

# Review of Lectures 9 to 13

## AOSC 433/633 & CHEM 433/633

Ross Salawitch

Class Web Site: <http://www.atmos.umd.edu/~rjs/class/spr2013>

Today:

- Health affects: i.e., why it is that so much research is funded in this area
- Photolysis and kinetics
- One atmosphere, one chemistry
- Non-linearity of tropospheric ozone production
- Recent improvements in air quality and future challenges

26 March 2013

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## Relationship Between UV and Column Ozone

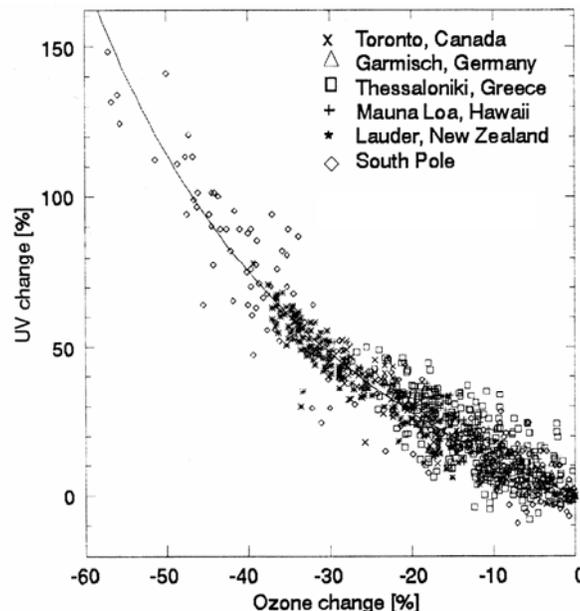


Fig. 2. Dependence of erythemal ultraviolet (UV) radiation at the Earth's surface on atmospheric ozone, measured on cloud-free days at various locations, at fixed solar zenith angles. Legend: South Pole [8]; Mauna Loa, Hawaii [9]; Lauder, New Zealand [10]; Thessaloniki, Greece (updated from Ref. [11]); Garmisch, Germany [12]; and Toronto, Canada (updated from Ref. [13]).

Madronich et al., *J. of Photochemistry and Photobiology B*, Vol. 46, 5–19, 1998.

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# Biological Effects of UV Radiation (Lecture 10)

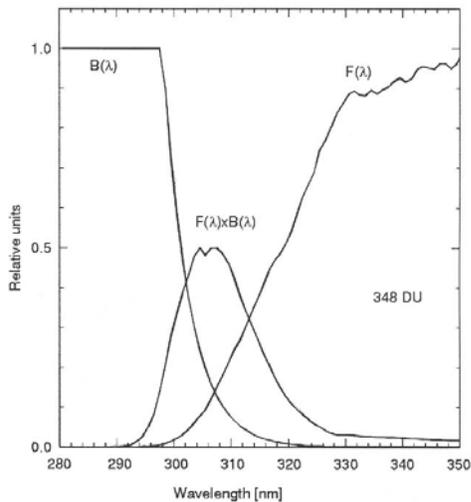


Fig. 1. Biologically active UV radiation. The overlap between the spectral irradiance  $F(\lambda)$  and the erythemal action spectrum  $B(\lambda)$  given by McKinlay and Diffey [6] shows the spectrum of biologically active radiation,  $F(\lambda)B(\lambda)$ . The area under the product function  $F(\lambda)B(\lambda)$  is the biologically active dose rate. For a total ozone column of 348 DU.

Humans are:

- strongly affected by exposure to UV-C radiation (100 to 280 nm)
- moderately affected by exposure to UV-B radiation (280 to 315 nm)
- weakly affected by exposure to UV-A radiation (315 to 400 nm)

⇐ From Mandronich et al., *J. Photochemistry and Photobiology*, vol. 46, pg. 5, 1998

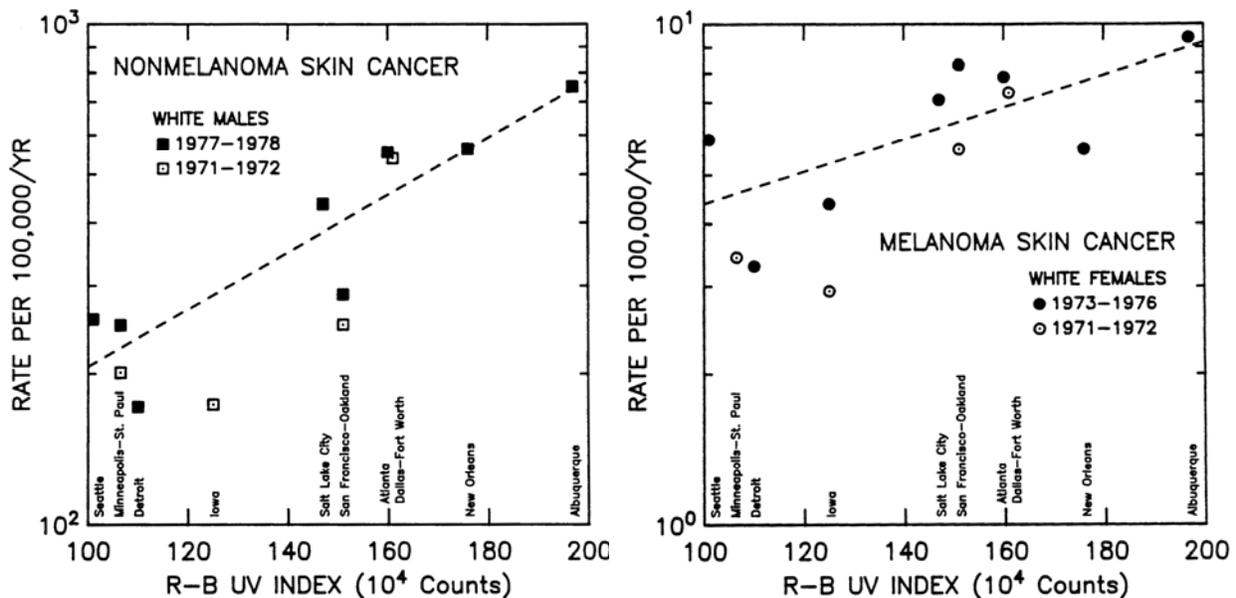
**The “biologically active dose rate” maximizes in the UV-B region at ~305 nm, where  $\sigma_{O_3} = 3 \times 10^{-19} \text{ cm}^2 \Rightarrow \tau(0 \text{ km}) = 2.4$  (for  $O_3$  column= 300 DU)**

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## Relationship Between Cancer and UV



Scotto and Fraumeni, *Cancer Epidemiology*, W. B. Saunders and Co, Philadelphia, 1982.

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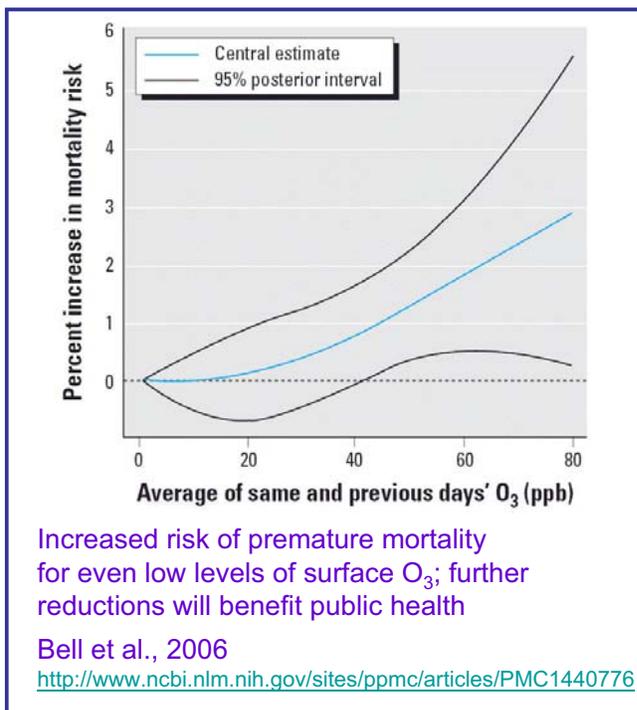
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# Air Quality Standards and Why We Care (Lecture 12)

Year	Averaging Period	EPA Surface Ozone Standard
1979	1 hr	125 ppb
1997	8 hr	85 ppb
2008	8 hr *	75 ppb
2013 #	???	???

