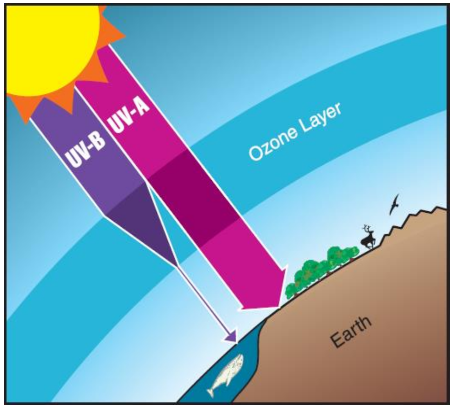

Atmospheric Chemistry
Stratospheric ozone

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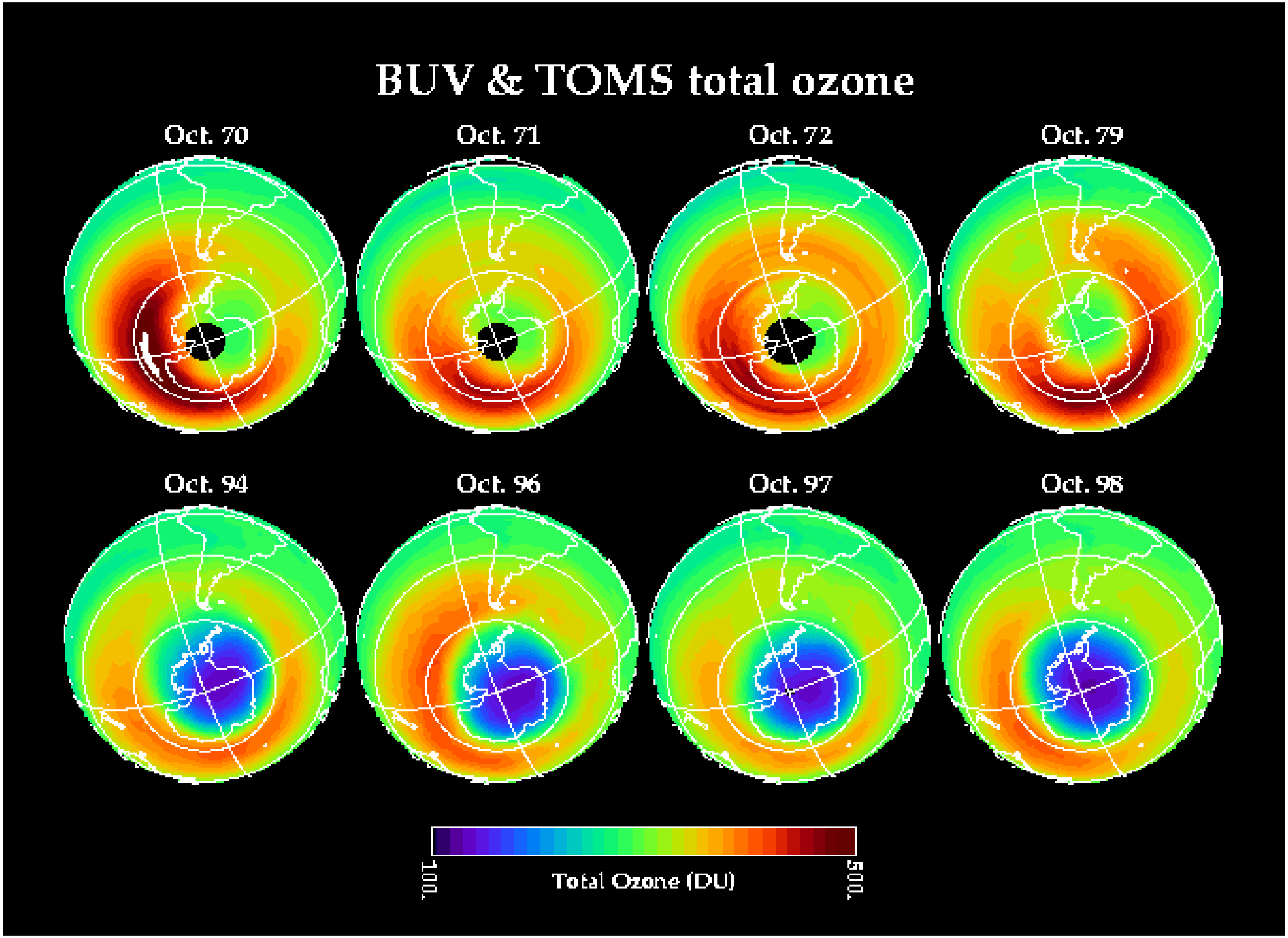
Stratospheric ozone

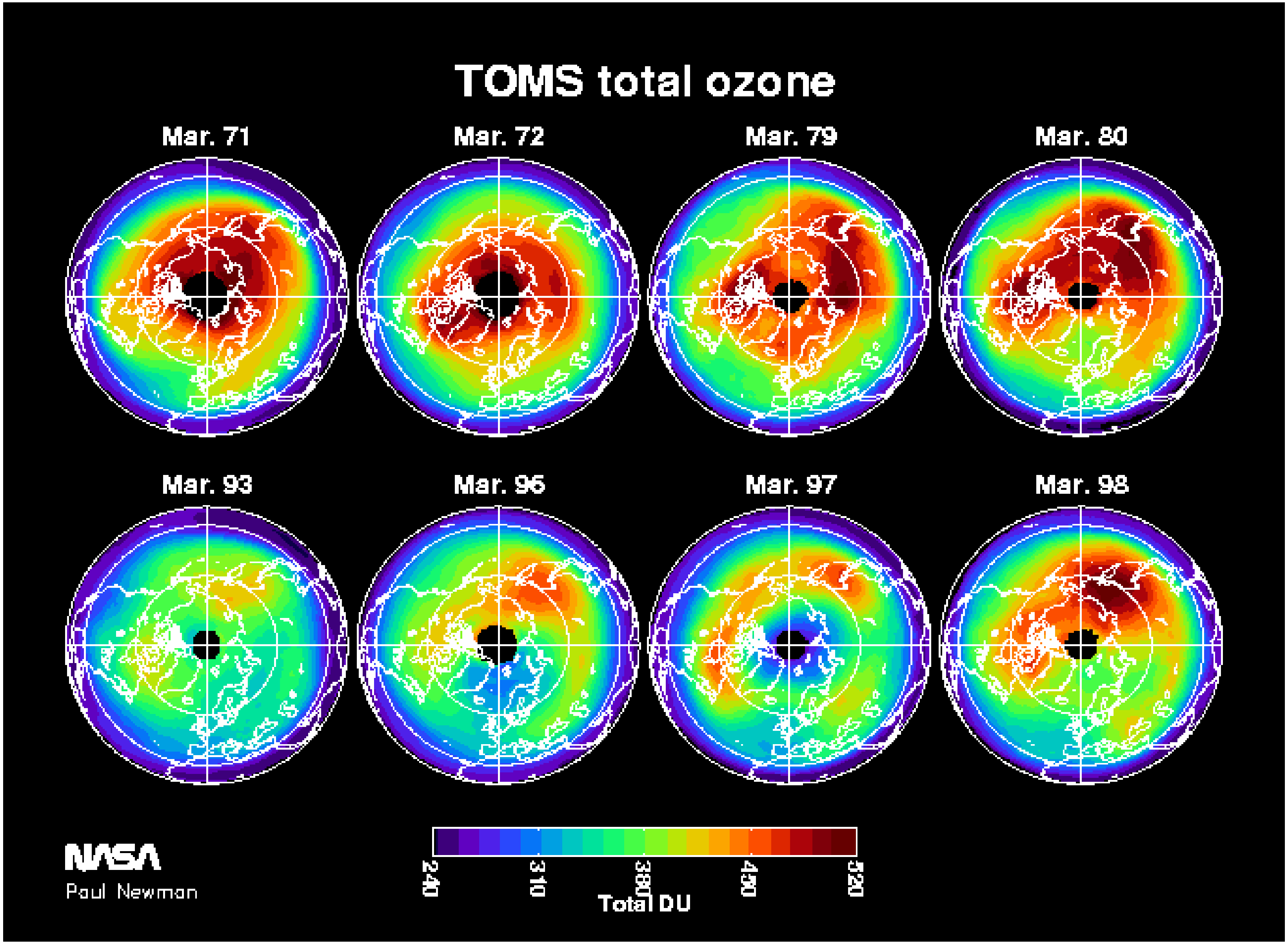
Important concepts in this lecture:

- Chapman mechanism
- Chemical ”families”
  O_x, HO_x, NO_x, ClO_x and their reservoirs
- Catalytic destruction of ozone
- Heterogenous chemical reactions (multi-phase)
- Polar stratospheric clouds (PSC)

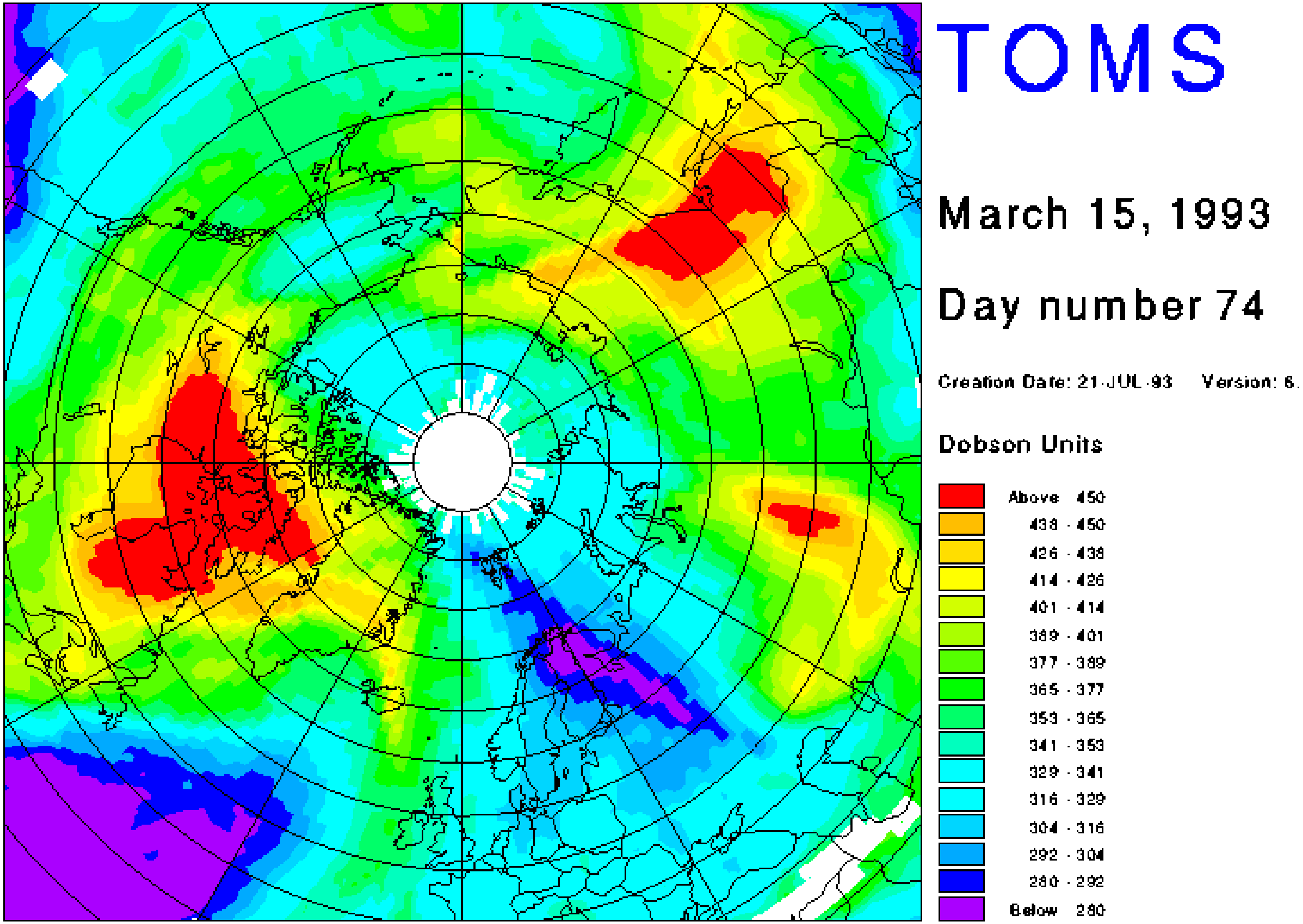
Stratospheric ozone – Southern hemisphere



