Review of Lectures 9 to 16

AOSC / CHEM 433 & AOSC 633

Ross Salawitch & Walt Tribett

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

https://www.videoblocks.com/video/earth-sunset-spacewalk-view-from-space-station-r7dydlcsgjd23vml0

11 April 2019

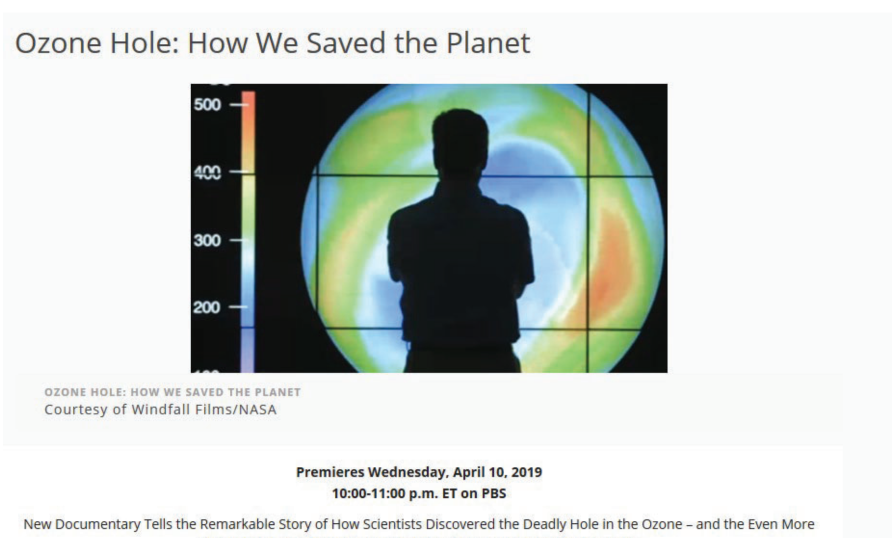
Announcements

1. Exam on Tuesday
  - **Conceptual questions only: <u>no calculators</u>**
  - **Closed book; no notes**

2. ELMS gradebook should be current except for AT 15
  - **Please let us know of any issues**

3. Review of Problem Set #3 will be held Mon, 15 April, 5 pm in ATL 2428

4. Will show movie on Thurs, 25 April, 6:00 pm, ATL 3400: attendance is voluntary



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 → O_3 + M

O_3 + photon → $O(^1D)$ + O_2

$O(^1D)$ + H_2O → OH + OH

OH + O_3 → HO_2 + O_2

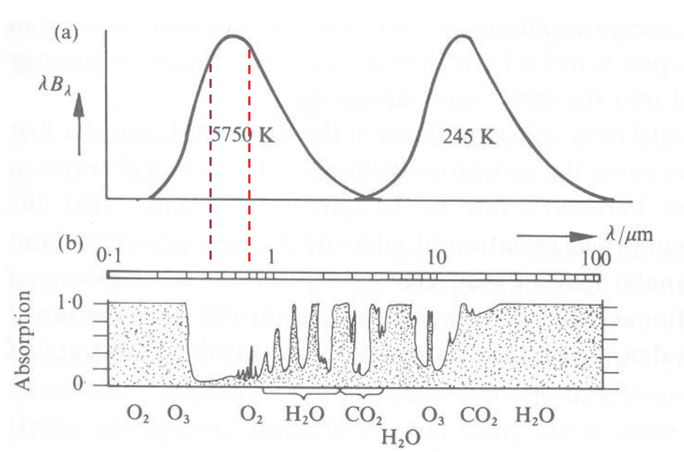
HO_2 + O → OH + O_2

Termination

HO_2 + HO_2 → 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)



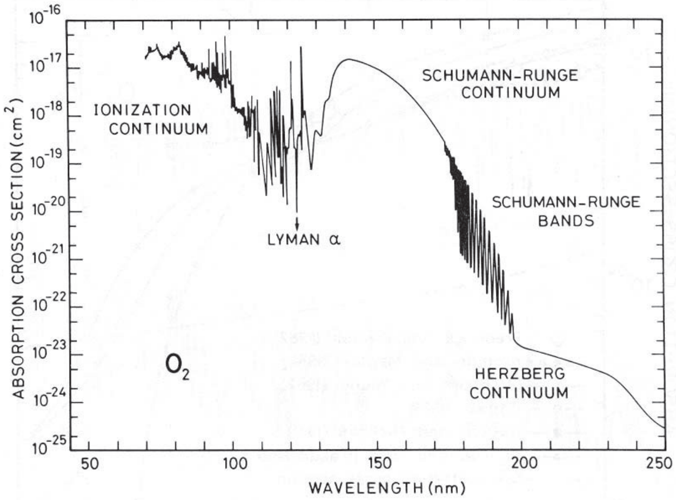
Panel (a) : Curves of black-body energy versus wavelength for 5750 K (Sun's approximate temperature) and for 245 K (Earth's mean temperature).
The curves are drawn with equal area since, integrated over the entire Earth at the top of the atmosphere, the solar (downwelling) and terrestrial (upwelling) 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 of the 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:

$$\int_0^{\infty} [O_2]\, dz' \approx 4 \times 10^{24} \text{ molecules/cm}^2$$

O_2 Optical Depth for $\theta = 0°$, z = 0 km			
	σ_{max} (cm^2)	τ (0 km)	$e^{-\tau\,(0\text{ km})}$
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: $$\frac{\text{Column } O_3}{\text{Column Air}} = \frac{8\times10^{18}}{2\times10^{25}} = 0.4 \text{ parts per million} \Rightarrow \text{Ozone is a trace species!}$$

O_3 Optical Depth for $\theta = 0°$, $z = 0$ km				
	σ_{max} (cm^2)	τ (0 km)	$e^{-\tau\,(0\text{ km})}$	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

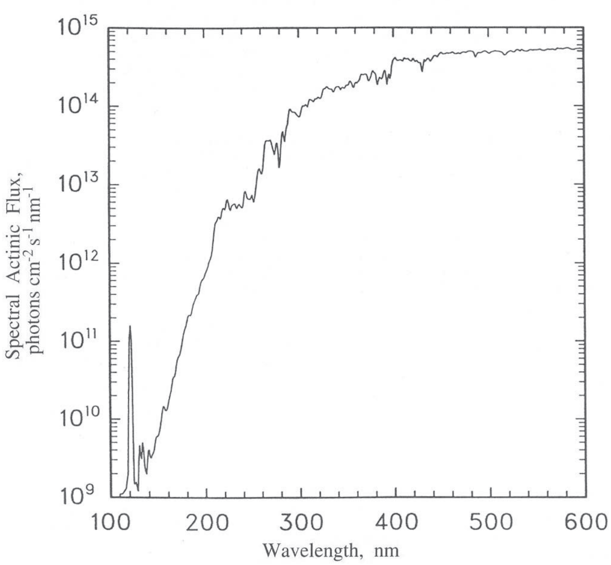
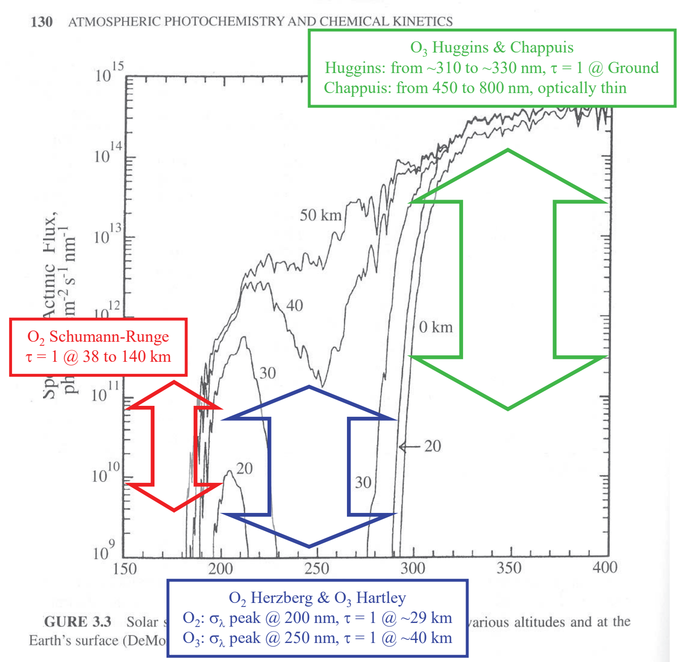


FIGURE 6. Solar spectral actinic flux (photons cm^{-2} s^{-1} nm^{-1}) at the top of Earth's atmosphere.

