Mid-Latitude Stratospheric Chemistry

AOSC/CHEM 433 & AOSC 633

Ross Salawitch & Walter Tribett

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2019

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

2 April 2019

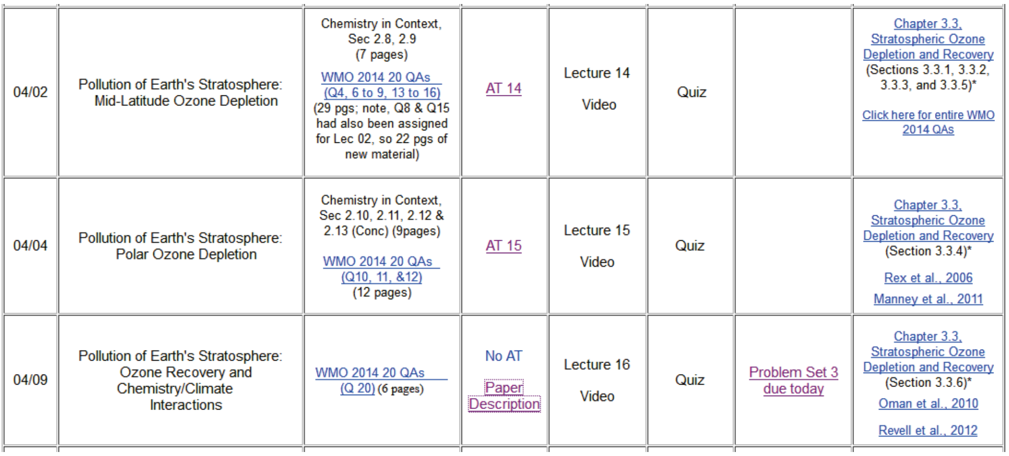
Announcements

- Problem Set #3 has been posted:

  https://www.atmos.umd.edu/~rjs/class/spr2019/problem_sets/ACC_2019_ps03.pdf

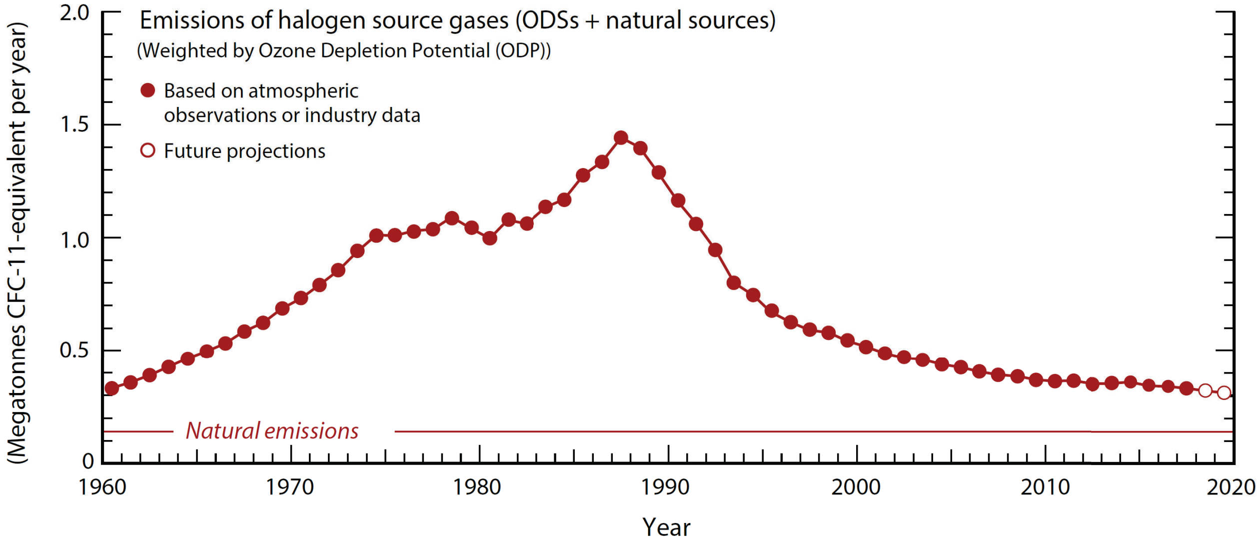
  and is due a week from today. Please get started early.
- No AT for Lecture 16, a week from today. Please try to complete the short reading.
- Students enrolled in 633 and those in 433 should turn in a few sentence description of their paper/project by next Tuesday:

  https://myelms.umd.edu/courses/1256337/quizzes/1270627



04/02	Pollution of Earth's Stratosphere: Mid-Latitude Ozone Depletion	Chemistry in Context, Sec 2.8, 2.9 (7 pages) WMO 2014 20 QAs (Q4, 6 to 9, 13 to 16) (29 pgs; note, Q8 & Q15 had also been assigned for Lec 02, so 22 pgs of new material)	AT 14	Lecture 14 Video	Quiz		Chapter 3.3, Stratospheric Ozone Depletion and Recovery (Sections 3.3.1, 3.3.2, 3.3.3, and 3.3.5)* Click here for entire WMO 2014 QAs
04/04	Pollution of Earth's Stratosphere: Polar Ozone Depletion	Chemistry in Context, Sec 2.10, 2.11, 2.12 & 2.13 (Conc) (9pages) WMO 2014 20 QAs (Q10, 11, &12) (12 pages)	AT 15	Lecture 15 Video	Quiz		Chapter 3.3, Stratospheric Ozone Depletion and Recovery (Section 3.3.4)* Rex et al., 2006 Manney et al., 2011
04/09	Pollution of Earth's Stratosphere: Ozone Recovery and Chemistry/Climate Interactions	WMO 2014 20 QAs (Q 20) (6 pages)	No AT Paper Description	Lecture 16 Video	Quiz	Problem Set 3 due today	Chapter 3.3, Stratospheric Ozone Depletion and Recovery (Section 3.3.6)* Oman et al., 2010 Revell et al., 2012

