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

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2020
https://myelms.umd.edu/courses/1291919

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 13

27 October 2020

Student Papers

- **Mandatory for 633 students:** paper grade will count towards final grade in an amount equal to each exam
- **Optional for 433 students:** can use paper grade to replace a ***single*** problem set grade: advisable for anyone who failed to turn in a problem set or would otherwise like to replace the grade on a problem set
- **Due Thursday, 10 Dec 2020 (last day of class)**
- **5 to 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
- Paper can build on a topic covered in class or can be on a topic related to Atmospheric Chemistry & Climate not covered in class: should have about 5 to 10 citations to material outside of that provided in class
- Request all students who will complete a paper provide a **2 to 3 sentence description of their topic one week** from today: **Tues, 3 Nov 2020**
  https://umd.instructure.com/courses/1291919/quizzes/1351196
  Please use next week to speak to exchange email with me about a topic
- Delighted to provide feedback on your paper, if given the opportunity: i.e., if you turn in a draft at least two weeks prior to the due date

Student Papers, Continued

- Academic journal articles can be accessed while through the University of Maryland library "reload button" available at:

  https://lib.guides.umd.edu/reload-button

- The link explains how to download the plugin to access a journal article. Must first go webpage of the article, then click on the "re-load button", which I have implemented as a bookmark within Mozilla Firefox.

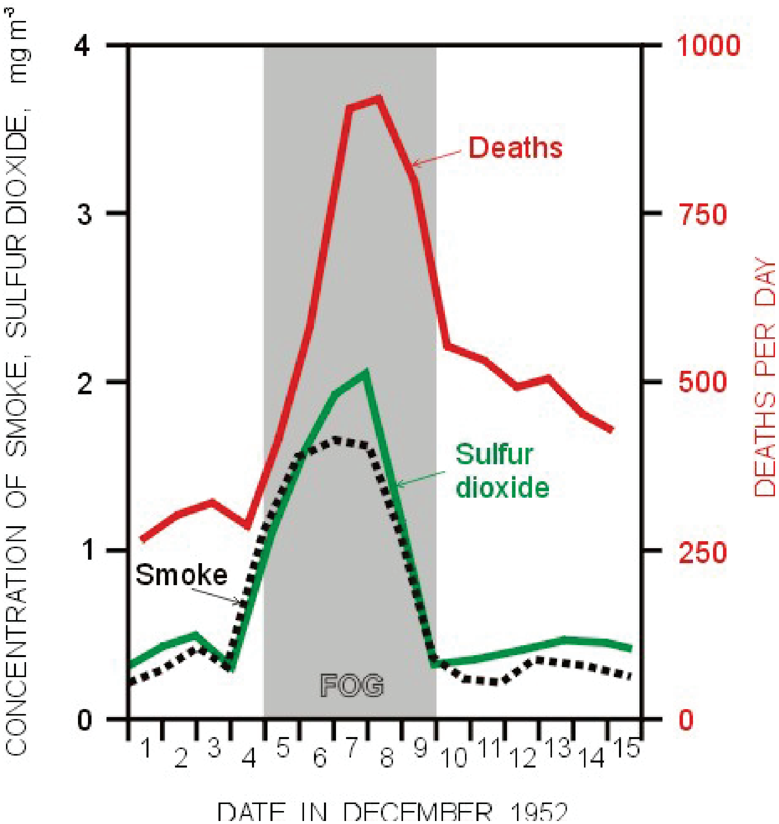
- This re-load feature works well in Google Chrome.

- May not work in Microsoft Edge.

- Please contact me if you encounter any trouble installing the reload button and accessing journal articles

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

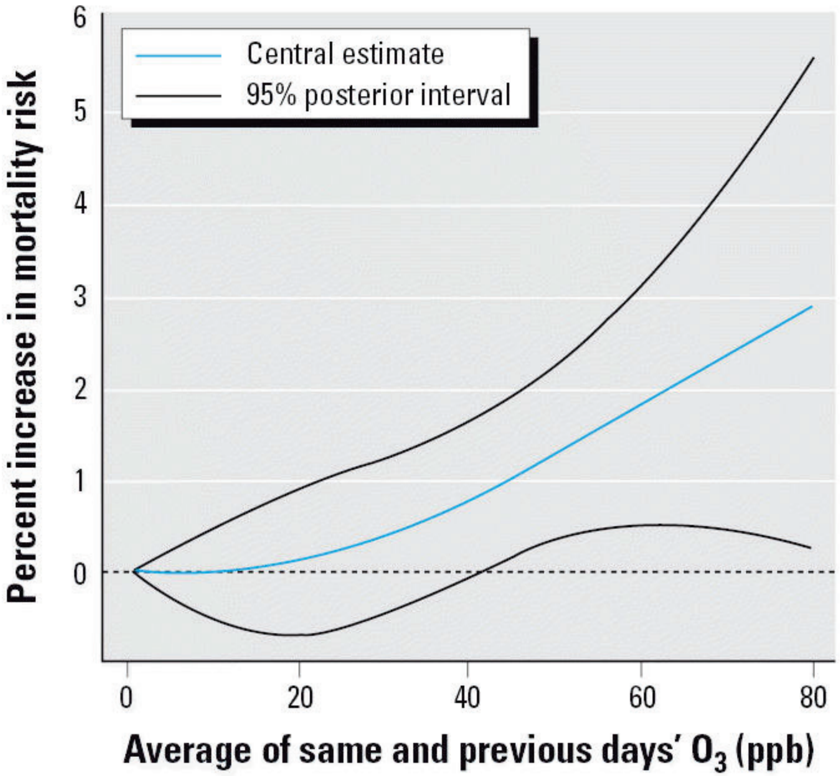
Air Quality Standards and Why We Care

For more information, have a look at:

https://www.weforum.org/agenda/2018/11/deadly-air-pollution-shortens-lives-by-nearly-2-years-researchers

https://aqli.epic.uchicago.edu/pollution-facts

Air Quality Standards and Why We Care



Increased risk of premature mortality at even low levels of surface O_3

Reductions in surface O_3 will benefit public health regardless of present conditions

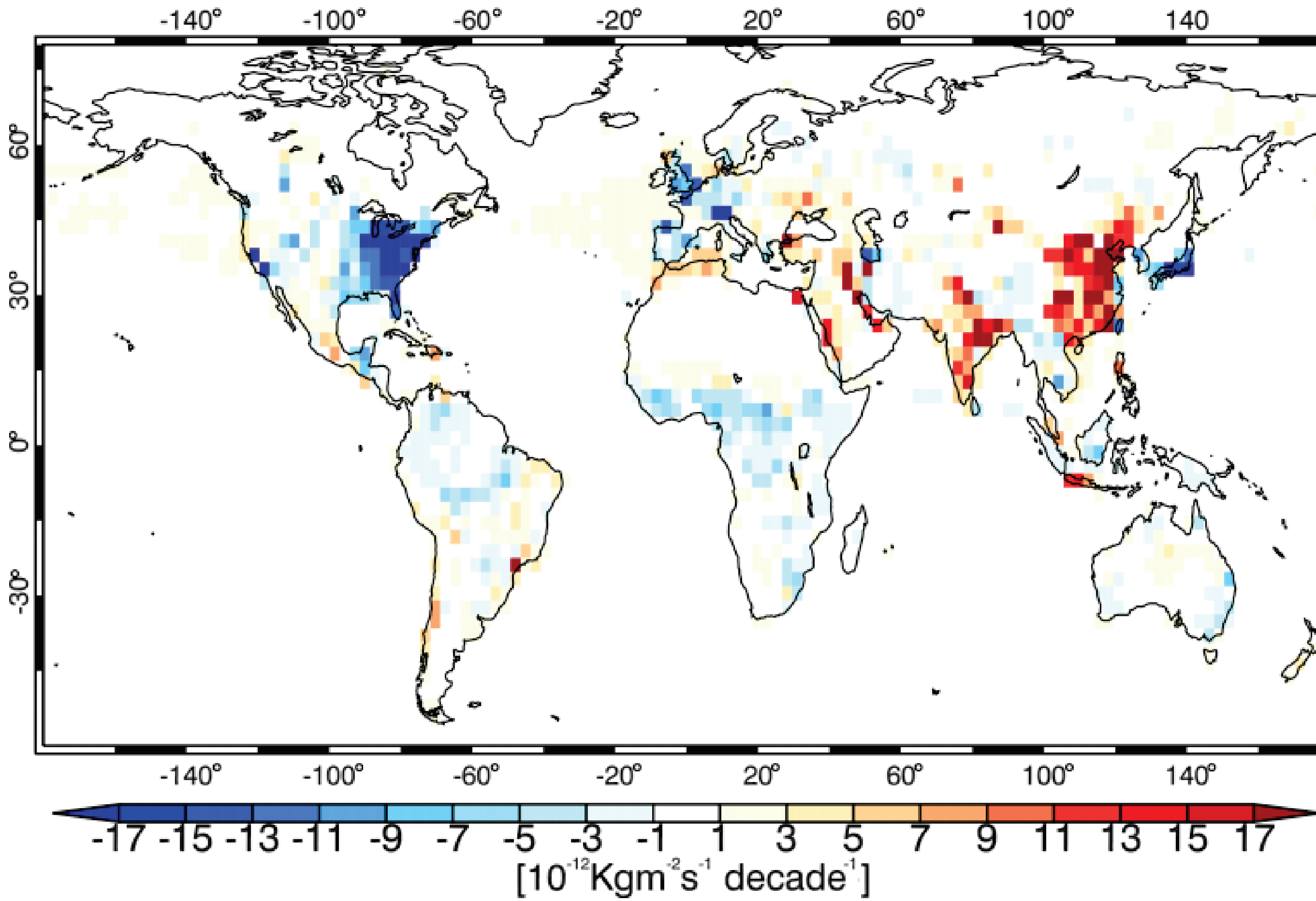
Bell et al., 2006
http://www.ncbi.nlm.nih.gov/sites/ppmc/articles/PMC1440776

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

\# 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

NOx emission trend: 2005–2014



Global distribution of the trend in the surface emission of NO_x ($NO + NO_2$) in units of kg m^{-2} s^{-1} per decade, from the assimilation of multiple satellite data sets.

Miyazaki *et al.*, *ACP*, 2017
https://www.atmos-chem-phys.net/17/807/2017/

Why do we care ?

(CNN) — Many premature deaths around the globe are due to air pollution, which can cause heart, lung and other diseases. New research suggests that a rapid reduction in air pollution emissions would save millions of lives.

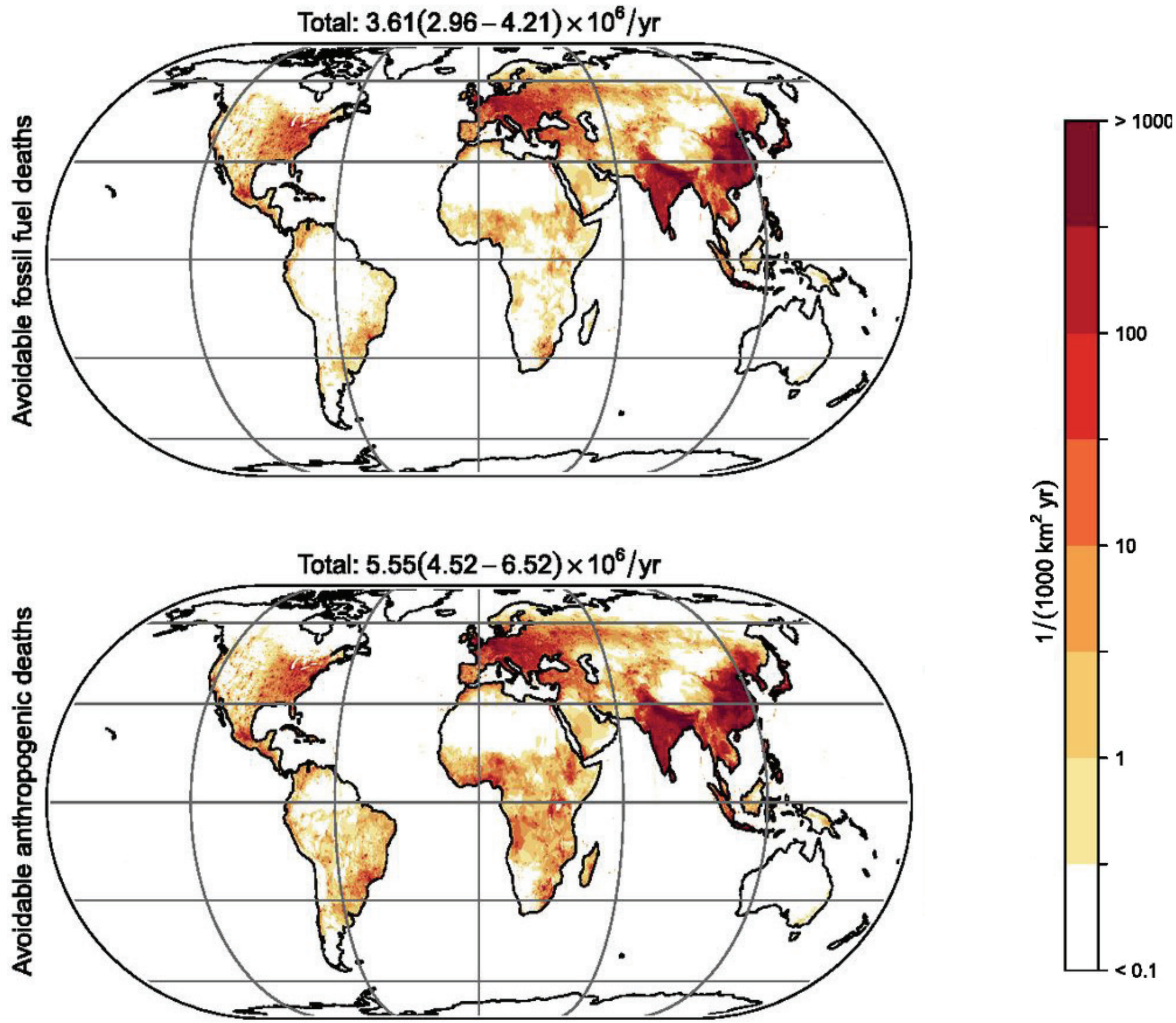
Worldwide, 3.61 million people are dying each year due to outdoor pollution caused by fossil fuels, an international team of researchers estimates. Fossil fuels, including coal, oil and natural gas, are responsible for about 78% of global greenhouse gas emissions, according to the US Environmental Protection Agency (and about 76% of US greenhouse gas emissions).

An additional 1.94 million premature deaths occur as a result of air pollution from other sources, including residential energy use and agricultural activities, according to the authors.

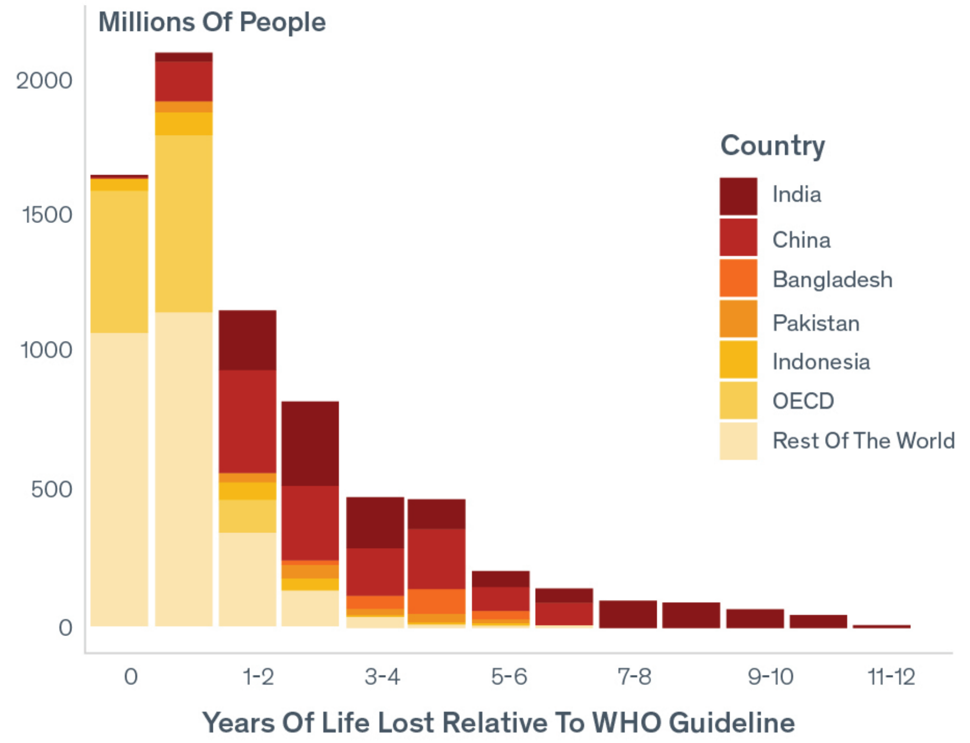
Beyond the direct health benefits, rapidly decreasing fossil fuel emissions would increase rainfall in drought-prone regions and boost food security, they say.

https://www.cnn.com/2019/03/25/health/air-pollution-emissions-study/index.html

Why do we care ?



Lelieveld et al., PNAS, 2019 https://www.pnas.org/content/116/15/7192



If all areas not in compliance with the WHO $PM_{2.5}$ guideline in 2016 were to permanently reduce their particulate pollution levels to meet the guideline, then, globally:

- 288 million people, all in northern India would live at least 7 years longer on average. These people represent 23 percent of India's current population.
- 347 million people in Asia would live 5-7 years longer on average. These include 35 percent of Nepal's population, 16 percent of Bangladeshis, 13 percent of Chinese, 10 percent of Pakistanis, 9 percent of Indians, and 1 percent of Indonesians.

https://aqli.epic.uchicago.edu/pollution-facts

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/m³)	
Carbon monoxide			
8-hr average	9	10,000	
1-hr average	35	40,000	
Nitrogen dioxide			
Annual average	0.053	100	← 1 hr 100 ppb is primary standard, Feb 2010
Ozone			
8-hr average	0.075	147	← 8 hr 70 ppb is standard, Oct 2015
1-hr average	0.12	235	
*Particulates**			
PM_{10}, annual average	—	~~50~~	← No annual average standard, Dec 2012
PM_{10}, 24-hr average	—	150	
$PM_{2.5}$, annual average	—	~~15~~	← Lowered to 12 μg/m³, Dec 2012
$PM_{2.5}$, 24-hr average†	—	35	
Sulfur dioxide			
Annual average	0.03	80	
24-hr average	0.14	365	← 1 hr , 75 ppb is primary standard, Jun 2010
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.

Chemistry in Context

Criteria pollutant: common-place and detrimental to human welfare

Tropospheric Pollutants (The Air We Breathe)

Primary Pollutants

Table 1.2 U.S. National Ambient Air Quality Standards

Pollutant	Standard (ppm)	Approximate Equivalent Concentration ($\mu g/m^3$)
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.

Primary Pollutants

Chemistry in Context

Primary pollutant emitted directly into the atmosphere and retains same chemical form

Tropospheric Pollutants (The Air We Breathe)

Secondary Pollutants

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

Secondary Pollutants

Secondary pollutant: formed by atmospheric reactions involving chemical precursors. Control generally more challenging than primary pollutants because mitigation of secondary pollutants requires identification of the precursor compounds, quantification of sources, and detailed understanding of the chemical reactions that form the secondary pollutant (*chemical mechanism*)

Significant Improvements in U.S. Air Quality, 1980 to 2006

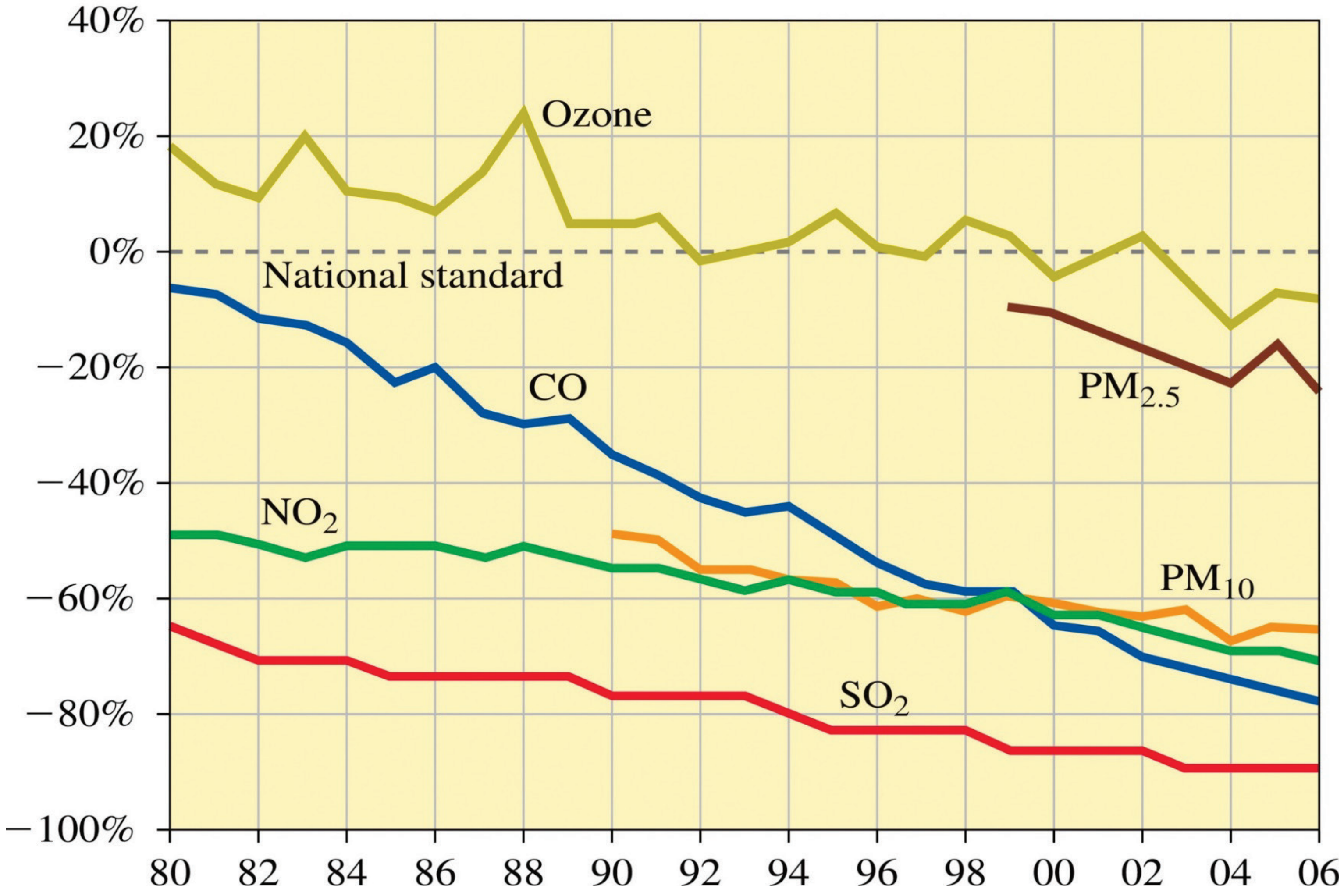
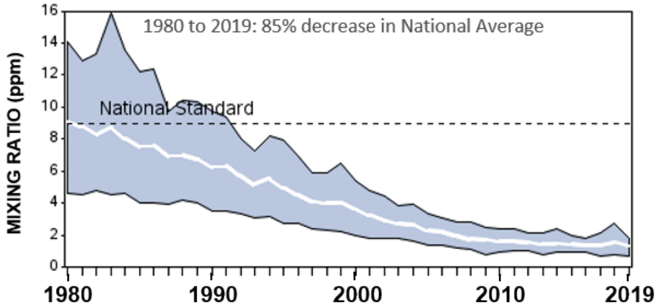


