Mid-Latitude Stratospheric Chemistry

AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2017

Today:

- **Importance of how a chemical cycle is completed wrt odd-oxygen loss**
- **Role of halogens and aerosol loading on mid-latitude ozone**
- **Connection to recent research**

Lecture 14

30 March 2017

Ozone Depletion and Halocarbons

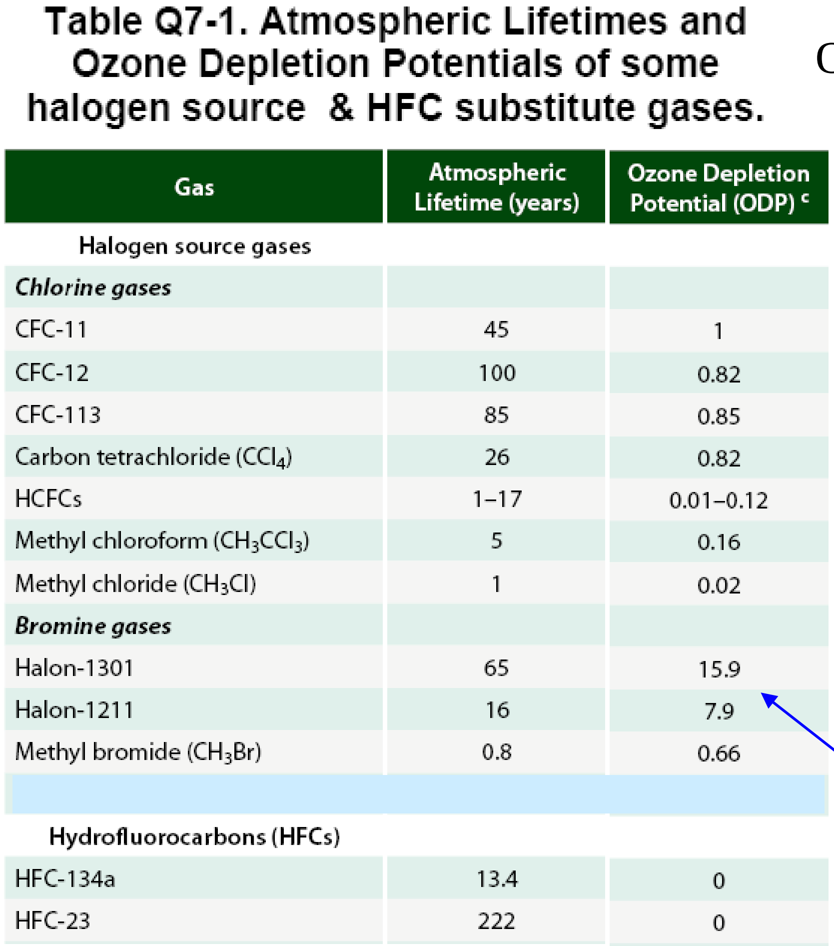


Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

Gas	Atmospheric Lifetime (years)	Ozone Depletion Potential (ODP) ^{c}
Halogen source gases		
Chlorine gases		
CFC-11	45	1
CFC-12	100	0.82
CFC-113	85	0.85
Carbon tetrachloride (CCl_4)	26	0.82
HCFCs	1–17	0.01–0.12
Methyl chloroform (CH_3CCl_3)	5	0.16
Methyl chloride (CH_3Cl)	1	0.02
Bromine gases		
Halon-1301	65	15.9
Halon-1211	16	7.9
Methyl bromide (CH_3Br)	0.8	0.66
Hydrofluorocarbons (HFCs)		
HFC-134a	13.4	0
HFC-23	222	0

continuous

$$\text{ODP (species "}i\text{")} = \frac{\text{global loss of O}_3\text{ due to unit mass emission of "}i\text{"}}{\text{global loss of O}_3\text{ due to unit mass emission of CFC-11}}$$

continuous

$$\approx \frac{(\alpha\, n_{\mathrm{Br}} + n_{\mathrm{Cl}})}{3}\;\frac{\tau_i}{\tau_{\text{CFC-11}}}\;\frac{MW_{\text{CFC-11}}}{MW_i}$$

where :

τ is the global atmospheric lifetime

MW is the molecular weight

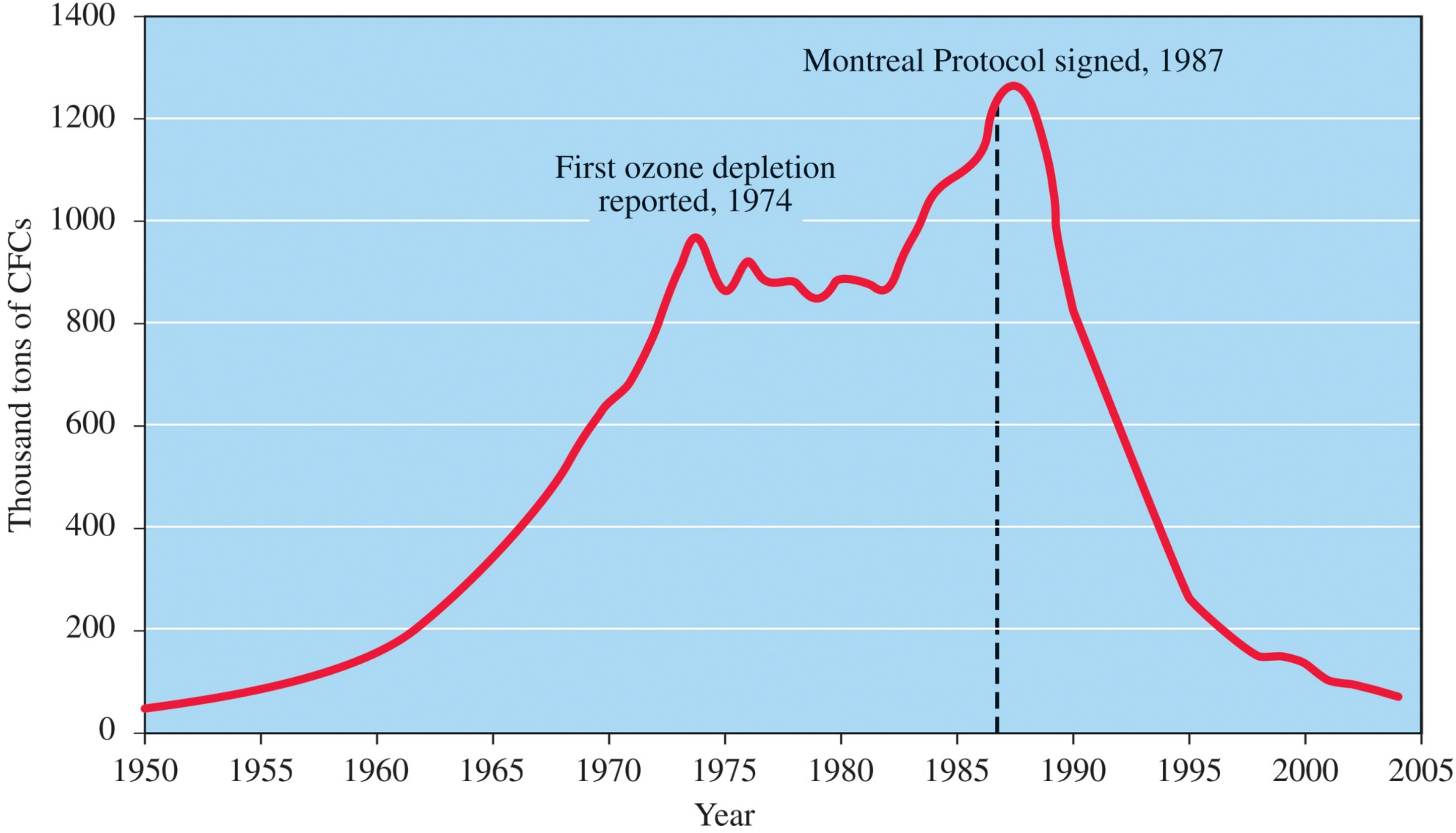
n is the number of chlorine or bromine atoms

α is the effectiveness of ozone loss by bromine relative to ozone loss by chlorine

$\boxed{\alpha = 60}$

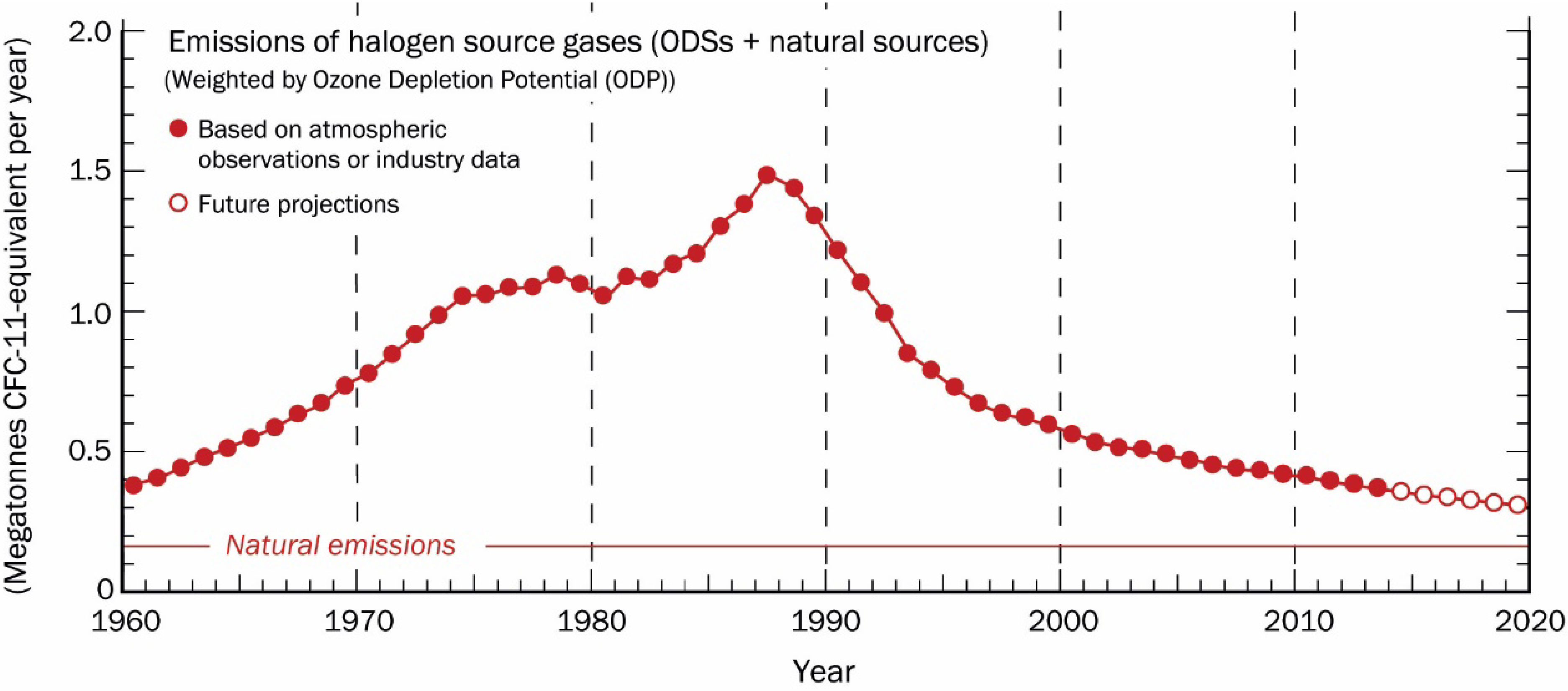
Halons (anthropogenic halocarbons containing <u>bromine</u>) much worse for ozone than CFCs (anthropogenic halocarbons containing <u>chlorine</u>)

Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons



Global <u>Production</u> of CFCs, Fig. 2.19, Chemistry in Context

Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons



Global <u>Production</u> of CFCs, Fig Q0-1, WMO 2014 QAs

Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons

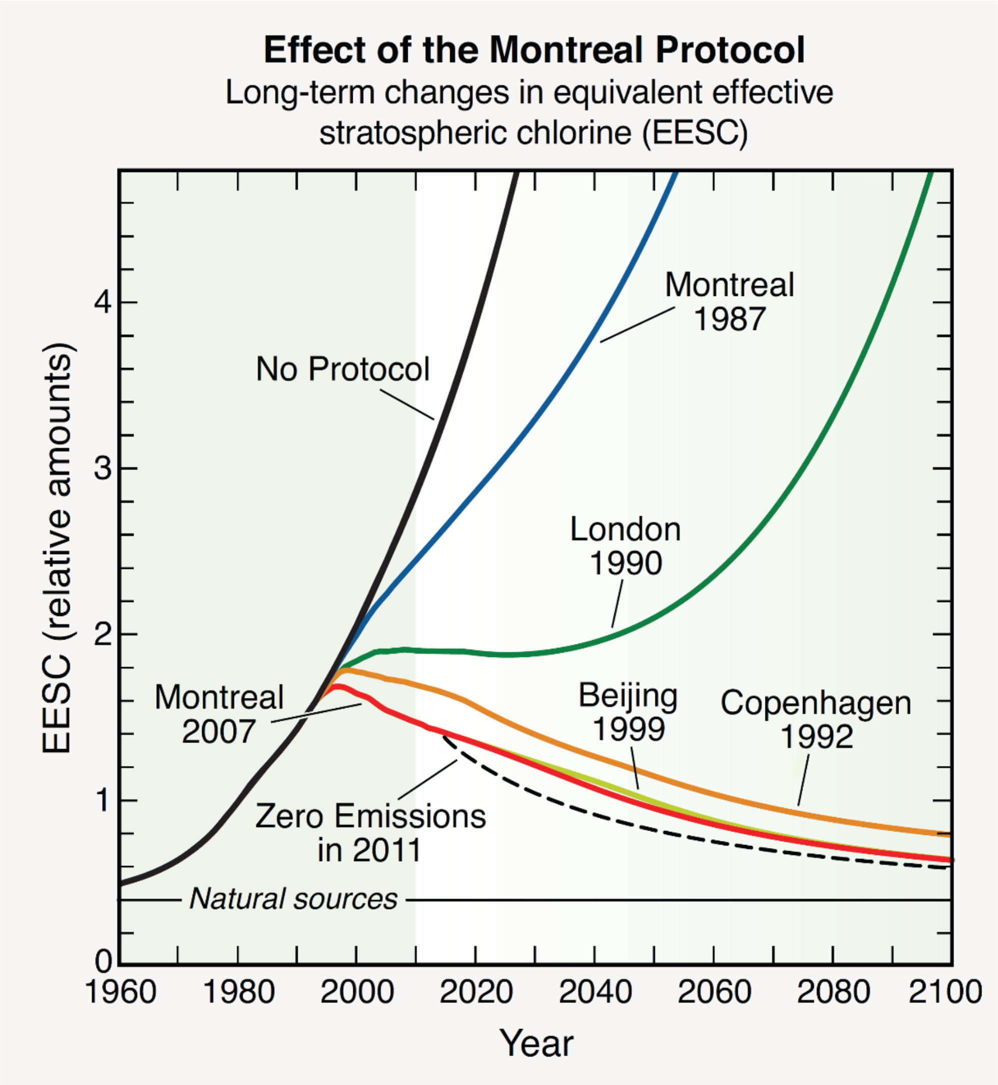


Figure Q15-1, WMO 2010 QAs

Chlorine Source Gases

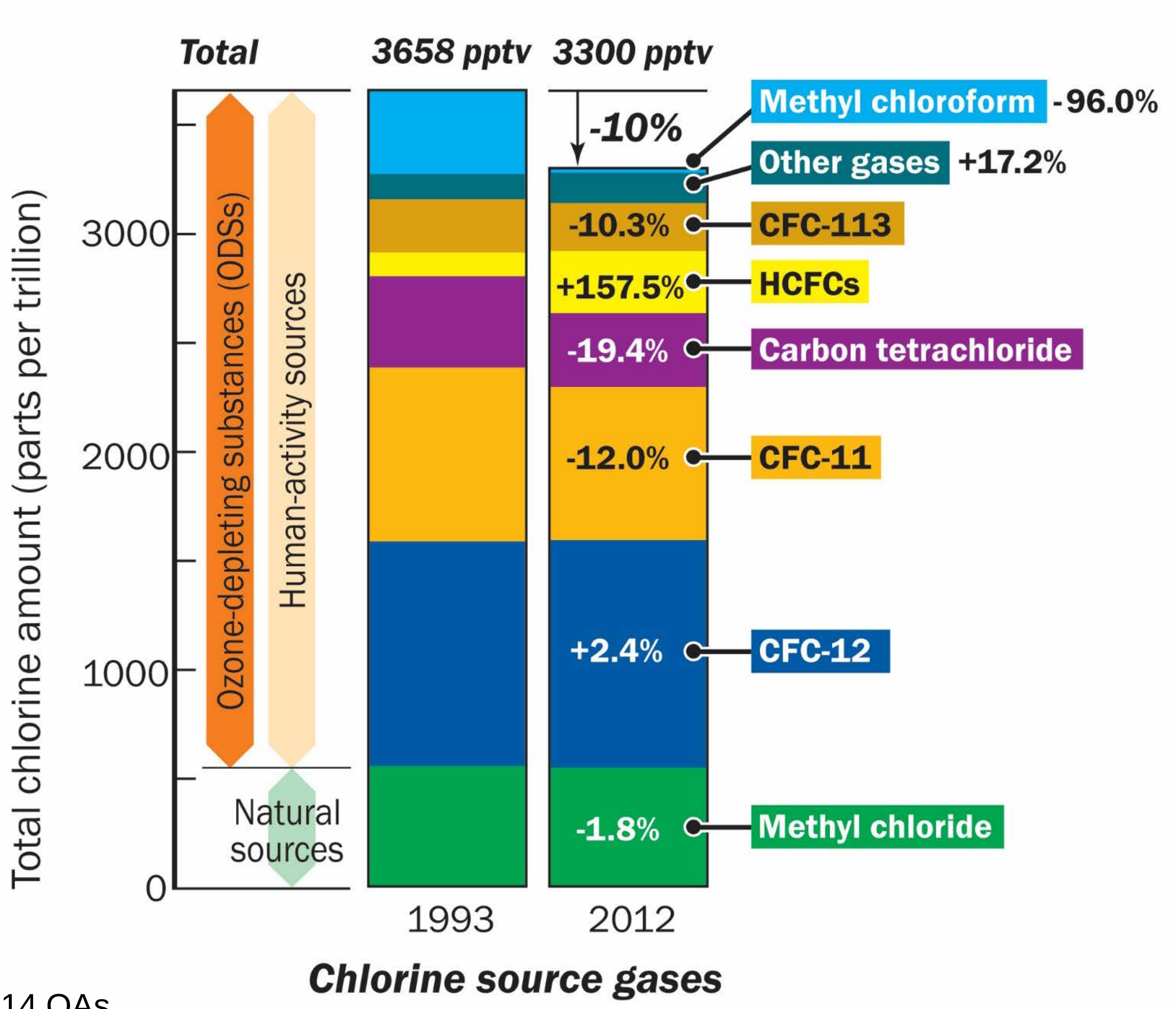
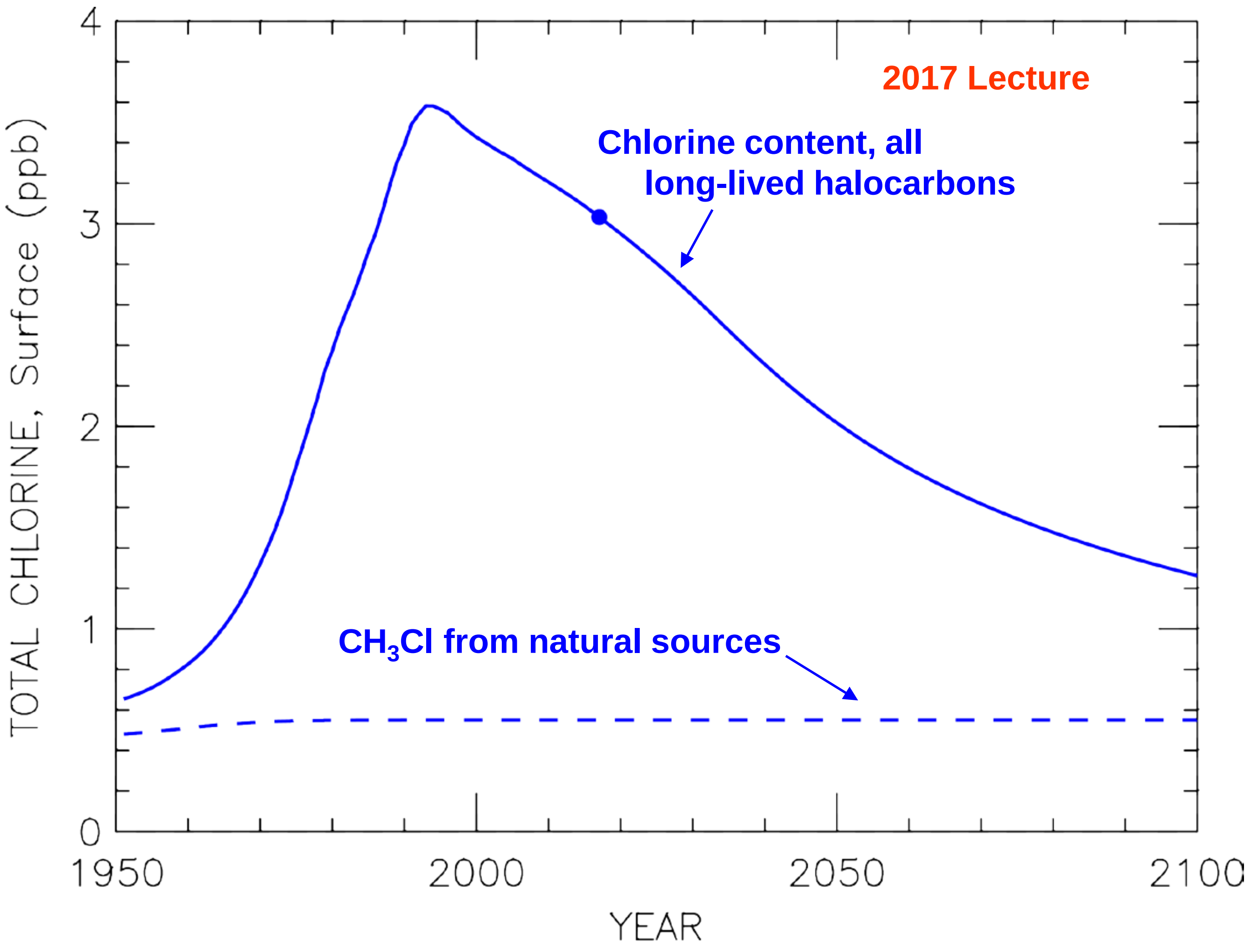


