STRATOSPHERIC CHEMISTRY

1. **Stratospheric ozone: distribution**
2. **Chapman mechanism**
3. **Catalytic loss cycles**
   - **Hydrogen oxide radicals (HO_x)**
   - **Nitrogen oxide radicals (NO_x)**
   - **Chlorine oxide and bromine oxide radicals (ClO_x, BrO_x)**
4. **Polar ozone loss**
5. **Role of aerosol chemistry in the stratosphere**

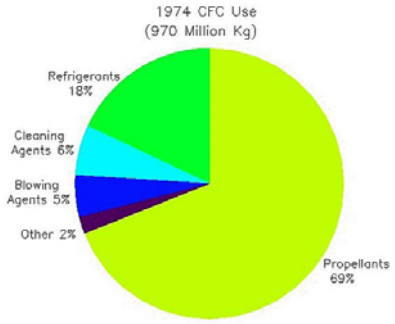
Anthropogenic perturbations to stratospheric ozone

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$
$$\text{Net: } O + O_3 \rightarrow 2O_2$$

Catalysts:

X = OH ← increasing CH_4 from troposphere
X = NO ← increasing N_2O from troposphere, supersonic fleet
X = Cl, Br ← Chlorofluorocarbons (CFCs) - Freons

“wonder gas” CFCs were invented in 1928



Use of CFCs increases rapidly

Chlorofluorocarbons and Halons

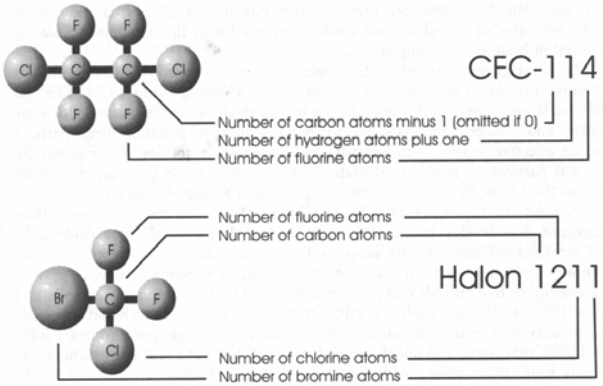
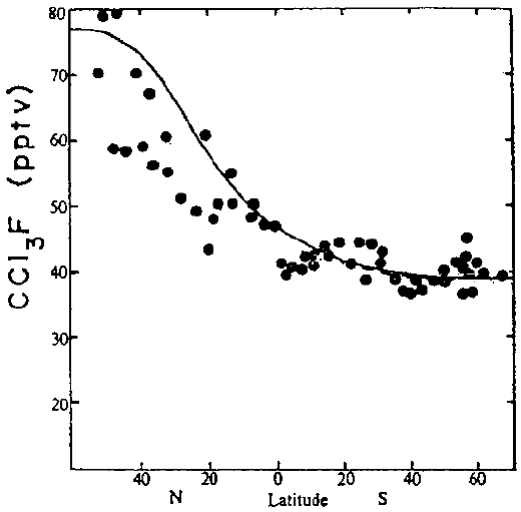


Figure 2.4 Names of CFCs and Halons. CFCs and halons are identified by numbering systems in which each digit is related to the number of one type of atom in the molecule. Source: UNEP Division of Technology, Industry, and Economics.

CCl_3F measurements in 1971: cruise from England to Antactica



CFC-11

J. E. Lovelock, R. J. Maggs and R. J. Wade, Halogenated hydrocarbons in and over the Atlantic, Nature, 241, 194-196 (1973)

CATALYTIC CYCLES FOR OZONE LOSS: Chlorine (ClO_x = Cl + ClO) radicals

- Initiation:

  $CCl_3F + h\nu \rightarrow CCl_2F + Cl$ wavelengths<230 nm

  $CCl_2F + h\nu \rightarrow CFCl + Cl$

- Propagation:

  $Cl + O_3 \rightarrow ClO + O_2$

  $ClO + O \rightarrow Cl + O_2$

  Net: $O_3 + O \rightarrow 2O_2$

  O_3 loss rate: $\frac{d[O_x]}{dt} = -2k[ClO][O]$

- Termination:

  $Cl + CH_4 \rightarrow HCl + CH_3$

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

Recycling:

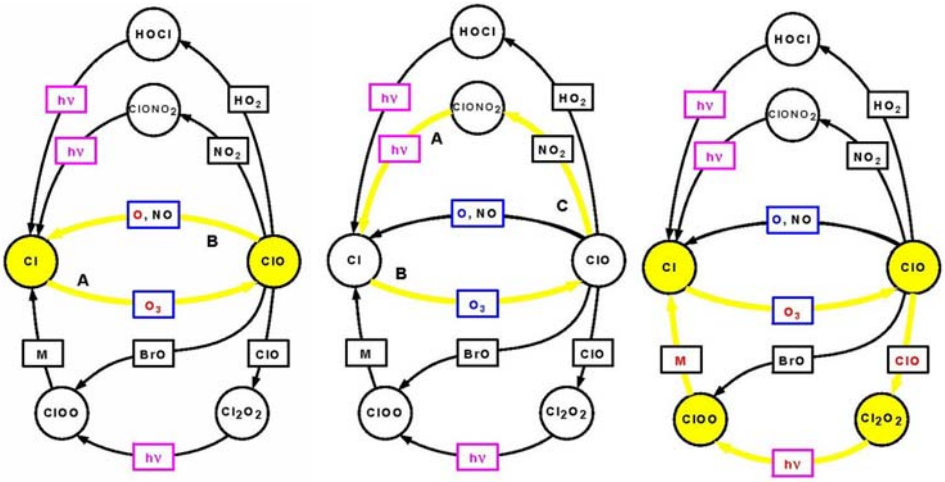
$HCl + OH \rightarrow Cl + H_2O$

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

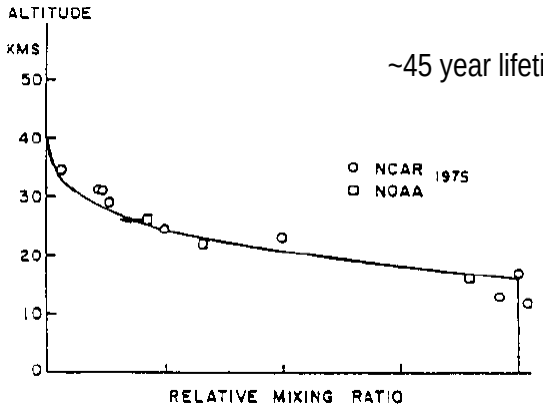
Molina & Rowland, 1974 …1995 Nobel Prize

Three Cl_x catalytic cycles

1. Cl/ClO
2. $Cl/ClONO_2/ClO$
3. $Cl/ClO/Cl_2O_2$

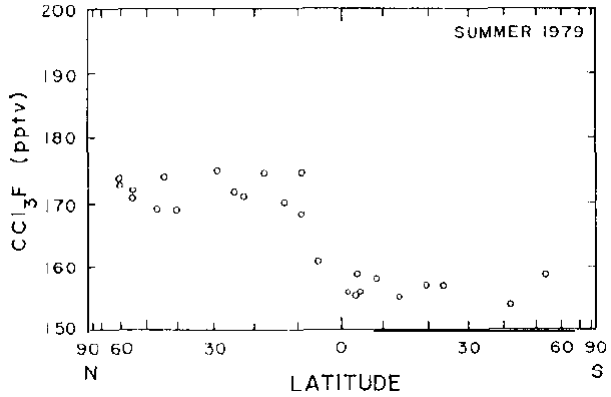


Vertical profile of CFC-11 in the stratosphere: 1975



~45 year lifetime

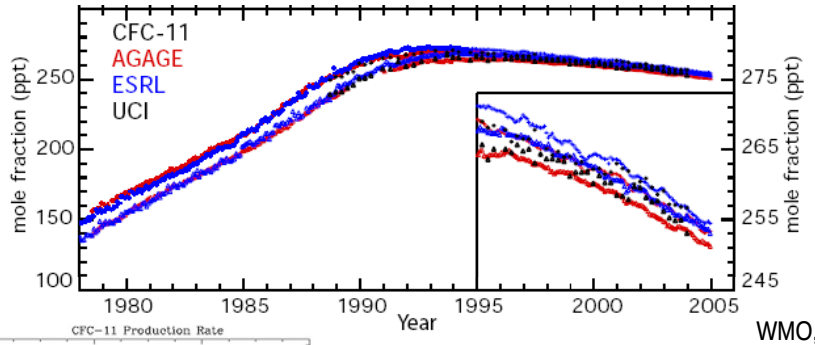
CCl_3F measurements in 1979 at remote locations



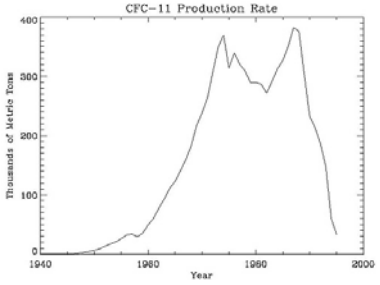
Lovelock et al. had found 40-80 pptv in 1971: doubling in 8 years!

