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

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/spr2022
https://myelms.umd.edu/courses/137772

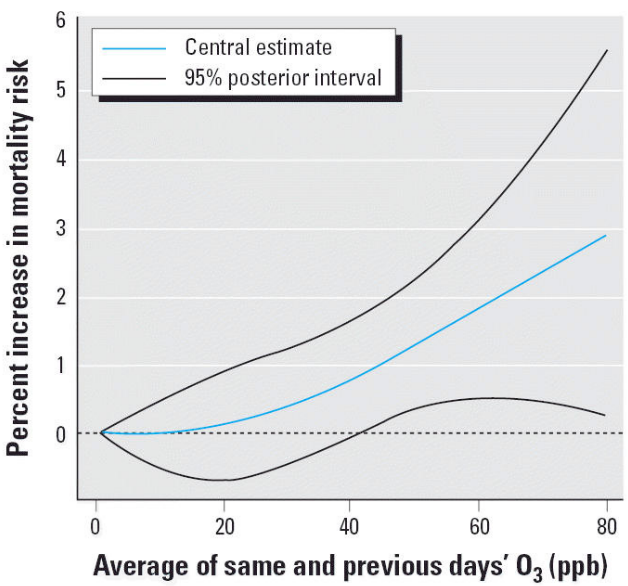
Today:
- **Tropospheric ozone production mechanism (CO, NO_x, and VOCs)**
- **Recent improvements of air quality**
- **Coupling of meteorology, and perhaps climate change, to air quality**

Lecture 13

17 March 2022

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



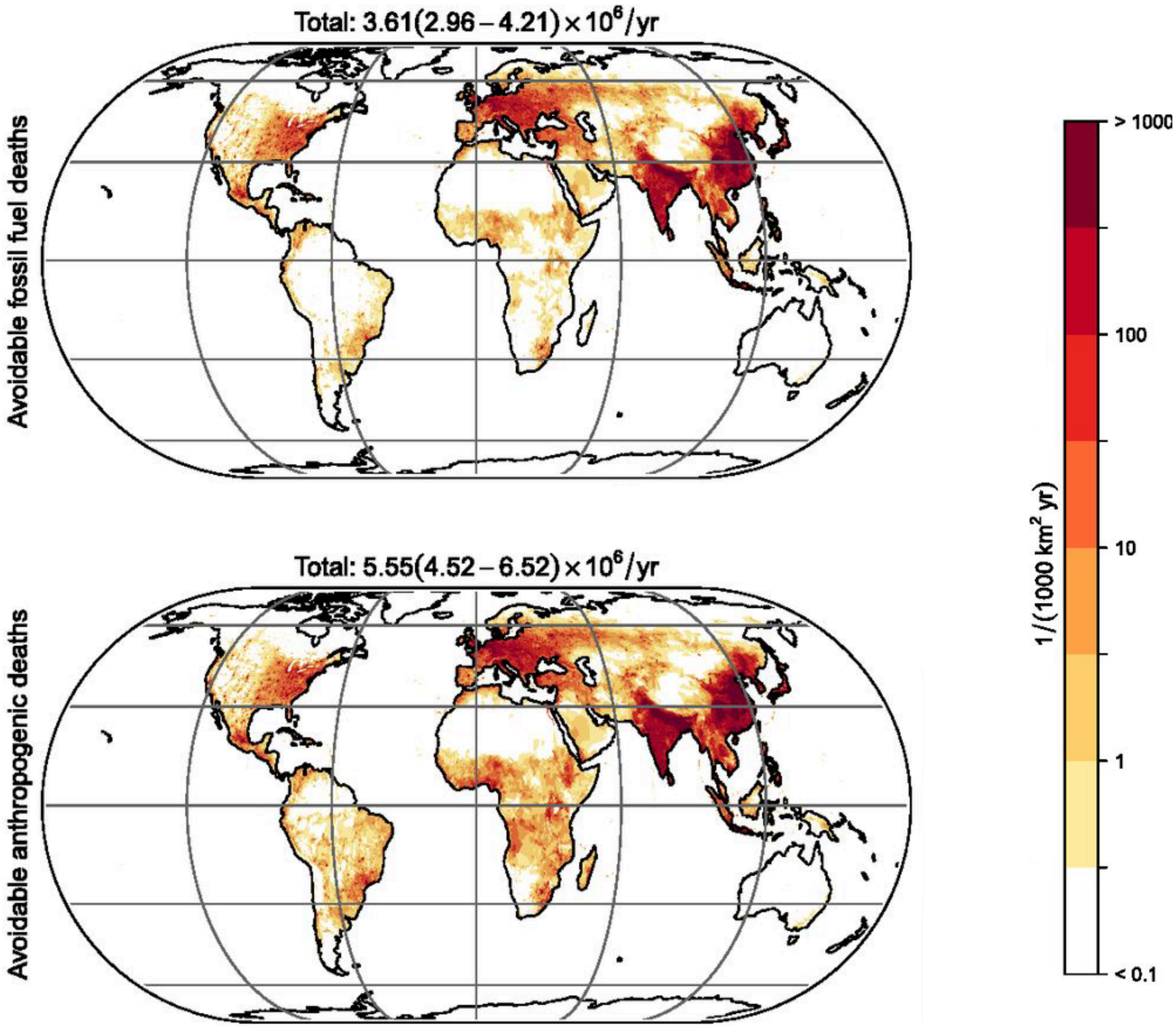
Increased risk of premature death (mortality) for all levels of surface O_3

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

Avoidable Deaths and Fossil Fuel Use



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

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

NO_2 (radical) and N_2O (long-lived GHG)

Nitrogen Dioxide: NO_2

Radical involved with numerous aspects of tropospheric and stratospheric chemistry

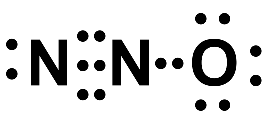
https://www.youtube.com/watch?v=0XTkO8KypUY

NO_2 when present in large amounts can appear as a *reddish-brown haze*

https://www.pca.state.mn.us/air/nitrogen-dioxide-no2

Nitrous Oxide aka Dinitrogen monoxide: N_2O

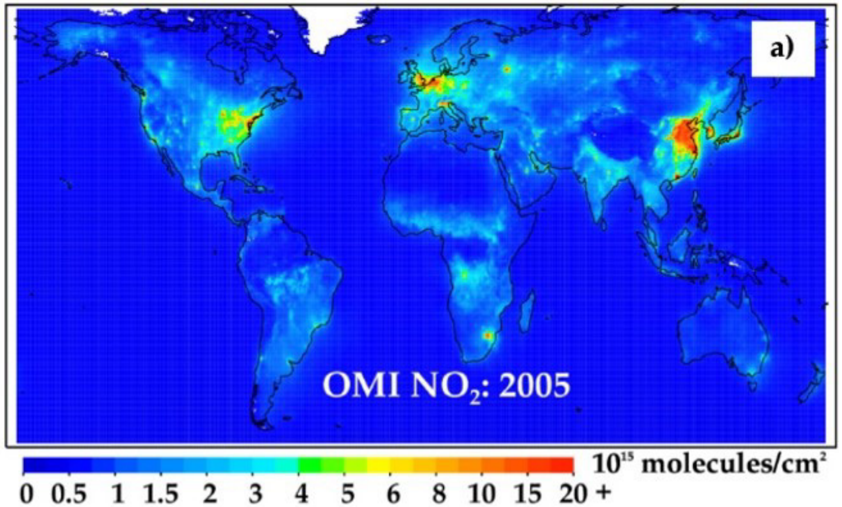
Very long-lived, nearly inert, well mixed greenhouse gas
Rising abundance linked mainly to human use of fertilizer
Causes global warming
Decomposes in the stratosphere, leading to production of NO_2



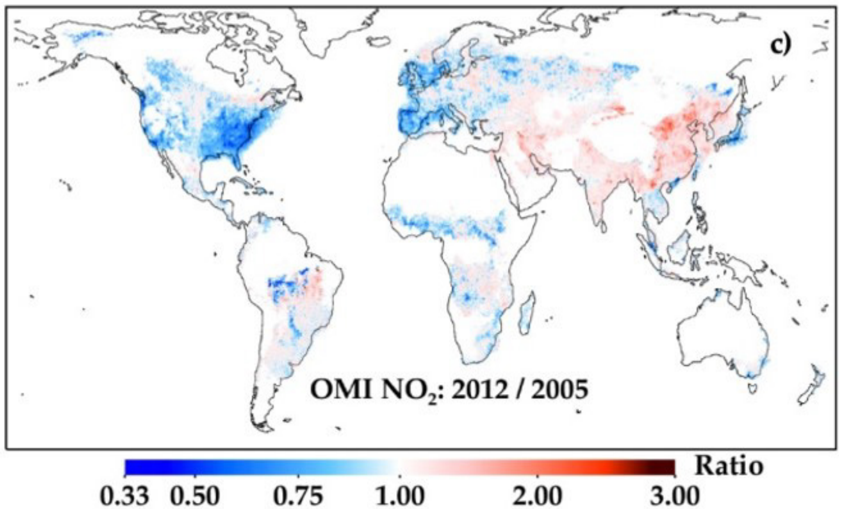
https://www.youtube.com/watch?v=ZlHIQhJlWNs

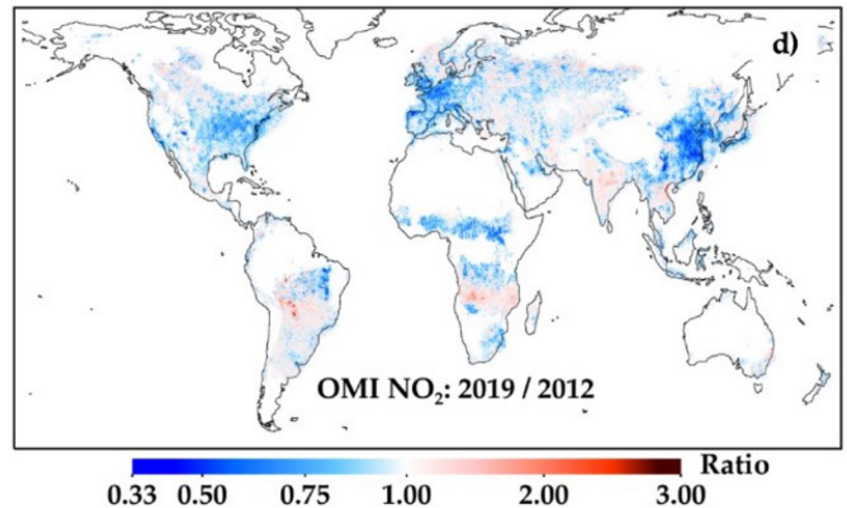
Nitrous: "Relating to or containing nitrogen"

https://www.yourdictionary.com/nitrous



Lecture 2, Slide 40 (Handout)





Top: Tropospheric vertical column NO_2 (Trop NO_2) measured in 2005
Bottom Left: Ratio of Trop NO_2 measured in 2012 and 2005
Bottom Right: Ratio of Trop NO_2 measured in 2019 and 2012
All observations from the NASA OMI instrument

Goldberg *et al.*, *ERL*, 2021
https://iopscience.iop.org/article/10.1088/1748-9326/ac2c34/meta

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	← 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/m^3, 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.

