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

Ross Salawitch & Walt Tribett

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

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**

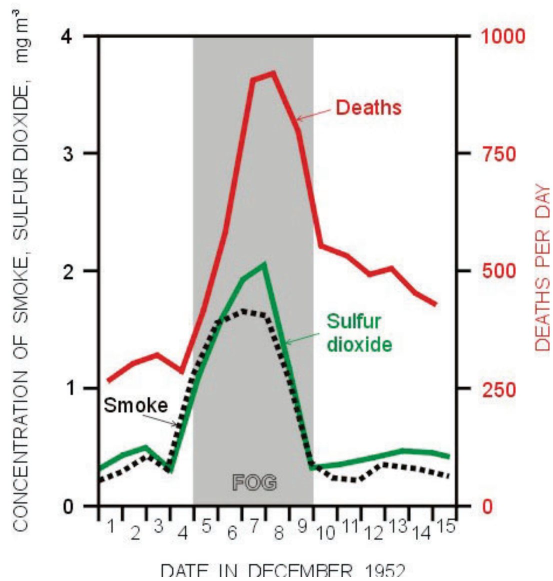
Lecture 12
26 March 2019

Student Projects

- **Mandatory for 633 students:** project grade will count towards final grade in an amount equal to each exam
- **Optional for 433 students:** can use project grade to either 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 Friday, 10 May 2019… you're welcome to complete sooner
- ~6 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
- ~12 min project presentations at TBD time on 10 May: everyone welcome to attend
- Request all students who will complete a project to provide a **2 to 3 sentence description 2 weeks** from today: **Tues, 9 April 2019**
  Please use next **2 weeks** to speak to me about a project topic
- 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

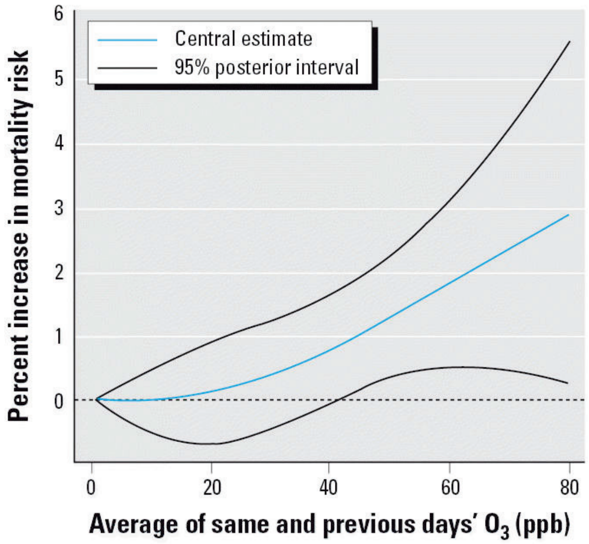
Table 2. Decreases in ozone (the population-weighted annual average 8-h daily maximum) and premature mortalities when European emissions are removed, for eight NH regions.

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



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

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.

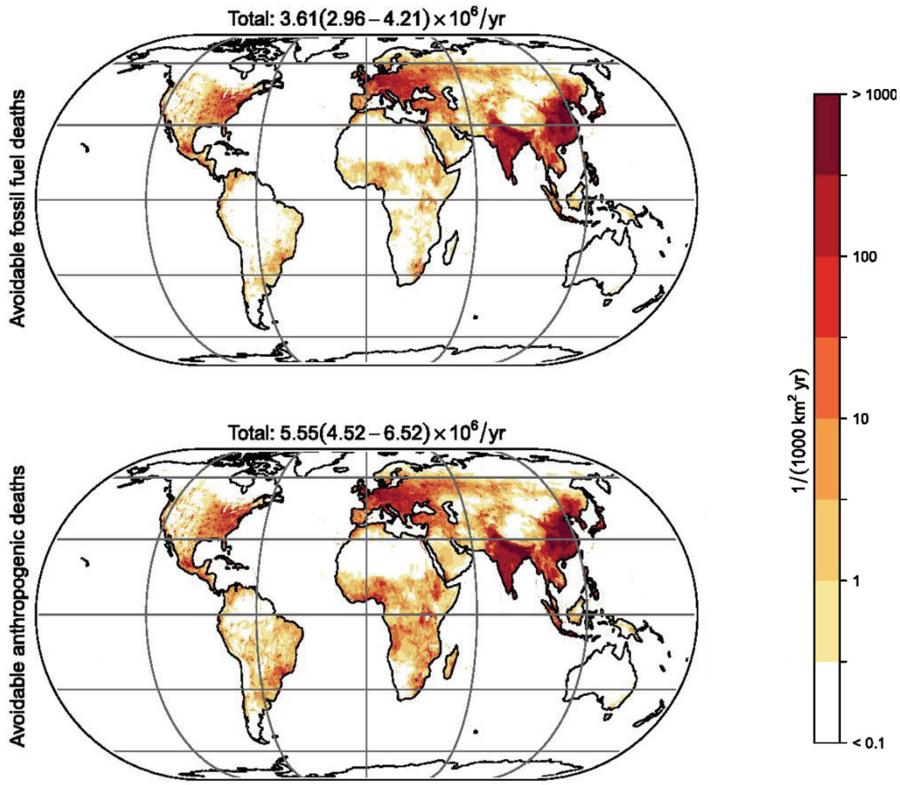
Worldwide, 3.61 million people are dying each year due to outdoor pollution caused by fossil fuels, an international team of researchers estimates. Fossil fuels, including coal, oil and natural gas, are responsible for about 78% of global greenhouse gas emissions, according to the US Environmental Protection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



https://www.pnas.org/content/early/2019/03/19/1819989116

Tropospheric Pollutants (The Air We Breathe)

Criteria 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	← 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.

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

Chemistry in Context

Criteria pollutant: common-place and detrimental to human welfare

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

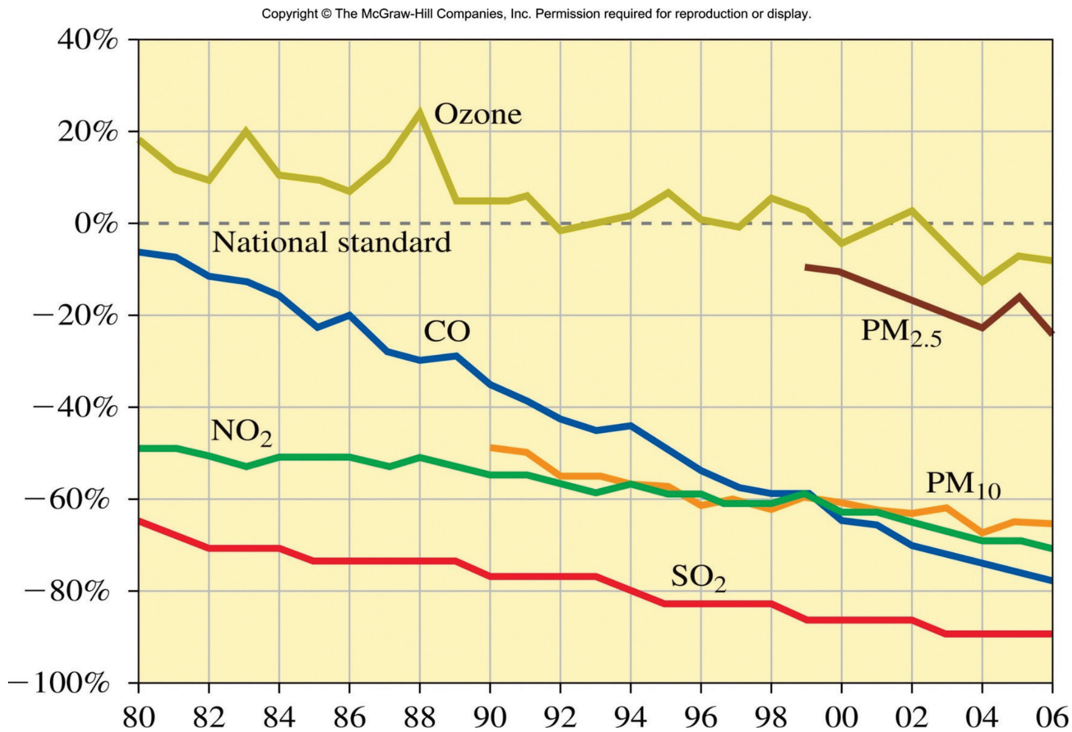
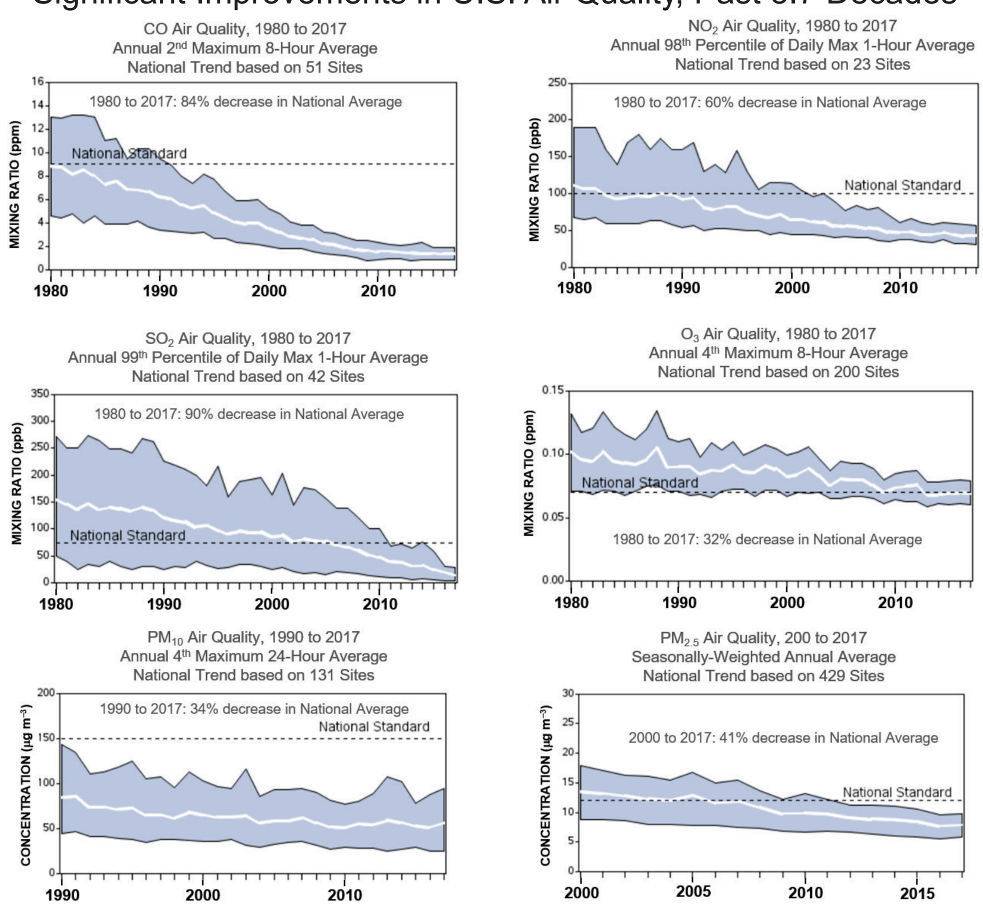


