Review of Lectures 9 to 16

AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2015

- Review of Problem Set #4 will be held Mon, 13 April 6:30 pm
- Unfortunately the last day to withdraw is Mon, 13 April
  apologies for scheduling exam one day after this important deadline

- ELMS gradebook current: please let us know of any inconsistencies
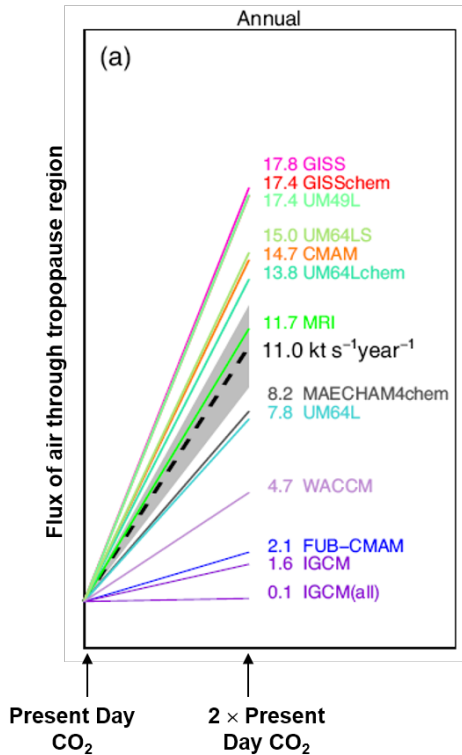
9 April 2015
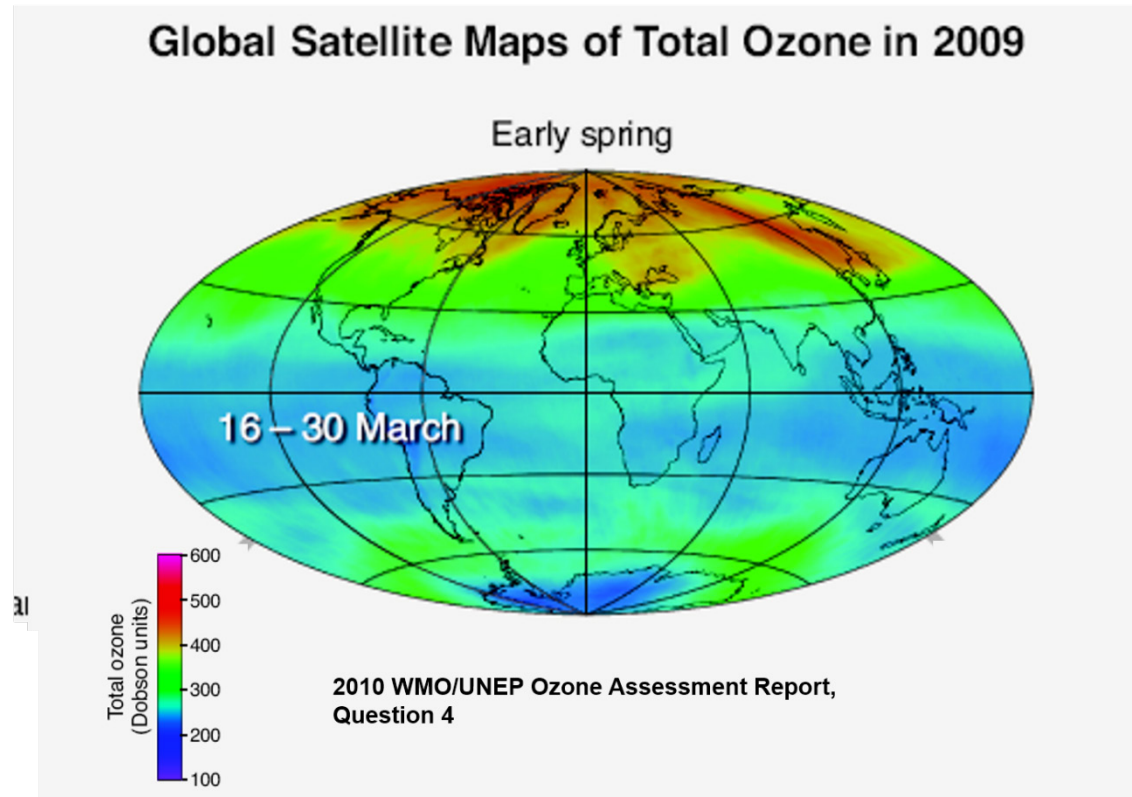
More Chemistry and Climate Coupling

Figure 5-17. Trends in exchange of air from troposphere-to-stratosphere computed by 14 CCMs.

Trends (units of Gg s^{-1} year $^{-1}$) are represented by the slope of each line.

Dashed line is the multi-model mean.

After Butchart *et al.*, *Clim. Dyn.*, 2006.

WMO/UNEP Ozone Assessment Report 2007

Global Satellite Maps of Total Ozone in 2009

Early spring

16 – 30 March

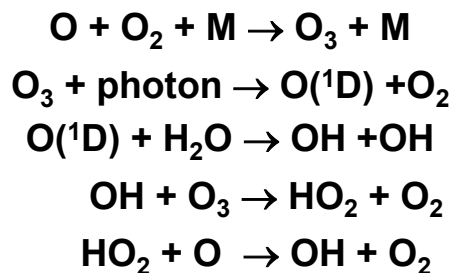2010 WMO/UNEP Ozone Assessment Report, Question 4

Importance of Radicals

- With a few exceptions, the only reactions between molecules that proceed at appreciable rates are those involving at least one radical

- Radicals require significant energy to form: a bond must be broken

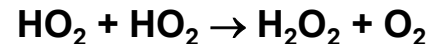- Radical formation is tied to absorption of photons that "photodissociate" a compound, leading to radical formation

Initiation

$O_2 + photon \rightarrow O + O$

Propagation

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

$O_3 + photon \rightarrow O(^1D) + O_2$

$O(^1D) + H_2O \rightarrow OH + OH$

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O \rightarrow OH + O_2$

Termination

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
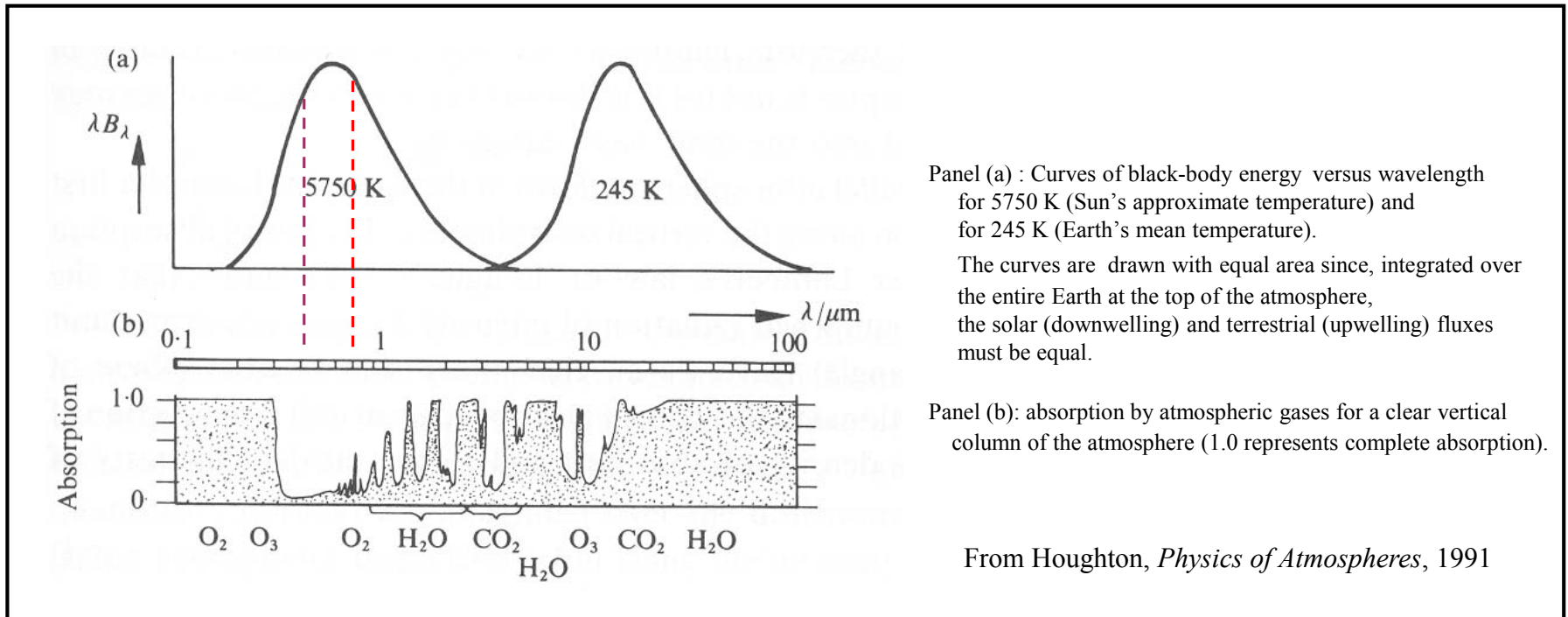
Atmospheric Radiation

- Solar irradiance (downwelling) at top of atmosphere occurs at wavelengths between ~200 and 2000 nm (~5750 K "black body" temperature)

Panel (a) : Curves of black-body energy versus wavelength for 5750 K (Sun's approximate temperature) and for 245 K (Earth's mean temperature).

The curves are drawn with equal area since, integrated over the entire Earth at the top of the atmosphere, the solar (downwelling) and terrestrial (upwelling) fluxes must be equal.

Panel (b): absorption by atmospheric gases for a clear vertical column of the atmosphere (1.0 represents complete absorption).

From Houghton, *Physics of Atmospheres*, 1991

- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) of molecules

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Absorption Cross Section of O_2
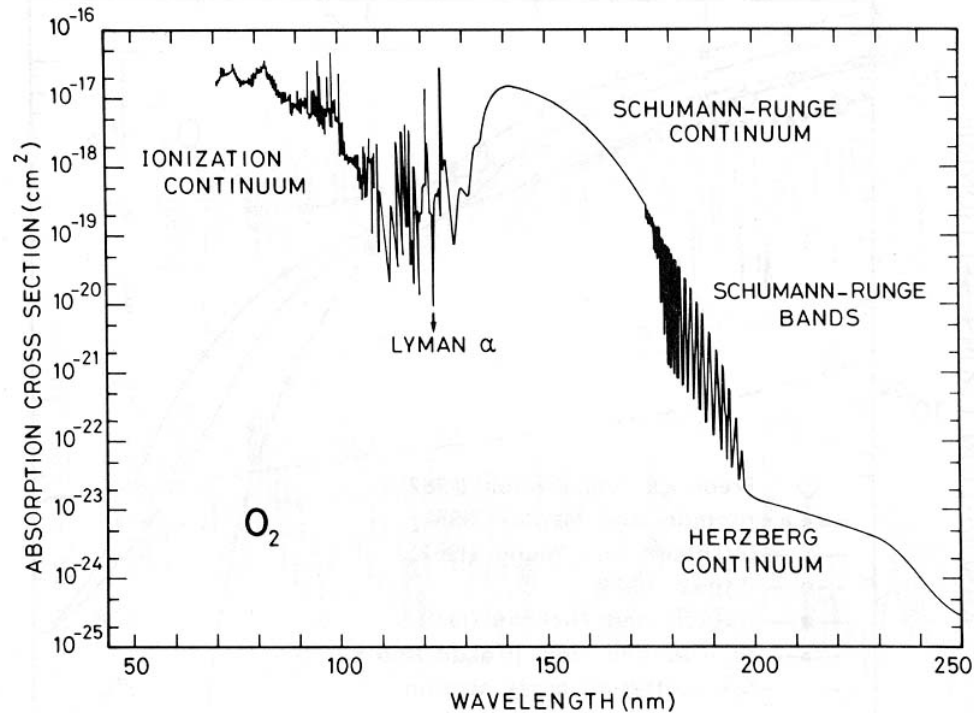
From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986

- O_2 can not dissociate longward of ~250 nm
- All absorption shown above is dissociative (e.g., leads to production of two O atoms)
- Structure in the O_2 cross section is related to whether the initial transition involves an unbound electronic state (smooth) or involves a specific vibrational level of an electronic state (banded, due to requirement of specific quanta of energy)

Optical Depth of O_2 Absorption

Recall the *Beer-Lambert Law*:

$$F(z,\lambda) = F_{TOA}(\lambda)\, e^{-\tau(z, \lambda)} \qquad \text{(TOA : Top of Atmosphere)}$$

where:

$$\tau(z, \lambda) = m \int_{z}^{\infty} \sigma_\lambda\, [C]\, dz' \qquad (\tau\text{: optical depth})$$

Also:

$$\int_{0}^{\infty} [O_2]\, dz' \approx 4 \times 10^{24} \text{ molecules/cm}^2$$

O_2 Optical Depth for $\theta = 0°$, $z = 0$ km			
	$\sigma_{max}\,(cm^2)$	$\tau\,(0\,km)$	$e^{-\tau\,(0\,km)}$
Schumann-Runge Continuum	10^{-17}	4×10^7	0.
Schumann-Runge Bands	10^{-20}	4×10^4	0.
	3×10^{-23}	120	7.6×10^{-53}
Herzberg Continuum	10^{-23}	40	4.2×10^{-18}

Optical Depth of O_3 Absorption

A typical mid-latitude column abundance for O_3 is 300 Dobson units (DU):

$$1 \text{ DU} = 2.687 \times 10^{16} \text{ molecules/cm}^2; \quad 300 \text{ DU} = 8 \times 10^{18} \text{ molecules/cm}^2$$

Aside:
$$\frac{\text{Column } O_3}{\text{Column Air}} = \frac{8 \times 10^{18}}{2 \times 10^{25}} = 0.4 \text{ parts per million} \Rightarrow \text{Ozone is a trace species !}$$

O_3 Optical Depth for $\theta = 0°$, z = 0 km				
	σ_{max} (cm^2)	τ (0 km)	$e^{-\tau\,(0\,km)}$	O_3 Column, $\tau = 1.0$
Hartley (~220 to 280 nm)	10^{-17}	80	1.8×10^{-35}	3.7 DU
Huggins (~310 to 330 nm)	10^{-19}	0.8	0.45	372 DU
Chappuis (~500 to 700 nm)	3×10^{-21}	0.024	~1.0	12,400 DU

Solar Spectral Actinic Flux

FIGURE 6. Solar spectral actinic flux (photons cm^{-2} s^{-1} nm^{-1}) at the top of Earth's atmosphere.

