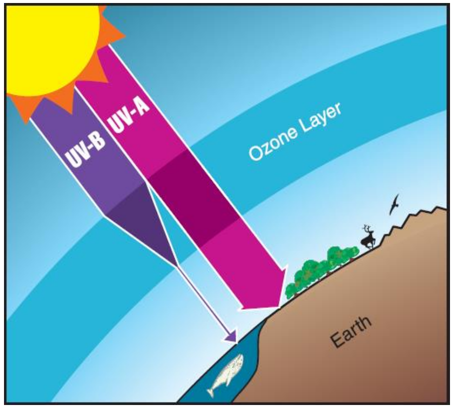

Atmospheric Chemistry

Stratospheric ozone

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Stratospheric ozone

Important concepts of this lecture:

- **Chapman mechanism**

  O_x – odd oxygen family

- **Catalytic ozone destruction with**

  HO_x, NO_x, ClO_x cycles ,

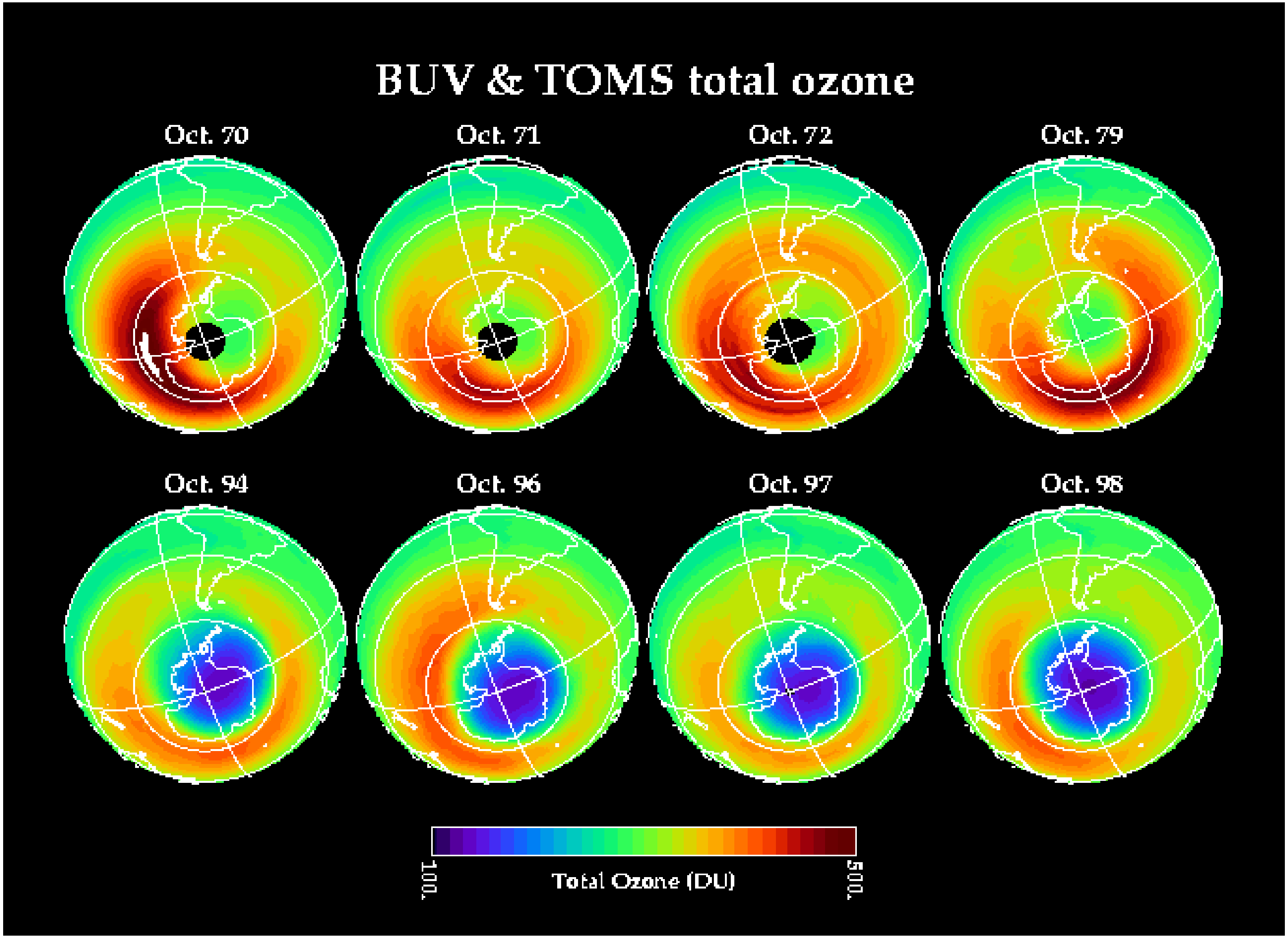
  including initiation, propagation, null cycles and reservoirs

- **The Antarctic ozone hole**

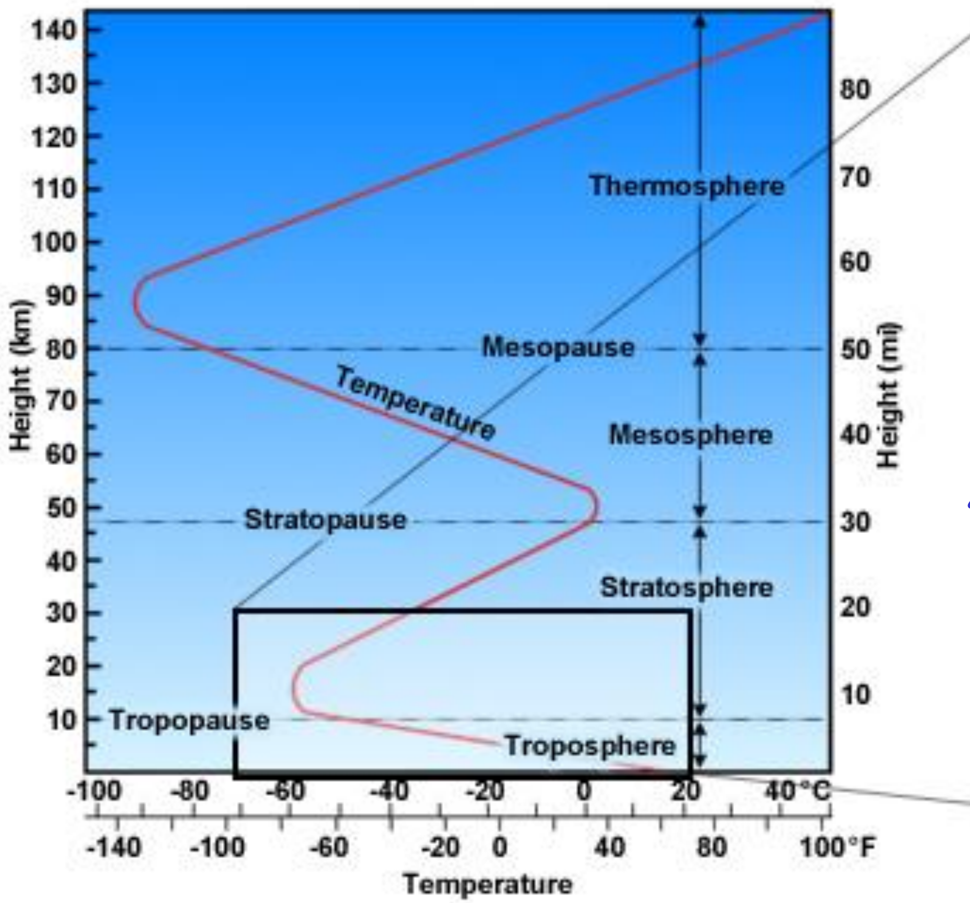
ClO-ClO mechanism

HNO_3 and PSC heterogenous chemistry

Stratospheric ozone – Southern hemisphere



Why is the stratosphere?



Why T-inversion?!

1. *Energy absorption by ozone lead to dissociation (O3->O+O2) 280-315 nm*
2. *Recombination give heat release (O+O2->O3)*

As a result of T-inversion the stratosphere is stable, it has slow vertical mixing compared to the troposphere.

Spectrum of solar radiation vs. altitude

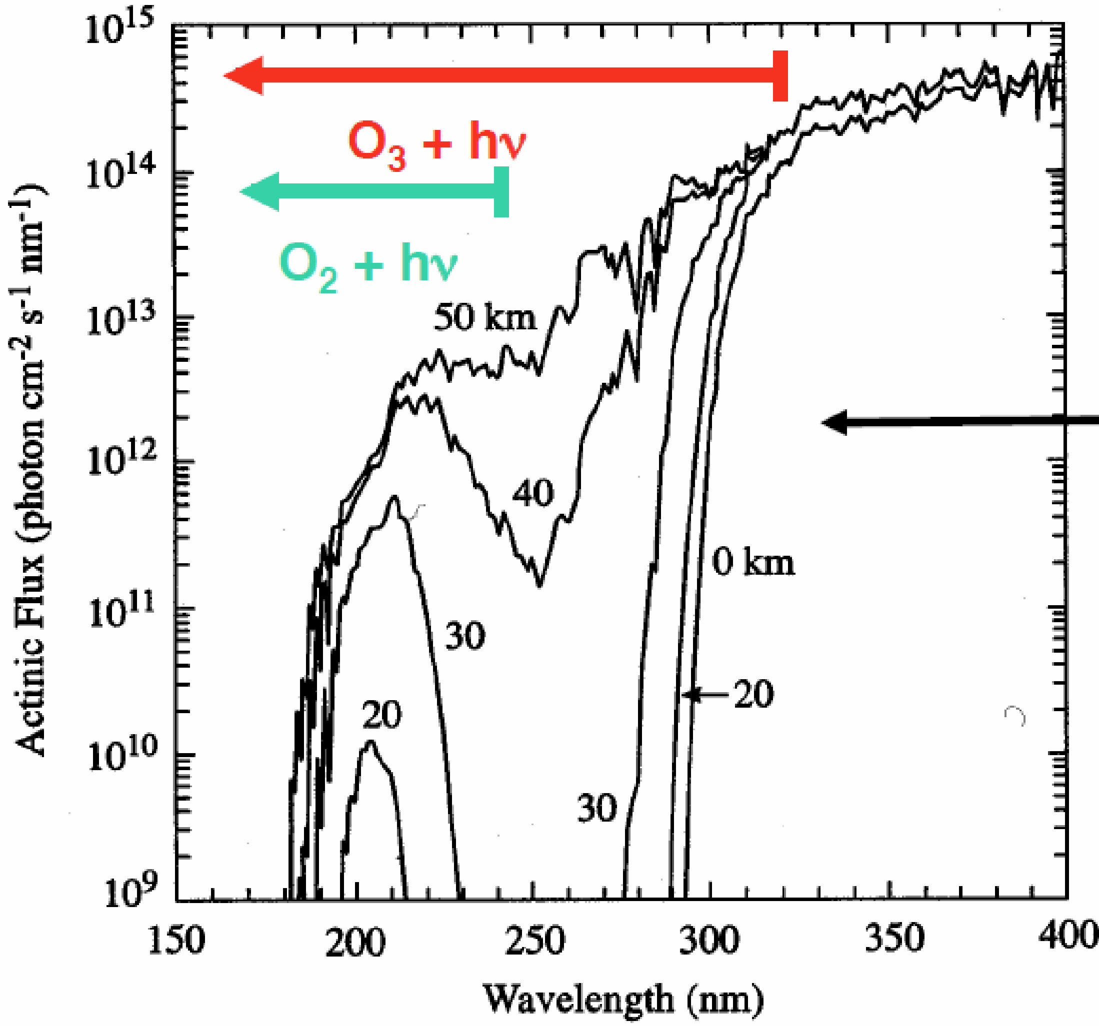
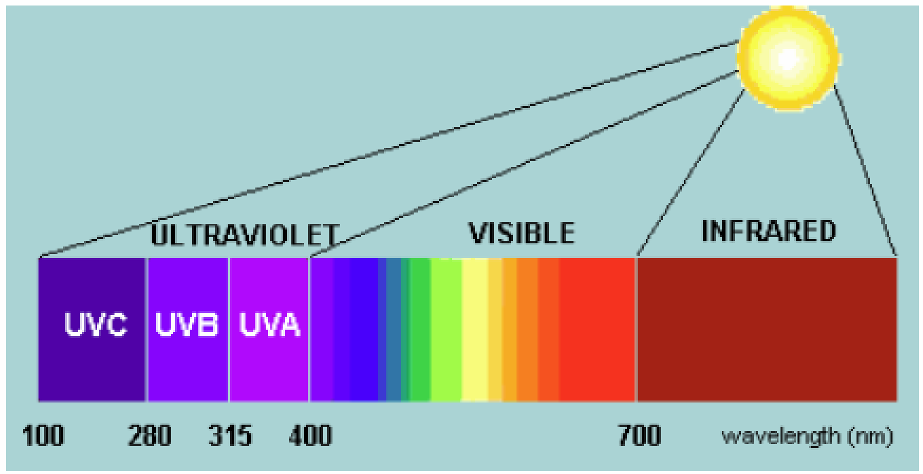


Fig. 10-2 Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W. B., et al. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. JPL Publication 97-4. Pasadena, Calif.: Jet Propulsion Lab, 1997.