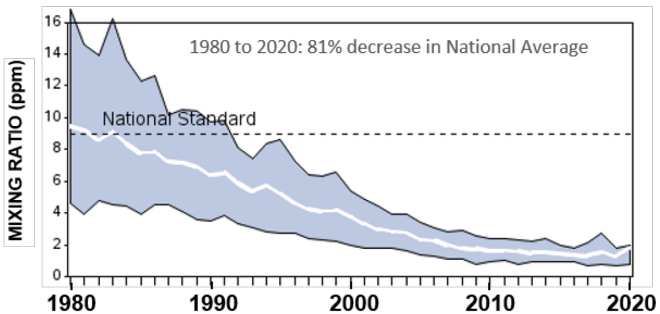
Source: U.S. Environmental Protection Agency. Standards also exist for lead, but are not included here.

Chemistry in Context

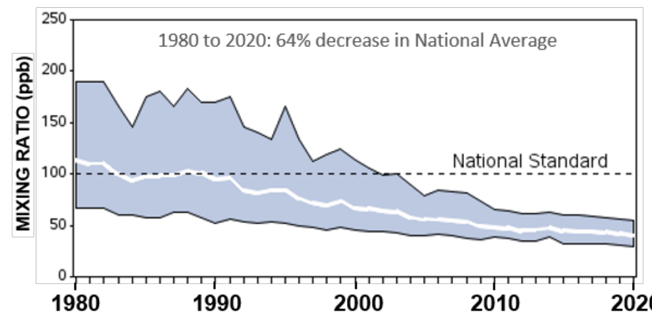
Criteria pollutant: common-place and detrimental to human welfare

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

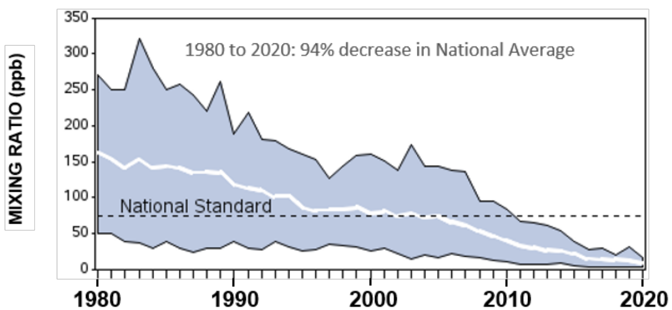
CO Air Quality, 1980 to 2020
Annual 2nd Maximum 8-Hour Average
National Trend based on 36Sites



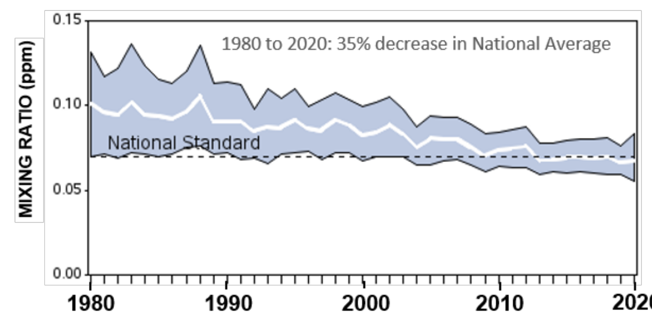
NO_2 Air Quality, 1980 to 2020
Annual 98th Percentile of Daily Max 1-Hour Average
National Trend based on 20 Sites



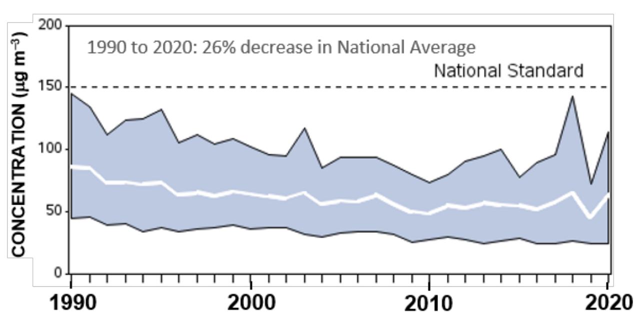
SO_2 Air Quality, 1980 to 2020
Annual 99th Percentile of Daily Max 1-Hour Average
National Trend based on 32 Sites



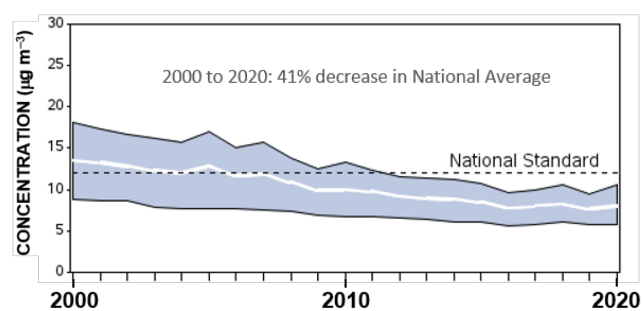
O_3 Air Quality, 1980 to 2020
Annual 4th Maximum 8-Hour Average
National Trend based on 188 Sites



PM_{10} Air Quality, 1990 to 2020
Annual 4th Maximum 24-Hour Average
National Trend based on 100 Sites

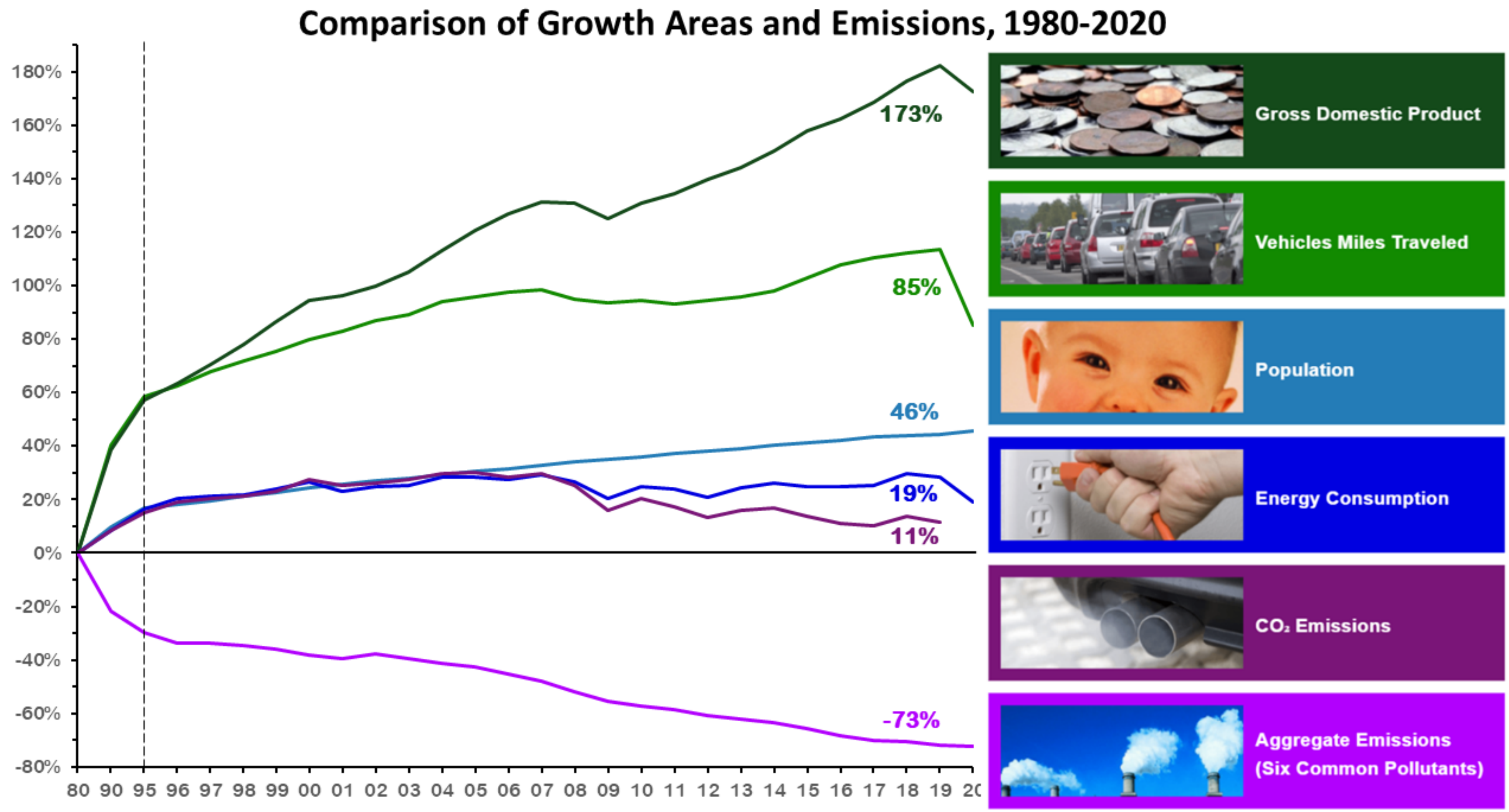


$PM_{2.5}$ Air Quality, 2000 to 2020
Seasonally-Weighted Annual Average
National Trend based on 390 Sites



