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/spr2017

Lecture 13

28 March 2017

Problem Set #3 has been posted

- Longest problem set of the semester: 300 points total
- This time, same for 433 & 633

Lecture 10: Photolysis Frequency

For a specific spectral interval, the photolysis frequency (***partial J value***) of a gas is given by the product of its absorption cross section and the solar irradiance:

$$J_{gas}(z,\lambda) = \text{Quantum\_Yield}(\lambda)\ \sigma_{gas}(\lambda,T)\ F(z,\lambda)$$

Units: $s^{-1}\ nm^{-1}$

The total ***photolysis frequency*** (***J value***) is found by integrating $J_{gas}(z,\lambda)$ over all wavelengths for which the gas photodissociates:

$$J_{gas}(z) = \int_{\lambda_{min}}^{\lambda_{max}} J_{gas}(z,\lambda)\, d\lambda$$

Units: s^{-1}

Problem Set #3 has been posted

- Longest problem set of the semester: 300 points total
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Lecture 12: Rates of Reactions

$NO_2 + h\nu \rightarrow NO + O$ (1)

Rate of reaction (1) = $J_{NO2} \times [NO_2]$

$HO_2 + NO \rightarrow OH + NO_2$ (2)

Rate of reaction (2) = $k_{HO2+NO} \times [HO_2] \times [NO]$

Units: molecules cm^{-3} s^{-1}

JPL 2015 Bimolecular Rates Table entry

$HO_2 + NO \rightarrow NO_2 + OH$	183–1270	3.3×10^{-12}	–270	8.0×10^{-12}	1.15	20	C12

Arrhenius Expression for k_{HO2+NO} is

Units: cm^3 s^{-1}

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 (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/m³ (1.011 to 1.012) and 1.003 per 10 μg/m³ (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 Air Pollution

Posted by Caleb Finch and Jiu-Chiuan Chen on Tue, 28 Feb 2017

Air Pollution Exposure May Increase Risk of Dementia

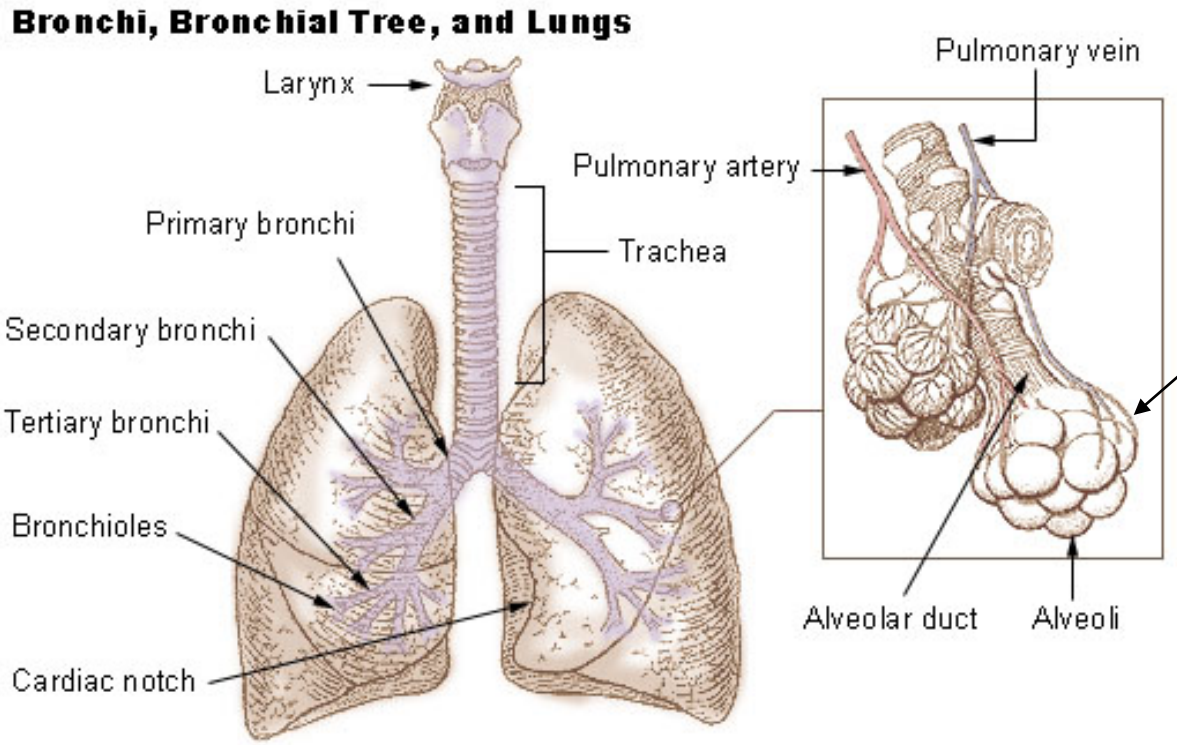
We designed this study to answer three broad questions. First, we wanted to know whether older people living in locations with higher levels of outdoor PM2.5 have an increased risk for cognitive impairment, especially dementia. We also wanted to know whether people who carry the high-risk gene for Alzheimer's disease, APOE4, are more sensitive to the damage potentially caused by long-term exposure to PM2.5 in the air.

We focused on older women and female mice because APOE4 confers a greater Alzheimer's disease risk in women than in men.

We found that women exposed to higher levels of PM2.5 had faster rates of cognitive decline and a higher risk of developing dementia. Older women living in places where PM2.5 levels exceeded the U.S. Environmental Protection Agency's standard had an 81% greater risk of global cognitive decline and were 92% more likely to develop dementia, including Alzheimer's. This environmental risk raised by long-term PM2.5 exposure was two to three times higher among older women with two copies of the APOE4 gene, compared with women who had only the background genetic risk with no APOE4 gene.

http://www.pbs.org/wgbh/nova/next/body/air-pollution-exposure-may-increase-risk-of-dementia/

