

Recognised (early 60's) that the exptl concn of O₃ was less than Chapman mechanism predicted

∴ other sinks for O₃ loss.

The other sinks are chain reactions involving radical species X, where X can be any of,

NO, Cl, Br, OH, H

← these are catalysts, reformed in each cycle.

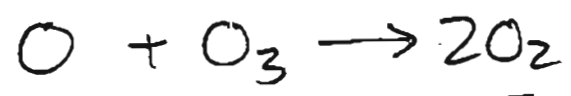
Small concns in atom



	X =	Cl	NO	OH
X + O ₃ → XO + O ₂	2.1	13.1	7.8	
XO + O → X + O ₂	1.1	≈ 0	≈ 0	

Activation energies E_a, kJ mol⁻¹ for the catalysed rxs.

Net rx. is



(previous Rx. 4)

Compare uncatalysed

but rates may be different (rx.) E_a = 18.4 kJ mol⁻¹

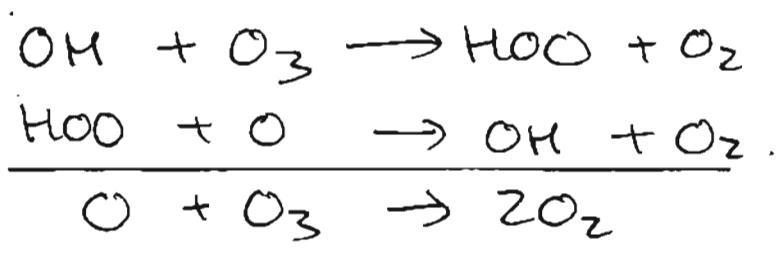
So,

- absorption of solar radu < 300 nm in stratosphere prevents this damaging radiation from reaching surface, and makes stratosphere warmer than upper troposphere
- UV-B (~300-~~315~~325 nm) can leak through to dissociate tropospheric O₃

More detail on the catalysed destruction of O_3 (46)
 The HO_x , NO_x and ClO_x cycles

\downarrow $H^\bullet, OH^\bullet, HOO^\bullet$ \downarrow NO^\bullet, NO_2^\bullet \downarrow Cl^\bullet, ClO^\bullet all involving free radicals

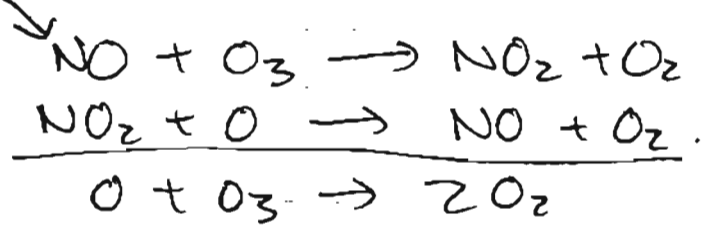
From $O^* + H_2O$ or $H_2O + h\nu$ in stratosphere



HO_x

From $N_2O + O^*$ (excited O) or $N + O_2$

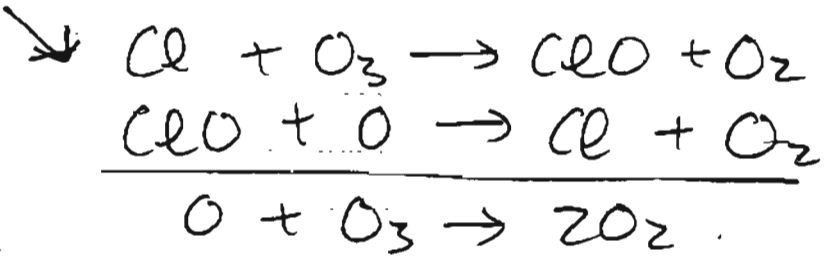
or supersonic aircraft or volcanoes



NO_x

From several Cl molecs. inc. CFC's as well as natural sources

e.g. CH_3Cl



ClO_x

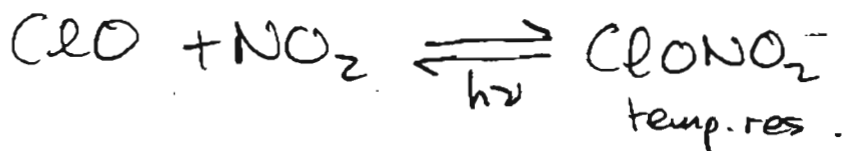
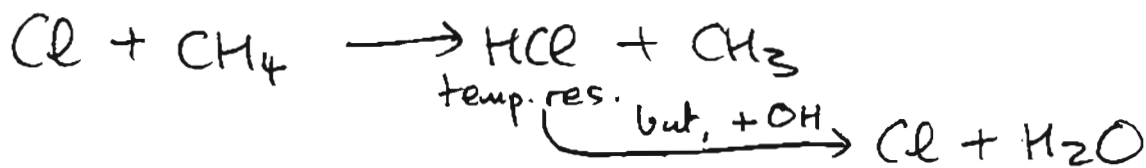
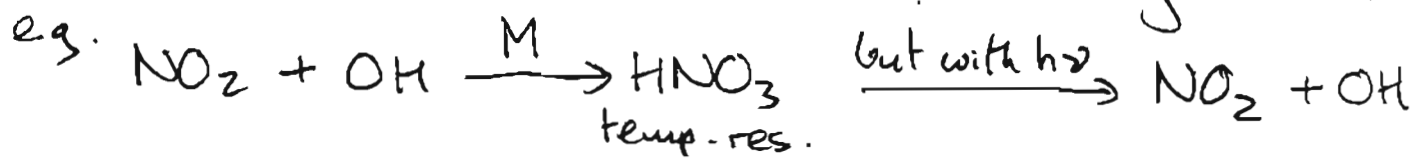
Same for Br^\bullet (indeed, the C-Br bond is weaker)

