# Mid-Latitude Stratospheric Chemistry

## AOSC/CHEM 433 & AOSC/CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/spr2022
https://myelms.umd.edu/courses/137772

**Today:**
- **Background on CFCs**
- **Ozone Depletion Potenial**
- **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 15**

**31 March 2021**

# Photolysis Frequency

For a specific spectral interval, the photolysis frequency (***partial J value***) of a gas is given by the product of its absorption cross section and the solar irradiance:

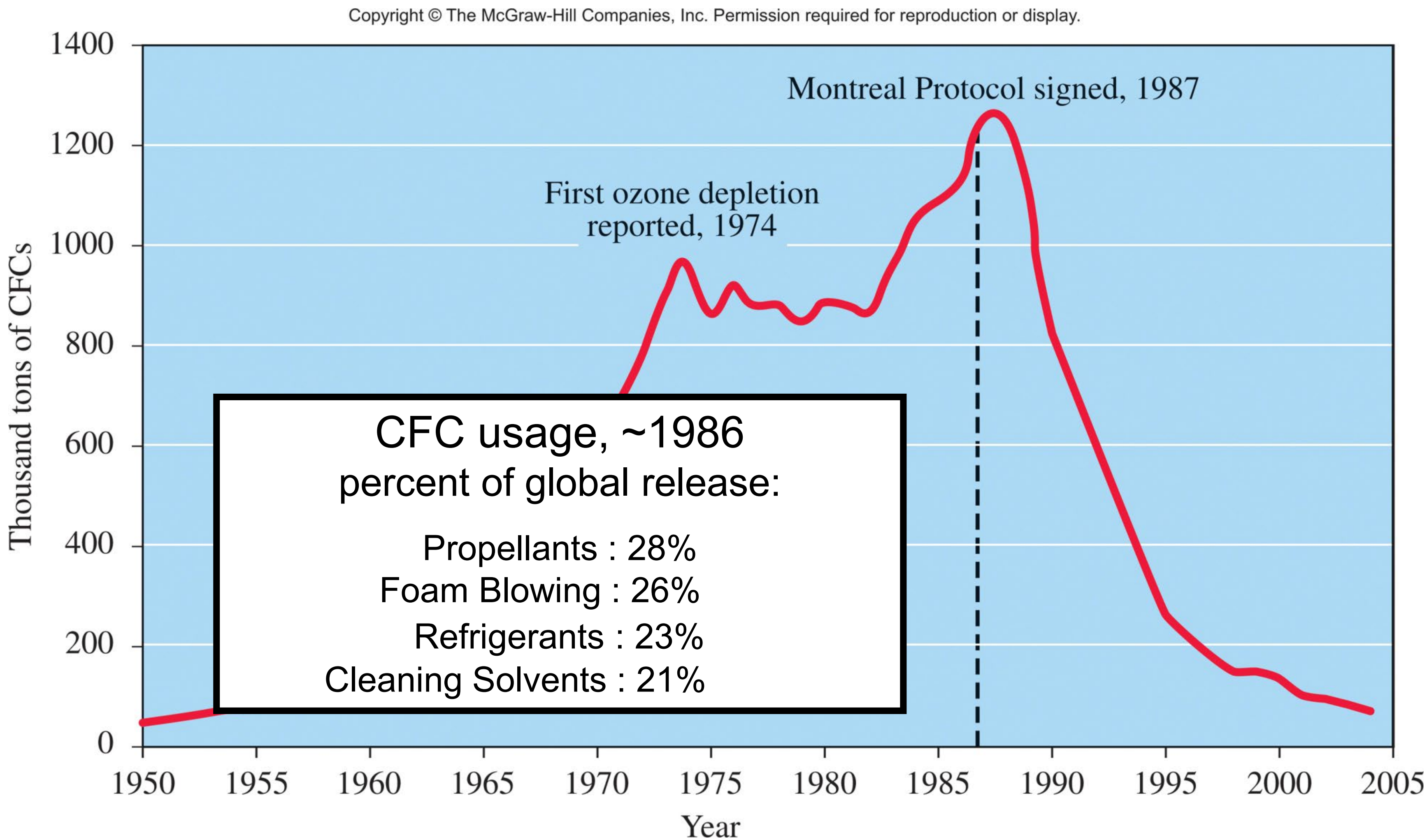
$$J_{gas}(z,\lambda) = \text{Quantum\_Yield}(\lambda)\ \sigma_{gas}(\lambda,T)\ F(z,\lambda) \quad : \text{Units: } s^{-1}\ nm^{-1}$$

The total ***photolysis frequency*** (***J value***) is found by integrating $J_{gas}(z,\lambda)$ over all wavelengths for which the gas photodissociates:

$$J_{gas}(z) = \int_{\lambda_{min}}^{\lambda_{max}} J_{gas}(z,\lambda)\, d\lambda = \int_{\lambda_{min}}^{\lambda_{max}} \text{Quantum\_Yield}(\lambda)\sigma_{gas}(\lambda,T)\ \underbrace{F(z,\lambda)}\ d\lambda \qquad \text{Units: } s^{-1}$$

***Second column of table, prior slide, gives numerical values of this quantity***

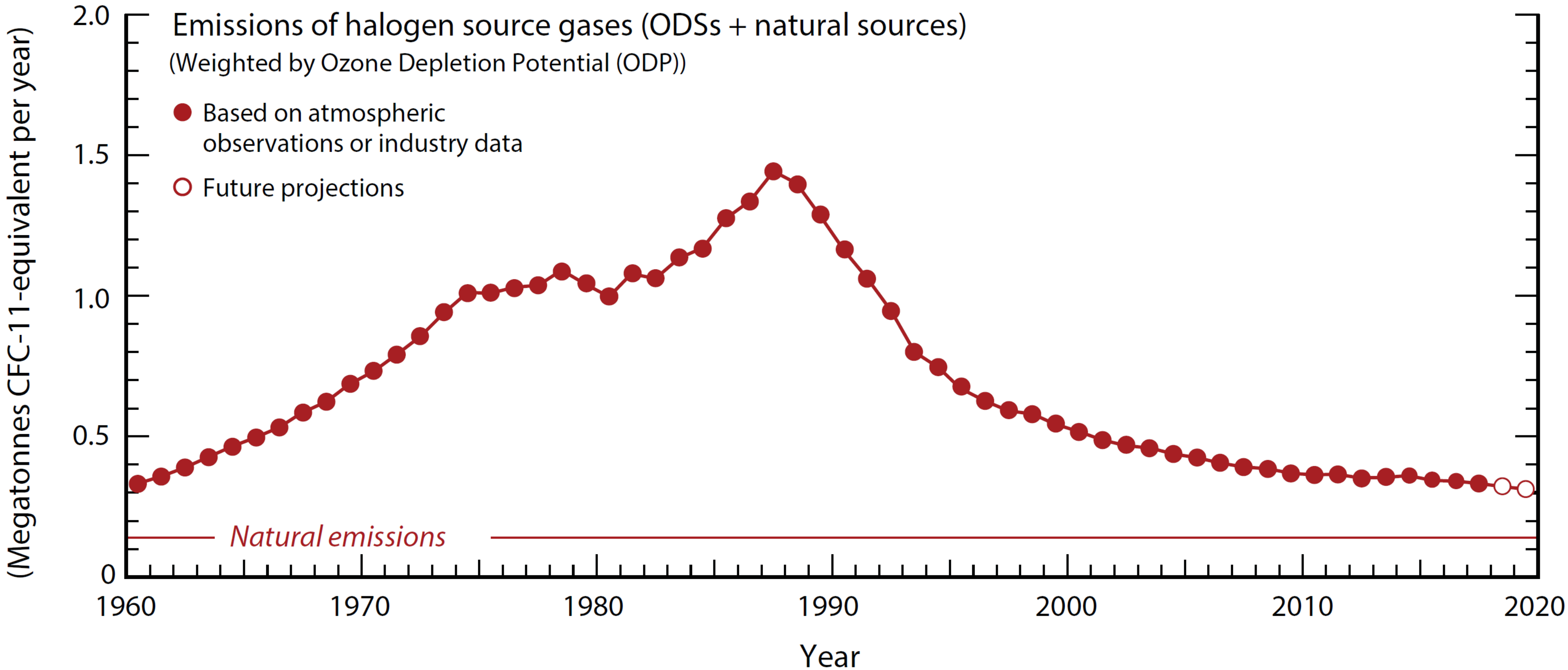
# Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons




Global Production of CFCs, Fig. 2.19, Chemistry in Context

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

Global Emmisions of all CFCs, **Fig Q0-1, *WMO/UNEP Twenty QAs Ozone***

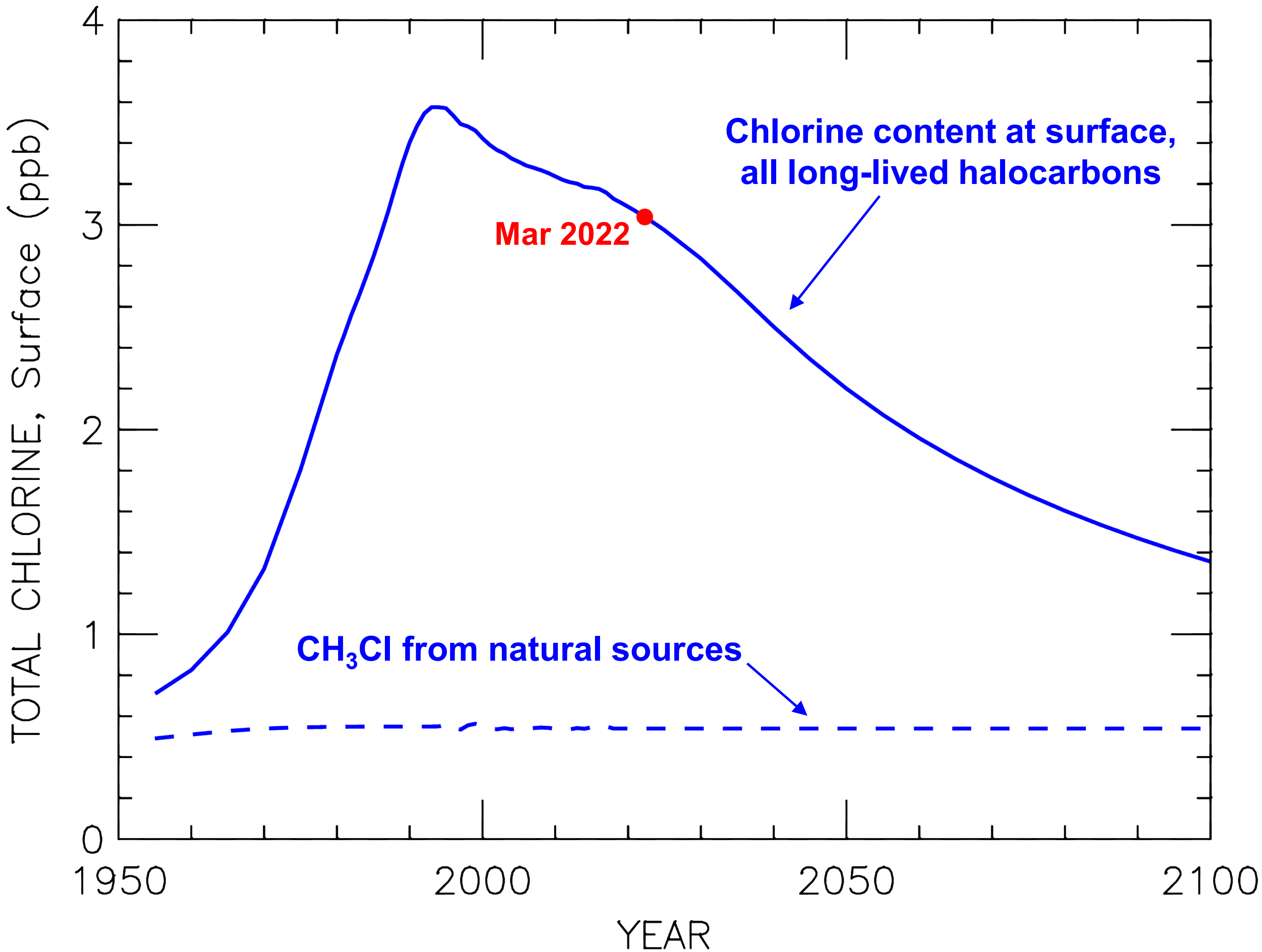



**Why was the introduction of Freon-12 as a refrigerant gas in the 1930s hailed as a great triumph?**

**By what mechanism does Freon-12 fall apart and in what region of the atmosphere does this occur?**

# Montreal Protocol Has Banned Industrial Production of CFCs & Other ODS

Projections Based on 2018 World Meteorological Organization
Scientific Assessment of Ozone Depletion Report




2018 WMO Scientific Assessment of Ozone Depletion Report:
https://www.esrl.noaa.gov/csd/assessments/ozone/2018

# Chlorine Source Gases

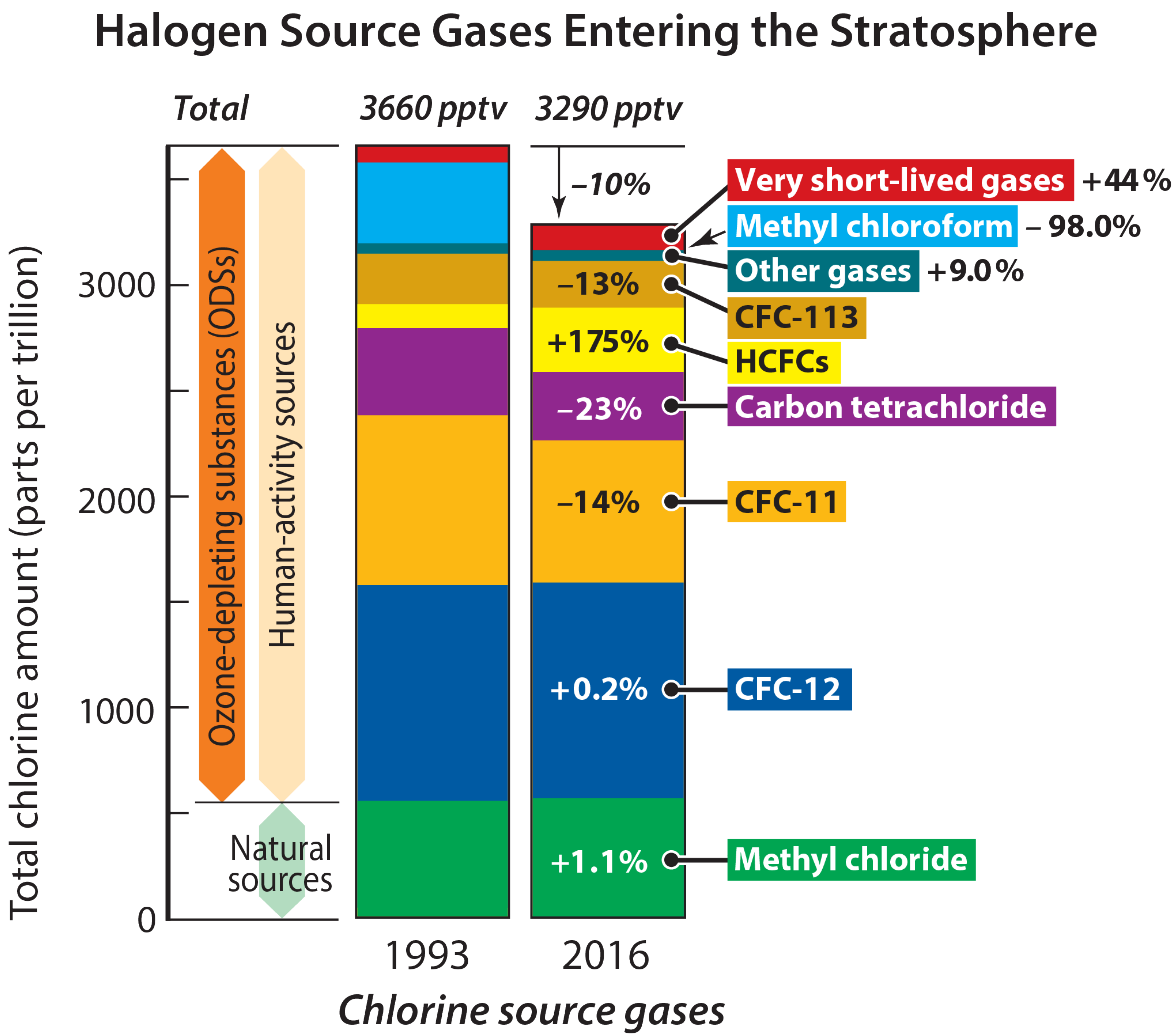



**Fig Q6-1, *WMO/UNEP Twenty QAs Ozone***

# Ozone Depletion Potential and Halocarbons

**Table Q6-1.** Atmospheric lifetimes, global emissions, Ozone Deletion Potentials, and Global Warming Potentials of some halogen source gases and HFC substitute gases.