Stratospheric ozone – Northern hemisphere

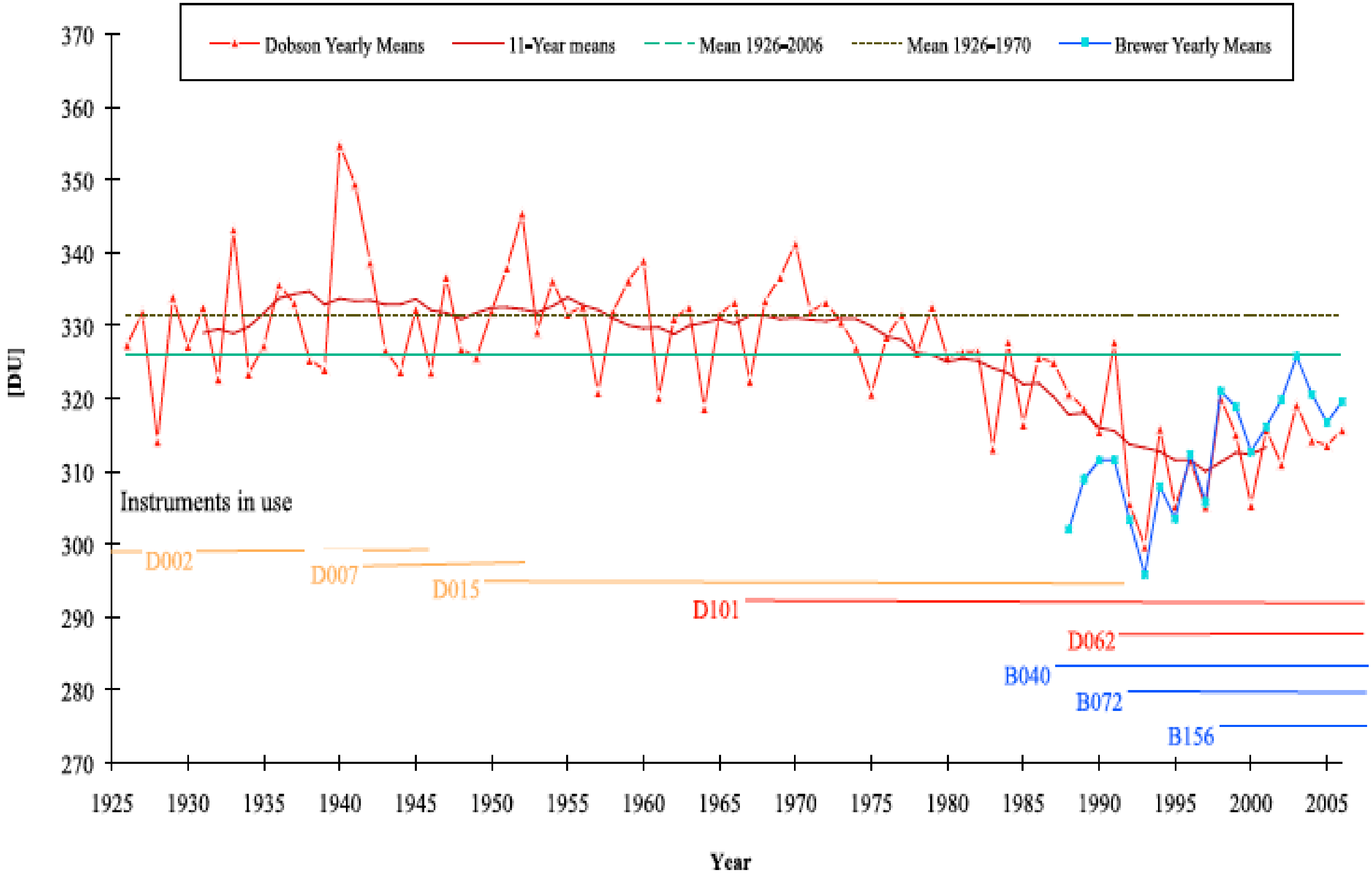


Arctic ozone hole – Satellite data



Stratospheric ozone – Northern hemisphere

Long term ozone observations at Arosa Switzerland



Stratospheric ozone

The stratospheric ozone layer

- Ozone: O_3
- ~ 3 mm thick if all ozone is concentrated to a layer at ground level (=300 Dobson Units, DU).
- Protects life on Earth by absorbing UV radiation from the sun ($\lambda < 320$ nm, UVb).
- The ozone layer is vital for life on Earth.

Depletion of stratospheric ozone – Effects

A depleted ozone layer casues a number of negative effects:

- Increased risk of skin cancer (e.g. malignant melanoma)
- Increased risk of skin burns
- Increased risk of eye injuries such as cataract (*grå starr*)
- Suppression of the immune system
- Increased risk of damage to natural ecosystems
- Increased risk of damage to crops and forests

A 10% thinning of the ozone layer is expected to result in a 26% increase in the number of skin cancer cases.

The EU Environmental Agency (EEA) estimates that the levels of ozone depleting compounds reached their highest values in 1997, but the skin cancer prevalence will not reach its highest levels until 2055, with 78 million new cases globally per year!!

Stratospheric ozone - Effects

UVc ($200 < \lambda < 280$ nm)	does not reach Earth´s surface
UVb ($280 < \lambda < 320$ nm)	harmful
UVa ($320 < \lambda < 400$ nm)	less harmful

If the ozone layer is depleted by 1%, UVb at Earth´s surface will increase by ~2%.

Thinning of the stratospheric ozone leads to increased irradiation at Earth´s surface, in particular of UVb, which leads to serious consequences for life on Earth.

UV radiation can break the DNA molecules forming the genetic code, resulting in skin cancer (e.g. malignant melanoma).

Stratospheric ozone

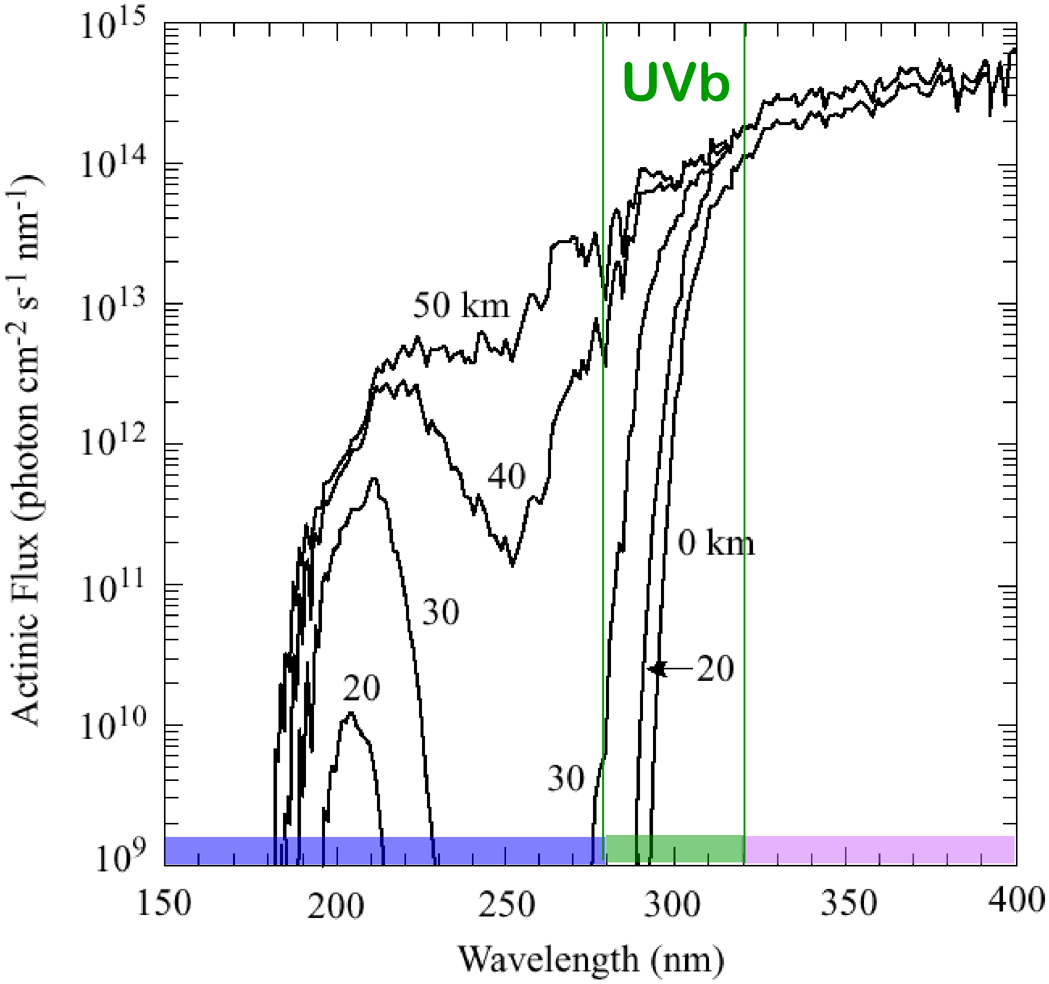
UVc ($200 < \lambda < 280$ nm)

O_2 photolysis: $\lambda < 240$ nm

UVb ($280 < \lambda < 320$ nm)

O_3 photolysis: $\lambda < 320$ nm

UVa ($320 < \lambda < 400$ nm)

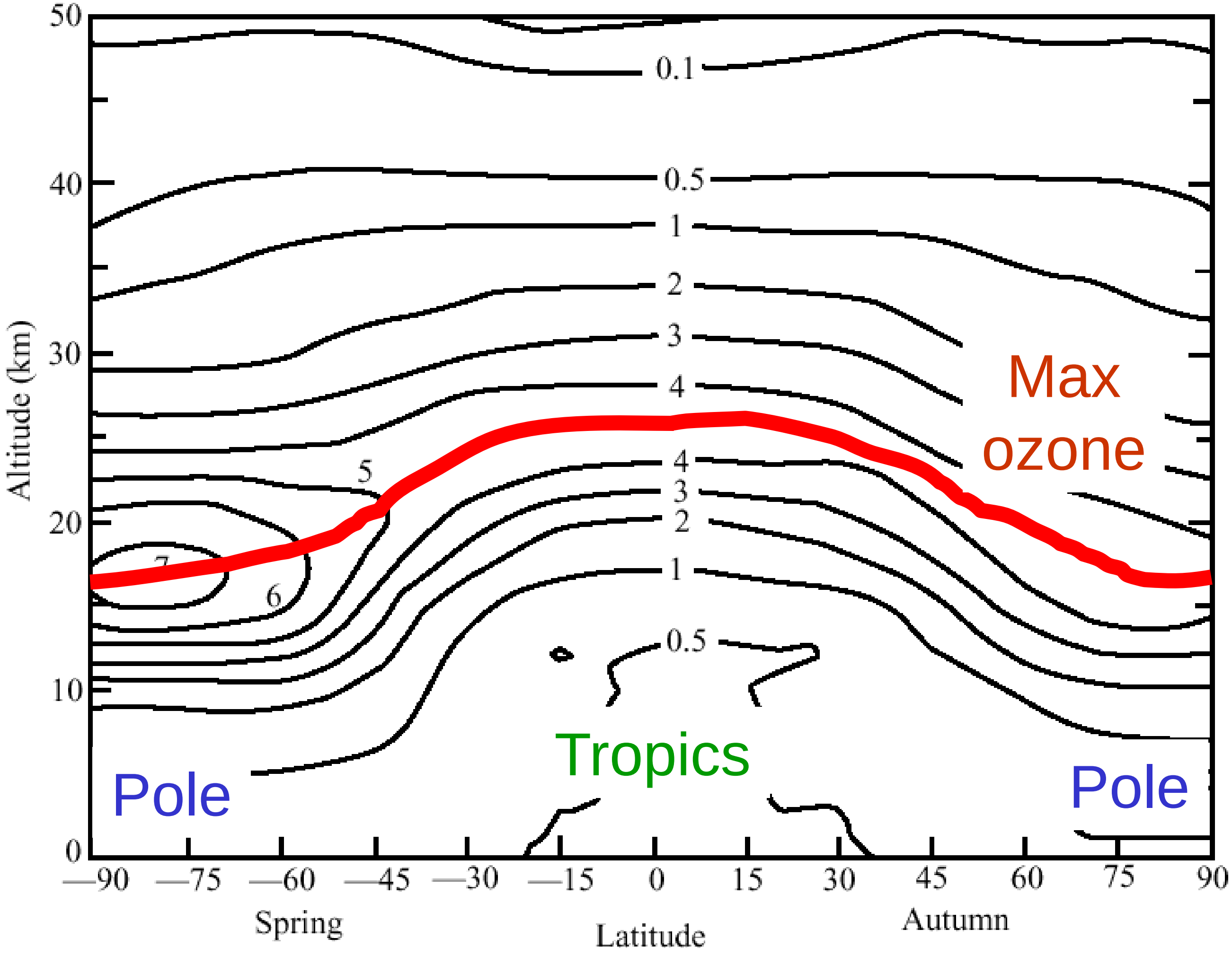


The natural ozone layer

The natural ozone layer before the ozone hole.

Data from measurements in the 1960-ies.

