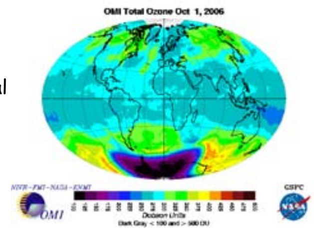
Polar Ozone Loss

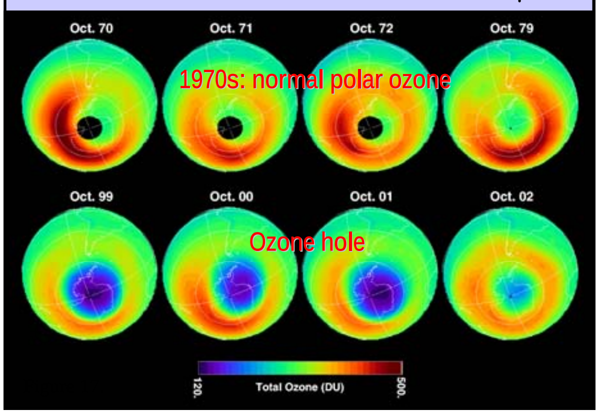
Severe depletion of stratospheric O_3 occurs every spring (since 1980's) over the poles (especially South Pole).

Example of:

- far reach of human activities
- environmental catastrophe and political blame game
- scientific process and ability of humans to correct



The Antarctic ozone hole viewed from space



Discovery of the Antarctic ozone hole: 1985

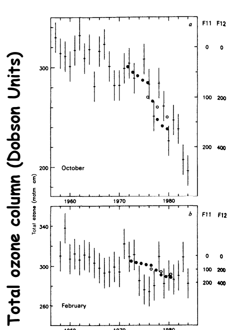
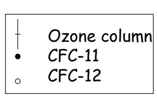


Fig. 2 Monthly means of total O_3 at Halley Bay, and Southern Hemisphere measurements of F-11 (●, p.p.t.v. (parts per thousand by volume) $CFCl_3$) and F-12 (○, p.p.t.v. CF_2Cl_2). *a*, October, 1957–84. *b*, February, 1958–84. Note that F-11 and F-12 amounts increase down the figure.

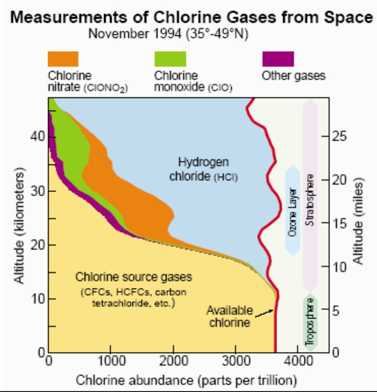


Total ozone observations at Halley Bay (76°S, 27°W), Antarctica: 1956-1985

Farman et al., Nature, 315, May 1985

"Large losses of ozone in Antarctic reveal seasonal ClO_x/NO_x interactions"

Chlorine Partitioning in Stratosphere

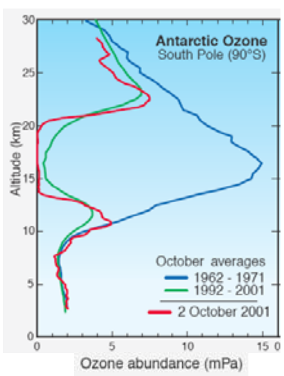


Most Cl is in its reservoir form (HCl, $ClONO_2$), not active form (Cl_x).

Gas-phase processes deplete strat. O_3, but are not capable of creating the O_3 "hole".

Why is there an ozone "hole" over polar regions?

Vertical distribution of ozone at the South Pole



Chlorine from CFCs predicted to be most effective ~ 40 km.

So why is depletion at 15 – 20 km?

Discovery of Antarctic Ozone Hole

The Conundrum:

- Known catalytic reactions with chlorine not fast enough to explain near complete depletion in couple months.
- Why only in spring?
- Why only between 15 – 25 km?
- Why only in polar region?

Debate Over Causes of Ozone Hole

There was also a real scientific debate over the relative roles of chemistry and meteorology.

Turns out to be both (of course!)

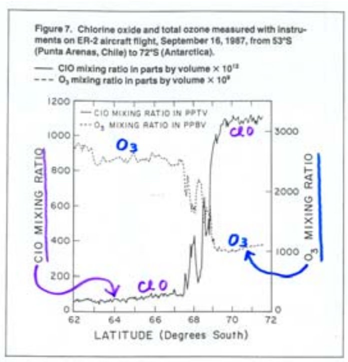
Chlorine: The Smoking Gun?

ClO and O_3 certainly anti-correlated.

