2 Stratospheric ozone chemistry

2.1 Chapman‘s reactions

1 source, photolysis of O_2, +
1 sink, recombination to O_2:
$O_2 + h\nu\ (\lambda < 242\ \mathrm{nm}) \rightarrow 2\ O$
$O + O_2 + M \rightarrow O_3 + M$
$O + O_3 \rightarrow 2\ O_2$
Net sum:
-

Second sink: Photolysis
$O_3 + h\nu \rightarrow O + O_2$

Chapman 1930

- Localized ozone layer too high in agreement with wrong measurements based, in turn, on wrong optical properties: ozone formation < 200 nm ignored
- Failed to recognize all sinks

2.2 Homogeneous catalysis of the ozone sink reaction

The sink reaction

$O + O_3 \rightarrow 2\ O_2$ can be catalyzed:

$X + O_3 \rightarrow XO + O_2$

$XO + O \rightarrow X + O_2$

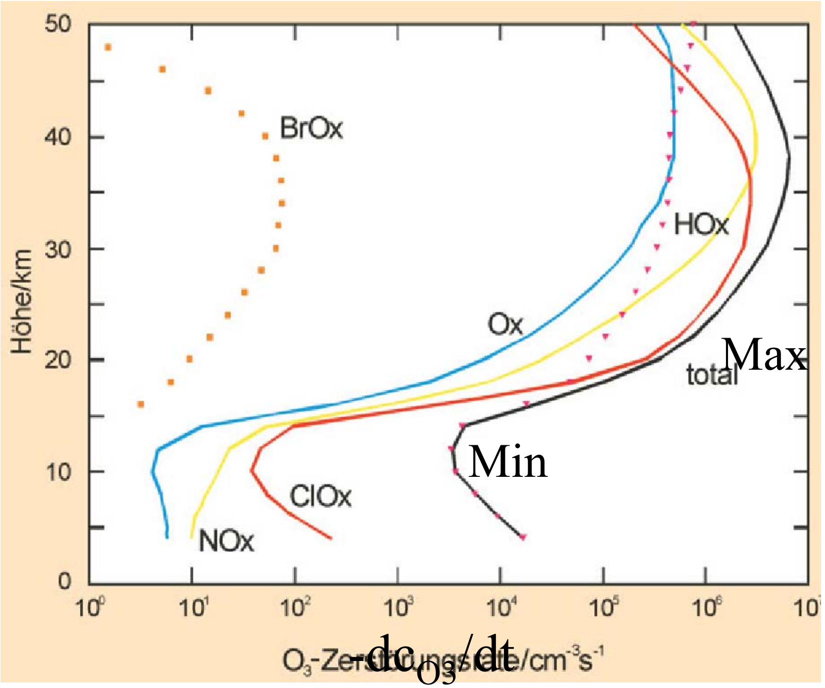
Sum:

$O_3 + O \rightarrow 2\ O_2$

X = Cl, Br (anthropogenic),

X = OH, NO (natural) *

- This results in an other steady-state concentration and vertical profile
- vertical distribution of sinks (1D model results):



** NO, like NO_2, because not really short-lived is usually not called a radical, although the electron shell contains an unpaired electron*

2.2.1 Homogeneous catalysis of the ozone sink reaction: OH

Catalyzed sink reaction

$O + O_3 \rightarrow 2\ O_2$

example X=OH

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O \rightarrow OH + O_2$

Sum:

$O_3 + O \rightarrow 2\ O_2$

OH source reactions:

(3a) $N_2O + h\nu \rightarrow N_2 + O(^1D)$

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

(5) $H_2O_2 + h\nu \rightarrow 2\ OH$

2.2.2 Homogeneous catalysis of the ozone sink reaction: Cl, Br

Catalyzed sink reaction

$O + O_3 \rightarrow 2\ O_2$

example X=Cl:

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

example X=Br:

$Br + O_3 \rightarrow BrO + O_2$

$BrO + O \rightarrow Br + O_2$

Deactivation reactions (sinks of effective radicals)

Formation of temporary reservoir substances

X=Cl:

$Cl + CH_4 \rightarrow HCl + CH_3$ *(fast)*

$CH_3 + O_2 \rightarrow CH_3OO$

$ClO + NO_2 + M \rightarrow ClONO_2 + M$ *(major)*

$c_{ClO} \sim c_{NO2}^{-1}$

Fate of X reservoirs

$HCl + OH \rightarrow Cl + H_2O$ *(slow)*

$ClONO_2 + h\nu \rightarrow ClO + NO_2$

X=Br:

$Br + CH_4 \rightarrow HBr + CH_3$ *(slo*

$Br + HO_2 \rightarrow HBr + O_2$

$BrO + NO_2 + M \rightarrow BrONO_2 + M$ (

$HBr + h\nu \rightarrow Br + H$ *(faster)*

$BrONO_2 + h\nu \rightarrow BrO + NO_2$ *(faster)*

$c_{Br}/c_{Br\text{-}Res} > c_{Cl}/c_{Cl\text{-}Res}$

$\tau_{Br} > \tau_{Cl}$

Further deactivation reaction ?

Formation of temporary reservoir substances

X=Cl: Fate of ClO (1)

$CH_3OO + ClO \rightarrow CH_3O + ClOO$

chlorine peroxide radical

$\rightarrow CH_3OCl + O_2$

methylhypochlorite

+HCl *(het)*

$\rightarrow CH_3OH + Cl_2$

Some rates and quantum yields involved are unknown → not totally clear

Uncertainties remain

Fate of ClO (2): Reaction with itself

The Cl catalyzed sink reaction in the absence of O atoms (i.e. efficient ozone destruction) is even accelerated:

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

(2) $ClO + O \not\rightarrow Cl + O_2$

(3) $2\ ClO + M \rightarrow ClOOCl + M$

chlorine peroxide (or ‚ClO dimer‘)

(4a) $ClOOCl + h\nu \rightarrow Cl + ClOO$

(5) $ClOO + M \rightarrow Cl + O_2 + M$

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

*Sum (4a+5+2*1):*

$2\ O_3 \rightarrow 3\ O_2$

ClOOCl is key species for ozone depletion: $O_3 \rightarrow ClO \rightarrow ClOOCl \rightarrow \rightarrow Cl$

Uncertainties remain:

Availability of ozone depleting radi

(3) $ClO + ClO \rightarrow ClOOCl$

(-3) $ClOOCl \rightarrow ClO + ClO$

(4a) $ClOOCl + h\nu \rightarrow 2\,ClO$

Sum:

(3+4a) –

(4b) $\rightarrow Cl + ClOC$

$\phi_{(4a)}$ yield: 100%

(5) $ClOO \rightarrow Cl + O_2$

Sum:

(3+4b+5) $2\,ClO \rightarrow 2\,Cl + O_2$ *No te*

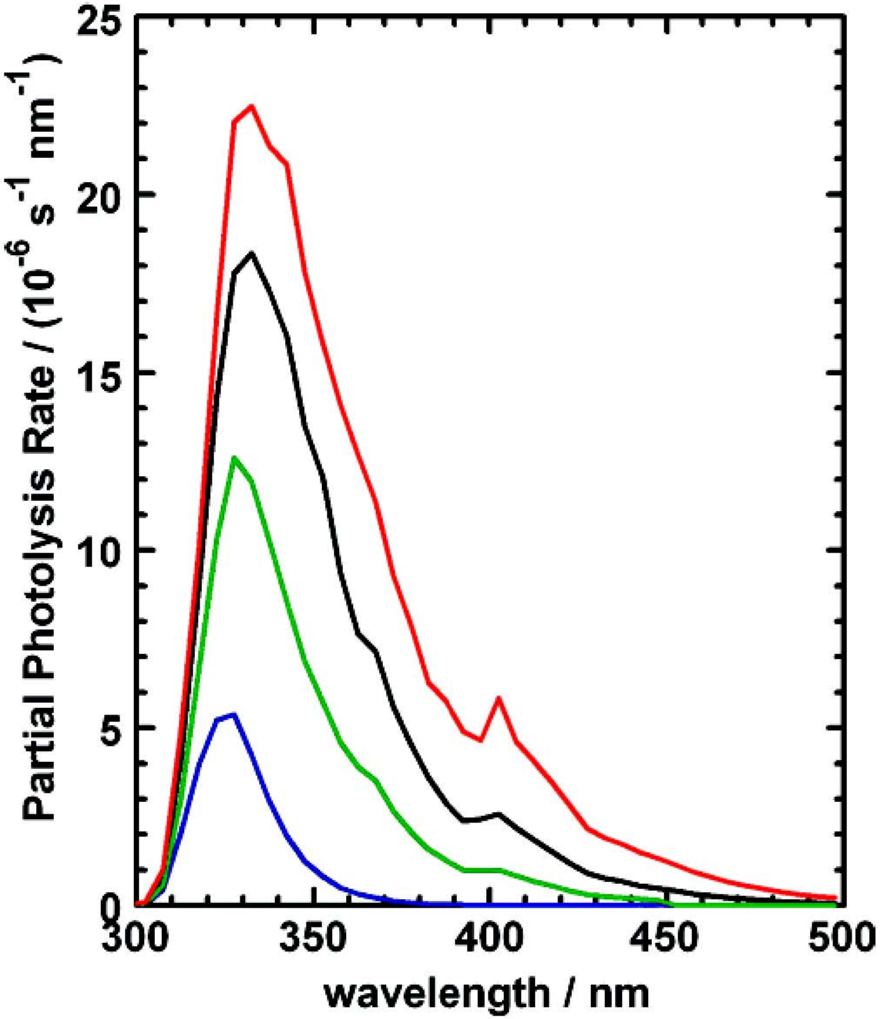


Figure 10. Partial photolysis rates of ClOOCl in the atmosphere calculated for different cross sections. Conditions: altitude 20 km; solar zenith angle 86°; O_3 concentrations and temperature values measured in the polar vortex for March 2000.[46] Cross sections: Burkholder et al. (red);[6] JPL 2006 (black);[18] Huder and DeMore (green);[7] present values (blue).

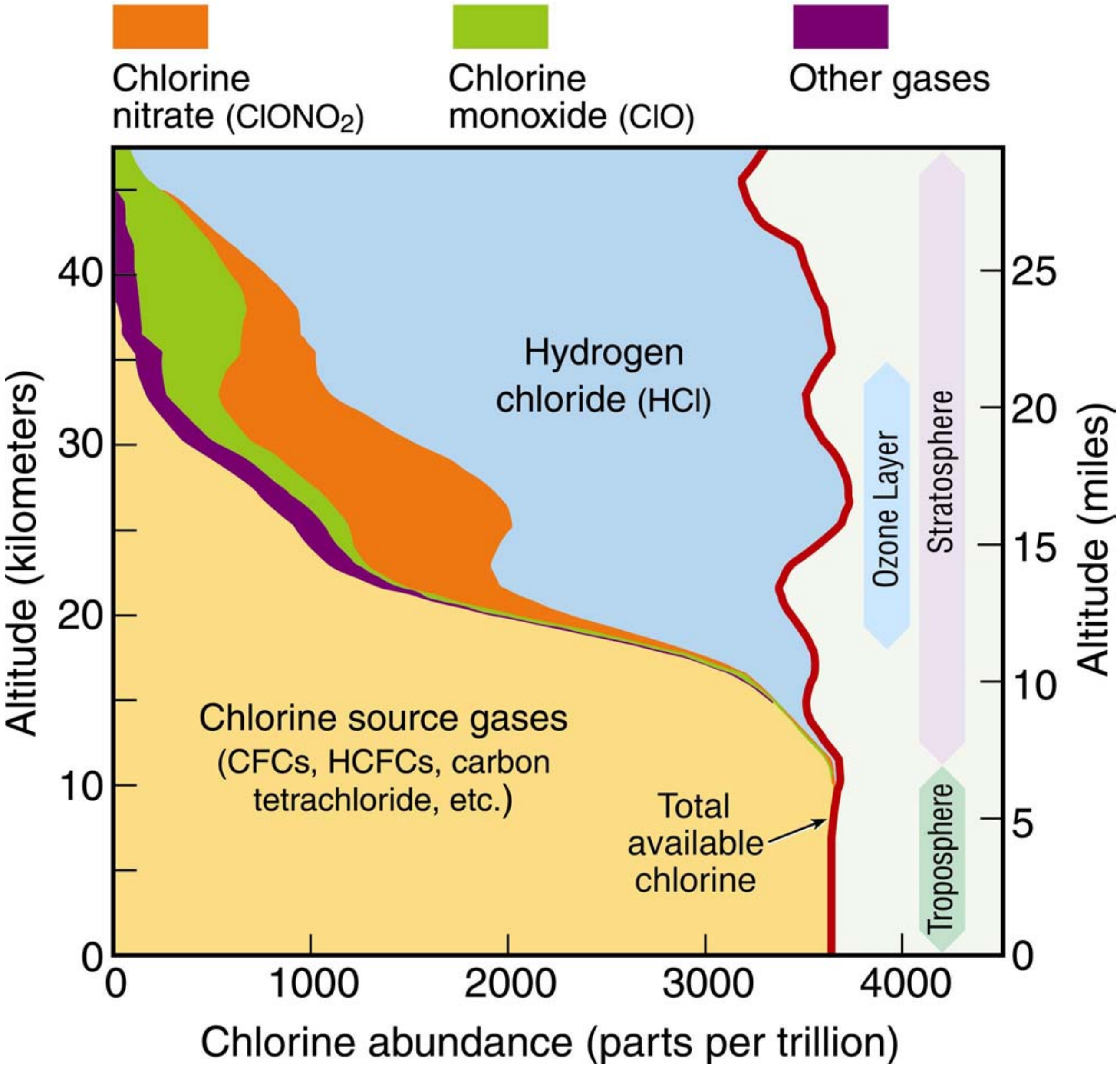
Cross section measured < 410 nm (Burkholder

