Review of Lectures 9 to 16

AOSC 433/633 & CHEM 433

Ross Salawitch

- Exam on Thursday:
  - Conceptual questions only: no calculators
  - Closed book; no notes
- ELMS gradebook should be current
  - please let us know of any issues
- Please note:
  - Last day to drop a course with a "W" is 12 April
  - Students dropping a course on Testudo have until 11pm on 12 April
  - Drop/Add services for Spring 2017 will no longer be available after 11pm on 12 April
  - Students who need to come in person to drop a course have until 5 pm on 12 April

11 April 2017

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 → O + O

Propagation

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

O_3 + photon → $O(^1D) + O_2$

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

$OH + O_3 \rightarrow HO_2 + O_2$

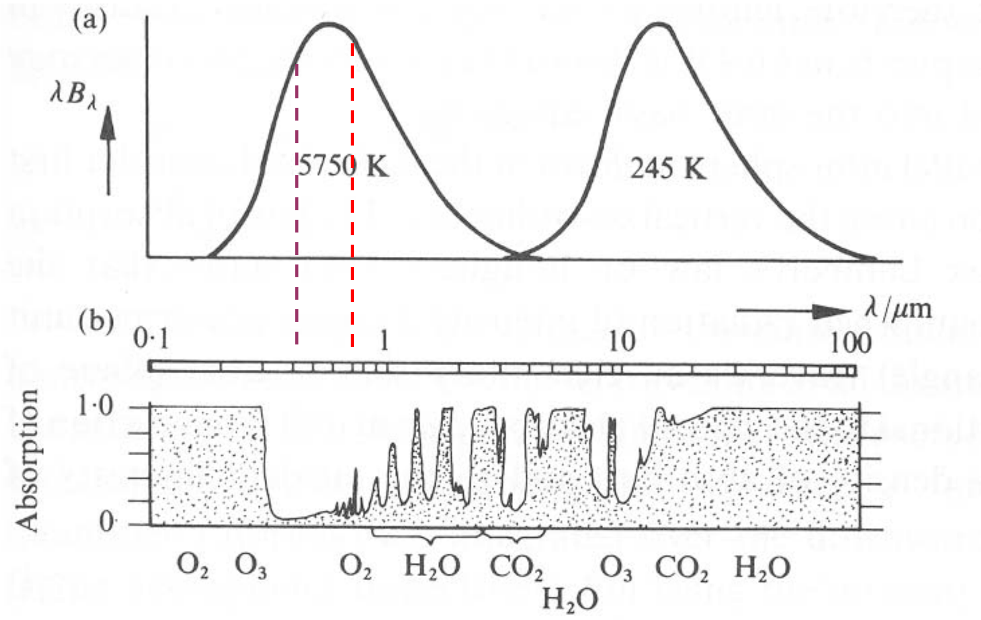
$HO_2 + O \rightarrow OH + O_2$

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).

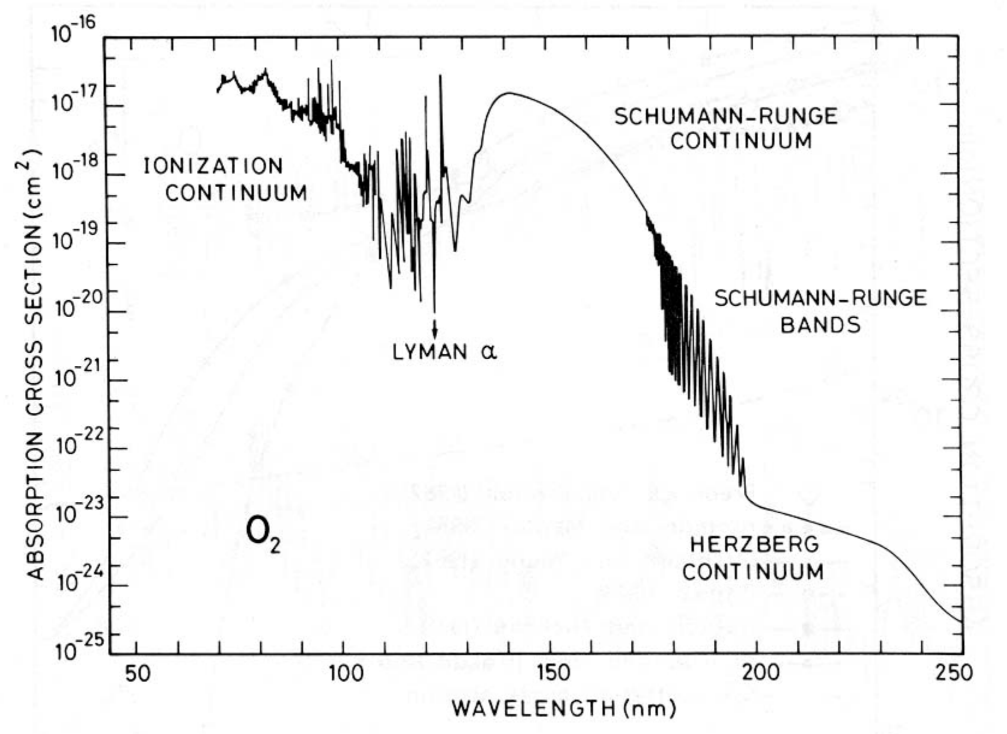
The curves are drawn with equal area since, integrated over the entire Earth at the top of the atmosphere, the solar (downwelling) and terrestrial (upwelling) fluxes must be equal.

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

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*:

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

where:

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

Also:

$$\int_{0}^{\infty} [O_2]\,dz' \approx 4\times10^{24}\ \text{molecules/cm}^2$$

O_2 Optical Depth for $\theta = 0°$, $z = 0$ km

	σ_{max} (cm^2)	τ (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):

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

Aside:

$$\frac{\text{Column } O_3}{\text{Column Air}} = \frac{8\times10^{18}}{2\times10^{25}} = 0.4 \text{ parts per million } \Rightarrow \text{Ozone is a trace species!}$$

O_3 Optical Depth for θ = 0°, z = 0 km

	σ_{max} (cm^2)	τ (0 km)	$e^{-\tau\,(0\ \mathrm{km})}$	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

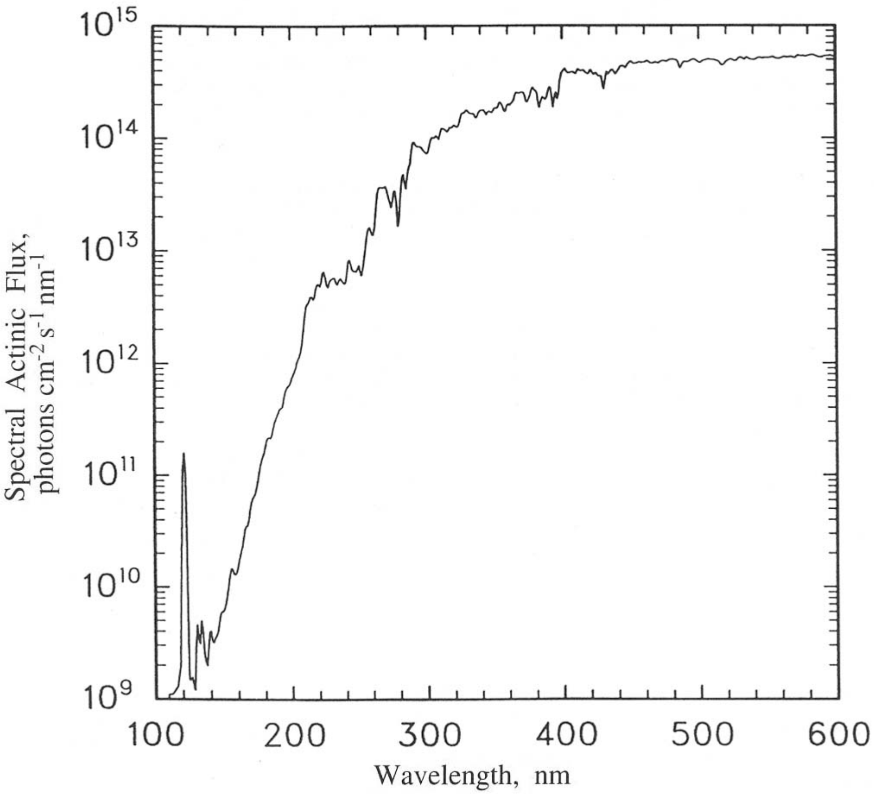
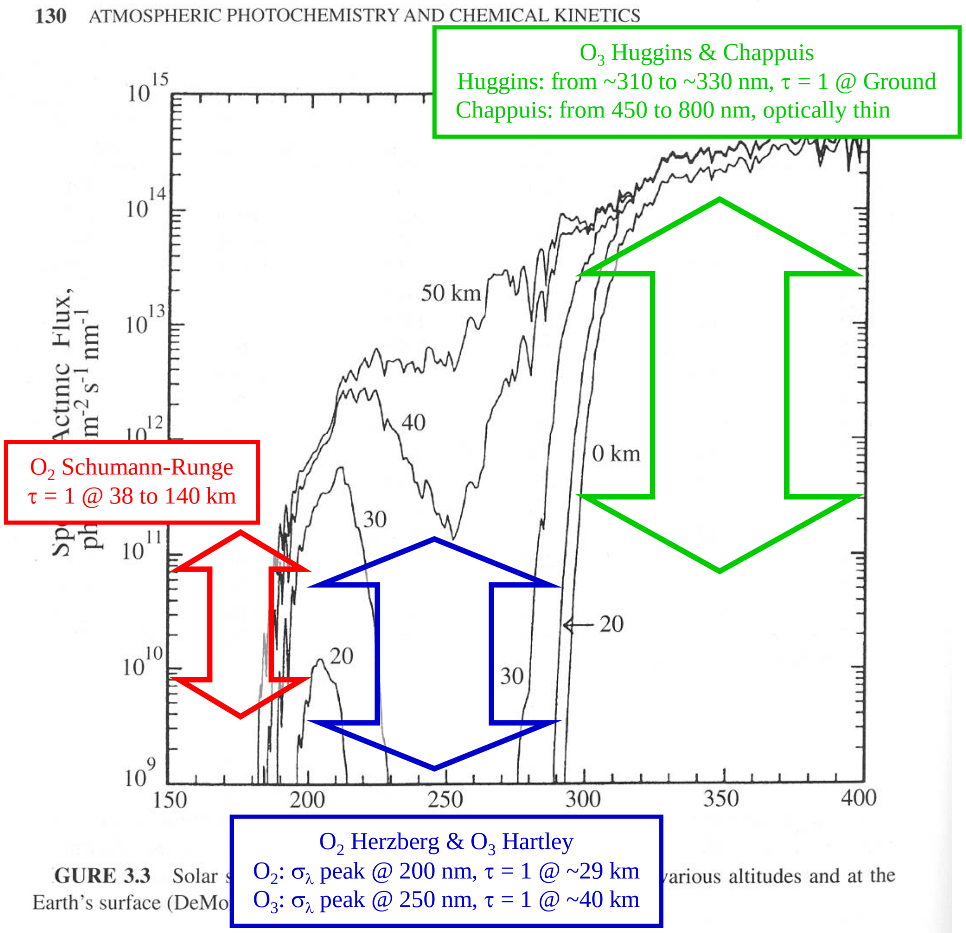


FIGURE 6. Solar spectral actinic flux (photons cm^{-2} s^{-1} nm^{-1}) at the top of Earth's atmosphere.

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



O_3 Huggins & Chappuis
Huggins: from ~310 to ~330 nm, $\tau = 1$ @ Ground
Chappuis: from 450 to 800 nm, optically thin

O_2 Schumann-Runge
$\tau = 1$ @ 38 to 140 km

O_2 Herzberg & O_3 Hartley
O_2: σ_λ peak @ 200 nm, $\tau = 1$ @ ~29 km
O_3: σ_λ peak @ 250 nm, $\tau = 1$ @ ~40 km

GURE 3.3 Solar s … various altitudes and at the Earth's surface (DeMo

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

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:

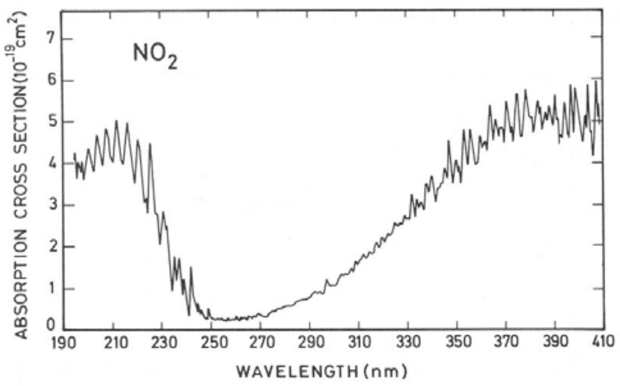
$$J_{gas}(z) = \int_{\lambda_{min}}^{\lambda_{max}} J_{gas}(z,\lambda)\, d\lambda$$

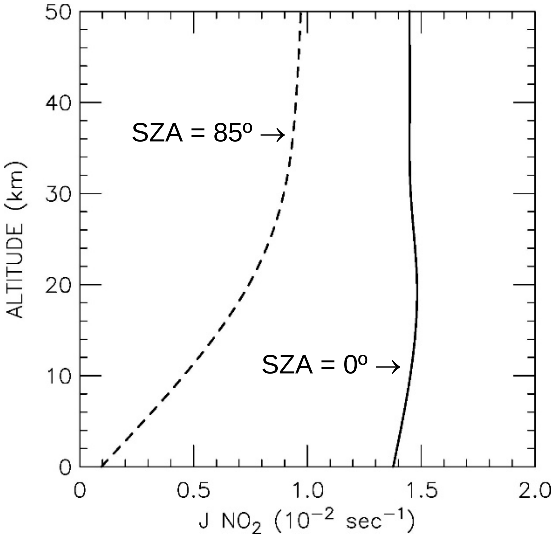
Units: s^{-1}

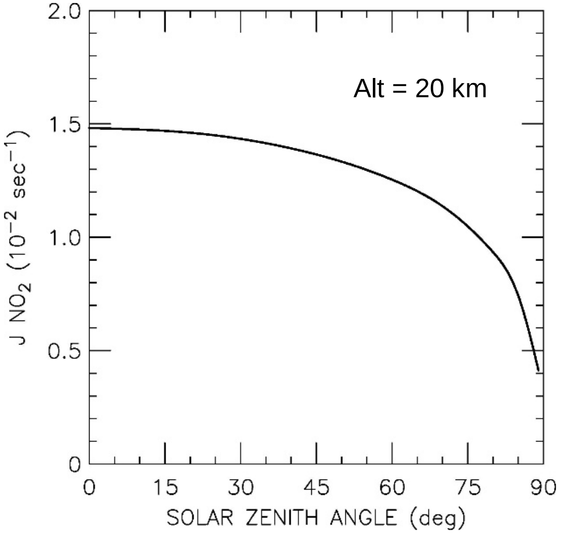
$$\text{Rate of Reaction} = \frac{dO_3}{dt} = J\ [O_3];\quad \text{Units of } J \text{ are } s^{-1}$$