\* The 8 hr standard is met when the 3-yr average of the annual 4<sup>th</sup> highest daily maximum 8 hr O<sub>3</sub> is less than 75 ppb.



# In 2011 Obama directed EPA to postpone revising surface O<sub>3</sub> standard so regulation would not interfere with economic recovery:  
<http://www.bloomberg.com/news/2011-09-02/obama-tells-epa-to-withdraw-ozone-air-quality-standards-hit-by-republicans.html>

On 6 March 2013, Obama nominated Gina McCarthy to be EPA administrator:  
<http://ehstoday.com/environment/obama-epa-nominee-gina-mccarthy-i-m-confident-she-s-going-do-outstanding-job-leading-epa>  
<http://www.washingtonpost.com/blogs/wonkblog/wp/2013/03/04/why-gina-mccarthy-for-epa-could-be-obamas-most-important-nominee>

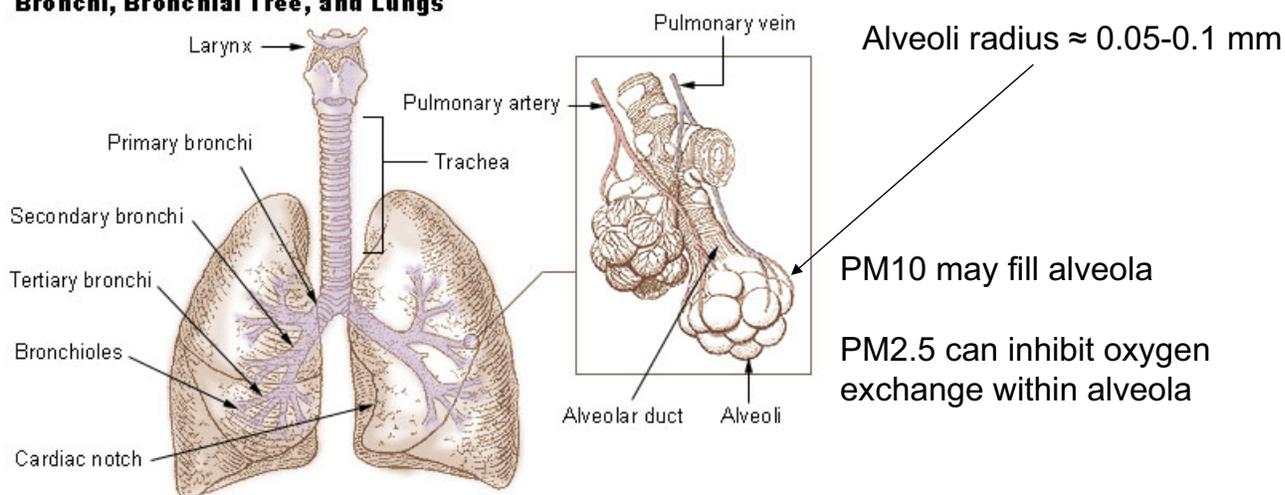
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## Health Effects of Aerosols (Lecture 13)

### Bronchi, Bronchial Tree, and Lungs



Leads to increase risk of respiratory illnesses, cardiopulmonary disease, ischemic heart disease, heart attack, etc.

This is without even considering chemical effects

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# Health Affects of Aerosols (Lecture 13)

## Long-term exposure to air pollution is associated with survival following acute coronary syndrome

Cathryn Tonne and Paul Wilkinson – Feb 19, 2013

**Table 4** Sensitivity of the PM<sub>2.5</sub> associations with mortality following admission for acute coronary syndrome

Hazard ratio (95% CI) per 10 µg/m <sup>3</sup> PM <sub>2.5</sub>	
Fully adjusted model	
Education in place of income	1.22 (1.06, 1.40)
Employment in place of income	1.20 (1.04, 1.38)
Income with random effect for hospital	1.17 (1.04, 1.33)
Income with time trend using 3 df	1.20 (1.04, 1.38)

**"We found that for every 10µg/m<sup>3</sup> increase in PM<sub>2.5</sub> there was a 20% increase in the death rate. For example, over one year of follow-up after patients had been admitted to hospital with ACS, there would be 20% more deaths among patients exposed to PM<sub>2.5</sub> levels of 20 µg/m<sup>3</sup>, compared to patients exposed to PM<sub>2.5</sub> levels of 10µg/m<sup>3</sup>."**

<http://eurheartj.oxfordjournals.org/content/early/2013/02/18/eurheartj.ehs480.full>

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# Health Affects of Surface Ozone and Aerosols

**Table 3.** Relative Risk of Death Attributable to a 10-ppb Change in the Ambient Ozone Concentration.\*

Cause of Death	Single-Pollutant Model†			Two-Pollutant Model‡	
	Ozone (96 MSAs)	Ozone (86 MSAs)	PM <sub>2.5</sub> (86 MSAs)	Ozone (86 MSAs)	PM <sub>2.5</sub> (86 MSAs)
	<i>relative risk (95% CI)</i>				
Any cause	1.001 (0.996–1.007)	1.001 (0.996–1.007)	1.048 (1.024–1.071)	0.989 (0.981–0.996)	1.080 (1.048–1.113)
Cardiopulmonary	1.014 (1.007–1.022)	1.016 (1.008–1.024)	1.129 (1.094–1.071)	0.992 (0.982–1.003)	1.153 (1.104–1.204)
Respiratory	1.029 (1.010–1.048)	1.027 (1.007–1.046)	1.031 (0.955–1.113)	1.040 (1.013–1.067)	0.927 (0.836–1.029)
Cardiovascular	1.011 (1.003–1.023)	1.014 (1.005–1.023)	1.150 (1.111–1.191)	0.983 (0.971–0.994)	1.206 (1.150–1.264)
Ischemic heart disease	1.015 (1.003–1.026)	1.017 (1.006–1.029)	1.211 (1.156–1.268)	0.973 (0.958–0.988)	1.306 (1.226–1.390)

\* MSA denotes metropolitan statistical area, and PM<sub>2.5</sub> fine particulate matter consisting of particles that are 2.5 µm or less in aerodynamic diameter. Ozone concentrations were measured from April to September during the years from 1977 to 2000, with follow-up from 1982 to 2000;

There is biologic plausibility for a respiratory effect of ozone. In laboratory studies, ozone can increase airway inflammation<sup>24</sup> and can worsen pulmonary function and gas exchange.<sup>25</sup> In addition, exposure to elevated concentrations of tropospheric ozone has been associated with numerous adverse health effects, including the induction<sup>26</sup> and exacerbation<sup>27,28</sup> of asthma, pulmonary dysfunction,<sup>29,30</sup> and hospitalization for respiratory causes.<sup>31</sup>

In our two-pollutant models, the adjusted estimates of relative risk for the effect of ozone on the risk of death from cardiovascular causes were significantly less than 1.0, seemingly suggesting a protective effect. Such a beneficial influence of ozone, however, is unlikely from a biologic standpoint.

In summary, we investigated the effect of tropospheric ozone on the risk of death from any cause and cause-specific death in a large cohort, using data from 96 metropolitan statistical areas across the United States and controlling for the effect of particulate air pollutants. We were unable to detect a significant effect of exposure to ozone on the risk of death from cardiovascular causes when particulates were taken into account, but we did demonstrate a significant effect of exposure to ozone on the risk of death from respiratory causes.