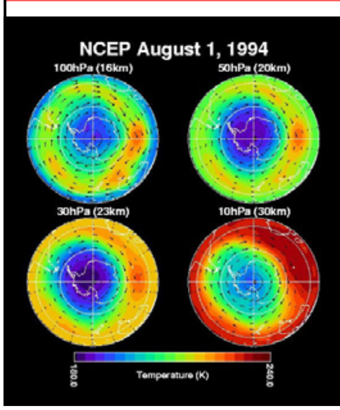
But how is there so much ClO?

What is the mechanism for ClO to destroy ozone so fast?

Can't be ClO + O…



The Antarctic Polar Vortex: Wind and temperature



- Lack of sunlight between June and September → **cooling** of Antarctic stratosphere and adiabatic **downwelling**
- Large latitudinal temperature gradient (sunlight/polar night) →strong zonal winds = Polar night jet (150 km/h at 20 km)
- Antarctic polar vortex: region poleward of polar night jet
- **Isolation** of polar vortex: little mixing of warmer air from lower latitudes occurs
- **Sustained cold temperatures** over Antarctica during winter (~183K at 20km in early August).

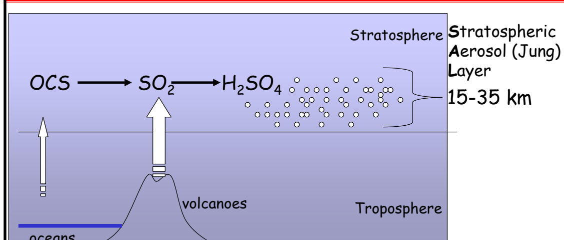
Polar Stratospheric Clouds (PSC)

http://earthobservatory.nasa.gov/

Temperatures as low as 183K can exist at 15-20 km altitude, where even small amounts of water can condense to produce PSCs.

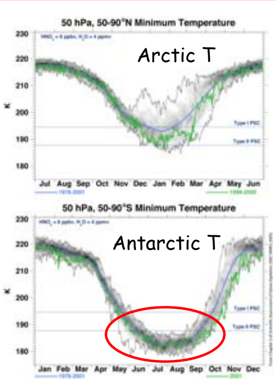
	Type I PSC	Type II PSC
Composition:	Nitric Acid Trihydrate (HNO_3-3 H_2O) Ternary solution (H_2O, H_2SO_4, HNO_3)	Water Ice
Formation Temp.:	195 K	188 K
Particle diameter:	1 μm	>10 μm
Altitudes:	10-24 km	10-24 km
Settling rates:	1 km/30 days	> 1.5 km/day

PSC Formation Starts on S.A.L



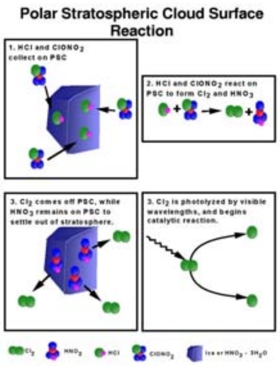
- Extends vertically from 15 to 35 km
- Aerosol composition primarily H_2SO_4-H_2O
- Typical particle radius ~ 700 nm
- Typical particle number density ~ 10 cm^{-3}

PSC Formation Requires Very Low T



Polar Vortex cuts off warm, ozone/NO_x rich mid-latitude air

Chlorine activation on polar stratospheric clouds



$$HCl + ClONO_2 \xrightarrow{PSCs} Cl_2 + HNO_3$$

Conversion of chlorine reservoirs HCl and $ClONO_2$ to Cl_2 and HNO_3 on PSCs

→Cl_2 photolyzes in sunlight (spring) releasing Cl and catalytic ozone loss begins

→HNO_3 remains on PSCs and settles out of stratosphere suppressing NO_x levels: $ClO + NO_2 + M \rightarrow ClONO_2 + M$ cannot deactivate ClO radicals.

Chlorine activation on PSCs

Reactions taking place on polar stratospheric clouds:

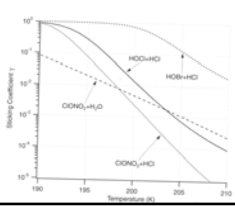
$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$
$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$$
$$HOCl + HCl \rightarrow Cl_2 + H_2O$$
$$BrONO_2 + H_2O \rightarrow HNO_3 + HOBr$$
$$HCl + BrONO_2 \rightarrow HNO_3 + BrCl$$
$$HCl + HOBr \rightarrow H_2O + BrCl$$