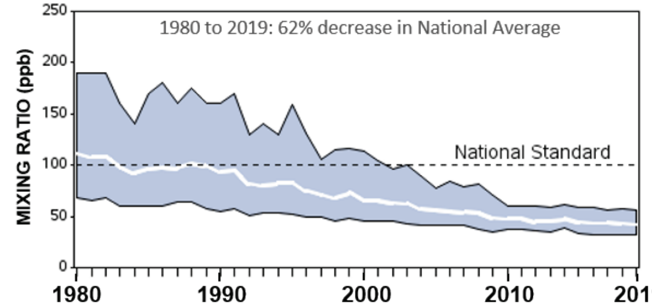
Figure 1.8, Chemistry in Context

Significant Improvements in U.S. Air Quality, Past 4 Decades

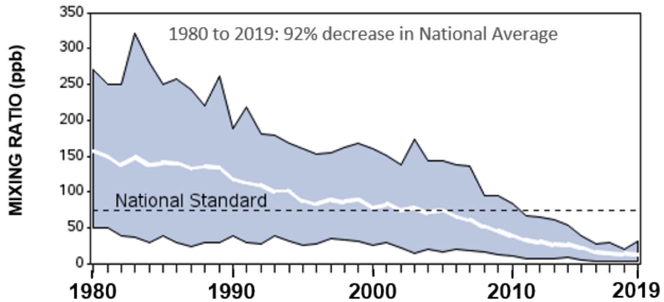
CO Air Quality, 1980 to 2019
Annual 2nd Maximum 8-Hour Average
National Trend based on 41 Sites



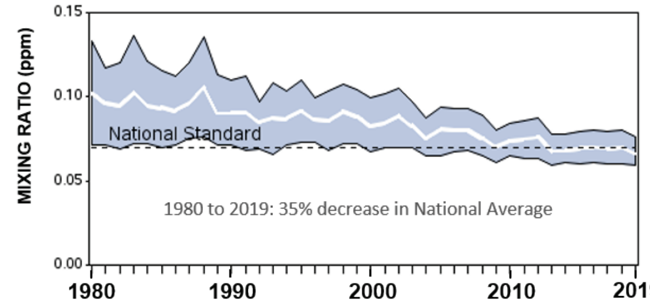
NO_2 Air Quality, 1980 to 2019
Annual 98th Percentile of Daily Max 1-Hour Average
National Trend based on 21 Sites



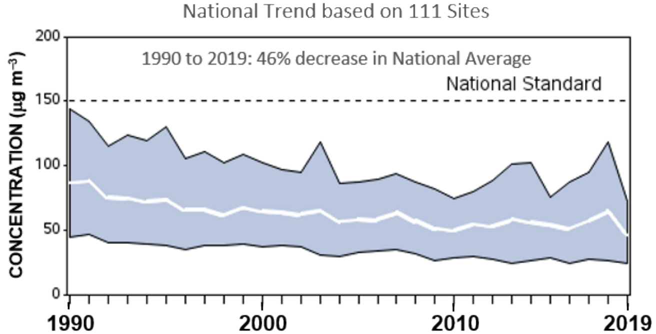
SO_2 Air Quality, 1980 to 2019
Annual 99th Percentile of Daily Max 1-Hour Average
National Trend based on 35 Sites



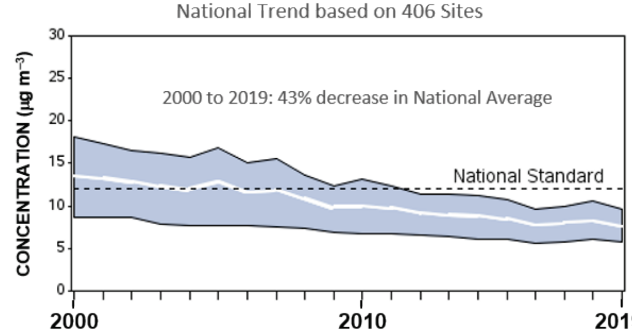
O_3 Air Quality, 1980 to 2019
Annual 4th Maximum 8-Hour Average
National Trend based on 193 Sites



PM_{10} Air Quality, 1990 to 2019
Annual 4th Maximum 24-Hour Average
National Trend based on 111 Sites

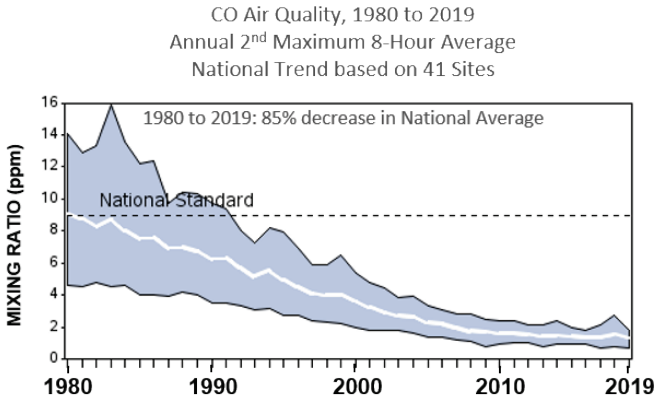


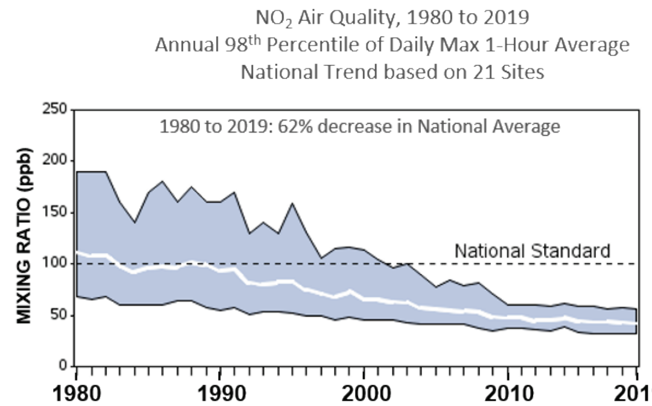
$PM_{2.5}$ Air Quality, 2000 to 2019
Seasonally-Weighted Annual Average
National Trend based on 406 Sites

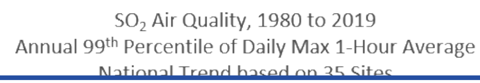


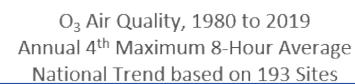
https://www.epa.gov/air-trends

Significant Improvements in U.S. Air Quality, Past 4 Decades

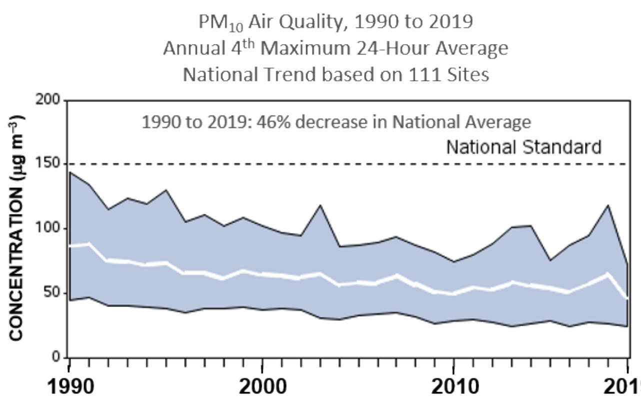


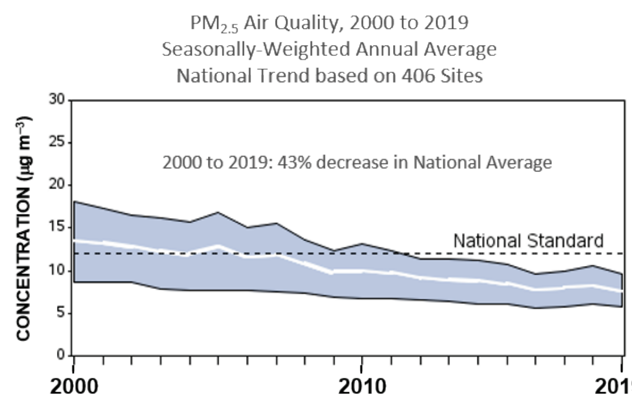






What three pollutants that are most directly tied to elevated levels of tropospheric ozone emerge from the tailpipes of automobiles ***and*** what is the chemical origin of these pollutants?

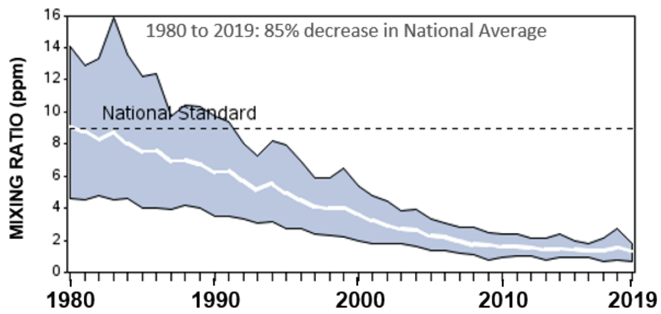




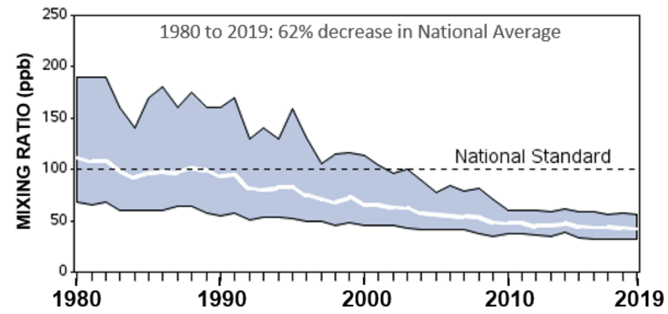
https://www.epa.gov/air-trends

Significant Improvements in U.S. Air Quality, Past 4 Decades

CO Air Quality, 1980 to 2019
Annual 2nd Maximum 8-Hour Average
National Trend based on 41 Sites



NO_2 Air Quality, 1980 to 2019
Annual 98th Percentile of Daily Max 1-Hour Average
National Trend based on 21 Sites



SO_2 Air Quality, 1980 to 2019
Annual 99th Percentile of Daily Max 1-Hour Average
National Trend based on 35 Sites

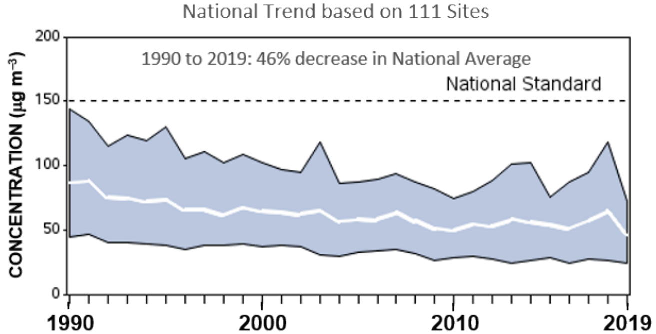
O_3 Air Quality, 1980 to 2019
Annual 4th Maximum 8-Hour Average
National Trend based on 193 Sites

What three pollutants that are most directly tied to elevated levels of tropospheric ozone emerge from the tailpipes of automobiles ***and*** what is the chemical origin of these pollutants?

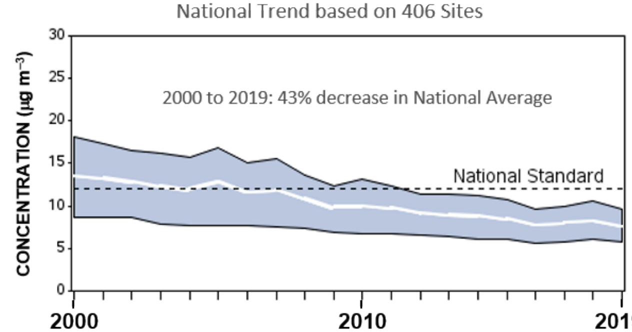
One of the most important actions for air quality undertaken by governments of the developed world has been mandatory use of catalytic convertors on automobiles, coupled with robust inspection programs.

Which pollutants, involved in the formation of tropospheric ozone, are controlled by catalytic convertors?

PM_{10} Air Quality, 1990 to 2019
Annual 4th Maximum 24-Hour Average
National Trend based on 111 Sites



$PM_{2.5}$ Air Quality, 2000 to 2019
Seasonally-Weighted Annual Average
National Trend based on 406 Sites



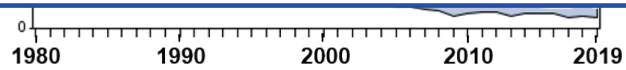
https://www.epa.gov/air-trends

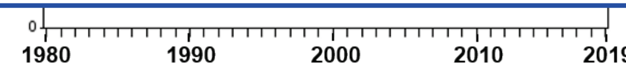
Significant Improvements in U.S. Air Quality, Past 4 Decades

CO Air Quality, 1980 to 2019
Annual 2nd Maximum 8-Hour Average
National Trend based on 41 Sites

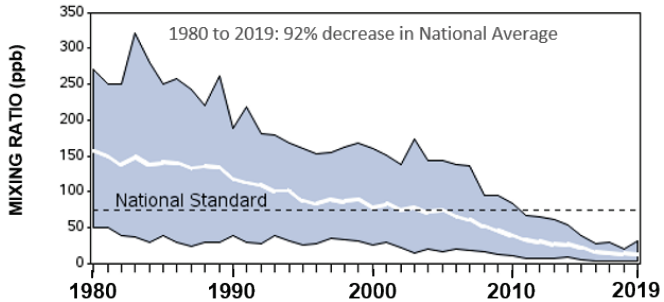
NO$_2$ Air Quality, 1980 to 2019
Annual 98th Percentile of Daily Max 1-Hour Average
National Trend based on 21 Sites

What aspect of air pollution mentioned in Chapter 1 is ***most uniquely*** associated with human use of coal?

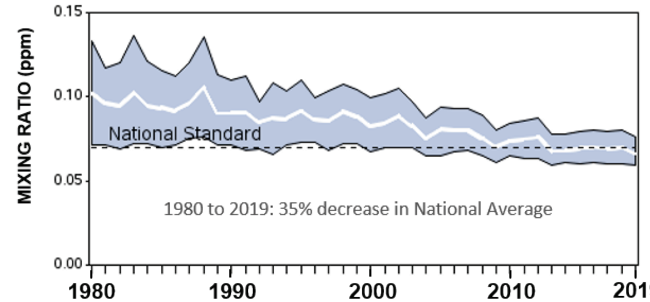




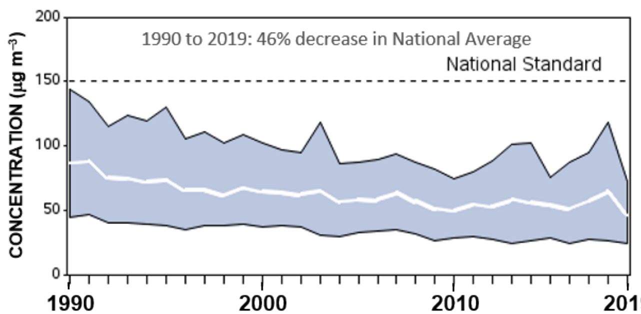
SO$_2$ Air Quality, 1980 to 2019
Annual 99th Percentile of Daily Max 1-Hour Average
National Trend based on 35 Sites



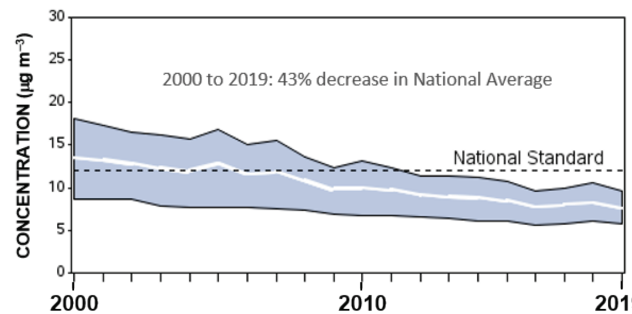
O$_3$ Air Quality, 1980 to 2019
Annual 4th Maximum 8-Hour Average
National Trend based on 193 Sites



PM$_{10}$ Air Quality, 1990 to 2019
Annual 4th Maximum 24-Hour Average
National Trend based on 111 Sites



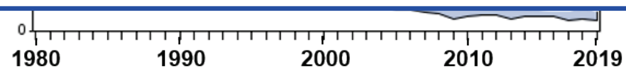
PM$_{2.5}$ Air Quality, 2000 to 2019
Seasonally-Weighted Annual Average
National Trend based on 406 Sites



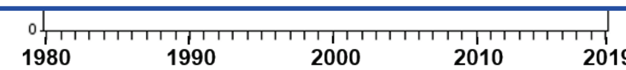
https://www.epa.gov/air-trends

Significant Improvements in U.S. Air Quality, Past 4 Decades

CO Air Quality, 1980 to 2019
Annual 2nd Maximum 8-Hour Average
National Trend based on 41 Sites



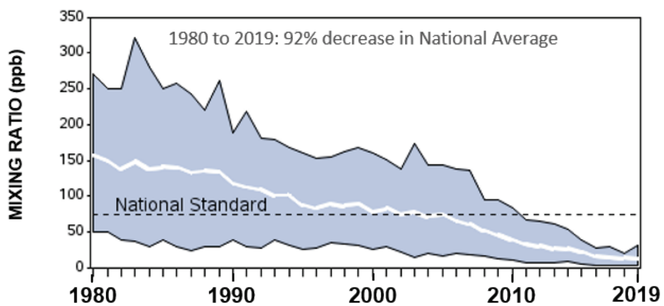
NO_2 Air Quality, 1980 to 2019
Annual 98th Percentile of Daily Max 1-Hour Average
National Trend based on 21 Sites



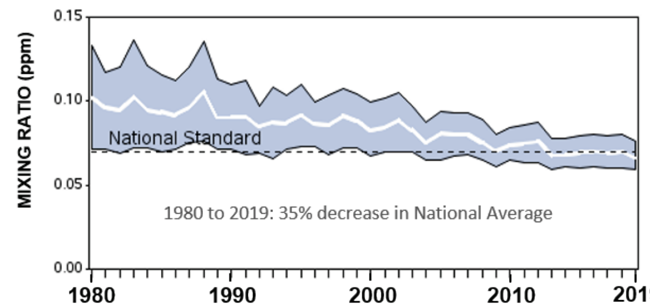
What aspect of air pollution mentioned in Chapter 1 is ***most uniquely*** associated with human use of coal?

For the aspect of air pollution that is most uniquely associated with human use of coal, what property of this pollutant determines whether it can penetrate deeply into human lungs?

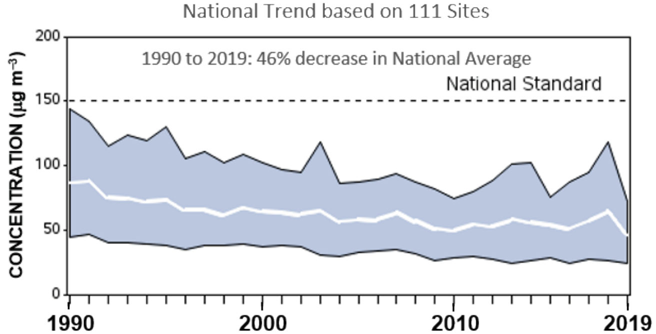
SO_2 Air Quality, 1980 to 2019
Annual 99th Percentile of Daily Max 1-Hour Average
National Trend based on 35 Sites



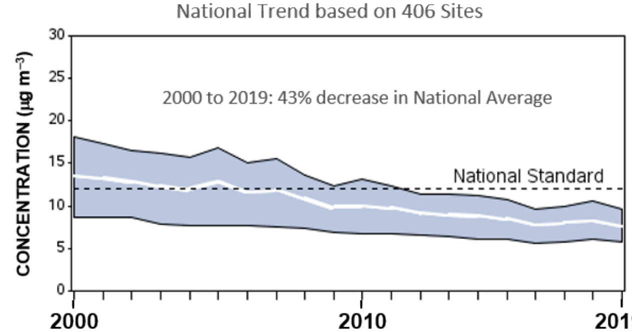
O_3 Air Quality, 1980 to 2019
Annual 4th Maximum 8-Hour Average
National Trend based on 193 Sites



PM_{10} Air Quality, 1990 to 2019
Annual 4th Maximum 24-Hour Average
National Trend based on 111 Sites

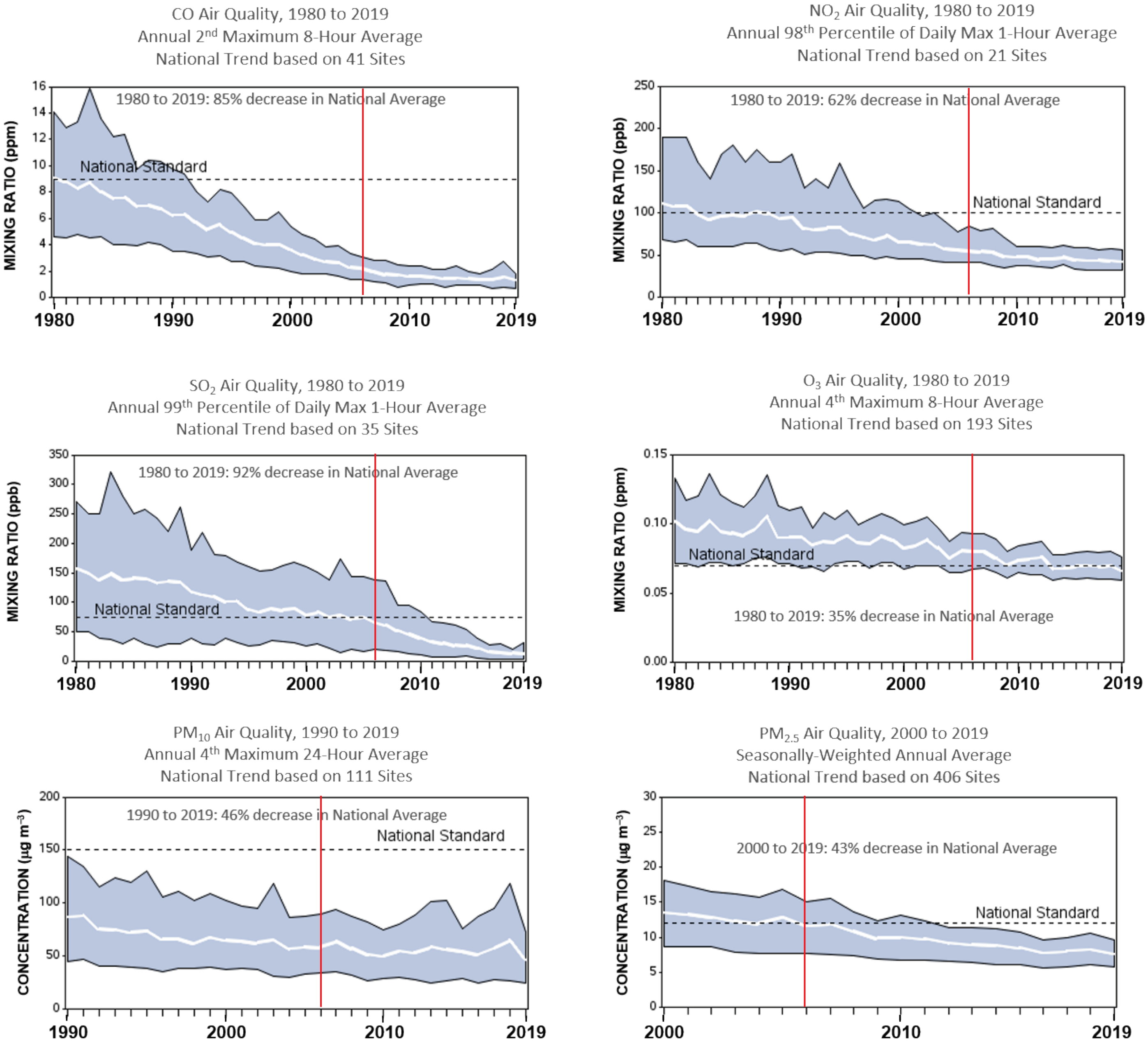


$PM_{2.5}$ Air Quality, 2000 to 2019
Seasonally-Weighted Annual Average
National Trend based on 406 Sites