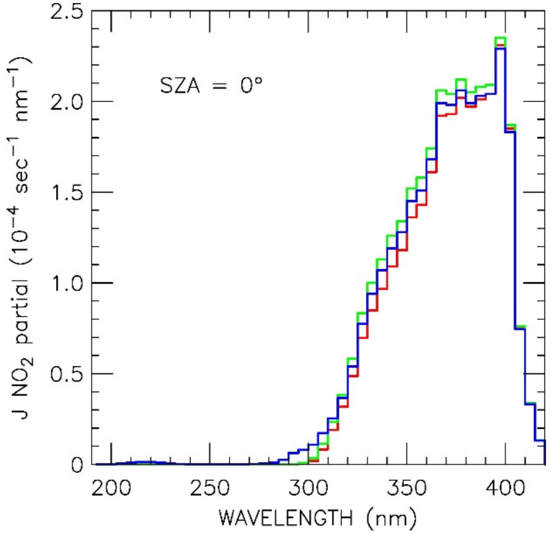
More precisely, calculations of photolysis frequencies consider the "spectral actinic flux", which represents the amount of available photons integrated over all angles, rather than "solar irradiance". These two quantities differ because of scattering of solar radiation by gases and aerosols, and reflection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

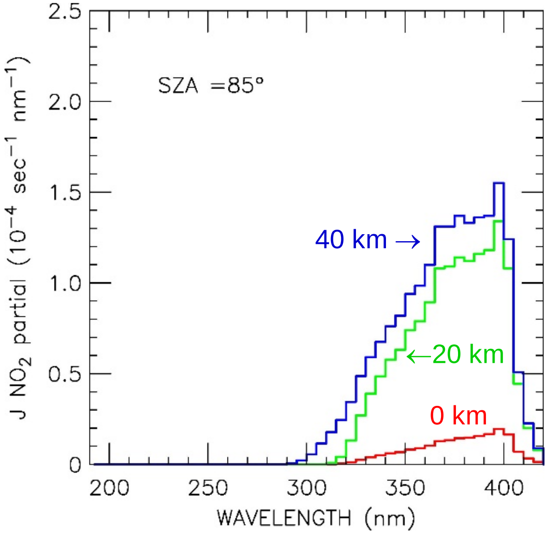
NO_2 Photolysis



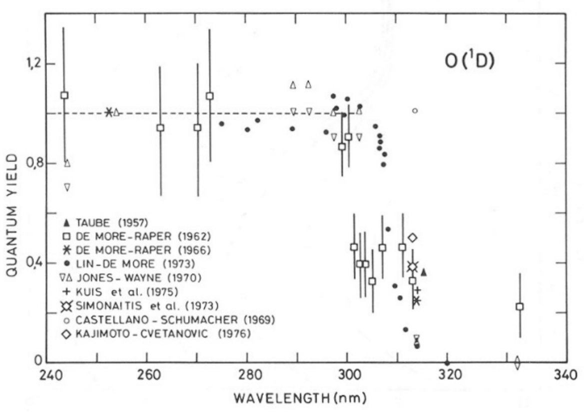


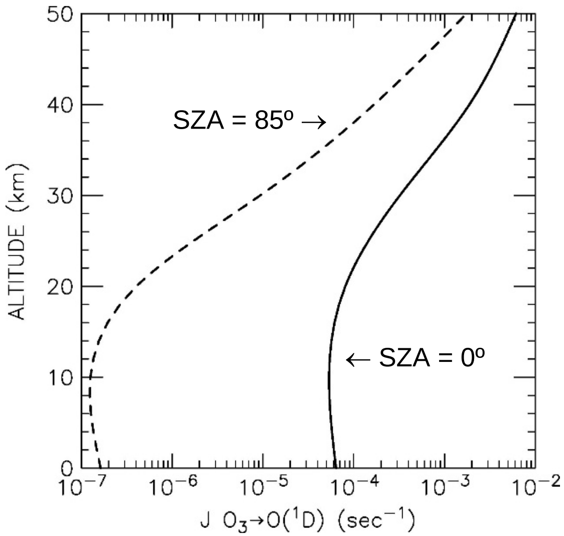


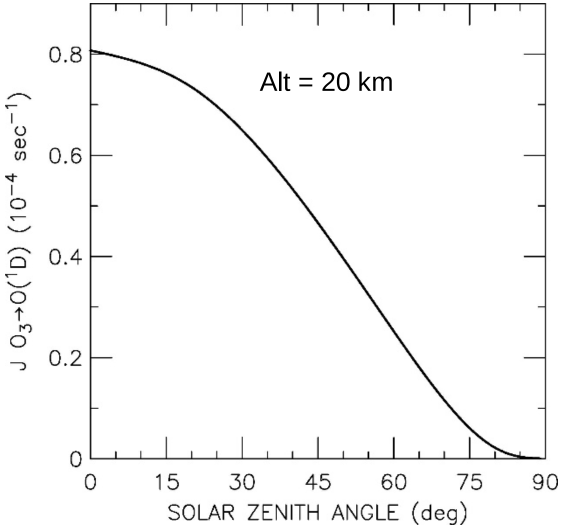


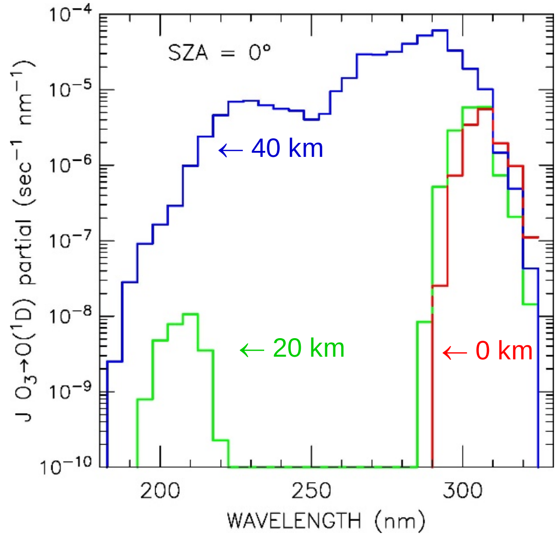


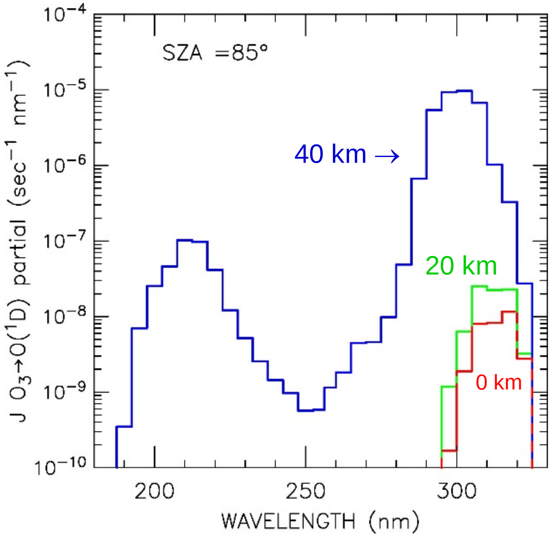
$O_3 \rightarrow O(^1D)$ Photolysis











Bimolecular Gas Phase Reactions

$$\overset{8.9\ \text{kcal/mole}}{\mathrm{OH}} + \overset{-17.8\ \text{kcal/mole}}{\mathrm{CH_4}} \rightarrow \overset{35.1\ \text{kcal/mole}}{\mathrm{CH_3}} + \overset{-57.8\ \text{kcal/mole}}{\mathrm{H_2O}}$$

ΔEnthalpy = –13.8 kcal/mole

Exothermic !

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

E_A / R ⇒ Activation Energy / Gas Constant

Arrhenius Expression for rate constant:

$$k = 2.45\times10^{-12} \times e^{-1775/T}\ \mathrm{cm^3\ sec^{-1}}$$

Energy Term

A factor

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

Entropy Term

R = 8.3143 ×10^7 erg / (K mole)
= 2.87 ×10^6 erg / (K gm) for air

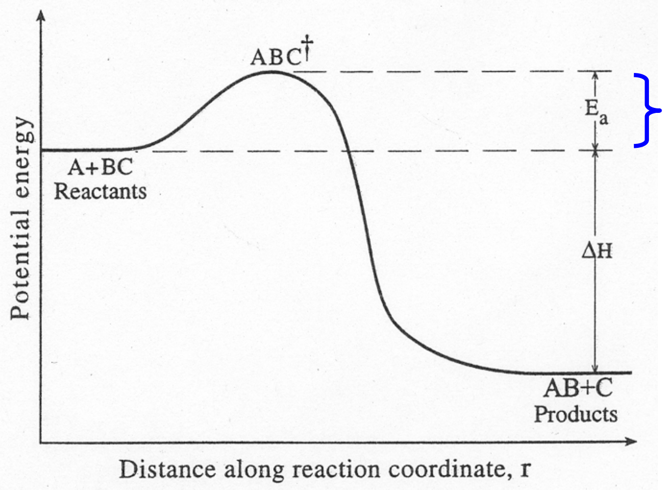


Figure 3.3 Barrier energies for the forward reaction (E_a) and the reverse reaction ($E_a + \Delta H$).

Yung and DeMore, *Photochemistry of Planetary Atmospheres*, Oxford, 1999.