| Gas | Atmospheric Lifetime (years) | Ozone Depletion Potential (ODP)[b] |
|---|---|---|
| **Halogen Source Gases** | | |
| **Chlorine Gases** | | |
| CFC-11 ($CCl_3F$) | 52 | 1 |
| Carbon tetrachloride ($CCl_4$) | 32 | 0.87 |
| CFC-113 ($CCl_2FCClF_2$) | 93 | 0.81 |
| CFC-12 ($CCl_2F_2$) | 102 | 0.73 |
| Methyl chloroform ($CH_3CCl_3$) | 5.0 | 0.14 |
| HCFC-141b ($CH_3CCl_2F$) | 9.4 | 0.102 |
| HCFC-142b ($CH_3CClF_2$) | 18 | 0.057 |
| HCFC-22 ($CHF_2Cl$) | 12 | 0.034 |
| Methyl chloride ($CH_3Cl$) | 0.9 | 0.015 |
| **Bromine Gases** | | |
| Halon-1301 ($CBrF_3$) | 65 | 15.2 |
| Halon-1211 ($CBrClF_2$) | 16 | 6.9 |
| Methyl bromide ($CH_3Br$) | 0.8 | 0.57 |
| **Hydrofluorocarbons (HFCs)** | | |
| HFC-23 ($CHF_3$) | 228 | 0 |
| HFC-143a ($CH_3CF_3$) | 51 | 0 |
| HFC-125 ($CHF_2CF_3$) | 30 | 0 |
| HFC-134a ($CH_2FCF_3$) | 14 | 0 |
| HFC-32 ($CH_2F_2$) | 5.4 | 0 |
| HFC-152a ($CH_3CHF_2$) | 1.6 | 0 |
| HFO-1234yf ($CF_3CF{=}CH_2$) | 0.03 | 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 :

$\tau$ is the global atmospheric lifetime

$MW$ is the molecular weight

$n$ is the number of chlorine or bromine atoms

$\alpha$ is the effectiveness of ozone loss by bromine relative to ozone loss by chlorine

# Ozone Depletion

**According to Section 2.8 of Chemistry in Context, how much depletion of stratospheric ozone at mid-latitudes (60°S to 60°N) has occurred?**

**According to the Question 12 of the WMO/UNEP QAs, how much depletion of the Global Total Ozone layer has occurred?**

**Also, state whether your are either "good" or "concerned" with the different estimates for depletion of the ozone layer given in Question 12 of the WMO/UNEP QAs, compared to Section 28 of Chemistry in Context (i.e, your answer to the prior question).**

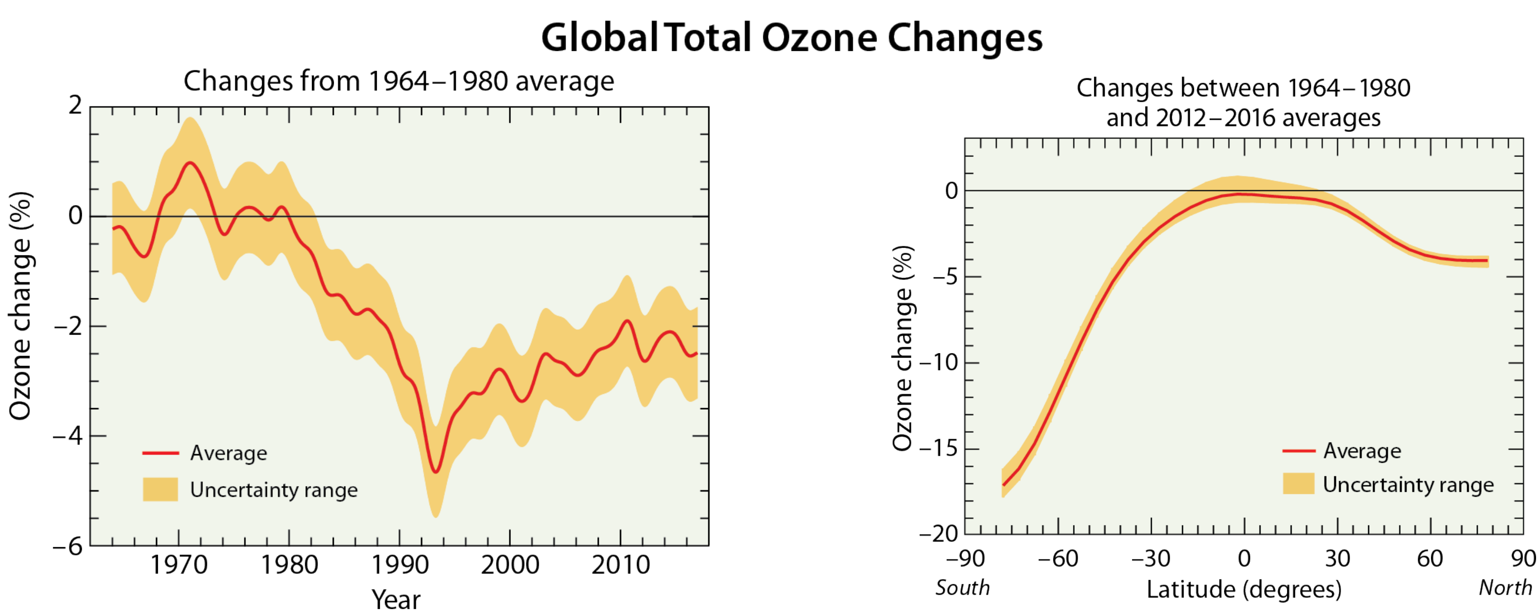
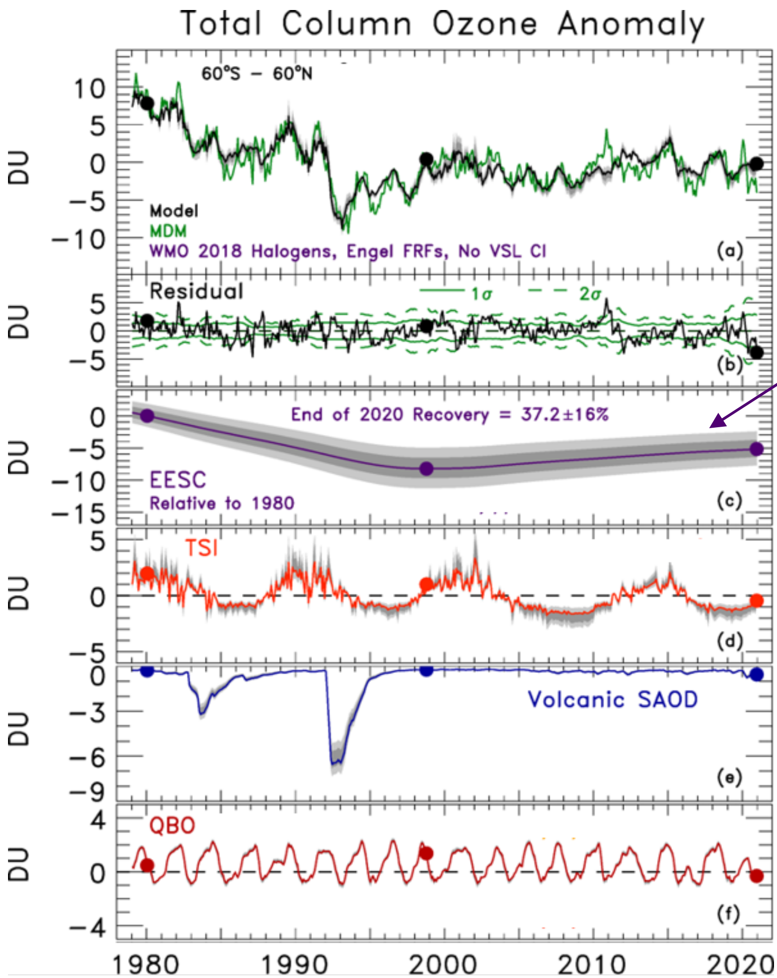



Fig Q12-1, *WMO/UNEP Twenty QAs Ozone*

# Mid-Latitude Ozone Depletion

***Total column ozone anomaly*** is deseasonalized, cosine latitude weighted average of total column ozone collected between 60°S and 60°N, relative to the mean total column abundance over the entire time period.




**"Expected" recovery of near global ozone layer for end of 2019 relative to maximum depletion since 1980, driven by atmospheric halogens**

Circles (•) placed at 1980, column minimum due to EESC, & end of 2020

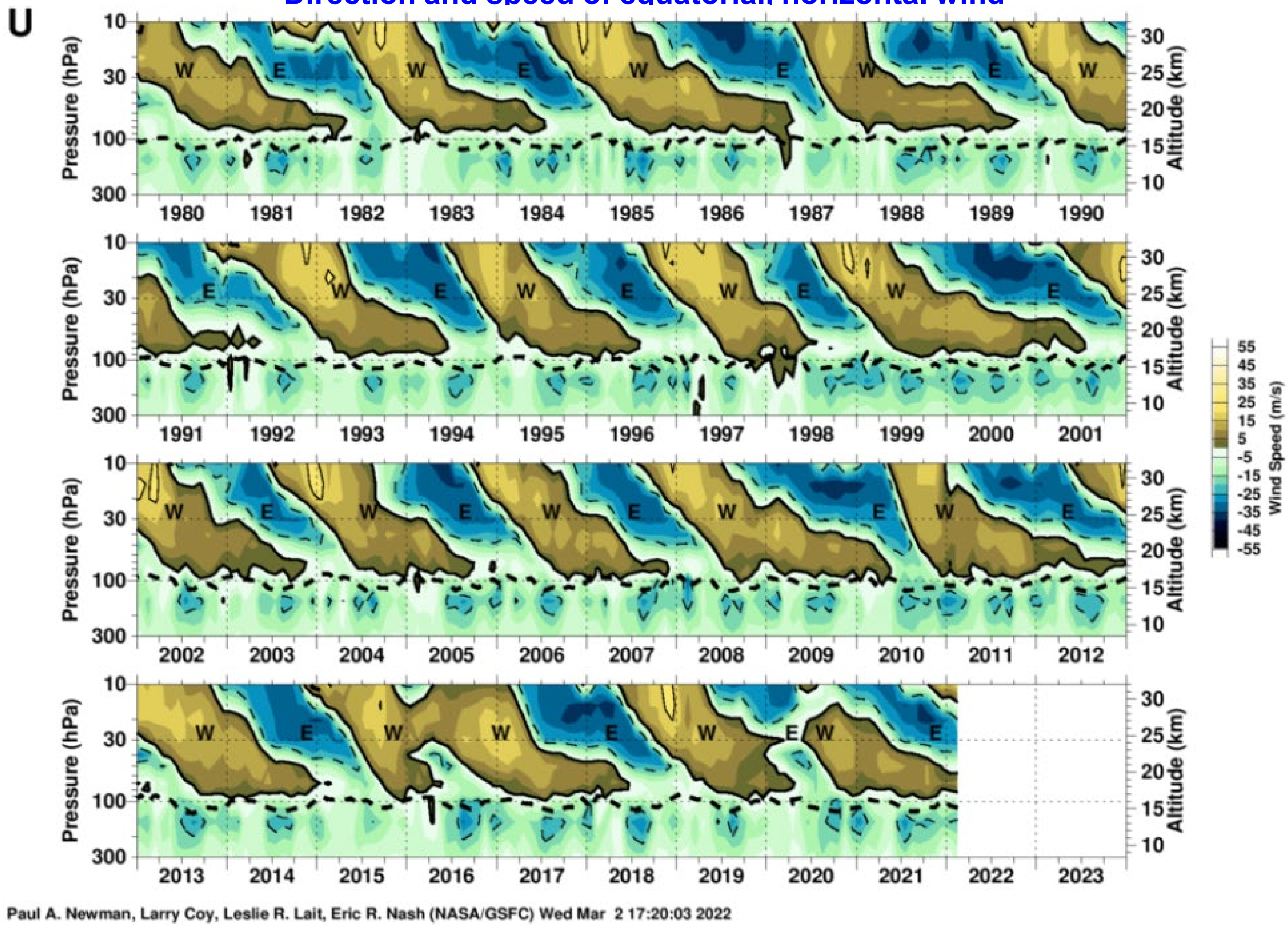
Multiple linear regression of <u>total ozone column</u> anomaly as a function of <u>equivalent effective stratospheric chlorine</u> (**EESC**), total solar irradiance (**TSI**), stratospheric aerosol optical depth (**SAOD**), and the quasi-biennial oscillation (**QBO**) has long been used to quantitatively assess factors that drive variations in the thickness of the ozone layer.

