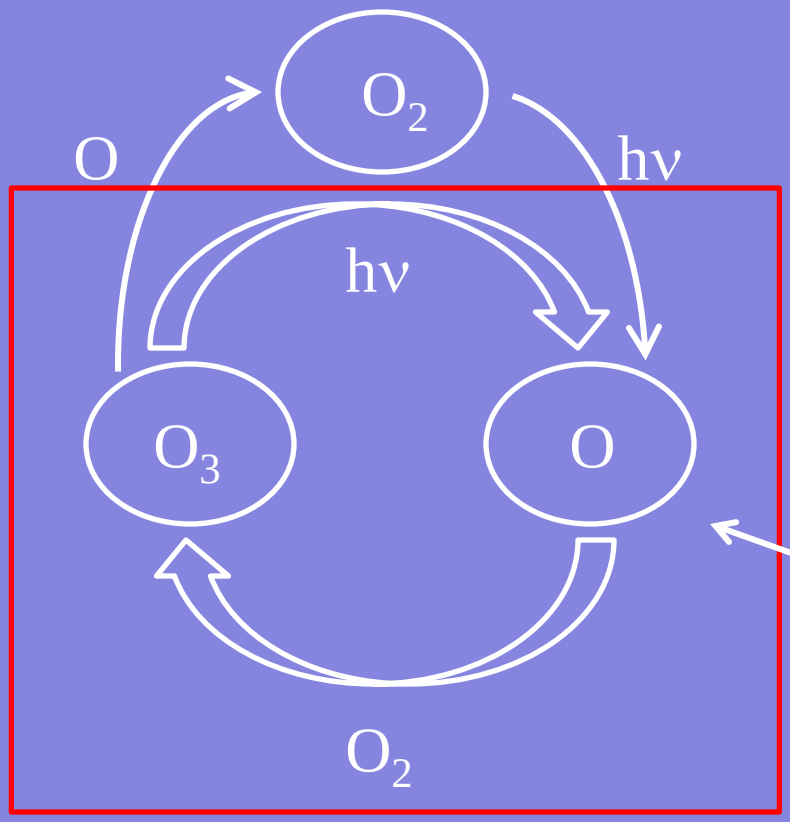
ATOC 3500 – Week 8/9
Catalytic Cycles and Stratospheric Ozone
Part 3

- Review of Chapman chemistry, odd oxygen
- Prediction vs. observations, need for catalysts
- Sources for catalysts
- Enhancing the rate of ozone destruction
- The 1995 Chemistry Nobel Prizes!!



rate1 = k_1 [O_2] [hν] = J_{O2} [O_2]
rate2 = k_2[O][O_2][M]
rate3 = J_{O3} [O_3]
rate4 = k_4[O][O_3]

Note that the only loss for "odd oxygen" (= O + O_3) is Reaction 4.

$$\frac{d[O_x]}{dt} = 2J_1[O_2] - 2k_4[O][O_3]$$

Chapman chemistry (in steady state)

$$O_2 + h\upsilon \rightarrow O + O$$

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

$$O_3 + h\upsilon \rightarrow O_2 + O$$

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

Slow and exactly balance

Fast and approx. balance

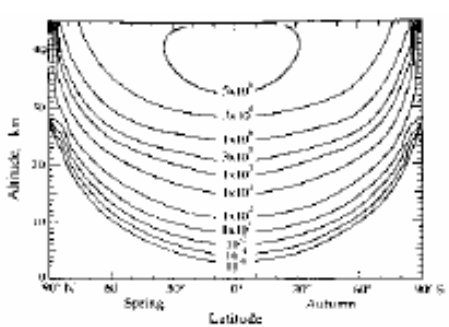
$$J_{O_2}[O_2] = k_4[O][O_3]$$

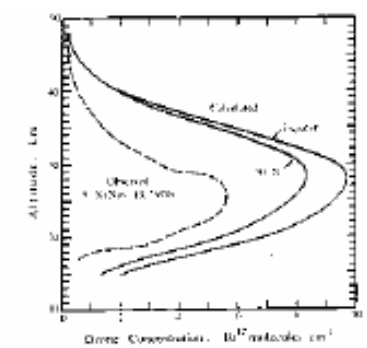
$$[O][O_3] = \frac{J_{O_2}}{k_4}[O_2]$$

$$k_2[O][O_2][M] \sim J_{O_3}[O_3]$$

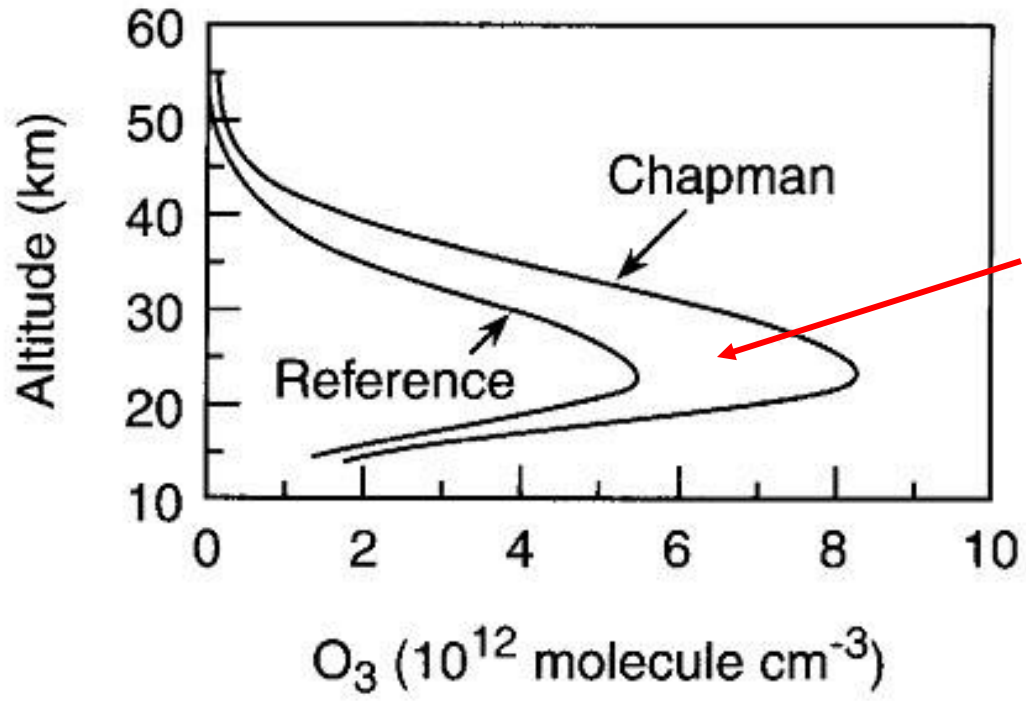
$$\frac{[O]}{[O_3]} \sim \frac{J_{O_3}}{k_2}\frac{1}{[O_2][M]}$$

$$[O_3] \sim 0.21\left(\frac{k_2}{k_4}\right)^{\frac{1}{2}}\left(\frac{J_{O_2}}{J_{O_3}}\right)^{\frac{1}{2}}[M]^{\frac{3}{2}}$$





However, we saw that observations of ozone were larger than predicted ozone using Chapman' mechanism! We need a faster Reaction 4 (can't really reduce photolysis of O_2.



What's missing?