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



Global Production of CFCs, Fig Q0-1, Update for 2019 QAs

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

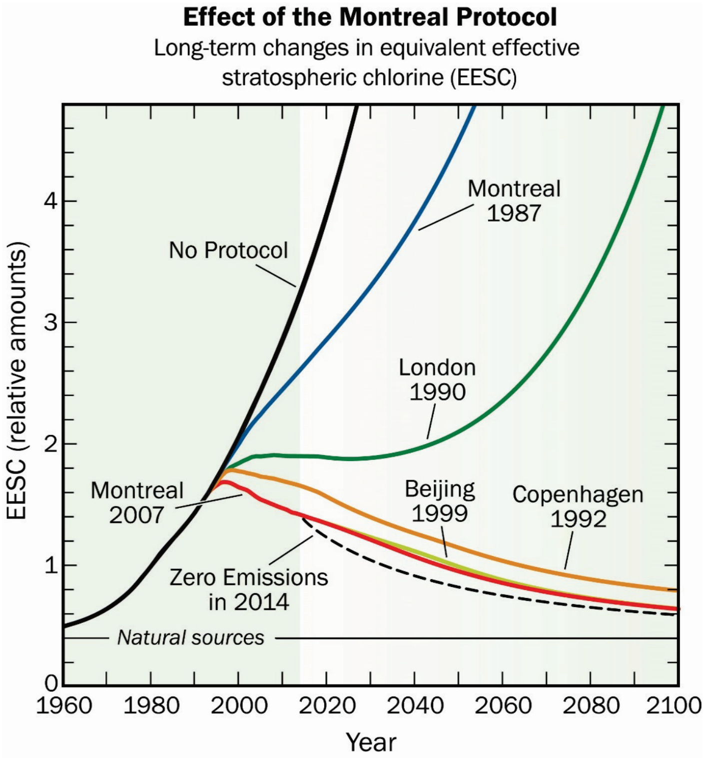
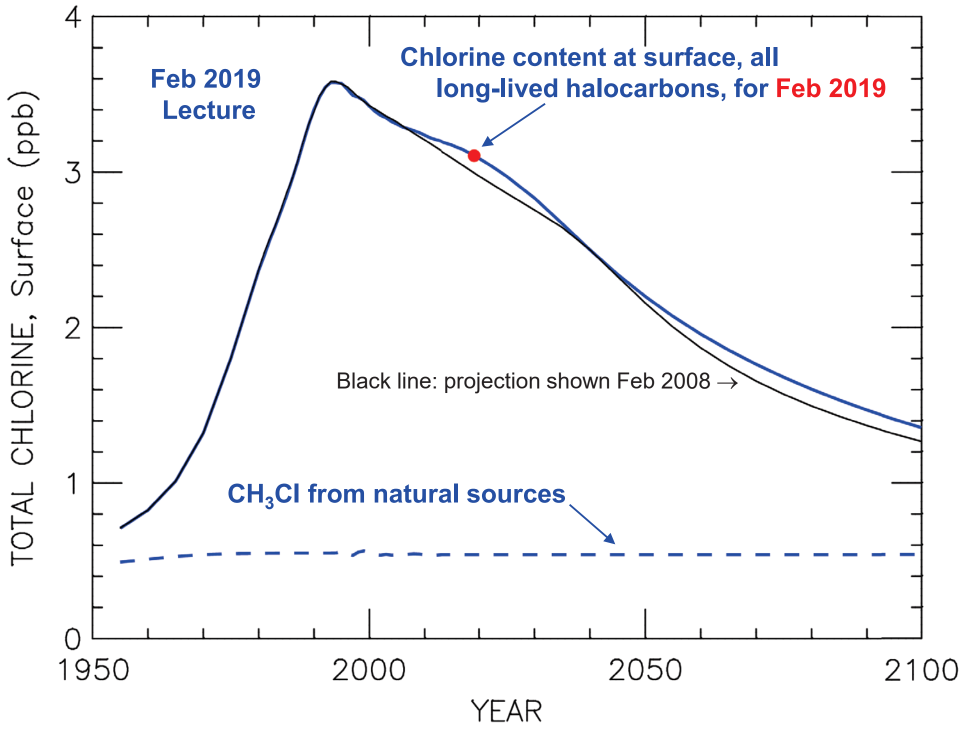


Figure Q15-1, WMO 2014 QAs

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 issued 4 Feb 2019:
https://www.esrl.noaa.gov/csd/assessments/ozone/2018

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

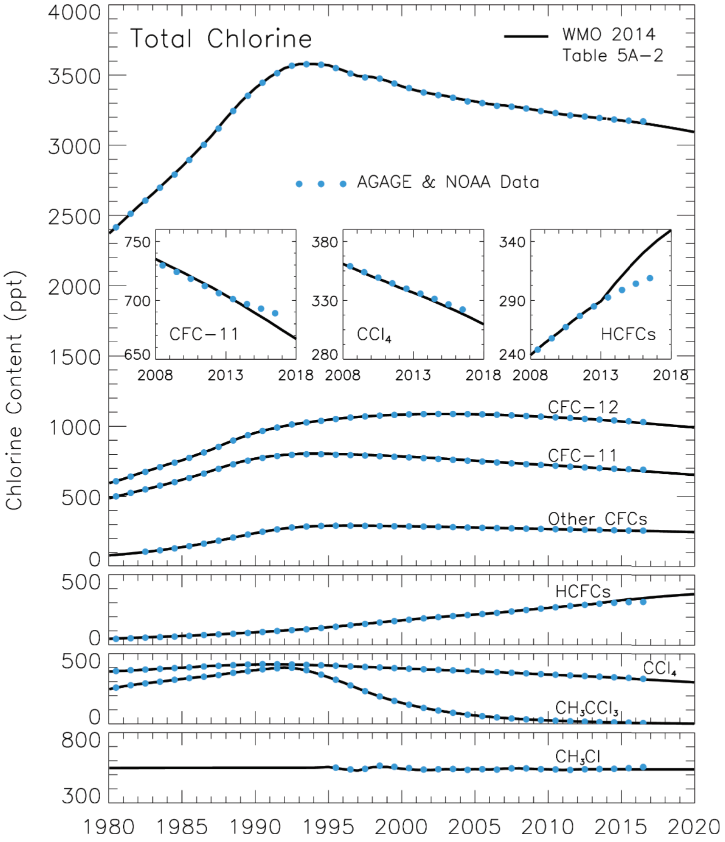
Interviews, documents and advertisements collected by The New York Times and independent investigators indicate that a major source — possibly the overwhelming one — is factories in China that have ignored a global ban and kept making or using the chemical, CFC-11, mostly to produce foam insulation for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

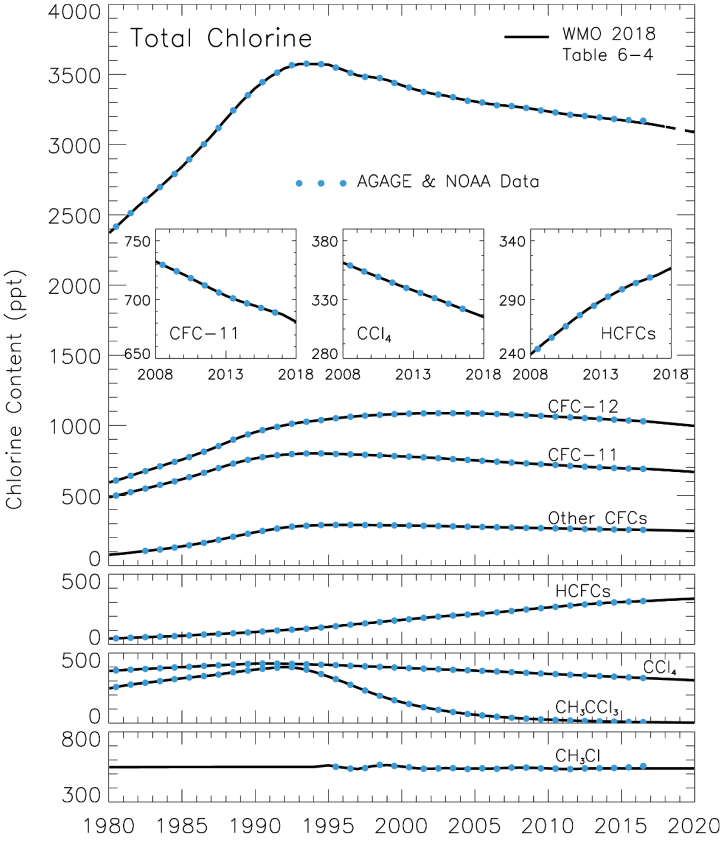
Billboards in Xingfu, China, promoting locally made refrigerators. The city has around 1,700 businesses involved in the production of cooking and refrigeration equipment. Gilles Sabrié for The New York Times