Jerrett et al., 2009

<http://www.nejm.org/doi/full/10.1056/nejmoa0803894>

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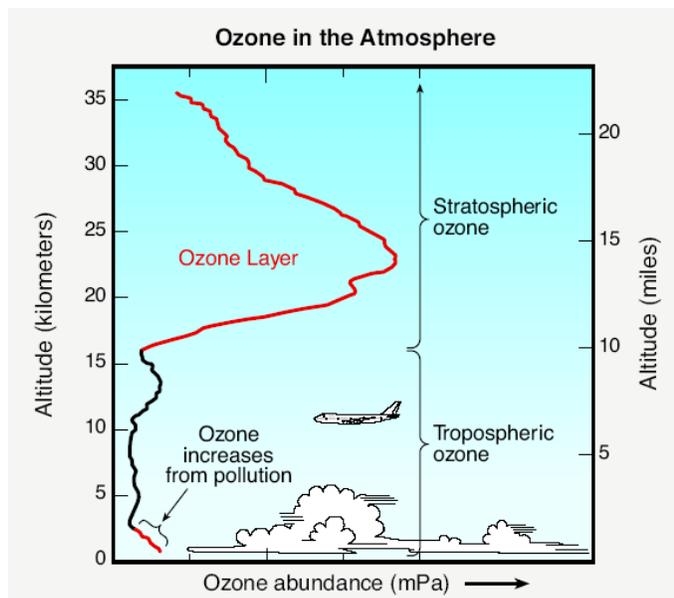
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# Typical Ozone Profile (Reading, Lecture 2)

## Ozone column:

$$\int_{z_1}^{z_2} [\text{O}_3(z)] dz$$



**Figure Q1-2.** Ozone in the atmosphere. Ozone is present throughout the troposphere and stratosphere... Increases in ozone occur near the surface as a result of pollution from human activities.

WMO/UNEP 2010 Ozone Twenty Questions

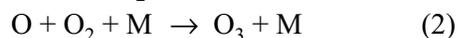
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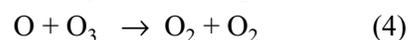
9

## Chapman Chemistry (Lecture 9)

- Production of *stratospheric*  $\text{O}_3$  initiated when  $\text{O}_2$  is photo-dissociated by UV sunlight
- $\text{O}_3$  formed when resulting O atom reacts with  $\text{O}_2$  :



- $\text{O}_3$  removed by photo-dissociation (UV sunlight) or by reaction with O :



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

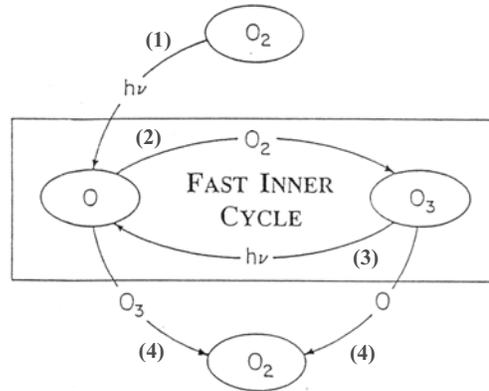
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## Chapman Chemistry (Lecture 9)

- The cycling between O and O<sub>2</sub> (rxns 2 and 3) occurs *much* more rapidly than leakage into (rxn 1) or out of the system (rxn 4)
- The sum O + O<sub>3</sub> 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

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## Chapman Chemistry (Lecture 9)

$$[\text{O}_3] = \left( \frac{J_1 k_2}{J_3 k_4} \right)^{1/2} f_{\text{O}_2} [\text{M}]^{3/2}$$

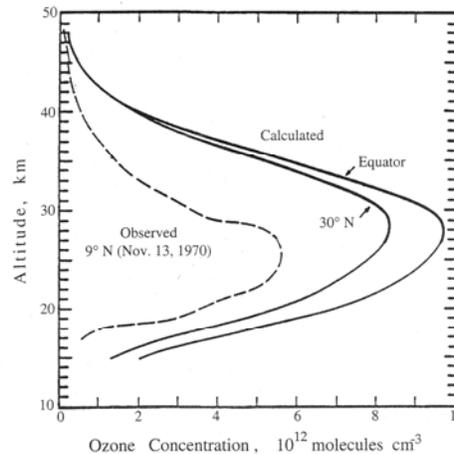


FIGURE 4.6 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970.

[O<sub>3</sub>] falls off with increasing altitude (high in stratosphere), at a rate determined by [M]<sup>3/2</sup>, because:

[O<sub>3</sub>] falls off with decreasing altitude (low in stratosphere) due to a rapid drop in J<sub>1</sub>, reflecting:

Observed [O<sub>3</sub>] < Chapman [O<sub>3</sub>]: why ???

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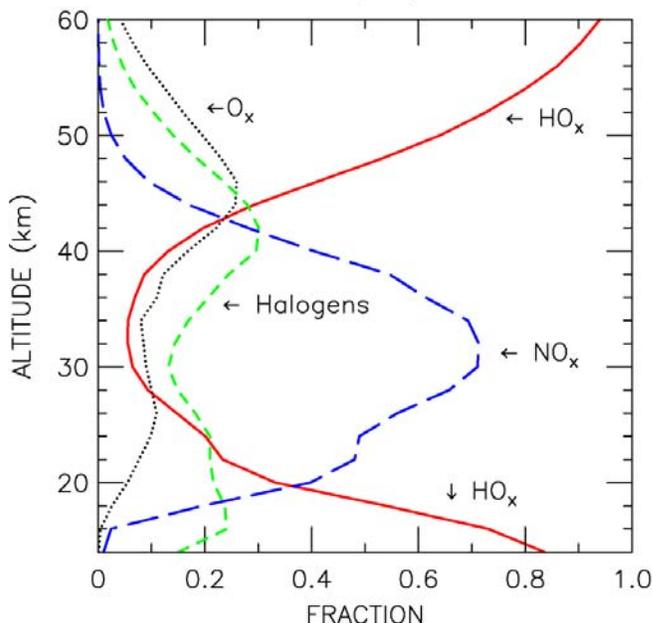
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# Stratospheric Photochemistry: Odd Oxygen Loss By Families (Lecture 9)

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.

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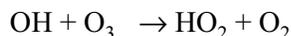
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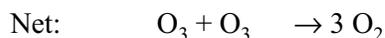
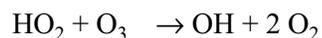
## One Atmosphere – One Photochemistry (Lecture 9)

### Stratosphere

HO<sub>2</sub> formation:

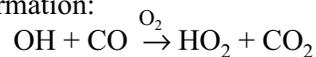


HO<sub>2</sub> loss:

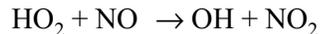


### Troposphere

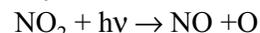
HO<sub>2</sub> formation:



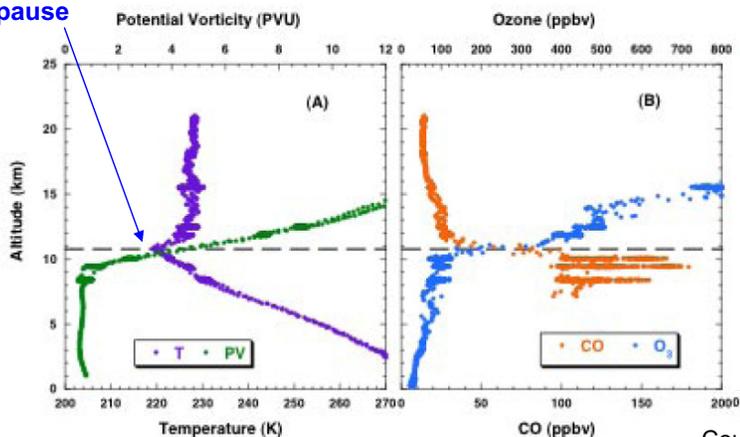
HO<sub>2</sub> loss:



Followed by:



Tropopause



Above Tropopause:  
Lots of O<sub>3</sub>, little CO

Below Tropopause:  
Lots of CO, little O<sub>3</sub>

Courtesy of Laura Pan, NCAR

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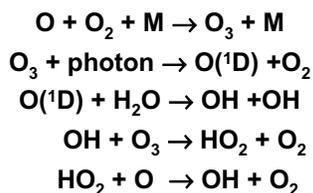
## Importance of Radicals (Lectures 9 & 10)