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

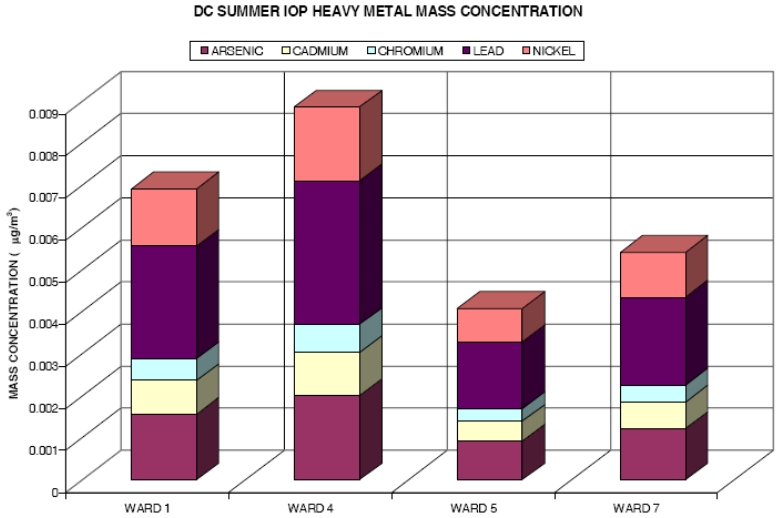


Figure 5: Heavy Metal Content of Fine PM for Summer IOP

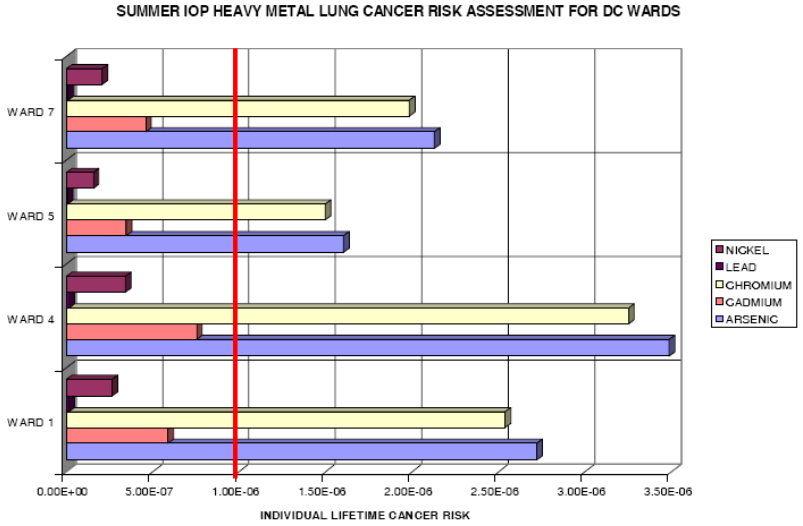
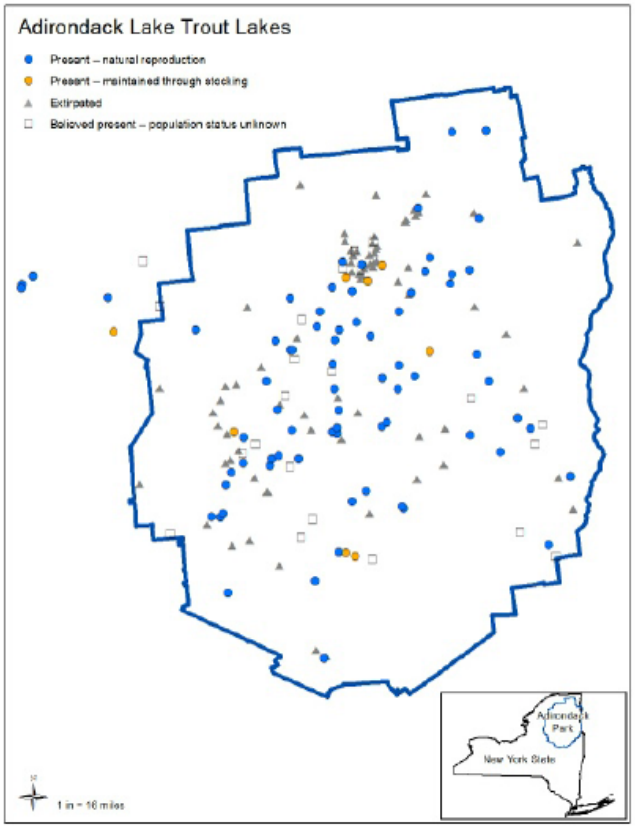


Figure 10: Summer IOP Lifetime Excess Lung Cancer Risk by DC Wards.

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

In 1944

At present

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)

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

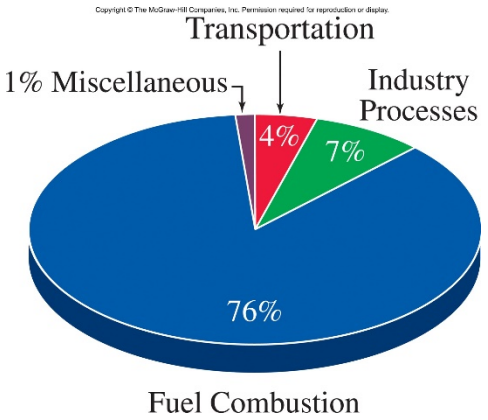
$$SO_3\,(aq) + H_2O\,(l) \rightarrow H_2SO_4\,(aq)$$

Followed by:

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

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

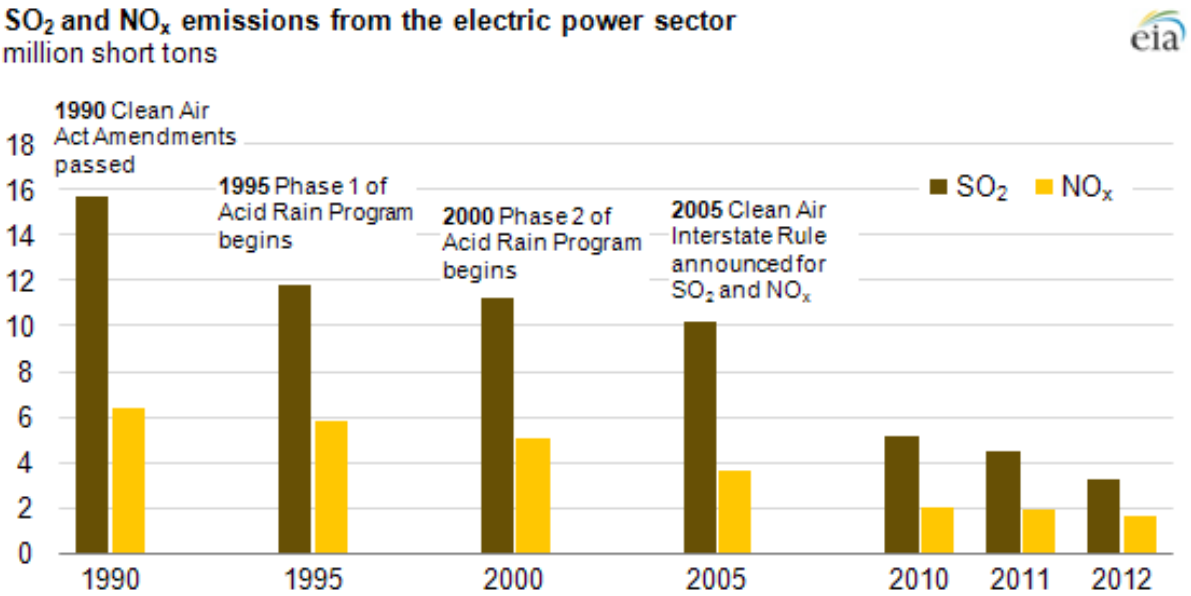
SO_2 Sources (US)



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

Emissions from transportation are small and largely unchanged.

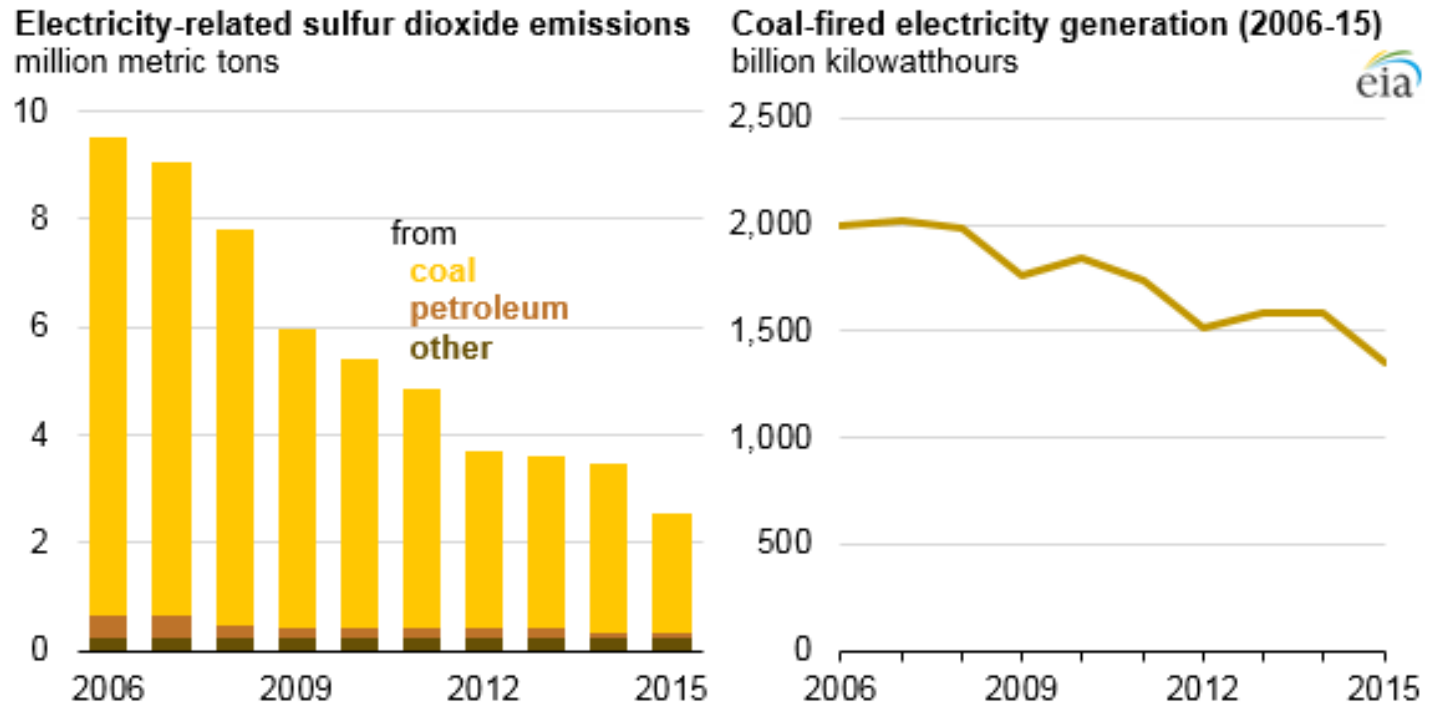
Figure 6.14, Chemistry in Context. US SO_2 emission sources, 2007



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

SO_2 Sources (US)

Sulfur dioxide emissions from U.S. power plants have fallen faster than coal generation



Source: U.S. Energy Information Administration, *Electric Power Annual*

Sulfur dioxide (SO2) emissions produced in the generation of electricity at power plants in the United States declined by 73% from 2006 to 2015, a much larger reduction than the 32% decrease in coal-fired electricity generation over that period. From 2014 to 2015, the most recent year with complete power plant emissions data, SO2 emissions fell 26%—the largest annual drop in percentage terms in the previous decade. Nearly all

https://www.eia.gov/todayinenergy/detail.php?id=29812

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

What happens to the $CaSO_3 \cdot H_2O$?