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



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:

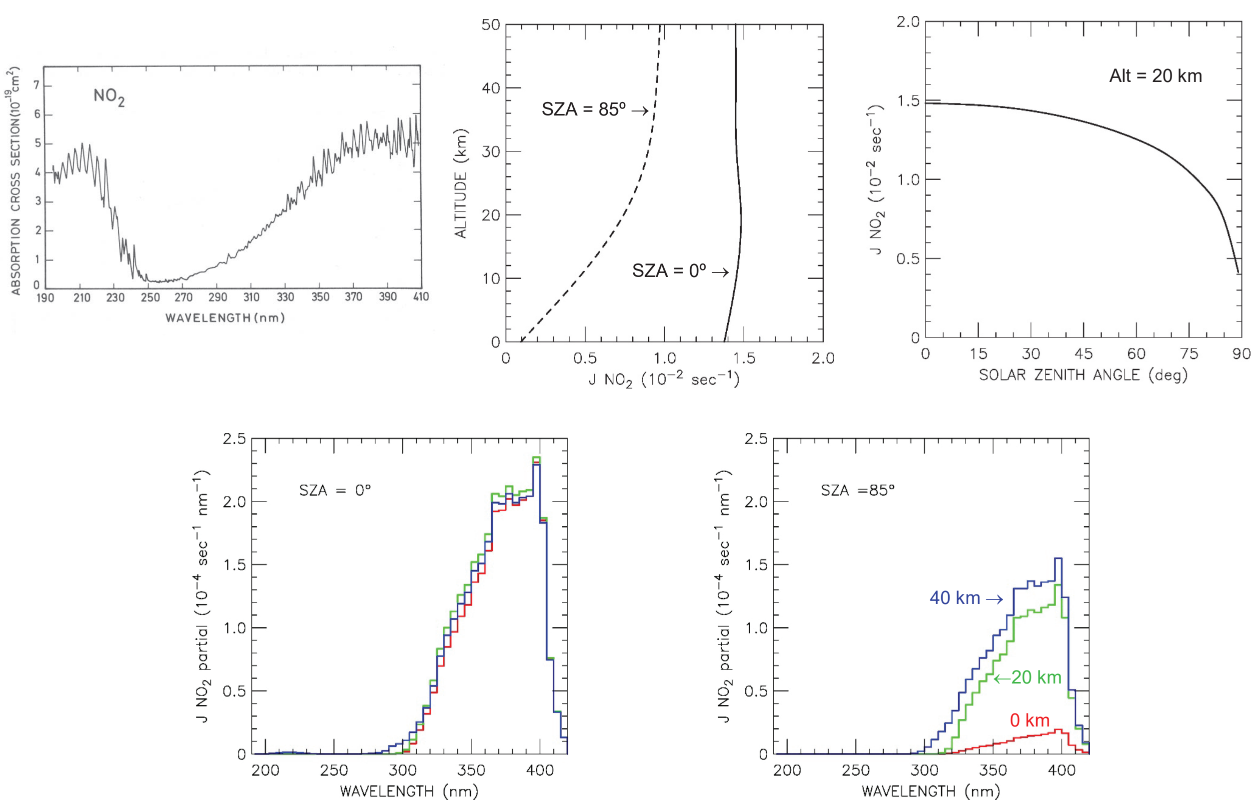
$$J_{gas}(z) = \int_{\lambda_{min}}^{\lambda_{max}} J_{gas}(z,\lambda)\, d\lambda$$

Units: s^{-1}

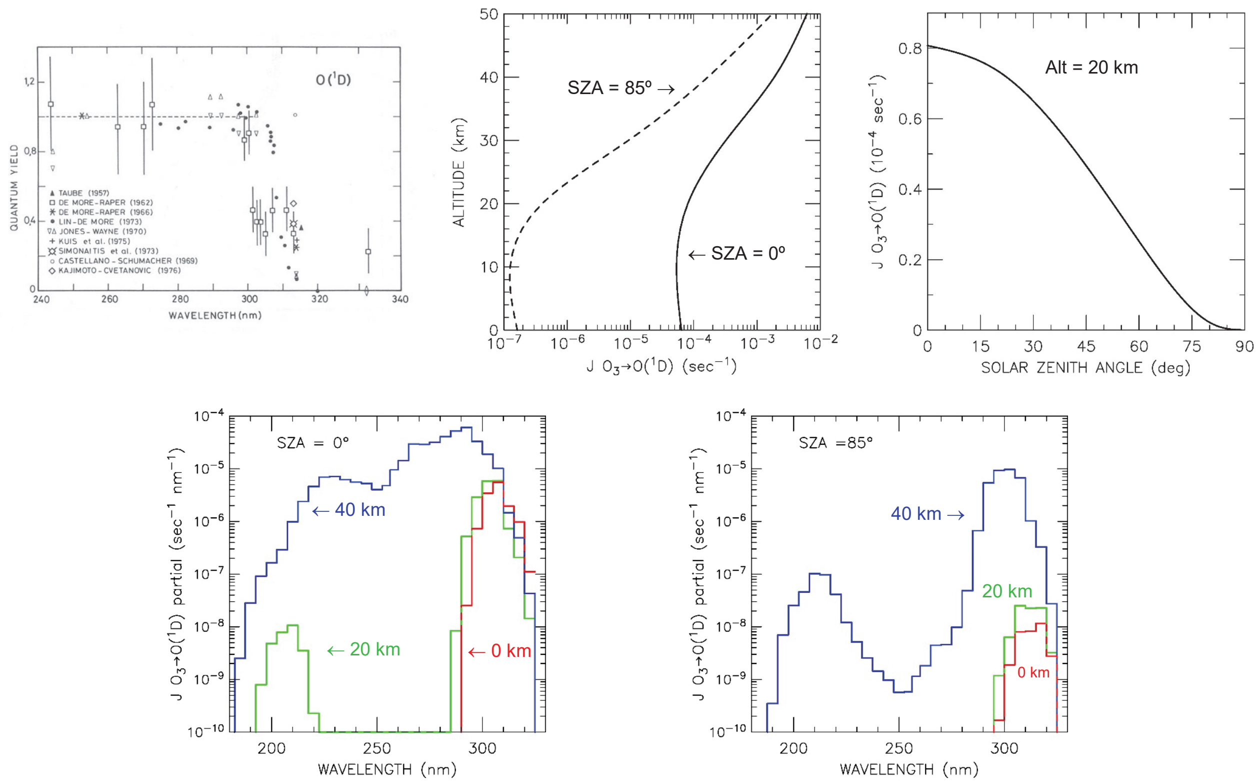
$$\text{Rate of Reaction} = \frac{dO_3}{dt} = J\ [O_3];\quad \text{Units of } J \text{ are } s^{-1}$$

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

8.9 kcal/mole | **–17.8 kcal/mole** | **35.1 kcal/mole** | **–57.8 kcal/mole**

$$OH + CH_4 \rightarrow CH_3 + H_2O$$

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:

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

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

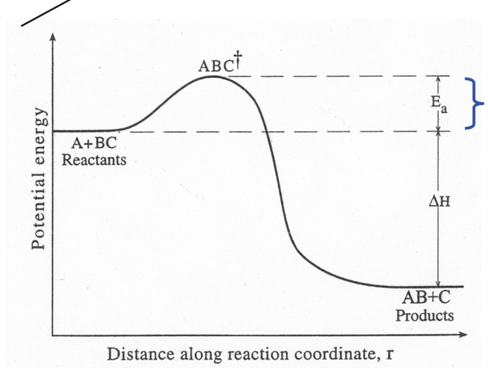


Figure 3.3 Barrier energies for the forward reaction (E_a) and the reverse reaction ($E_a + \Delta H$).