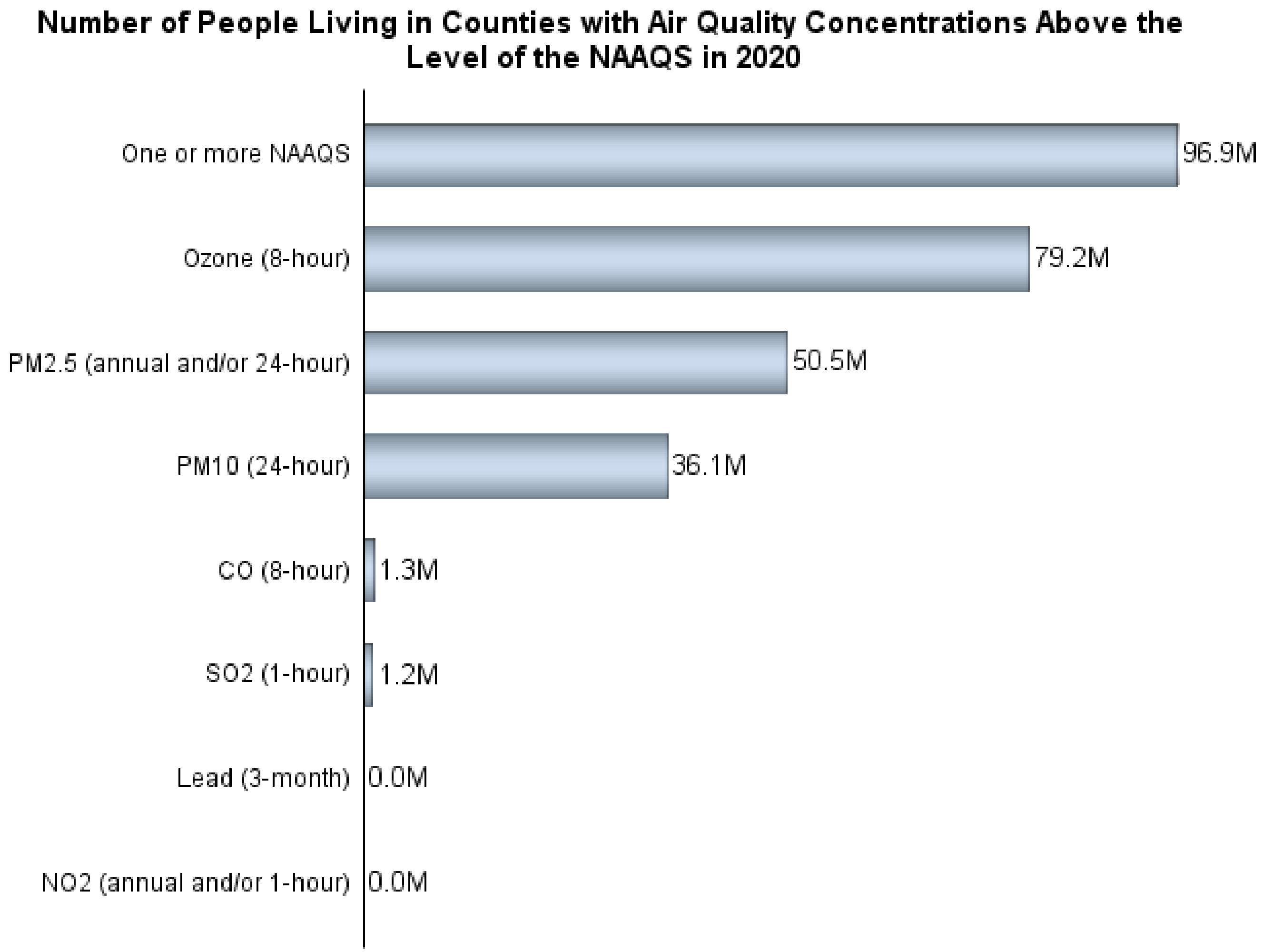
https://www.epa.gov/air-trends

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

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

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

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

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

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

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

Oxidation of CO in the presence of NO_x (NO & NO_2) leads to production of tropospheric 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$_3$:

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

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

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

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

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

Net: $CO + O_2 + OH \rightarrow$

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

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

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

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: can occur via either:

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

or

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

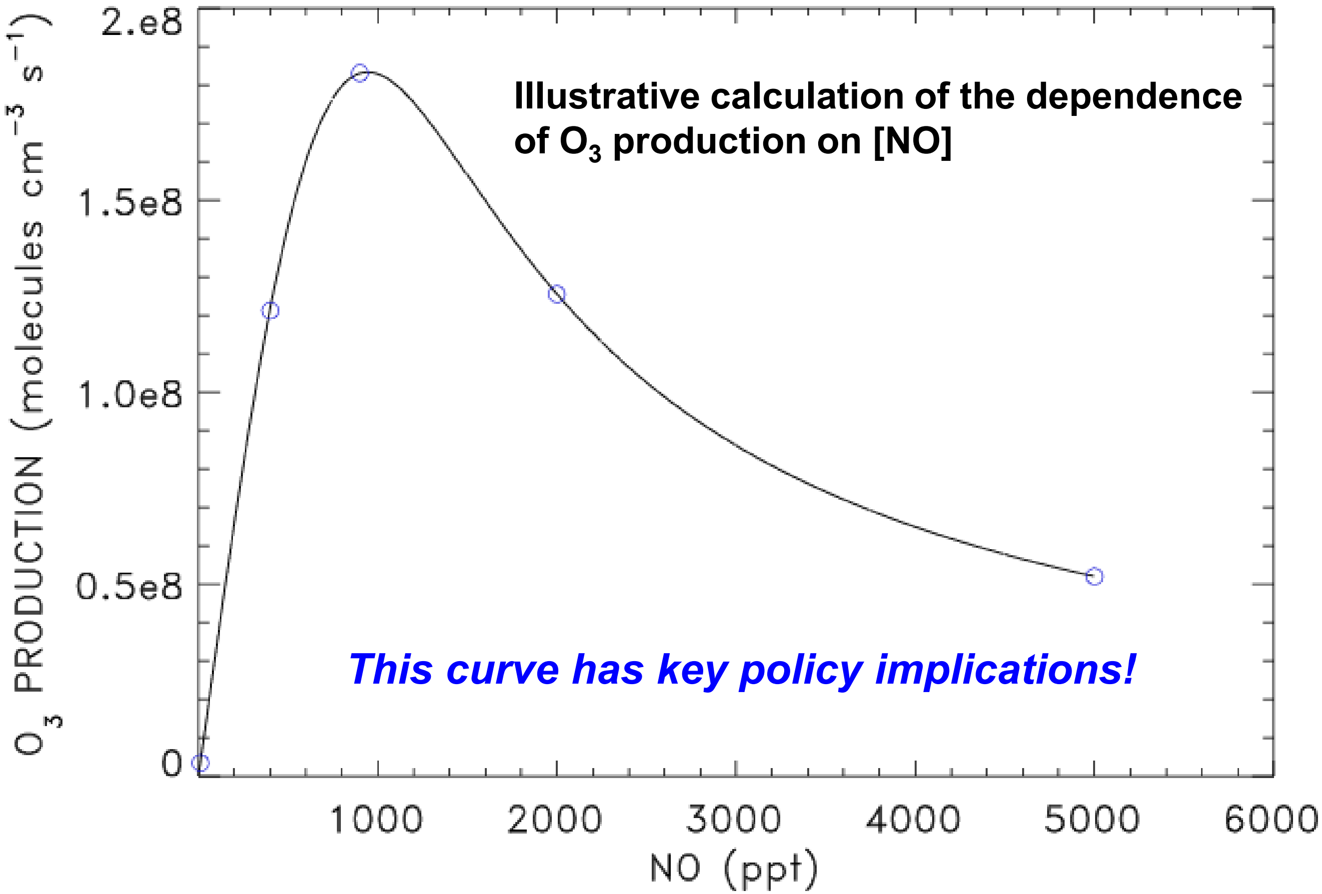
Tropospheric Ozone Production versus NO

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.