Atmospheric concns. of chlorine-containing species seems to have maxed out at ~ 4 ppbv (1998) and slight decreases are evident in some cases (see Montreal Protocol (below))
 Historical levels were $\sim 1-2$ ppbv.

Additional rxs in stratospheric chemistry (47)

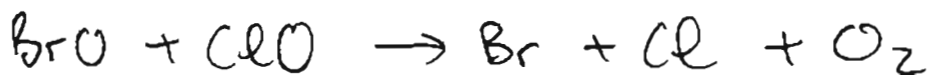
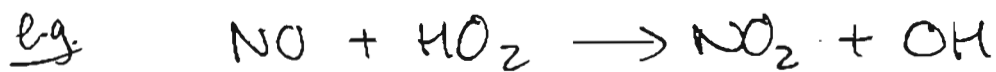
1. Temporary reservoirs
2. Interactions between catalytic cycles
3. Null (do-nothing cycles)
4. Initiation/termination rxs.

1. Temporary reservoirs ... species later released
Catalytically active species, e.g. NO_x , ClO_x , can form less active species ... but they can be regenerated

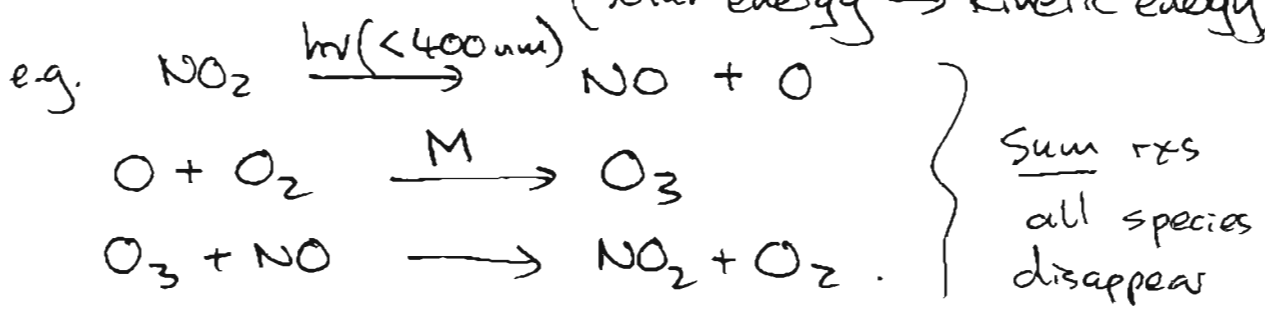


2. Interaction between cycles

ie. X from one cycle reacting with X from another



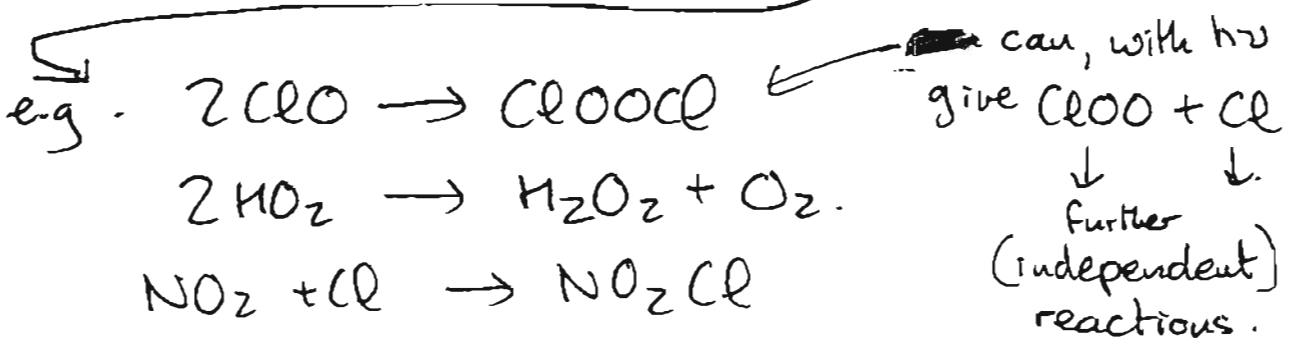
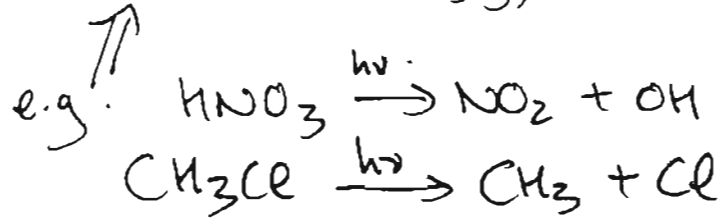
3. Null cycles ... no net change
(solar energy → kinetic energy)



