Pollution of Earth's Troposphere: Acid Rain & Aerosols
AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Sites: http://www.atmos.umd.edu/~rjs/class/spr2015

Lecture 13

26 March 2015

Overview of Aerosols

- Aerosols aka particulate matter (PM)
- Size generally ranges from 0.005 μm to 100 μm diameter
- Can be liquid or solid
- Dust: solid, produced by grinding or crushing operation
- Fumes: formed by condensation of gases
- Smoke or soot: carbon particles resulting from incomplete combustion
- SOA: secondary organic aerosol, formed by condensation of decomposition products of VOCs (volatile organic compounds) including isoprene (C_5H_8) which is mainly biogenic and benzene (C_6H_6) which is mainly anthropogenic
- PM can be emitted directly as carbonaceous material (primary pollutant) or formed in atmosphere upon condensation/transformation of gaseous emissions of SO_2, NO_x, and NH_3

  Eastern US: sulfates dominate due to greater reliance on coal-fired power plants
  Western US: carbon and nitrates dominate due to agriculture & transportation

Overview of Aerosols

- Health effects driven by size and chemical composition
- Smaller particles most hazardous
- Benzene-like compounds called polycyclic aromatic hydrocarbons (PAH) most hazardous

http://www.barnesandnoble.com/w/polycyclic-aromatic-hydrocarbons-pierre-a-haines

- Fall speed of aerosols varies as $(\text{diameter})^2$

  2 μm diameter particle has residence time in 1 km of atmosphere of 2 months, if removed by only gravitational settling

  ⇨ small particles are suspended in the atmosphere until removed by _____ ?

Health Effects of Air Pollution

International New York Times

Air Pollution Raises Stroke Risk

By NICHOLAS BAKALAR MARCH 24, 2015 4:30 PM 7 Comments

Air pollution — even for just one day — significantly increases the risk of stroke, a large review of studies has found.

Researchers pooled data from 103 studies involving 6.2 million stroke hospitalizations and deaths in 28 countries.

The analysis, published online in BMJ, found that all types of pollution except ozone were associated with increased risk for stroke, and the higher the level of pollution, the more strokes there were.

Daily increases in pollution from nitrogen dioxide, sulfur dioxide, carbon monoxide and particulate matter were associated with corresponding increases in strokes and hospital admissions. The strongest associations were apparent on the day of exposure, but increases in particulate matter had longer-lasting effects.

The exact reason for the effect is unclear, but studies have shown that air pollution can constrict blood vessels, increase blood pressure and increase the risk for blood clots. Other research has tied air pollution to a higher risk of heart attacks, stroke and other ills.

http://well.blogs.nytimes.com/2015/03/24/air-pollution-raises-stroke-risk

BMJ: British Medical Journal

Short term exposure to air pollution and stroke: systematic review and meta-analysis

Anoop S V Shah,[1] Kuan Ken Lee,[1] David A McAllister,[2] Amanda Hunter,[1] Harish Nair,[2] William Whiteley,[3] Jeremy P Langrish,[1] David E Newby,[1] Nicholas L Mills[1]

[1]BHF/University Centre for Cardiovascular Science, University of Edinburgh, Edinburgh EH16 4SB, UK

[2]Centre of Population Health Sciences, University of Edinburgh, Edinburgh, UK

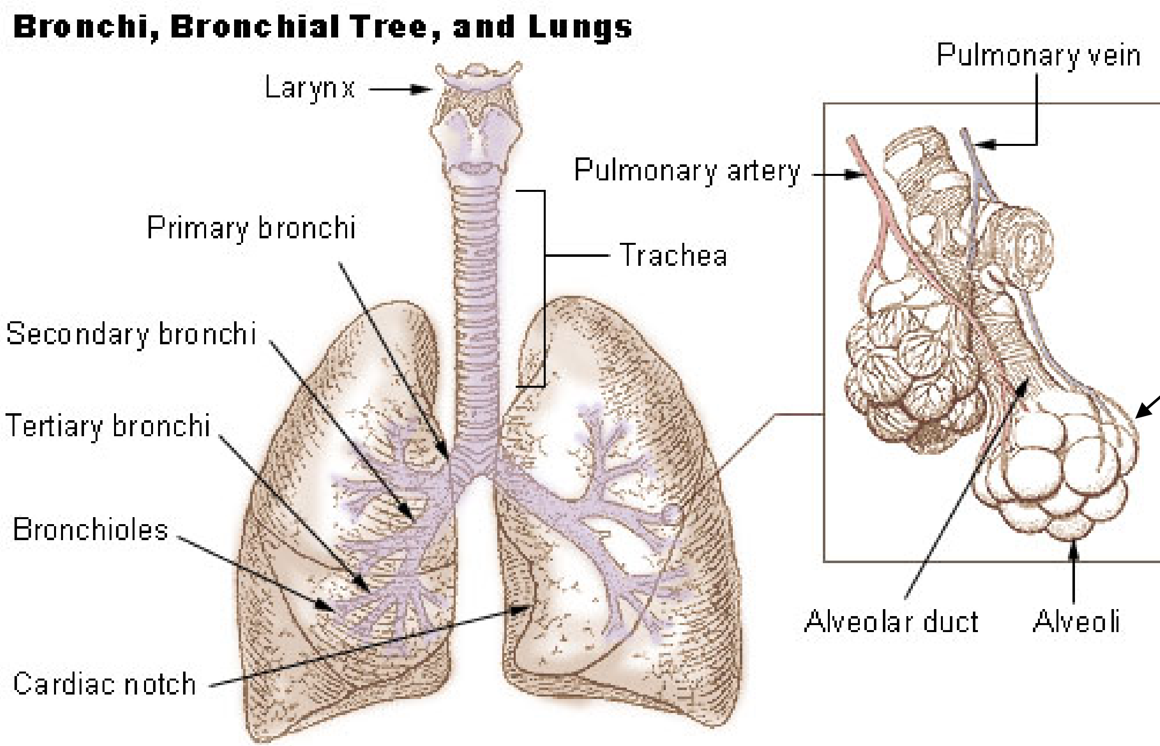
[3]Centre for Clinical Brain Sciences, University of Edinburgh, Edinburgh, UK

Admission to hospital for stroke or mortality from stroke was associated with an increase in concentrations of carbon monoxide (relative risk 1.015 per 1 ppm, 95% confidence interval 1.004 to 1.026), sulphur dioxide (1.019 per 10 ppb, 1.011 to 1.027), and nitrogen dioxide (1.014 per 10 ppb, 1.009 to 1.019). Increases in $PM_{2.5}$ and PM_{10} concentration were also associated with admission and mortality (1.011 per 10 Î¼g/m^3 (1.011 to 1.012) and 1.003 per 10 $\mu g/m^3$ (1.002 to 1.004), respectively).

Gaseous and particulate air pollutants have a marked and close temporal association with admissions to hospital for stroke or mortality from stroke. Public and environmental health policies to reduce air pollution could reduce the burden of stroke.

The lead author, Dr. Anoop Shah, a lecturer in cardiology at the University of Edinburgh, said that there was little an individual can do when air pollution spikes. "If you're elderly, or have co-morbid conditions, you should stay inside," he said. But policies leading to cleaner air would have the greatest impact, he said. "It's a question of getting cities and countries to change."

Health Effects of Aerosols



Alveoli radius ≈ 50 to 100 μm

PM10 may fill alveola

PM2.5 can inhibit oxygen exchange within alveola

Exposure to elevated levels of particulate matter leads to increase risk of respiratory illnesses, cardiopulmonary disease, ischemic heart disease, and heart attacks

Health Effects of Aerosols

Assessment of Public Health Risks Associated with Atmospheric Exposure to $PM_{2.5}$ in Washington, DC, USA

Natasha A. Greene[1*], and Vernon R. Morris[1,2]

[1]Program in Atmospheric Sciences, Howard University, Washington, DC 20059, USA
[2]Department of Chemistry, Howard University, Washington, DC 20059, USA

Our findings show that there are significant risks of ward-specific pediatric asthma emergency room visits (ERV). Results also illustrate lifetime excess lung cancer risks, exceeding the $1x10^{-6}$ threshold for the measured levels of particulate matter and heavy metals (chromium and arsenic) on behalf of numerous subpopulations in the DC selected wards.

