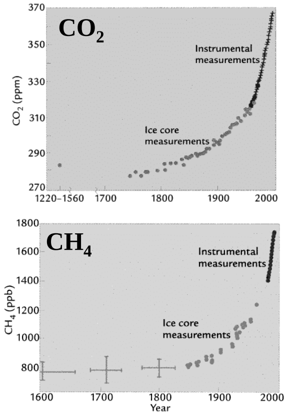
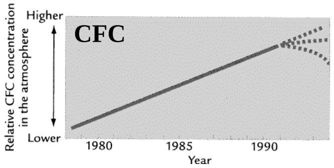
Anthropogenic Climate Changes

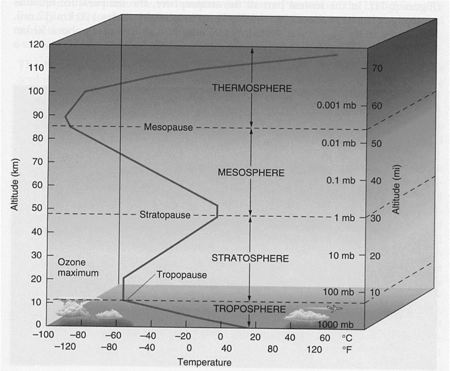




- ☐ Human production of freons (CFCs) ➔ Ozone Hole Depletion
- ☐ Human production of CO2 and CH4 ➔ Global Warming
- ☐ Human change of land use ➔ Deforestation

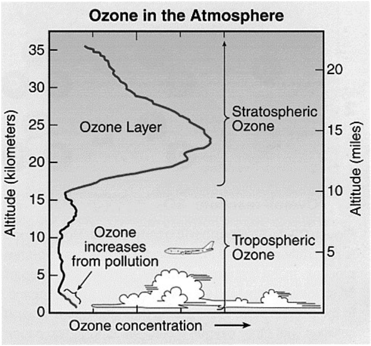
(from *Earth's Climate: Past and Future*)

Standard Atmosphere



(from *Understanding Weather & Climate*)

Measurements of Ozone



(from WMO Report 2003)

(1) Number Density

Number of molecules per cubic centimeter (molecules/cm^3).

The number density is typically about 5x10^{12} molecules/cm^3 near 20 to 25 km altitude, near the peak of ozone concentration in the stratosphere.

(2) Layer Thickness

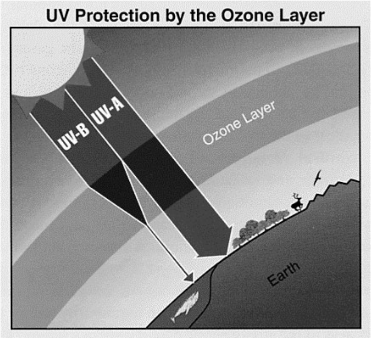
The thickness of pure ozone would have at 1 atm pressure.

One atmosphere-centimeter (1 atm-cm) is equal to 2.687x10^{19} molecules/cm^2.

One Dobson Unit (DU) is equivalent to a layer of pure ozone 0.001 cm thick at 1 atm pressure.

A typical midlatitude ozone column depth is about 300 DU (0.3 atm-cm).

Why is Ozone Important?



(from *WMO Report 2003*)

- ☐ The stratospheric ozone layer reduces the amount of UV-B radiation from the sun reaching Earth's surface.
- ☐ UV-B exposure can damage human's immune system, increase risk of skin cancer, and damage terrestrial plant life, single-cell organisms, and aquatic ecosystem.

How Is Ozone Formed?