Chlorine/Bromine activation + sequestration of HNO_3 in PSCs

Low temperature heterogeneous reactions

$$ClONO_2 + H_2O \xrightarrow{aerosol} HOCl + HNO_3$$
$$ClONO_2 + HCl \xrightarrow{aerosol} Cl_2 + HNO_3$$
$$HOCl + HCl \xrightarrow{aerosol} Cl_2 + H_2O$$
$$HOBr + HCl \xrightarrow{aerosol} BrCl + H_2O$$
$$BrONO_2 + H_2O \xrightarrow{aerosol} HOBr + HNO_3$$

Reactions converting chlorine from the long-lived reservoirs HCl and $ClONO_2$ to Cl_2, HOCl, BrCl which readily photolyze and release Cl_x. Similarly $BrONO_2$, and HOBr are converted to BrCl and HOBr.



Rapid ozone destruction mechanisms after sunrise

Polar sunrise: $Cl_2 + h\nu \rightarrow Cl + Cl$, $BrCl + h\nu \rightarrow Br + Cl$

Molina and Molina (1987): ClO dimer catalytic cycle

$2(Cl + O_3 \rightarrow ClO + O_2)$
$ClO + ClO + M \rightarrow Cl_2O_2 + M$
$Cl_2O_2 + h\nu \rightarrow ClOO + Cl$
$ClOO + M \rightarrow Cl + O_2 + M$
Net: $2O_3 \rightarrow 3O_2$

~75 % of ozone removal in ozone hole

McElroy et al. (1986) and Tung et al. (1986): Bromine/chlorine coupling

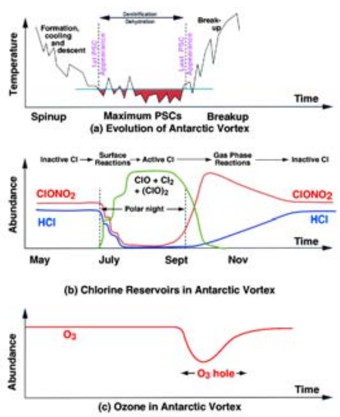
$Cl + O_3 \rightarrow ClO + O_2$
$Br + O_3 \rightarrow BrO + O_2$
$BrO + ClO \rightarrow Br + ClOO$
$ClOO + M \rightarrow Cl + O_2 + M$
Net: $2O_3 \rightarrow 3O_2$

~20% of ozone removal in ozone hole

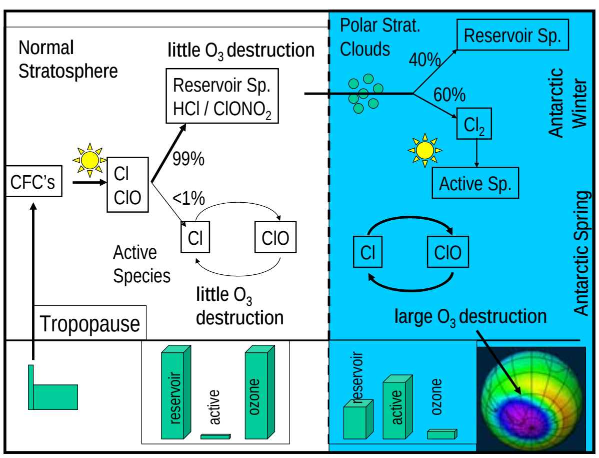
Evolution of Antarctic Vortex

Reactive chlorine and chlorine reservoirs

Ozone levels



Wallace & Hobbs



Antarctic Ozone Hole Today

http://ozonewatch.gsfc.nasa.gov/

Antarctic Ozone Hole: Key Points

- Why only in spring?

Wintertime processing on PSCs needed for active chlorine production and denitrification. Sunlight required to generate Cl atoms from Cl_2 and ClOOCl.

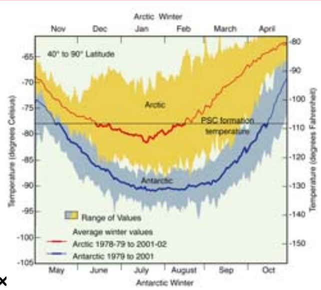
- Why only between 15 – 25 km?

Where PSCs form (on aerosol layer), and where the ClOOCl mechanism is fastest.

- Why only in (south) polar region?

PSCs are required and only form under cold conditions achieved during polar winter (and mainly only Antarctic winter).

An Arctic ozone hole?

