Tropospheric Ozone and Air Quality
AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2017

Today:
- **Tropospheric ozone production mechanism (CO, NO_x, and VOCs)**
- **Recent improvements of air quality**
- **Coupling of meteorology, and perhaps climate change, to air quality**

Lecture 12

16 March 2017

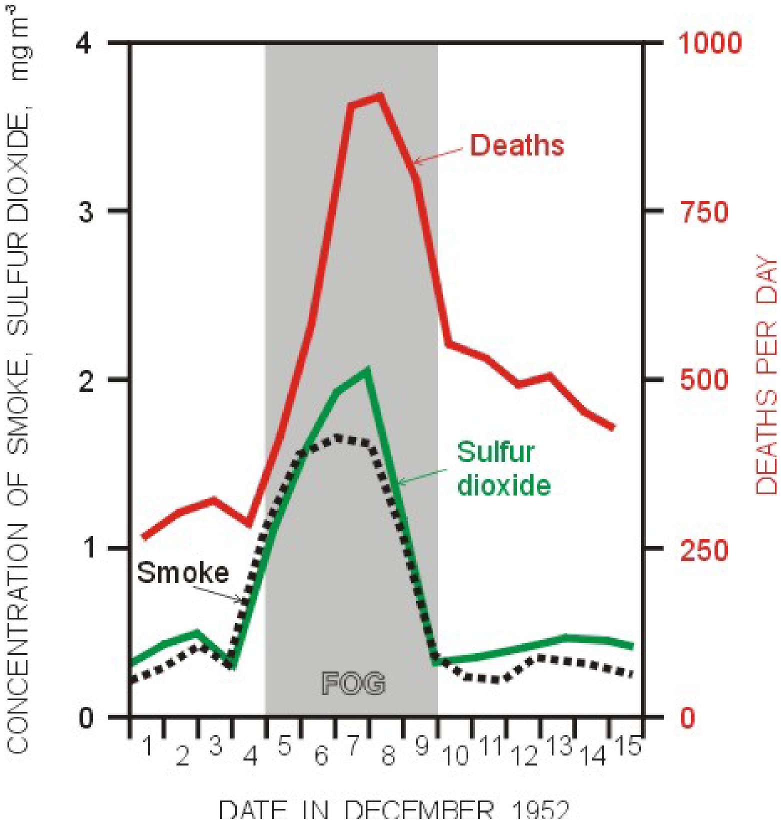
Student Projects

- **Mandatory for 633 students:** project grade will count towards final grade in an amount equal to each exam
- Due Wednesday, 10 May 2017… you're welcome to complete sooner
- ~8 pages single spaced (not including reference list or figures) on a topic related to class (your choice …we're happy to discuss potential topics)
- Must be ***new work for this class*** but can be related to your dissertation or some other topic in which you've had prior interest
- ~10 min project presentations 6:30 pm, 10 May: everyone encouraged to attend
- Request all students who will complete a project to provide a **2 to 3 sentence description** **2 weeks** from today: **Thurs, 30 March 2017**

  Please use next **2 weeks** to speak to me about a project topic
- Finally, I am delighted to provide feedback on your project (paper & presentation) if given the opportunity

Why do we care ?

Many thousands of deaths attributed to London Smog of 1952:



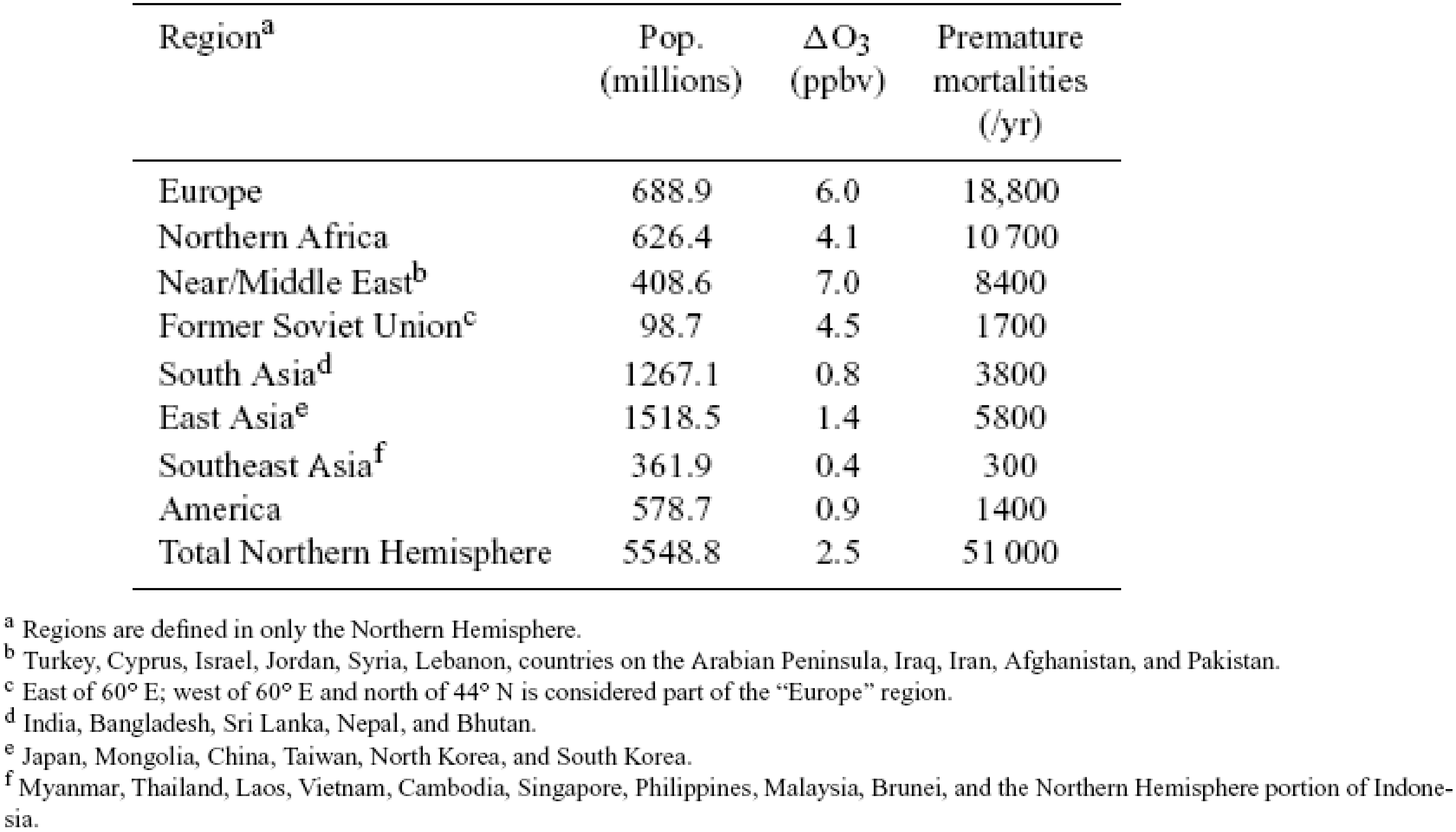
http://www.ems.psu.edu/~lno/Meteo437/Smoglond.jpg

http://www.nickelinthemachine.com/wordpress/wp-content/uploads/smog-d.jpg

Why do we care ?

Today, epidemiologists relate many thousands of deaths (annually) to air pollution

Table 2. Decreases in ozone (the population-weighted annual average 8-h daily maximum) and premature mortalities when European emissions are removed, for eight NH regions.



Region[a]	Pop. (millions)	ΔO_3 (ppbv)	Premature mortalities (/yr)
Europe	688.9	6.0	18,800
Northern Africa	626.4	4.1	10 700
Near/Middle East[b]	408.6	7.0	8400
Former Soviet Union[c]	98.7	4.5	1700
South Asia[d]	1267.1	0.8	3800
East Asia[e]	1518.5	1.4	5800
Southeast Asia[f]	361.9	0.4	300
America	578.7	0.9	1400
Total Northern Hemisphere	5548.8	2.5	51 000

[a] Regions are defined in only the Northern Hemisphere.

[b] Turkey, Cyprus, Israel, Jordan, Syria, Lebanon, countries on the Arabian Peninsula, Iraq, Iran, Afghanistan, and Pakistan.

[c] East of 60° E; west of 60° E and north of 44° N is considered part of the "Europe" region.

[d] India, Bangladesh, Sri Lanka, Nepal, and Bhutan.

[e] Japan, Mongolia, China, Taiwan, North Korea, and South Korea.

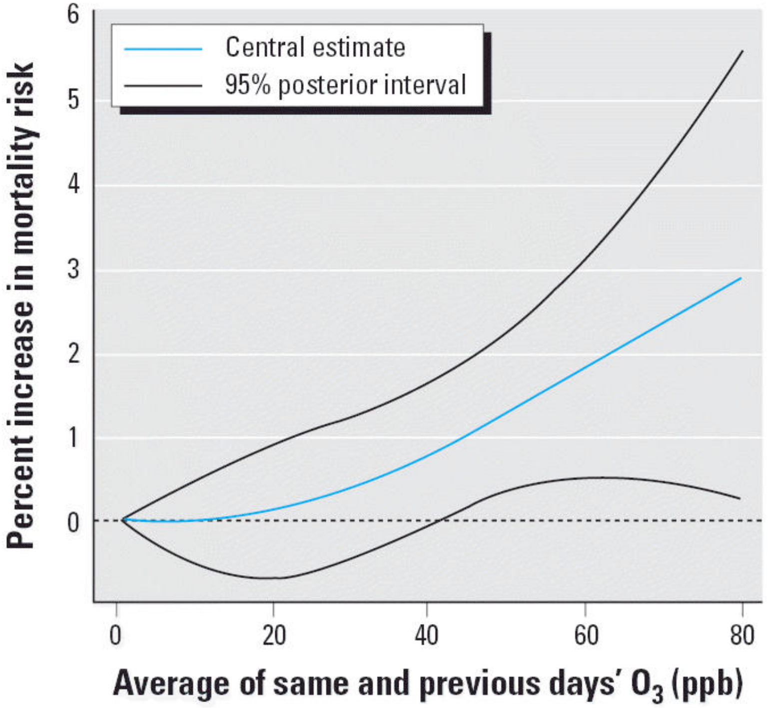
[f] Myanmar, Thailand, Laos, Vietnam, Cambodia, Singapore, Philippines, Malaysia, Brunei, and the Northern Hemisphere portion of Indonesia.

Duncan *et al.*, *Atmos. Chem. Phys.*, 2008

Air Quality Standards and Why We Care

Year	Averaging Period	EPA Surface Ozone Standard
1979	1 hr	125 ppb
1997	8 hr	85 ppb
2008	8 hr	75 ppb
2015[#]	8 hr [*]	70 ppb

[*] The 8 hr standard is met when the 3-yr average of the annual 4th highest daily maximum 8 hr O_3 is less than 70 ppb



Increased risk of premature mortality for even low levels of surface O_3; further reductions will benefit public health

Bell et al., 2006
http://www.ncbi.nlm.nih.gov/sites/ppmc/articles/PMC1440776

[#] On October 1, 2015 the EPA lowered the NAAQS for ground-level ozone to 70 ppb, based on extensive scientific evidence about the harmful effects of tropospheric ozone

Tropospheric Pollutants (The Air We Breathe)

Criteria Pollutants

U.S. NAAQS frequently updated
http://www.epa.gov/air/criteria.html

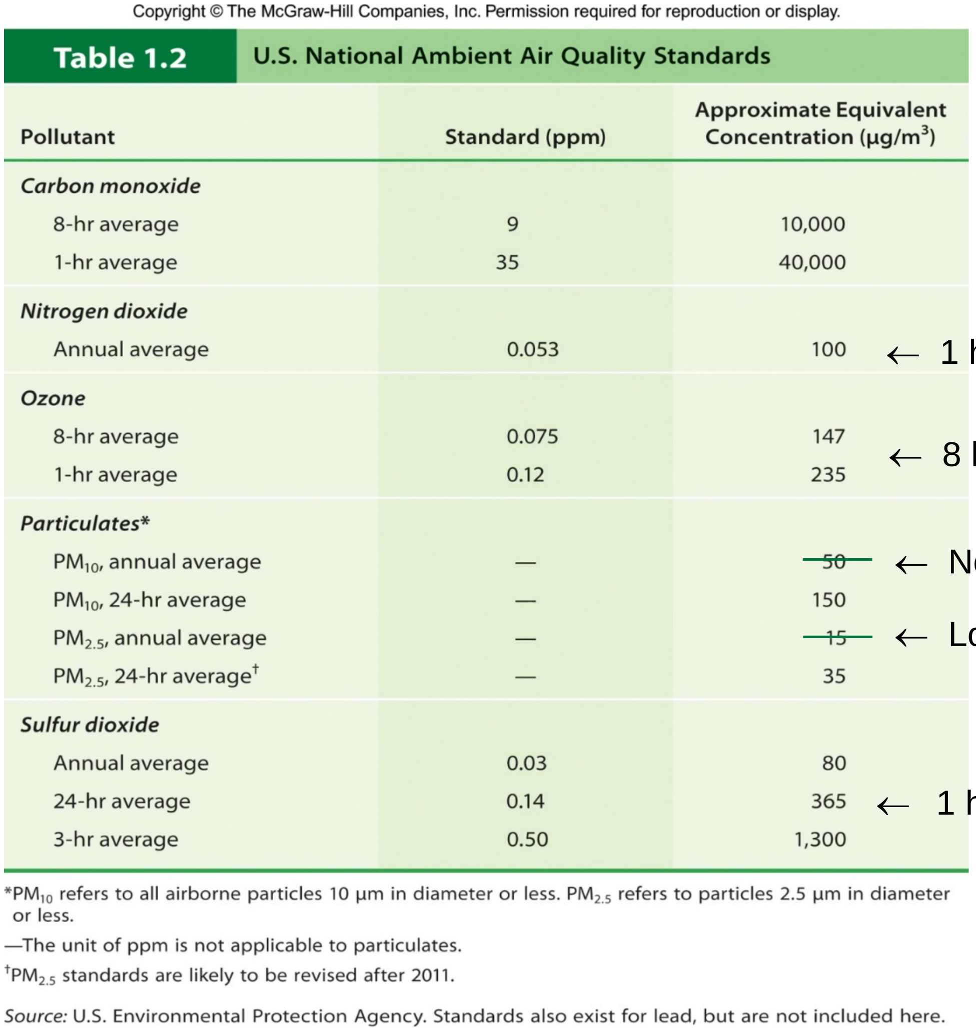


Table 1.2 U.S. National Ambient Air Quality Standards

Pollutant	Standard (ppm)	Approximate Equivalent Concentration (μg/m^3)
Carbon monoxide		
8-hr average	9	10,000
1-hr average	35	40,000
Nitrogen dioxide		
Annual average	0.053	100
Ozone		
8-hr average	0.075	147
1-hr average	0.12	235
*Particulates**		
PM_{10}, annual average	—	~~50~~
PM_{10}, 24-hr average	—	150
$PM_{2.5}$, annual average	—	~~15~~
$PM_{2.5}$, 24-hr average†	—	35
Sulfur dioxide		
Annual average	0.03	80
24-hr average	0.14	365
3-hr average	0.50	1,300

*PM_{10} refers to all airborne particles 10 μm in diameter or less. $PM_{2.5}$ refers to particles 2.5 μm in diameter or less.