What happens to the CO_2 ?

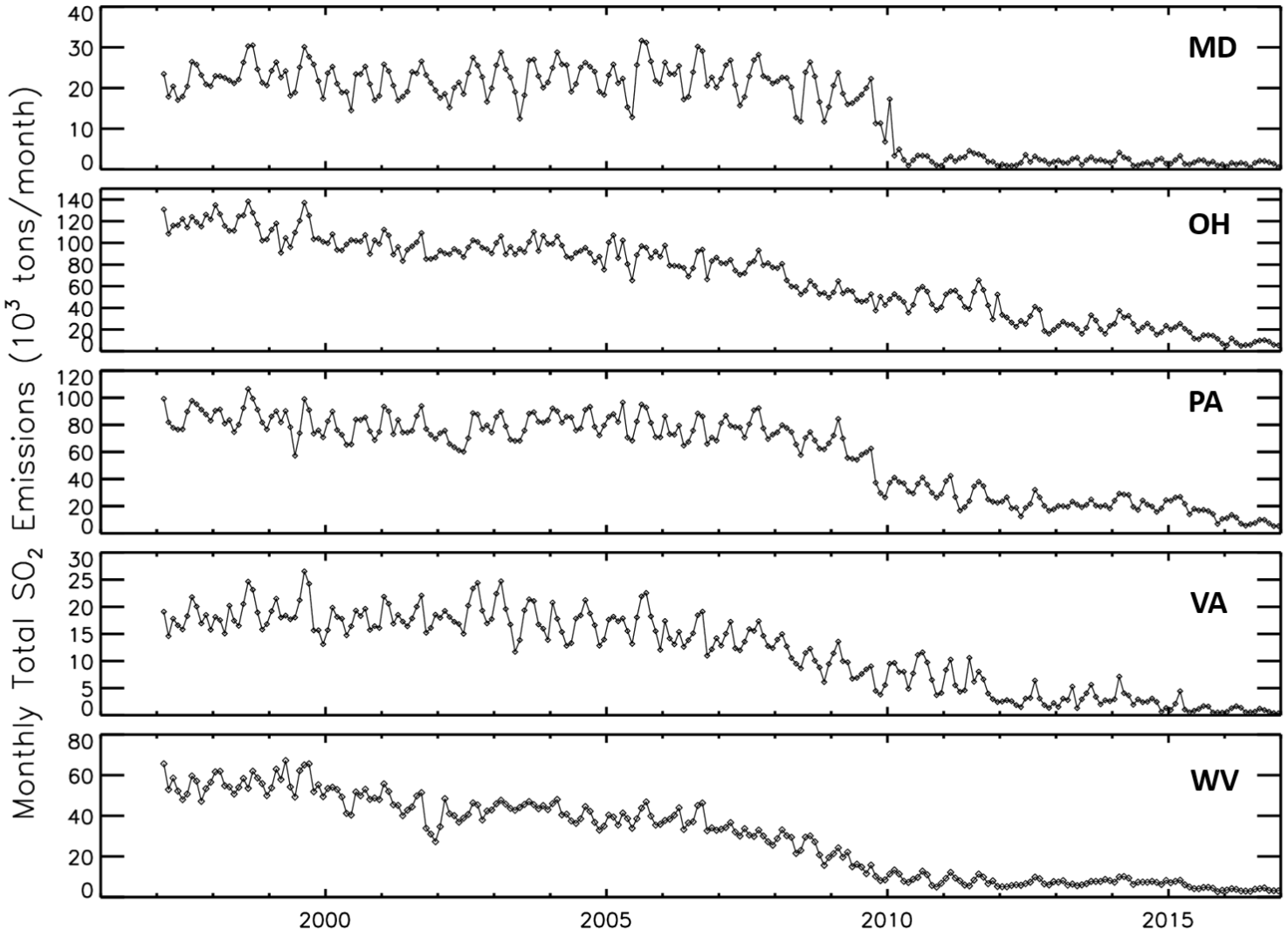
Md Coal Plants with Capacity over 400 Mw

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

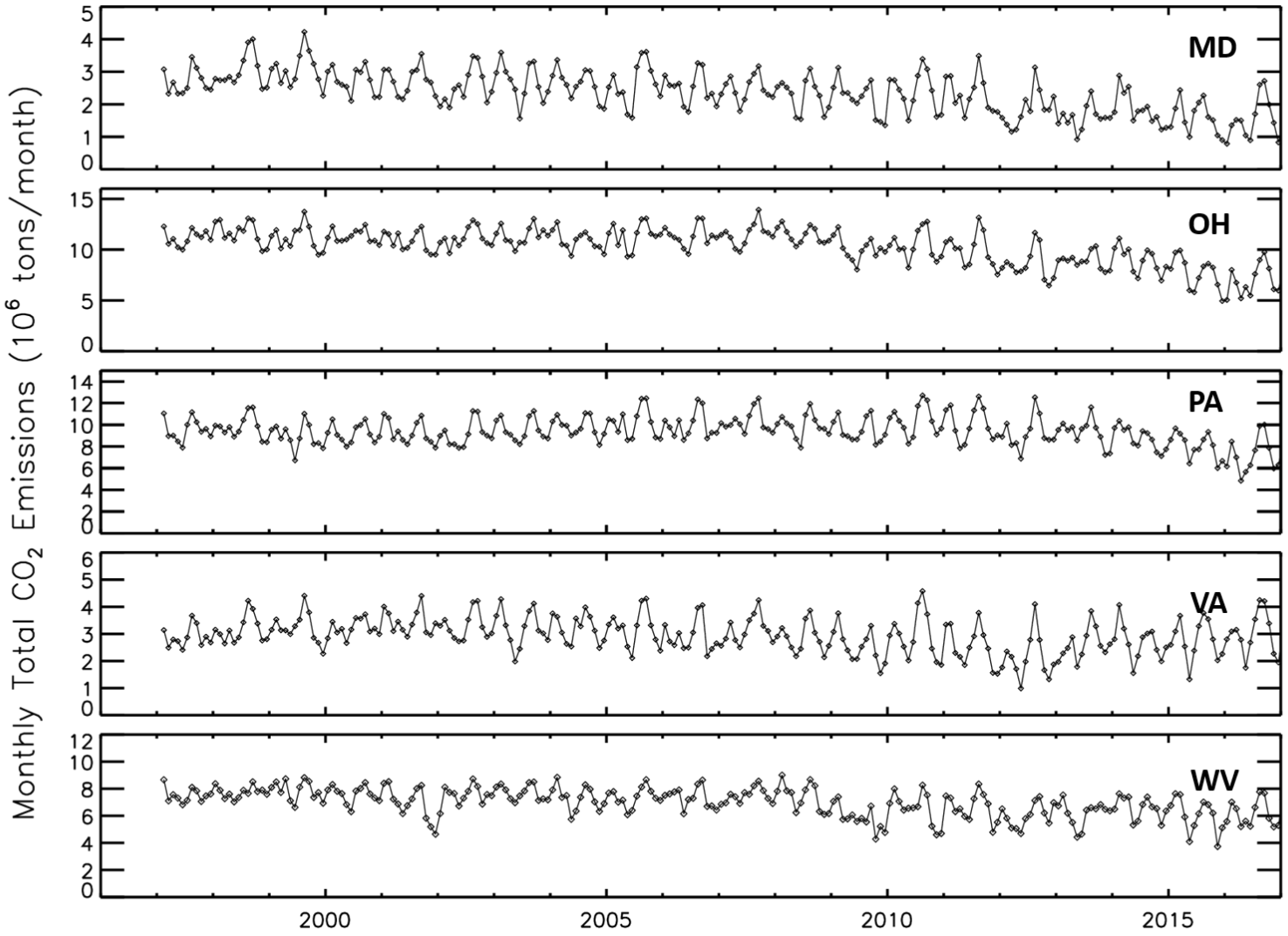
Sources: http://www.sourcewatch.org/index.php/Maryland_and_coal
http://raven-power.com/plants/brandon-shores
http://www.industcards.com/st-coal-usa-md.htm