Only this part reaches the Earth's surface (λ > 290 nm).



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!!

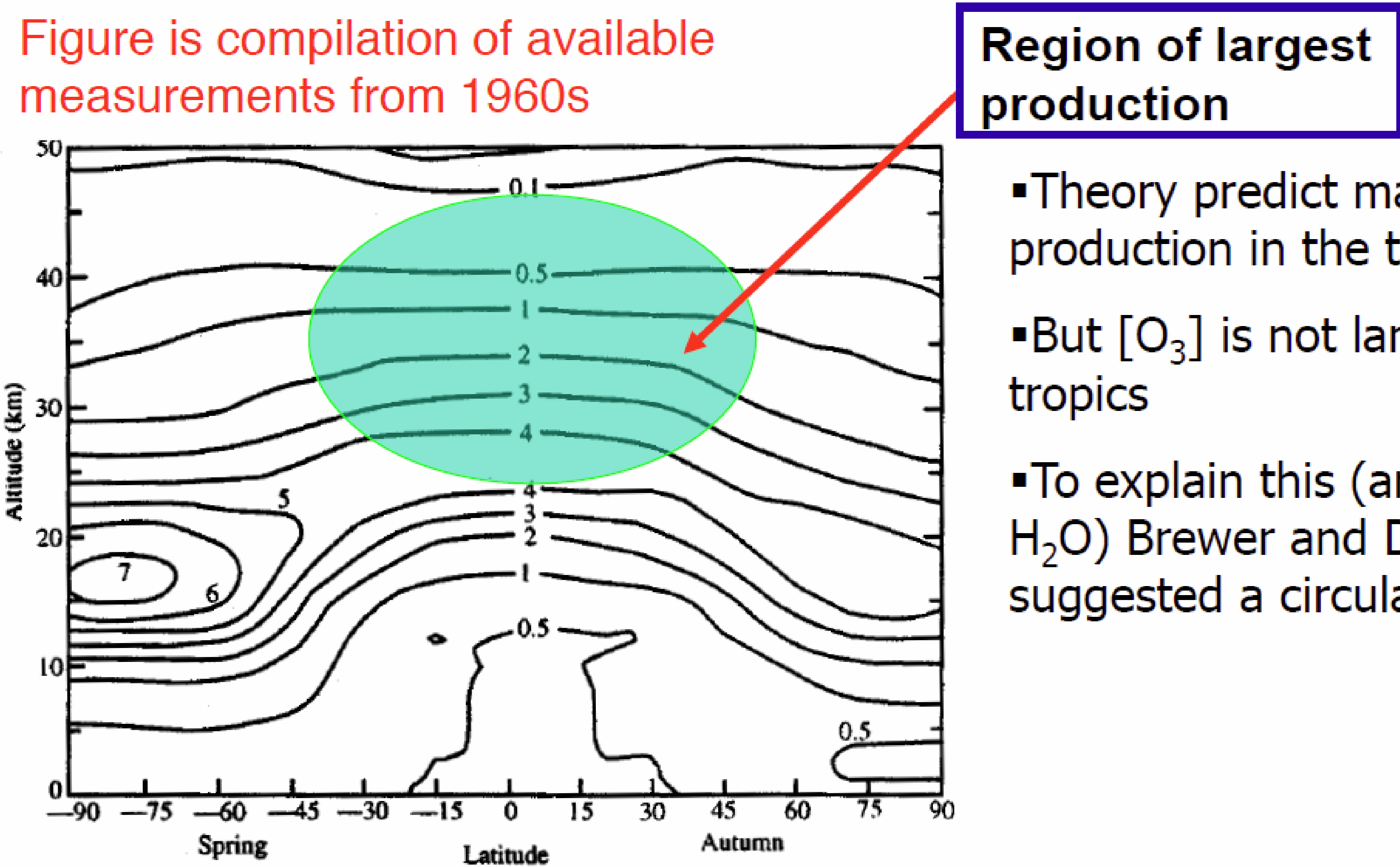
Stratospheric ozone - Effects

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

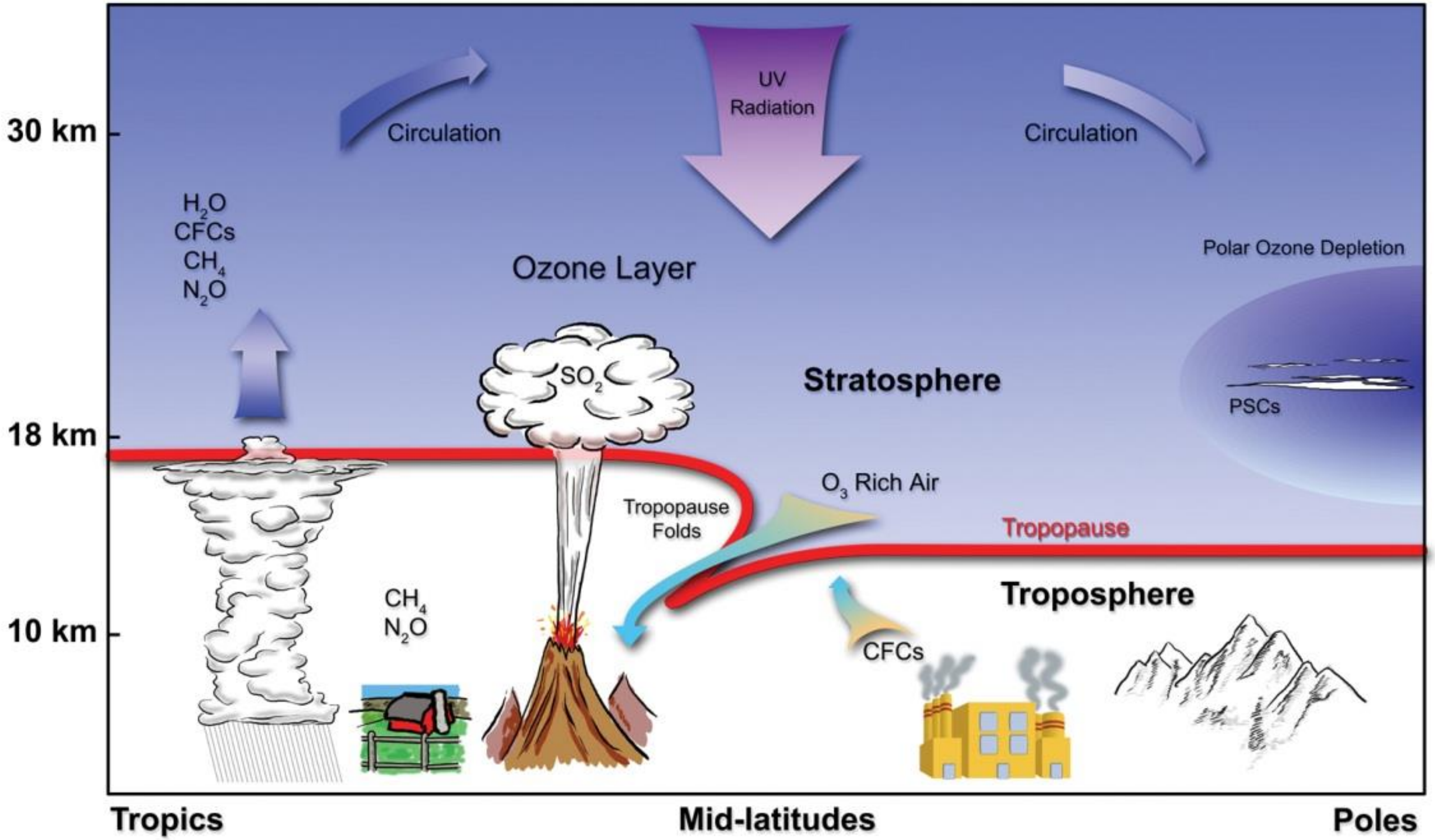
UV radiation can break the DNA molecules forming the genetic code, resulting in skin cancer (e.g. malignant melanoma).

The natural ozone layer

Figure is compilation of available measurements from 1960s

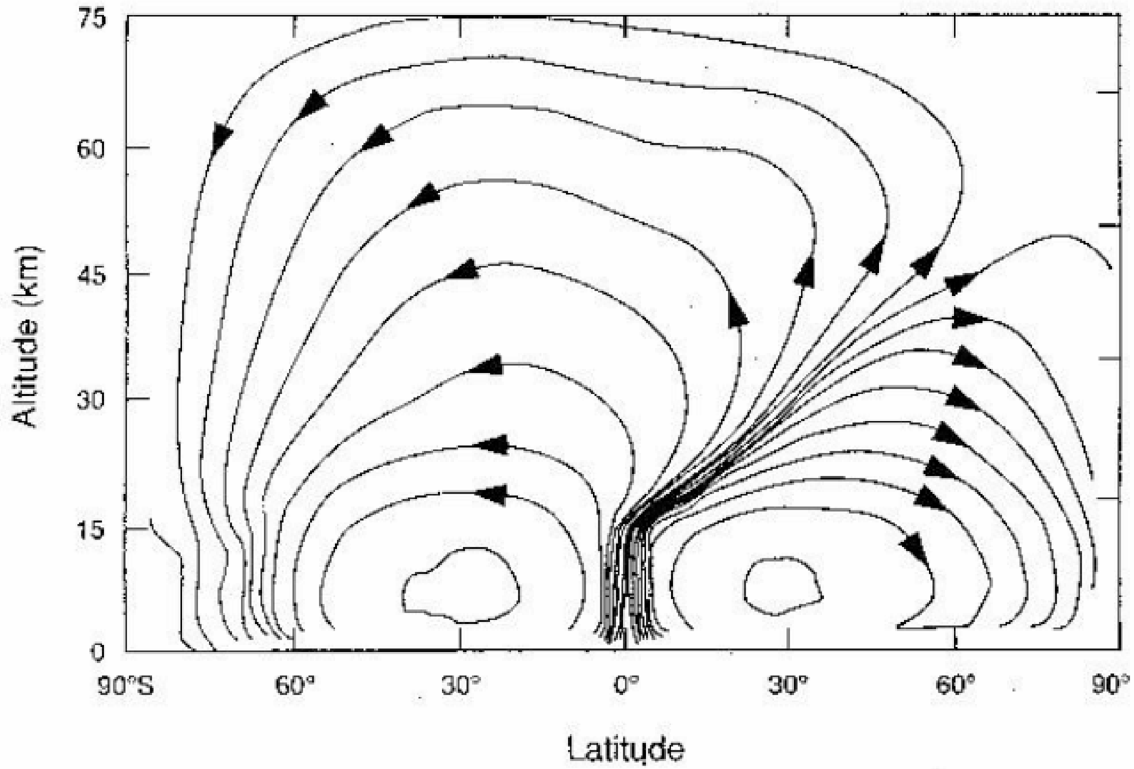


- Theory predict maximum O_3 production in the tropics
- But $[O_3]$ is not largest in the tropics
- To explain this (and low strat. H_2O) Brewer and Dobson suggested a circulation pattern



30 km
18 km
10 km
Circulation
UV Radiation
Circulation
H_2O
CFCs
CH_4
N_2O
Ozone Layer
Polar Ozone Depletion
SO_2
Stratosphere
PSCs
O_3 Rich Air
Tropopause Folds
Tropopause
Troposphere
CH_4
N_2O
CFCs
Tropics
Mid-latitudes
Poles

Brewer-Dobson circulation



Observation

- O_3 columns are smallest in tropics despite this being the main stratospheric O_3 production region

Explanation

- Rising tropospheric air with low ozone
- B-D circulation transports O_3 from tropics to mid- and high latitudes
- Recall that τ_{Ox} is quite long in the lower stratosphere.

