of Ozone, but is itself removed by the reaction: $ClO + NO_2 + M \rightarrow ClONO_2 + M$. Thus a decrease in the levels of $NO_2$ helps maintain large levels of ozone-destroying ClO.
- As the clouds grow, they begin to settle out of the stratosphere, taking the Nitric Acid with them.  This removal of nitrogen compunds is termed "denitrification".  It further encourages denoxification.

**Denitrification**
- If PSC particles grow large enough for sedimentation ⇒ N is taken from higher altitude to lower.  Ex: particle size 9.5 micron will fall from 20km to 10km in 1 week.

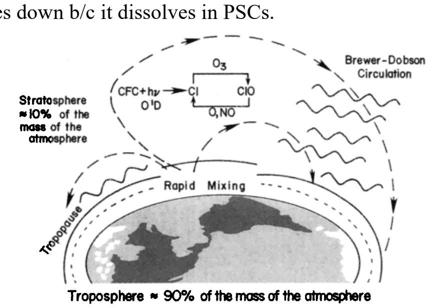
**Dehydration**
- Sedimentation of ice particles.  N species will come out.

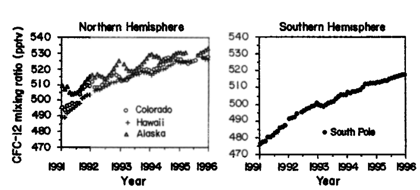
**Arctic**
- Less ozone depletion than in SH.  No ozone hole.
- Explanation is climatological: T is 10° warmer than in SH, therefore do not get PSCs.  Occasionally NH is very cold, then you get a high % of PSCs, though they may not be there for an extended period of time.  They need to be there for an extended period (ie. whole winter) to form a hole.

**Antarctica**
- Temp determines presence of PSCs, thus SH has them & thus $O_3$ hole




- SH: $NO_x$ & $H_2O$ decrease b/c they are tied to PSCs.  $H_2O$ b/c it is inside PSCs
- SH: $O_3$ curve is similar to, but just above $NO_x$ & $H_2O$
- NH: HCl goes down b/c it dissolves in PSCs.



P. 282: "The latitudinal gradients in Antarctic ozone depletion are related to the dynamical structure of the polar winter stratosphere, whose circulation can be viewed as a vortex. Briefly, the absence of solar illumination in high-latitude winter leads to a cooling over the poles and hence a large temp gradient near the polar terminator. This thermal gradient implies rapid zonal (E-W) flow characterizing the 'jet' at the edge of the vortex, while the air within the vortex is relatively isolated in comparison with surrounding mid-latitude regions, allowing deep depletion to develop. Differences in the pre-1970's ozone abundances in the 2 ploar votices are related to differences in atmospheric waves and circulation patterns, which are in turn driven by factors relating to surface topography (e.g., distribution of mountains, oceans, and continents). In brief, the north polar vortex is generally more disturbed by atmospheric waves forced from beneath by flow over a more variable surface topography. These lead to greater mixing and faster downward motion, which both increases the natural wintertime Arctic ozone abundances (by bringing down ozone-rich air from above) and warms the lower stratosphere (through adiabatic compression). Temperatures in the Antarctic vortex are both colder and less variable than those of the Arctic, which strongly influences the polar ozone depletion in the two hemispheres "

**Ozone summary**

1) Over decades, CFCs accumulate in the global troposphere and are slowly carried into the stratosphere.
2) Under illumination by UV solar radiation above roughly 20-30km, CFCs are decomposed into Chlorine atoms (Cl) & Chlorine monoxide (ClO)
3) The free chlorine partitions itself through normal chemical processes primarily into hydrogen chloride (HCl) and chlorine nitrate (ClONO2), with only a small fraction ~1% remaining in the catalytically active forms, Cl and ClO
4) In early winter, the Polar Stratospheric Vortex (PSV) winds up as the sun drops down below the horizon & the stratosphere cools strongly.
5) The vortex entraps ozone & the partitioned chlorine species, & isolates them from the rest of the atmosphere.
6) The dark isolated vortex continues to cool by radiating the residual heat into space as IR radiation. This further strengthens the vortex and seals its walls to form a containment vessel.
7) As the vortex air cools below 195K, Type-1 PSCs begin to condense from the nitric acid vapor trapped in the vortex.
8) The inert chlorine reservoir species HCl and $ClONO_2$ stick to and react on the Type-1 PSC ice surfaces & are converted to molecular chlorine ($Cl_2$) gas.
9) If temperatures drop below about 185-190K, Type 2 PSCs begin to form, leading to "denitrification" of the lower stratosphere.
10) The “heterogeneous” chemical processing continues throughout the winter, during which the inert chlorine reservoirs are larglely converted to “preactivated” molecular chlorine vapor, and nitrogen oxides are removed.
11) When sunlight first returns to the Polar vortex in early spring, the molecular chlorine is photodissociated and fully activated into Cl and ClO.
12) The extraordinarily high concentrations of active chlorine in the form of ClO (~ 100 times the normal abundance) rapidly destroys ozone through halogen catalytic reaction cycles, which are accelerated by the formation of the chlorine monoxide dimer ($Cl_2O_2$) and the presence of bromine monoxide. Chlorine monoxide dimer (Cl2O2) is more reactive than ClO.
13) Local Ozone concentrations decrease in a matter of weeks by 90 % or more at some altitudes, with the amount of total column ozone decreasing to less than half its initial value.
14) As time progresses, the polar vortex begins to warm up, becoming less stable and starting to leak as it slows down; the vortex may collapse in a final ‘warming’ event
15) During the period of vortex breakdown, ozone-rich stratospheric air is transported from the mid-latitudes into the polar region, and the ozone hole rapidly ‘fills in’; nitrogen oxides & nitirc acid also are replenished
16) During late spring & summer, the normal chemical composition of the stratosphere is reestablished, and the polar region becomes primed for the next ozone hole.