Unit:
10^{12} molecules O_3 cm^{-3}



Ozone production in the stratosphere

Production of ozone occurs via photolysis of O_2

(1) $O_2 + h\nu \rightarrow O + O$ ($\lambda < 240$ nm, UV)

(2) $O + O_2 + M \rightarrow O_3 + M$

Atomic oxygen O in its ground-level triplet state $O(^3P)$, very reactive

Photolysis is also a sink for ozone

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ ($\lambda < 320$ nm, UV)

$O(^1D) + M \rightarrow O + M$ (stabilization of $O(^1D)$)

Atomic oxygen in an excited singlet state $O(^1D)$, extremely reactive

Net reaction for photolysis of ozone:

(3) $O_3 + h\nu \rightarrow O_2 + O$

Photolysis is not a final sink for ozone since atomic oxygen O is recycled by reaction 2. Ozone destruction requires:

(4) $O_3 + O \rightarrow 2O_2$

Chapman mechanism (1930)

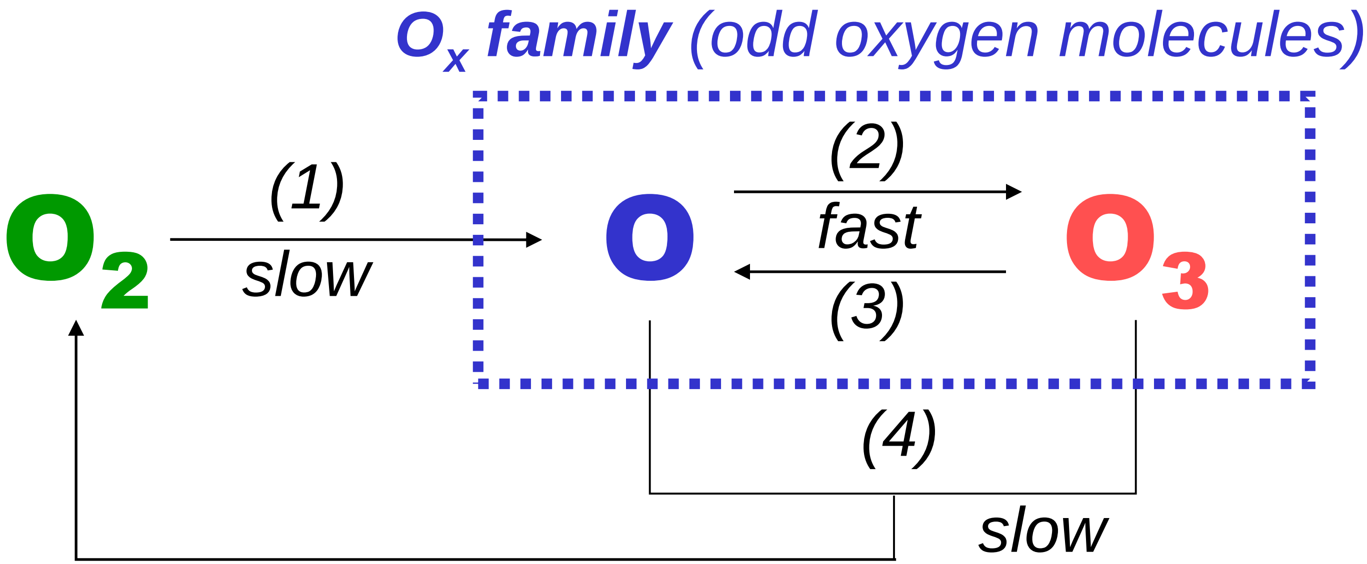
The Chapman mechanism for stratospheric ozone

(1) $O_2 + h\nu \rightarrow O + O$ ($\lambda < 240$ nm)

(2) $O + O_2 + M \rightarrow O_3 + M$ (2x) (fast)

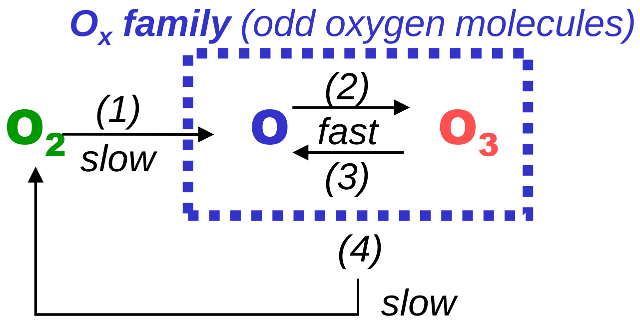
(3) $O_3 + h\nu \rightarrow O_2 + O$ (fast, $\lambda < 320$ nm)

(4) $O_3 + O \rightarrow 2O_2$



O_x according to the Chapman mechanism

Check that the short-lived O is in a steady state,
i.e. production and losses ~ constant over its lifetime.
Lifetime (τ_O) for *O* can be written
τ_O = (mass in the reservoir)/(loss rate)



$$\tau_O = \frac{[O]}{k_2[O][O_2][M]} = \frac{1}{k_2[O_2][M]} = \frac{1}{k_2 C_{O_2} n_a^2}$$

$C_{O_2} =$ 0.21 mol/mol (mixing ratio of O_2)

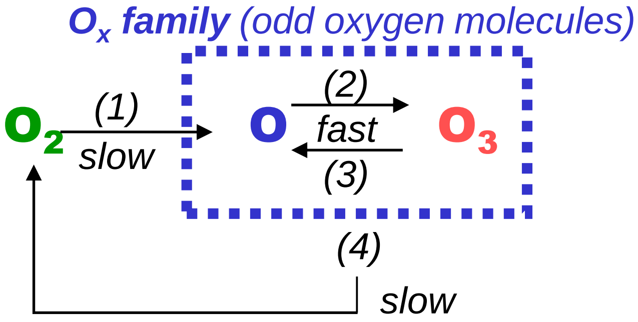
$n_a =$ Number concentration of air molecules

Lifetime **(τ_O) ~ seconds** or less.

Production of O varies on longer time scales.

$\Rightarrow$ **Steady state for [O].**

O_x according to the Chapman mechanism



***O_x* family** *(odd oxygen molecules)*

O_2 $\xrightarrow[\text{slow}]{(1)}$ O $\underset{(3)}{\overset{(2)}{\rightleftarrows}}$ O_3

fast

(4) slow

Steady state conditions for [O].

$\Rightarrow$ O production rate = O loss rate

Only the fast reactions (2) and (3) are important.

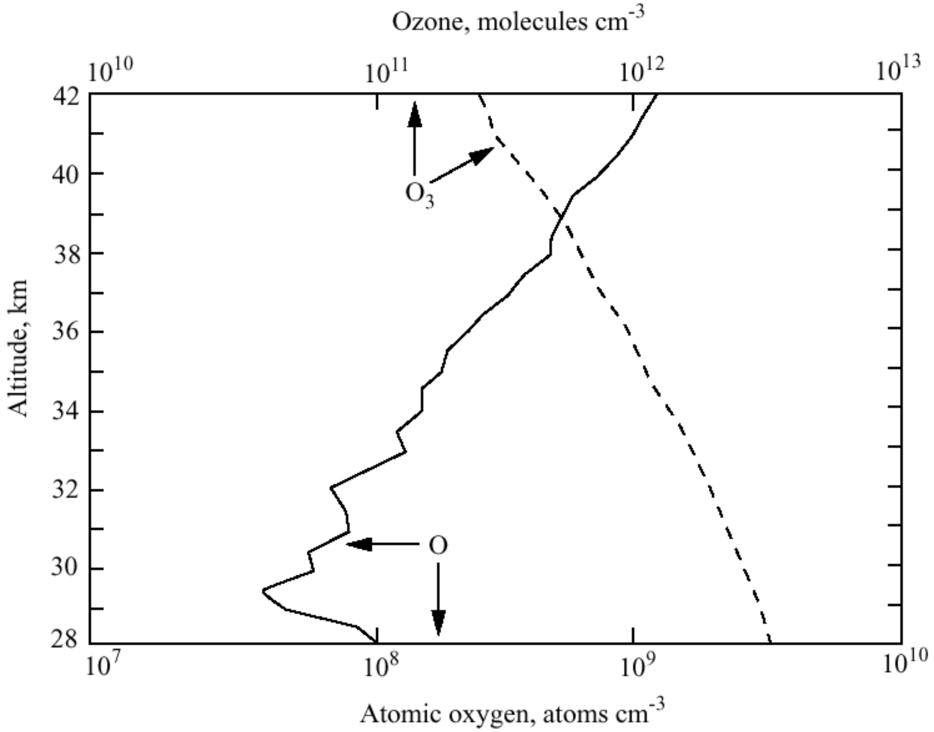
$$0 = \frac{d}{dt}[O] = k_3[O_3] - k_2[O][O_2][M] \Rightarrow k_3[O_3] = k_2[O][O_2][M] \Rightarrow$$

$$\frac{[O]}{[O_3]} = \frac{k_3}{k_2 C_{O_2} n_a^2} \Rightarrow [O_3] >> [O]$$

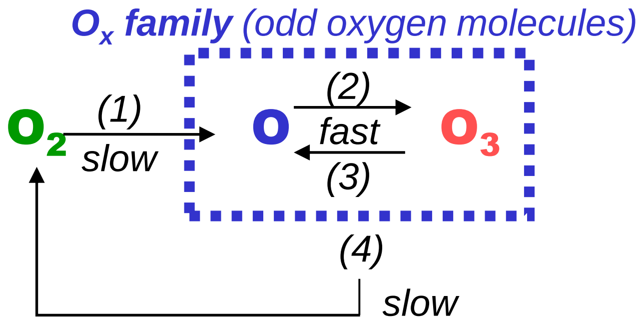
$[O_3]$ >> [O] throughout the stratosphere.

$$[O_x] = [O_3] + [O] \approx [O_3]$$

O_3 production and loss determined by the slow reactions (1) and (4).



O_x lifetime

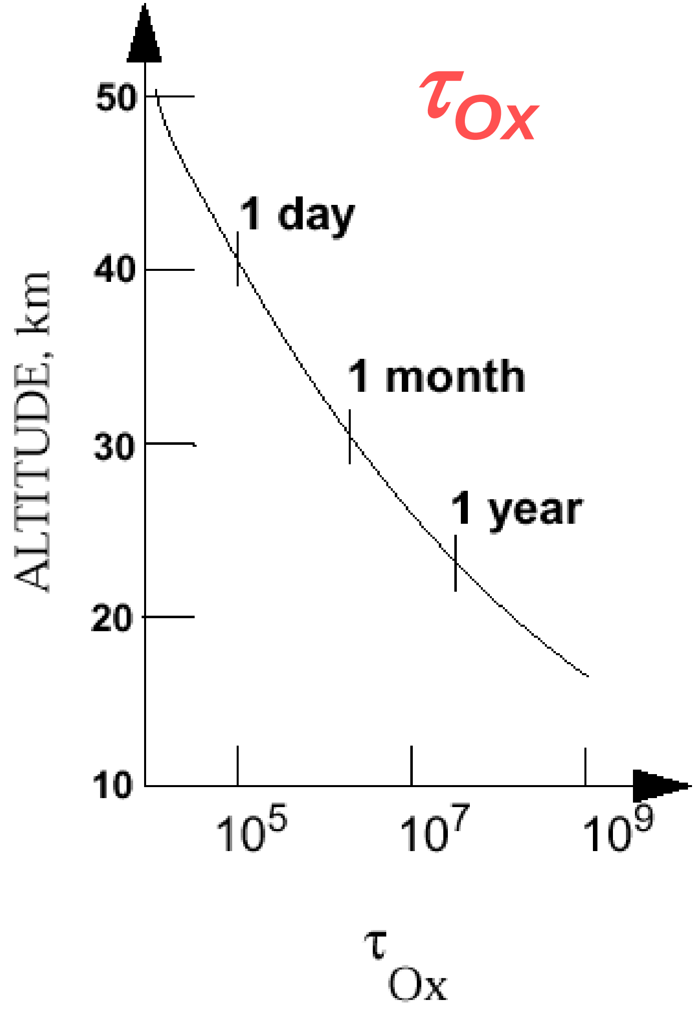


O_3 production determined by (1)
O_3 loss determined by (4)
O_3 lifetime determined by (4)

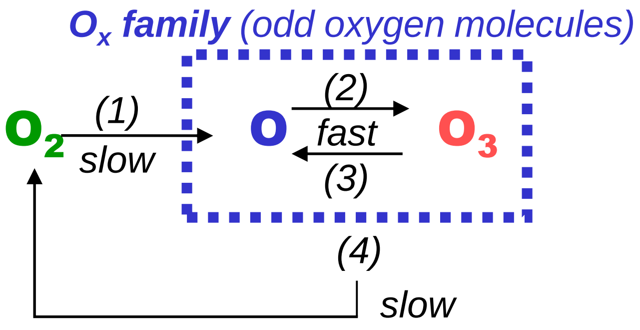
Lifetime (τ_{Ox}) for O_x

$$\tau_{O_x} = \frac{[O_x]}{2k_4[O][O_3]} \approx \frac{1}{2k_4[O]}$$

Steady-state conditions valid for O_x in large parts of the stratosphere, but maybe not in the lower part.



Chapman mechanism – Ozone levels



Steady-state conditions can be assumed for O_x in large parts of the stratosphere.

$$0 = \frac{d}{dt}[O_x] = 2k_1[O_2] - 2k_4[O][O_3] \; \text{Þ}$$

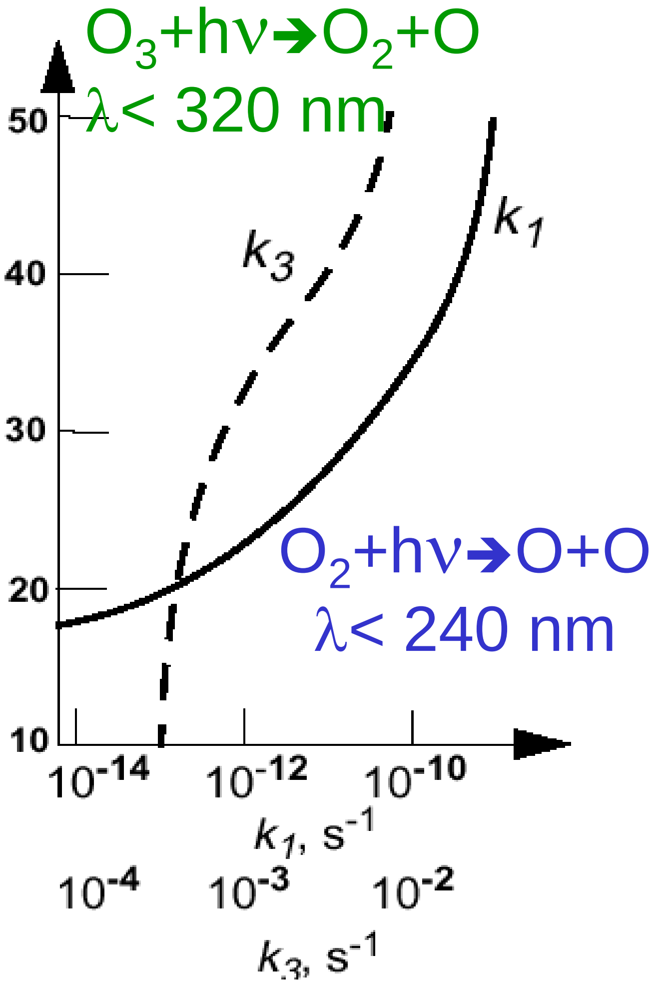
$$2k_1[O_2] = 2k_4[O][O_3] \; \text{Þ}$$

Stratospheric O_3 levels (Chapman):

$$[O_3]^2 = \frac{k_1 k_2}{k_3 k_4} C_{O_2}^2 n_a^3$$

Photolysis rates k_1 and k_3 vary with altitude z in the stratosphere.