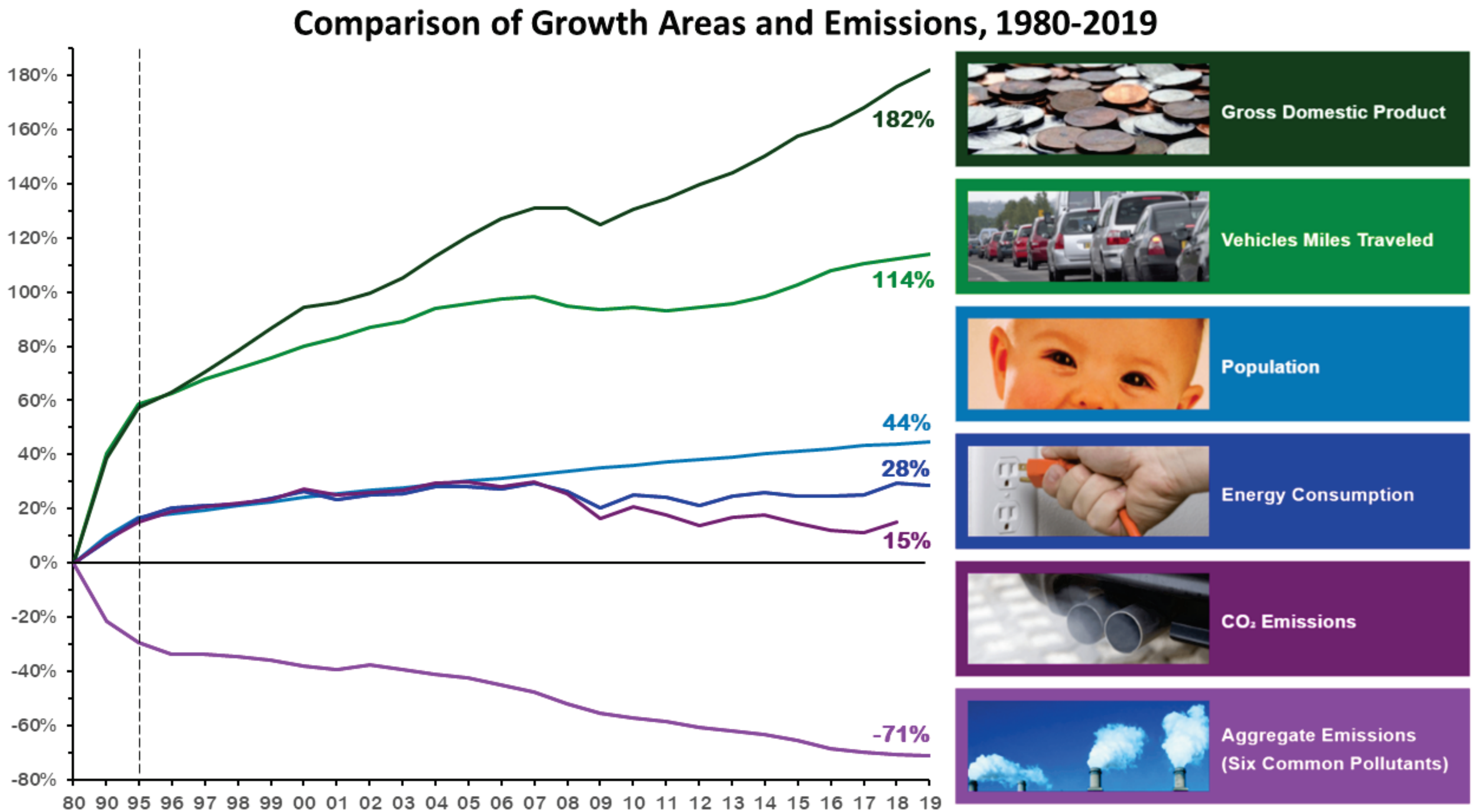
https://www.epa.gov/air-trends

Significant Improvements in U.S. Air Quality, Past 4 Decades



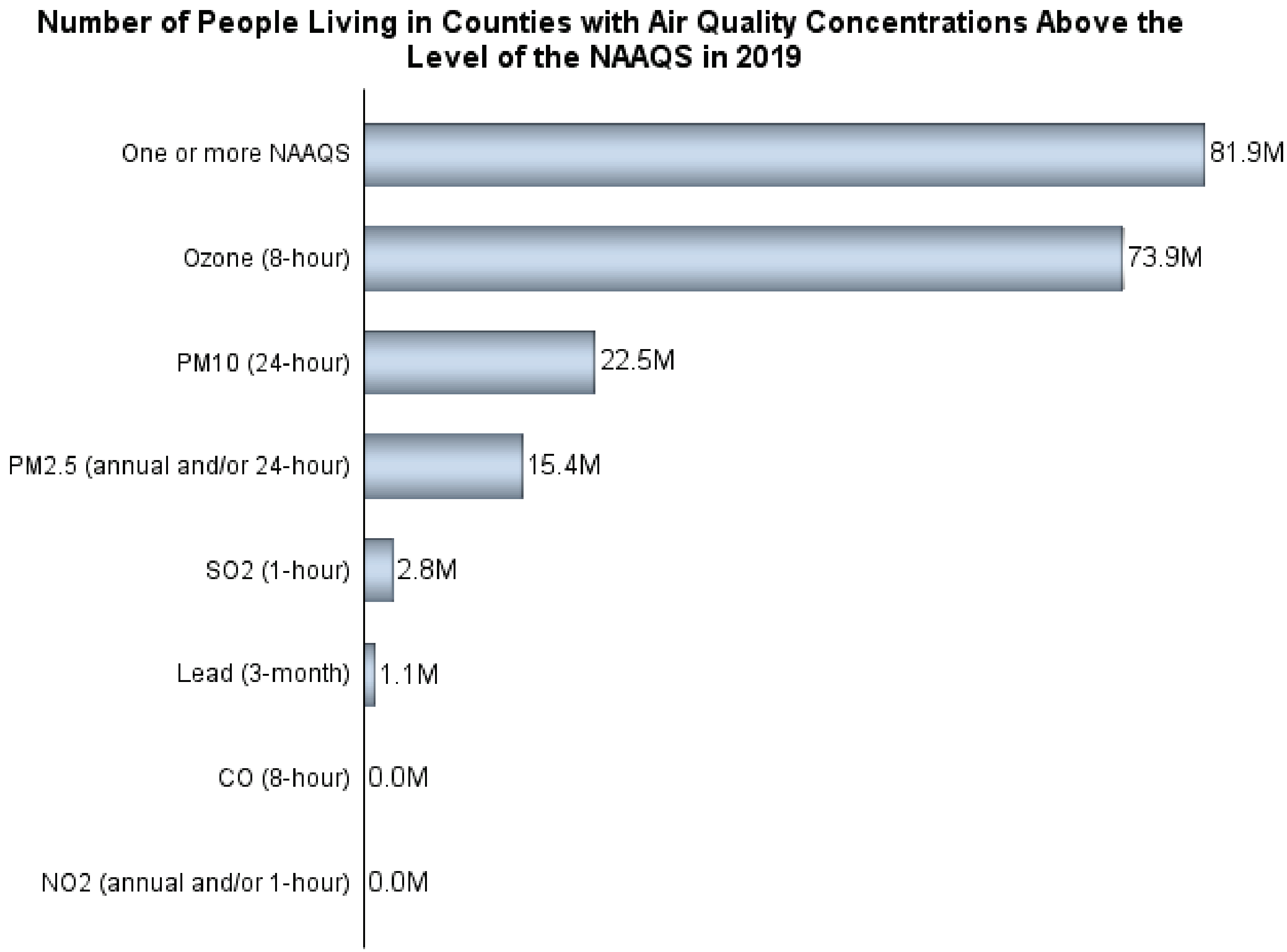
https://www.epa.gov/air-trends

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



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

Alas, much of the Developing World still experiences poor Air Quality



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

Tropospheric Ozone Production

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

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

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

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

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

Tropospheric Ozone Production

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

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

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

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

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

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

Oxidation of CO in the presence of NO_x (NO & NO_2) leads to production of tropospheric O_3

Tropospheric Ozone Production

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

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

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

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

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

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

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

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

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

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

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

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

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

Oxidation of CO in the presence of NO_x (NO & NO_2) leads to production of tropospheric O_3

***Key chemical aspect* :**

NO converted to NO_2 without consumption of O_3

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: **????????** $\rightarrow$ **????????**

Tropospheric Ozone Production

Suppose NO is converted to NO_2 by reaction with O_3 :

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

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

$$NO + O_3 \rightarrow NO_2 + O_2$$

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

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

$$\text{Net: } CO + O_2 + OH \rightarrow CO_2 + HO_2$$

No ozone production!

Tropospheric Ozone Production

***Suppose* NO *is converted to* NO$_2$ *by reaction with* O$_3$:**

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

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

$$NO + O_3 \rightarrow NO_2 + O_2$$

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

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

$$\text{Net: } CO + O_2 + OH \rightarrow CO_2 + HO_2$$

Next key question: ????????

Tropospheric Ozone Production

***Suppose* NO *is converted to* NO_2 *by reaction with* O_3 :**

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

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

$$NO + O_3 \rightarrow NO_2 + O_2$$

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

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

$$\text{Net: } CO + O_2 + OH \rightarrow CO_2 + HO_2$$

Next key question: how does HO_2 go back to OH ?

Tropospheric Ozone Production

Suppose NO is converted to NO_2 by reaction with O_3 :

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

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

$$NO + O_3 \rightarrow NO_2 + O_2$$

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

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

~~Net: $CO + O_2 + OH \rightarrow CO_2 + HO_2$~~

$$HO_2 + O_3 \rightarrow OH + 2\ O_2$$

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

Tropospheric Ozone Production

***Suppose* NO *is converted to* NO_2 *by reaction with* O_3 :**

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

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

$$NO + O_3 \rightarrow NO_2 + O_2$$

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

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

~~Net: $CO + O_2 + OH \rightarrow CO_2 + HO_2$~~

$$HO_2 + O_3 \rightarrow OH + 2\ O_2$$

$$\text{Net: } CO + O_3 \rightarrow CO_2 + O_2$$

Have now consumed O_3 because it is used to convert NO to NO_2 and HO_2 to OH !

Tropospheric Ozone Production

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

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

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

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

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

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

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 *crucial* 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

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$\text{Net:} \quad CO + 2\,O_2 \rightarrow CO_2 + O_3$$

$$RH + OH \rightarrow R + H_2O$$
$$R + O_2 + M \rightarrow RO_2 + M$$
$$RO_2 + NO \rightarrow RO + NO_2$$
$$RO + O_2 \rightarrow HO_2 + R'CHO$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$2 \times \quad NO_2 + h\nu \rightarrow NO + O$$
$$2 \times \quad O + O_2 + M \rightarrow O_3 + M$$
$$\text{Net:} \quad RH + 4O_2 \rightarrow R'CHO + H_2O + 2\,O_3$$

VOC: Volatile Organic Compounds

Produced by trees, fossil fuel vapor, and non-controlled auto emissions

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

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

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

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

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

Tropospheric Ozone Production

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

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

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

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

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

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

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

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

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

High NO_x ($NO+NO_2$) forces termination via this route!

Tropospheric Ozone Production

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

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

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

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

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

High NO_x ($NO+NO_2$) forces termination via this route!

As NO rises, [HO_2]/[OH] ratio falls (HO_2 titrated to OH)

As NO_x rises, [HO_2] falls faster than [NO] rises

⇨ What will happen to production of O_3 ?

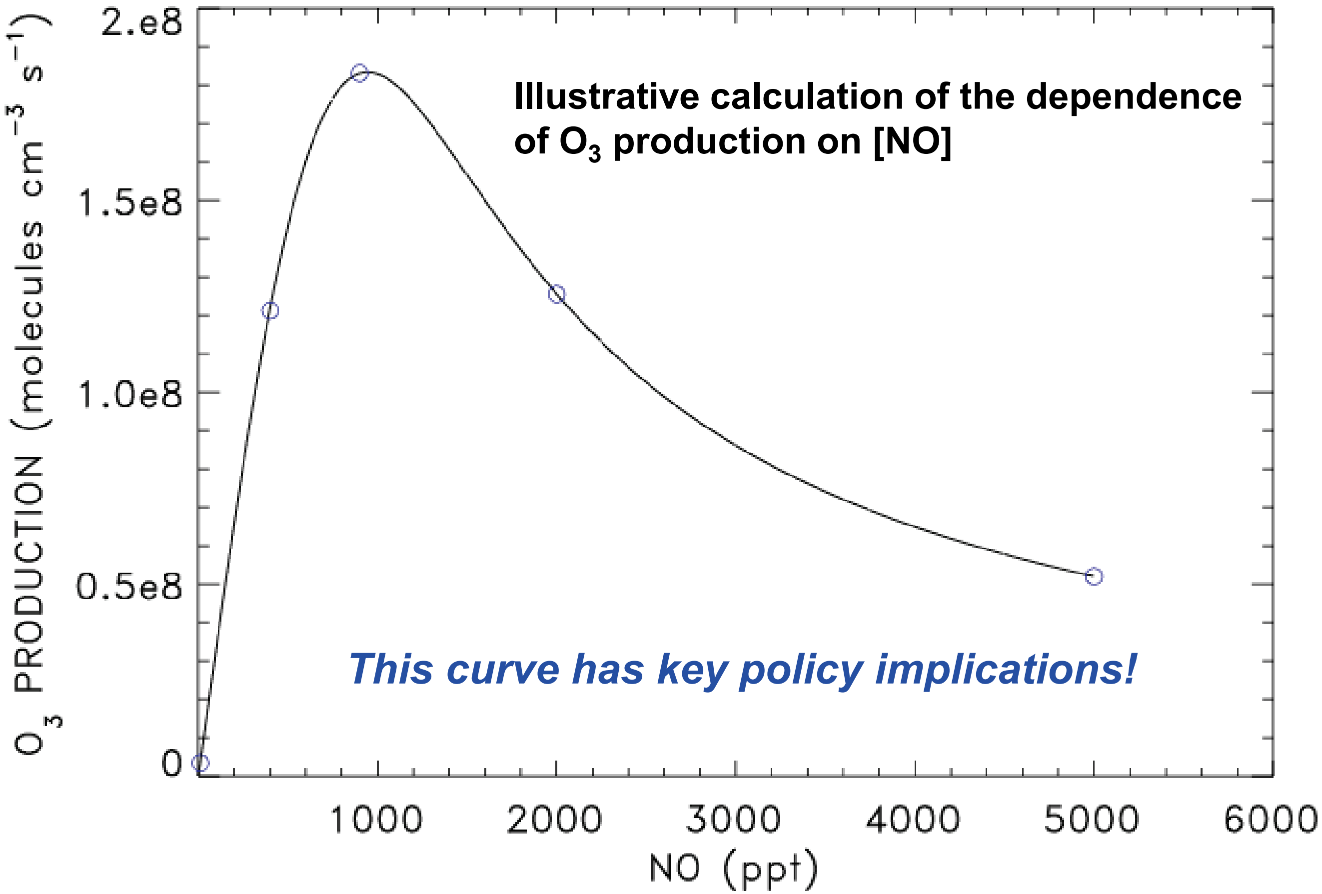
Tropospheric Ozone Production versus NO

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.



Tropospheric Ozone Production versus NO_x and VOCs

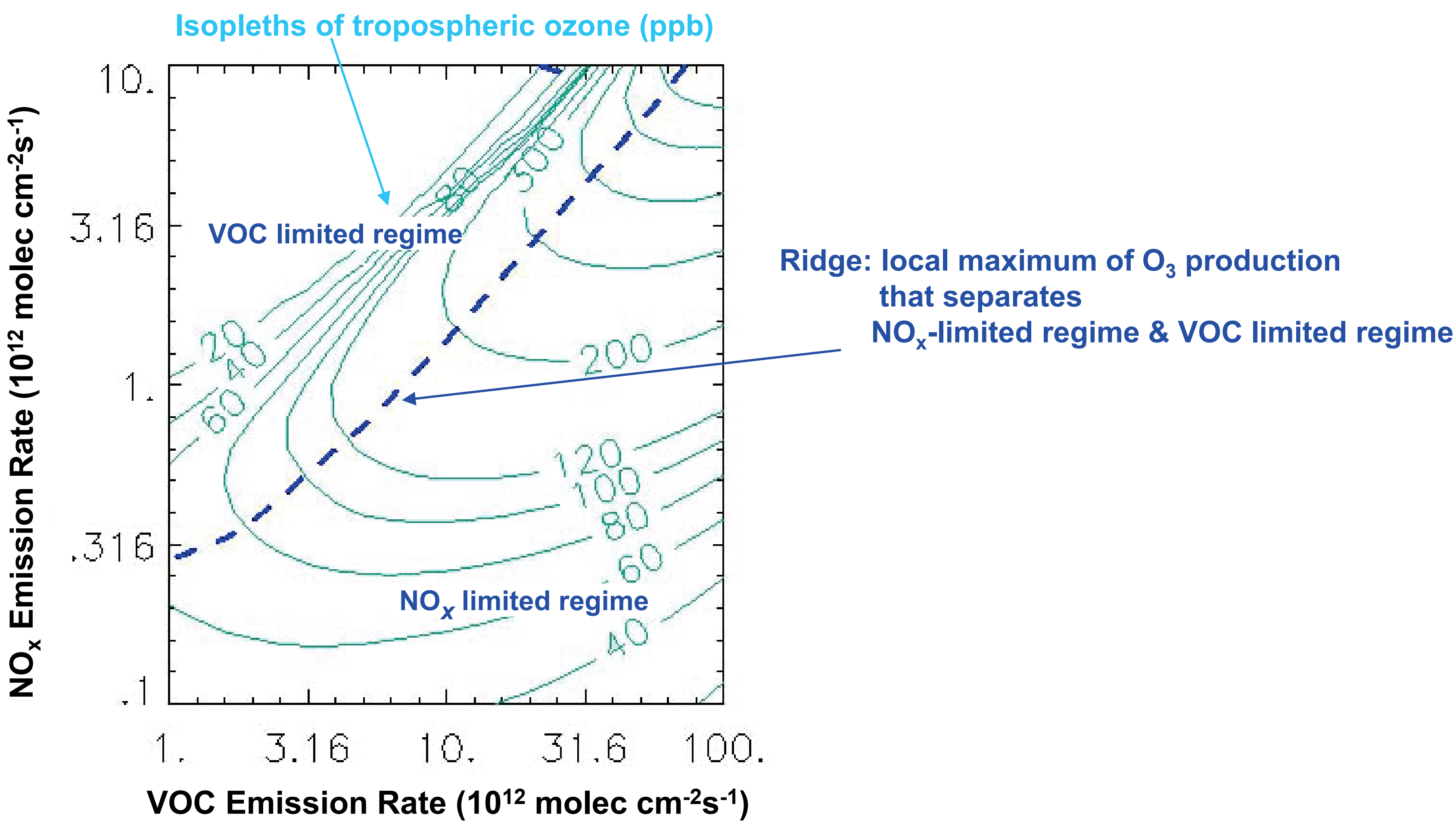


Figure: http://www-personal.umich.edu/~sillman/ozone.htm

Tropospheric Ozone Production versus NO_x and VOCs

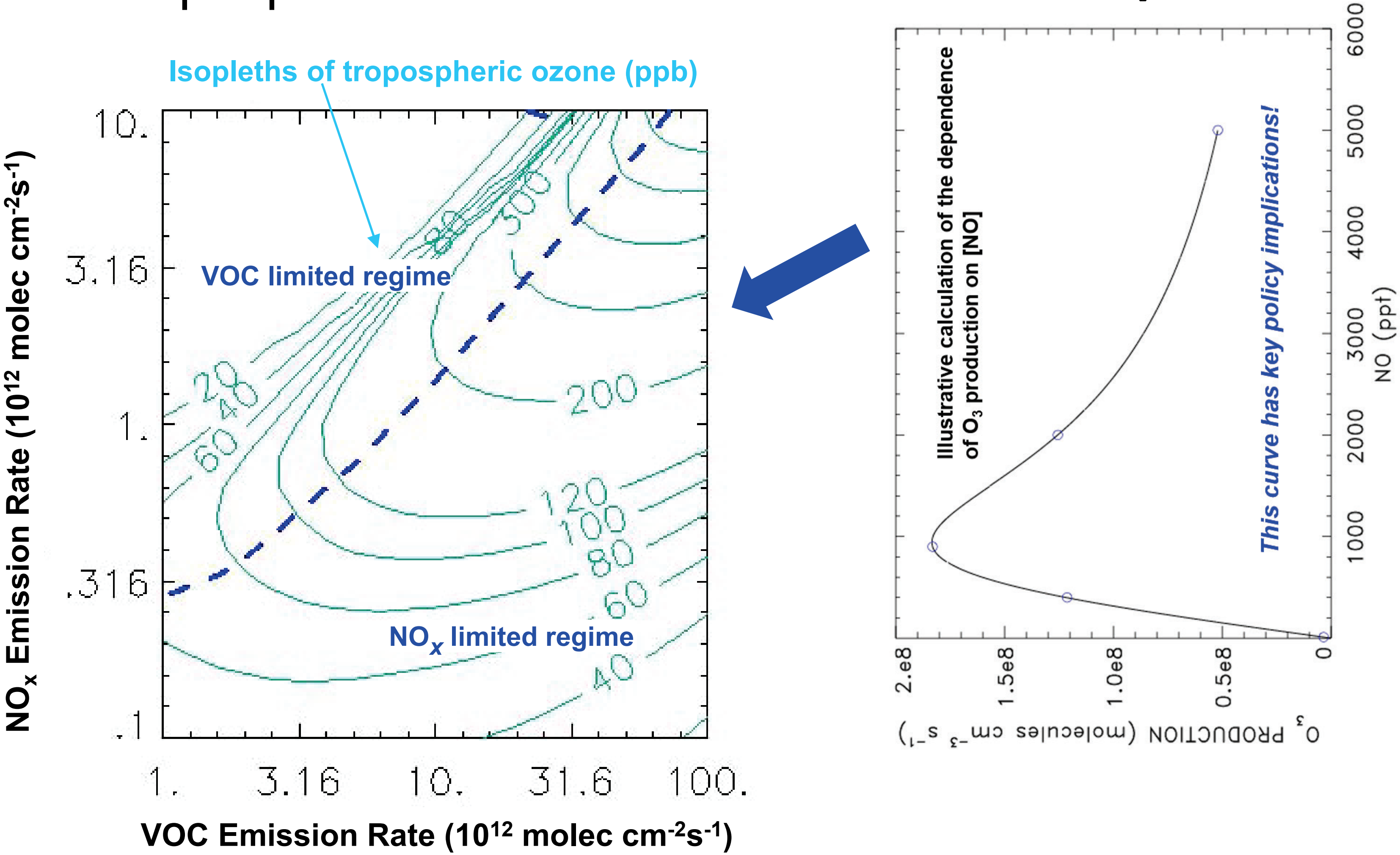
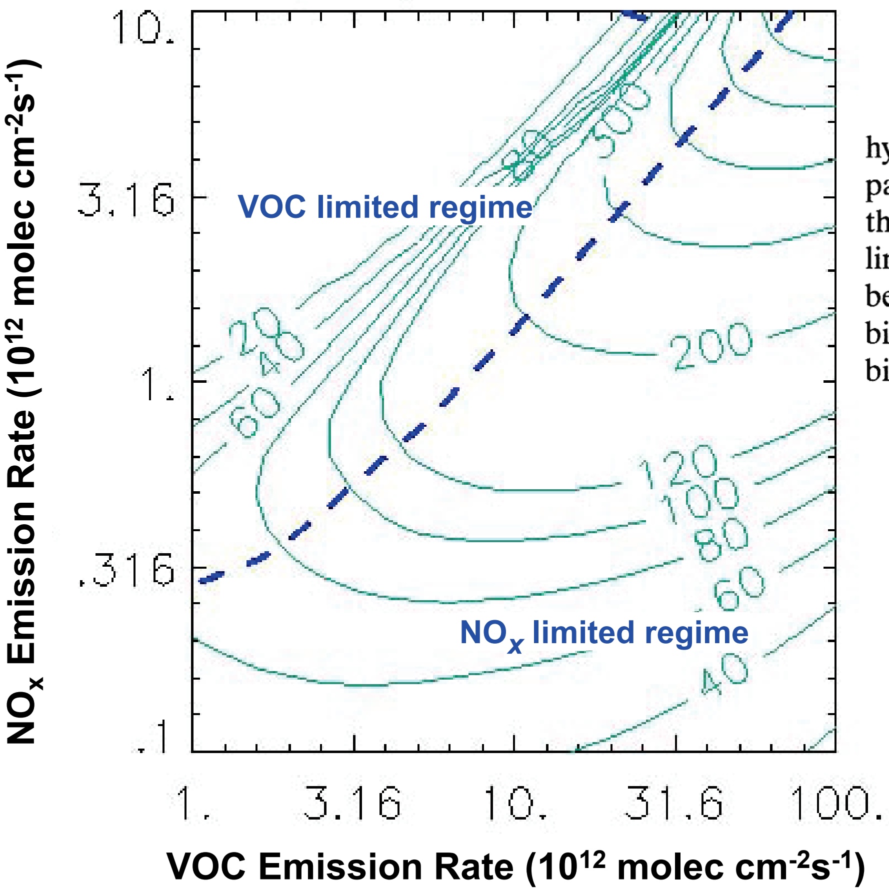