450 nm because of excitatic

Cross section $\sigma_{(4) > 310\ nm}$ had been overestimated, ClOOCl is longer lived - and ozone sinks are incomplete (Pope et al., 2007)

Measurements of reactive chlorine from space

November 1994 (35° – 49°N)



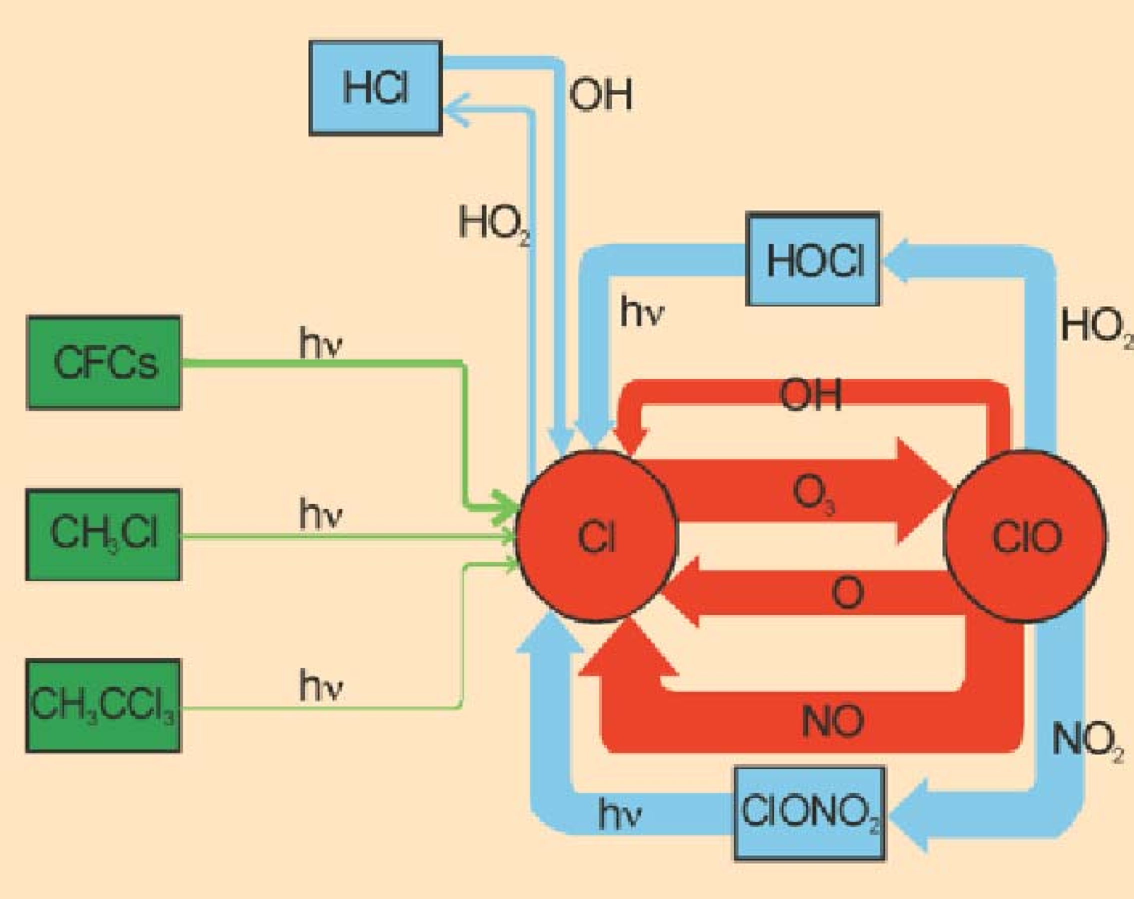
Ozone chemistry for X = Cl (catalyst, source, reservoir) including coupling reactions ClO_x/HO_x and ClO_x/NO_x:

Total flux between X and XO is proportional to $-dc_{O3}/dt$

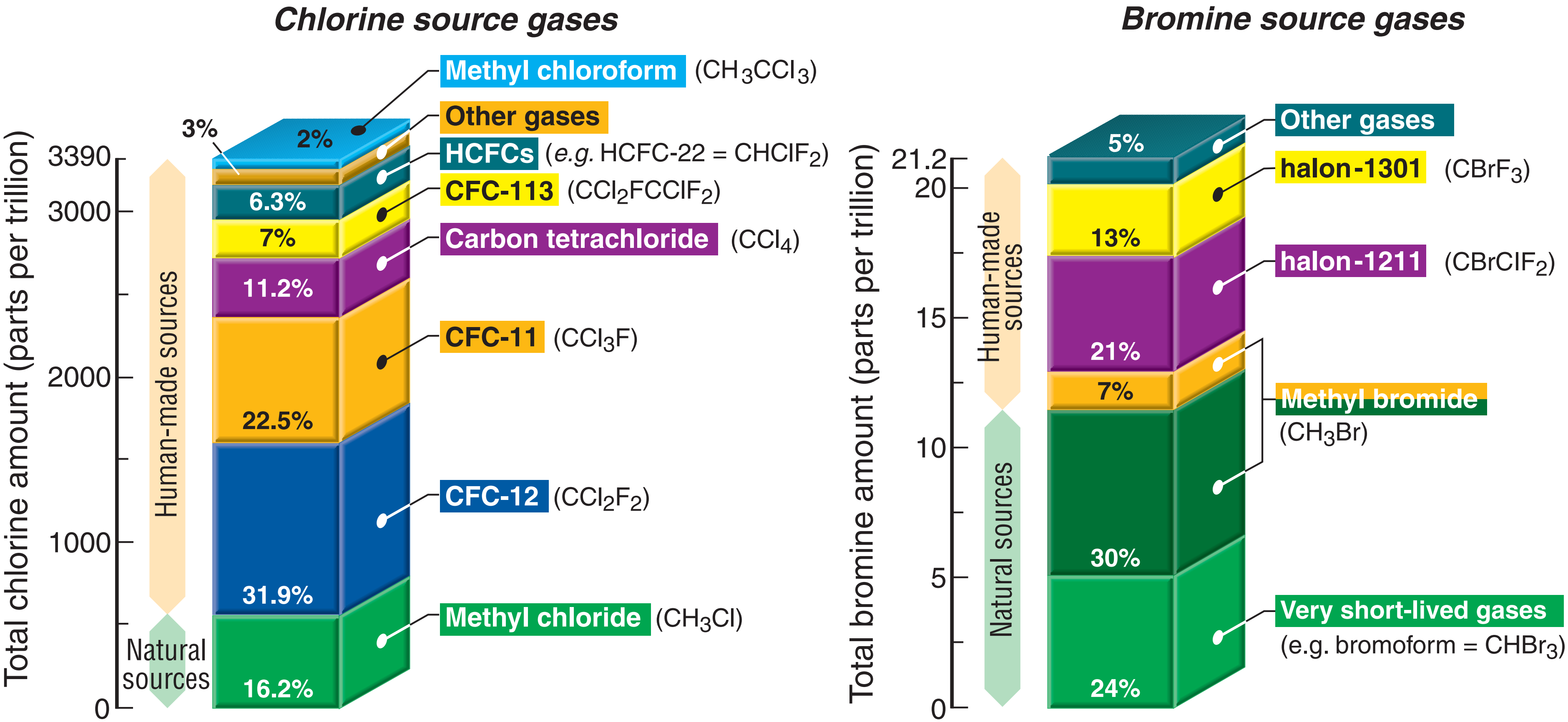
Temporary reservoir HCl

Direct photolysis of RCl‘s insignificant for $-dc_{O3}/dt$ e.g.:

$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$

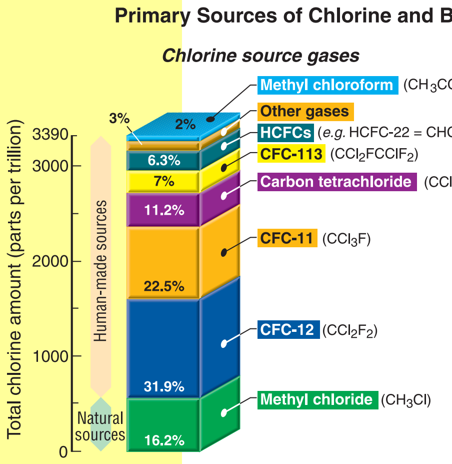


Primary Sources of Chlorine and Bromine for the Stratosphere in 2004



Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007

Nomenclature for halogenated hydrocarbons:



Chlorofluorocarbons (CFCs)
Freons (F, trade name)

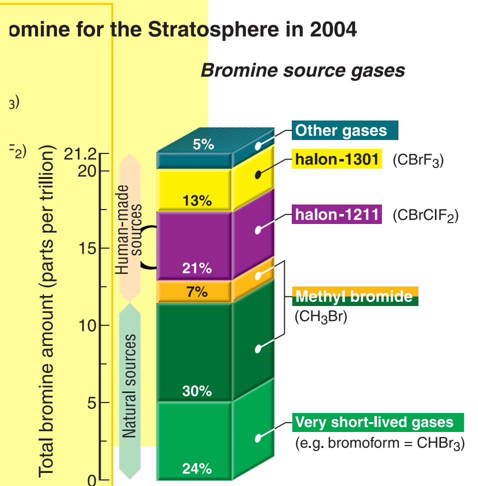
‚F-xyz‘ or ‚CFC-xyz‘ or ‚HCFC-xyz‘
with:
x = number of C atoms –1
y = number of H atoms +1
z = number of F atoms
general: $C_{x-1}H_{y+1}Cl_nF_z$

dt.: *Chlorfluorkohlenwasserstoffe*

commonly:
FCKW for Fluorchlorkohlenwasserstoffe

Halogenated hydrocarbons in general:

Halons
‚Halon-wxyz‘ for $C_wH_nF_xCl_yBr_z$
e.g.
CF_3Br = Halon-1301
CF_2ClBr = Halon-1211; CH_3Br would be Halon-1001



2.2.3 Homogeneous catalysis of the ozone sink reaction: NO

Catalyzed sink reaction

$O + O_3 \rightarrow 2\ O_2$

example X=NO (Crutzen, 1970)

(1a) $NO + O_3 \rightarrow NO_2 + O_2$

(2a) $NO_2 + O \rightarrow NO + O_2$

Sum:

(1a+2a) $O_3 + O \rightarrow 2\ O_2$

(2b) $NO_2 + h\nu \rightarrow NO + O$

(3) $O + O_2 \rightarrow O_3$

(2a) vs.(2b) competition decides upon NO effect on O_3:

(2a) destroys O which otherwise would recycle O_3 and recycles O_3-destroying NO

Deactivation by formation of reservoir compound:

(1b) $NO + HO_2 \rightarrow HNO_3$

Yield ≈ 15% at 298 K but ≈ 50% at 223 K (Butkovskaya et al., 2005).

→ additional HO_x sink

→ lower NO_x/HNO_3

NO source reactions:

(3a) $N_2O + h\nu \rightarrow N_2 + O(^1D)$ 1% (1967: „≈ 20%“)

(3b) $\rightarrow NO + N(^4S)$

(4a) $N_2O + O(^1D) \rightarrow N_2 + O_2$

(4b) $\rightarrow 2\ NO$ 60% $k=67\times10^{-12}$ cm³/molec/s (1990)

Catalyzed sink reaction

$O + O_3 \rightarrow 2\ O_2$

example X=NO (Crutzen, 1970)

(1a) $NO + O_3 \rightarrow NO_2 + O_2$

(2a) $NO_2 + O \rightarrow NO + O_2$

Sum:

(1a+2a) $O_3 + O \rightarrow 2\ O_2$

(2b) $NO_2 + h\nu \rightarrow NO + O$

(3) $O + O_2 \rightarrow O_3$

Sum:

(1a+2b+3) -

The catalyzing radicals are coupled:

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

$ClO + HO_2 \rightarrow HOCl + O_2$

$Cl + HO_2 \rightarrow HCl + O_2$

$NO + HO_2 \rightarrow OH + NO_2$

Catalyzed sink reaction

$O + O_3 \rightarrow 2\ O_2$

example X=NO (Crutzen, 1970)

(1a) $NO + O_3 \rightarrow N$

(2a) $NO_2 + O \rightarrow N$

Sum:

(1a+2a) $O_3 + O \rightarrow 2$

(2b) $NO_2 + h\nu \rightarrow N$

(3) $O + O_2 \rightarrow O_3$

Sum:

(1a+2b+3) -

Effect of emissions in the stratosphere?