- 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

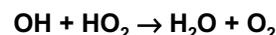
### Initiation



### Propagation



### Termination



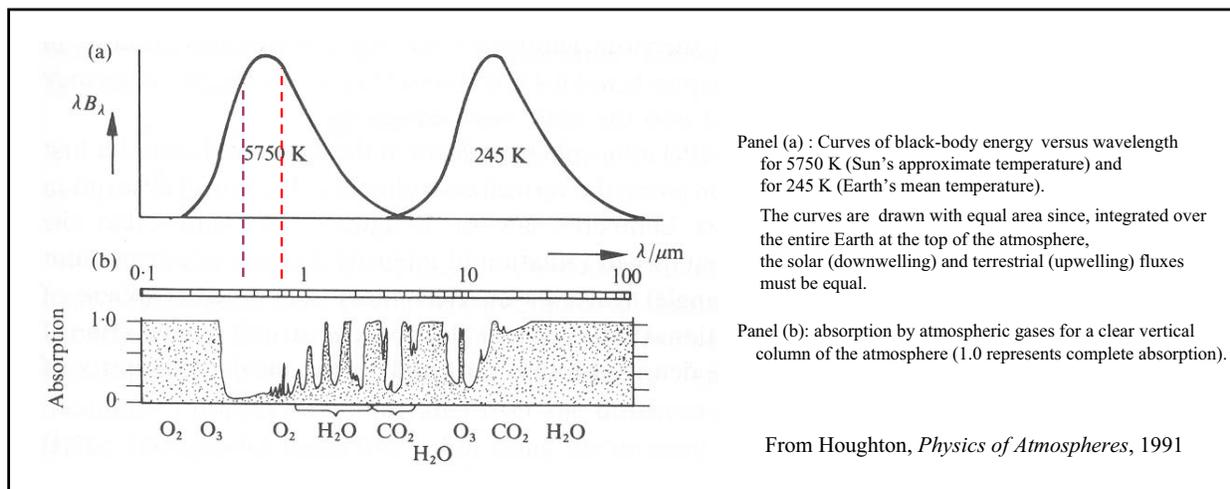
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## Atmospheric Radiation (Lecture 10)

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



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

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## Beer-Lambert Law (Lecture 10)

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

where:

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

$F$  : solar irradiance (photons/cm<sup>2</sup>/sec)

$\sigma_{\lambda}$  : absorption cross section

$C$  : concentration of absorbing gas (molecules/cm<sup>3</sup>)

$m$  : ratio of slant path to vertical path, equal to  $1/\cos(\theta)$  for  $\theta < \sim 75^\circ$

$\theta$  : solar zenith angle

Governs basics of radiative transfer in the UV and near IR regions

## Photolysis Frequency (Lecture 10)

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:

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

Units: s<sup>-1</sup> nm<sup>-1</sup>

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

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

Units: s<sup>-1</sup>

$$\text{Rate of Reaction} = \frac{d\text{O}_3}{dt} = J [\text{O}_3]; \quad \text{Units of } J \text{ are s}^{-1}$$

*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.*

# Solar Spectral Actinic Flux (Lecture 10)

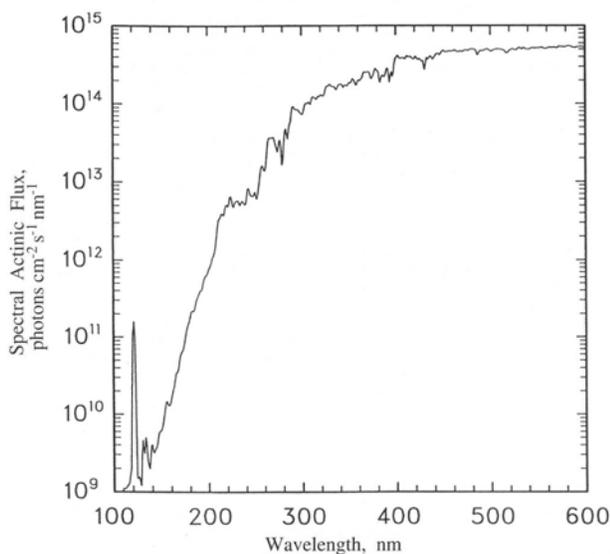


FIGURE 6. Solar spectral actinic flux (photons  $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ ) at the top of Earth's atmosphere.

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

130 ATMOSPHERIC PHOTOCHEMISTRY AND CHEMICAL KINETICS

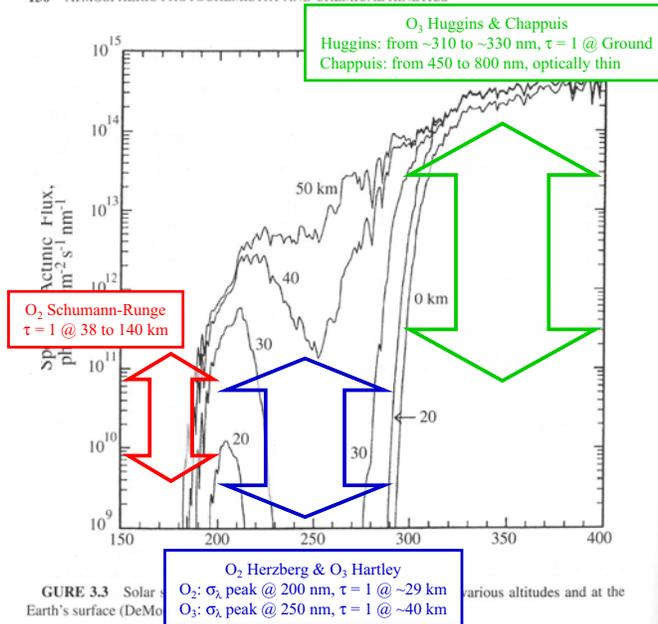


FIGURE 3.3 Solar actinic flux at various altitudes and at the Earth's surface (DeMore et al., 1994).

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

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## Admission Ticket Lecture 11

**Gibbs Free energy involves both enthalpy and entropy. Briefly describe the relative roles of the change in enthalpy and entropy in affecting the rate of a chemical reaction.**

**Under what conditions will each term tend to dominate the rate of a chemical reaction.**

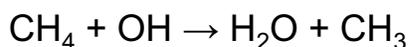
**Briefly: why is kinetic information needed, in addition to thermodynamic information, to quantify our understanding of atmospheric chemistry?**

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## CH<sub>4</sub> is lost by reaction with OH (Lecture 6)



$$\frac{d\text{CH}_4}{dt} = \text{Production} - \text{Loss} = \text{Production} - k[\text{OH}][\text{CH}_4]$$

Arrhenius Expression for rate constant:

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

$$\text{Lifetime of CH}_4 = \frac{\text{Abundance}}{\text{Loss}} = \frac{[\text{CH}_4]}{k[\text{OH}][\text{CH}_4]} = \frac{1}{k[\text{OH}]}$$

Commonly T = 272 K and **[OH] = 1 × 10<sup>6</sup> molec cm<sup>-3</sup>** are used (see Box 1-3 of

[http://www.unep.ch/ozone/Assessment\\_Panels/SAP/Scientific\\_Assessment\\_2010/03-Chapter\\_1.pdf](http://www.unep.ch/ozone/Assessment_Panels/SAP/Scientific_Assessment_2010/03-Chapter_1.pdf))

yielding :

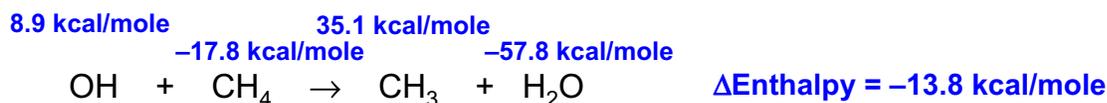
$$\begin{aligned} \text{Lifetime of CH}_4 &= \frac{1}{3.59 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \cdot 1 \times 10^6 \text{ molecules cm}^{-3}} = \\ &= \frac{1}{3.59 \times 10^{-9} \text{ s}^{-1}} = 8.9 \text{ yr} \end{aligned}$$

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## Bimolecular Gas Phase Reactions



$$\text{Rate of Reaction} = \frac{d\text{CH}_4}{dt} = k[\text{OH}][\text{CH}_4]$$

**Exothermic !**

Arrhenius Expression for rate constant:

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

**A factor** →

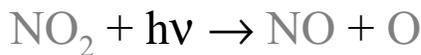
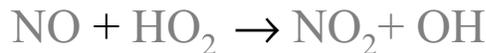
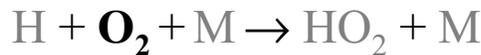
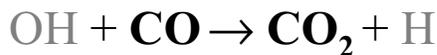
**E<sub>A</sub> / R** ⇒ Activation Energy / Gas Constant

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## Tropospheric Ozone Production (Lecture 12)