Tropospheric Ozone Production versus NO_x and VOCs

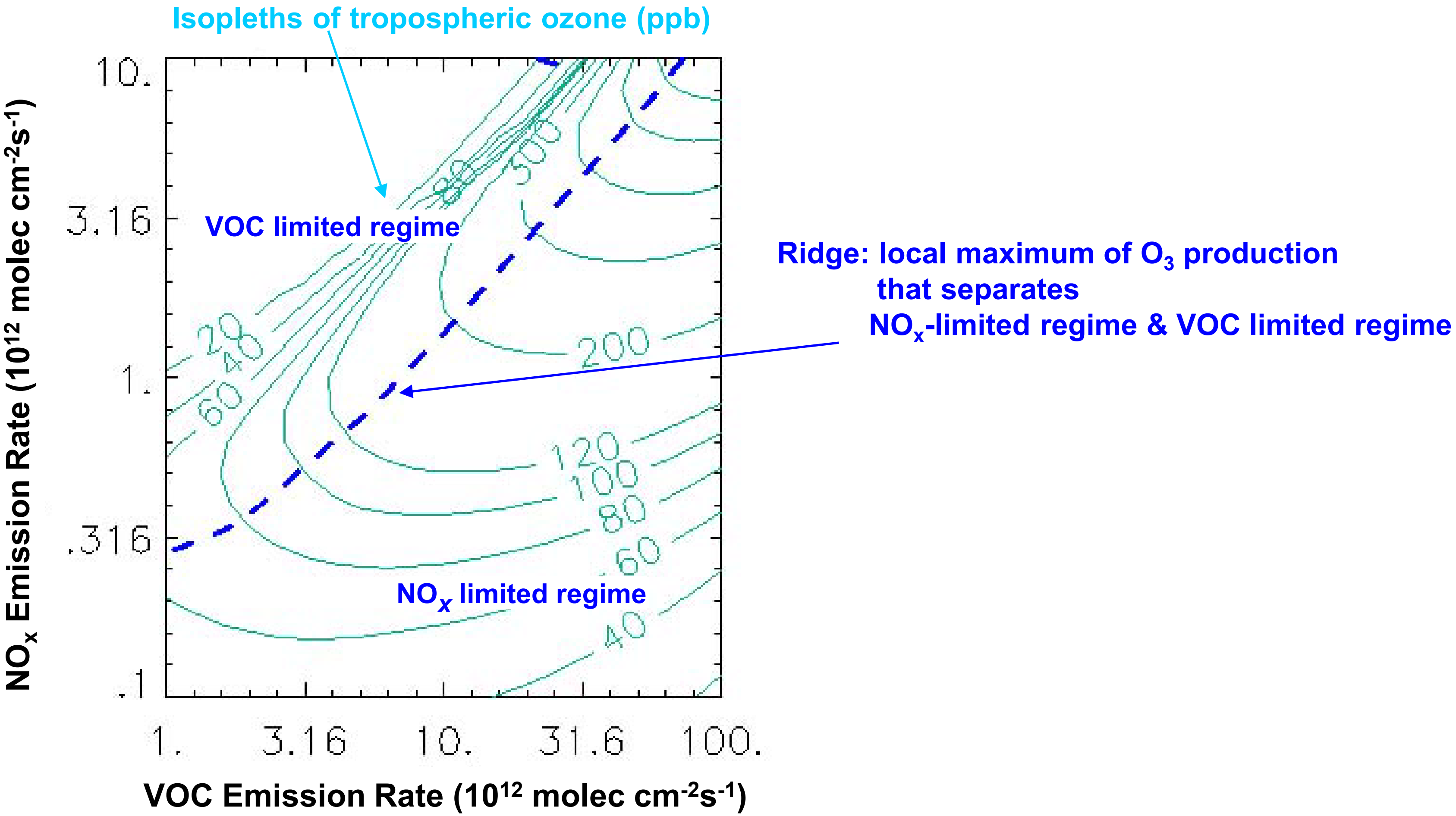


Figure: http://www-personal.umich.edu/~sillman/ozone.htm

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

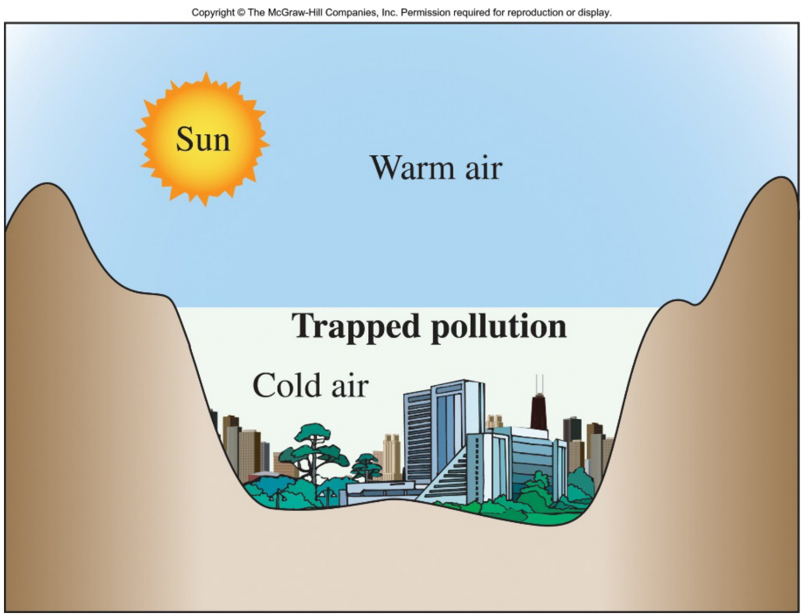
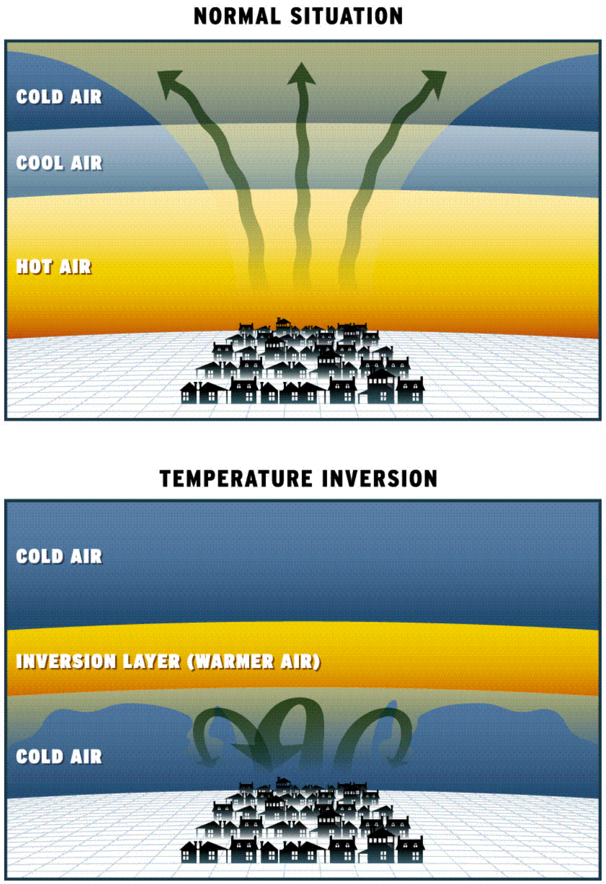


Figure 1.10, Chemistry in Context



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

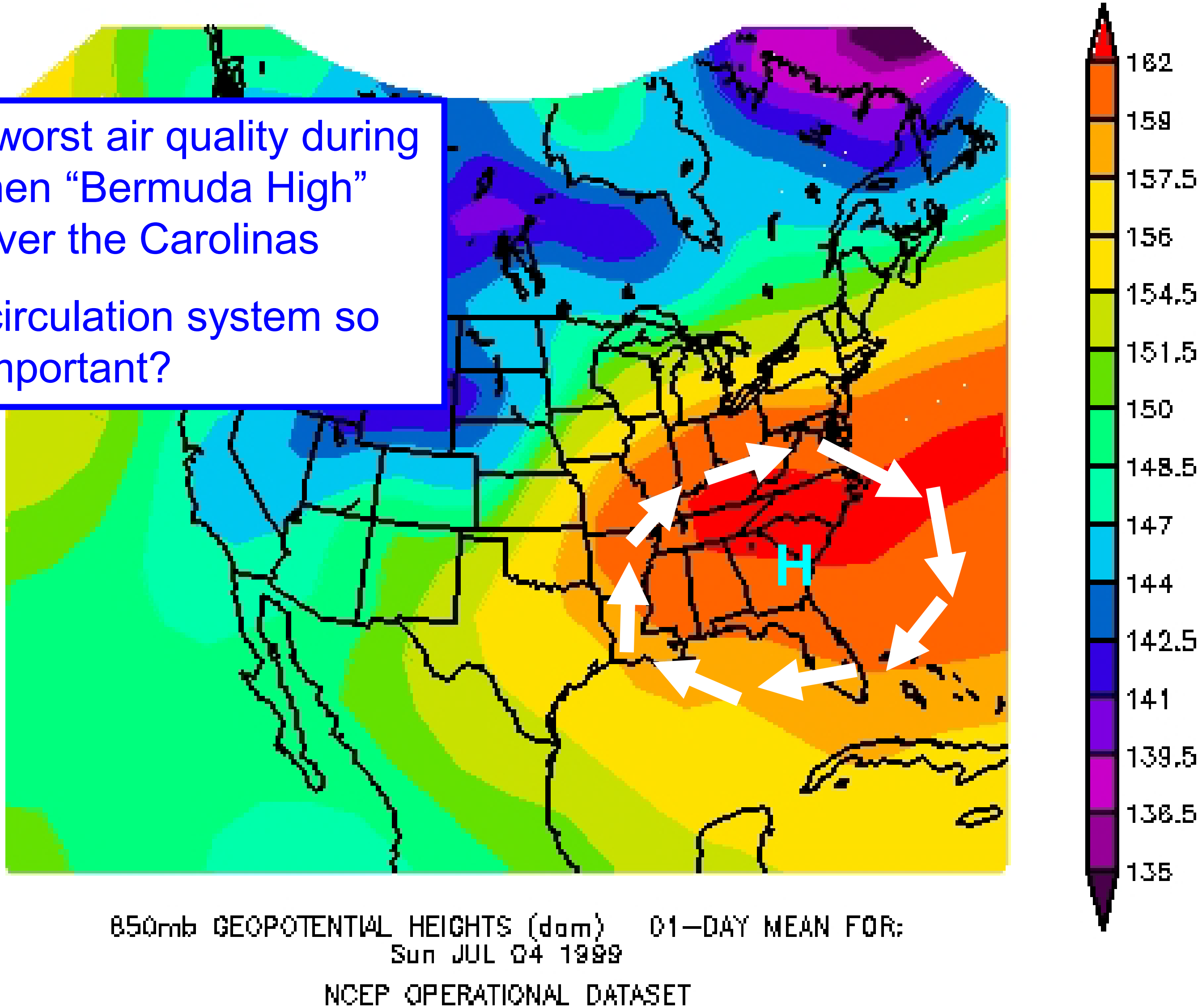
Air pollutants can accumulate in cities ringed by mountains, such as Los Angeles, Mexico City, and Salt Lake City