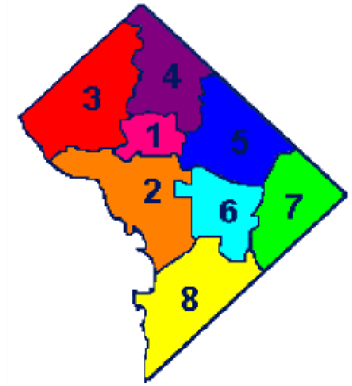


Figure 1: Washington, DC Wards Schematic

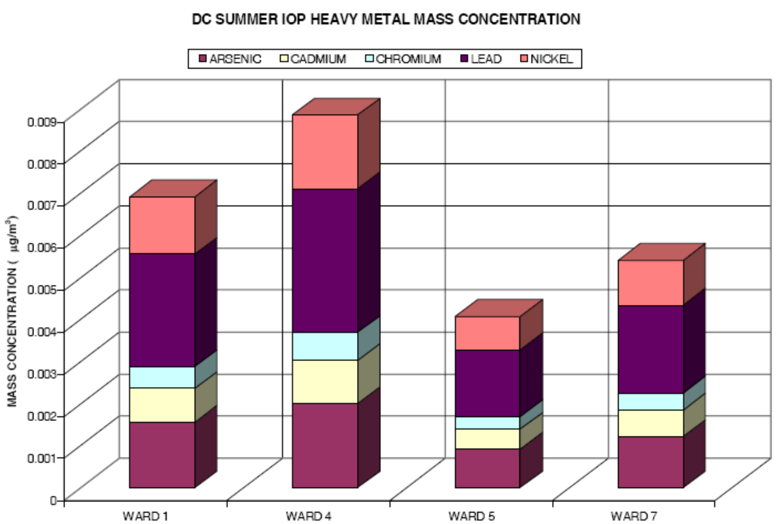


Figure 5: Heavy Metal Content of Fine PM for Summer IOP

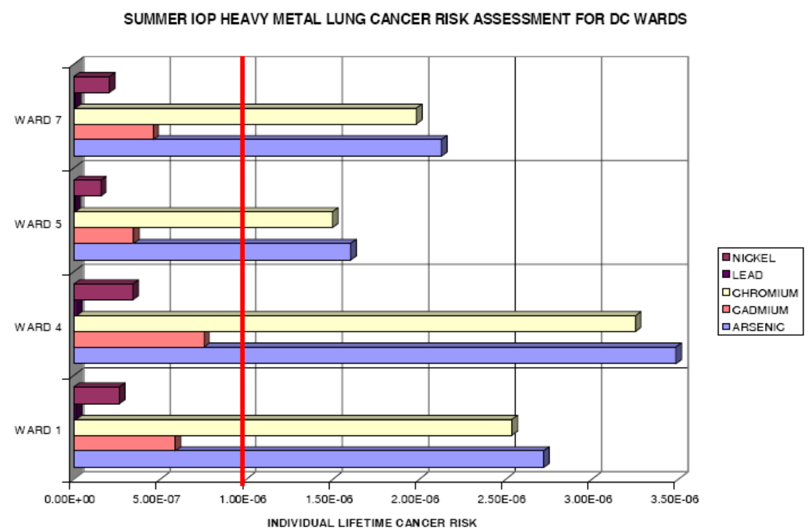
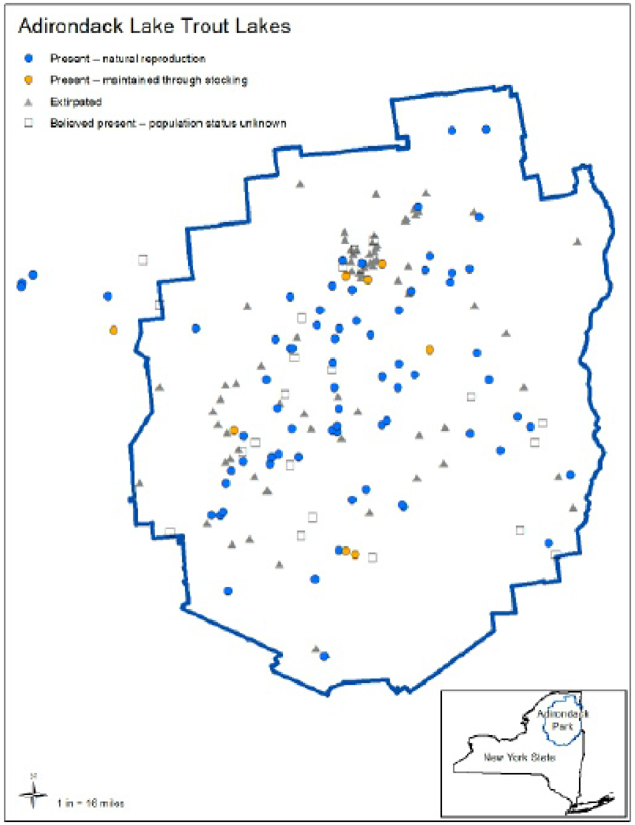


Figure 10: Summer IOP Lifetime Excess Lung Cancer Risk by DC Wards.

Int J. Environ. Res. Public Health 2006, 3(1), 86-97

Lake Acidification



Adirondack Park, New York

- Largest American park outside of Alaska (9,300 square miles)
- Suffered worse damage due to acid rain than any other region in the U.S.
- 700 lakes had become too acidic to support native aquatic species
- Considerable recent progress after extensive legislative battles:

The EPA states that from 1990 to 2013, there was a seventy-seven percent decrease in sulfur dioxide emissions and a forty-nine percent decrease in total nitrogen oxide emissions.

Charles Driscoll is a professor at Syracuse University who has been studying acid rain in the Adirondacks for decades. Driscoll noted that because of the reductions that many lakes are now once again supporting species like brook trout. However, he also said that some lakes will take centuries to recover.

"We've seen a partial recovery, but there is still quite a bit of damage, particularly on soils and streams," Driscoll said. "I think that we're part way there … but we need additional reductions to more fully recover."

http://www.nature.org/ourinitiatives/regions/northamerica/unitedstates/newyork/adirondacks-lake-trout-report-december-2014.pdf

See also http://www.adirondackalmanack.com

Cultural Degradation

Figure 6.22, Chemistry in Context.
Limestone statue of George Washington, NYC

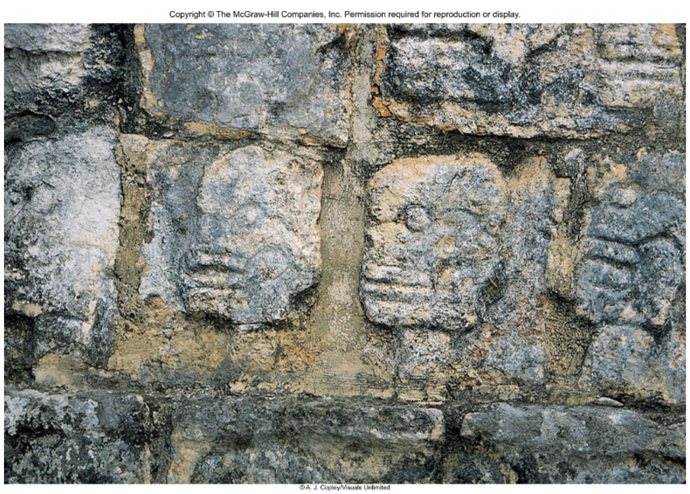


Figure 6.24, Chemistry in Context.
Mayan art, Mexico.

Marble limestone, composed mainly of calcium carbonate ($CaCO_3$), slowly dissolves in the presence of hydrogen ion:

$CaCO_3$ (s) + H^+ (aq) $\rightarrow$ Ca^{2+} (aq) + HCO_3^- (aq)

HCO_3^- (aq) + H^+ (aq) $\rightarrow$ H_2CO_3 (aq) $\rightarrow$ CO_2 (g) + H_2O (l)

or:

$CaCO_3$(s)+2 H^+(aq) $\rightarrow$ Ca^{2+} (aq) + CO_2 (g) + H_2O (l)

Acid Rain: SO_2

Chemical formula of coal: $C_{135}H_{96}O_9NS$ (S varies with coal type)

Combustion of leads to release of sulfur dioxide (SO_2)

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

SO_2 reacts with O_2 to form sulfur trioxide (SO_3)

$$2SO_2\ (g) + O_2\ (g) \rightarrow 2\ SO_3\ (g)$$

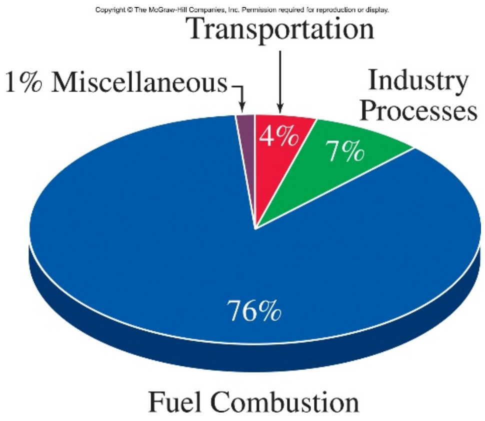
$$SO_3\ (aq) + H_2O\ (l) \rightarrow H_2SO_4\ (aq)$$

Followed by:

$$H_2SO_4\ (aq) \leftrightarrow H^+ + HSO_4^-$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$$

SO_2 Sources (US)



Primary source of SO_2 is fuel combustion; emissions from this sector are decreasing.

Emissions from transportation are small and largely unchanged.