4. Initiation and termination rxs.

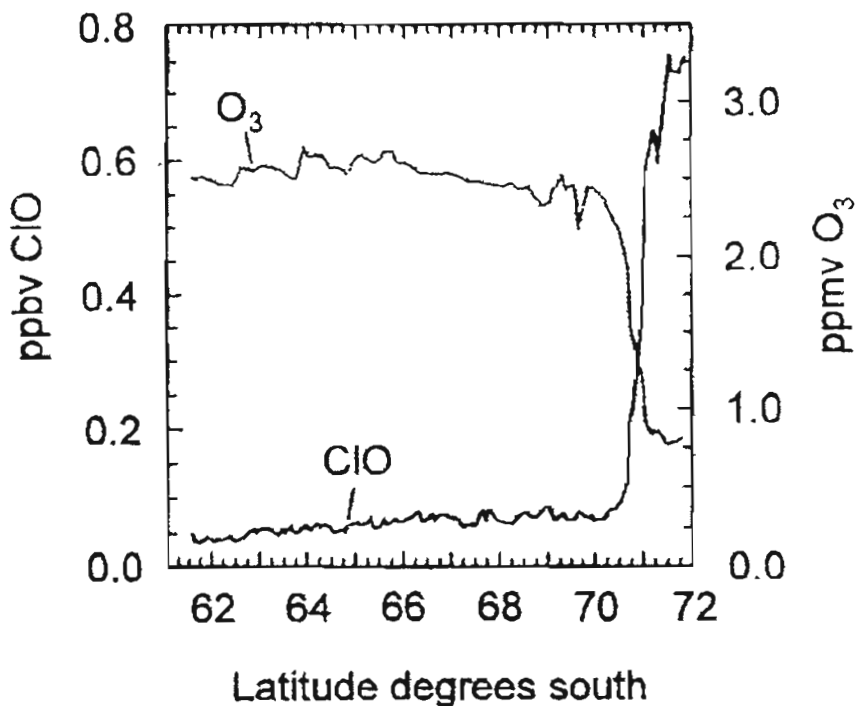
↓
generation of free rads from non-radical precursors (most depend on solar energy).

↓
conversion of free rads to non-rads.



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Polar Ozone "Holes" (the precipitating event for the Montreal Protocol)



Environ. Sci. Technol., 1991; data of September 21, 1987

- “Polar Sunrise” experiments have shown that this effect is seen (but not every year) in the Arctic also.
- The curious effect of the break-up of the Ross Antarctic ice shelf (January-March 2002): D.W.J. Thompson and S. Solomon, *Science*, 2002, 296, 895 attributed to stratospheric **cooling** from the polar ozone hole having two effects: tropospheric warming; changing polar vortex —> W Antarctic becomes warmer, E Antarctic cooler.

"Polar ozone hole"

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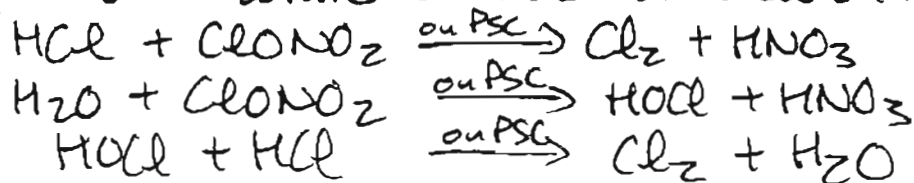
First detected -- early 80's in Antarctica -- occurs because of unusual climate factors and the "awakening" of temporary Cl reservoirs at Polar Sunrise.

1. Air circulation in the Antarctic is essentially circumpolar, i.e. get a giant polar vortex. Area within vortex like a big chemical reactor where polar stratospheric clouds (PSC) form during winter.

Two types: Type I PSC (193K), particles of $\text{HNO}_3/\text{H}_2\text{O}$
Type II PSC (187K), pure water/ice ^{form}

Also, within vortex are all kinds of Cl and N-containing species, especially HCl and ClONO_2

During the dark winter various rxns. occur on the particles:



2. Spring -- sun appears (Oct.) -- solar radiation does its thing.
 $\text{Cl}_2 \rightarrow 2\text{Cl}$, $\text{HOCl} \rightarrow \text{Cl} + \text{OH}$