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

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

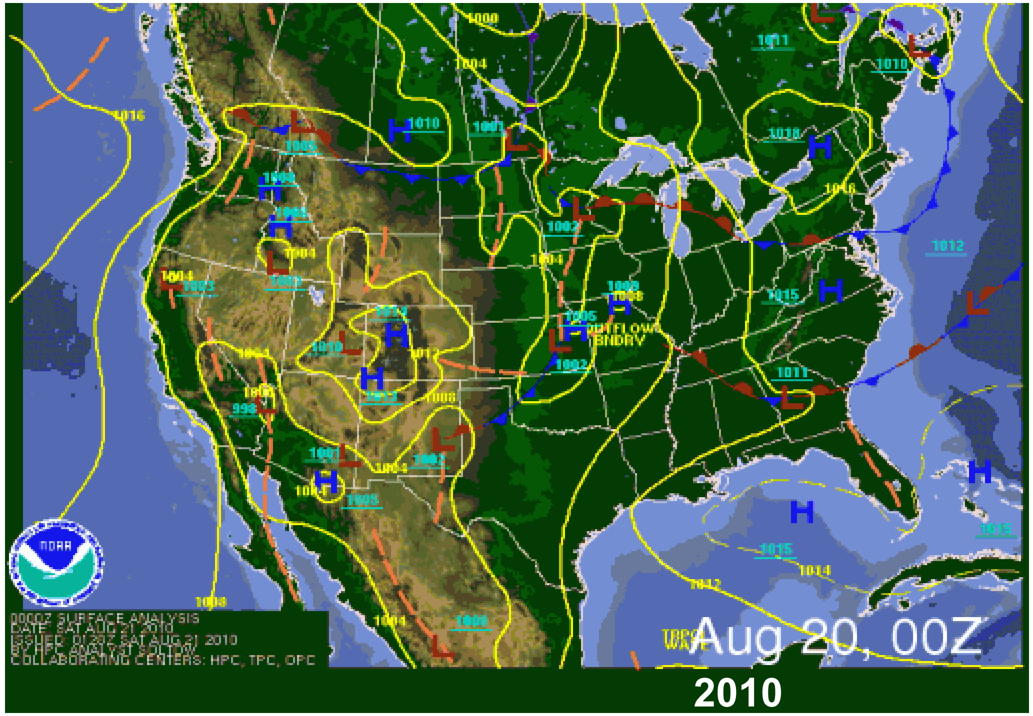
Maryland has worst air quality during summer, when "Bermuda High" sets up over the Carolinas

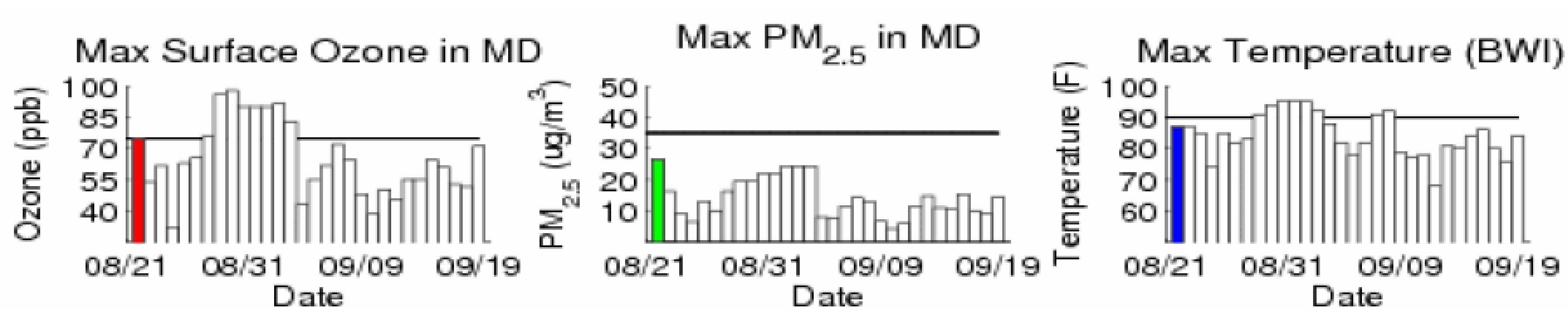
Why is this circulation system so important?



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

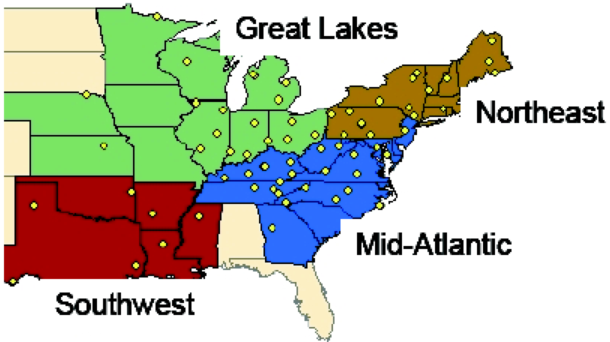


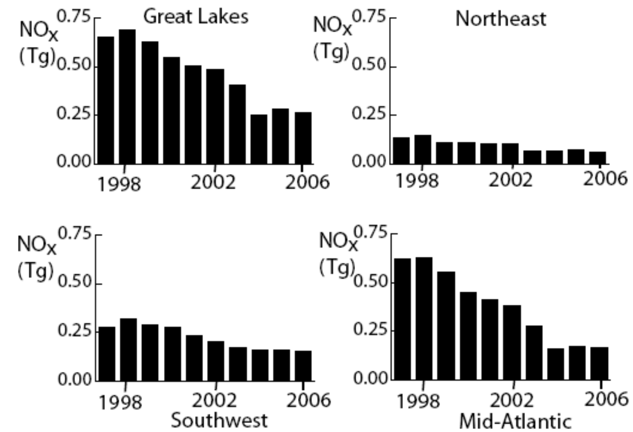


2010

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

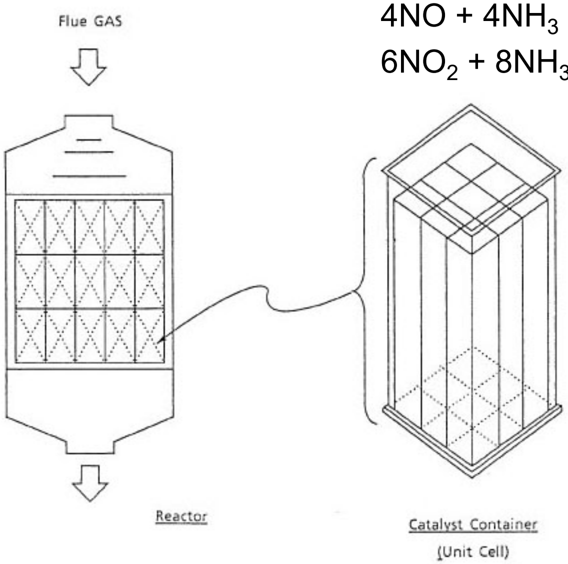
Removal of NO_x from Power Plants





NOx Control:
SCR Selective Catalytic Reduction

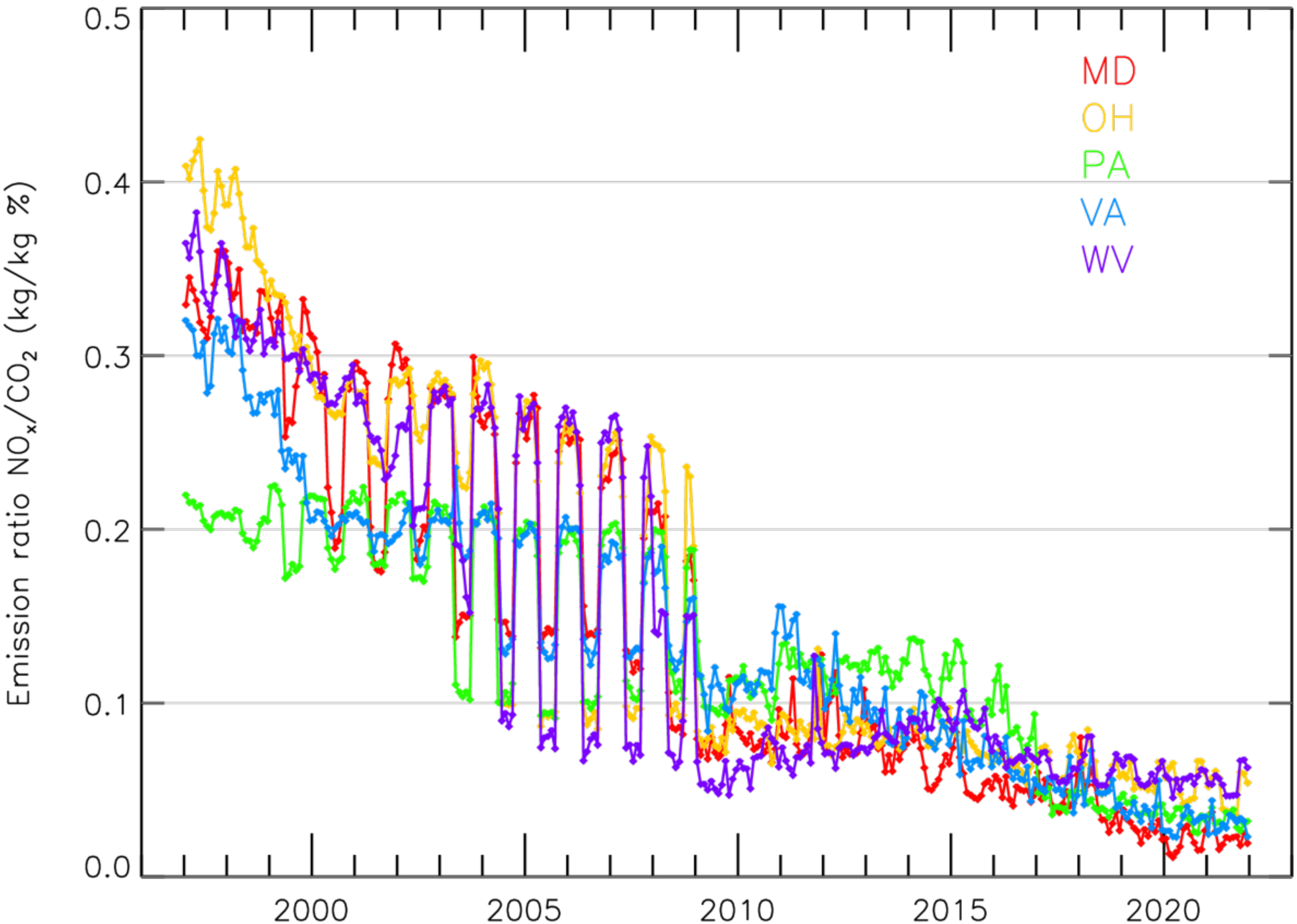
$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$