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

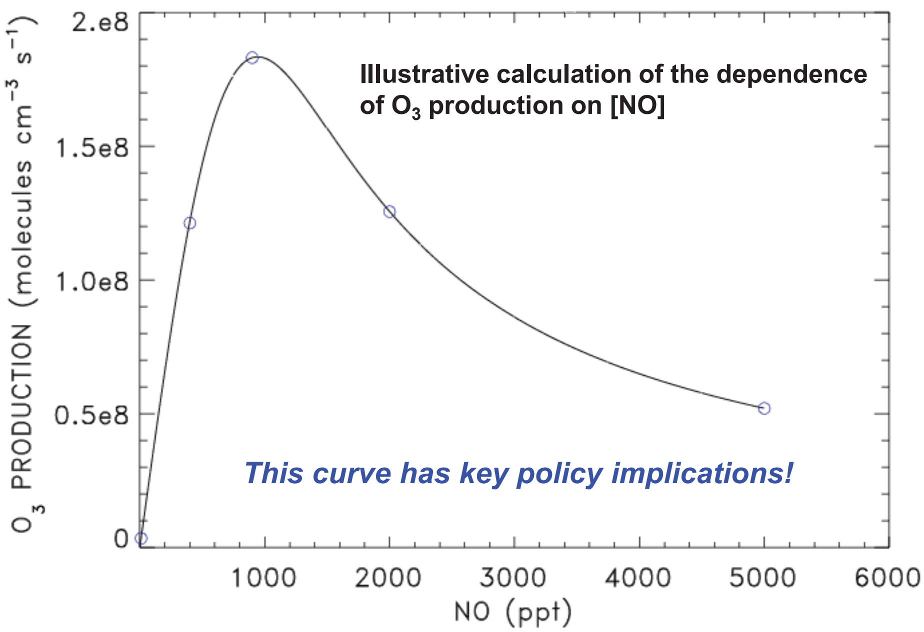
Tropospheric Ozone Production versus NO

Production of Tropospheric O_3 limited by: ___________ ?

As NO_x rises:

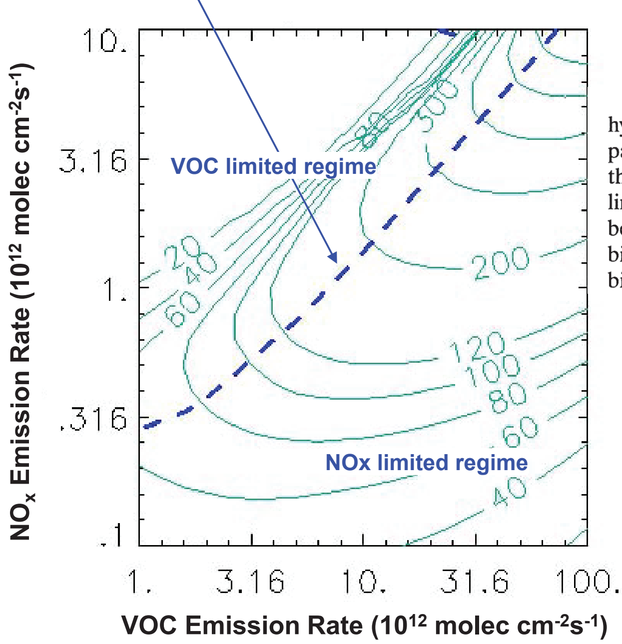
$[HO_2]$ falls faster than [NO] rises,

leading to a decrease in the value _____________



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

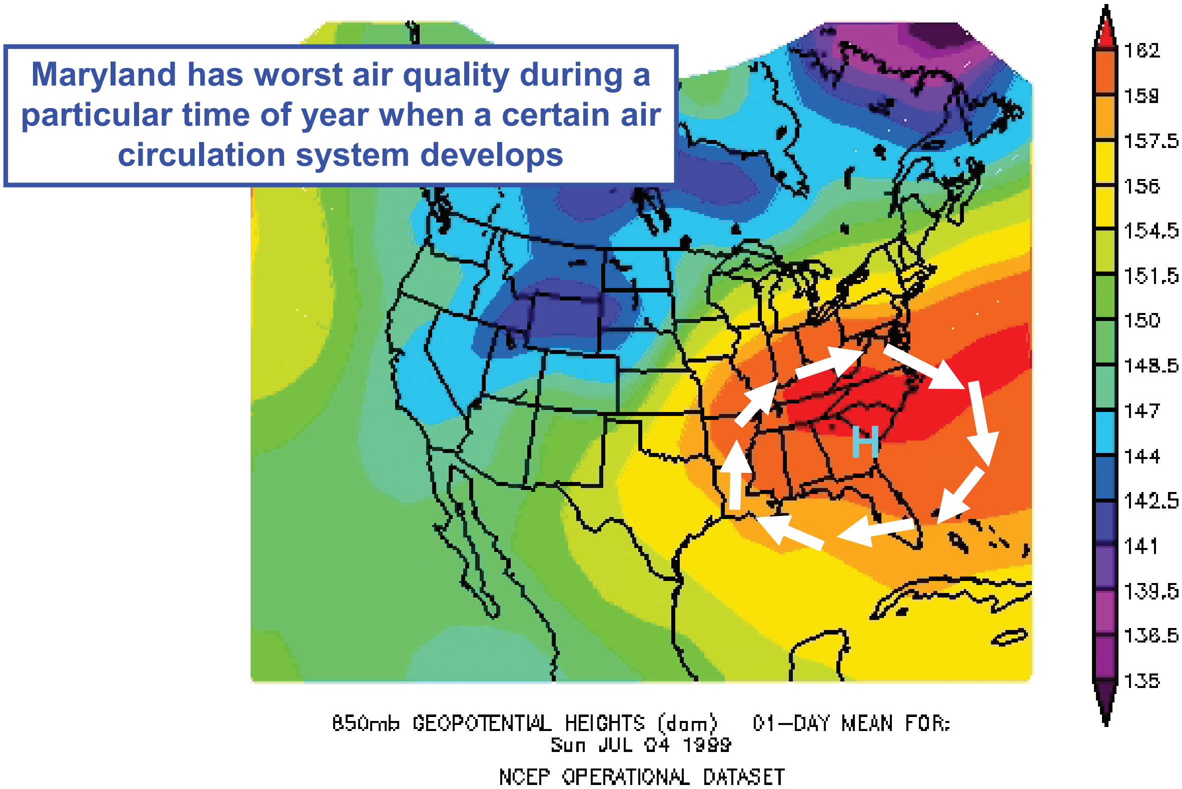


An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O_3 pollution may have been partly misdirected. Measurements and model calculations now show that O_3 production over most of the United States is primarily NO_x limited, not hydrocarbon limited. The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