Figure 6.14, Chemistry in Context. US SO_2 emission sources, 2007

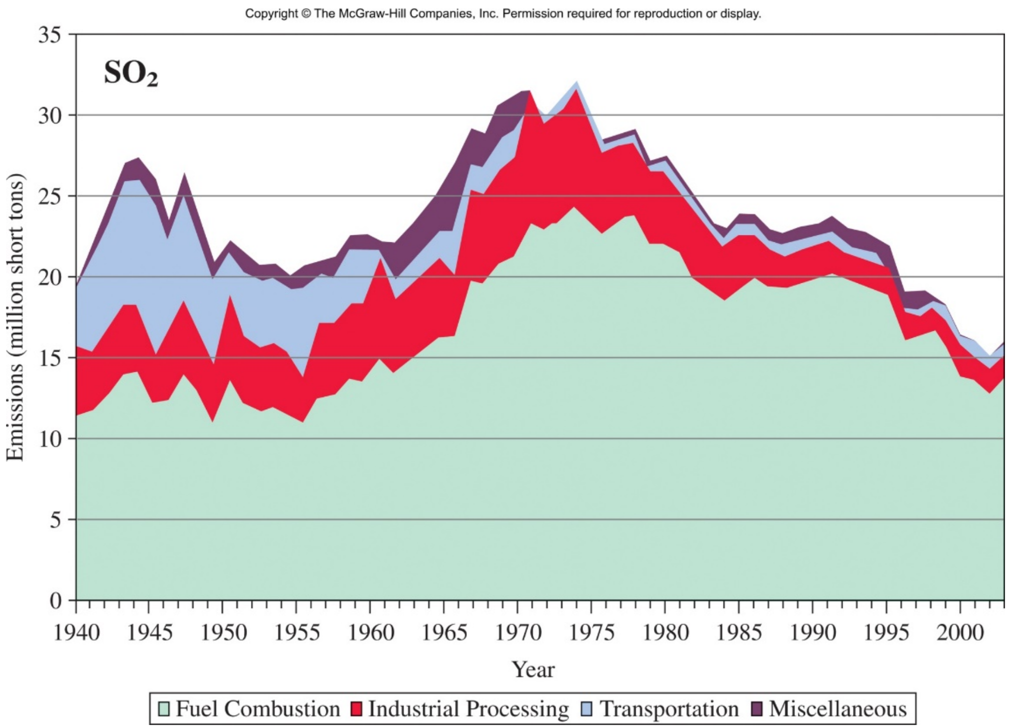
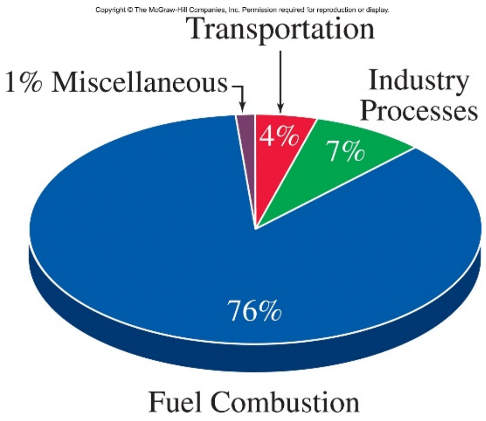


Figure 6.21, Chemistry in Context. US SO_2 emissions, 1940 to 2003

SO_2 Sources (US)



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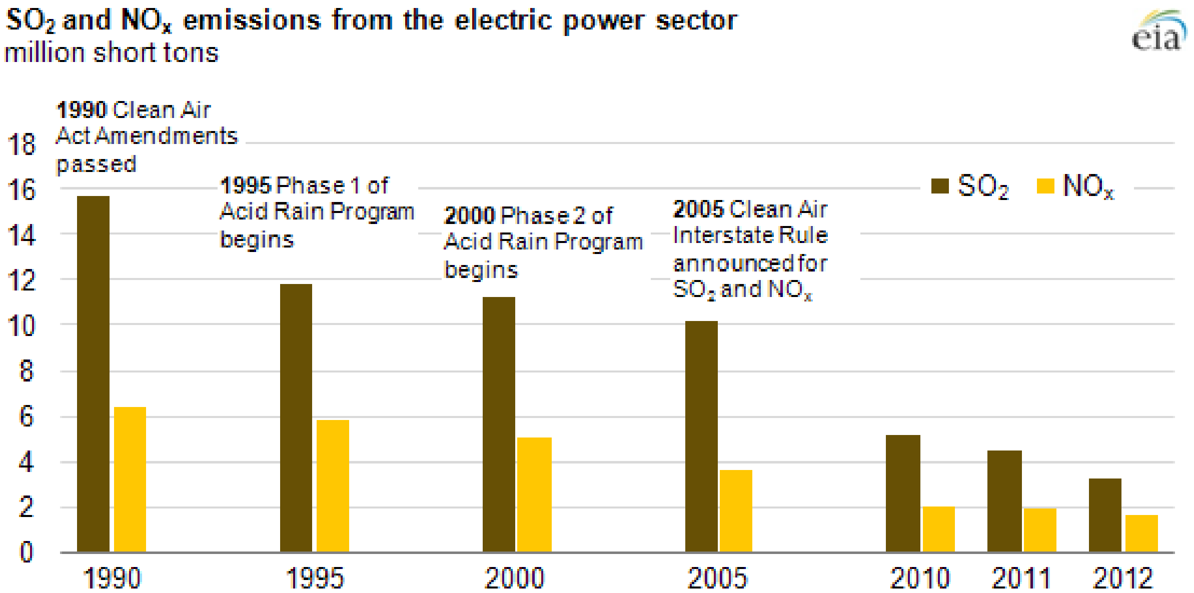

http://www.eia.gov/todayinenergy/detail.cfm?id=10151

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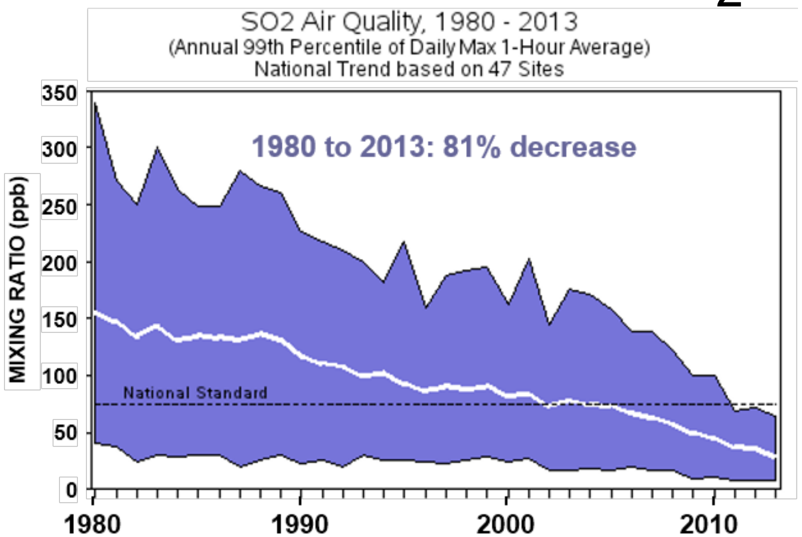
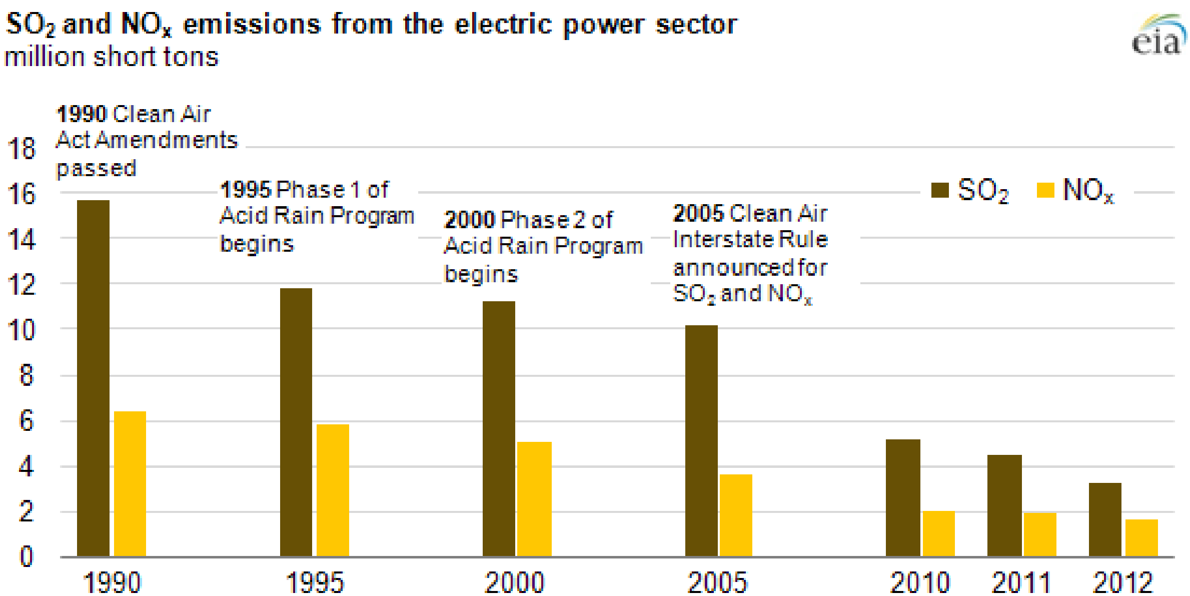


Observed SO_2 dropping, largely in compliance with NAAQS 1 hr standard of 75 ppb

http://www.epa.gov/airtrends



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Removal of SO_2 from Power Plants

SO_2 Control: Flue Gas Desulphurization

Pulverized limestone ($CaCO_3$) is mixed with water to make a slurry sprayed into flue gas, resulting in:

$$CaCO_3 + SO_2 + 2H_2O \rightarrow CaSO_3{\cdot}H_2O + CO_2$$

Cost on order $200 million per unit

Another technology using lime, CaO, exists but is not in widespread use due to high cost of lime