Figure: http://www-personal.umich.edu/~sillman/ozone.htm

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

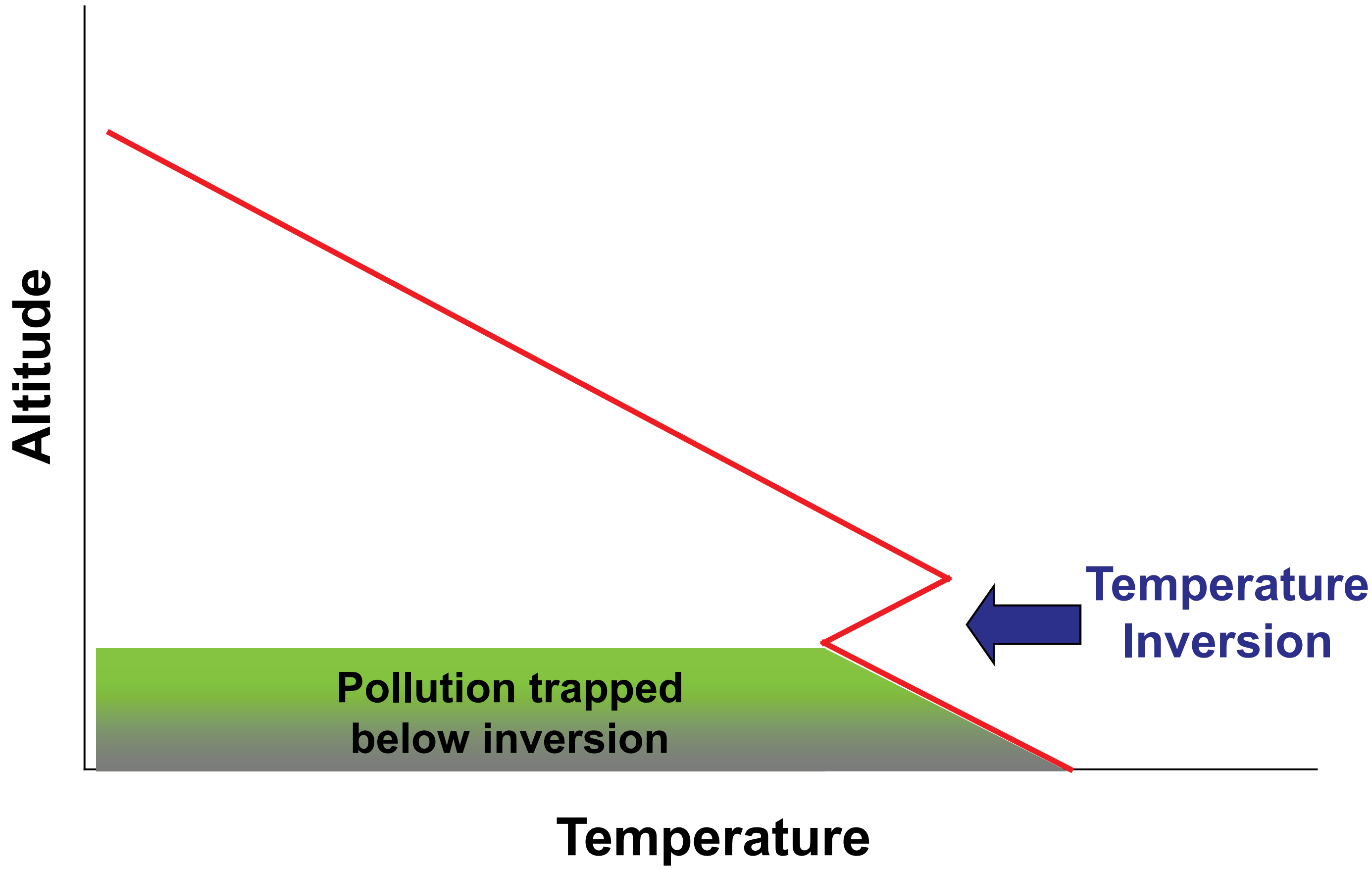
Figure: http://www-personal.umich.edu/~sillman/ozone.htm

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



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

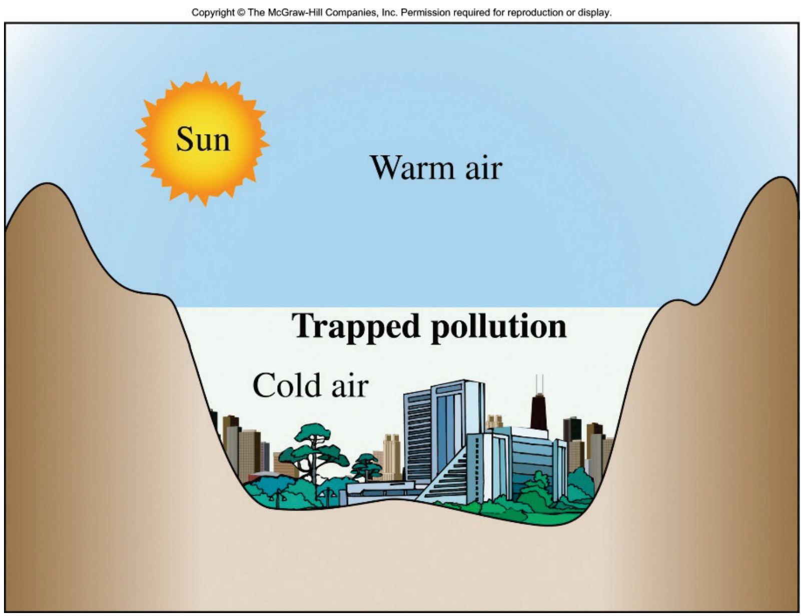
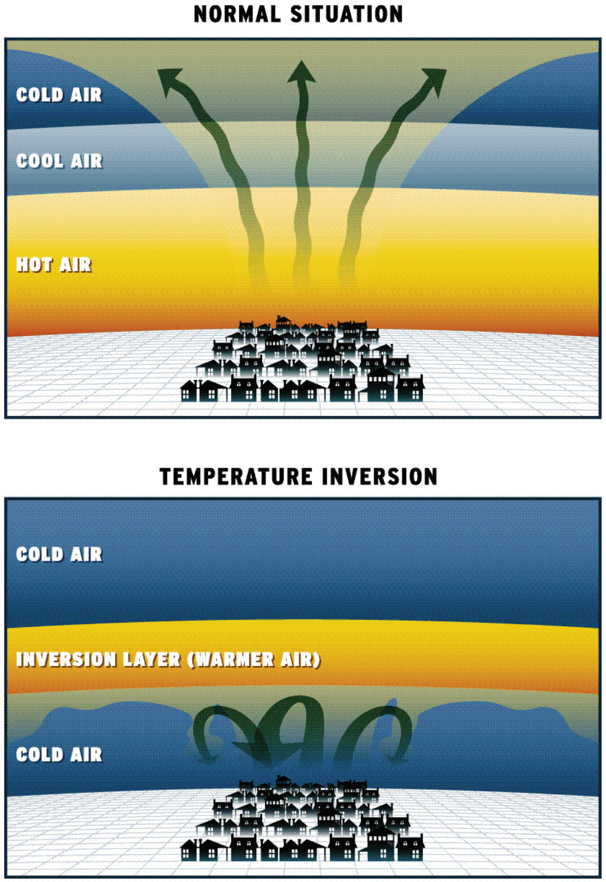


Figure 1.10, Chemistry in Context



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

Temperature Inversions and Air Quality

Temperature inversion: increase in temperature with height

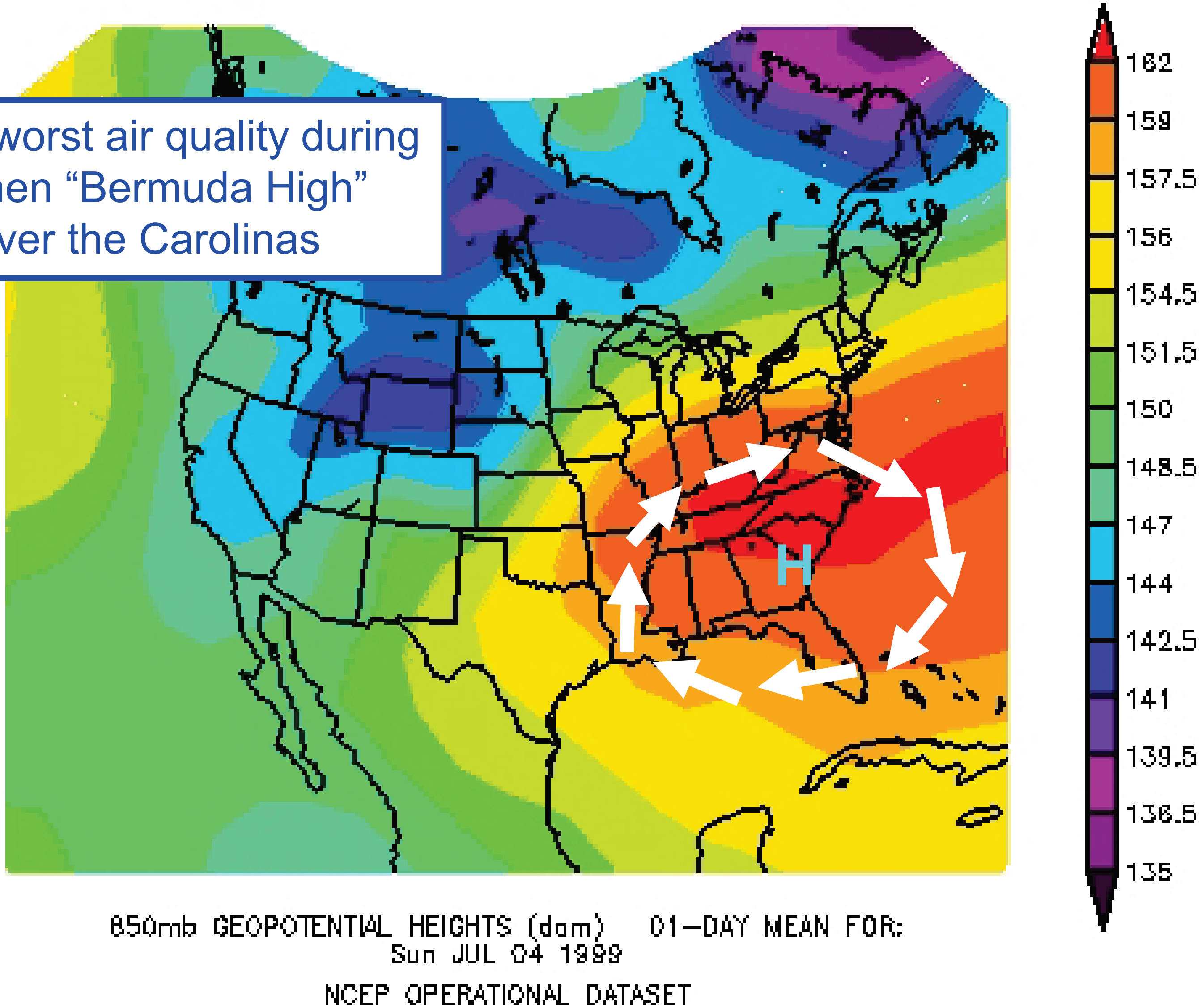
Inversions important for Air Quality because they inhibit vertical mixing of air

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

http://mashable.com/2014/04/30/most-polluted-cities-us/

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

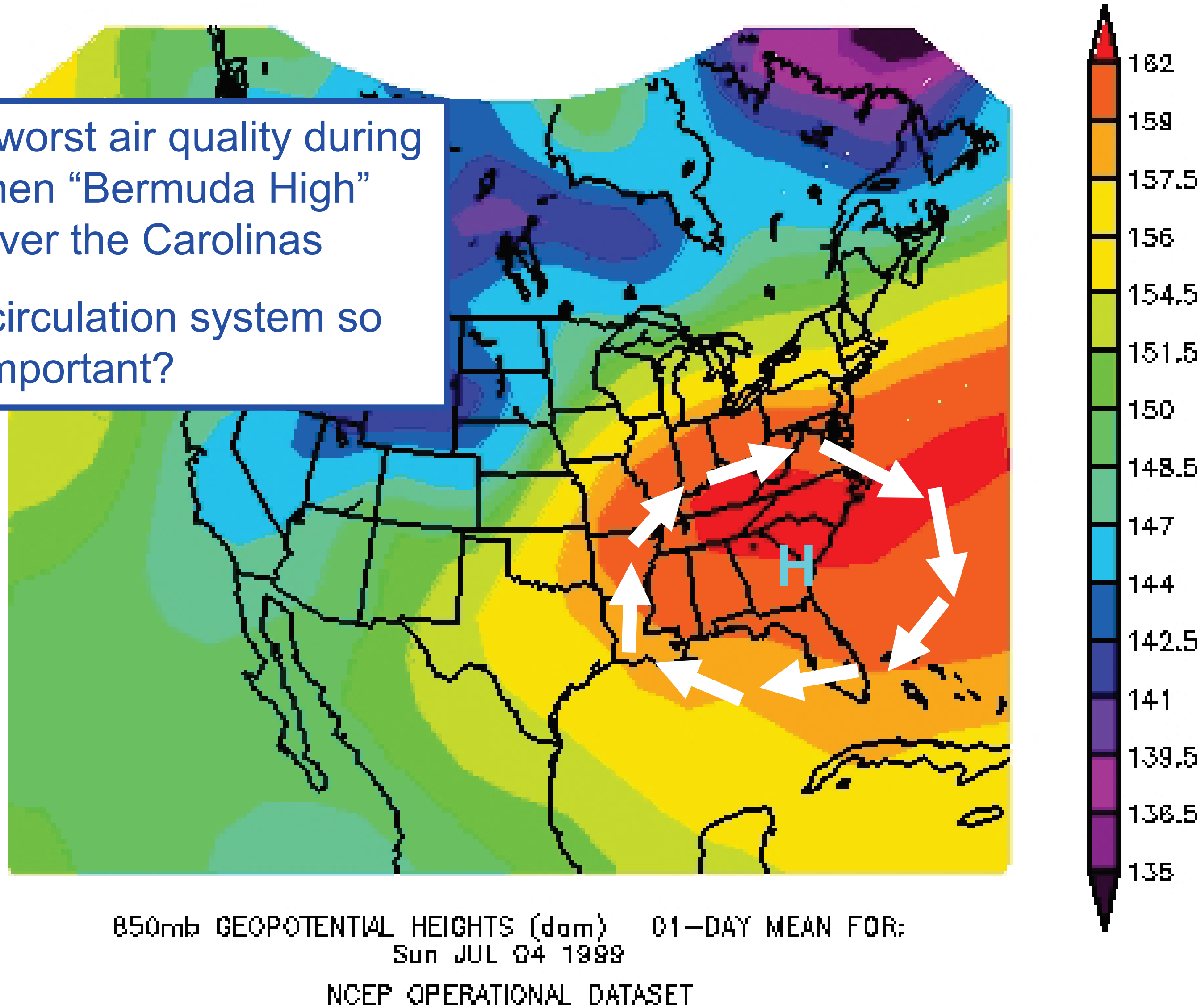


http://www.mde.state.md.us/assets/document/BJH%20-%20Basics%20on%20Ozone%20Transport.ppt

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

Maryland has worst air quality during summer, when "Bermuda High" sets up over the Carolinas

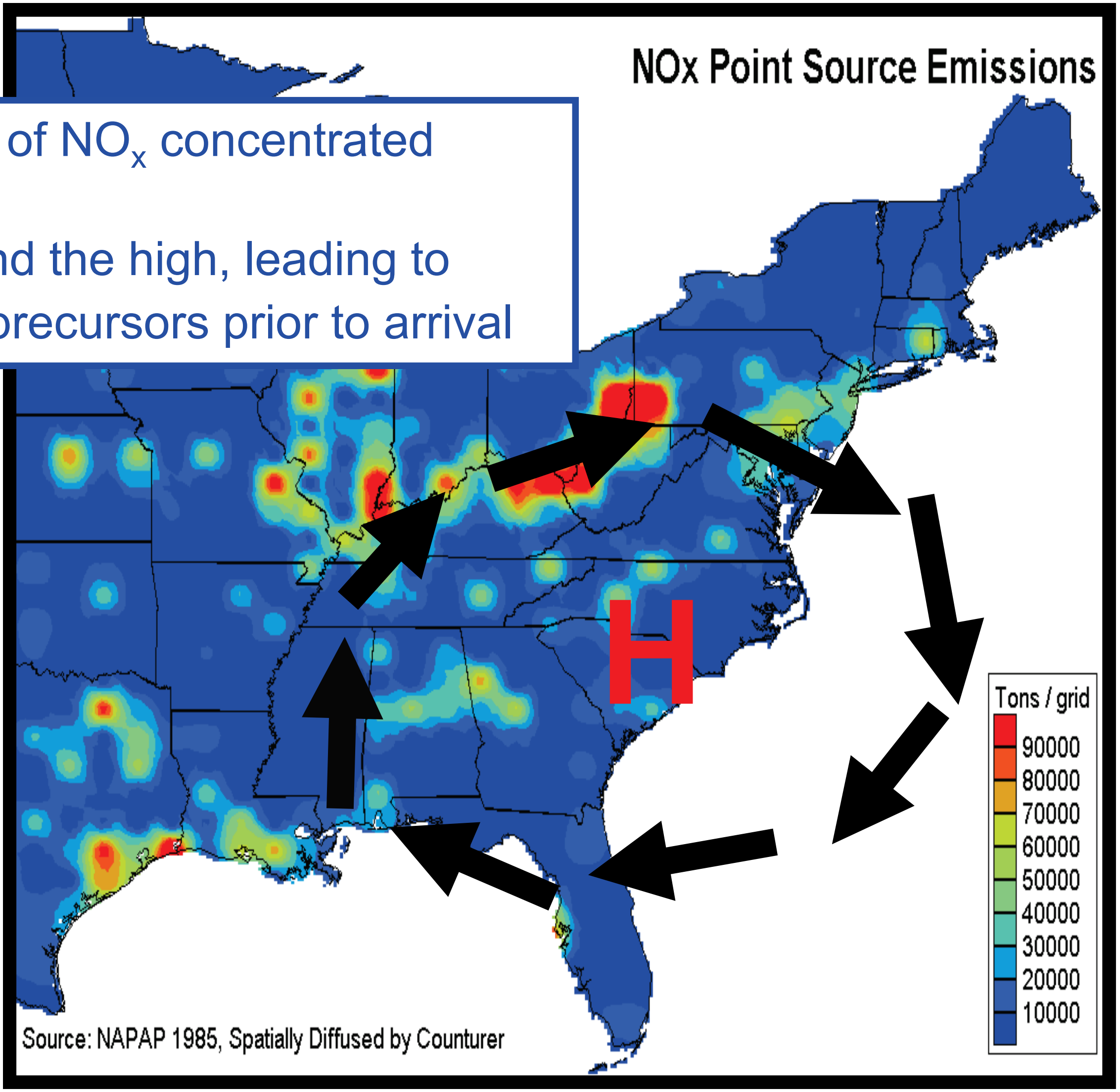
Why is this circulation system so important?