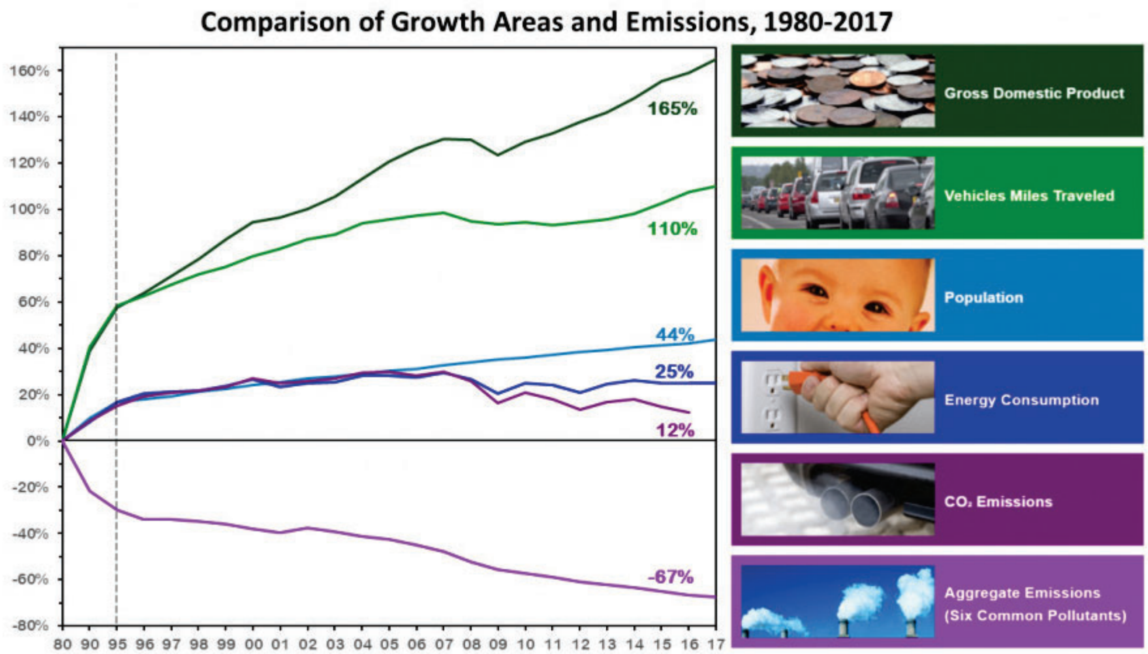
Figure 1.8, Chemistry in Context

Significant Improvements in U.S. Air Quality, Past 3.7 Decades



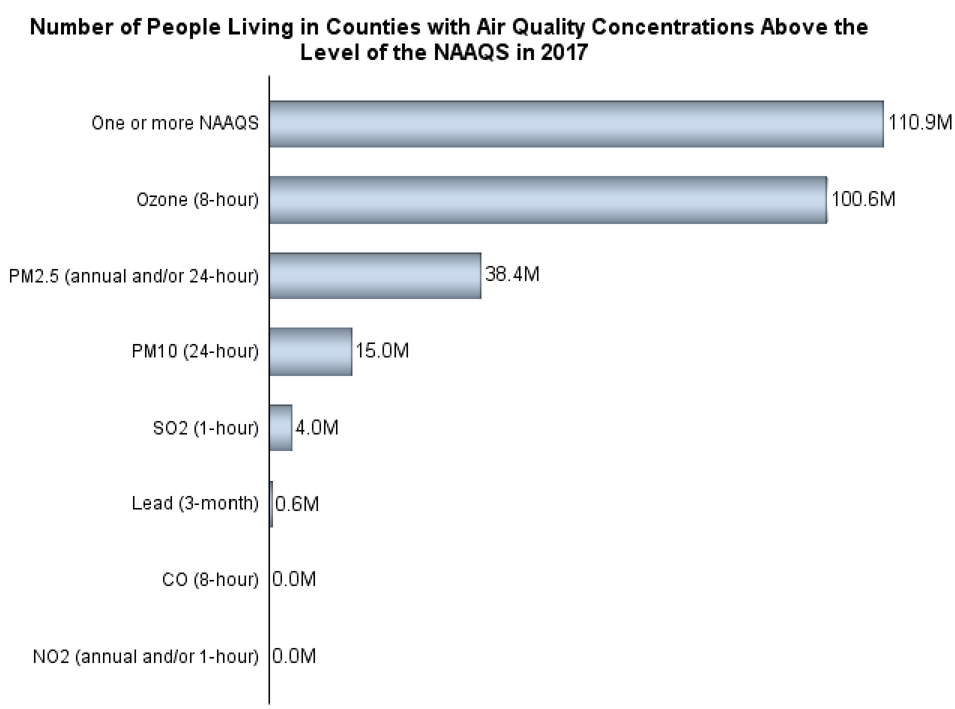
https://www.epa.gov/air-trends

Significant Improvements in U.S. Air Quality, Past 3.7 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

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

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

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: $\rightarrow$

Tropospheric Ozone Production

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

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

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

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

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] + Σ k_i [RO_2]$_i$ [NO]

Tropospheric Ozone Production

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

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

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:

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

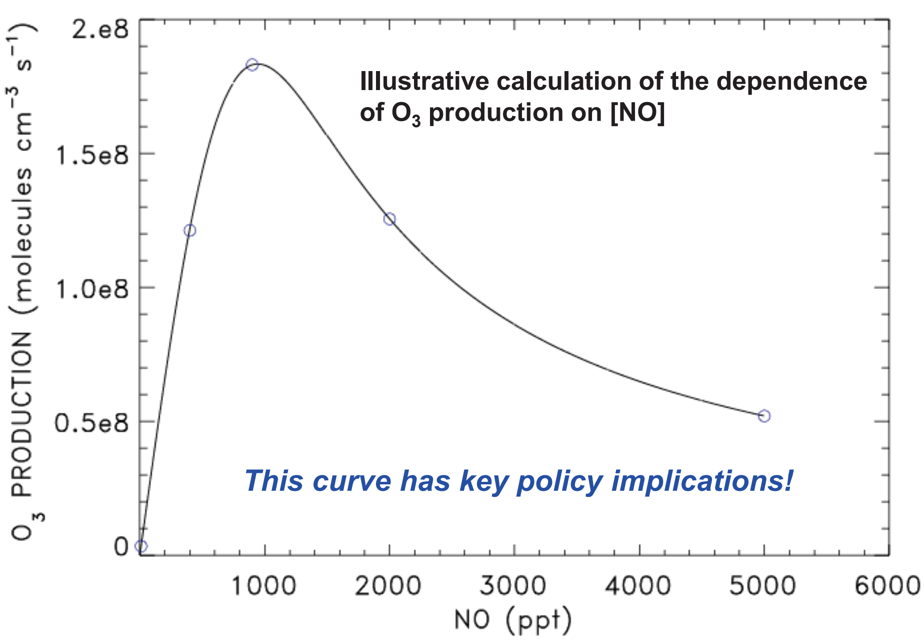
or

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

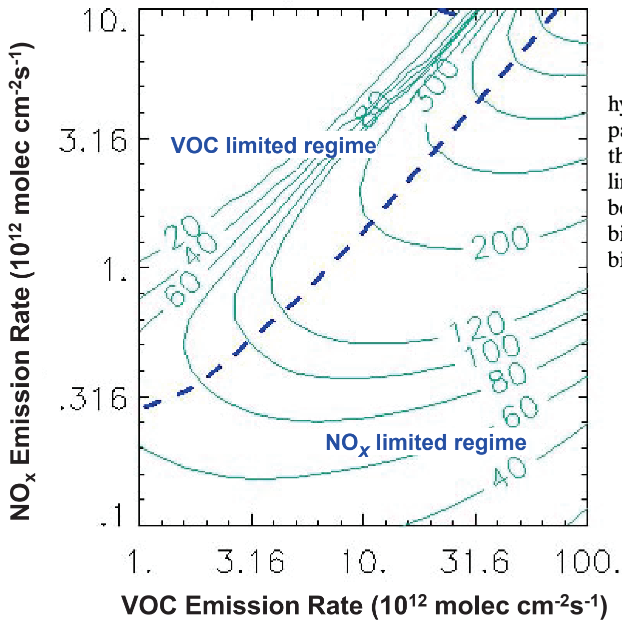
Tropospheric Ozone Production versus NO

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



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

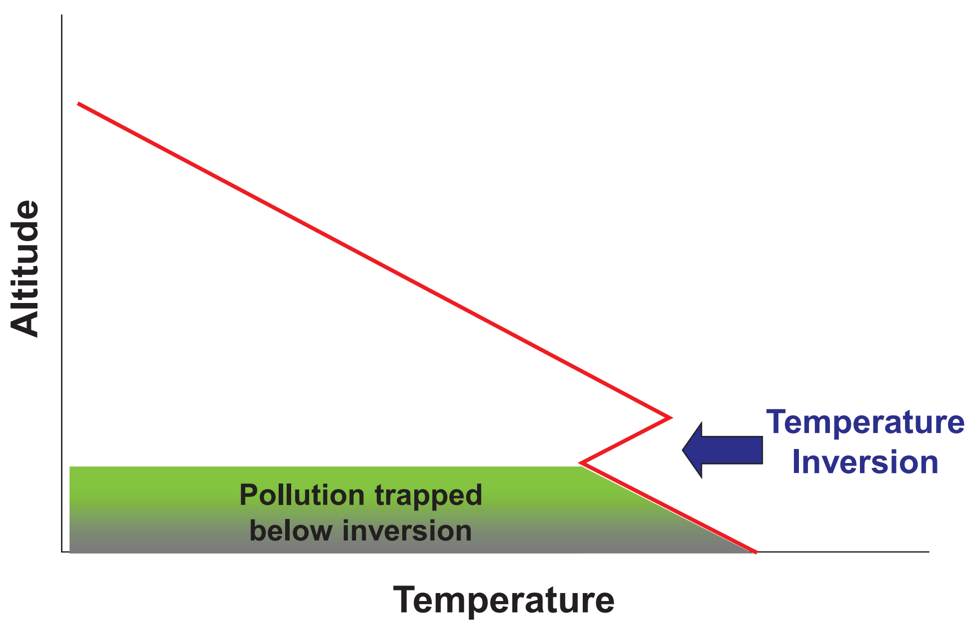
Figure: http://www-personal.umich.edu/~sillman/ozone.htm

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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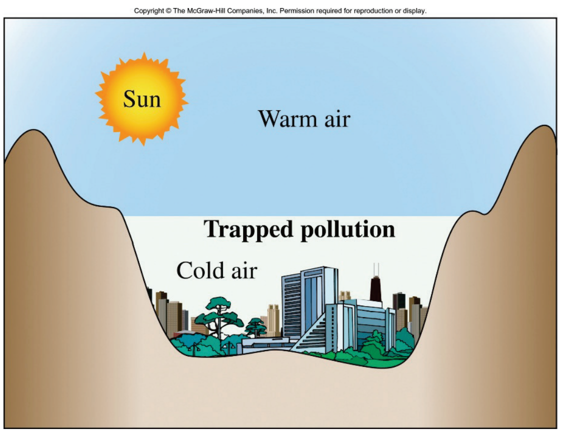
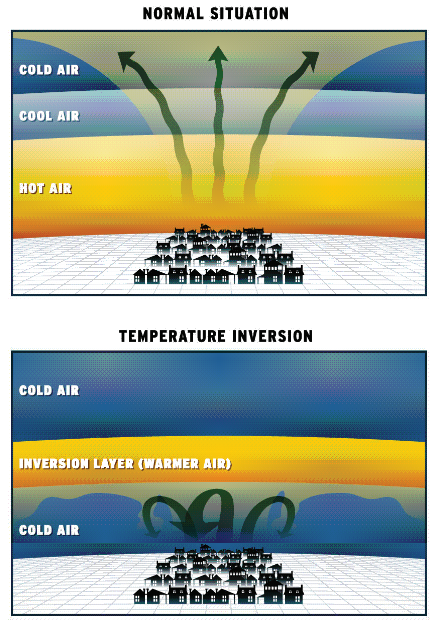
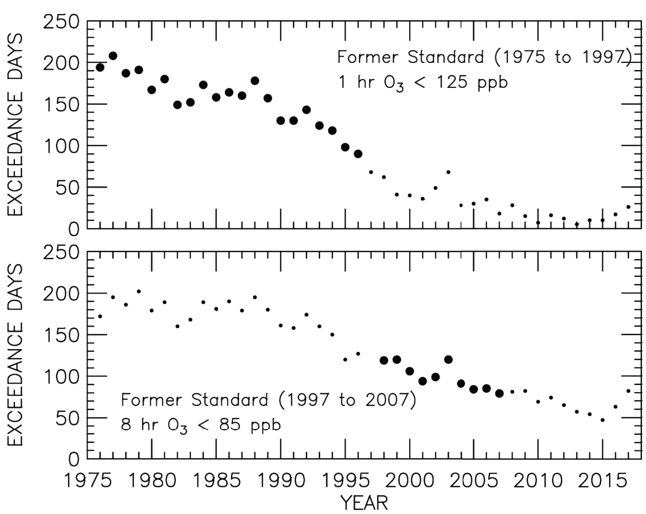