Faster

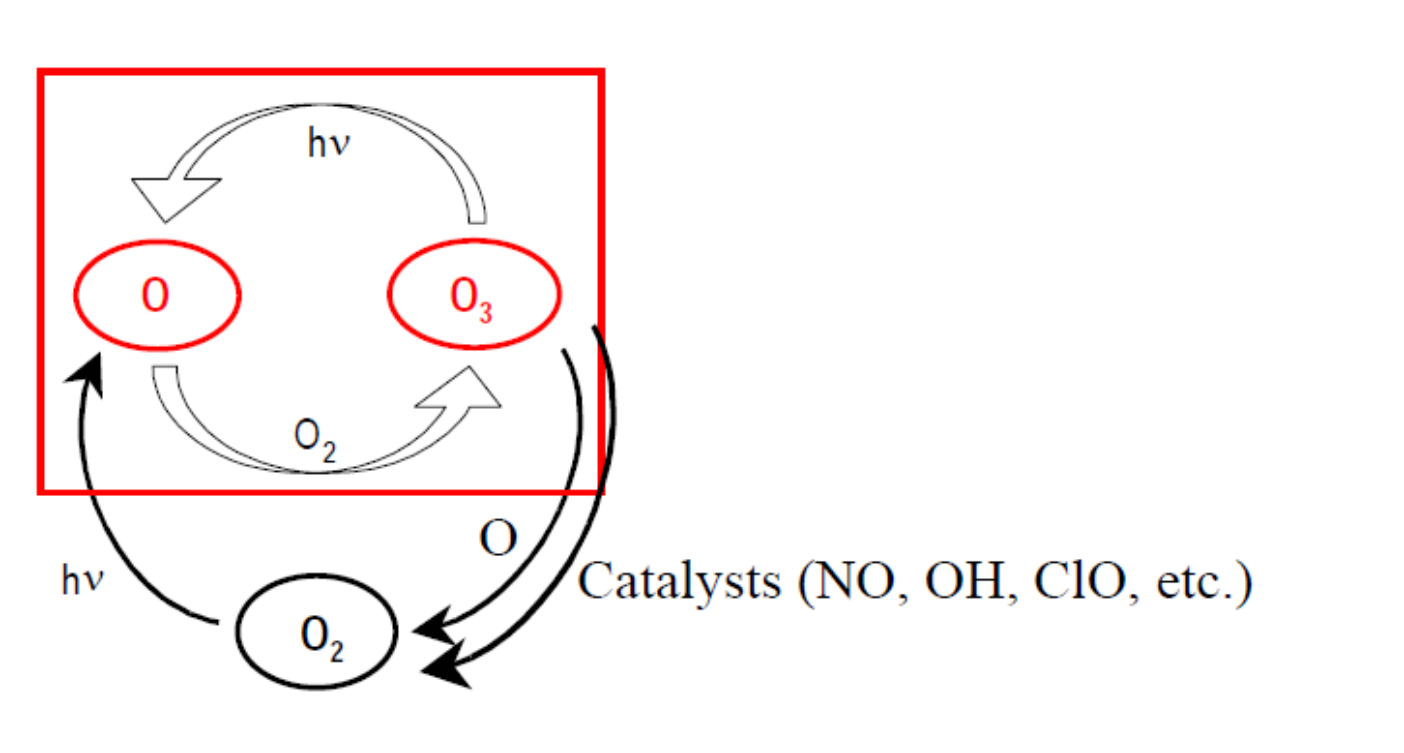
$$O_3 + O \rightarrow O_2 + O_2$$

FIGURE 12.5 Model-calculated ozone vertical profiles for a Chapman or O_x model, with only O_2, O, and O_3 as reactive species and the reference atmosphere chosen to be typical of 1960 conditions (adapted from Kinnison *et al.*, 1988).

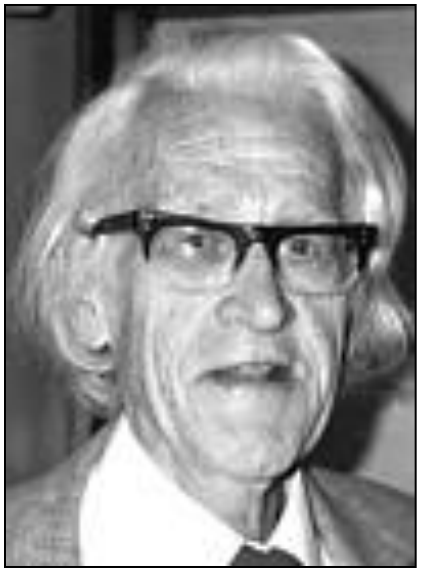
• Steady state ozone is determined by the ratio of P to L.

• Production is determined by J_{O2} and $[O_2]$ (sunlight and air pressure) which don't change much over time.

• The only explanation for the overprediction of ozone by Chapman theory is that there must be additional losses. These will be due to catalysts.



http://www.accessexcellence.org/WN/SUA06/nobchem.html



Water in the stratosphere would lead to catalytic destruction of ozone by ‘speeding up’ reaction (4) of Chapman’s mechanism – thus, introducing the concept of catalytic destruction of ozone

$$H + O_3 \rightarrow OH + O_2$$

$$\underline{OH + O \rightarrow H + O_2}$$

$$\text{Net - } O_3 + O \rightarrow O_2 + O_2$$

Bates, D.R. and M. Nicolet, The Photochemistry of the Atmospheric Water Vapor, J. Geophys. Res., 55, 301, 1950

Catalysis

$H + O_3 \rightarrow OH + O_2$ rate = $k_a[H][O_3]$

$OH + O \rightarrow H + O_2$ rate = $k_b[OH][O]$

Net - $O_3 + O \rightarrow O_2 + O_2$

$$\frac{d[O_3]}{dt} \approx -2k_4[O][O_3] - 2k_b[OH][O]$$

Replace k_4 $[O][O_3]$ with apparent loss

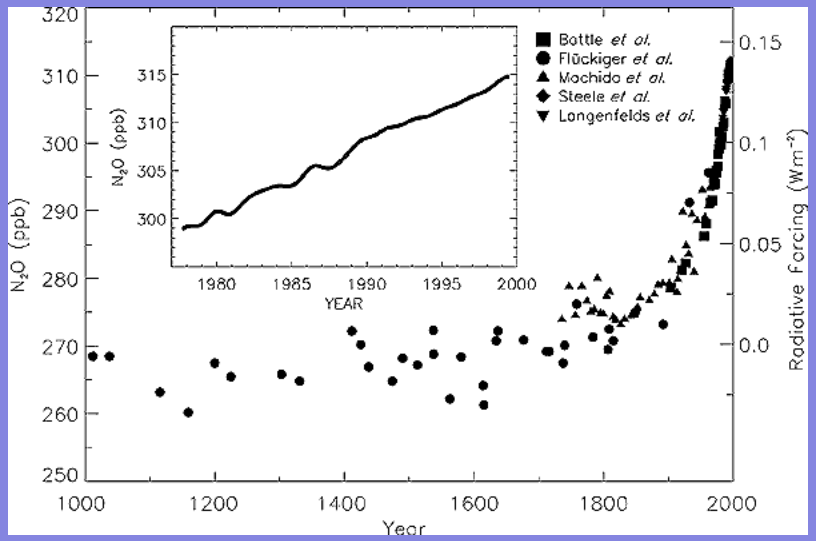
$$k_4^{app} = k_4\left[1 + \frac{k_b[OH]}{k_4[O_3]}\right] \qquad [O_3] = 0.21^2\left(\frac{k_2}{k_4^{app}}\right)^{\frac{1}{2}}\left(\frac{J_{O_2}}{J_{O_3}}\right)^{\frac{1}{2}}[M]^{\frac{3}{2}}$$

$> k_4$

Paul J. Crutzen

"Influence of Nitrogen Oxides on Atmospheric Ozone Content" *Quarterly Journal of the Royal Meteorological Society* 96 (1970):320.