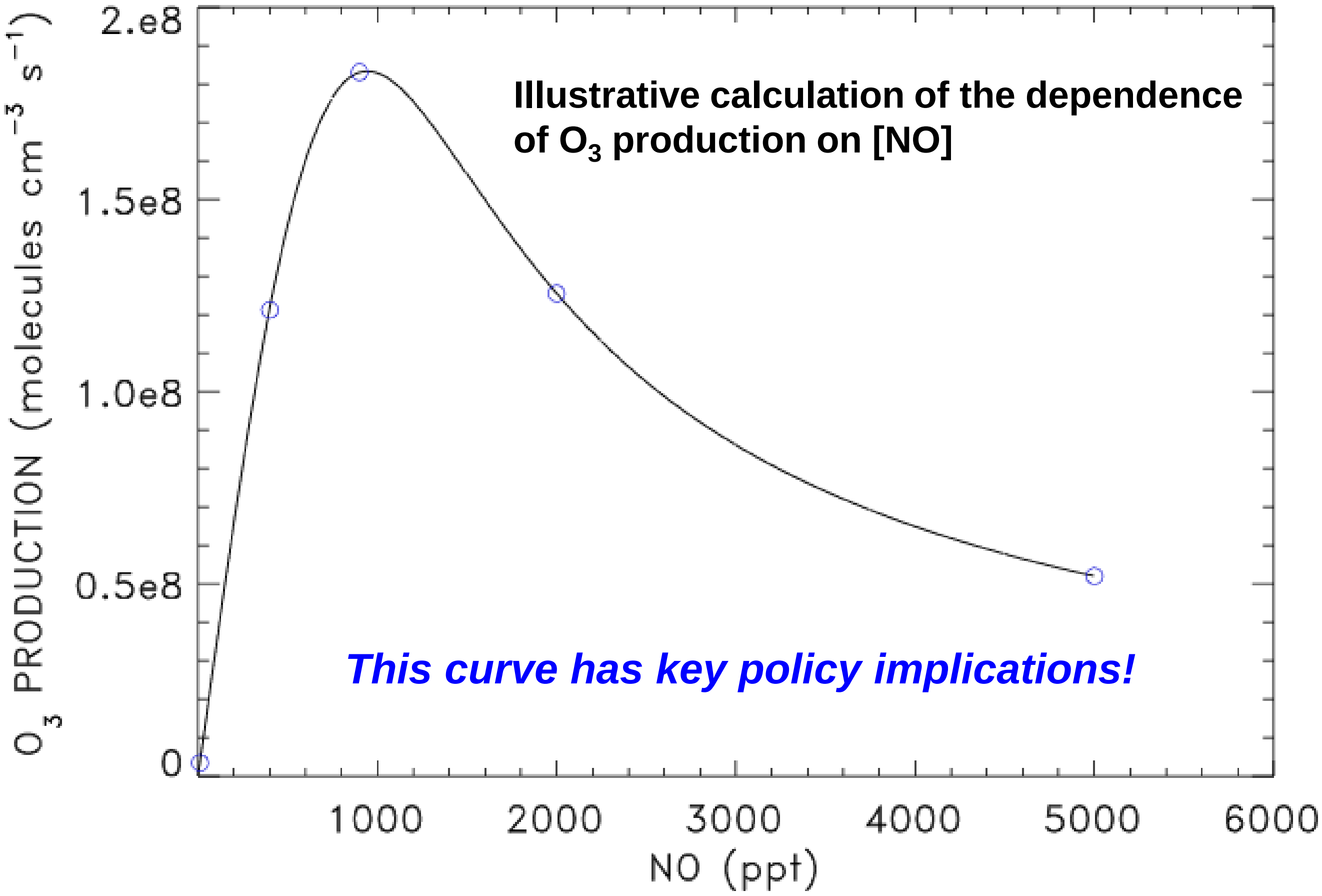
Tropospheric Ozone Production versus NO

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 ______________

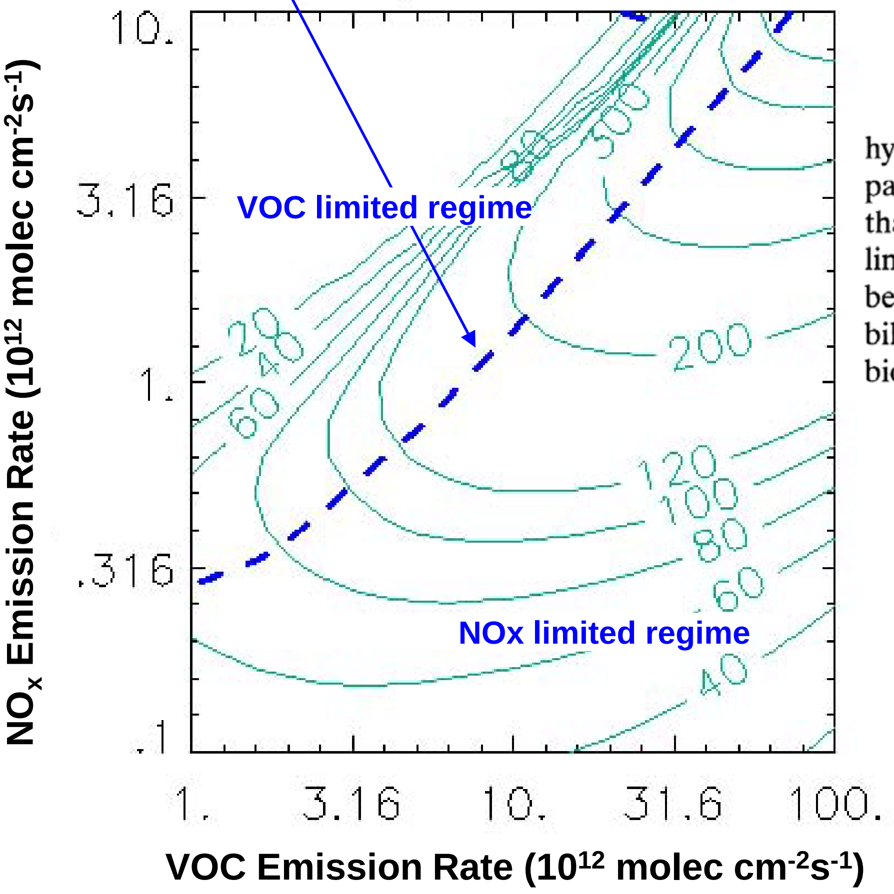


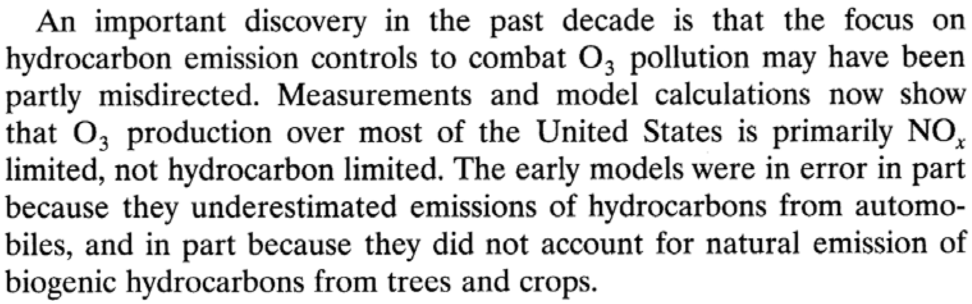
Illustrative calculation of the dependence of O_3 production on [NO]

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



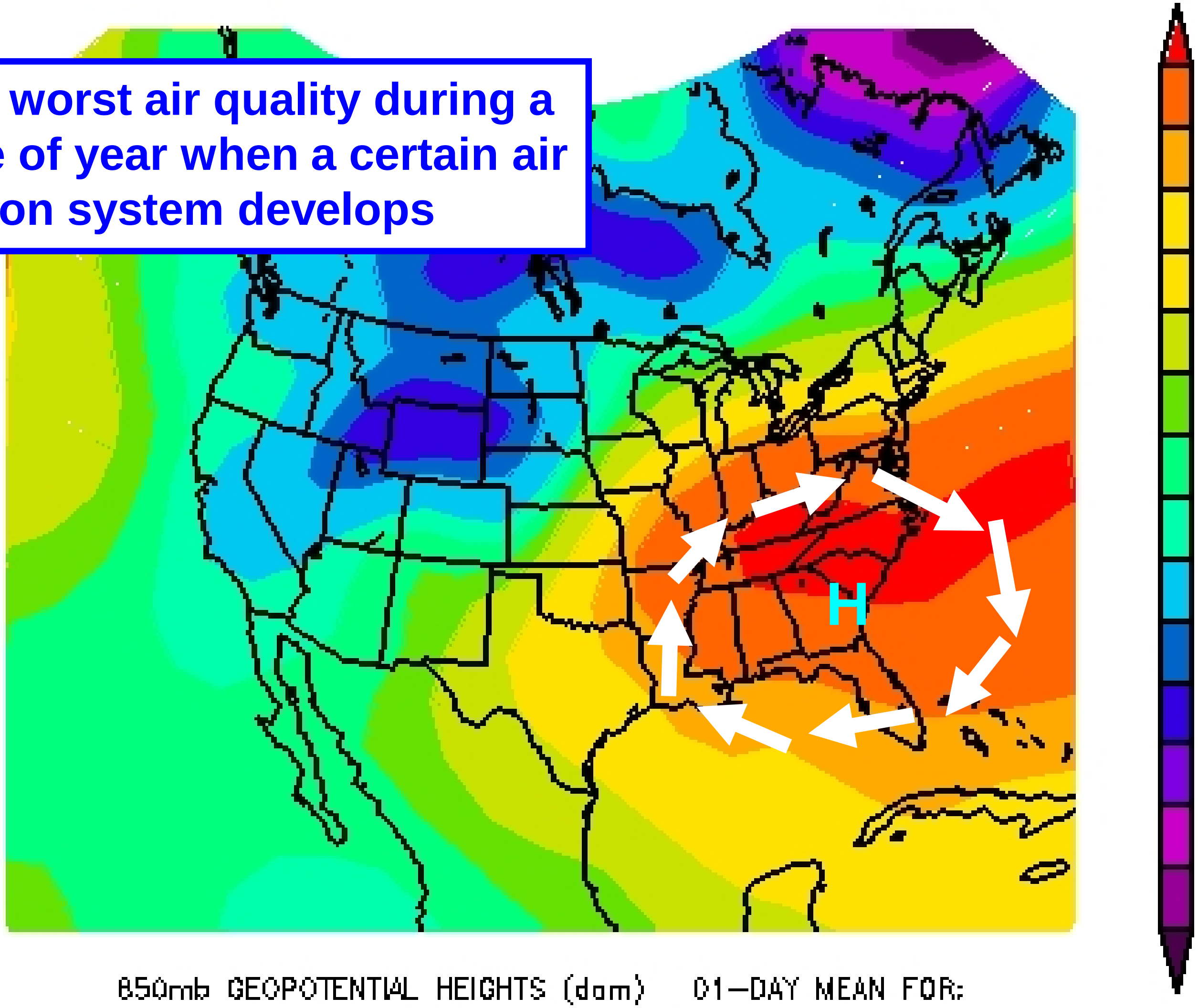

An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O_3 pollution may have been partly misdirected. Measurements and model calculations now show that O_3 production over most of the United States is primarily NO_x limited, not hydrocarbon limited. The 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

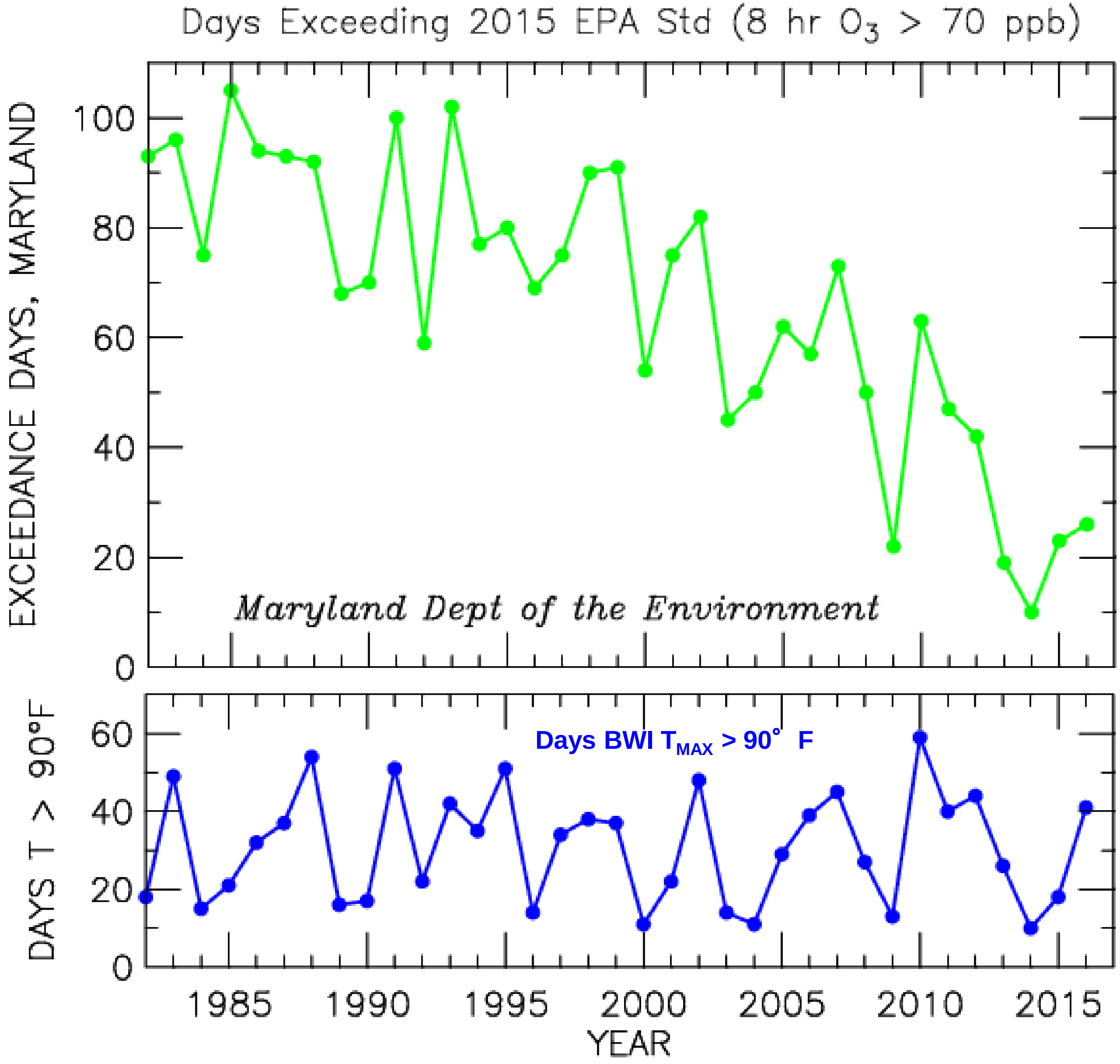


850mb GEOPOTENTIAL HEIGHTS (dam) 01–DAY MEAN FOR:
Sun JUL 04 1999

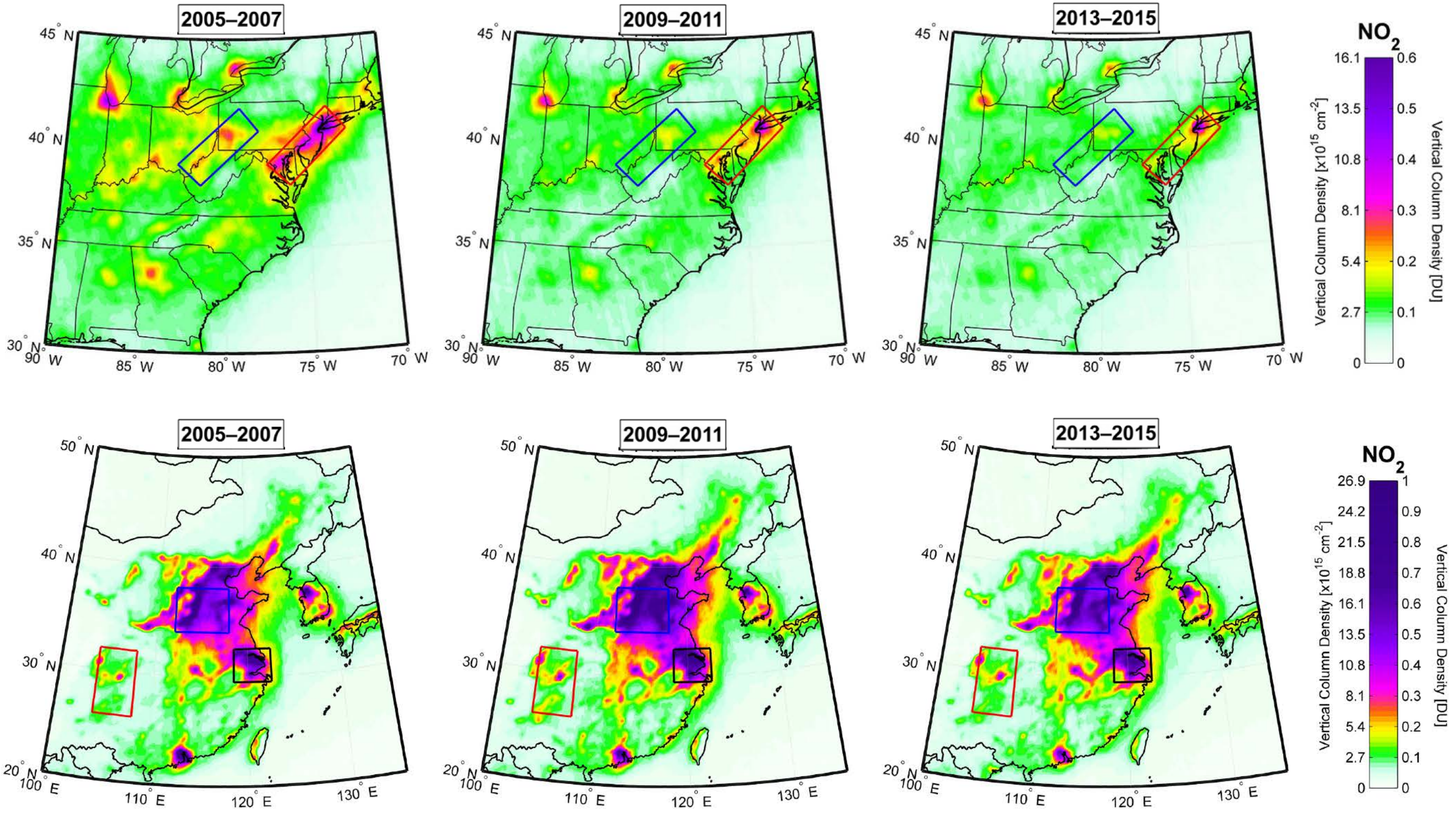
NCEP OPERATIONAL DATASET

http://www.mde.state.md.us/assets/document/BJH%20-%20Basics%20on%20Ozone%20Transport.ppt