Fig Q7-1, WMO 2014 QAs

And Atmospheric Levels of these Pollutants are Declining



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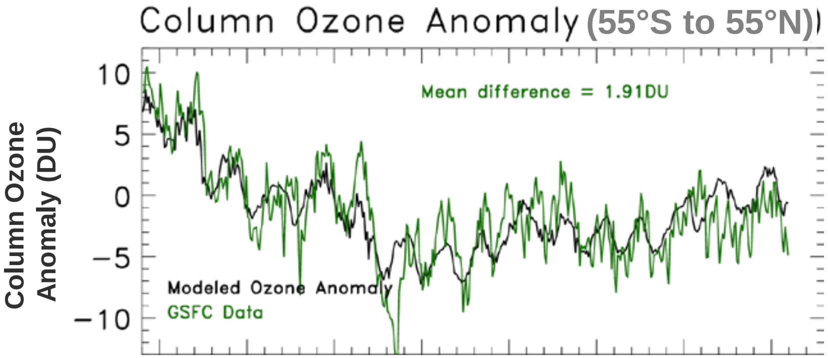
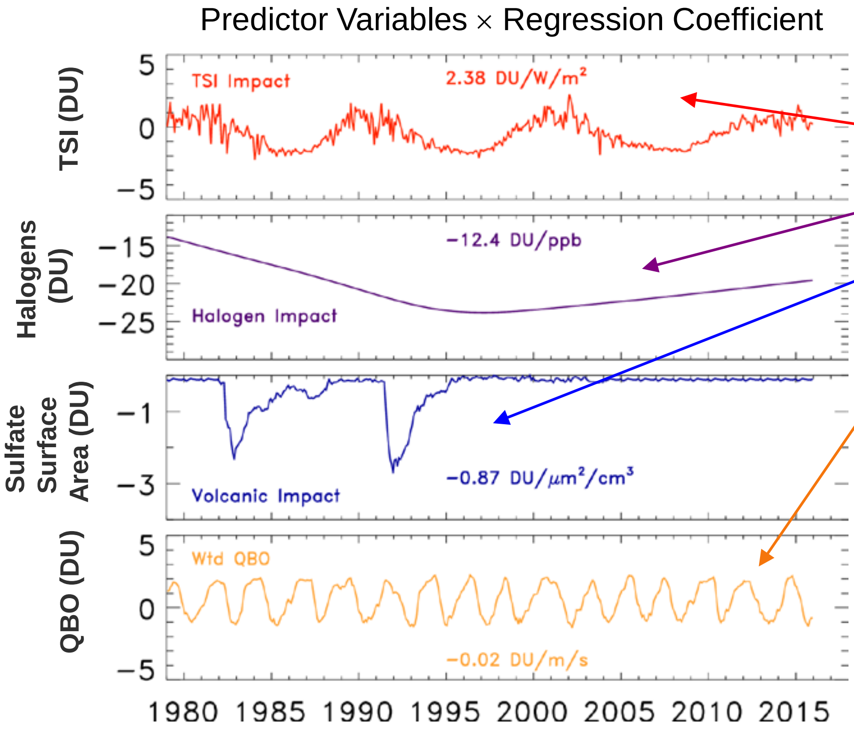
Ozone Depletion at Mid-Latitudes



Ozone data from
http://acdb-ext.gsfc.nasa.gov/Data_services/merged



Column Ozone Anomaly (DU) =
19.6 DU +
2.38 DU / W m^{-2} × TSI +
−12.4 DU / ppb × Halogens +
−0.87 DU × ln (SSA) +
−0.02 DU / m s^{-1} × QBO

where
TSI = total solar irradiance
Halogens=stratospheric chlorine & bromine loading
SSA = Sulfate Surface Area
QBO = Quasi-biennial oscillation of the direction of winds in the tropical lower strat

Chapman Chemistry

$$[O_3] = \left(\frac{J_1\, k_2}{J_3\, k_4} \right)^{1/2} f_{O2}\, [M]^{3/2}$$

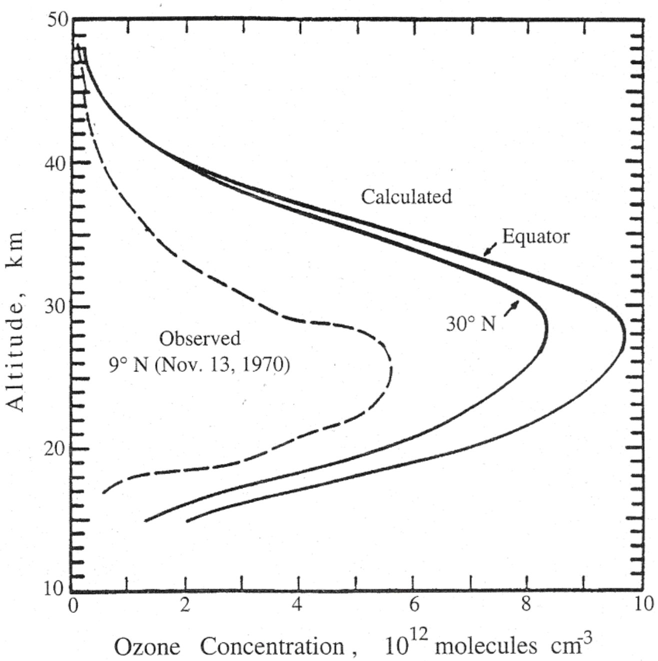


FIGURE 4.6 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970.

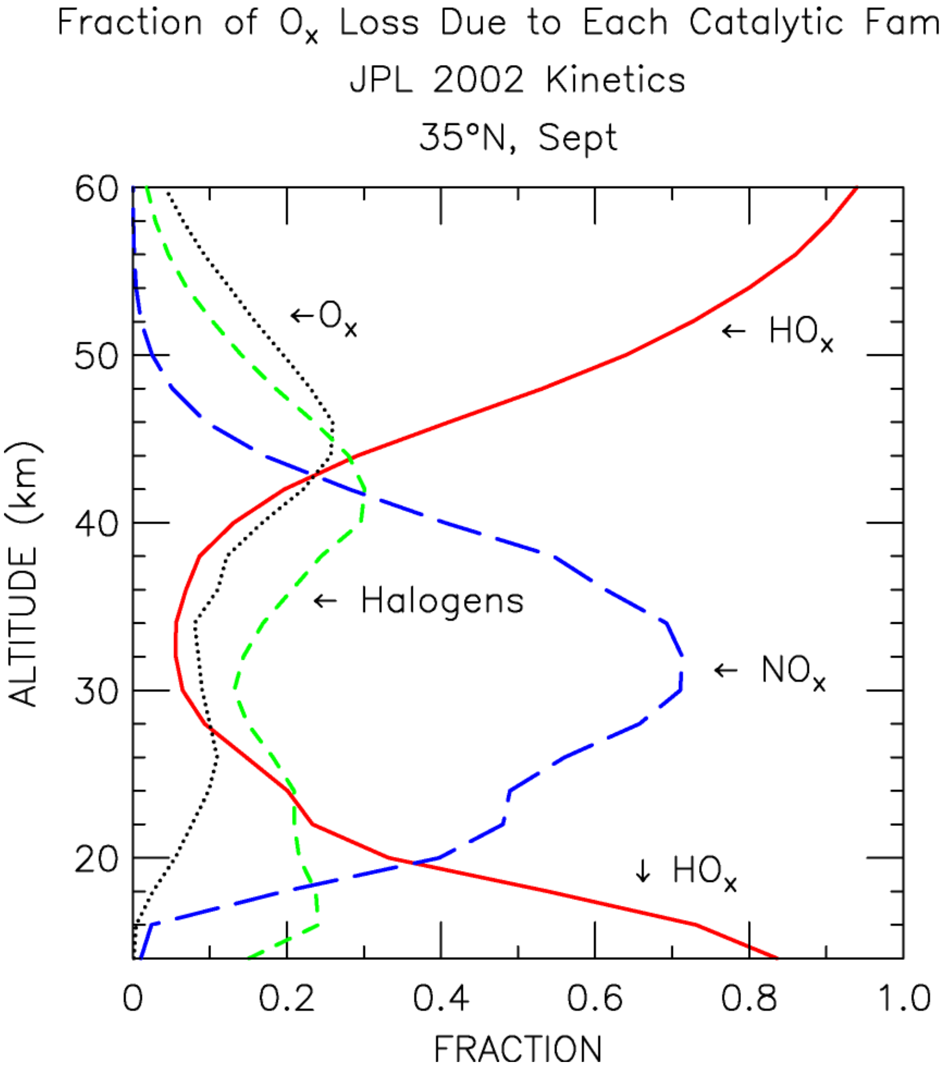
$[O_3]$ falls off with increasing altitude (high in stratosphere), at a rate determined by $[M]^{3/2}$, because:

$[O_3]$ falls off with decreasing altitude (low in stratosphere) due to a rapid drop in J_1, reflecting:

Observed $[O_3]$ < Chapman $[O_3]$: why ?!?

Lecture 9

Stratospheric Photochemistry: Odd Oxygen Loss By Families



Calculated fraction of Ozone loss due to various family of radicals.

After Osterman et al., GRL, 1997.

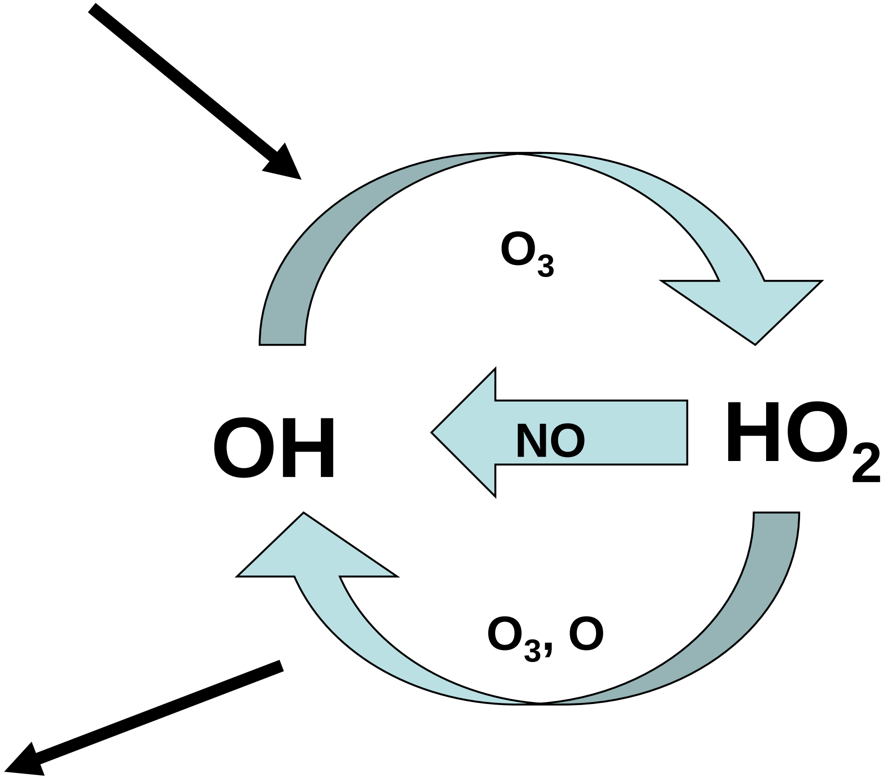
Lecture 9

HO_x : OH and HO_2

OH and HO_2 are central to stratospheric and tropospheric photochemistry

Production : $O^1D + H_2O \rightarrow OH + OH$

$O^1D + CH_4 \rightarrow OH + CH_3$



O_3

OH

NO

HO_2

O_3, O

Loss: $OH + HO_2 \rightarrow H_2O + O_2$

$OH + HNO_3 \rightarrow H_2O + NO_3$

HO_x : OH and HO_2

OH and HO_2 are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

HO_2 formation:

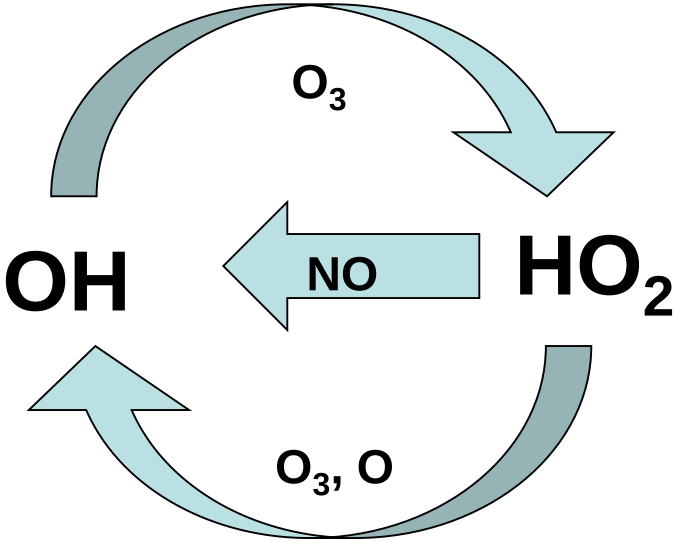
$OH + O_3 \rightarrow HO_2 + O_2$ (1)

HO_2 loss:

$HO_2 + NO \rightarrow OH + NO_2$ (2)

or $HO_2 + O \rightarrow OH + O_2$ (3)

or $HO_2 + O_3 \rightarrow OH + O_2 + O_2$ (4)



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or $HO_2 + O \rightarrow OH + O_2$ (3)

or $HO_2 + O_3 \rightarrow OH + O_2 + O_2$ (4)

HO_2 loss step (2):

$$\left.\begin{aligned}
&\cancel{OH} + O_3 \rightarrow \cancel{HO_2} + O_2\\
&\cancel{HO_2} + NO \rightarrow \cancel{OH} + NO_2\\
\hline
&\text{Net:}\quad O_3 + NO \rightarrow O_2 + NO_2
\end{aligned}\right.$$

This is followed quickly by:

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

Yielding final "net":

$$O_3 \rightarrow O + O_2$$

Null cycle

with respect to production & loss of odd oxygen

HO_x : OH and HO_2

OH and HO_2 are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

HO_2 formation:

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (1)$$

HO_2 loss:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (2)$$

or $$HO_2 + O \rightarrow OH + O_2 \qquad (3)$$

or $$HO_2 + O_3 \rightarrow OH + O_2 + O_2 \qquad (4)$$

HO_2 loss step (3):

$$\left.\begin{array}{lrl} & OH + O_3 & \rightarrow HO_2 + O_2 \\ & HO_2 + O & \rightarrow OH + O_2 \\ \hline \text{Net:} & O_3 + O & \rightarrow O_2 + O_2 \end{array}\right\}$$

HO_2 loss step (4):

$$\left.\begin{array}{lrl} & OH + O_3 & \rightarrow HO_2 + O_2 \\ & HO_2 + O_3 & \rightarrow OH + O_2 + O_2 \\ \hline \text{Net:} & O_3 + O_3 & \rightarrow O_2 + O_2 + O_2 \end{array}\right\}$$

Catalytic Ozone (Odd Oxygen) Loss Cycles

Odd Oxygen Loss - HO_x

$$\frac{d\,(\text{Odd Oxygen})}{dt} = -\,2\,k_4\,[HO_2][O_3]\;-2\,k_3\,[HO_2][O] \qquad \text{Eq (7)}$$

The reactions:

$$HO_2 + O \rightarrow OH + O_2 \qquad (3)$$
$$HO_2 + O_3 \rightarrow OH + O_2 + O_2 \qquad (4)$$

are rate limiting steps for O_3 loss by two catalytic cycles:

Cycle (1) Net :

$$O_3 + O \rightarrow 2\,O_2$$

Cycle (2) Net :

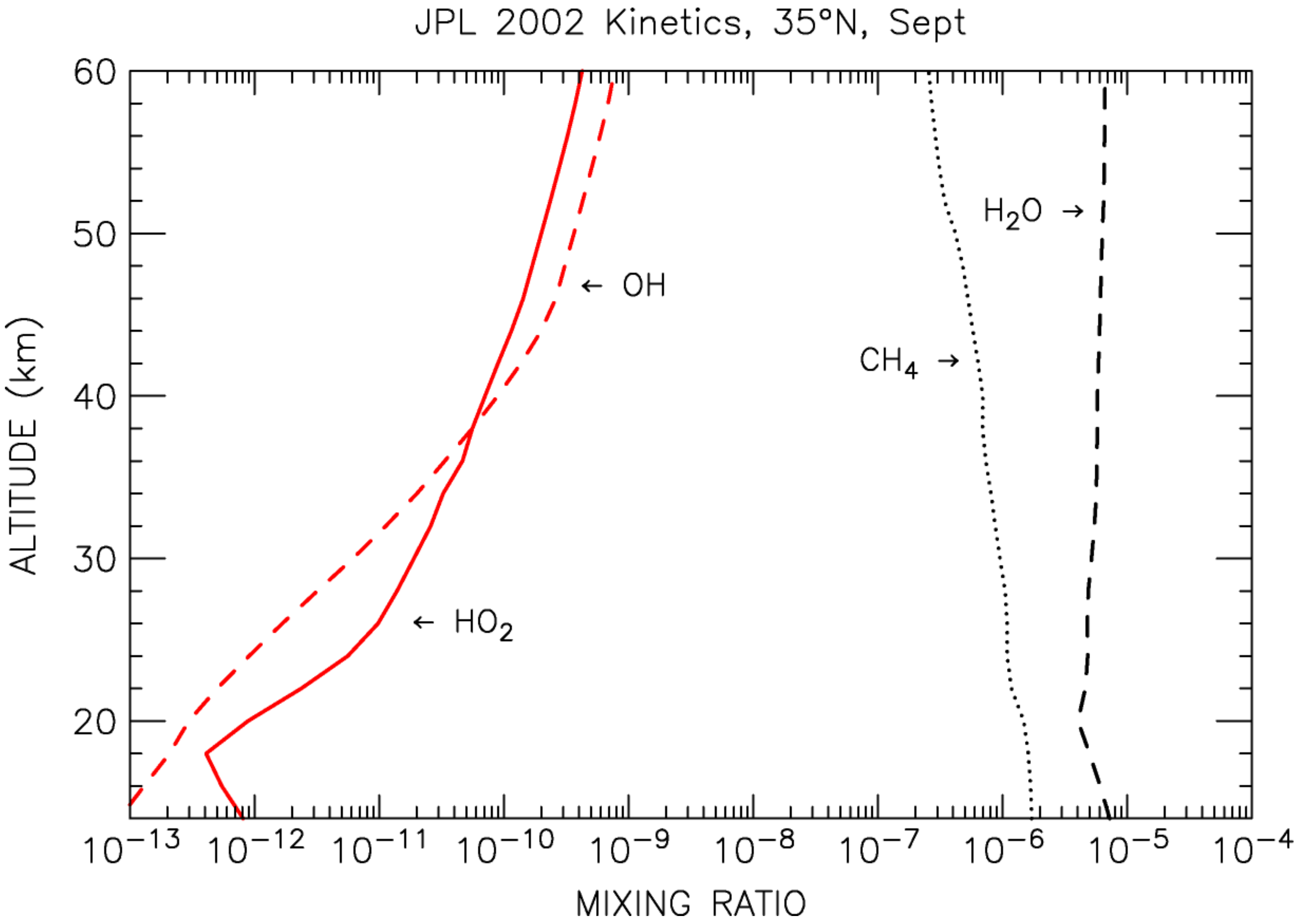
$$O_3 + O_3 \rightarrow 3\,O_2$$

As a convenient short hand, **we consider HO_2 to be odd oxygen**

Then:

clear now that reactions (3) and (4) each consume two odd oxygens at rates determined by $2\,k_3\,[HO_2]\,[O]$ and $2\,k_4\,[HO_2][O_3]$

OH, HO_2, H_2O, and CH_4

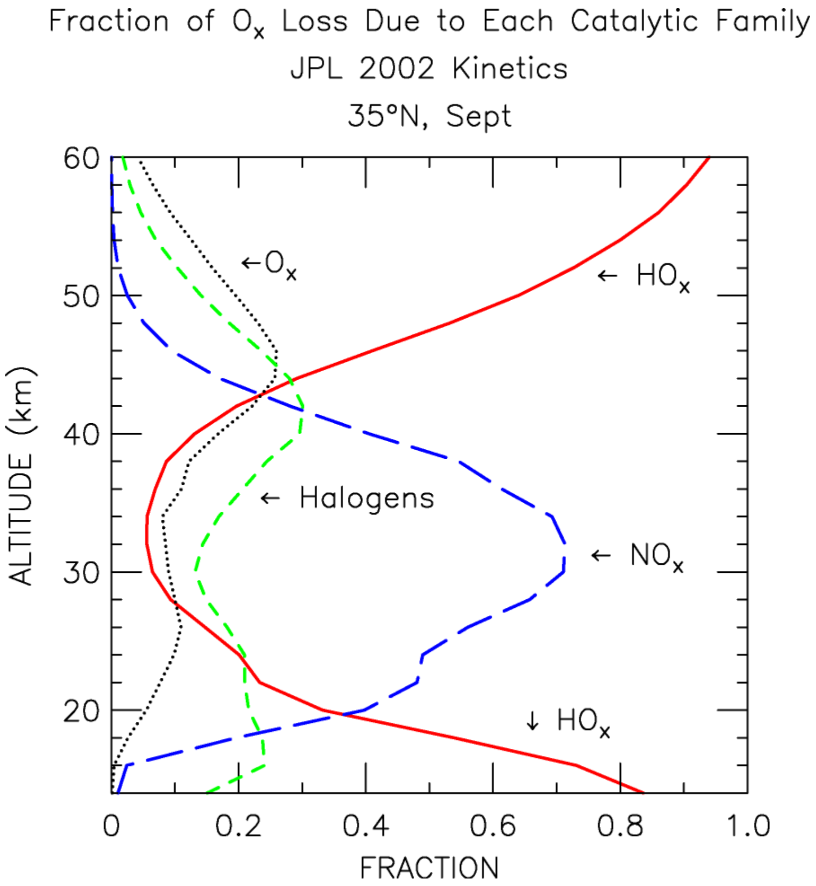


Odd Oxygen Loss - HO_x

At what altitudes will loss of ozone by these rate limiting steps be dominant ?