Note: EESC = Inorganic Stratospheric Chlorine + 60× Inorganic Stratospheric Bromine

McBride *et al.*, In Prep, 2022

# Quasi-Biennial Oscillation of Stratospheric Winds

**Direction and speed of equatorial, horizontal wind**




https://acd-ext.gsfc.nasa.gov/Data_services/met/qbo/qbo.html

# Chapman Chemistry

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

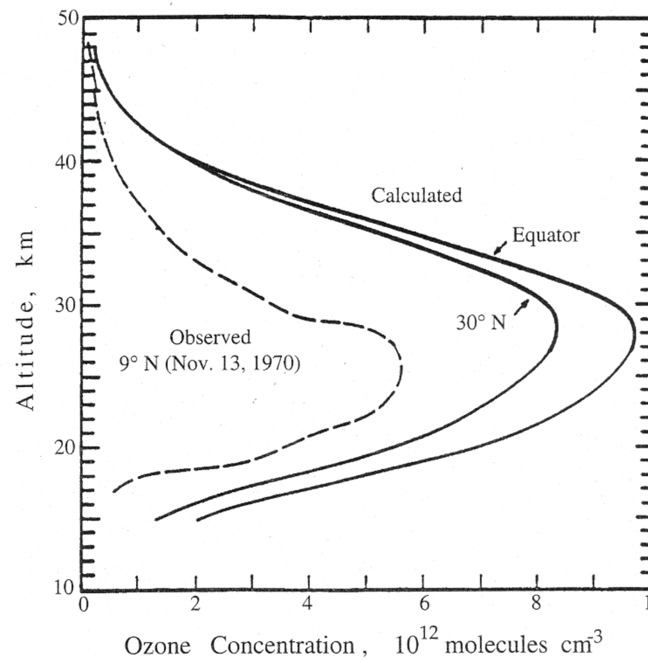



**FIGURE 4.6** Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970.

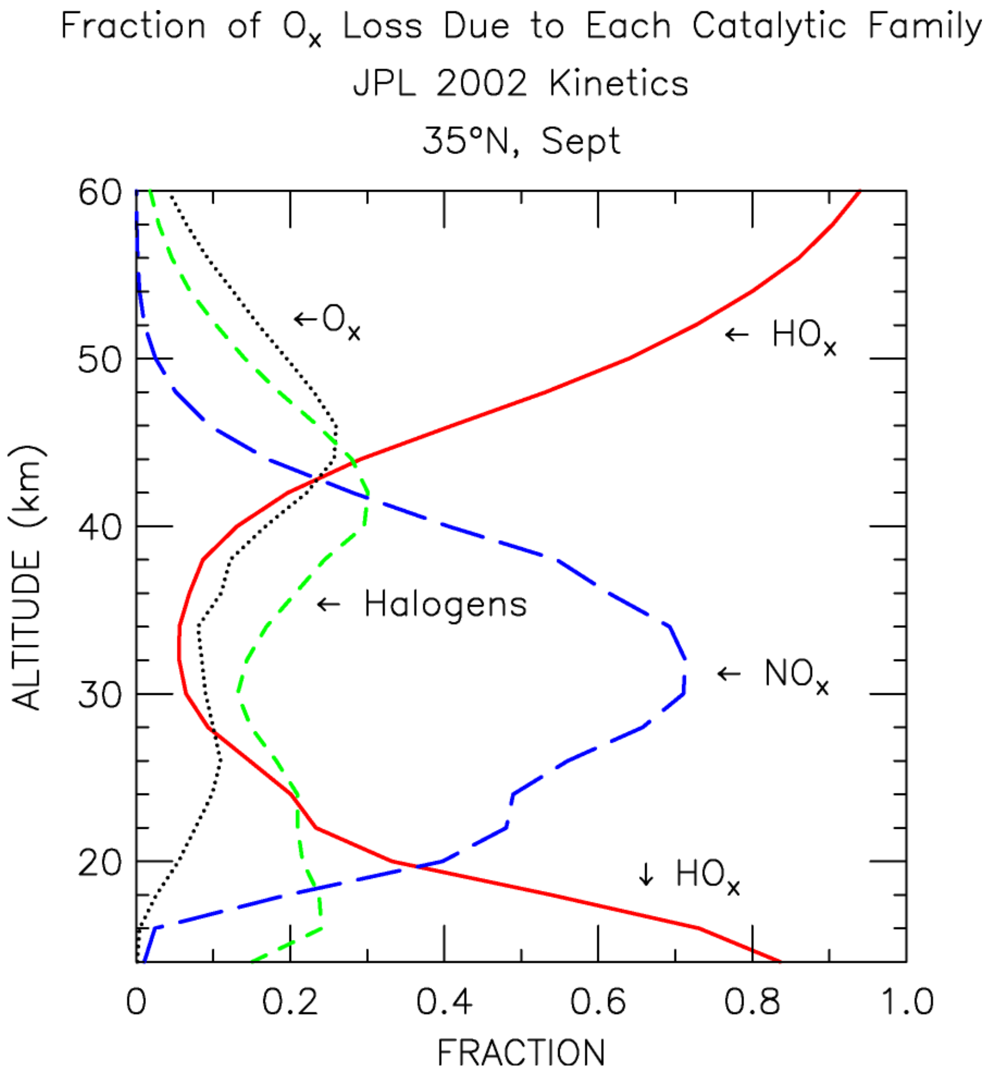
$[O_3]$ falls off with increasing altitude (high in stratosphere), at a rate determined by $[M]^{3/2}$, because:

$[O_3]$ 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 10, Slide 10**

# Stratospheric Photochemistry: Odd Oxygen Loss By Families




**Lecture 9, Slide 10**

Calculated fraction of odd oxygen loss due to various families of radicals

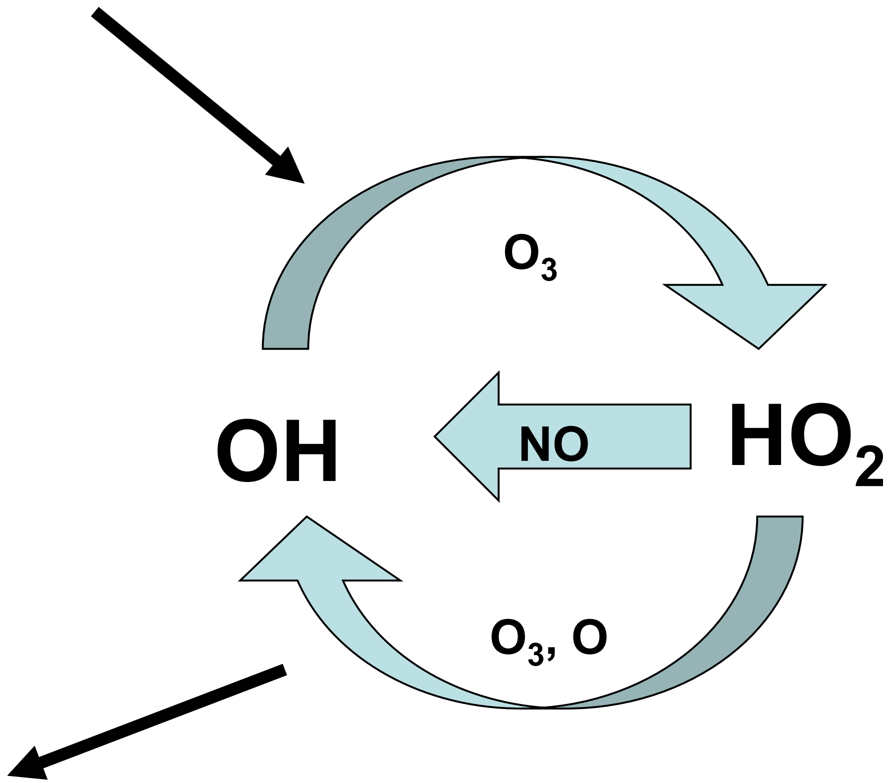
After Osterman *et al.*, *GRL*, 24, 1107, 1997;
Sen *et al.*, *JGR*, 103, 3571. 1998;
Sen *et al.*, *JGR*, 104, 26653, 1999.

# $HO_x$ : OH and $HO_2$

OH and $HO_2$ are central to stratospheric and tropospheric photochemistry

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

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




**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:

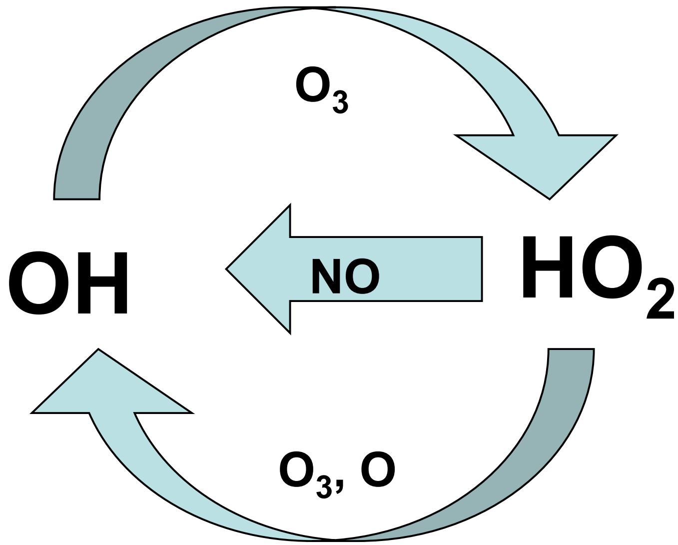
$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (1)$$

$HO_2$ loss:

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

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

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



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$HO_2$ loss step (2):

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

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

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**

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$HO_2$ loss step (3):

$$\begin{array}{ll} & OH + O_3 \rightarrow HO_2 + O_2 \\ & HO_2 + O \rightarrow OH + O_2 \\ \hline \text{Net:} & O_3 + O \rightarrow O_2 + O_2 \end{array}$$

$HO_2$ loss step (4):

$$\begin{array}{ll} & OH + O_3 \rightarrow HO_2 + O_2 \\ & HO_2 + O_3 \rightarrow OH + O_2 + O_2 \\ \hline \text{Net:} & O_3 + O_3 \rightarrow O_2 + O_2 + O_2 \end{array}$$

**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 <u>rate limiting steps</u> 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:

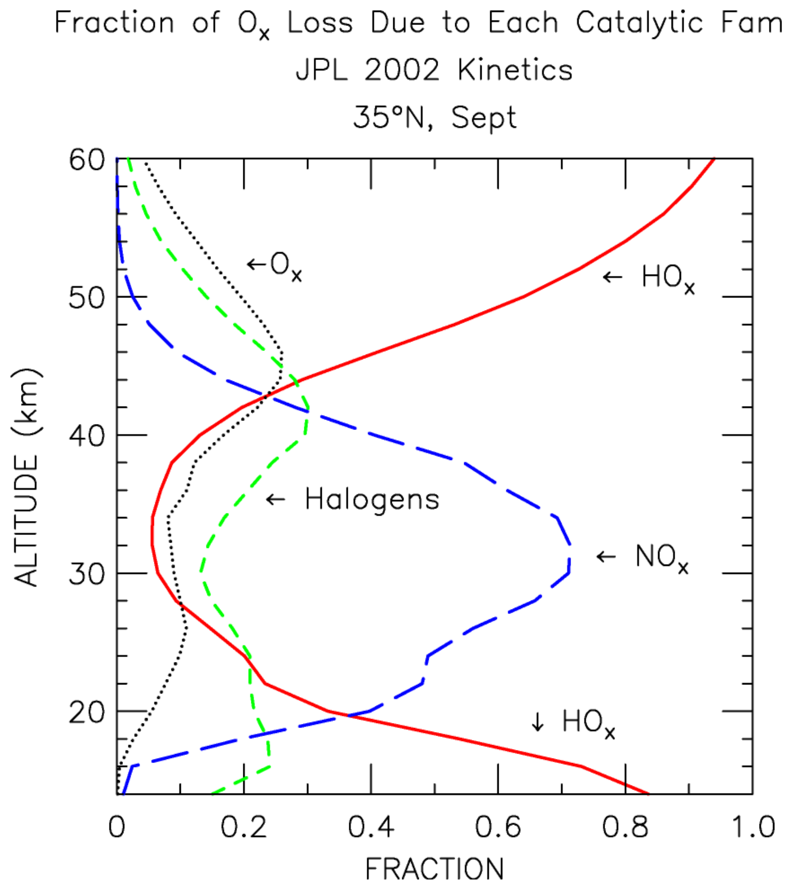
clear now that reactions (3) and (4) each consume two odd oxygens at rates determined by $2\,k_3\,[HO_2]\,[O]$ and $2\,k_4\,[HO_2][O_3]$

# Odd Oxygen Loss - $HO_x$

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

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

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



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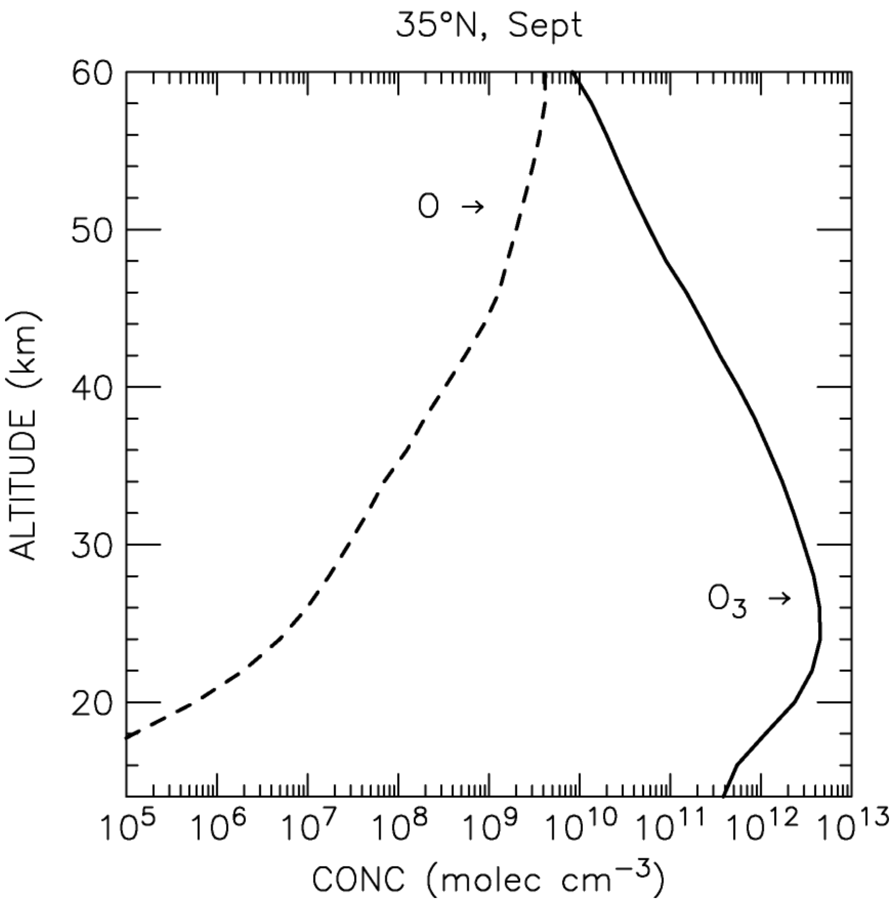
Hint:



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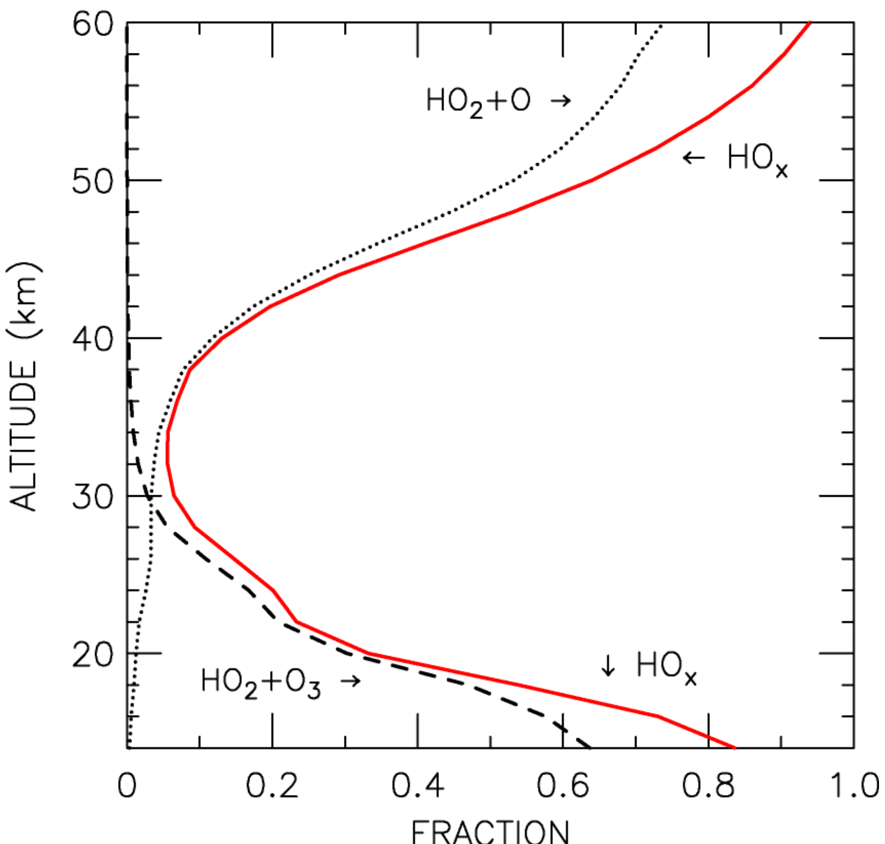
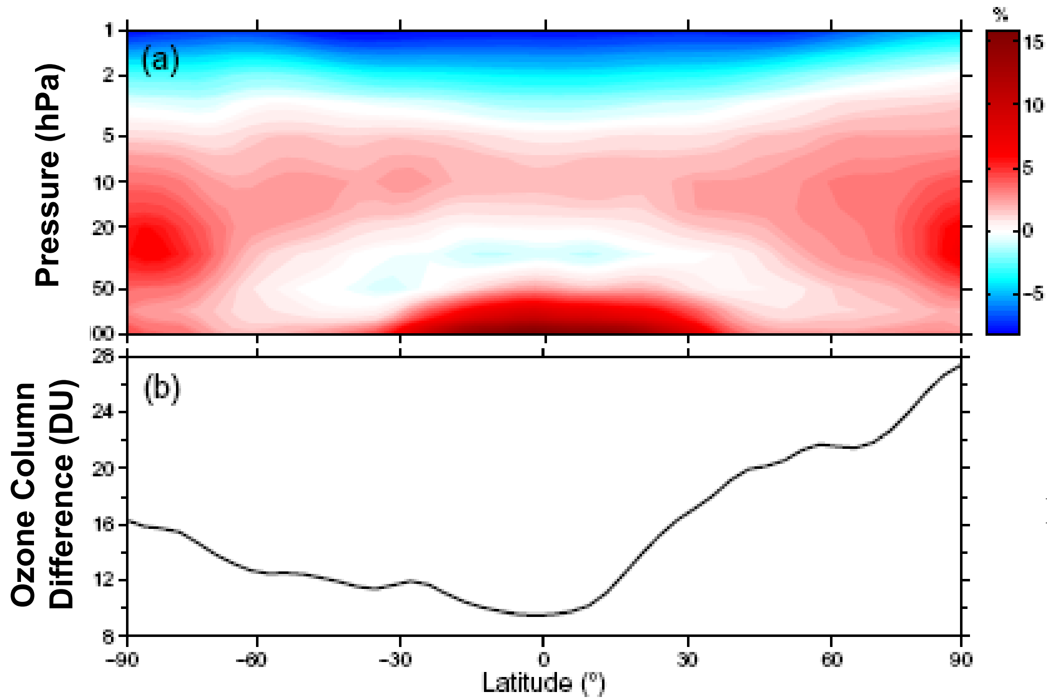


# $CH_4$ and Stratospheric Ozone




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

Stratospheric $O_3$ difference in the 2090s found for a computer simulation run using $CH_4$ from RCP 8.5 minus that of a simulation using $CH_4$ from RCP 2.6

Rising $CH_4$ leads to:

a) ozone loss in the upper stratosphere by increasing the speed of OH and $HO_2$ ($HO_x$) mediated loss cycles.

b) a cooler stratosphere, slowing the rate of all ozone loss cycles

c) speeds up the rate of $Cl+CH_4$, shifting chlorine from ClO into HCl (i.e., deactivates chlorine)

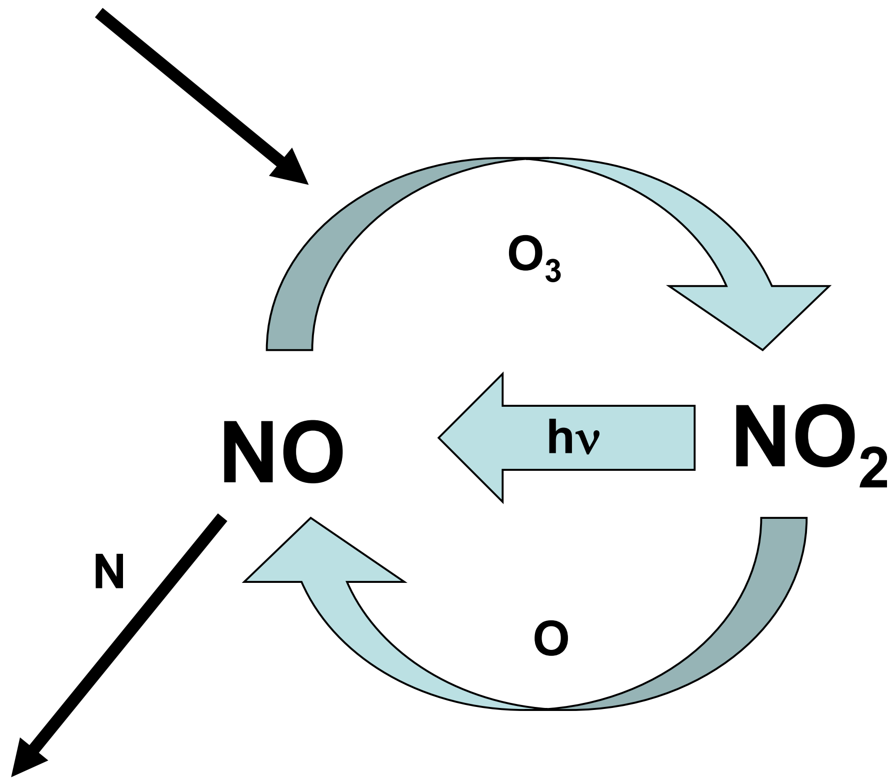
d) more $HO_2$ in the lowermost stratosphere where there is sufficient CO to result in $O_3$ production by "smog chemistry"

**Computer models project stratospheric column $O_3$ will increase as $CH_4$ rises**

# $NO_x$ : 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:

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$NO_2$ loss:

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

or

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$NO_2$ loss step (2):

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + h\nu \rightarrow NO + O$$

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

$NO_2$ loss step (3):

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

Net: $O_3 + O \rightarrow 2\ O_2$

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**

# $N_2O$ and $NO_y$

**Loss of $N_2O$ occurs mainly in the stratosphere due to:**

**photolysis – main sink**

**reaction with electronically excited $O(^1D)$ – minor sink**

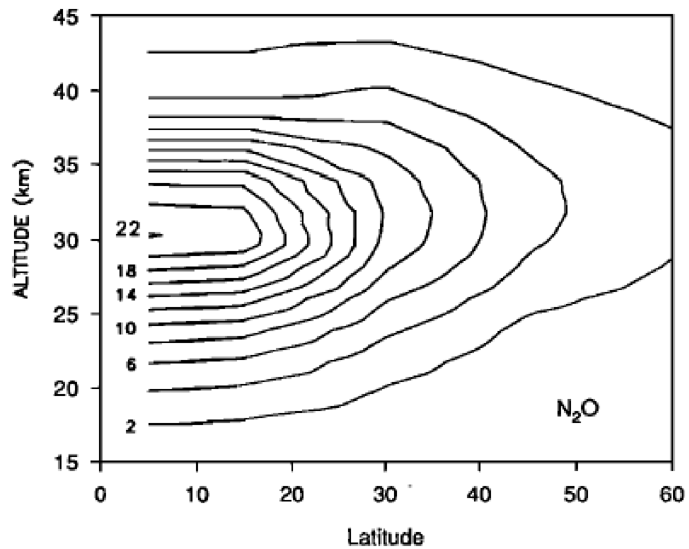


Fig. 11. Diurnally averaged loss rate for $N_2O$ ($10^2$ molecules $cm^{-3}$ $s^{-1}$) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate includes destruction of $N_2O$ by reaction with $O(^1D)$ as well as photolysis.

Minschwaner, Salawitch, and McElroy, *JGR*, 1993

**The minor sink for $N_2O$ loss has a path that results in "reactive nitrogen":** **Lecture 6**

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

**Reactive nitrogen ($NO_y$) is crucial to stratospheric chemistry**

**Oxides of nitrogen catalyze loss of stratospheric $O_3$ & participate in a series of chemical reactions that affect partitioning of hydrogen and chlorine radicals, etc.**

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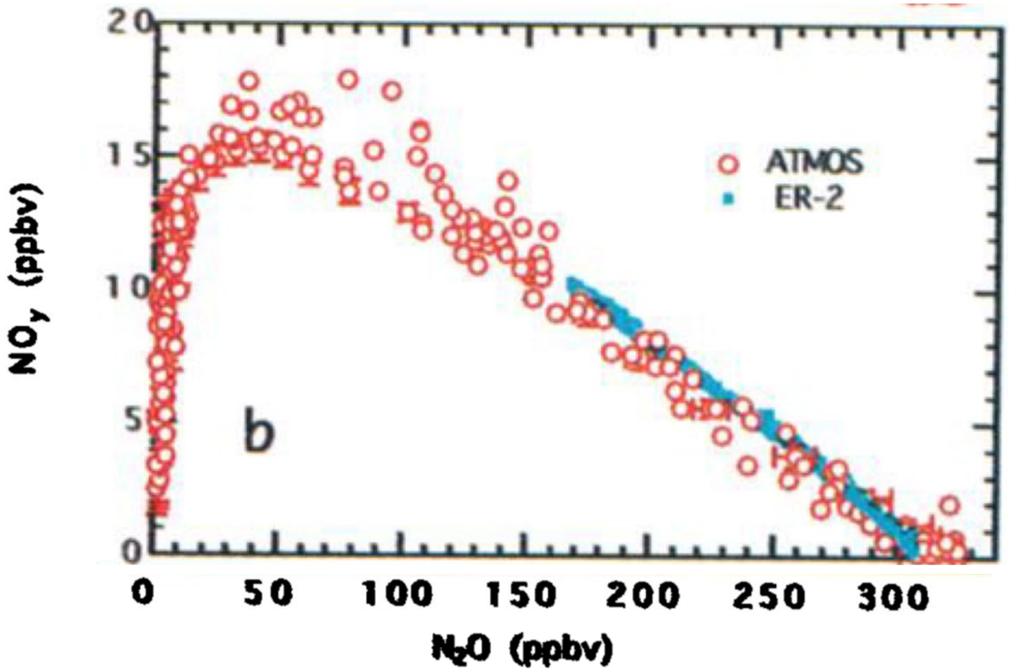


**ATMOS: NASA Atmospheric Trace Molecule Spectroscopy Experiment that flew on the Nov 1994 STS-66 Space Shuttle mission**

**ER-2: NASA Earth Reconnaissance 2 research aircraft that can sample air at 20 km (~66,000 feet), civilian version of the U2 spy plane**

Chang *et al.*, *GRL*, 1996

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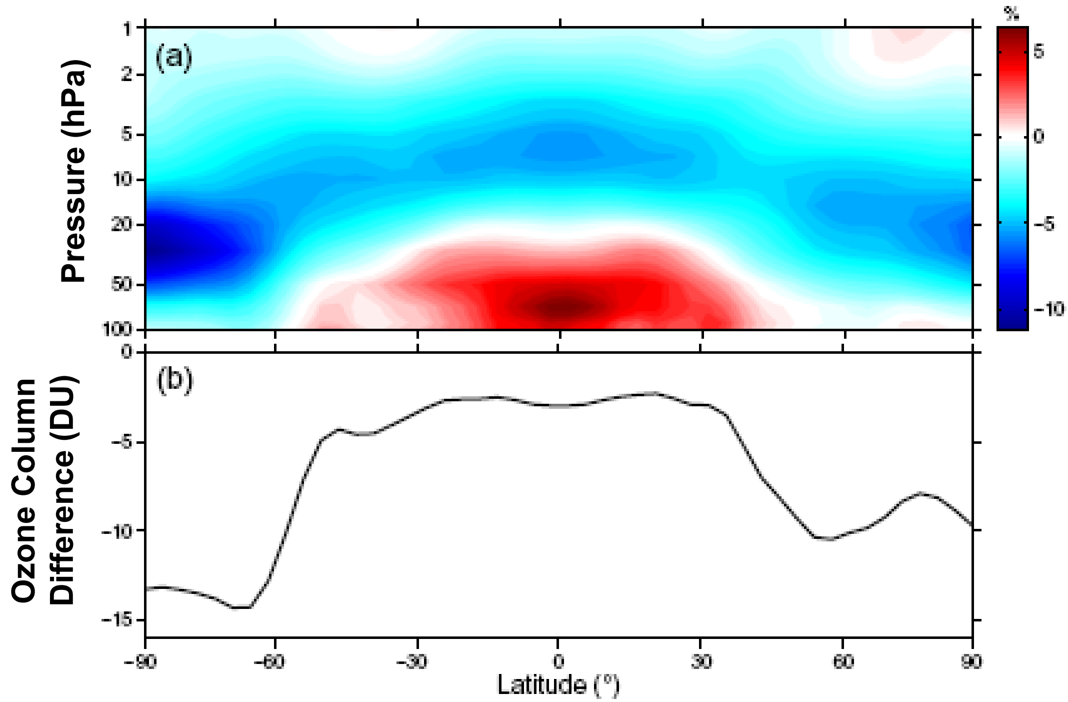
# $N_2O$ and Stratospheric Ozone