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

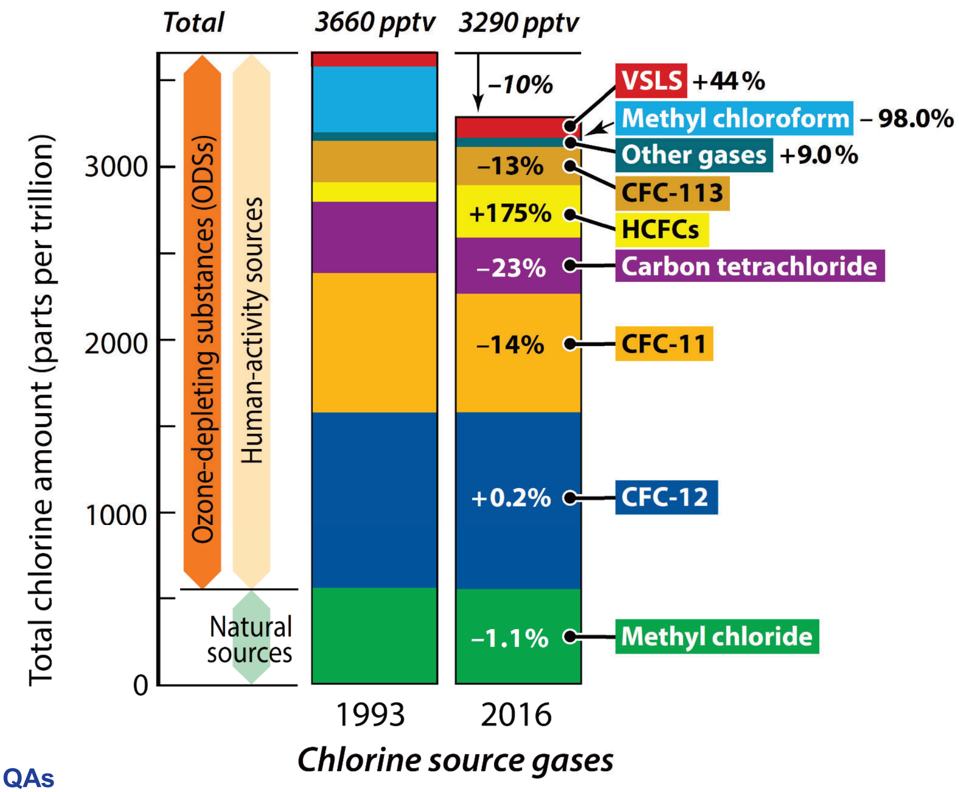
Organic Halogens Versus Time



Organic Halogens Versus Time



Chlorine Source Gases



Update for 2019 QAs

Ozone Depletion Potential 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[e]		
CFC-11	52	1
CFC-12	102	0.73
CFC-113	93	0.81
Carbon tetrachloride (CCl_4)	26	0.72
HCFCs	1–18	0.01–0.10
Methyl chloroform (CH_3CCl_3)	5	0.14
Methyl chloride (CH_3Cl)	0.9	0.015
Very short-lived Cl-containing gases	less than 0.5	[b, d] very low
Bromine gases		
Halon-1301	72	15.2
Halon-1211	16	6.9
Methyl bromide (CH_3Br)	0.8	0.57
Hydrofluorocarbons (HFCs)		
HFC-134a	14	0
HFC-23	228	0
HFC-143a	51	0
HFC-125	31	0
HFC-152a	1.6	0
HFC-32	5.4	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

Ozone Depletion

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

According to the Question 13 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 13 of the WMO/UNEP QAs, compared to Section 28 of Chemistry in Context (i.e, your answer to the prior question).

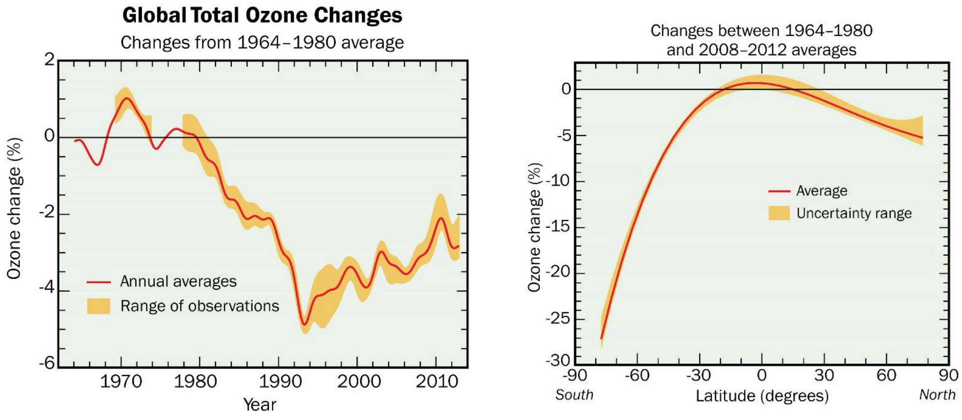
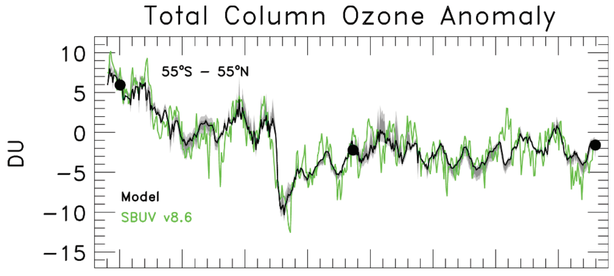
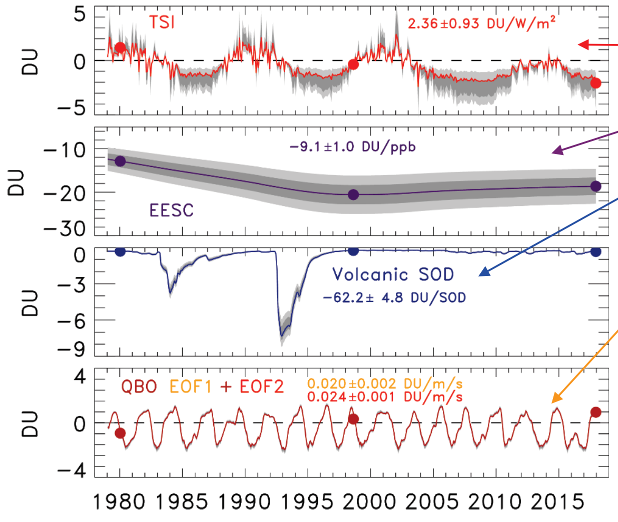