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

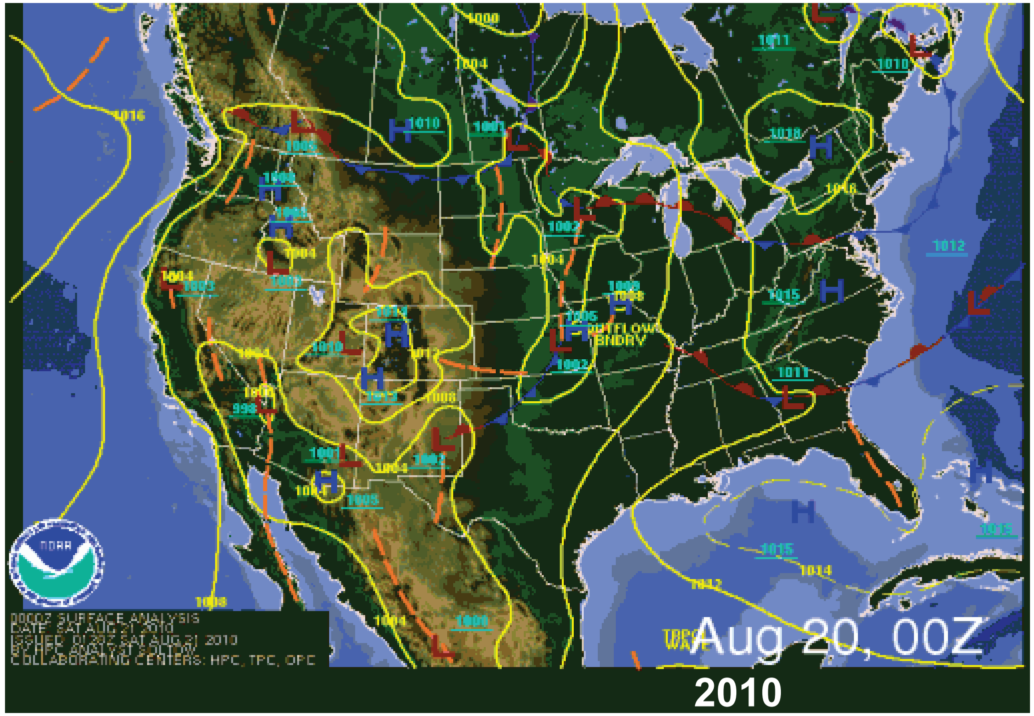
Day-to-day meteorology (weather!) affects severity and duration of pollution episodes

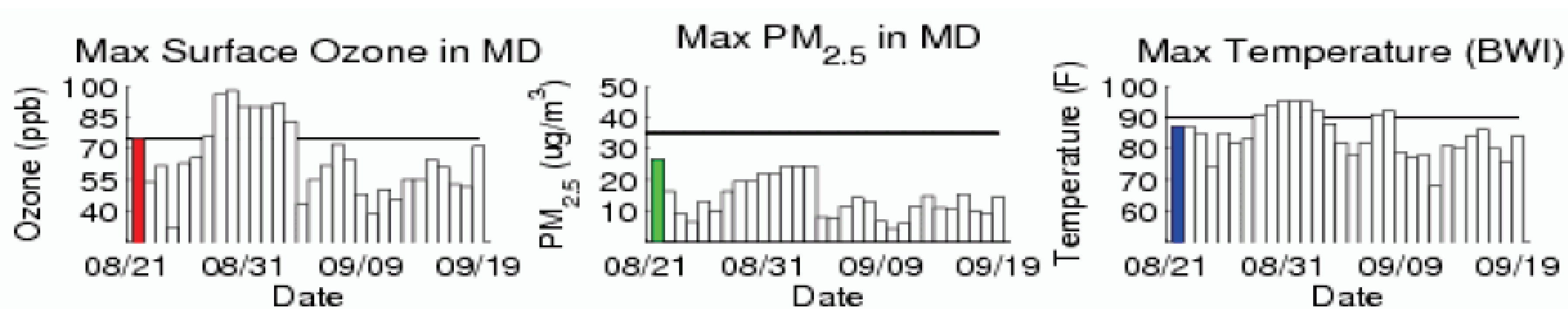
- Large power plant emissions of NO_x concentrated along the Ohio River valley
- Air circulates clockwise around the high, leading to significant build up of ozone precursors prior to arrival



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

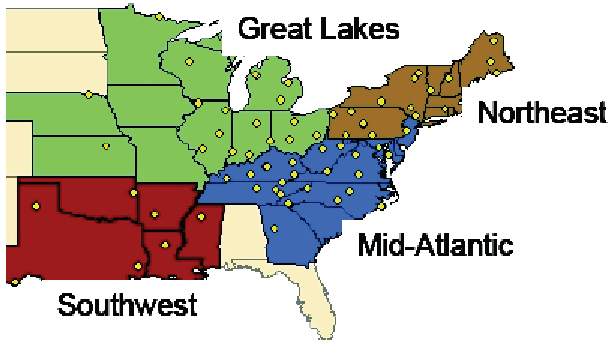


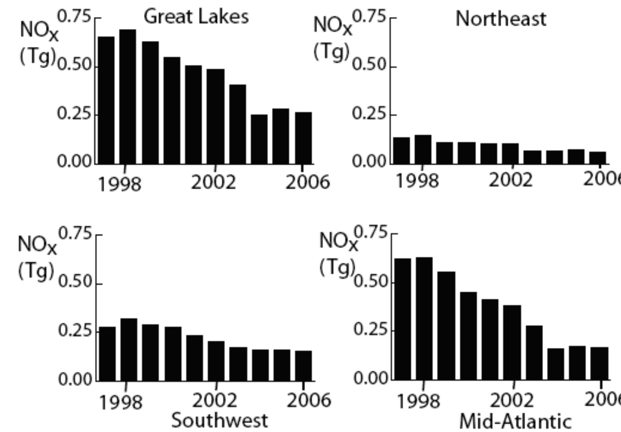


2010

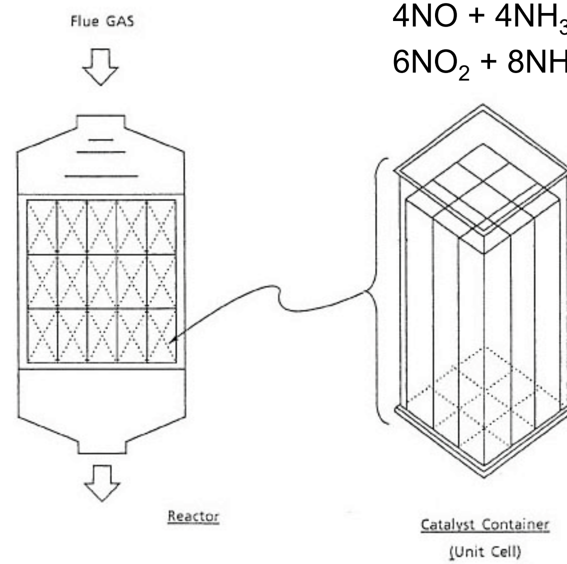
Produced by: Daniel Silversmith, UMCP
Directed by: Tim Canty & Ross Salawitch

Removal of NO_x from Power Plants





NOx Control:
SCR Selective Catalytic Reduction



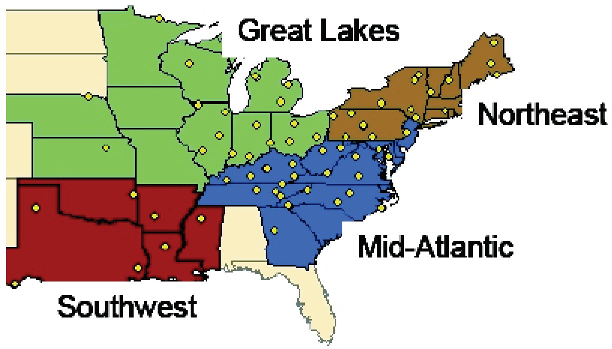
$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

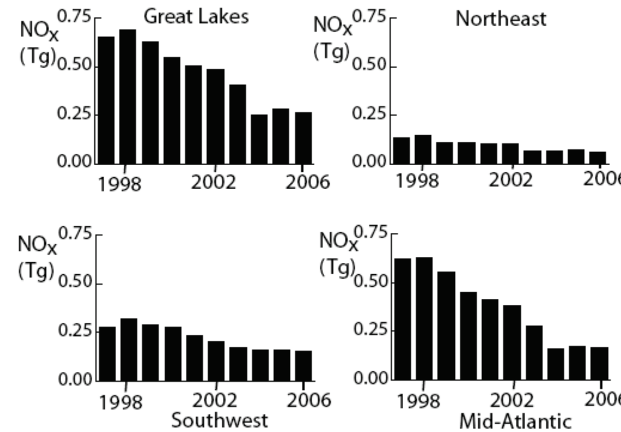
$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$

Catalyst
Maximize NOx $\rightarrow N_2$
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

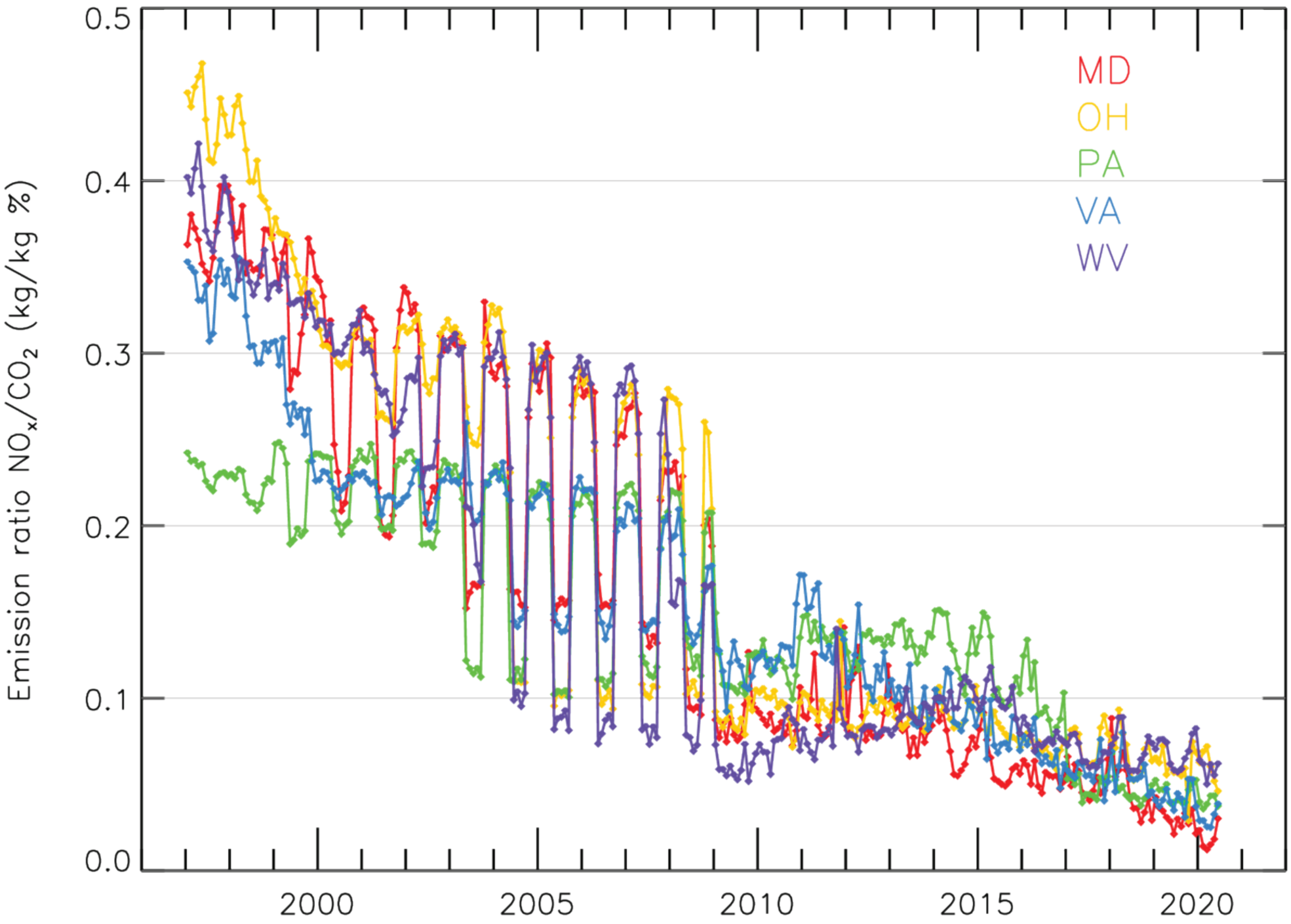




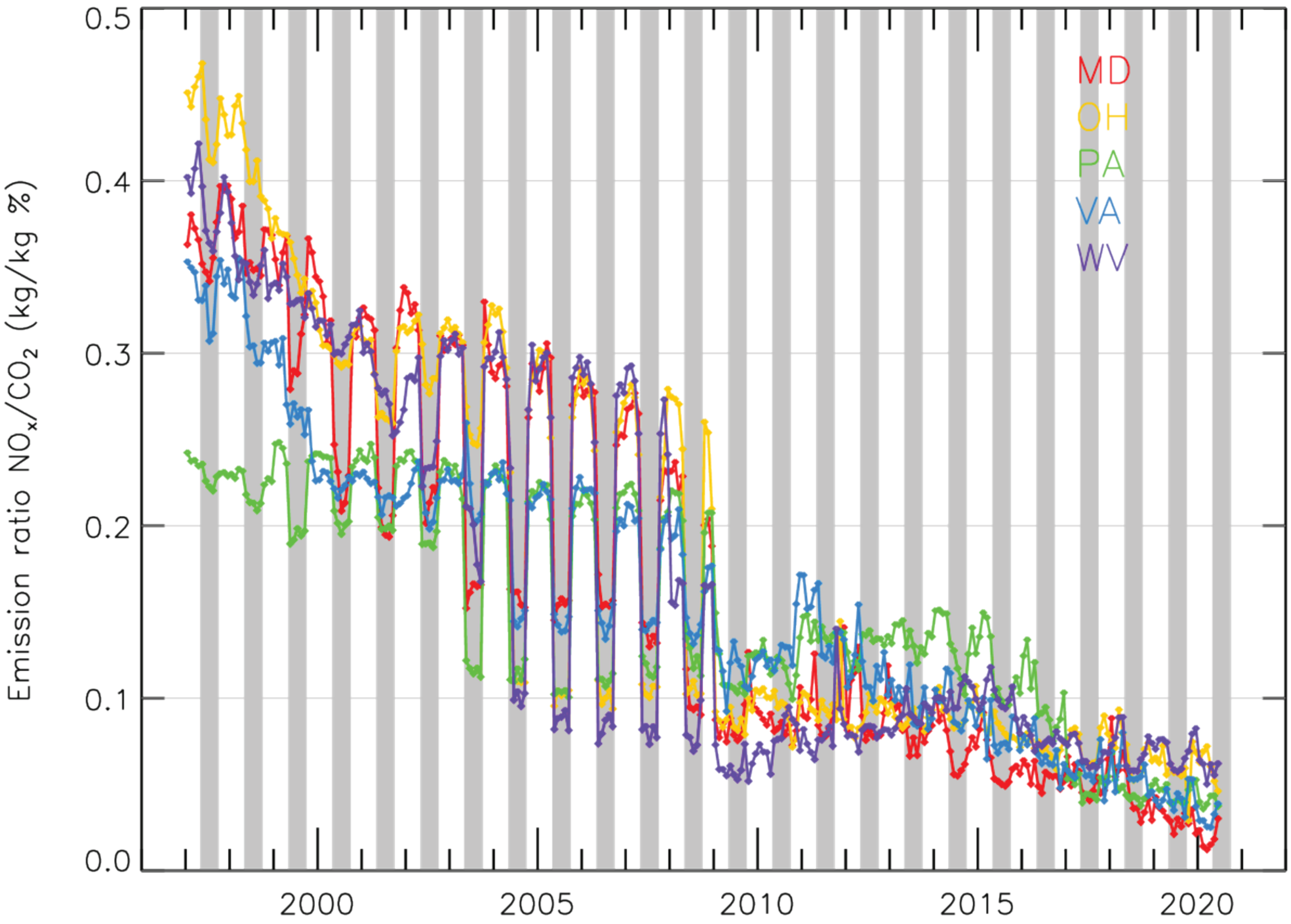
SCR at Brandon Shores

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

Trends in power plant emissions of NOx

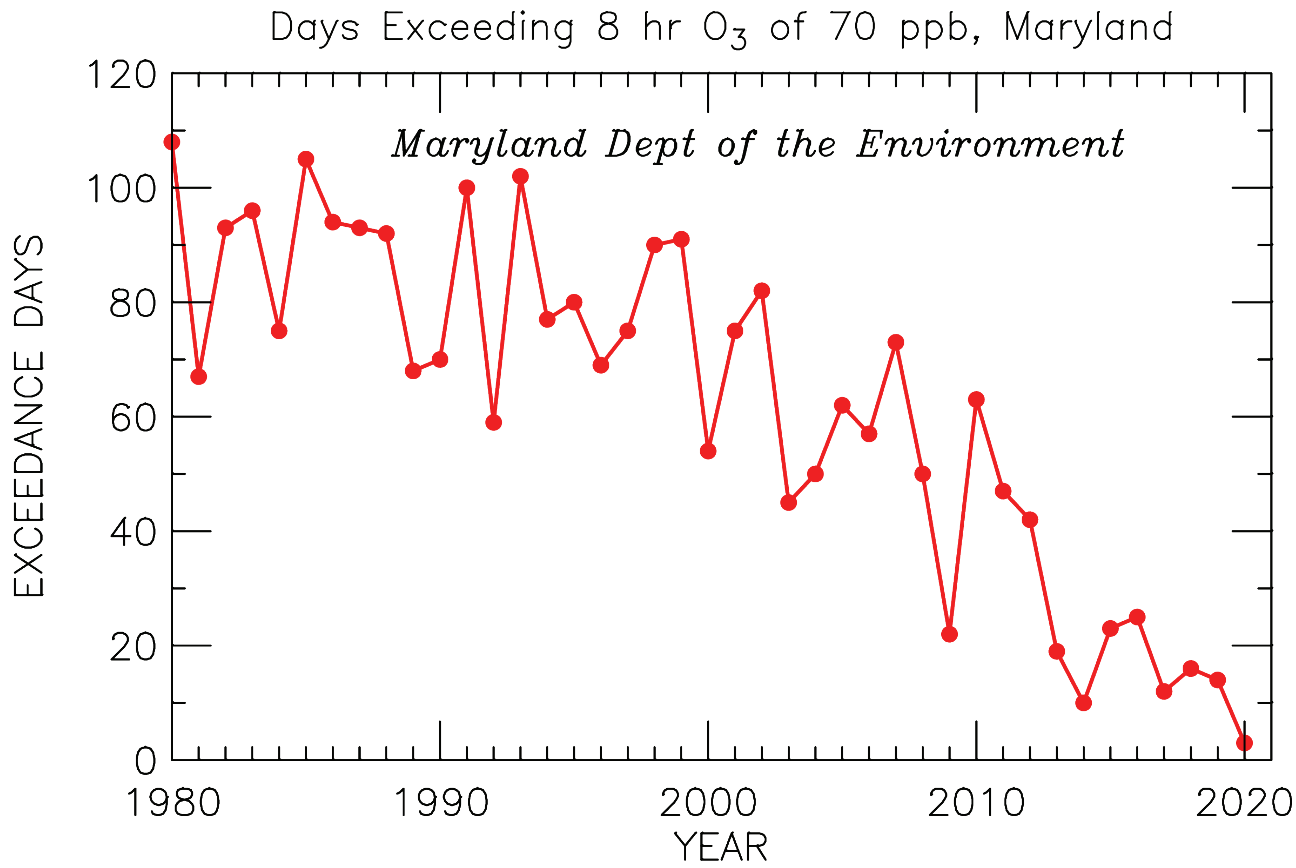


Trends in power plant emissions of NOx



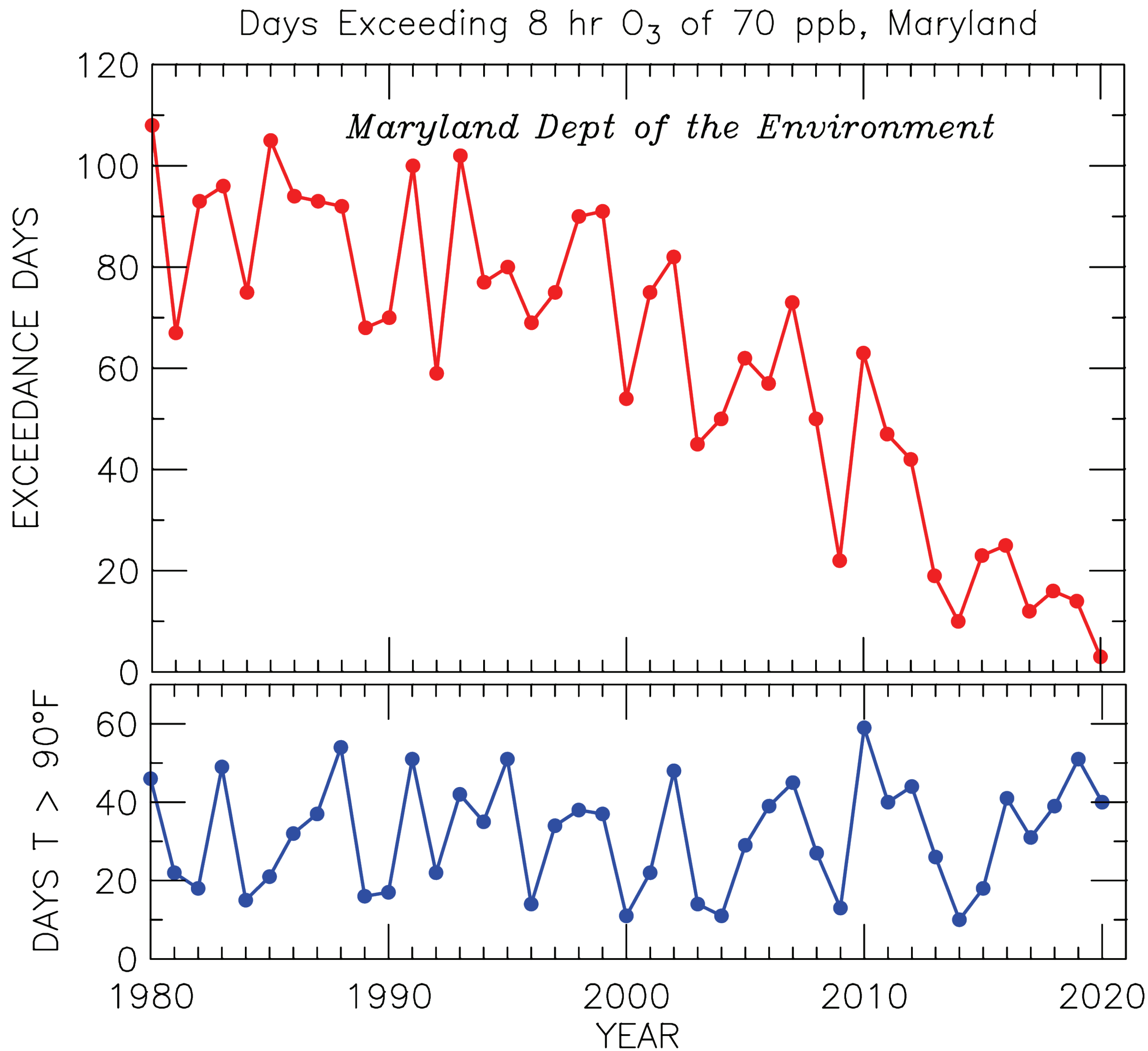
Shading denotes “ozone season”, April to Sept

Significant Improvements in *Local* Air Quality since early 1980s



http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

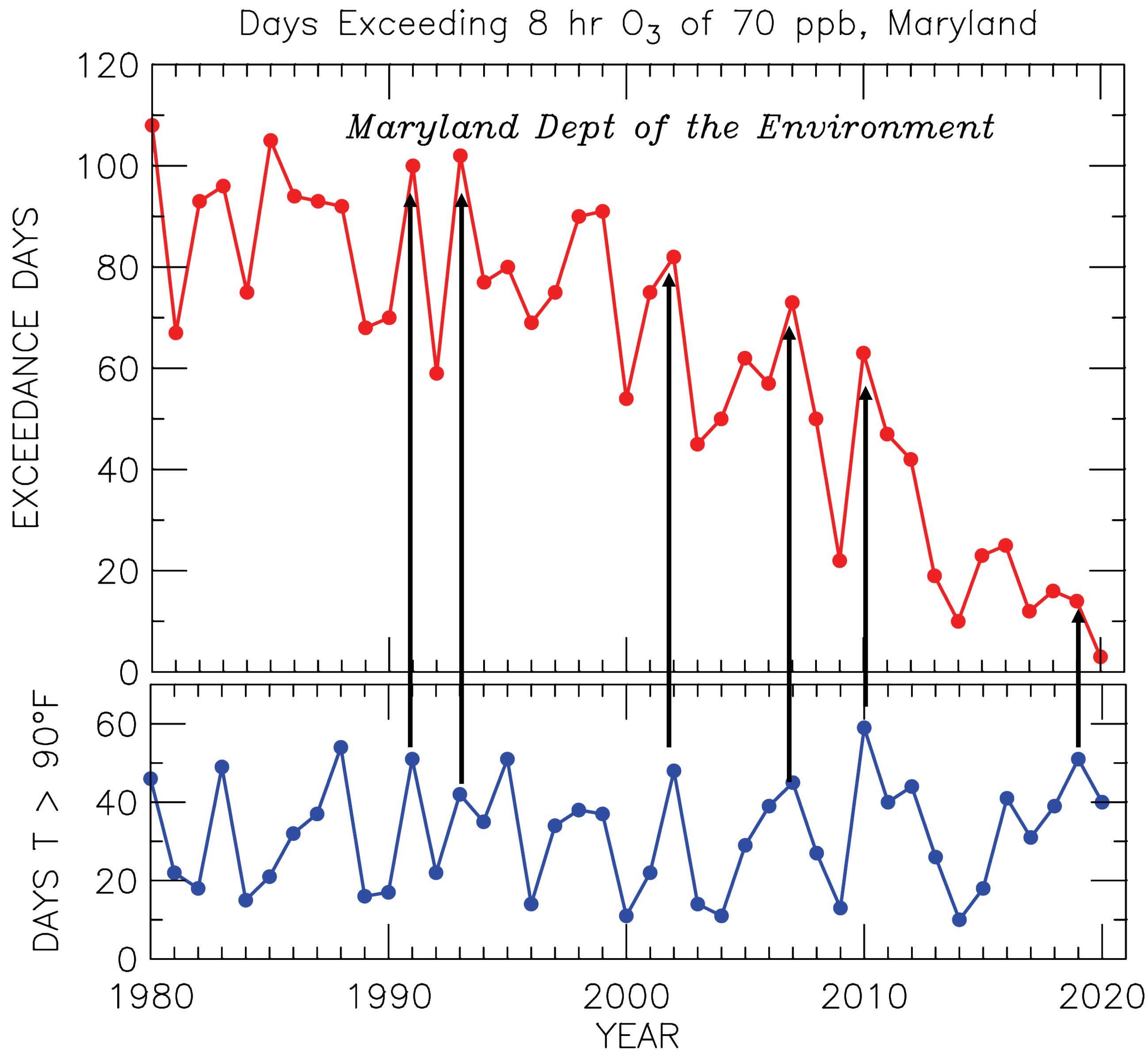
Significant Improvements in *Local* Air Quality since early 1980s