Both $k_1(z)$ and $k_3(z)$ depend on $[O_3]$.



Chapman mechanism – Results

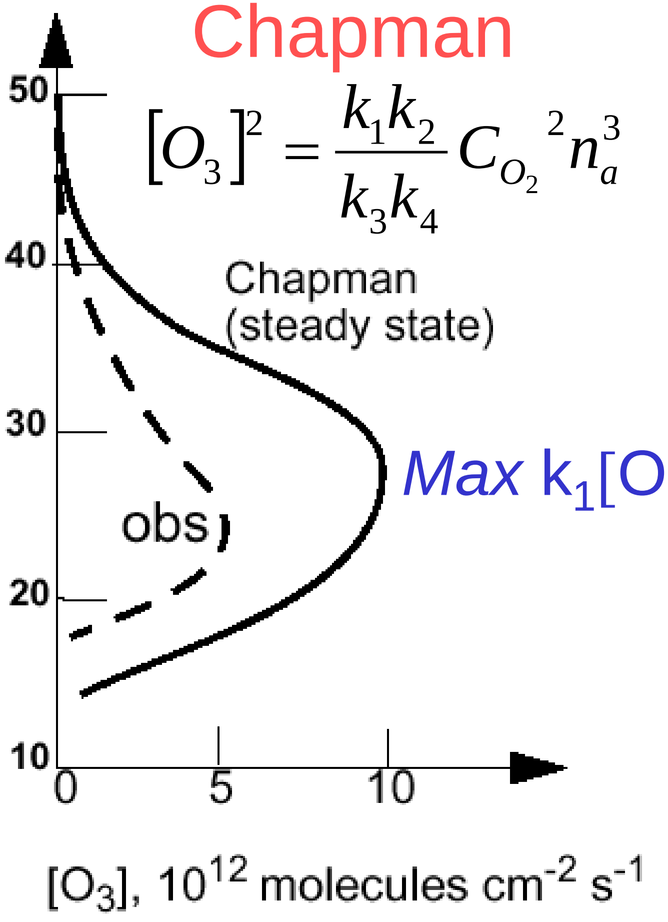
The Chapman mechanism can explain qualitatively the O_3 maximum at 20-30 km altitude.

O_x production $=2k_1[O_2]$ via reaction (1) depends strongly on altitude.

Photolysis rate (k_1) increases with altitude while $[O_2]$ decreases due to the pressure drop.

Observed natural ozone levels are significantly lower than predicted by the Chapman mechanism. ⇒

Additional sinks needed!



Chapman

$$[O_3]^2 = \frac{k_1 k_2}{k_3 k_4} C_{O_2}{}^2 n_a^3$$

Max $k_1[O_2]$

Catalytic ozone loss

Ozone can be consumed in catalytic processes, meaning that the component causing ozone destruction is not consumed.

(1) $O_3 + h\nu \rightarrow O_2 + O$

(2) $O_3 + X \rightarrow O_2 + XO$

(3) $O + XO \rightarrow O_2 + X$ (X conserved)

(Net) $2O_3 \rightarrow 3O_2$

X can be different components

X = OH : OH, HO_2

X = Cl : Cl, ClO

X = NO : NO, NO_2

X = Br : Br, BrO

Catalytic ozone loss - HO_x

Water vapour levels in the stratosphere are low (3-5 ppm)
Origin: transport from troposphere ($H_2O + O(^1D) \rightarrow 2OH$)

(5) $O_3 + h\nu \rightarrow O_2 + O$ (initiation)

(6) $OH + O_3 \rightarrow HO_2 + O_2$ (propagation)

(7) $HO_2 + O \rightarrow OH + O_2$ (propagation)

(Net) $2O_3 \rightarrow 3O_2$

HO_x family: hydroxyl radical OH, hydroperoxyl radical HO_2

Reaction (6) and (7) destroys ozone without consuming HO_x radicals (=catalysts).

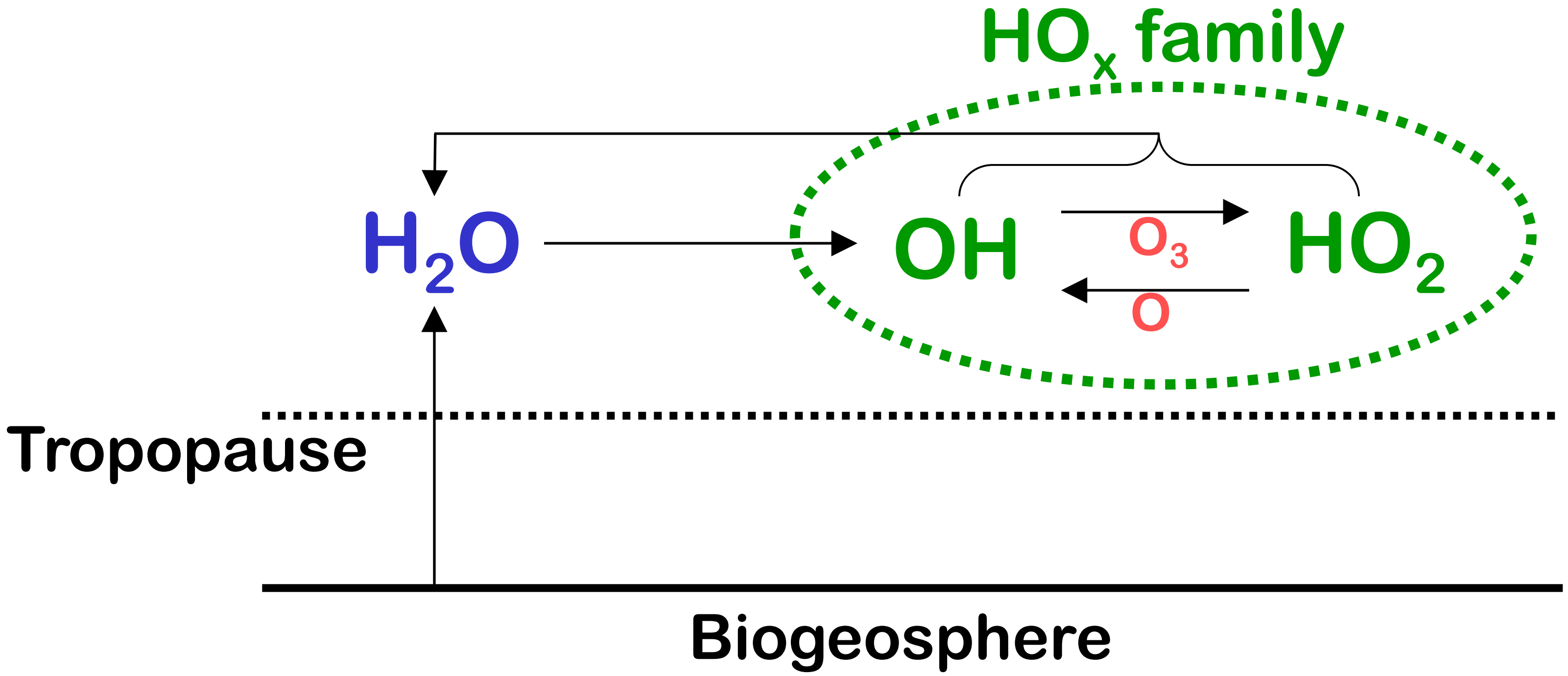
The catalytic ozone loss cycle is broken when the HO_x radical chain is terminated by mutual destruction of two HO_x radicals.

(8) $OH + HO_2 \rightarrow H_2O + O_2$ (termination)

Catalytic ozone loss - HO_x

HO_x is an important O_3 sink, but it is not enough as only complement to the Chapman mechanism to fully account for the observed natural ozone levels (1960-ies).

Additional catalytic sinks are needed!



Catalytic ozone loss - NO_x

Nitrogen oxides in the stratophere originate from aircraft (NO) and from Earth´s surface (N_2O).

(9) $NO + O_3 \rightarrow NO_2 + O_2$ (propagation)

(10) $NO_2 + h\nu \rightarrow NO + O$ (photolysis, radical production)

(2) $O + O_2 + M \rightarrow O_3 + M$

Null cycle! No net effect on ozone, but results in a fast exchange between NO ↔ NO_2

NO_x family

nitric oxide NO

nitrogen dioxide NO_2

An additional O sink is needed to break the null cycle:

(11) $NO_2 + O \rightarrow NO + O_2$

Catalytic ozone loss - NO_x

(9) $NO + O_3 \rightarrow NO_2 + O_2$
(11) $NO_2 + O \rightarrow NO + O_2$
(Net) $O_3 + O \rightarrow 2O_2$

Reaction (11) destroys O_x (=ozone) without consuming NO_x radicals (=catalysts).

Each cycle destroys two O_x molecules (=2 O_3 molecules)!

Reaction (11) is limiting for the ozone loss. The alternative is photolysis of NO_2. Reaction (11) does not occur in the troposphere where [O] is negligible.

$$-\frac{d}{dt}[O_3] \approx -\frac{d}{dt}[O_x] = 2k_{11}[NO_2][O]$$

Note! NO_x (and HO_x) results in a net loss of ozone in the stratosphere but ozone production in the troposphere.

Catalytic ozone loss - NO_x

The catalytic cycle is broken by consuming NO_x radicals.

(12) $NO_2 + OH + M \rightarrow HNO_3 + M$ (termination)

This happens during daytime, when OH is produced by photolysis (5). Nighttime (no OH) the following reactions take place:

(13) $NO_2 + O_3 \rightarrow NO_3 + O_2$ (propagation)
(14) $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$ (termination)

Reaction (14) only happens nighttime since NO_3 is rapidly photolyzed
(15) $NO_3 + h\nu \rightarrow NO_2 + O$ (photolysis)

Both HNO_3 (τ=weeks) and N_2O_5 (τ=hours, days) are non-radicals.

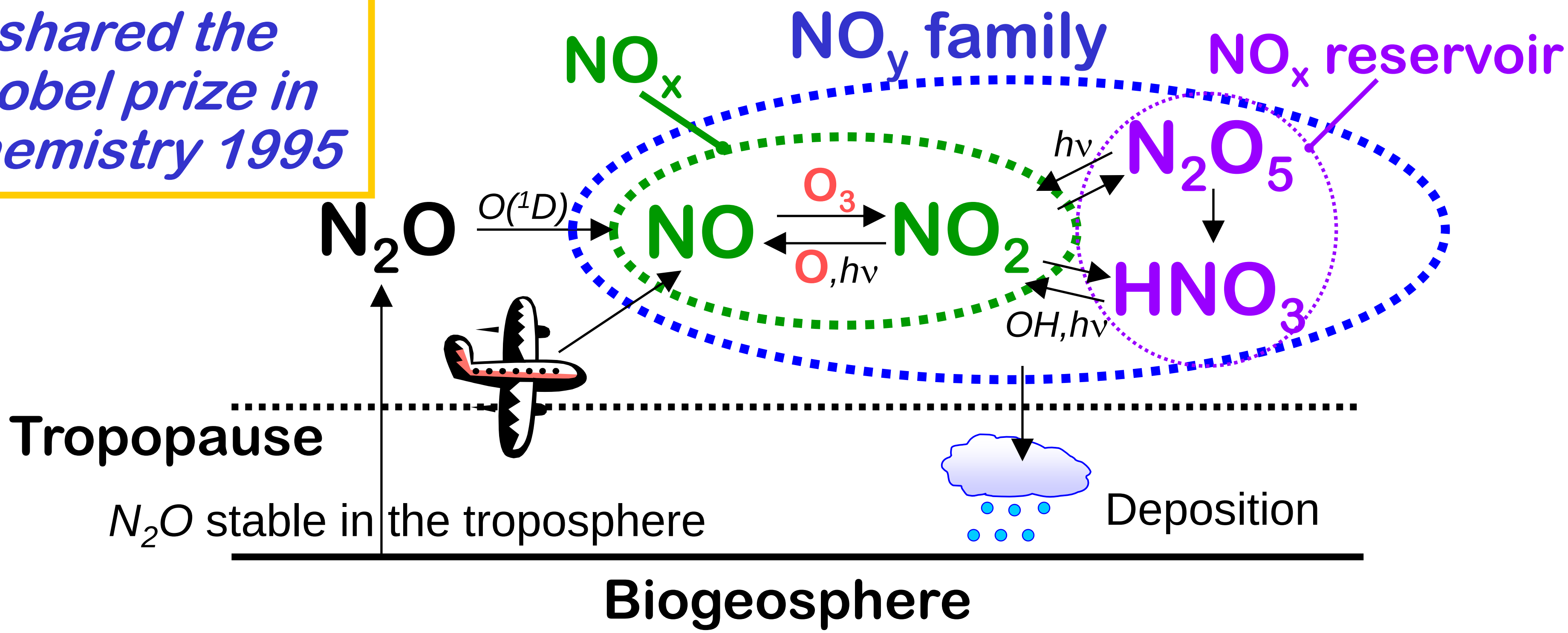
Together, HNO_3 and N_2O_5 form a **NO_x reservoir**.