Fig Q13-1, WMO 2014 QAs

Ozone Depletion at Mid-Latitudes



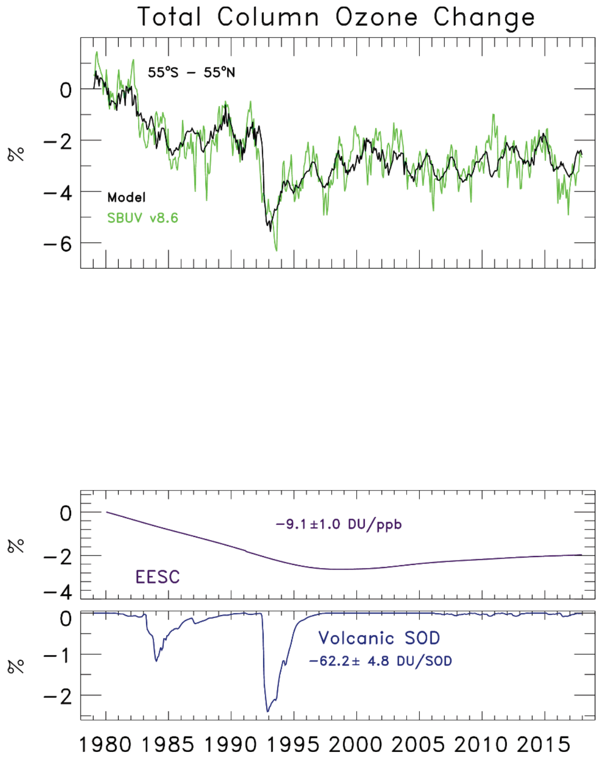
Ozone data from
http://acdb-ext.gsfc.nasa.gov/Data_services/merged



Column Ozone Anomaly (DU) =
2.36 DU / W m^{-2} × TSI +
−9.1 DU / ppb × Halogens +
−62.2 DU × SOD +
0.022 DU / m s^{-1} × Wind Speed

where
TSI = total solar irradiance
Halogens=stratospheric chlorine & bromine loading
SOD = Stratospheric Optical Depth
WS = Wind speed of the tropical lower strat

Ozone Depletion at Mid-Latitudes



Ozone data from
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Chapman Chemistry

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

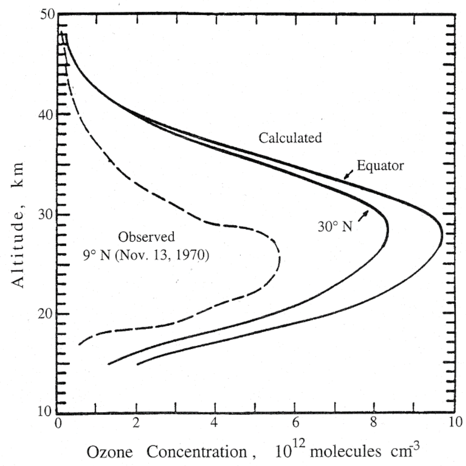


FIGURE 4.6 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970.

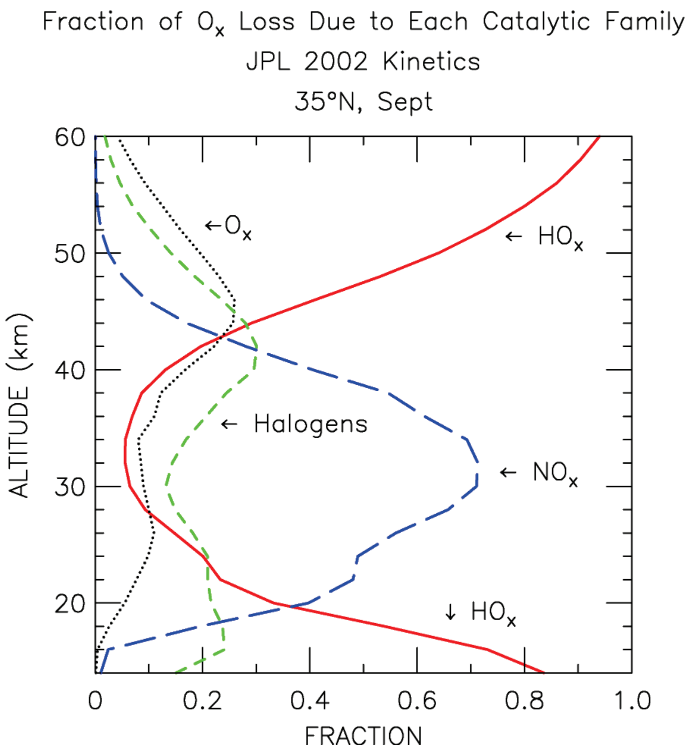
$[O_3]$ falls off with increasing altitude (high in stratosphere), at a rate determined by $[M]^{3/2}$, because:

$[O_3]$ 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, Slide 5

Stratospheric Photochemistry: Odd Oxygen Loss By Families

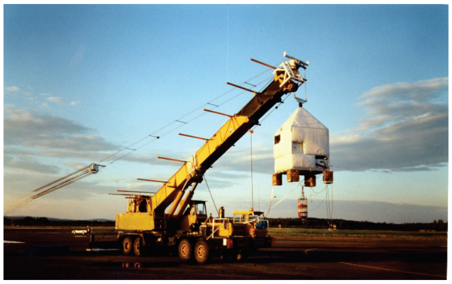


Lecture 9, Slide 10

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.

Fairbanks, Alaska : Summer 1998



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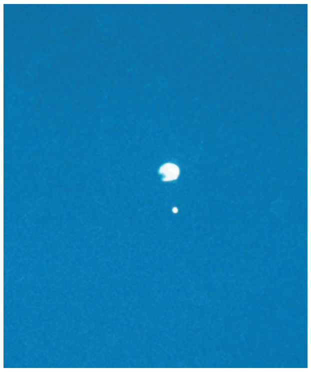
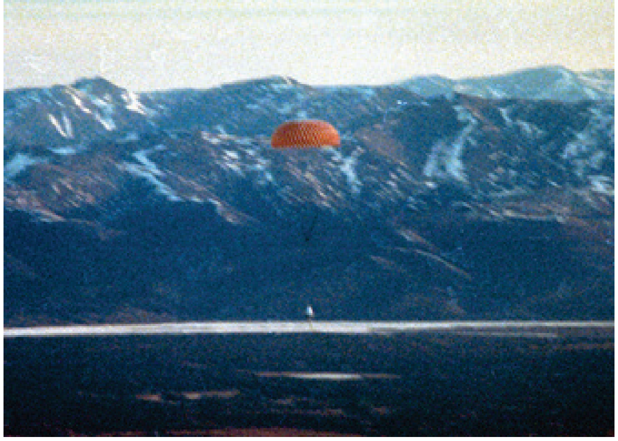
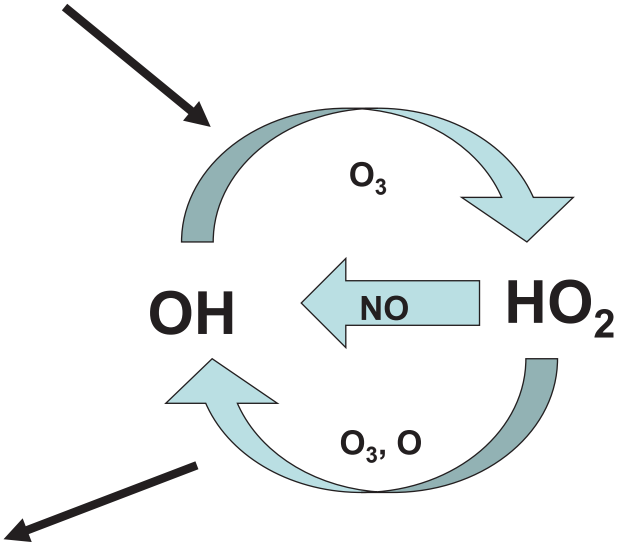