Number of days, each summer, for which T at BWI exceeded 90°F at some part of the day

http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

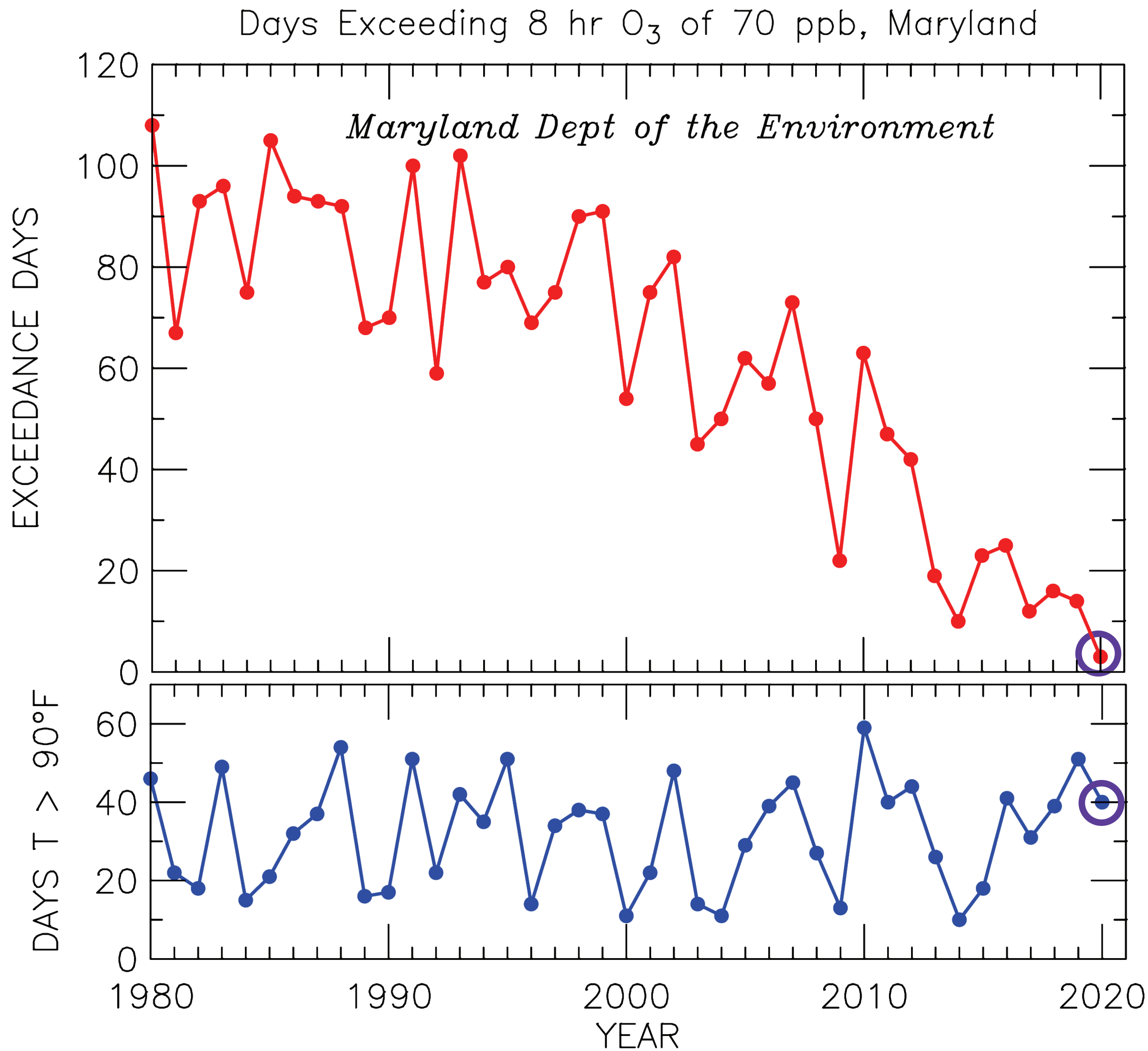
Significant Improvements in *Local* Air Quality since early 1980s



Number of days, each summer, for which T at BWI exceeded 90°F at some part of the day

http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

Significant Improvements in *Local* Air Quality since early 1980s

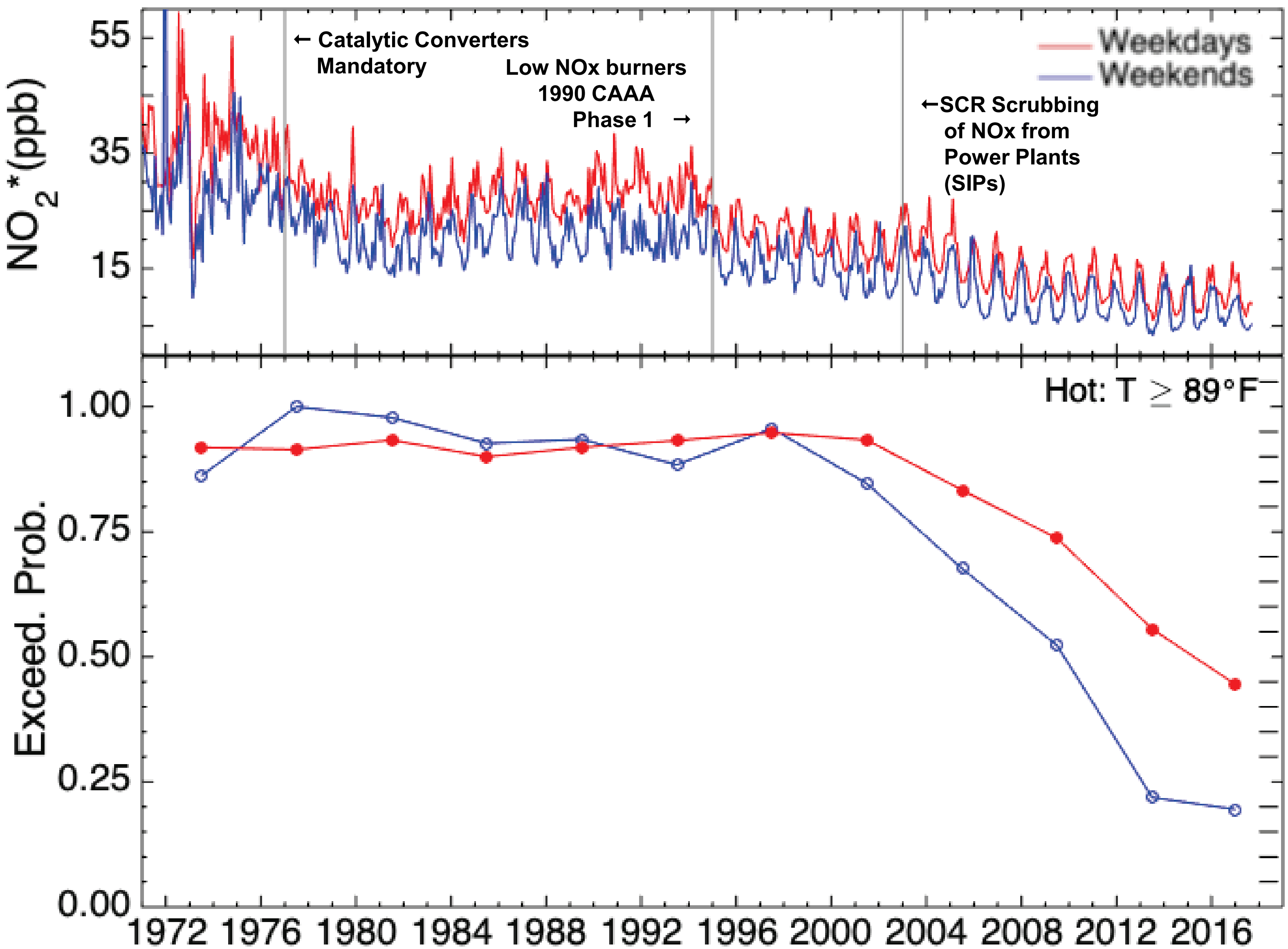


Number of days, each summer, for which T at BWI exceeded 90°F at some part of the day

3 surface ozone exceedances in Maryland during 2020. Would have expected many more (i.e., 12 to 16) given relation between Exceedance Days & Days T > 90°F from prior recent years.

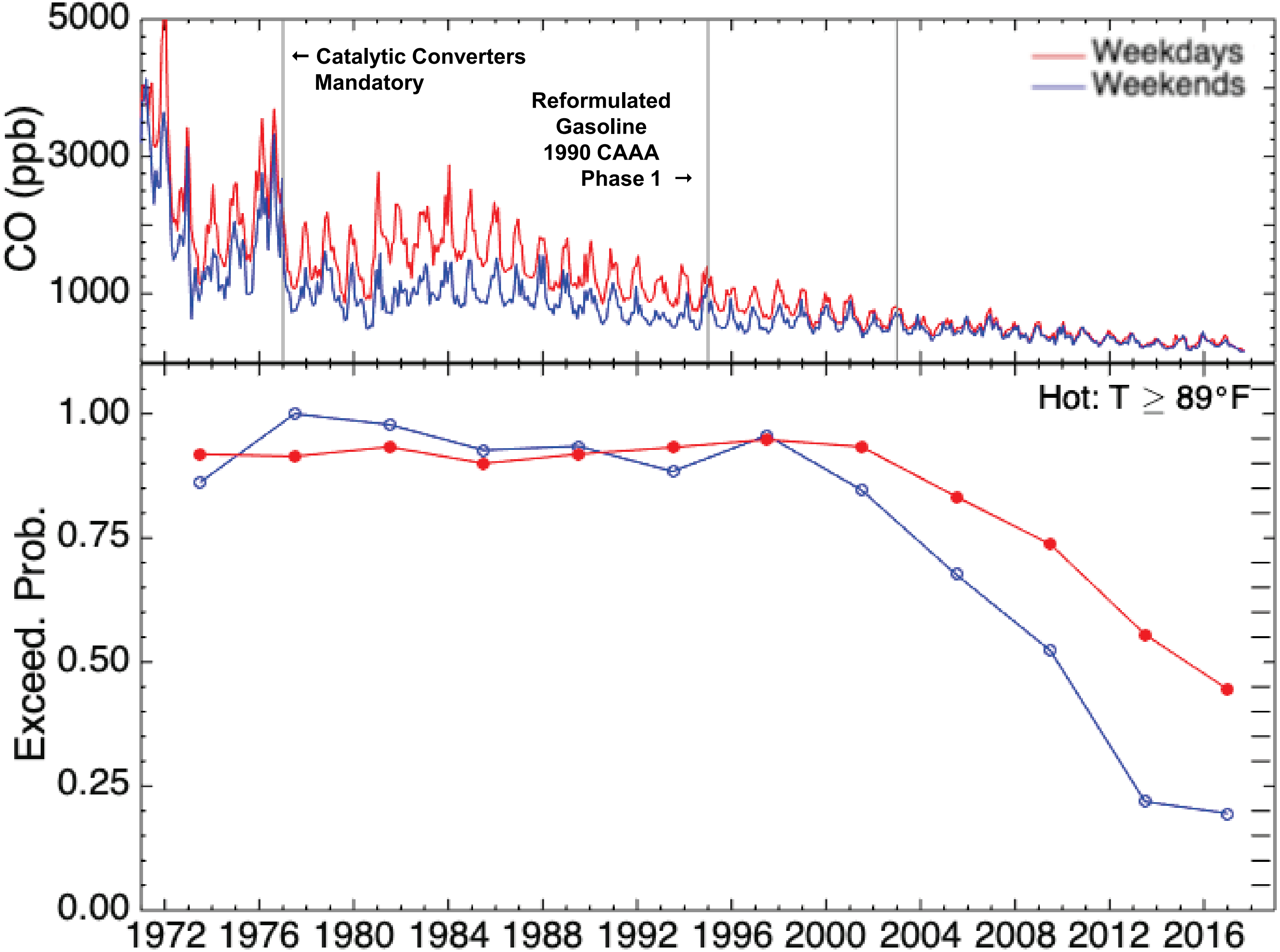
http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

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



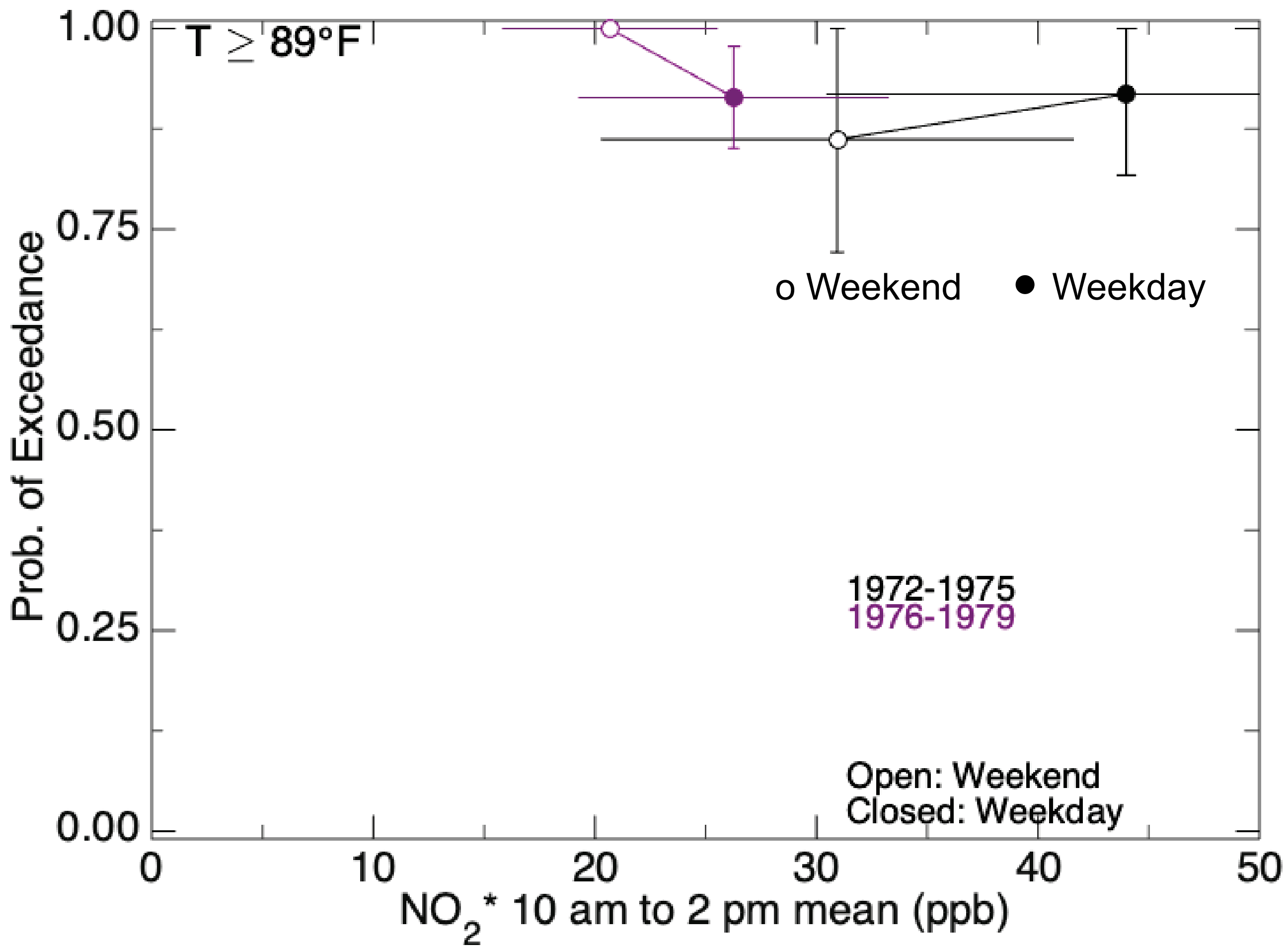
Figures above research product of UMCP Graduate Student Sandra Roberts

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



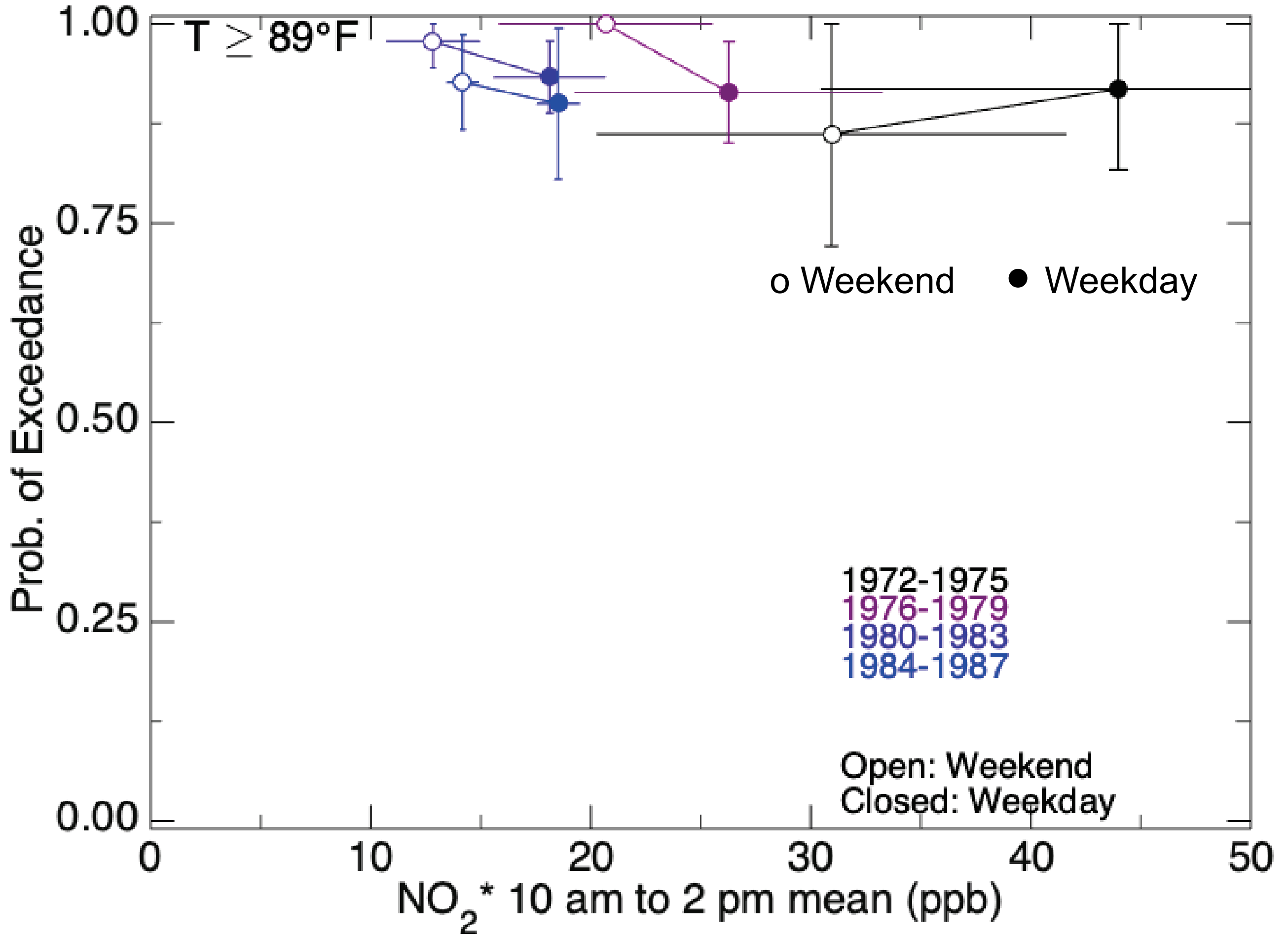
Figures above research product of UMCP Graduate Student Sandra Roberts

Probability of Surface O_3 Exceedance (DC, MD, No. VA) vs Daytime NO_2
Hot Summer Days (T_{BWI} > 89° F)



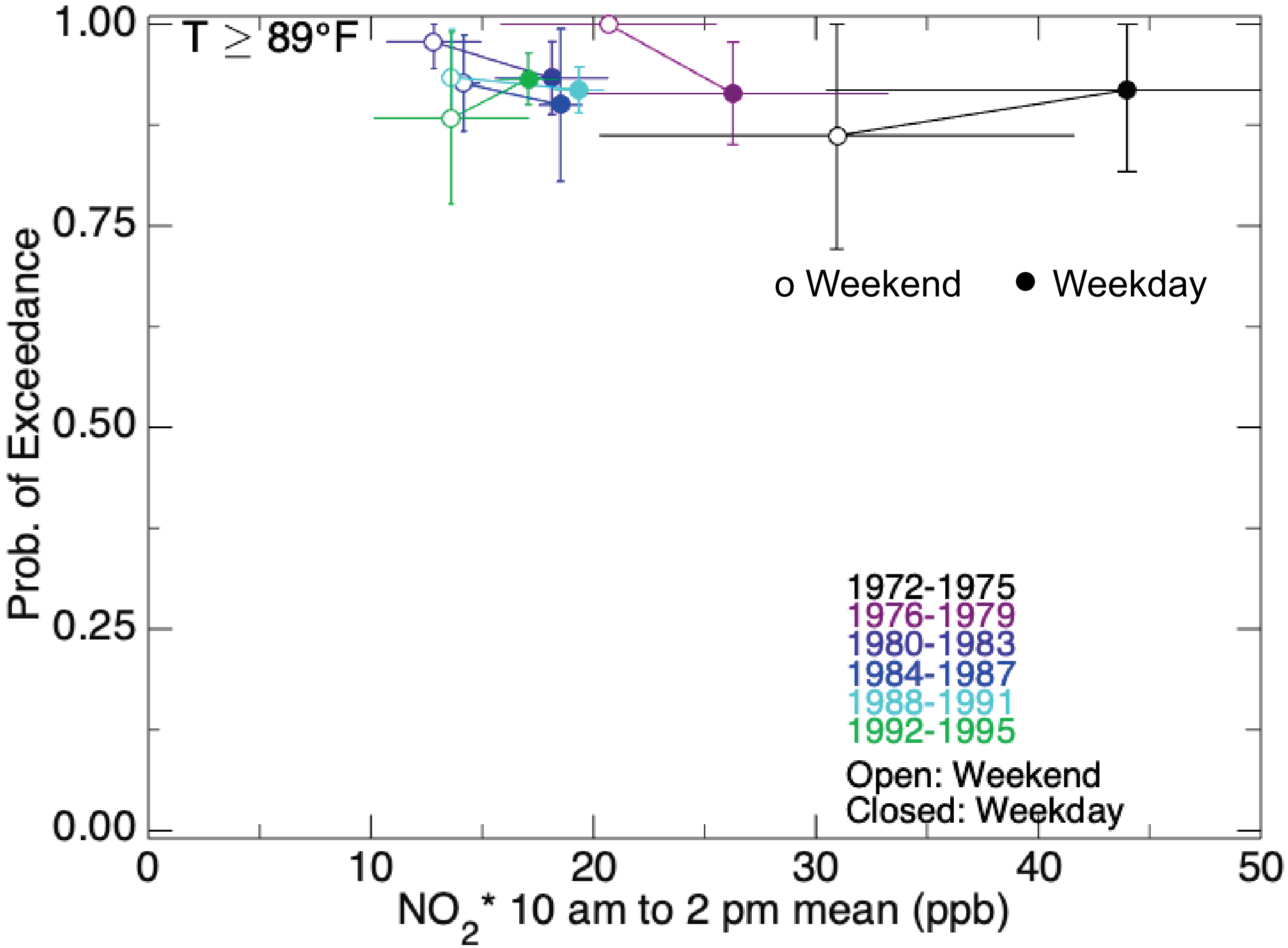
Analysis in this framework motivated by Pusede and Cohen, ACP, 2012
http://www.atmos-chem-phys.net/12/8323/2012/acp-12-8323-2012.html
Figures above research product of UMCP Graduate Student Sandra Roberts