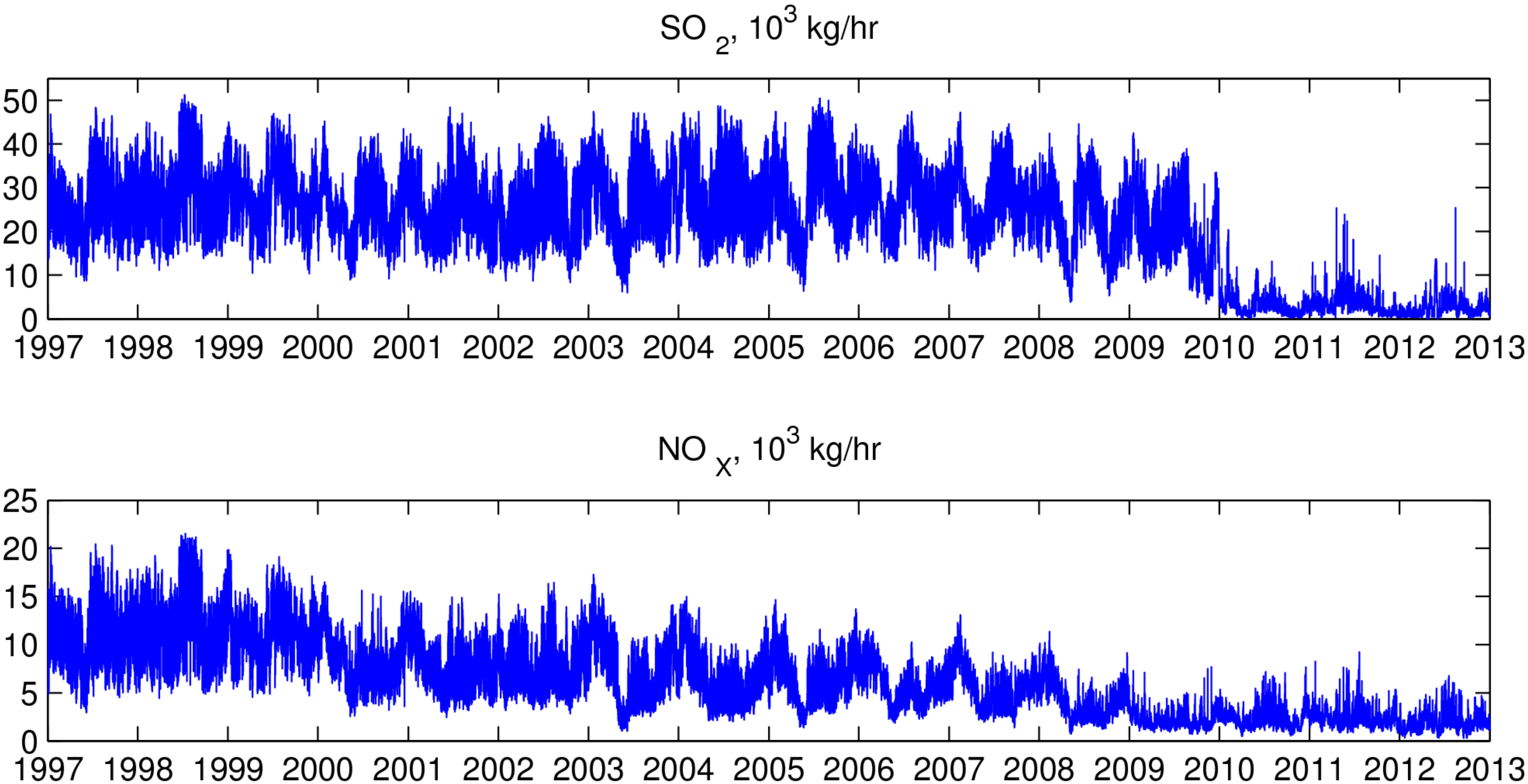
Md Coal Plants with Capacity over 400 Mw

Plant	County	Capacity, MW	Year Built	SCR	FGD
Brandon Shores	Anne Arundel	1273	1984, 1991	Partial	Yes
Morgantown	Charles	1252	1970, 1971	Yes	Yes
Chalk Point	Prince Georges	728	1964, 1965	No	Yes
Dickerson	Montgomery	588	1959, 1960, 1962	No	Yes
Herbert Wagner	Anne Arundel	977	1959, 1966	Partial	No
Crane	Baltimore	400	1961, 1963	Partial	No

Note: A 7th coal plant, R. Paul Smith Power Station in Williamsport (near Hagerstown), closed on 1 Sept 2012

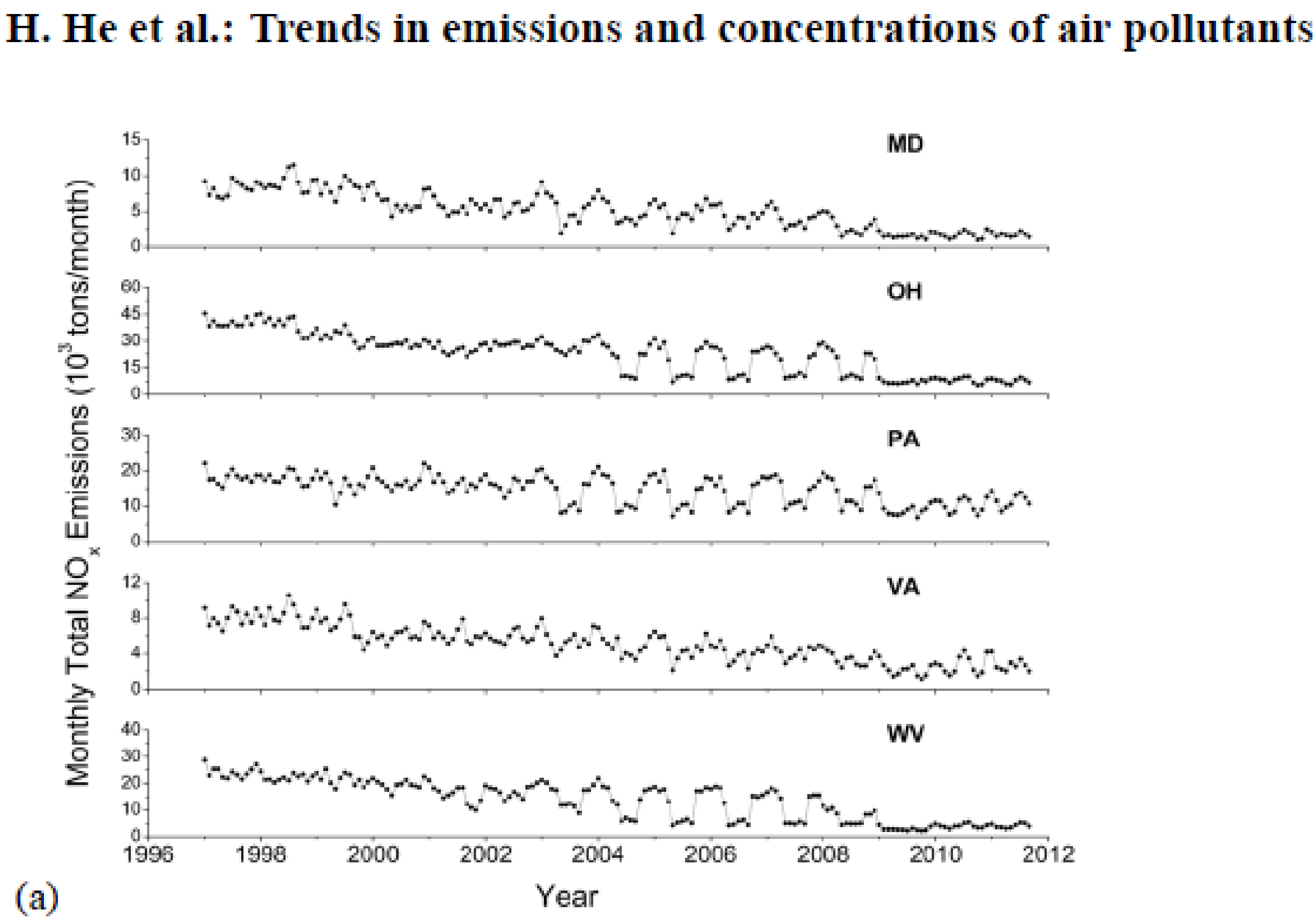
Sources: http://www.sourcewatch.org/index.php/Maryland_and_coal
http://raven-power.com/plants/brandon-shores
http://www.industcards.com/st-coal-usa-md.htm

Maryland Trends



Courtesy: K. Vinnikov

Trends in power plant NO_x emission, region



He et al., *ACP*, 2013

SO_2 From Space (US)