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



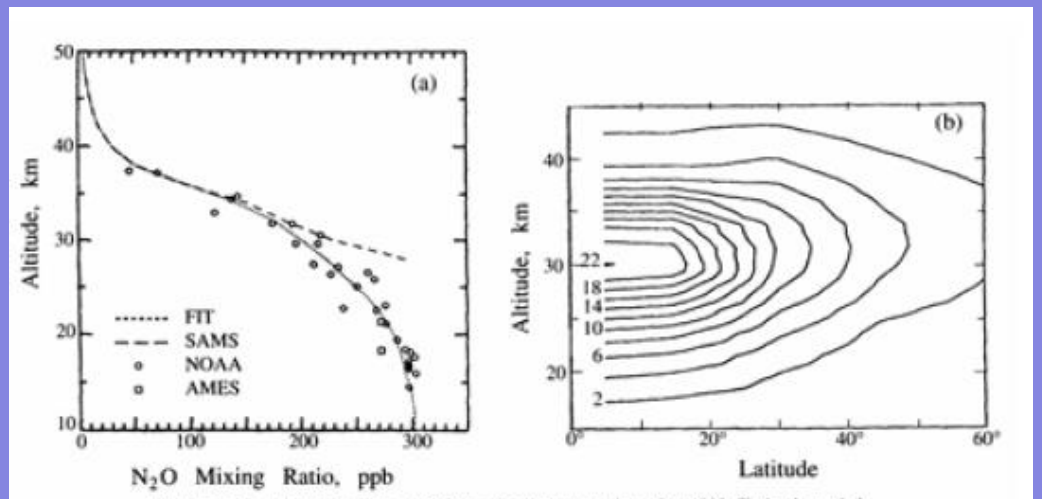


FIGURE 4.7 (a) Vertical profiles of N_2O over the tropics at equinox circa 1980. Circles denote balloon-borne measurements at 9° N and 5° S; squares represent aircraft measurements between 1.6° S and 9.9° N. Dashed curve refers to the average of satellite measurements at 5° N, equinox, between 1979 and 1981. This compilation of data was presented by Minschwaner et al. (1993), where the original sources of data can be found. The dotted curve indicates the vertical profile used by Minschwaner et al. to estimate the lifetime of N_2O. (b) Calculated diurnally averaged loss rate for N_2O (in units of 10^{12} molecules cm^{-3} s^{-1}) as a function of altitude and latitude, at equinox. The loss rate includes both photolysis and reaction with $O(^1D)$ (Minschwaner et al, 1993).

Formation of NO_x

$O_3 + h\nu \rightarrow O_2 + O(^1D)$	J_{O3}
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	J_{N2O}
$N_2O + O(^1D) \rightarrow N_2 + O_2$	$k_{2a} = 5 \times 10^{-11}\ cm^3\ s^{-1}$
$\rightarrow NO + NO$	$k_{2b} = 6.7 \times 10^{-11}\ cm^3\ s^{-1}$

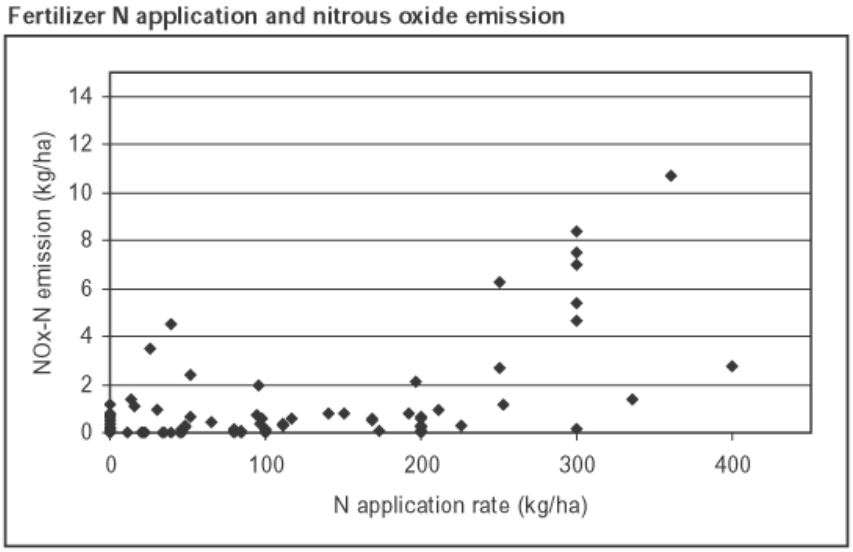
3-4% of the loss of N_2O in the stratosphere results in the formation of nitric oxide (NO).

NO acts as the main catalyst for ozone destruction.

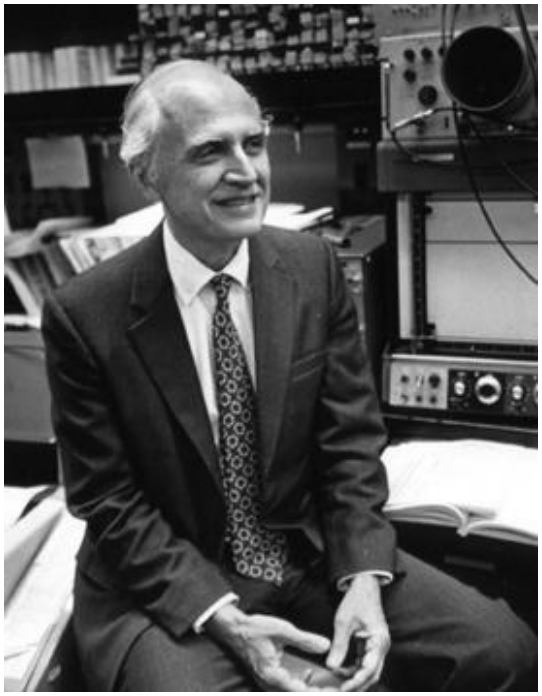
Since much of the N_2O is from natural processes, this is considered a natural loss for ozone. The additional N_2O that is produced by agriculture is considered an ozone-depleting practice.