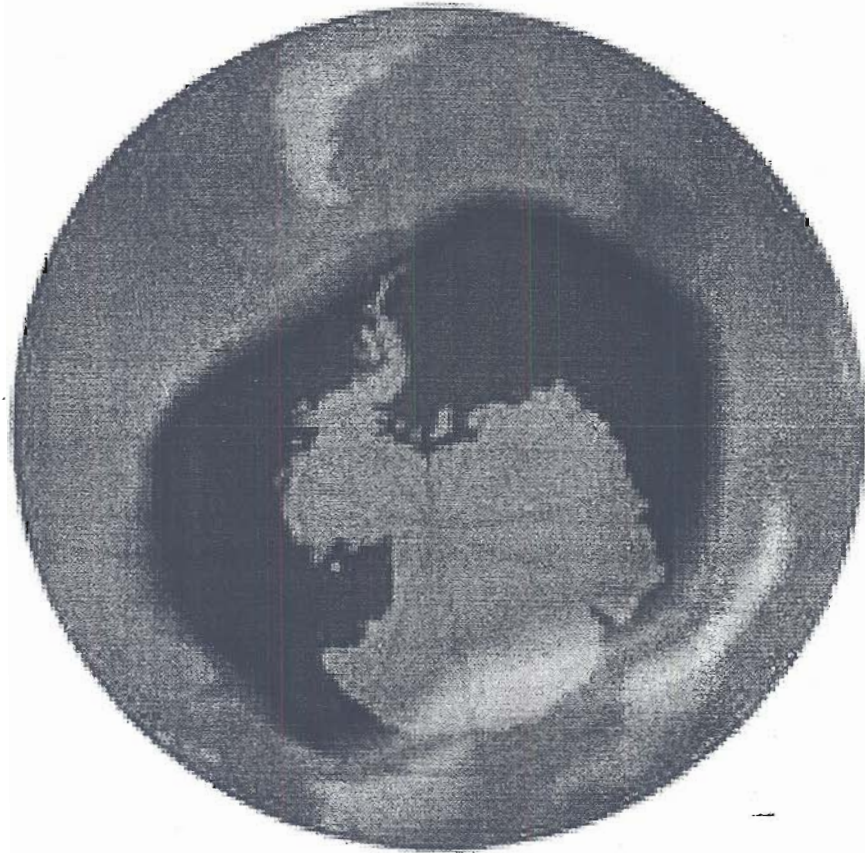
and the rest you know. Destruction of O_3 happens so fast that within days, O_3 levels are ~50% of winter levels.

Increasing sunlight makes more O_3 , the PSCs dissipate and the Cl-active species are trapped and the O_3 levels recover.

Similar effects in the Arctic (but not every year).

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S. America



Antarctica, spring 2006 (October) ... a big "hole"
"Hole" is a misnomer ... it's a reduction in
ozone concentrations (which can be as much as
70% destruction).

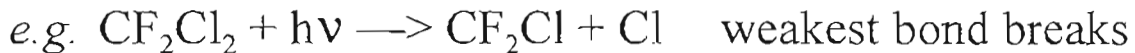
trade name Freon (Dupont)

~~14/28~~
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The CFC (chlorofluorocarbon) story

- CFCs do not absorb radiation < 250 nm (not present in troposphere) ^{because}
- Chemically unreactive: no tropospheric sinks
- Slow migration to stratosphere, $t_{1/2} \sim 5$ yr; globally well mixed
- In stratosphere, **slow** reaction with $t_{1/2}$ many decades:

$\rightarrow < 250$ nm



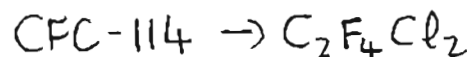
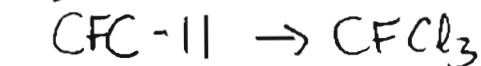
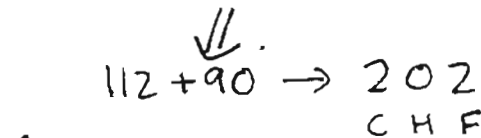
- Hence CFCs are a source of stratospheric **chlorine atoms** which are catalysts for destroying stratospheric ozone: "X" in the chain sequence on the previous pages
- Photolysis **initiates** the chain reactions; up to 10^4 cycles per chlorine atom \leftarrow wow !!
- CFCs **increase** an existing "sink strength", thereby lowering the steady state concentration of ozone. [originally, it was thought that this was a new sink]

CFC Numbering System e.g. CFC-112

- Add 90 to the number; the three digits represent the numbers of C, H, F atoms; make up the rest of the "unused bonds" with Cl. Example: CFC-112 is $\text{C}_2\text{F}_2\text{Cl}_4$

What were/are CFCs used for?

- Refrigerants (non-toxic, non-flammable)
- Propellants for foams
- Propellants for aerosols



replaced SO_2 and NH_3

Same numbering system for HCFC's and HFC's

The Road to the Montreal Protocol

- CFCs first discovered in the atmosphere 1974
- Many were increasing at 6%/year in the late 1970s
- Travel to the stratosphere takes 5-10 years
- —> N. American and European ban on aerosol use 1978
- —> Montreal Protocol 1987 with a ban on “hard” CFCs + CH_3CCl_3 + CCl_4 to take place January 1, 1996
 ✓ 27 countries signed up
- 5 revisions (at least), 1990, 1992, 1995, 1997, 1999
- 10 year extension for developing countries (originally by 2010)
- Halons (e.g., CF_3Br) phased out January 1, 1994
 Brominated CFC analogues

CFC-11 (CFCl_3)
 CFC-12 (CF_2Cl_2)