130   ATMOSPHERIC PHOTOCHEMISTRY AND CHEMICAL KINETICS

O$_3$ Huggins & Chappuis
Huggins: from ~310 to ~330 nm, τ = 1 @ Ground
Chappuis: from 450 to 800 nm, optically thin

O$_2$ Schumann-Runge
τ = 1 @ 38 to 140 km

O$_2$ Herzberg & O$_3$ Hartley
O$_2$: σ_λ peak @ 200 nm, τ = 1 @ ~29 km
O$_3$: σ_λ peak @ 250 nm, τ = 1 @ ~40 km
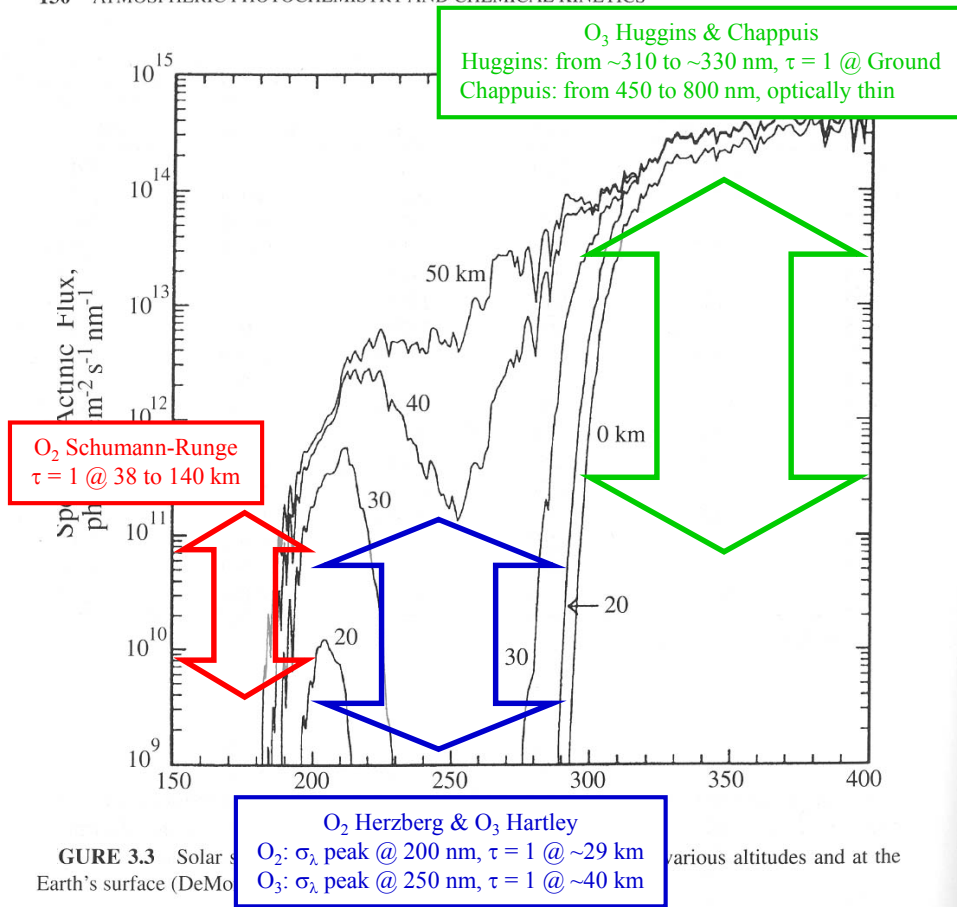
GURE 3.3   Solar s... ...arious altitudes and at the Earth's surface (DeMo...

From DeMore et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation No. 11, 1994.

From Seinfeld and Pandis, *Atmospheric Chemistry and Physics*, 1998.

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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:

$$J_{gas}(z,\lambda) = \text{Quantum\_Yield}(\lambda)\ \sigma_{gas}(\lambda,T)\ F(z,\lambda)$$

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:

$$J_{gas}(z) = \int_{\lambda_{min}}^{\lambda_{max}} J_{gas}(z,\lambda)\,d\lambda$$

Units: s^{-1}

$$\boxed{\text{Rate of Reaction} = \frac{dO_3}{dt} = J\,[O_3]; \quad \text{Units of } J \text{ are } s^{-1}}$$

More precisely, calculations of photolysis frequencies consider the "spectral actinic flux", which represents the amount of available photons integrated over all angles, rather than "solar irradiance". These two quantities differ because of scattering of solar radiation by gases and aerosols, and reflection of radiation by clouds and the surface.
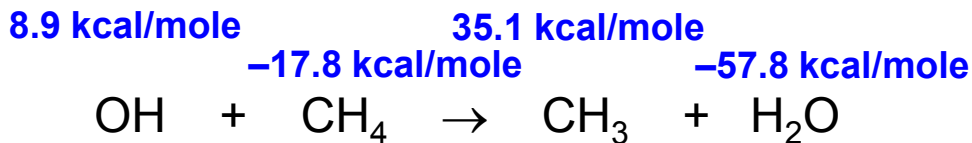
NO₂ Photolysis

O$_3 \rightarrow$ O(^{1}D) Photolysis

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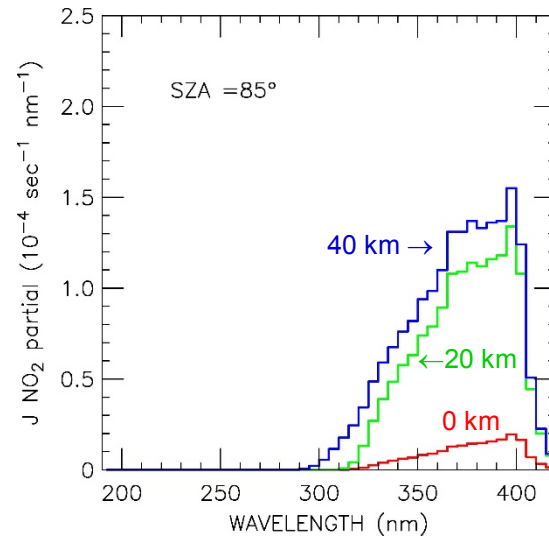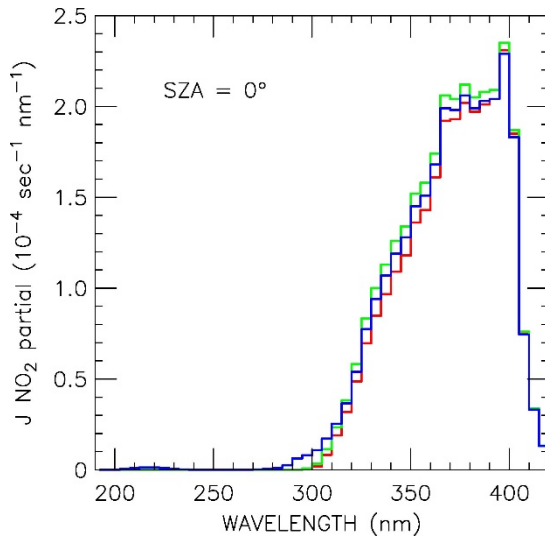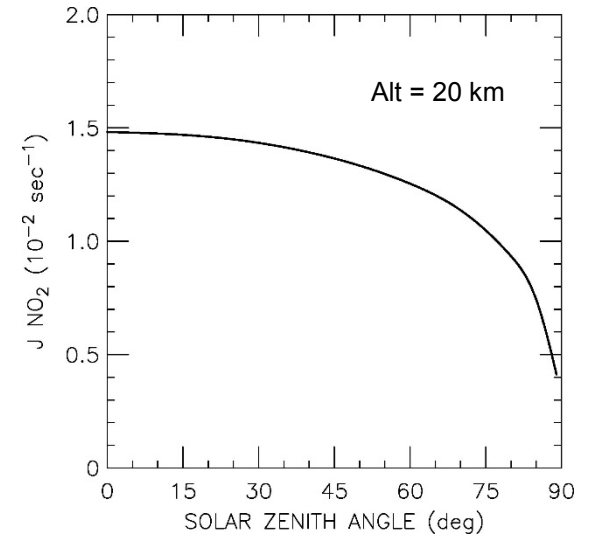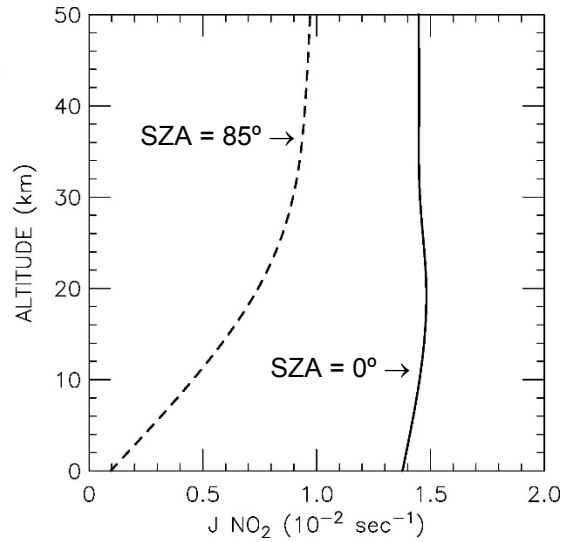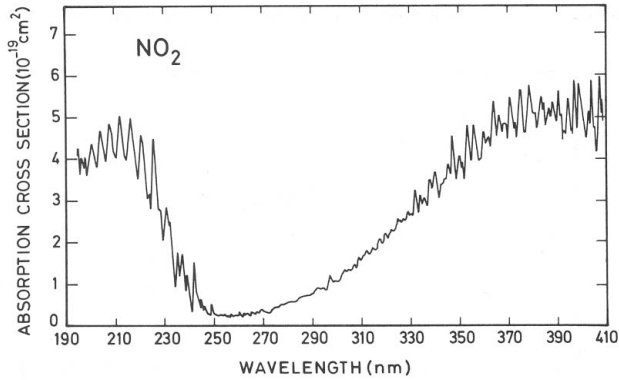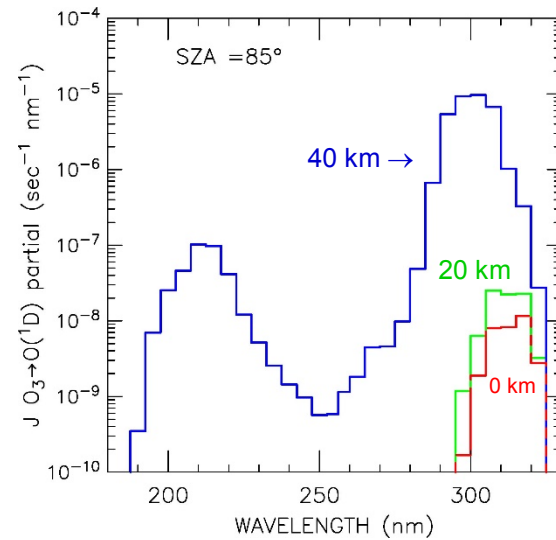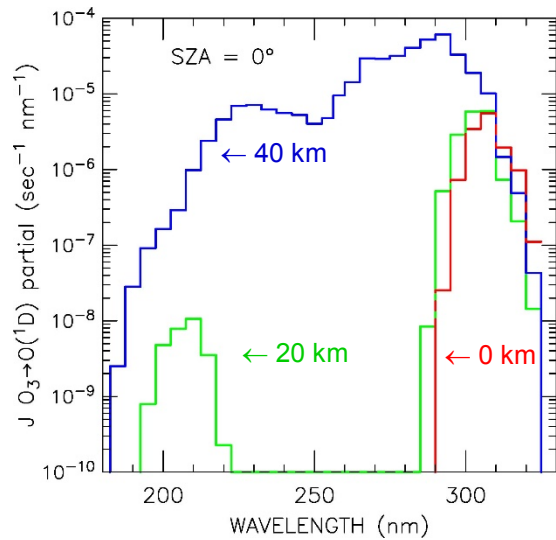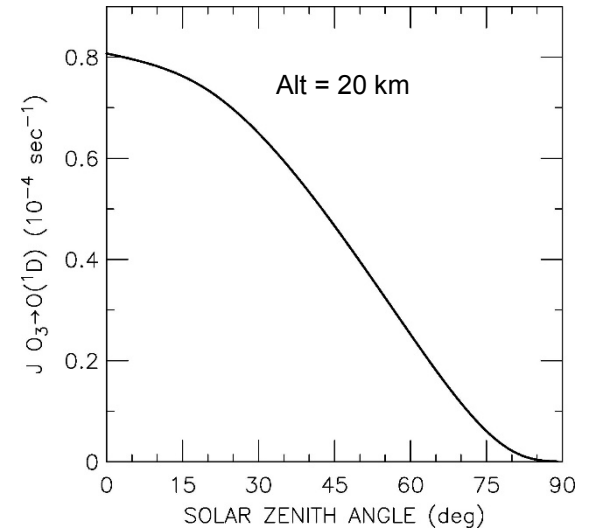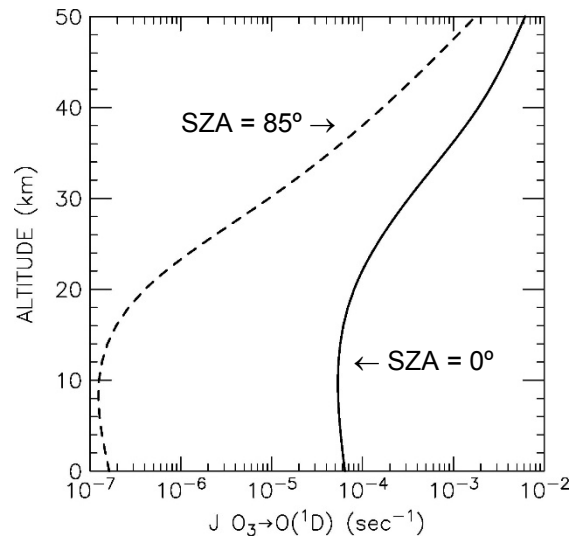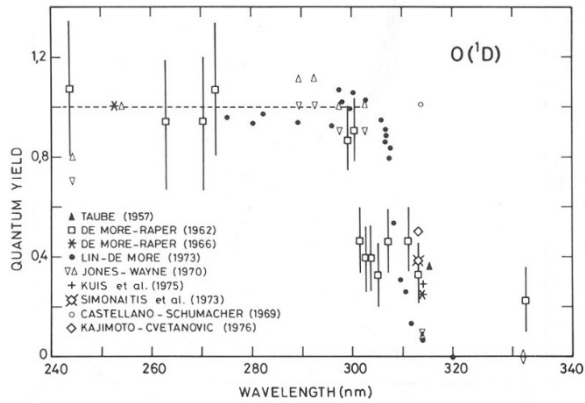
Bimolecular Gas Phase Reactions