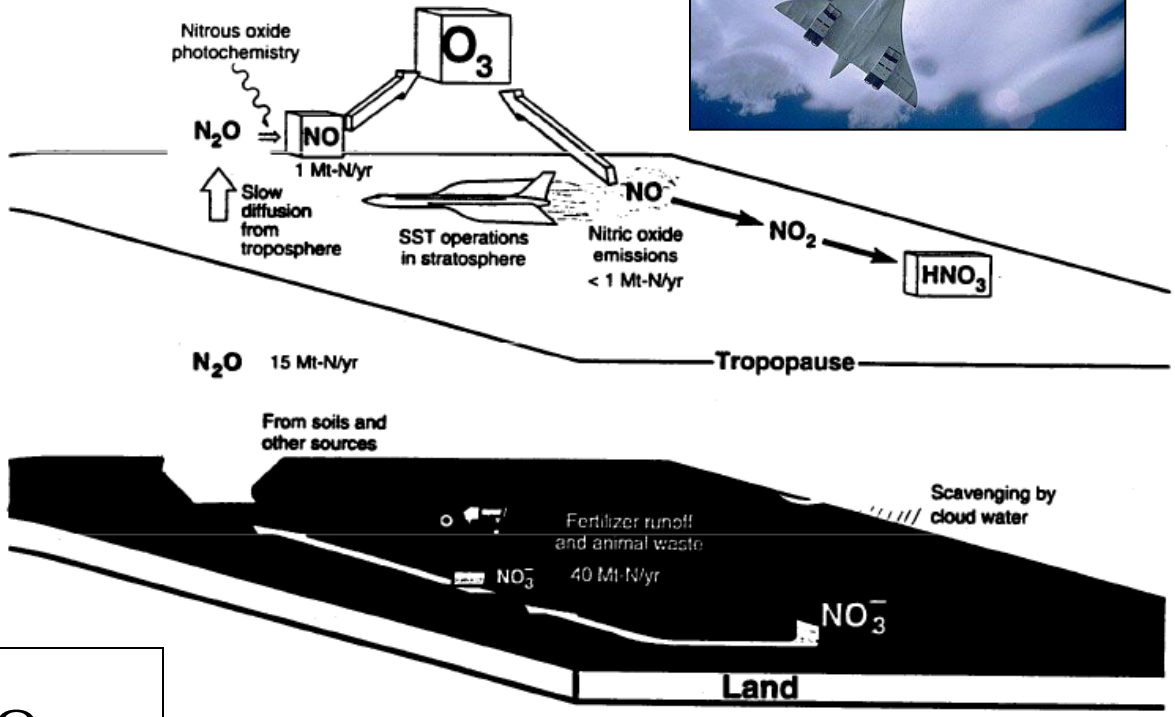
Key connections made by Crutzen

- mankind can increase N_2O emissions by fertilizing crops
- N_2O has a long lifetime in troposphere, so can reach the stratosphere
- Increase in tropospheric N_2O will increase stratospheric NO_x
- Increase in NO_x will result in decrease in steady state ozone
- e.g. **Mankind can alter stratospheric ozone without leaving the ground!**



Harold Johnston





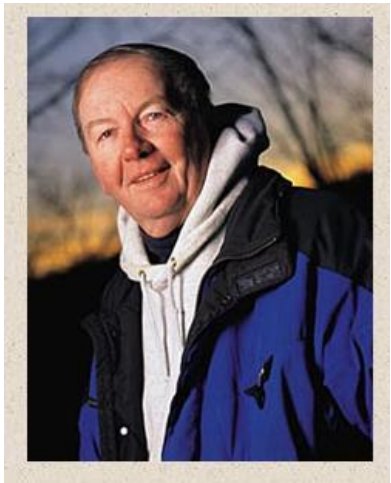
$$NO + O_3 \rightarrow NO_2 + O_2$$

$$\underline{NO_2 + O \rightarrow NO + O_2}$$

$$\text{Net - } O_3 + O \rightarrow O_2 + O_2$$

Direct Injection of emissions from SSTs

$$\frac{d[O_3]}{dt} \approx -2[O]\left(k_{O_3}[O_3] + k_{OH}[OH] + k_{NO}[NO]\right)$$



Richard Stolarski and Ralph Cicerone

$$Cl + O_3 \rightarrow ClO + O_2$$

$$\underline{ClO + O \rightarrow Cl + O_2}$$

$$\text{Net - } O_3 + O \rightarrow O_2 + O_2$$

$$\frac{d[O_3]}{dt} \approx -2[O]\left(k_{O_3}[O_3] + k_{OH}[OH] + k_{NO}[NO] + k_{clo}[ClO]\right)$$

Each of these cycles contributes to ozone loss at slightly different altitudes and in different proportions.

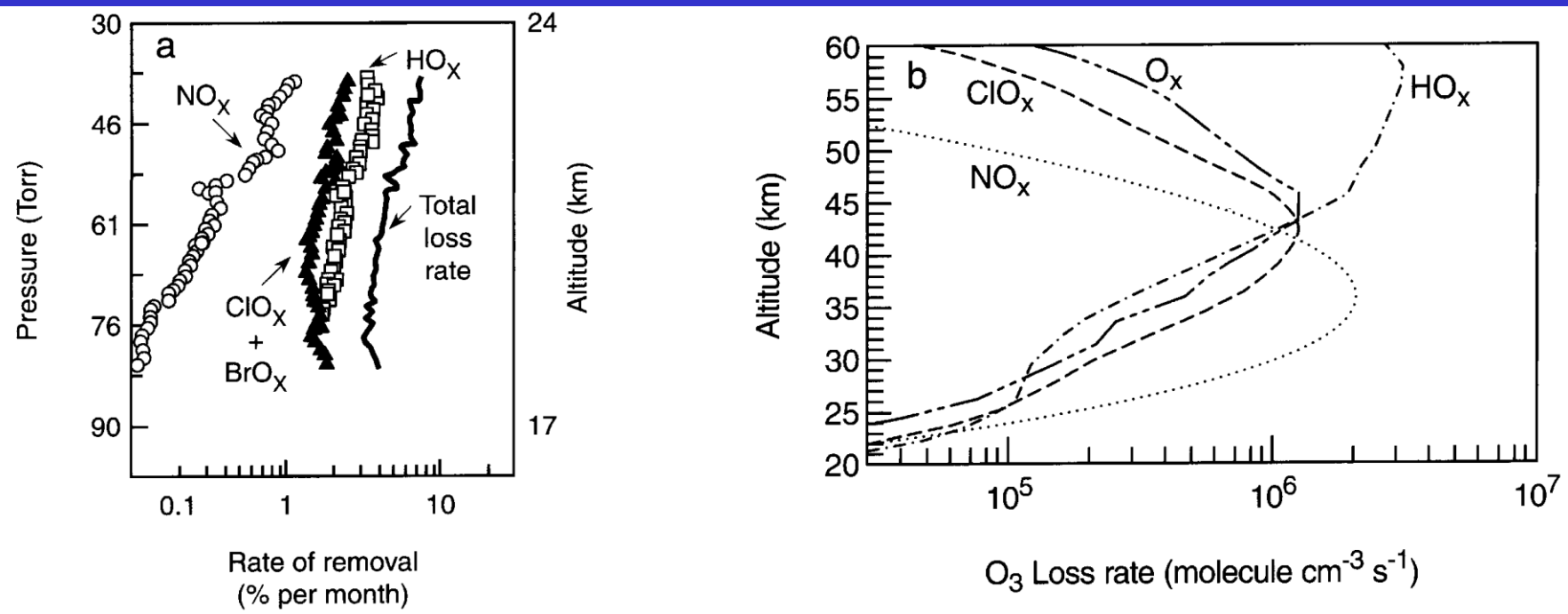
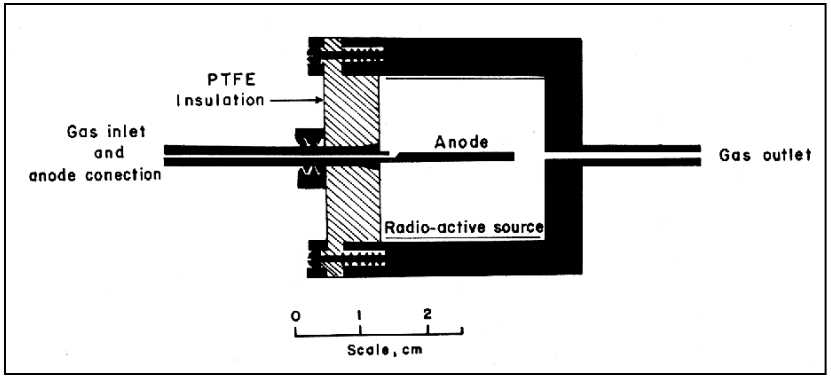
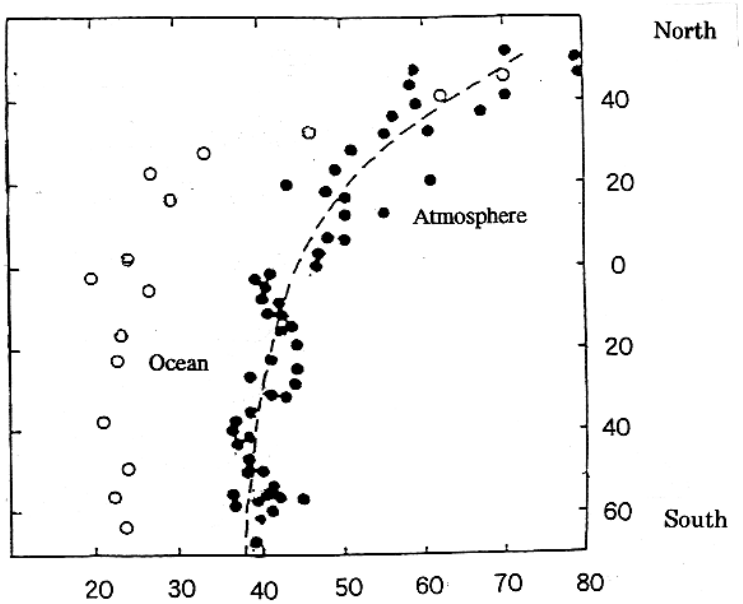