Dramatic Improvements Local Air Quality, Past 4 Decades

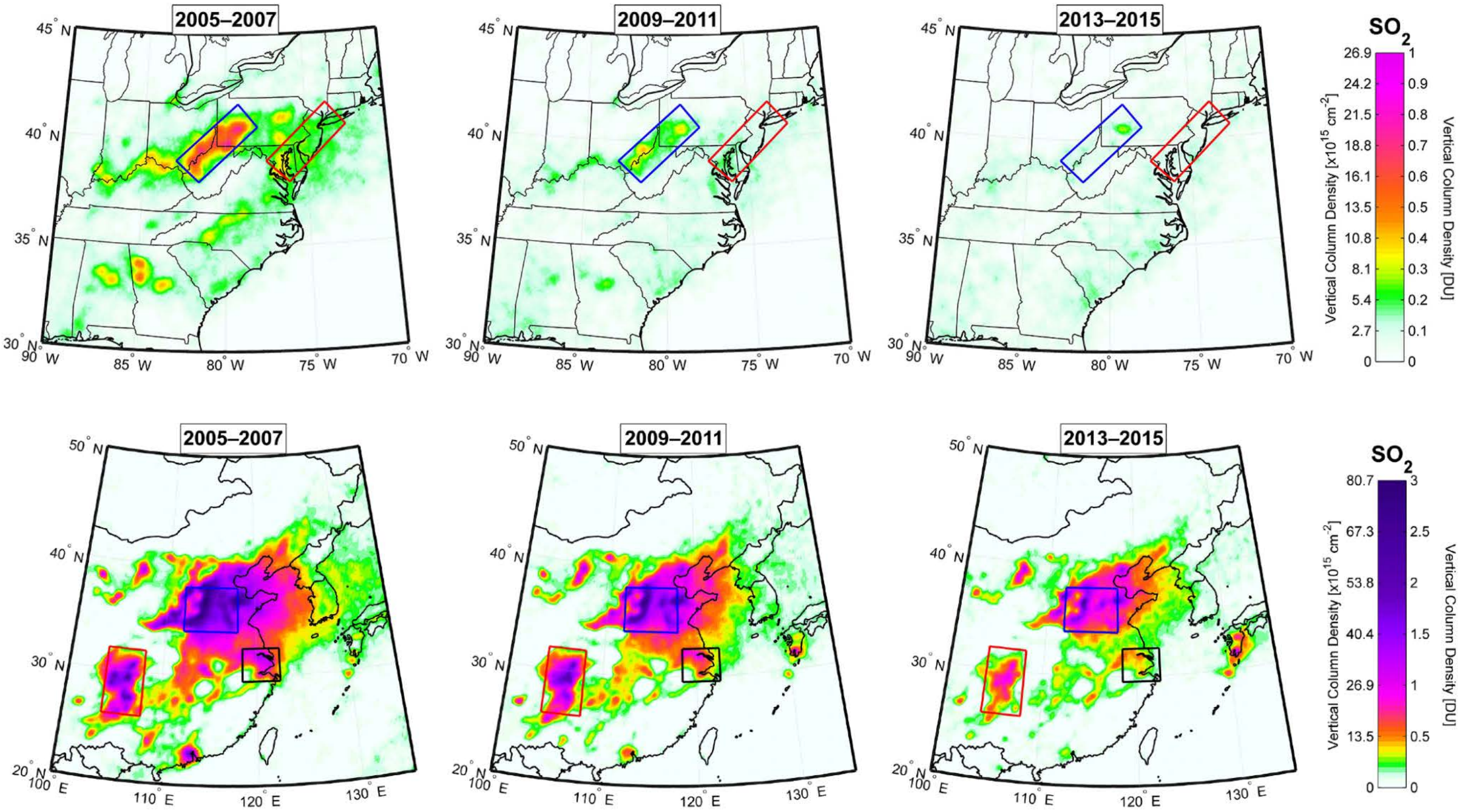


NO_2 Trends from Space



Krotkov *et al.*, *ACP*, 2016

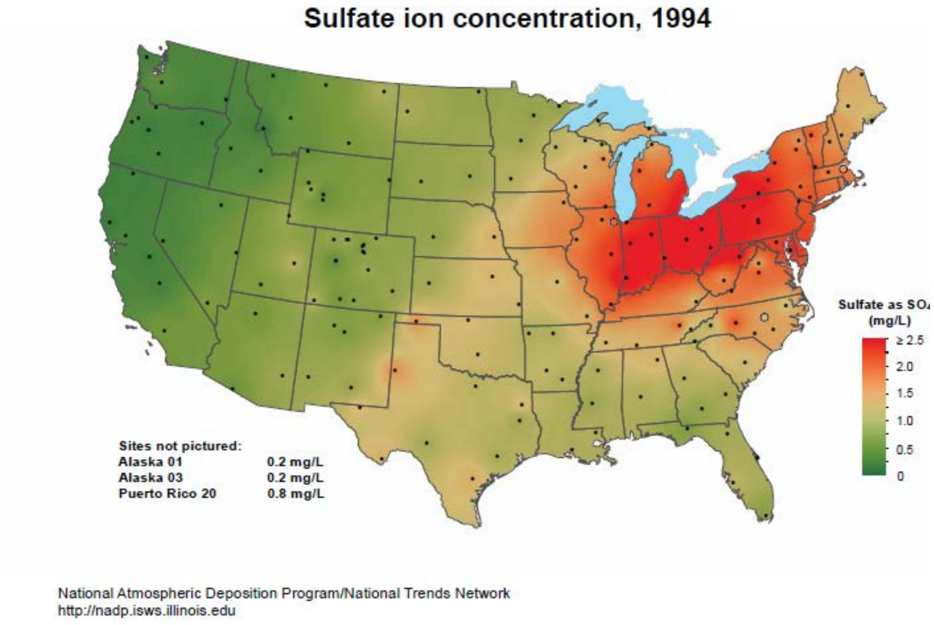
SO_2 Trends from Space



Krotkov *et al.*, *ACP*, 2016

Sulfate Deposition

1994



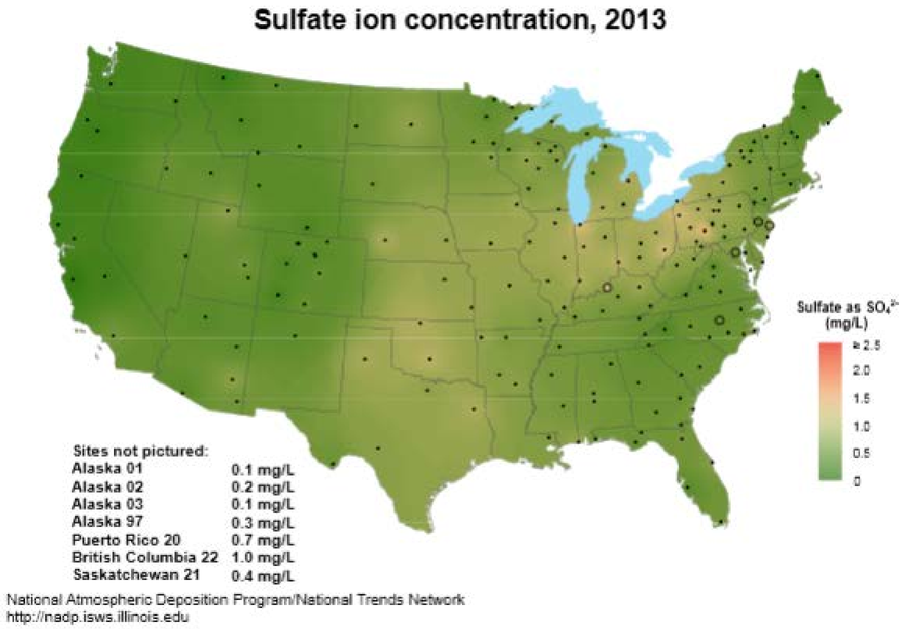
Sulfate ion concentration, 1994

Sites not pictured:

Alaska 01	0.2 mg/L
Alaska 03	0.2 mg/L
Puerto Rico 20	0.8 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

2013



Sulfate ion concentration, 2013

Sites not pictured:

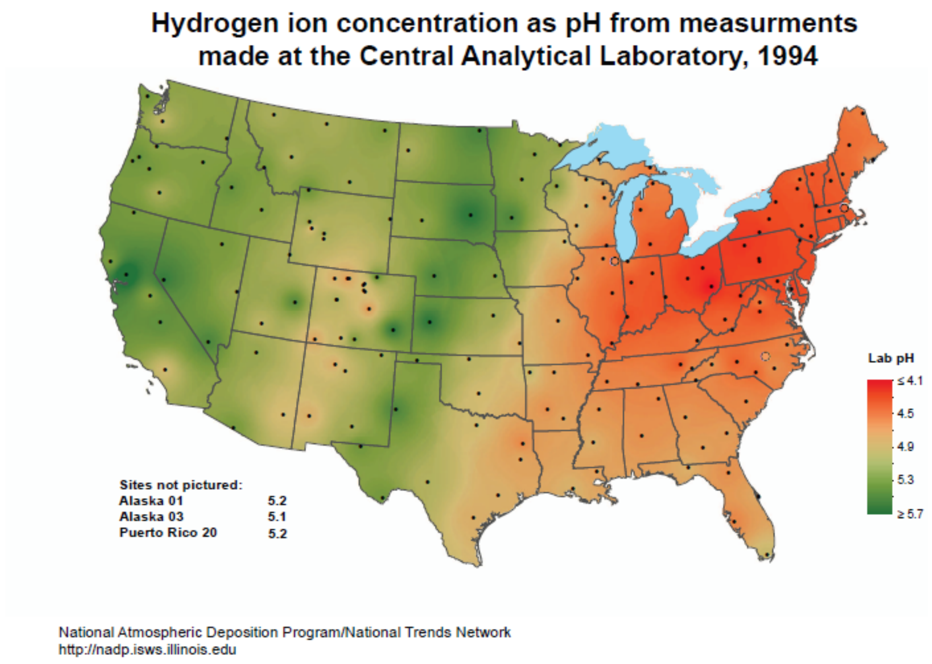
Alaska 01	0.1 mg/L
Alaska 02	0.2 mg/L
Alaska 03	0.1 mg/L
Alaska 97	0.3 mg/L
Puerto Rico 20	0.7 mg/L
British Columbia 22	1.0 mg/L
Saskatchewan 21	0.4 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

http://nadp.sws.uiuc.edu/

pH

1994

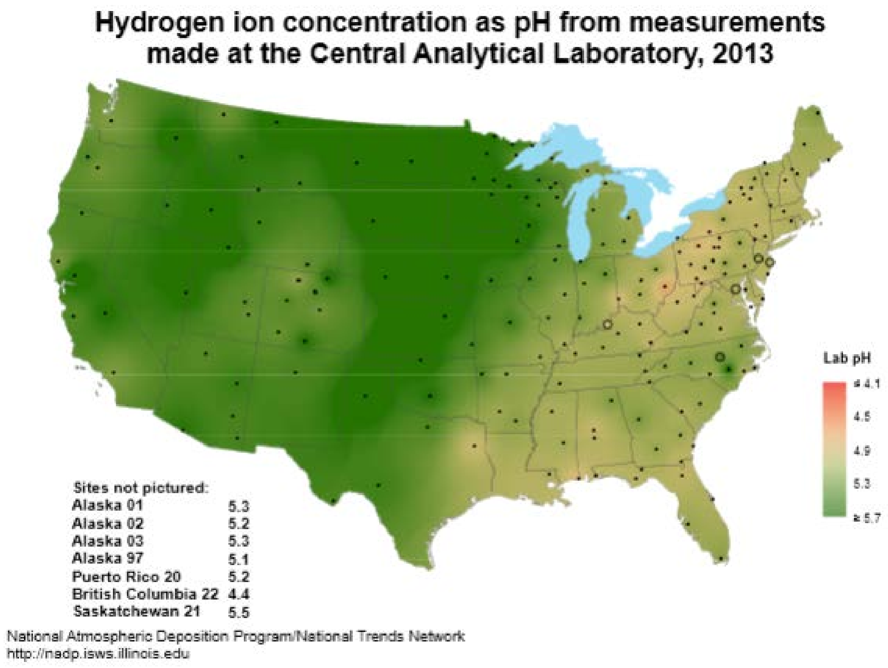


Hydrogen ion concentration as pH from measurments made at the Central Analytical Laboratory, 1994

Sites not pictured:	
Alaska 01	5.2
Alaska 03	5.1
Puerto Rico 20	5.2

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

2013



Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2013

Sites not pictured:	
Alaska 01	5.3
Alaska 02	5.2
Alaska 03	5.3
Alaska 97	5.1
Puerto Rico 20	5.2
British Columbia 22	4.4
Saskatchewan 21	5.5

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

http://nadp.sws.uiuc.edu/

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 :

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

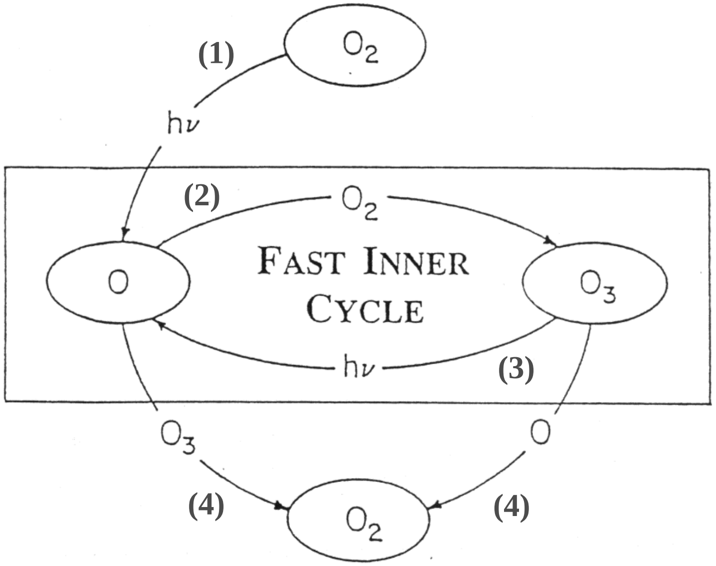
$$O + O_3 \rightarrow O_2 + O_2 \qquad (4)$$

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)