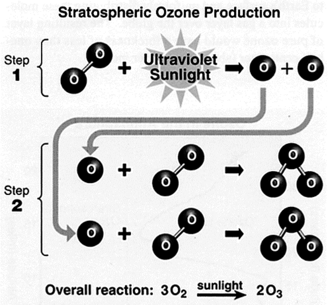
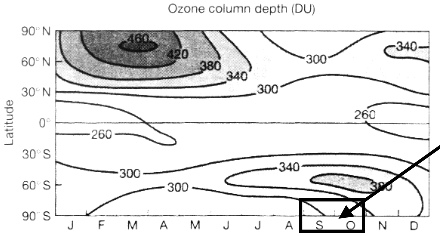


Figure Q2-1. Stratospheric ozone production. Ozone is naturally produced in the stratosphere in a two-step process. In the first step, ultraviolet sunlight breaks apart an oxygen molecule to form two separate oxygen atoms. In the second step, these atoms then undergo a binding collision with other oxygen molecules to form two ozone molecules. In the overall process, three oxygen molecules react to form two ozone molecules.

(from *WMO Report 2003*)

Ozone Distribution

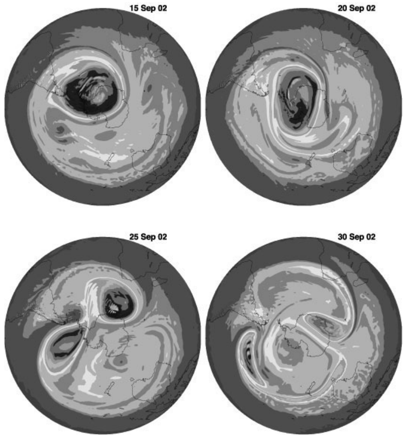


Antarctic Ozone Hole

(from *The Earth System*)

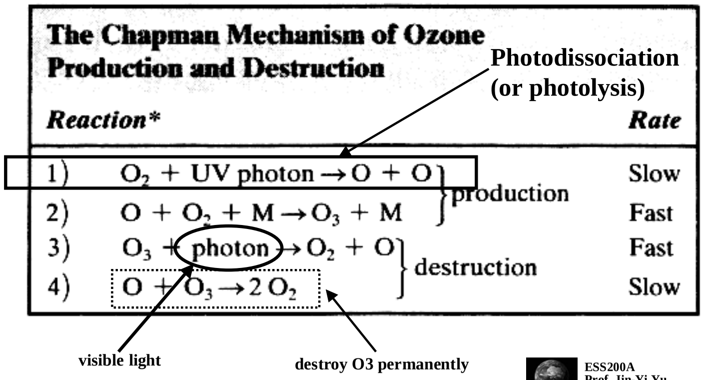
- ☐ The greatest production of ozone occurs in the tropics, where the solar UV flux is the highest.
- ☐ However, the general circulation in the stratosphere transport ozone-rich air from the tropical upper stratosphere to mid-to-high latitudes.
- ☐ Ozone column depths are highest during springtime at mid-to-high latitudes.
- ☐ Ozone column depths are the lowest over the equator.

Polar Vortex



Ozone Production and Destruction

(from *The Earth System*)



The Chapman Mechanism of Ozone Production and Destruction

Photodissociation (or photolysis)

Reaction*		Rate
1) O_2 + UV photon → O + O	production	Slow
2) O + O_2 + M → O_3 + M		Fast
3) O_3 + photon → O_2 + O	destruction	Fast
4) O + O_3 → 2 O_2		Slow

visible light

destroy O3 permanently

Radiation and Ozone

- ☐ **Ozone Production**

  UV photons are required for ozone production:

  O_2 + UV photon → O + O

  Below about 20 km, UV photons are absorbed by ozone. Therefore, O2 can be photolyzed only above 20 km. This is why the ozone layer is located in the stratosphere and not near Earth's surface.

- ☐ **Ozone Destruction**

  O3 can be split by radiation in the visible-light range:

  O_3 + photon → O_2 + O

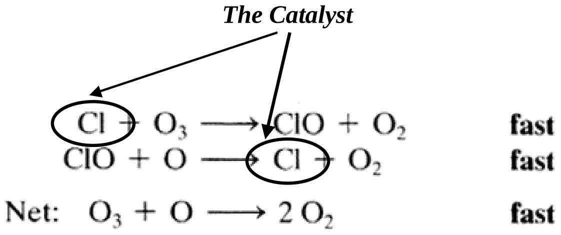
  Because many more visible photons than UV photons are available, O3 is photolyzed (ozone destruction) much faster than O_2 (ozone production).