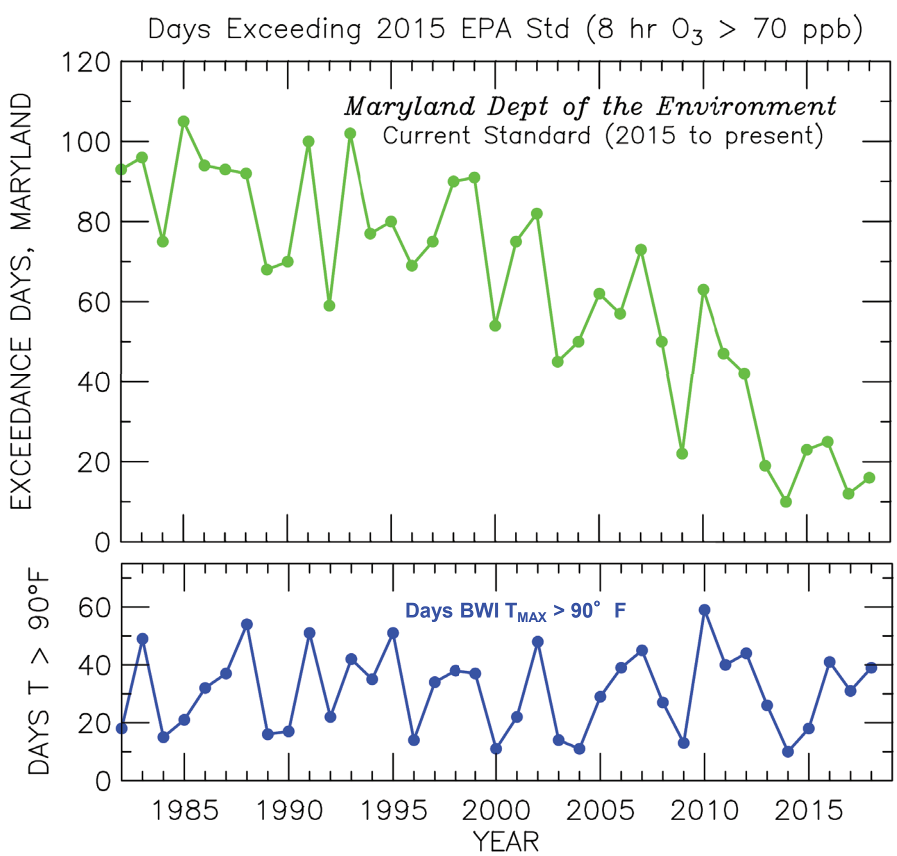
Figure: http://www-personal.umich.edu/~sillman/ozone.htm

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



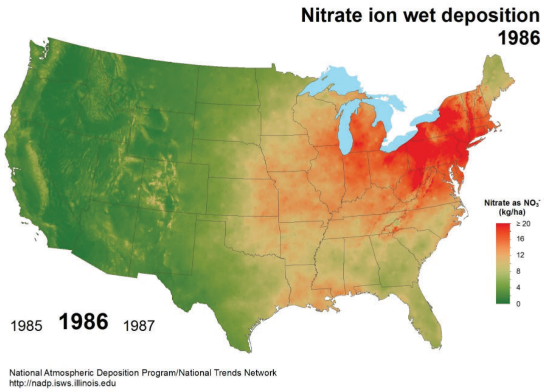
http://www.mde.state.md.us/assets/document/BJH%20-%20Basics%20on%20Ozone%20Transport.ppt

Dramatic Improvements Local Air Quality, Past 4 Decades

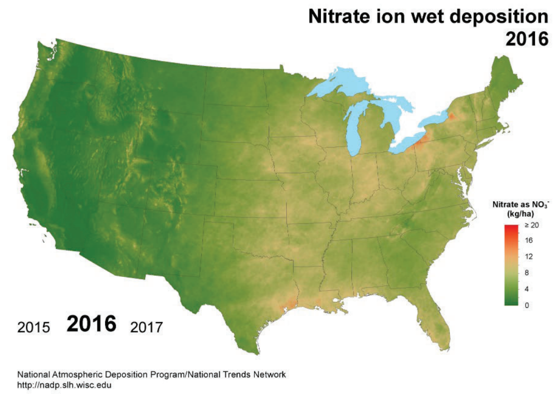


Nitrate Deposition

1986



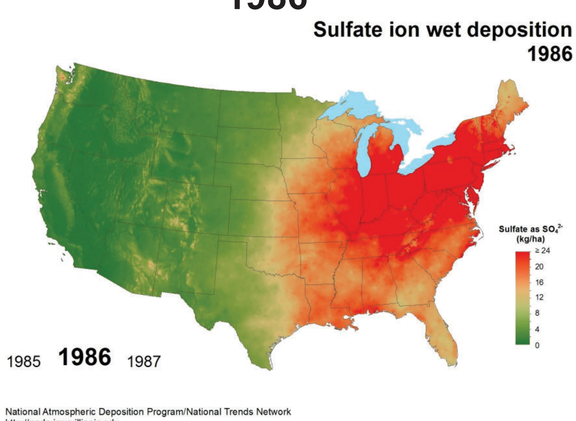
2016



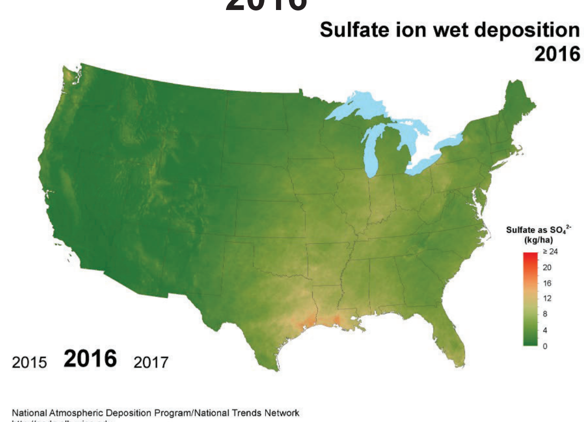
http://nadp.slh.wisc.edu/data/animaps.aspx