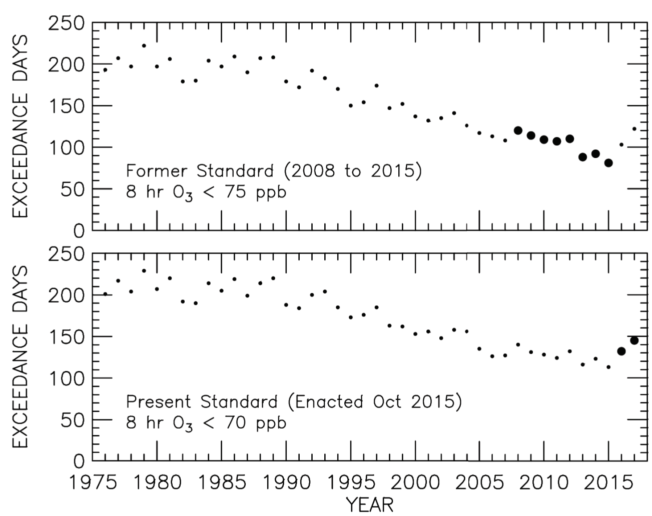
Figure 1.10, Chemistry in Context



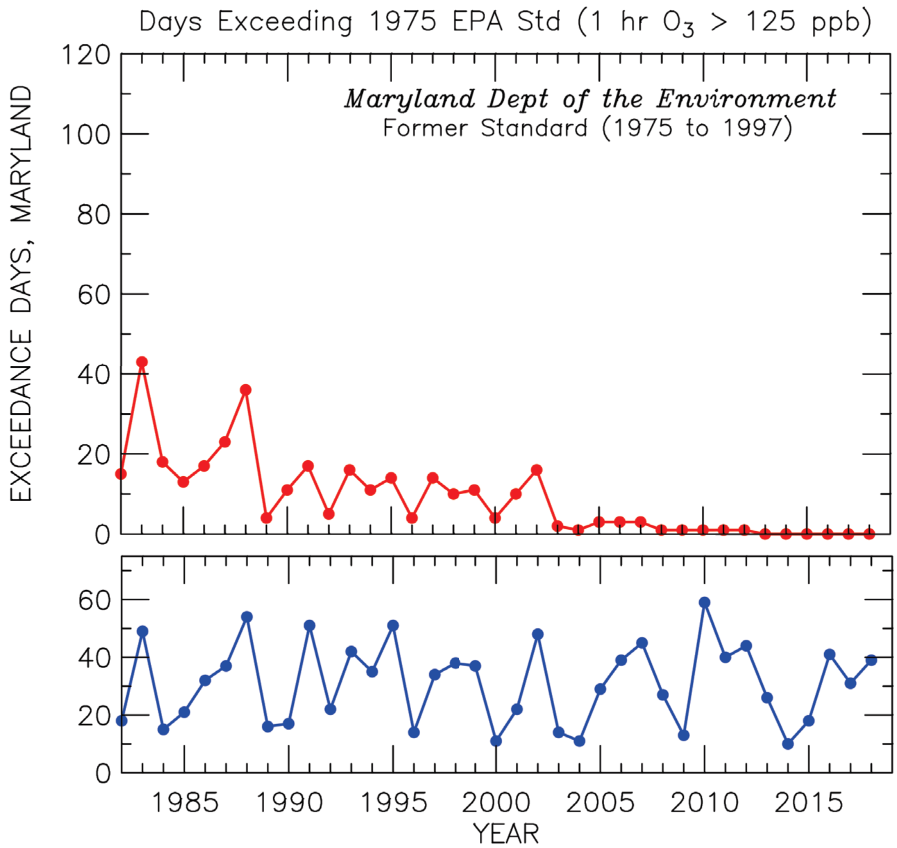
http://geographygems.blogspot.com/2011/09/smog.html

Dramatic Improvements California Air Quality, Past 4 Decades

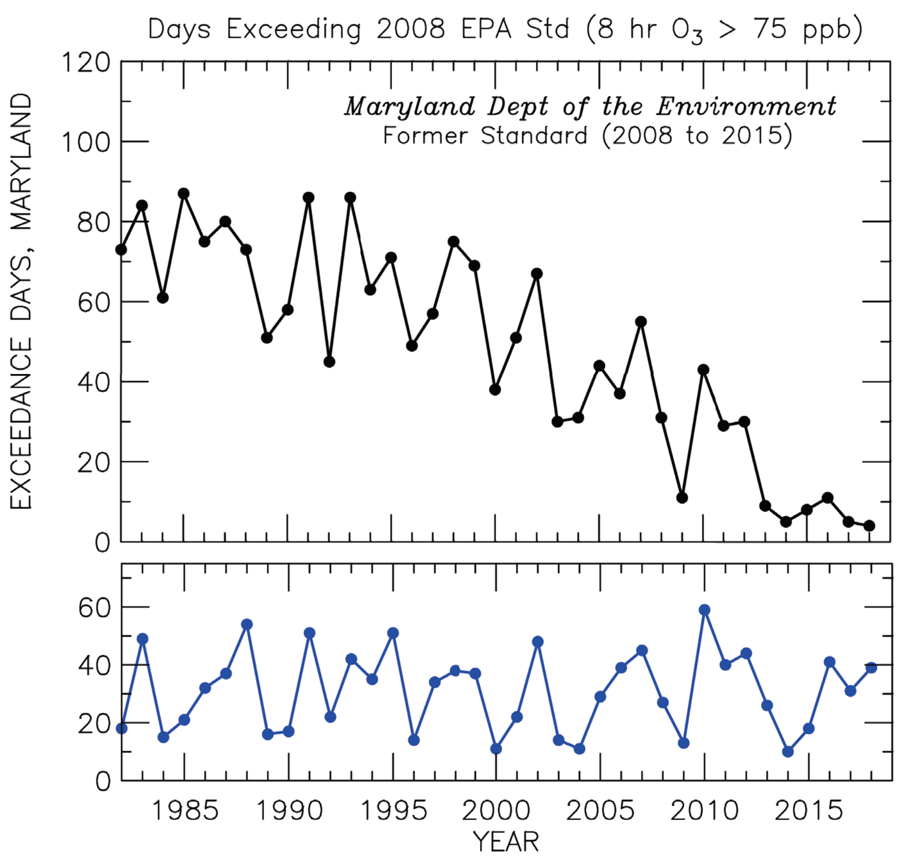




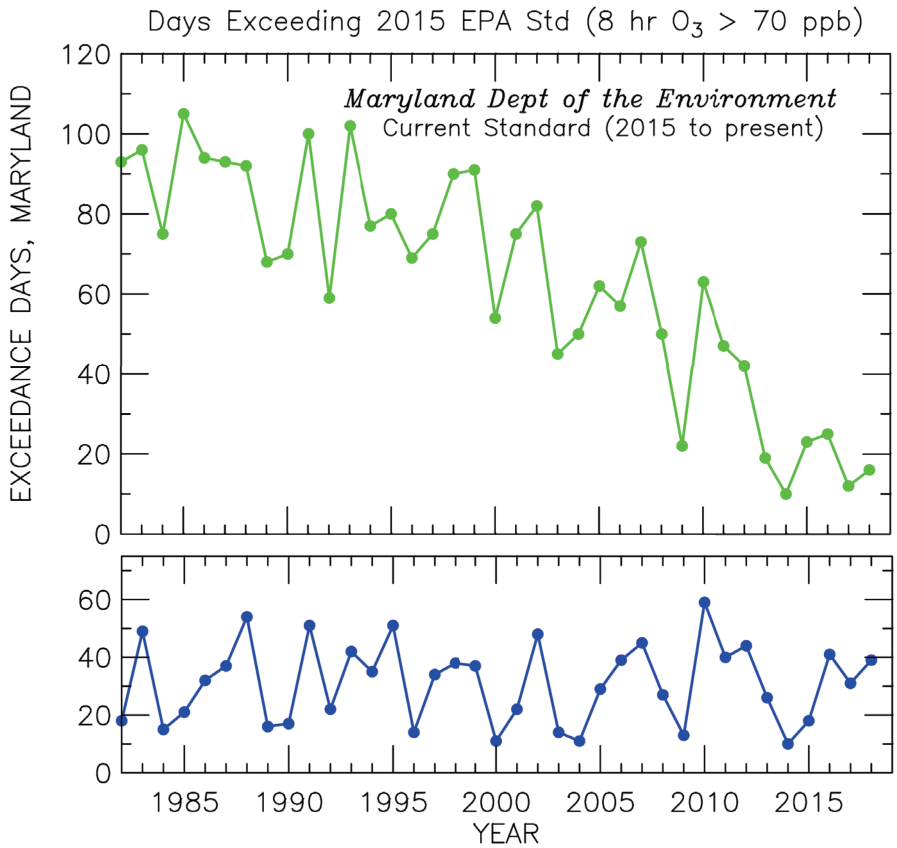
Dramatic Improvements Local Air Quality, Past 4 Decades