8.9 kcal/mole   **35.1 kcal/mole**
  −17.8 kcal/mole   **−57.8 kcal/mole**

OH   + CH_4 → CH_3 + H_2O **ΔEnthalpy = −13.8 kcal/mole**

Exothermic !

$$\text{Rate of Reaction} = \frac{dCH_4}{dt} = k\,[OH][CH_4]$$

E_A / R ⇒ Activation Energy / Gas Constant

Arrhenius Expression for rate constant:

$$k = 2.45 \times 10^{-12} \times e^{-1775/T} \; cm^3 \; sec^{-1}$$

Energy Term

A factor
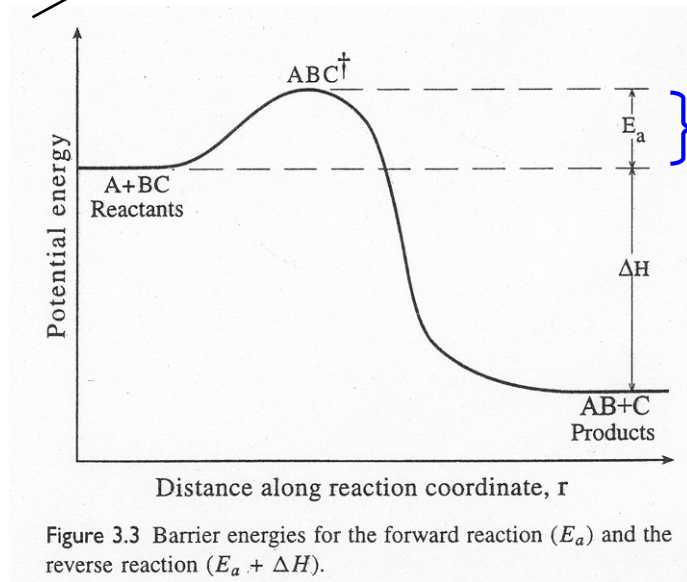
R = 8.3143 ×10⁷ erg / (K mole)
= 2.87 ×10⁶ erg / (K gm) for air

$$k_c \; e^{\Delta S / R}$$

Entropy Term

Figure 3.3 Barrier energies for the forward reaction (E_a) and the reverse reaction ($E_a + \Delta H$).

Yung and DeMore, *Photochemistry of Planetary Atmospheres*, Oxford, 1999.
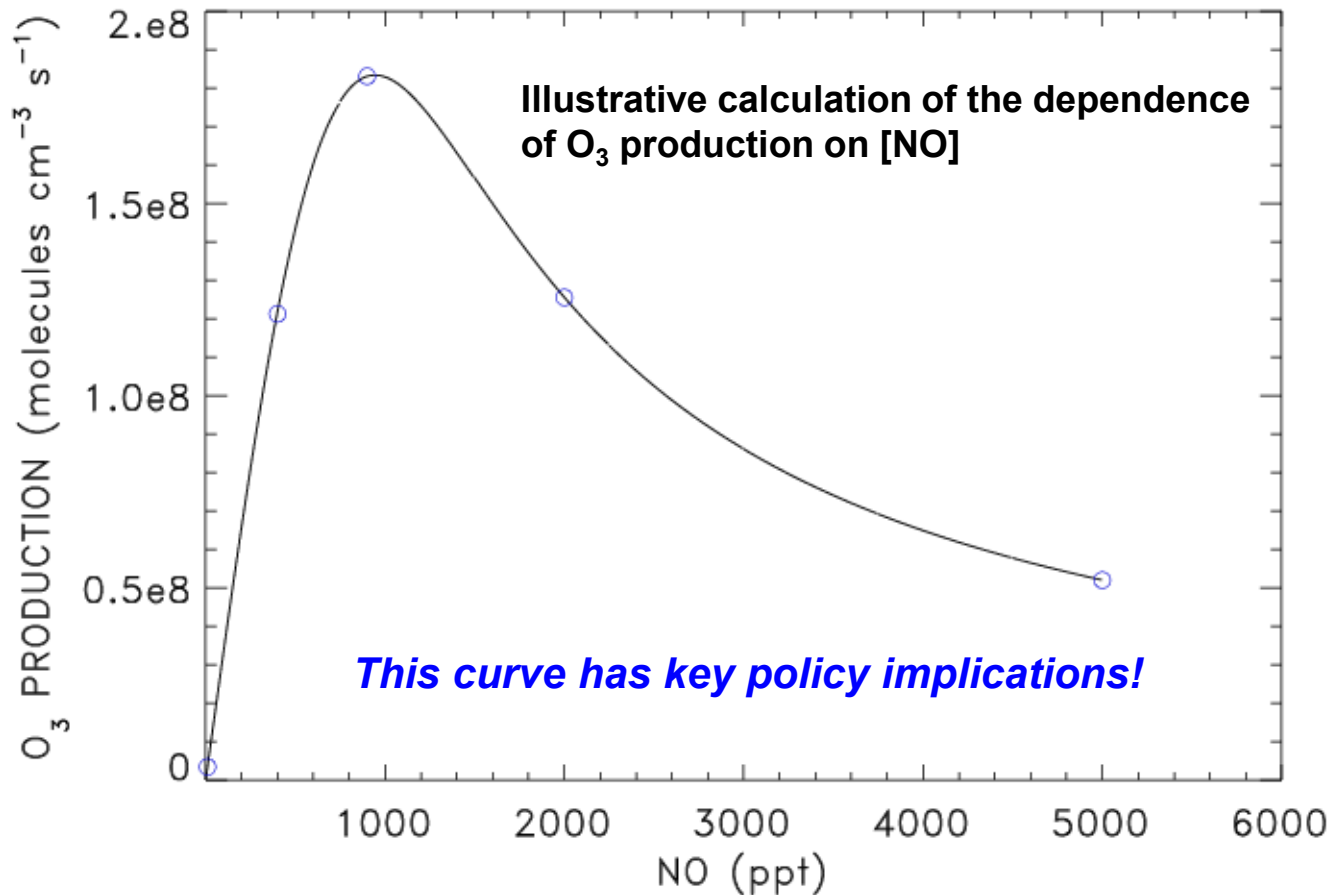
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Tropospheric Ozone Production versus NO

Production of Tropospheric O_3 limited by: _____ ?
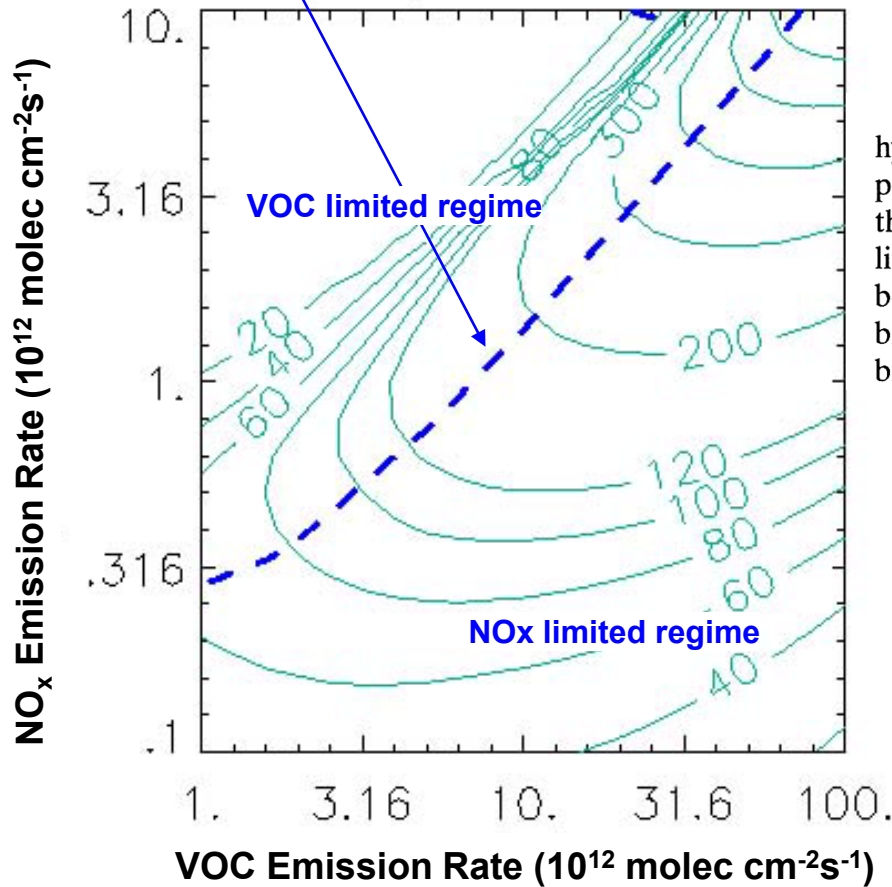
As NO_x rises:

$[HO_2]$ falls faster than $[NO]$ rises,

leading to a decrease in the value _____

Illustrative calculation of the dependence of O_3 production on [NO]

This curve has key policy implications!

Tropospheric Ozone Production versus NO$_x$ and VOCs

Ridge: local maximum for O$_3$ that separates the NOx-limited regime from and VOC limited regime

VOC limited regime

NOx limited regime

NO$_x$ Emission Rate (10^{12} molec cm^{-2}s^{-1})

VOC Emission Rate (10^{12} molec cm^{-2}s^{-1})

An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O$_3$ pollution may have been partly misdirected. Measurements and model calculations now show that O$_3$ production over most of the United States is primarily NO$_x$ limited, not hydrocarbon limited. The early models were in error in part because they underestimated emissions of hydrocarbons from automobiles, and in part because they did not account for natural emission of biogenic hydrocarbons from trees and crops.