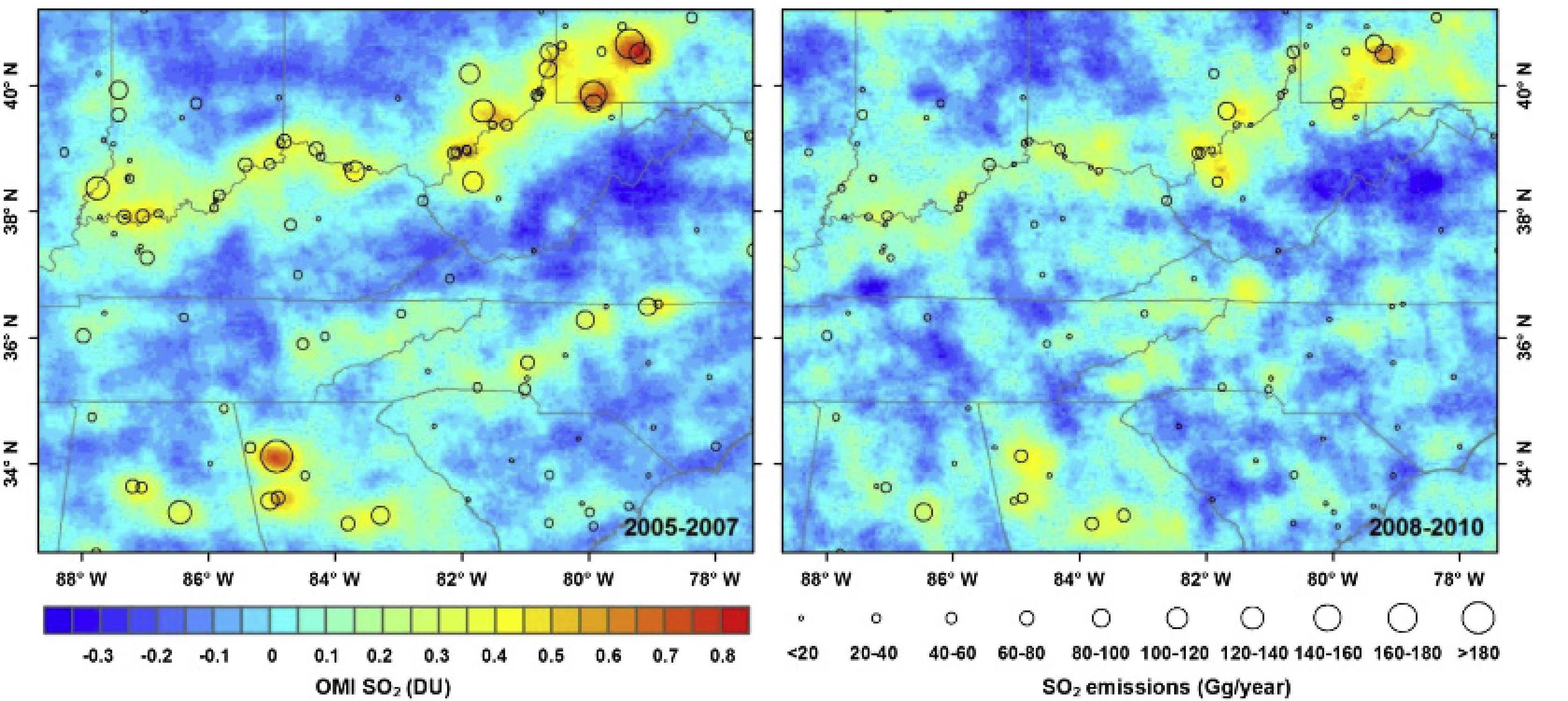
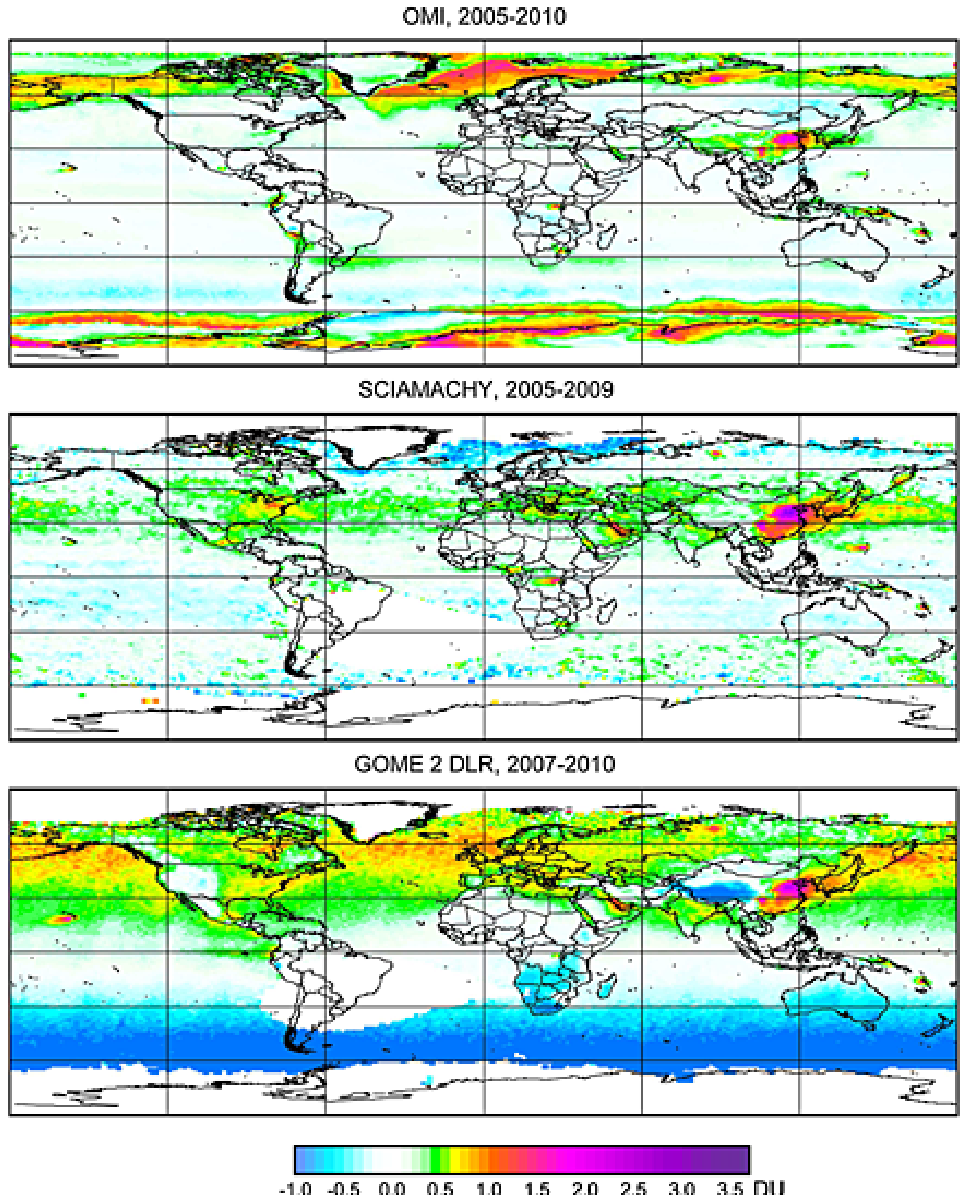


Fig. 4. Mean SO_2 burdens over the Ohio River Basin for 2005–2007 (left) and 2008–2010 (right) measured by OMI, confirming a substantial reduction in SO_2 pollution around the largest coal-fired power plants, as a result of the implementation of SO_2 emission control measures (adapted from NASA Earth Observatory, as reported in Fioletov et al., 2011).

Streets et al., Atmos. Envir., 2013

SO_2 From Space (Global)

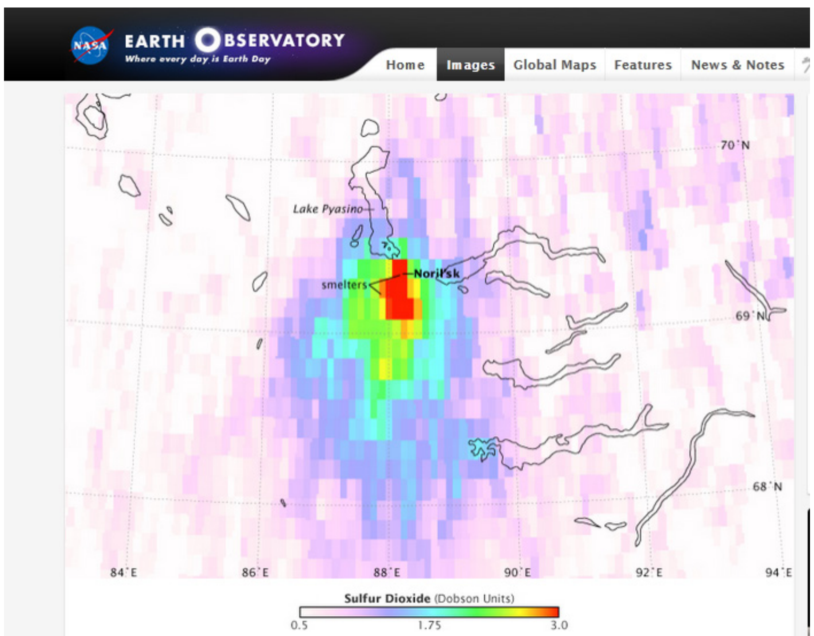


Fioletov et al., JGR, 2013

SO_2 From Space (Norilsk, Russia)

Copper and nickel smelters in Norilsk, Russia are largest anthropogenic point source of SO_2

http://news.bbc.co.uk/1/hi/in_pictures/6529225.stm



Enhanced SO_2 in this region readily apparent from space

http://earthobservatory.nasa.gov/IOTD/view.php?id=36063

Acid Rain: NO_x

NO_x plays major role in tropospheric O_3 formation.