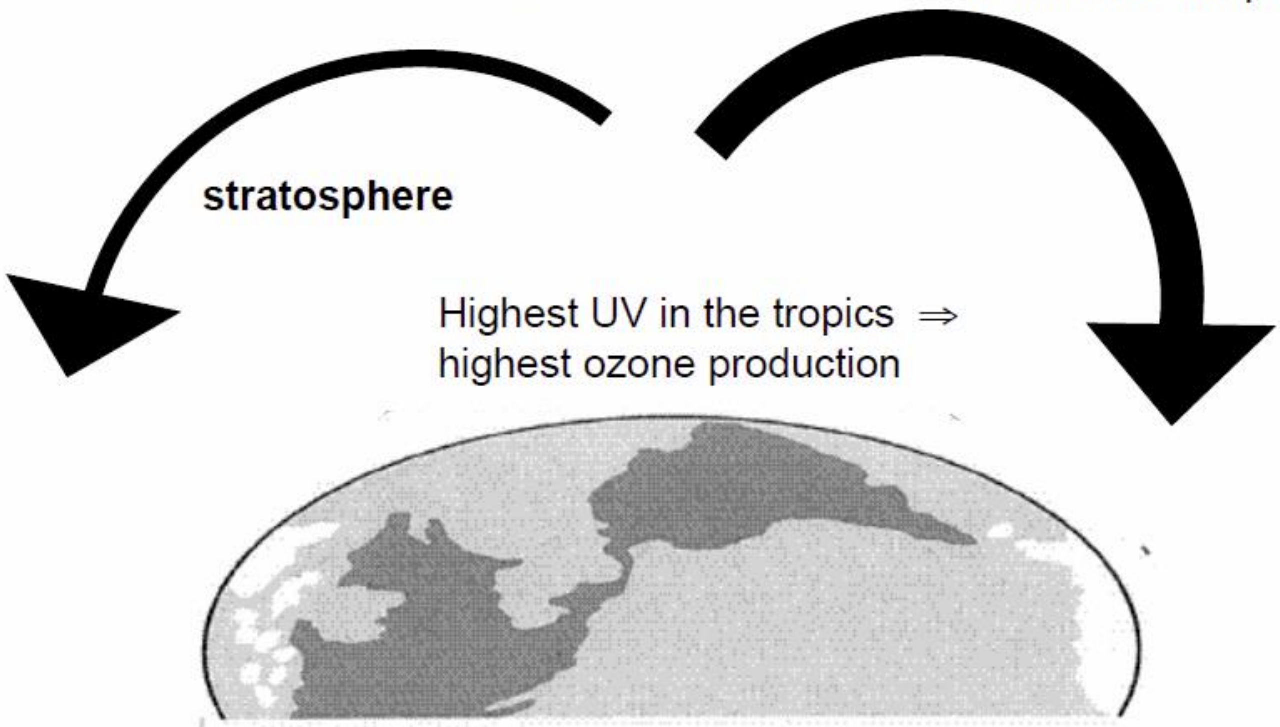
Other comments

- O_3 maxima occur toward high latitudes in late winter/early spring - the result of the descending branch of the B-D circulation
- Virtually no seasonal change in the tropics
- More accurate data has led to improvements in our understanding of this simple circulation pattern.

Brewer – Dobson circulation

From the tropics to the mid- & high latitudes

Circulation stronger in the northern hemisphere



Chapman mechanism (1930)

The Chapman mechanism for stratospheric ozone

(R1) $O_2 + h\nu \rightarrow O(^3P) + O(^3P)$ (λ< 240 nm, UVC slower)

(R2) $O(^3P) + O_2 + M \rightarrow O_3 + M$ (2x, fast)

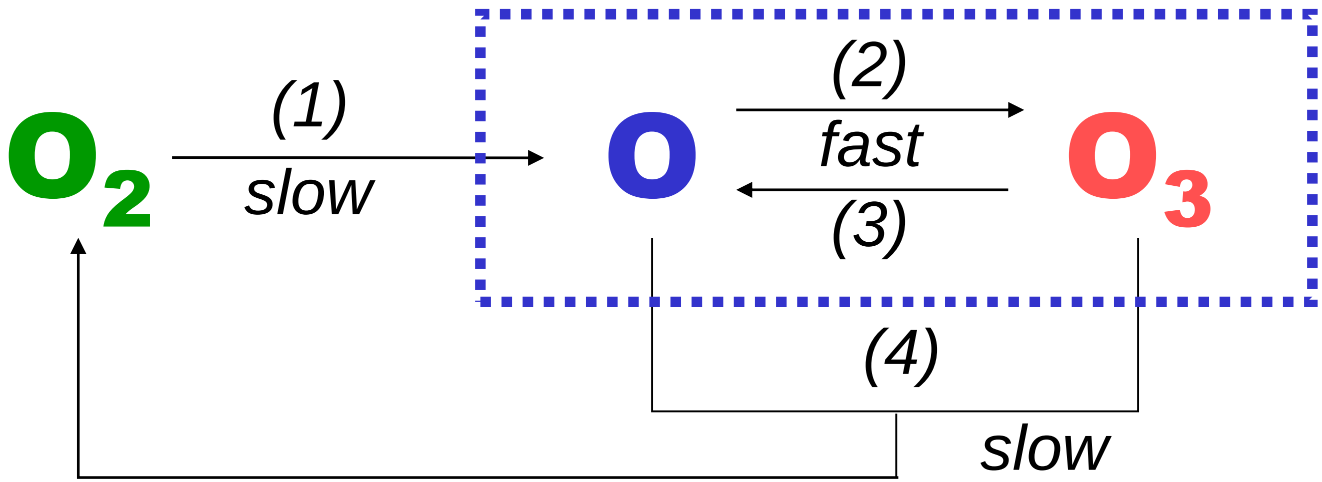
$O_3 + h\nu \rightarrow O_2 + O(^1D)$ (λ< 320 nm, UVC+UVB)

$O(^1D) + M \rightarrow O(^3P) + M$

(R3) net: $O_3 + h\nu \rightarrow O_2 + O(^3P)$ → (R2) (fast)

(R4) $O_3 + O(^3P) \rightarrow 2O_2$ (slower)

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



O_x according to the Chapman mechanism

Check that the short-lived *O* is in a steady state ($O=O(^3P)$),

i.e. production and losses ~ constant over its lifetime.

Lifetime (τ_O) for *O* can be written

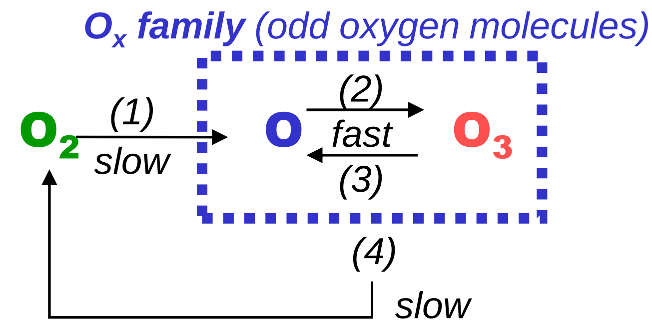
τ_O = (mass in the reservoir)/(loss rate)

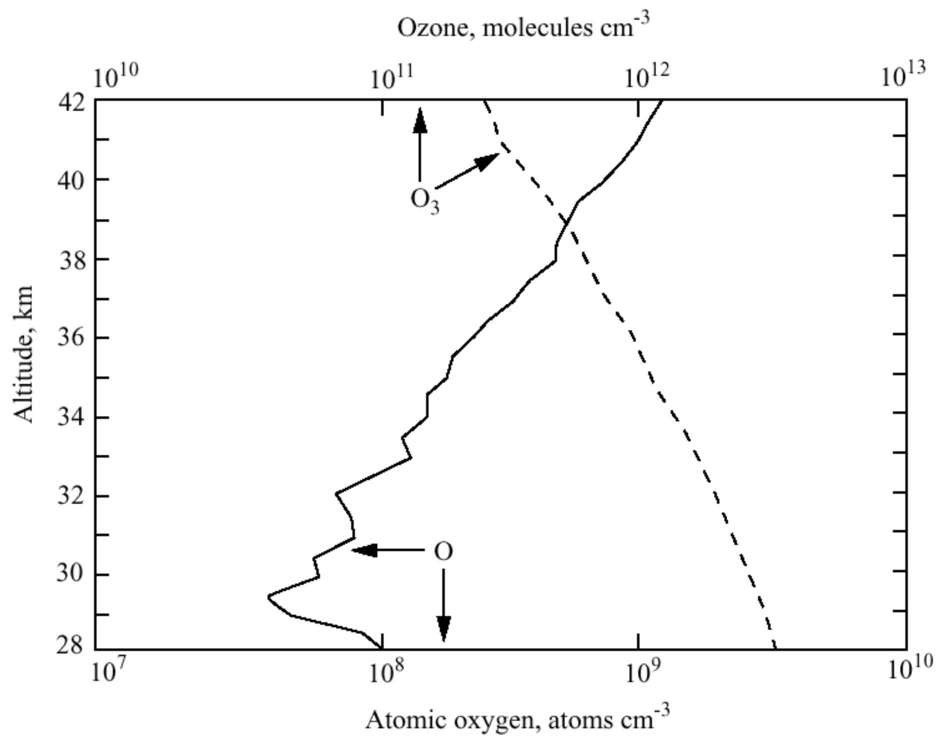
Lifetime **(τ_O) ~ seconds** or less.

Production of *O* varies on longer time scales.

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

O_x according to the Chapman mechanism



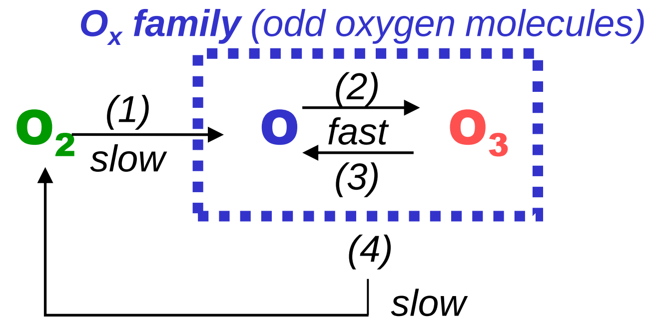


[O_3] >> [O] throughout the stratosphere.

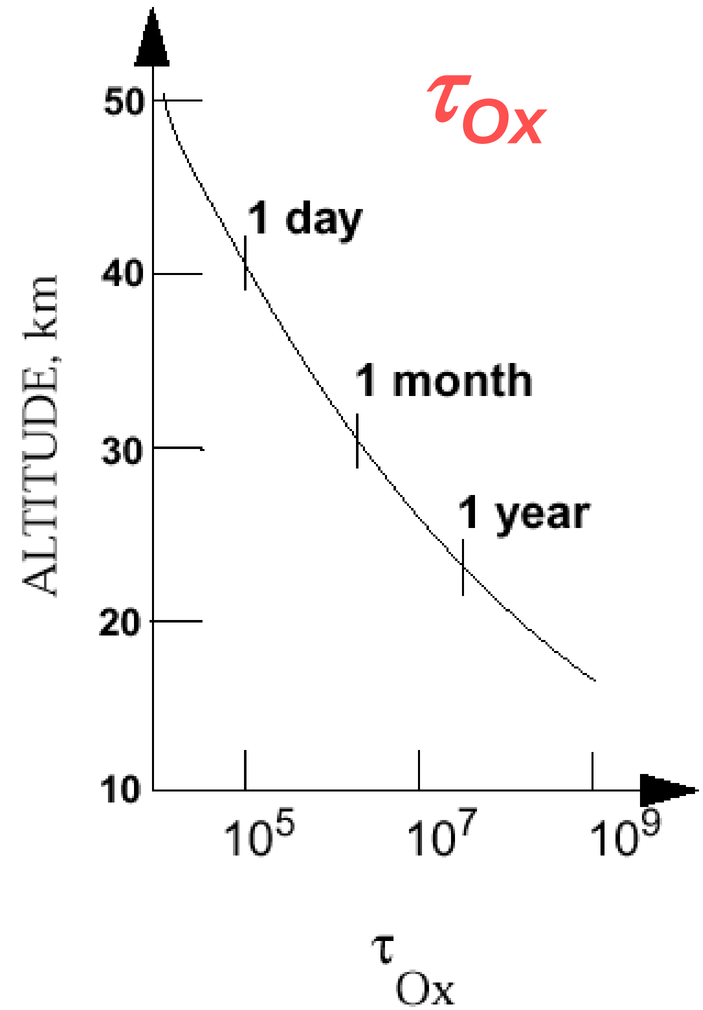
$$[O_x] = [O_3] + [O] \approx [O_3]$$

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

O_x lifetime

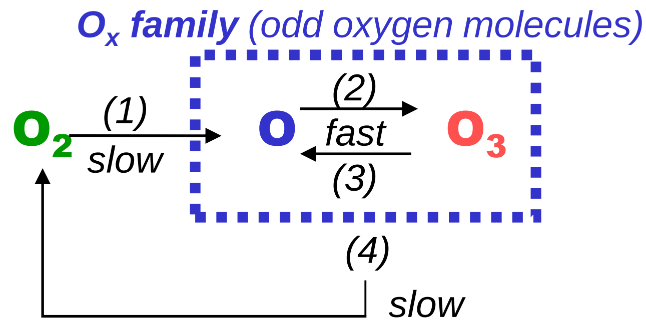


O_3 production determined by (1)
O_3 loss determined by (4)
O_3 lifetime determined by (4)



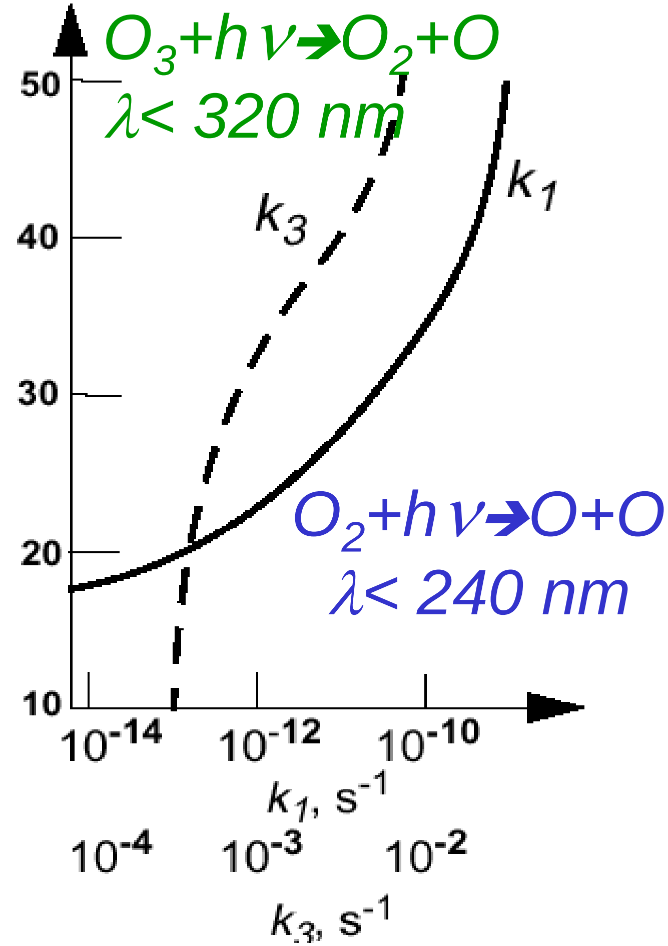
Steady-state conditions valid for O_x in large parts of the stratosphere, but maybe not in the lower part.