Jacob, Chapter 12, Introduction to Atmospheric Chemistry, 1999

Figure: http://www-personal.umich.edu/~sillman/ozone.htm

Day-to-day meteorology (weather!) affects severity and duration of pollution episodes

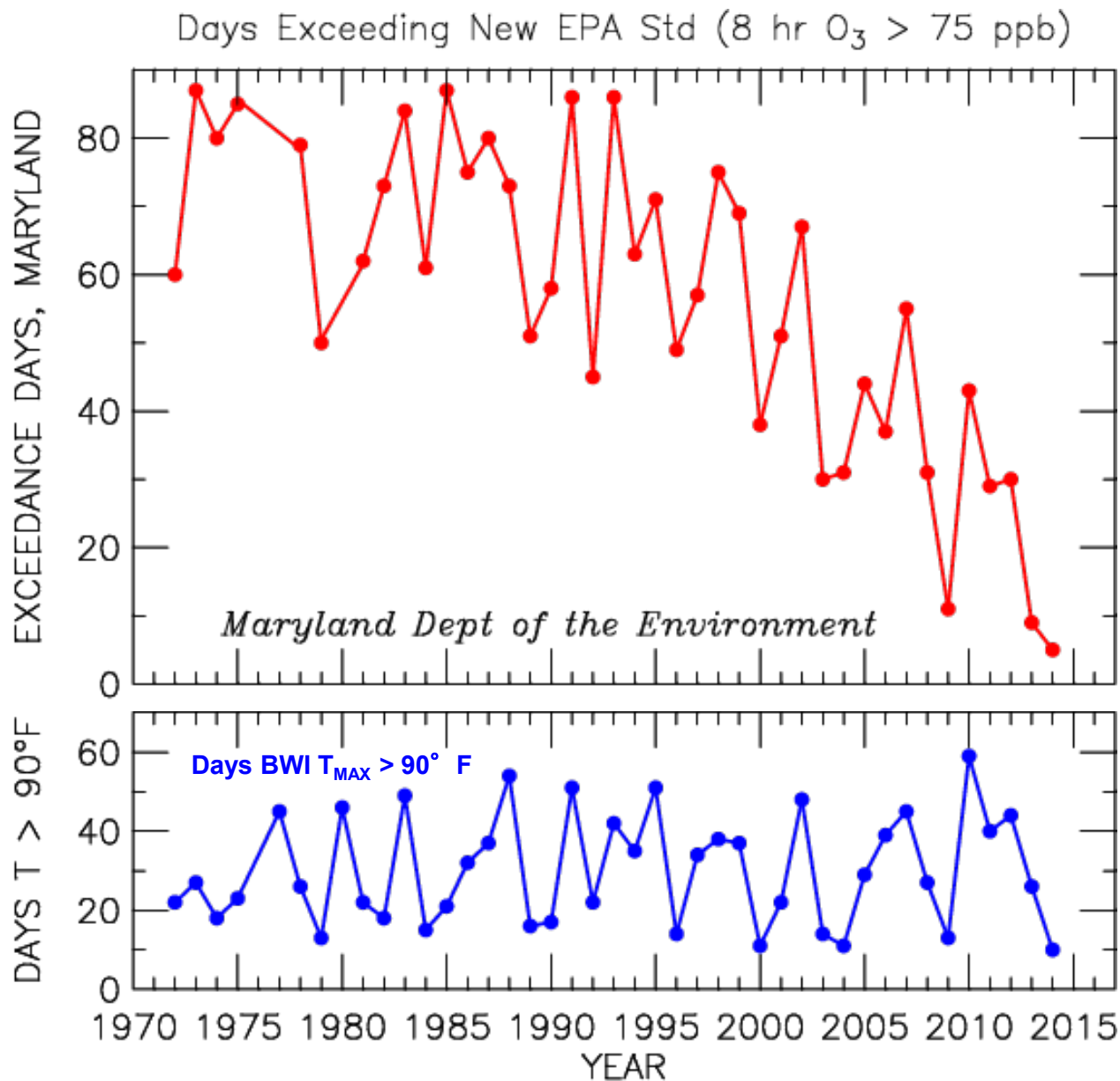**Maryland has worst air quality during a particular time of year when a certain air circulation system develops**
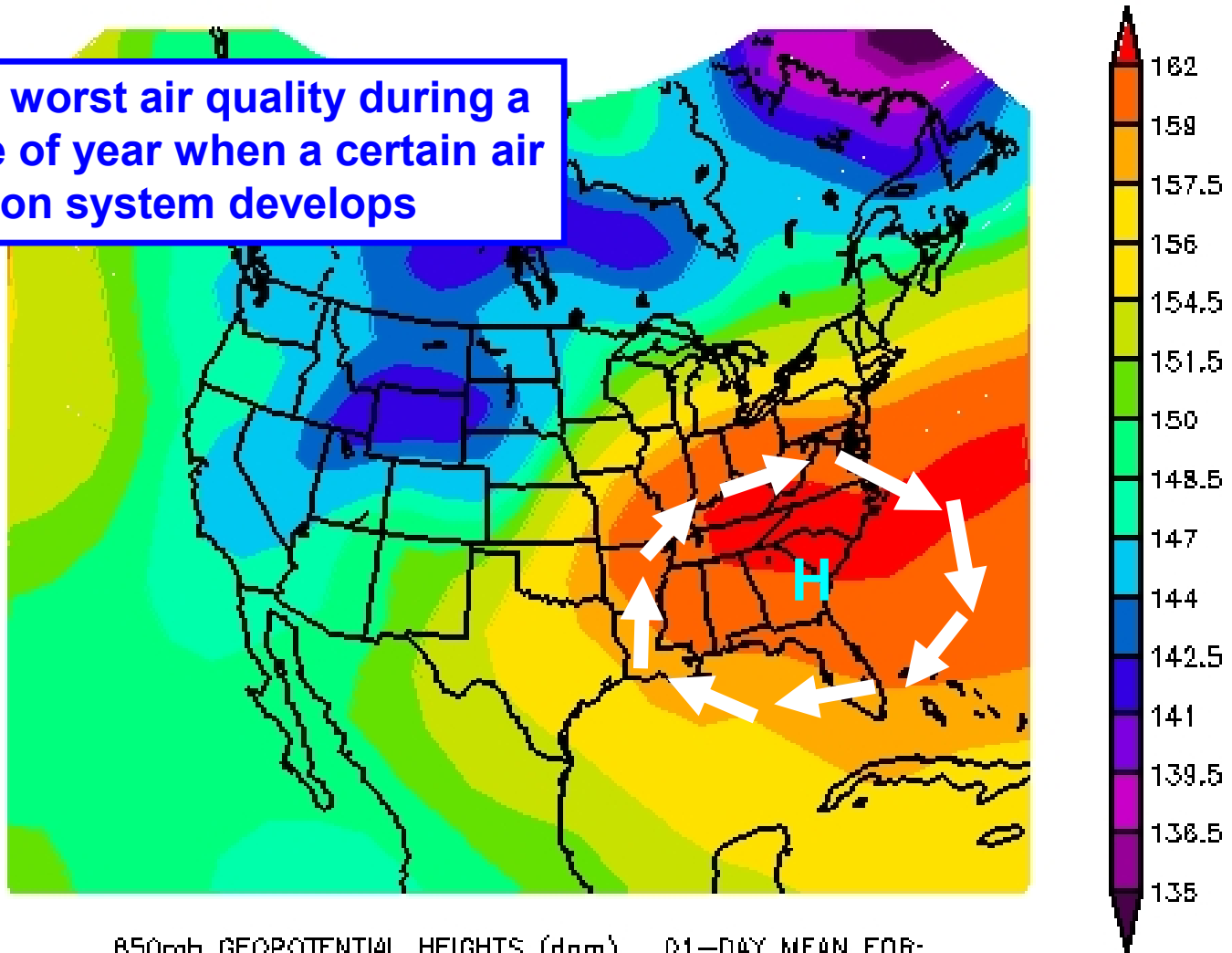
850mb GEOPOTENTIAL HEIGHTS (dam)   01—DAY MEAN FOR:
Sun JUL 04 1999
NCEP OPERATIONAL DATASET

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Dramatic Improvements Local Air Quality, Past 4 Decades

Days Exceeding New EPA Std (8 hr O_3 > 75 ppb)

EXCEEDANCE DAYS, MARYLAND

Maryland Dept of the Environment

DAYS T > 90°F
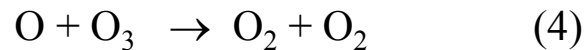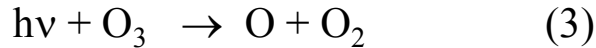
Days BWI T_{MAX} > 90° F

YEAR

16

Stratospheric Ozone: Chapman Chemistry

• Production of O_3 initiated when O_2 is photodissociated by UV sunlight

• O_3 formed when resulting O atom reacts with O_2 :

$$h\nu + O_2 \;\rightarrow\; O + O \qquad (1)$$
$$O + O_2 + M \;\rightarrow\; O_3 + M \qquad (2)$$
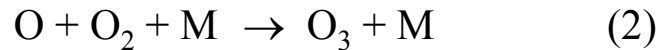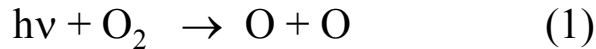
• O_3 removed by photodissociation (UV sunlight) or by reaction with O :

$$h\nu + O_3 \;\rightarrow\; O + O_2 \qquad (3)$$
$$O + O_3 \;\rightarrow\; O_2 + O_2 \qquad (4)$$

This reaction sequence was first worked out in the 1930s by Sidney Chapman,
an English mathematician and geophysicist

Chapman Chemistry

- The cycling between O and O_2 (rxns 2 and 3) occurs *much* more rapidly than leakage into (rxn 1) or out of the system (rxn 4)

- The sum $O + O_3$ is commonly called *"odd oxygen"*
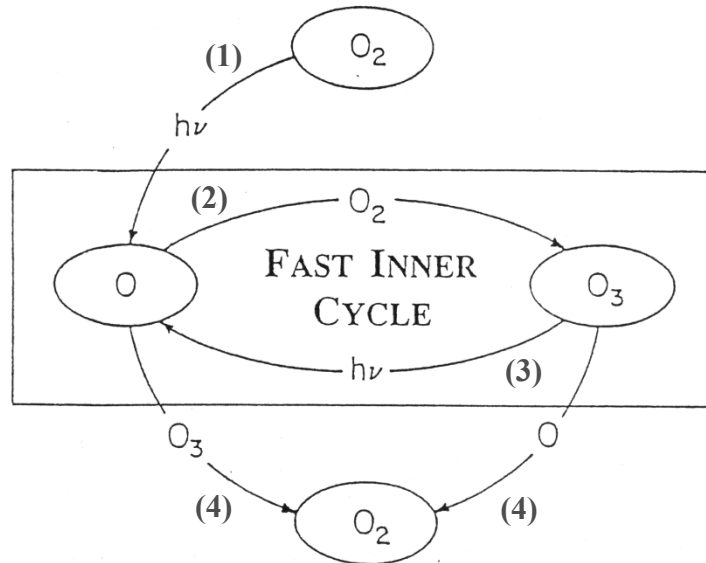
Rxn (1) produces two *odd oxygen* molecules
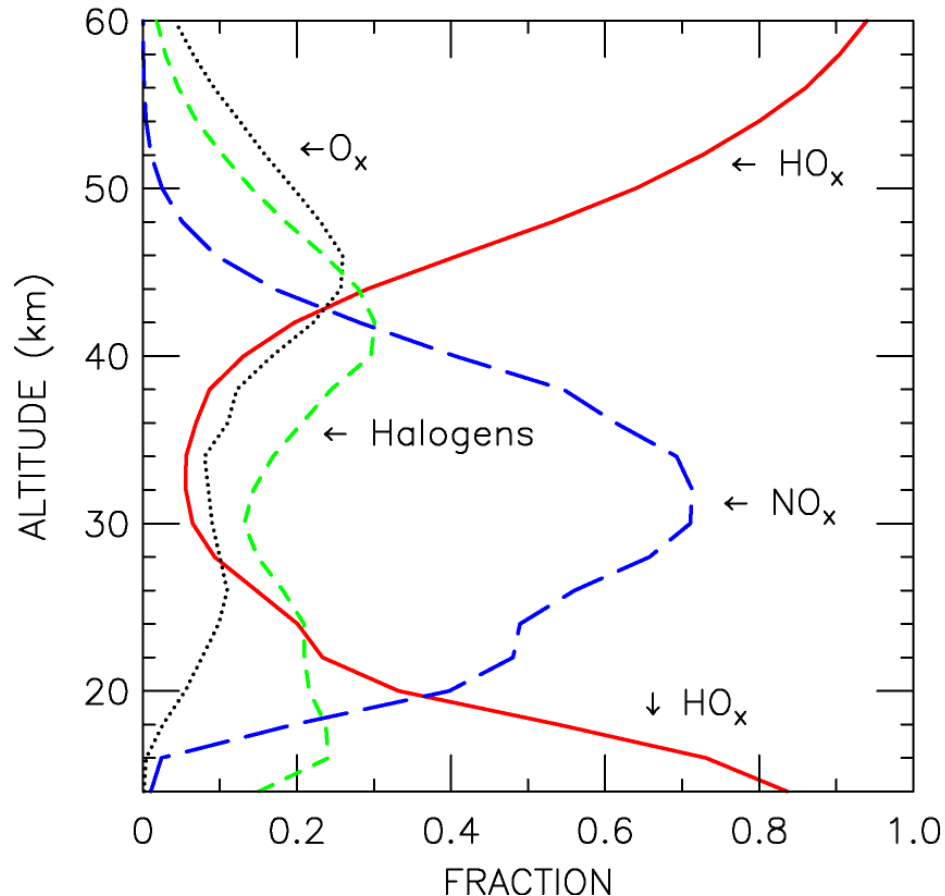Rxn (4) consumes two *odd oxygen* molecules

and reactions 2 and 3 recycle *odd oxygen* molecules

Stratospheric Photochemistry: Odd Oxygen Loss By Families

Fraction of O_x Loss Due to Each Catalytic Family

JPL 2002 Kinetics

35°N, Sept

Calculated fraction of odd oxygen loss due to various families of radicals
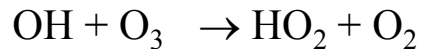
After Osterman et al., GRL, 24, 1107, 1997;
Sen et al., JGR, 103, 3571. 1998;
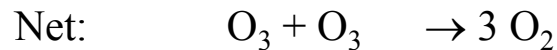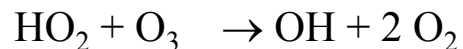Sen et al., JGR, 104, 26653, 1999.

