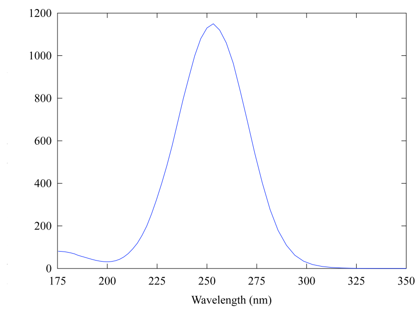
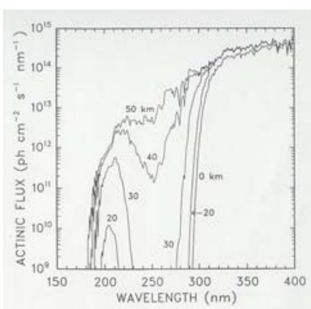
Role of Stratospheric Ozone

- Ozone strongly absorbs light in the wavelength range 220 – 300 nm (ultraviolet C region).
- Light of these wavelengths has sufficient energy to break chemical bonds ⇒ leads to chemical changes in cell tissues of living organisms.
- Consequences include: cancer, reduced functionality, decreased fertility, ….

Ozone Absorption Spectrum



Solar Intensity as a Function of Altitude



Formation of Stratospheric Ozone

- Ozone is formed after O_2 absorbs UV light (λ < 220 nm) and dissociates to form oxygen atoms:

  O_2 + sunlight (λ < 220 nm) → 2 O

- Atomic oxygen combines with molecular oxygen to for ozone:

  $O + O_2 \rightarrow O_3$

Formation of Stratospheric Ozone

- The rate of ozone formation reaches a maximum in the stratosphere at an altitude of between 25 and 30 km.
- The rate of O_3 formation is a balance between UV light available, filtering of UV light by O_3, and loss through chemical reactions.

Natural Ozone Loss Processes

- Ozone reacts via one of several mechanism to form molecular oxygen:

  Homogeneous chemistry:

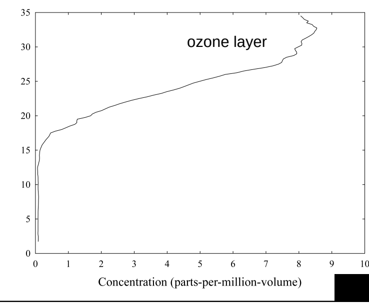
  $O + O_3 \rightarrow 2\ O_2$ slow

Natural Ozone Loss Processes

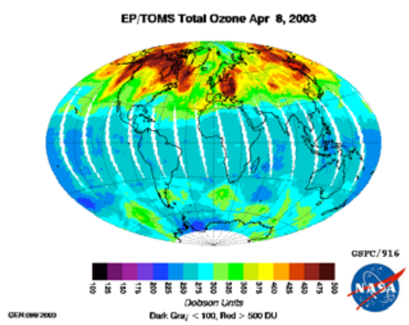
Catalytic cycles:

	$NO + O_3 \rightarrow NO_2 + O_2$	moderate
	$O + NO_2 \rightarrow NO + O_2$	fast
net:	$O + O_3 \rightarrow 2\ O_2$	
	$OH + O_3 \rightarrow HO_2 + O_2$	moderate
	$O + HO_2 \rightarrow OH + O_2$	fast
net:	$O + O_3 \rightarrow 2\ O_2$	

O_3 Concentration *vs* Altitude—July 27, 2000: Boulder, CO



Typical Global Ozone Map



Anthropogenic Species Affecting Stratospheric Ozone

- Chlorofluorocarbons (CFC's) are chemical compounds that contain carbon, chlorine, and fluorine atoms. Examples:
  CFC-12: CCl_2F_2 CFC-22: $CHClF_2$
  CFC-23: CHF_3 CFC-114: $CClF_2CClF_2$
- Halons are chemical compounds that contain carbon, bromine, and/or chlorine and fluorine atoms. Examples:
  Halon-1211: $CBrClF_2$ Halon-1301: $CBrF_3$

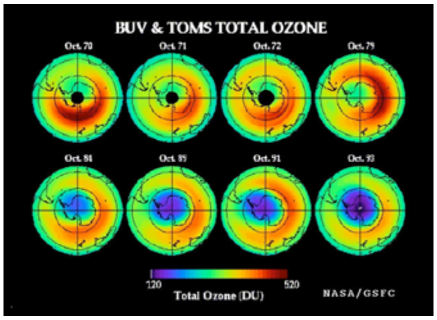
Anthropogenic Species Affecting Stratospheric Ozone

- Properties of these compounds:
  - Unreactive, particularly to tropospheric oxidants (OH, NO_3)
  - Only absorb light in UV C spectral region
- These species are transported to the equator and through the tropopause into the stratosphere intact. There they diffuse above the ozone layer, absorb sunlight, and dissociate, releasing chlorine or bromine atoms.