Catalytic ozone loss – NO_x

The O_3 sinks attributable to NO_x and HO_x are sufficient as complement to the Chapman mechanism to account for the observed natural ozone levels (1970-ies).

Before the discovery of the ozone hole!

Paul Crutzen shared the Nobel prize in Chemistry 1995



NO_x

NO_y family

NO_x reservoir

N_2O

$O(^1D)$

$NO \xrightarrow{O_3} NO_2$

$NO_2 \xrightarrow{O, h\nu} NO$

N_2O_5

$h\nu$

HNO_3

$OH, h\nu$

Tropopause

N_2O stable in the troposphere

Deposition

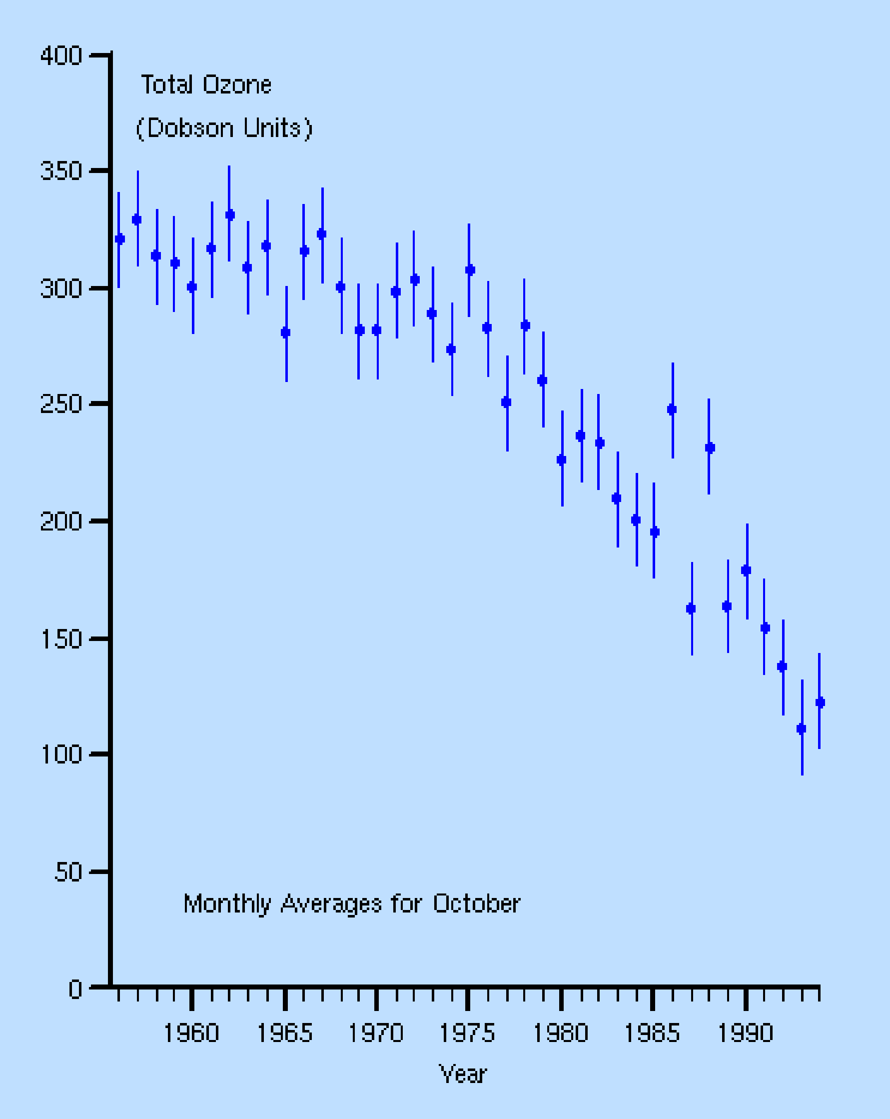
Biogeosphere

Stratospheric ozone – Antarctica

The ozone hole was first observed 1981 at Halley Bay, Antarctica.

The resultats were so astonishing that the scientists first would not believe their own data, and waited to publish them until 1985.

J.C. Farman, B.G. Gardiner and J.D. Shanklin.
Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction
Nature, 1985



Halley Bay – Antarctica

Ozone hole firs observed at Halley Bay, Antarctica, around 1980. Data published 1985.

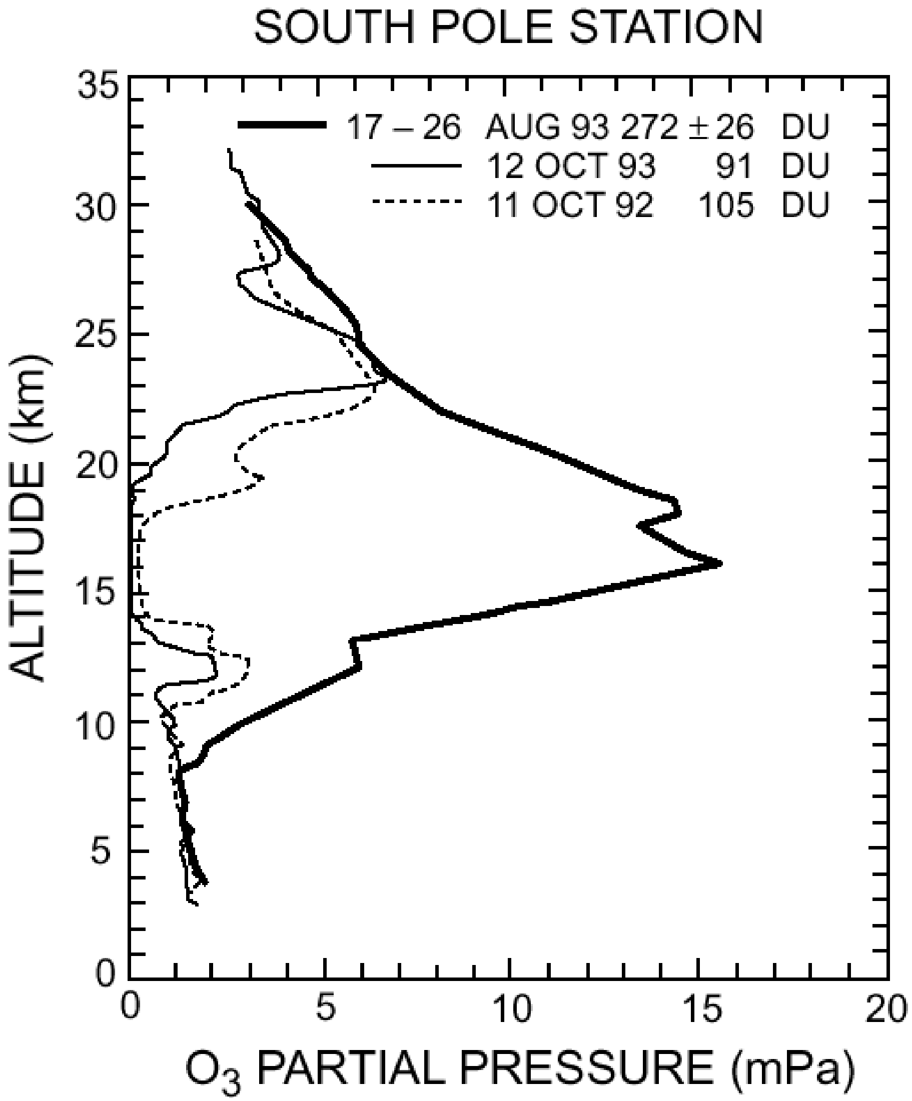
The base at Halley Bay is operated by the British Antarctic Survey and lies on a sheet of ice in the Weddel Sea. The winter night at Halley Bay lasts 105 days!

Stratospheric ozone hole

The ozone hole is largest in October, when spring comes to Antarctica.

The ozone layer can disappear almost completely at some altitudes.

Data from ozone sondes (balloons) launched from the South Pole.

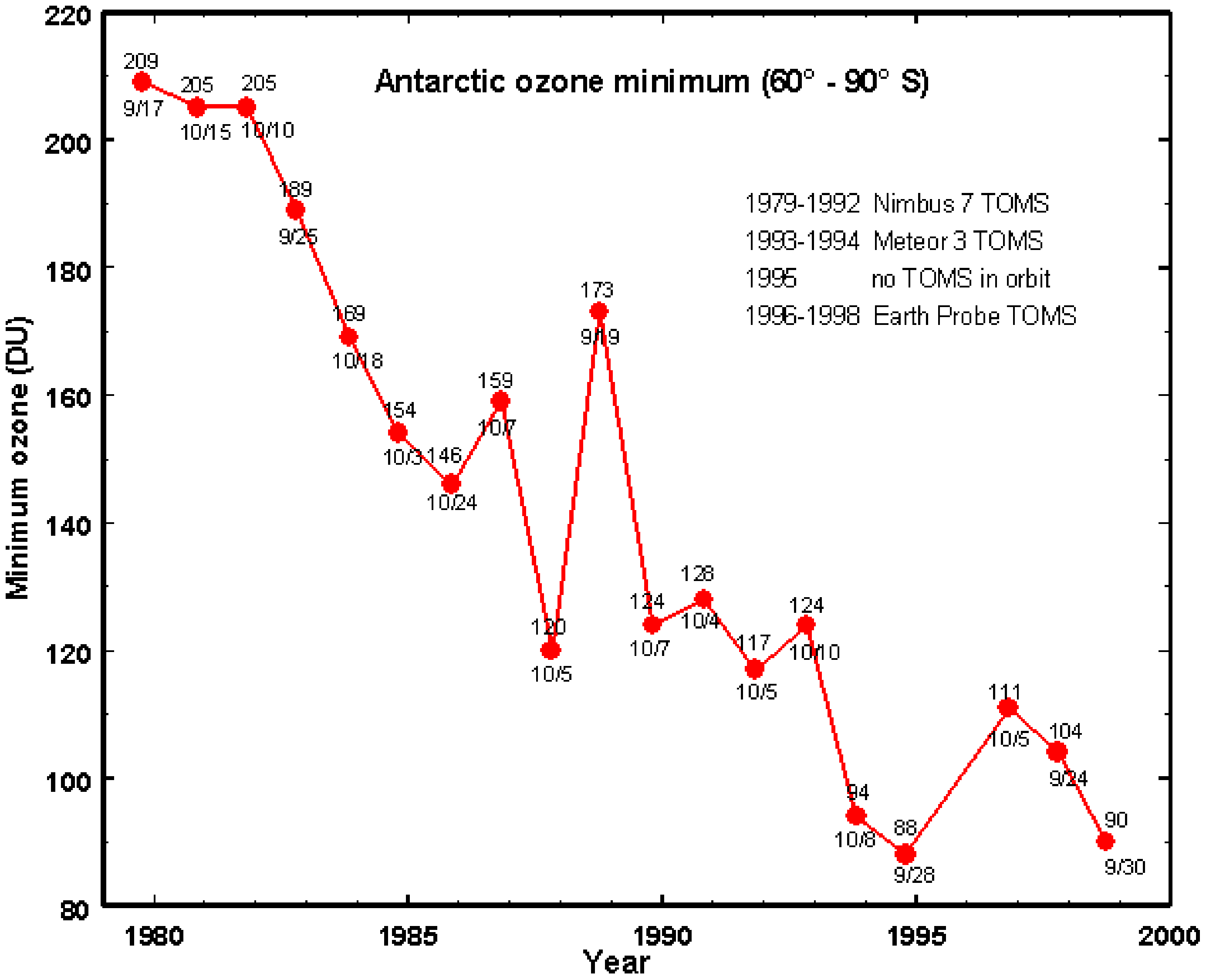


Stratospheric ozone – Antarctica

Ozone minimum
measured
17 Sept – 24 Oct

Lowest measured
ozone column:

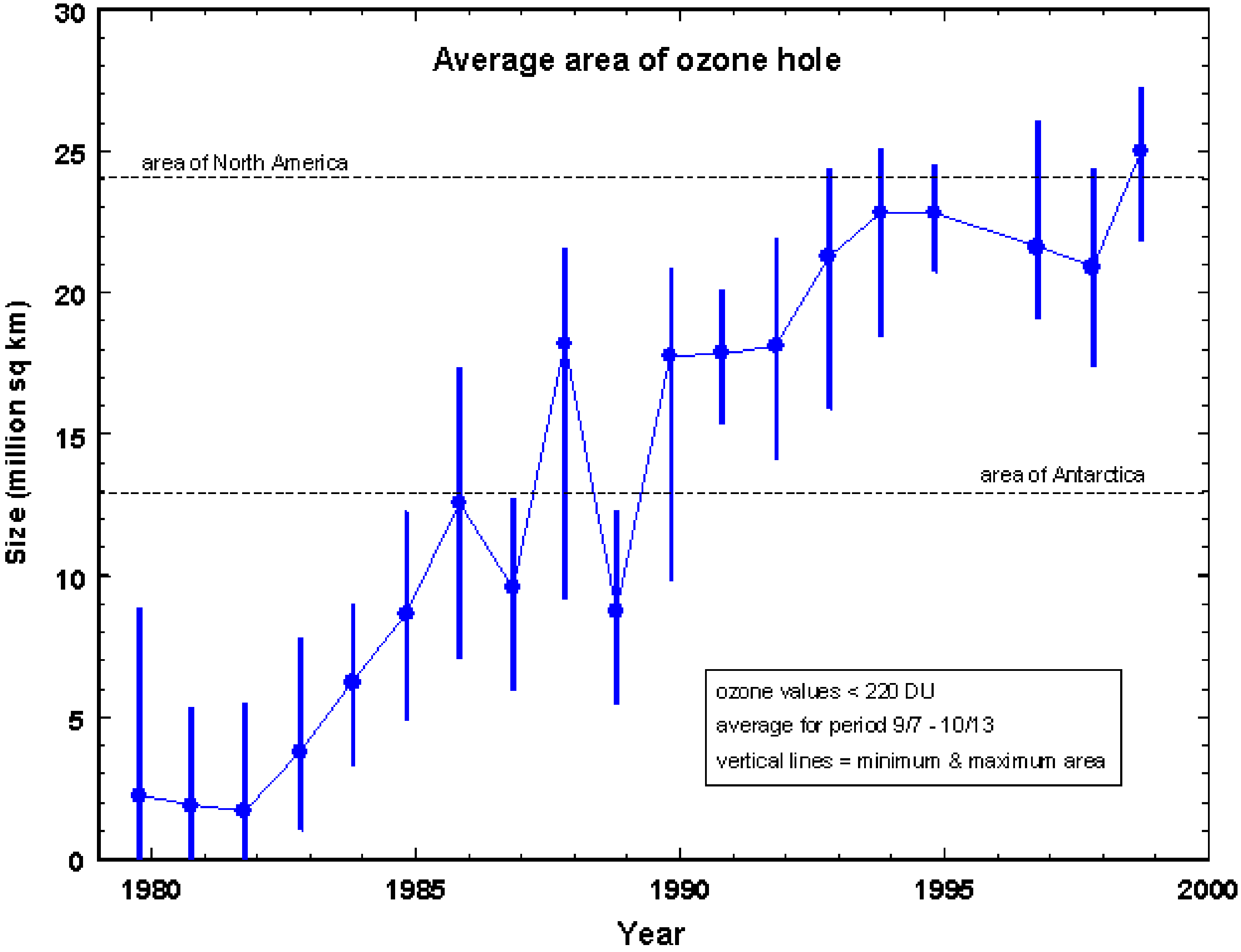
88 DU



Stratospheric ozone – Antarctica

The extension of the ozone hole is defined as the area having < 220 DU (Dobson Units) ozone.

This area is now as large as the entire North American continent when at maximum.



Stratospheric ozone – CFCs

Ozone depleting substances:

CFC: ChloroFluoroCarbons ("hard CFC")
HCFC: HydroChloroFluoroCarbons ("soft CFC")
Halons, methyl bromide, certain solvents

Volatile compounds containing chlorine and bromine.

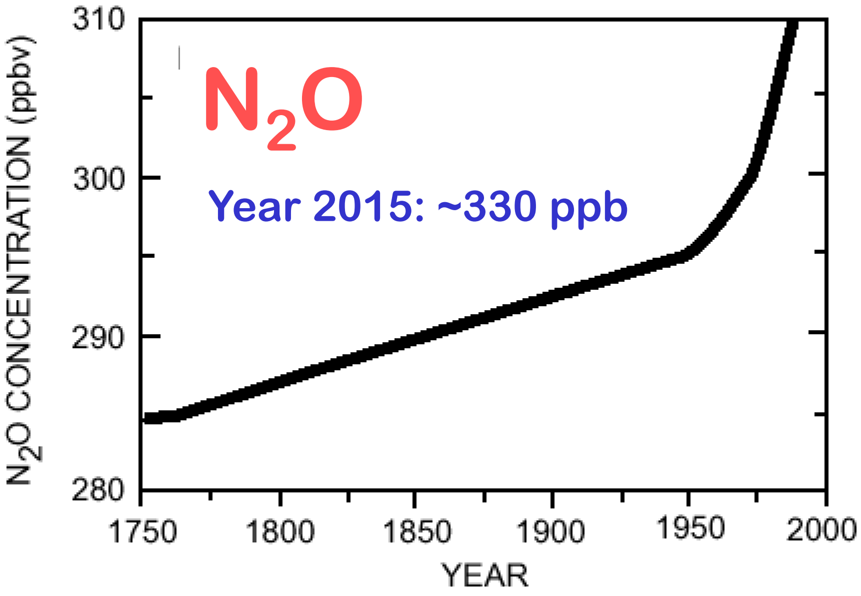
Extremely stable in the troposphere
➔ They can be transported up to the stratosphere.

Use of these substances:

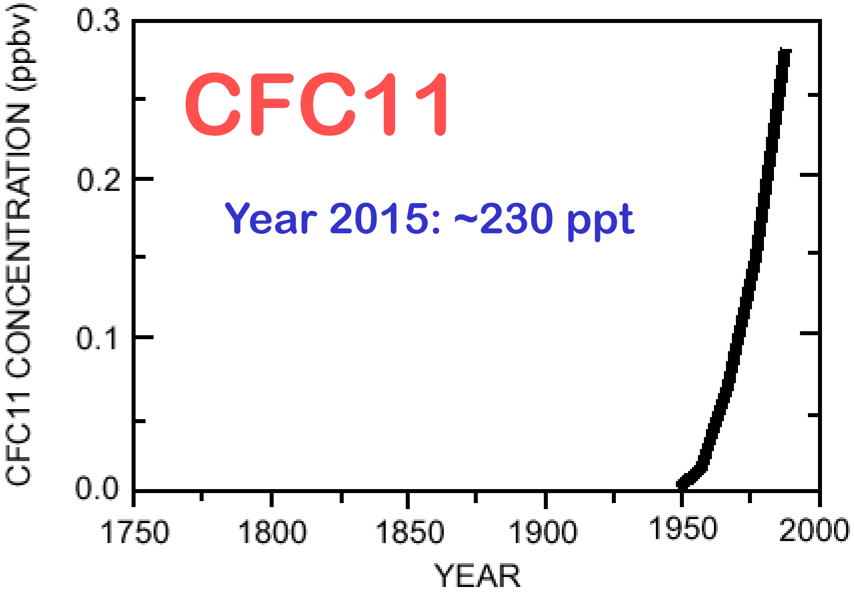
- Cooling medium
- Blower for plastics
- Dry cleaning fluid
- Cleaning detergent
- Solvents
- Propellant gas in spray cans

Catalytic ozone loss – CFC

CFCs and HCFC are not found in nature.
Industrial-scale production started in the 1930-ies.
CFC has a lifetime in the atmosphere of 50-300 years.
Cl-levels in the atmosphere:
1980 level: 2 ppb (reached again 2050?)
Natural level: ~0.7 ppb (reached earliest 2100)



Year 2015: ~330 ppb



Year 2015: ~230 ppt

Catalytic ozone loss - ClO_x

CFCs are photolysed by UV radiation in the stratosphere.

(20) $CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$ (initiation)

ClO_x family: Cl and ClO (radicals)

(21) $Cl + O_3 \rightarrow ClO + O_2$
(22) $ClO + O \rightarrow Cl + O_2$
(Net) $O_3 + O \rightarrow 2O_2$

Reaction (21) and (22) destroys O_x (=ozone) without consuming ClO_x radicals (=catalysts).

Each cycle destroys two O_x molecules (=2 O_3 molecules)!

Reaction (22) is limiting for the ozone loss.

$$-\frac{d}{dt}[O_3] \text{ » } -\frac{d}{dt}[O_x] = 2k_{22}[ClO][O]$$

Catalytic ozone loss - ClO_x

The catalytic cycle is broken when ClO_x radicals are comsumed.

(23) $Cl + CH_4 \rightarrow HCl + CH_3$
(24) $ClO + NO_2 + M \rightarrow ClNO_3 + M$ (termination)

Both HCl (τ=weeks) and $ClNO_3$ ($\tau \approx$1 day) are non-radicals.

Together, HCl and $ClNO_3$ form a **ClO_x reservoir**.

Cl_y family: ClO_x+ its ClO_x reservoirs
Cl and ClO (radicals), HCl and $ClNO_3$ (non-radicals)

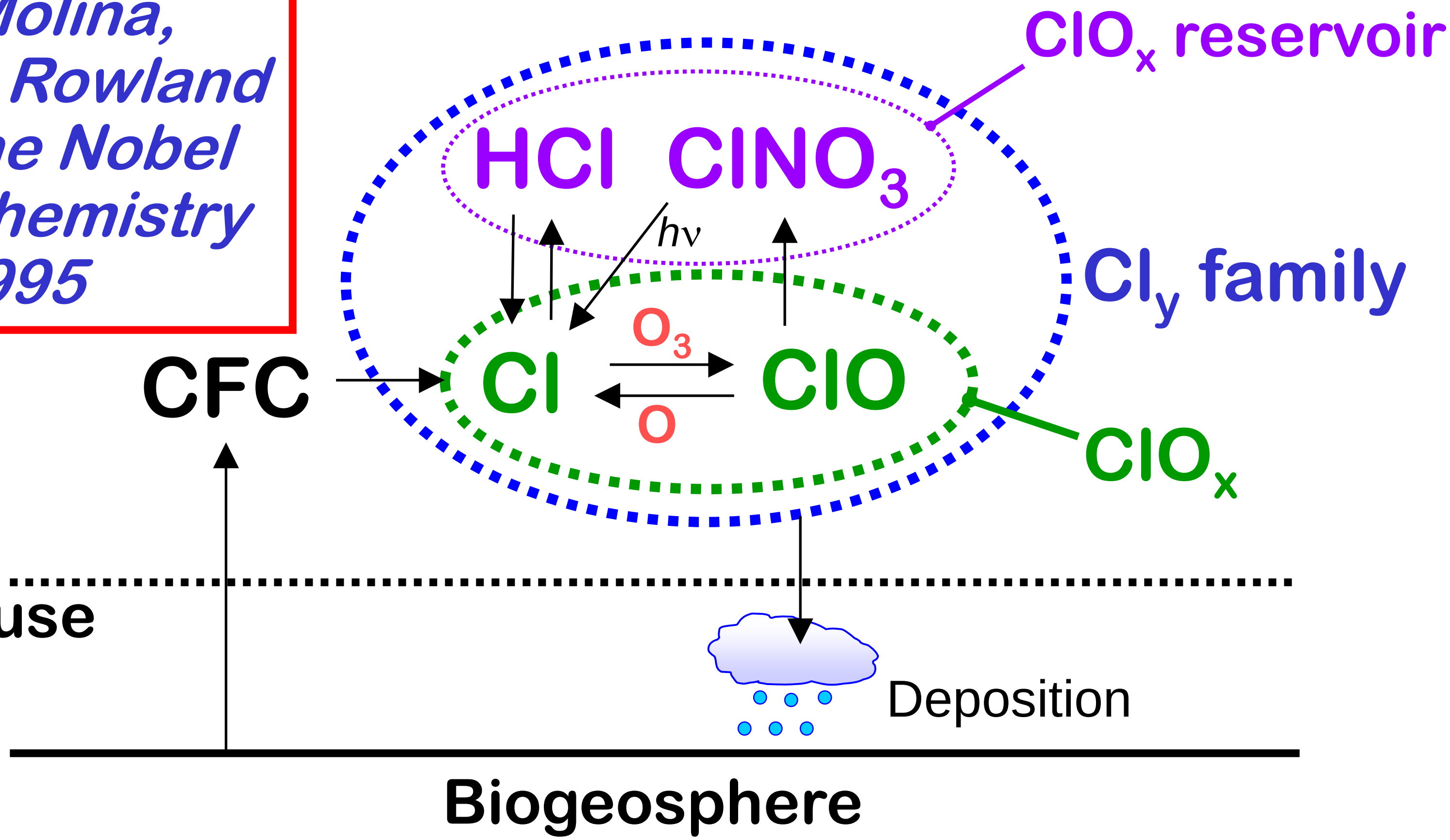
The reservoirs return to ClO_x

(25) $HCl + OH \rightarrow Cl + H_2O$
(26) $ClNO_3 + h\nu \rightarrow Cl + NO_3$ (photolysis)

Catalytic ozone loss – ClO_x

1980-ies: The evidence that CFCs can seriously damage the stratospheric ozone layer led to the signing of the Montreal protocol in 1987. CFC production stopped in 1996.

Mario Molina, Sherwood Rowland shared the Nobel prize in Chemistry in 1995



Catalytic ozone loss - ClO

The catalytic cycle with ClO_x radicals was rewarded the Nobel prize but could not explain the ozone hole !!

Early spring in Antarctica is relatively dark and levels of O are low.

(11) $NO_2 + O \rightarrow NO + O_2$ and...
(22) $ClO + O \rightarrow Cl + O_2$ ...are not efficient !

Yet another catalytic cycle involving ClO is needed:

(27) $ClO + ClO + M \rightarrow ClOOCl + M$ (ClO dimer)
(28) $ClOOCl + h\nu \rightarrow + ClOO + Cl$ (split in ”wrong” place)
(29) $ClOO + M \rightarrow Cl + O_2 + M$
(30) $Cl + O_3 \rightarrow ClO + O_2$ (2x)
(Net) $2O_3 \rightarrow 3O_2$

Reaction (27) is limiting for the ozone loss, which makes the loss rate proportional to $[ClO]^2$, as opposed to the ClO_x mechanism (22).

Catalytic ozone loss - ClO

Why are the levels of ClO radicals so high during spring in Antarctica?