500 supersonic airplanes would destroy 50 % (Johnston, 1971), 12 % (Johnston et al., 1974)

k_{1a} (NO/O_3) was underestimated, k_{2a}/k_{2b} was uncertain

→ today: Ozone production from SSA because of Cl and OH deactivation!

The catalyzing radicals are coupled:

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

$ClO + HO_2 \rightarrow HOCl + O_2$

$Cl + HO_2 \rightarrow HCl + O_2$

$NO + HO_2 \rightarrow OH + NO_2$

History of the ozone hole over Antarctica:

Farman et al. 1985: (Dobson-Instrument) Halley Ba

Chubachi, 1985: Syowa 1984

Solomon et al.: PSC can activate Cl (1986)

Molina & Molina: ClO recycled via ClOOCl (1987)

US Natl. Ozone Expedition, NOAA 1986

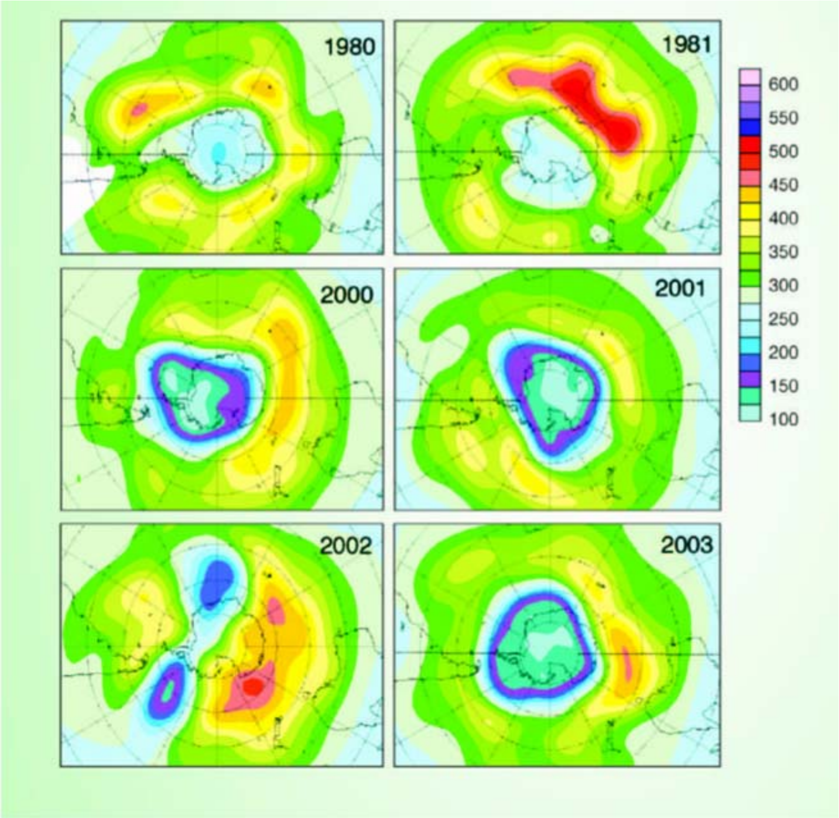
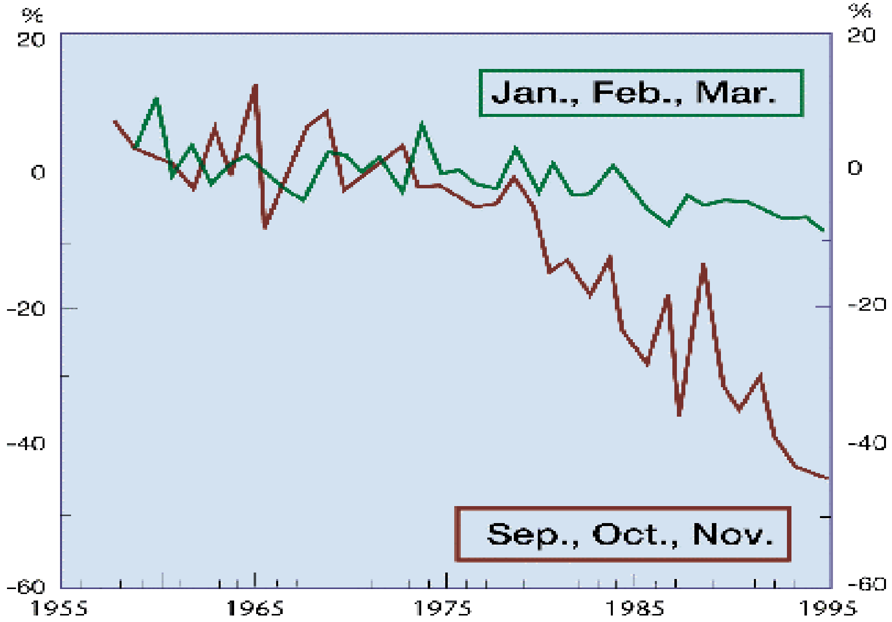
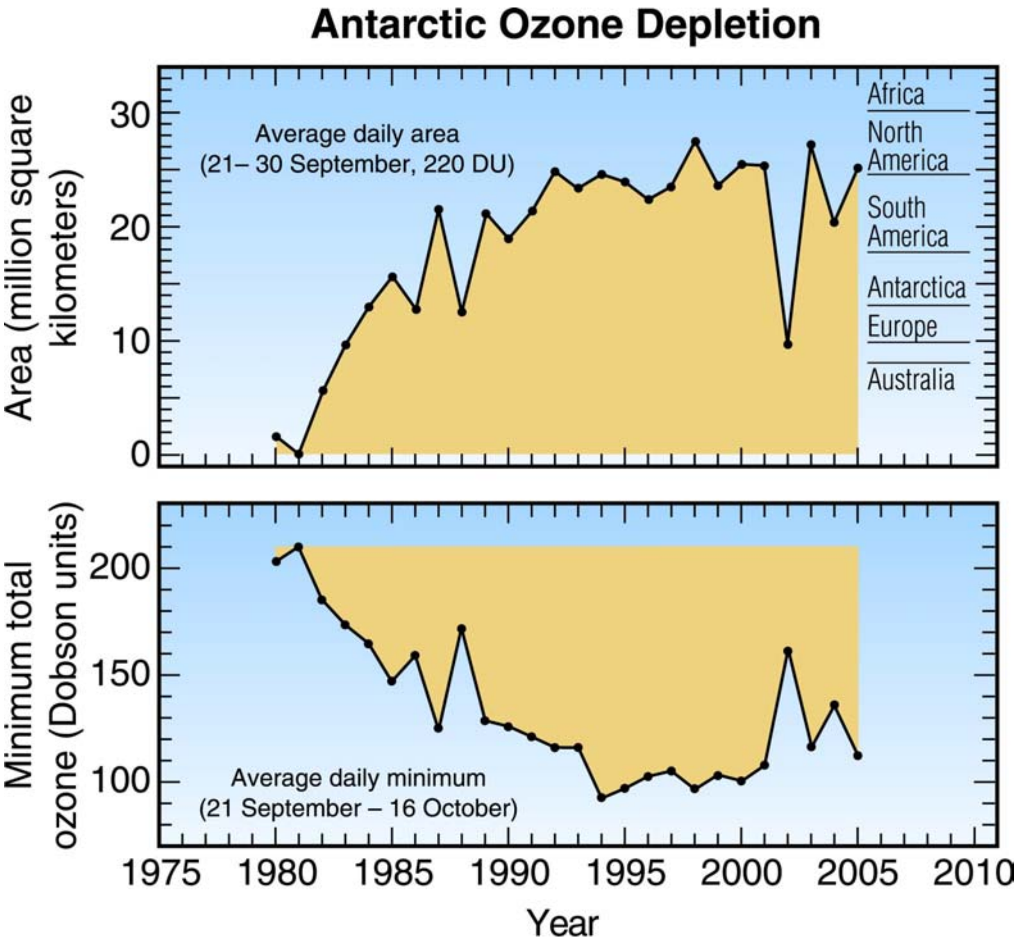


Figure 1 **Satellite maps of total ozone over Antarctica on 24 September, when the ozone hole is near its annual peak, in 1980, 1981, 2000, 2001, 2002 and 2003. The colour scale shows the amount of ozone in Dobson units, indicating the depth of the hole. The images are based on multiple satellite records and analyses and are available from many sources, including the World Ozone and Ultraviolet Radiation Data Centre in Toronto, Canada, http://woudc.ec.gc.ca/cgi-bin/selectMap.**



Seasonal ozone deviations from pre-ozone-hole (1957-1978) averages over Antarctica show a rapid decline during the austral spring and lesser decline during the summer.

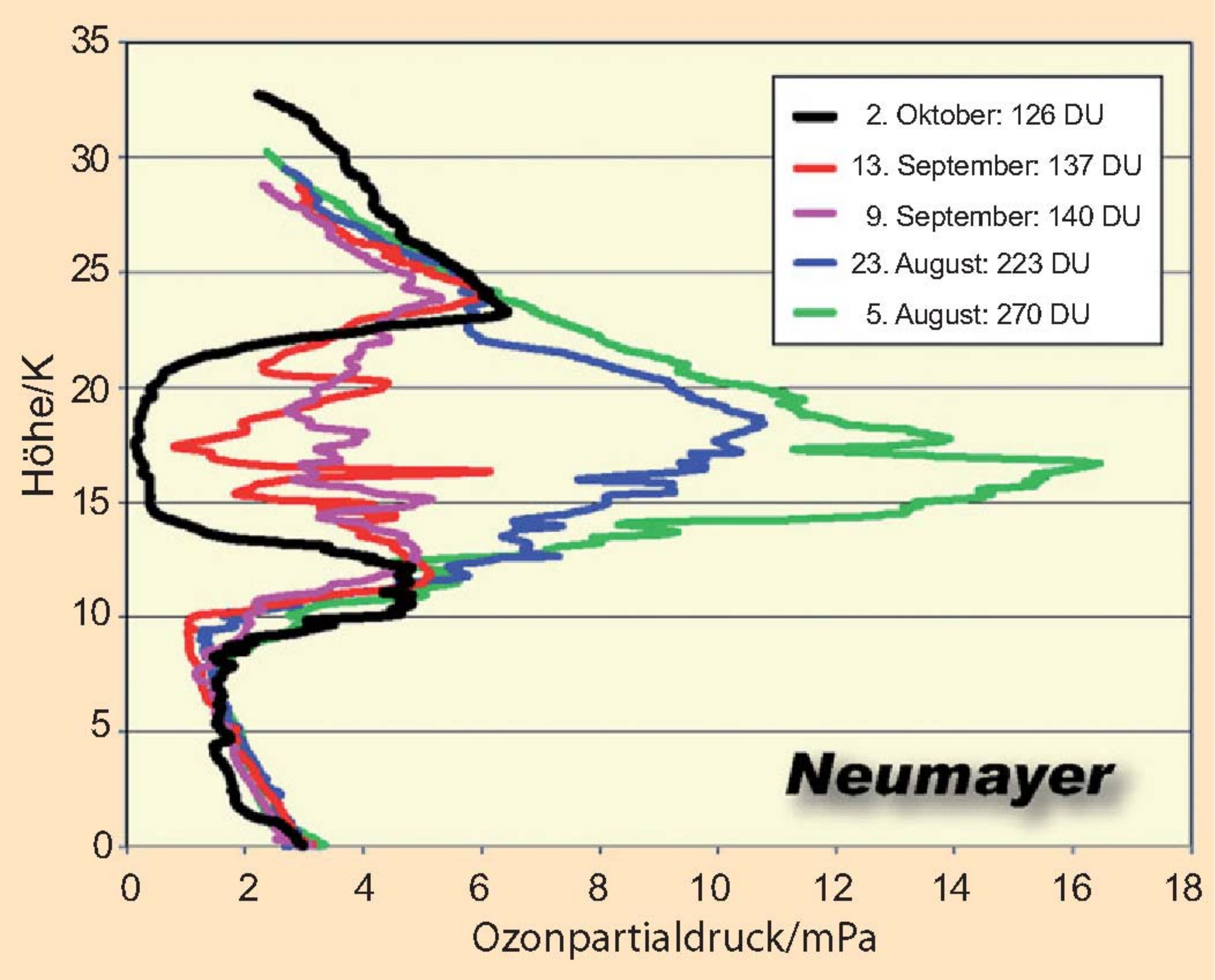
(Source: The Changing Ozone Layer by R.D. Bojkov © World Meteorological Organization, 1995)