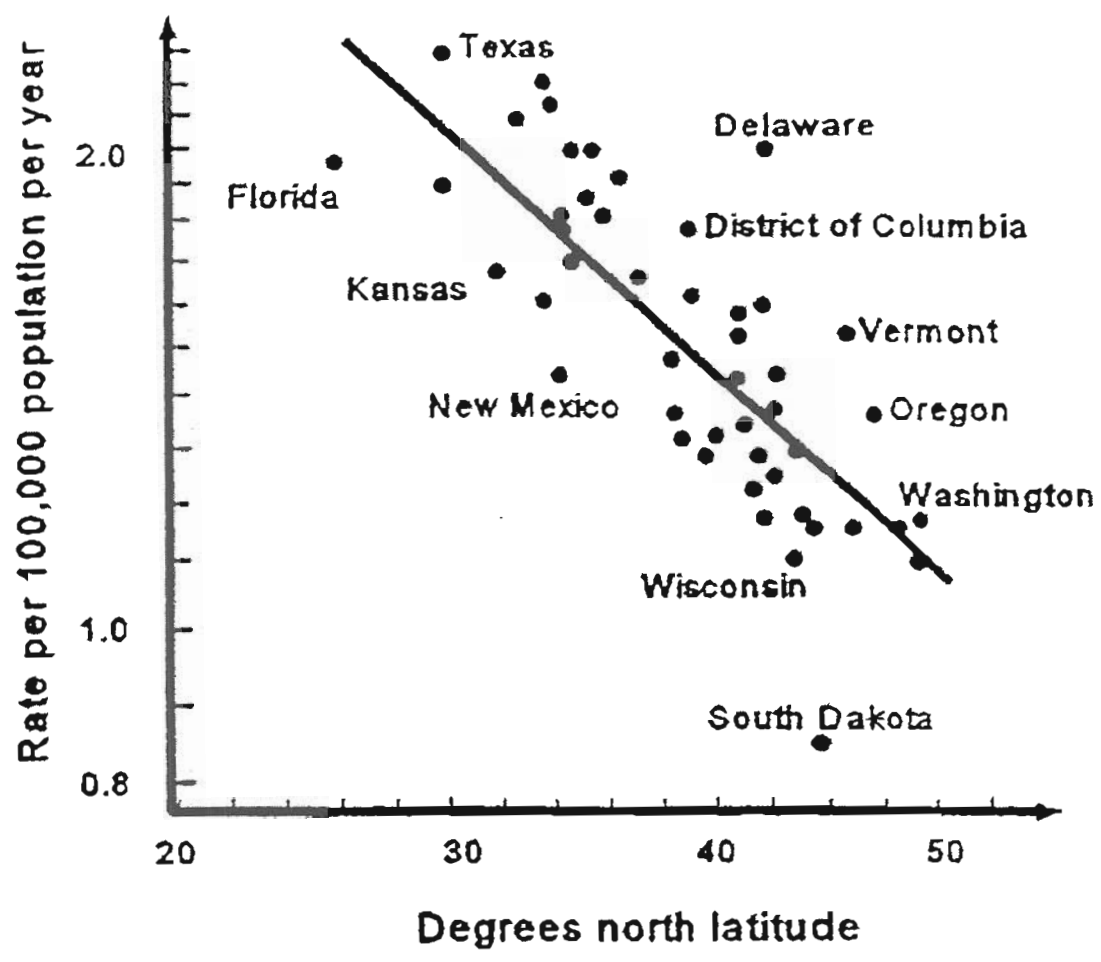
The Montreal Protocol is historic because it is the first instance of international action on the basis of a future anticipated environmental threat

Mario Molina and Sherwood Rowland received the 1995 Nobel Prize in Chemistry for their seminal work on stratospheric ozone depletion: *Nature*, 1974, 249, 810

By ~2003, 191 nations have signed up.
 ~2008, 193 nations have signed up
 ✓
 (of 196 UN member states).

Why have CFCs been banned?

- CFC lifetimes 100+ years: photolysis is inefficient
- Loss of stratospheric ozone allows more UV-B radiation to reach the earth's surface
- Relationship between UV radiation and skin cancer (melanoma deaths among white US males)

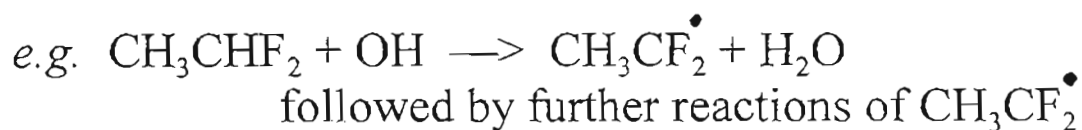


- High UV at noon, in summer, high altitude, in the tropics

UV-B effects upon plants and other animal species
(including plankton)