Heterogeneous chemical processes (multiple phases involved) constitute an efficient sink for the ClO_x reservoir.
Polar stratospheric clouds (PSC) provide a surface.

(32) $ClNO_3 + HCl \xrightarrow{PSC} Cl_2 + HNO_3$

(33) $Cl_2 + h\nu \rightarrow 2Cl$

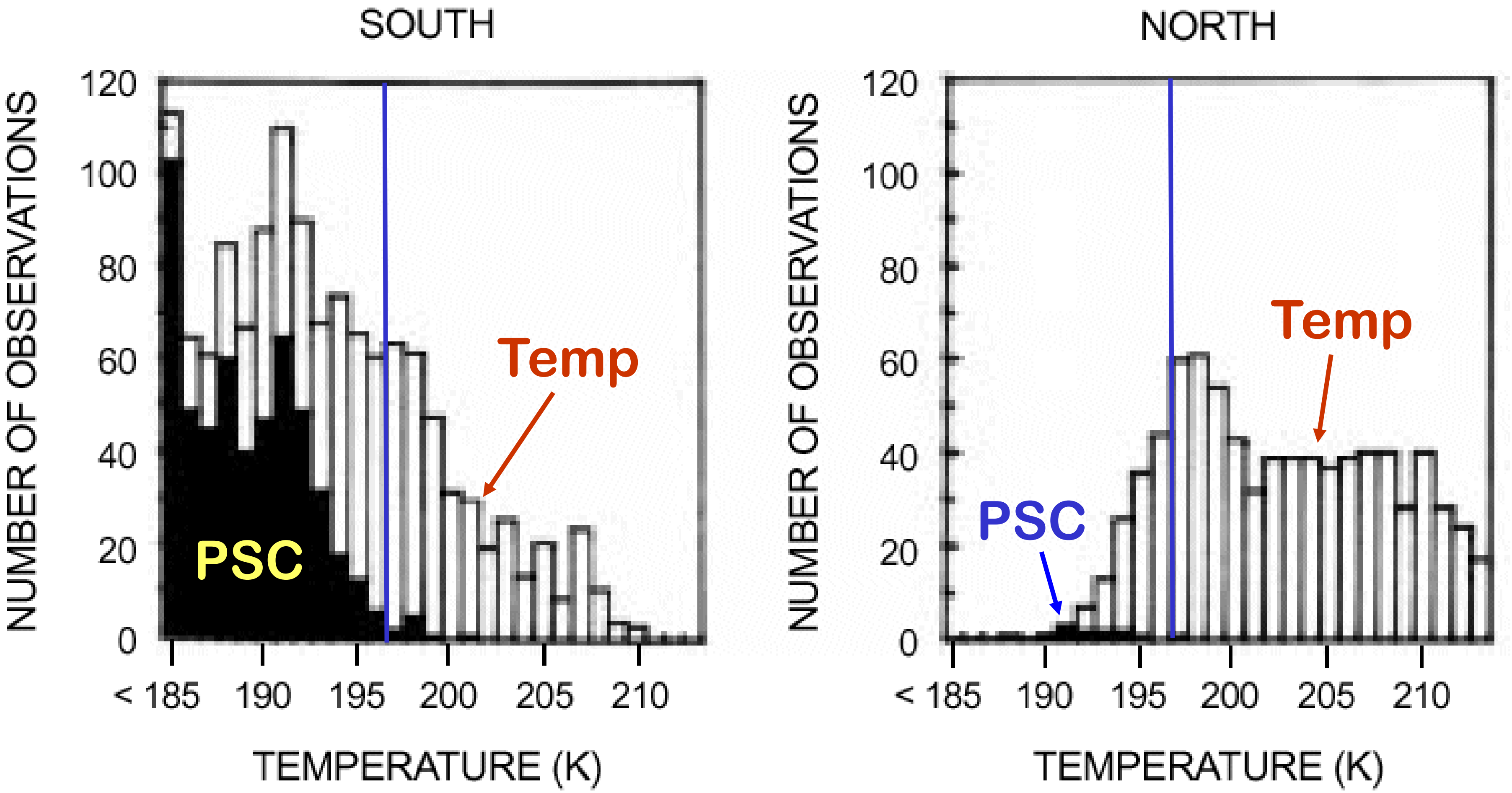
Reaction (32) is so fast that either all $ClNO_3$ or HCl is titrated out.

The ratio ClO_x/Cl_y is normally ~0.1, but can reach 1 during early spring.
The ClO_x reservoir becomes completely empty !

Polar stratospheric clouds (PSC) are essential in forming of the ozone hole.

Stratospheric ozone

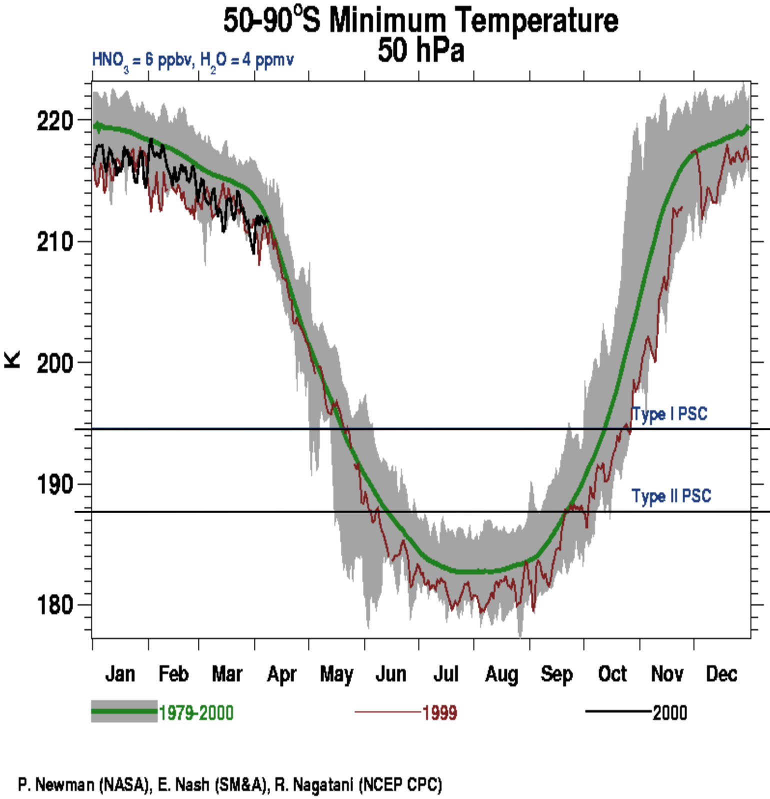
Polar stratospheric clouds (PSC) are formed at temperatures lower than ~ 197 K, which is more frequent at the South Pole than at the North Pole.



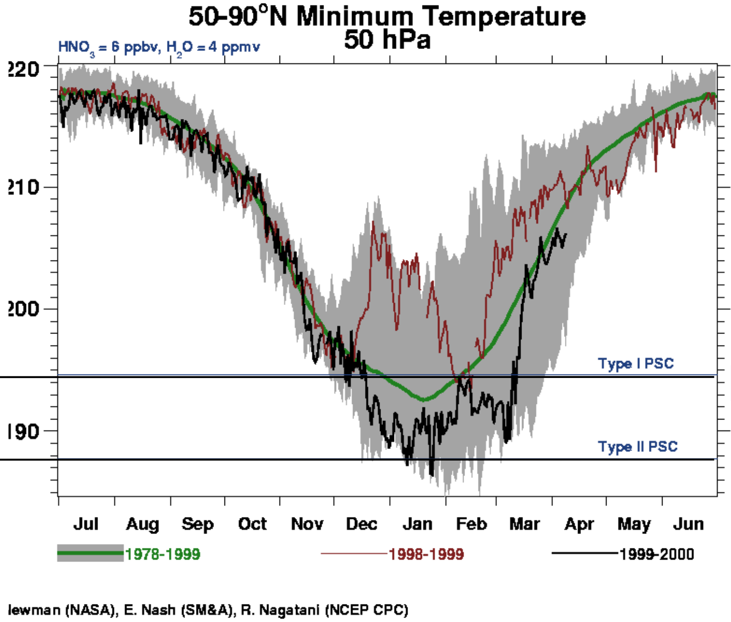
Temperatures in the stratosphere

Minimum temperatures at 50 hPa

Antarctic, 50-90° S



Arctic, 50-90° N



PSC-1

PSC-2

(H_2O)

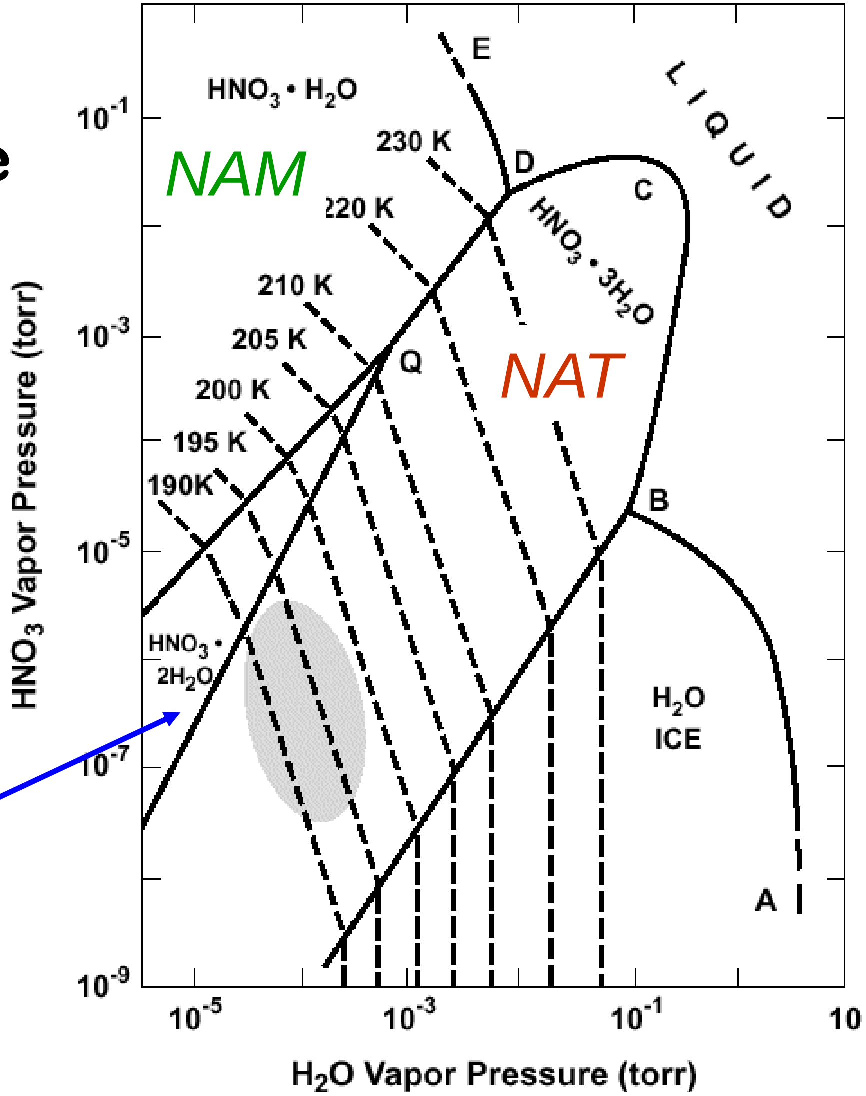
Stratospheric ozone

Hydrated nitric acid (*HNO_3*) forms ice crystals at higher temperatures compared to pure water → more PSC.

$HNO_3 \cdot H_2O$
Nitric Acid Monohydrate (NAM)

$HNO_3 \cdot 3H_2O$
Nitric Acid Trihydrate (NAT)

$HNO_3 \cdot 2H_2O$
Nitric Acid Dihydrate (NAD)



Stratospheric ozone

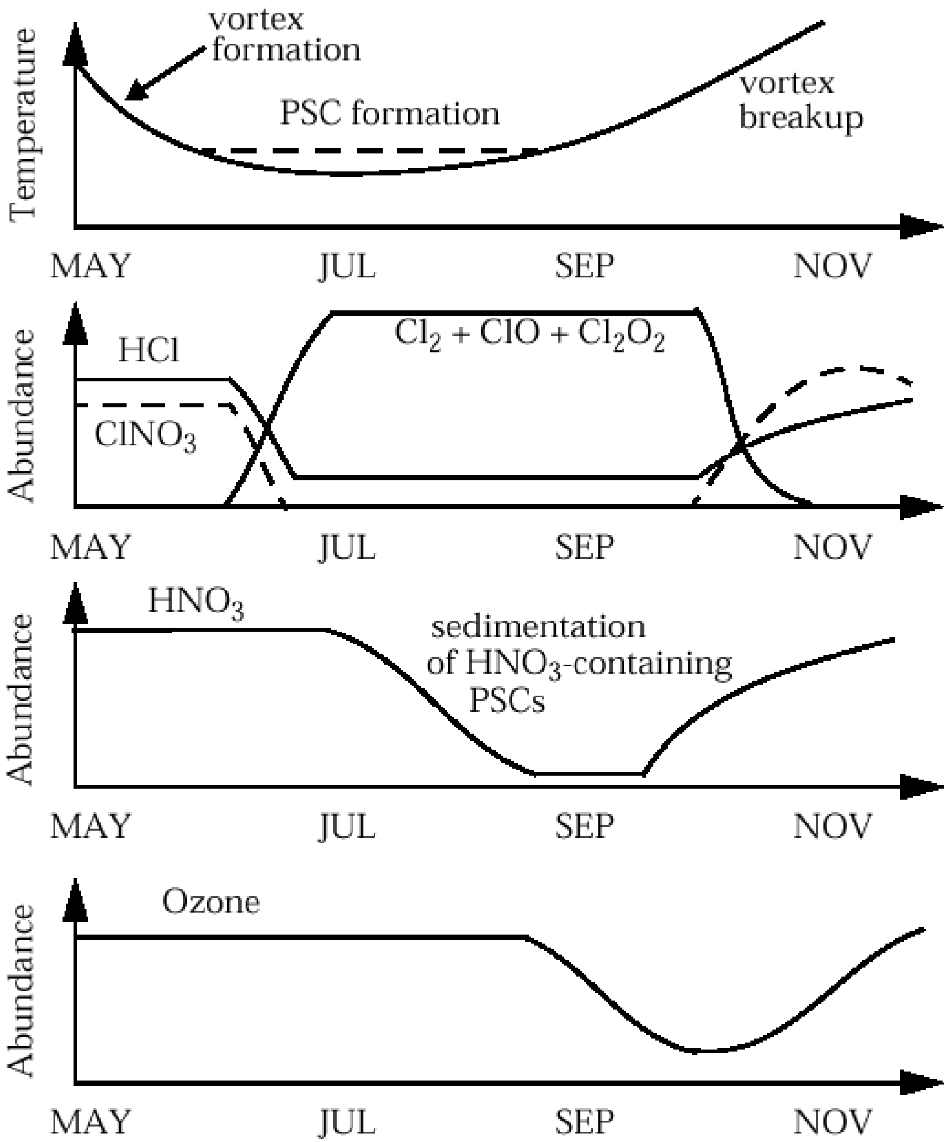
The polar vortex is formed as the sun sets in Antarctica. Polar stratospheric clouds (PSC) are formed.