—The unit of ppm is not applicable to particulates.

†$PM_{2.5}$ standards are likely to be revised after 2011.

Source: U.S. Environmental Protection Agency. Standards also exist for lead, but are not included here.

← 1 hr 100 ppb is primary standard, Feb 2010

← 8 hr 70 ppb is standard, Oct 2015

← No annual average standard, Dec 2012

← Lowered to 12 μg/m^3, Dec 2012

← 1 hr , 75 ppb is primary standard, Jun 2010

Chemistry in Context

Criteria pollutant: common-place and detrimental to human welfare

Tropospheric Ozone Production

$$OH + \mathbf{CO} \rightarrow \mathbf{CO_2} + H$$

$$H + \mathbf{O_2} + M \rightarrow HO_2 + M$$

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

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + \mathbf{O_2} + M \rightarrow \mathbf{O_3} + M$$

$$\text{Net:} \quad \mathbf{CO + 2\,O_2 \rightarrow CO_2 + O_3}$$

NO & NO_2 : Emitted by fossil fuel combustion & biomass burning

$$N_2 + O_2 \xrightarrow{\text{High T}} 2\,NO$$

CO: Emitted by fossil fuel combustion & biomass burning

Complete combustion:

$$2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O$$

Extreme, incomplete combustion:

$$2\,C_8H_{18} + 17\,O_2 \rightarrow 16\,CO + 18\,H_2O$$

OH & HO_2: ????

Tropospheric Ozone Production

Suppose NO is converted to NO_2 by reaction with O_3 :

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$\mathbf{NO + O_3 \rightarrow NO_2 + O_2}$$

$$NO_2 + h\nu \rightarrow NO + O$$

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

Net:

Tropospheric Ozone Production

$$\mathrm{OH} + \mathbf{CO} \rightarrow \mathbf{CO_2} + \mathrm{H}$$

$$\mathrm{H} + \mathbf{O_2} + \mathrm{M} \rightarrow \mathrm{HO_2} + \mathrm{M}$$

$$\mathbf{HO_2 + NO \rightarrow OH + NO_2}$$

$$\mathrm{NO_2} + h\nu \rightarrow \mathrm{NO} + \mathrm{O}$$

$$\mathrm{O} + \mathbf{O_2} + \mathrm{M} \rightarrow \mathbf{O_3} + \mathrm{M}$$

$$\text{Net:} \quad \mathbf{CO} + \mathbf{2\,O_2} \rightarrow \mathbf{CO_2} + \mathbf{O_3}$$

Chain Mechanism for production of ozone

Chemical Initiation: $H_2O+O(^1D) \rightarrow 2OH$ & human emission of NO, CO

Since method for conversion of NO to NO_2 is <u>*crucial*</u> for whether O_3 is produced by this chain mechanism, chemists consider production of tropospheric ozone to be "limited" by $k[HO_2][NO]$

Tropospheric Ozone Production

$$\begin{aligned}
CO + OH &\rightarrow CO_2 + H \\
H + O_2 + M &\rightarrow HO_2 + M \\
HO_2 + NO &\rightarrow OH + NO_2 \\
NO_2 + h\nu &\rightarrow NO + O \\
O + O_2 + M &\rightarrow O_3 + M
\end{aligned}$$

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

$$\begin{aligned}
RH + OH &\rightarrow R + H_2O \\
R + O_2 + M &\rightarrow RO_2 + M \\
RO_2 + NO &\rightarrow RO + NO_2 \\
RO + O_2 &\rightarrow HO_2 + R'CHO \\
HO_2 + NO &\rightarrow OH + NO_2 \\
2 \times \quad NO_2 + h\nu &\rightarrow NO + O \\
2 \times \quad O + O_2 + M &\rightarrow O_3 + M
\end{aligned}$$

Net: $RH + 4O_2 \rightarrow R'CHO + H_2O + 2\,O_3$

VOC: Volatile Organic Compounds

Produced by trees and fossil fuel vapor

Strong source of HO_x (OH & HO_2) & O_3 (depending on NO_x levels)

Examples of RH and R'CHO : CH_4 (methane) → CH_2O (formaldehyde)
: C_2H_6 (ethane) → CH_3CHO (acetaledhyde)
: C_3H_8 (propane) → CH_3COCH_3 (acetone)

Ozone Production "limited" by $k[HO_2][NO] + \Sigma\, k_i\, [RO_2]_i\, [NO]$

Tropospheric Ozone Production

$$\begin{aligned}
CO + OH &\rightarrow CO_2 + H \\
H + O_2 + M &\rightarrow HO_2 + M \\
HO_2 + NO &\rightarrow OH + NO_2 \\
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Net: $CO + 2\,O_2 \rightarrow CO_2 + O_3$

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HO_2 + NO &\rightarrow OH + NO_2 \\
2 \times \quad NO_2 + h\nu &\rightarrow NO + O \\
2 \times \quad O + O_2 + M &\rightarrow O_3 + M
\end{aligned}$$

Net: $RH + 4O_2 \rightarrow R'CHO + H_2O + 2\,O_3$

Chain Mechanism for production of ozone

Chemical Initiation: Human emission of NO, CO and either human (RO_2) or natural (HO_2) hydrogen radicals

Ozone production: k[HO_2][NO]

Termination: can occur via either:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

or

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

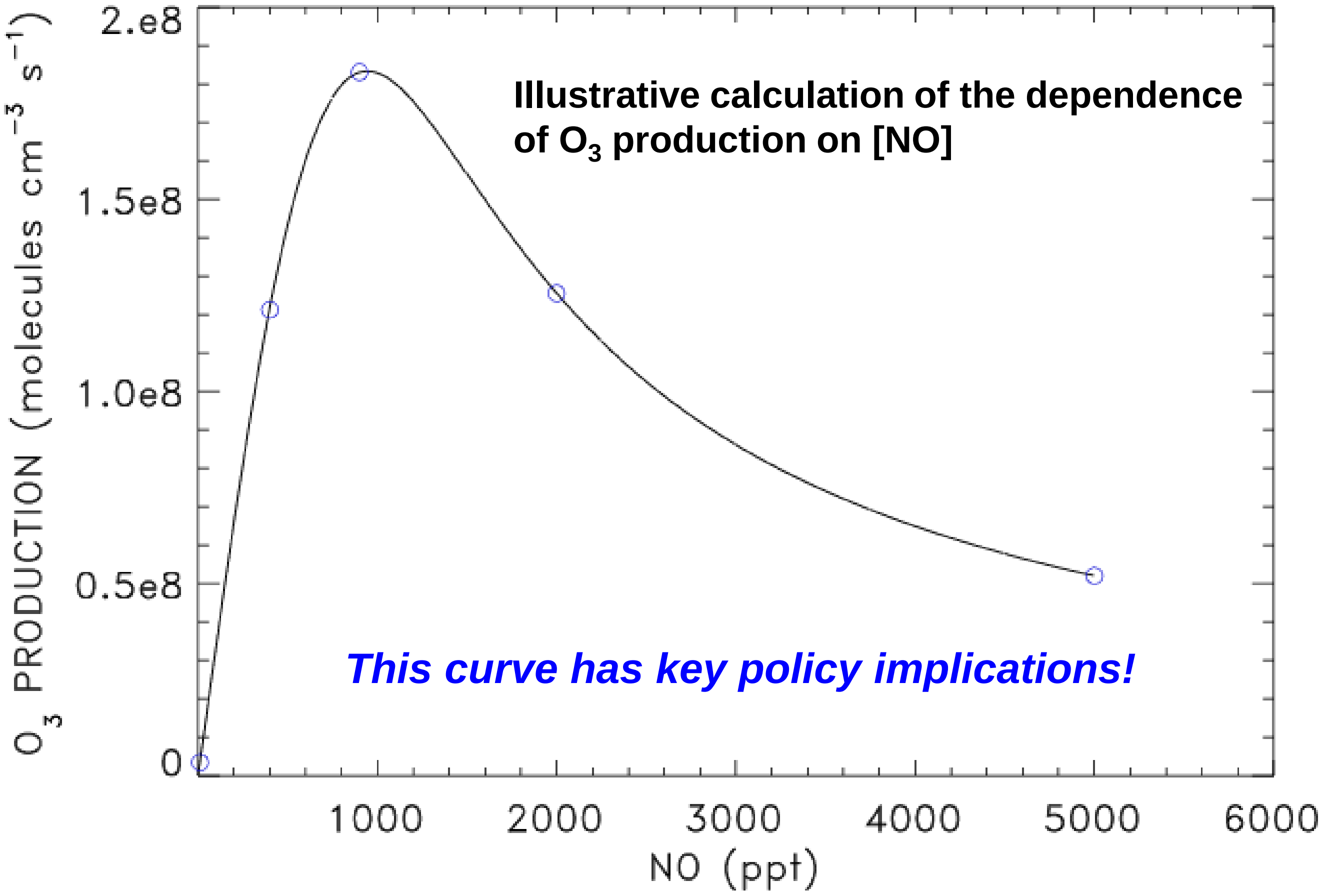
Tropospheric Ozone Production versus NO

As NO_x rises:

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

leading to a decrease in the value of the product of k $[HO_2]$ [NO],

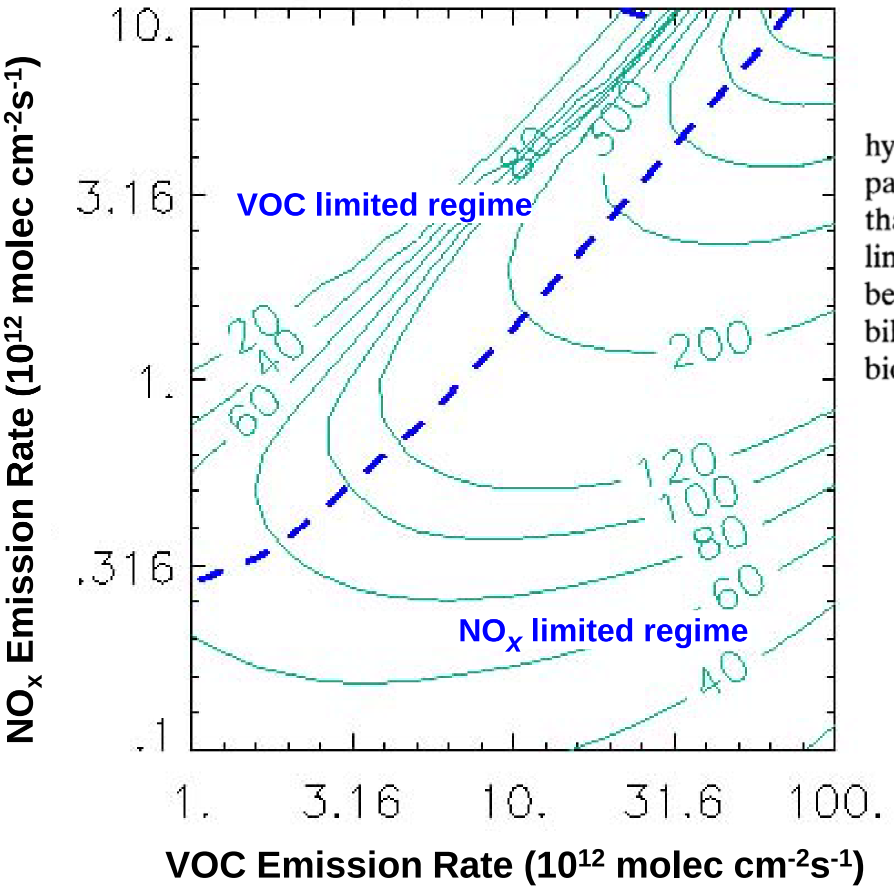
and hence the production rate of O_3.