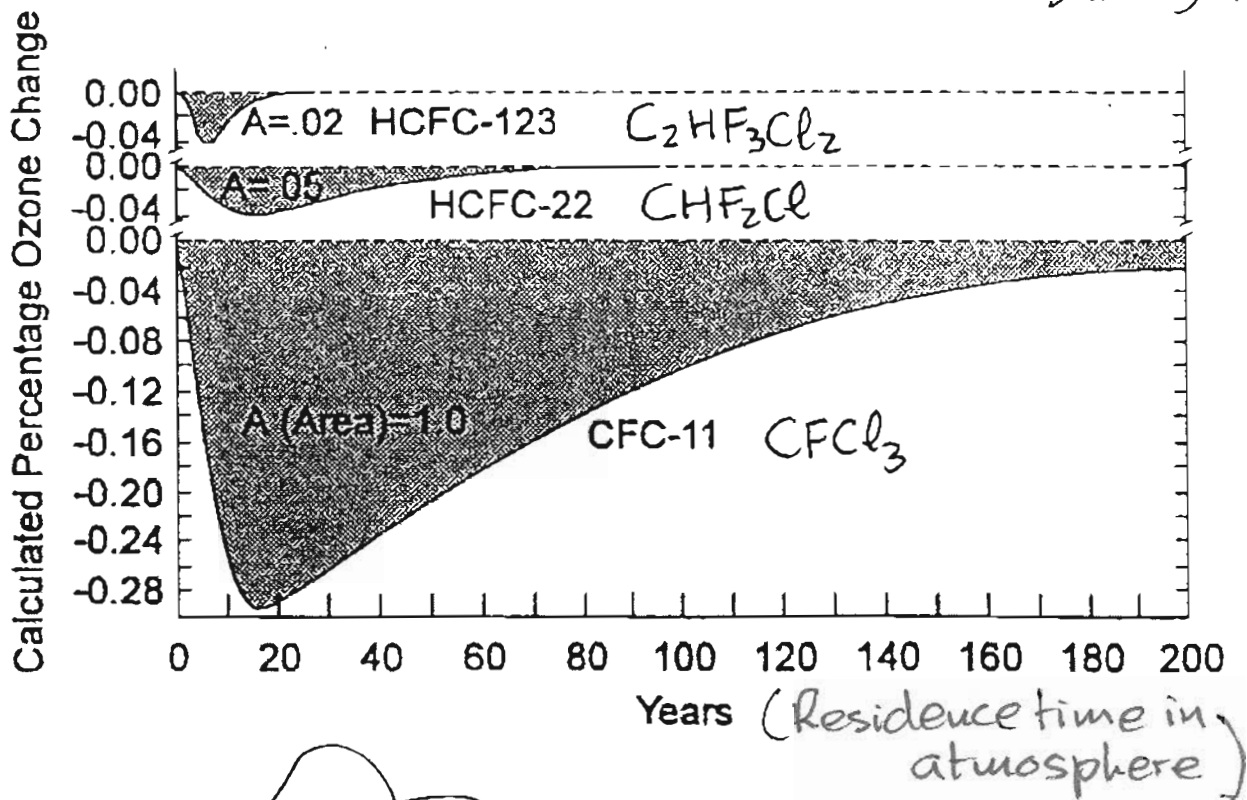
CFC Replacement Compounds

- HCFCs (hydrochlorofluorocarbons) and HFCs (hydrofluorocarbons): desired properties are **chemical stability**, **low toxicity**, appropriate **boiling point**
- CFC replacements must undergo **tropospheric** oxidation
(i.e. shouldn't make it to stratosphere)
- Since CFCs deplete stratospheric ozone replacements should **avoid or minimize Cl atoms**
- Because **hydrocarbons** oxidize in the troposphere replacement compounds should **include H atoms**. As will be discussed in Chapter 3, HCFCs and HFCs can react with tropospheric OH radicals.



- CFCs and their replacements are also greenhouse gases: polar C-F and C-Cl bonds. Fully fluorinated compounds must be avoided (no hydrogen atoms to react with OH) and high global warming potential

Ozone Depleting Potential (ODP) (See Table 2.2 in Bunce)



Relative areas are ODPs based on equal masses. CFC-11 is $CFCl_3$, HCFC-22 is CHF_2Cl , HCFC-123 is $C_2HF_3Cl_2$

defined as the ratio of the long-term impact on ozone from a specific chemical to the impact from an equivalent mass of CFC-11

- takes into account the reactivity, atmospheric lifetime and molar mass (inc. the no. of Cl atoms in the species) ... hence CCl_4 has an ODP of 1.1-1.2

Most CFC's have ODP's from 0.1 → 1.0
 HCFC's → " → 0.01 → 0.1 (~10x lower)
 HFC's → " → 0 → 0

CFCs, HFCs, HCFCs: ODP vs Global Warming Potential

<i>Compound</i>		<i>ODP (CFCl₃ = 1)</i>	<i>GWP (CO₂ = 1)</i>
HCFC-22	CHF ₂ Cl	0.05	4300
HCFC-123	CF ₃ CHCl ₂	0.02	300
HCFC-124	CF ₃ CHFCI	0.02	1500
HFC-125	CF ₃ CHF ₂	0.0	5300
HFC-134a	CF ₃ CH ₂ F	0.0	3300
HCFC-141b	CH ₃ CFCl ₂	0.1	4300
HCFC-142b	CH ₃ CF ₂ Cl	0.06	1800
HFC-152a	CH ₃ CHF ₂	0.0	410

Note: HFCs have ODP = zero; GWPs taken from the IPCC Report and <http://216.239.33.100/search?q=cache:4ApslDfh9poC:tis.eh.doe.gov/oepa/rules/60/60fr52357.pdf+global+warming+potential+HCFC&hl=en> (20 year horizon). **They are much larger than the values in the text**

Response of industry to CFC phase-out

- aerosol propellants: CO₂; CH₃OCH₃-H₂O; C₄H₁₀-CH₂Cl₂
- foam blowing agents: [HCFC-22]; HCFC-141b; cyclopentane
- refrigerants: HFC-134a; hydrocarbons (in Europe)
- Note concern about CF₃CO₂H as a highly stable breakdown product of several HFCs, including HFC-134a

Trends from atmospheric measurements.