FIGURE 12.8 (a) Rates of removal of O_3 at 38°N in May 1993 due to NO_x, (ClO_x + BrO_x), and HO_x chemistry, respectively, as a function of altitude in the stratosphere (adapted from Wennberg *et al.*, 1994); (b) 24-h average rates of removal of O_3 as a function of altitude (adapted from Osterman *et al.*, 1997).

Dr. James E. Lovelock, Inventor

The electron capture detector

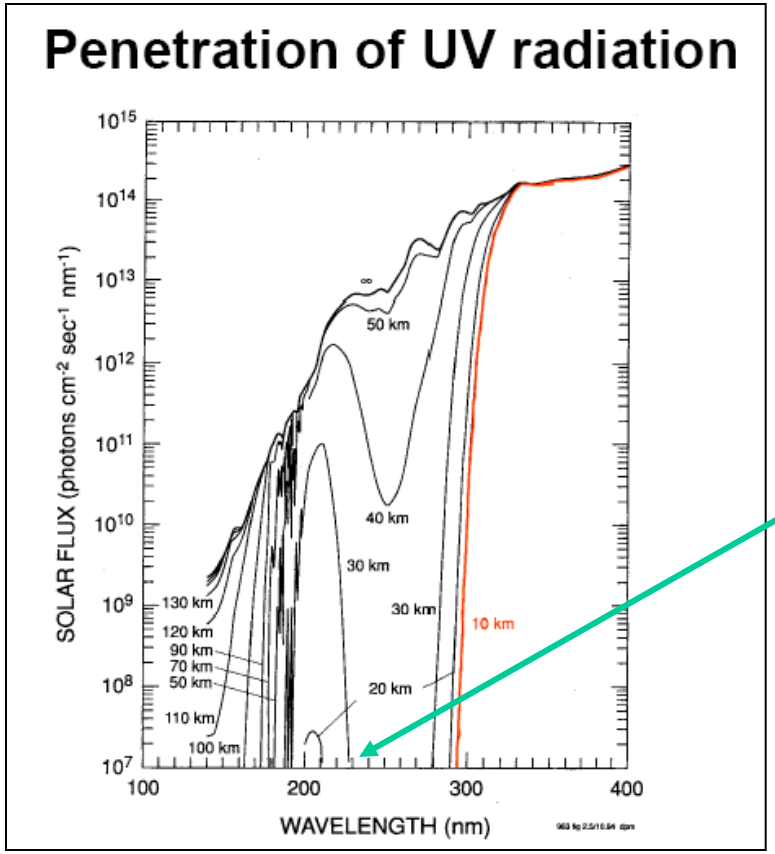




"…are unusually stable chemically and only slightly soluble in water and might therefore persist and accumulate in the atmosphere … The presence of these compounds constitutes no conceivable hazard."

Distribution of CCl_3F in and over the North and South Atlantic Ocean, Nature, Vol. 241, January 19, 1973

Chlorofluorocarbons are quite stable in the troposphere because they do not absorb sunlight. They photolyze high in the stratosphere.



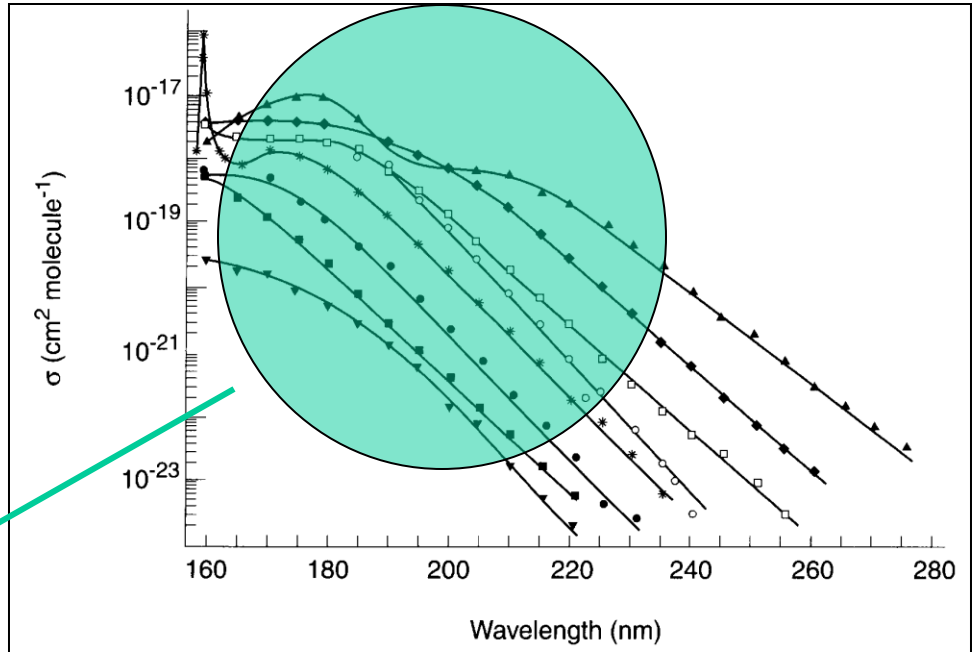


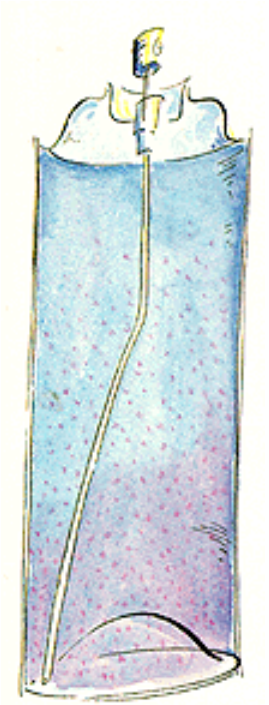
FIGURE 12.14 Semilogarithmic plot of the absorption cross sections of the halogenated methanes at 298K: ∗, $CHCl_3$; ■, $CHClF_2$; □, CH_2Cl_2; ●, CH_2ClF; ▲, CCl_4; ◆, CCl_3F (CFC-11); ○, CCl_2F_2 (CFC-12); ▼, $CClF_3$ (adapted from Hubrich and Stuhl, 1980).