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



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

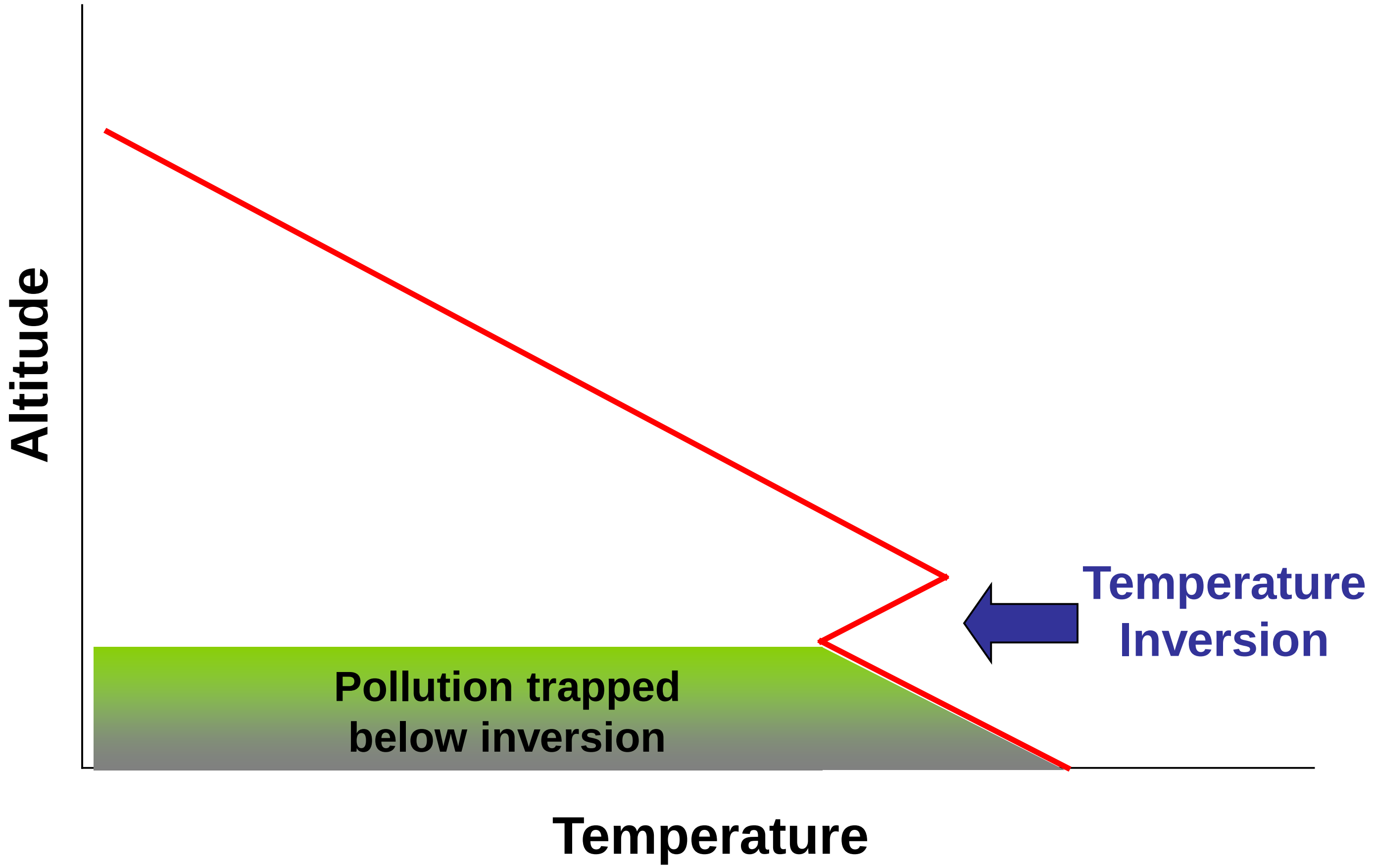
Figure: http://www-personal.umich.edu/~sillman/ozone.htm

Temperature Inversions and Air Quality

Temperature inversion: increase in temperature with height

Inversions important for Air Quality because they inhibit vertical mixing of air

Air pollutants can accumulate in cities ringed by mountains, such as Los Angeles, Mexico City, and Salt Lake City



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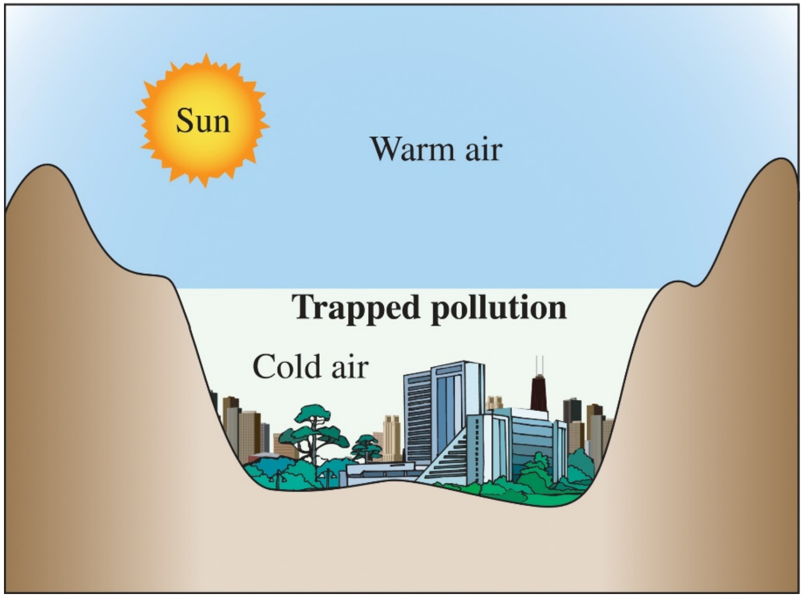
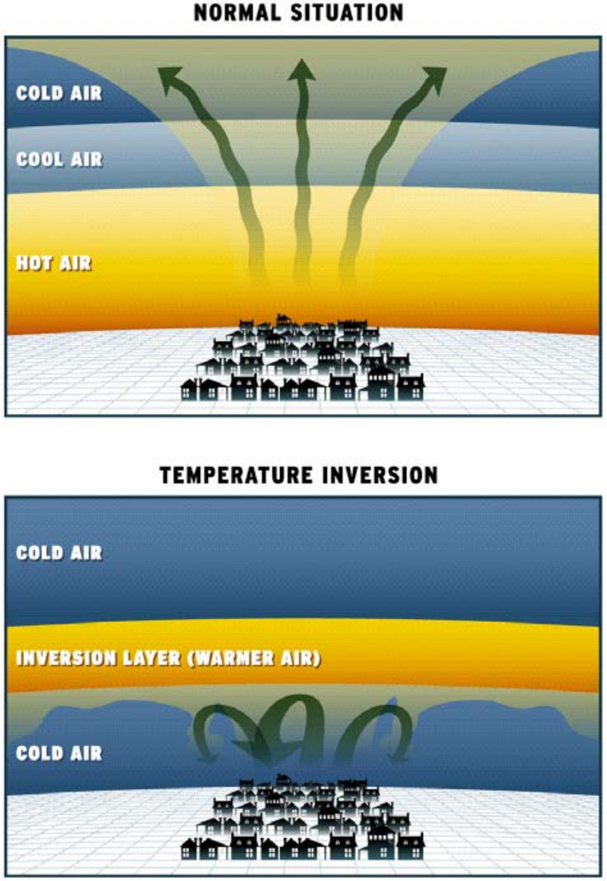


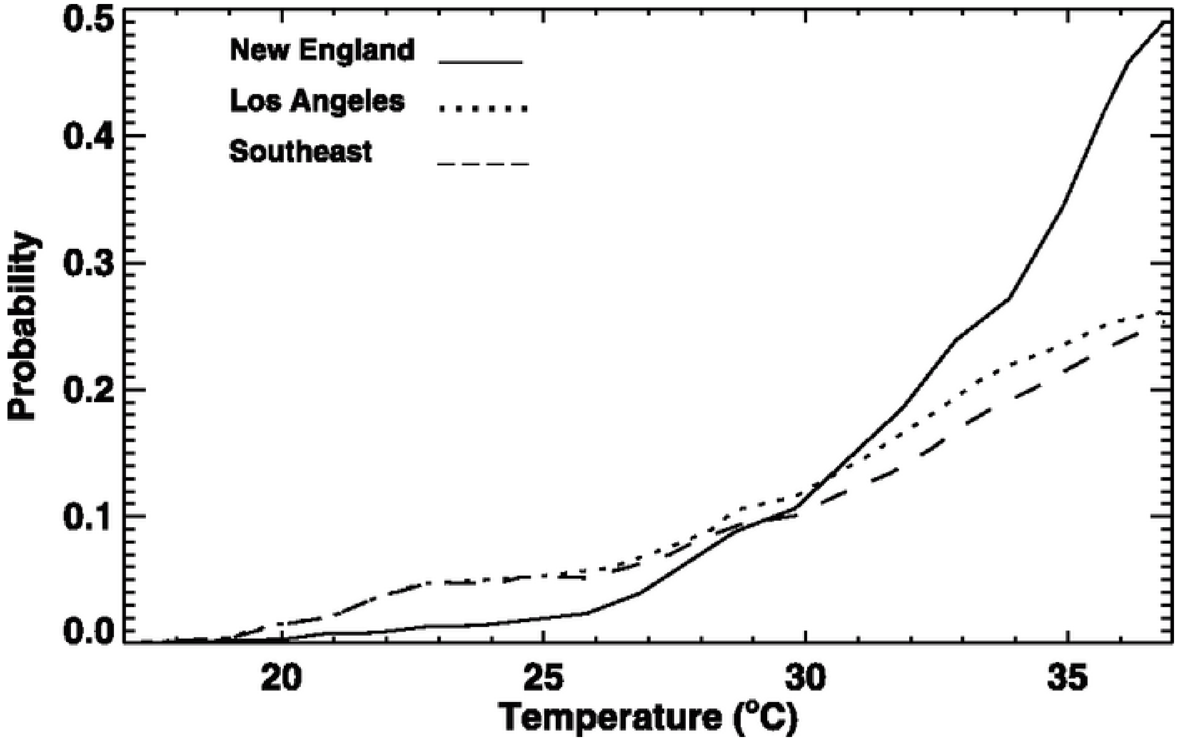
Figure 1.10, Chemistry in Context



http://geographygems.blogspot.com/2011/09/smog.html

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

Probability of ozone exceedance vs. daily max. temperature

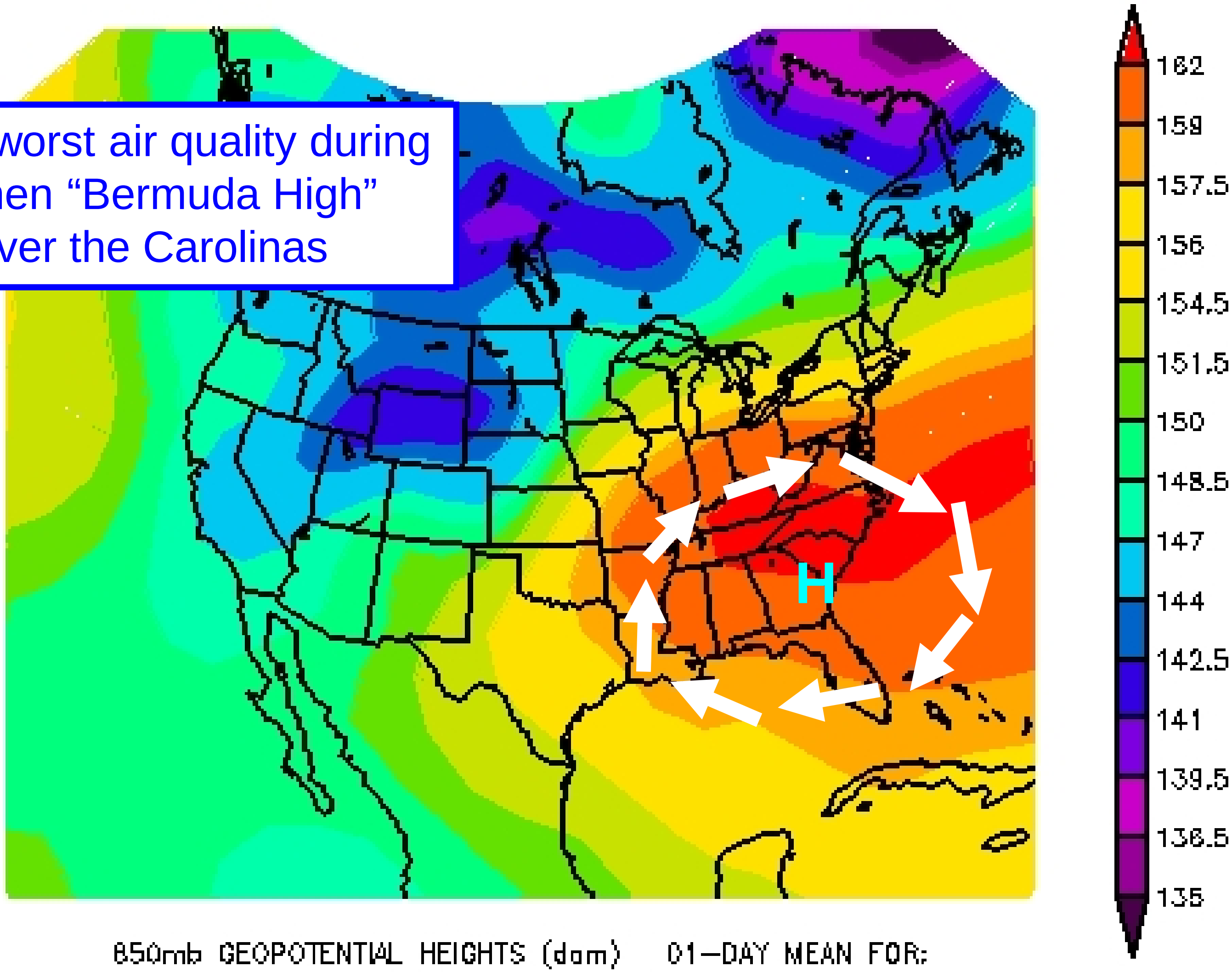


Lin et al. 2001

Why does probability of high ozone rise with increasing temperature?