  Also, O3 can be photolyzed all the way sown to Earth's surface.

Other Ozone Destruction Processes

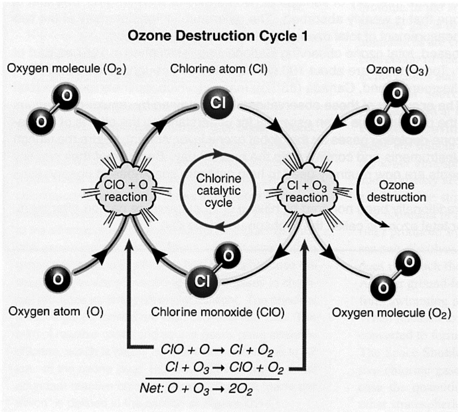
- ☐ Other atmospheric trace constituents, such as nitrous oxide (N2O), water vapor, and freons, can also be photolyzed. They produce highly reactive radicals that keep ozone abundances lower than they would otherwise be.
- ☐ These radicals include: nitric oxide (NO), atomic chlorine (Cl), bromine (Br) radicals, and hydroxyl (OH) radicals.
- ☐ These radicals can destroy stratospheric ozone through ***"catalytic cycles".***
- ☐ A catalytic cycle is a set of chemical reactions facilitated by the presence of a ***catalyst***.
- ☐ A catalyst is a substance that increases the rate of a chemical reaction but is itself unchanged by the reaction.

The Chlorine Catalytic Cycle



$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$
$$\text{Net:}\ O_3 + O \longrightarrow 2\,O_2$$

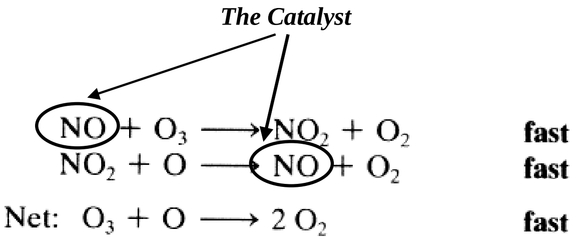
The Chlorine Catalytic Cycle



$ClO + O \rightarrow Cl + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
$\text{Net: } O + O_3 \rightarrow 2O_2$

(from *WMO Report 2003*)

The Nitrogen Catalytic Cycle



$$NO + O_3 \longrightarrow NO_2 + O_2 \quad \text{fast}$$
$$NO_2 + O \longrightarrow NO + O_2 \quad \text{fast}$$
$$\text{Net:} \quad O_3 + O \longrightarrow 2\,O_2 \quad \text{fast}$$

(from *The Earth System*)

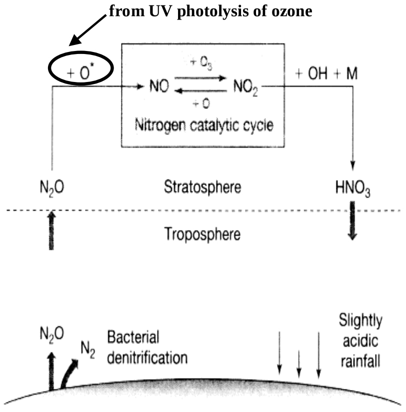
Where do those ozone-depleting catalysts come from?

(1) Cl – related to natural and man-made substances

(2) Br – related to natural and man-made substances

(3) NO2 reacts with Cl and Br to produce reservoirs for Cl and Br.

The Odd Nitrogen Cycle



(from *The Earth System*)

- ❑ **N2O**: from Earth's surface, where it is produced by microbial activity in soil and in the ocean.
- ➔ In the stratosphere, some of N2O reacts to form NO, the rest is photolyzed back to N2 and O2.
- ➔ The NO so produced participates in the ozone-destroying nitrogen catalytic cycle.
- ➔ Once for a while, the resulting NO2 molecule interacts with a hydroxyl radical (OH), producing nitric acid (HNO3).
- ➔ Nitric Acid (HNO3) then diffuses down into the troposphere and dissolves into rain.