Sulfate Deposition

1986

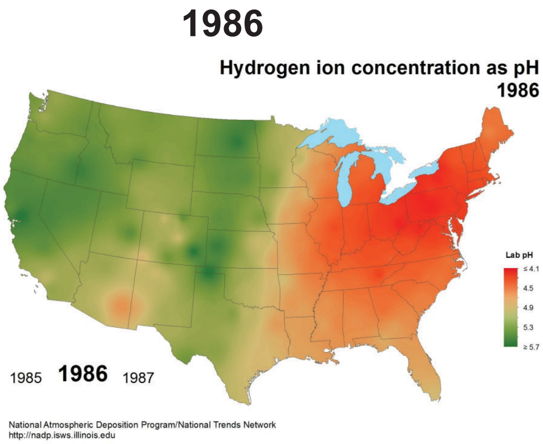


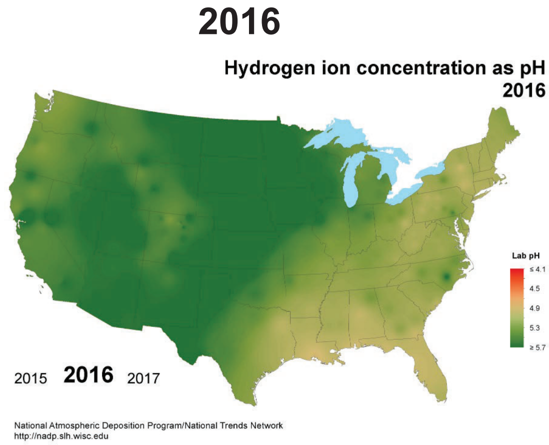
2016



http://nadp.slh.wisc.edu/data/animaps.aspx

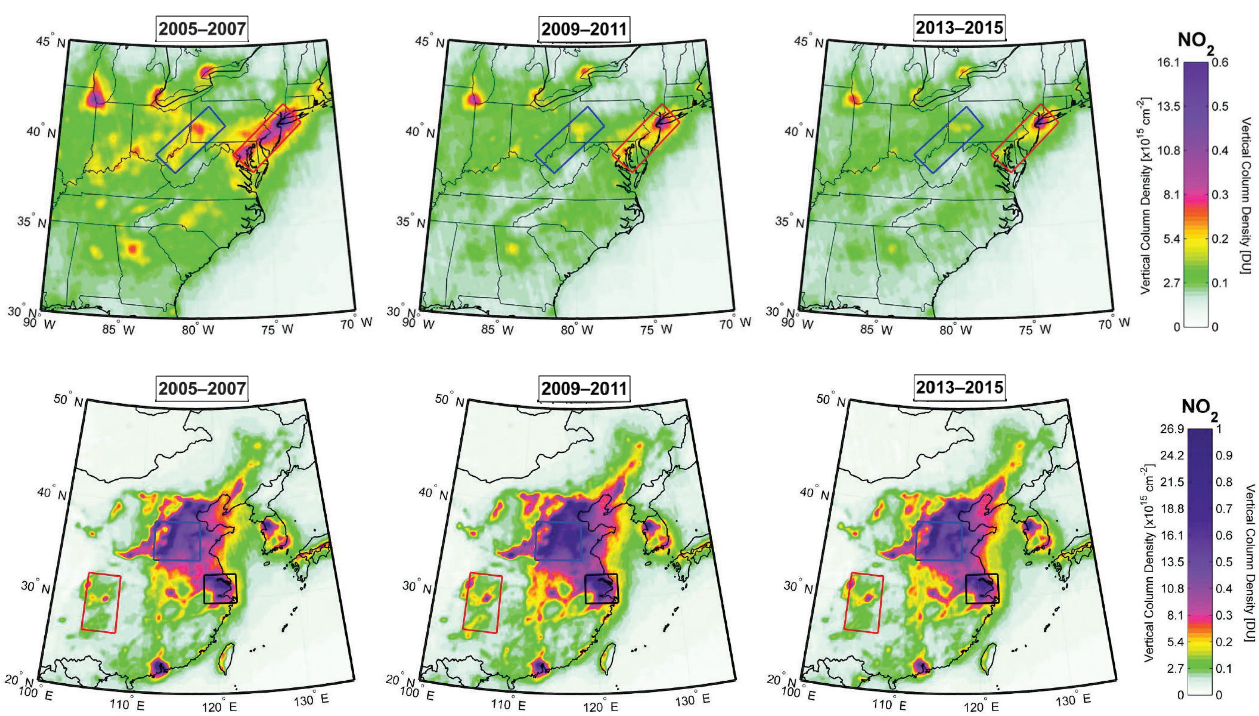
pH





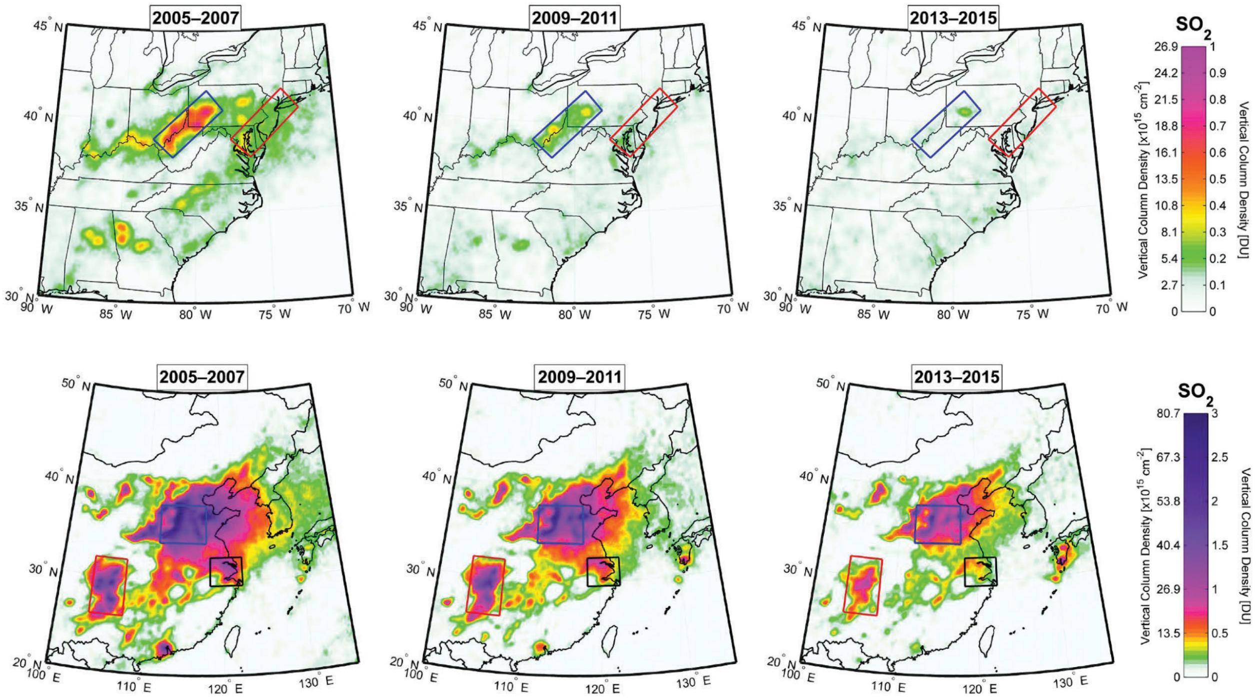
http://nadp.slh.wisc.edu/data/animaps.aspx

NO_2 Trends from Space



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

SO_2 Trends from Space



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

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 :

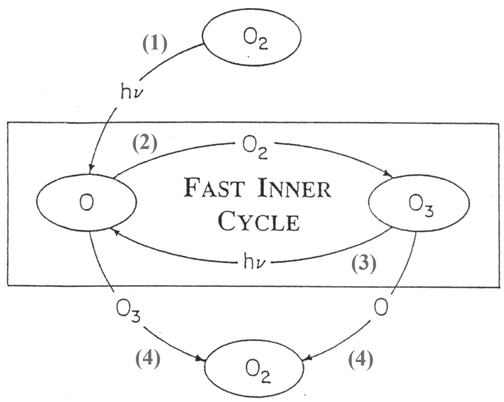
$$h\nu + O_3 \rightarrow O + O_2 \qquad (3)$$
$$O + O_3 \rightarrow O_2 + O_2 \qquad (4)$$

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)

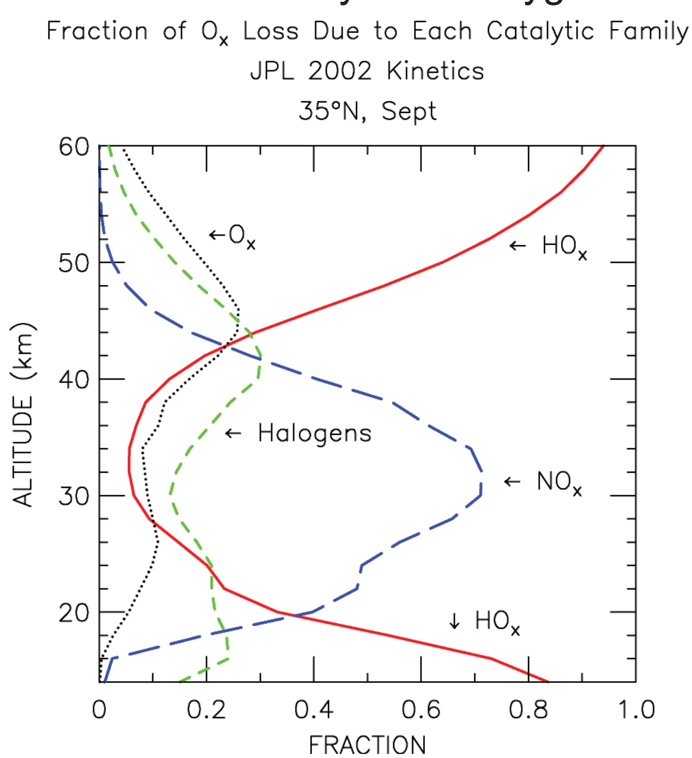
- The sum O + O_3 is commonly called *"odd oxygen"*



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:

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

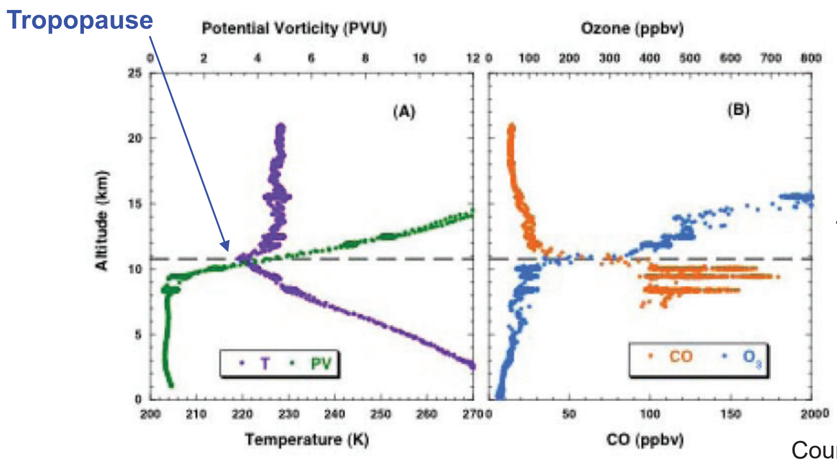
HO_2 loss:

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

Followed by:

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

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



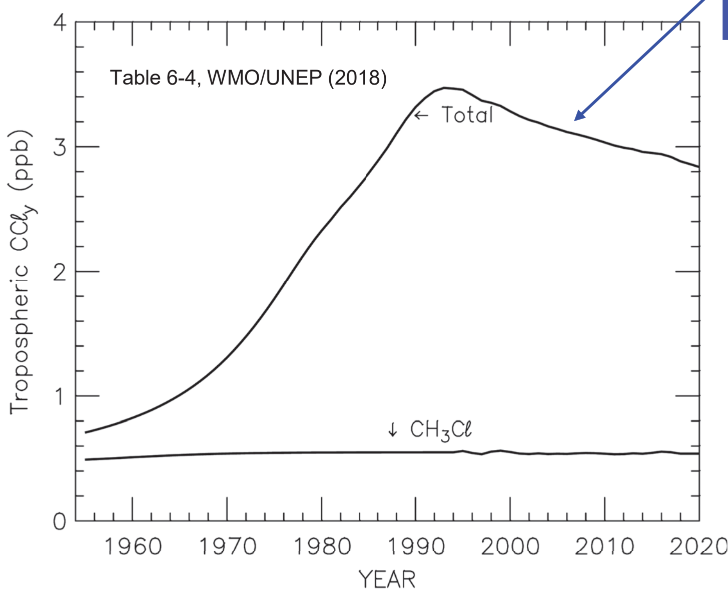
Above Tropopause:
Lots of O_3, little CO

Below Tropopause:
Lots of CO, little O_3

Courtesy of Laura Pan, NCAR

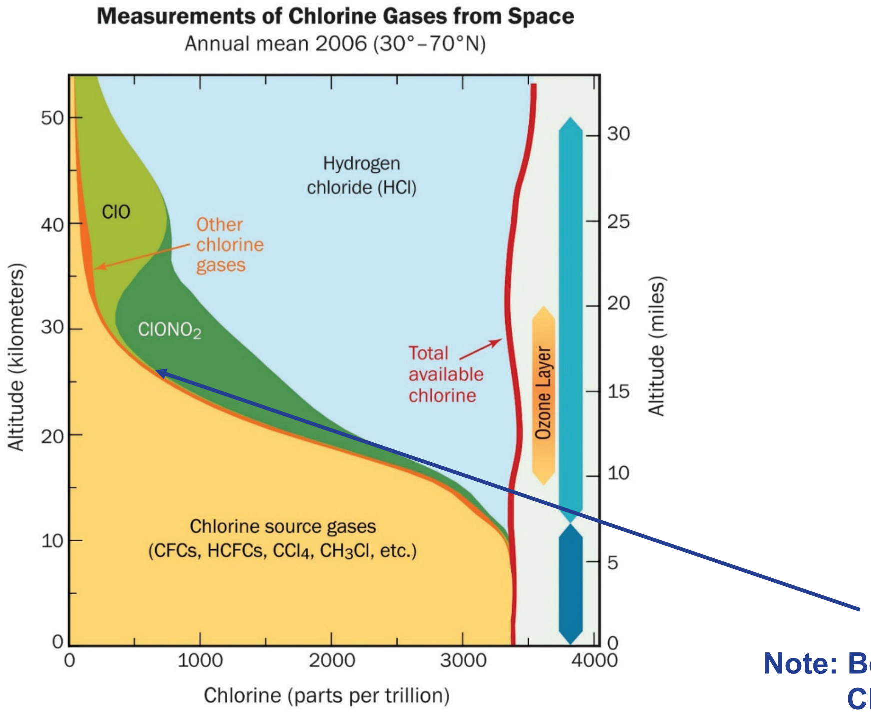
Tropospheric Chlorine Loading

Total Organic Chlorine (CCl_y):
- **Peaked at ~3.5 ppb around 1993**
- **Slowly declining**
- **Montreal Protocol and Amendments have banned production of CFCs**



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

Chlorine Abundance, Mid-Latitude Stratosphere



Note: Below ~30 km, ClO << $ClNO_3$ and HCl

Fig Q8-2, WMO 2014 QAs

Chlorine Source Gases

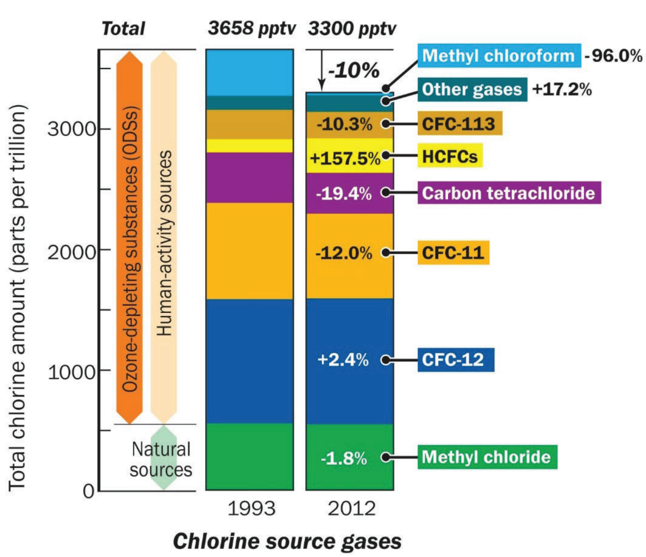
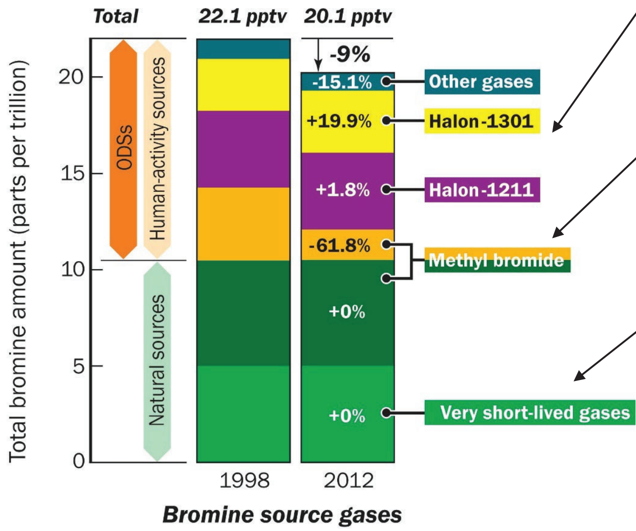


Fig Q7-1, WMO 2014 QAs

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[a]		
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