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

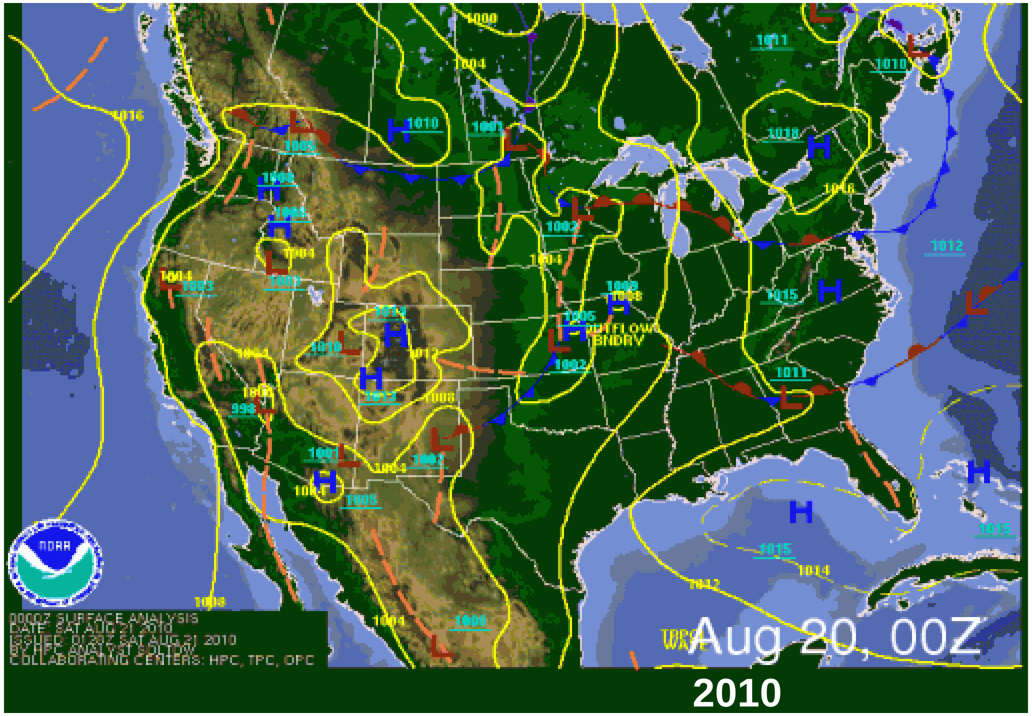


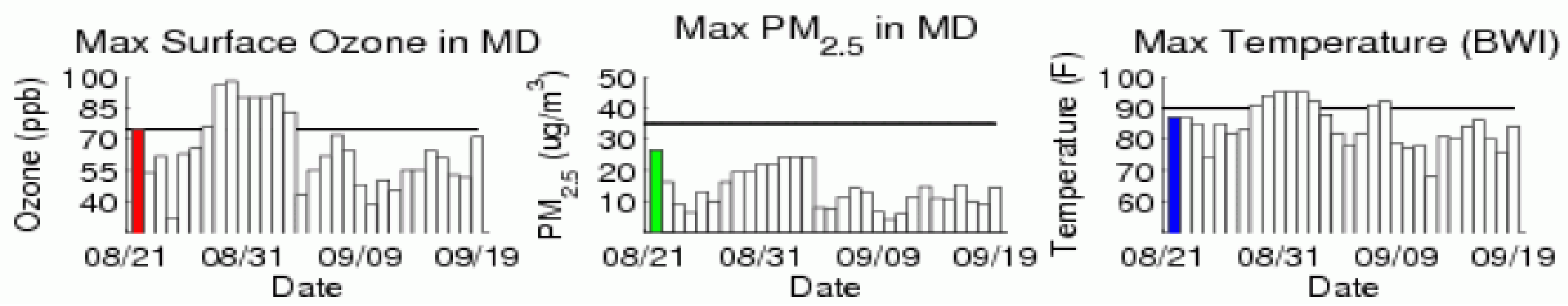
850mb GEOPOTENTIAL HEIGHTS (dam) 01-DAY MEAN FOR:
Sun JUL 04 1999

NCEP OPERATIONAL DATASET

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

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





2010

Produced by: Daniel Silversmith, UMCP
Directed by: Tim Canty & Ross Salawitch

Significant Improvements in U.S. Air Quality, Past 3 Decades

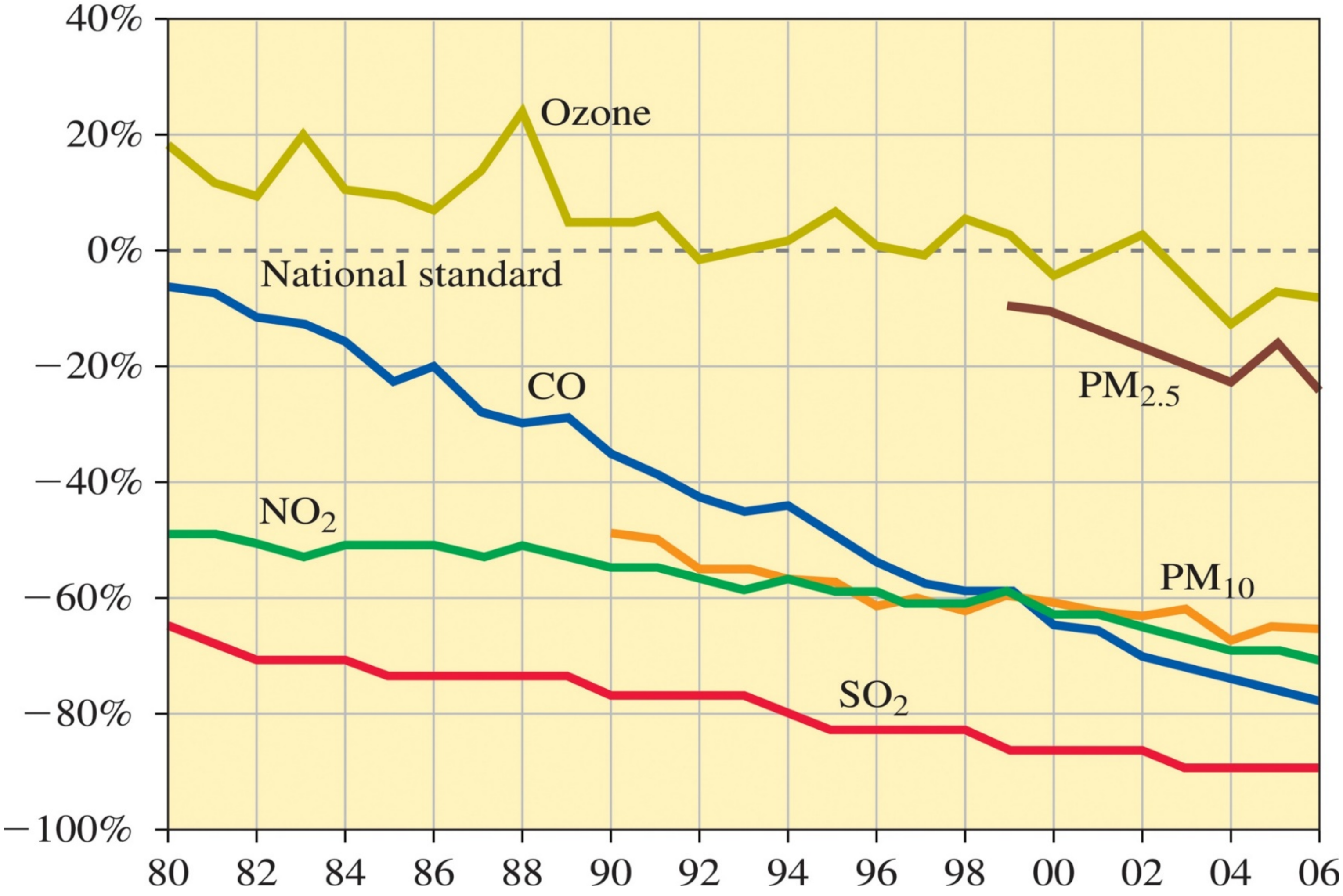
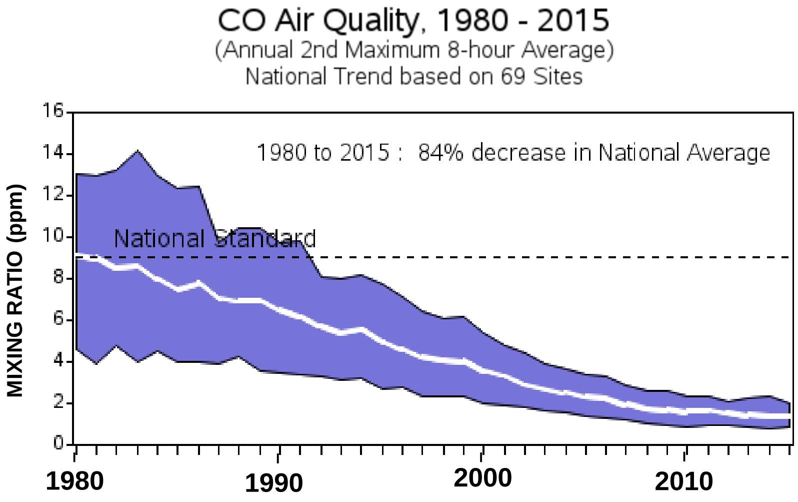
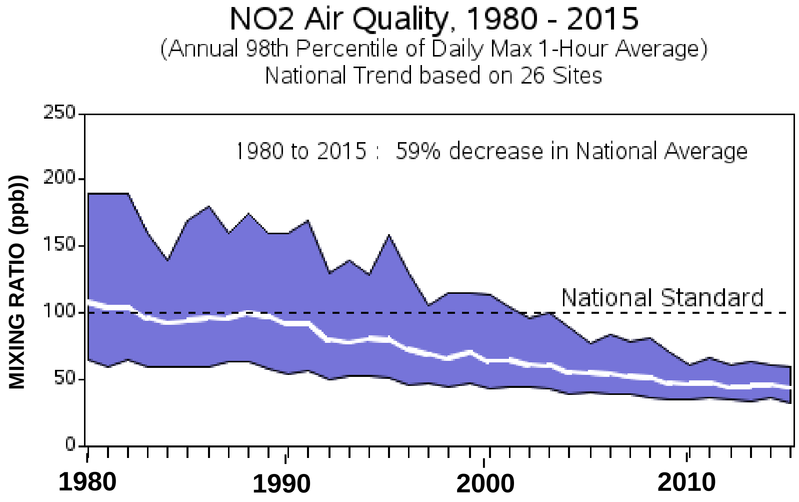
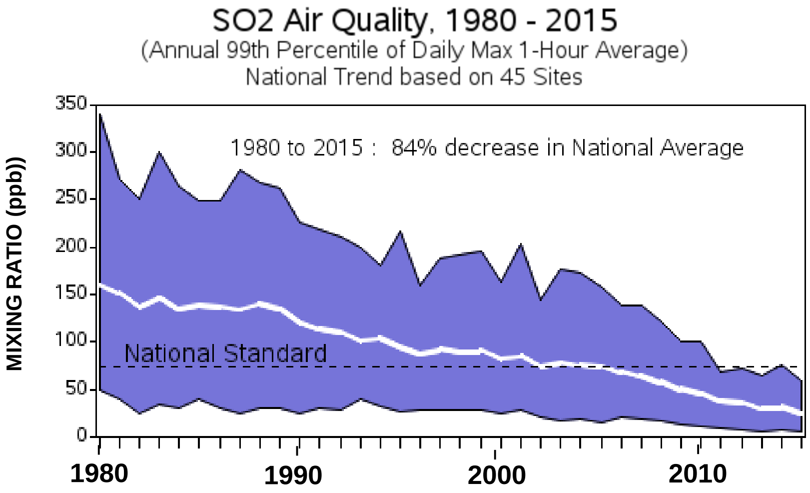


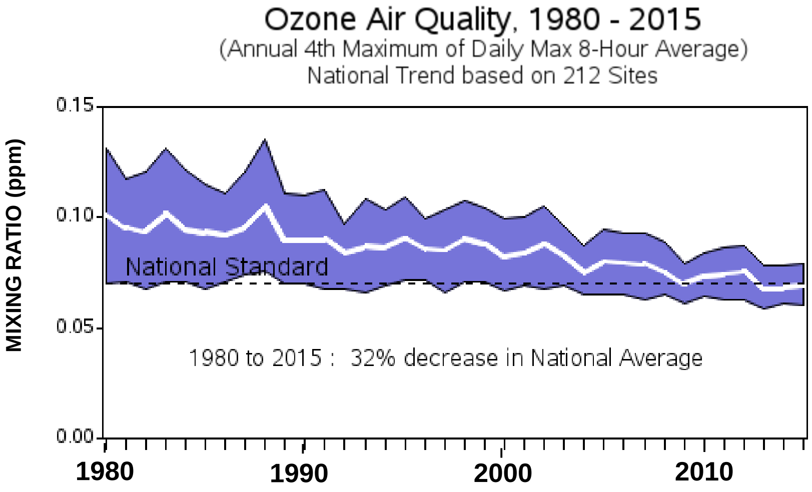
Figure 1.8, Chemistry in Context

Significant Improvements in U.S. Air Quality, Past 3 Decades


CO Air Quality, 1980 - 2015
(Annual 2nd Maximum 8-hour Average)
National Trend based on 69 Sites