Dramatic Improvements Local Air Quality, Past 4 Decades

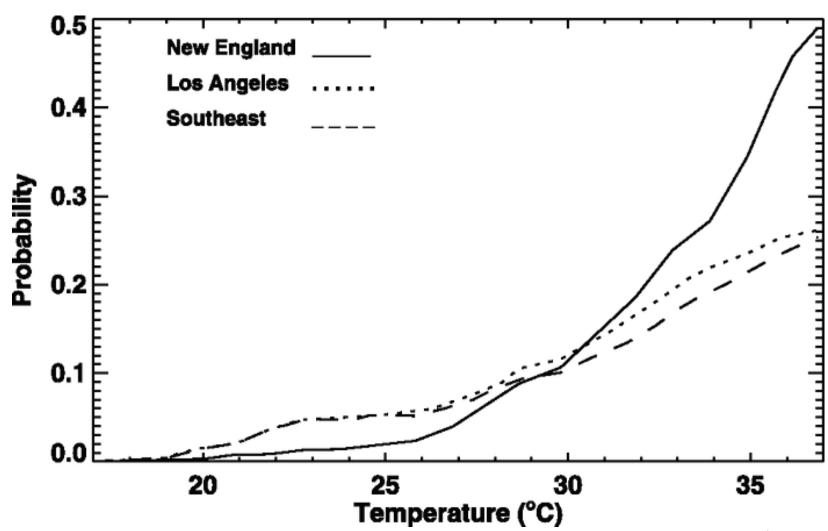


Dramatic Improvements Local Air Quality, Past 4 Decades



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

Probability of ozone exceedance vs. daily max. temperature

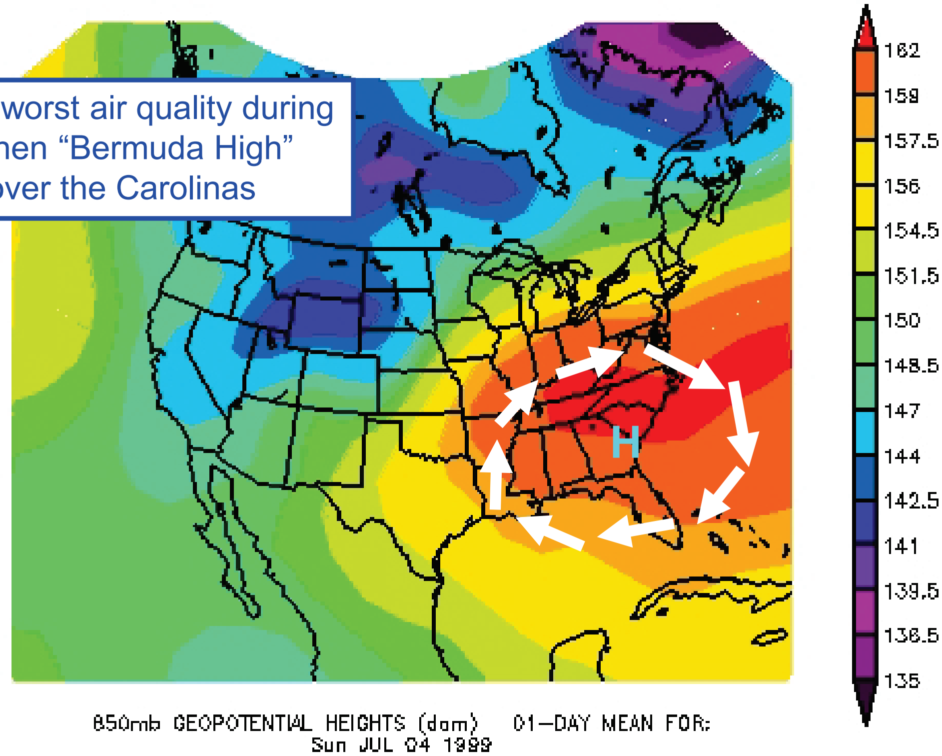


Lin et al. 2001

Why does probability of high ozone rise with increasing temperature?

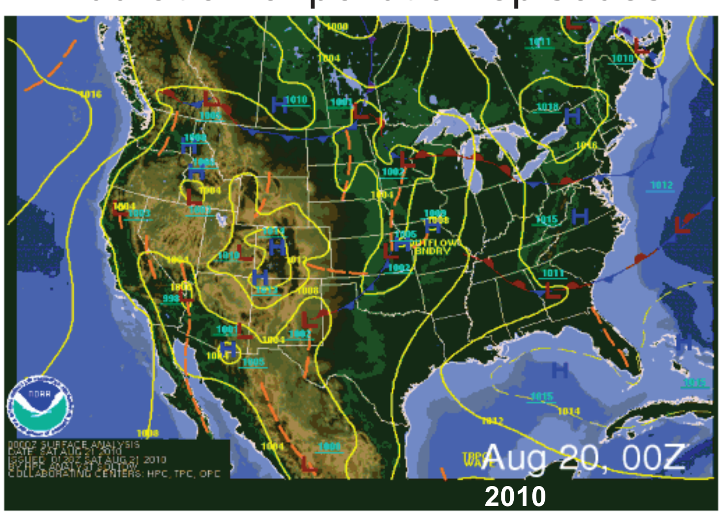
Day-to-day meteorology (weather!) affects severity and duration of pollution episodes

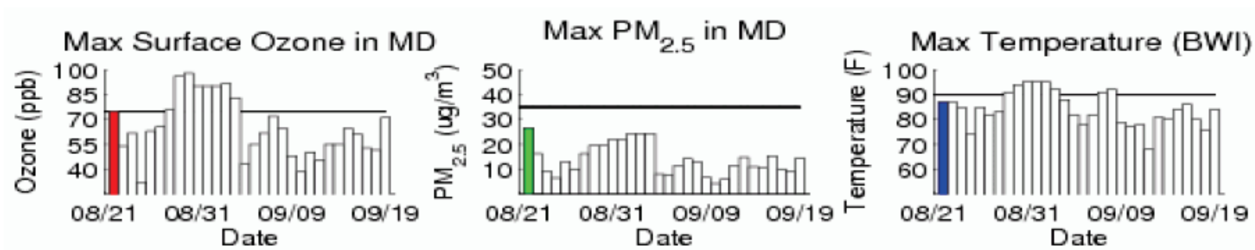
Maryland has worst air quality during summer, when "Bermuda High" sets up over the Carolinas



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

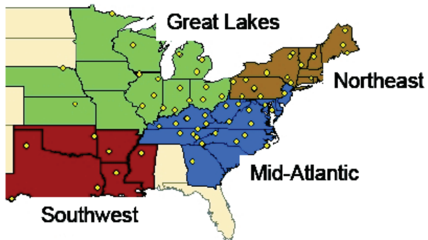


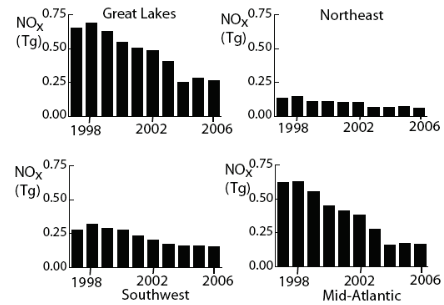


2010

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

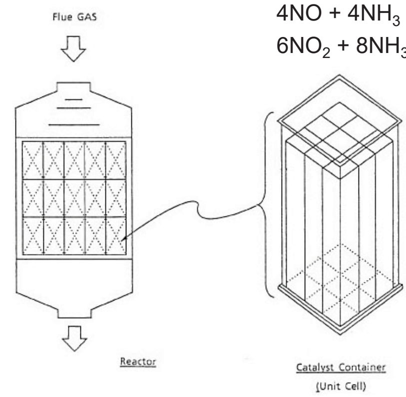
Removal of NO_x from Power Plants





NO_x Control:
SCR Selective Catalytic Reduction

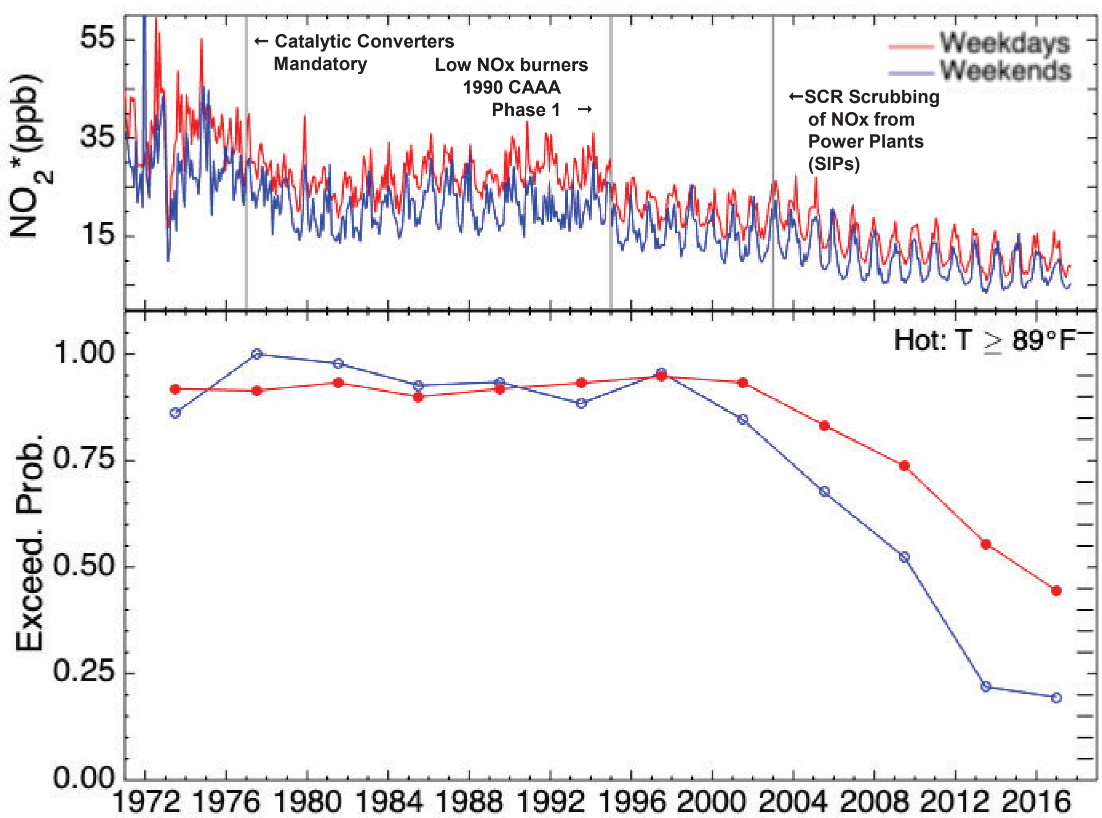
$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$