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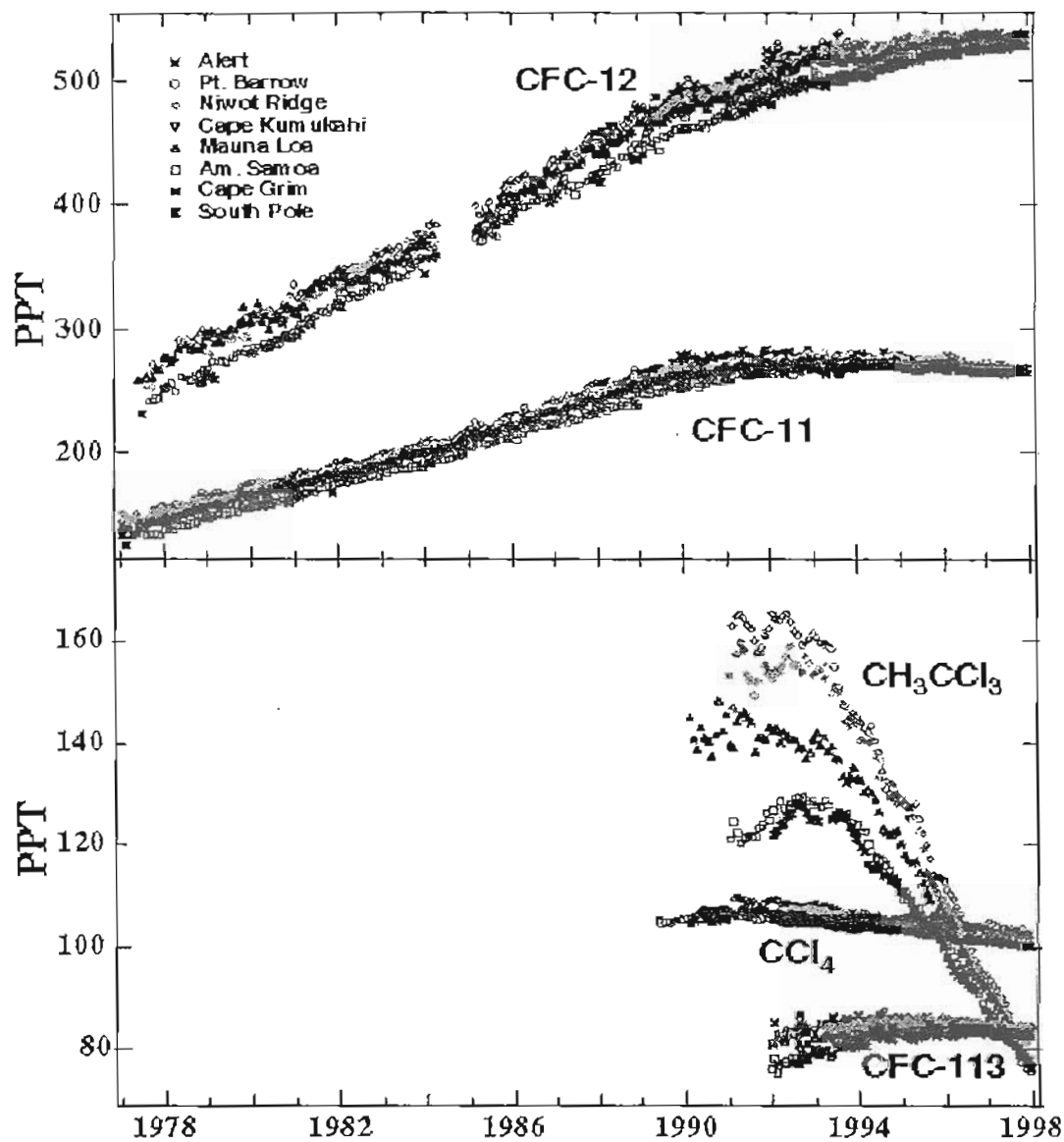


FIG. 18. Trends of various controlled ozone-depleting chlorine species. [Analysis provided by the Climate Monitoring and Diagnostics Laboratory (CMDL).]

Figure from

http://www.cpc.ncep.noaa.gov/products/assessments/assess_98/fig18.gif



Scientific Assessment of Ozone depletion 2006

LONG-LIVED COMPOUNDS <http://esrl.noaa.gov/csd/assessments/2006>

Chapt. 1.