Mario Molina and F. Sherwood Rowland

Mario Molina and F. Sherwood Rowland

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

$$CF_2Cl_2\ h\nu \rightarrow CF_2Cl + Cl$$



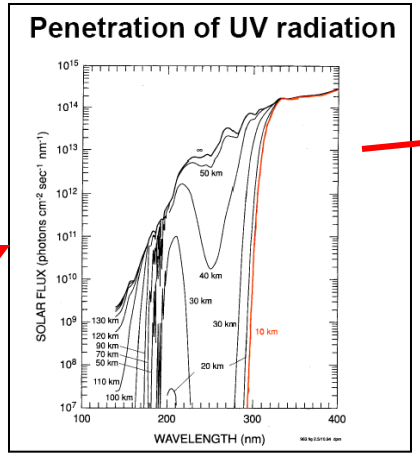
The deadly weapon!

Predicted tens of percents of ozone loss

M. J. Molina and F. S. Rowland "Stratospheric Sink for Chlorofluoromethanes: Chlorine atomic-atalysed destruction of ozone," *Nature* 249 (28 June 1974):810

Note the typo! (should be “atom-catalyzed”)

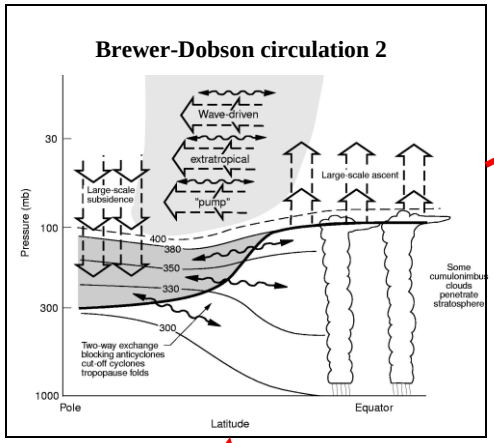
The pieces come together!



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

$CF_2Cl_2\ h\nu \rightarrow CF_2Cl + Cl$

release



transport

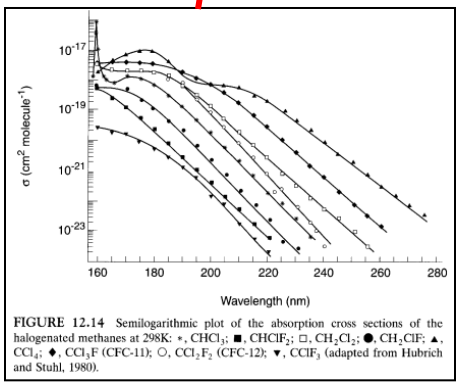
"spark"

$Cl + O_3 \rightarrow ClO + O_2$

$\underline{ClO + O \rightarrow Cl + O_2}$

Net - $O_3 + O \rightarrow O_2 + O_2$

"flame"



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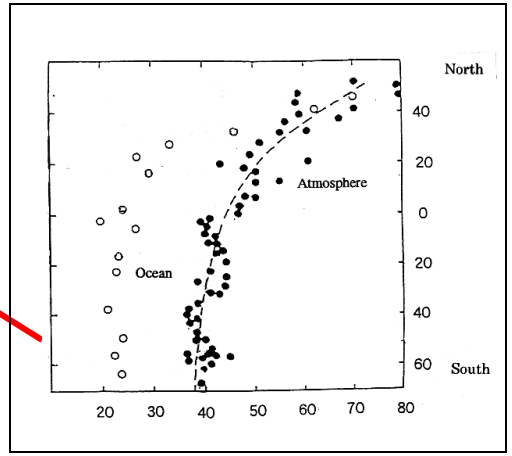
Unreactive in troposphere