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

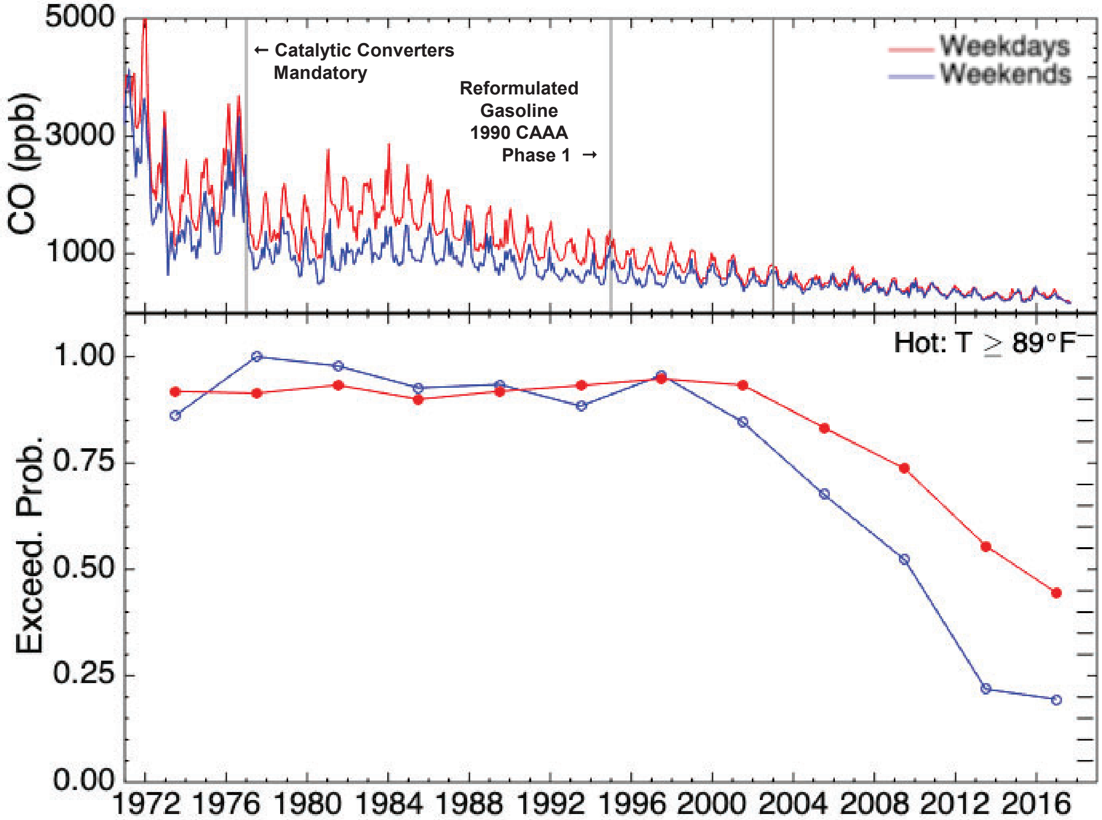
Slide courtesy John Sherwell, Md Dept of Natural Resources
http://www.dnr.maryland.gov/bay/pprp

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



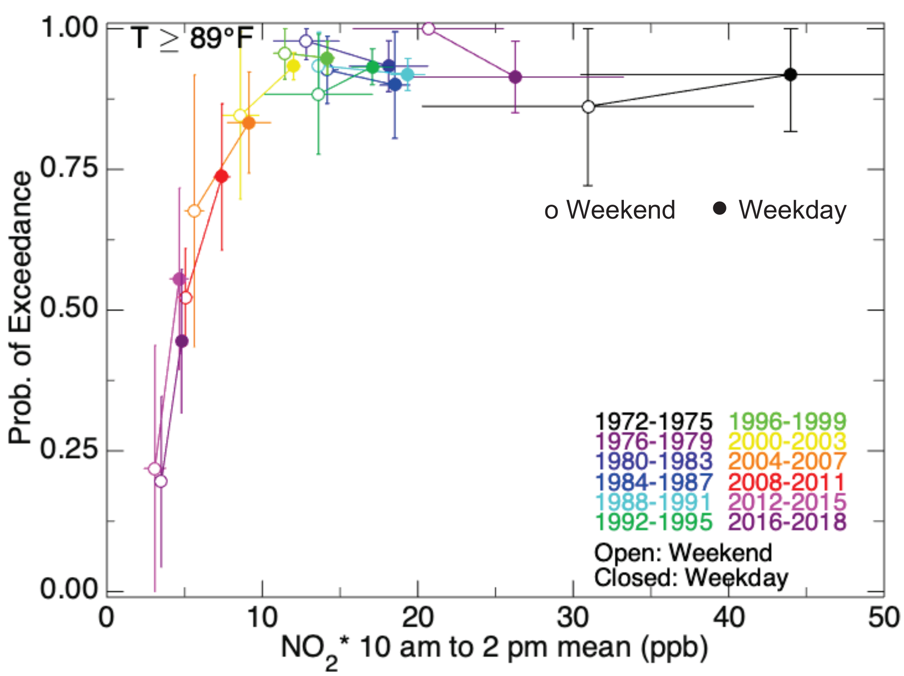
Figures above research product of UMCP Graduate Student Sandra Roberts

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

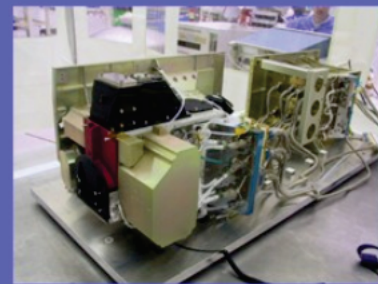
http://www.atmos-chem-phys.net/12/8323/2012/acp-12-8323-2012.html

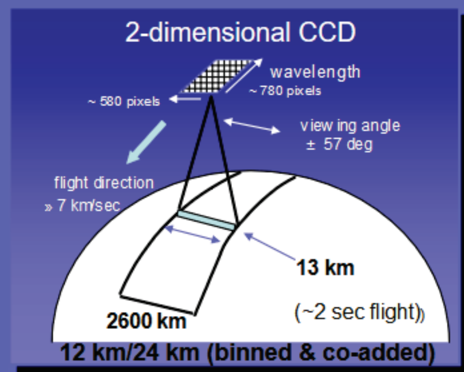
Figures above research product of UMCP Graduate Student Sandra Roberts