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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 $O_3$

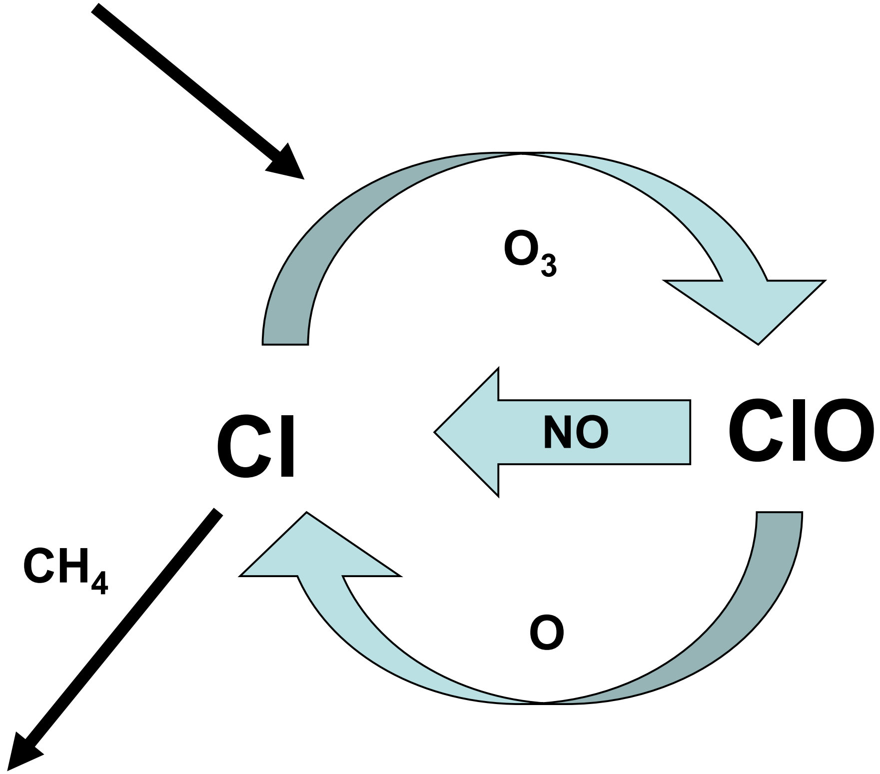
**Computer models project stratospheric column $O_3$ will decline as $N_2O$ rises**

**Lecture 6**

# $ClO_x$ : 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):

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

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

Followed by: $$NO_2 + h\nu \rightarrow NO + O$$

Final net: $$O_3 + h\nu \rightarrow O + O_2$$

ClO loss step (3):

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

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

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**

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Followed by: $NO_2 + h\nu \rightarrow NO + O$

Final net: $O_3 + h\nu \rightarrow O + O_2$

**According to Chemistry and Context, what two chemical reactions were first proposed by Rowland and Molina as a mechanism for *ozone destruction* and if these two chemical reactions occur in sequence, what is the net effect?** →

ClO loss step (3):

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$$ClO + O \rightarrow Cl + O_2$$

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

Can show:

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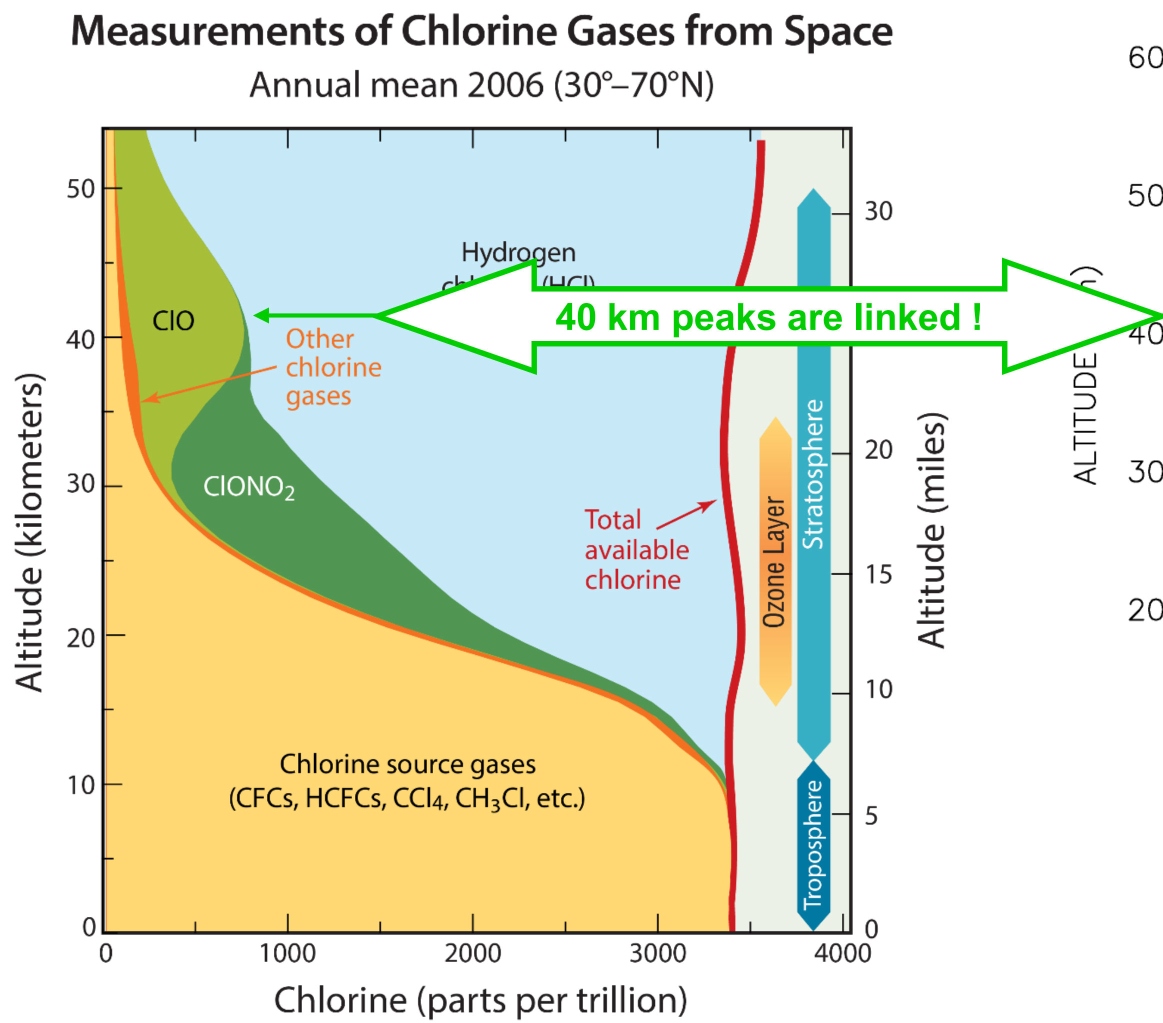
# Proof Halocarbons Reach The Stratosphere



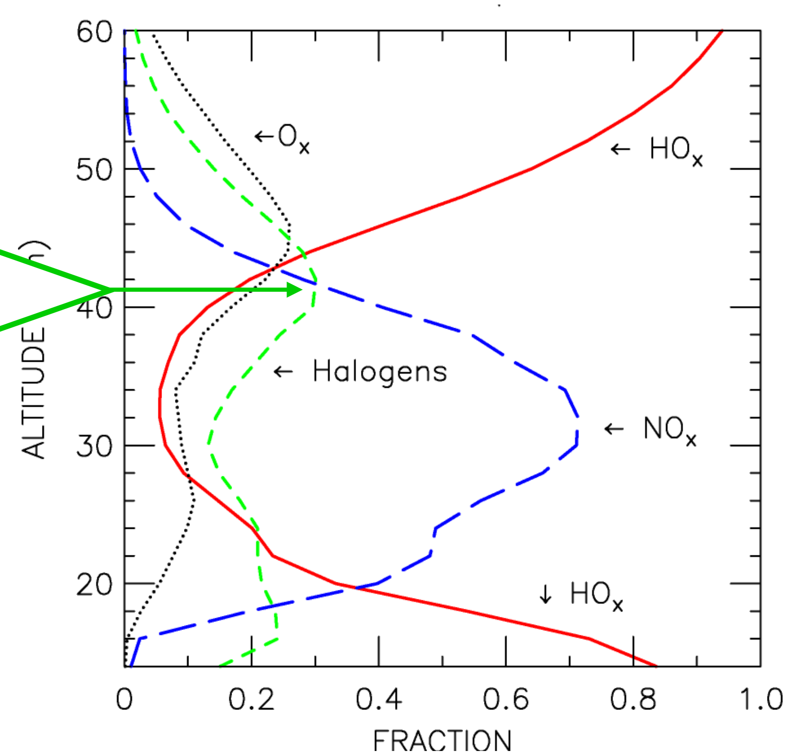




Fig Q7-2, *WMO/UNEP Twenty QAs Ozone*

# Trends in Ozone, ~40 km

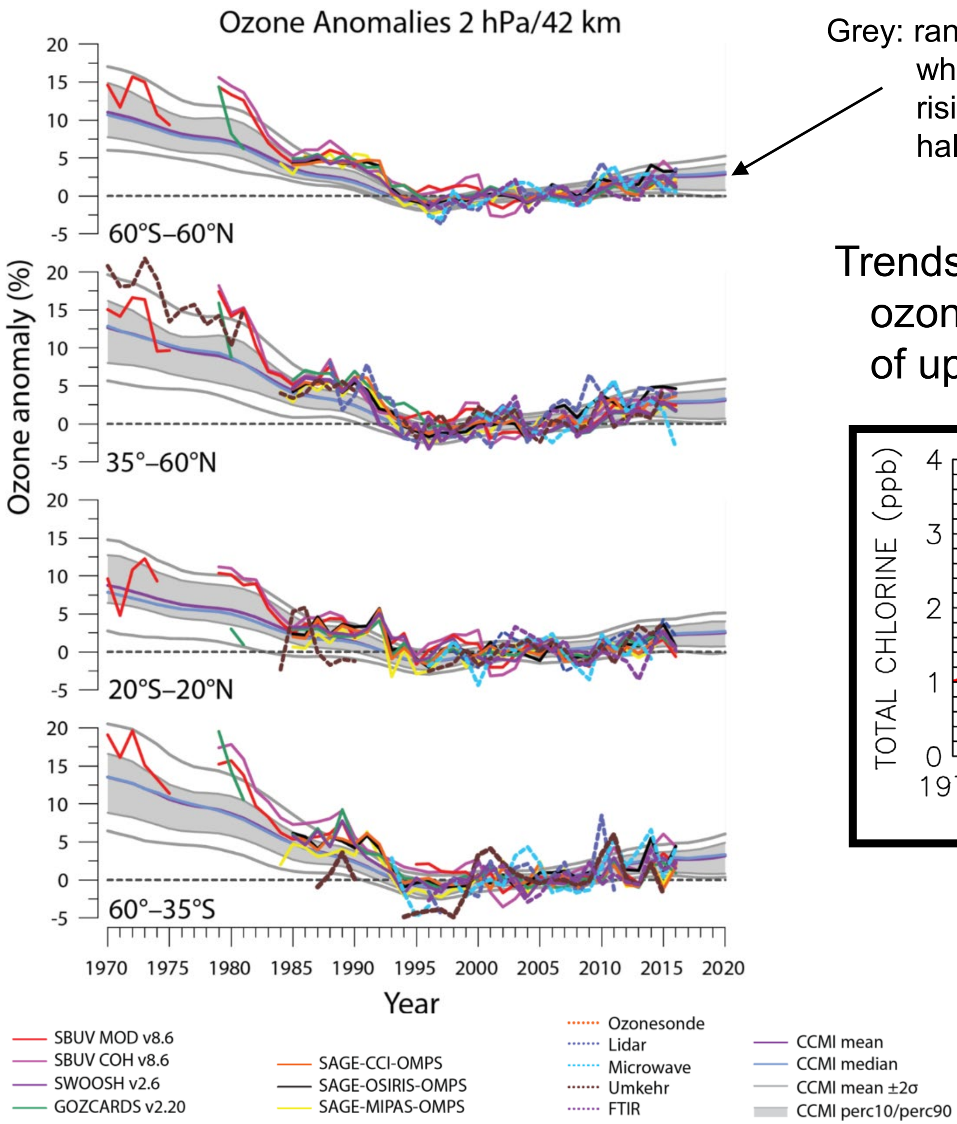
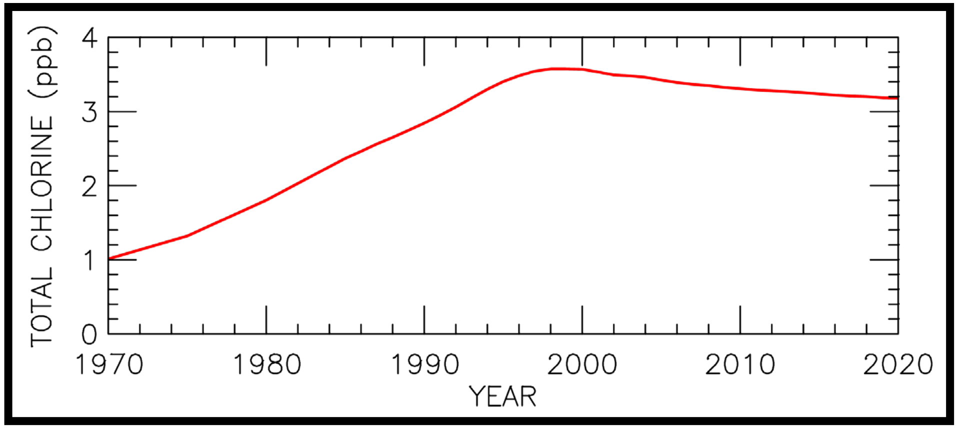