chlorofluorocarbons



source

$O_2 + h\nu \rightarrow O + O$

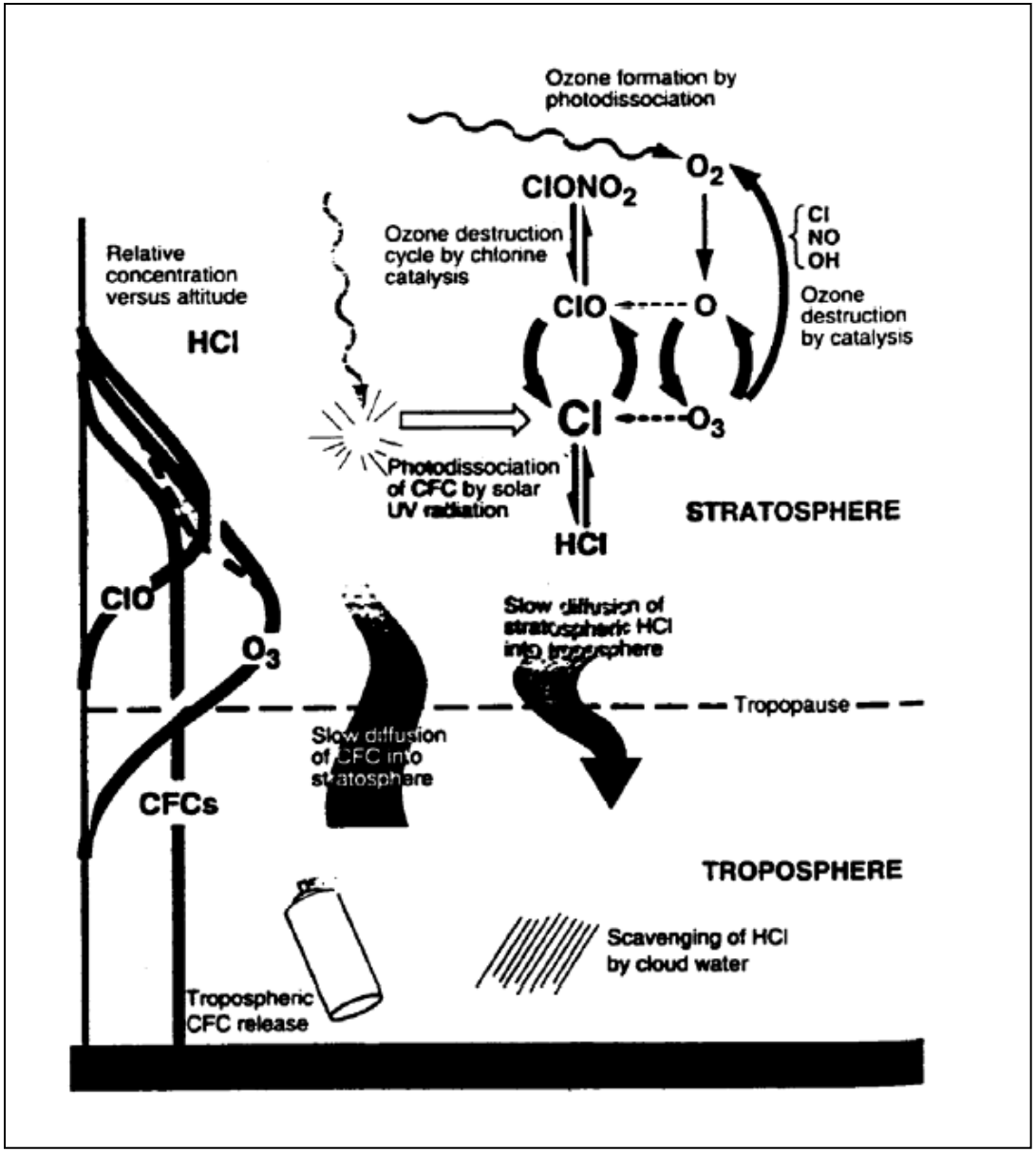
$O + O_2 + M \rightarrow O_3 + M$

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

$O_3 + O \rightarrow O_2 + O_2$

destruction

Schematically



Rowland (1974): *"The work is going very well, but it may mean the end of the world."*

x10!

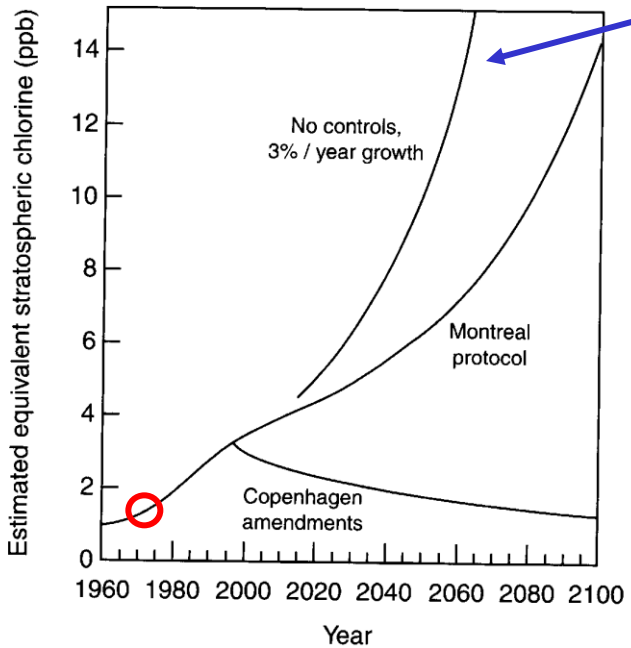


FIGURE 13.1 Estimated equivalent effective stratospheric chlorine for a continued 3% growth per year, for controls contained in the Montreal Protocol, and for those in the Copenhagen amendments (adapted from World Meteorological Organization, 1995).

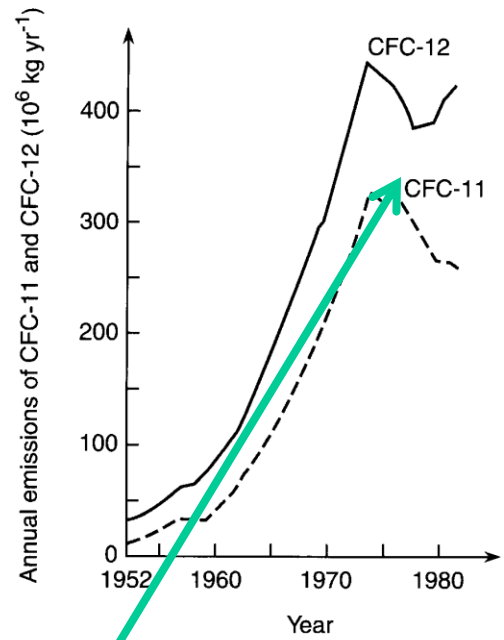


FIGURE 12.11 Estimated annual worldwide releases of CFC-11 and CFC-12 from 1952 to 1980. Data from Chemical Manufacturers' Association (adapted from National Research Council, 1984).

Industry pauses while it waits for word that ozone is, in fact, being depleted – i.e., let scientists look for the smoking gun!

So, all we need is
to observe ozone losses in conjunction with
increases in CFCs, easy, right?

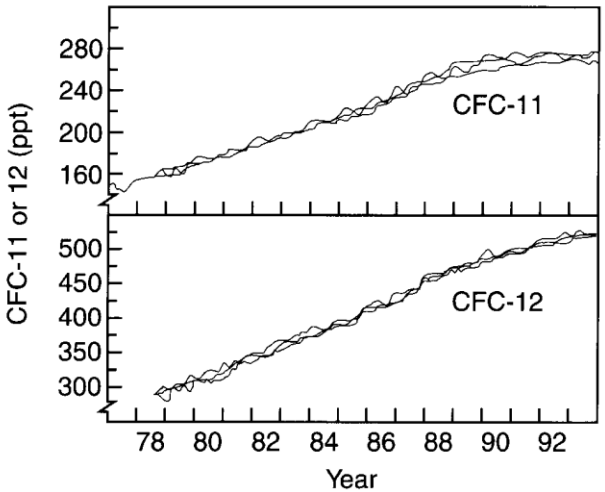
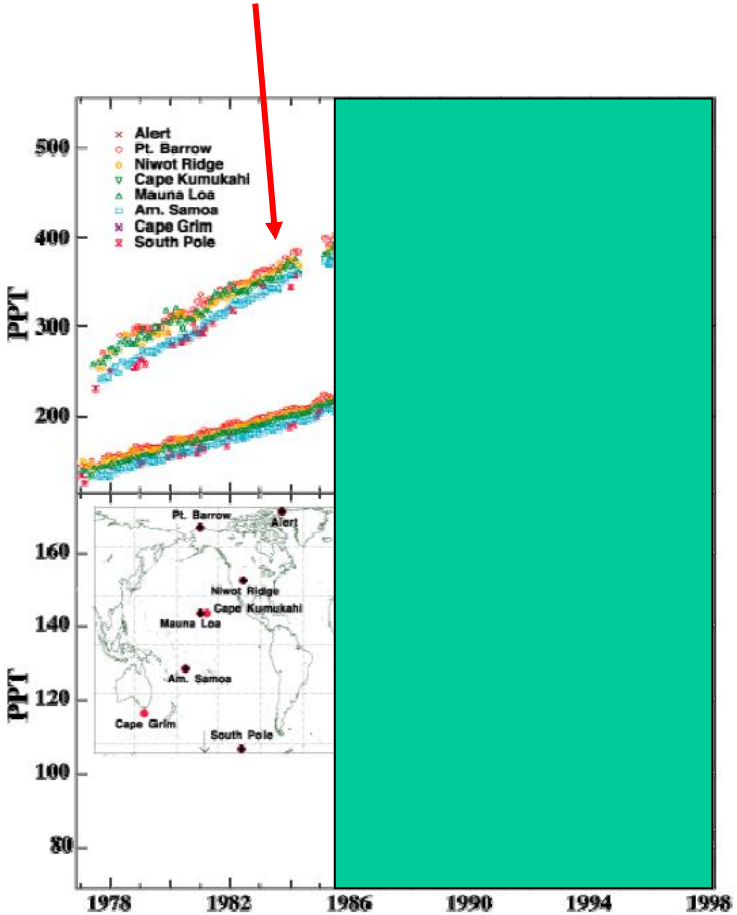