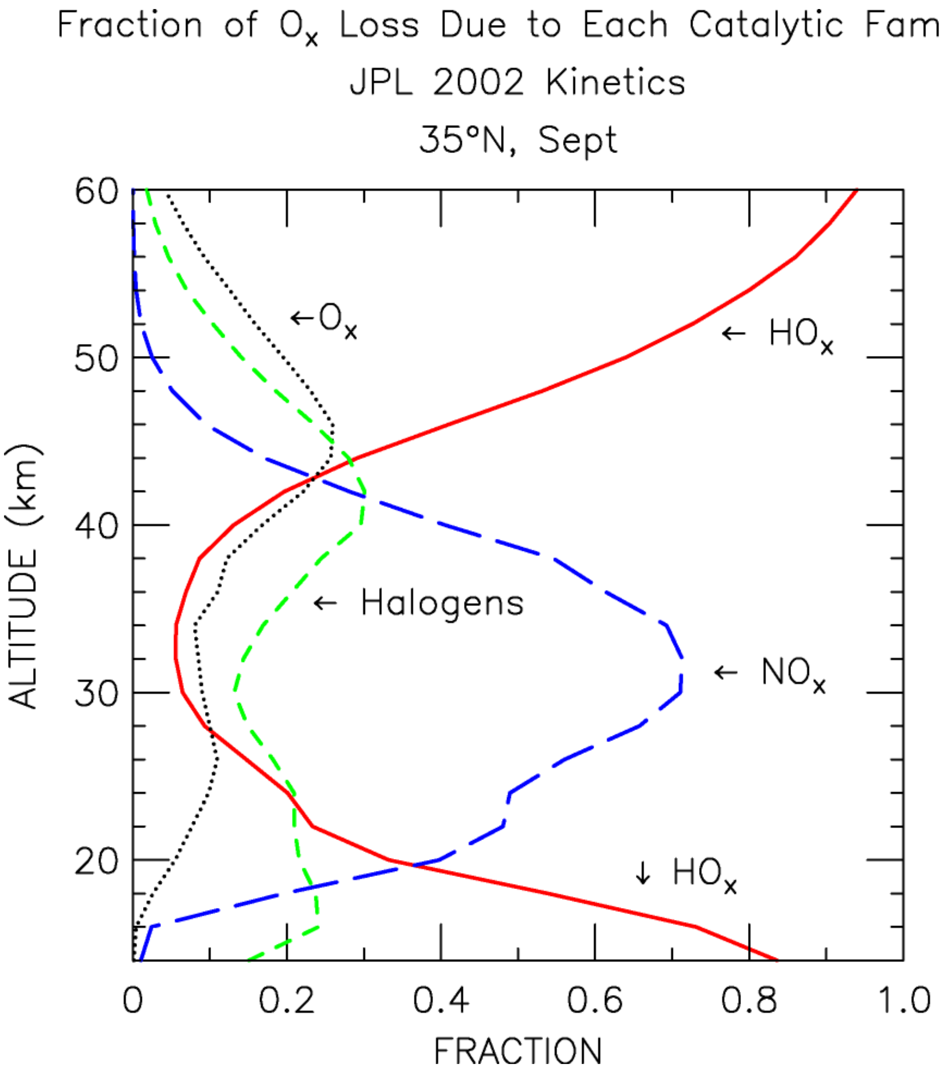
- The sum O + O_3 is commonly called *"odd oxygen"*



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



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

Troposphere

HO_2 formation:

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2$$

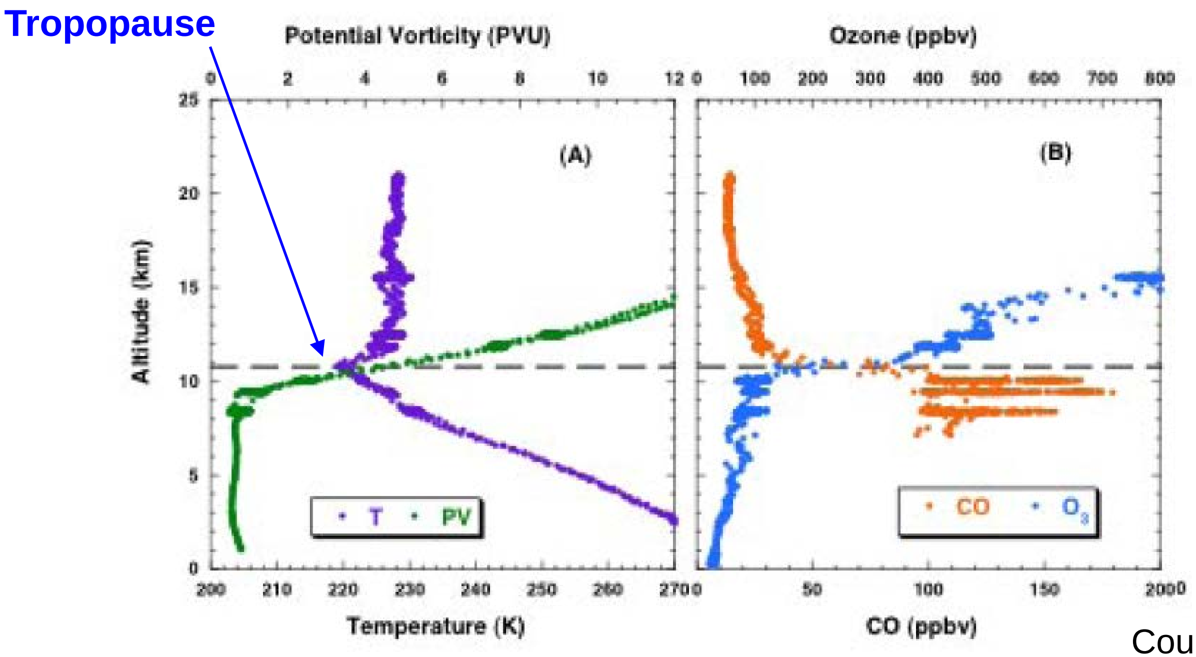
HO_2 loss:

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

Followed by:

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

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



Tropopause

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**

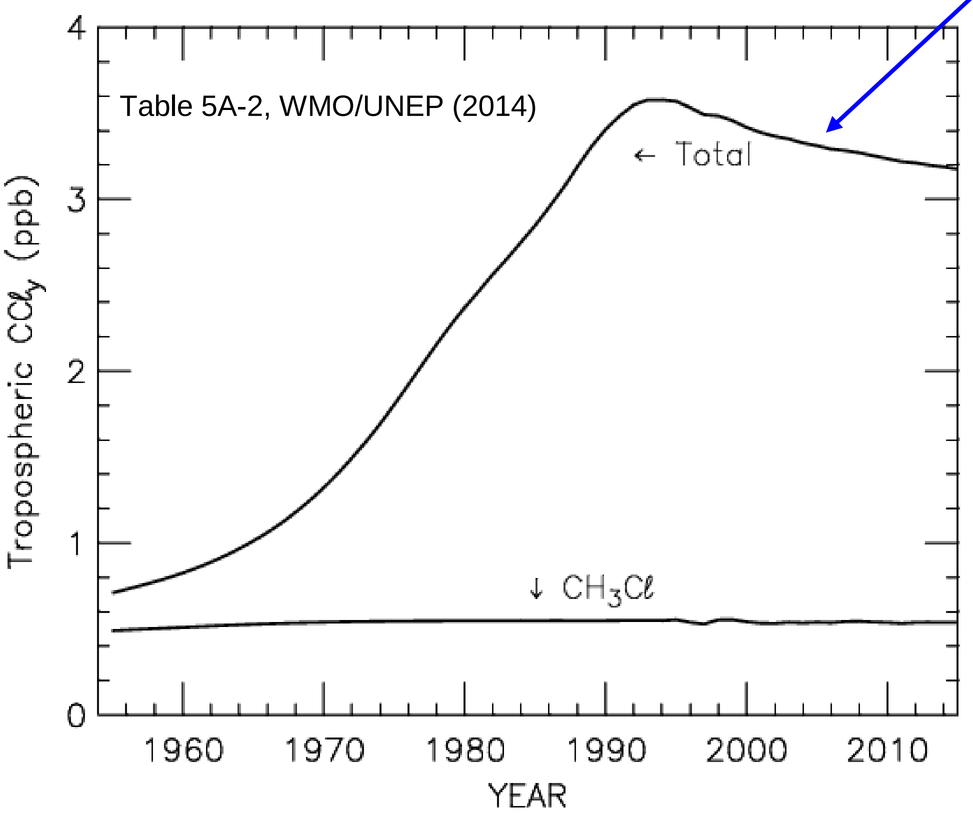
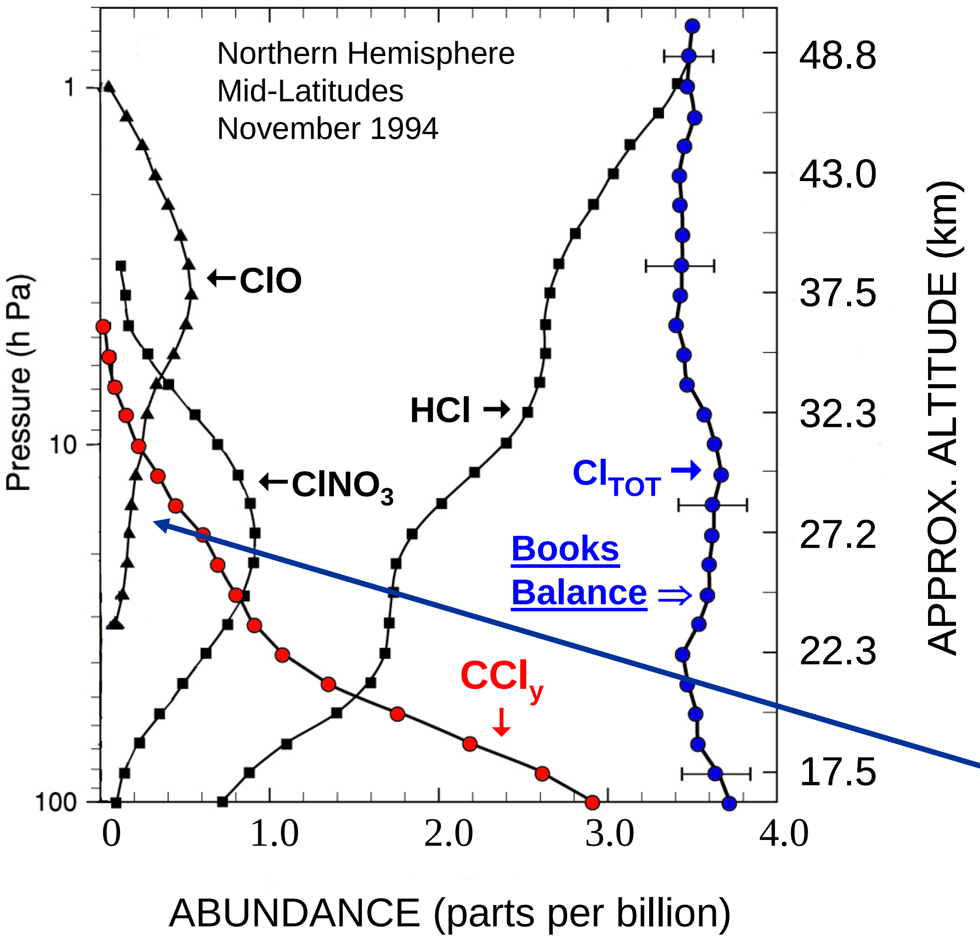


Table 5A-2, WMO/UNEP (2014)

CFCs:
- **long lived (50 to 100 yr lifetime)**
- **decompose in the stratosphere**
- **lose memory of emission location when enter stratosphere**

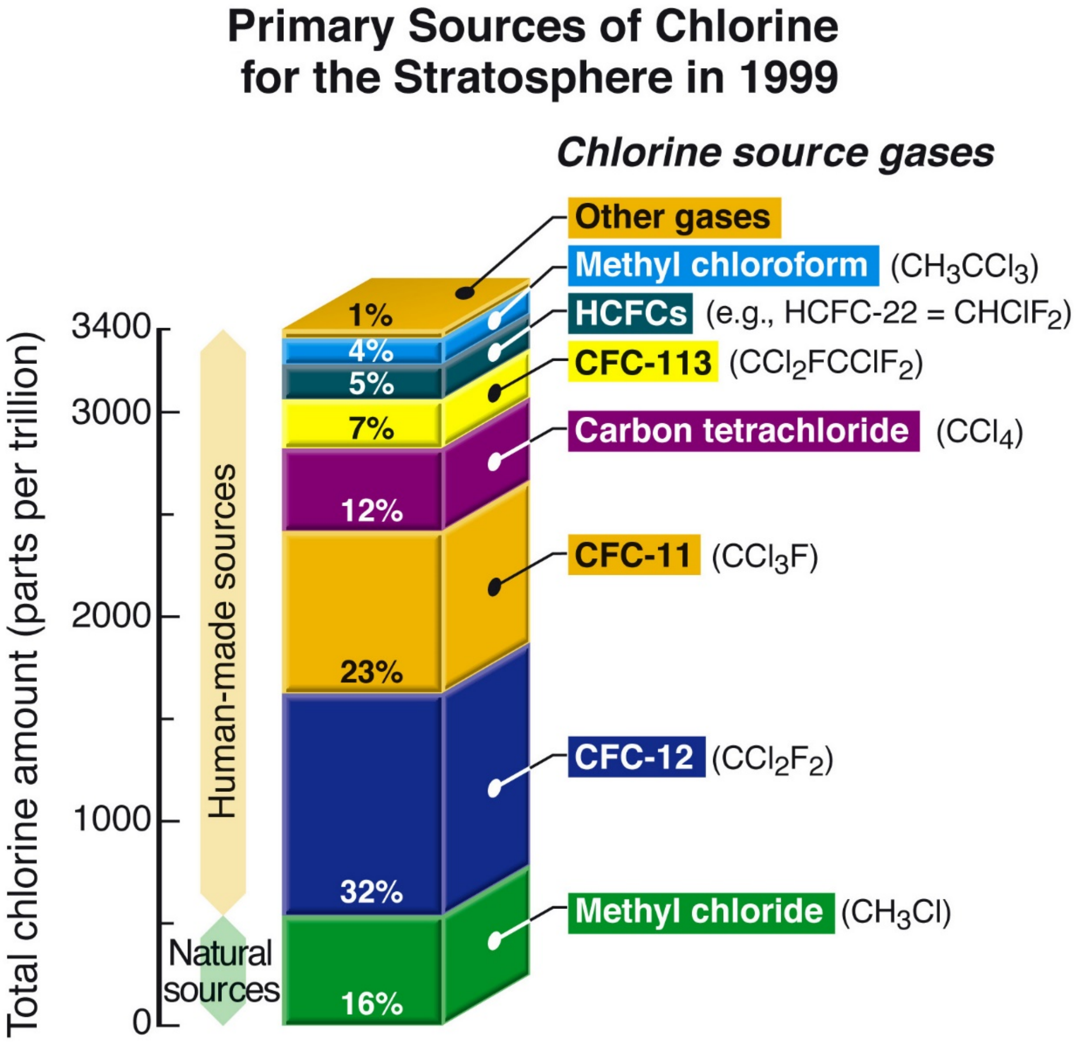
Chlorine Abundance, Mid-Latitude Stratosphere