Bromine Source Gases



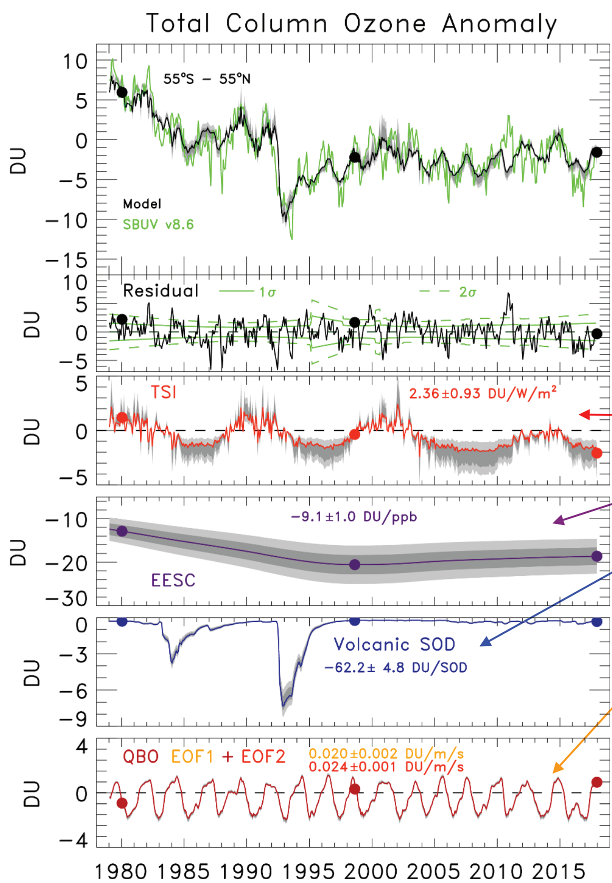
Halons:
- fire extinguishing agents
- production in developed world halted by Montreal Protocol
- present emissions primarily from "banks"

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

Fig Q7-1, WMO 2014 QAs

Ozone Depletion at Mid-Latitudes



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

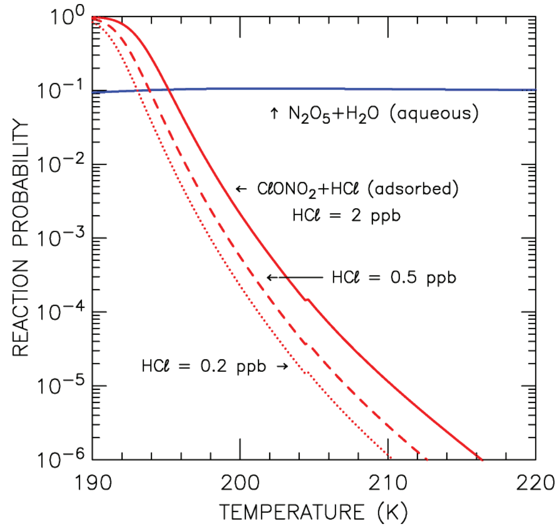
Column Ozone Anomaly (DU) =

$$2.36 \ \mathrm{DU / W\ m^{-2}} \times \mathrm{TSI} \ + $$
$$-9.1 \ \mathrm{DU / ppb} \times \mathrm{Halogens} \ + $$
$$-62.2 \ \mathrm{DU} \times \mathrm{SOD} \ + $$
$$0.022 \ \mathrm{DU / m\ s^{-1}} \times \mathrm{Wind\ Speed}$$

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

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

- <u>Cold Temperatures</u> → Polar Stratospheric Clouds (**<u>PSCs</u>**)
- Reactions on PSC surfaces lead to elevated **<u>ClO</u>**

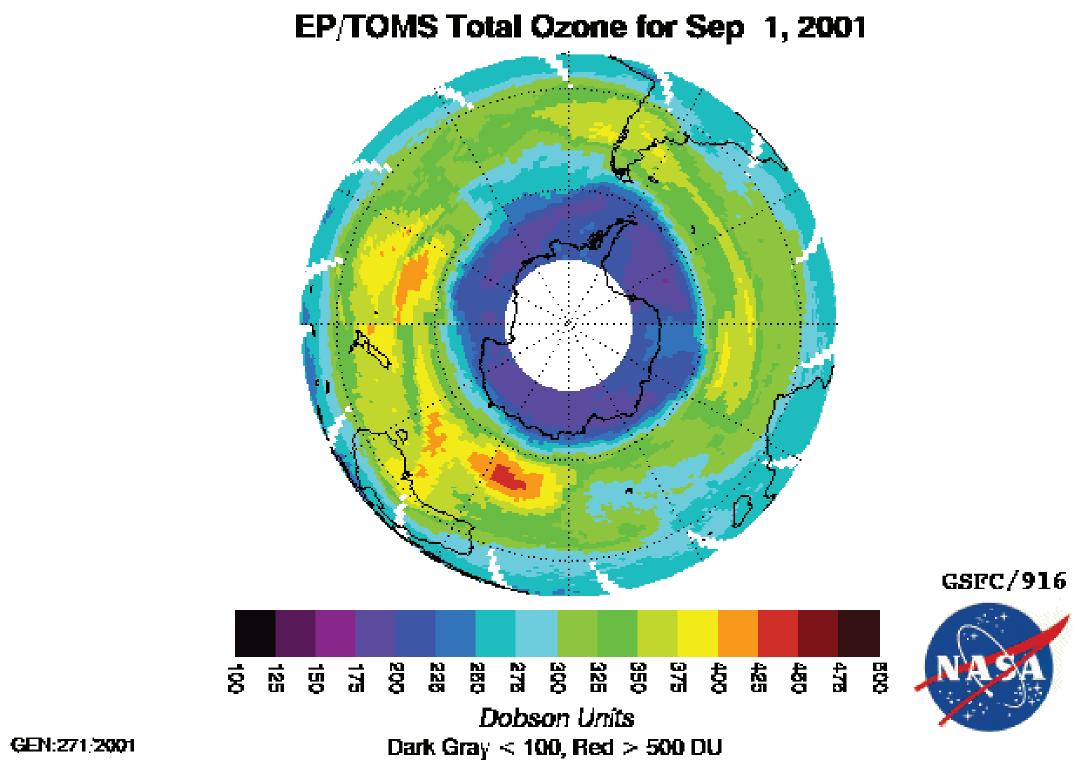
  HCl + $ClNO_3$ → Cl_2 (gas) + HNO_3 (solid)