**NO & NO<sub>2</sub>: Emitted by fossil fuel combustion & biomass burning**



**CO: Emitted by fossil fuel combustion & biomass burning**

**Complete combustion:**



**Extreme, incomplete combustion:**



**OH & HO<sub>2</sub>: ???**

## Tropospheric Ozone Production (Lecture 12)

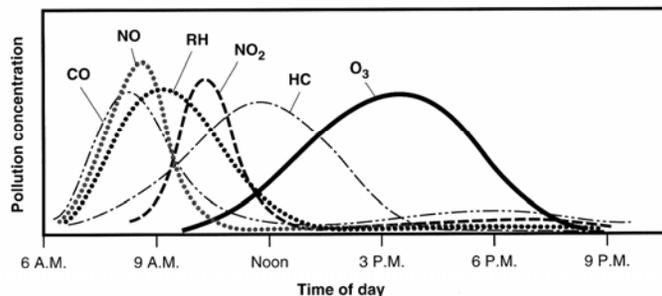
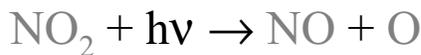
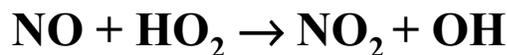
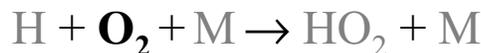
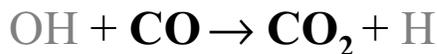
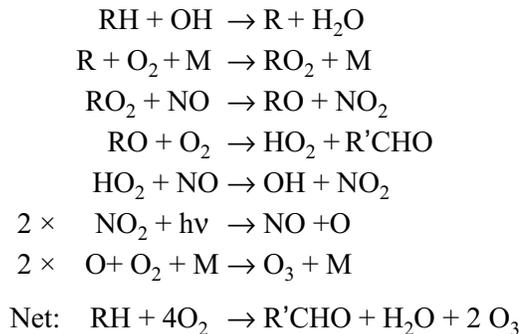
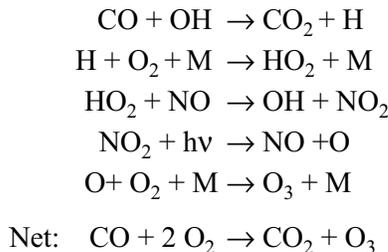


Figure 6.10 The time evolution of the principal chemical components of photochemical smog: carbon monoxide (CO), reactive hydrocarbons (RH), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), hydrocarbon by-products (HC), and ozone (O<sub>3</sub>). This behavior of the pollutants is observed during a day in a smoggy city. The sequential appearance of the pollutants is related to the timing of the emissions and rates at which CO, NO, and reactive hydrocarbons are transformed into secondary pollutants by photochemical reactions, as explained in the text.

# Tropospheric Ozone Production (Lecture 12)



## Chain Mechanism for production of ozone

**Chemical Initiation: Human emission of NO, CO and either human (RO<sub>2</sub>) or natural (HO<sub>2</sub>) hydrogen radicals**

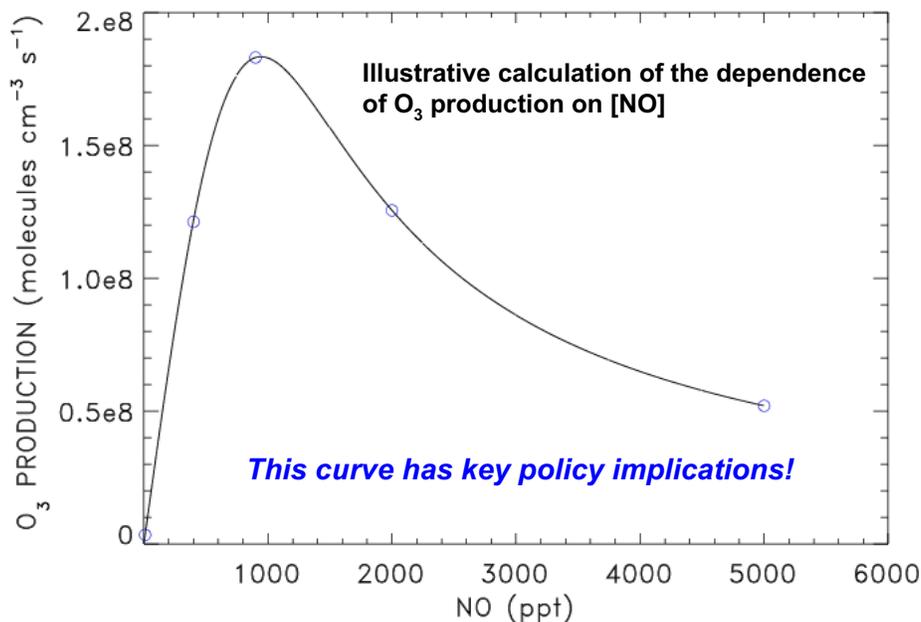
**Ozone production:  $k[\text{HO}_2][\text{NO}]$**

**Termination: refers to “loss of radicals” in the chain mechanism**

# Tropospheric Ozone Production versus NO (Lecture 12)

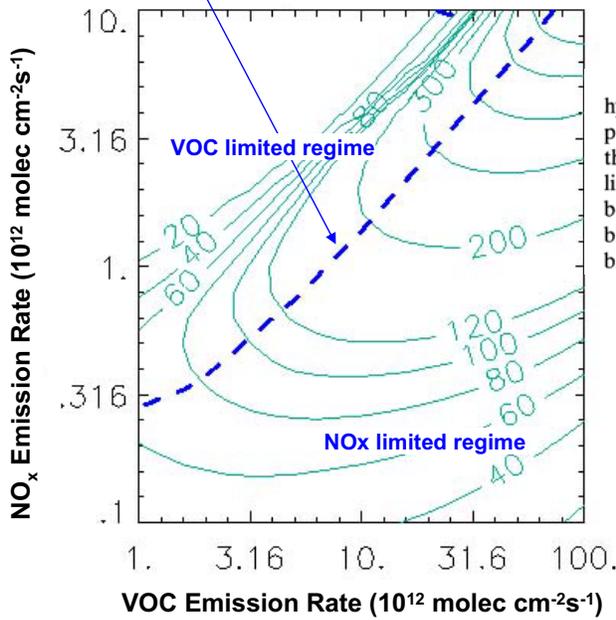
**As NO<sub>x</sub> rises:**

**[HO<sub>2</sub>] falls faster than [NO] rises, leading to a decrease in the value of the product of  $k [\text{HO}_2] [\text{NO}]$ , and hence the production rate of O<sub>3</sub>.**



# Tropospheric Ozone Production versus NO<sub>x</sub> and VOCs (Lecture 12)

Ridge: local maximum for O<sub>3</sub> that separates the NO<sub>x</sub>-limited regime from and VOC limited regime



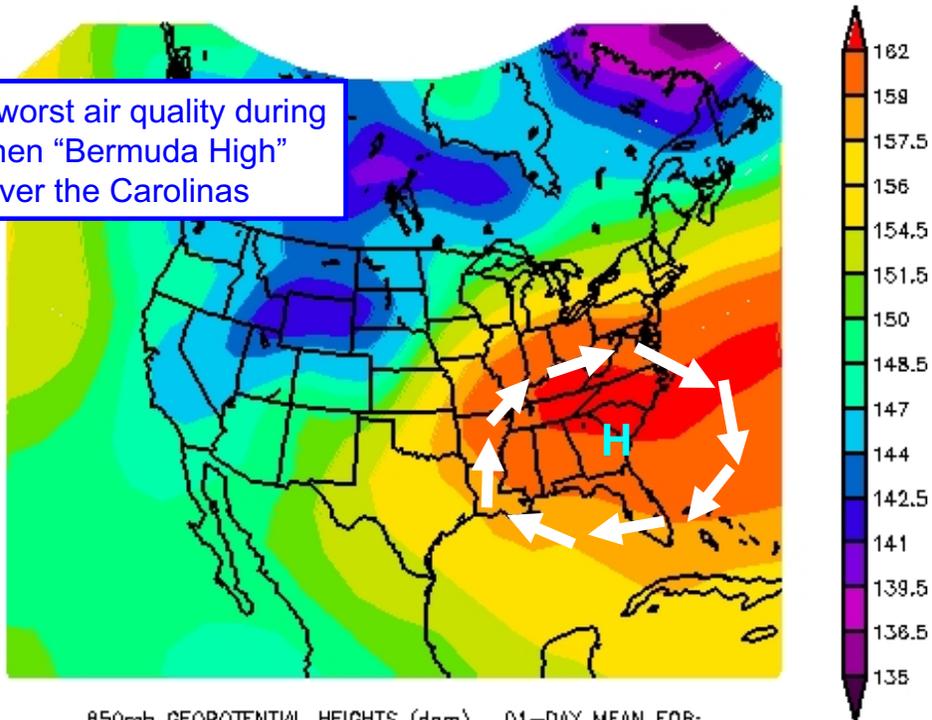
An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O<sub>3</sub> pollution may have been partly misdirected. Measurements and model calculations now show that O<sub>3</sub> production over most of the United States is primarily NO<sub>x</sub> limited, 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 summer, when "Bermuda High" sets up over the Carolinas