Note: Below ~30 km,
ClO << ClNO$_3$ and HCl

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

Chlorine Source Gases



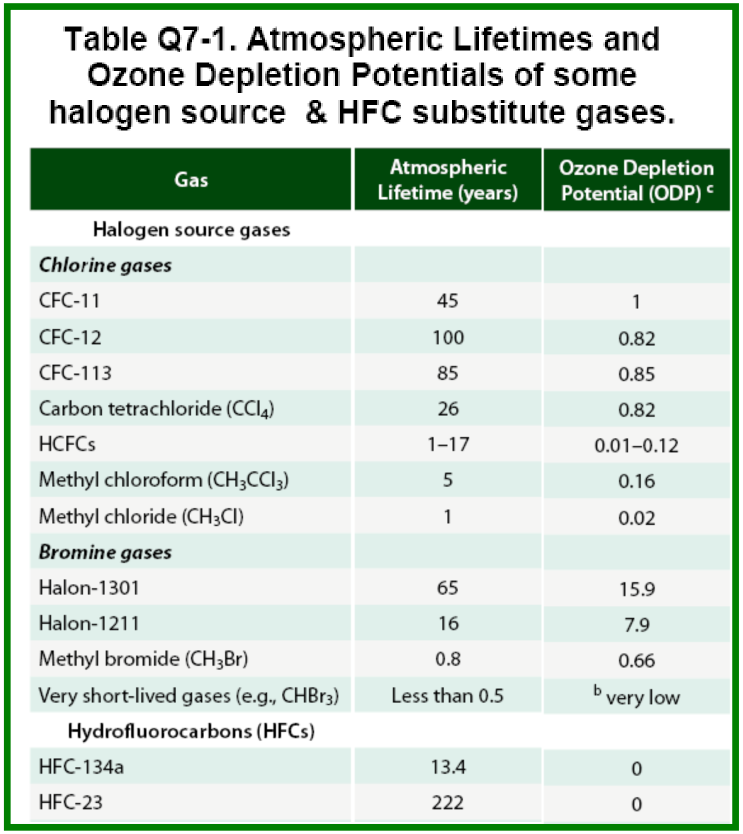
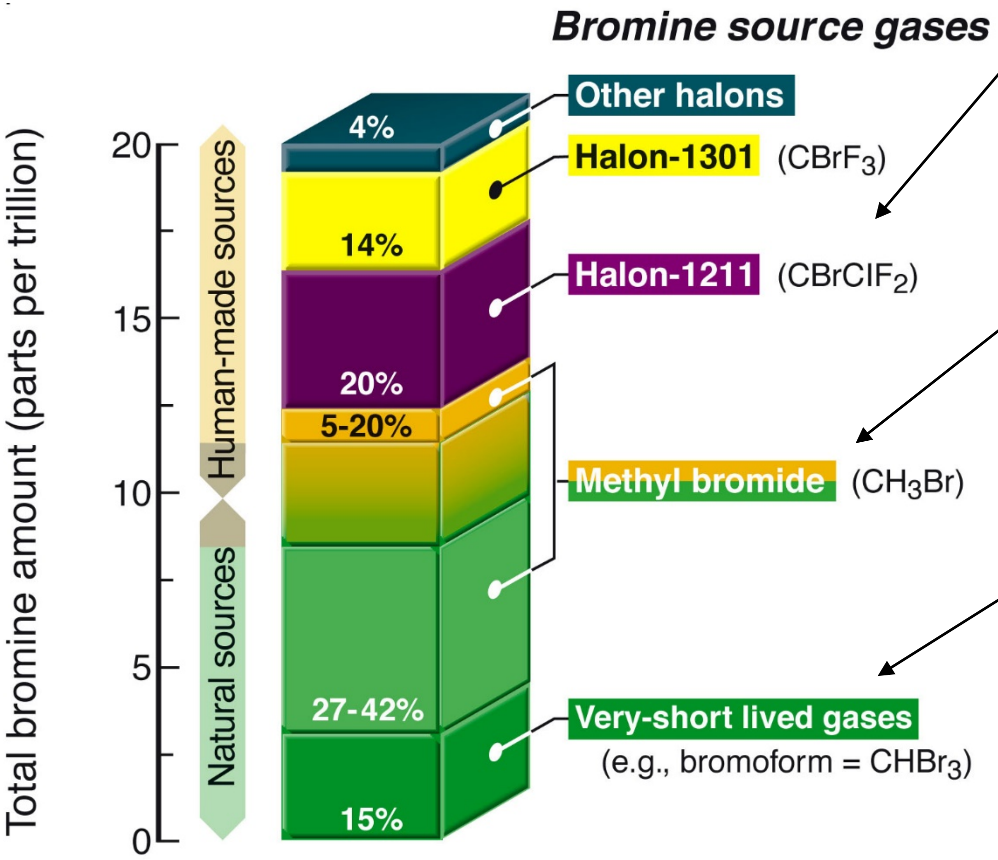


Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

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



Halons:

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

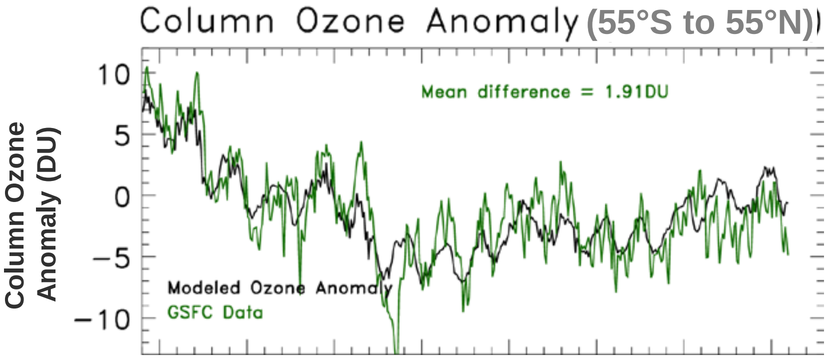
CH_3Br:

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

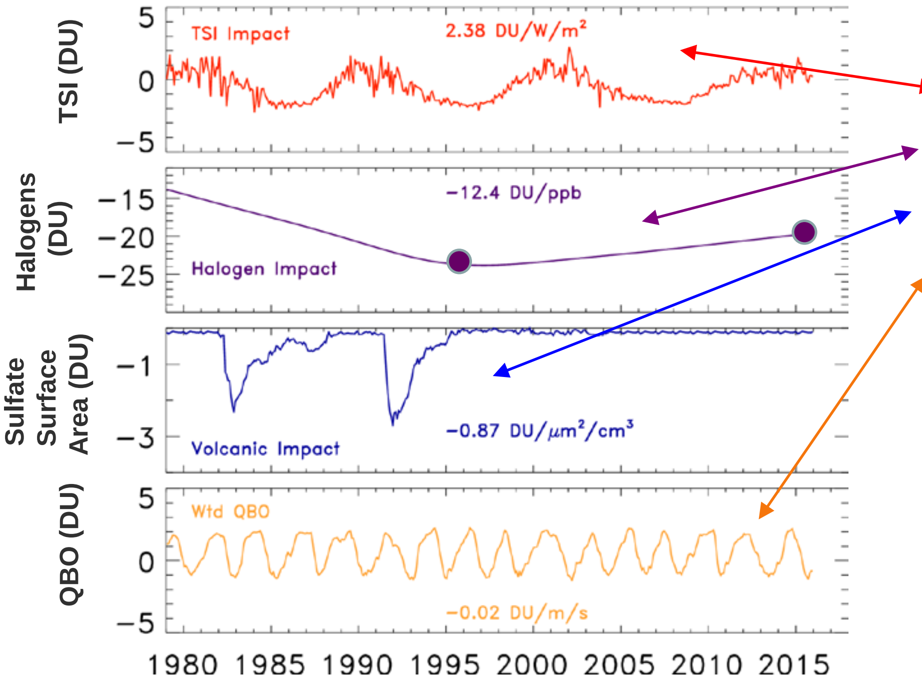
VSL Gases (e.g., $CHBr_3$, CH_2Br_2):

- 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)

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


Predictor Variables × Regression Coefficient

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

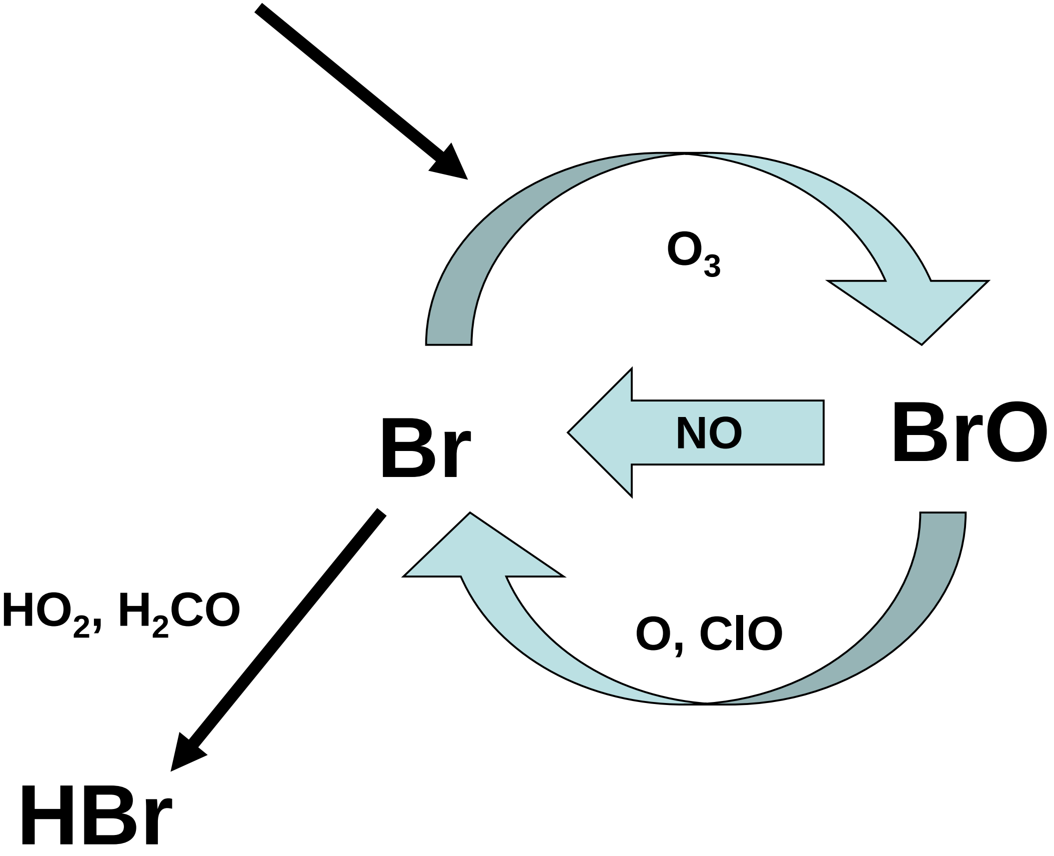
QBO = Quasi-biennial oscillation of the direction of winds in the tropical lower strat

BrO_x : BrO and Br

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

Production : $CH_3Br + h\nu \rightarrow$ Inorganic bromine
$\text{Halons} + h\nu \rightarrow$ Inorganic bromine
} Considered in global models

$CHBr_3 + h\nu \rightarrow$ Inorganic bromine
$CH_2Br_2 + h\nu \rightarrow$ Inorganic bromine
} Generally neglected in global models



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:

$$BrO + NO \rightarrow Br + NO_2 \qquad (2)$$

or $$BrO + O \rightarrow Br + O_2 \qquad (3)$$

or $$BrO + ClO \rightarrow BrCl + O_2 \qquad (4a)$$

$$\rightarrow ClOO + Br \qquad (4b)$$

$$\rightarrow OClO + Br \qquad (4c)$$

BrO loss step (2):

$$\begin{aligned} Br + O_3 &\rightarrow BrO + O_2 \\ BrO + NO &\rightarrow Br + NO_2 \\ \hline \text{Net:} \quad O_3 + NO &\rightarrow NO_2 + O_2 \\ \text{Followed by:} \quad NO_2 + h\nu &\rightarrow NO + O \\ \hline \text{Final net:} \quad O_3 + h\nu &\rightarrow O + O_2 \end{aligned}$$

BrO loss step (3):

$$\begin{aligned} Br + O_3 &\rightarrow BrO + O_2 \\ BrO + O &\rightarrow Br + O_2 \\ \hline \text{Net:} \quad O_3 + O &\rightarrow 2\,O_2 \end{aligned}$$

Can show:

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

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
  - fetime 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 >> ClO/Cl_y

  $Br + CH_4 \rightarrow HBr + CH_3$ is endothermic and has rate constant of zero

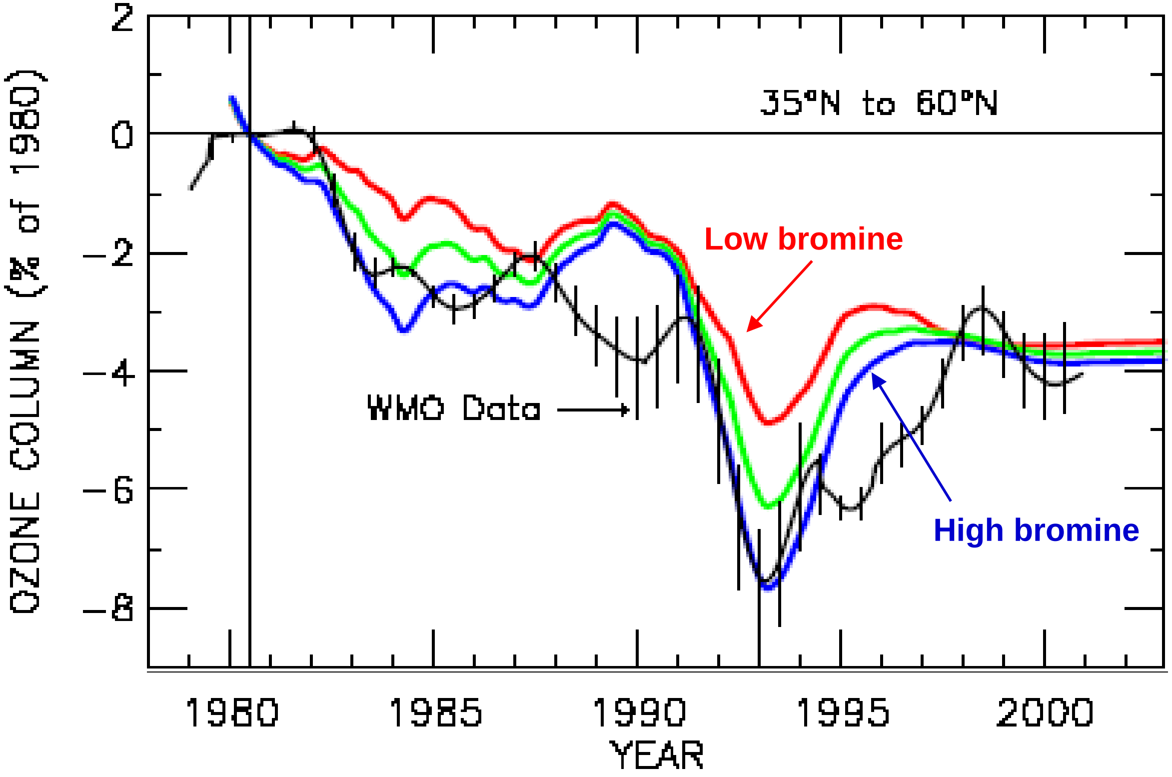
  $Cl + CH_4 \rightarrow HCl + CH_3$ is exoothermic and proceeds at reasonable rate