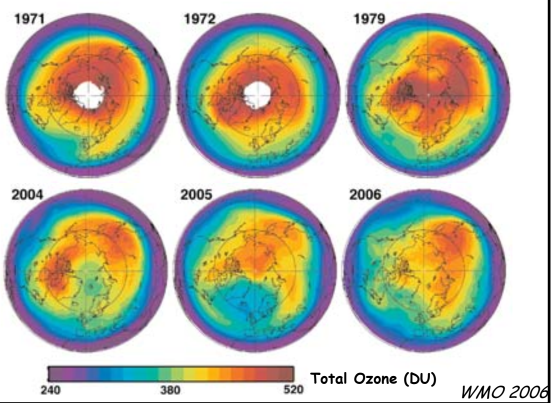


Arctic vortex

- No land mass (warmer)
- Less symmetric
- Planetary wave activity (Tibet, North America…)

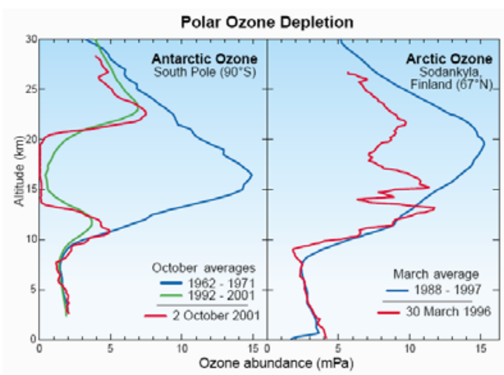
→ **Overlap between cold temperatures and sunlight are limited in the Arctic and ozone depletion episodic and minor**

Arctic Ozone depletion: March



WMO 2006

Comparison: Arctic, Antarctic lower stratosphere



Aerosol chemistry on sulfate aerosols

Role of N_2O_5 hydrolysis:

$$N_2O_5 + H_2O \xrightarrow{aerosol} 2\ HNO_3$$

→ Converts active nitrogen (NO_x) to long-lived reservoir (HNO_3) [NO_x/NO_y ratio decreases], and slows down O_x loss through NO_x cycles.

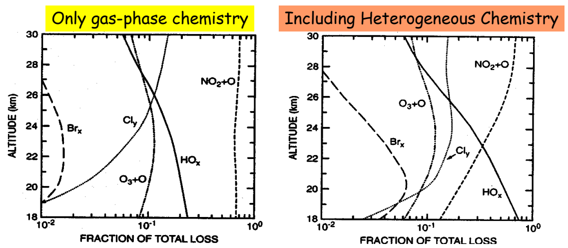
But at the same time it enhances O_x loss through ClO_x, BrO_x, and HO_x cycles. Lower NO_x result in:

- Slower deactivation of ClO_x through $ClO+NO_2+M \rightarrow ClONO_2+M$
- Slower deactivation of BrO_x through $BrO+NO_2+M \rightarrow BrONO_2+M$
- Slower deactivation of HO_x through $OH+NO_2+M \rightarrow HNO_3+M$

➔ Concentrations of ClO_x, BrO_x, and HO_x increase!

➔ Ozone becomes more sensitive to human-induced increases in chlorine and bromine species in the lower stratosphere.

Effect of N_2O_5 + Aerosols→ $2HNO_3$



HO_x becomes most important catalyst in aerosol layer!

Vertical distribution of ozone trends at midlatudes

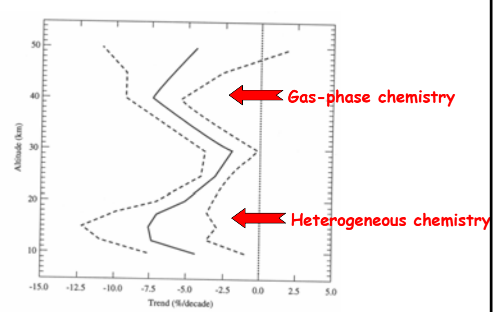
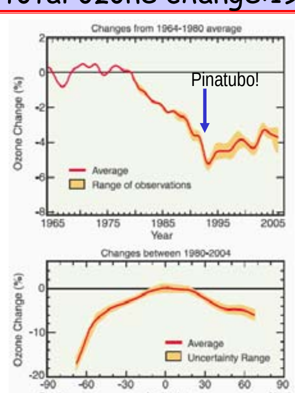


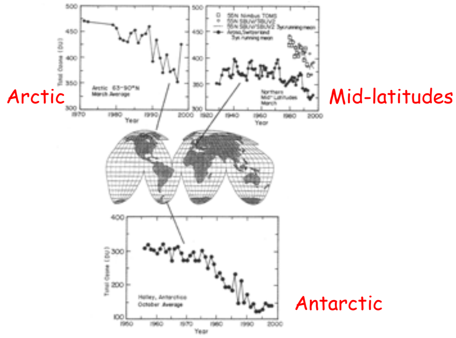
Fig. 10-15 Vertical distribution of the O_3 trend at northern midlatitudes for the period 1980–1996: best estimate (solid line) and uncertainties (dashed lines). Adapted from *Scientific Assessment of Ozone Depletion: 1998*, Geneva: WMO, 1999.