Total ozone column density N/A = 2.46×10^{19} molec/cm²:=1000 DU

Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007

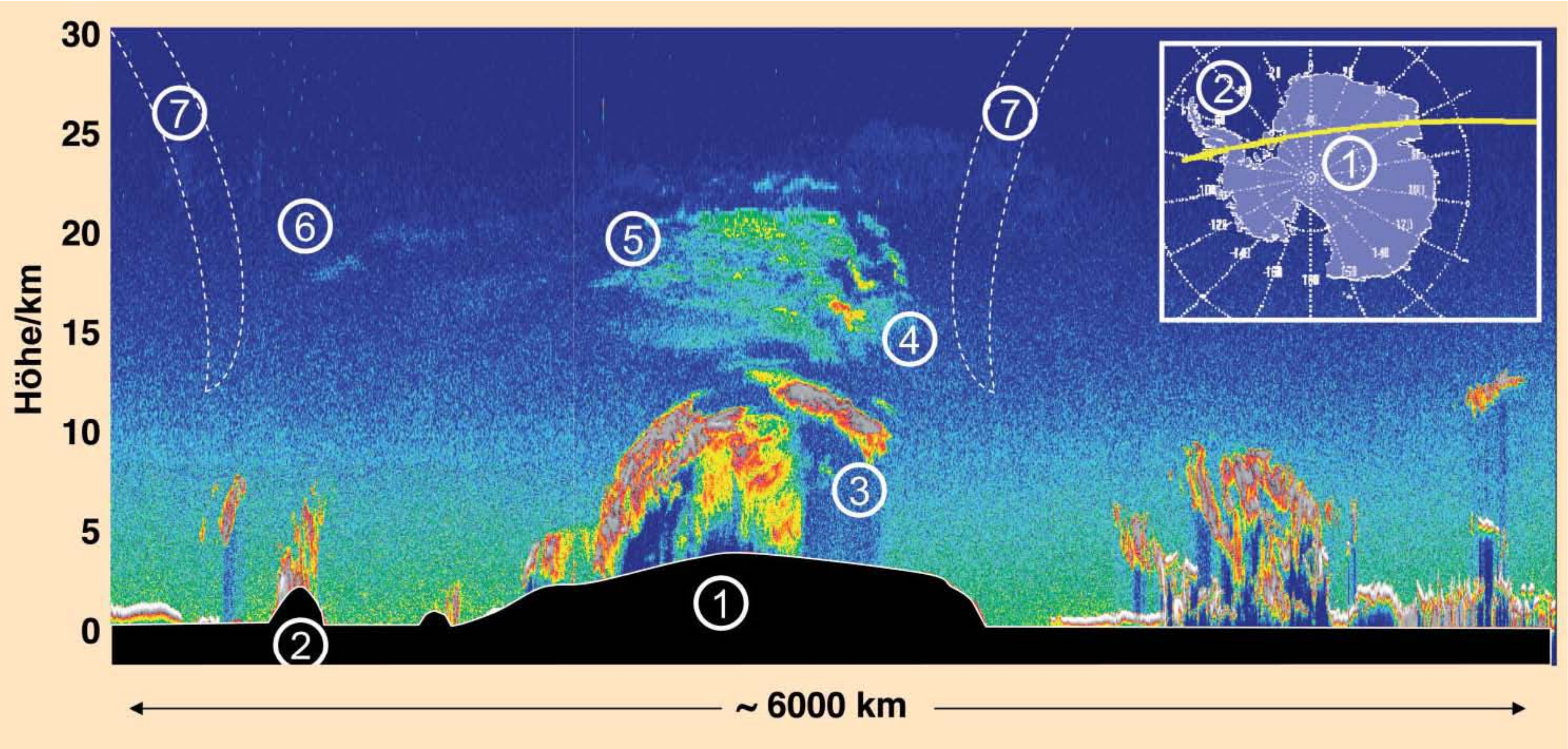
Temporal dynamics of ozone loss over Antarctica: 2006, 71°S



Losses mostly in 12-25 km altitude

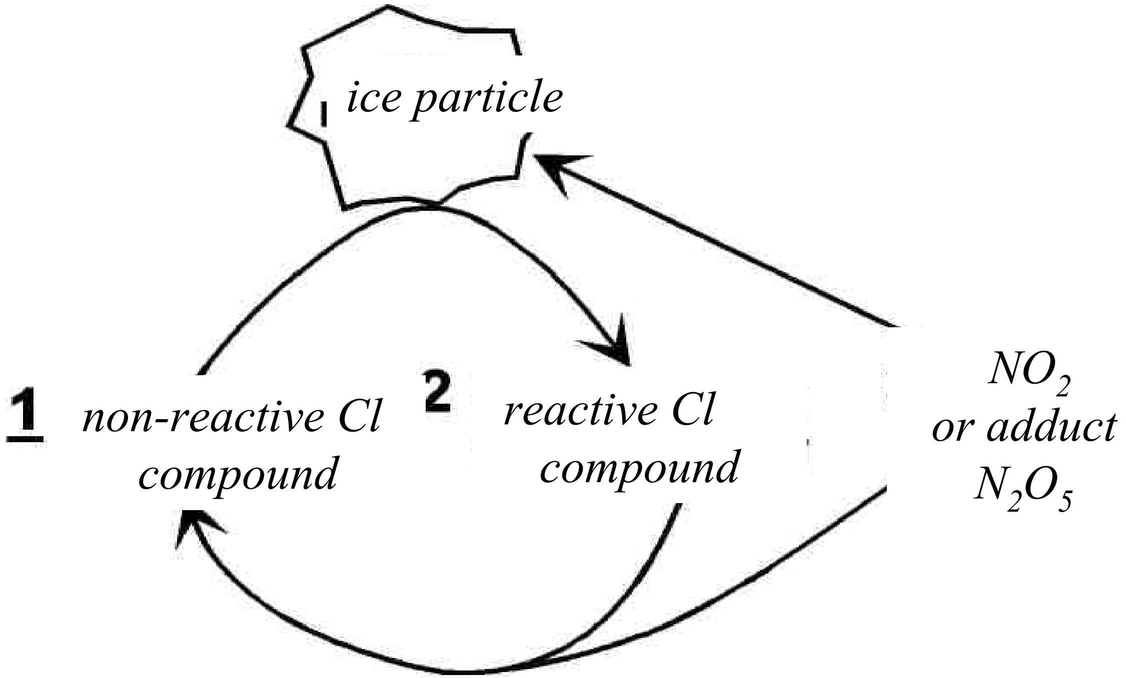
1994/97 vs. 1979: -50% spring 60°S_90°S

2.3 Heterogeneous reactions in polar stratospheric clouds



Satellite (Calipso, NASA) based lidar data, 22.6.06: 1 = Antarctica, 2 = Antarctic Peninsula, 3 = cirrus, 4 = $H_2O(l)$ PSCs, 5 = H_2SO_4-HNO_3-$H_2O(l)$ or HNO_3*3 $H_2O(s)$ (NAT) PSCs, 6 = lee wave clouds, 7 = position of polar vortex

2.3 Heterogeneous reactions in polar stratospheric clouds
Overview



$\underline{1}$ = $ClONO_2$, HCl

2 = Cl_2, HOCl $\xrightarrow{h\nu}$ Cl

3 = NO_2 , N_2O_5

Deactivation by formation of reservoir compounds:

$Cl + CH_4 \rightarrow HCl + CH_3$

$Cl + HO_2 \rightarrow HCl + O_2$

$Cl + H_2 \rightarrow HCl + H$

$ClO + NO_2 \rightarrow ClONO_2$

Slow

As long as there is NO_2 available!

Deactivation by NO_y compounds:

$HNO_3 + h\nu \not\rightarrow NO + HO_2$

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + ClO + M \rightarrow ClONO_2 + M$

Activation through recycling reactions:

$HCl_{\text{in Ice}} + n\ H_2O \rightarrow H_3O^+(H_2O)_{n-1}Cl^-$

$Cl^- + ClONO_2 \rightarrow Cl_2 + NO_3^-$

Sum:

$HCl_{\text{in Ice}} + ClONO_2 \rightarrow Cl_2 + HNO_{3(s)}$

$H_2O(s) + ClONO_2 \rightarrow HOCl + HNO_{3(s)}$

$HOCl + HCl \rightarrow Cl_2 + H_2O$

Denitrification: Sedimentation of HNO_3–containing ice particles of the PSCs

$H_2O(s) + N_2O_5 \rightarrow 2\ HNO_3(s)$

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

Gas-phase activation reactions:

$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$

$N_2O + h\nu \rightarrow N_2 + O(^1D)$

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

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

1.5 Heterogeneous reactions

$$- dc_{i(g)} / dt = k^{het\,(1)} c_{i(g)}$$

$$k^{het\,(1)} = \gamma_i \,(S/V)\, \beta_i \langle v_i \rangle / 4$$

$$\beta_i = (1 + Kn_i) \;/\; (1 + 1.71\, Kn_i + 1.33\, Kn_i^2)$$

$$\langle v_i \rangle = (8\, RT / \pi M_i)^{0.5}$$

with:

$c_{i(g)}$ = concentration of trace gas i far from the interface,
k^{het} = loss rate to condensed phase,
γ_i = surface reaction propability, can be T dependent
S/V = total (aerosol + ground) surface concentration
$\langle v_i \rangle$ = mean velocity of gas molecules,
R = molar gas constant, T = absolute temperature, M_i = molar mass,
β_i = correction for non-continuum effects (for $r < 0.05\mu m$; Fuchs & Sutugin, 1971)
With:
  $Kn_i = \lambda_i / r$ = Knudson number, r = particle radius
  $\lambda_i = (\sqrt{2}\, \pi\sigma_i^2\, N_i/V)^{-1}$ = mean free path of gas molecules,
  $\pi\sigma_i^2$ = collision cross-section of gas molecules in air,
  N_i/V = molecule number concentration.

Kinetic description of heterogeneous reactions

γ_i = reaction probabilites

	Ice	**NAT**	**SAT**
$ClONO_2 + HCl \rightarrow$	0.2	0.1	0.001_0.1
$N_2O_5 + HCl \rightarrow$	0.3	0.003	-
$HOCl + HCl \rightarrow$	0.3	0.1	-
$ClONO_2 + H_2O \rightarrow$	> 0.1	0.0001_0.01	0.001_0.01
$N_2O_5 + H_2O \rightarrow$	0.02	0.0003	0.01

$$NO \xrightarrow{+\,O_3} NO_2 \xrightarrow{+\,O_3} NO_3 \overset{+\,NO_2}{=} N_2O_5$$

Example: Loss of N_2O_5 on particle surfaces: $N_2O_5 + 2\,H_2O\,(l) \rightarrow 2\,NO_3^- + 2\,H_3O^+$

with: $\beta_i \approx 1$

$<v_i> = (8\,RT / \pi M_i)^{0.5} \approx 5 \times 10^4$ cm/s

γ_i = reaction probability $\approx 0.0003\text{-}0.02$

$S/V \approx (0.01\text{-}1) \times 10^{-6}\ cm^{-1}$ for stratospheric aerosol

k^{het} = loss rate to condensed phase = $\gamma_i\,(S/V)\,\beta_i <v_i> / 4$:

$$k^{het} \approx (0.0003\text{-}0.02) \times (0.01\text{-}1) \times 10^{-6} \times 5 \times 10^4 / 4\ s^{-1} \approx (0.04\text{-}250) \times 10^{-6}\ s^{-1},$$

$$\tau_{het.loss} \approx 1\ h - 300\ d$$

Kinetic description of heterogeneous reactions

γ_i = reaction probabilites

Concept: Resistance model

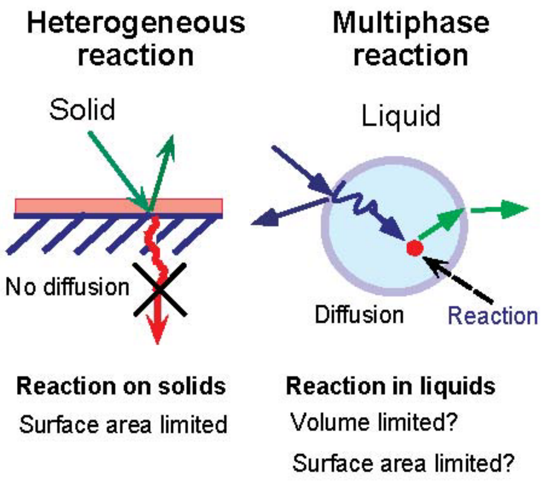
The larger γ the lower the resistance, the higher the conductivity Γ.
In analogy to electrical circuits: serial and parallel processes dealt as resistances.