  $ClNO_3$ + H_2O → HOCl + HNO_3

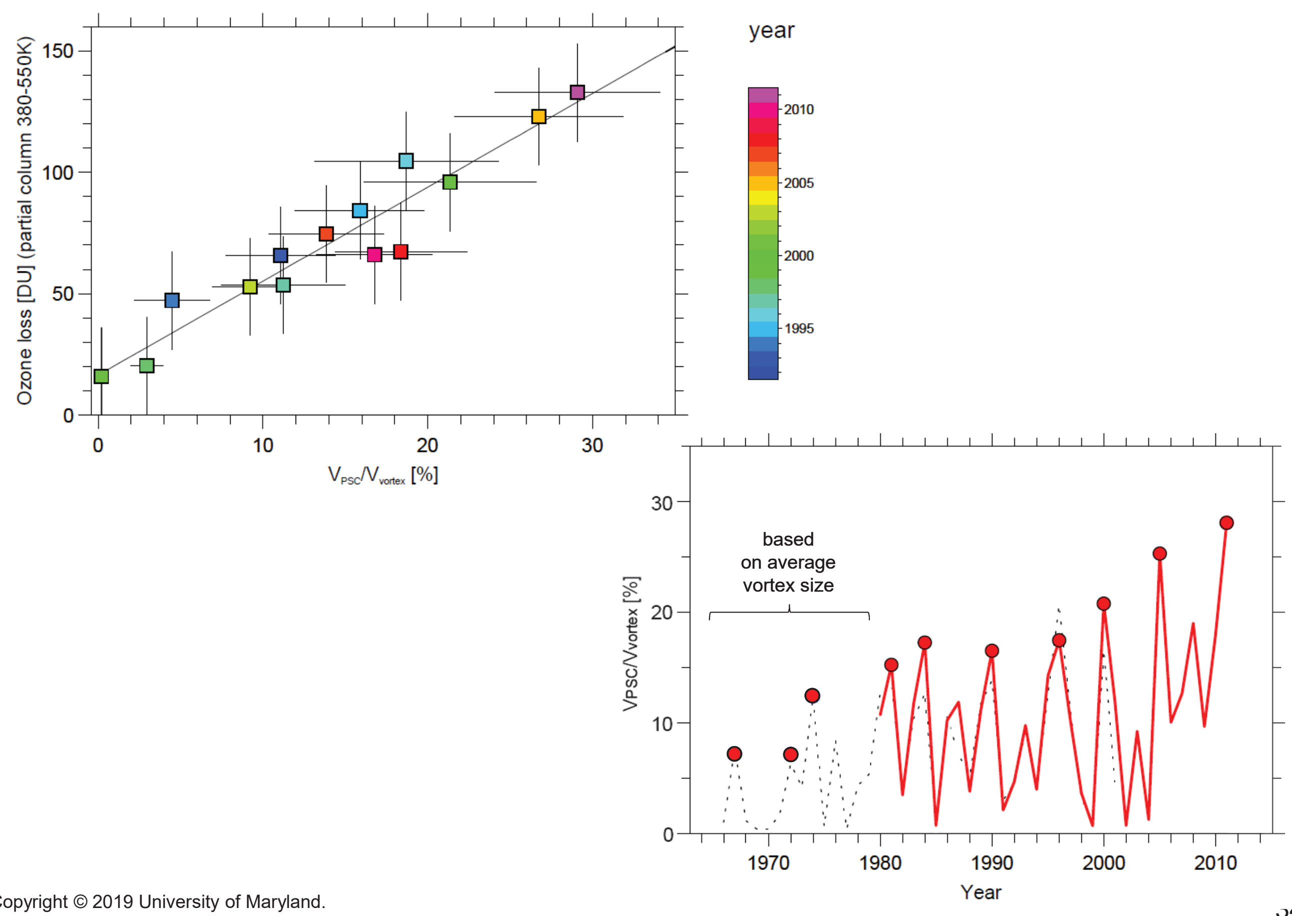
  Cl_2 + SUNLIGHT + O_3 → ClO

  HOCl + SUNLIGHT + O_3 → ClO

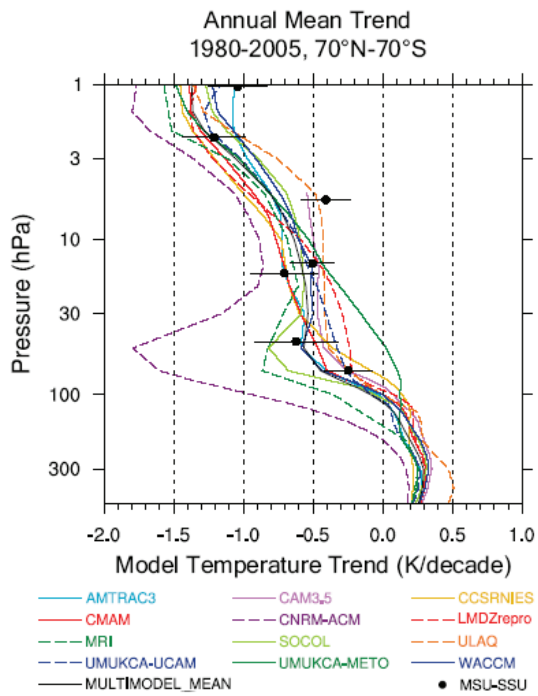
  HNO_3 SEDIMENTS (PSCs fall due to gravity)
- Elevated **ClO** + <u>Sunlight</u> destroys O_3
- BrO : Reaction Partner For ClO ⇒ Additional O_3 Loss



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)

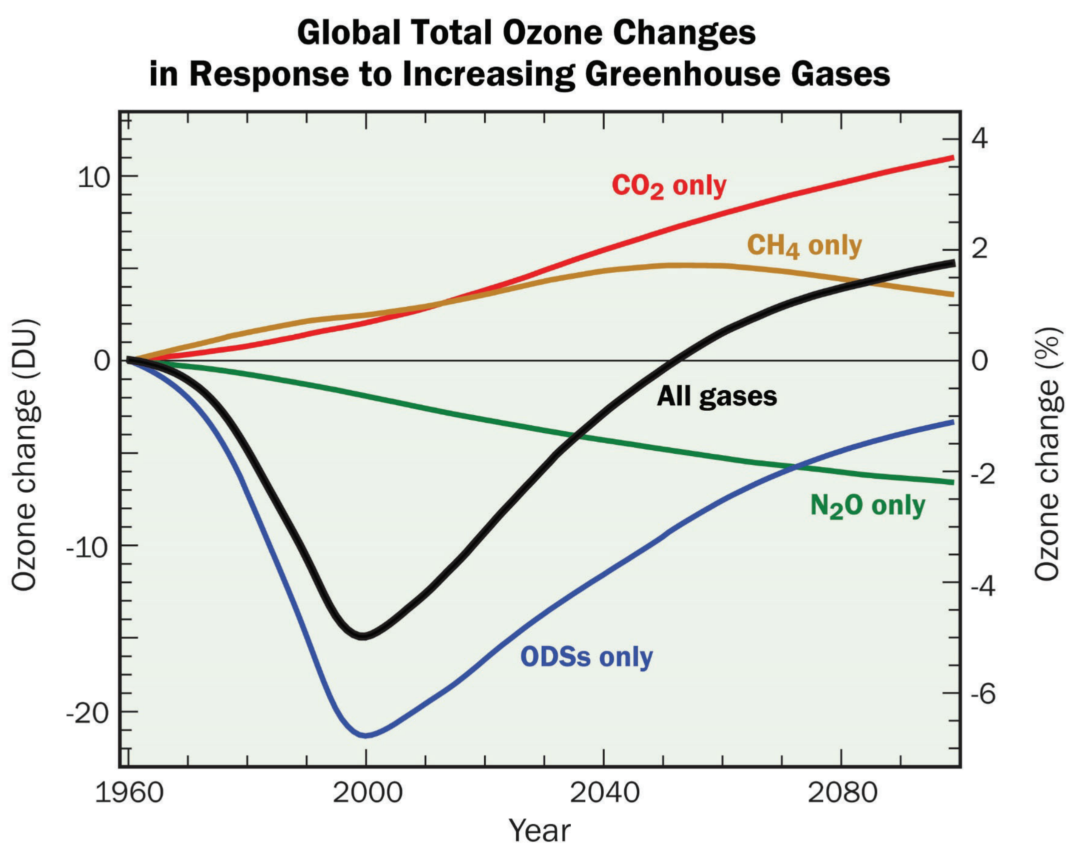
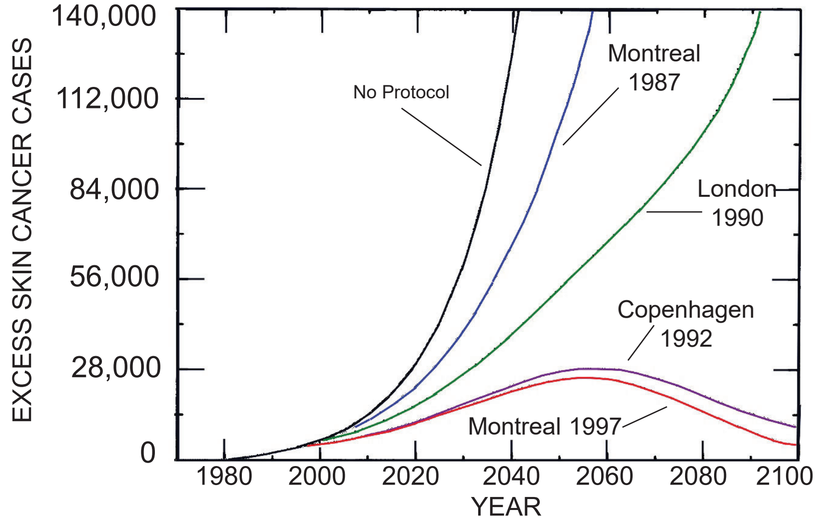


Fig Q20-3, WMO 2014 QAs

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, 16 April, 2:00 pm to 3:15 pm**
- **ATL 2416**
- **Closed book, no notes**

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

- **Conceptual questions only: <u>no calculator</u>**

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

- **Ross & Walt will be present:**
  please let us know if a question requires clarification

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