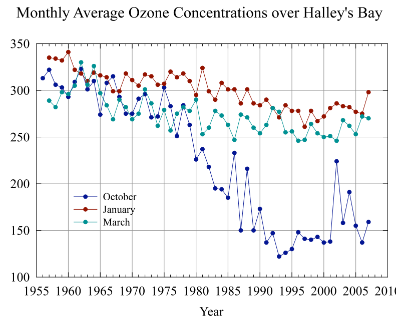
The Antarctic Ozone Hole

- In the early 80's, measurements of ozone over Antarctica showed a significant decrease in the total column ozone during the Austral spring. The effect lasted from mid-September to late November at which time the ozone "hole" recovered and concentrations returned to normal values.

Monthly Average Antarctic Ozone



Average October O_3 Concentration Over Halley's Bay



The Antarctic Ozone Hole

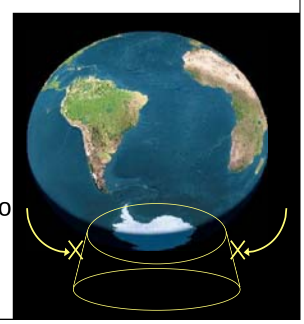
- Unique Properties of the Polar Stratosphere:

  1. There is no sunlight during the Antarctic winter—no photochemistry can occur.

The Antarctic Ozone Hole

- Unique Properties of the Antarctic Stratosphere:

  2. Strong polar vortex forms each winter—isolates air within vortex with no fresh air input from lower latitudes.



The Antarctic Ozone Hole

- Unique Properties of the Antarctic Stratosphere:

  3. The Antarctic stratosphere is very cold —10 – 20 K colder than Arctic stratosphere —this allows the formation of polar stratospheric clouds (PSC's).
     - pure water ice crystals
     - nitric acid trihydrate (NAT) ($HNO_3 \cdot 3H_2O$)

Chemistry of the Ozone Hole

- The following chemical reactions occur within the polar vortex over Antarctica:

  $Cl + O_3 \rightarrow ClO + O_2$ very fast

  $ClO + ClO \rightarrow ClOOCl$
- ClOOCl is relatively stable at the low temperatures of the southern stratosphere.
- The concentration of ClOOCl builds up during the Austral winter until mid-September.

Chemistry of the Ozone Hole

- ClOOCl strongly absorb UV B/C sunlight and dissociates:

  ClOOCl + sunlight → ClOO + Cl

  ClOO → Cl + O_2

  2 x Cl + O_3 → ClO + O_2

The net results of these reaction is:

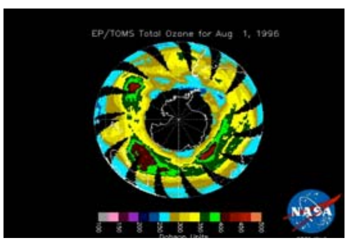
  2 O_3 → 3 O_2

  and chlorine is free to repeat the cycle.

Formation of Antarctic Ozone Hole

- When the sun rises over Antarctica in mid-September, photolysis of ClOOCl begins, and the stratosphere is flooded with a rush of chlorine atoms which deplete the ozone and form the ozone hole.
- This catalytic cycle continues to destroy ozone until the polar vortex breaks apart in late November, and the polar stratosphere is replenished with ozone from lower latitudes.

Development of 1996 Ozone Hole



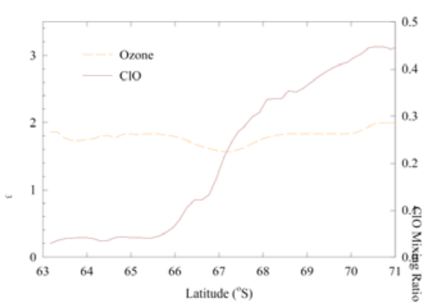
ER-2 Stratospheric Research Platform

NASA Dryden Flight Research Center Photo Collection
http://www.dfrc.nasa.gov/gallery/photo/index.html
NASA Photo: EC99-45225-1 Date: October 1999 Photo by: Jim Ross
Lockheed ER-2 #809 high altitude research aircraft in flight

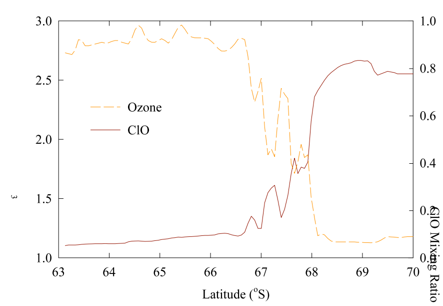
ER-2 carries a suite of 15 instruments to measure concentrations of various atmospheric species.