Individual processes in series: $\Gamma = \gamma^{-1} = \Sigma_i \Gamma_I = \Sigma_i (\gamma^{-1})_i$

Parallel individual processes: $\Gamma = \gamma^{-1} = (\Sigma_i \gamma_i)^{-1}$

$$\gamma = \Sigma_i \gamma_i$$

Kinetic description of heterogeneous reactions: solid surface



Processes:	*Condensed phase: Solid*
Transport in the gas phase Initial interaction	Γ_g
Reversible sorption	Accommodation (‘sticking’) coefficient α
Reaction on surface	Reactive uptake coefficient γ_r
Overall process Γ	Total experimental uptake/reaction probability, coefficient γ_{tot}

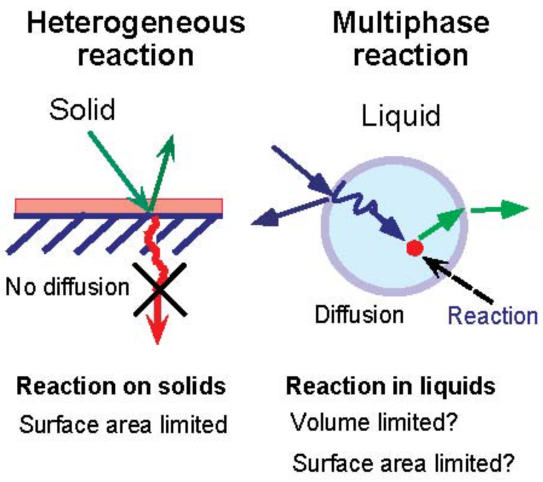
Def.: α: = fraction of gas-surface collisions taken up by surface (reversible)

γ_r: = fraction of gas-surface collisions leading to irreversible uptake, tabulated *

$\gamma_{tot}^{-1} \approx \gamma_r$ if surface and/or bulk reaction dominate the overall process kinetics =

= reaction is slow while gas-phase diffusion and reversible sorption are fast

Kinetic description of heterogeneous reactions: solid surface



Processes:	*Condensed phase: Solid*
Transport in the gas phase Initial interaction	Γ_g
Reversible sorption	Accommodation ('sticking') coefficient α
Reaction on surface	Reactive uptake coefficient γ_r
Overall process Γ	Total experimental uptake/reaction probability,

Def.: α: = fraction of gas-su

γ_r: = fraction of gas-su

$\gamma_{tot}^{-1} \approx \gamma_r$ if surface and/or bul

= reaction is slow v

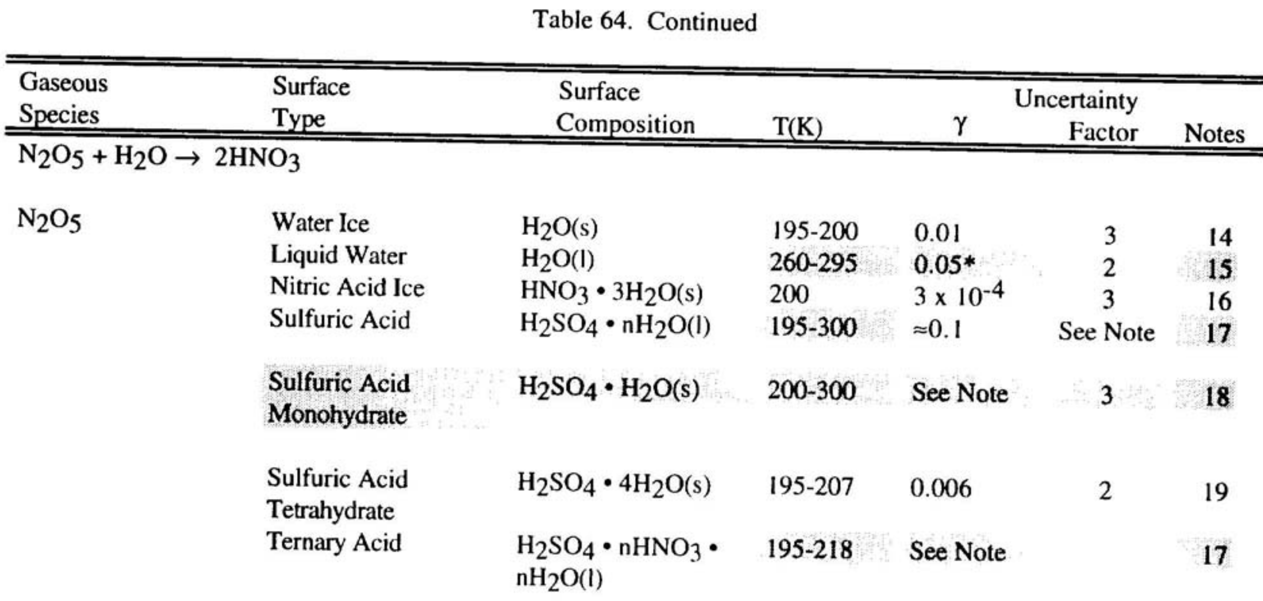


Table 64. Continued

Gaseous Species	Surface Type	Surface Composition	T(K)	γ	Uncertainty Factor	Notes
$N_2O_5 + H_2O \rightarrow 2HNO_3$						
N_2O_5	Water Ice	$H_2O(s)$	195-200	0.01	3	14
	Liquid Water	$H_2O(l)$	260-295	0.05*	2	15
	Nitric Acid Ice	$HNO_3 \cdot 3H_2O(s)$	200	3×10^{-4}	3	16
	Sulfuric Acid	$H_2SO_4 \cdot nH_2O(l)$	195-300	≈0.1	See Note	17
	Sulfuric Acid Monohydrate	$H_2SO_4 \cdot H_2O(s)$	200-300	See Note	3	18
	Sulfuric Acid Tetrahydrate	$H_2SO_4 \cdot 4H_2O(s)$	195-207	0.006	2	19
	Ternary Acid	$H_2SO_4 \cdot nHNO_3 \cdot nH_2O(l)$	195-218	See Note		17

1.5.1 Heterogeneous reactions on solids

$$\gamma_{tot} = (1/\alpha + 1/\gamma_r)^{-1} \approx \alpha \qquad \text{if } \alpha \ll \gamma_r$$
$$\approx \gamma_r \qquad \text{if } \gamma_r \ll \alpha$$

Reversible sorption and irreversible reaction can take place in parallel rather than in series, too. Then:

$$\gamma = \gamma_r + \alpha$$
with $\gamma_r \geq \alpha$, eventually $\gamma_r \approx \alpha$.

Laboratory experiments often do not allow to unambiguously differentiate between γ and α. In these cases γ are tabulated * as ‘α‘ – subject to change if more definitive data become available.

* Chemical kinetics and photochemical data for use in stratospheric modeling Eval. No. 12 (JPL-Publ-97-4; NAS 1.26112606; NASA CR-97-112606), 1997 (updated 2005), http://ntrs.nasa.gov/search.jsp

1.2.3 Heterogeneous reactions in polar stratospheric clouds

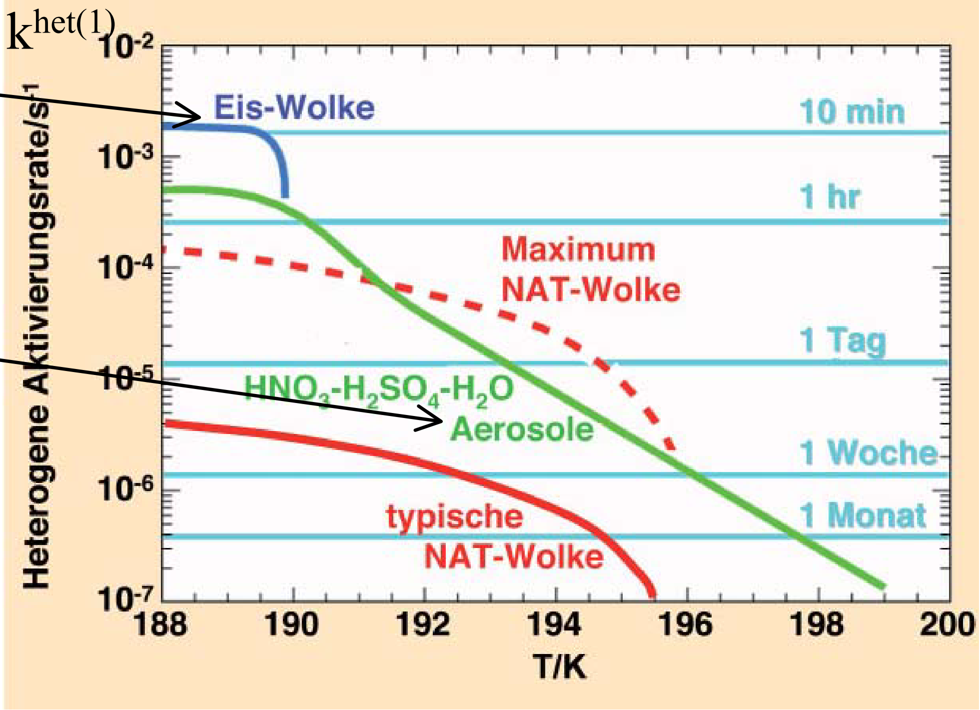
PSC properties

Solid or liquid, < 200 K growth of sulfuric acid particles, < 188 K partly solid
wide range of particle/droplet sizes
$S/V = (0.01\text{-}1)\times10^{-6}\ \mathrm{cm}^{-1}$
$V/V = (1\text{-}100)\times10^{-12}$

Reaction rate of $ClONO_2/Cl^-$: $k^{het(1)} = -dc_{ClONO2}/dt/c_{ClONO2}$ (s^{-1})

‚Type II PSC‘
$D \approx 5\text{-}50\ \mu m$

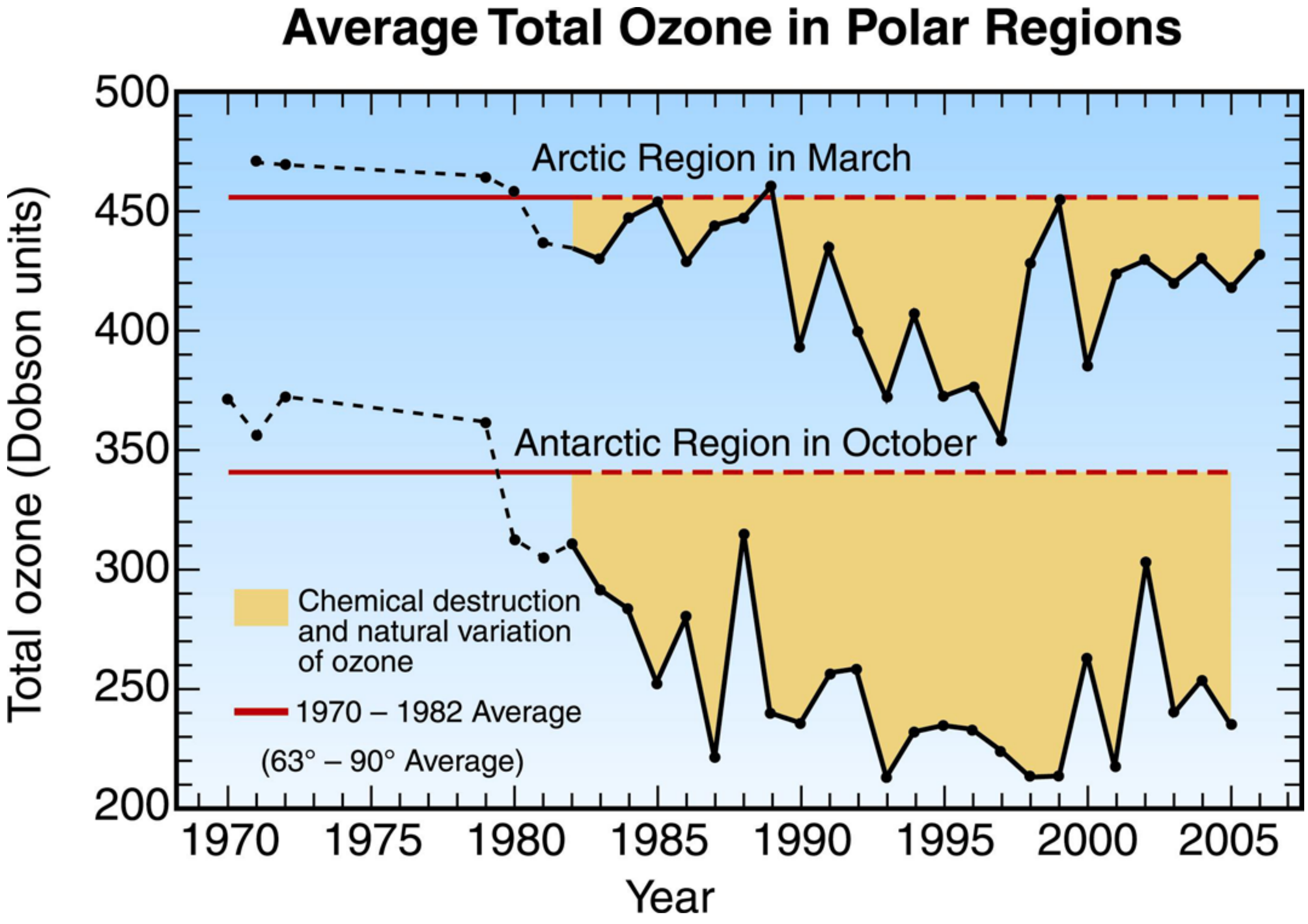
‚Type I PSC‘
$D \approx 0.5\ \mu m$



Changing chemistry at sunrise:

- Advection: vortex opens and zonal transport of ozone rich air is possible again
- Temperature increase: ice crystals melt, release NO_2, $ClONO_2$ is formed again, binding Cl
- Photochemistry: O_2 photolysis supplies fresh O_3