Global total ozone change:1964-2005



WMO, 2006

Stratospheric Ozone Depletion



→ Downward trends in ozone column on a global scale

Regulations on the production of CFCs

- **Vienna convention (1985):** "Convention for the Protection of the ozone layer" signed by 20 nations (research, future protocols)
- **Montreal Protocol (1987):** "Protocol on substances that deplete the ozone layer" ratified in 1989. Legally binding controls freezing production to 1985 levels.
- **London Amendment (1990):** phaseout of production by 2000 for developed nations and by 2010 for developing nations.
- **Copenhagen Agreement (1992):** Phaseout for developed nations by 1996.
- HCFC production allowed as short-term substitutes for CFCs. HCFC production to be phased out by 2030 (developed nations), 2040 (developing nations).

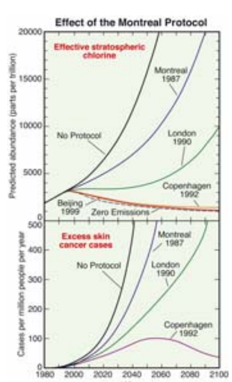
First environmental problem solved on an international basis!

The Solution: Montreal Protocol

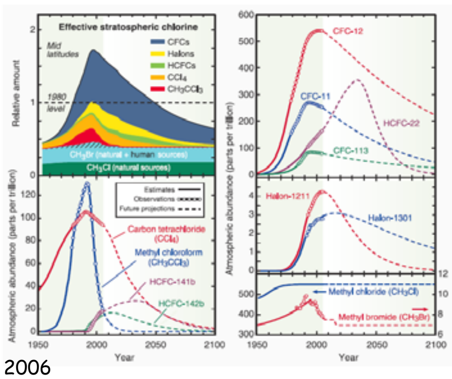
The persistent observations of the ozone hole from 1984 – 1987 led to legally binding international agreements.

The Montreal Protocol and its amendments eventually called for a near complete ban on the production and use of CFCs.

A suitable and easy replacement for CFCs, known as HCFCs, made these acts easier to swallow.



Past and expected future abundances of halogen source gases

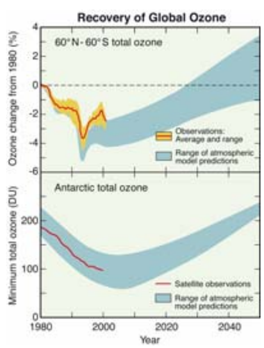


WMO, 2006

Ozone Recovery

Computer model predictions:
- Antarctic ozone will recover to pre-1980 values by ~2040.
- Extra-polar ozone should recover by 2020-2040.

Predictions assume strict adherence to Montreal Protocol.



Questions

1. One "geo-engineering" scheme to reduce global warming is to inject sulfur into the stratosphere to enhance the stratospheric aerosol layer – which reflects incoming solar radiation. How would that affect stratospheric ozone at present?
2. How might volcanic eruptions in the distant past (before CFCs) affect stratospheric ozone?

What would have happened?

Newman, et al. *ACP* 2009

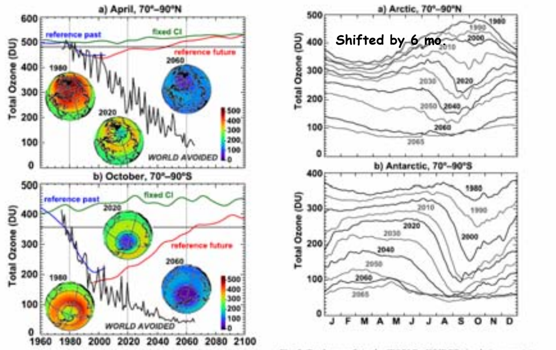


Fig. 5. Total ozone from the *WORLD AVOIDED* simulation over (a)

Positive Feedback: O_3 Destruction and T

Less O_3 → less heating

Less heating → colder strat

Colder stratosphere → ??

Newman, et al. *ACP* 2009

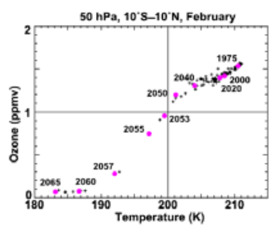


Fig. 8. The February *WORLD AVOIDED* ozone versus temperature (also at 50 hPa and 10° S–10° N, as in Fig. 7). Certain years are highlighted in magenta.