One Atmosphere – One Photochemistry

Stratosphere

HO$_2$ formation:
$$OH + O_3 \rightarrow HO_2 + O_2$$
HO$_2$ loss:
$$HO_2 + O_3 \rightarrow OH + 2\,O_2$$

Net: $\quad O_3 + O_3 \rightarrow 3\,O_2$

Troposphere

HO$_2$ formation:
$$OH + CO \xrightarrow{O_2} HO_2 + CO_2$$
HO$_2$ loss:
$$HO_2 + NO \rightarrow OH + NO_2$$
Followed by:
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

Net: $\quad CO + 2\,O_2 \rightarrow CO_2 + O_3$

Tropopause

(A) Potential Vorticity (PVU) / Temperature (K) vs Altitude (km) — T, PV

(B) Ozone (ppbv) / CO (ppbv) vs Altitude (km) — CO, O$_3$
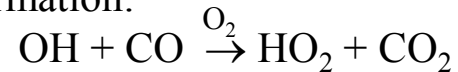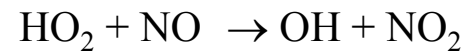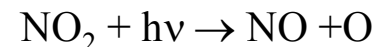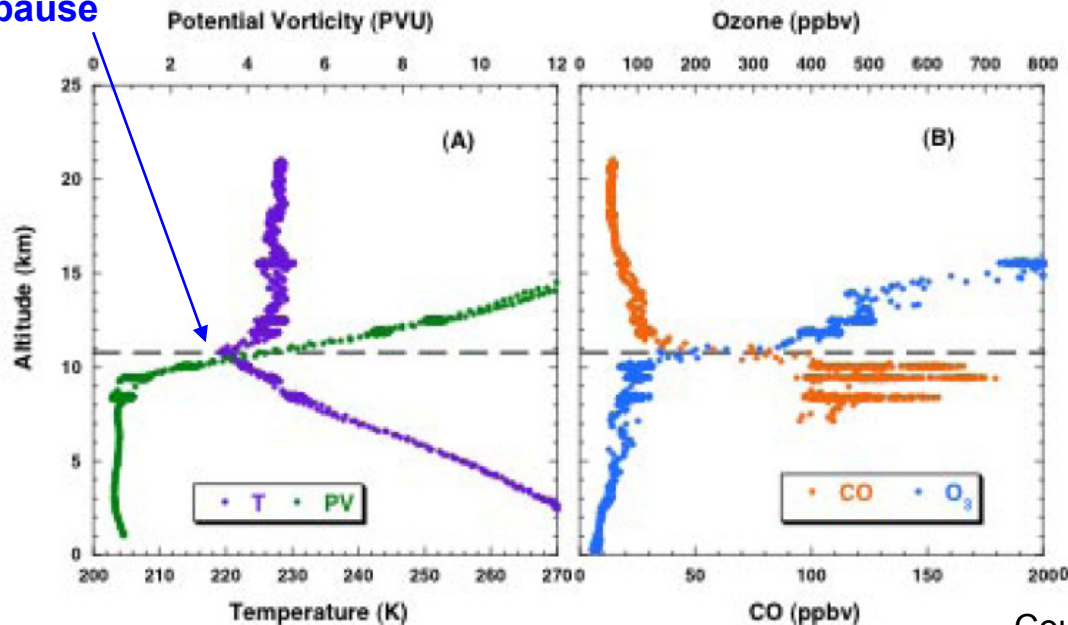
Above Tropopause:
Lots of O$_3$, little CO
Below Tropopause:
Lots of CO, little O$_3$

Courtesy of Laura Pan, NCAR

Tropospheric Chlorine Loading

Total Organic Chlorine (CCl_y):
- **Peaked at ~3.6 ppb around 1993**
- **Slowly declining**
- **Montreal Protocol and Amendments have banned production of CFCs**

Table 5A-2, WMO/UNEP (2014)
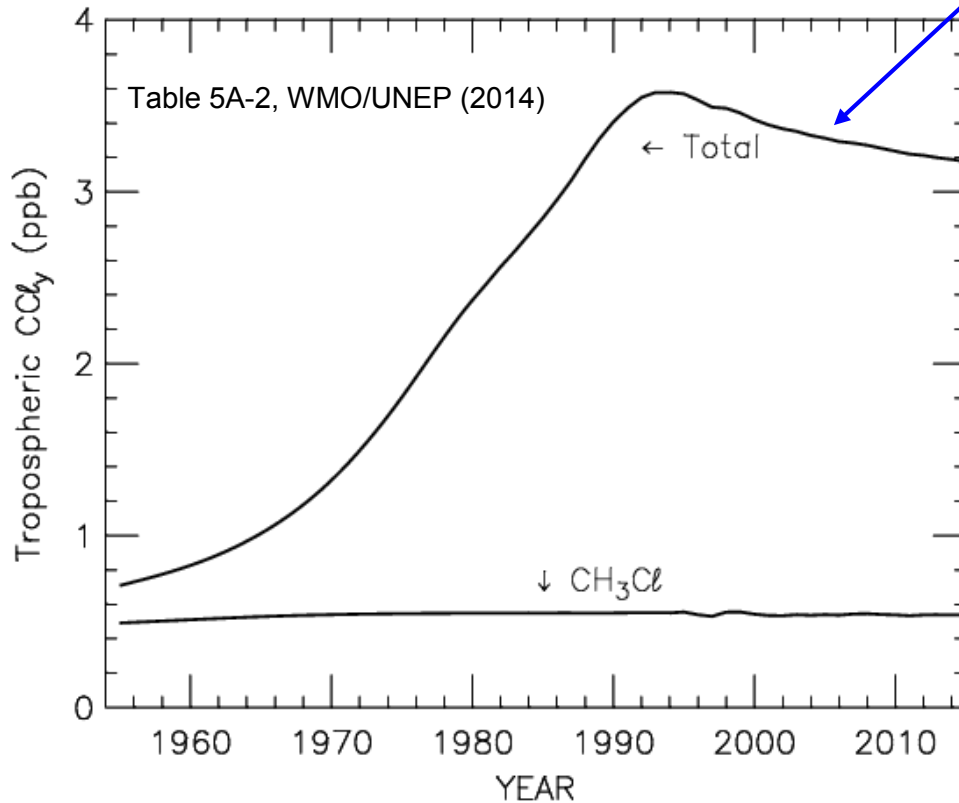
CFCs:
- **long lived (50 to 100 yr lifetime)**
- **decompose in the stratosphere**
- **lose memory of emission location when enter stratosphere**

Chlorine Abundance, Mid-Latitude Stratosphere

Northern Hemisphere
Mid-Latitudes
November 1994

←ClO

HCl →

←ClNO$_3$

Cl$_{TOT}$ →

Books
Balance ⇒

CCl$_y$
↓

48.8
43.0
37.5
32.3
27.2
22.3
17.5

APPROX. ALTITUDE (km)

Pressure (h Pa)

ABUNDANCE (parts per billion)
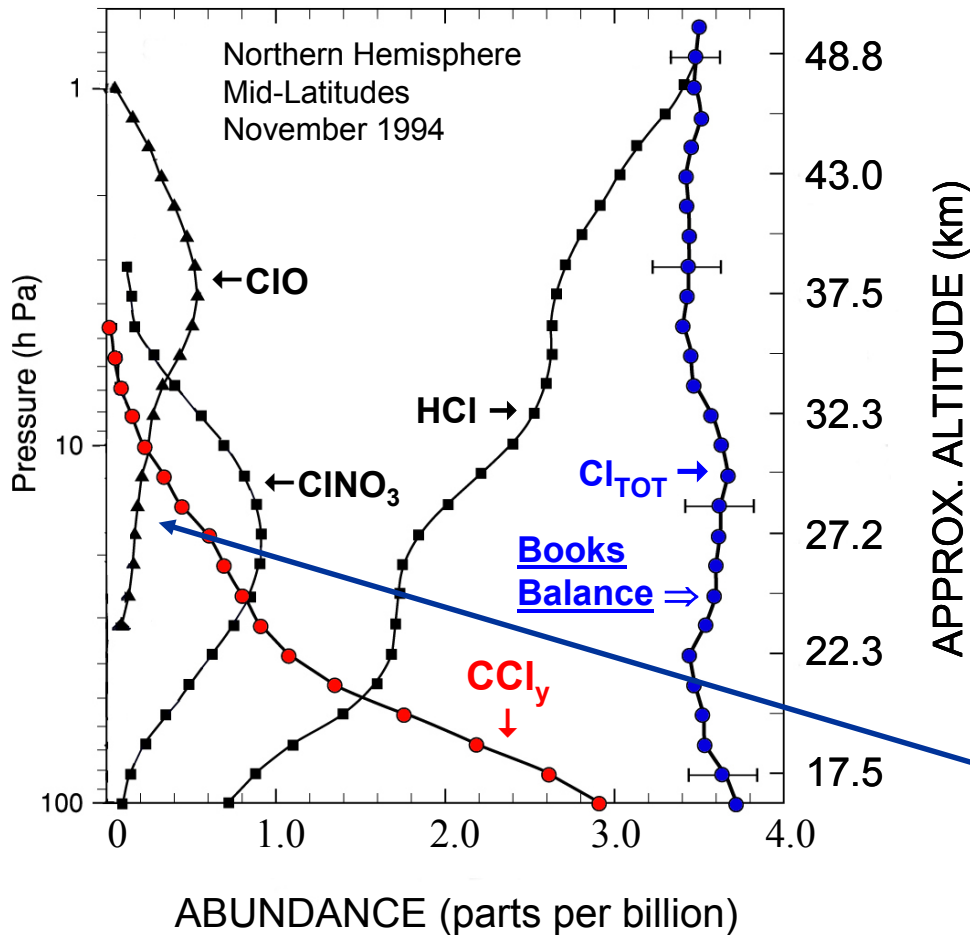
**Note: Below ~30 km,
ClO << ClNO$_3$ and HCl**

Zander et al., GRL, 1996

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Chlorine Source Gases

Primary Sources of Chlorine for the Stratosphere in 1999

Chlorine source gases

Bar chart showing total chlorine amount (parts per trillion) on y-axis from 0 to 3400:
- Other gases — 1%
- Methyl chloroform (CH_3CCl_3) — 4%
- HCFCs (e.g., HCFC-22 = $CHClF_2$) — 5%
- CFC-113 (CCl_2FCClF_2) — 7%
- Carbon tetrachloride (CCl_4) — 12%
- CFC-11 (CCl_3F) — 23%
- CFC-12 (CCl_2F_2) — 32%
- Methyl chloride (CH_3Cl) — 16%

Human-made sources span the upper portion; Natural sources the bottom.
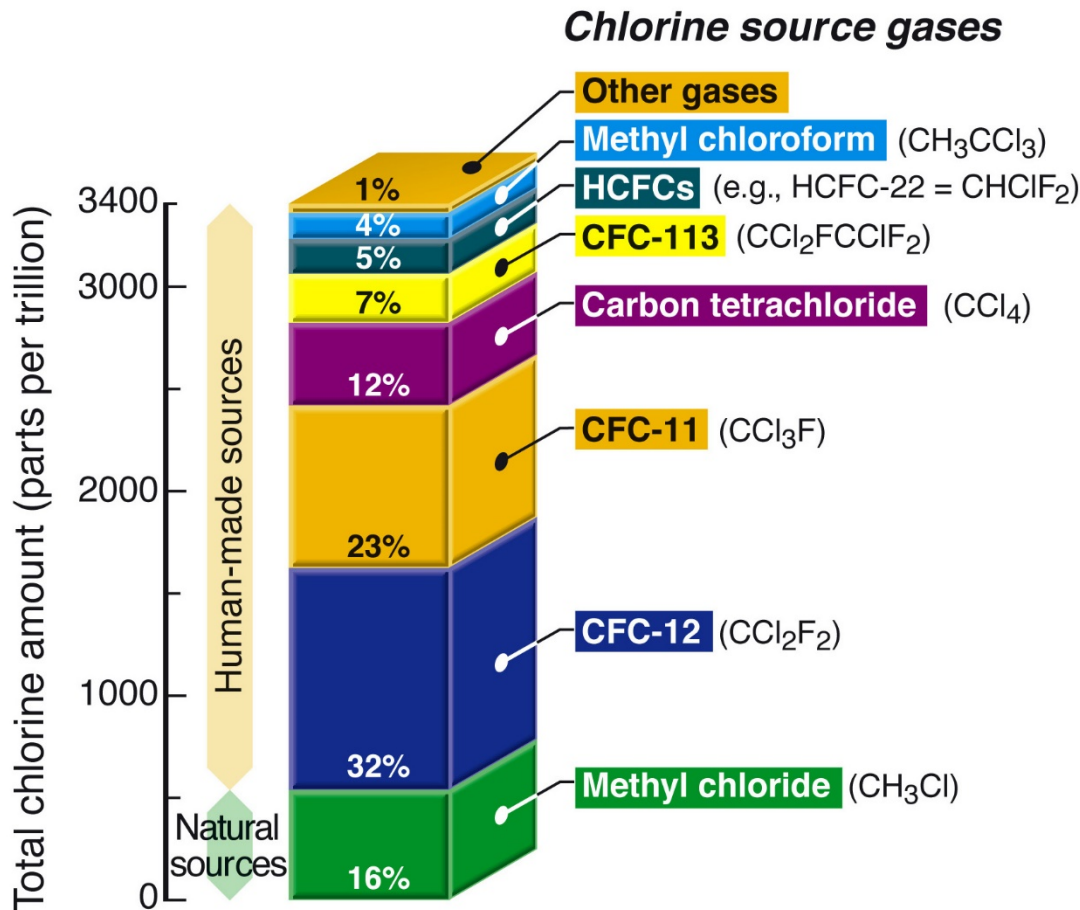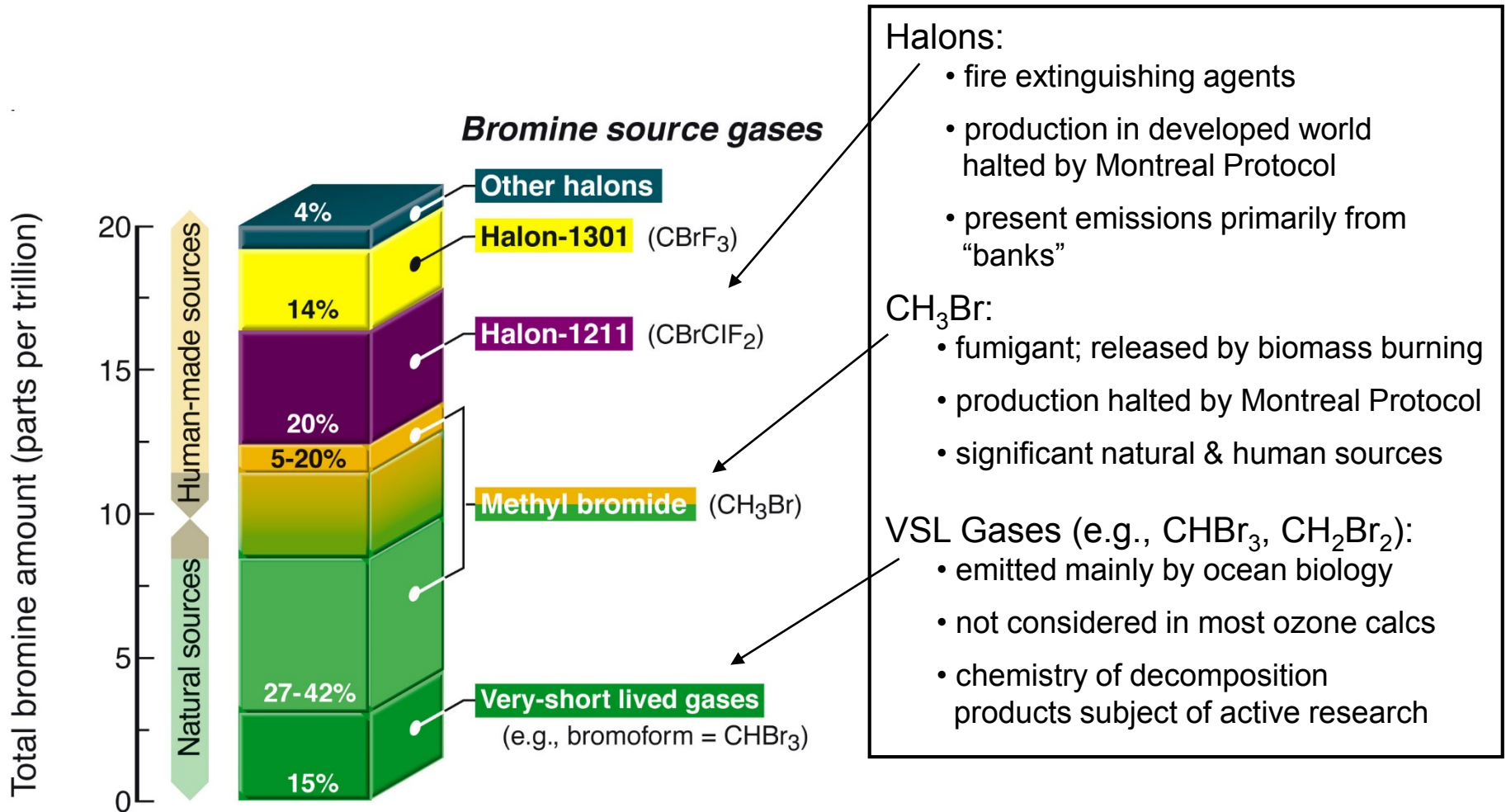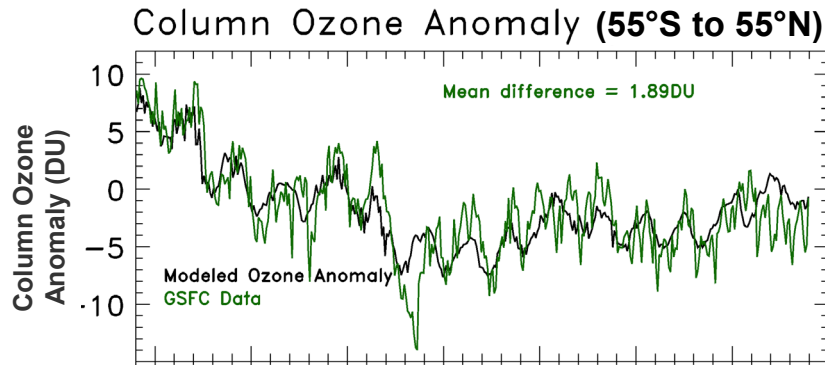
Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