2.4 Long-term trends

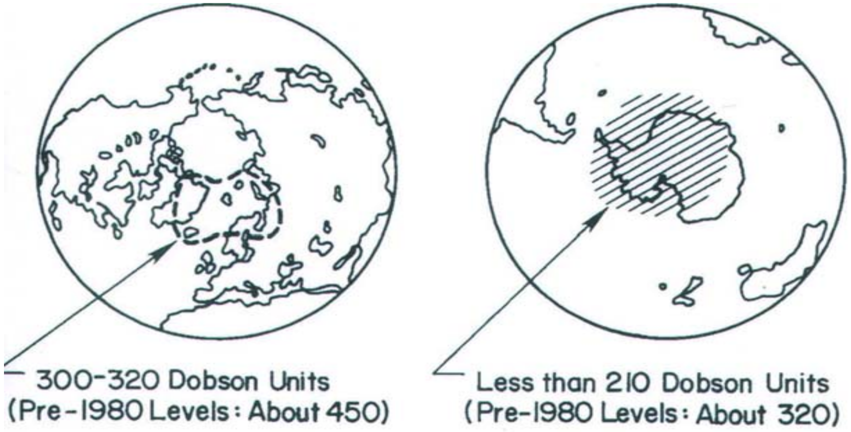


Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007

Stratospheric ozone chemistry

T < 190 K

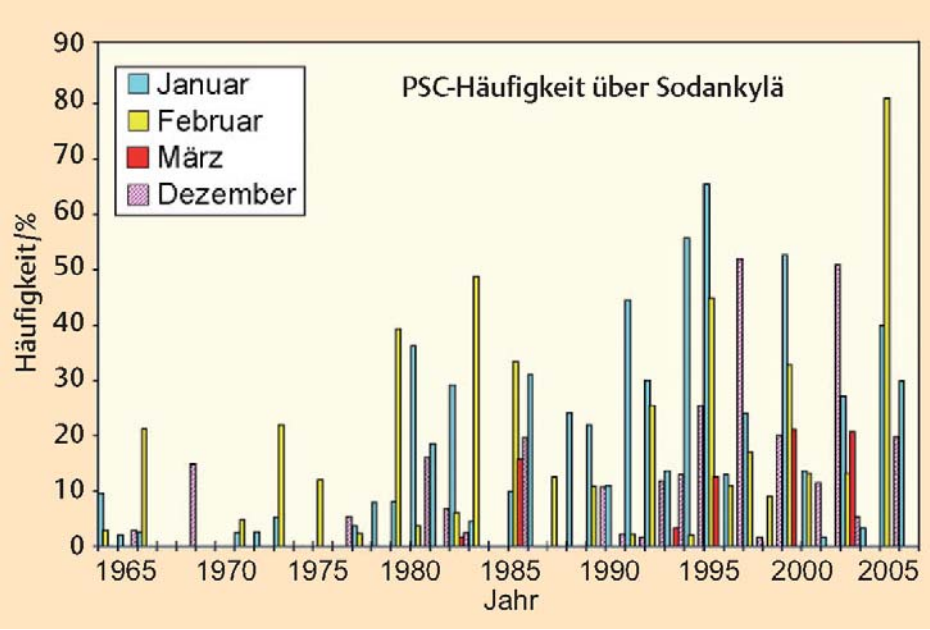
Arctic stratosphere?

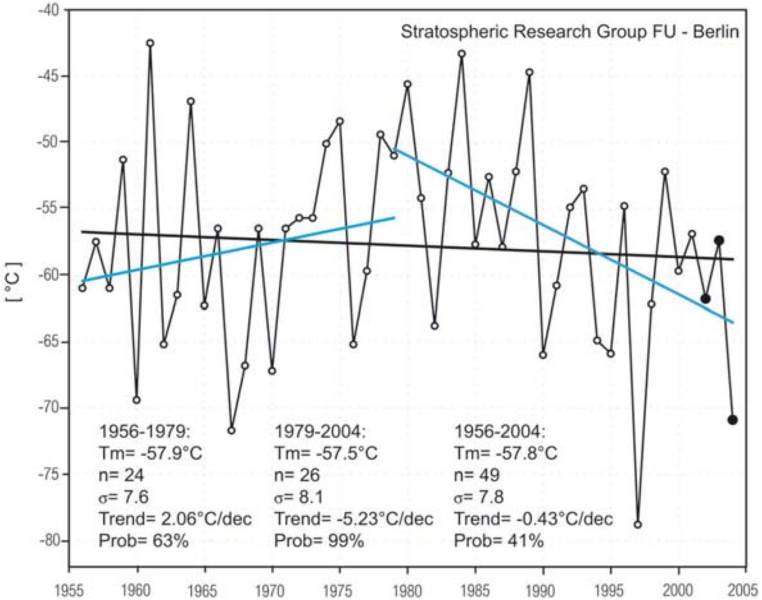


Arctic spring (March) and Antarctic Spring (September)

(WMO, 1999)

Frequency of PSCs, temperature trends:





(Labitzke & van Loon, 1999, updated 2004)

Emission reduction efficiency ?

Basis for comparison of different substances = ?

→ Ozone depletion potentials

ODP: = (global ozone loss due to unit mass emission of i

(global ozone loss due to unit mass emission of CFC-11)

-assuming steady-state conditions (time dependent calculations are possible, but not common)

- assuming constant emissions (for compounds that are removed by linear processes, this is equivalent to assumin an emission pulse and integrating over the entire decay of the compound)

- not dependent on time

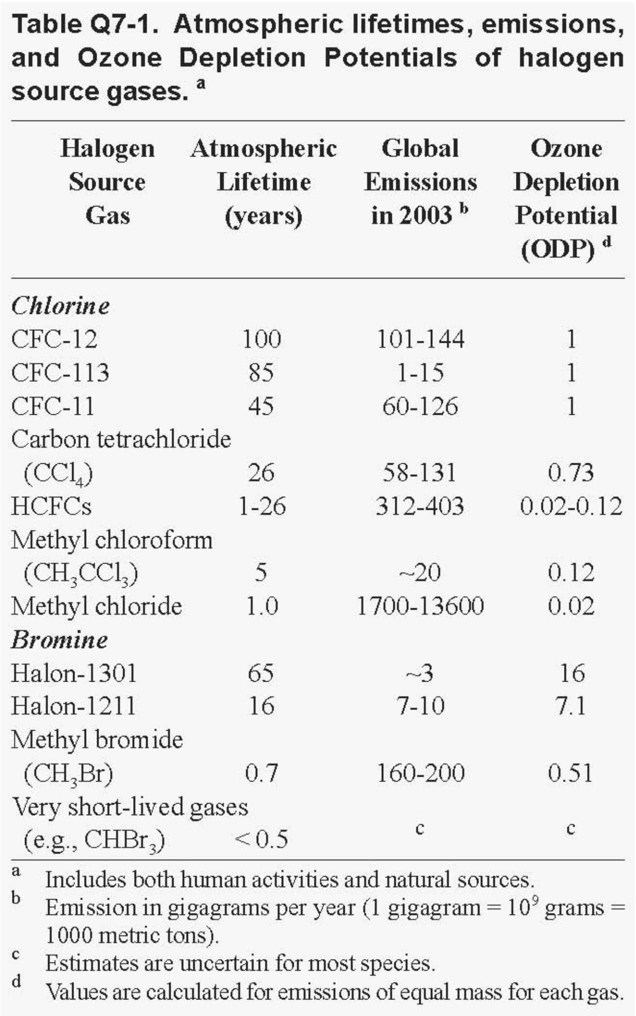


Table Q7-1. Atmospheric lifetimes, emissions, and Ozone Depletion Potentials of halogen source gases. [a]

Halogen Source Gas	Atmospheric Lifetime (years)	Global Emissions in 2003 [b]	Ozone Depletion Potential (ODP) [d]
Chlorine			
CFC-12	100	101-144	1
CFC-113	85	1-15	1
CFC-11	45	60-126	1
Carbon tetrachloride (CCl_4)	26	58-131	0.73
HCFCs	1-26	312-403	0.02-0.12
Methyl chloroform (CH_3CCl_3)	5	~20	0.12
Methyl chloride	1.0	1700-13600	0.02
Bromine			
Halon-1301	65	~3	16
Halon-1211	16	7-10	7.1
Methyl bromide (CH_3Br)	0.7	160-200	0.51
Very short-lived gases (e.g., $CHBr_3$)	<0.5	c	c

[a] Includes both human activities and natural sources.

[b] Emission in gigagrams per year (1 gigagram = 10^9 grams = 1000 metric tons).

[c] Estimates are uncertain for most species.

[d] Values are calculated for emissions of equal mass for each gas.

Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007

Total atmospheric lifetime (or residence time):

$$\tau_i = \text{burden/(total loss rate)} = b_i / \tau_i^{-1} = b_i / [\Sigma_i (\tau_i^{-1})]^{-1}$$

$$\tau_i^{-1} = \tau_{i\ \text{strat}}^{-1} + \tau_{i\ \text{trop}}^{-1} + \tau_{i\ \text{dep}}^{-1} = \Sigma_j\ \tau_{ij}^{-1}$$

j: tropospheric reactions
stratospheric reactions
deposition

For CFCs:

$$\tau_{\text{trop}} \approx \infty$$

$$\sigma_{> 260\ \text{nm}} < 10^{-21}\ \text{cm}^2 \quad \rightarrow \tau_{j\ \text{strat}} \approx \infty$$

$$\tau_{\text{CFC}} \approx \tau_{\text{strat}}$$

For most organic substances, however:

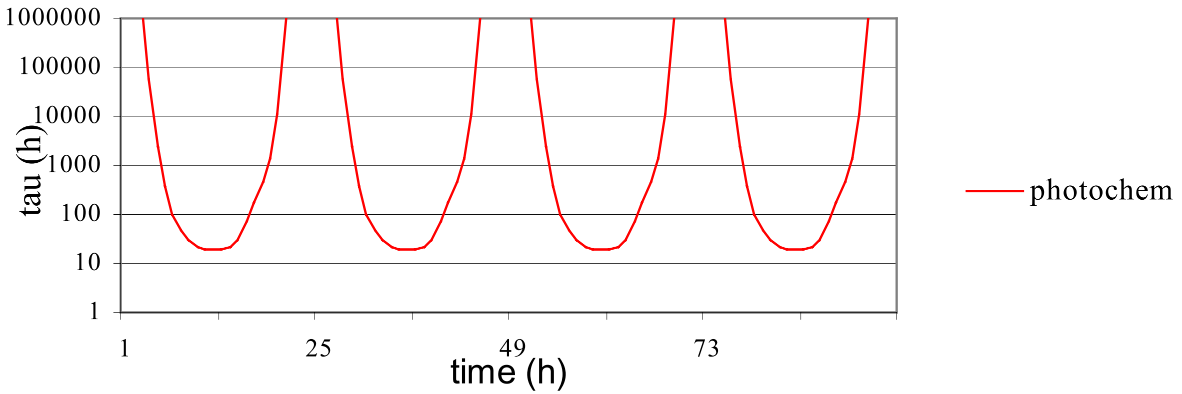
$$\tau_{i\ \text{trop}} \approx \tau_{i\ \text{OH}}$$

$$\tau_i \approx \tau_{i\ \text{trop}}$$

For most organic substances:

$$-dc_i/dt = k_{OH}^{(2)}\, c_{OH}\, c_i\ ;\ \tau_{OH} = (k_{OH}^{(2)}\, c_{OH})^{-1}$$

$$\tau = (\Sigma\, k\, c)^{-1}$$



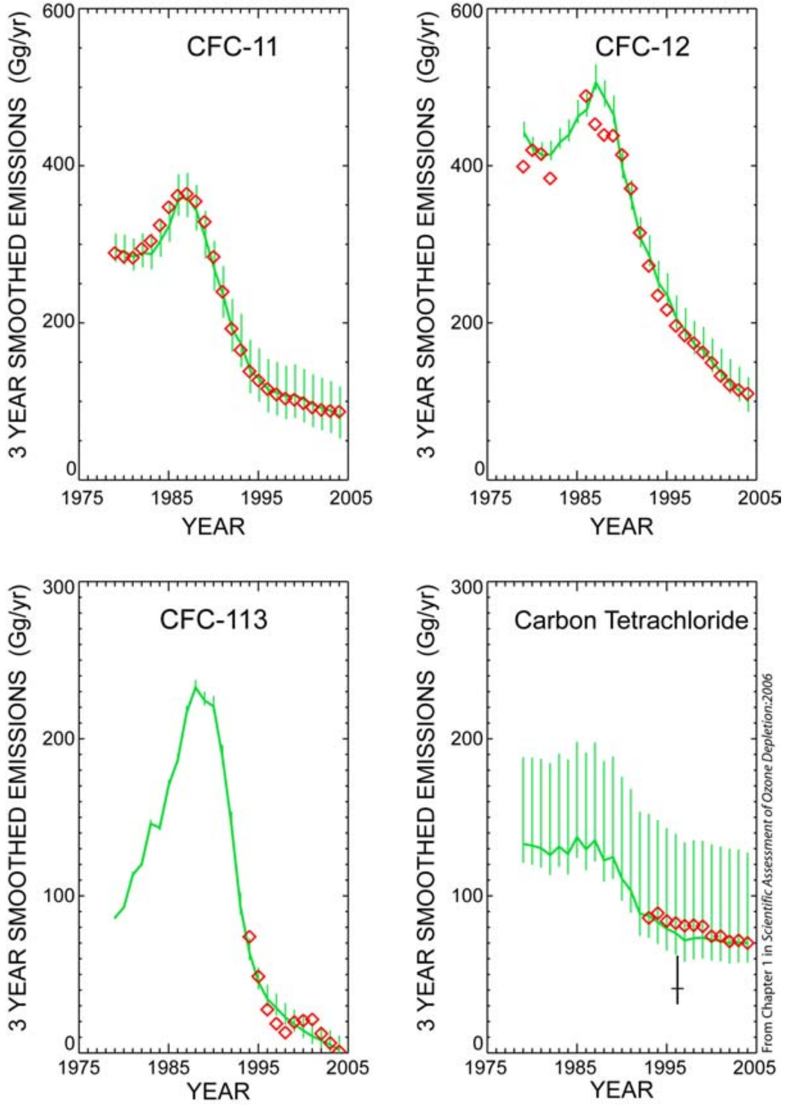
$$\tau_{photochem} = (\overline{k_{OH} * c_{OH}})^{-1}$$
$$\neq (k_{OH} * \overline{c_{OH}})^{-1}$$