Trends in power plant emission, region



Thanks to Doyeon Ahn for this wonderful analysis of CEMS (Continuous Emission Monitoring System) Data provided by EPA

Trends in power plant emission, region



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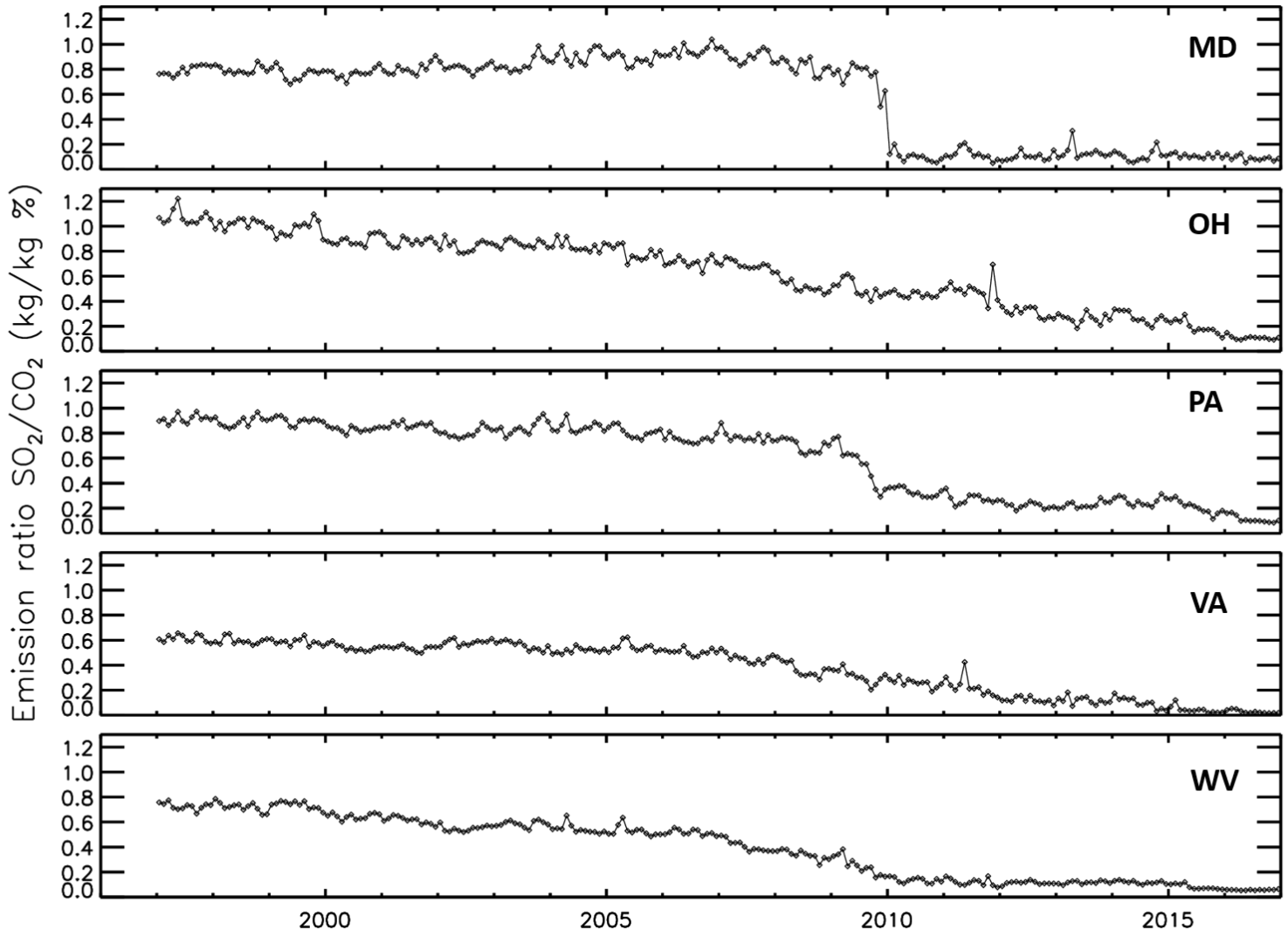

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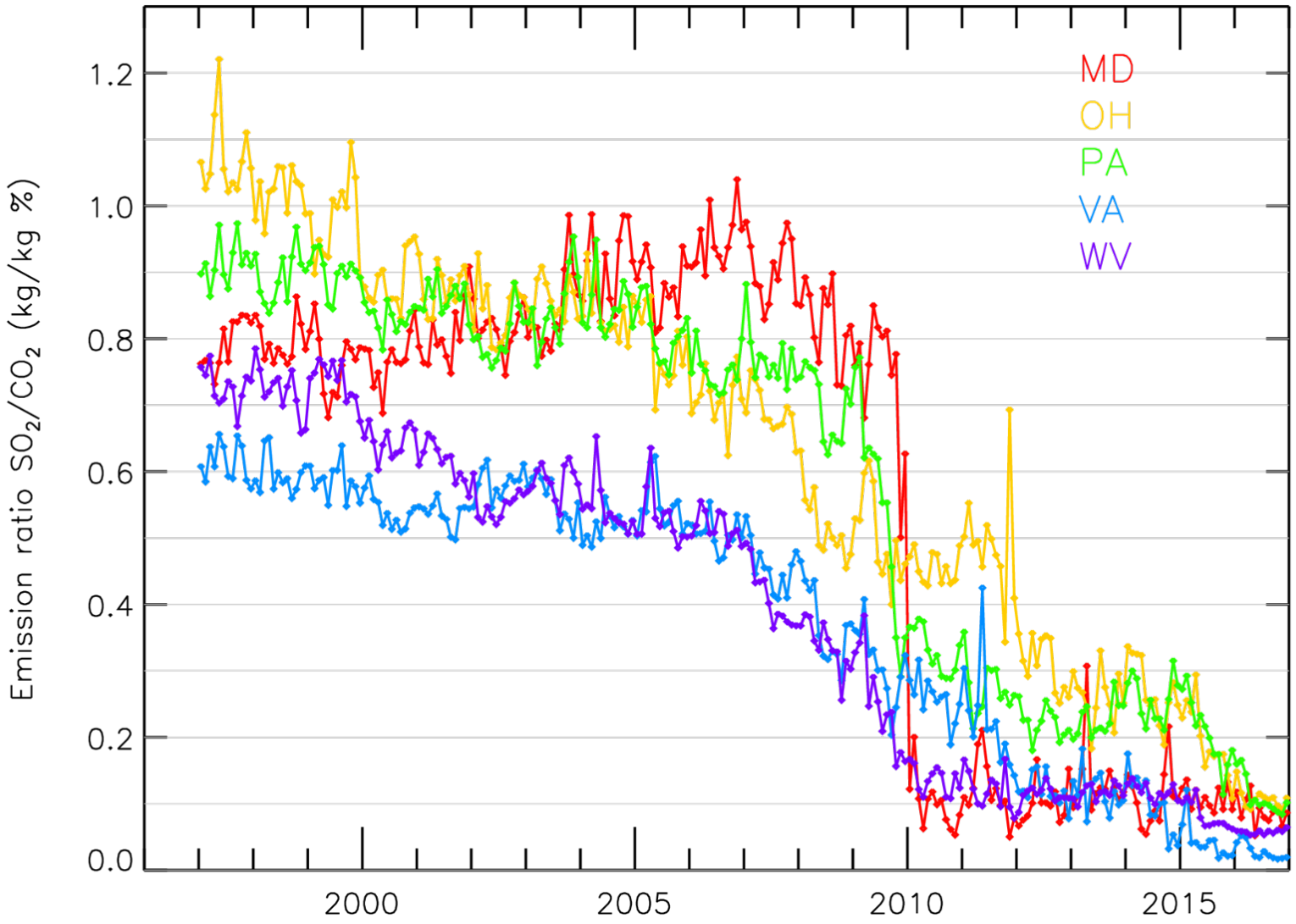
Trends in power plant emission, region