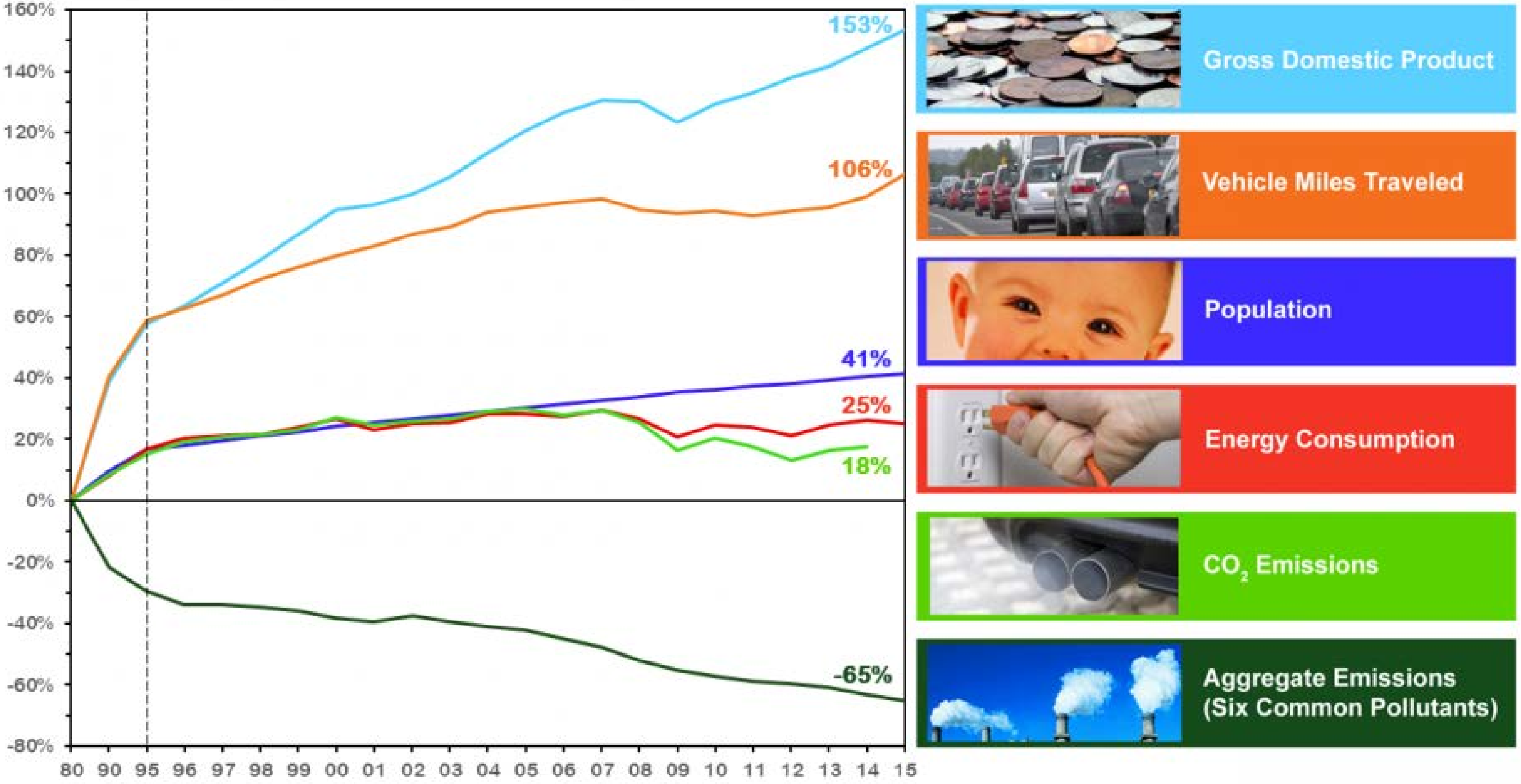

NO2 Air Quality, 1980 - 2015
(Annual 98th Percentile of Daily Max 1-Hour Average)
National Trend based on 26 Sites


SO2 Air Quality, 1980 - 2015
(Annual 99th Percentile of Daily Max 1-Hour Average)
National Trend based on 45 Sites


Ozone Air Quality, 1980 - 2015
(Annual 4th Maximum of Daily Max 8-Hour Average)
National Trend based on 212 Sites

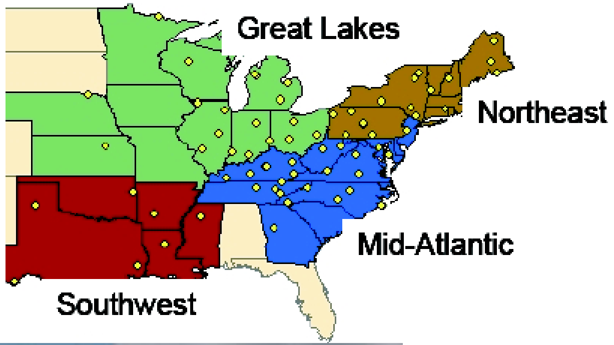
http://www.epa.gov/airtrends

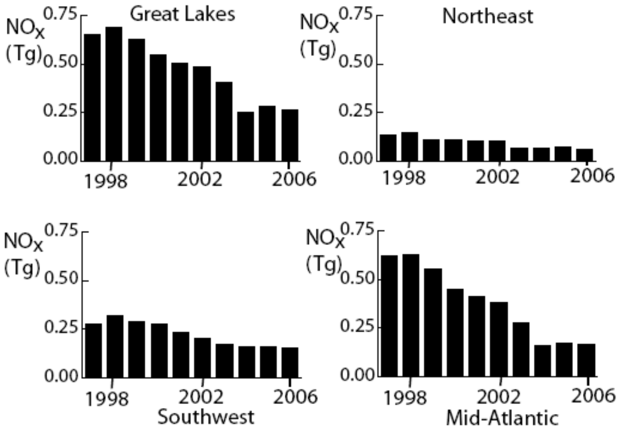
Significant Improvements in U.S. Air Quality, Past 3.5 Decades



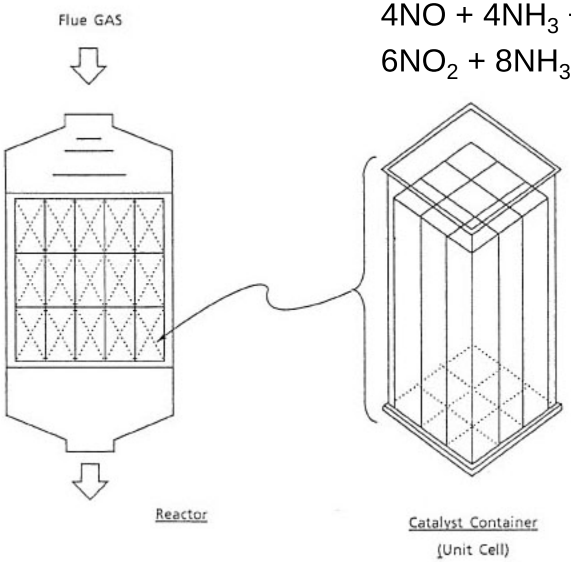
https://www.epa.gov/air-trends/air-quality-national-summary

Removal of NO_x from Power Plants





NO*x* Control:
SCR Selective Catalytic Reduction



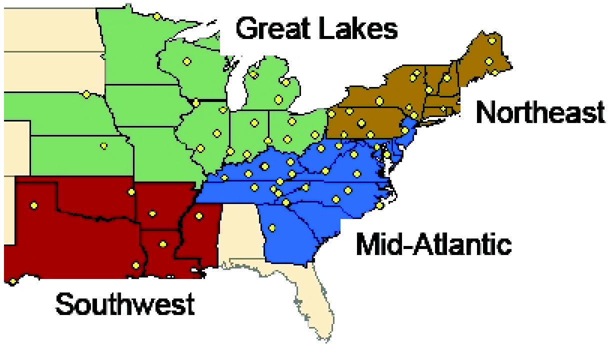
$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

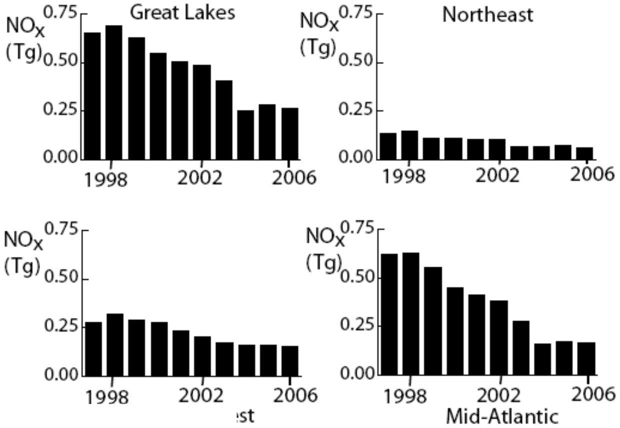
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

Catalyst
- Maximize $NO_x \rightarrow N_2$
- Minimize $SO_2 \rightarrow SO_3$

Slide courtesy John Sherwell, Md Dept of Natural Resources
http://www.dnr.maryland.gov/bay/pprp

Removal of NO_x from Power Plants





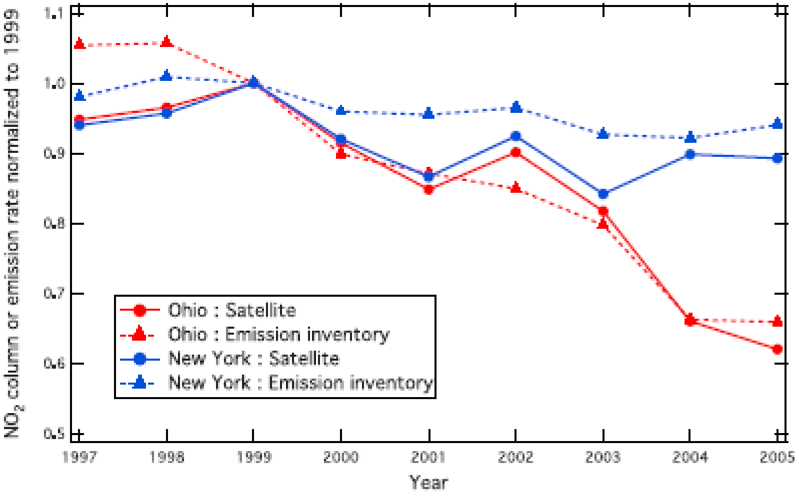
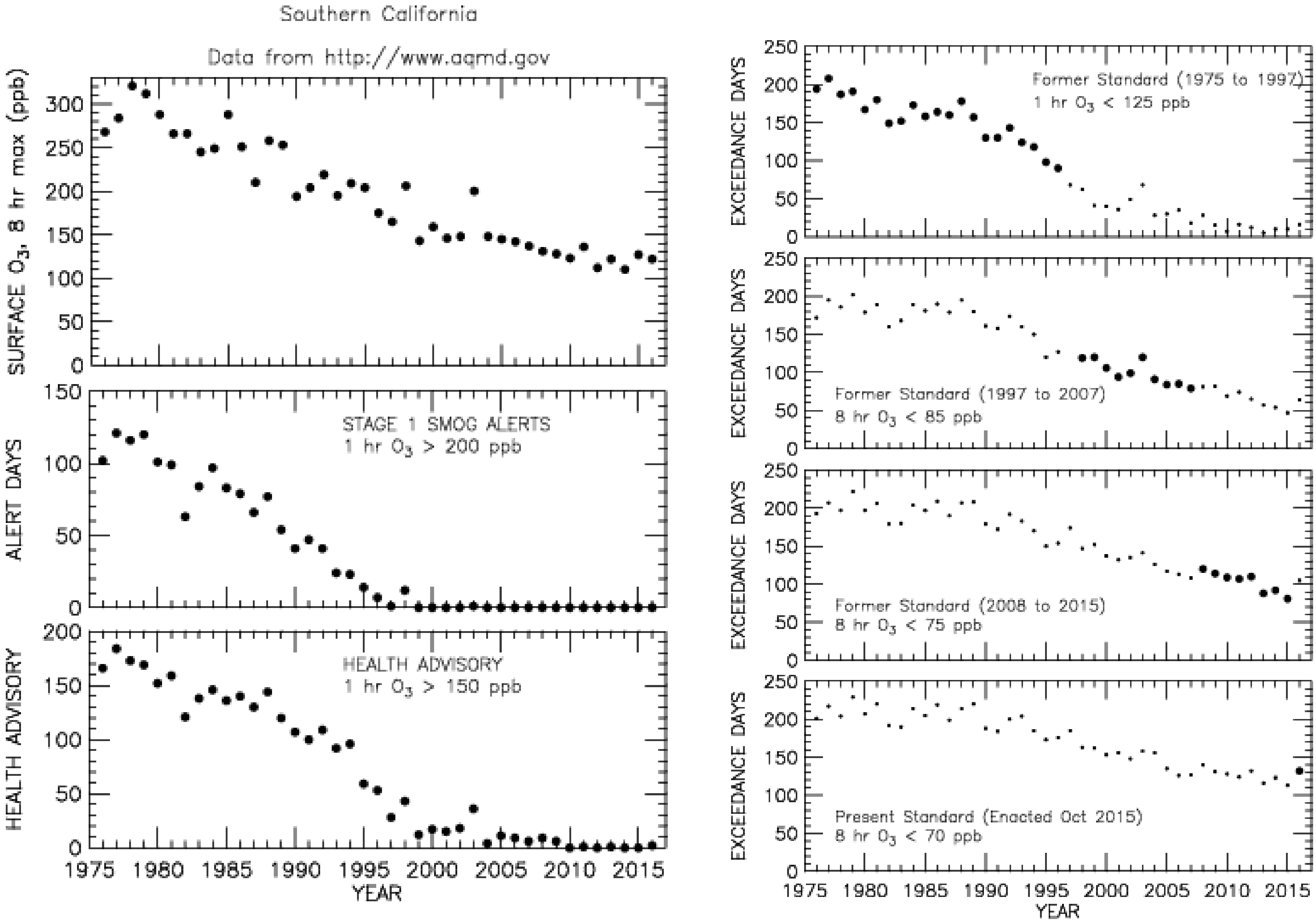