diurnal means: differ by orders of magnitude according to averaging time

annual mean 44°N: 740 h (2 weeks resolution) vs. 310 h

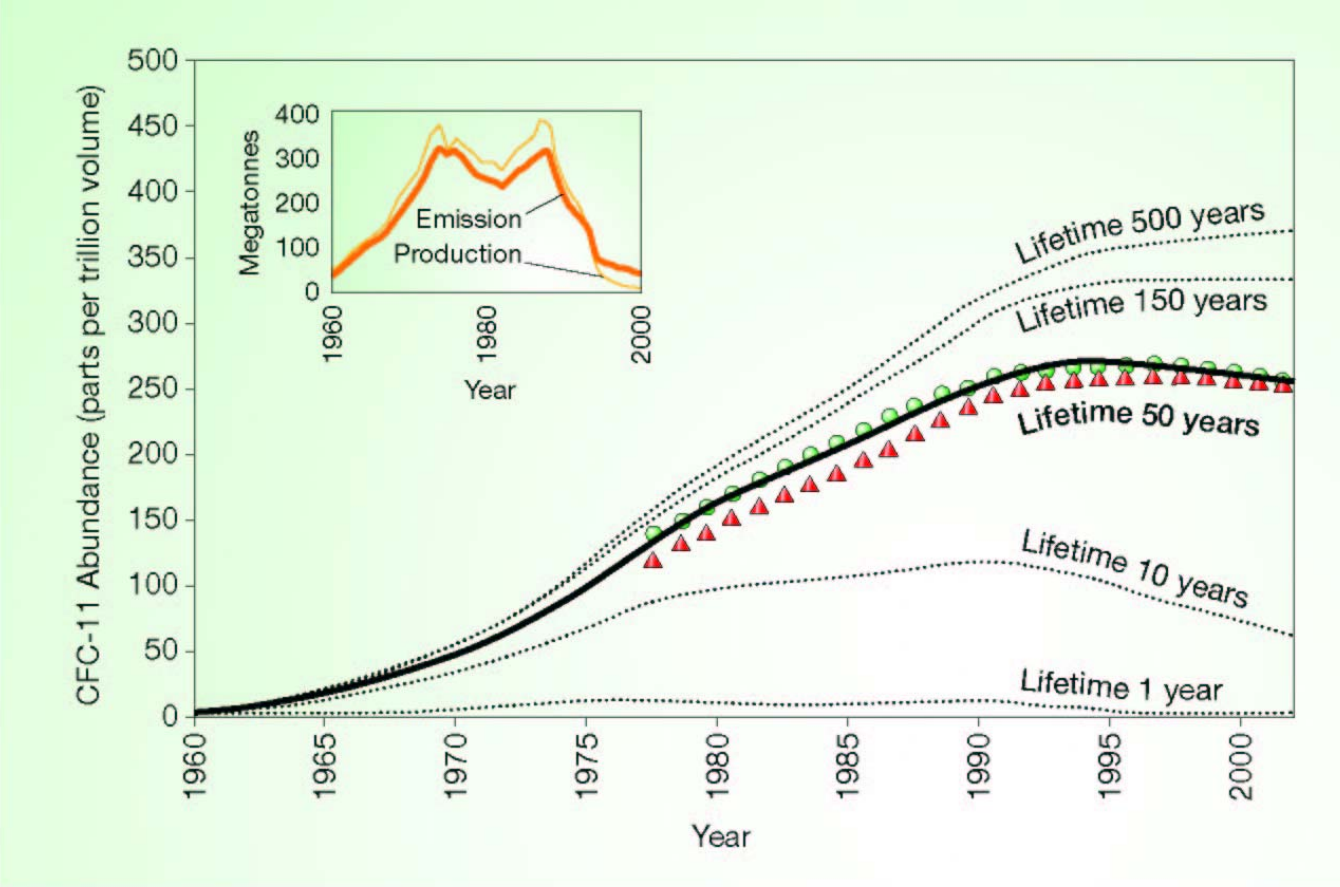
annual mean 12°N: 173 h vs. 168 h

CFC trends



Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007

CFC lifetimes - uncertainties



CFC-11 in the atmosphere. The curves represent predicted abundance of CFC-11 for different atmospheric lifetimes. Actual data for Northern (circles) and Southern (triangles) Hemispheres show that CFC-11's atmospheric lifetime is about 50 years.

Solomon, 2004

CFC trends

Stabilization, reduction: $db/dt = F_e - b/\tau \leq 0!$

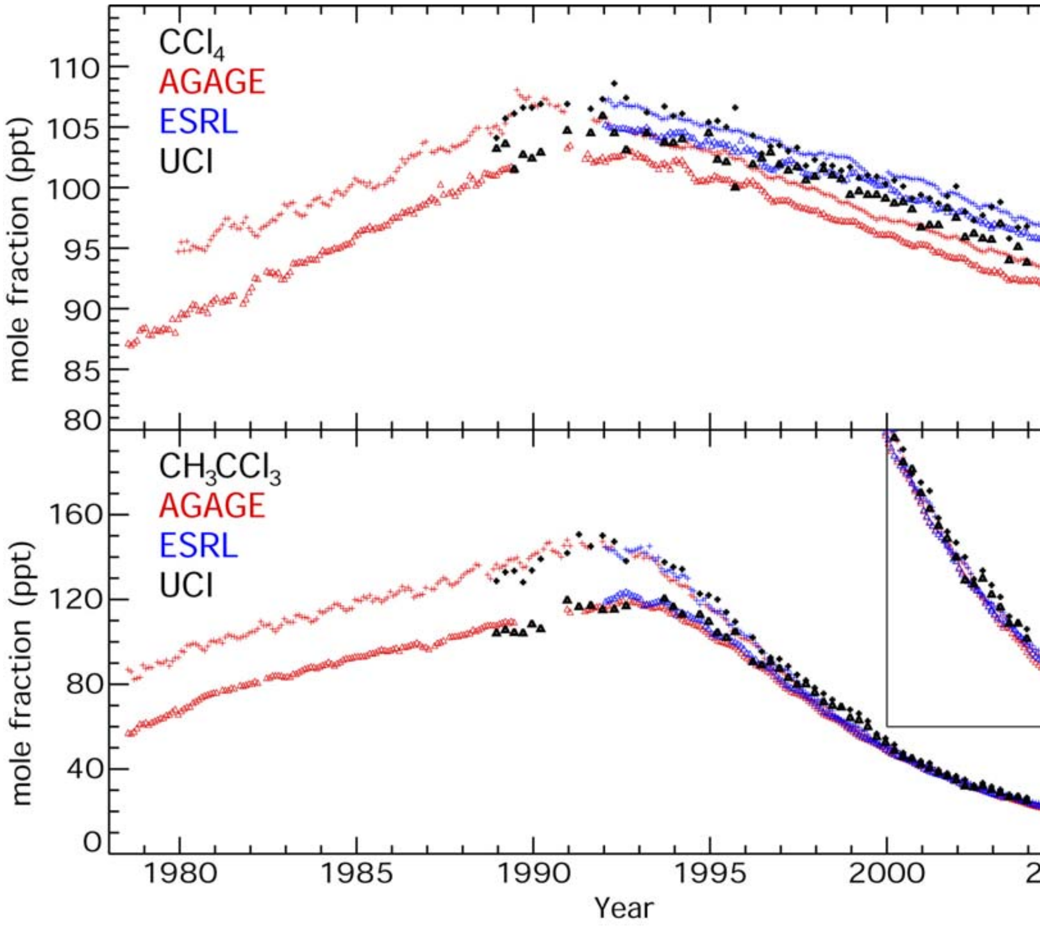
$db/dt/b = F_e/b - 1/\tau$

$F_e = db/dt + b/\tau$

	τ	db/dt/b (2003-04)
CCl_4	26 a	-(1.1±0.1) %/a
CH_3CCl_3	5 a	-(18 ± 1) %/a

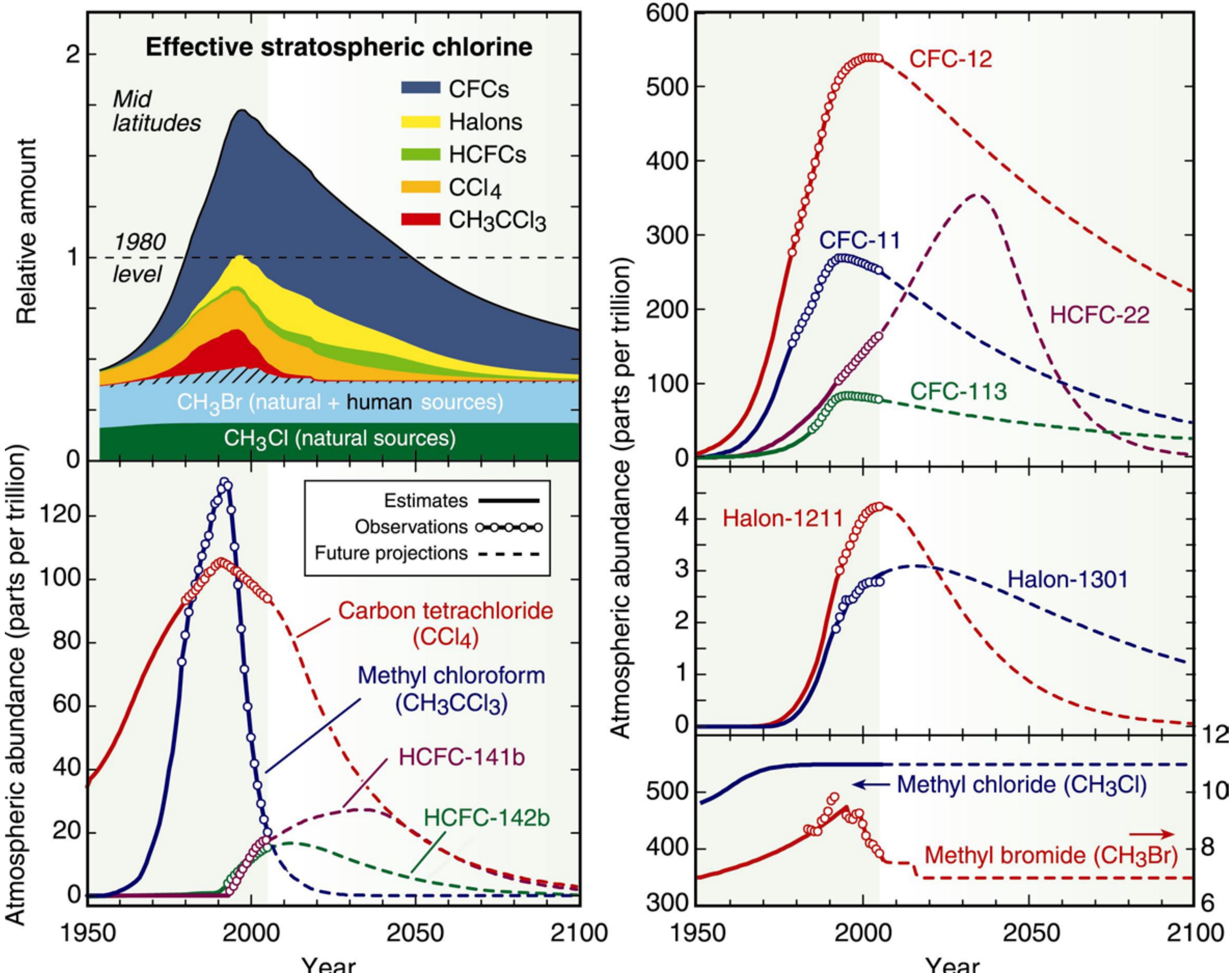
Even with $F_e = 0$ the CCl_4 levels could not have been reduced < -4 %/a

Reported lifetimes assume uniform mixing in the global atmosphere – the more uncertain the shorter τ is!