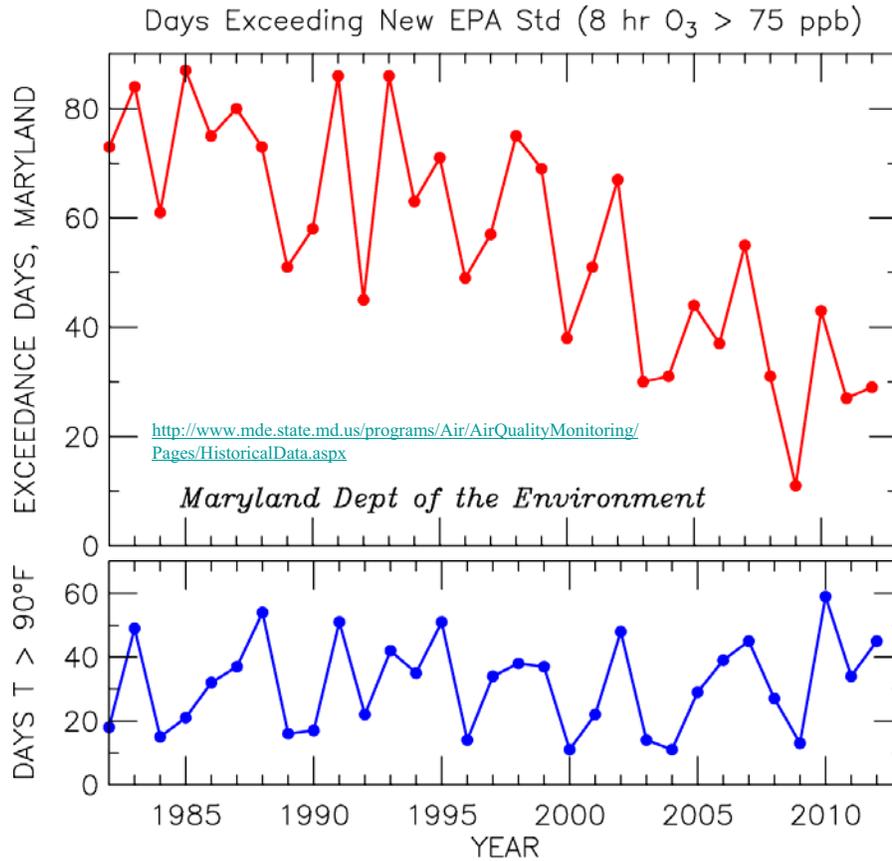


850mb GEOPOTENTIAL HEIGHTS (dam) 01-DAY MEAN FOR:  
Sun JUL 04 1999

NCEP OPERATIONAL DATASET

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

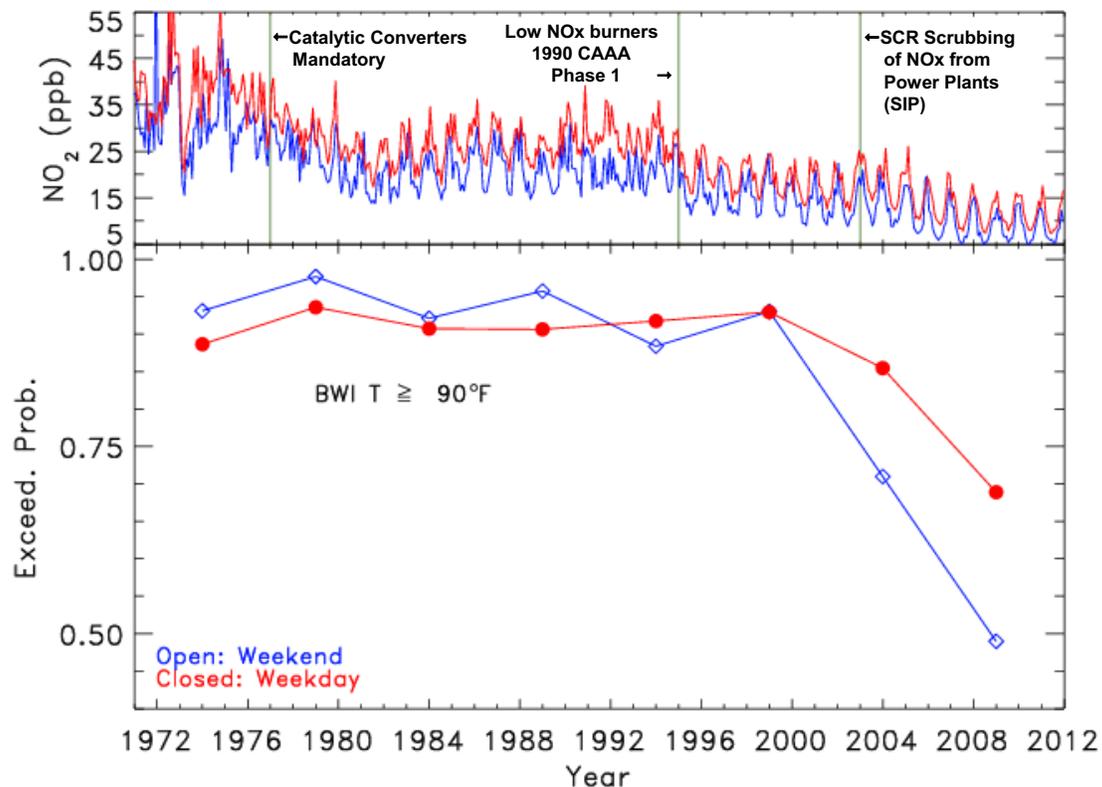
# Significant Improvements in Local Air Quality since early 1980s



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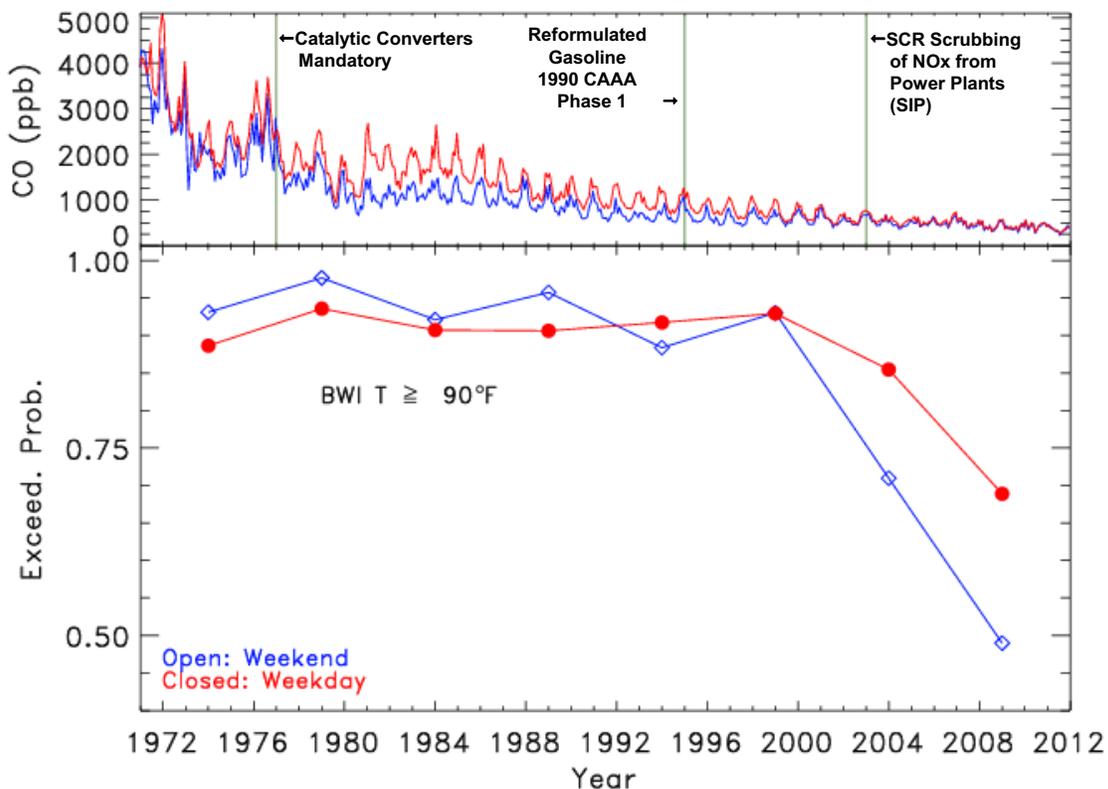
## Probability of Surface O<sub>3</sub> Exceedance: DC, MD, and Northern VA