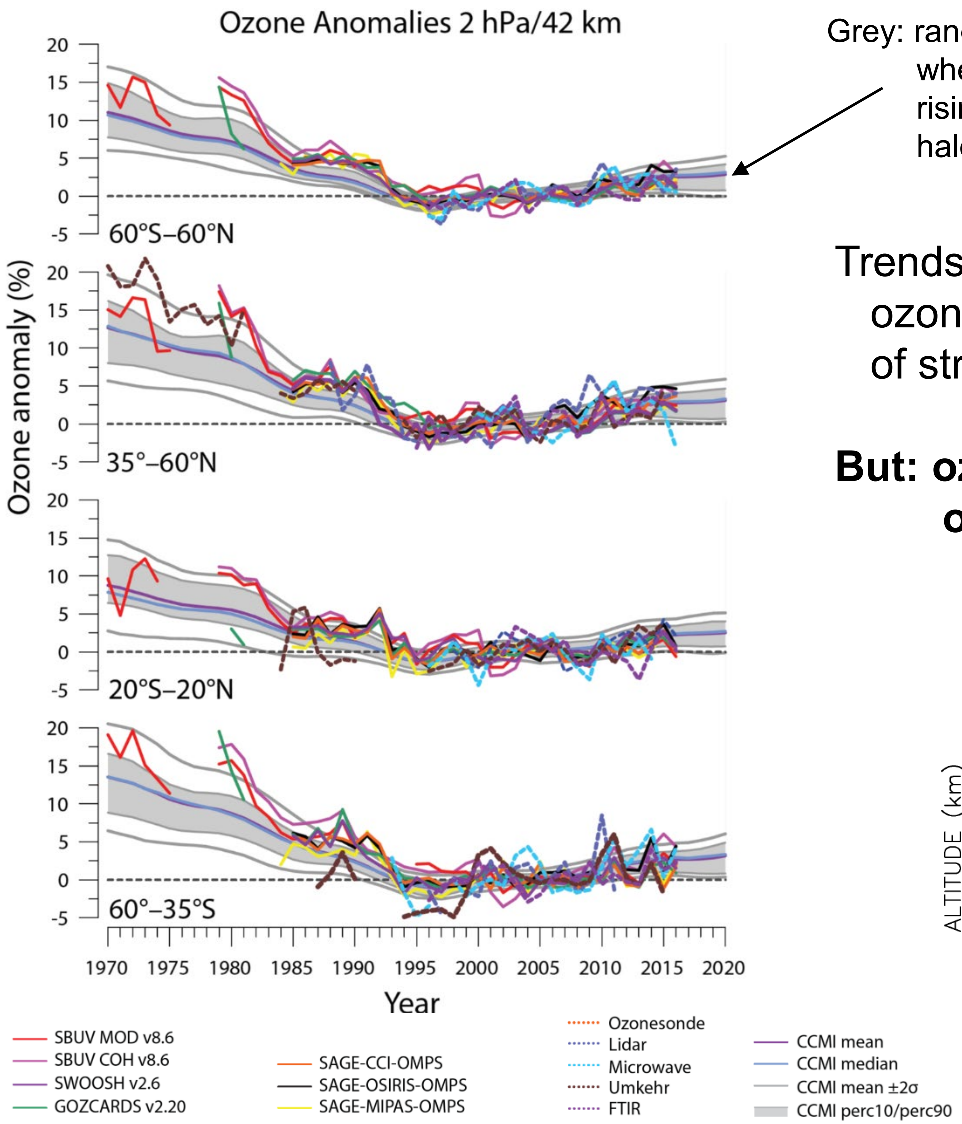

**Fig 3-15, *WMO/UNEP Ozone Report***

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 upper stratospheric chlorine loading



# Trends in Ozone, ~40 km

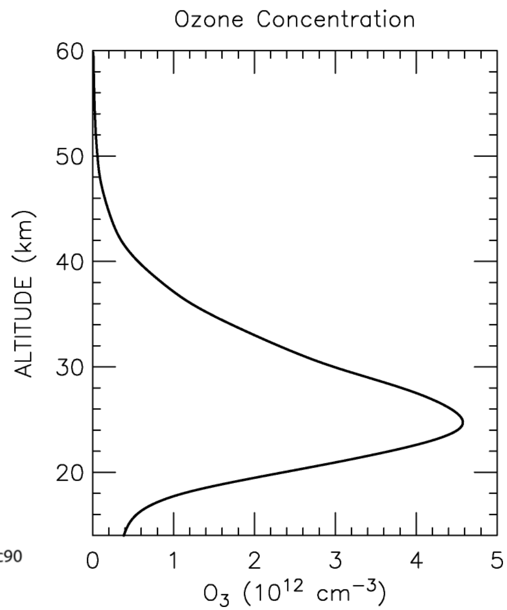



Grey: range of model calculations, where models are forced by rising levels of stratospheric halogens

Fig 3-15, ***WMO/UNEP Ozone Report***

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

**But: ozone at 40 km has little effect on surface UV radiation**



# Trends in Ozone vs Altitude

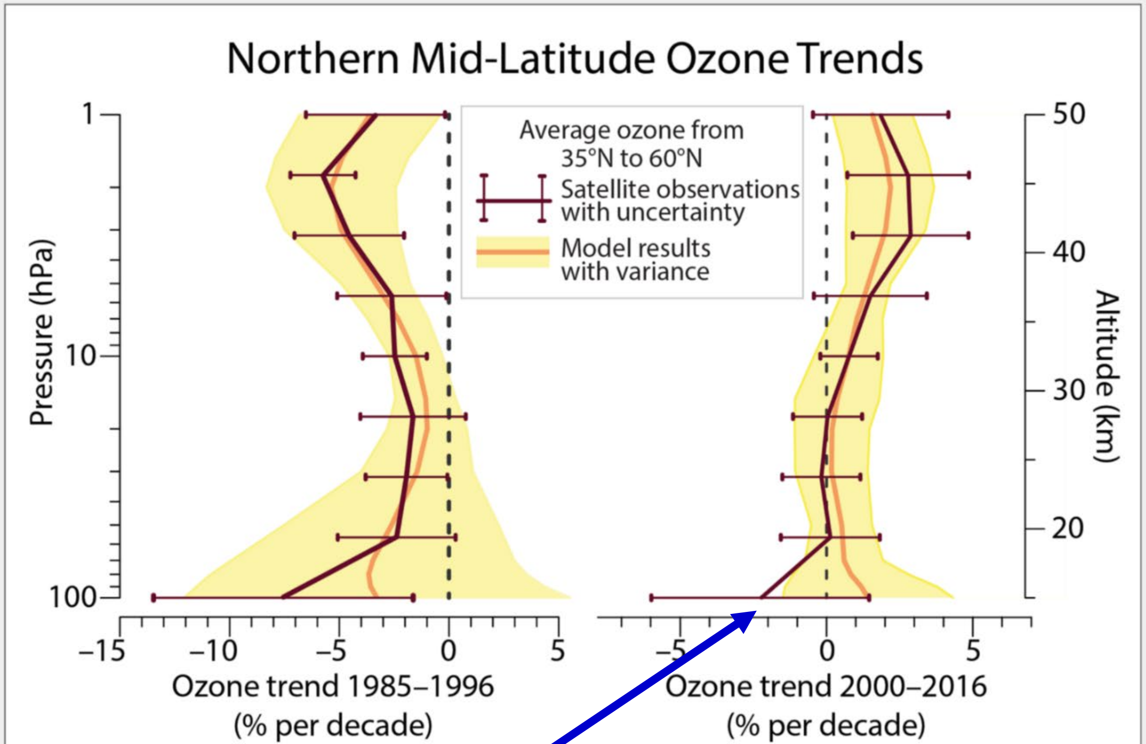
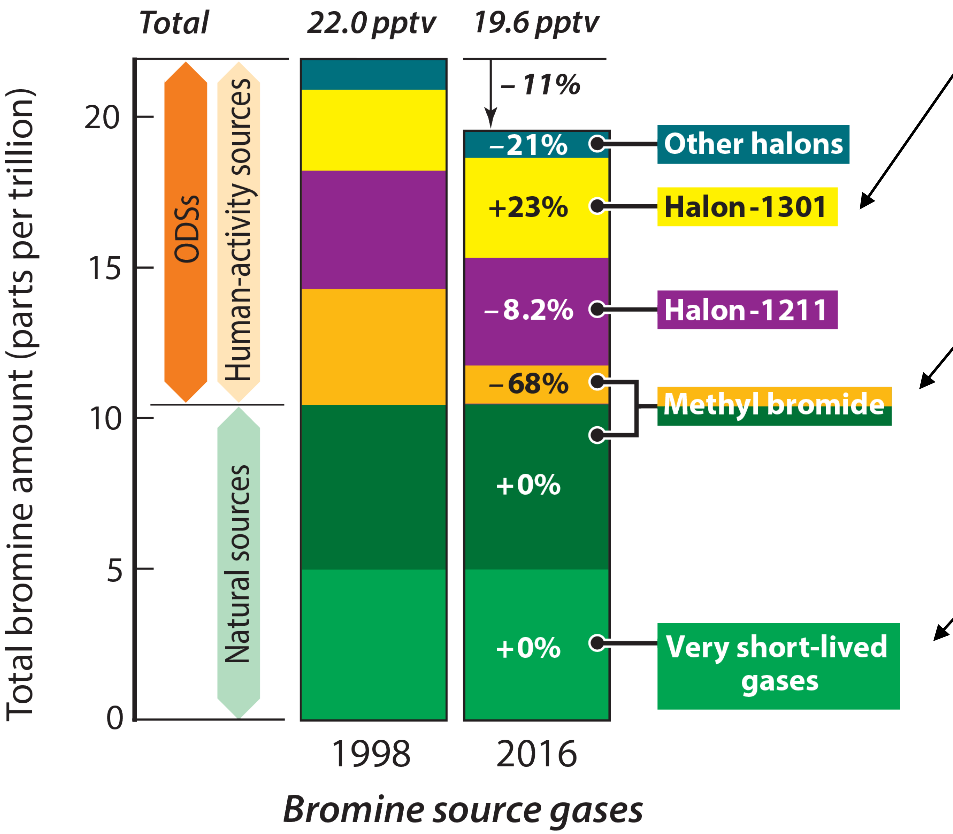



**Figure ES-7. Ozone trends in the stratosphere.** The largest relative depletion of ozone outside the polar regions occurred prior to 1997 in the northern mid-latitude, upper stratosphere *(left panel)*. The largest recovery has occurred in the same region, with an upward trend of about 3% per decade since 2000 above 40-km altitude *(right panel)*. Ozone trends derived from satellite observations are shown in brown, with uncertainty ranges given by horizontal lines. Ozone trends derived from a set of chemistry-climate models are shown in orange, with the model variance given by the yellow envelope. Ozone trends from chemistry-climate models agree very well with the measured trends. [See also Figure 3-23]

**Fig ES-7, *WMO/UNEP Ozone Report Executive Summary***

**Three complications to understanding ozone trends in the lower stratosphere:**
**1) aerosol surface area; 2) bromine, particularly from biogenic sources that exists in inorganic form just above the tropopause; 3) unreported emissions of CFC-11 (yikes!)**

# Bromine Source Gases




Halons:

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

$CH_3Br$:

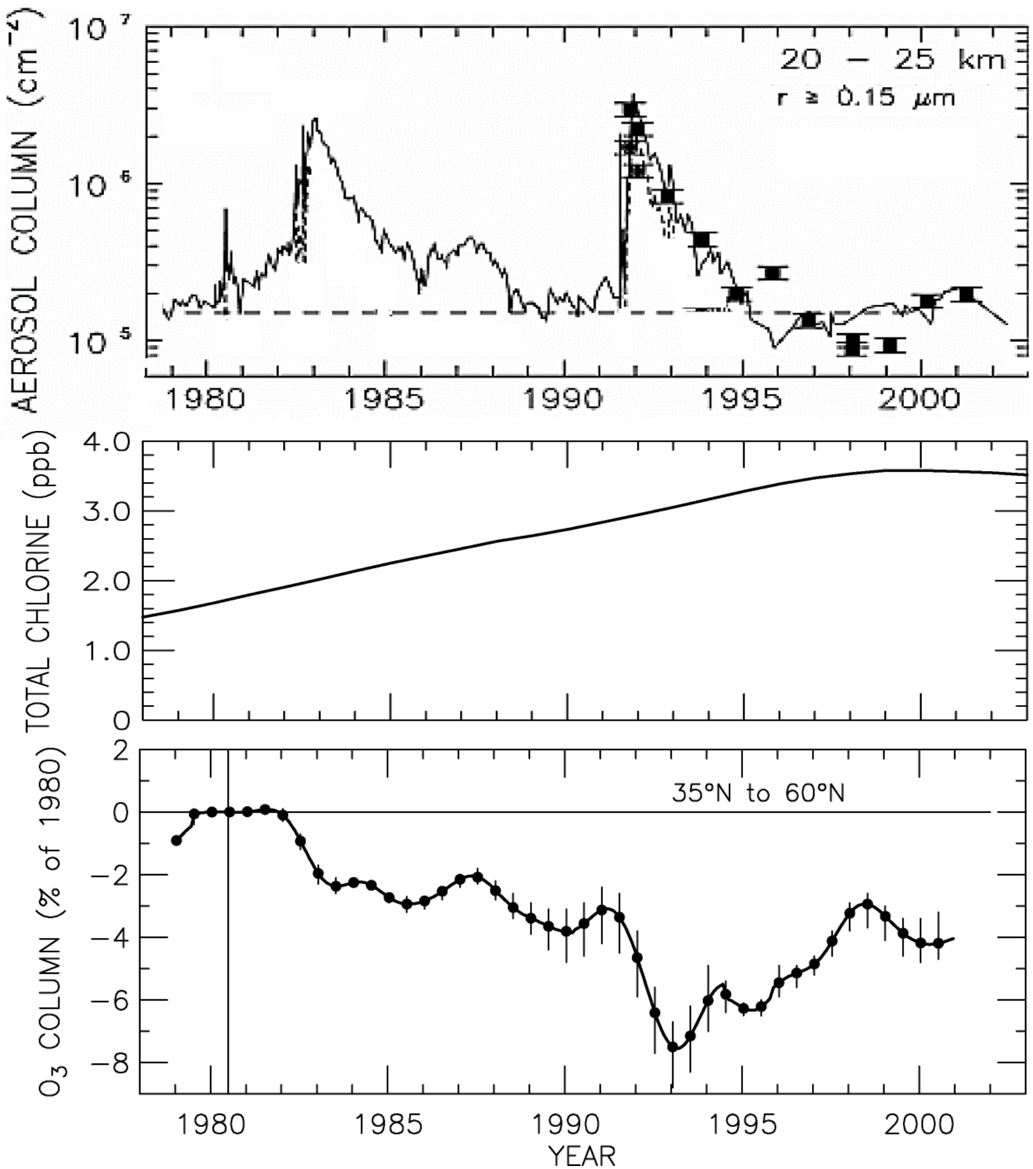
- fumigant; released by biomass burning
- production halted by Montreal Protocol
- significant natural & human sources

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

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

**Fig Q6-1, *WMO/UNEP Twenty QAs Ozone***

# Total Column Ozone Time Series, NH




Stratospheric aerosol loading,

Deshler et al., 2003.