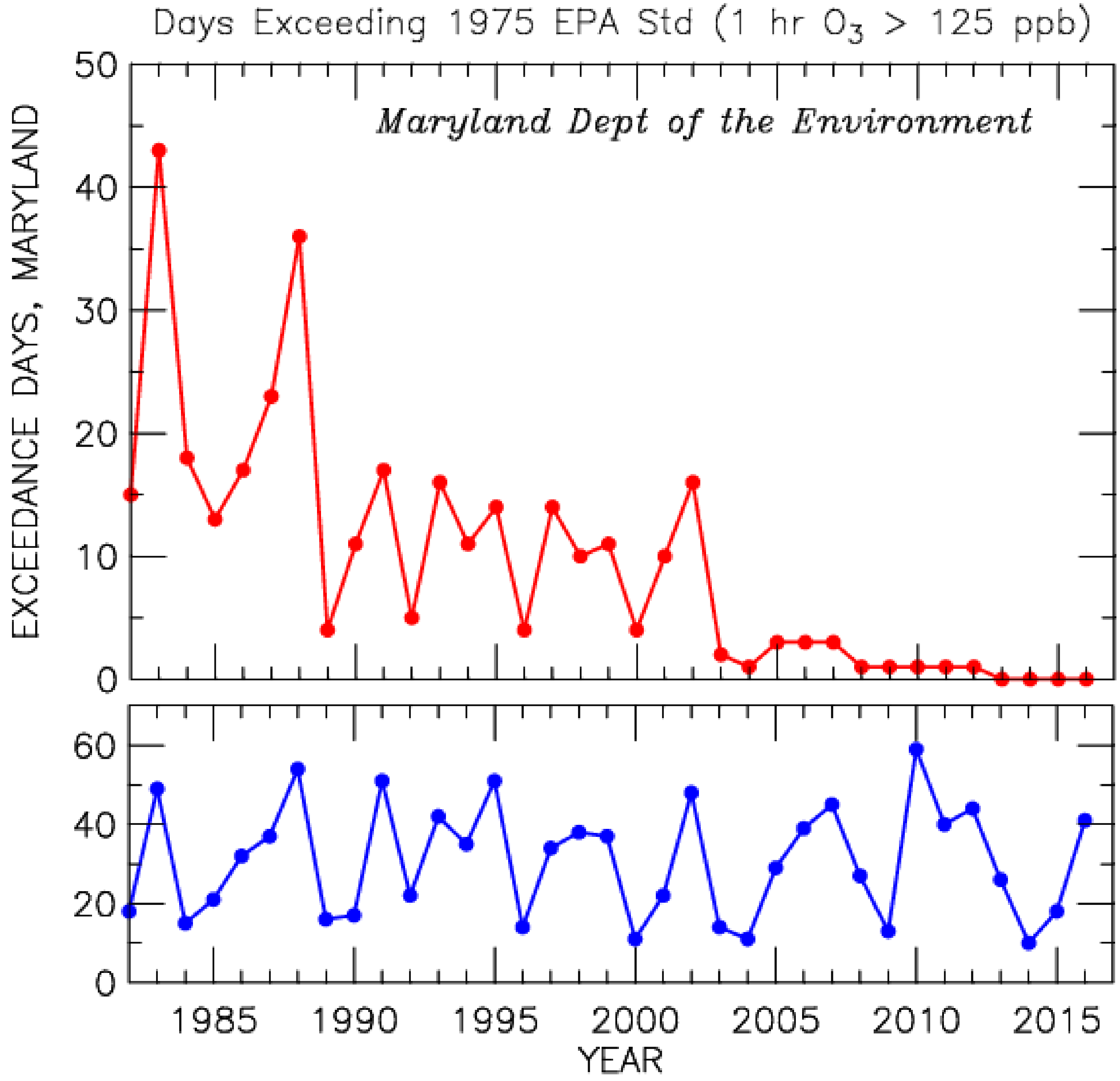
Figure 2. The trends in summertime (June–August) mean NO_2 columns from the GOME and SCIAMACHY satellites and the bottom-up NO_x emission rates in the Ohio River Valley and the northeast U.S. urban corridor during 1997–2005. SCIAMACHY data are used for 2003–2005, while GOME data are utilized for the earlier period. Data are normalized to 1999 values.

Kim *et al.*, *GRL*, 2006

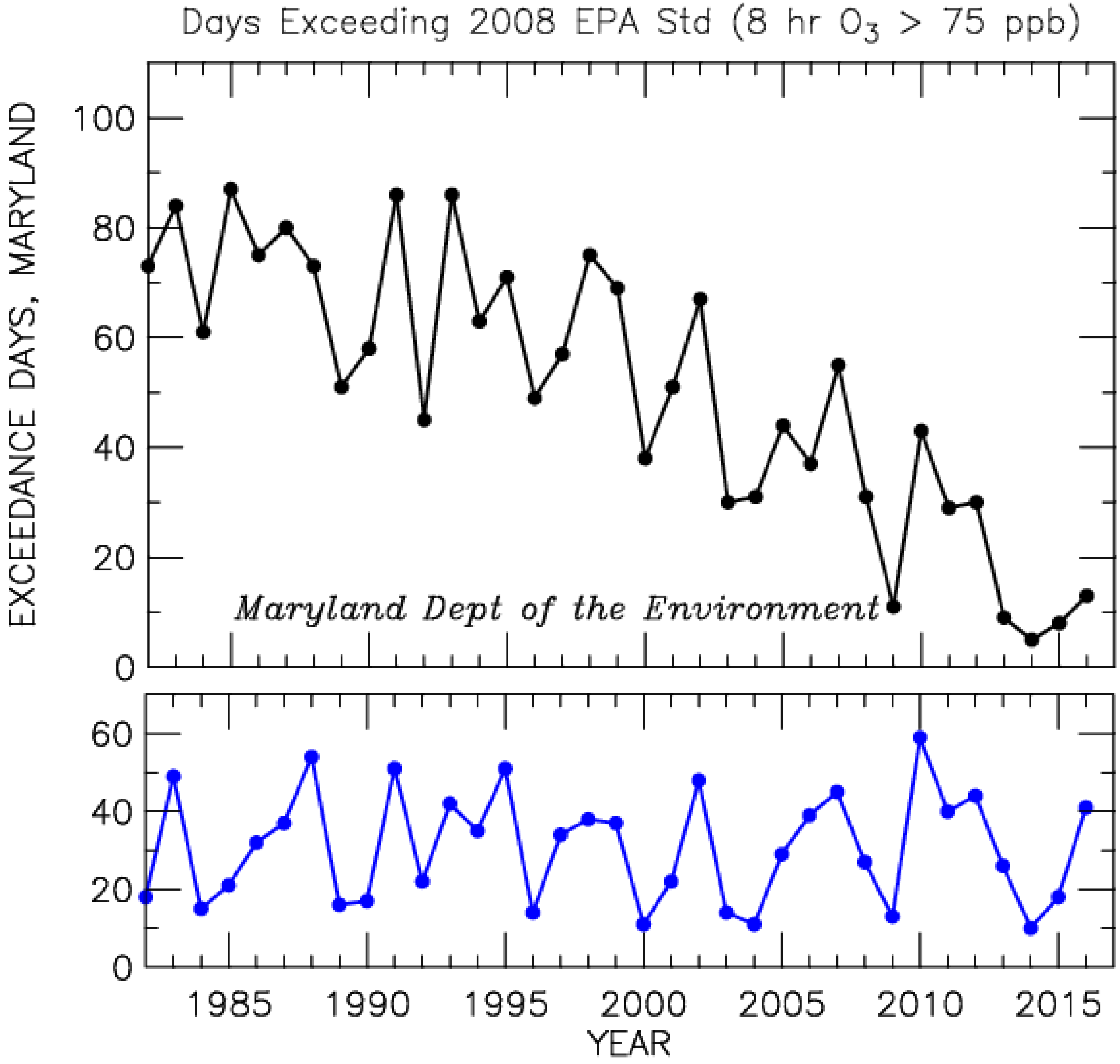
Dramatic Improvements California Air Quality, Past 4 Decades



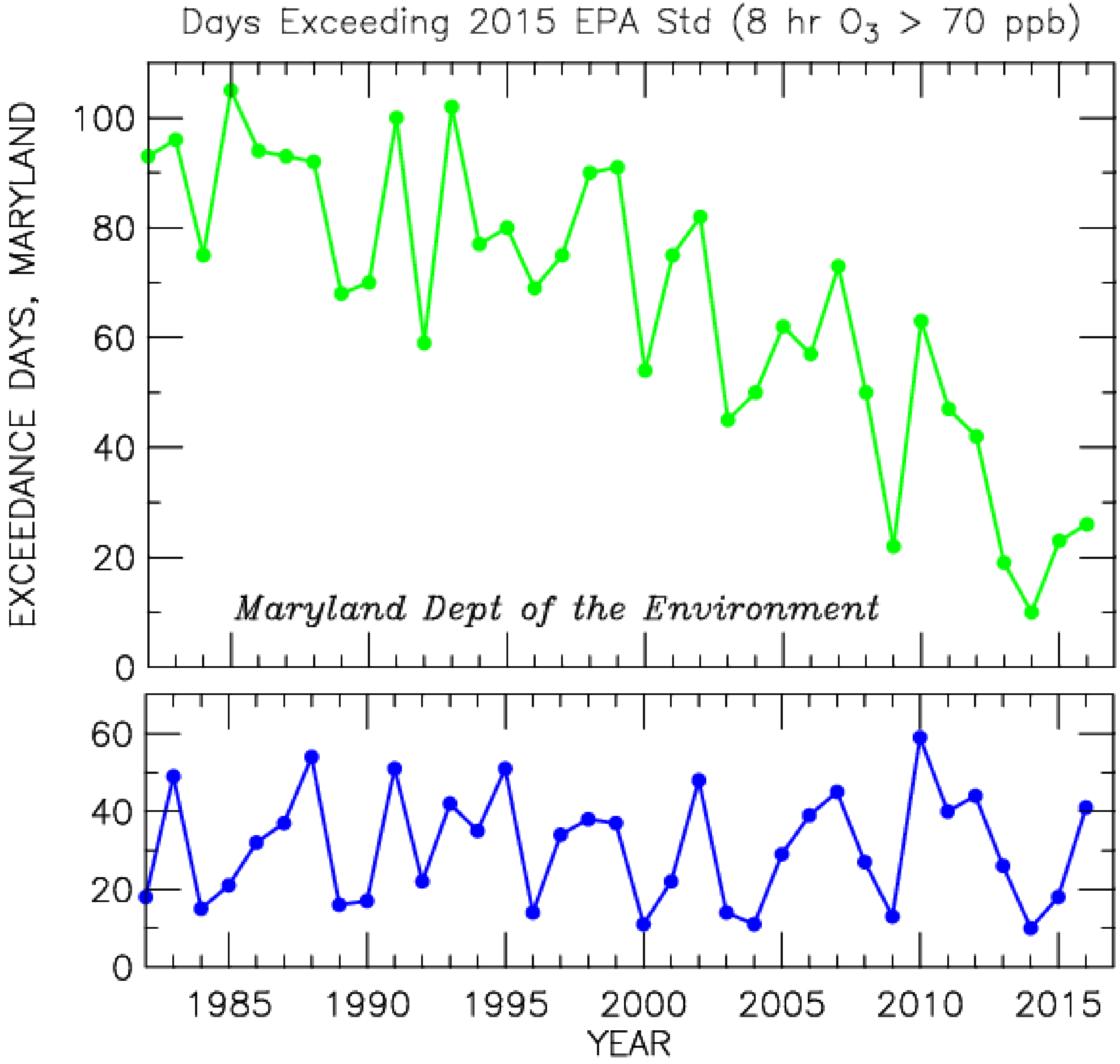
Dramatic Improvements Local Air Quality, Past 4 Decades