ClO$_x$ reservoir is emptied.

Cl, *Cl*$_2$ are released ➔ *ClO* and *ClOOCl* form.

When the sun rises again over Antarctica *ClOOCl* is photolyzed and the catalytic *ClO* cycle starts.

[*HNO*$_3$] are very low due to sedimentation ➔ no new source of *NO*$_2$ och *ClNO*$_3$.



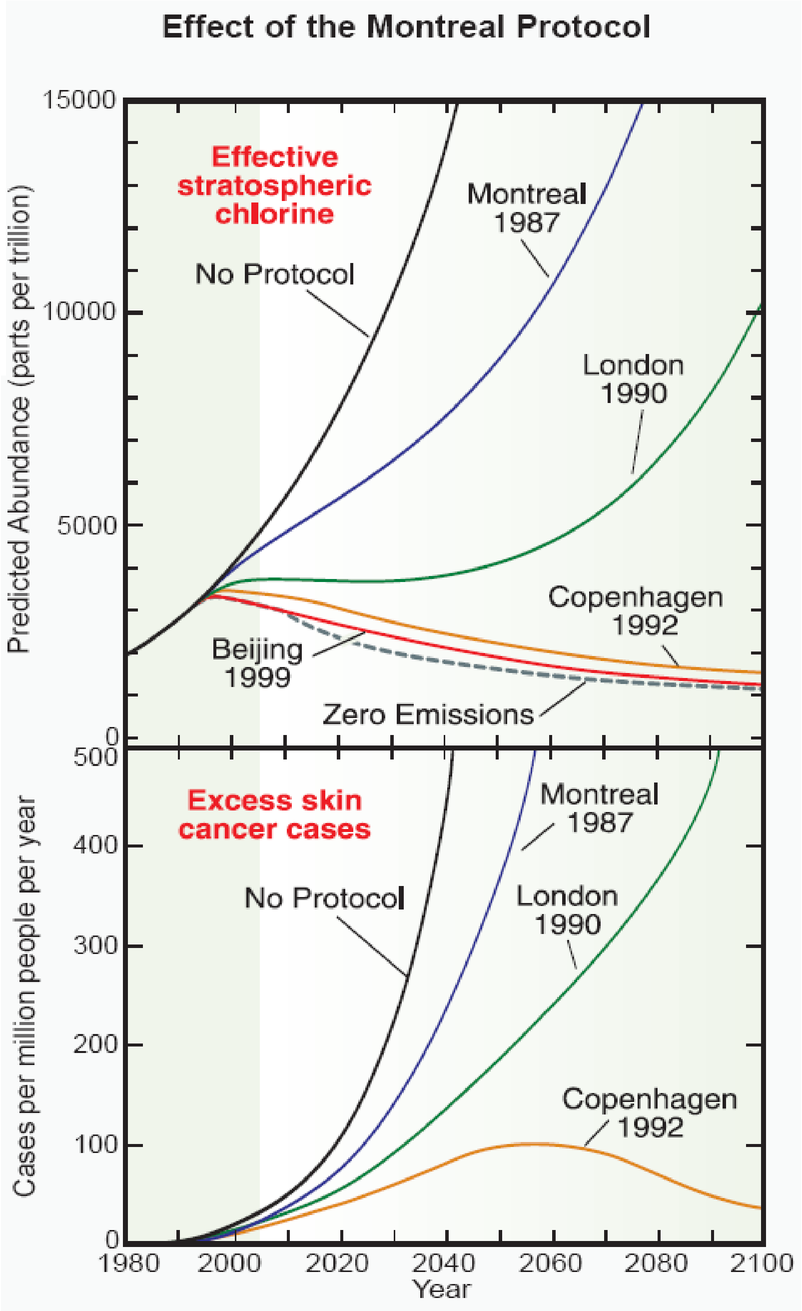
Stratospheric ozone – Effect of protocols

Stratospheric chlorine levels

Already decreasing owing to the protocols!

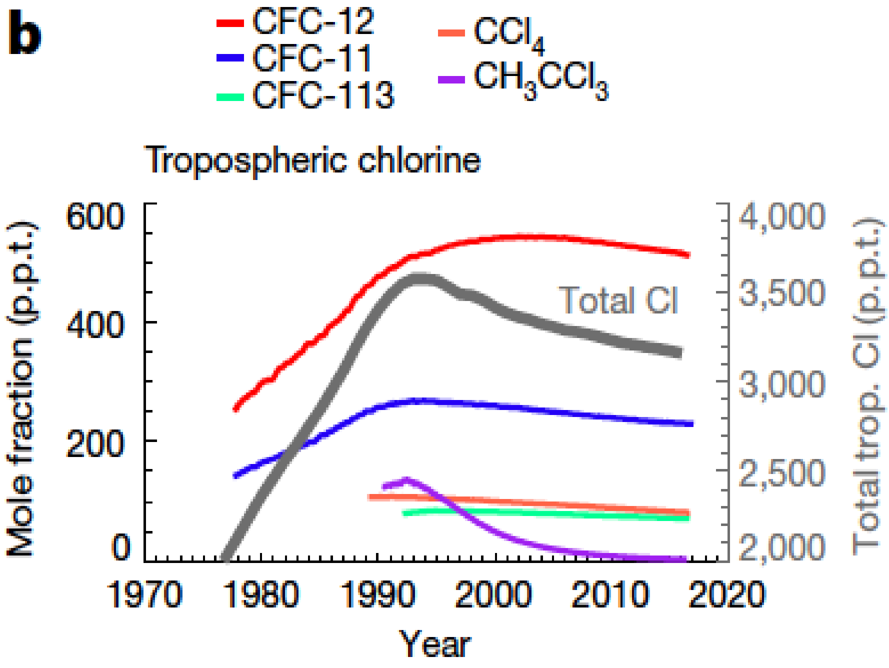
Number of extra cases of skin cancer

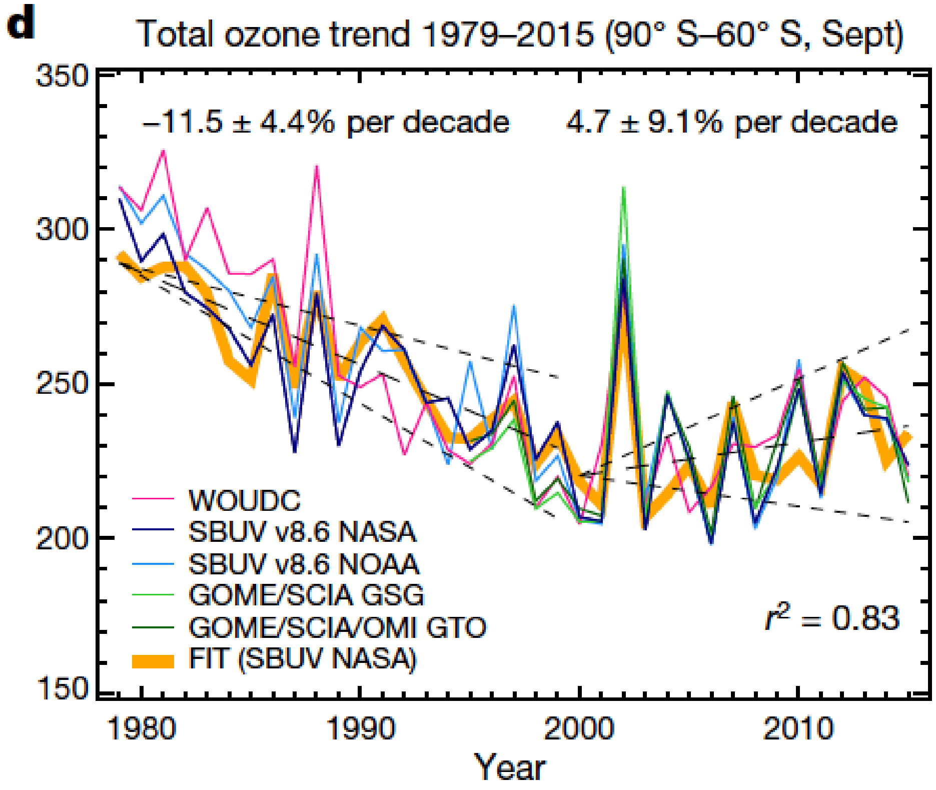
Increasing until 2055 despite the protocols!



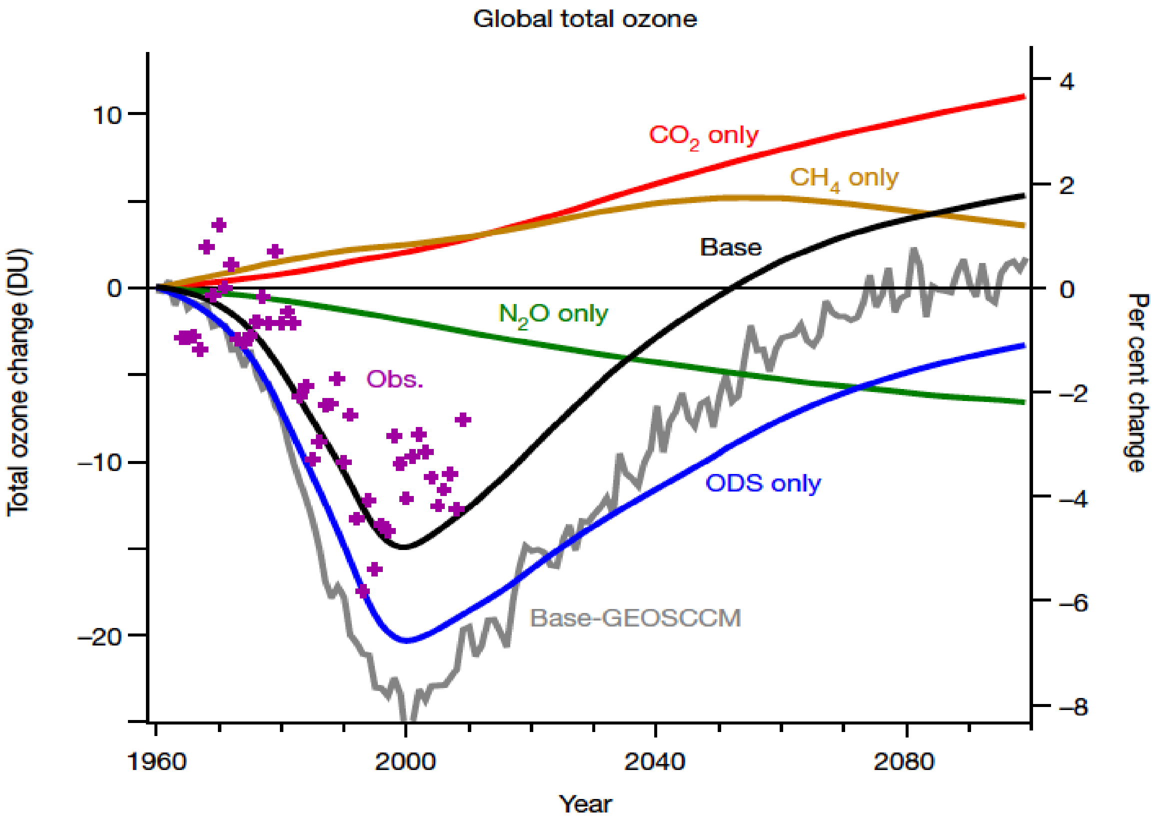
Stratospheric ozone - Recovery

- Large inter-annual variations driven by dynamic circulation patterns make it hard to find significant trends in stratospheric ozone recovery.
- Significant trends only seen over Antarctica in September





Stratospheric ozone - Recovery



Decreasing ODS (ozone-depleting substances) → recovery of ozone

Increased GHG (CO_2 & CH_4) cause cooling in the upper stratosphere → slower gas-phase ozone destruction

Increased N2O → increase [NOx] → increased ozone depleation