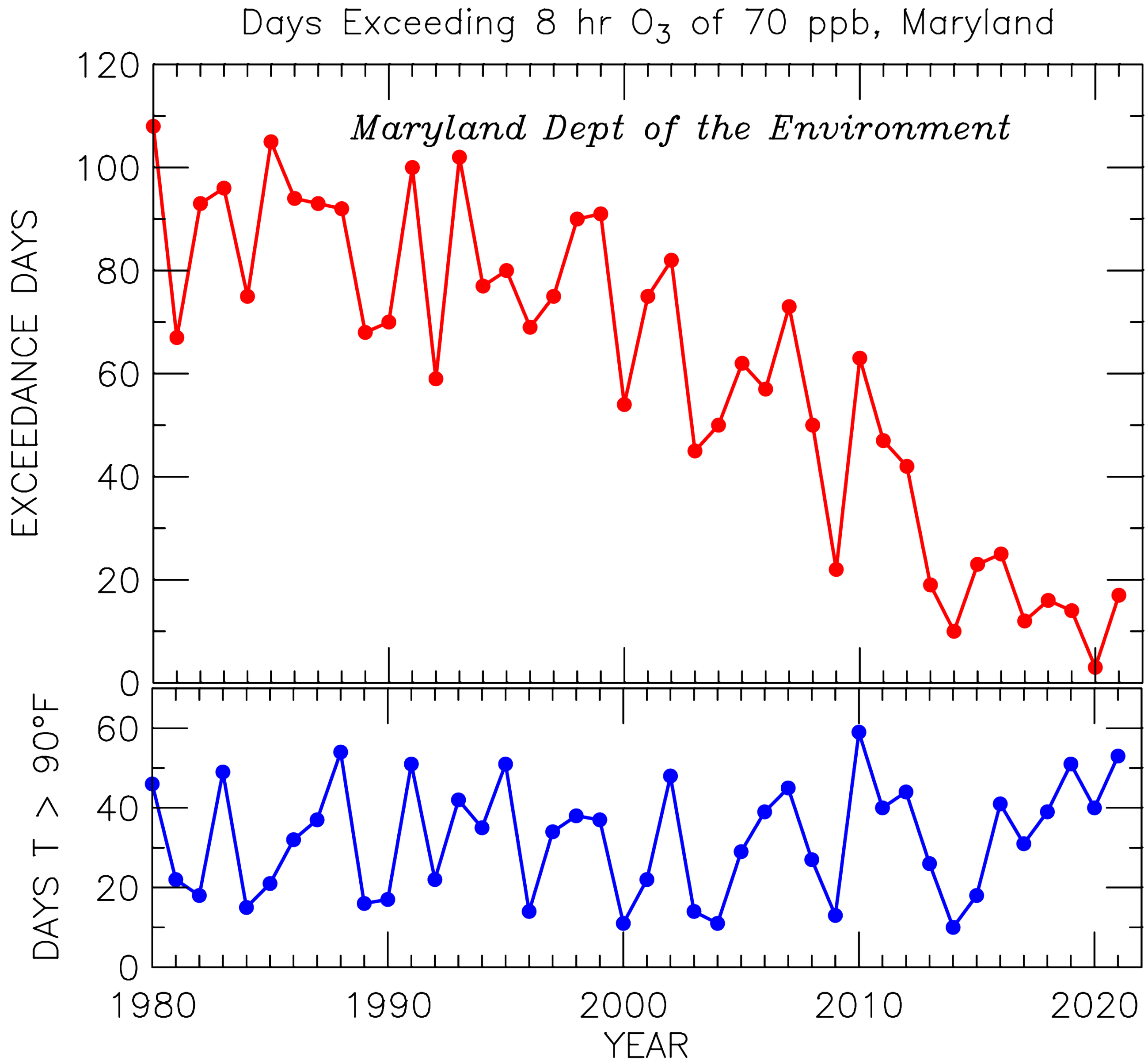
Catalyst
- Maximize $NOx \rightarrow N_2$
- Minimize $SO_2 \rightarrow SO_3$

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

Trends in power plant emissions of NOx



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

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

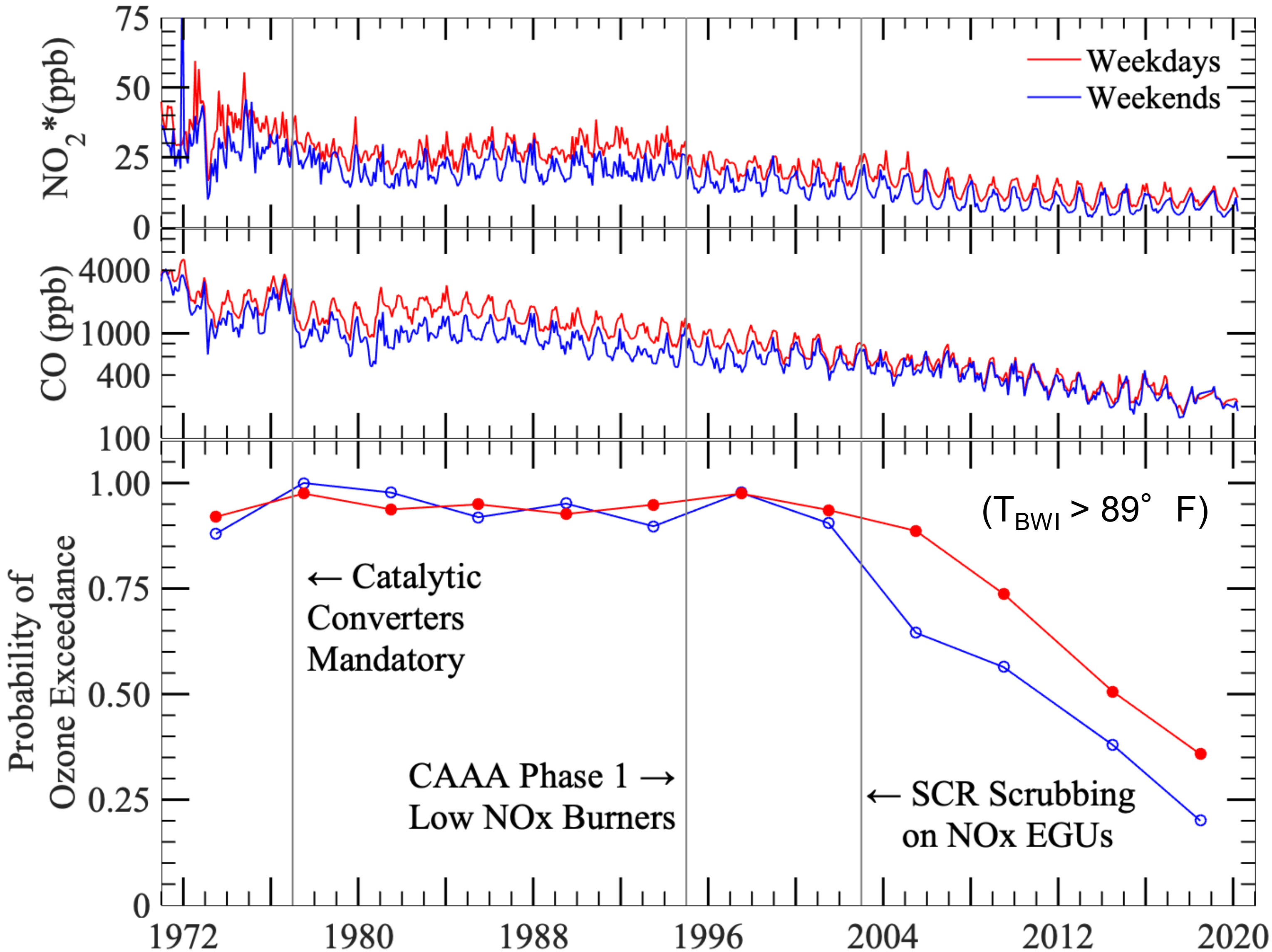
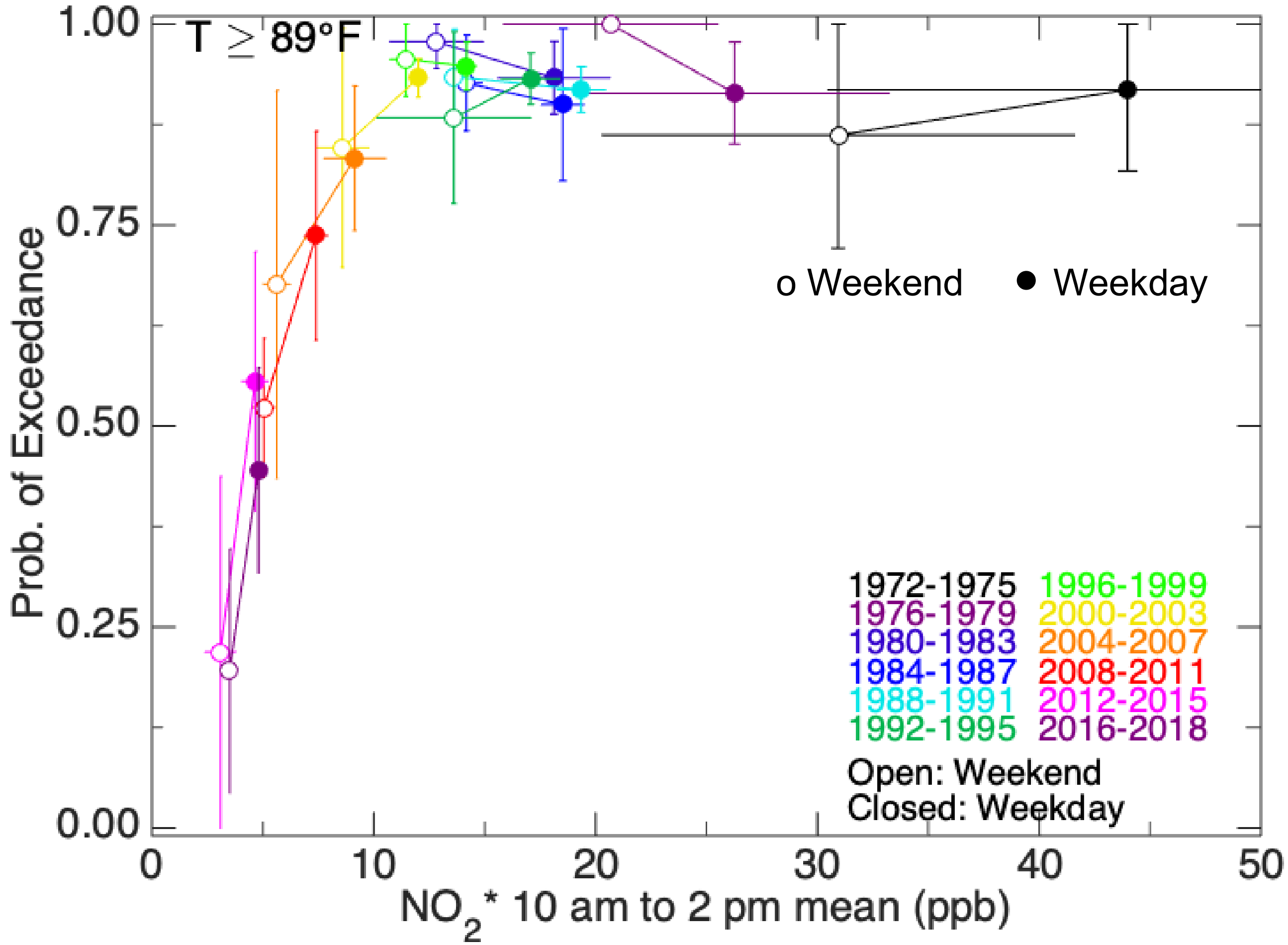