In Lecture 12, we emphasize the critical importance of radical termination:

$$NO_2\,(g) + OH\,(g) + M \rightarrow HNO_3\,(g) + M$$

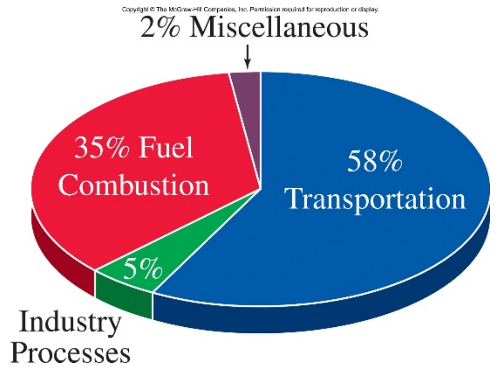
Nitric acid, HNO_3, is soluble. Hence, in the presence of droplets, HNO_3 (g) can become HNO_3 (aq)

HNO3 (aq) then dissociate:

$$HNO_3(aq) \leftrightarrow H^+\,(aq) + NO_3^-\,(aq)$$

and well "oops, we did it again"

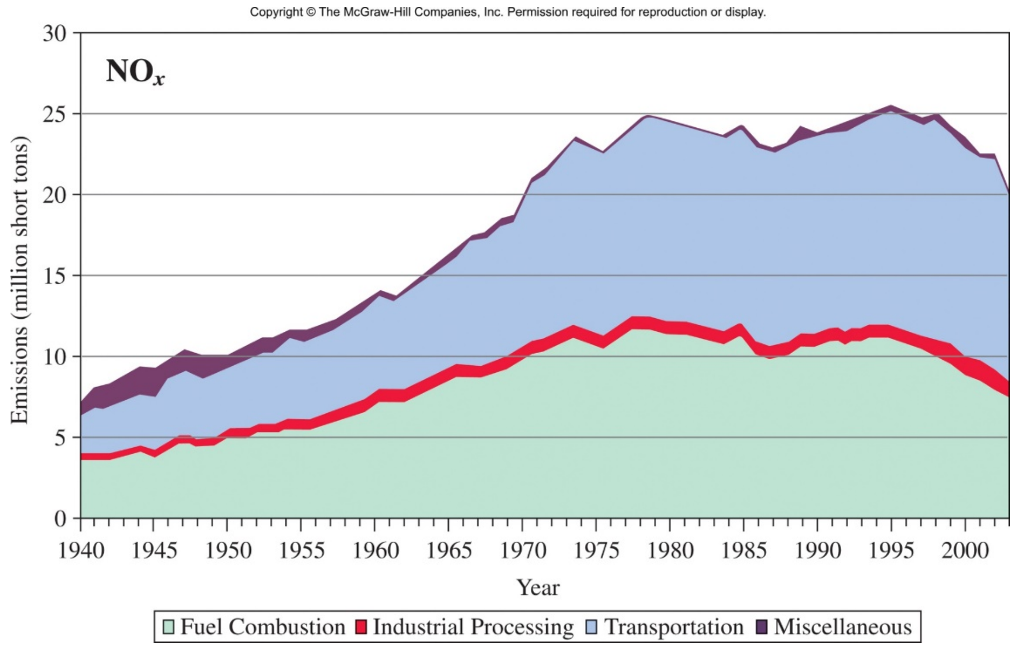
NO_x Sources (US)



Primary source of NO_2 is transportation; EPA inventory suggests emissions from this sector are holding steady, whereas the UMd Atmos Chem group believes emission in the mid-Atlantic have fallen dramatically (Anderson et al., Atmos Envor, 2014)

Emissions from fuel combustion primary driver of inventory decline

Figure 6.16, Chemistry in Context. US NO_x emission sources, 2007



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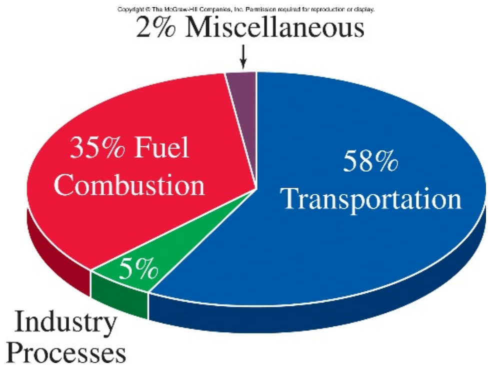

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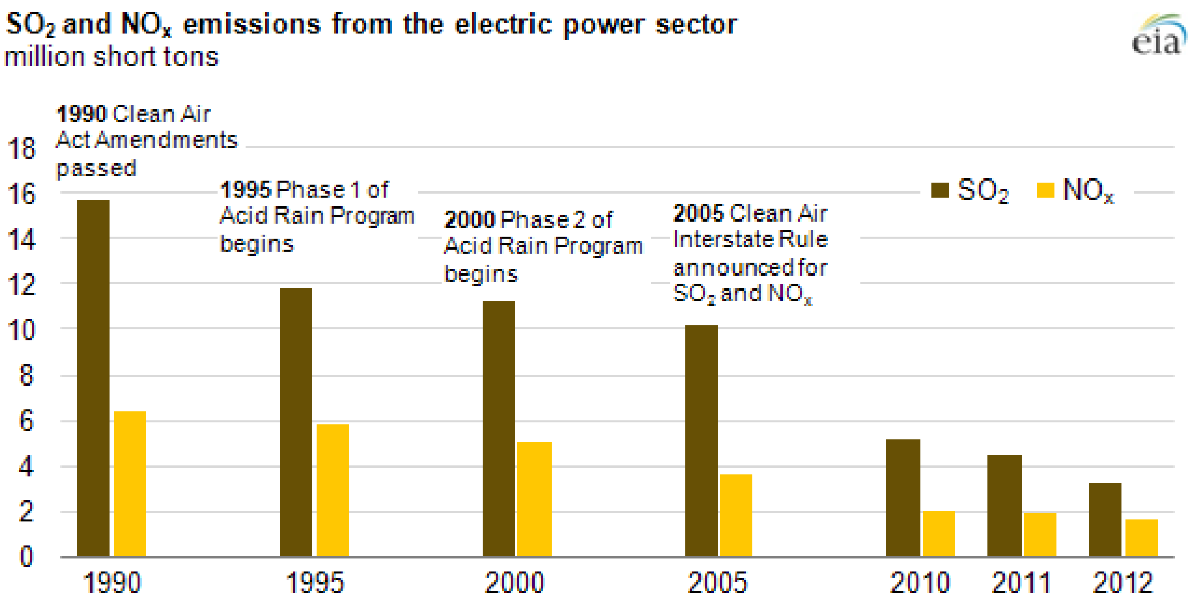

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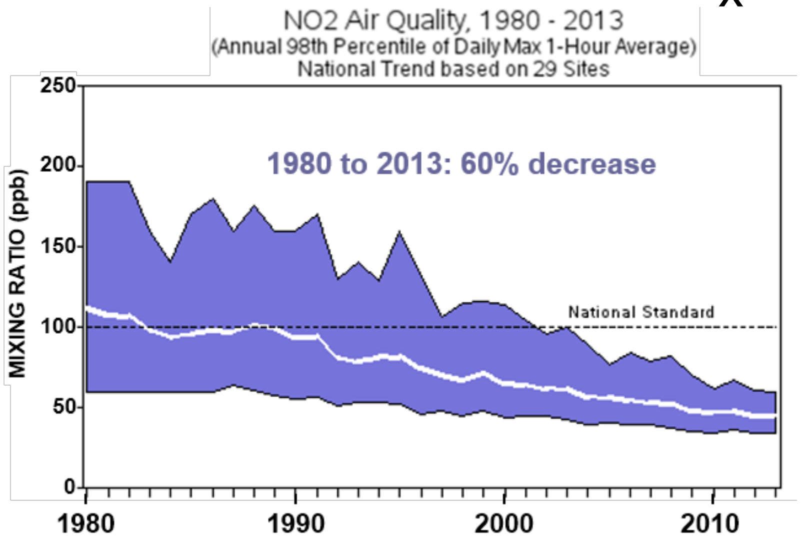

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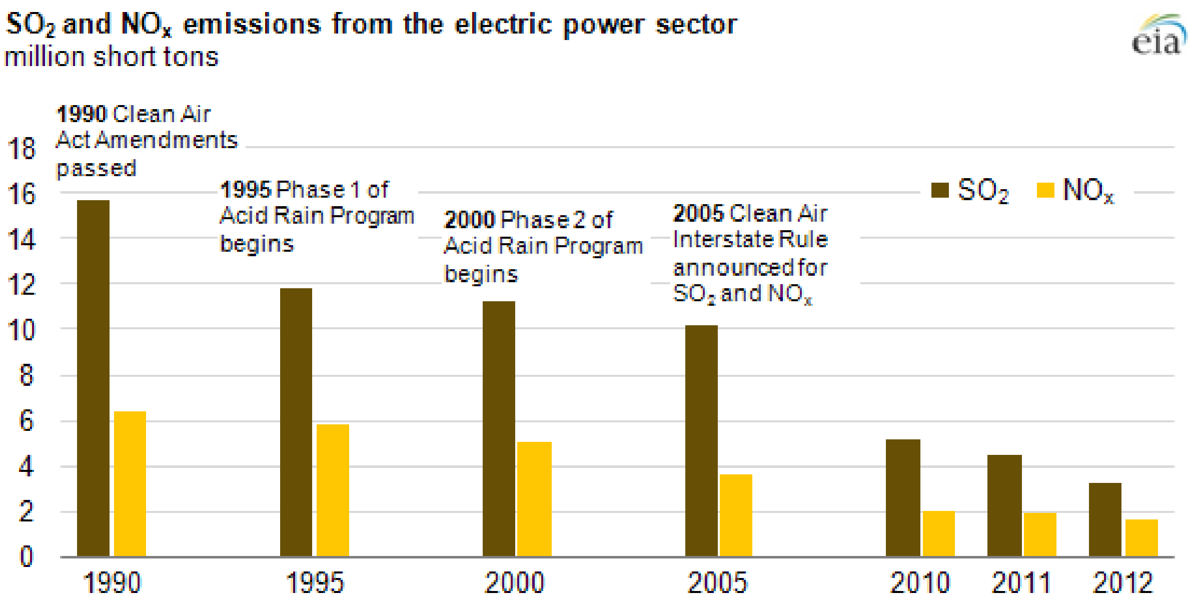