$HO_2 + O \rightarrow OH + O_2$ (3)
$HO_2 + O_3 \rightarrow OH + O_2 + O_2$ (4)

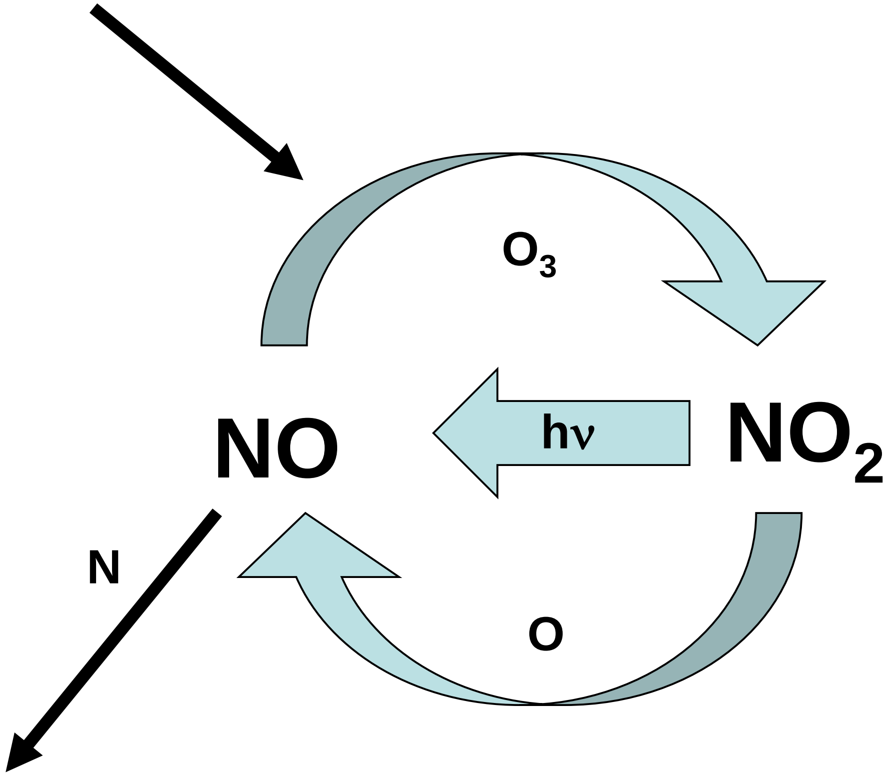
One dominates at low altitude, the other at high altitude ⇒ which is which ?!?



NO_x : NO and NO_2

NO and NO_2 are central to stratospheric and tropospheric photochemistry

Stratospheric **Production :** **$O^1D + N_2O \rightarrow NO + NO$**



Final sinks : **$N + NO \rightarrow N_2 + O$ (uppermost stratosphere)**
HNO_3 solubility & rainout (lowermost stratosphere)

NO_x : NO and NO_2

NO and NO_2 are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

NO_2 formation:

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

NO_2 loss:

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

or

$$NO_2 + O \rightarrow NO + O_2 \qquad (3)$$

NO_2 loss step (2):

$$\begin{array}{lll} & NO + O_3 & \rightarrow NO_2 + O_2 \\ & NO_2 + h\nu & \rightarrow NO + O \\ \hline \text{Net:} & O_3 + h\nu & \rightarrow O + O_2 \end{array}$$

NO_2 loss step (3):

$$\begin{array}{lll} & NO + O_3 & \rightarrow NO_2 + O_2 \\ & NO_2 + O & \rightarrow NO + O_2 \\ \hline \text{Net:} & O_3 + O & \rightarrow 2\,O_2 \end{array}$$

Can show:

$$\frac{dO_3}{dt} + \frac{dO}{dt} = \frac{d\,(\text{Odd Oxygen})}{dt} = -2\,k_3\,[NO_2][O]$$

As a convenient short hand, **we consider NO_2 to be odd oxygen**

NO_y versus N_2O

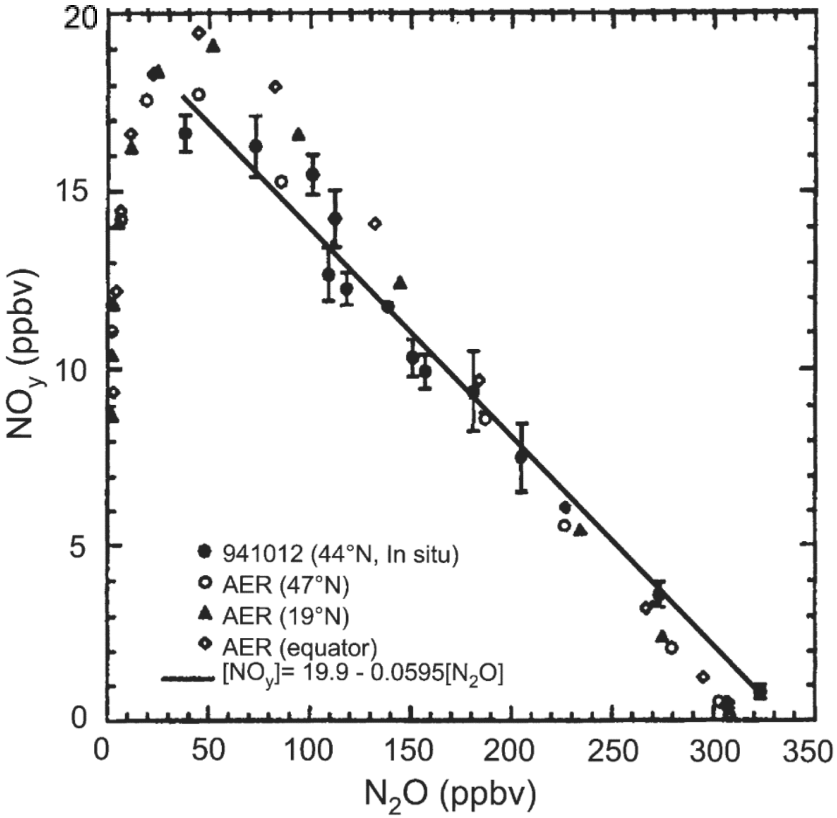
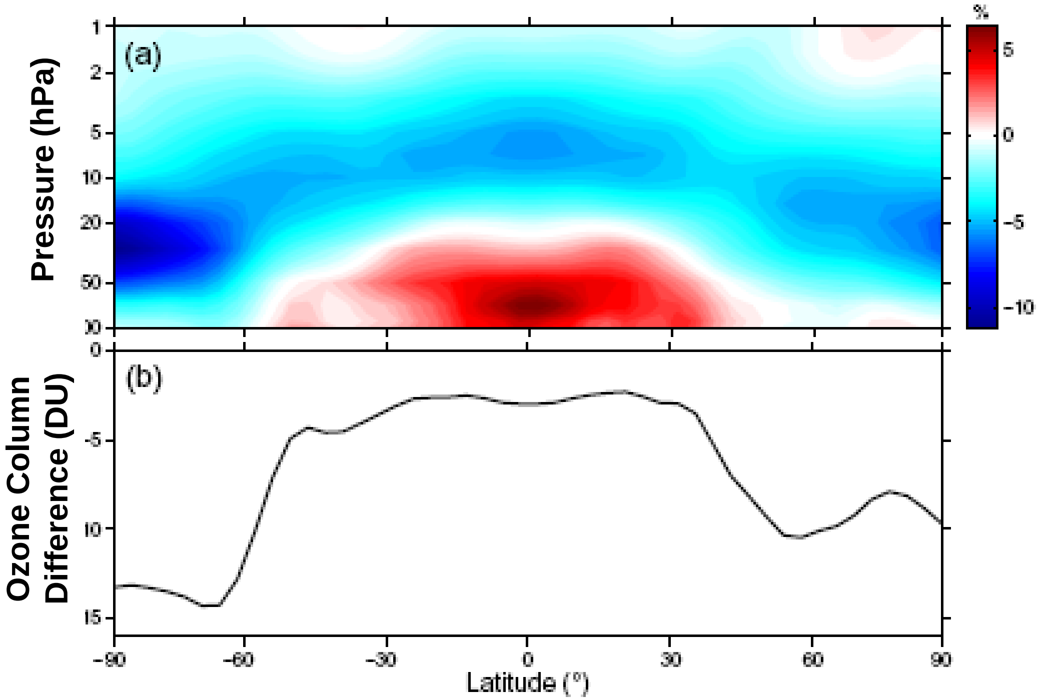


Figure 6-8, WMO (1999)

$NO_y = NO + NO_2 + NO_3 + 2 \times N_2O_5 + HONO + HONO_2 + HO_2NO_2 + ClNO_3 + BrNO_3$

N_2O and Stratospheric Ozone



Revell *et al.*, *ACP*, 2012

Stratospheric O_3 difference in the 2090s found for a computer simulation run using N_2O from RCP 8.5 minus that of a simulation using N_2O from RCP 2.6

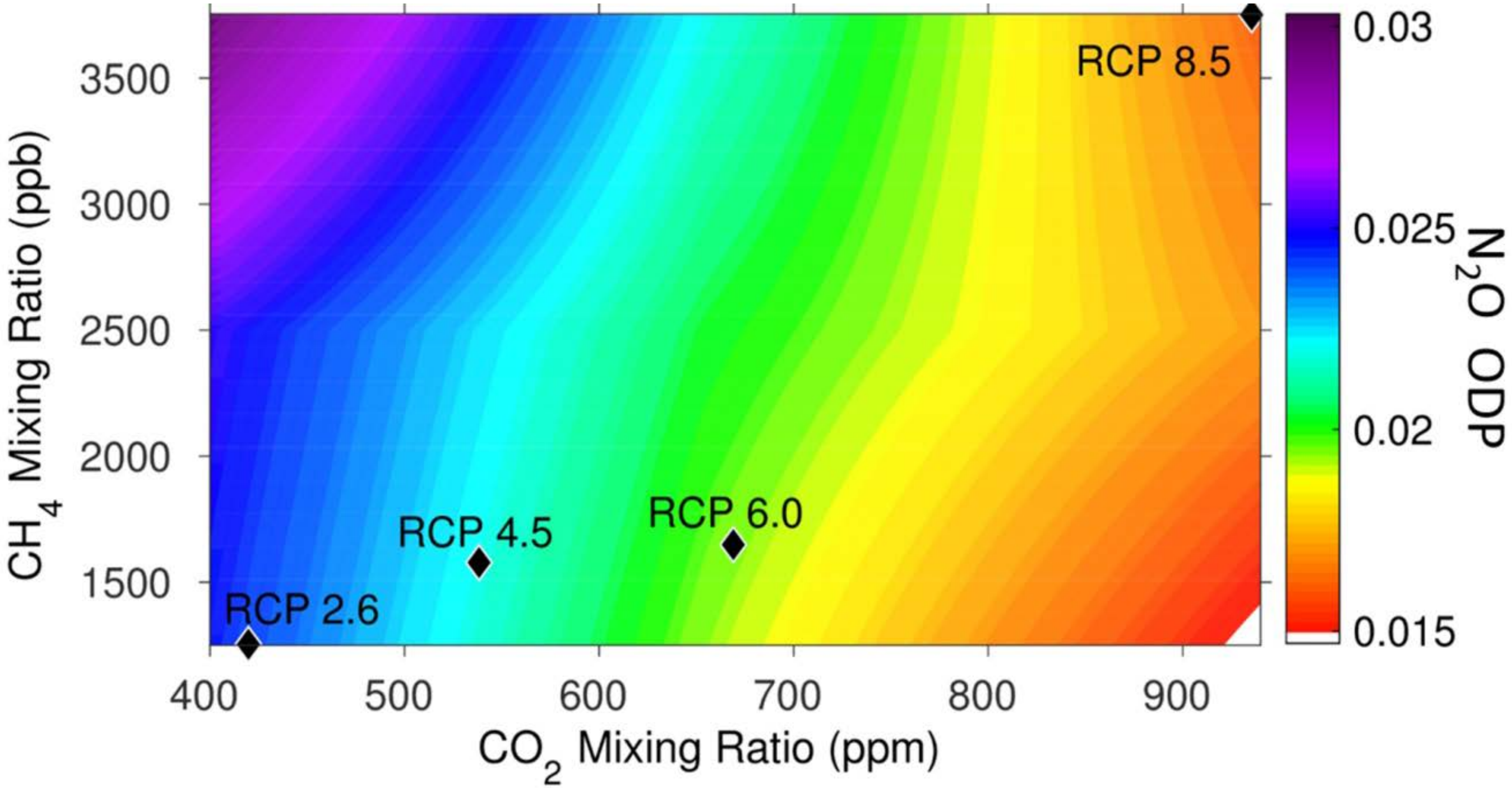
Rising N_2O leads to:

a) ozone loss in the middle & upper stratosphere by increasing the speed of NO and NO_2 (NO_x) mediated loss cycles.