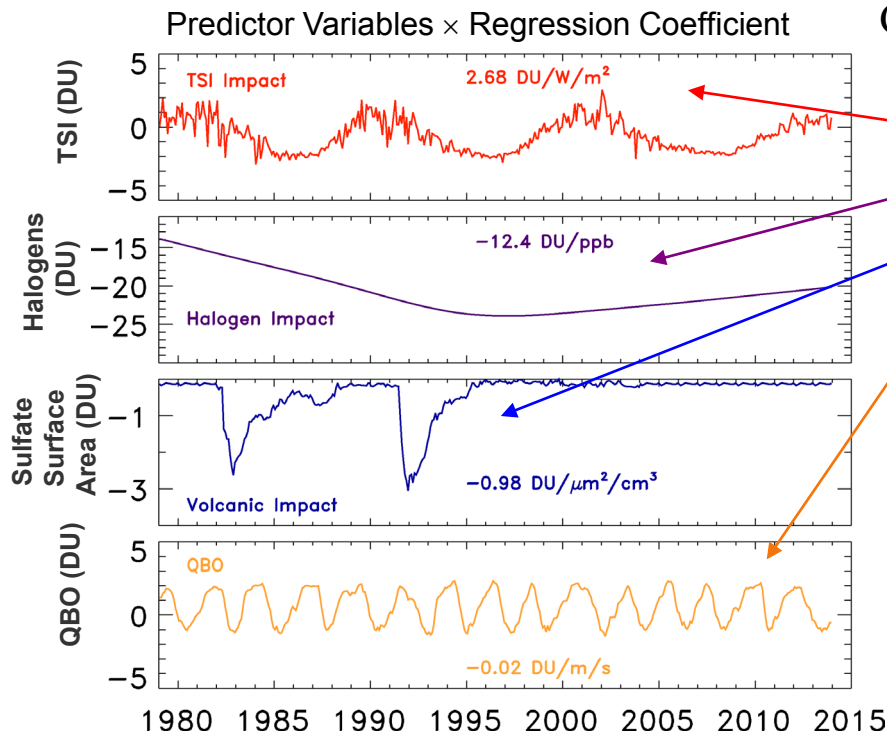| Gas	Atmospheric Lifetime (years)	Ozone Depletion Potential (ODP) [c]
Halogen source gases		
Chlorine gases		
CFC-11	45	1
CFC-12	100	0.82
CFC-113	85	0.85
Carbon tetrachloride (CCl_4)	26	0.82
HCFCs	1–17	0.01–0.12
Methyl chloroform (CH_3CCl_3)	5	0.16
Methyl chloride (CH_3Cl)	1	0.02
Bromine gases		
Halon-1301	65	15.9
Halon-1211	16	7.9
Methyl bromide (CH_3Br)	0.8	0.66
Very short-lived gases (e.g., $CHBr_3$)	Less than 0.5	[b] very low
Hydrofluorocarbons (HFCs)		
HFC-134a	13.4	0
HFC-23	222	0

Bromine Source Gases

Bromine source gases

Total bromine amount (parts per trillion)

- Human-made sources
- Natural sources

- Other halons — 4%
- Halon-1301 ($CBrF_3$) — 14%
- Halon-1211 ($CBrClF_2$) — 20%
- Methyl bromide (CH_3Br) — 5-20%
- Very-short lived gases (e.g., bromoform = $CHBr_3$) — 27-42%, 15%

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

Ozone Depletion at Mid-Latitudes

Column Ozone Anomaly (55°S to 55°N)

Mean difference = 1.89DU

Modeled Ozone Anomaly
GSFC Data

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

Predictor Variables × Regression Coefficient

TSI Impact — 2.68 DU/W/m²

Halogen Impact — −12.4 DU/ppb

Volcanic Impact — −0.98 DU/μm²/cm³

QBO — −0.02 DU/m/s

Column Ozone Anomaly (DU) =

$$
\begin{aligned}
& 19.5 \quad \text{DU} + \\
& 2.68 \quad \text{DU} / \text{W m}^{-2} \quad \times \text{TSI} + \\
& -12.4 \quad \text{DU} / \text{ppb} \quad \times \text{Halogens} + \\
& -0.98 \quad \text{DU} \quad \times \ln(\text{SSA}) + \\
& -0.20 \quad \text{DU} / \text{m s}^{-1} \quad \times \text{QBO}
\end{aligned}
$$

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

BrO$_x$: BrO and Br

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

Production : **CH$_3$Br + hν → Inorganic bromine**
Halons+ hν → Inorganic bromine **} Considered in global models**

CHBr$_3$ + hν → Inorganic bromine
CH$_2$Br$_2$ + hν → Inorganic bromine **} Generally neglected in global models**

Br

NO

O$_3$

BrO

O, ClO

HO$_2$, H$_2$CO

HBr
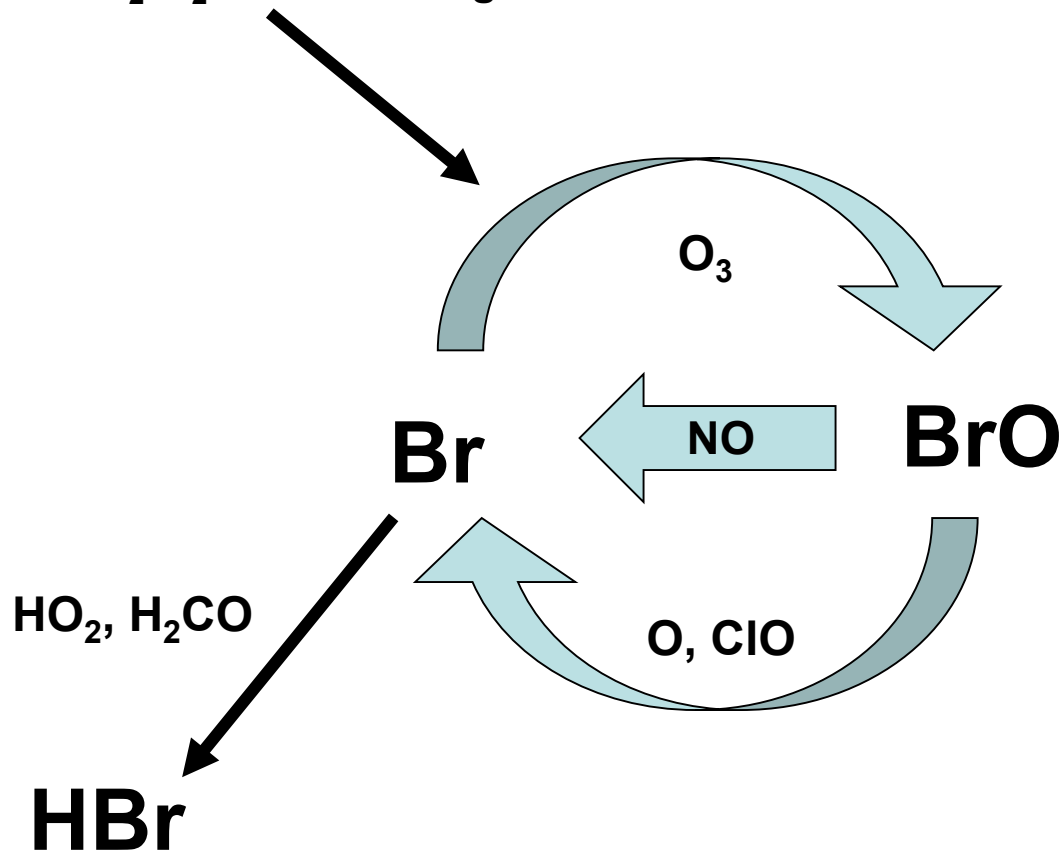
Final sink : HBr solubility & rainout (lowermost stratosphere)
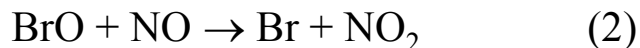
BrO$_x$: BrO and Br

BrO is central to <u>stratospheric</u> photochemistry, at mid-latitudes and polar regions:
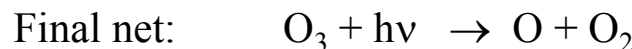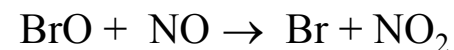
Rapid inner cycle:

BrO formation:
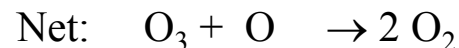$$Br + O_3 \rightarrow BrO + O_2 \qquad (1)$$
BrO loss:
$$BrO + NO \rightarrow Br + NO_2 \qquad (2)$$
$$\text{or} \quad BrO + O \rightarrow Br + O_2 \qquad (3)$$
$$\text{or} \quad BrO + ClO \rightarrow BrCl + O_2 \qquad (4a)$$
$$\rightarrow ClOO + Br \qquad (4b)$$
$$\rightarrow OClO + Br \qquad (4c)$$

BrO loss step (2):
$$Br + O_3 \rightarrow BrO + O_2$$
$$BrO + NO \rightarrow Br + NO_2$$
$$\overline{\text{Net:} \quad O_3 + NO \rightarrow NO_2 + O_2}$$
Followed by: $NO_2 + h\nu \rightarrow NO + O$
$$\overline{\text{Final net:} \quad O_3 + h\nu \rightarrow O + O_2}$$
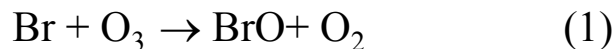
BrO loss step (3):
$$Br + O_3 \rightarrow BrO + O_2$$
$$BrO + O \rightarrow Br + O_2$$
$$\overline{\text{Net:} \quad O_3 + O \rightarrow 2\,O_2}$$
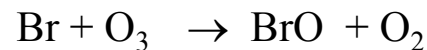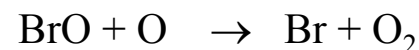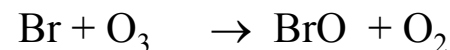
Can show:

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

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

Bromine Overview

Bromine is more efficient, per molecule, than chlorine at removing ozone because:

- Organic bromine compounds degrade faster than CFCs
    - lifetime of CH_3Br much shorter than lifetime of CFCs
    - Therefore Br_y liberated more easily from CBr_y than Cl_y liberated from CCl_y

- $BrO/Br_y \gg ClO/Cl_y$
    $Br + CH_4 \rightarrow HBr + CH_3$ is endothermic and has rate constant of zero
    $Cl + CH_4 \rightarrow HCl + CH_3$ is exothermic and proceeds at reasonable rate
    Also, $J_{BrONO2} > J_{ClONO2}$

- Loss due to BrO+ClO reaction generally counted as "bromine loss",
    even though loss of ozone by this cycle depends on Br_y and Cl_y
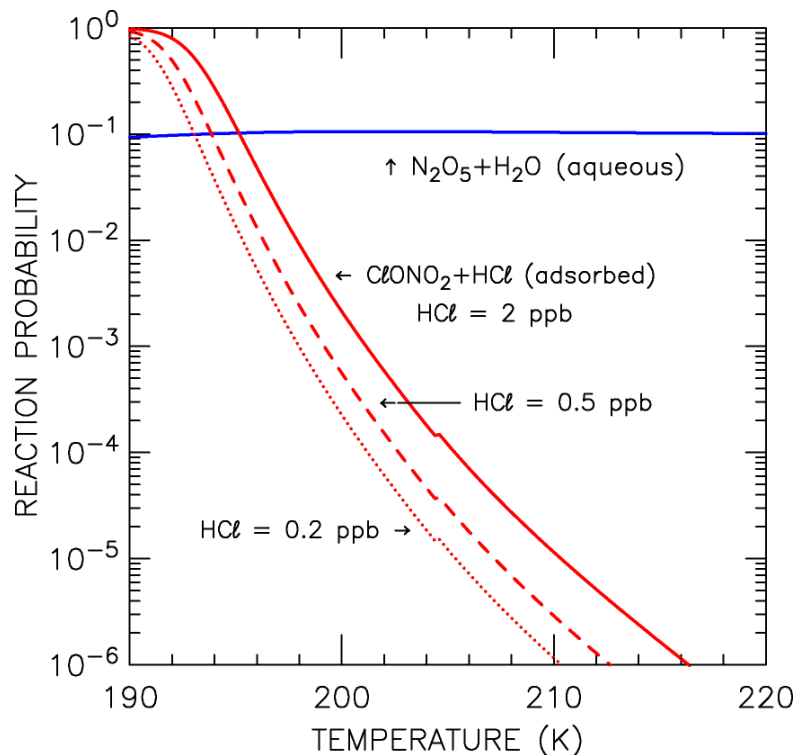
Ozone responds to:

    a) rise and fall of chlorine

    b) volcanic perturbations to aerosol loading

    c) amount of bromine in lowermost stratosphere
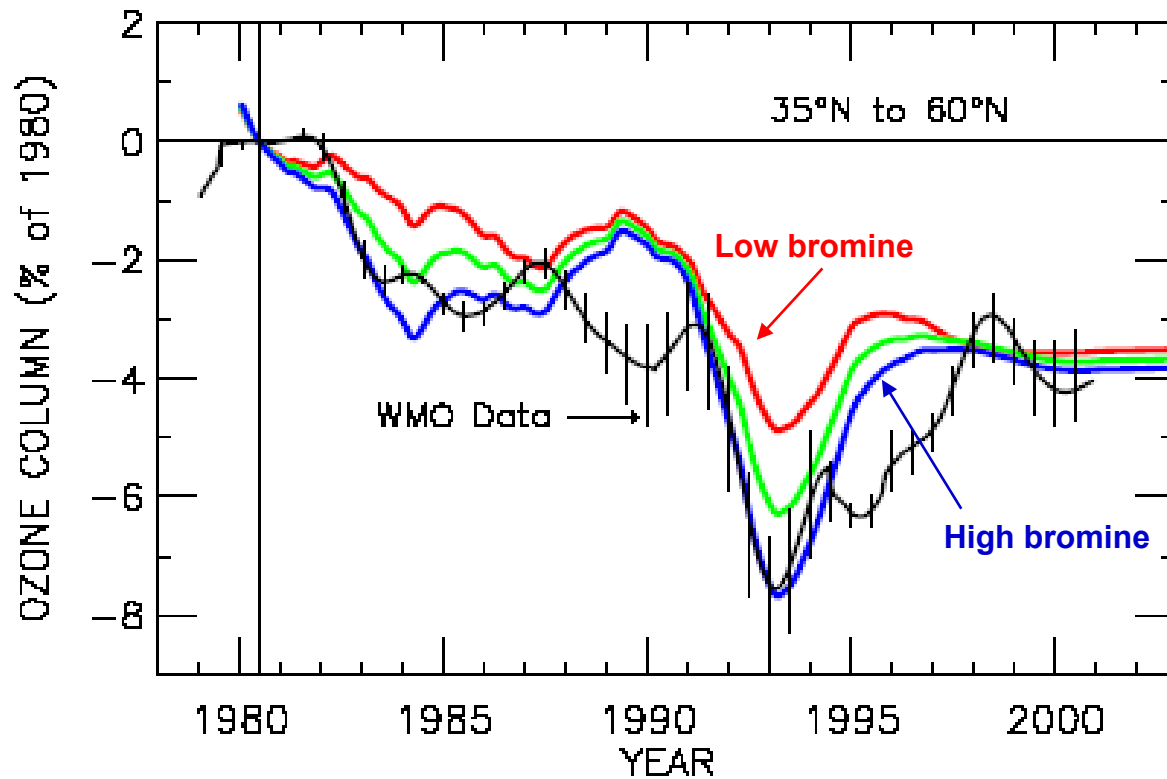
Salawitch *et al.*, *GRL*, 2004

Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

In all cases, γ must be measured in the laboratory

Reaction probabilities given for various surface types, with formulations of various degrees of complexity, in **Section 5** of the JPL Data Evaluation.

Atmospheric Chemistry and Physics by Seinfeld and Pandis provides extensive treatment of aqueous phase chemistry, properties of atmospheric aerosol, organic aerosols, etc.

POLAR OZONE LOSS

- COLD TEMPERATURES → POLAR STRATOSPHERIC CLOUDS (**PSCs**)
- REACTIONS ON PSC SURFACES LEAD TO ELEVATED **ClO**

$$HCl + ClNO_3 \rightarrow Cl_2 \text{ (gas)} + HNO_3 \text{ (solid)}$$
$$ClNO_3 + H_2O \rightarrow HOCl + HNO_3$$
$$Cl_2 + SUNLIGHT + O_3 \rightarrow ClO$$
$$HOCl + SUNLIGHT + O_3 \rightarrow ClO$$
$$HNO_3 \text{ SEDIMENTS (PSCs fall due to gravity)}$$

- ELEVATED **ClO** + SUNLIGHT DESTROYS O_3
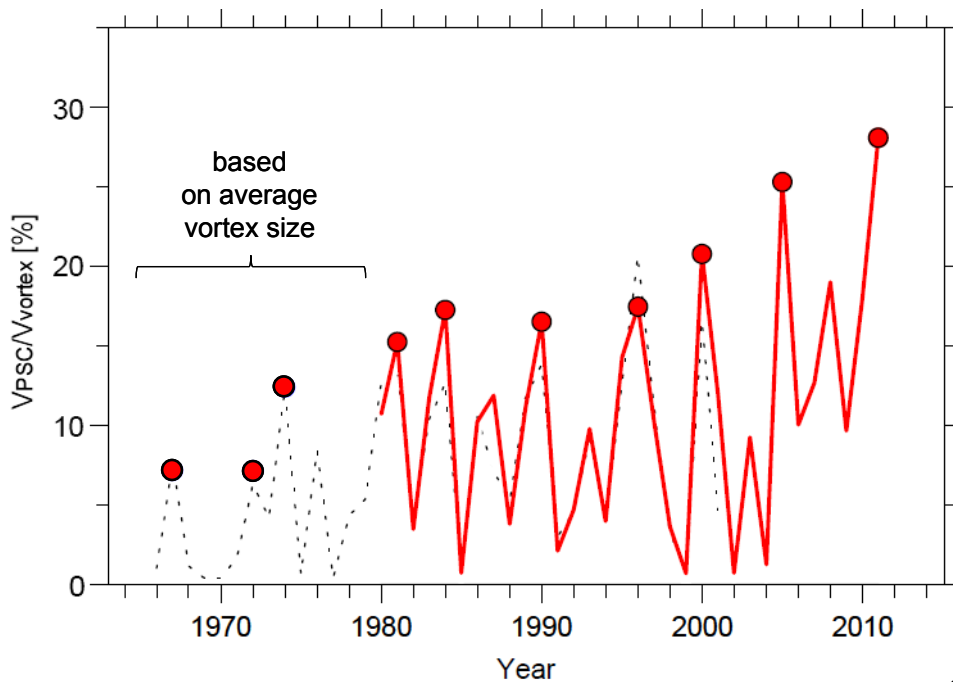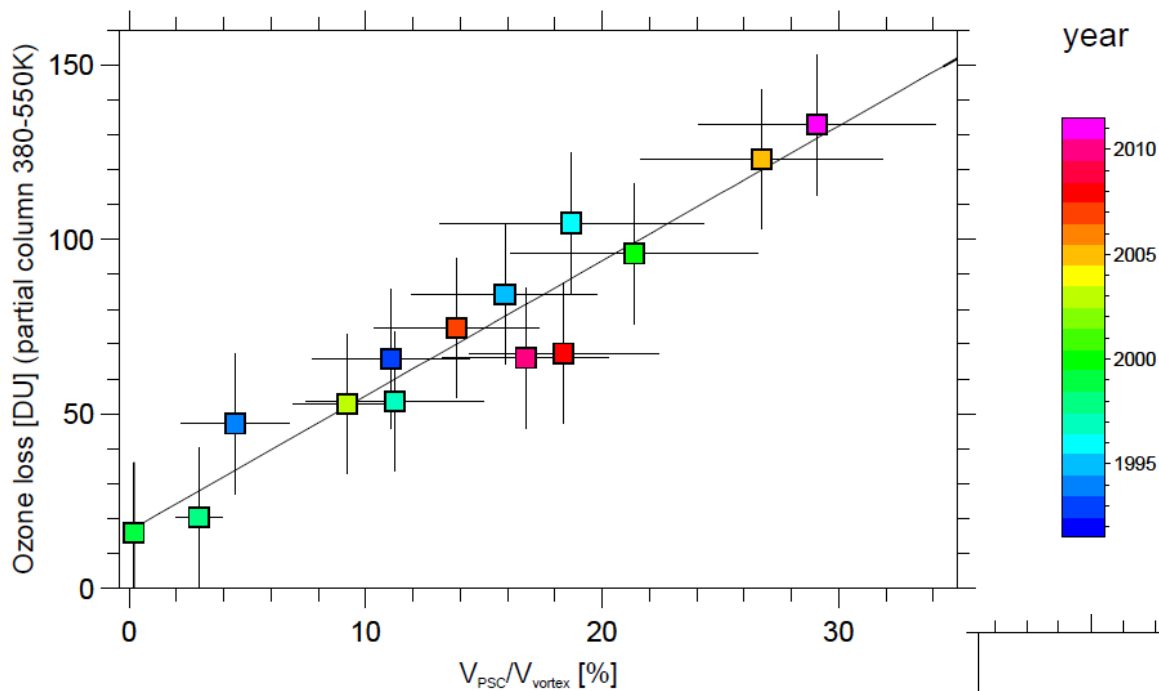- BrO : REACTION PARTNER FOR ClO $\Rightarrow$ ADDITIONAL O_3 LOSS
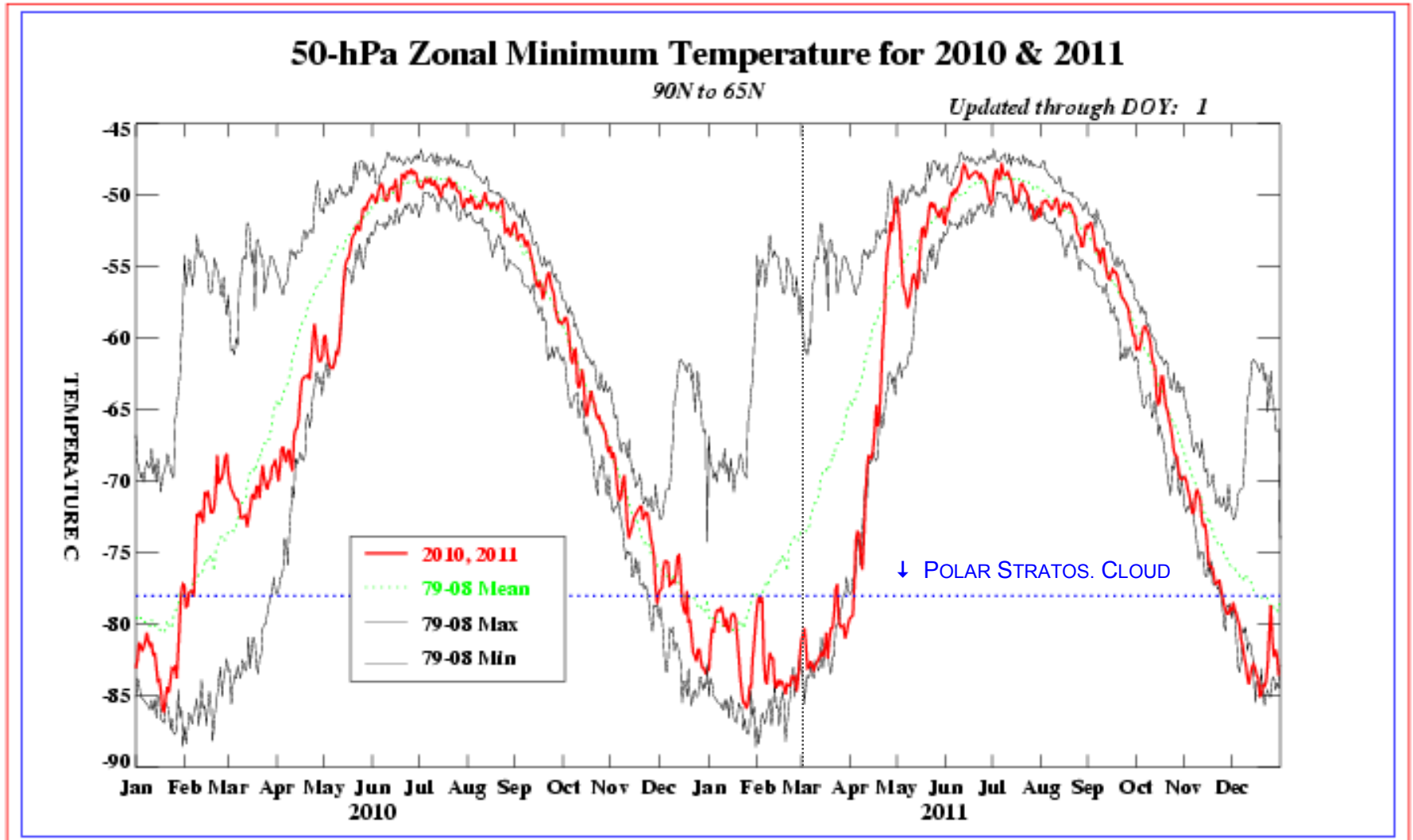
EP/TOMS Total Ozone for Sep 1, 2001