Chapman mechanism – Ozone levels



Stratospheric O_3 levels (Chapman):

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



Chapman mechanism – Results

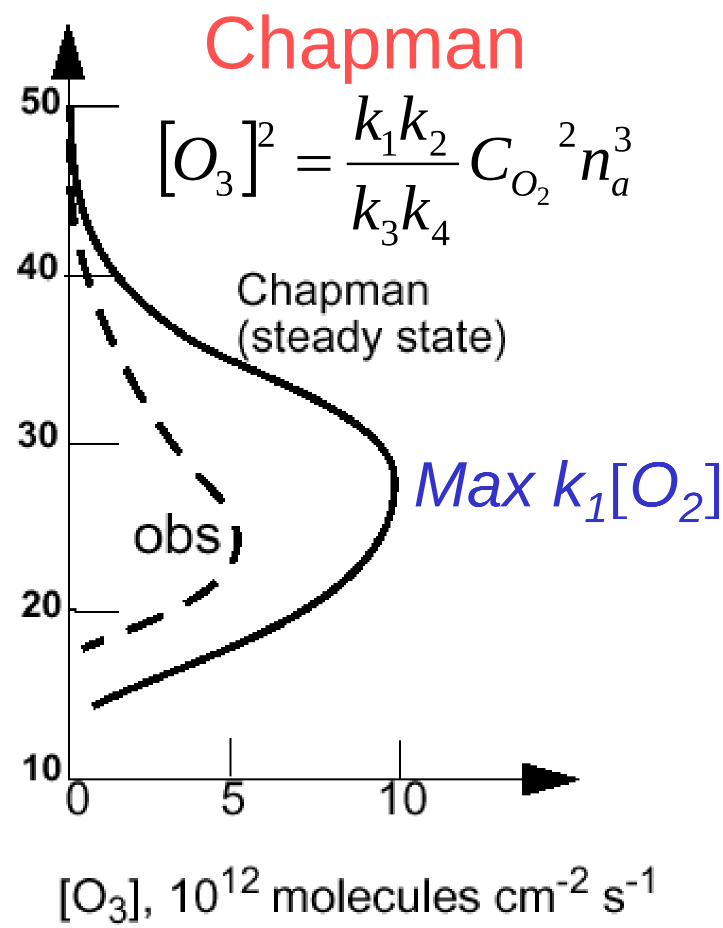
The Chapman mechanism can explain qualitatively the O_3 maximum at 20-30 km altitude.

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!



Catalytic ozone loss

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

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

Net reaction:

$$2O_3 \rightarrow 3O_2 \quad (OH\ \text{conserved})$$

Or:

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O \rightarrow OH + O_2$$

Net reaction:

$$O_3 + O \rightarrow 2O_2\ (OH\ \text{conserved})$$

Catalytic ozone loss

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

How does the cycle look for Br and Cl?

Catalytic ozone loss

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Net: $O_3 + O \rightarrow 2O_2$

$Br + O_3 \rightarrow BrO + O_2$

$BrO + O \rightarrow Br + O_2$

Net: $O_3 + O \rightarrow 2O_2$

$Br + O_3 \rightarrow BrO + O_2$

$BrO + O_3 \rightarrow Br + 2O_2$

Net: $2O_3 \rightarrow 3O_2$

Catalytic ozone loss - HO_x

From troposphere

$H_2O + O(^1D) \rightarrow 2OH$ (initiation step)

$CH_4 + O(^1D) \rightarrow OH + CH_3$ (initiation step)

(1) $OH + O_3 \rightarrow HO_2 + O_2$ (*propagation step*)

(2a) $HO_2 + O \rightarrow OH + O_2$ (*propagation step, >20 km*)

(2b) $HO_2 + O_3 \rightarrow OH + 2O_2$ (*propagation step, <40 km*)

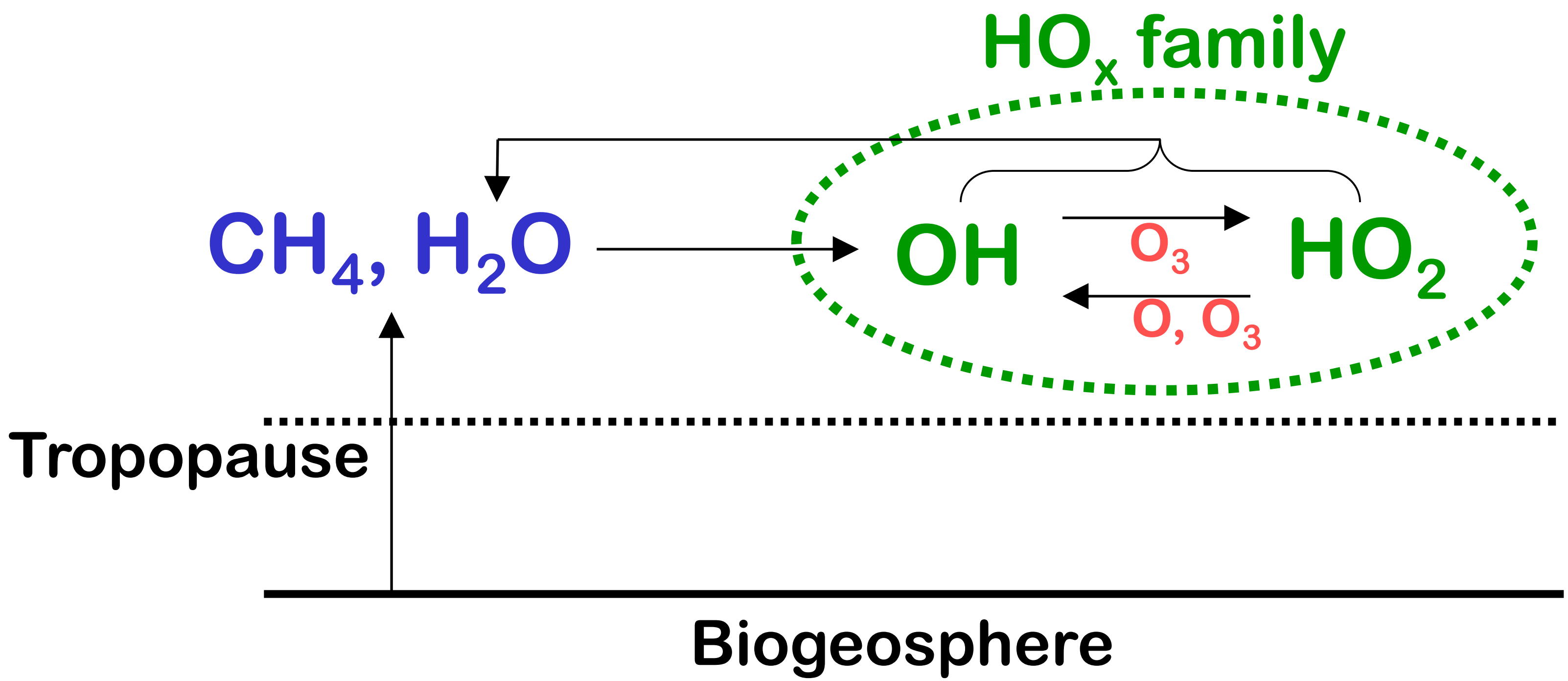
These catalytic ozone loss cycles (1+2a, or 1+2b) are broken by

$OH + HO_2 \rightarrow H_2O + O_2$ (*termination step*)

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 - NOx

From troposphere

$N_2O + O(^1D) \rightarrow 2\,NO$ (initiation step)

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

$NO_2 + O \rightarrow NO + O_2$ (propagation, >20 km)

From aircraft

NO and NO_2 are held up as reservoirs owing to:

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

$NO_2 + O_3 \rightarrow NO_3 + O_2$ (propagation)

$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ (nigthtime termination)

N_2O_5 and HNO_3 can be converted back to NO and NO_2, however they temporarily halt the catalytic cycle.

Catalytic ozone loss - NO_x

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

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

$O + O_2 + M \rightarrow O_3 + M$

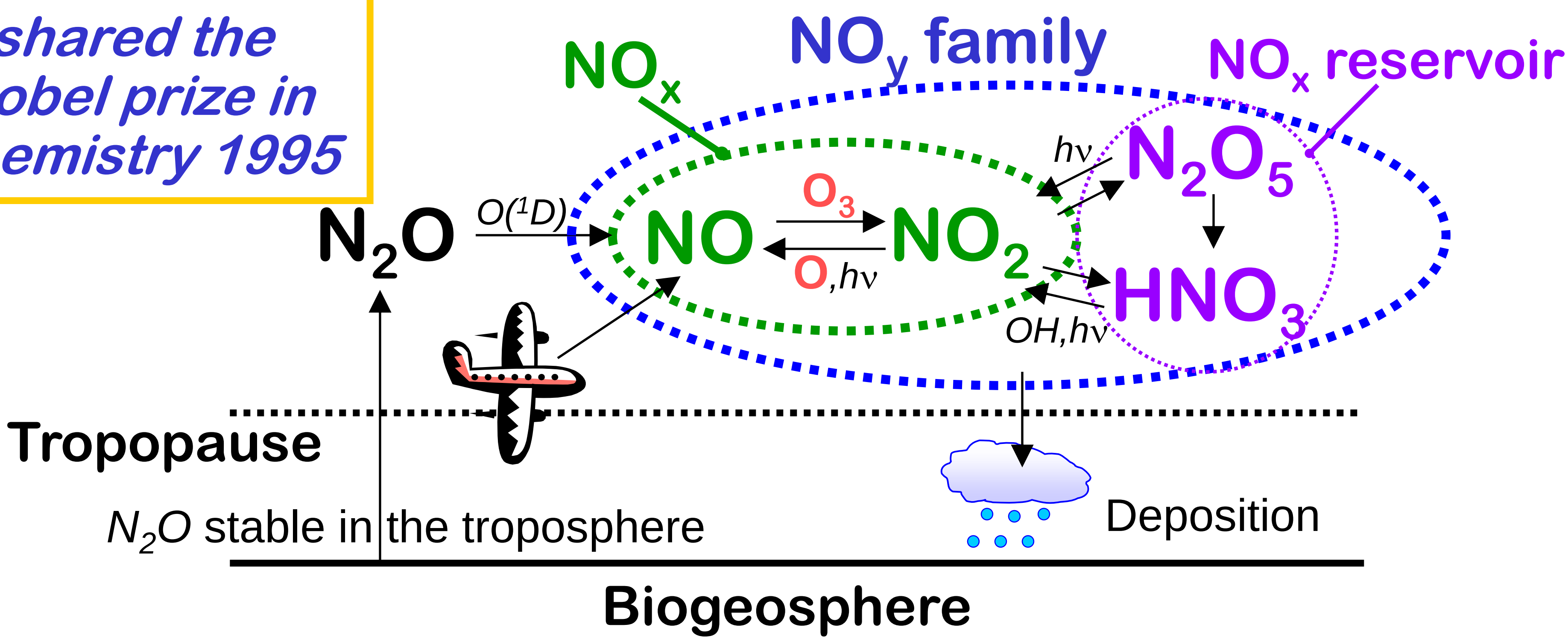
Null cycle! No net effect on ozone, and competes with the NOx catalytic ozone destruction. Especially efficient during daytime.

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



Other important types of cycles

O + O catalytic cycle (example)

$OH + O \rightarrow H + O_2$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + O \rightarrow OH + O_2$

Net: $O + O + M \rightarrow O_2 + M$

- Important at high altitudes where $[O]/[O_3]$ is higher

$O_3 + O_3$ catalytic cycle (example)

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O_3 \rightarrow OH + O_2 + O_2$

Net: $O_3 + O_3 \rightarrow O_2 + O_2 + O_2$

- Important at low altitudes where $[O]/[O_3]$ is low

Null cycle (example)

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + h\nu \rightarrow NO + O$

Net: $O_3 + h\nu \rightarrow O_2 + O$

- No O_X loss. Important because the NO_X tied up in null cycle is not removing O_X in catalytic cycles.