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## Probability of Surface O<sub>3</sub> Exceedance: DC, MD, and Northern VA

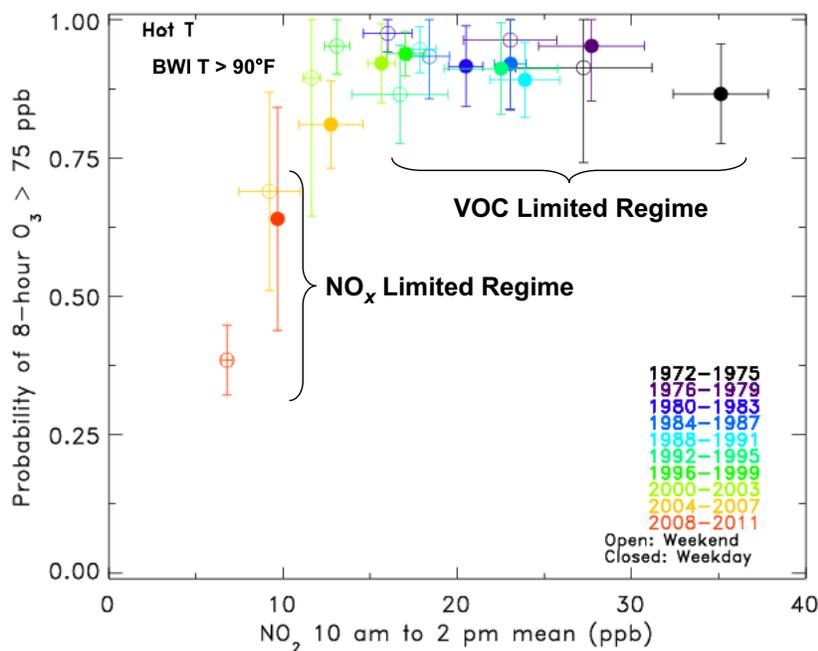


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## Probability of Surface O<sub>3</sub> Exceedance (DC, MD, No. VA) vs Daytime NO<sub>2</sub> Hot Summer Days (T<sub>BWI</sub> > 90°F)



Hosley, Canty, and Salawitch, in preparation, 2013

Analysis in this framework motivated by Pusede and Cohen, ACP, 2012

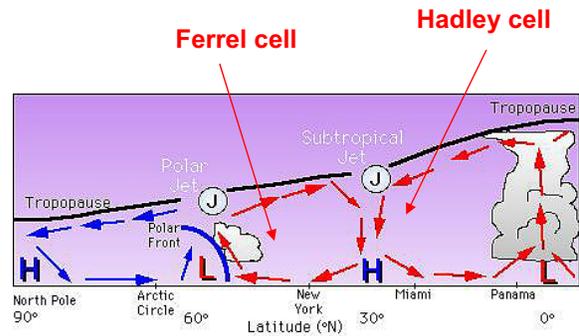
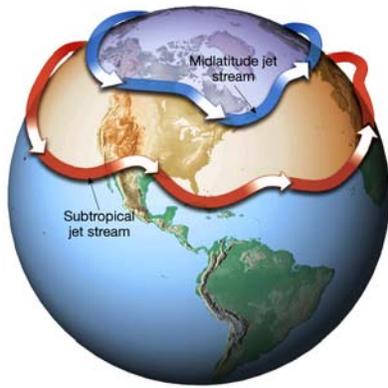
<http://www.atmos-chem-phys.net/12/8323/2012/acp-12-8323-2012.html>

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# Subtropical Jet



[http://www.ux1.eiu.edu/~cfjps/1400/FIG07\\_014A.jpg](http://www.ux1.eiu.edu/~cfjps/1400/FIG07_014A.jpg)

[http://www.fas.org/irp/imint/docs/rst/Sect14/jet\\_stream.jpg](http://www.fas.org/irp/imint/docs/rst/Sect14/jet_stream.jpg)

**Subtropical Jet: area where poleward descending branch of the Hadley Circulation meets the equatorward descending of the Ferrel Cell (see Lecture 3)**

**Semi-permanent area of high pressure, fair weather, low rainfall:  
conditions conducive to high ozone**

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## Climate Change and Air Pollution

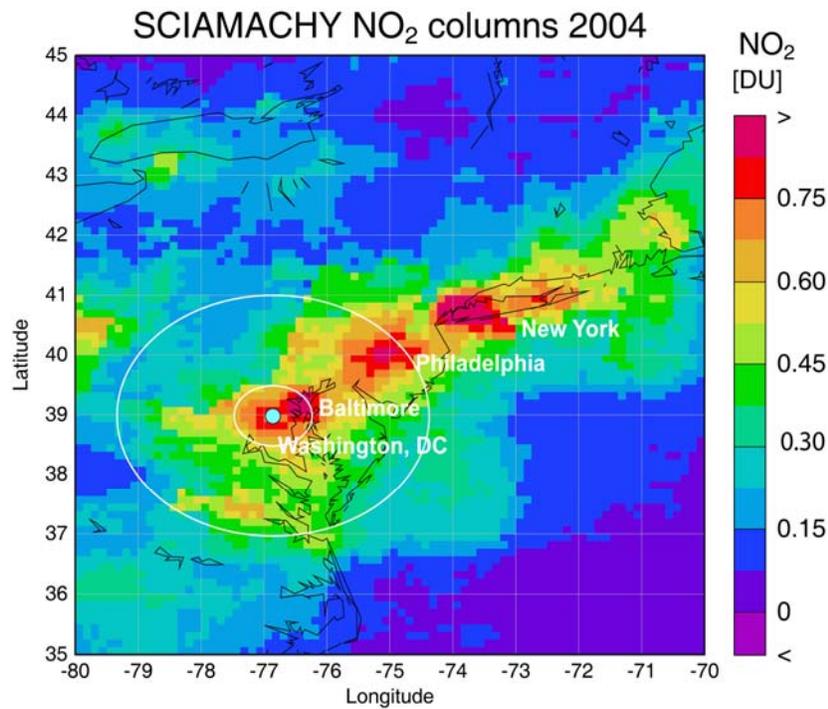
### Poleward expansion of the sub-tropical jet:

- **Surface ozone highs occur along Subtropical Jet**
- Number of days Subtropical Jet within 150 miles of Baltimore has increased by ~50% between 1979 and 2003, due to “frontal movement” (expansion of the Hadley Cell)
- Driving force: weakening of the equator to pole temperature gradient, caused by more rapid warming at high latitudes compared to tropics
- **As a consequence, models predict increase in severity and duration of surface O<sub>3</sub> episodes in the Mid-Atlantic, even for constant emissions**