GSFC/916

Dobson Units
Dark Gray < 100, Red > 500 DU

GEN:271:2001

32
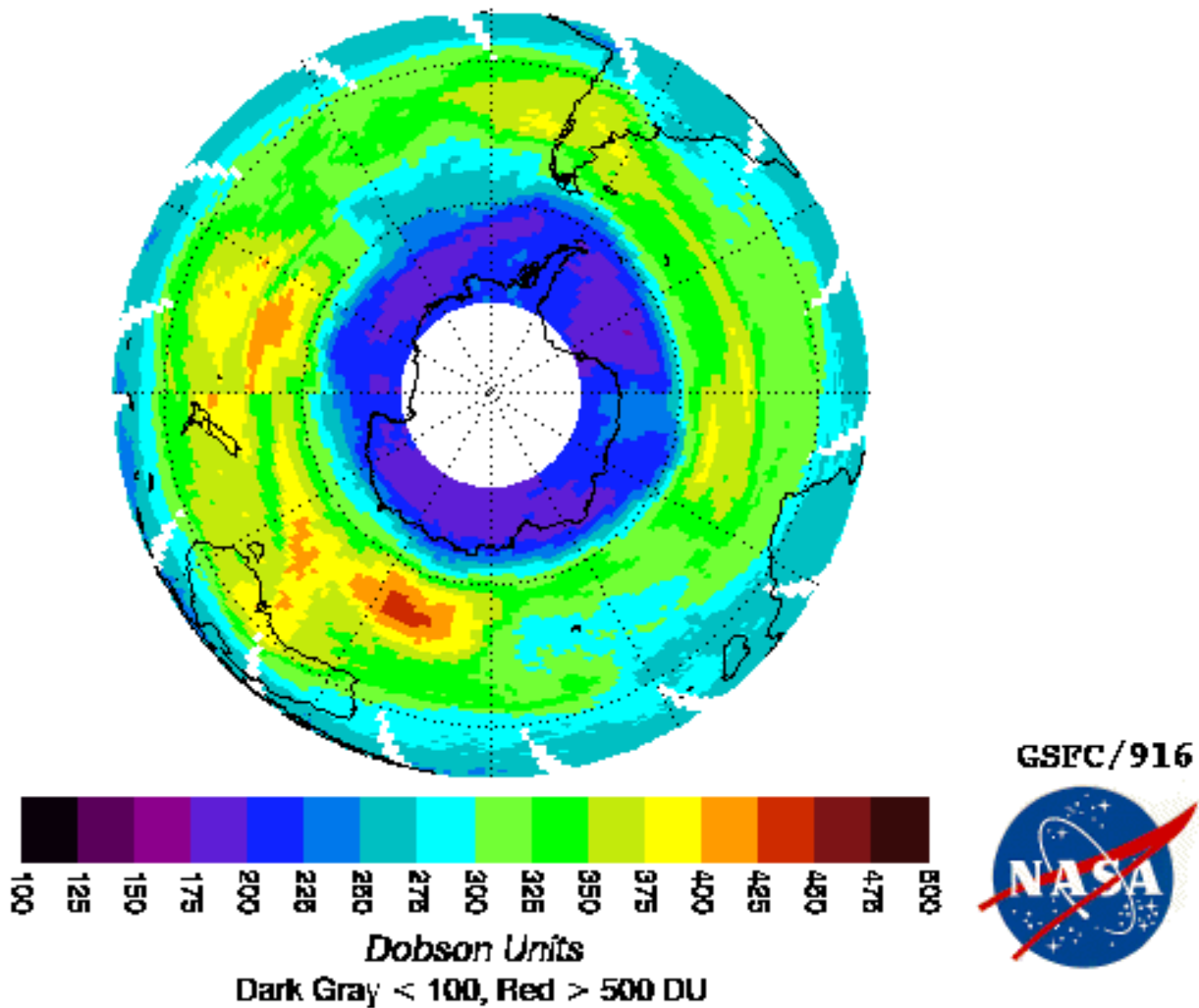
Arctic Ozone 2011 in Context of Prior Years
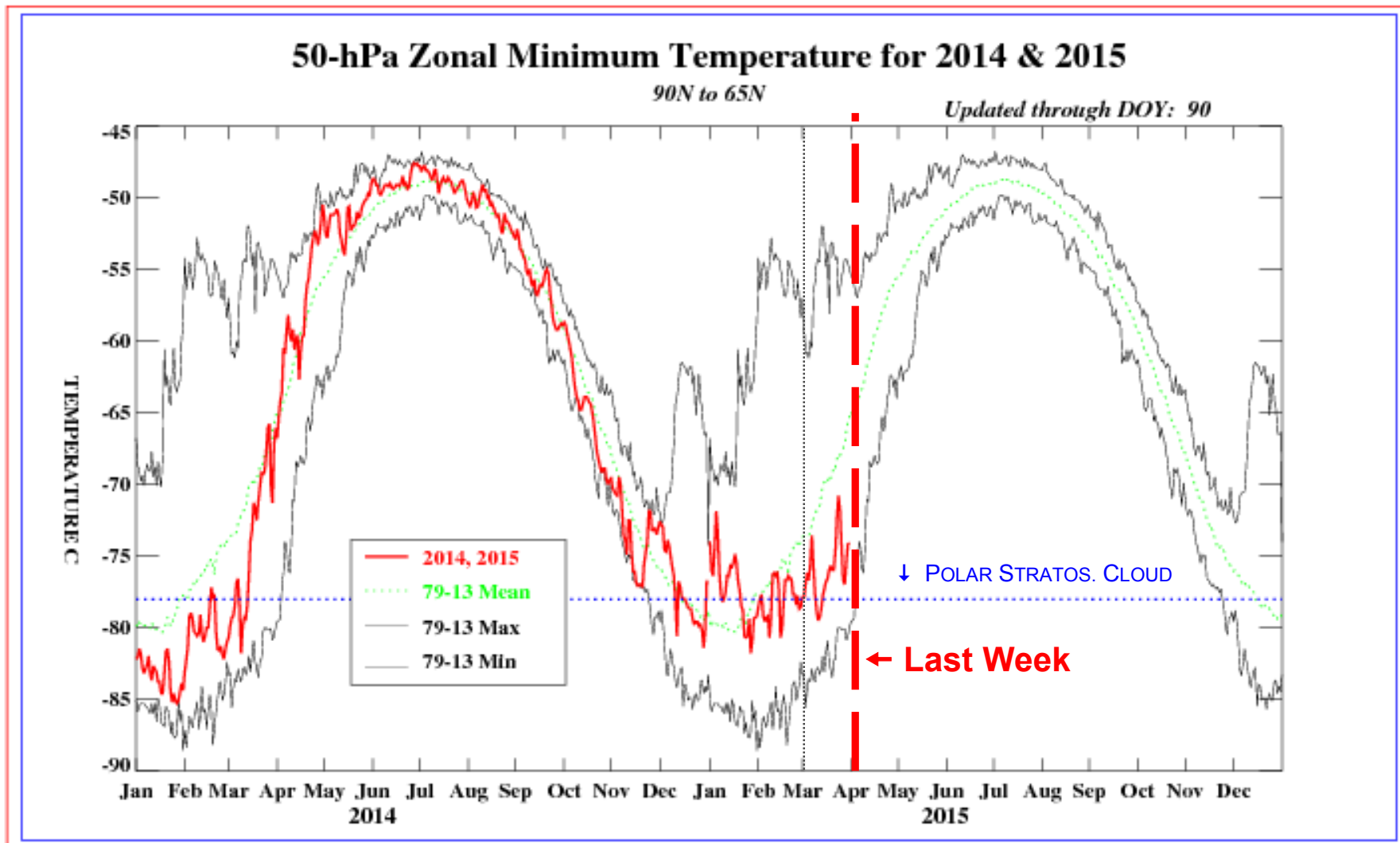
Arctic Temperature

50-hPa Zonal Minimum Temperature for 2010 & 2011

http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2011.gif

Arctic Temperature: Mar 2015

50-hPa Zonal Minimum Temperature for 2014 & 2015

http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbnhlo.gif

EXCESS SKIN CANCER CASES IN THE UNITED STATES, PER YEAR, DUE TO OZONE DEPLETION FOR VARIOUS CFC EMISSION SCENARIOS
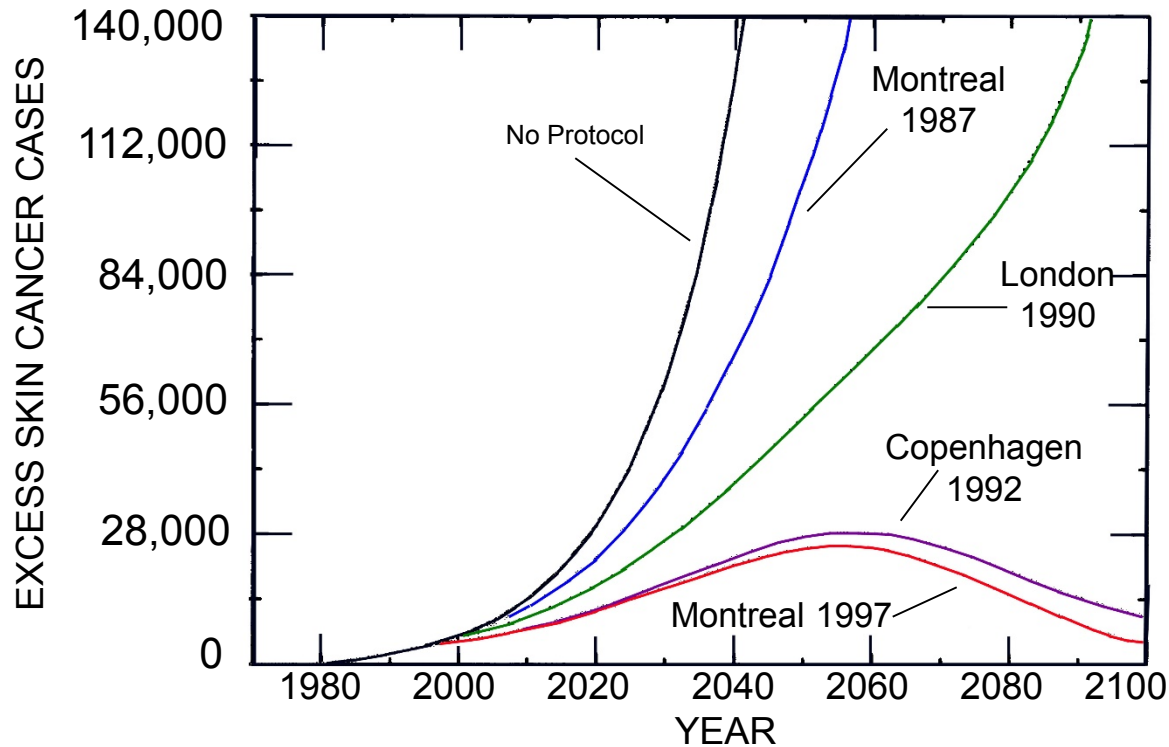
Longstreth *et al.*, *J. of Photochemistry and Photobiology B*, 46, 20–39, 1998.

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.

Second Exam

– **Tuesday, 14 April, 2:00 pm to 3:15 pm**

– **CSS 2416**

– **Closed book, no notes**

– **Focus mainly on Lectures 9 to 17**

– **Mix of conceptual questions and simple calculations**

– ***Please bring a calculator*** **(we'll have extras if you forget)**

– **use of iPad, iPhone or any other device able to go on the web**
   or store notes is not allowed

– **Backbone of course is the lectures and material from readings**
   highlighted in class

– **We'll be present:** ***please let us know if a question requires clarification***

– **Exam for 633 will differ somewhat from exam for 433**