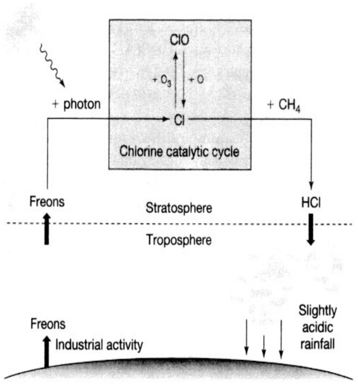
Other Sources of NO

- ❑ N2O is currently the largest source of stratospheric odd nitrogen (NO and NO2).

- ❑ How human activity affect NO?

  high-flying, supersonic transport airplanes
  - ➔ Jet plane-produced high temperatures from combustion.
  - ➔ combine N2 and O2 to form NO.
  - ➔ injected NO goes to the stratosphere and destroy ozone
  - ➔ This is why jet plans can affect stratospheric ozone layer (even though jet plans fly in the upper troposphere).

The Chlorine Cycle



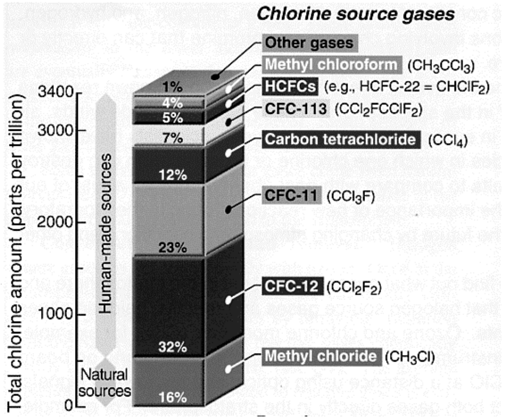
(from *The Earth System*)

- ☐ Natural sources of chlorine:

  (1) **Methyl chloride (CH3Cl):** produced by marine plankton. (2) **Hydrogen chloride (HCl):** produced by volcanic eruption and by evaporation of sea spray.

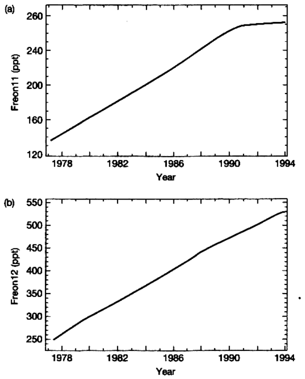
  These natural-generated chlorine are most removed by precipitation before they reach the stratosphere.
- ☐ The largest sources of stratospheric chlorine today are freons (CFCs), which are thropogenic compounds.
- ➔ CFCs do not react in either the troposphere or lower stratosphere
- ➔ CFCs go all the way to the upper stratosphere and are photolyzed by UV radiation.
- ➔ The Cl so produced proceeds to destroy ozone.
- ➔ Eventually, Cl react with CH4 and is diffused to the troposphere, where it is precipitated out.

Chlorine Sources



(from *WMO Report 2003*)

Man-Made Sources for CFCs



(from *The Earth System*)

- ☐ There are two kinds of CFCs: freon-11 (CCl3F) and freon-12 (CCl2F2).
- ☐ Freon-11 has been used:

  (1) as a propellant in spray cans

  (2) as a blowing agent for producing foams

  (3) to clean semiconductor chips.
- ☐ Freon-12 has been used as

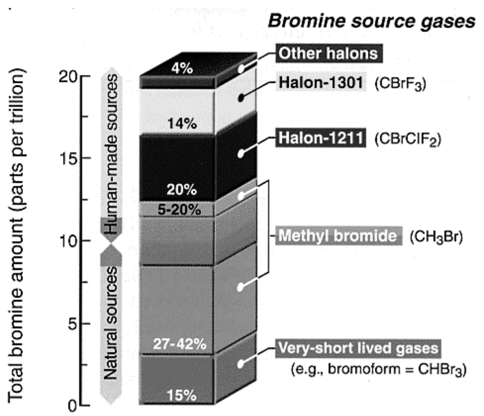
  (1) a refrigerant

  (2) working fluid in most car air conditioners.