Holding cycle (example)

$Cl + CH_4 \rightarrow HCl + CH_3$

$OH + HCl \rightarrow H_2O + Cl$

Net: $CH_4 + OH \rightarrow CH_3 + H_2O$

- Does not involve O_X directly, but Cl atoms "tied up" as HCl are not participating in catalytic cycles.

Holding cycles involve reservoir species.

Other processes of ozone loss

HOX, CLOX and NOX cycles not the only way to destruct ozon.
Members of one family can react with members of another!

All reaction rates are still not fully estimated. Some question marks remain in the ozone chemistry in the stratosphere.

Bromine – the most effective ozone killer

- Br – BrO catalytic cycle similar to Cl – ClO cycle.
- However, Br is **almost 60 times as effective** as Cl in destroying ozone. Why?
- 1) $BrONO_2$ is much less stable than $ClONO_2$:
  - $BrONO_2 + h\nu \rightarrow BrO + NO_2$ Effective also for long λ (visible light)
  - $BrONO_2 + h\nu \rightarrow Br + NO_3$ No such channel available for Cl
- 2) HBr formation thermodynamically unfavourable (unlike HCl formation)
  - $Br + CH_4 \rightarrow HBr + CH_3$ endothermic reaction
- Mixed bromine – chlorine cycle also strengthens ozone depletion:

  $BrO + ClO \rightarrow Br + Cl + O_2$

  $Br + O_3 \rightarrow BrO + O_2$

  $Cl + O_3 \rightarrow ClO + O_2$

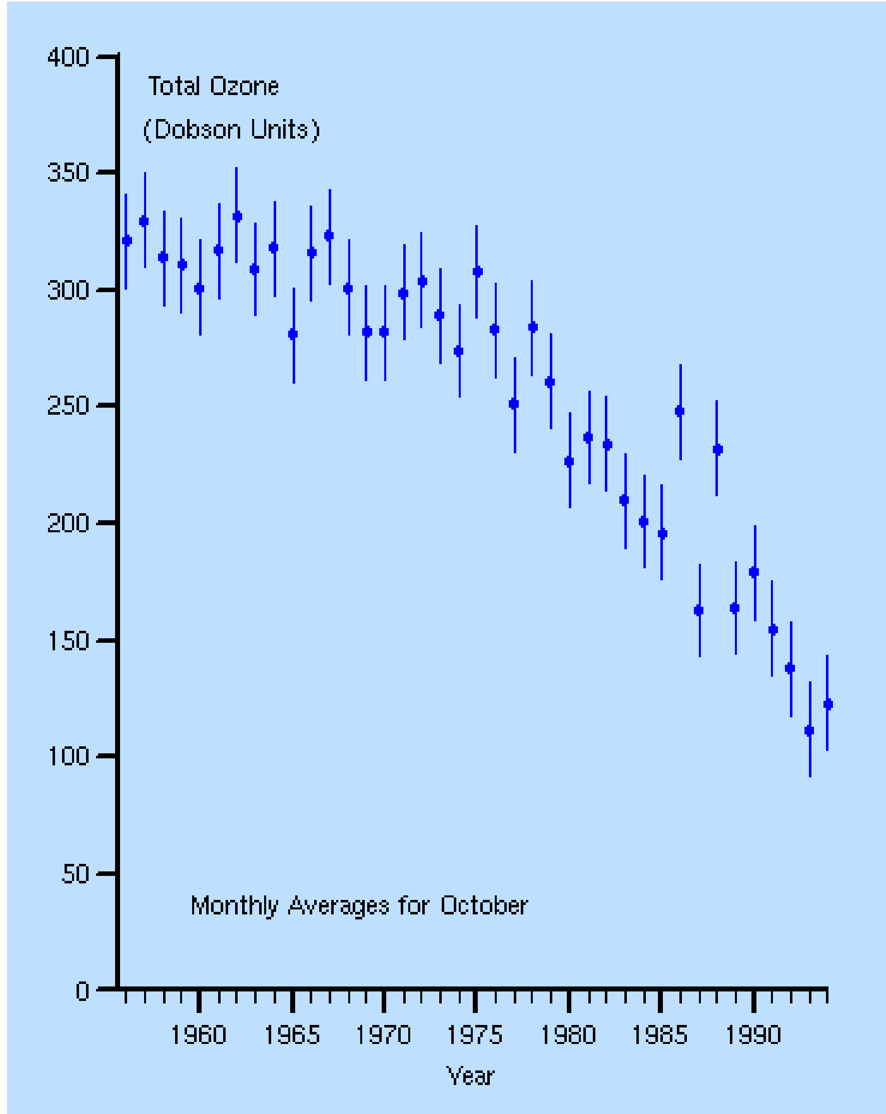
  Net: $O_3 + O_3 \rightarrow O_2 + O_2 + O_2$
- **Fortunately, atmospheric bromine levels are quite low**.
  - *The decision to use chlorine instead of bromine in CFCs is one of the luckiest decisions ever made. If bromine had been used instead, the ozone layer would probably have been gone before anyone noticed.*

Stratospheric ozone – Antarctica

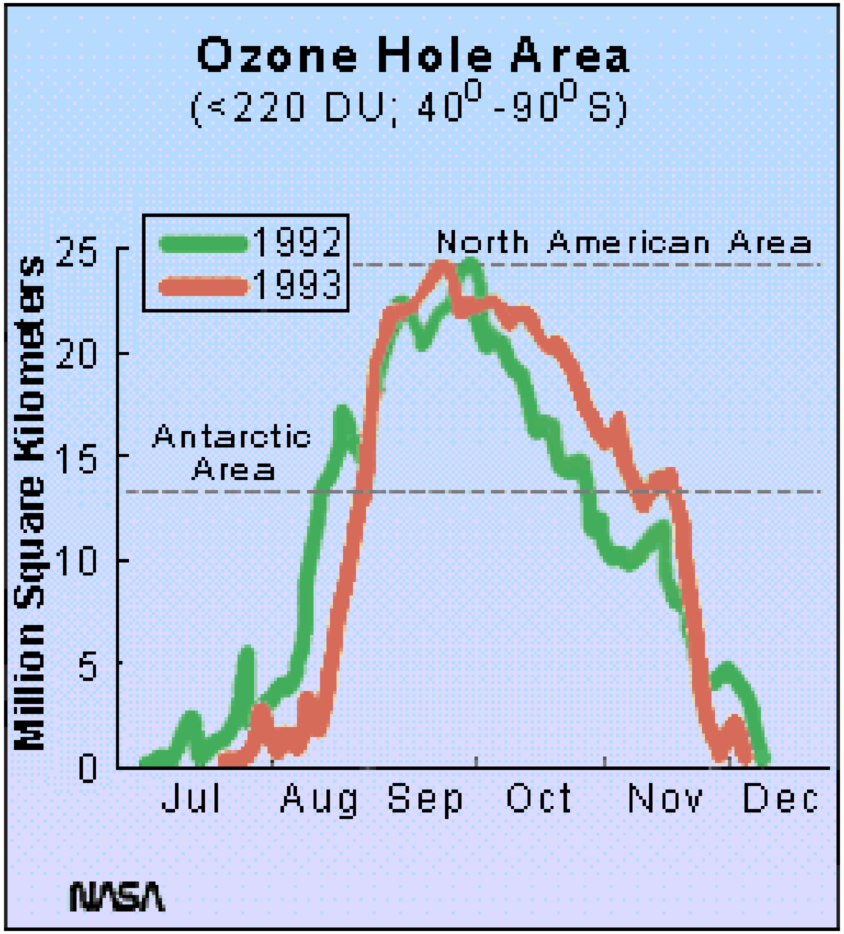
The ozone hole was first observed 1981 at Halley Bay, Antarctica.

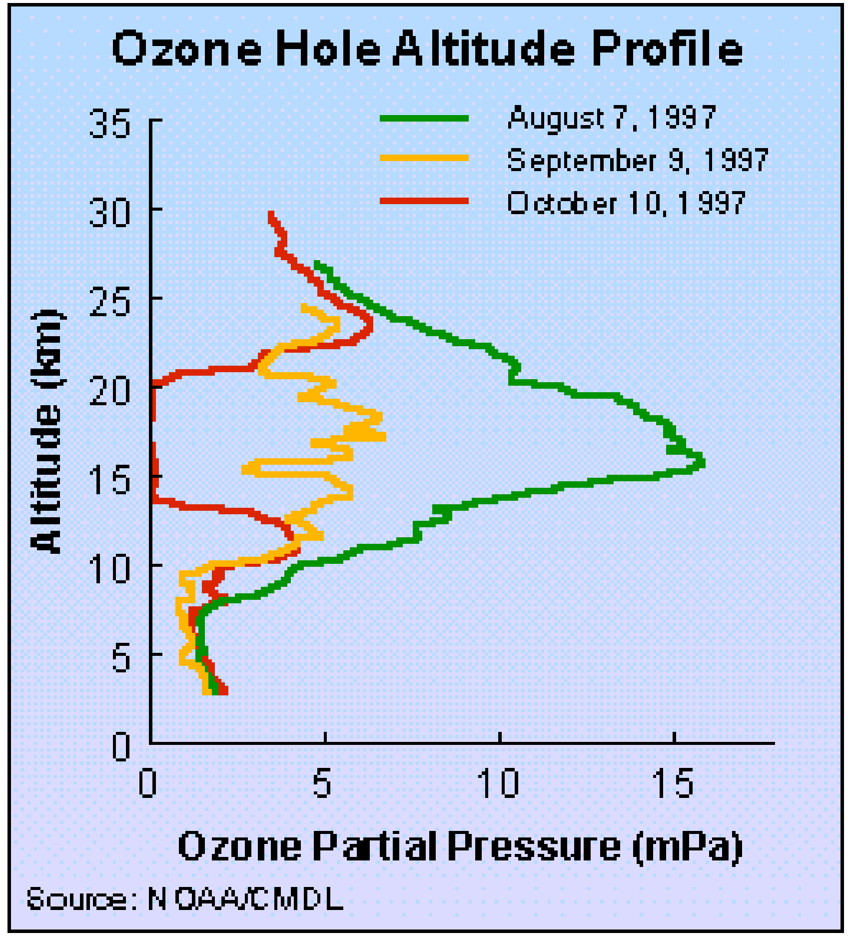
The resultats were so astonishing that the scientists first would not believe their own data, and waited to publish them until 1985.

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



Stratospheric ozonhole – Antarctica





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.

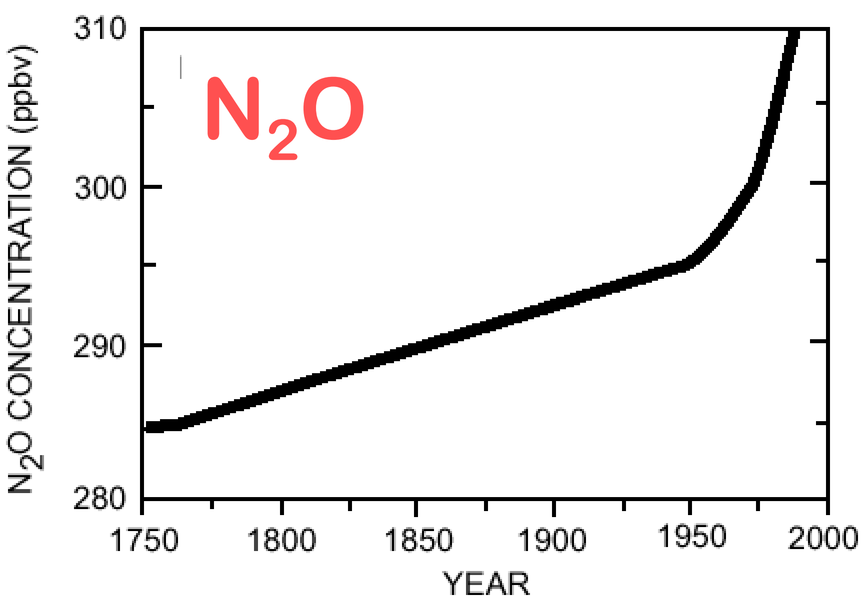
Use of these substances:

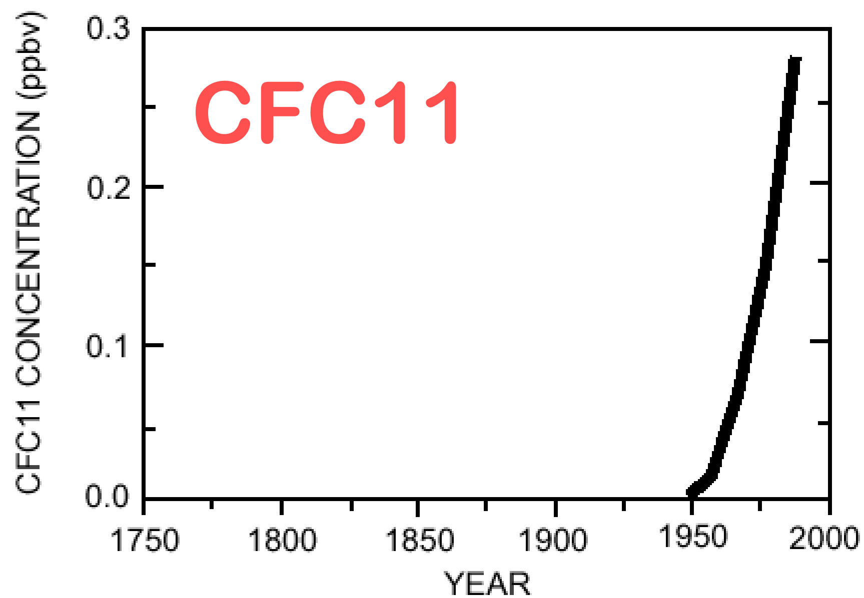
- Cooling medium
- Blower for plastics
- Dry cleaning fluid
- Cleaning detergent
- Solvents
- Propellant gas in spray cans

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)





Catalytic ozone loss - ClO_x

CFCs are photolysed by UV radiation in the stratosphere.