  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:

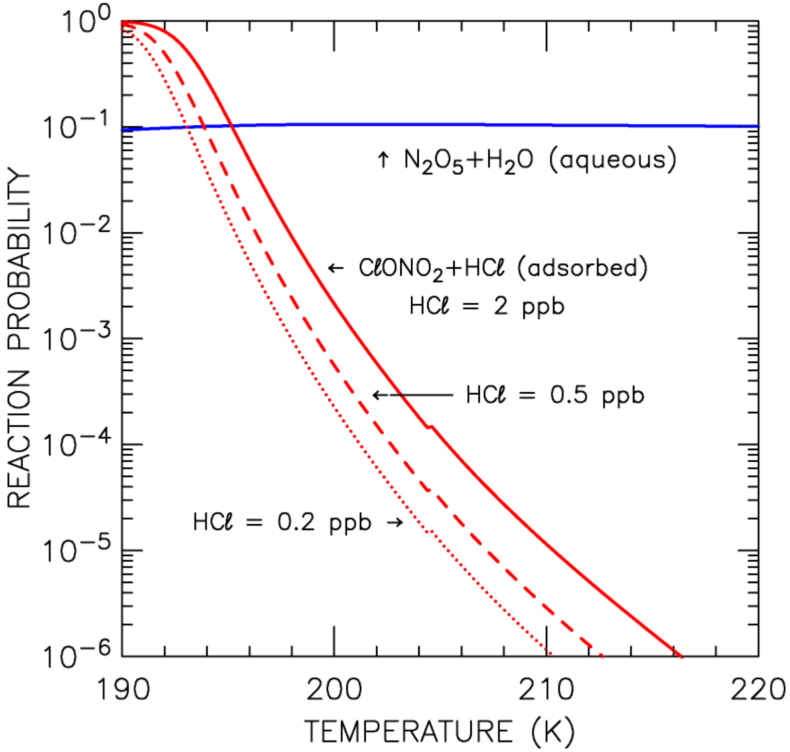
- a) rise and fall of chlorine
- b) volcanic perturbations to aerosol loading
- c) amount of bromine in lowermost stratosphere



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**

$HCl + ClNO_3 \rightarrow Cl_2$ (gas) + HNO_3 (solid)

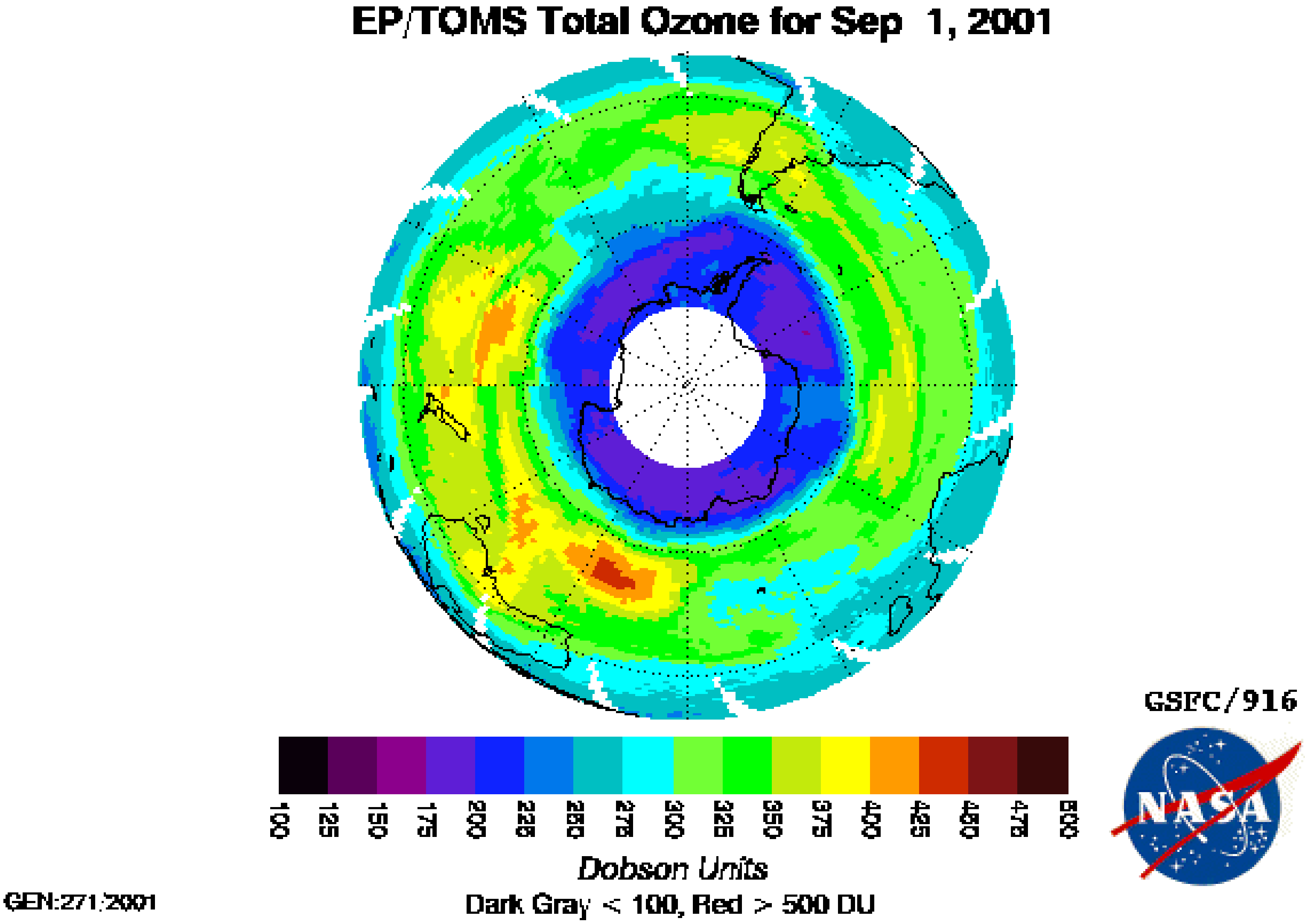
$ClNO_3 + H_2O \rightarrow HOCl + HNO_3$

Cl_2 + SUNLIGHT + $O_3 \rightarrow ClO$

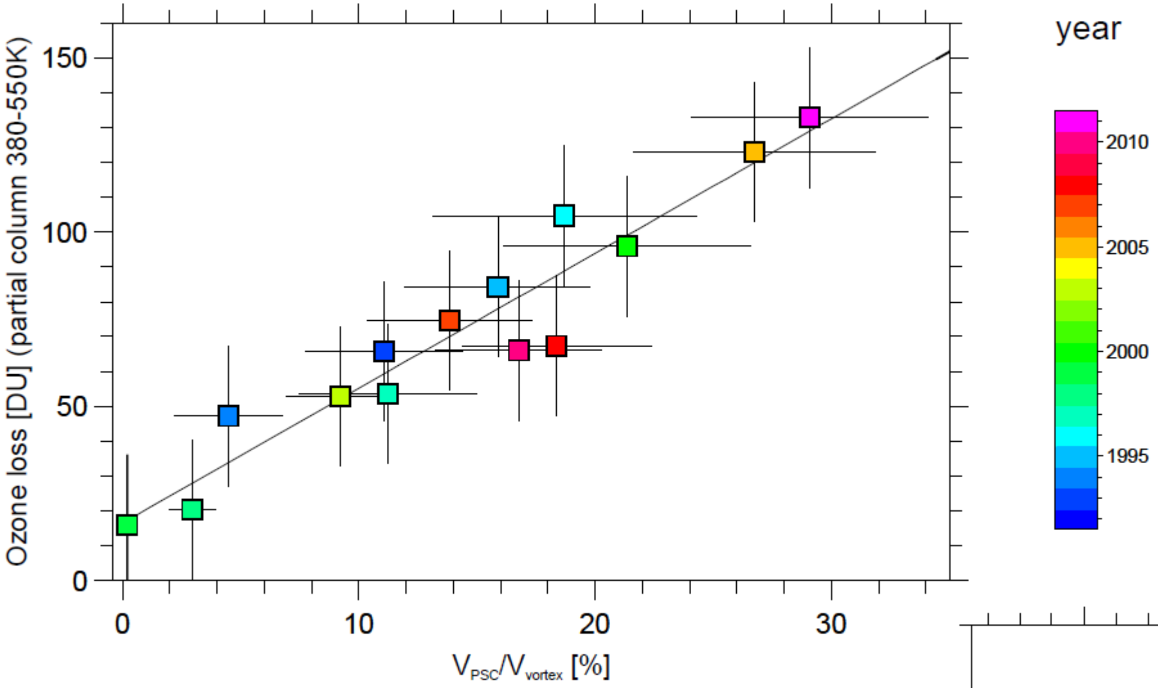
HOCl + SUNLIGHT + $O_3 \rightarrow ClO$

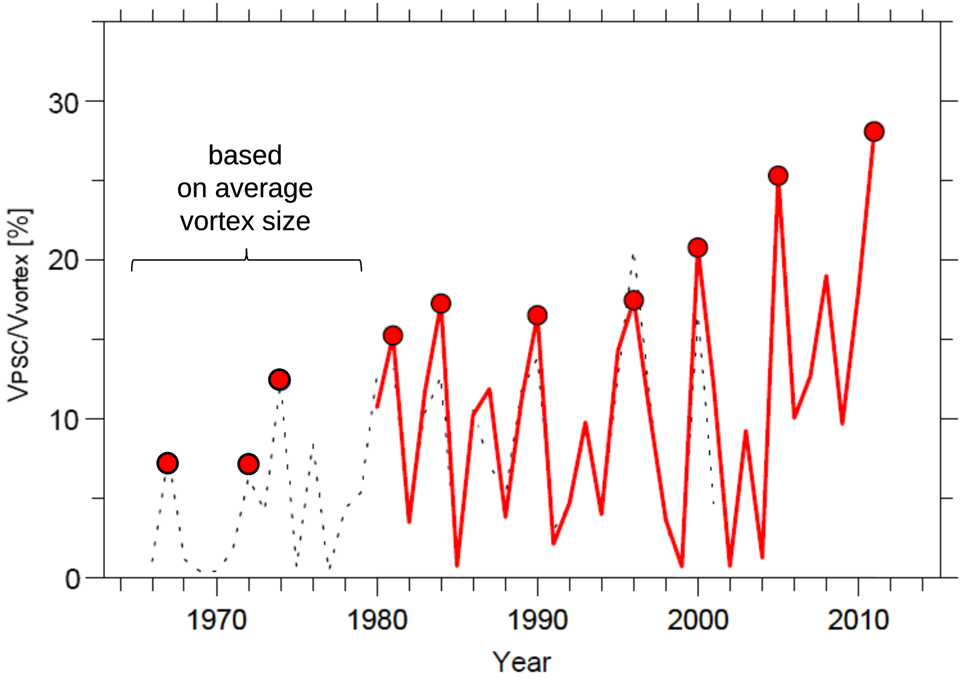
HNO_3 SEDIMENTS (PSCs fall due to gravity)

- ELEVATED **ClO** + SUNLIGHT DESTROYS O_3
- BrO : REACTION PARTNER FOR ClO $\Rightarrow$ ADDITIONAL O_3 LOSS

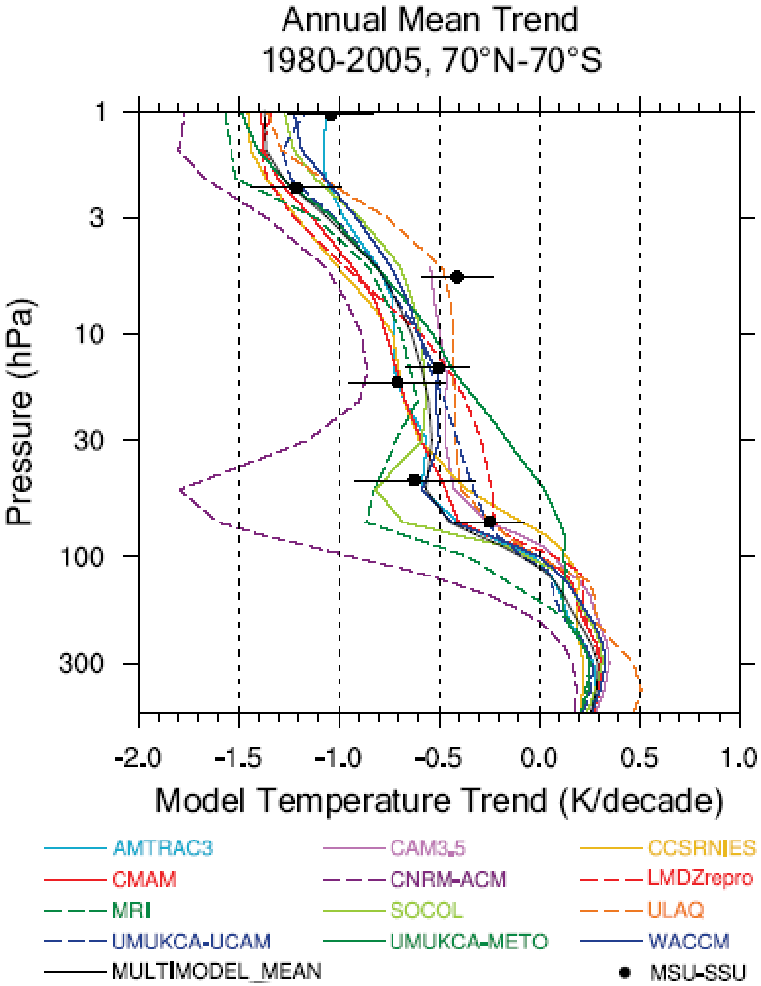

EP/TOMS Total Ozone for Sep 1, 2001
100
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
500
Dobson Units
Dark Gray < 100, Red > 500 DU
GSFC/916
GEN:271:2001