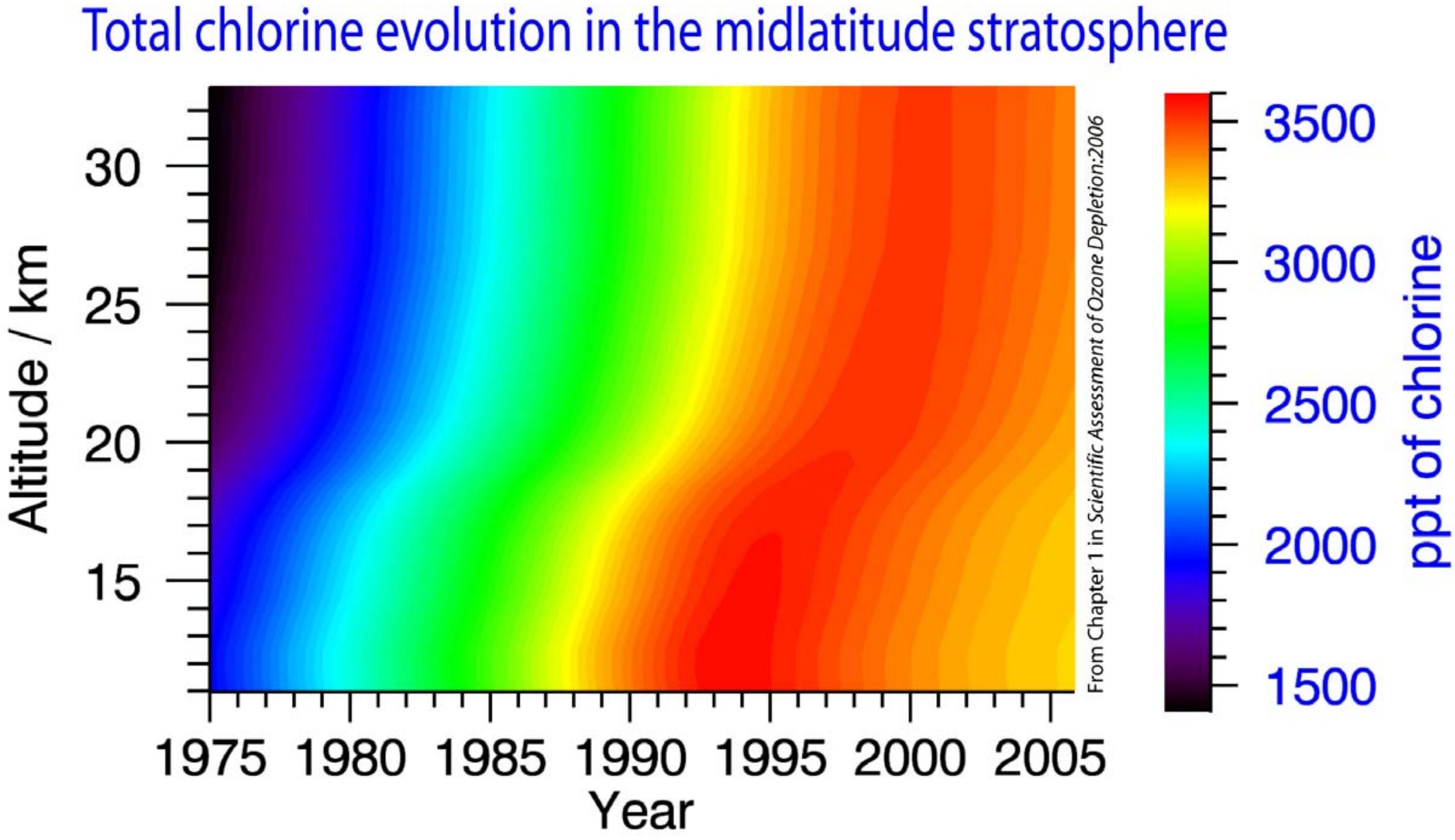
Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007

Stratospheric Cl trends



Past and Expected Future Abundances of Atmospheric Halogen Source Gases

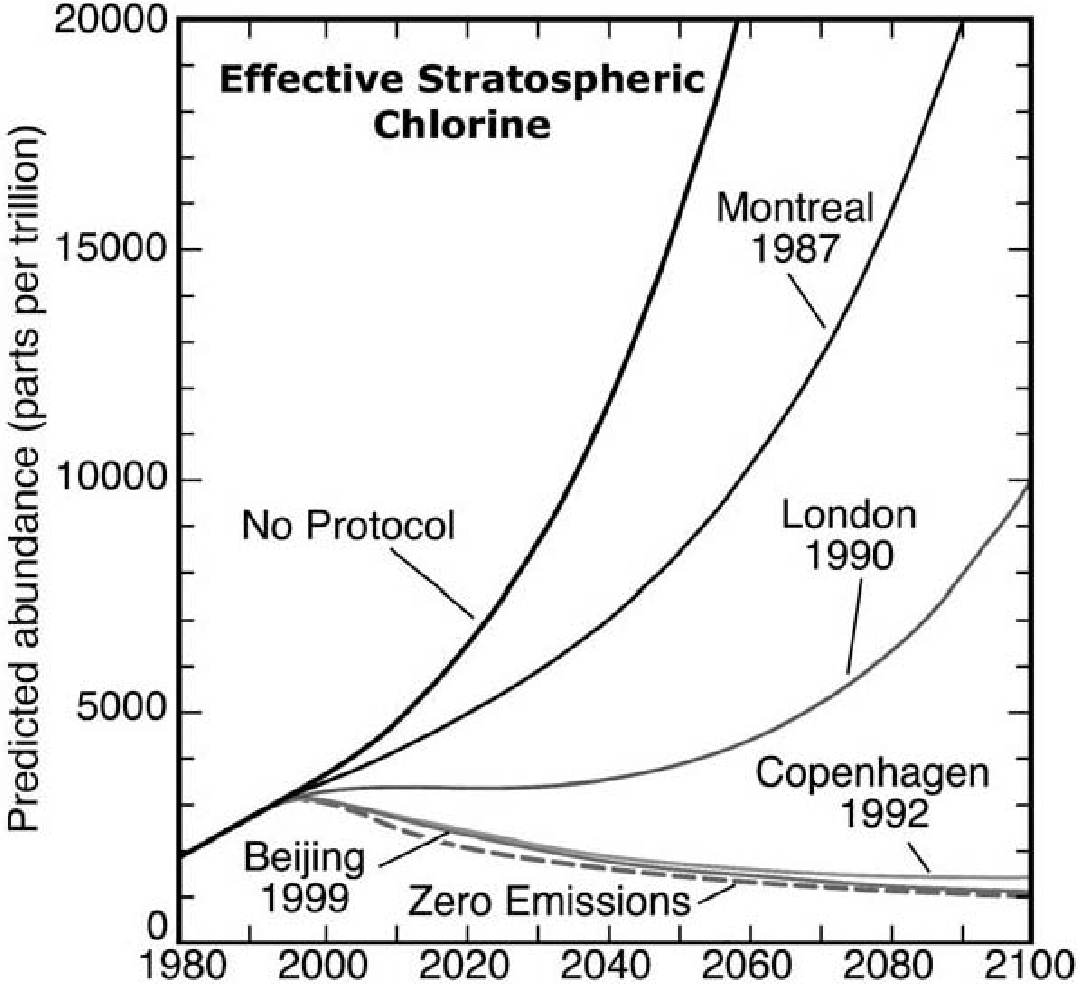
Cl trends

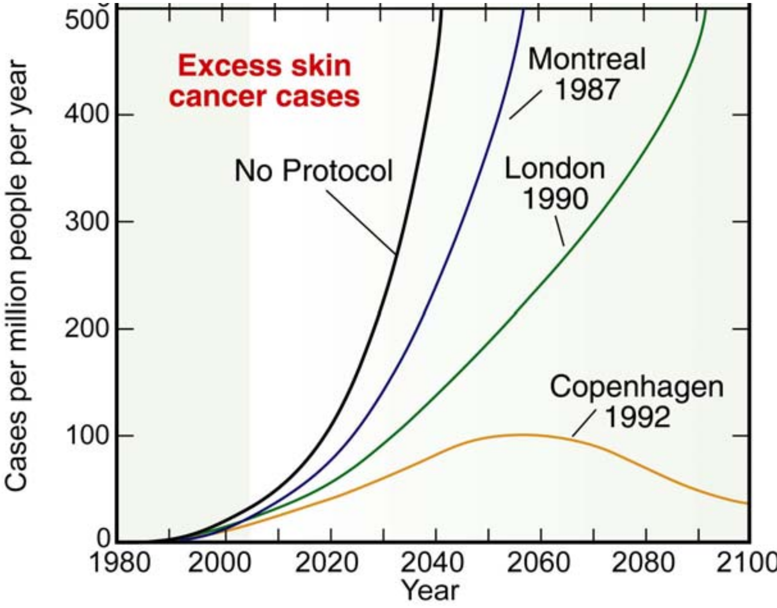


Src: WMO: Scientific Assessment of Ozone Depletion 2006, Geneva 2007

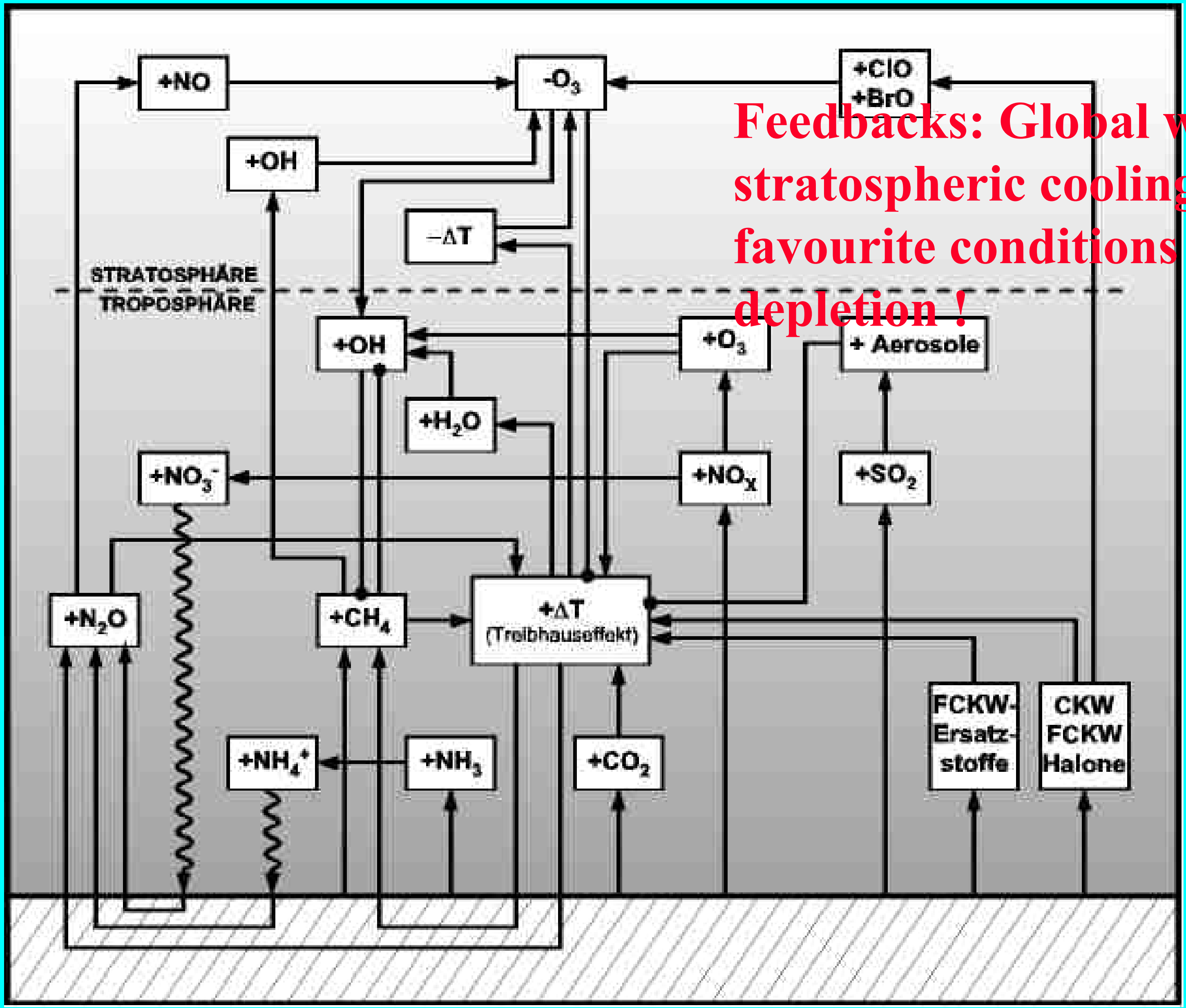
Cl trends

Protocols of the Vienna Convention (1985)





Atmospheric chemistry ⟷ Climate



Feedbacks: Global warming causes stratospheric cooling, hence, more favourite conditions for ozone depletion !

(Lammel, 1997)