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

ClO_x family: *Cl and ClO (radicals)*

(*) $Cl + O_3 \rightarrow ClO + O_2$

(**) $ClO + O \rightarrow Cl + O_2$

Net reaction:

$$O_3 + O \rightarrow 2O_2$$

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

http://www.ucar.edu/learn/images/o3split.gif

Catalytic ozone loss - ClO_x

The catalytic cycle is broken when ClO_x radicals are comsumed.

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

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)

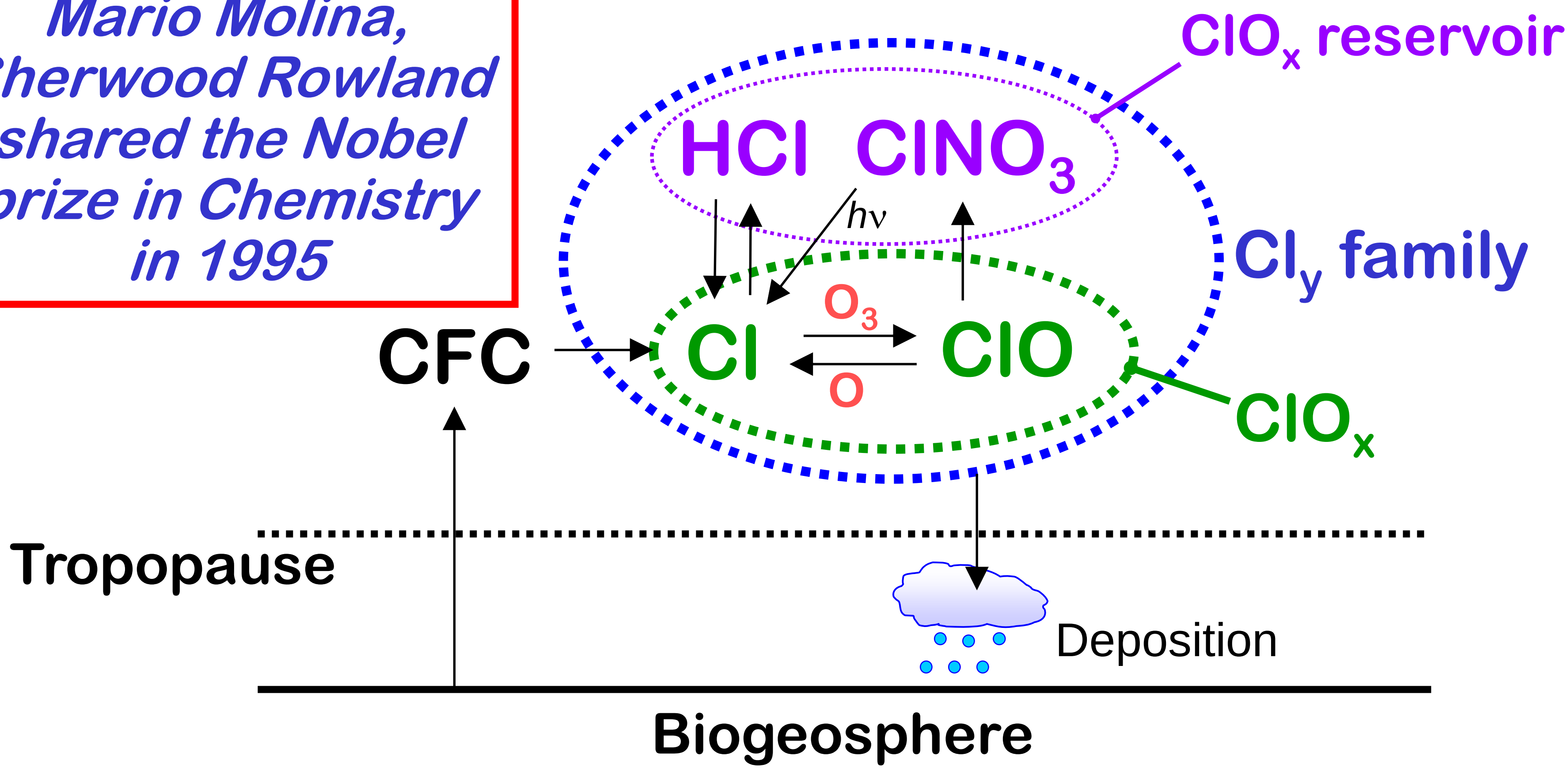
The reservoirs return to ClO_x

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

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.

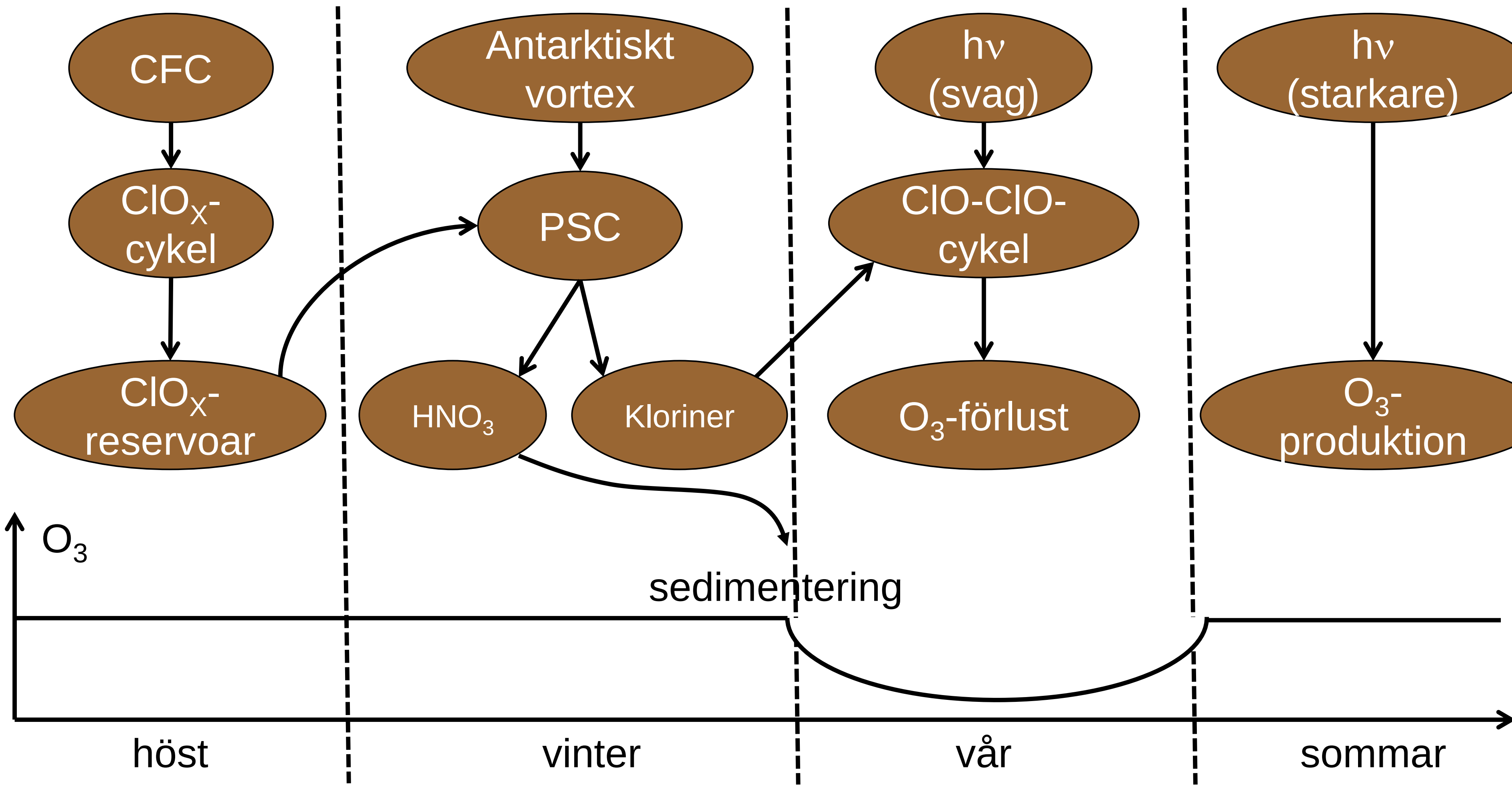
Mario Molina, Sherwood Rowland shared the Nobel prize in Chemistry in 1995



Catalytic ozone loss

The catalytic cycle with *ClO*$_x$ radicals was rewarded the Nobel prize but could not explain the ozone hole !!

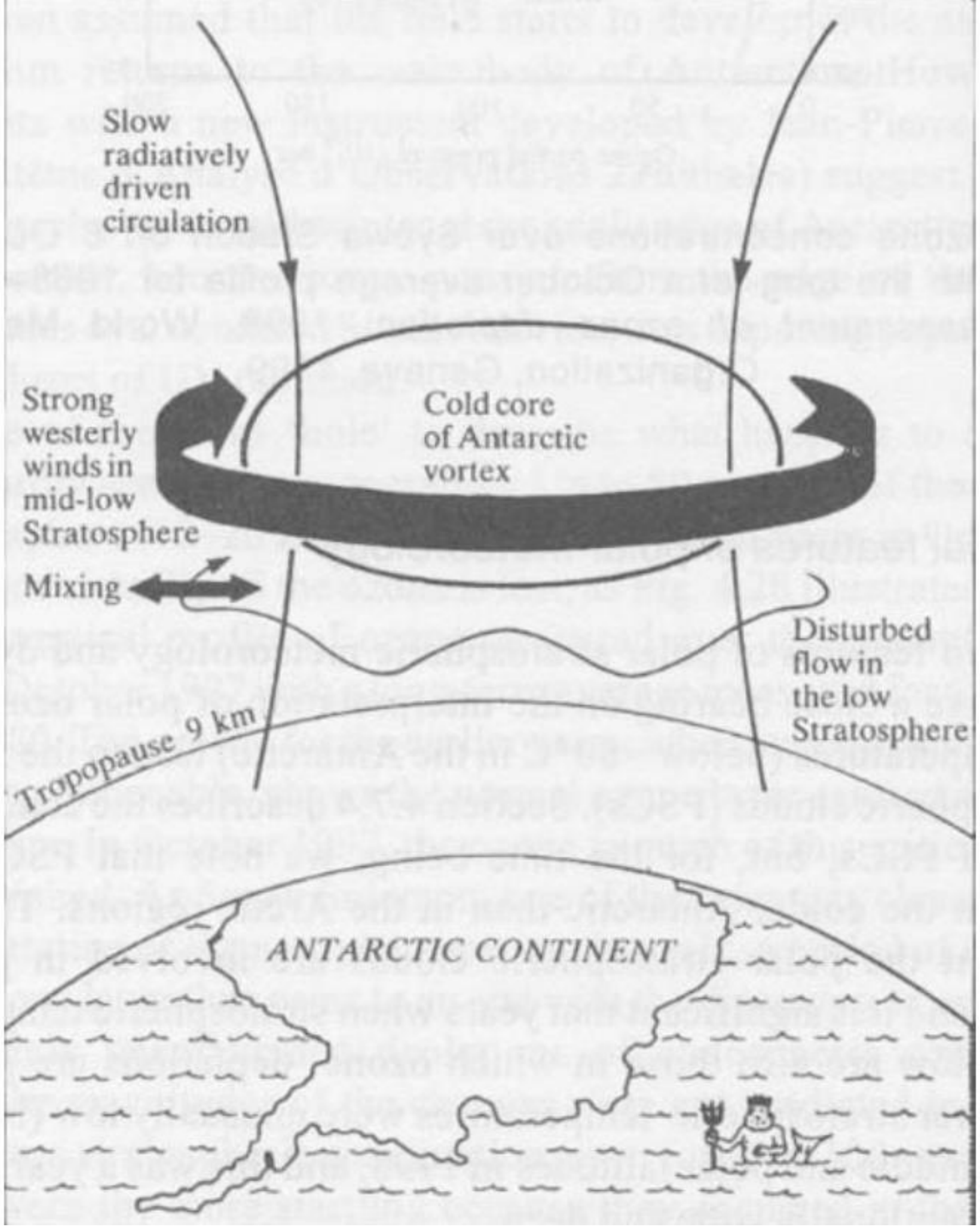
Stratosfäriskt ozon



Källor: Jacob, D. J., 1999. Introduction to Atmospheric Chemistry.