HO_x : OH and HO_2

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

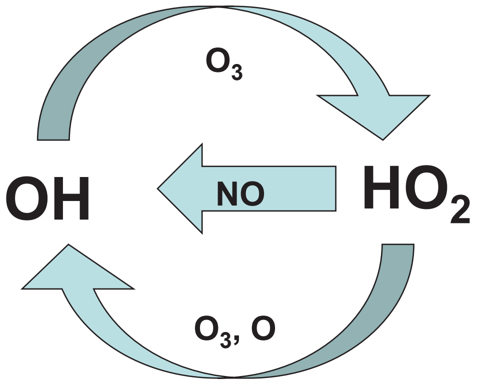
Rapid inner cycle:

HO_2 formation:

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

HO_2 loss step (2):

$$\cancel{OH} + O_3 \rightarrow \cancel{HO_2} + O_2$$
$$\cancel{HO_2} + NO \rightarrow \cancel{OH} + NO_2$$

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

HO_x : OH and HO_2

OH and HO_2 are central to stratospheric and tropospheric photochemistry

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

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

HO_2 loss step (3):

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

HO_2 loss step (4):

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

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 <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:

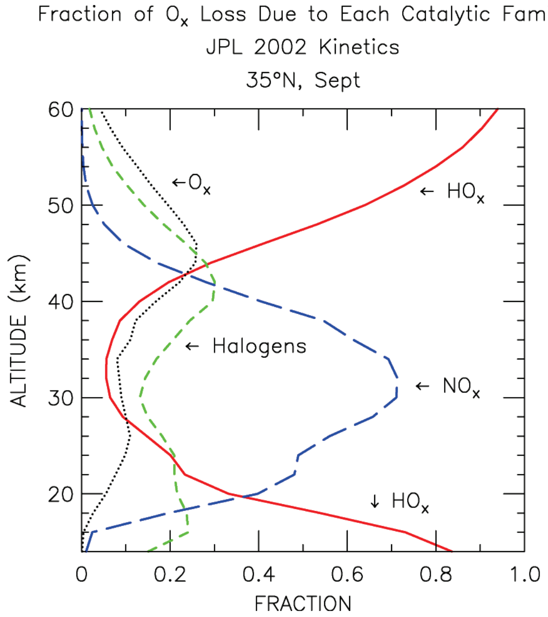
clear now that reactions (3) and (4) each consume two odd oxygens at rates determined by $2\,k_3\,[HO_2]\,[O]$ and $2\,k_4\,[HO_2][O_3]$

Odd Oxygen Loss - HO_x

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

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

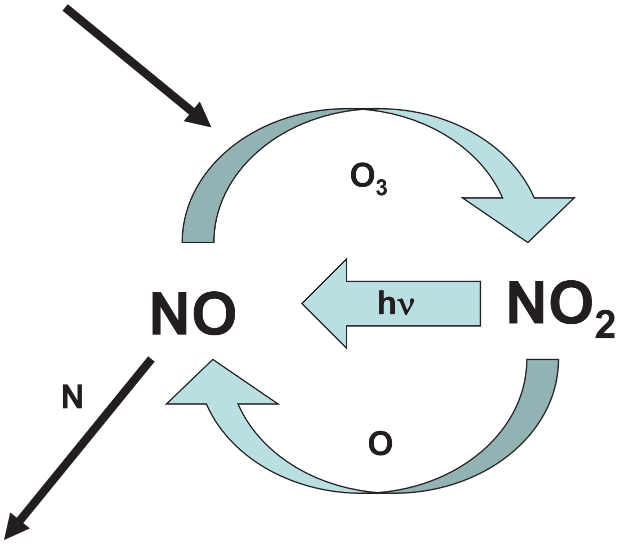
One dominates at low altitude, the other at high altitude ⇒ which is which ?!?



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):

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

NO_2 loss step (3):

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

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

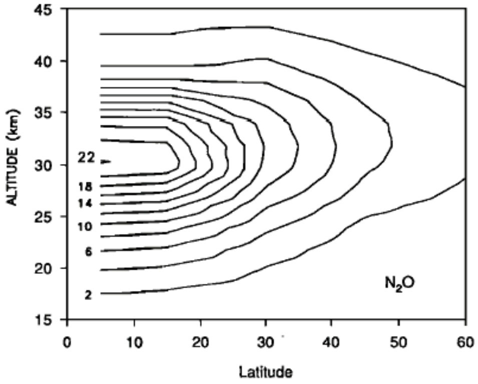


Fig. 11. Diurnally averaged loss rate for N_2O (10^2 molecules cm^{-3} s^{-1}) as a function of altitude and latitude, calculated with the line-by-line model, for equinox. The loss rate includes destruction of N_2O by reaction with $O(^1D)$ as well as photolysis.

Minschwaner, Salawitch, and McElroy, JGR, 1993

The minor sink for N_2O loss has a path that results in "fixed nitrogen": **Lecture 6, Slide 37**

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

Fixed 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.

N_2O and NO_y

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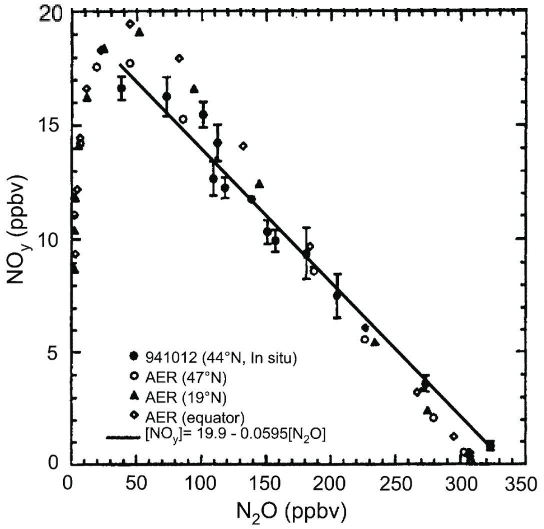

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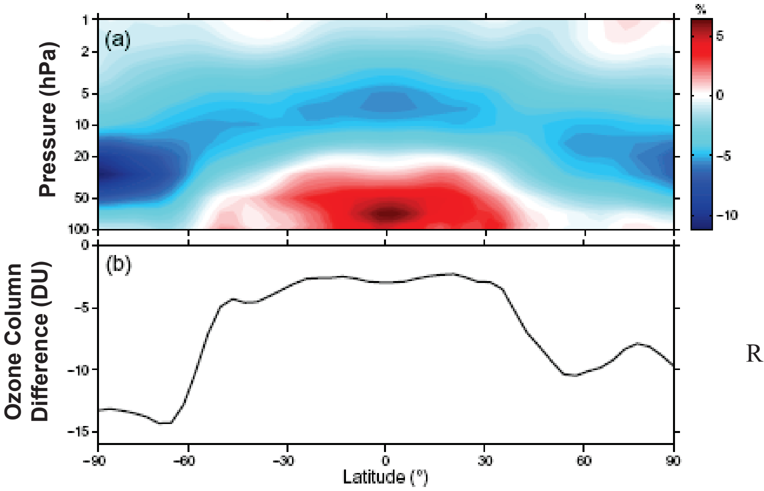
N_2O and Stratospheric Ozone