The Bromine Cycle

- ☐ Br is also a ozone-depleting catalyst
- ☐ The bromine cycle is similar to the chlorine cycle.
- ☐ The natural source of bromine is Methyl Bromine (Ch3Br), which is a byproduct of biological activity in the ocean. These natural source reacts in the troposphere.
- ☐ The man-made source of bromine is two chemical compounds: Halon-1211 (CF2ClBr) and Halon-1301 (CF3Br).
- ☐ These two halons are used in certain types of fire extinguishers.
- ☐ Halons diffuse up to the stratosphere, where they are photolyzed into bromine atmos. They eventually rain out.

Bromine Sources



(from *WMO Report 2003*)

Coupling Between Odd Nitrogen and Chlorine Cycles

reactive unreactive

$$\boxed{\mathrm{ClO}} + \mathrm{NO_2} + \mathrm{M} \longrightarrow \boxed{\mathrm{ClONO_2}} + \mathrm{M}.$$

- ❑ Throughout most of the lower stratosphere, the nitrogen and chlorine cycles are coupled by the above chemical reaction.
- ❑ The chlorine nitrate (ClONO2) formed in this reaction does not react directly with either ozone or atomic oxygen. Therefore, this coupling reaction keeps chlorine from being in its reactive forms (Cl and ClO) (which can destroy ozone).

Polar Stratospheric Clouds (PSCs)

(Sweden, January 2000; from NASA website)

- ❑ In winter the polar stratosphere is so cold (-80°C or below) that certain trace atmospheric constituents can condense.
- ❑ These clouds are called “polar stratospheric clouds” (PSCs).
- ❑ The particles that form typically consist of a mixture of water and nitric acid (HNO3).
- ❑ The PSCs alter the chemistry of the lower stratosphere in two ways:

  (1) by slow down the coupling between the odd nitrogen and chlorine cycles

  (2) by providing surfaces on which heterogeneous reactions can occur.

How PSCs Affect Chlorine?

- ❑ In most of the seasons, there are always abundant NO2 in the stratosphere to tie up a significant fraction of the available chlorine in the form of chlorine nitrate.
- ❑ In the wintertime Antarctic stratosphere, NO2 concentrations are low, because most of the odd nitrogen has been converted into HNO3 and become droplets in PSCs (polar stratospheric clouds).
- ❑ Therefore, the formation of PSCs allow reactive chlorine concentration to increases.

- ❑ The PSCs particles also help convert unreactive forms of chlorine into reactive chlorine by providing surfaces on which heterogeneous reaction can occur.

$$\mathrm{ClONO_2} + \mathrm{HCl} \longrightarrow \mathrm{Cl_2} + \mathrm{HNO_3}.$$ **On PCSs**

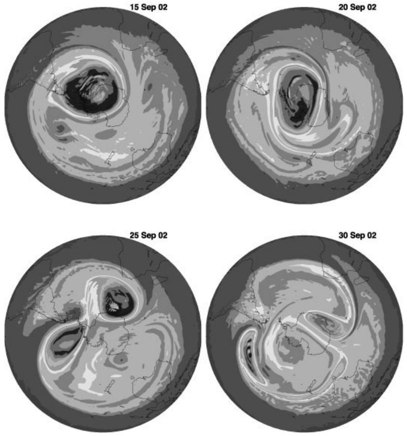
$$\mathrm{Cl_2} + \text{photon} \longrightarrow \boxed{\mathrm{Cl} + \mathrm{Cl}.}$$ **destroy ozone**

Three Factors for the Ozone Hole

- ❑ Chemical Reactions – polar stratospheric clouds (PSCs)
- ❑ Atmospheric Circulation – stratospheric polar vortex
- ❑ Sunlight – spring season

In Winter !!