1970-1994: rapid increase in CFC-11 atmospheric levels

1994-today: CFC-11 is decreasing

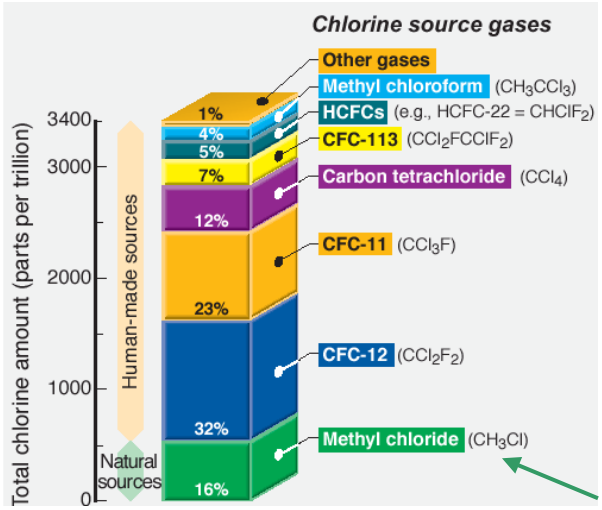


WMO, 2006



CFC-11 production rate

Primary sources of chlorine for the stratosphere in 1999



Lifetimes

5 yrs

640 yrs

26 yrs

45 yrs

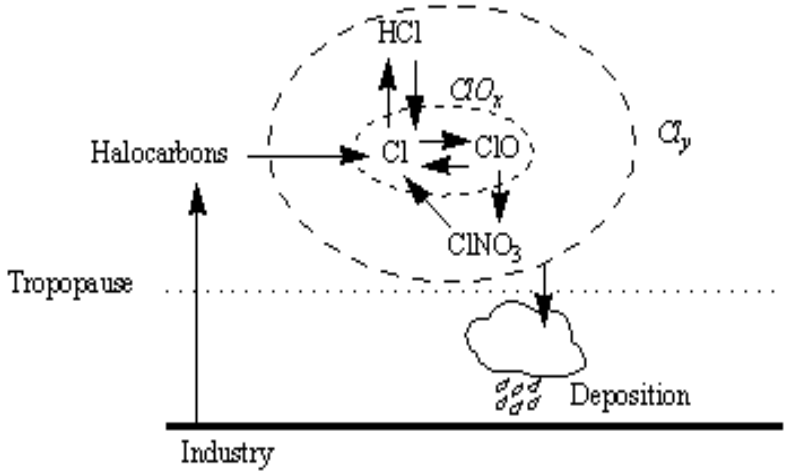
100 yrs

1 yr

Sources:tropical plants, ocean, biomass burning

WMO, Ozone assessment 2002

ATMOSPHERIC CYCLING OF ClO_x AND Cl_y



ClOx = Cl + ClO + 2Cl2O2

Cly = HCl + ClONO2 + HOCl + ClOx, inorganic chlorine

CCly = Σhalocarbons

Chlorine partitioning in the stratosphere

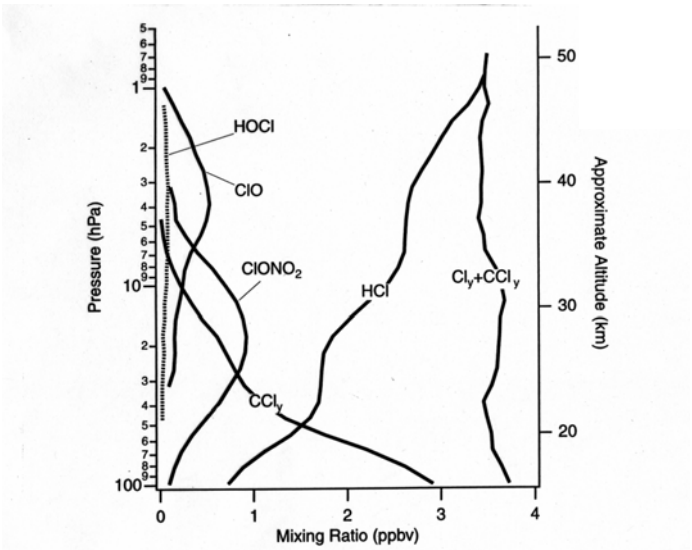
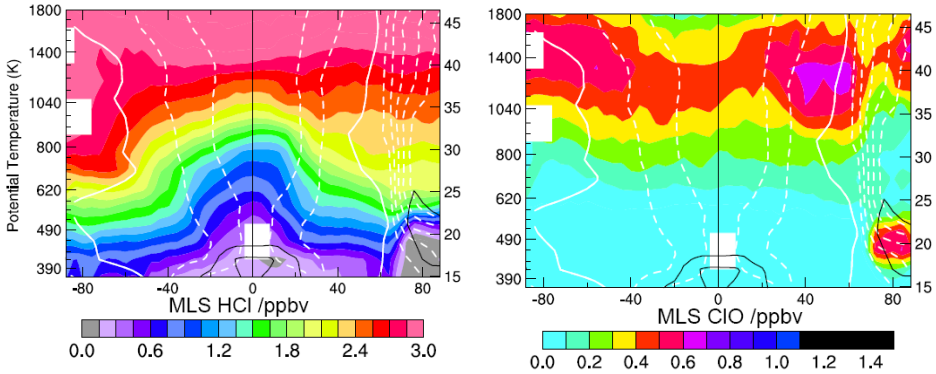