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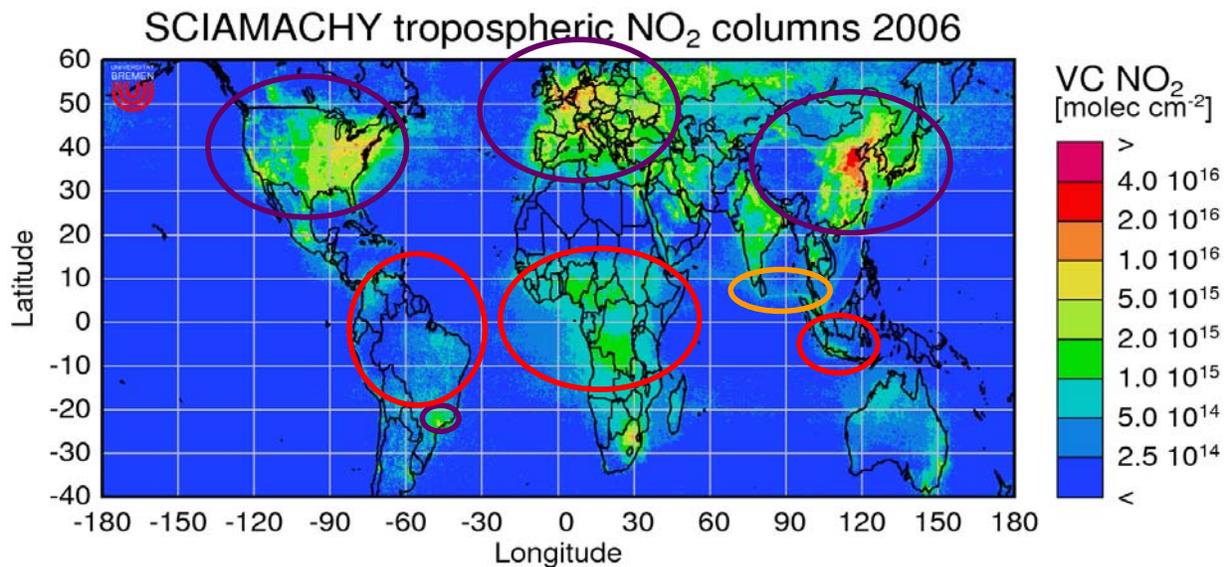
**Tropospheric NO<sub>2</sub> columns derived from SCIAMACHY measurements, 2004.**  
**The NO<sub>2</sub> hot-spots coincide with the locations of the labeled cities.**

Herman *et al.*, *NCAR Air Quality Remote Sensing from Space*, 2006

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**anthropogenic  
pollution**

**biomass  
burning**

**ships**

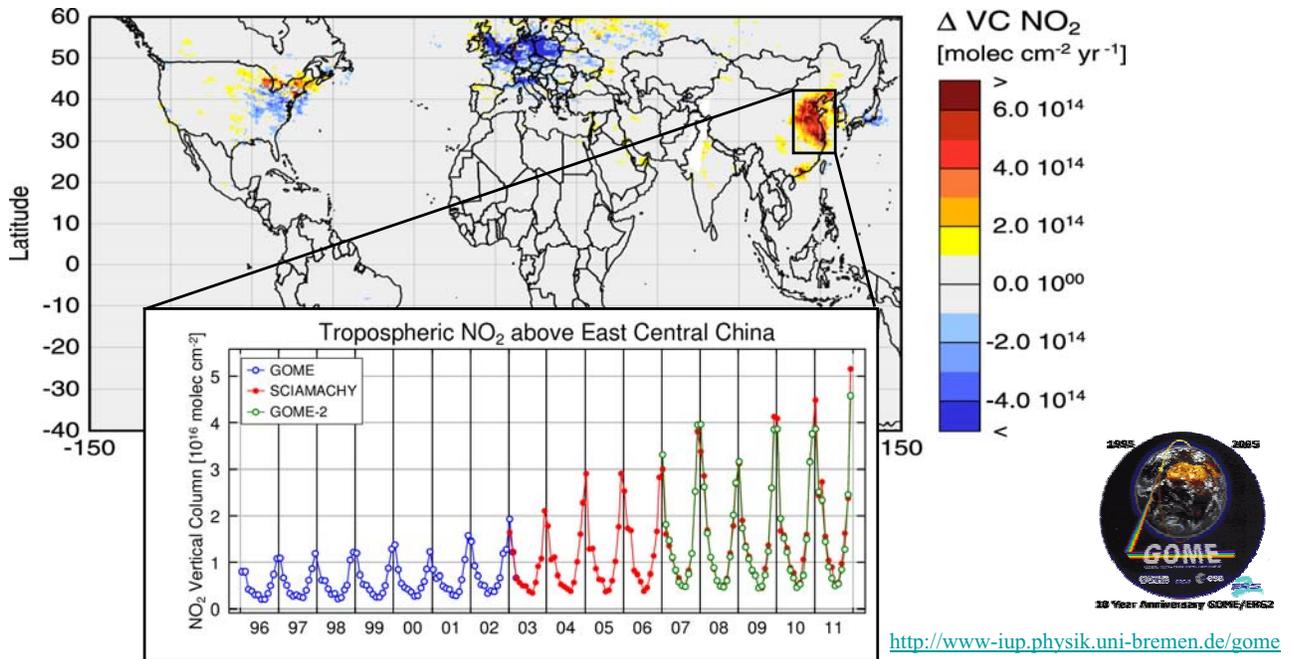
[http://www.doas-bremen.de/lectures/richter\\_nox\\_erca\\_100126.ppt](http://www.doas-bremen.de/lectures/richter_nox_erca_100126.ppt)

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## Change in tropospheric NO<sub>2</sub>, 2002 minus 1996 GOME: Global Ozone Monitoring Instrument



A. Richter et al., Increase in tropospheric NO<sub>2</sub> over China observed from space, *Nature*, 2005

[http://www.doas-bremen.de/lectures/richter\\_nox\\_erca\\_120203.ppt](http://www.doas-bremen.de/lectures/richter_nox_erca_120203.ppt)

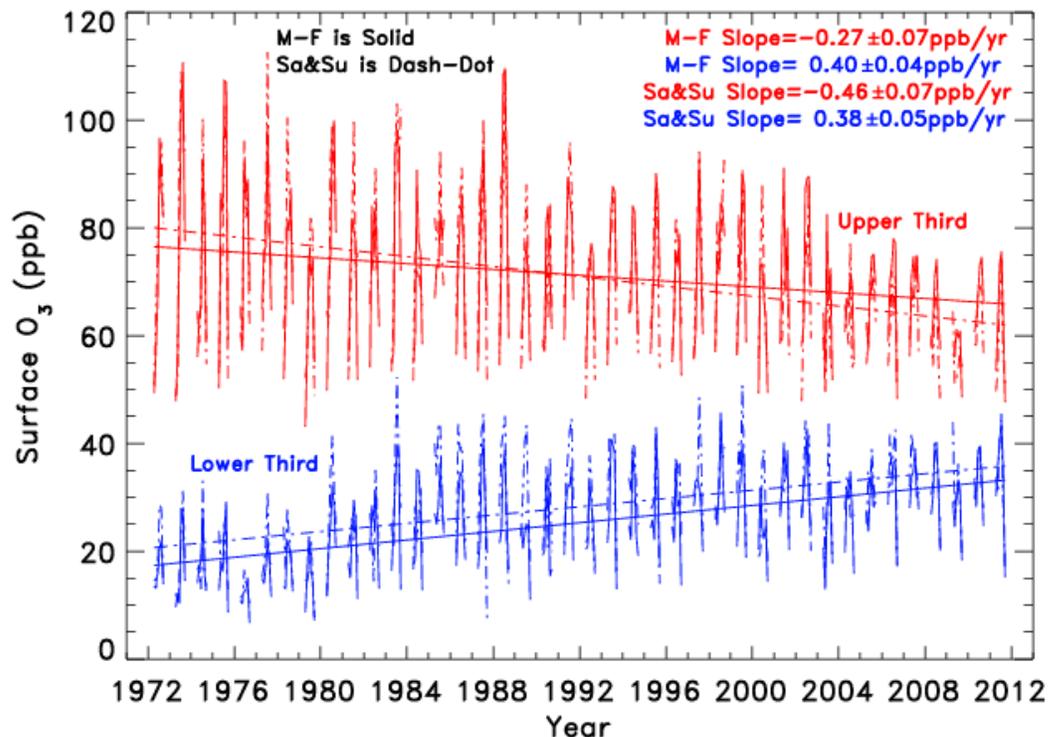
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## Surface O<sub>3</sub>: Temporal Transition from Local to Regional

Timeseries of top & bottom third monthly average o<sub>3</sub>  
weekend & weekday, hours: 10–19, months: apr to sep



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