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

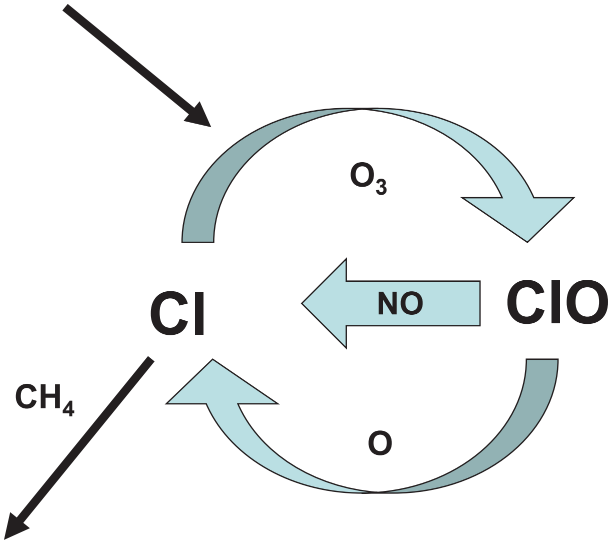
Computer models project stratospheric column O_3 will decline as N_2O rises

Lecture 6, Slide 38

ClO_x : ClO and Cl

ClO is central to <u>stratospheric</u> photochemistry, at mid-latitudes and polar regions

Production : CFCs +hν→ Inorganic chlorine



O_3

Cl

NO

ClO

CH_4

O

Final sinks : HCl solubility & rainout (lowermost stratosphere)

ClO_x : ClO and Cl

ClO is central to <u>stratospheric</u> photochemistry, at mid-latitudes and polar regions:

Rapid inner cycle:

ClO formation:

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

ClO loss:

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

$$\text{or} \quad ClO + O \rightarrow Cl + O_2 \qquad (3)$$

ClO loss step (2):

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

ClO loss step (3):

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

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

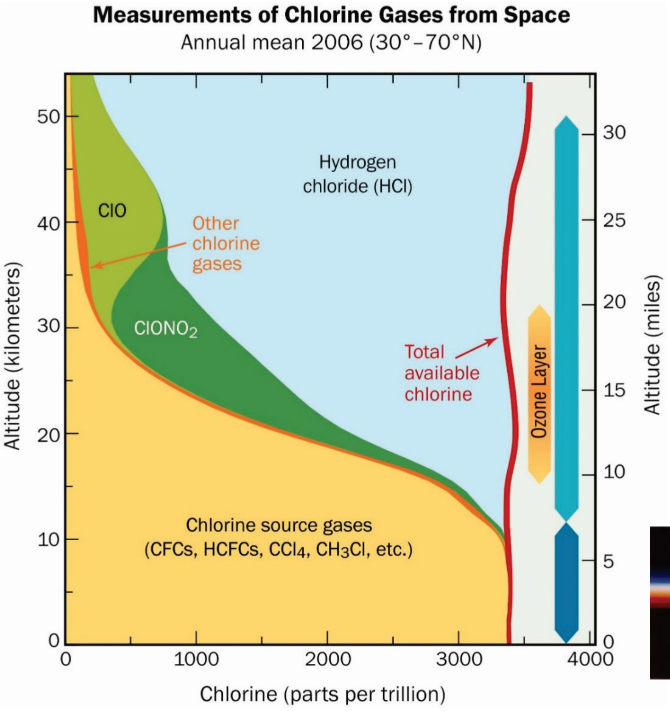
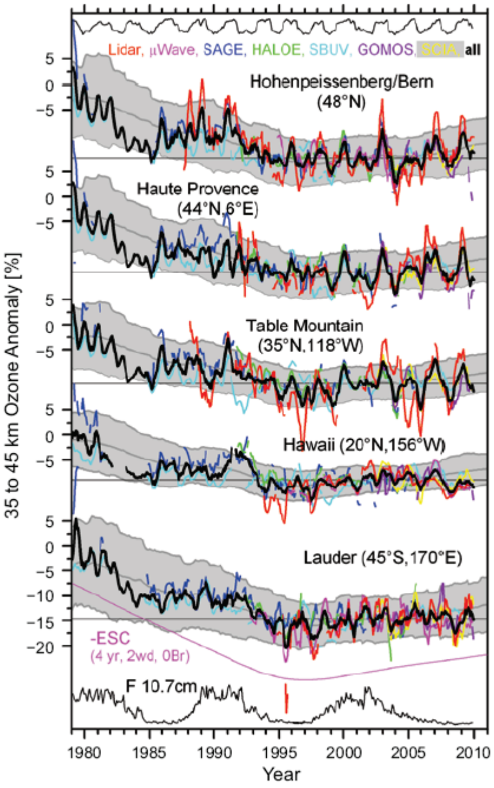


Fig Q8-2, WMO 2014 QAs

Trends in Ozone, ~40 km



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

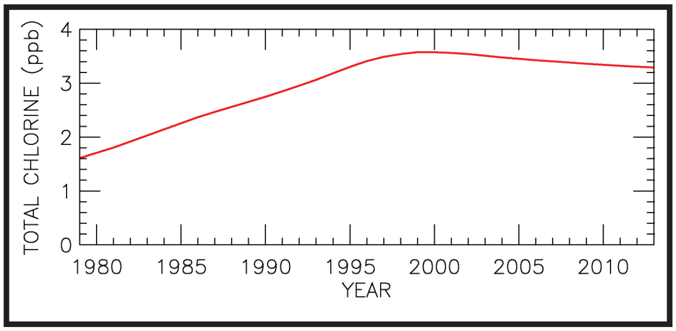
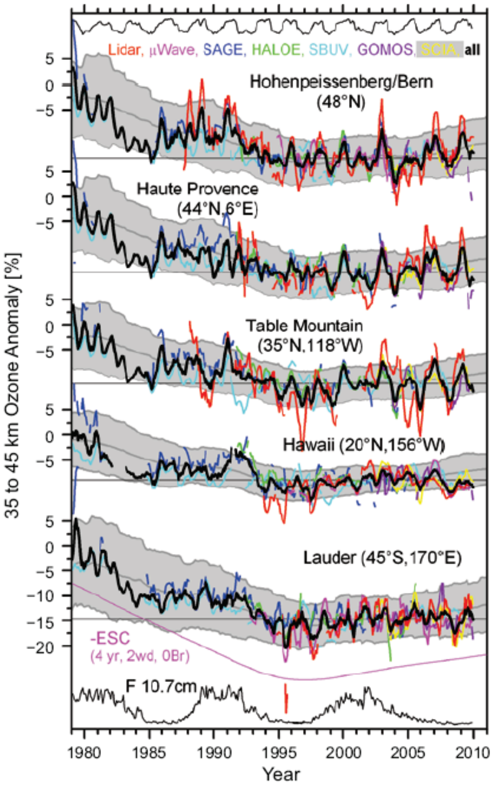