Stratospheric chlorine

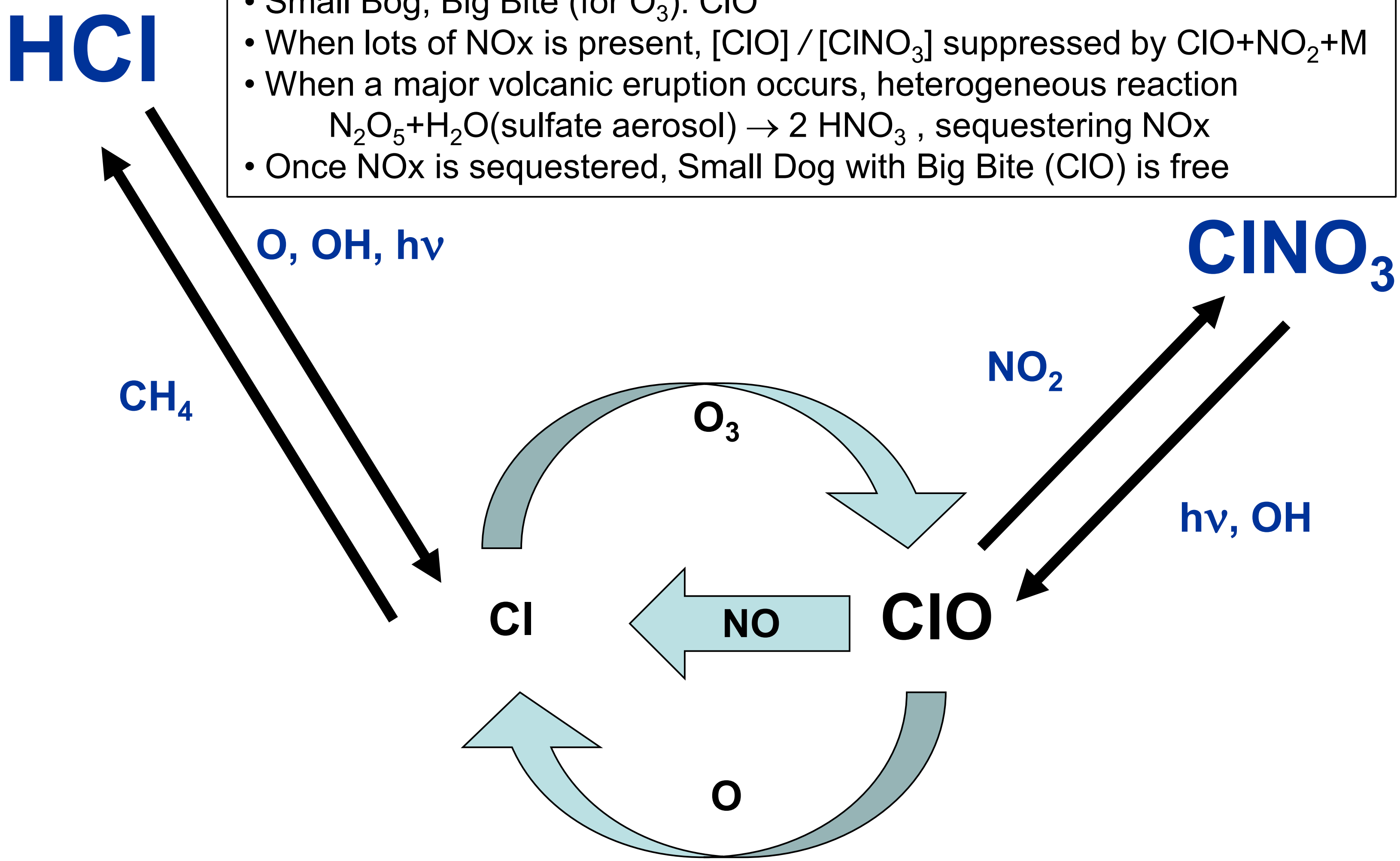
Change in ozone column relative to 1980, 35 to 60°N

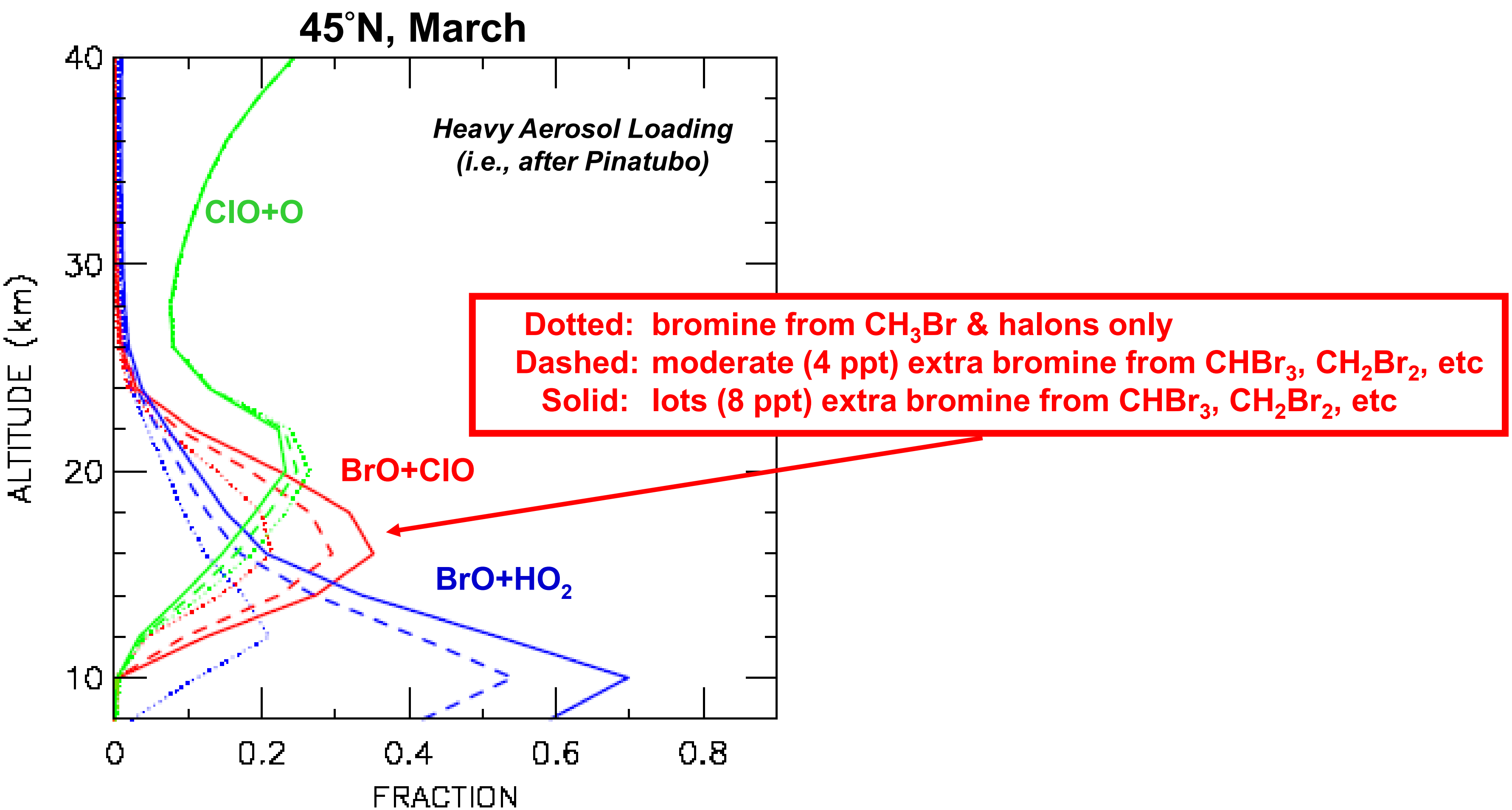
WMO/UNEP 2006 Ozone Report

# 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, $ClNO_3$ falls and ClO rises**

- Big Dogs in Chlorine Family: HCl & $ClNO_3$
- Small Bog, Big Bite (for $O_3$): ClO
- When lots of NOx is present, [ClO] / [$ClNO_3$] suppressed by ClO+$NO_2$+M
- When a major volcanic eruption occurs, heterogeneous reaction
  $N_2O_5+H_2O$(sulfate aerosol) $\rightarrow$ 2 $HNO_3$ , sequestering NOx
- Once NOx is sequestered, Small Dog with Big Bite (ClO) is free

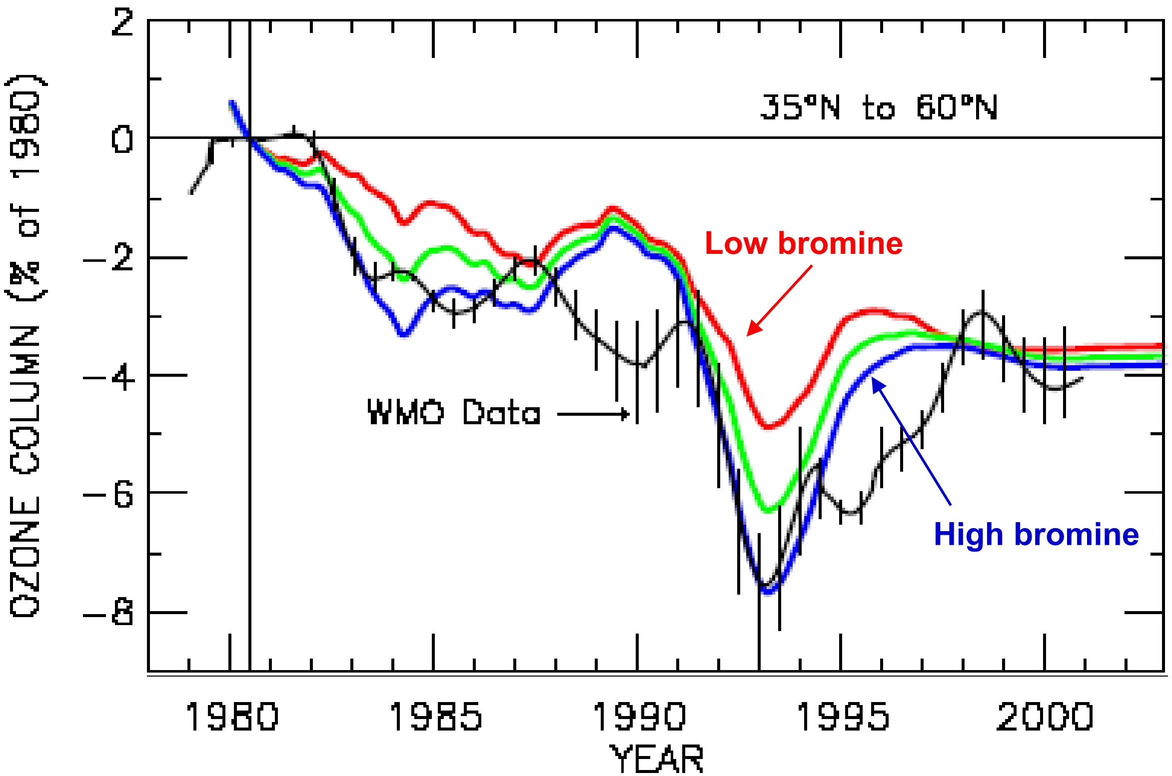





After Salawitch *et al.*, *GRL*, 2005

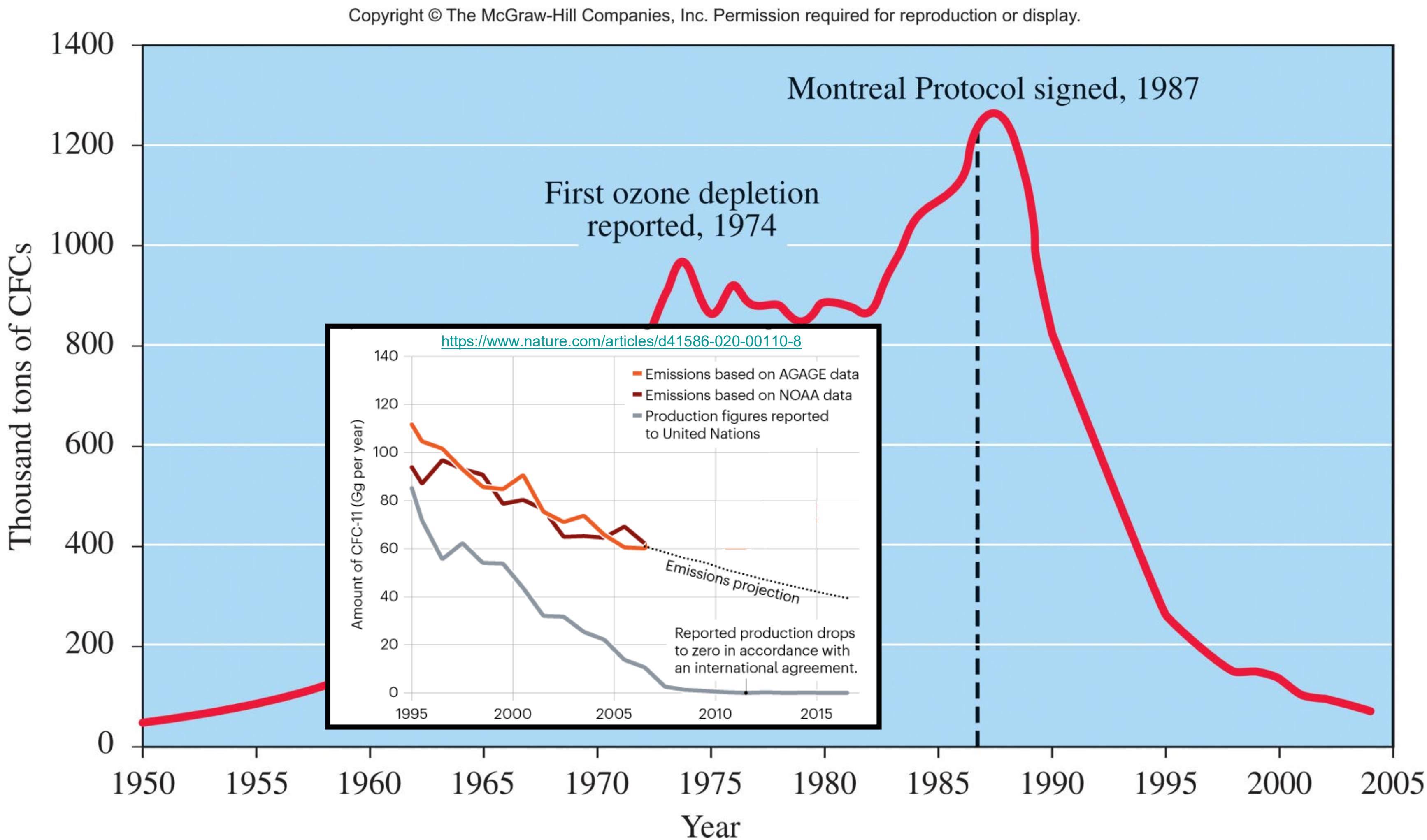
**Ozone responds to:**

- **a) rise and fall of chlorine**
- **b) volcanic perturbations to aerosol loading**
- **c) amount of bromine in lowermost stratosphere**