ER-2 flies at a maximum altitude of 18 km (lower stratosphere).

O_3 and ClO Across Polar Vortex Boundary—August, 1987



O_3 and ClO Across Polar Vortex Boundary—September, 1987



Influence of PSC's on Ozone Hole

- During the late 80s and early 90s, the chemistry was thought to be understood—models fairly accurately predicted Antacritic ozone concentrations
- However, following eruption of Mt. Pinatubo in 1991, subsequent ozone holes were much deeper than expected
  - Lead to realization of impact heterogenous chemistry on ozone depletion

Influence of PSC's on Ozone Hole

- Chemical reactions occuring on PSC's:

$ClONO_2(g) + HCl(s) \rightarrow Cl_2(g) + HNO_3(s)$

$k_{gas\ phase} < 2 \times 10^{-20}$

$\gamma = 0.3$ water ice

$\gamma = 0.3$ NAT

$\gamma = 0.3$ $H_2SO_4/H_2O/HNO_3$

$Cl_2 + h\nu \rightarrow 2\ Cl$

Influence of PSC's on Ozone Hole

- Chemical reactions occuring on PSC's:

$ClONO_2(g) + H_2O(s) \rightarrow HOCl(g) + HNO_3(s)$

$k_{gas\ phase} < 5 \times 10^{-21}$

$\gamma = 0.3$ water ice

$\gamma = 0.006$ NAT

$\gamma = 0.05$ $H_2SO_4/H_2O/HNO_3$

$HOCl + h\nu \rightarrow OH + Cl$

Influence of PSC's on Ozone Hole

- Chemical reactions occuring on PSC's:

$N_2O_5(g) + HCl(s) \rightarrow ClNO_2(g) + HNO_3(s)$

$k_{gas\ phase} < 8 \times 10^{-21}$

$\gamma = 0.03$ water ice

$\gamma = 0.003$ NAT

$\gamma = ?$ $H_2SO_4/H_2O/HNO_3$

$ClNO_2 + h\nu \rightarrow Cl + NO_2$

$\rightarrow ClO + NO$

Influence of PSC's on Ozone Hole

- Chemical reactions occuring on PSC's:

$HOCl(g) + HCl(s) \rightarrow Cl_2(g) + H_2O(s)$

$k_{gas\ phase}$ no information

$\gamma = 0.3$ water ice

$\gamma = 0.1$ NAT

$\gamma = 0.1 – 0.5$ $H_2SO_4/H_2O/HNO_3$

$Cl_2 + h\nu \rightarrow 2\ Cl$

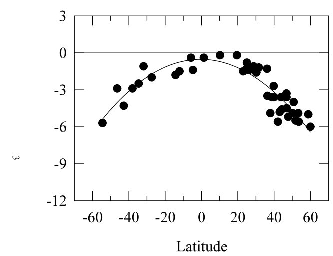
Influence of PSC's on Ozone Hole

- The full impact of PSC's on ozone loss was not understood until after the eruption of Mt. Pinatubo in June, 1991.
- The eruption was so violent that it injected ash, soot, and sulfur-containing compounds directly into the stratosphere. This lead to deeper ozone holes over Antarctica than expected which ultimately resulted in the study of the impact of aerosols on stratospheric ozone.

What has been done to correct ozone hole formation?

- Montreal Protocol (1987)—original treaty called for a freeze on production of CFC's at 1989 levels with phase-out by 2000. Other ozone depleting substances had longer time schedules for phase-out. Developing countries were given a ten-year lag time for implementation of the Montreal Protocol.

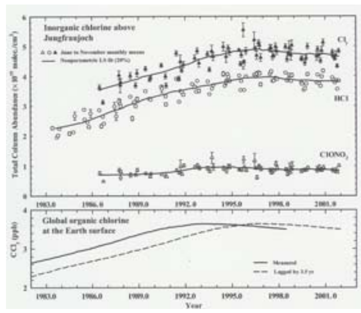
Trend of Ozone Loss per Decade: 1979 - 1994



What has been done to correct ozone hole formation?

- Copenhagen (1992)—based on new, more extensive measurements of global ozone concentrations, the phase-out of CFC's was accelerated to Jan. 1, 1996 and halon phase-out by 2000.

Total Atmospheric Chlorine Concentration



Conclusions

- The Ozone Hole over Antarctica, discovered in the early 80's, is the result of increased chlorine and bromine in the stratosphere from anthropogenic sources.
- Concentrations of atmospheric chlorine peaked in the late 90's and are beginning to decrease.

Conclusions

- If the conventions for elimination of ozone depleting substances outlined in the Montreal Protocol are followed, chemical models predict that stratospheric ozone concentrations will return to pre-1970 levels by middle of this century.