**Mid-latitudes –** General downward trend
NH winter/spring: ~ 4% $O_3$ decrease
NH summer/fall: ~ 2% $O_3$ decrease
SH all seasons: ~ 6% $O_3$ decrease

**GLOBAL WARMING**

- An increase in GHGs ⇒ more $CO_2$ in strat
- $CO_2$ is gas which cools the strat & thus vortex. It radiates & cools strat
- $CO_2$ warms troposphere , but cools the stratosphere.
- Increase $CO_2$ ⇒ cold T in vortex
- Cold T ⇒ more PSCs ⇒ more $O_3$ depletion.

**Active chlorine:** chlorine compounds that destroy ozone and interchange rapidly with one another in the sunlit atmosphere (mainly Cl, ClO, Cl2O2, OclO, and HOCl); chlorine that is not tied up in the reservoir gases (HCl and ClONO2).
**Chlorine loading:** Abundance of total chlorine in all forms (including CFCs) at a given location.

**Chlorofluorocarbons (CFCs)**: Chemicals, used in a variety of industrial applications, that are the dominant source of chlorine to the present-day stratosphere.

**Cly:** The sum of all chlorine gases liberated by decomposition of CFCs, including Cl, ClO, Hcl, ClONO2, HOCl, Cl2O2, and other trace species. **ClO dimer:** Cl2O2, a key intermediate in the formation of the Antarctic ozone hole. See the catalytic cycle involving this gas illustrated in Table 1. **Denitrification:** Removal of reactive nitrogen (NOy) from the stratosphere through sedimentation of large particles containing nitric acid. **Dehydration:** Removal of water vapor from the stratosphere through sedimentation of large particles containing water.

**Dobson Unit (DU):** Unit of measurement of total ozone column abundance, named for G. M. B. Dobson, a pioneer in measurement of ozone. One Dobson unit corresponds to 2.6 3 1016 molecules cm22 of total overhead column ozone.

**Frost point:** The temperature at which water condenses to form solid ice.
**NAT**: Nitric acid trihydrate, or HNO3 z (H2O)3). Some polar stratospheric clouds are probably composed of solid NAT particles.

**Nox**: NO 1 NO2, two reactive forms of nitrogen that interchange very rapidly with each other in the sunlit atmosphere. The amount of Nox is linked to NO2 and hence to formation of the ClONO2 reservoir.
**Noy**: The sum of the relatively reactive total nitrogen gases, including N, NO, NO2, ClONO2, NO3, N2O5, BrONO2, HNO3, and other trace species.

**Ozone hole**: Widespread removal of total ozone in Antarctic spring. The hole is reflected in both the steep latitudinal gradients in the observed ozone depletion and in its temporal evolution since the mid-1970s.

**Partitioning**: Distribution of chlorine between active compounds that destroy ozone and reservoirs that are inert toward ozone.
**Ppbv, pptv:** Parts per billion by volume or parts per trillion by volume, indicating relative abundance of a given gas (i.e., 1 ppbv 5 1 molecule per billion total air molecules).
**Processing**: General term describing conversion of chlorine to active forms. Chemical processing refers to in situ chemistry. Vortex processing refers to flow of air to midlatitudes from the vortex, while PSC processing refers to flow of air through PSCs associated with locally cold temperatures.

**Polar stratospheric clouds (PSCs):** Clouds that are observed to form at cold temperatures (below 200 K) in the polar stratospheres of both hemispheres.
**Reservoir**: Long-lived compound capable of storing Nox or active chlorine in a relatively inert form (mainly HNO3, Hcl, and ClONO2).

**Stratosphere**: The region of the atmosphere between 12 and 50 km (a few kilometers lower in polar regions and higher in the tropics) in which heating by ozone leads to increasing temperatures with increasing altitude.
**Sulfuric acid tetrahydrate (SAT)**: A solid form of sulfuric acid and water that can form under certain thermodynamic conditions.
**Tracer**: Long-lived chemical compound that can be used to trace the atmospheric airflow.

**Tropopause**: The transition region, in which temperatures reach a minimum, between the troposphere and stratosphere.
**Troposphere**: The region of the atmosphere between the surface and the stratosphere, in which temperatures decrease with increasing altitude.
**Type 1:** Polar stratospheric clouds that form at temperatures above the frost point.
**Type 1a (1b):** Solid (liquid) polar stratospheric clouds at temperatures above the frost point.
**Type 2**: Solid water ice polar stratospheric clouds that form when temperatures drop below the frost point.

**Vortex**: Dynamical structure of the stratosphere in polar winter caused by the absence of solar illumination, which leads to a cooling over the poles and a large temperature gradient relative to midlatitudes. This temperature gradient implies rapid zonal (east-west) flow characterizing the "jet" at the edge of the vortex, while the air within the vortex is relatively isolated in comparison with surrounding regions.

**References**

Solomon, S. 1999: Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.,* **37**, 275–316.