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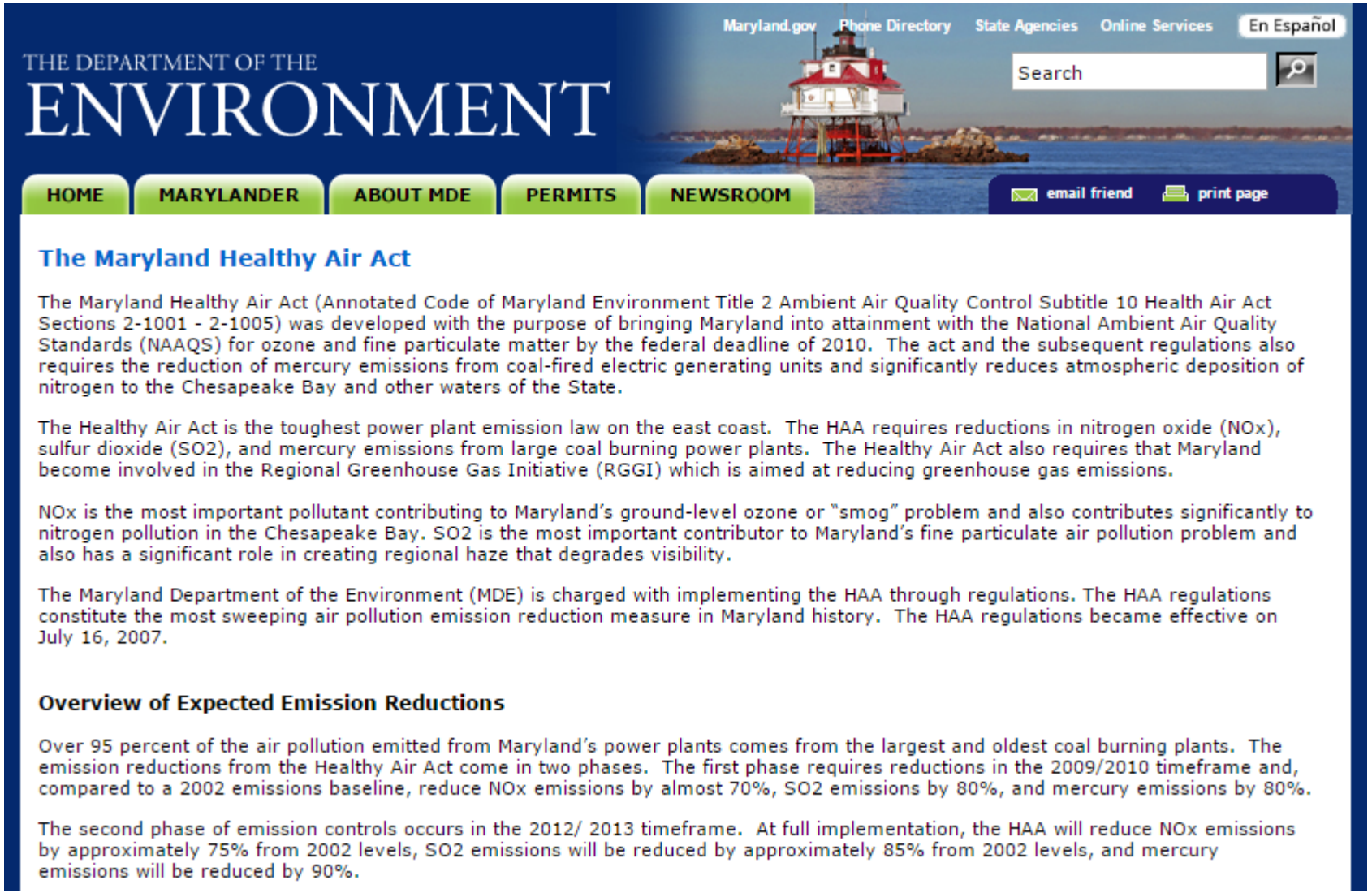
Maryland Healthy Air Act



The Maryland Healthy Air Act

The Maryland Healthy Air Act (Annotated Code of Maryland Environment Title 2 Ambient Air Quality Control Subtitle 10 Health Air Act Sections 2-1001 - 2-1005) was developed with the purpose of bringing Maryland into attainment with the National Ambient Air Quality Standards (NAAQS) for ozone and fine particulate matter by the federal deadline of 2010. The act and the subsequent regulations also requires the reduction of mercury emissions from coal-fired electric generating units and significantly reduces atmospheric deposition of nitrogen to the Chesapeake Bay and other waters of the State.

The Healthy Air Act is the toughest power plant emission law on the east coast. The HAA requires reductions in nitrogen oxide (NOx), sulfur dioxide (SO2), and mercury emissions from large coal burning power plants. The Healthy Air Act also requires that Maryland become involved in the Regional Greenhouse Gas Initiative (RGGI) which is aimed at reducing greenhouse gas emissions.

NOx is the most important pollutant contributing to Maryland's ground-level ozone or "smog" problem and also contributes significantly to nitrogen pollution in the Chesapeake Bay. SO2 is the most important contributor to Maryland's fine particulate air pollution problem and also has a significant role in creating regional haze that degrades visibility.

The Maryland Department of the Environment (MDE) is charged with implementing the HAA through regulations. The HAA regulations constitute the most sweeping air pollution emission reduction measure in Maryland history. The HAA regulations became effective on July 16, 2007.

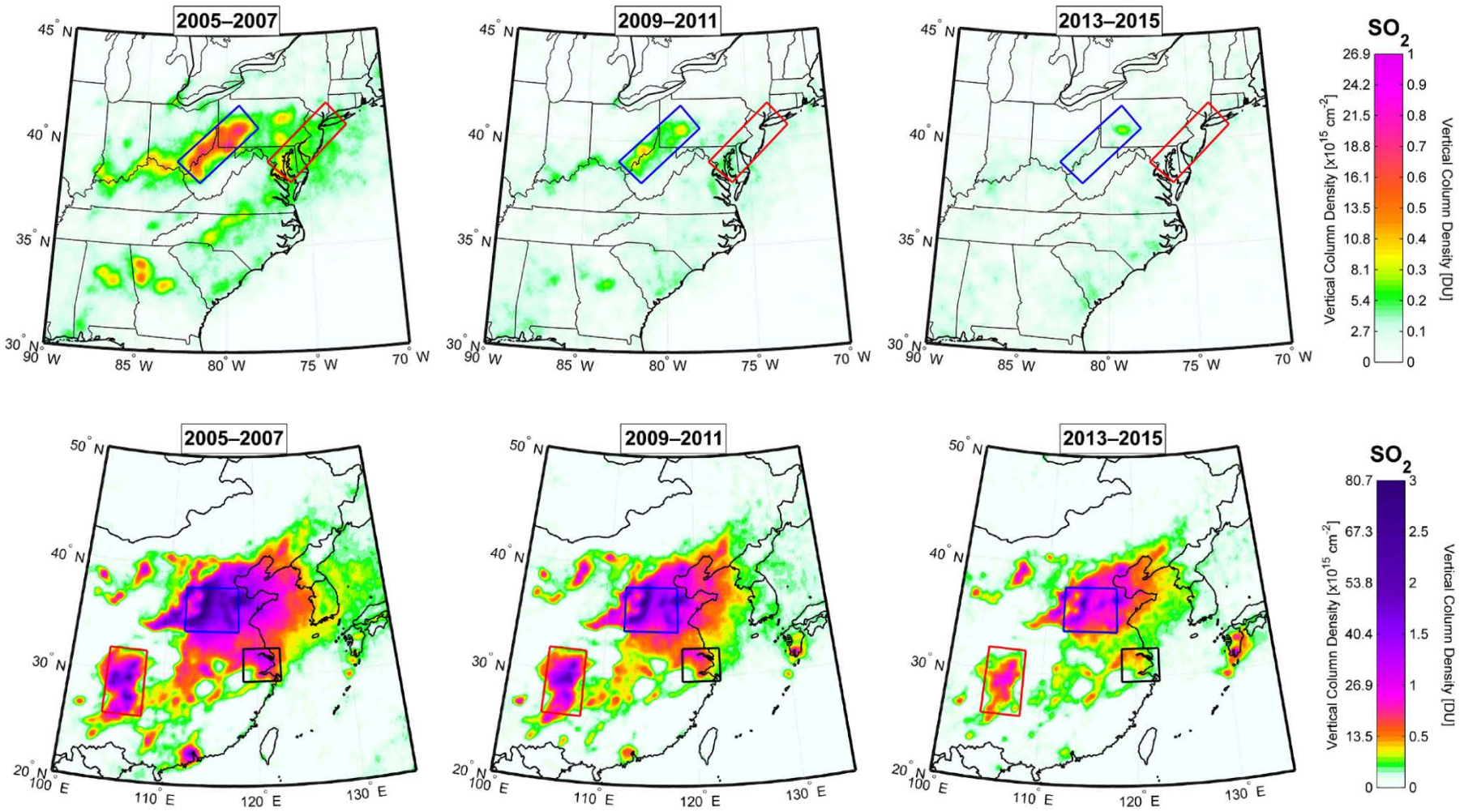
Overview of Expected Emission Reductions

Over 95 percent of the air pollution emitted from Maryland's power plants comes from the largest and oldest coal burning plants. The emission reductions from the Healthy Air Act come in two phases. The first phase requires reductions in the 2009/2010 timeframe and, compared to a 2002 emissions baseline, reduce NOx emissions by almost 70%, SO2 emissions by 80%, and mercury emissions by 80%.