b) speeds up the rate of $OH+NO_2+M \rightarrow HNO_3+M$ & $ClO+NO_2+M \rightarrow ClNO_3+M$ in the lowermost stratosphere, leading to slower ozone loss by these cycles & therefore more O_3 where these cycles dominate total loss of O_3

Computer models project stratospheric column O_3 will decline as N_2O rises

Future ODP of N_2O depends on CH_4 & CO_2



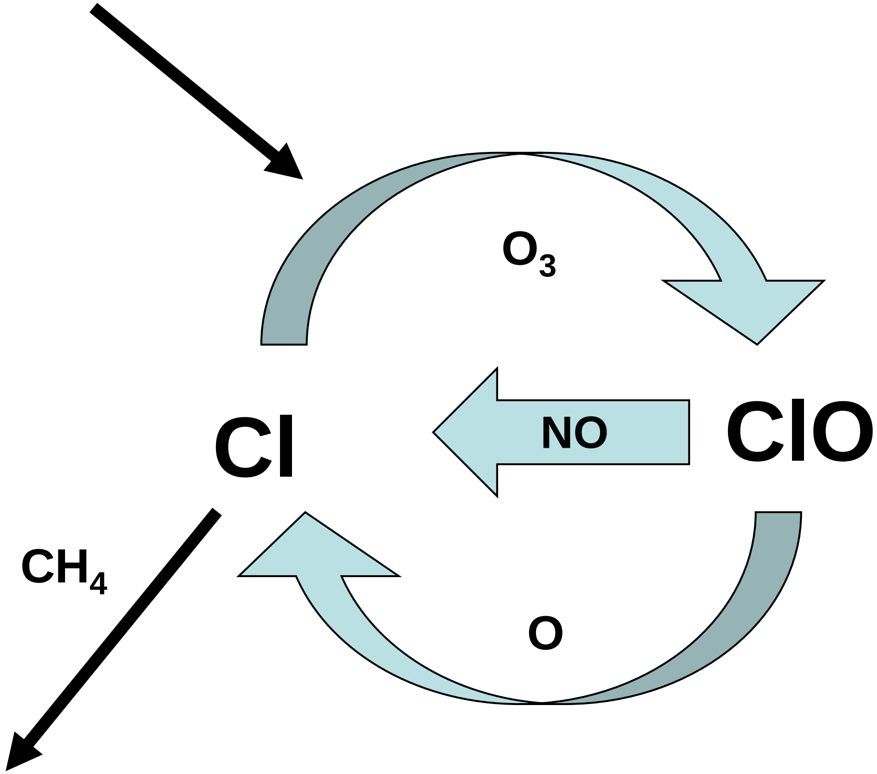
ODP of N_2O in year 2100 found by a Swiss three dimensional, chemistry climate model called SOCOL (Solar Climate Ozone Links)

Revell et al., GRL, 2015

ClO_x : ClO and Cl

ClO is central to stratospheric photochemistry, at mid-latitudes and polar regions

Production : **CFCs +hν→ Inorganic chlorine**



Final sinks : **HCl solubility & rainout (lowermost stratosphere)**

ClO_x : ClO and Cl

ClO is central to stratospheric photochemistry, at mid-latitudes and polar regions:

Rapid inner cycle:

ClO formation:

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

ClO loss:

$$ClO + NO \rightarrow Cl + NO_2 \qquad (2)$$

or $$ClO + O \rightarrow Cl + O_2 \qquad (3)$$

ClO loss step (2):

$$\begin{array}{ll} & Cl + O_3 \rightarrow ClO + O_2 \\ & ClO + NO \rightarrow Cl + NO_2 \\ \hline \text{Net:} & O_3 + NO \rightarrow NO_2 + O_2 \\ \text{Followed by:} & NO_2 + h\nu \rightarrow NO + O \\ \hline \text{Final net:} & O_3 + h\nu \rightarrow O + O_2 \end{array}$$

ClO loss step (3):

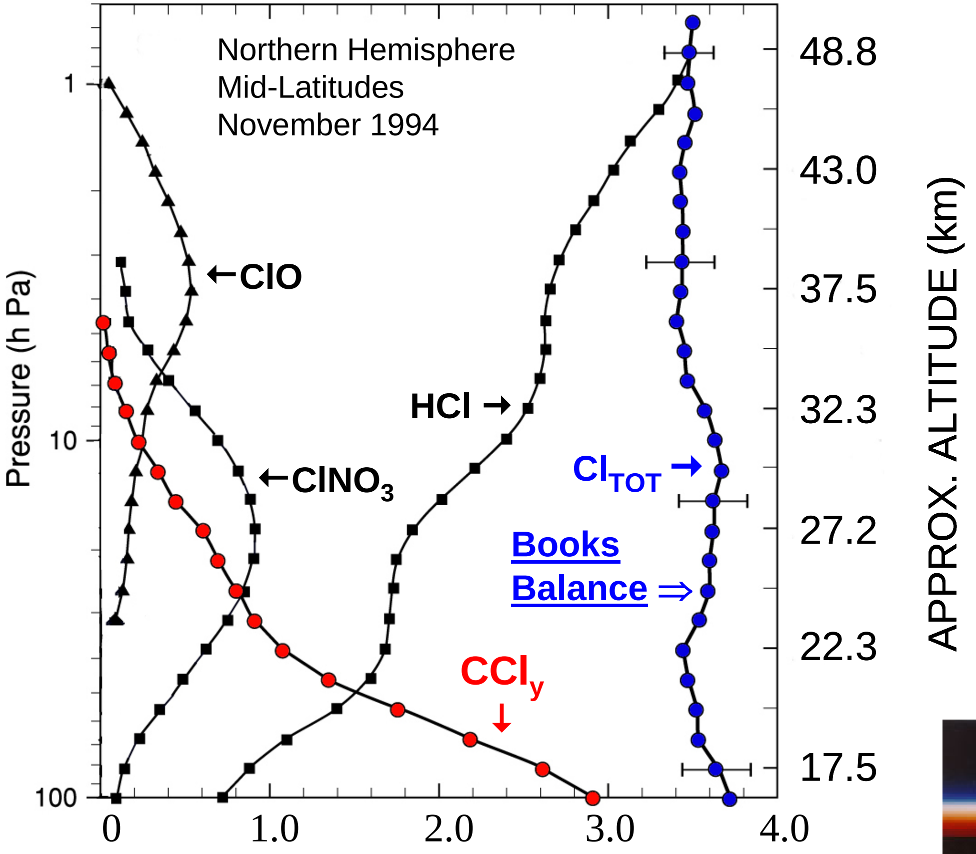
$$\begin{array}{ll} & Cl + O_3 \rightarrow ClO + O_2 \\ & ClO + O \rightarrow Cl + O_2 \\ \hline \text{Net:} & O_3 + O \rightarrow 2\,O_2 \end{array}$$

Can show:

$$\frac{dO_3}{dt} + \frac{dO}{dt} = \frac{d\,(\text{Odd Oxygen})}{dt} = -\,2\,k_3\,[ClO][O]$$

As a convenient short hand, **we consider ClO to be odd oxygen**

Proof Halocarbons Reach The Stratosphere



ABUNDANCE (parts per billion)

Zander *et al.*, *GRL*, 1996

Trends in Ozone, ~40 km

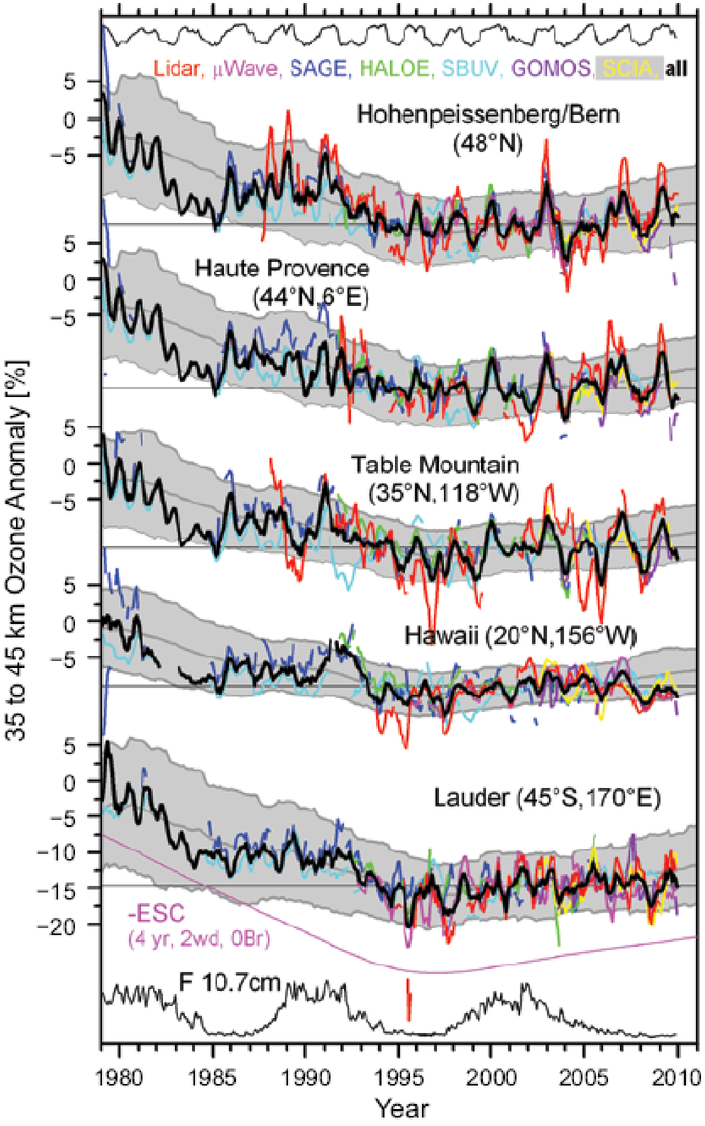
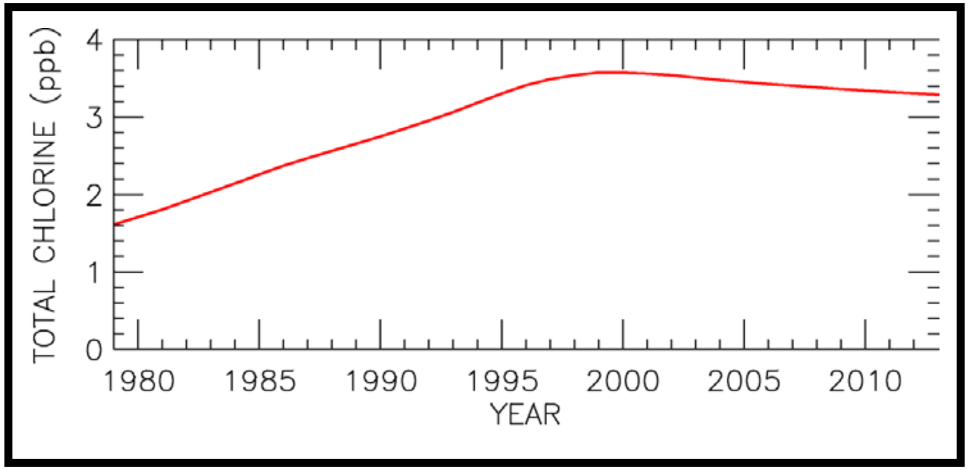