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

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




Global Production of CFCs, Fig. 2.19, Chemistry in Context

# Montreal Protocol Had Banned Most Industrial Production of CFCs & Other ODS

The New York Times

## *In a High-Stakes Environmental Whodunit, Many Clues Point to China*

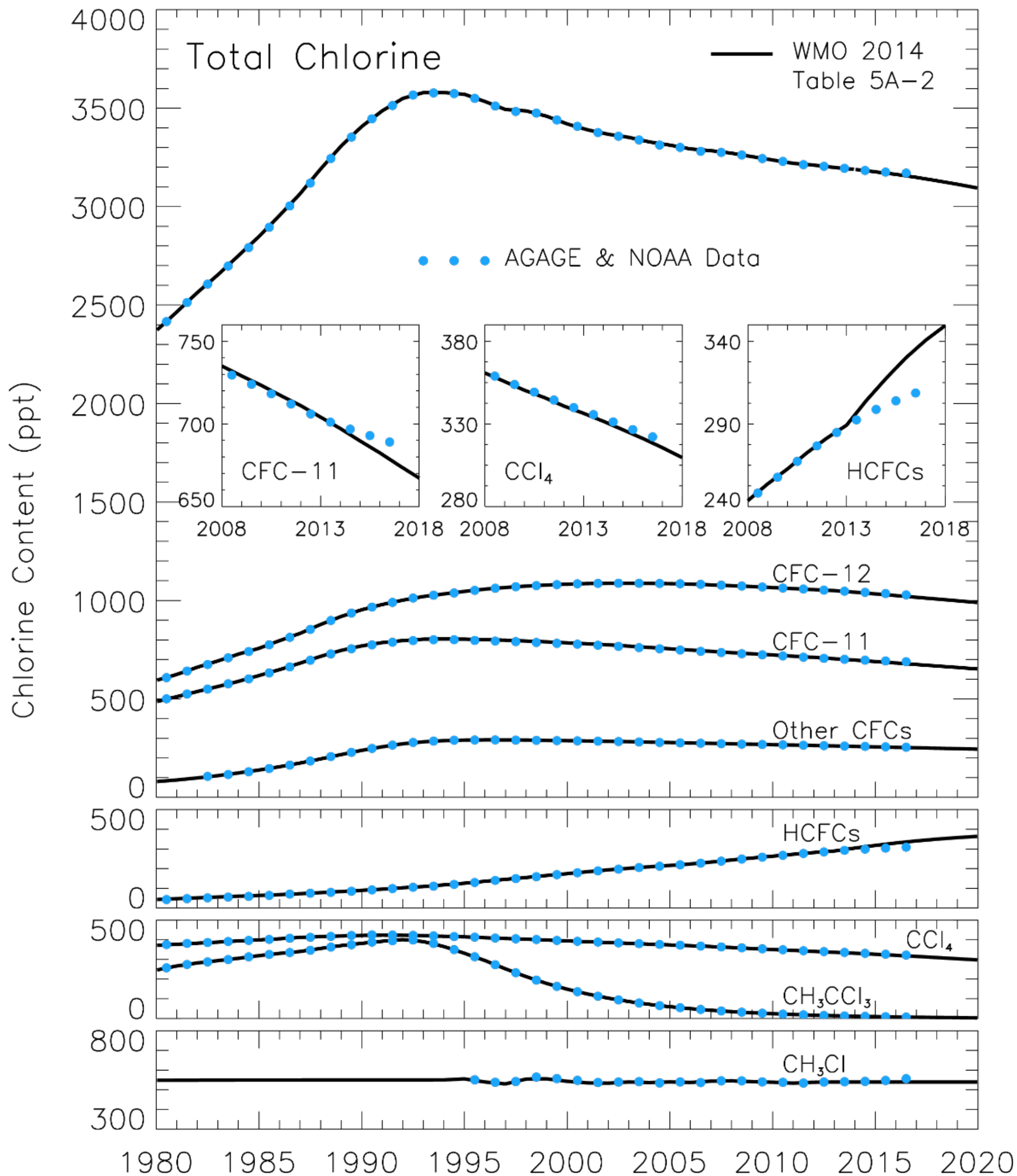
Interviews, documents and advertisements collected by The New York Times and independent investigators indicate that a major source — possibly the overwhelming one — is factories in China that have ignored a global ban and kept making or using the chemical, CFC-11, mostly to produce foam insulation for refrigerators and buildings.

"You had a choice: Choose the cheaper foam agent that's not so good for the environment, or the expensive one that's better for the environment," said Zhang Wenbo, owner of a refrigerator factory here in Xingfu, in Shandong Province, where he and many other small-scale manufacturers said that until recently, they had used CFC-11 widely to make foam insulation.

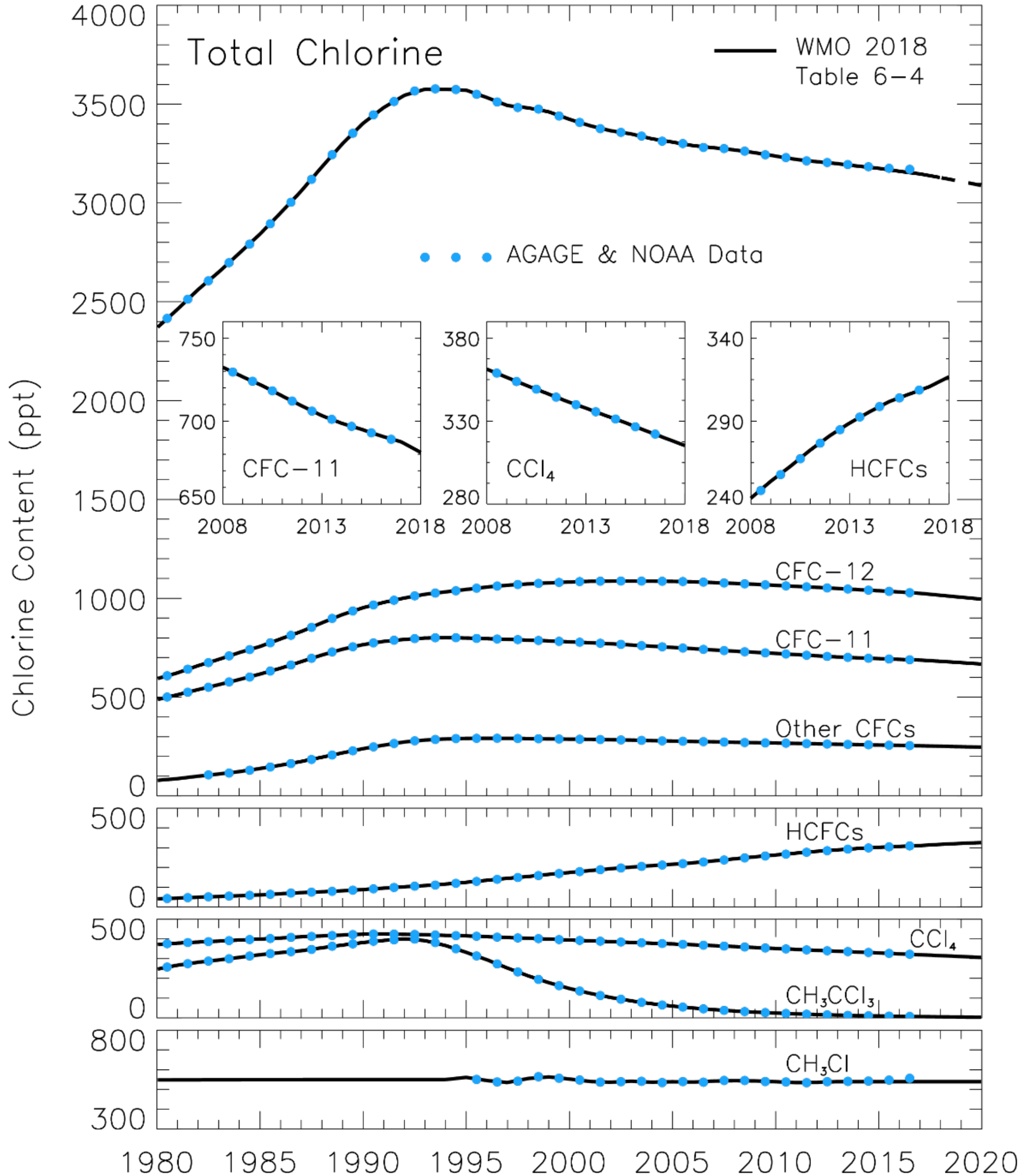
Billboards in Xingfu, China, promoting locally made refrigerators. The city has around 1,700 businesses involved in the production of cooking and refrigeration equipment. Gilles Sabrié for The New York Times

https://www.nytimes.com/2018/06/24/world/asia/china-ozone-cfc.html

# Organic Halogens Versus Time



# Organic Halogens Versus Time



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

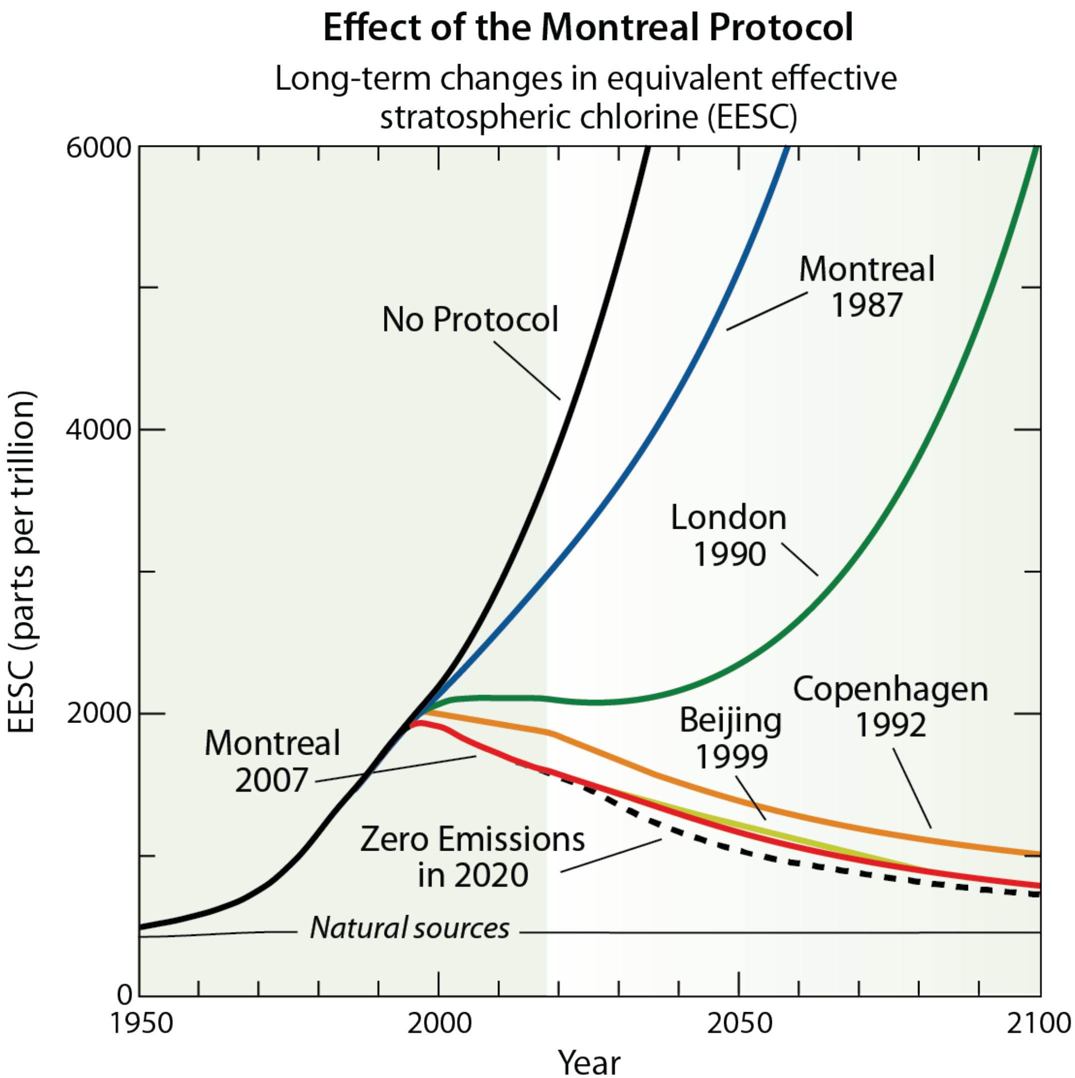
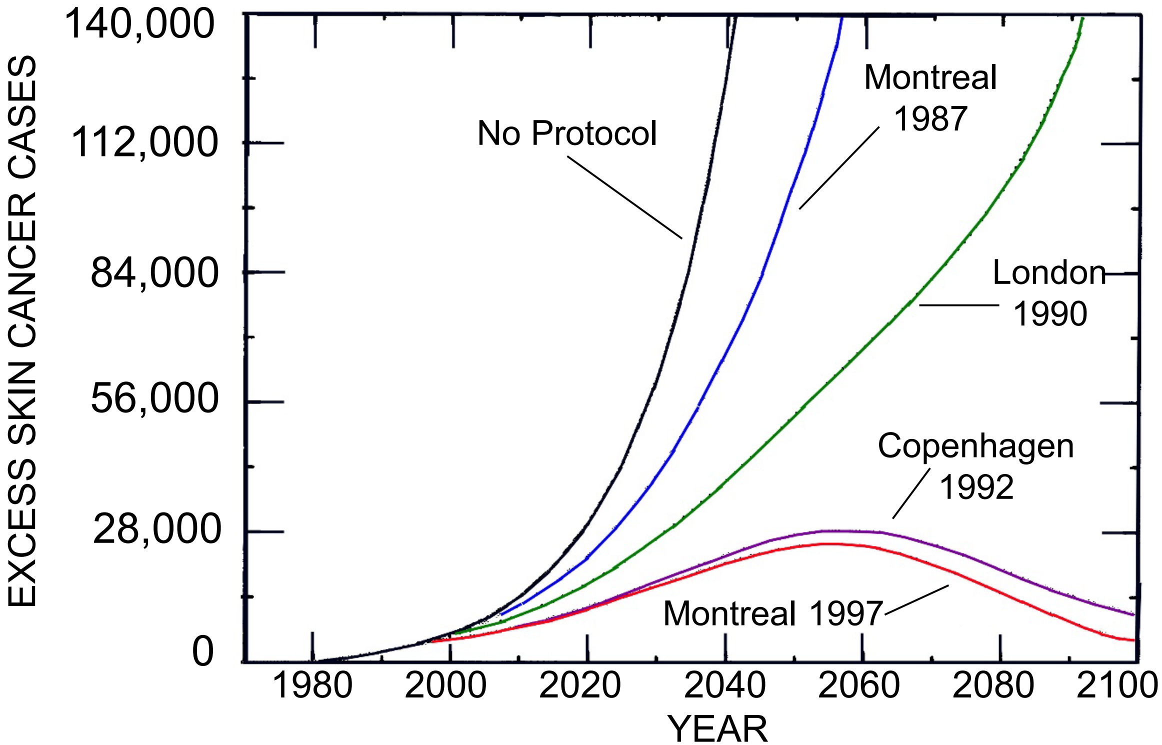



**Fig Q14-1, *WMO/UNEP Twenty QAs Ozone***

# 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.