The second phase of emission controls occurs in the 2012/ 2013 timeframe. At full implementation, the HAA will reduce NOx emissions by approximately 75% from 2002 levels, SO2 emissions will be reduced by approximately 85% from 2002 levels, and mercury emissions will be reduced by 90%.

http://www.mde.maryland.gov/programs/air/pages/md_haa.aspx

SO_2 Trends from Space



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

SO_2 From Space (US)

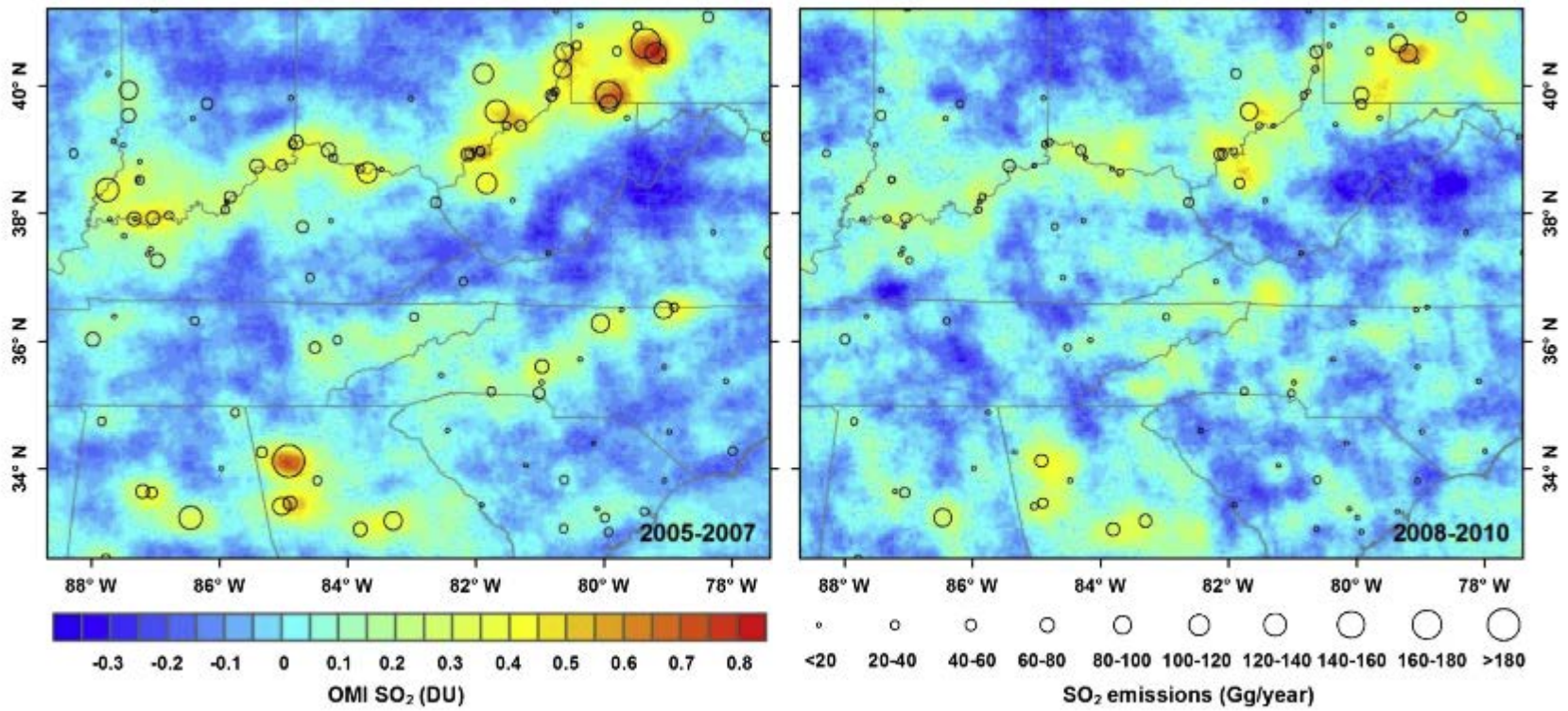
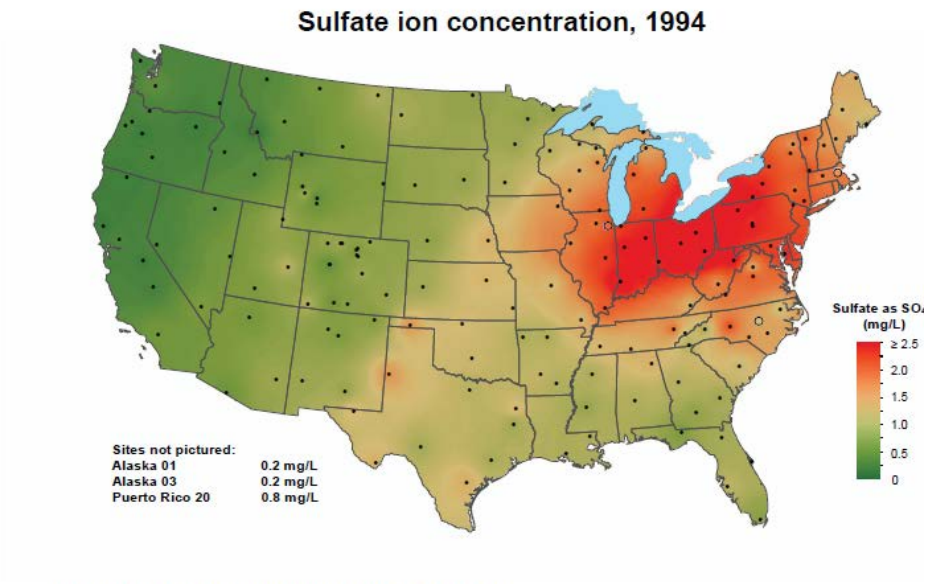


Fig. 4. Mean SO_2 burdens over the Ohio River Basin for 2005–2007 (left) and 2008–2010 (right) measured by OMI, confirming a substantial reduction in SO_2 pollution around the largest coal-fired power plants, as a result of the implementation of SO_2 emission control measures (adapted from NASA Earth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