Figure 4.6 Measurements of the major components of stratospheric chlorine versus pressure. Data were measured in November 1994 and between 20°N and 49°N [89].

HCl and ClO distribution in the stratosphere

(AURA satellite observations – MLS instrument)



Feb 15 2007

http://mls.jpl.nasa.gov/data/gallery.php

CATALYTIC CYCLES FOR OZONE LOSS: Bromine (BrO_x = Br + BrO) radicals

- Initiation:

  $CH_3Br + h\nu \rightarrow CH_3 + Br$

- Propagation:

  $Br + O_3 \rightarrow BrO + O_2$

  $BrO + O \rightarrow Br + O_2$

  Net: $O_3 + O \rightarrow 2O_2$

- Termination:

  $BrO + HO_2 \rightarrow HOBr + O_2$

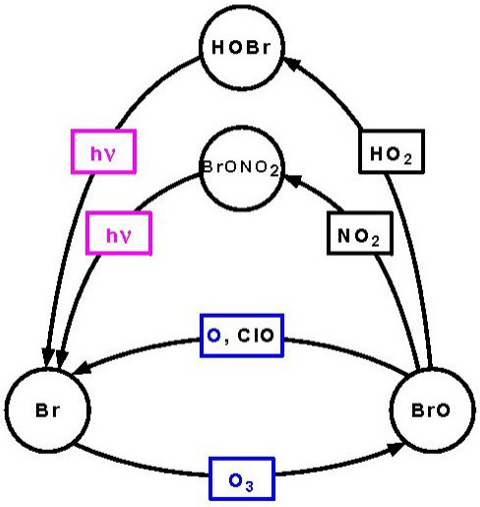
  $BrO + NO_2 + M \rightarrow BrNO_3 + M$

Recycling:

$HOBr + h\nu \rightarrow Br + OH$

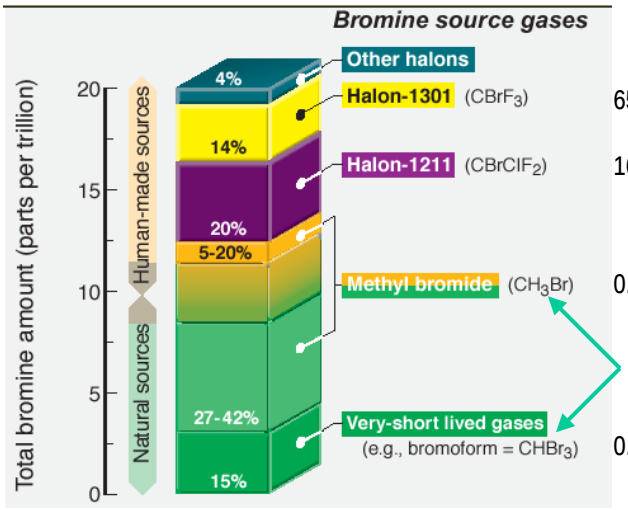
$BrNO_3 + h\nu \rightarrow BrO + NO_2$

Br_X Catalytic cycles



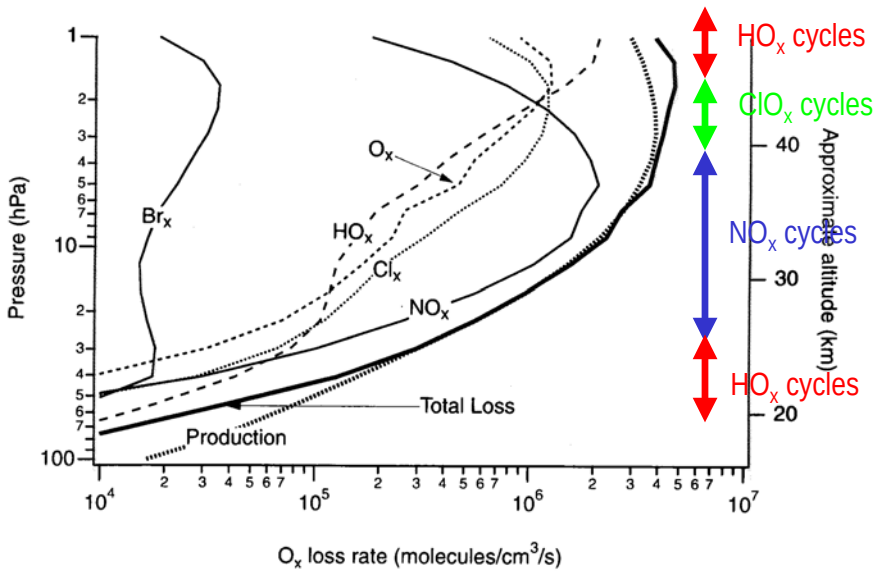
See Lary, JGR, 102, 21515-21526, 1997.

Primary sources of bromine for the stratosphere in 1999

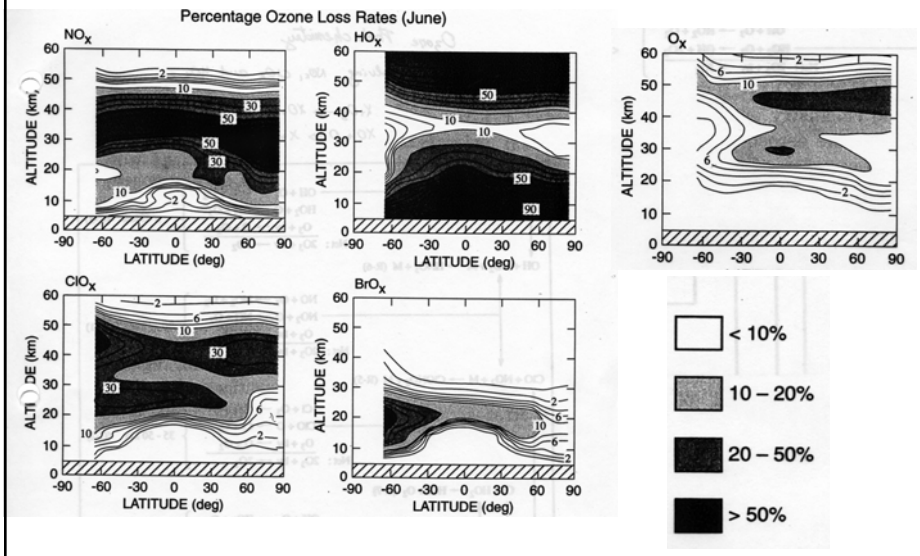


WMO, Ozone assessment 2002

Vertical distribution of O_x catalytic loss cycles

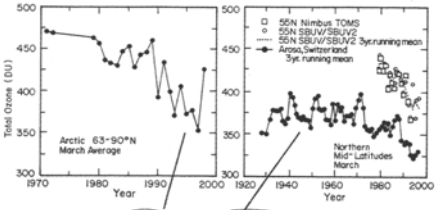


Relative rates of ozone loss

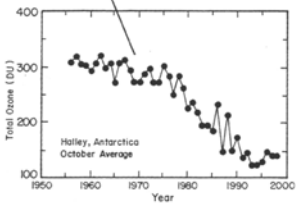


STRATOSPHERIC OZONE DEPLETION

Arctic



Mid-latitudes



Antarctic

→ Downward trends in ozone column on a global scale