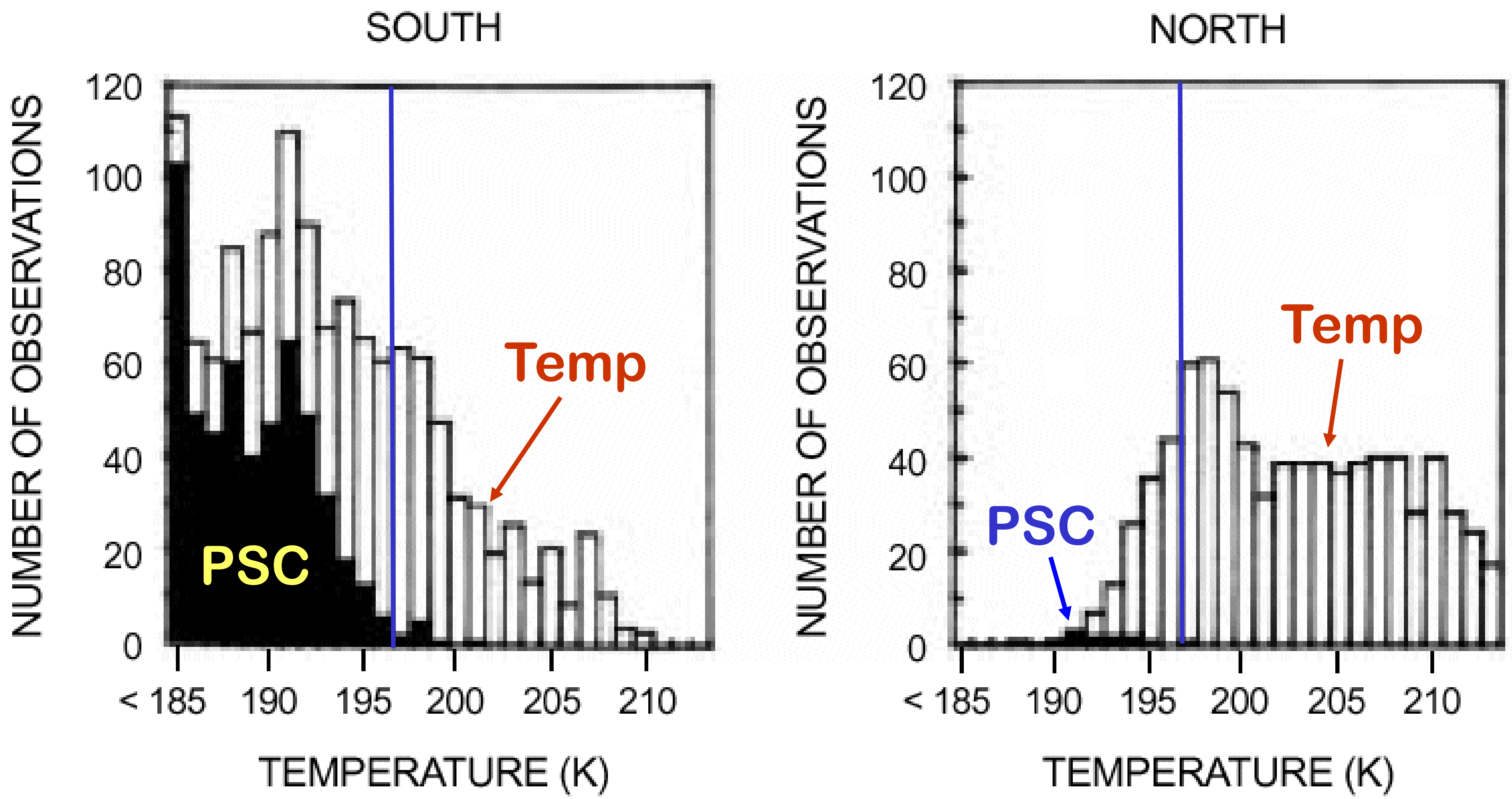
Antarctic polar vortex

The vortex forms in winter conditions. The air over the antartic is ”trapped” in the vortex, little exchange with rest of the atmosphere ⇒ no transport of new ozone from the mid-latitude or tropics via the B-D circulation.



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.



Polar stratospheric clouds (pärlemormoln)

Not to be confused with:
Aurora borealis (norrsken)

Catalytic ozone loss - ClO

Early spring in Antarctica is relatively dark (low photochemistry) and levels of O are low

$$NO_2 + O \rightarrow NO + O_2$$ and...

(*) $$ClO + O \rightarrow Cl + O_2$$ ...are not efficient !

Since there is for example no photolysis of NO_2

$$(NO_2 + h\nu \rightarrow NO + O)$$

Yet another cycle involving *ClO* is needed (CLO-CLO cycle):

$$ClO + ClO + M \rightarrow ClOOCl + M$$ (*ClO dimer*)

$$ClOOCl + h\nu \rightarrow + ClOO + Cl$$ (*split in "wrong" place*)

$$ClOO + M \rightarrow Cl + O_2 + M$$

$$Cl + O_3 \rightarrow ClO + O_2 \ (2x)$$

Net reaction:

$$2O_3 \rightarrow 3O_2$$

Loss rate proportional to $[ClO]^2$, as opposed to the ClO_x mechanism (*), which depends on abundance of O atoms ($=2k_{22}[ClO][O]$).

Catalytic ozone loss - ClO

Why are levels of *ClO*-radicals so high during Antarctic spring?

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

PSC

(*) $ClNO_3 + HCl \rightarrow Cl_2 + HNO_3$

$Cl_2 + h\nu \rightarrow 2Cl$

$Cl + O_3 \rightarrow ClO + O_2$

Reaction (*) 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.

Catalytic ozone loss - ClO

But isn't it possible that HNO_3 is photolyzed again and continue to supress ozone destruction?

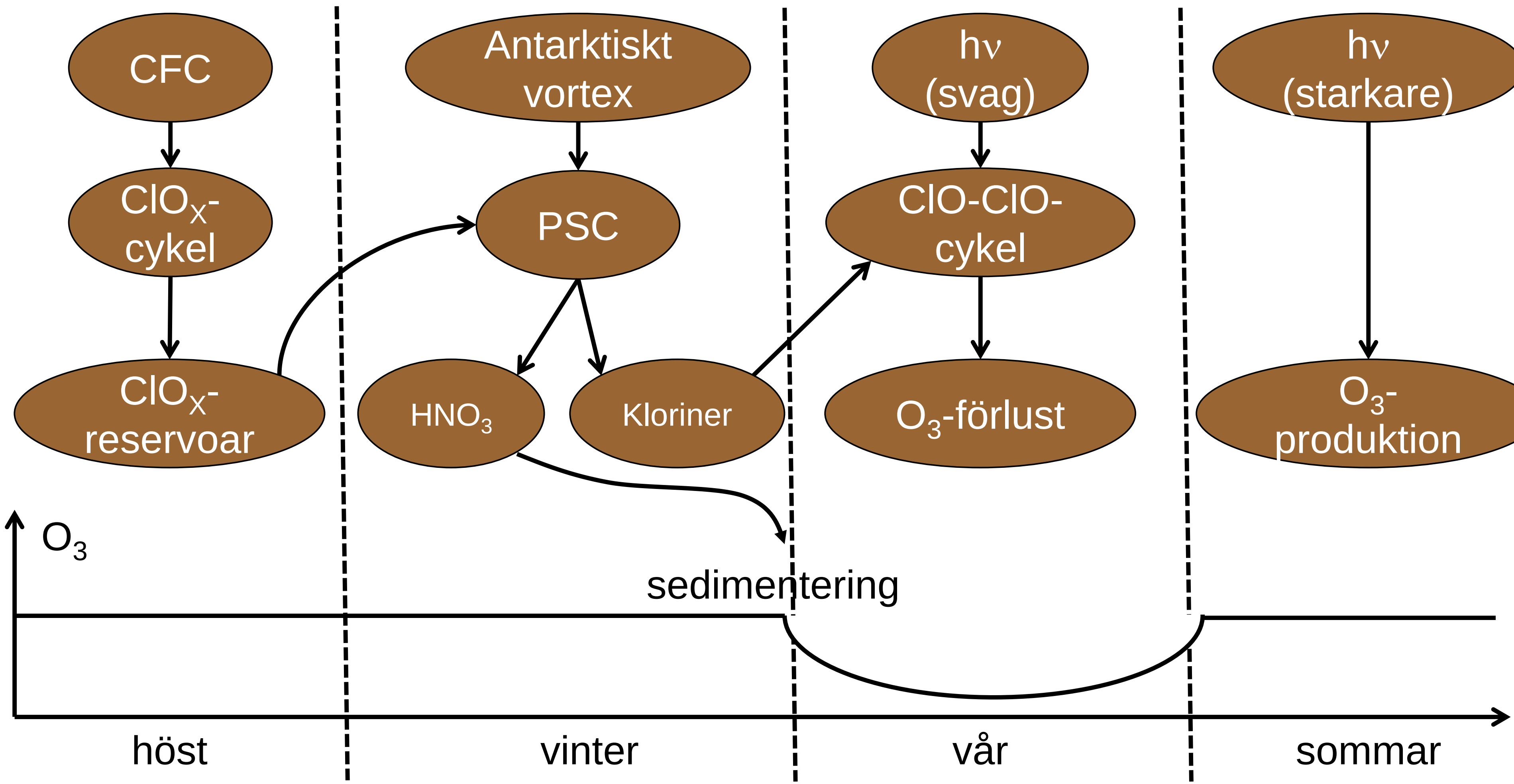
(*) $HNO_3 + h\nu \rightarrow NO_2 + OH$

(**) $ClO + NO_2 + M \rightarrow ClNO_3 + M$

, where ClO is consumed.

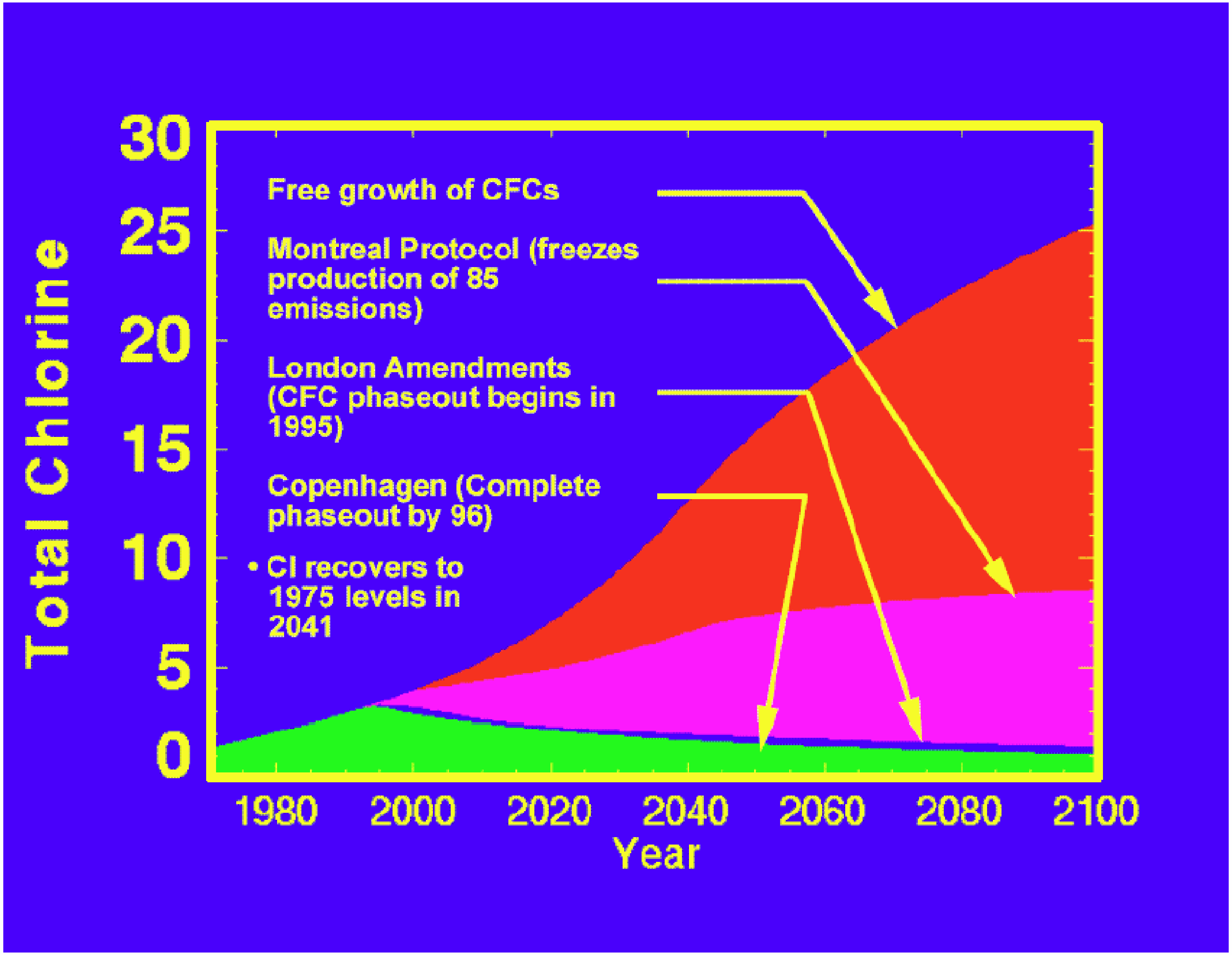
The answer is no! HNO_3-containing PSC have been sedimented to the troposphere.