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

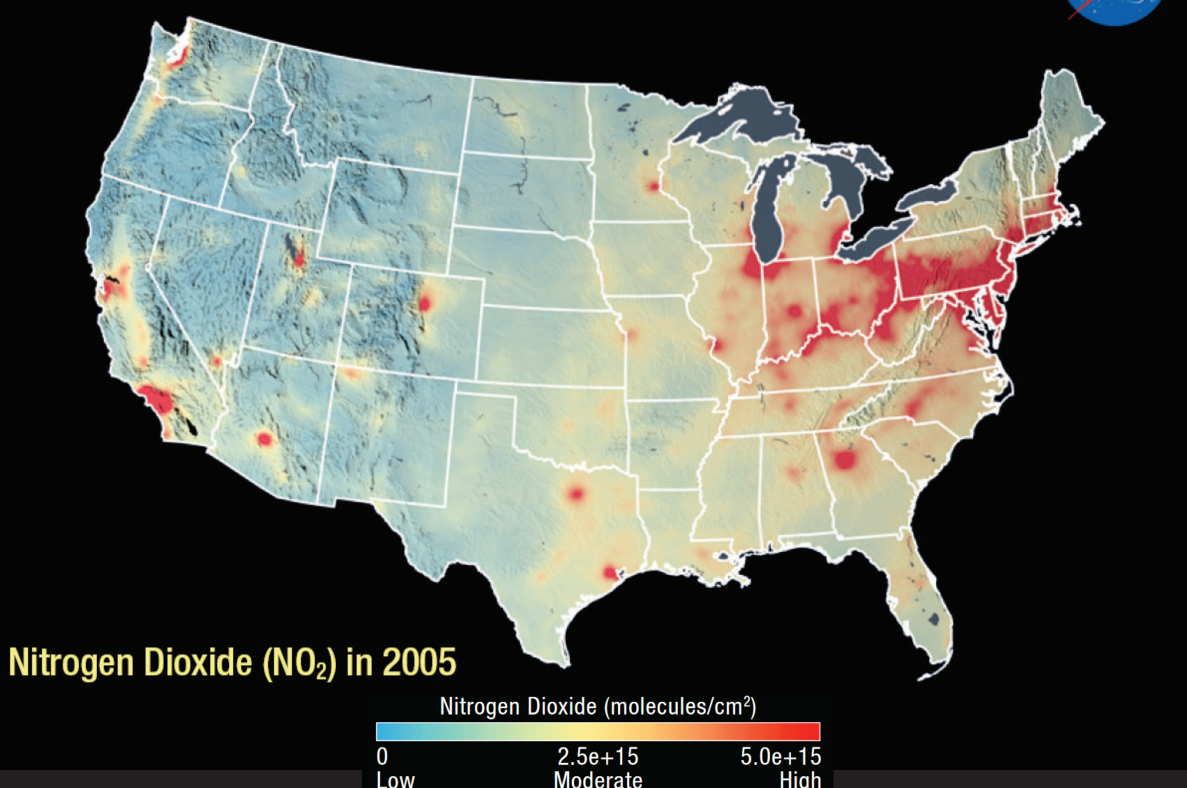




https://www.youtube.com/watch?v=krY5DjhjKGY

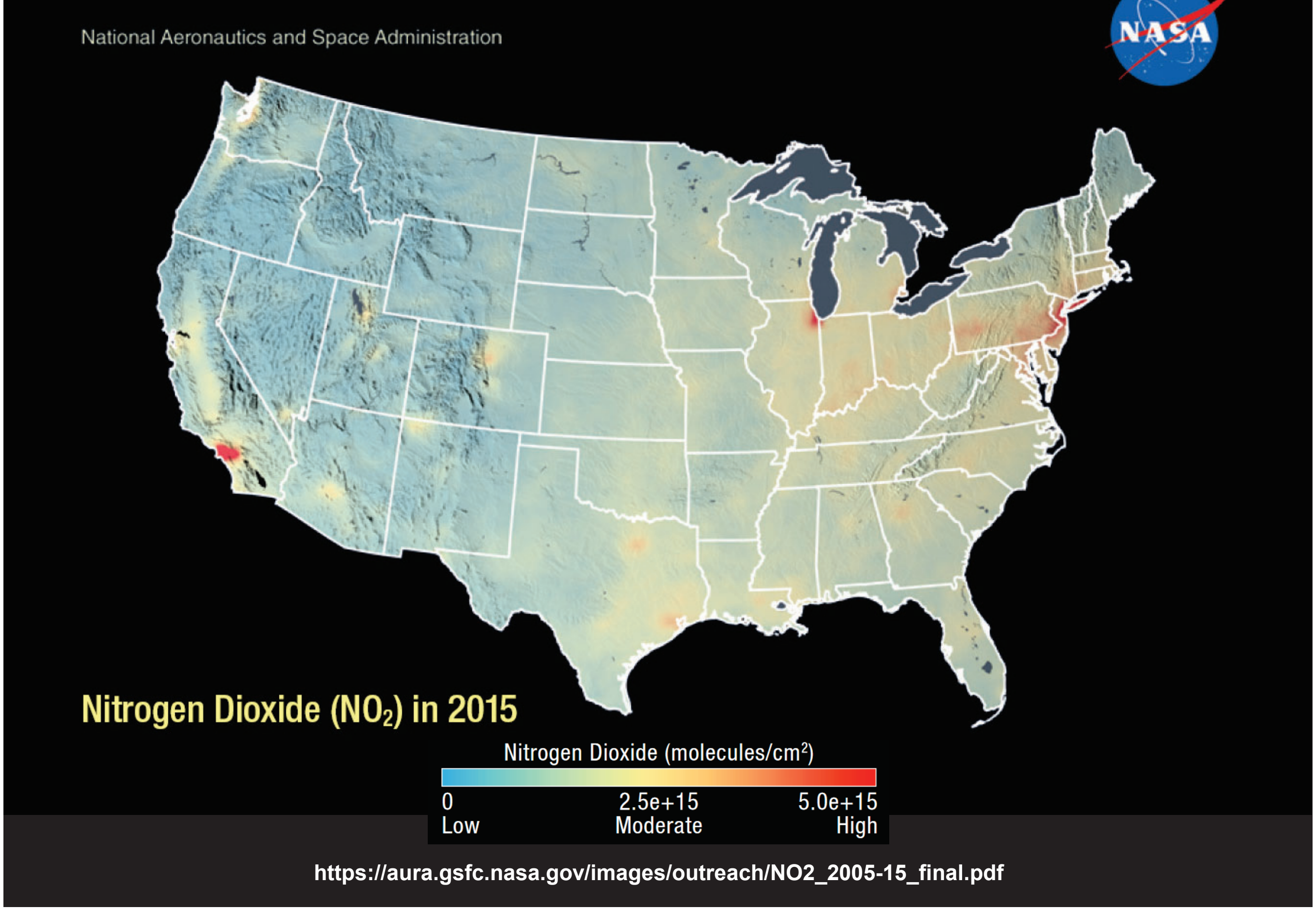
US Trends: NO_2

National Aeronautics and Space Administration

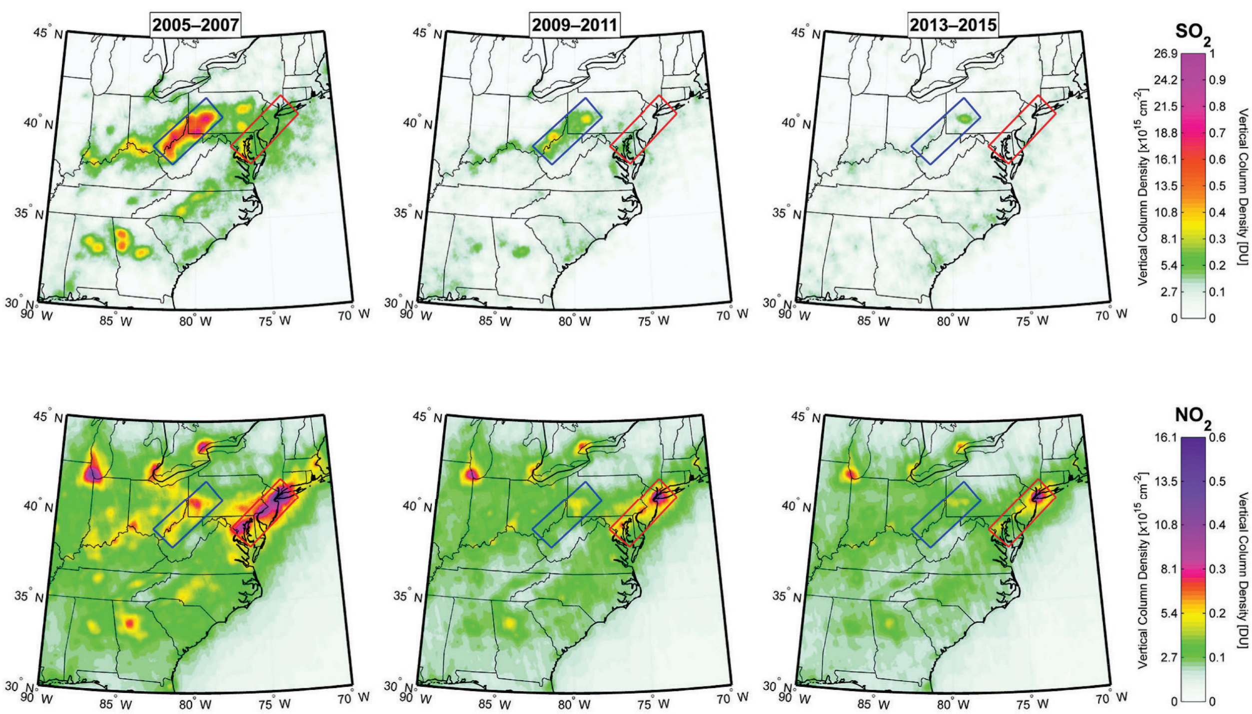


https://aura.gsfc.nasa.gov/images/outreach/NO2_2005-15_final.pdf

US Trends: NO_2

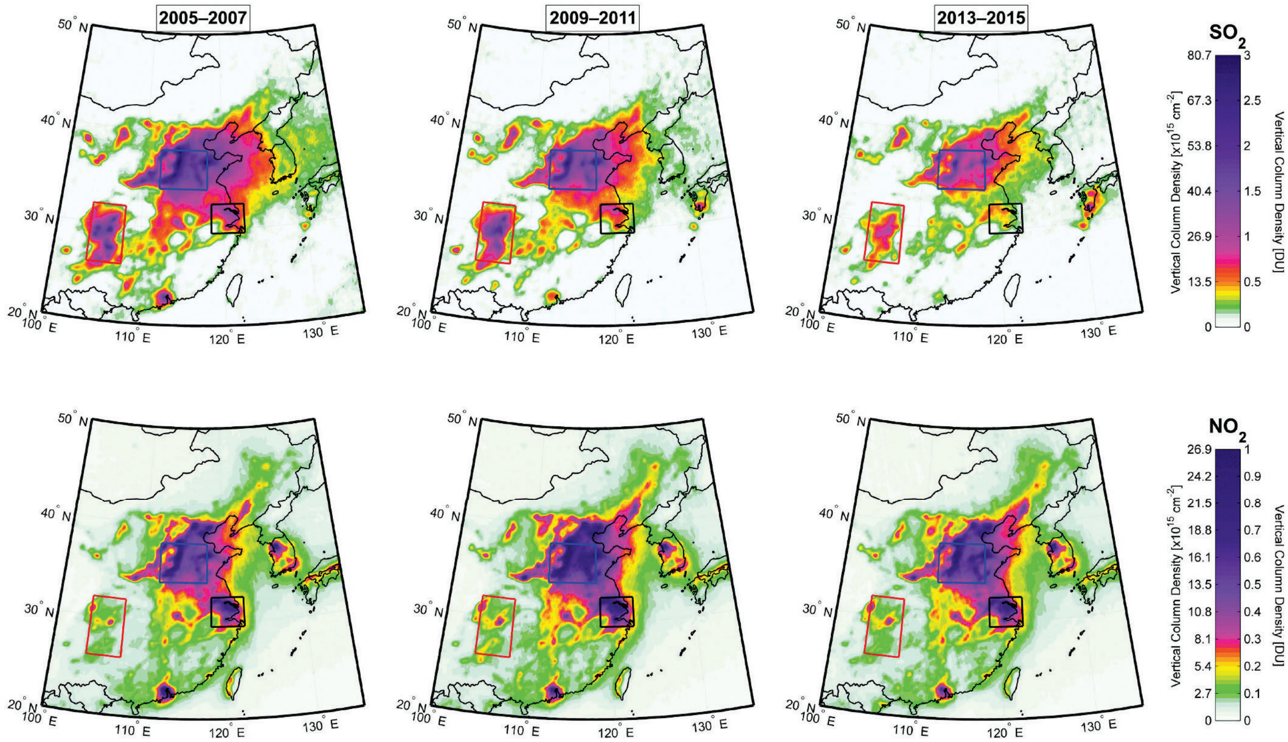


US Trends: NO_2 and SO_2



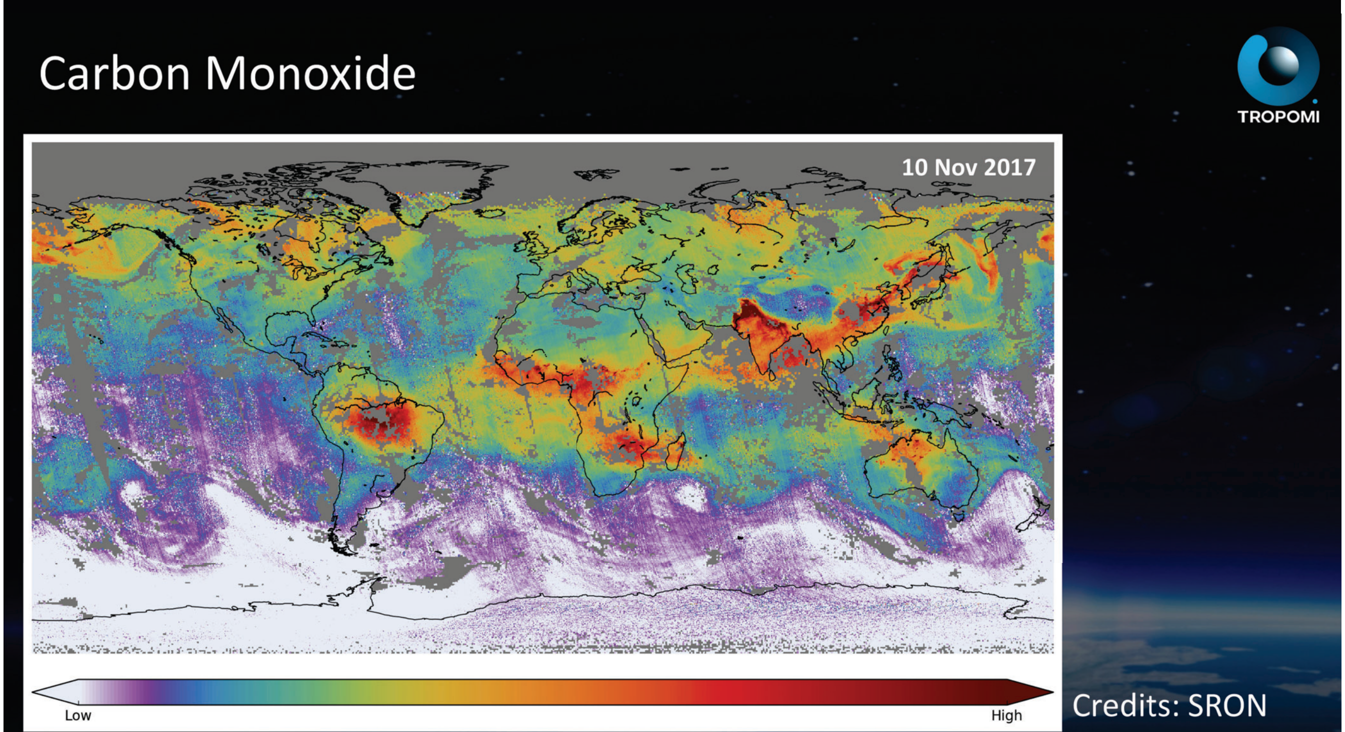
Krotkov *et al.*, *ACP*, 2016