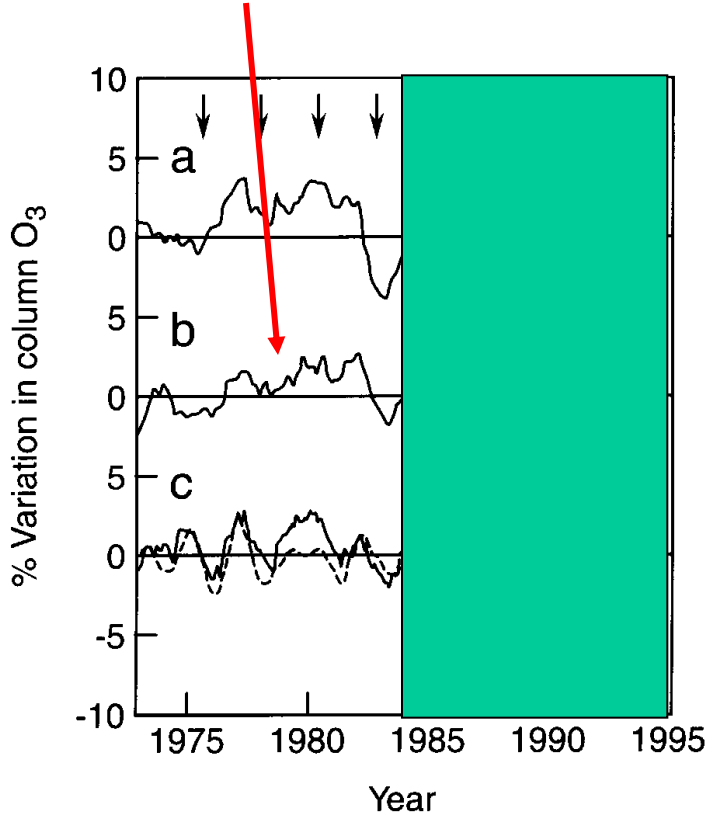
FIGURE 12.13 Concentrations of CFC-11 and CFC-12 in air in the 30°N to 90°N region as a function of time. The different curves represent measurements made at various locations (adapted from WMO, 1995).

Easy!?

CFCs nearly double over 15 years!

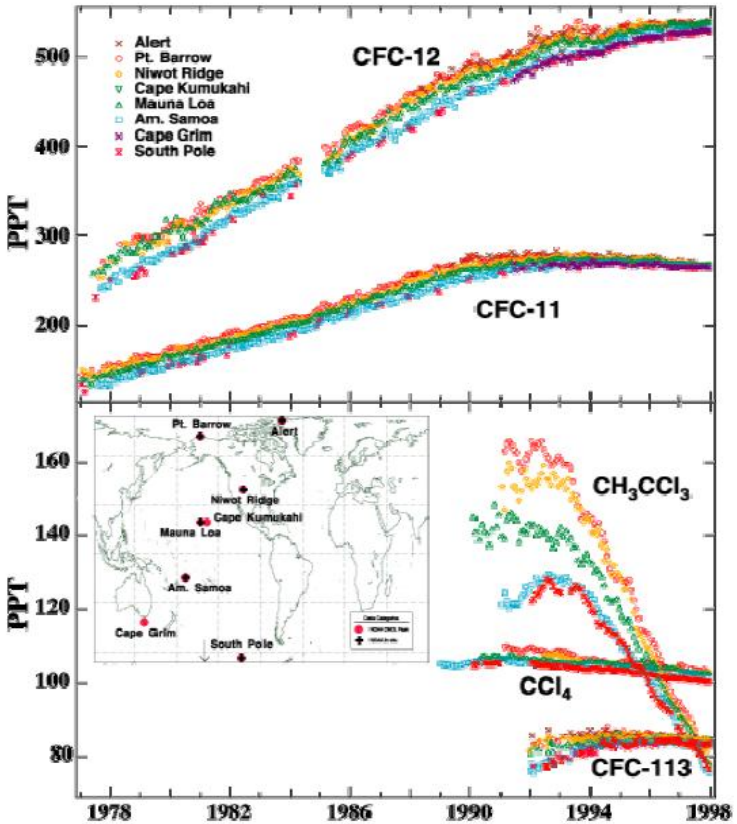


With no observable ozone loss!

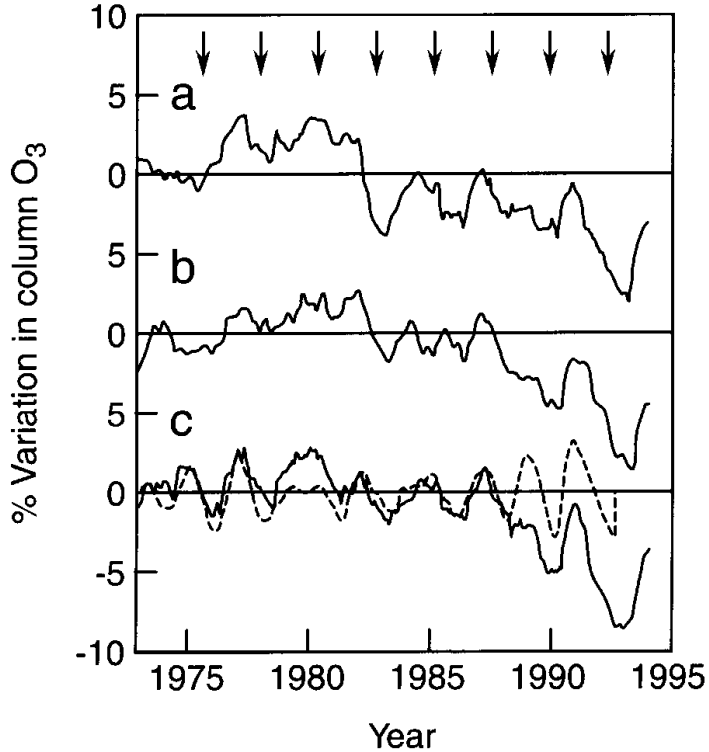


E 13.11 Percentage variations in total column ozone smoothed using a 12-month running mean for a network of stations in (a) Europe, (b) Eastern Siberia and the Far East, and (c) Western Siberia from 1973 to March 1994. The arrows show the expected QBO. In (c) the dashed line shows the component that has a periodicity expected for the QBO (adapted from Bojkov *et al.*, 1994).

CFCs nearly double over 15 years!



Until 1988!



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Summary of important points

- Stratospheric ozone is only produced by photolysis of O_2, a process that is governed by abundances of O_2 and sunlight. Mankind can't easily tamper with these parameters

- Sir Sydney Chapman (who spent a lot of time in Boulder at NCAR) nearly got it right. He could account for the formation of the ozone layer with just four simple reactions. But something was missing – there were other chemicals to consider.

- Gases that are long-lived in the troposphere eventually reach the stratosphere, where they break down into radicals that destroy ozone. It doesn't matter where these gases originate from – the troposphere is the great homogenizer. The 1995 Nobel Prizes in Chemistry were awarded to Paul Crutzen, Mario Molina, and Sherry Rowland for recognizing the importance of this concept.

The Big Surprise of 1985!

It doesn’t hurt your case to have a huge hole in the ozone appear right when government and the public is doubting your theories!