Stratosfäriskt ozon

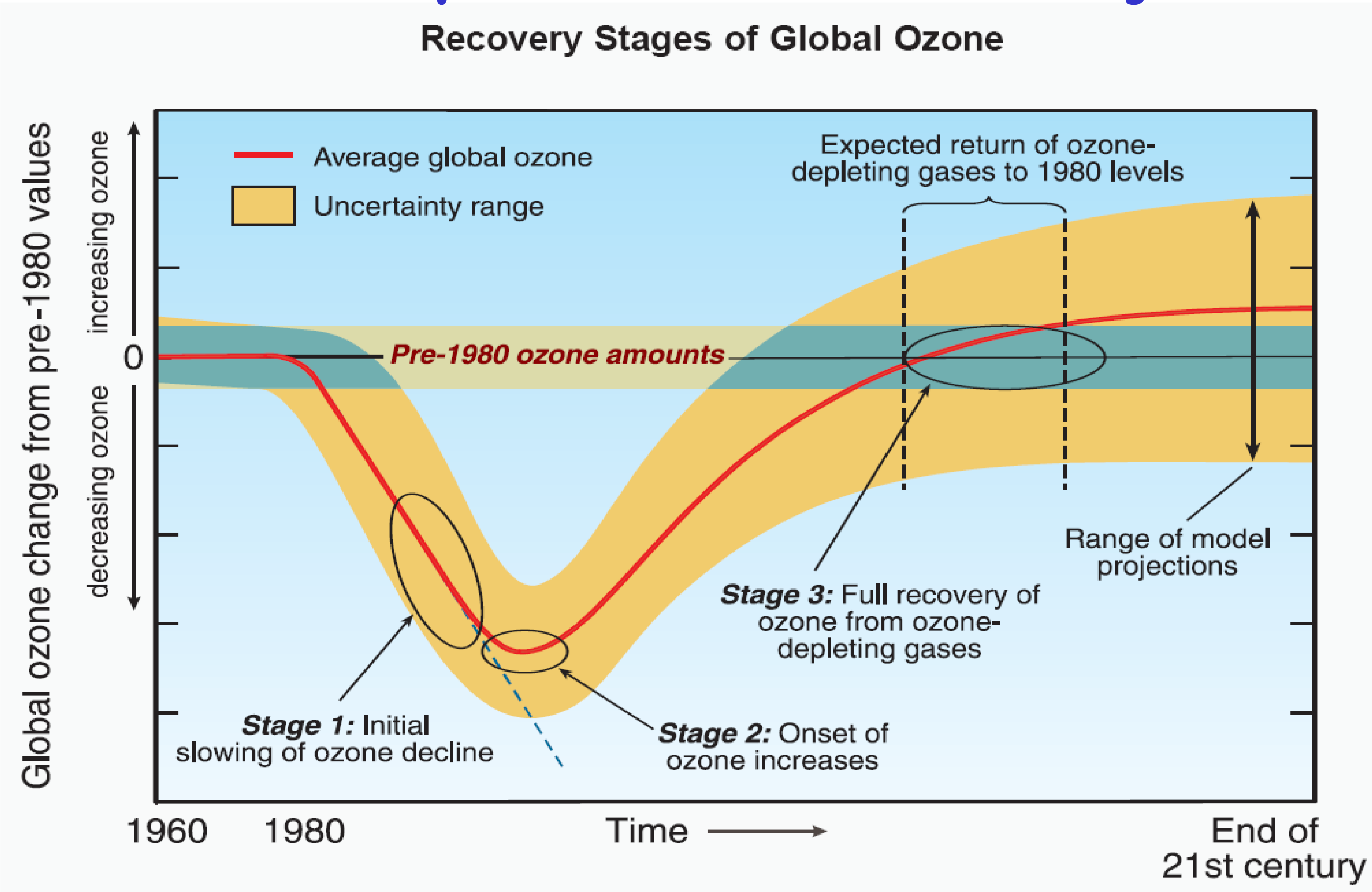


Källor: Jacob, D. J., 1999. Introduction to Atmospheric Chemistry.

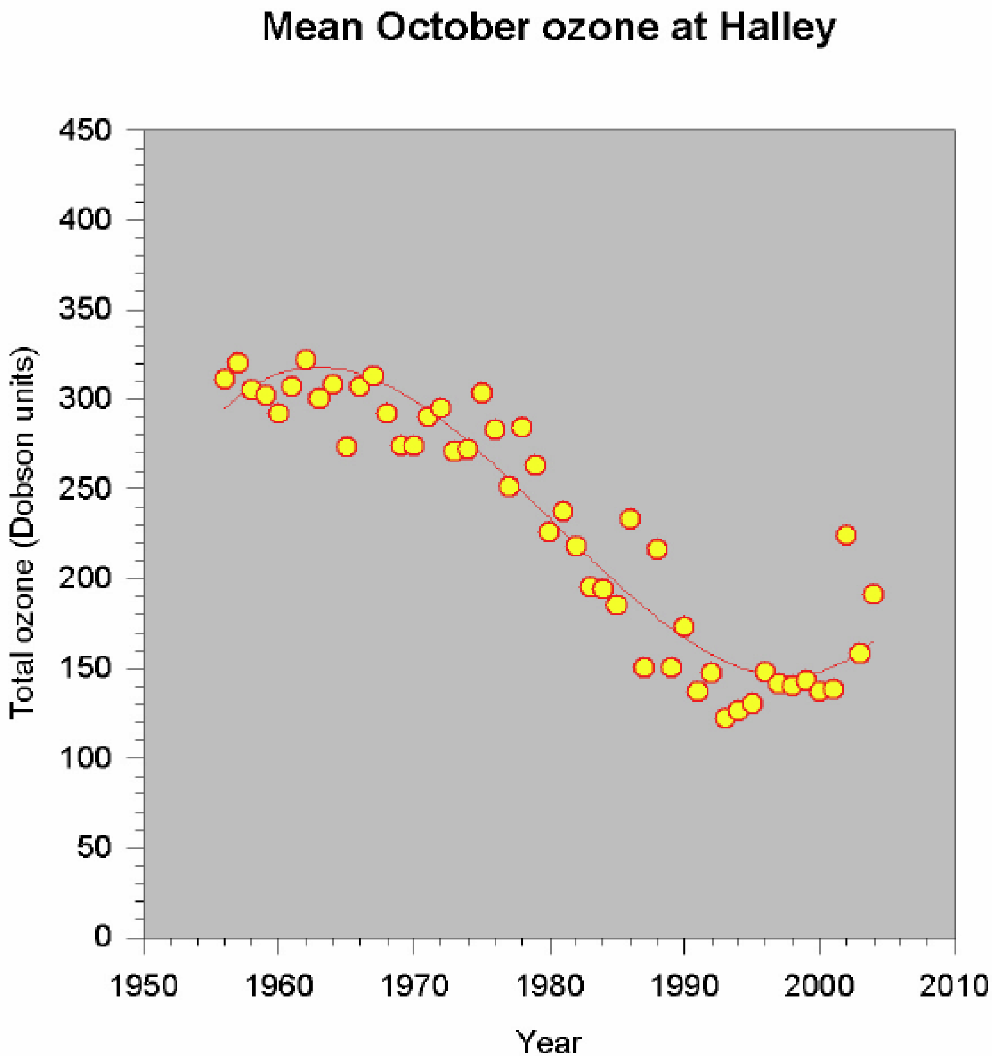
Without emission reductions, stratospheric chlorine levels would have grown catastrophically.

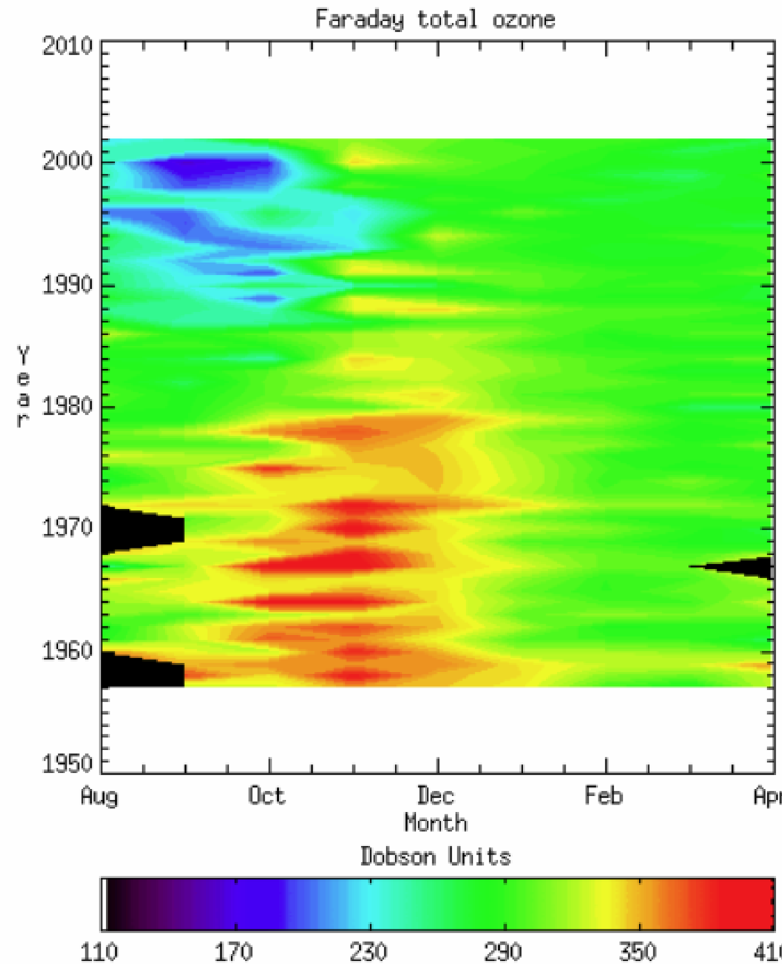


Stratospheric ozone - Recovery



Ozone trend at Halley bay, Antarctica





British Antarctic Survey, 2005

Stratospheric ozone - Recovery

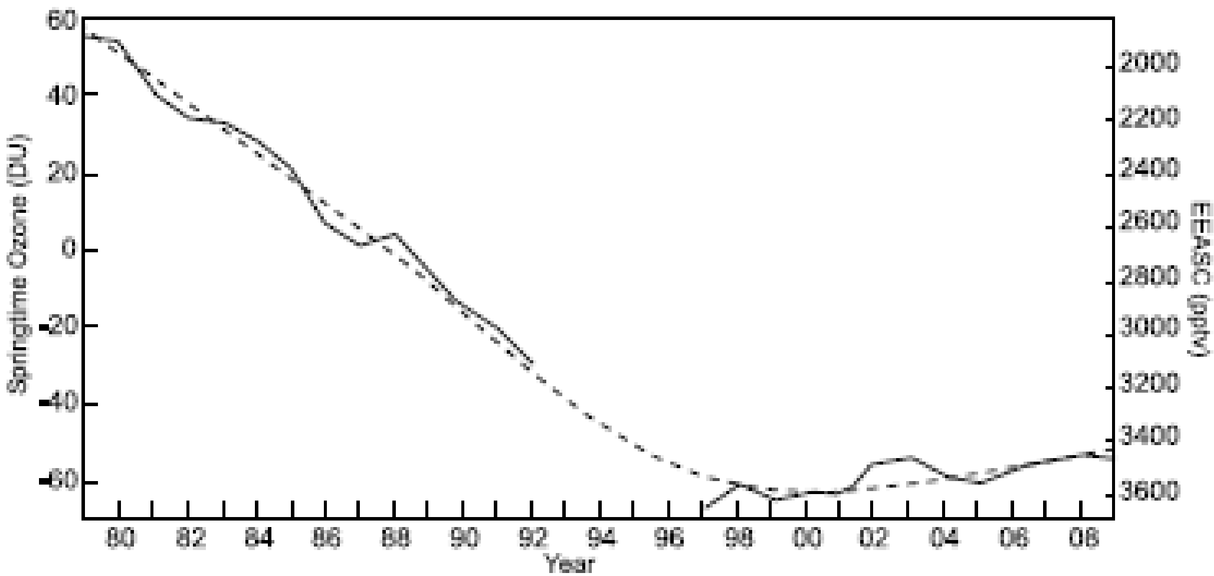


Figure 3. Anomalous springtime ozone that is independent of dynamically-induced changes (solid). The positive trend after 1996 is significant at the 99.5% level. EEASC, corresponding to a mean age of air of 5 yr and a bromine scale factor of 60 (dotted).

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