Figure above research product of UMCP Graduate Student Sandra Roberts

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

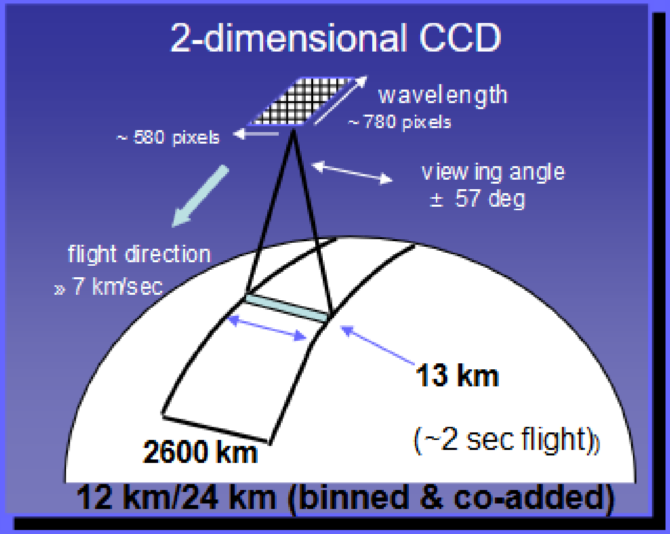


Analysis in this framework motivated by Pusede and Cohen, ACP, 2012
http://www.atmos-chem-phys.net/12/8323/2012/acp-12-8323-2012.html
Figures above research product of UMCP Graduate Student Sandra Roberts