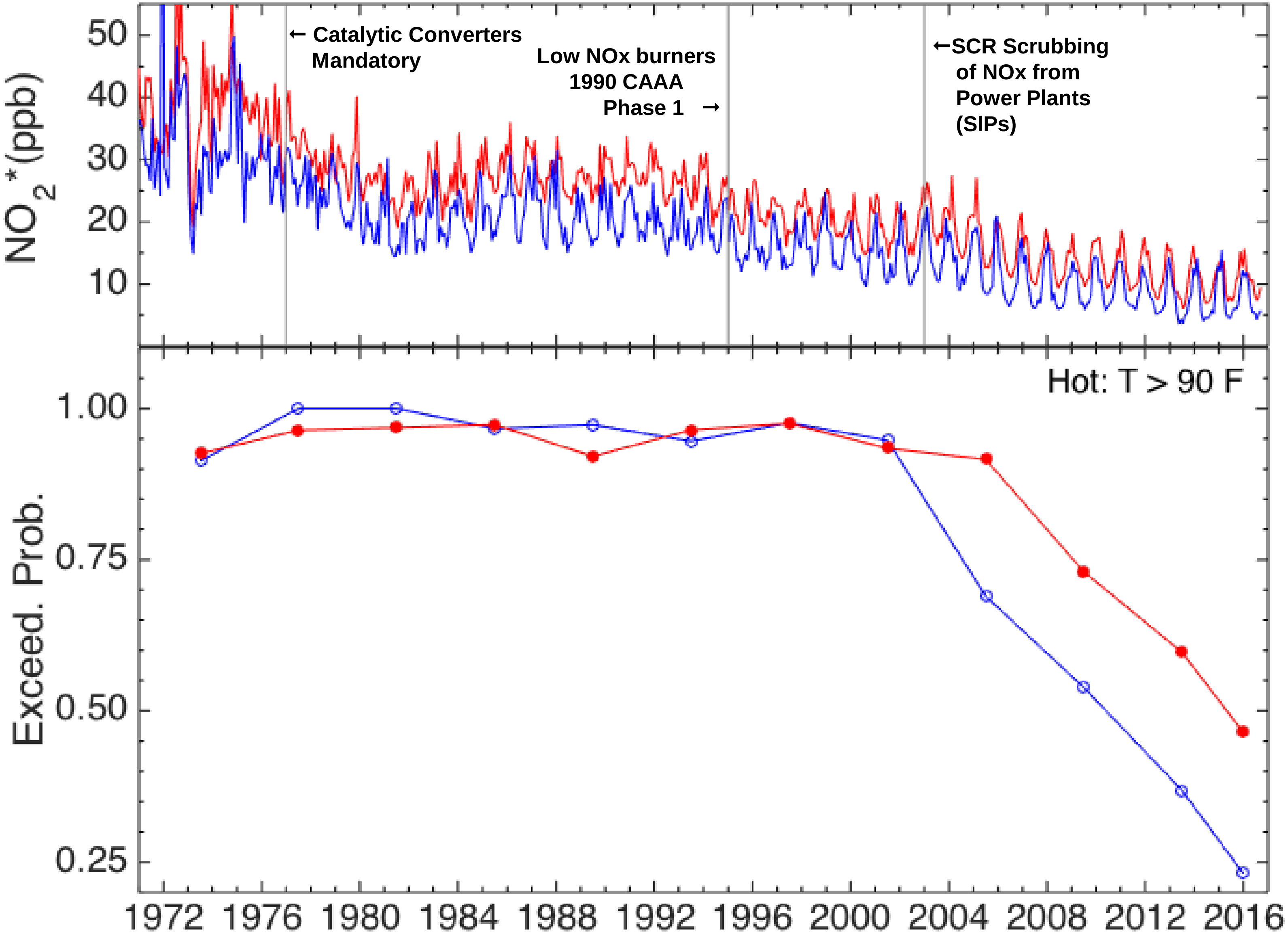
Dramatic Improvements Local Air Quality, Past 4 Decades



Dramatic Improvements Local Air Quality, Past 4 Decades

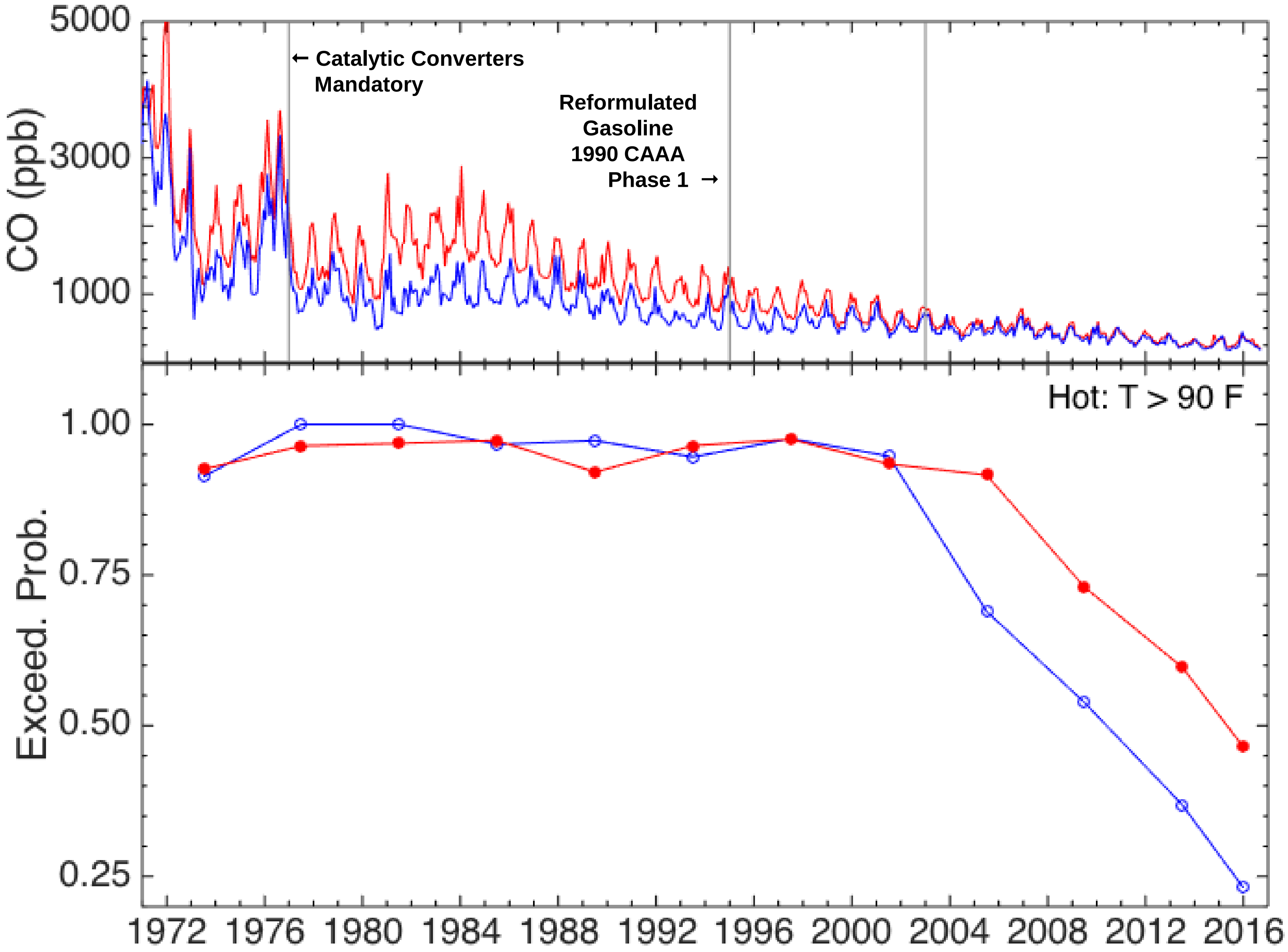


Probability of Surface O_3 Exceedance: DC, MD, and Northern VA



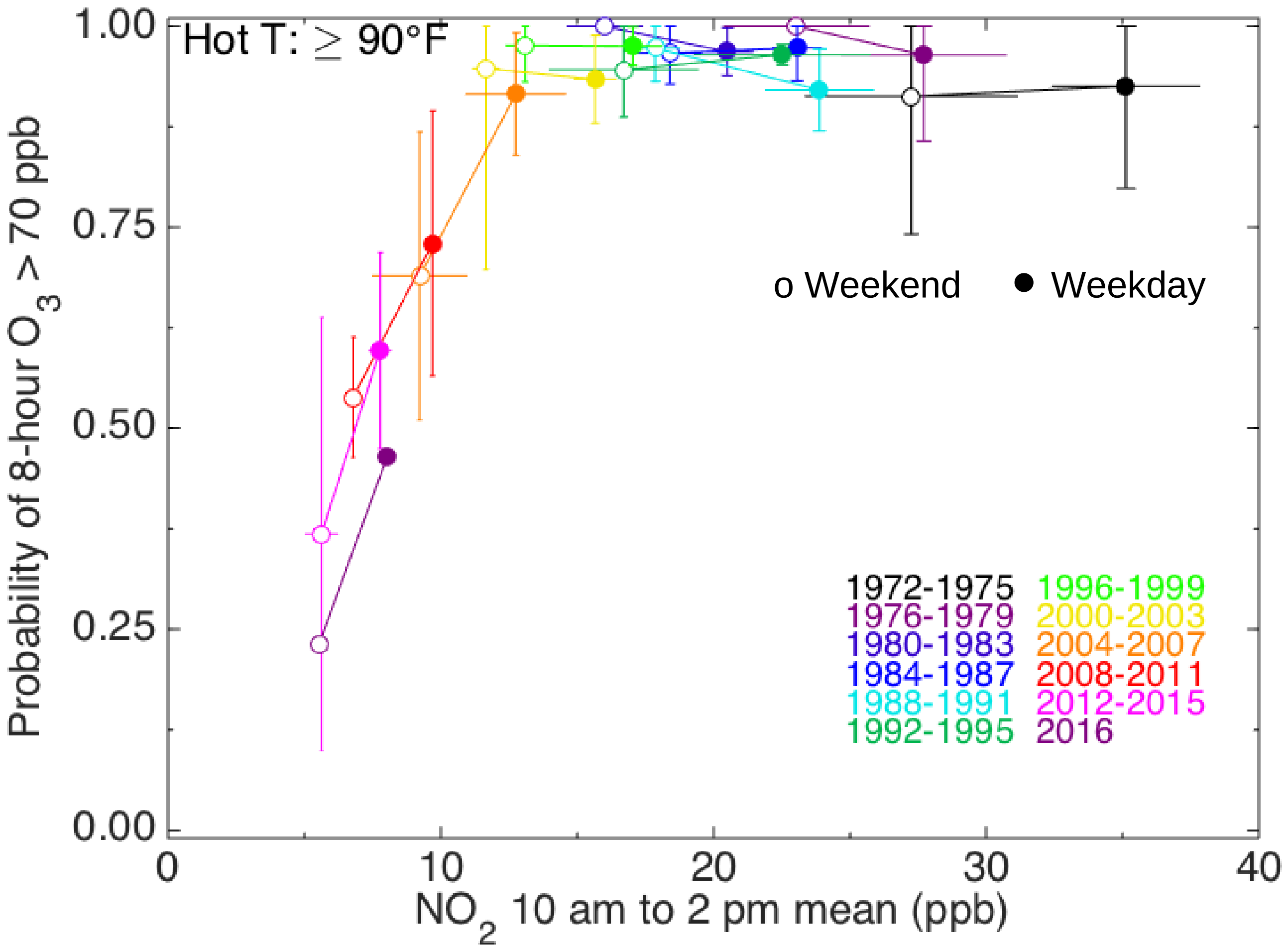
Figures above research product of UMCP Graduate Student Sandra Roberts

Probability of Surface O_3 Exceedance: DC, MD, and Northern VA



Figures above research product of UMCP Graduate Student Sandra Roberts

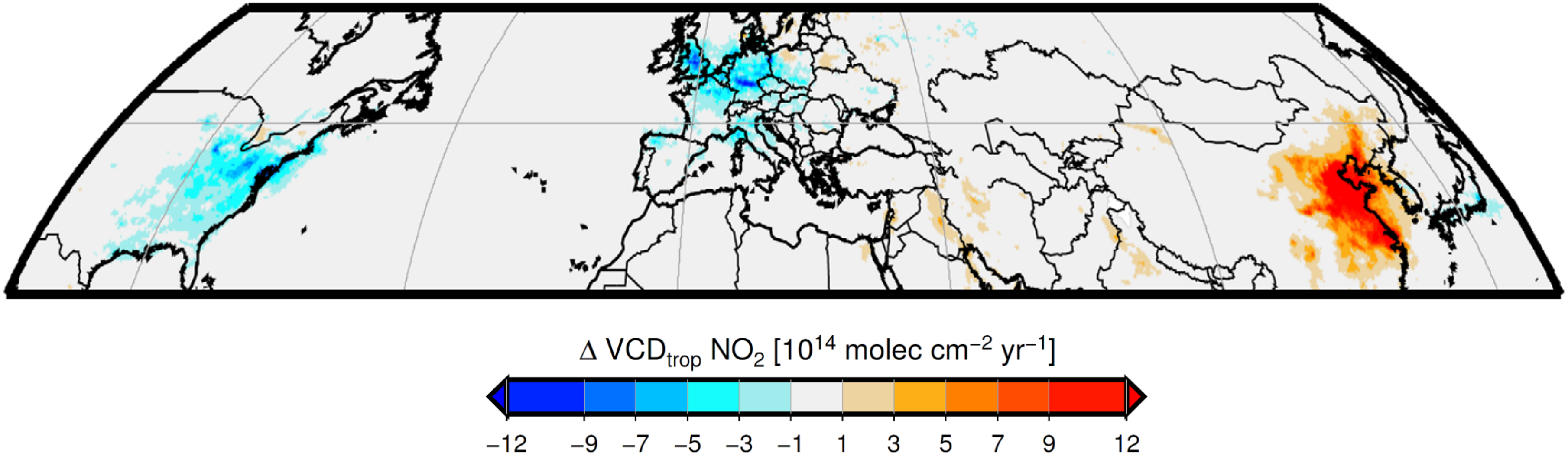
Probability of Surface O_3 Exceedance (DC, MD, No. VA) vs Daytime NO_2
Hot Summer Days (T_{BWI} > 90°F)