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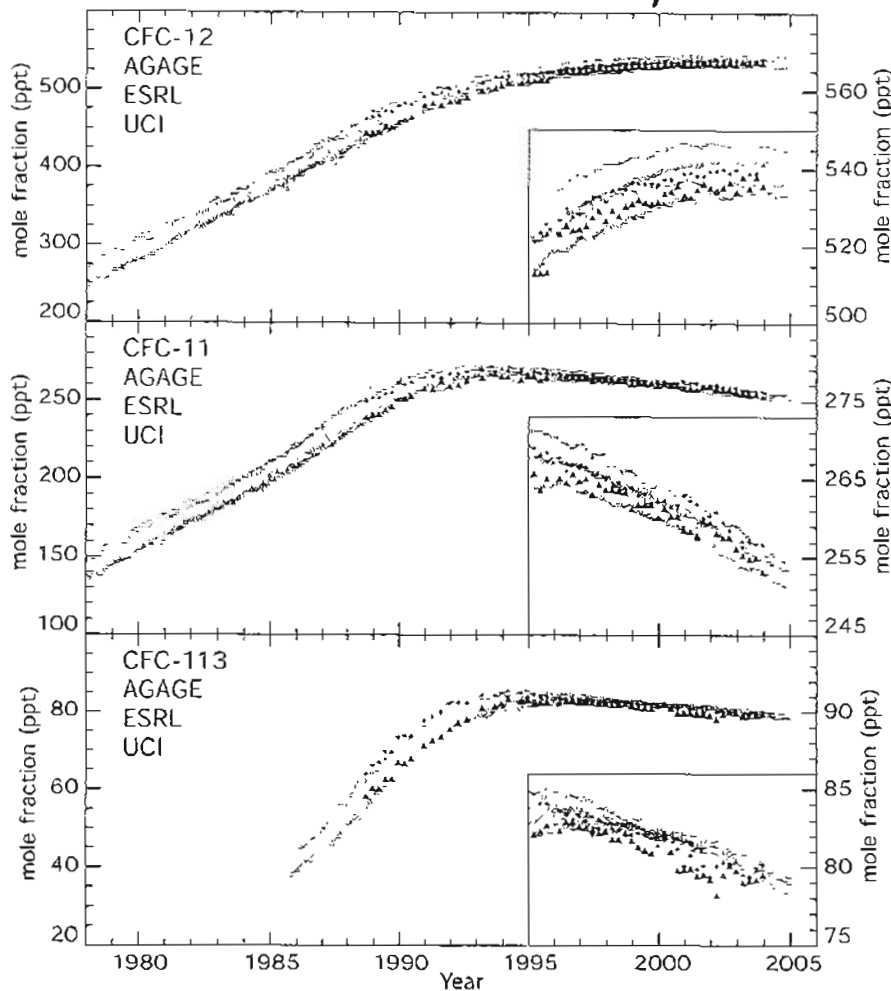


Figure 1-1. Hemispheric monthly means of the major chlorofluorocarbons CFC-12, CFC-11, and CFC-113 (crosses for Northern Hemisphere and triangles for Southern Hemisphere). Measurements from the AGAGE network (Prinn et al., 2000 updated), the NOAA/ESRL network (Montzka et al., 1999 updated; Thompson et al., 2004), and UCI (D.R. Blake et al., 1996; N.J. Blake et al., 2001) are shown. To increase visibility, recent measurements are depicted on a larger scale in the inserts (the scales are on the right-hand sides of the panels).

cate that Northern Hemispheric mole fractions are now decreasing. These observations are consistent with the analyses of Rinsland et al. (2005) using ATMOS and ACE satellite data. The measured annual column change above Jungfraujoch in 2003-2004 is -0.11×10^{14} molec cm^{-2} ($-0.16\%/yr$) (Zander et al., 2005) compared with 0.50×10^{14} molec cm^{-2} ($+0.71\%/yr$) in 1998 (*WMO 2002*) and 0.27×10^{14} molec cm^{-2} ($+0.39\%/yr$) in 1999-2000. Trends from column measurements in $\%/yr$ should be almost directly comparable with trends for similar periods derived from the sampling networks, because of the long lifetimes of the species being discussed. Averaged over

Kiruna (68°N) and Izaña (28°N), the column trend from 2000 to 2005 is $-0.09 \pm 0.10\%/yr$ (update from Kopp et al., 2003, and Schneider et al., 2005). Since the CFC-12 lifetime is approximately 100 years, the measured rate of change indicates that there are still significant emissions of CFC-12. Differences between measured Northern Hemisphere and Southern Hemisphere mole fractions have been decreasing since approximately the end of the 1980s (Figure 1-1). The hemispheric difference in 2004 was still approximately 3 ppt (0.6%), indicating that the remaining emissions are still occurring predominantly in the Northern Hemisphere.

Chemistry in the Troposphere: Photochemical Smog (Chapt. 3)

Overview:

- The atmosphere is an oxidizing system
- Tendency of organic components (natural and anthropogenic) to be oxidized to $\text{CO}_2 + \text{H}_2\text{O}$. These are called VOCs (volatile organic compounds)
e.g. $2\text{C}_2\text{H}_6 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}$
- Formation of toxic intermediates en route to $\text{CO}_2 + \text{H}_2\text{O}$
- Formation of **ozone** as a **byproduct** of VOC oxidation
- Central role of the hydroxyl radical, OH^\cdot , in initiating oxidation
- Interaction between VOC oxidation and NO_x chemistry
- Conditions for photochemical smog formation
 - strong sunlight
 - temperature $> \sim 20^\circ\text{C}$
 - polluted air, *i.e.*, greater than background levels of **both** VOCs and NO_x (Note Table 3.3, text, p. 81)