Figure 2-5, WMO/UNEP 2010

Trends in Ozone, ~40 km



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

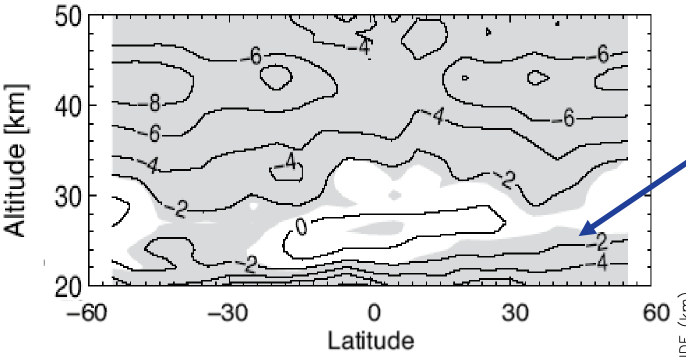
But: ozone at 40 km has little effect on surface UV radiation

Figure 2-5, WMO/UNEP 2010

Trends in Ozone vs Altitude

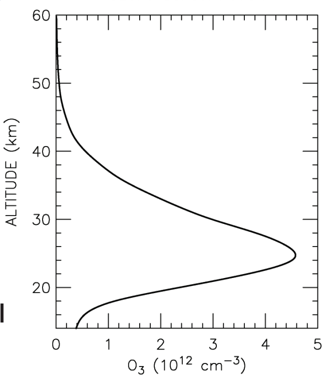
Two complications to understanding ozone trends in the lower stratosphere: aerosol surface area and bromine

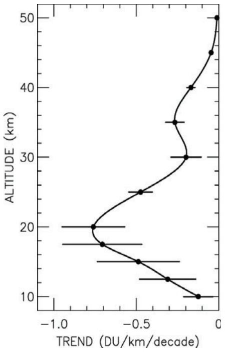
Units: % per decade



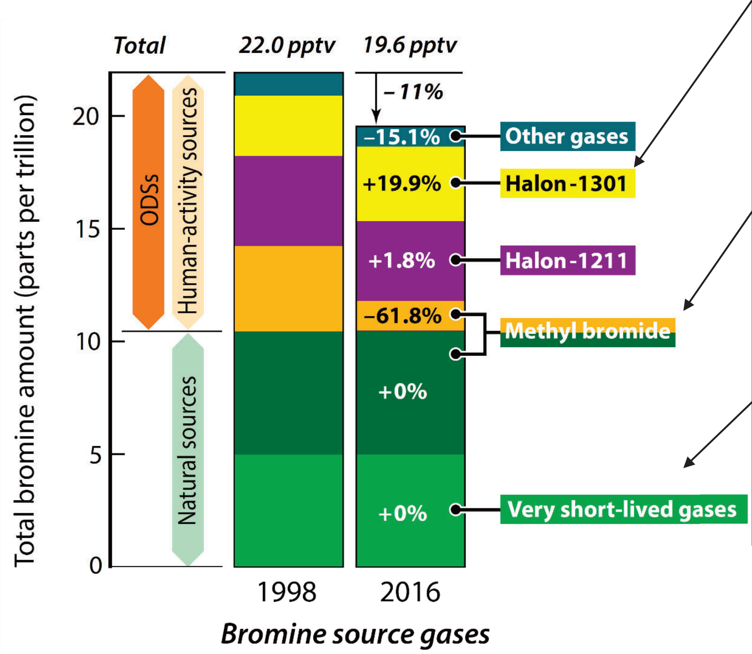
Trends in ozone as a function of latitude and altitude, for the time period 1979 to 2005, from the NASA SAGE I & SAGE II instruments. Shaded region indicates significance at the 2σ level

Figure 2-4, WMO/UNEP 2010





Bromine Source Gases



Halons:

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

CH_3Br:

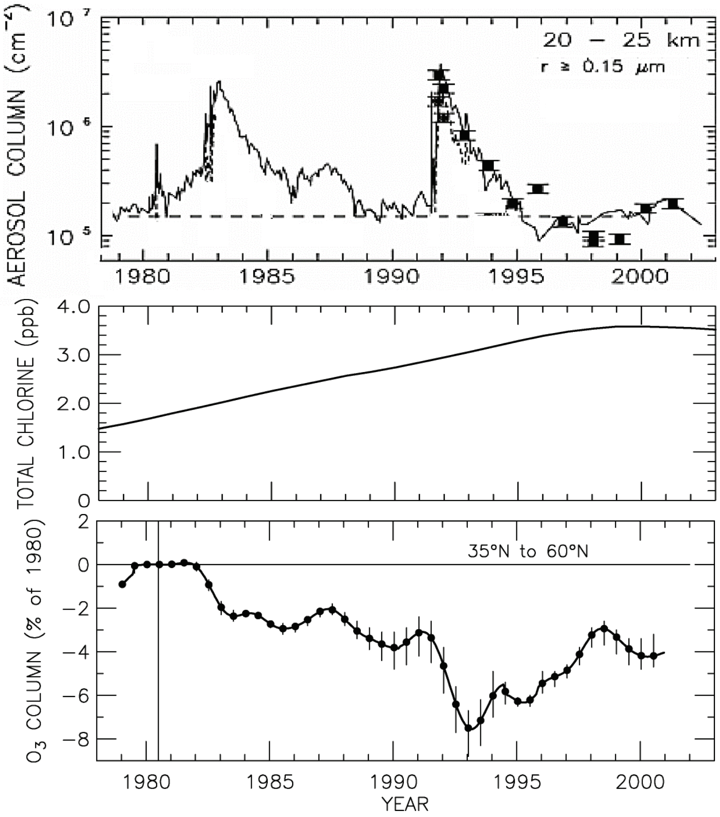
- fumigant; released by biomass burning
- production halted by Montreal Protocol
- significant natural & human sources

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

Update for 2019 QAs

Total Column Ozone Time Series, NH



Stratospheric aerosol loading,

Deshler et al., 2003.