Streets et al., Atmos. Envir., 2013

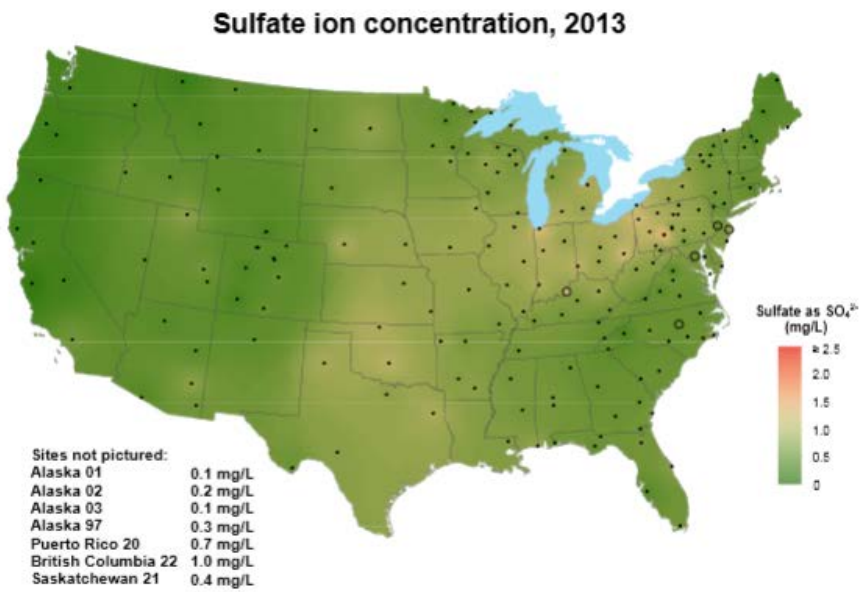
Sulfate Deposition

1994



National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

2013



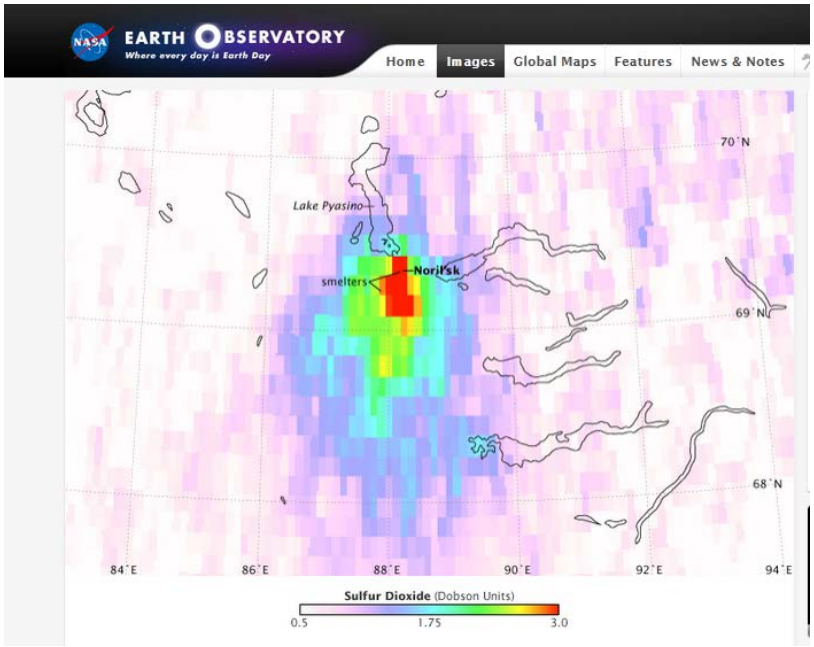
National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

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

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:

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

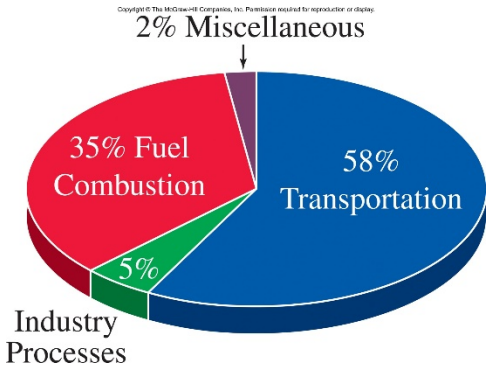
Nitric acid, HNO_3, is soluble. Hence, in the presence of droplets, HNO_3 (g) can become HNO_3 (aq)

HNO3 (aq) then dissociate:

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

and well "oops, we did it again"

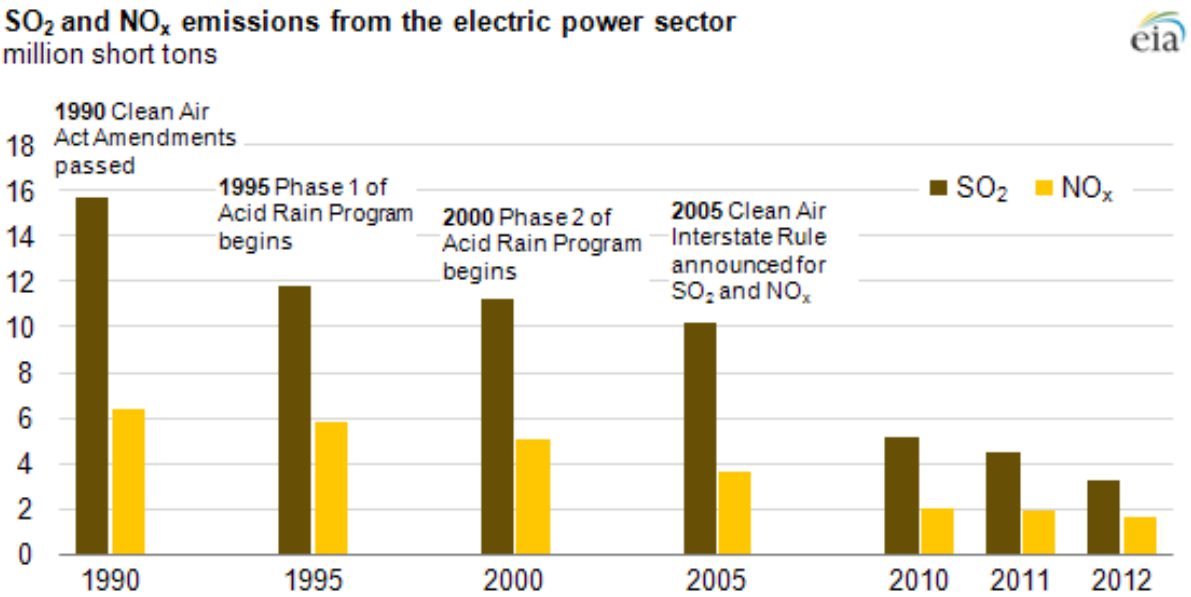
NO_x Sources (US)



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)

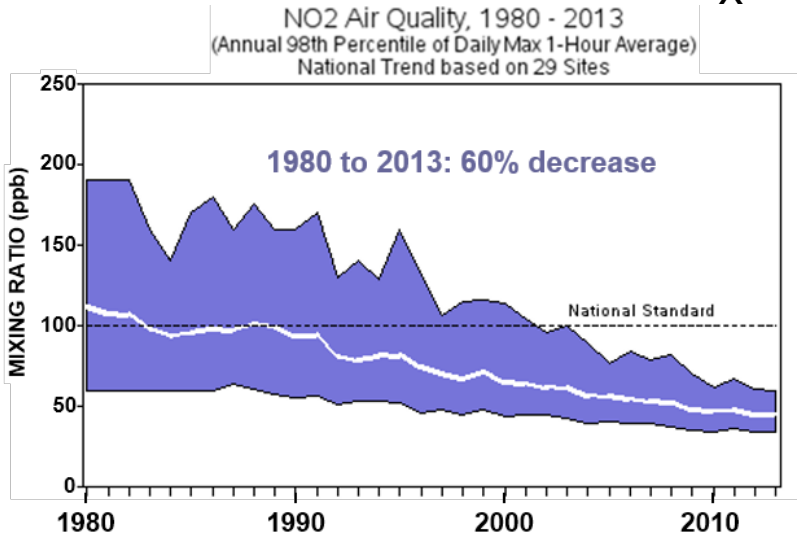
Emissions from fuel combustion primary driver of inventory decline

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



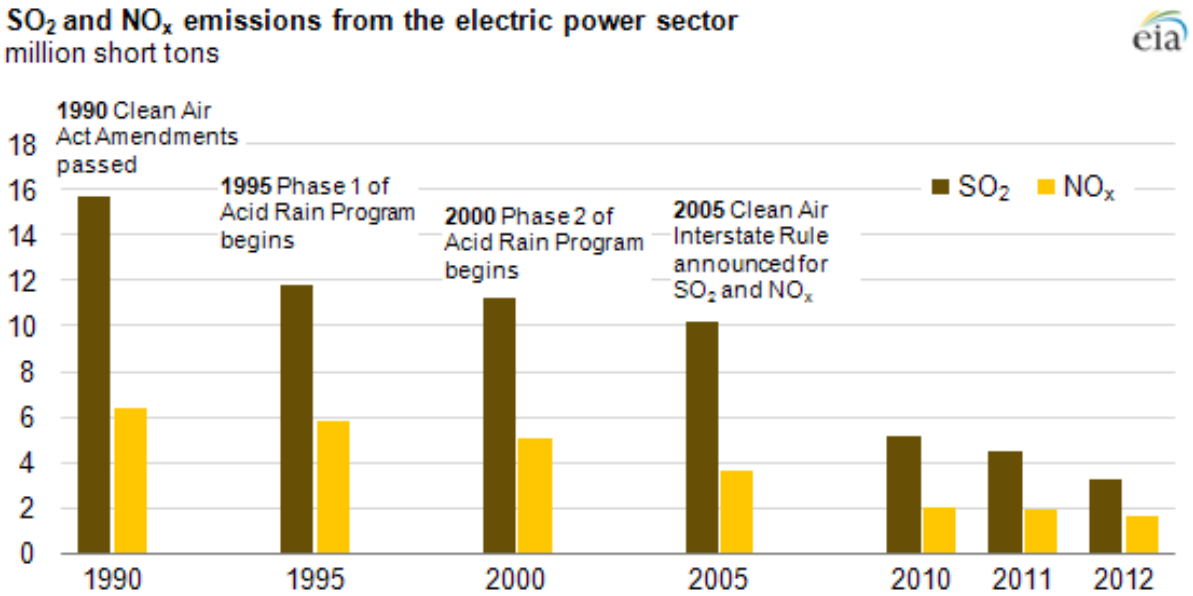
http://www.eia.gov/todayinenergy/detail.cfm?id=10151