Probability of Surface O_3 Exceedance (DC, MD, No. VA) vs Daytime NO_2
Hot Summer Days (T_{BWI} > 89° F)



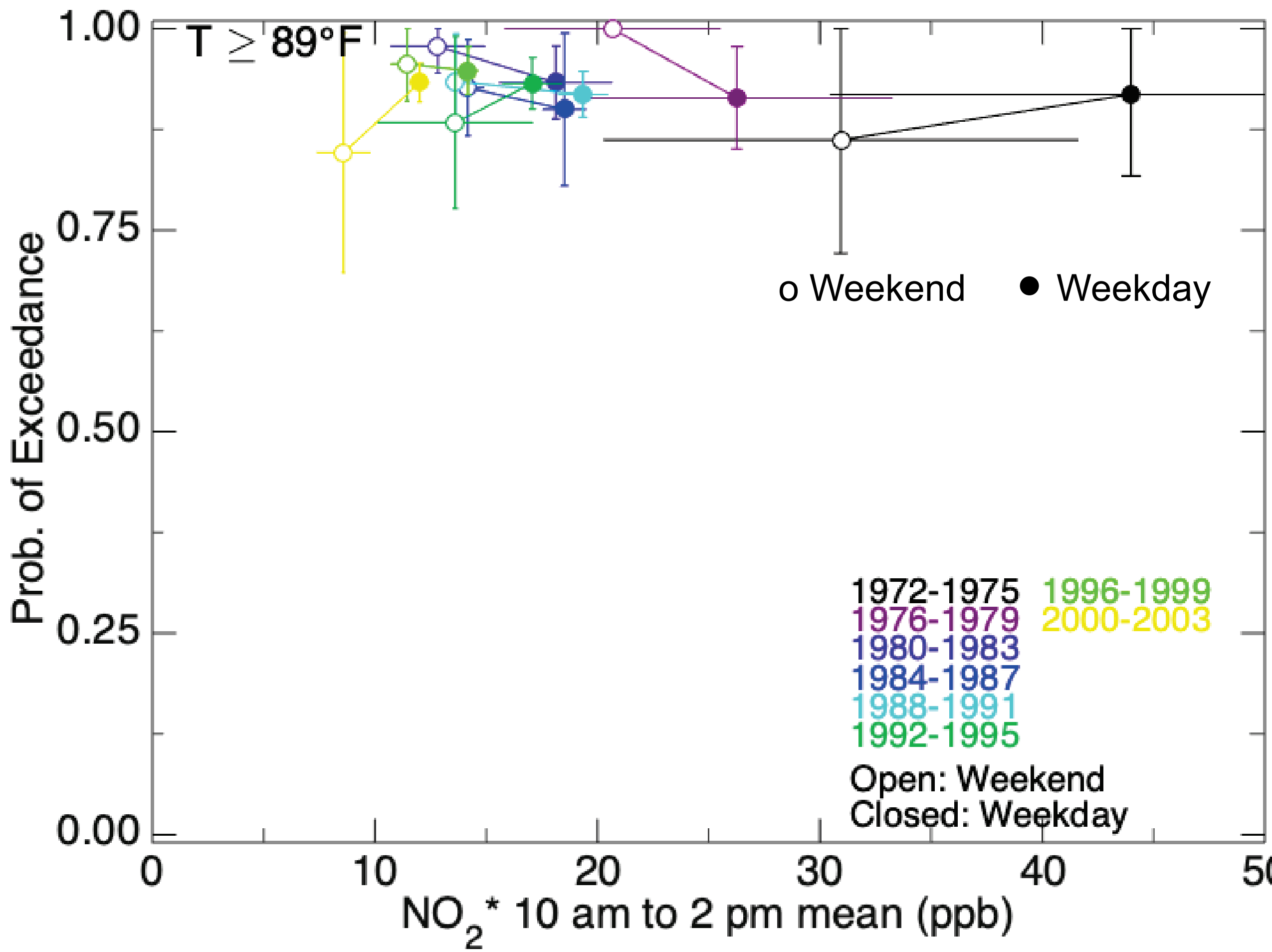
Analysis in this framework motivated by Pusede and Cohen, ACP, 2012
http://www.atmos-chem-phys.net/12/8323/2012/acp-12-8323-2012.html
Figures above research product of UMCP Graduate Student Sandra Roberts

Probability of Surface O_3 Exceedance (DC, MD, No. VA) vs Daytime NO_2
Hot Summer Days (T_{BWI} > 89° 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

Probability of Surface O_3 Exceedance (DC, MD, No. VA) vs Daytime NO_2
Hot Summer Days (T_{BWI} > 89° F)

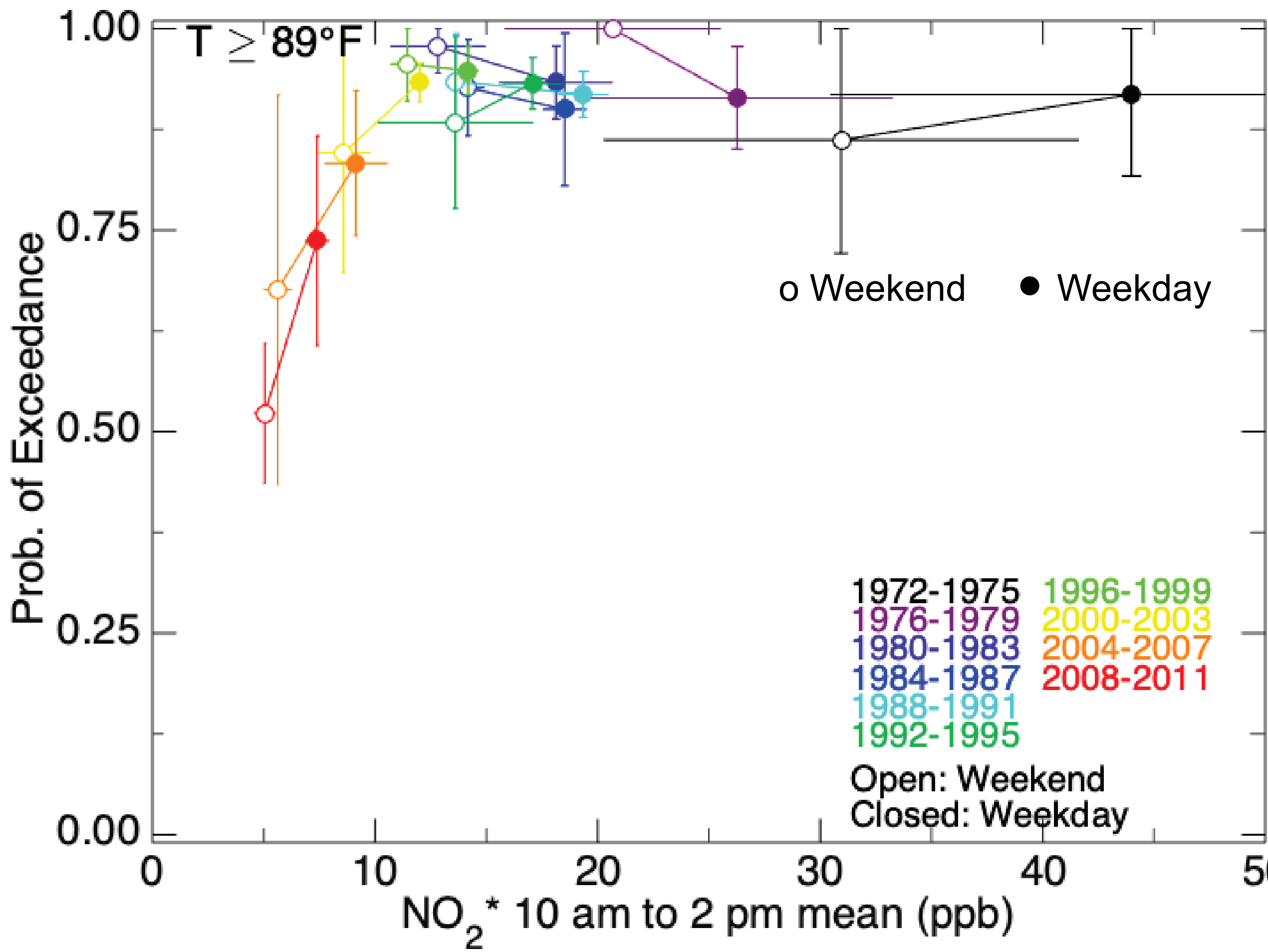


Analysis in this framework motivated by Pusede and Cohen, ACP, 2012

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

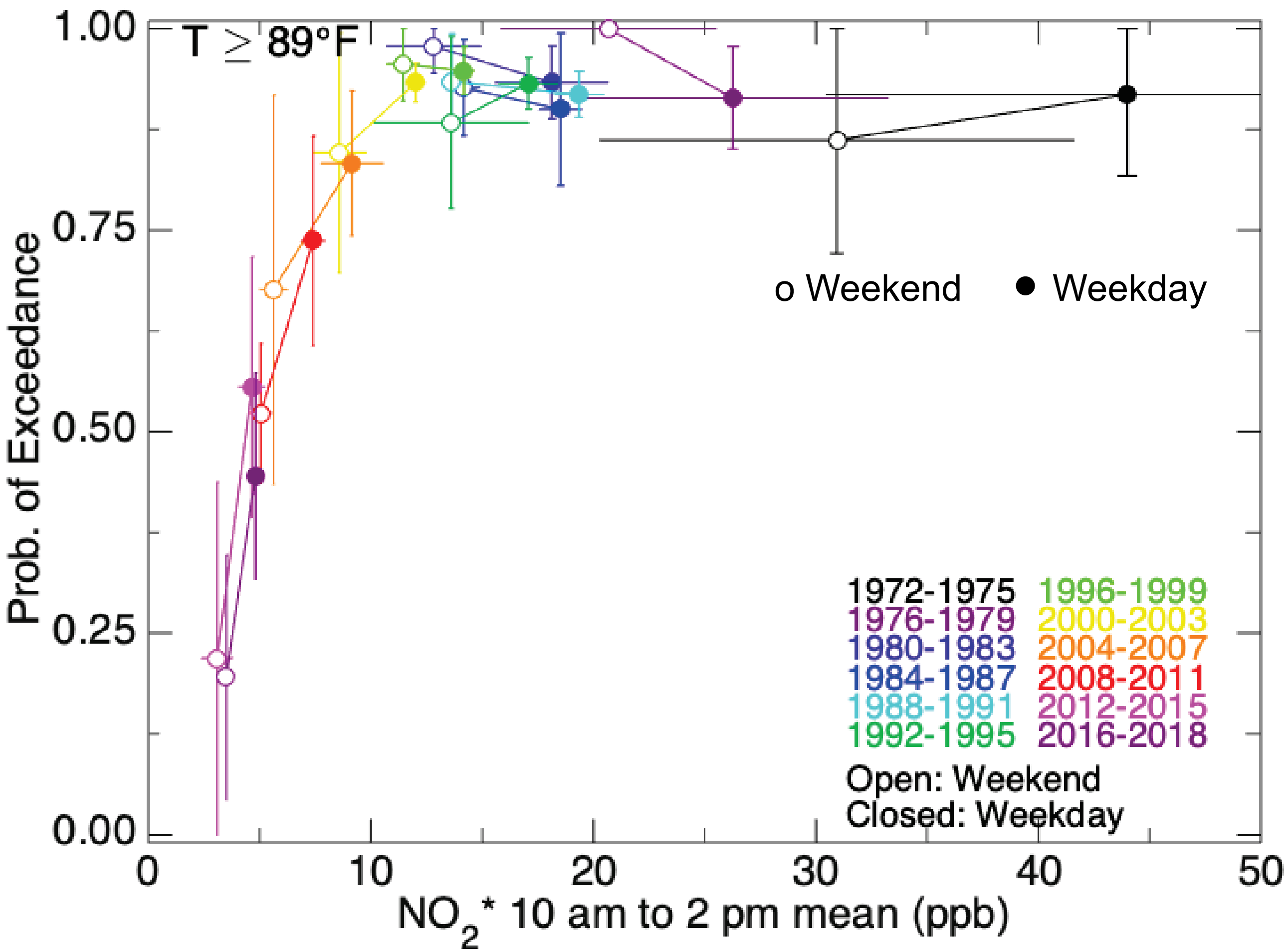
Figures above research product of UMCP Graduate Student Sandra Roberts

Probability of Surface O_3 Exceedance (DC, MD, No. VA) vs Daytime NO_2
Hot Summer Days (T_{BWI} > 89° 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

Probability of Surface O_3 Exceedance (DC, MD, No. VA) vs Daytime NO_2
Hot Summer Days (T_{BWI} > 89° F)

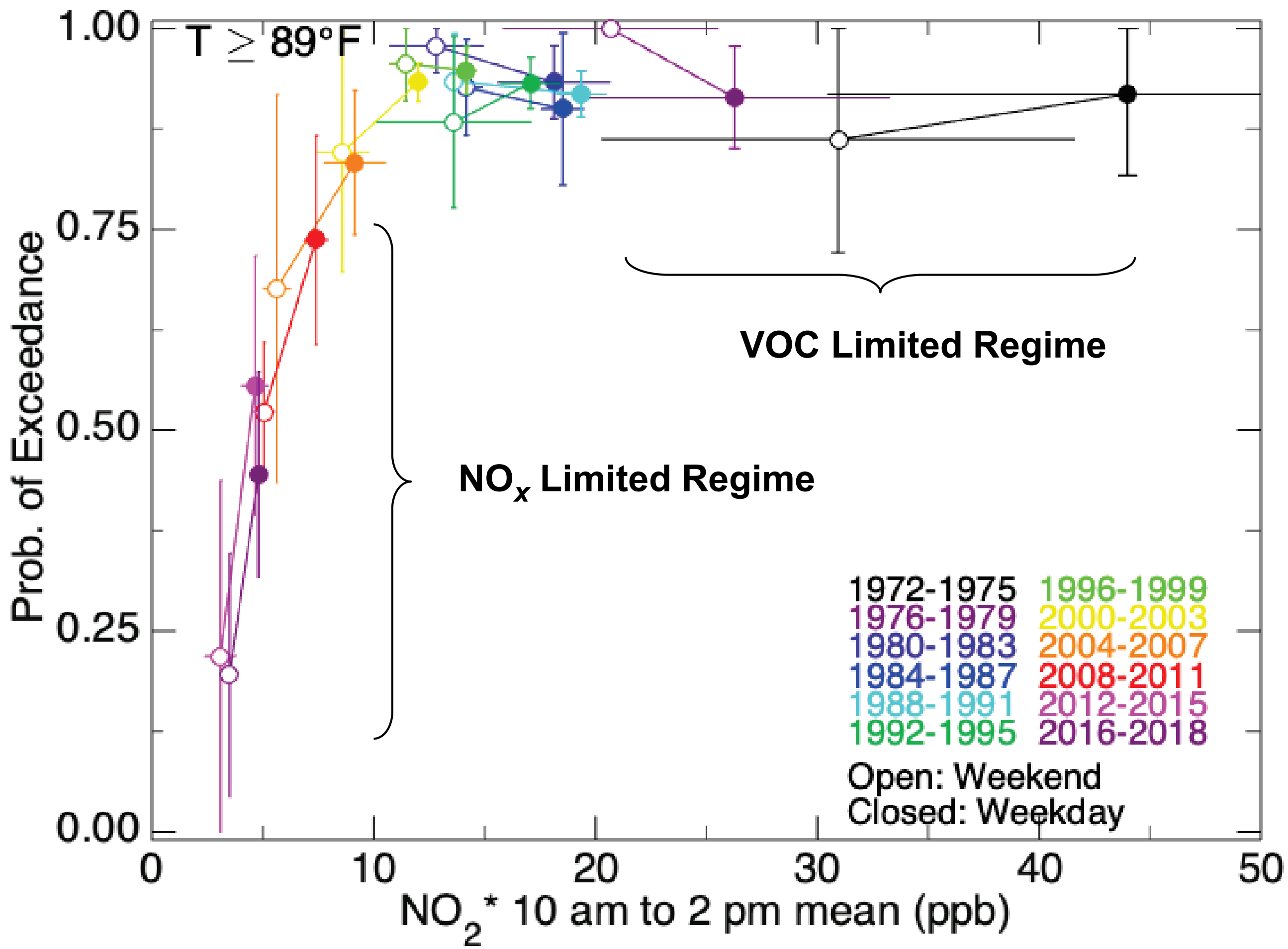


Analysis in this framework motivated by Pusede and Cohen, ACP, 2012

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

Figures above research product of UMCP Graduate Student Sandra Roberts

Probability of Surface O_3 Exceedance (DC, MD, No. VA) vs Daytime NO_2
Hot Summer Days (T_{BWI} > 89° F)



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

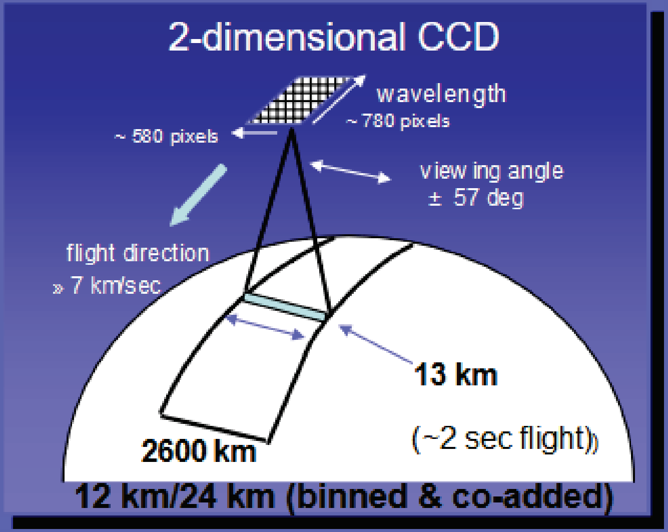
http://www.atmos-chem-phys.net/12/8323/2012/acp-12-8323-2012.html

Figures above research product of UMCP Graduate Student Sandra Roberts

NASA OMI Instrument on Aura

Ozone Monitoring Instrument

- The NASA EOS Aura platform, launched on July 15, 2004, carries the Ozone Monitoring Instrument (OMI)
- Joint Dutch-Finnish Instrument with Duch/Finish/U.S. Science Team
  - PI: P. Levelt, KNMI
  - Hyperspectral wide FOV Radiometer
    - 270-500 nm
    - 13x24 km nadir footprint (highest resolution from space !)
    - Swath width 2600 km (contiguous coverage)
  - Radicals: Column O_3, NO_2, BrO, OClO
  - O_3 profile ~ 5-10 km vert resolution
  - Tracers: Column SO_2 , HCHO
  - Aerosols (smoke, dust and sulfates)
  - Cloud top press., cloud coverage
  - Surface UVB
  - Tropospheric ozone