Figure 2-5, WMO/UNEP 2010

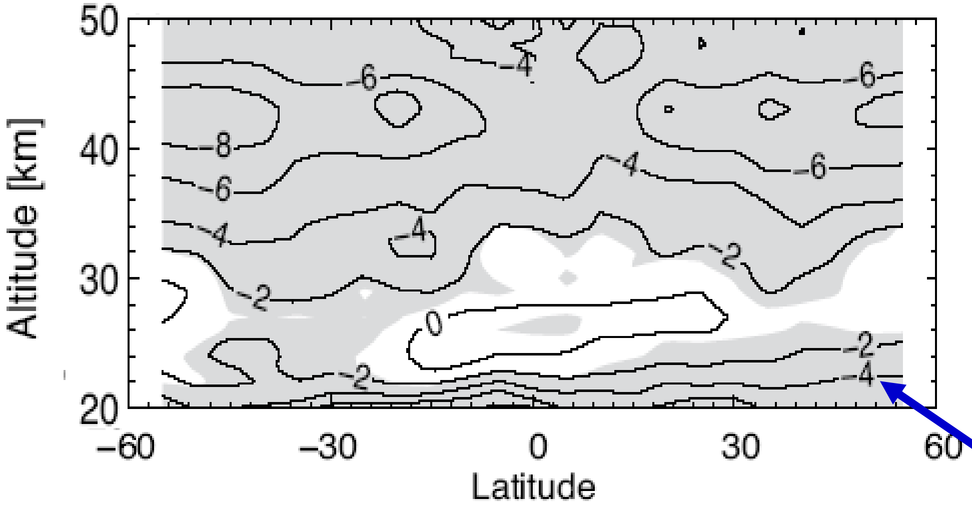
Grey: range of model calculations, where models are forced by rising levels of stratospheric halogens

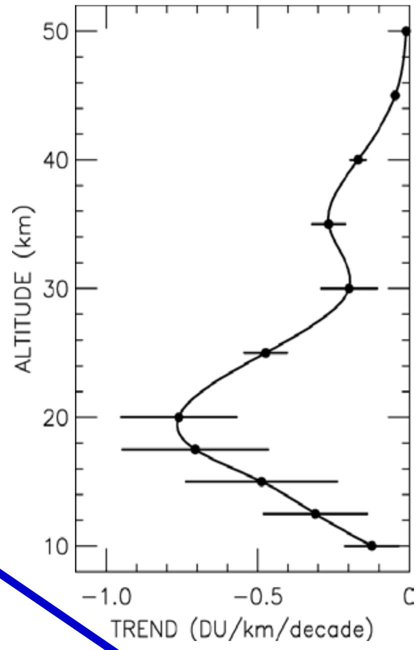
Trends in ozone at 40 km are "well understood" ozone generally ***anti-correlates*** with time history of stratospheric chlorine loading



Trends in Ozone vs Altitude

Units: % per decade



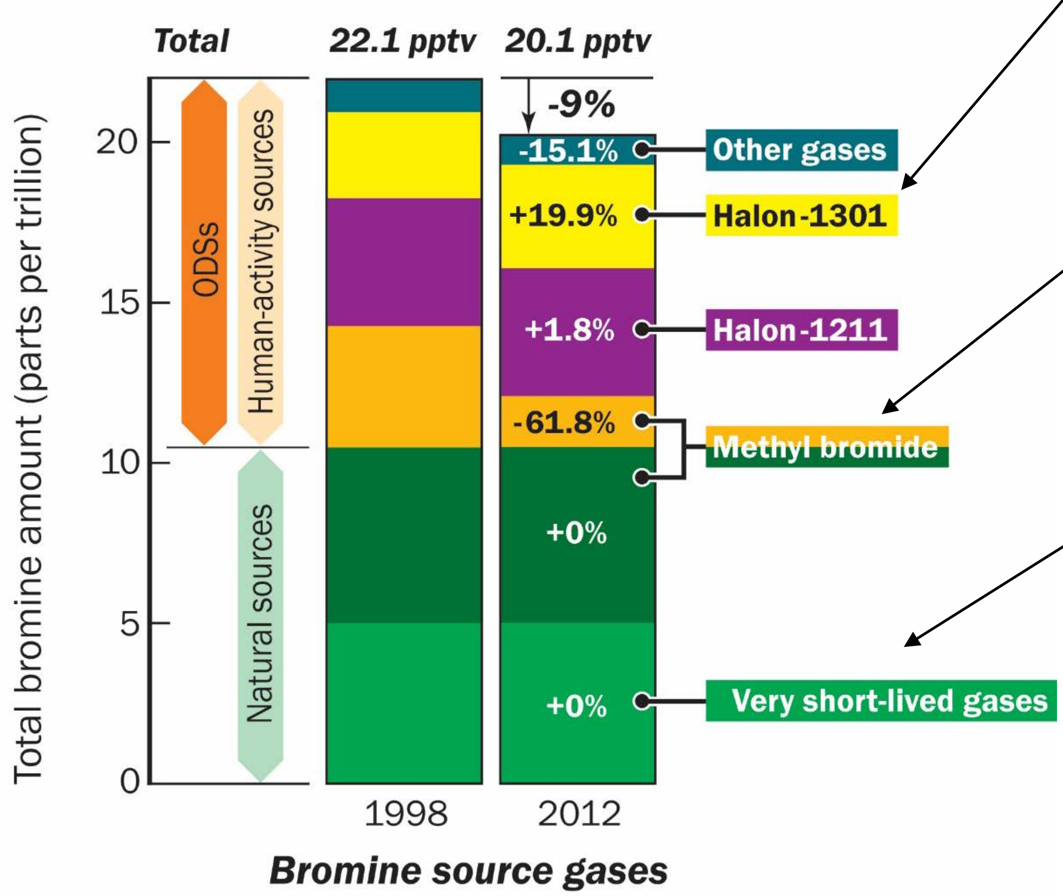


Trends in ozone as a function of latitude and altitude, for the time period 1979 to 2005, from the NASA SAGE I & SAGE II instruments. Shaded region indicates significance at the 2σ level.

Figure 2-4, WMO/UNEP 2010

Two complications to understanding ozone trends in the lower stratosphere: aerosol surface area and bromine

Bromine Source Gases



Halons:

- fire extinguishing agents
- production in developed world halted by Montreal Protocol
- present emissions primarily from "banks"

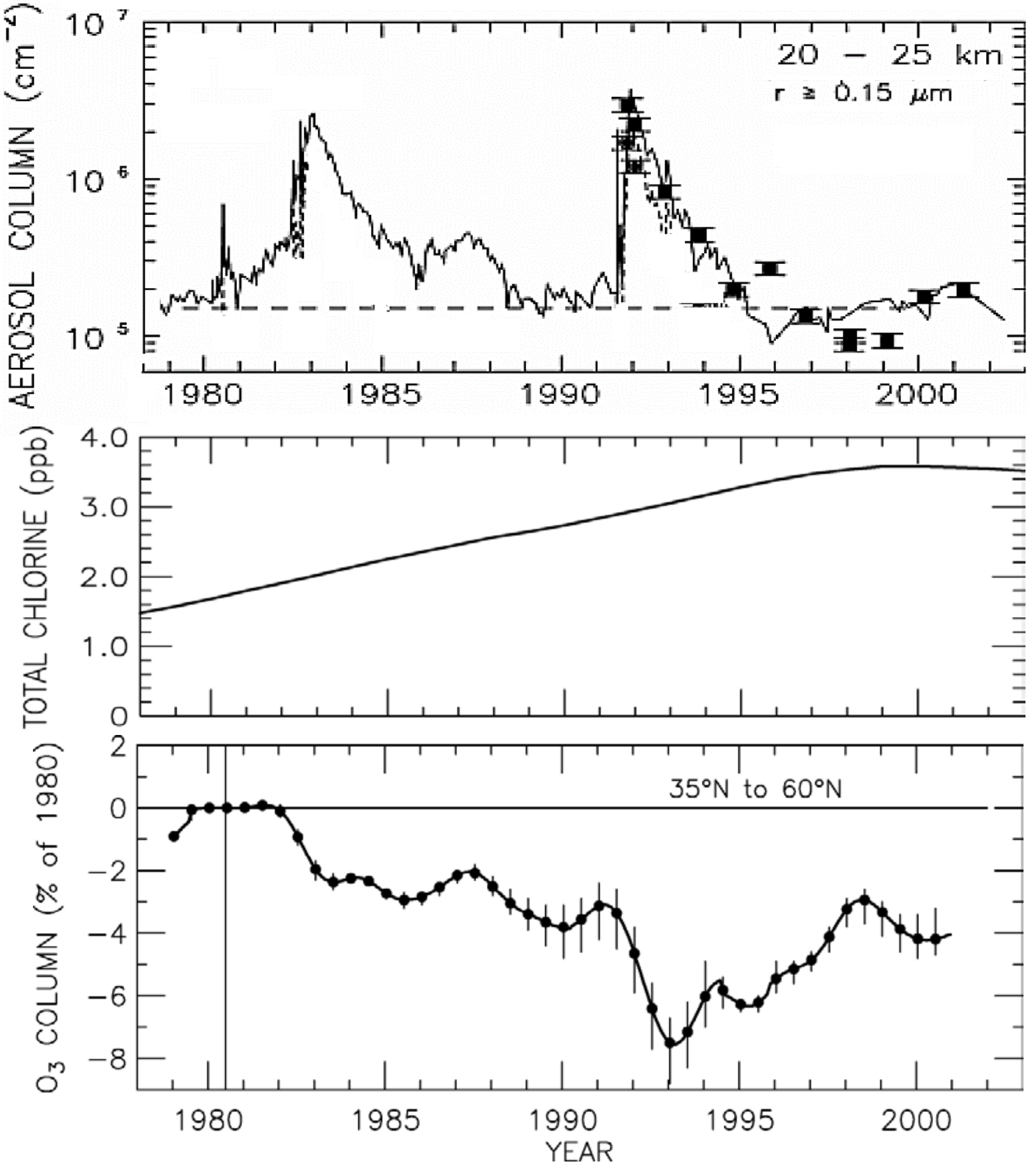
CH_3Br:

- fumigant; released by biomass burning
- production halted by Montreal Protocol
- significant natural & human sources

VSL Gases (e.g., $CHBr_3$, CH_2Br_2):

- emitted mainly by ocean biology
- not considered in most ozone calcs
- chemistry of decomposition products subject of active research

Total Column Ozone Time Series, NH



Stratospheric aerosol loading,

Deshler et al., 2003.