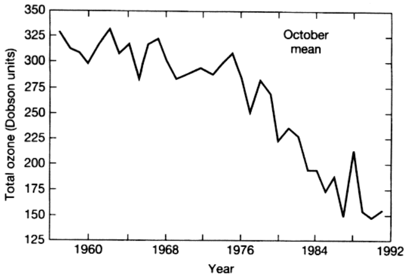
The Polar Vortex



- ❑ The wintertime circulation over the South Pole is characterized by a gigantic whirlpool of cold and dense air, called the polar vortex.
- ❑ The cold and dense cold air in the middle of the vortex is subsiding.
- ❑ The sinking air carries cloud particles along with it.
- ❑ Remove odd nitrogen from the stratosphere.
- ❑ Very little ozone and odd nitrogen can be brought into the south pole.

Antarctic Ozone Hole

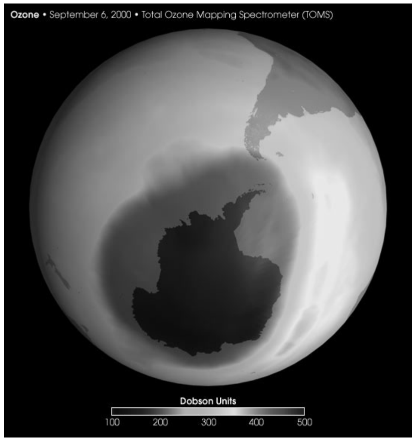
Mean Total Ozone Over Antarctic in October



(from *The Earth System*)

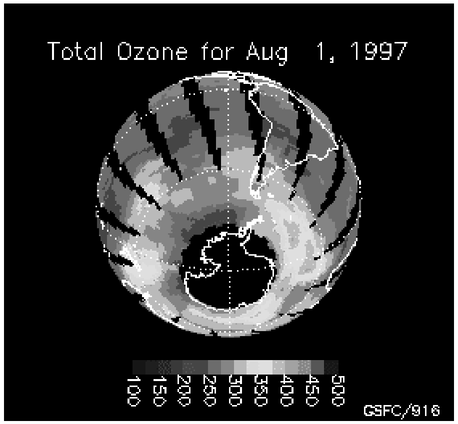
- ❑ The decrease in ozone near the South Pole is most striking near the spring time (October).
- ❑ During the rest of the year, ozone levels have remained close to normal in the region.

Satellite View of the Ozone Hole



September 6, 2000

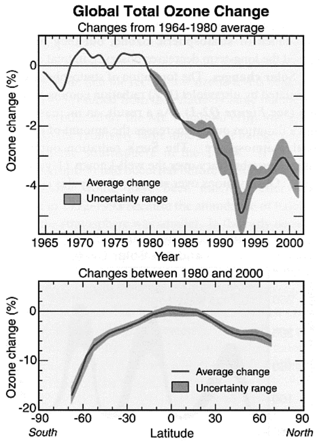
The 1997 Ozone Hole



Ozone Hole Depletion

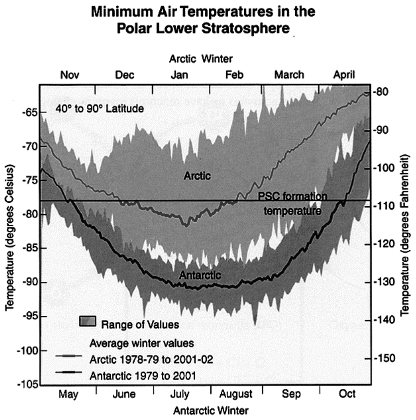
☐ Long Antarctic winter (May through September)
- ➔ The stratosphere is cold enough to form PSCs
- ➔ PSCs deplete odd nitrogen (NO)
- ➔ Help convert unreactive forms of chlorine (ClONO2 and HCl) into more reactive forms (such as Cl2).
- ➔ The reactive chlorine remains bound to the surface of clouds particles.
- ➔ Sunlight returns in springtime (September)
- ➔ The sunlight releases reactive chlorine from the particle surface.
- ➔ The chlorine destroy ozone in October.
- ➔ Ozone hole appears.
- ➔ At the end of winter, the polar vortex breaks down.
- ➔ Allow fresh ozone and odd nitrogen to be brought in from low latitudes.
- ➔ The ozone hole recovers (disappears) until next October.

Global Total Ozone Change



(from *WMO Report 2003*)

Why No Ozone Hole in Artic?



(from WMO Report 2003)