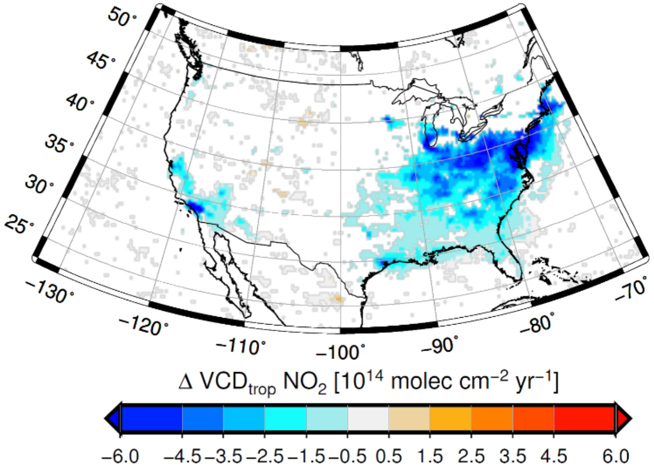
Analysis in this framework motivated by Pusede and Cohen, ACP, 2012
http://www.atmos-chem-phys.net/12/8323/2012/acp-12-8323-2012.html
Figures above research product of UMCP Graduate Student Sandra Roberts

Nitrogen Dioxide (NO_2): Combustion product that leads to formation of tropospheric ozone

Value in 2011 minus value in 2006

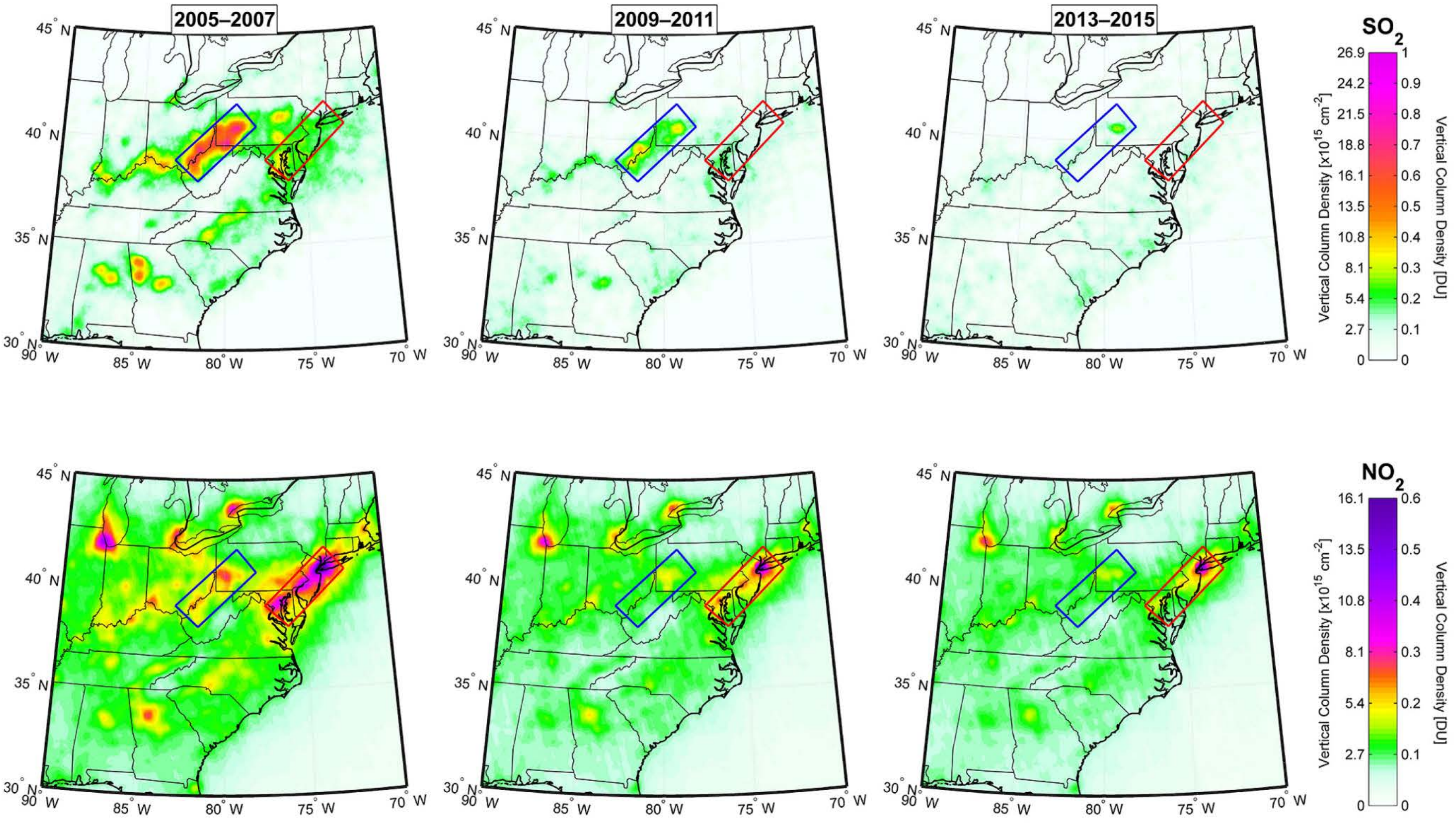


Value in 2011 minus value in 2006



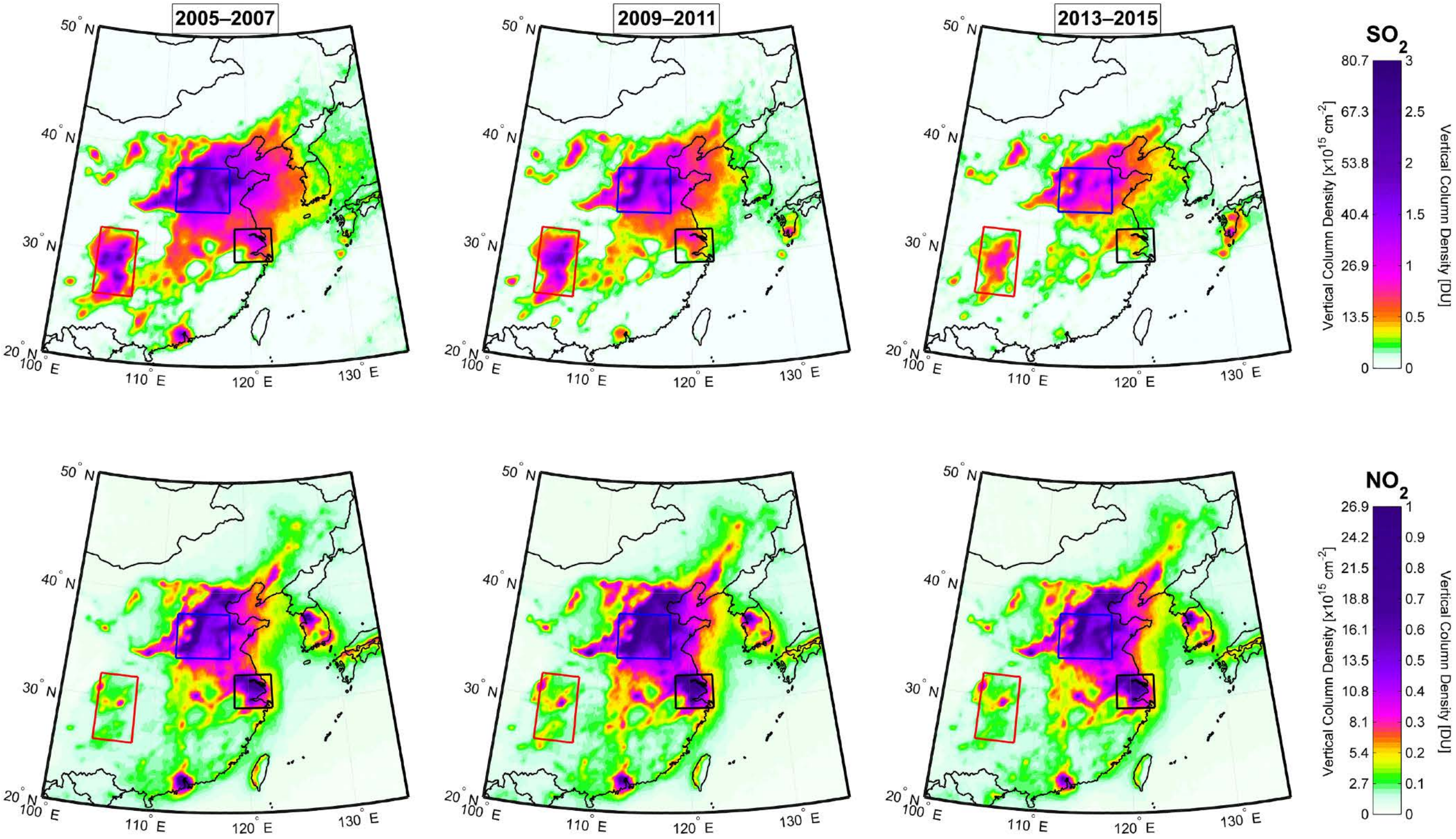
Hilboll *et al.*, *ACP*, 2013

US Trends: NO_2 and SO_2



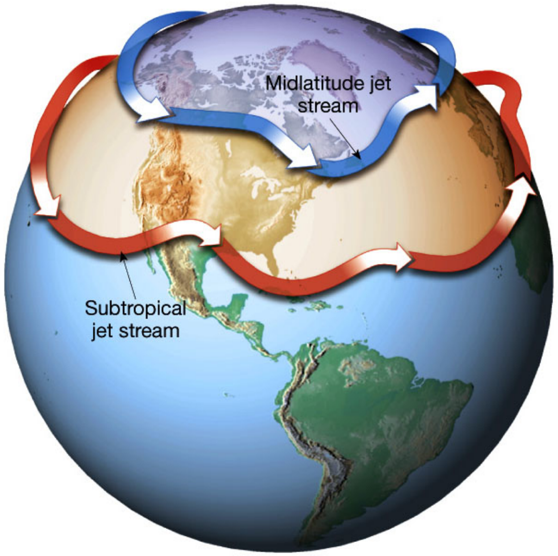
Krotkov *et al.*, *ACP*, 2016

China Trends: NO_2 and SO_2

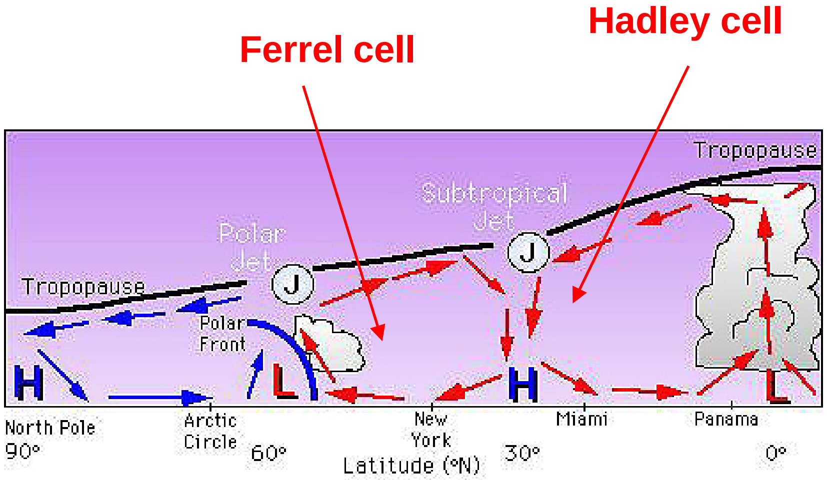


Krotkov *et al.*, *ACP*, 2016

Subtropical Jet



http://www.ux1.eiu.edu/~cfjps/1400/FIG07_014A.jpg



http://www.fas.org/irp/imint/docs/rst/Sect14/jet_stream.jpg

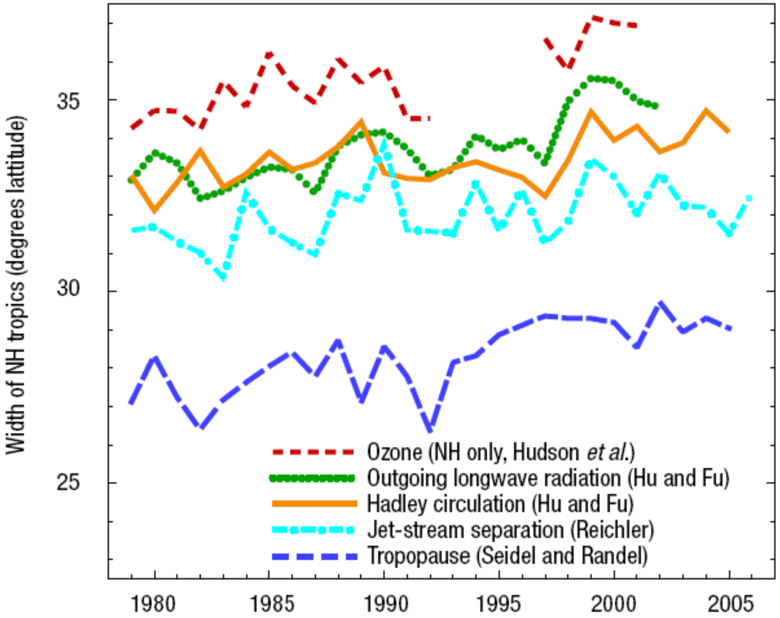
Subtropical Jet: area where poleward descending branch of the Hadley Circulation meets the equatorward descending of the Ferrel Cell (see Lecture 3)

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

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"
- Driving force: weakening of the equator to pole temperature gradient, caused by more rapid warming at high latitudes compared to tropics



Seidel et al., *Nature Geoscience*, 2008

- **Computer models predict increase in severity and duration of pollution episodes over Midwest , Mid-Atlantic, and Northeast U.S. in 2050, even for constant emissions**