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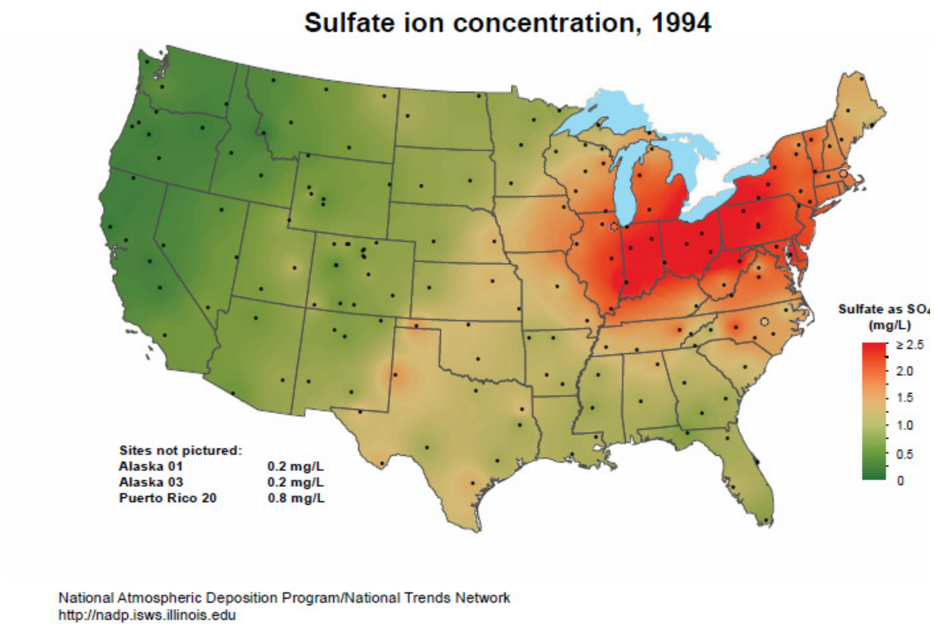
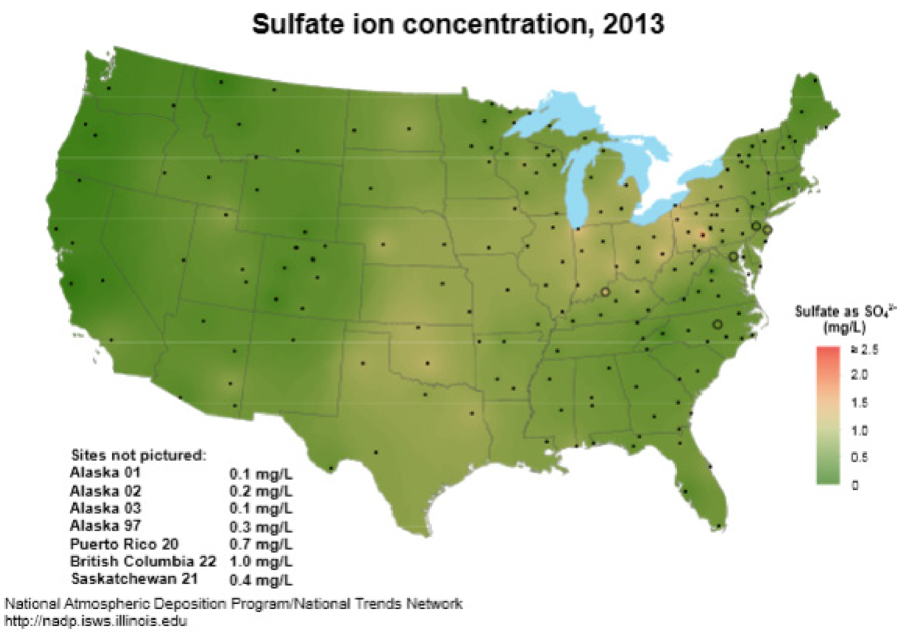
Sulfate Deposition

1994

2013

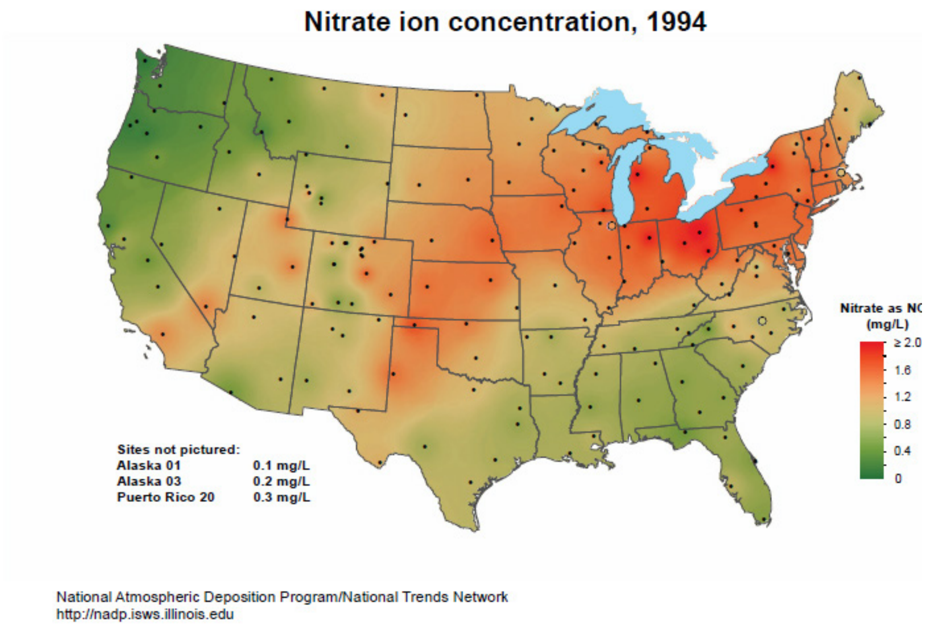




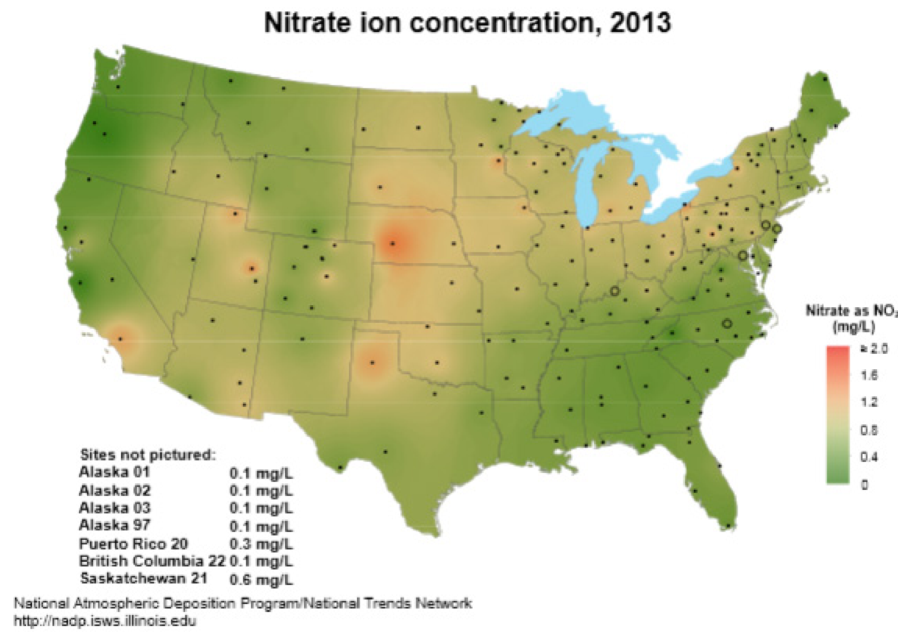
http://nadp.sws.uiuc.edu/

Nitrate Deposition

1994



2013



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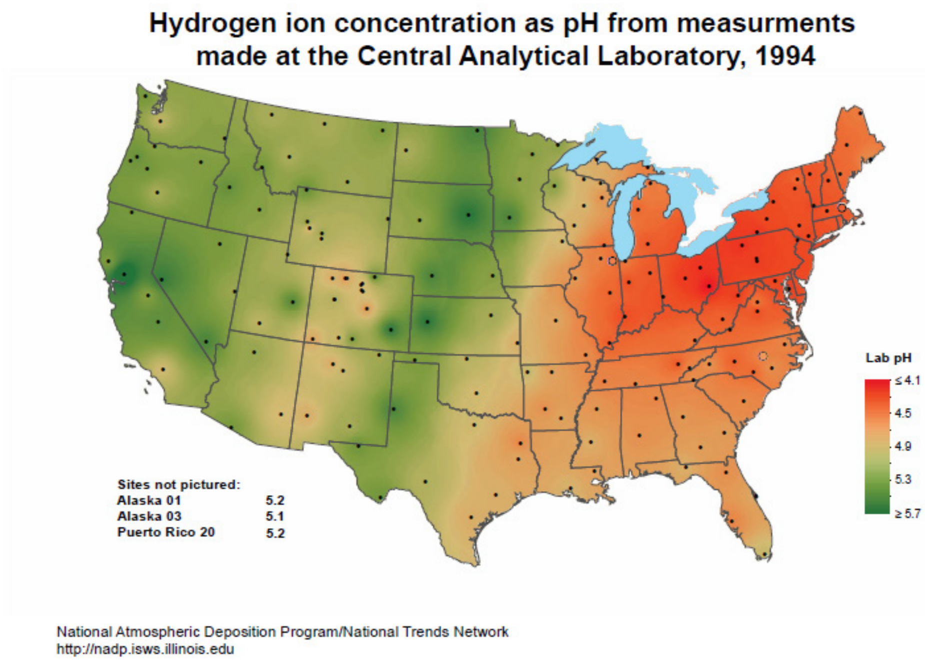
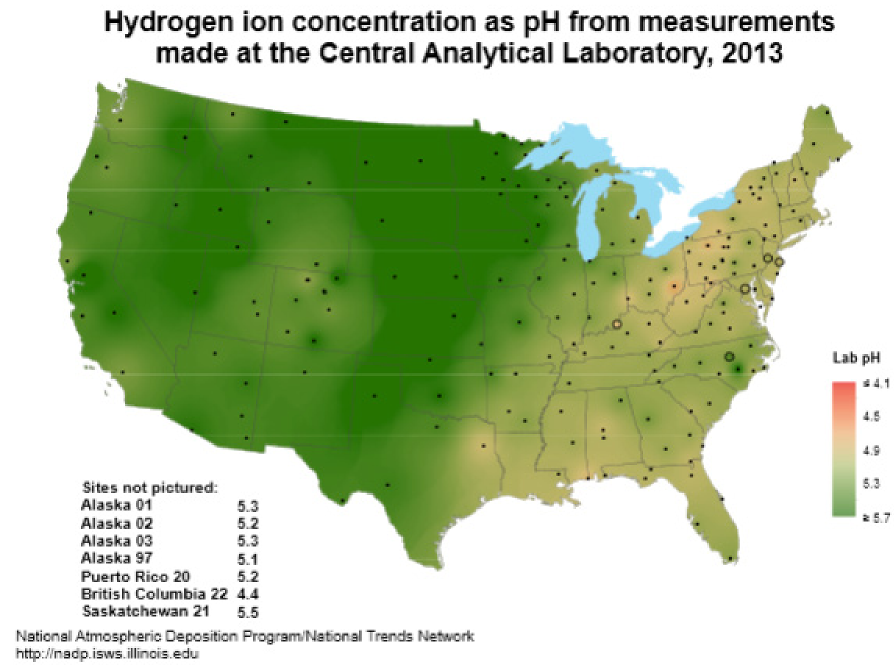
pH