NASA OMI Instrument on Aura

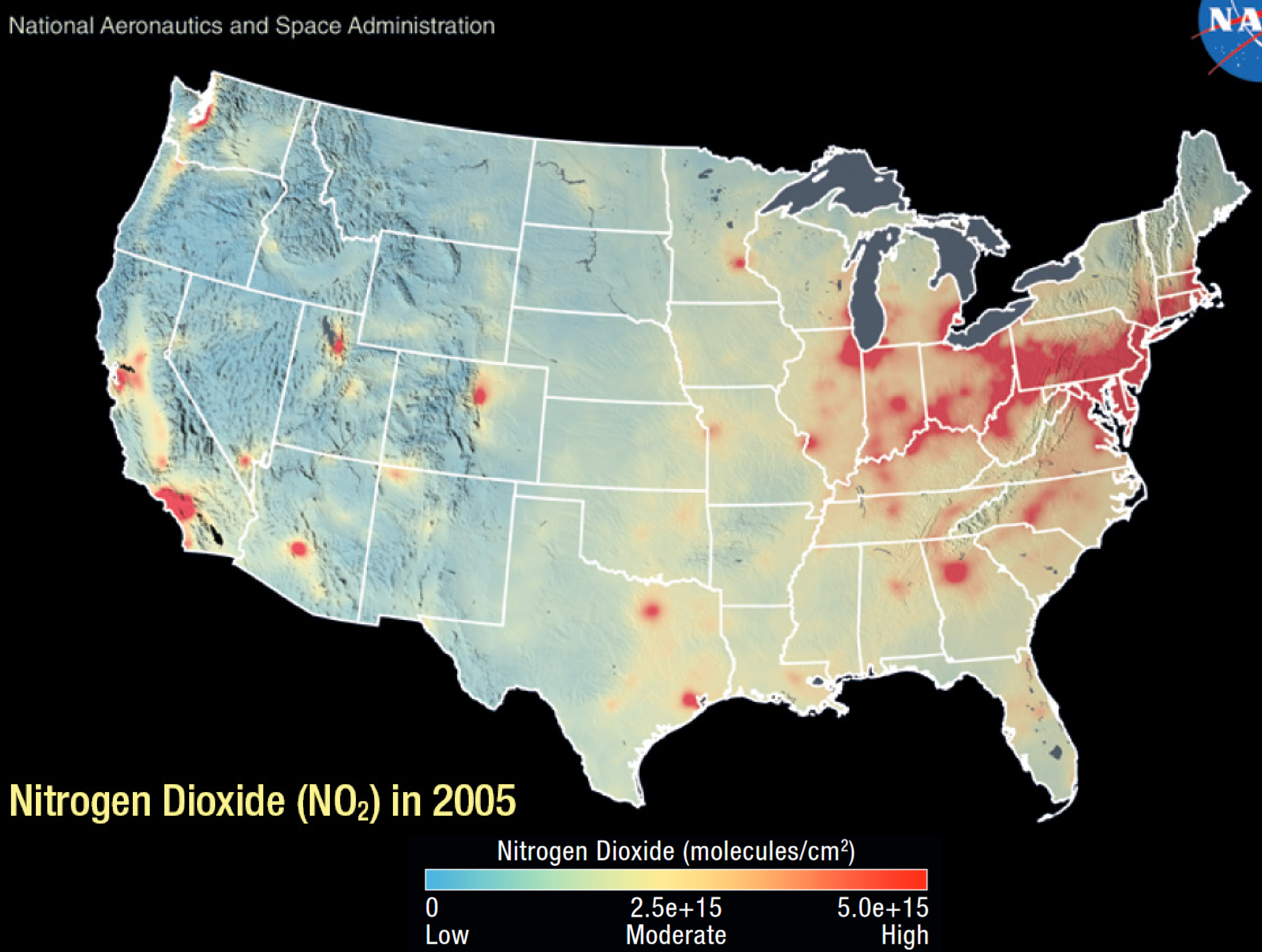
Ozone Monitoring Instrument

- 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

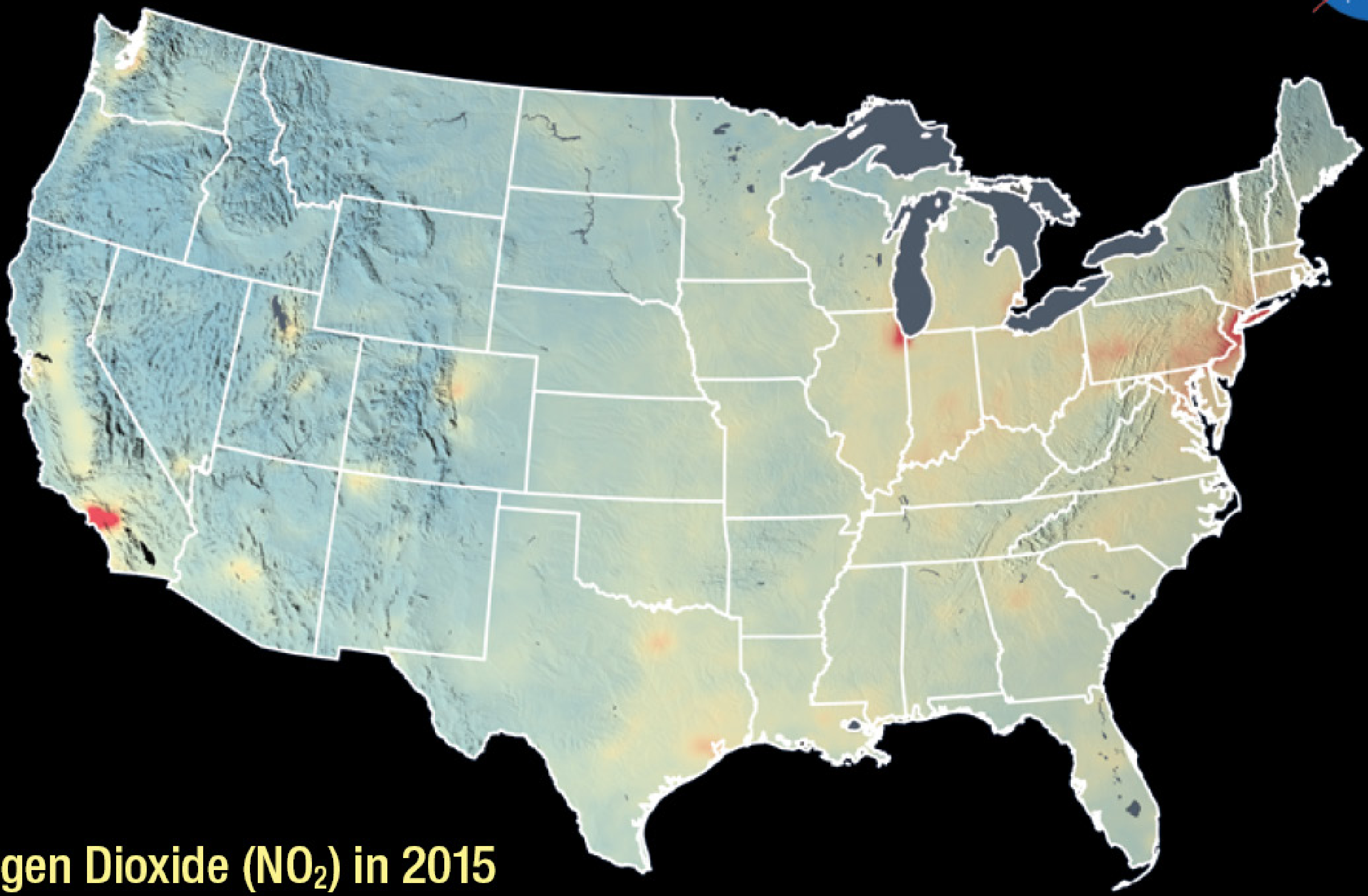
US Trends: NO_2



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

US Trends: NO_2

National Aeronautics and Space Administration



Nitrogen Dioxide (NO_2) in 2015

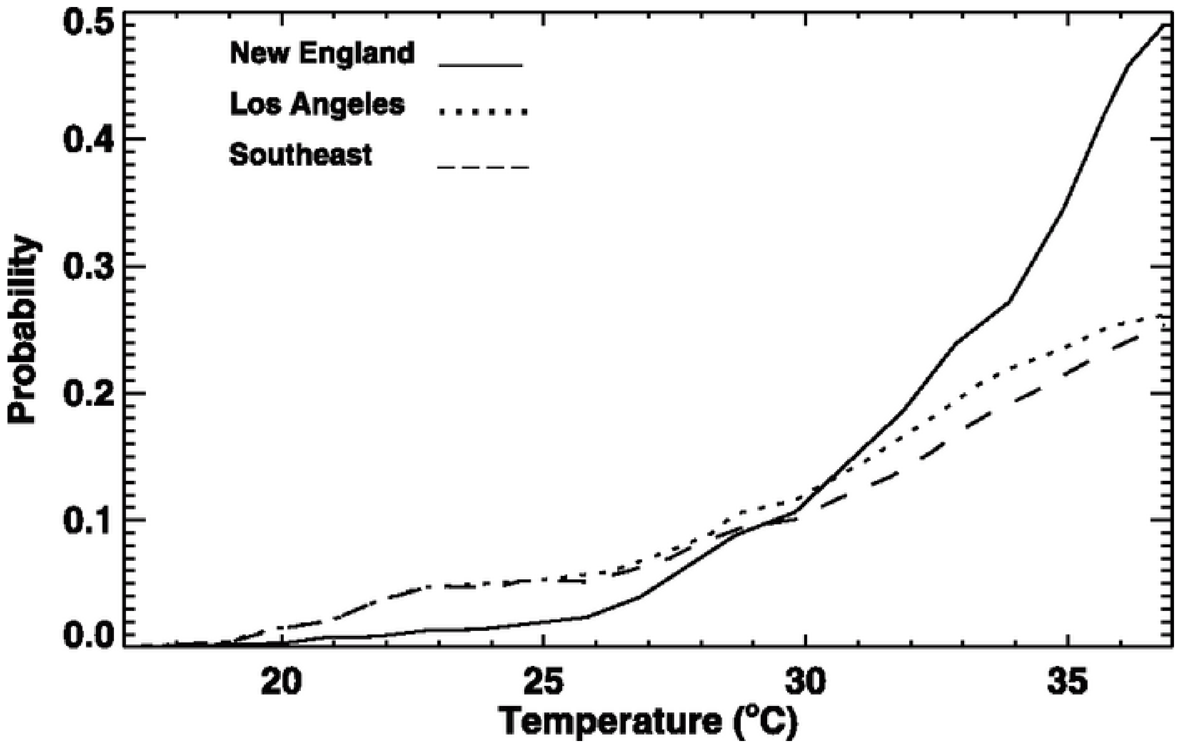
Nitrogen Dioxide (molecules/cm^2)

0	2.5e+15	5.0e+15
Low	Moderate	High

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

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

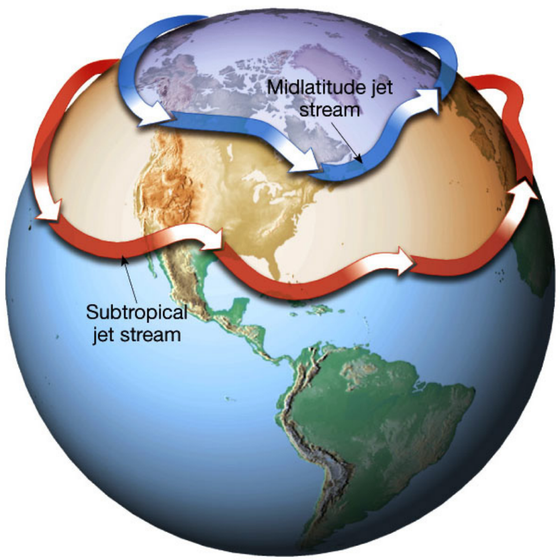
Probability of ozone exceedance vs. daily max. temperature



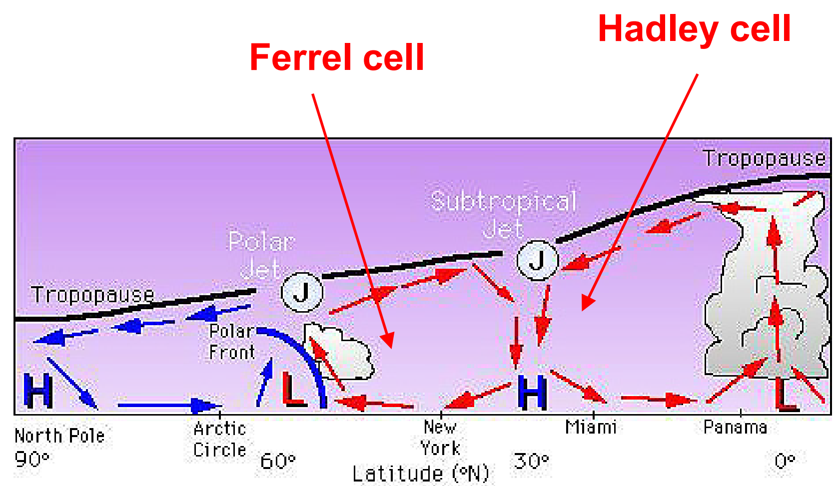
Lin et al. 2001

Why does probability of high ozone rise with increasing temperature?

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

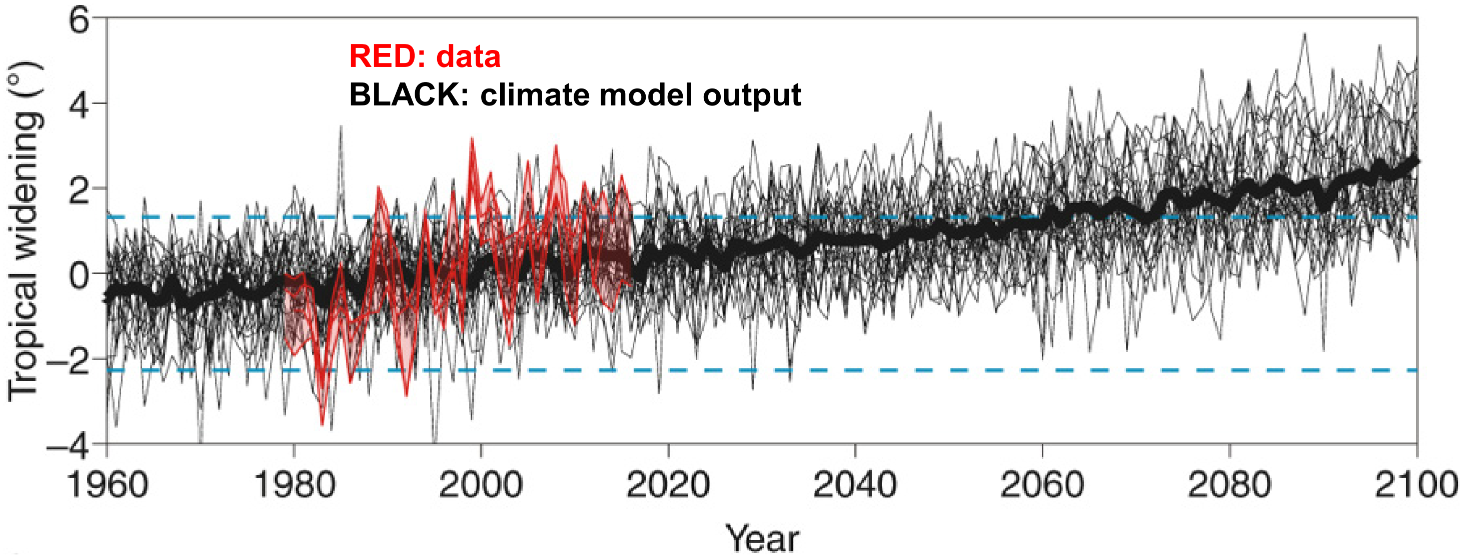
Climate Change and Air Pollution

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**