Arctic Ozone 2011 in Context of Prior Years





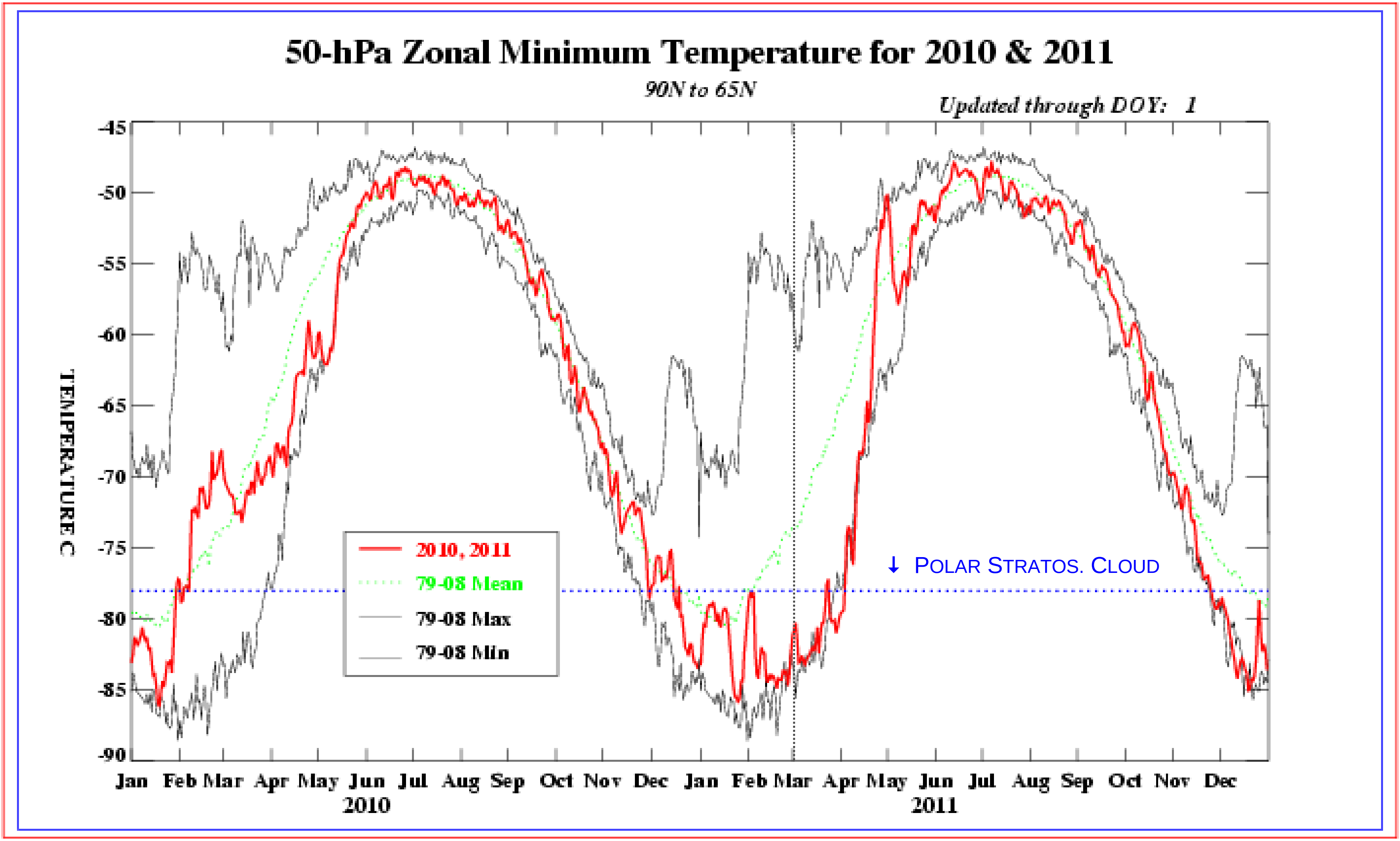
The Stratosphere Cools as the Surface Warms



**If the stratosphere *continues to cool*,
for which region of the stratosphere will
ozone be most vulnerable to future decline ?**

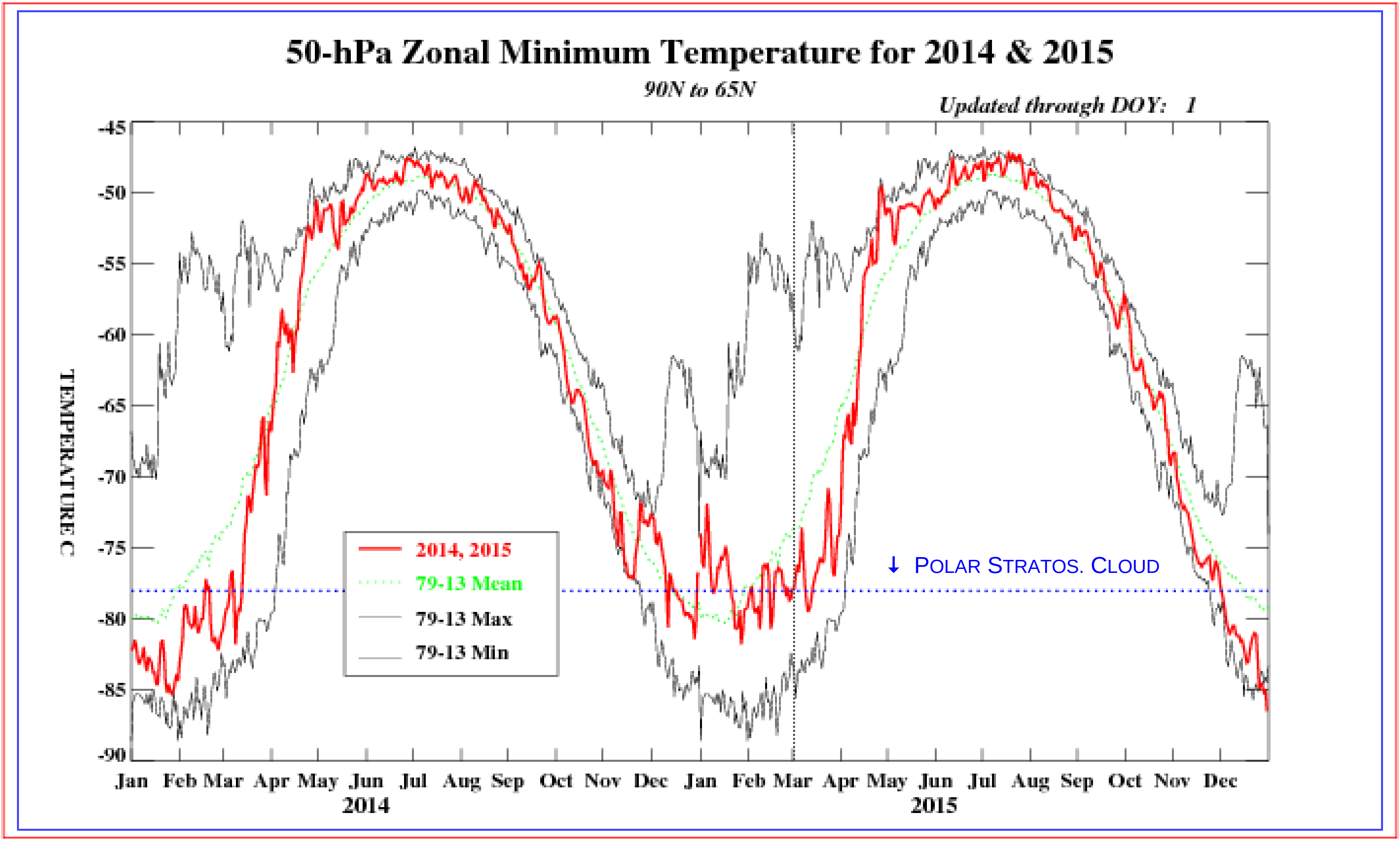
Figure 4−11, WMO/UNEP (2011)

Arctic Temperature: Mar 2011



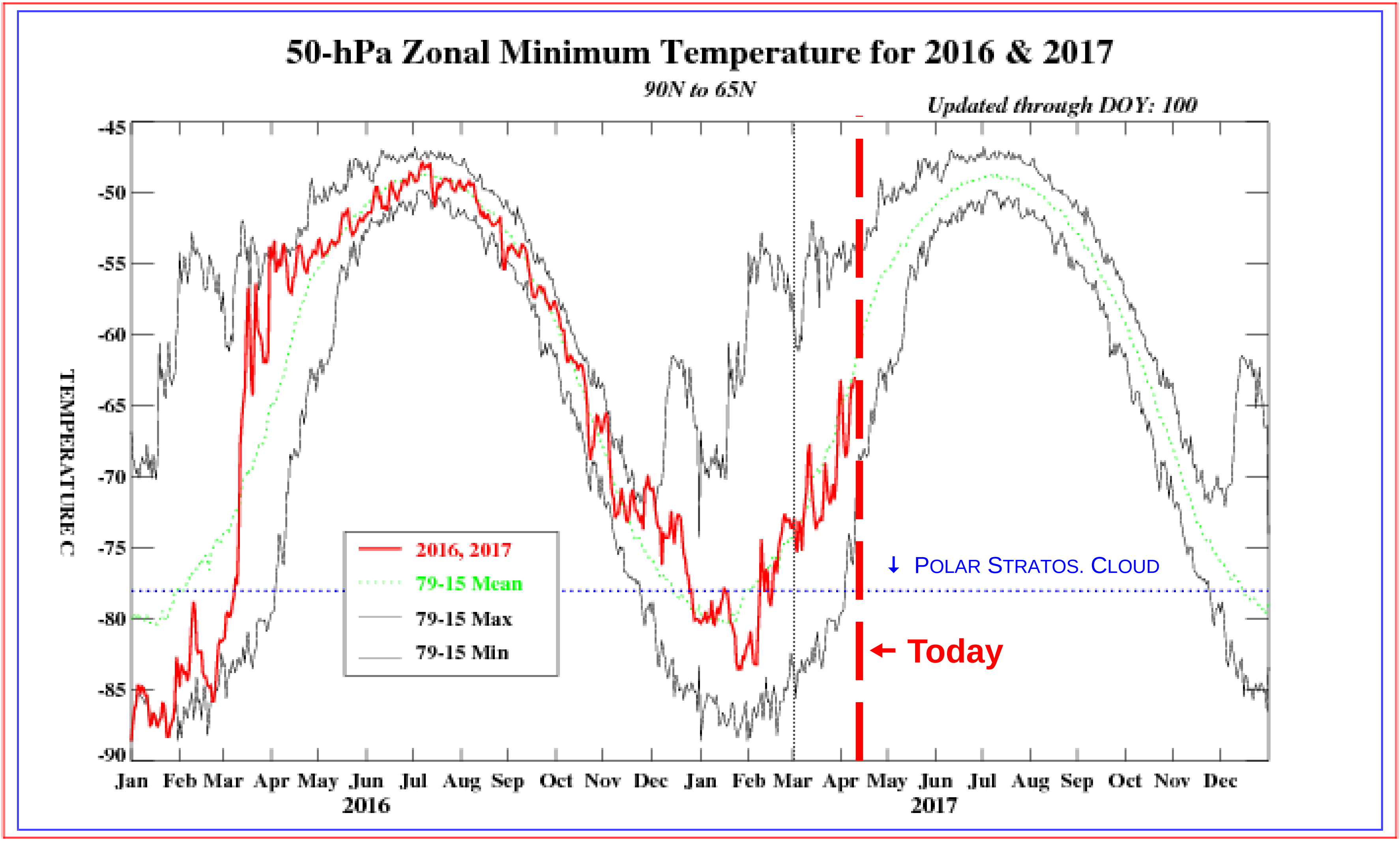
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2011.gif

Arctic Temperature: Mar 2015



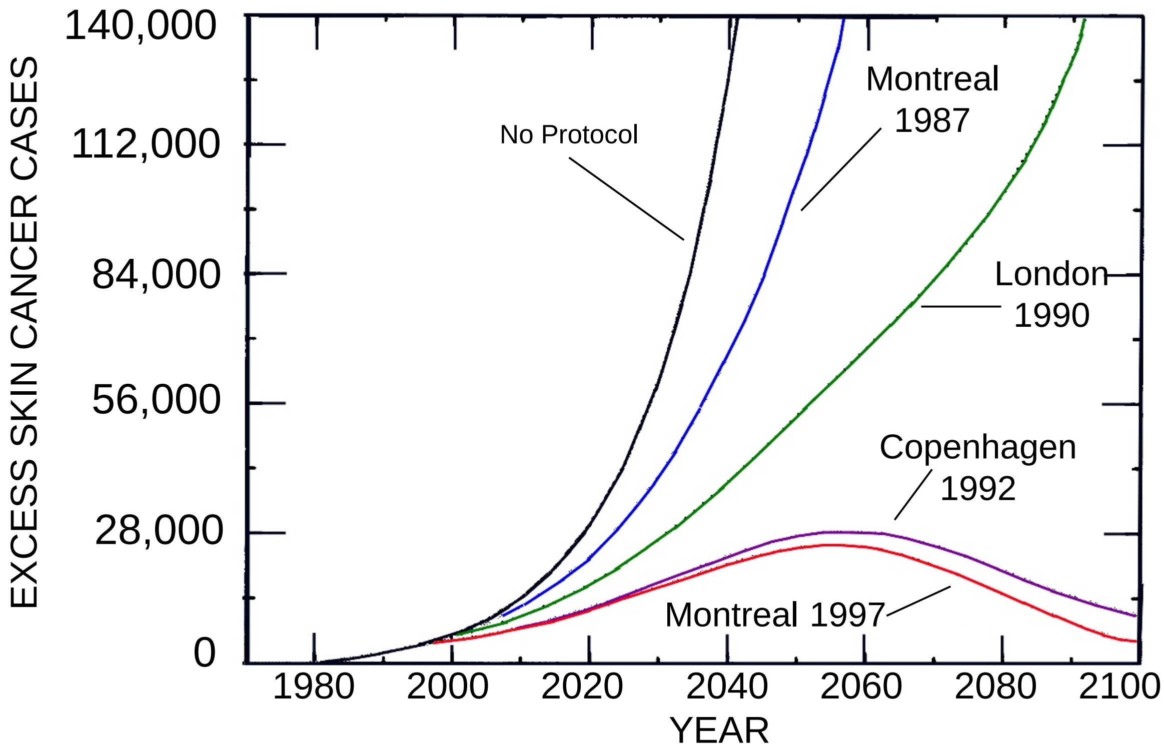
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2015.gif

Arctic Temperature: Mar 2017



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

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

- **Thursday, 13 April, 2:00 pm to 3:15 pm**
- **CSS 2416**
- **Closed book, no notes**

- **Focus mainly on Lectures 9 to 16**

- **Conceptual questions only: no calculator**

- **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**