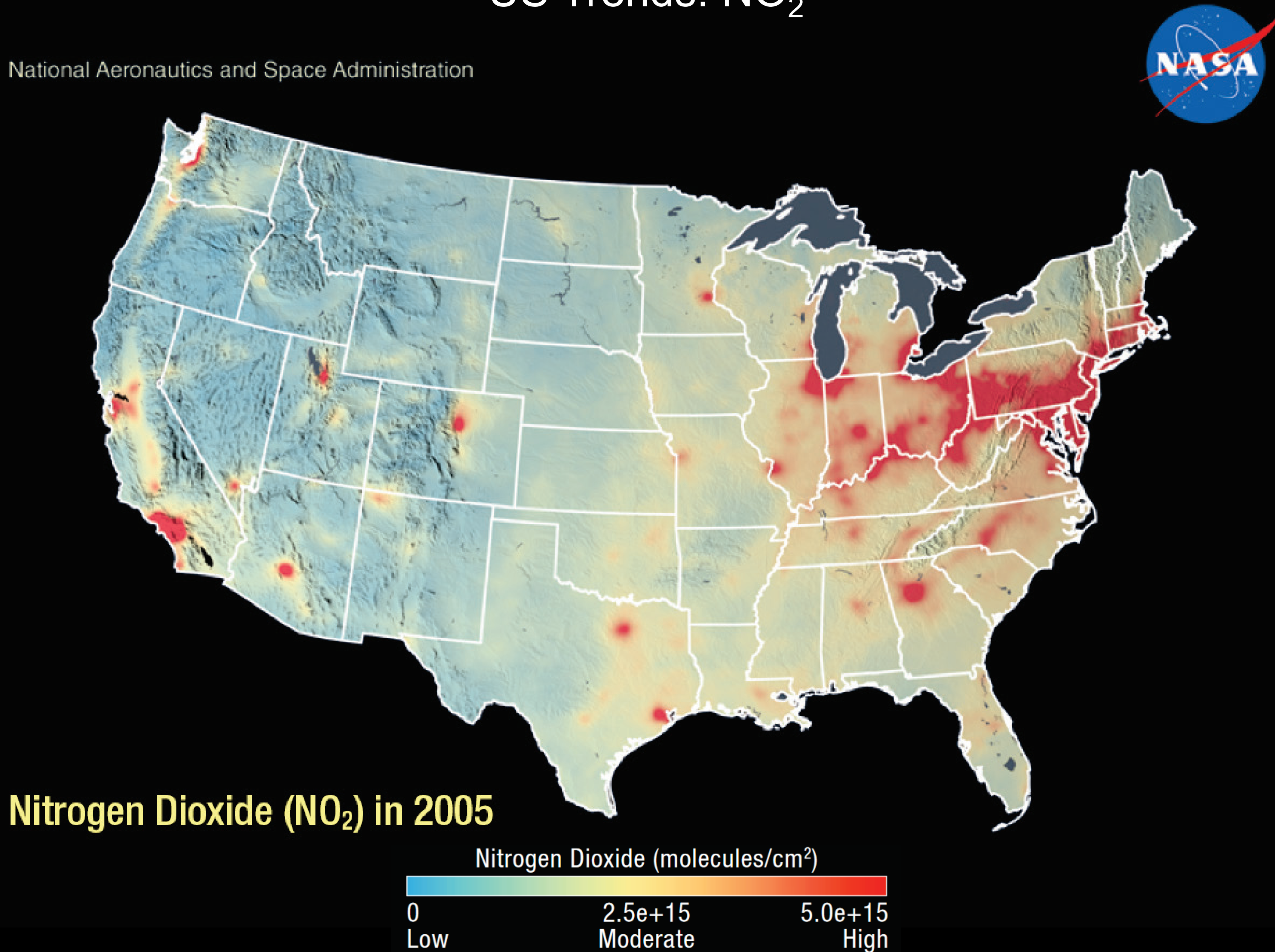


https://www.youtube.com/watch?v=krY5DjhjKGY

Let's Go to Second Video

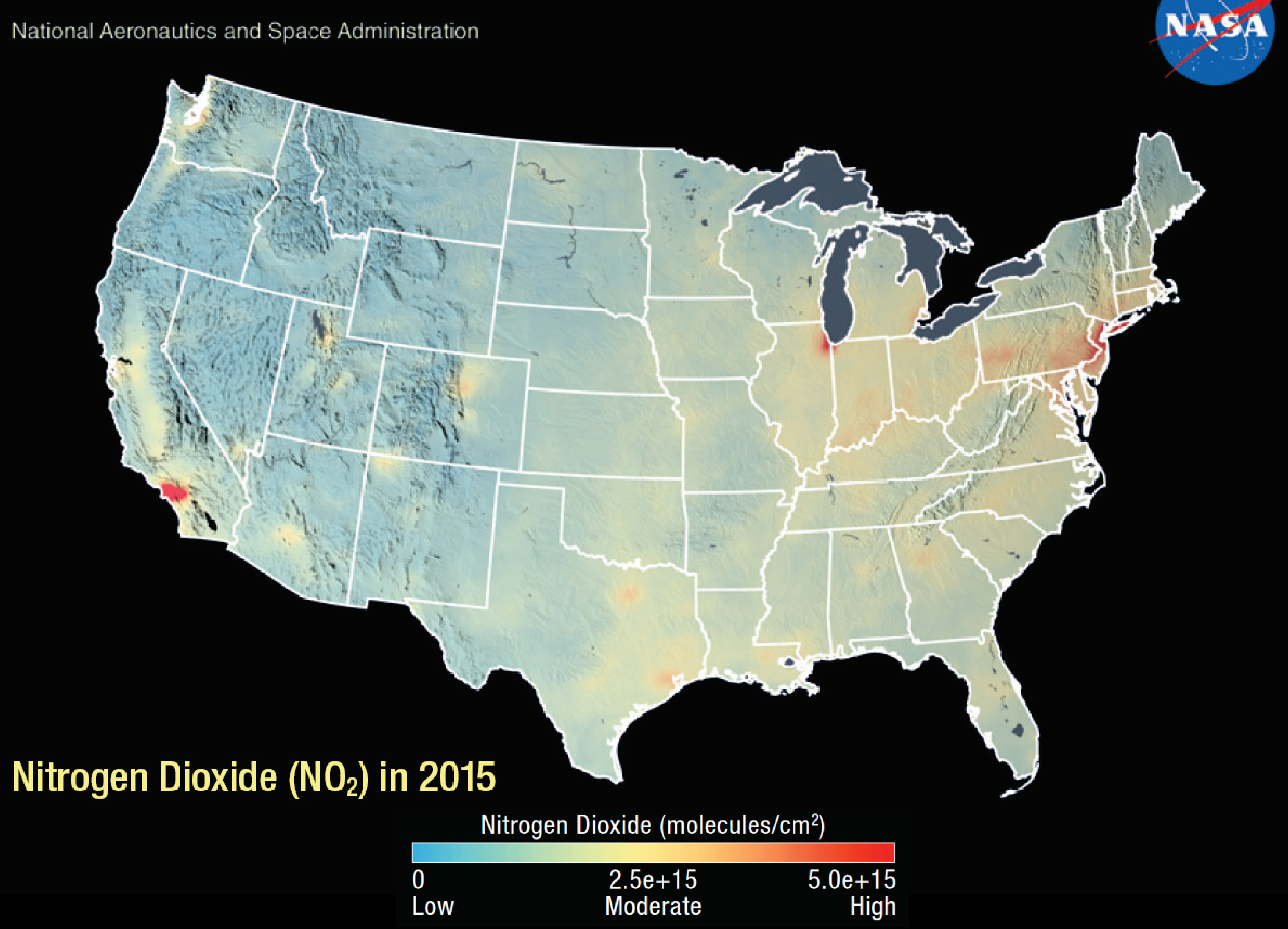
https://www.youtube.com/watch?v=LKe5FdKInJs

US Trends: NO_2



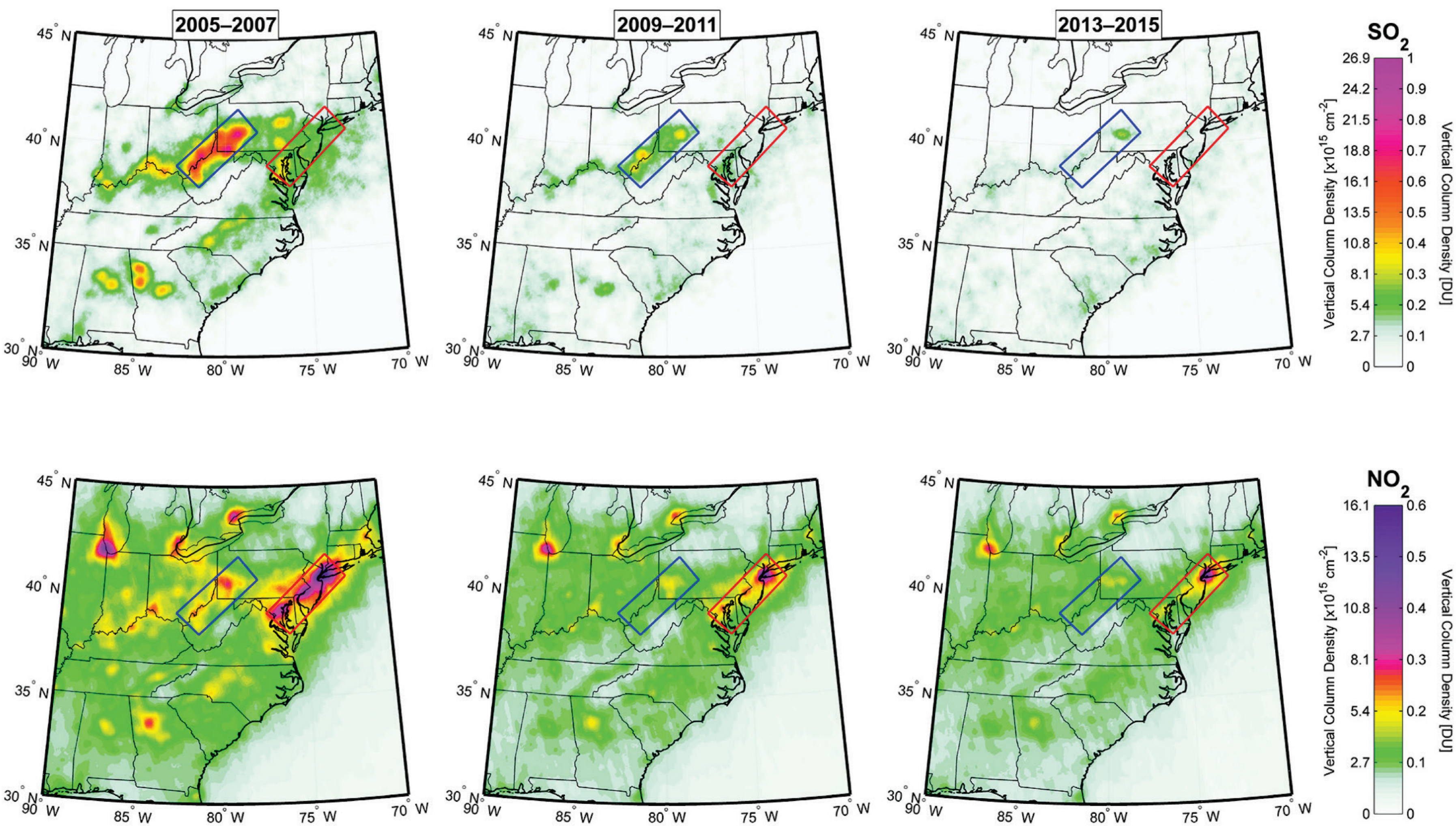
https://aura.gsfc.nasa.gov/images/outreach/NO2_2005-15_final.pdf

US Trends: NO_2



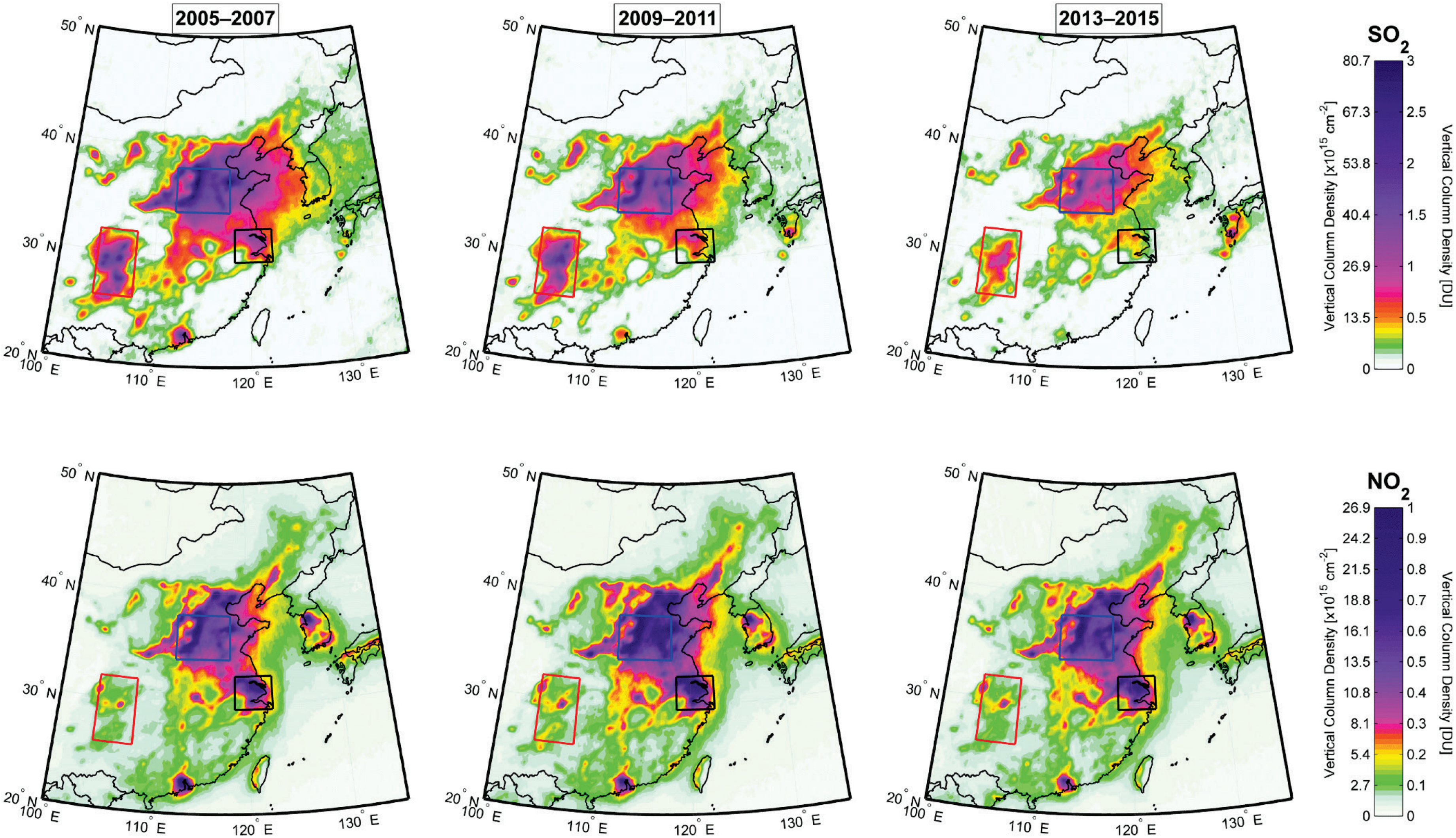
https://aura.gsfc.nasa.gov/images/outreach/NO2_2005-15_final.pdf

US Trends: NO_2 and SO_2



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

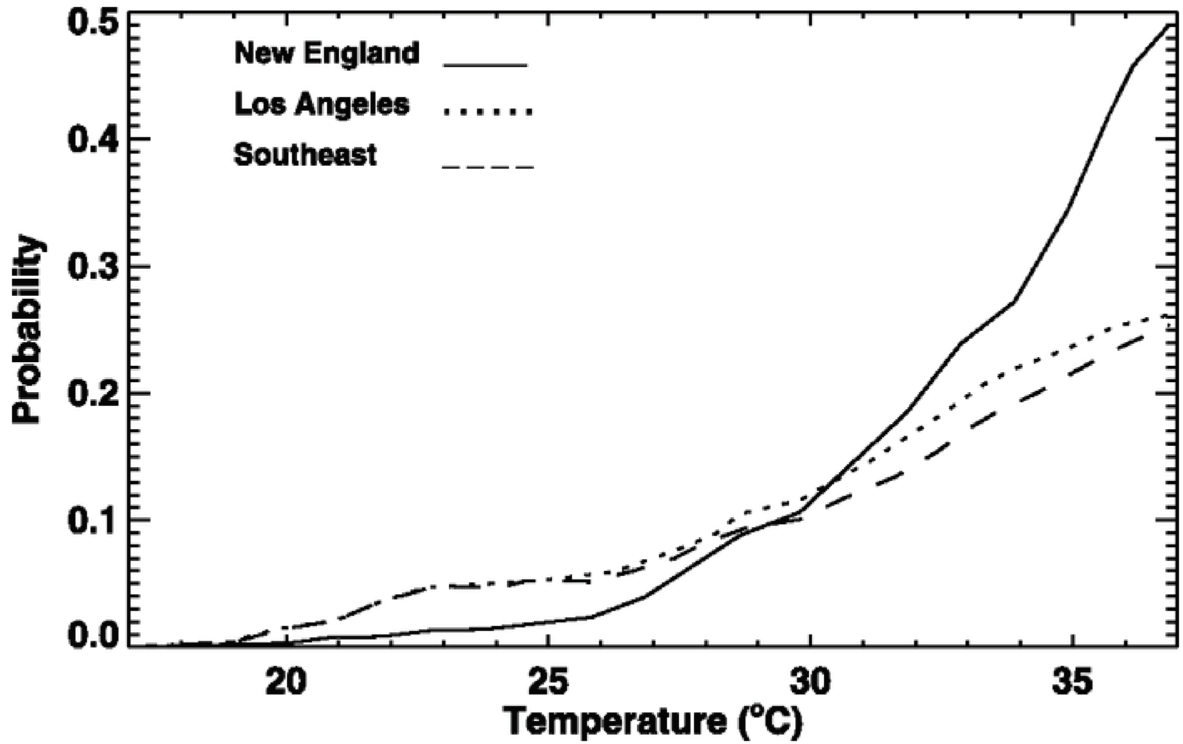
China Trends: NO_2 and SO_2



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

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

Probability of ozone exceedance vs. daily max. temperature

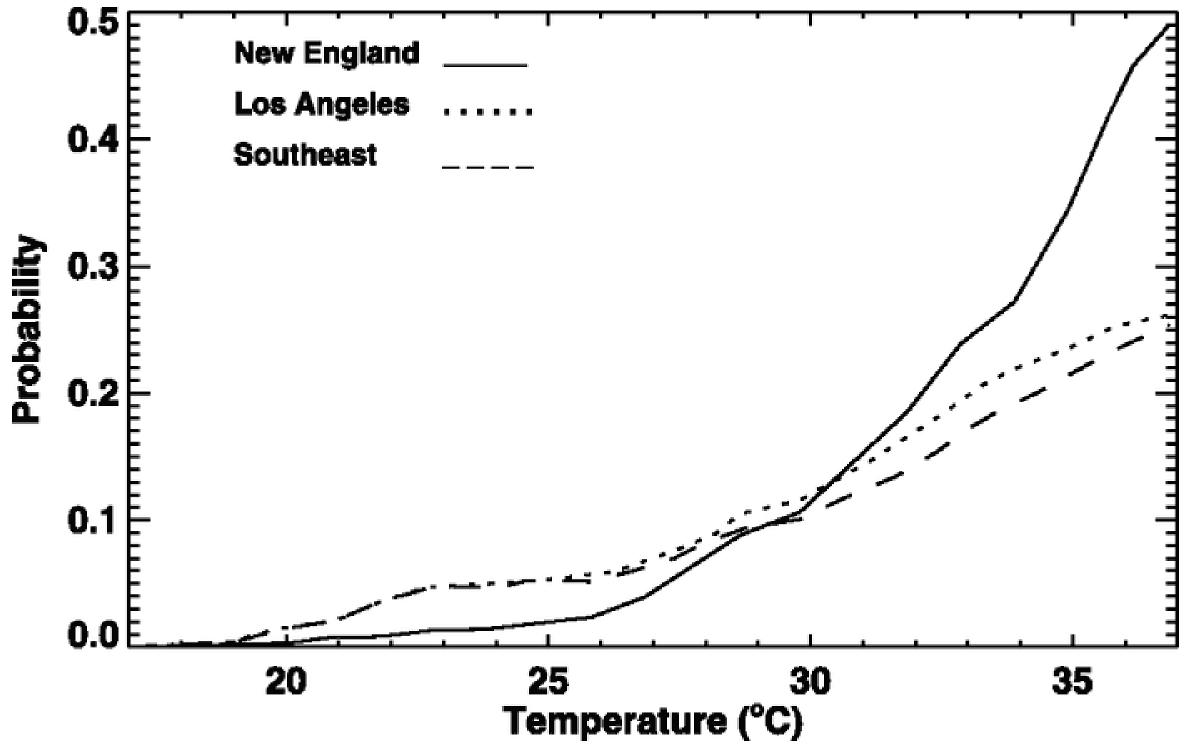


Lin et al. 2001

Why does probability of high ozone rise with increasing temperature?

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

Probability of ozone exceedance vs. daily max. temperature

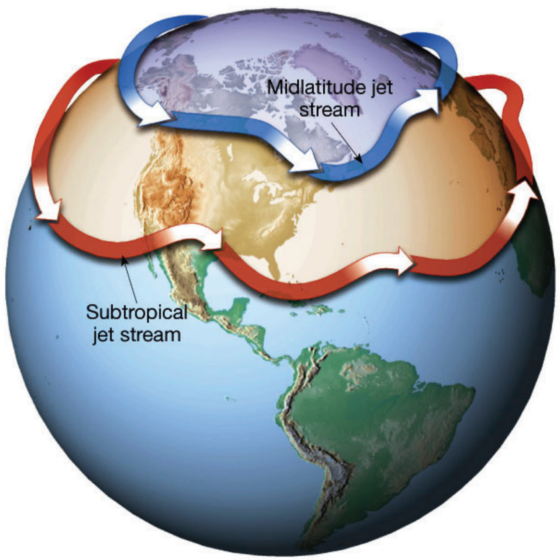


Lin et al. 2001

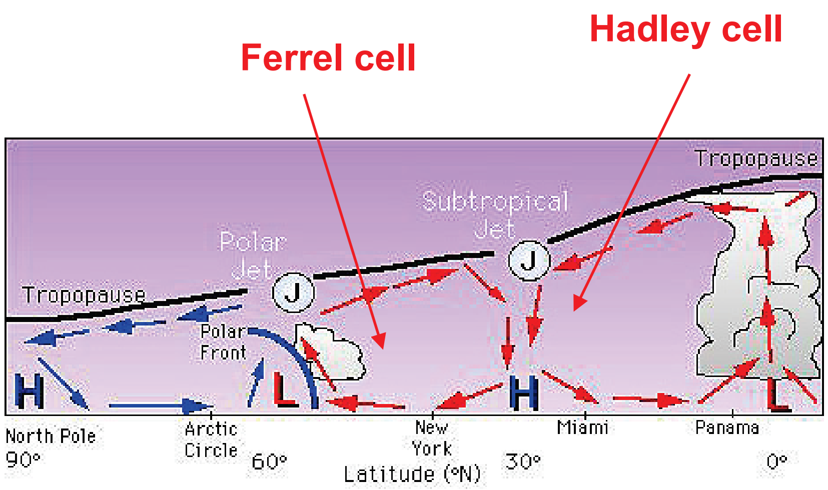
Why does probability of high ozone rise with increasing temperature?

Faster chemical reactions, increased anthropogenic emission (NO_x), increased biogenic emission (mainly isoprene, C_5H_8), and *stagnation of air*.

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

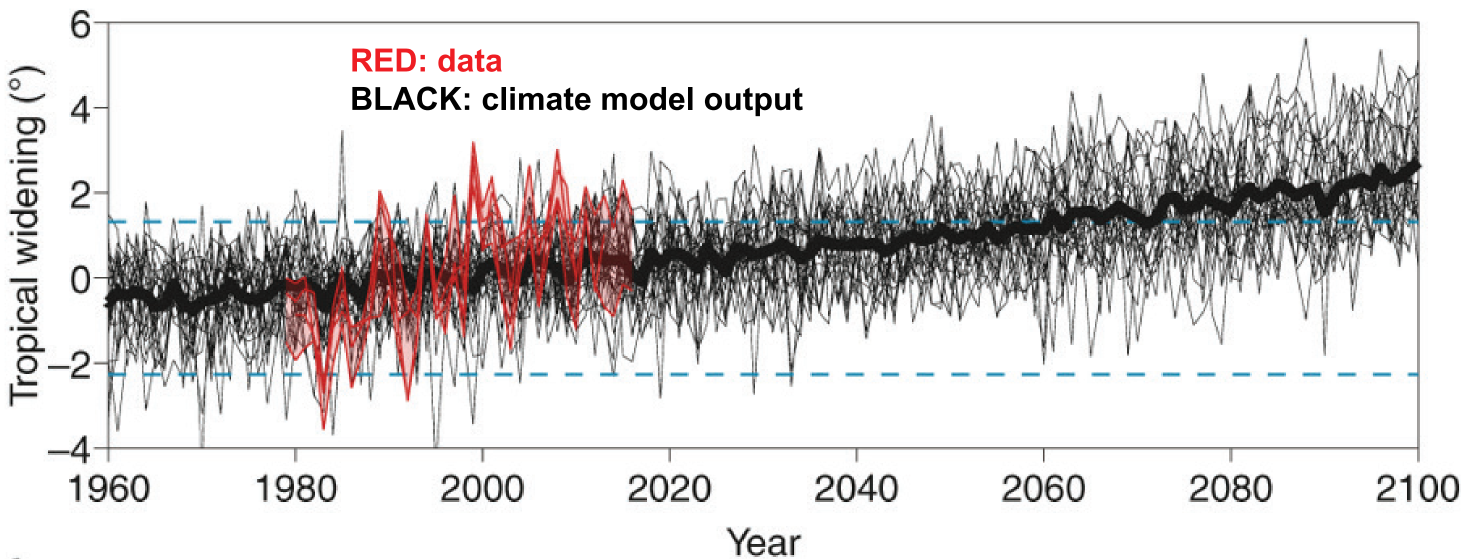
Climate Change and Air Pollution

Poleward expansion of the sub-tropical jet:

- Surface ozone highs occur along Subtropical Jet
- Driving forces:

  a) rising levels of GHGs lead to a weakening of the equator to pole due to more rapid warming at extra-tropical latitudes compared to tropics;

  b) prior increases in CFCs lead to ozone depletion in the extra-tropics, which exacerbates stratospheric cooling



Staten *et al*., Nature Climate Change, 2018
https://www.nature.com/articles/s41558-018-0246-2/

- **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**