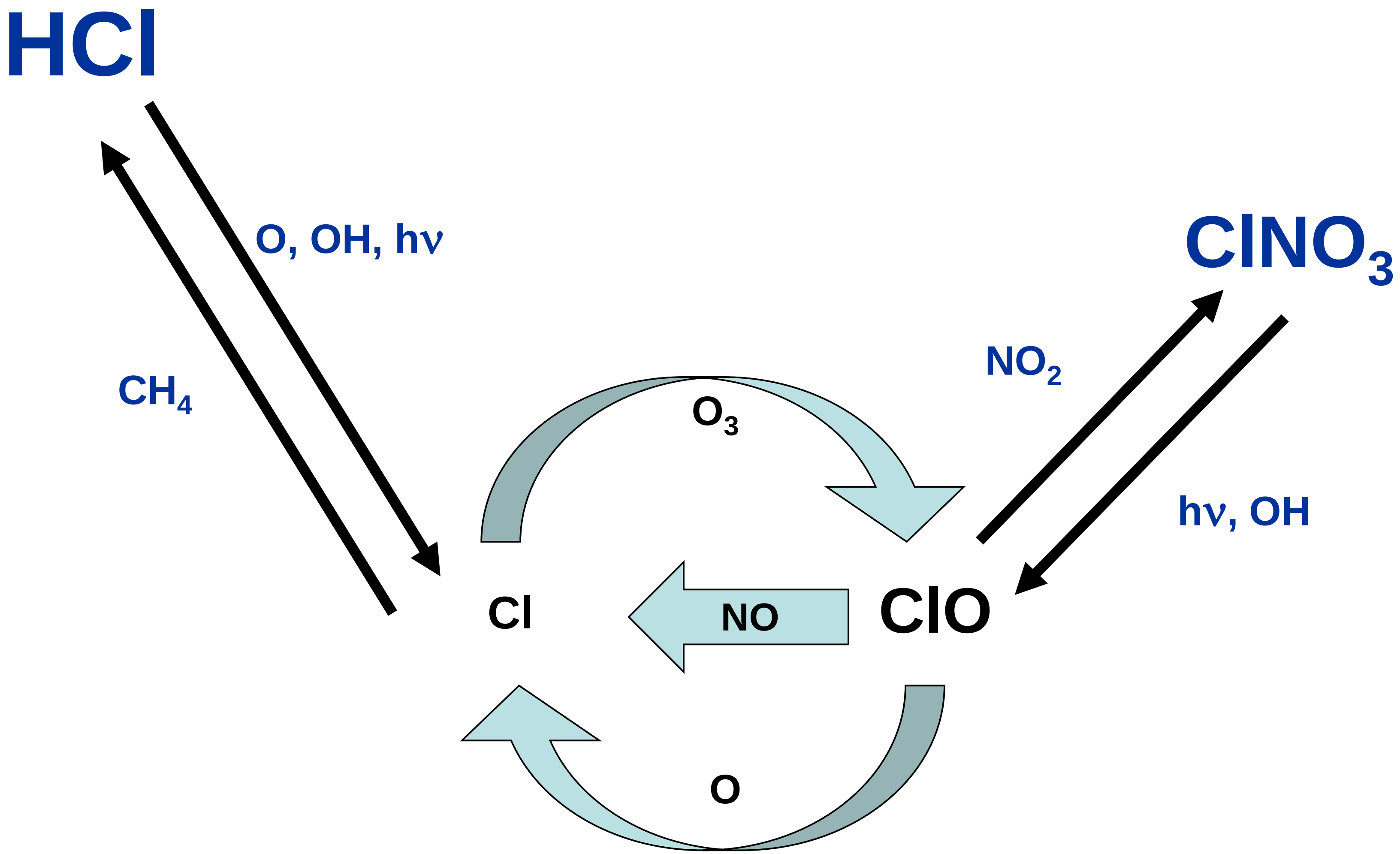
Stratospheric chlorine

Change in ozone column relative to 1980, 35 to 60°N

WMO/UNEP 2006 Ozone Report

Chemical reaction on surface of volcanic aerosol couples NO_2 and HNO_3

- As sulfate aerosol rises, NO_x (NO and NO_2) falls
- As NO_2 drops, ClNO2 falls and ClO rises

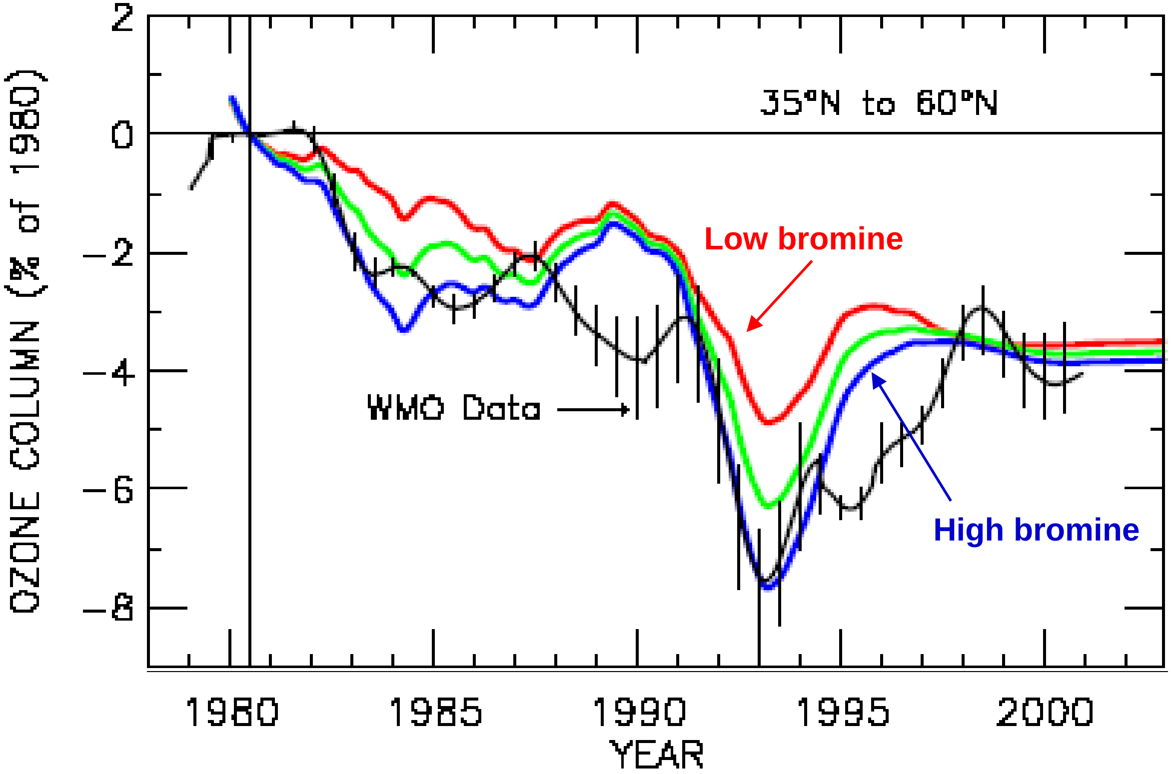


Ozone responds to:

a) rise and fall of chlorine

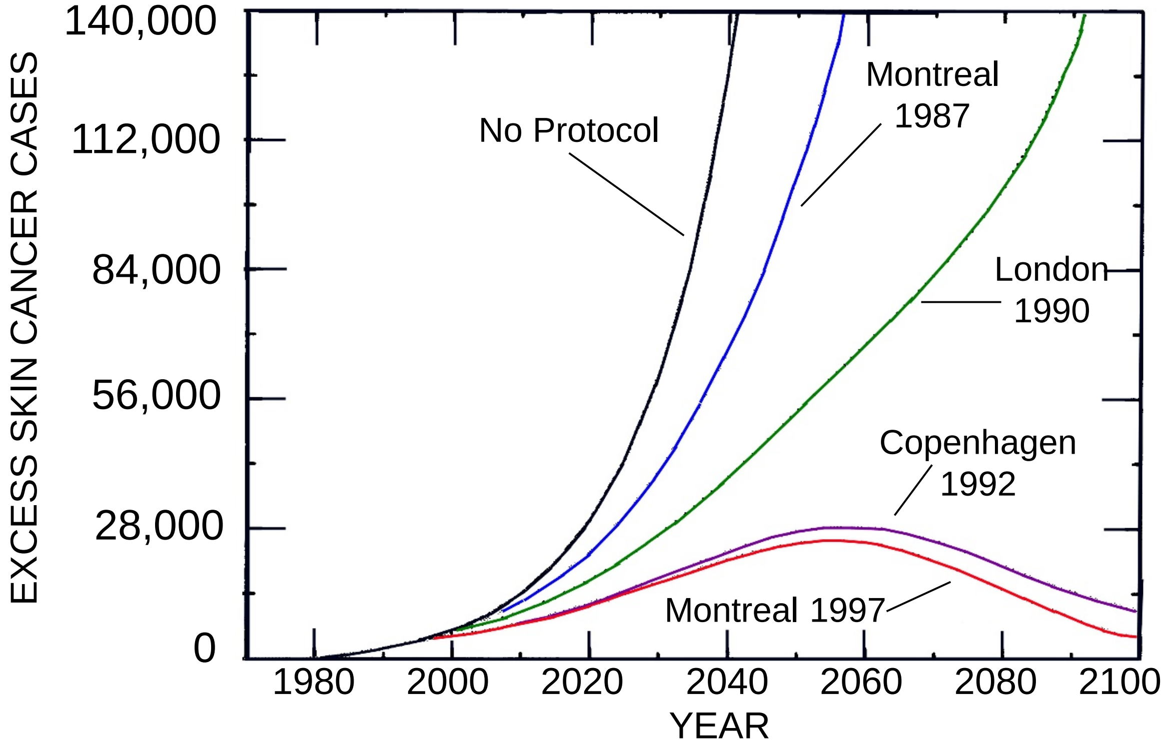
b) volcanic perturbations to aerosol loading

c) amount of bromine in lowermost stratosphere



Salawitch *et al.*, *GRL*, 2005

EXCESS SKIN CANCER CASES IN THE UNITED STATES, PER YEAR, DUE TO OZONE DEPLETION FOR VARIOUS CFC SCENARIOS



Longstreth *et al.*, *J. of Photochemistry and Photobiology B*, 46, 20–39, 1998.

See also Slaper *et al.*, Estimates of ozone depletion and skin cancer incidence to examine the Vienna Convention achievements, *Nature*, *384*, 256–258, 1996, who state:

> The no-restrictions and Montreal Protocol scenarios produce a runaway increase in skin cancer incidence, up to a quadrupling and doubling, respectively, by year 2100.