China Trends: NO_2 and SO_2



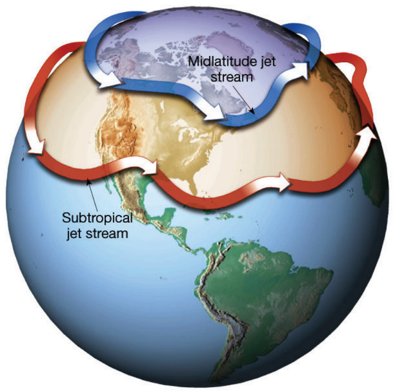
Krotkov *et al.*, *ACP*, 2016

TROPOMI: Early Results Presented in Washington, DC at Fall 2018 American Geophysical Union meeting

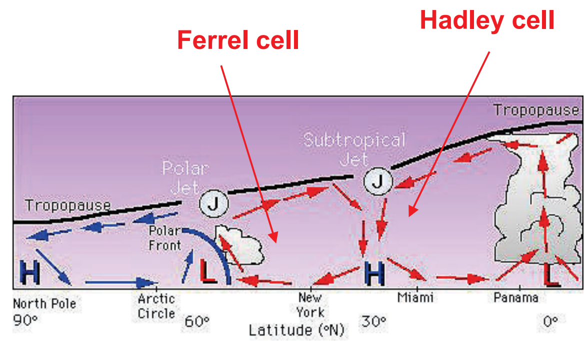


http://www.tropomi.eu/sites/default/files/files/agu_veefkind.pdf

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

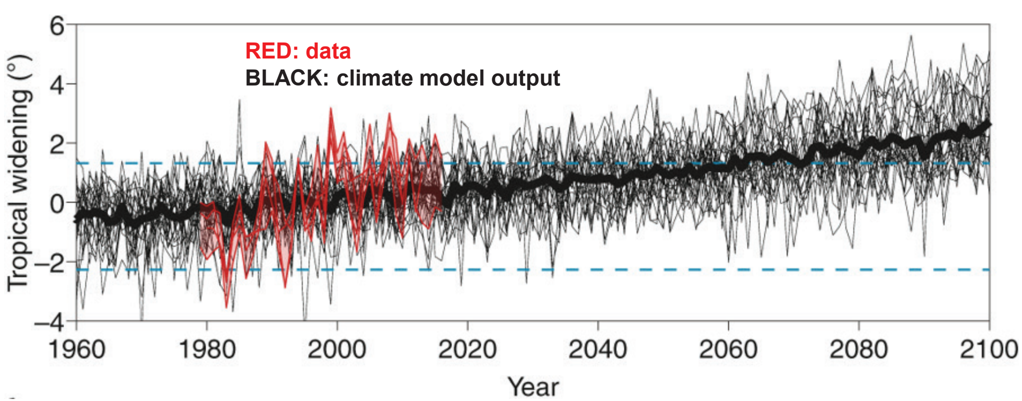
Climate Change and Air Pollution

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**