1994



2013



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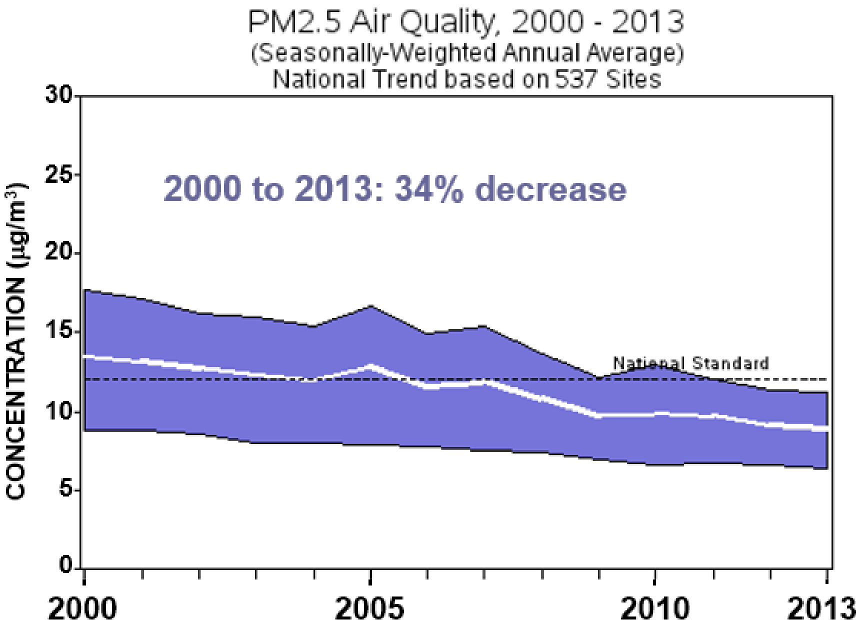
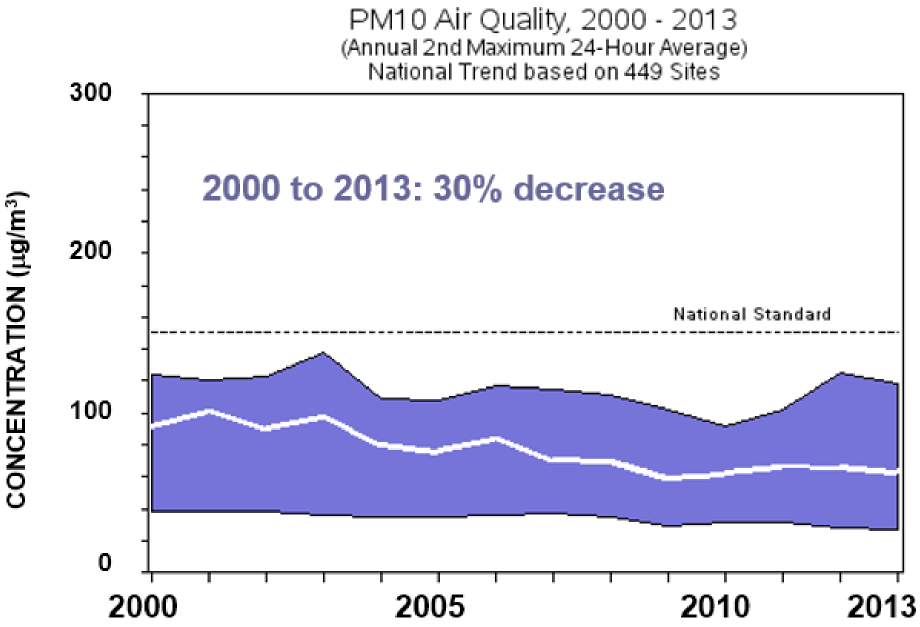
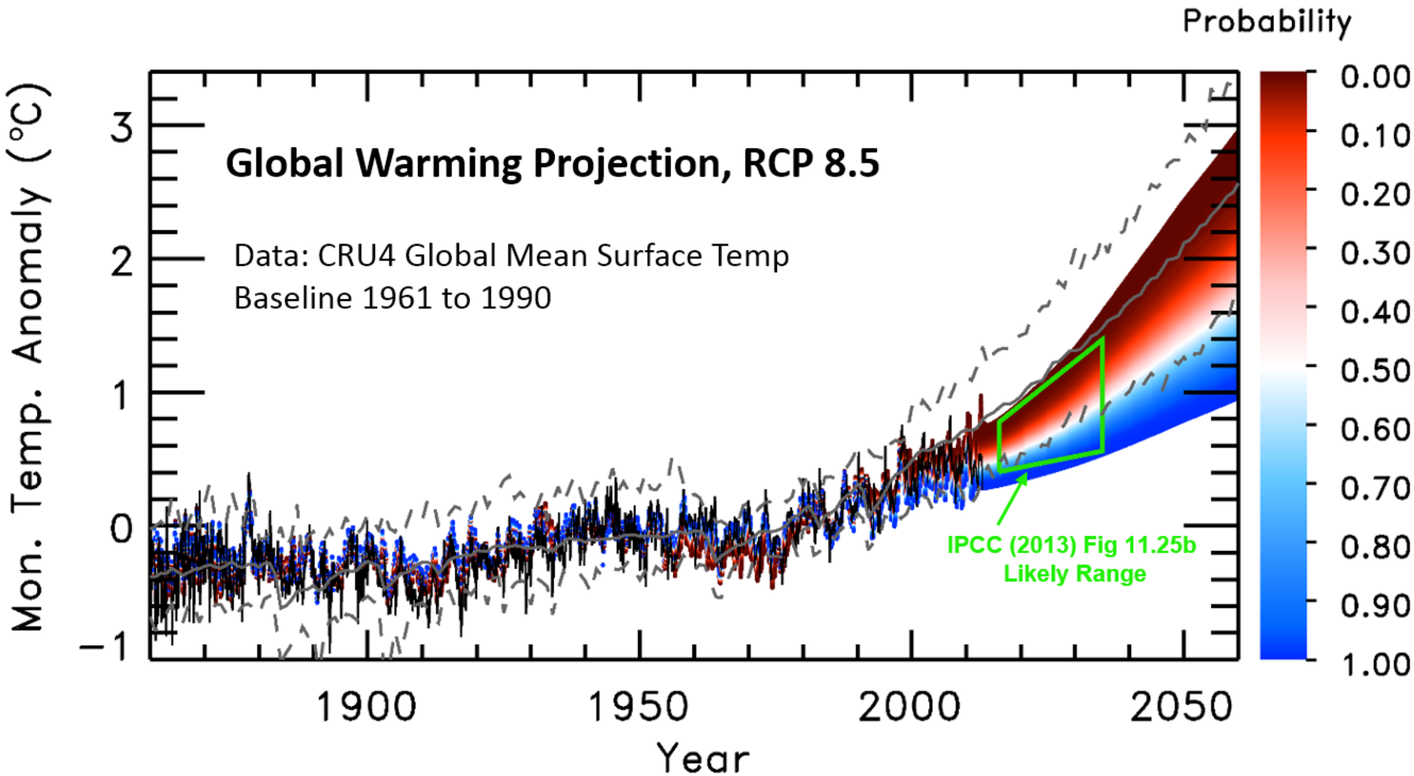
PM Trends





http://www.epa.gov/airtrends/

Uncertainty of Aerosol RF Effects Future Climate



If tropospheric aerosols have offset a <u>large fraction</u> of GHG induced warming, then the actual warming that may occur could be considerably *larger* than "best estimate"

If tropospheric aerosols have offset only a <u>tiny fraction</u> of GHG induced warming, then the actual warming that may occur could be considerably *smaller* larger "best estimate"