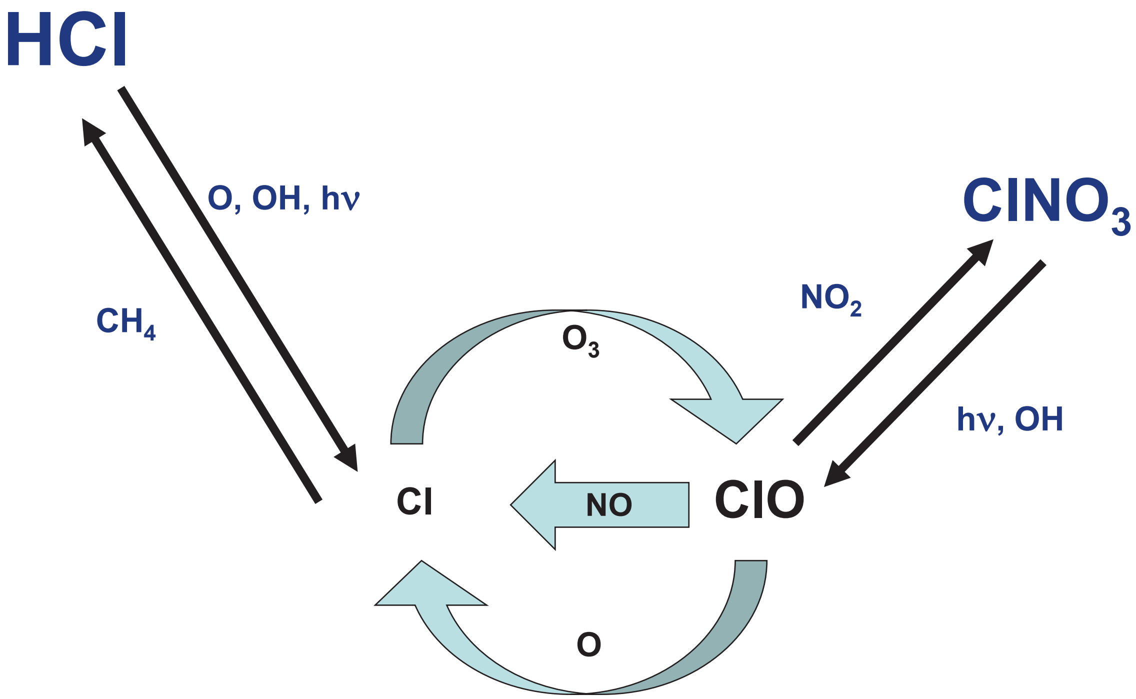
Stratospheric chlorine

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



HCl

O, OH, hν

CH_4

$ClNO_3$

NO_2

O_3

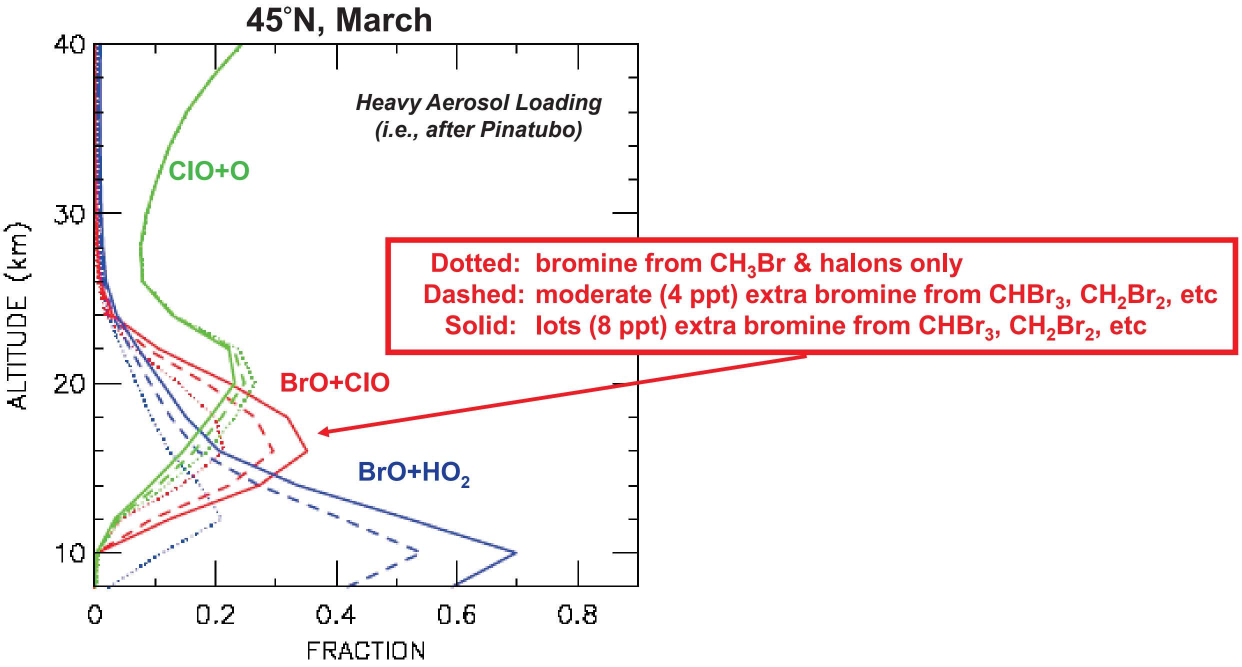
hν, OH

Cl

NO

ClO

O

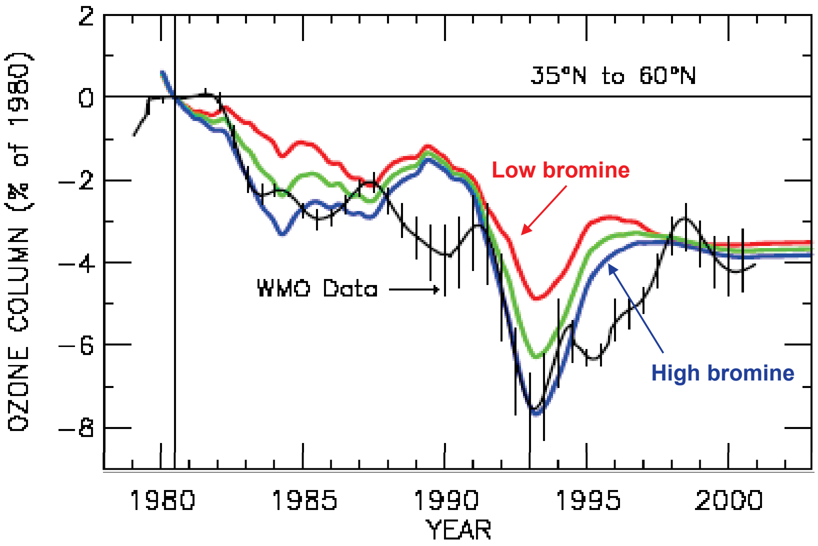


Dotted: bromine from CH_3Br & halons only
Dashed: moderate (4 ppt) extra bromine from $CHBr_3$, CH_2Br_2, etc
Solid: lots (8 ppt) extra bromine from $CHBr_3$, CH_2Br_2, etc

After Salawitch *et al*., *GRL*, 2004.

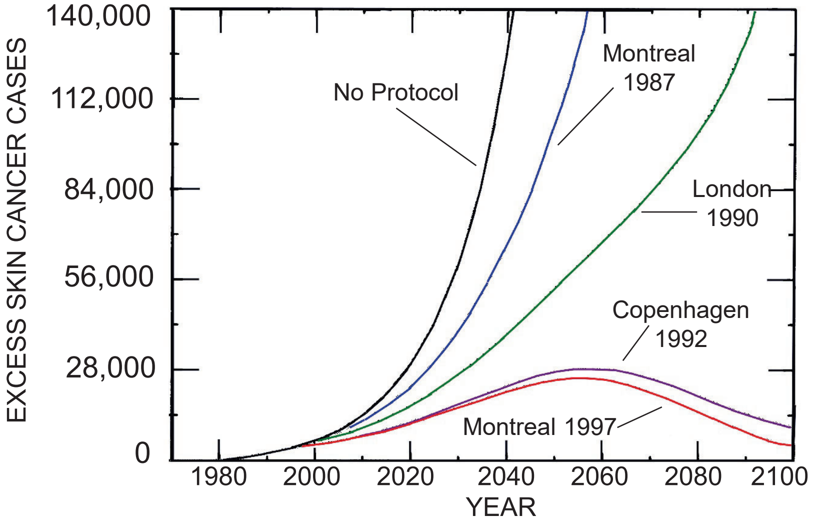
Ozone responds to:

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.