NO_x Sources (US)



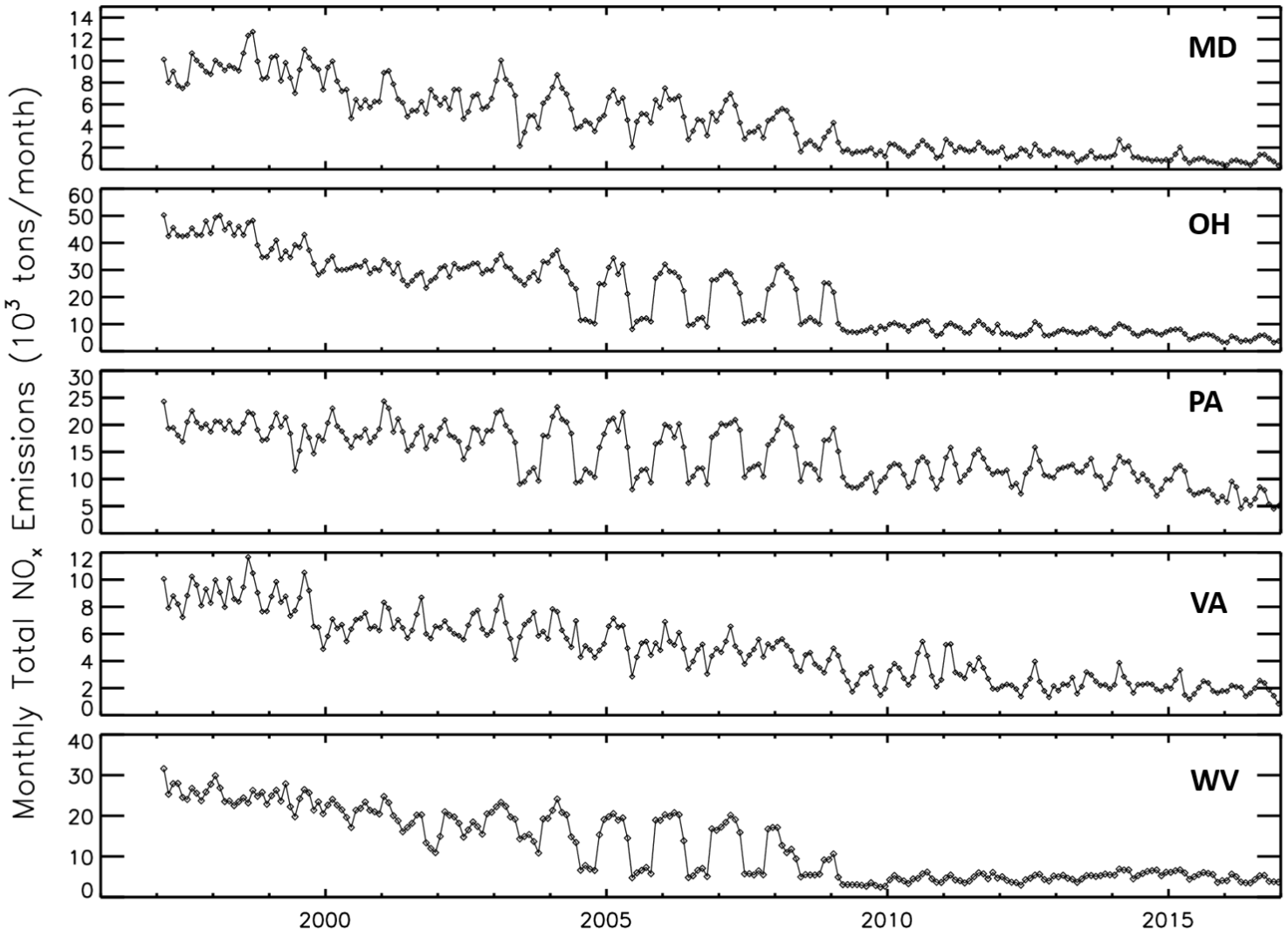
Observed NO_2 dropping, largely in compliance with NAAQS 1 hr standard of 100 ppb

http://www.epa.gov/airtrends



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

Trends in power plant emission, region



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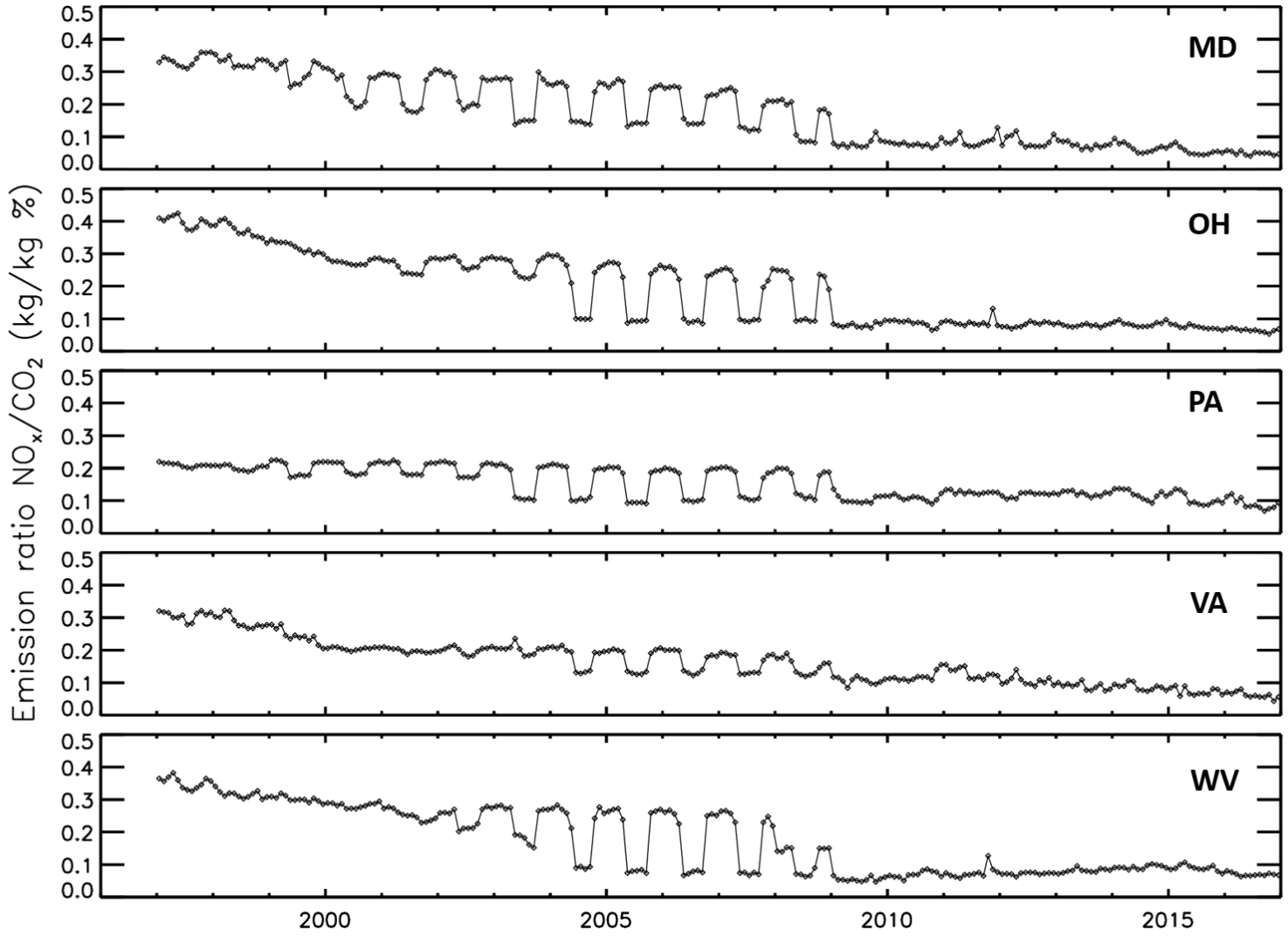
Trends in power plant emission, region



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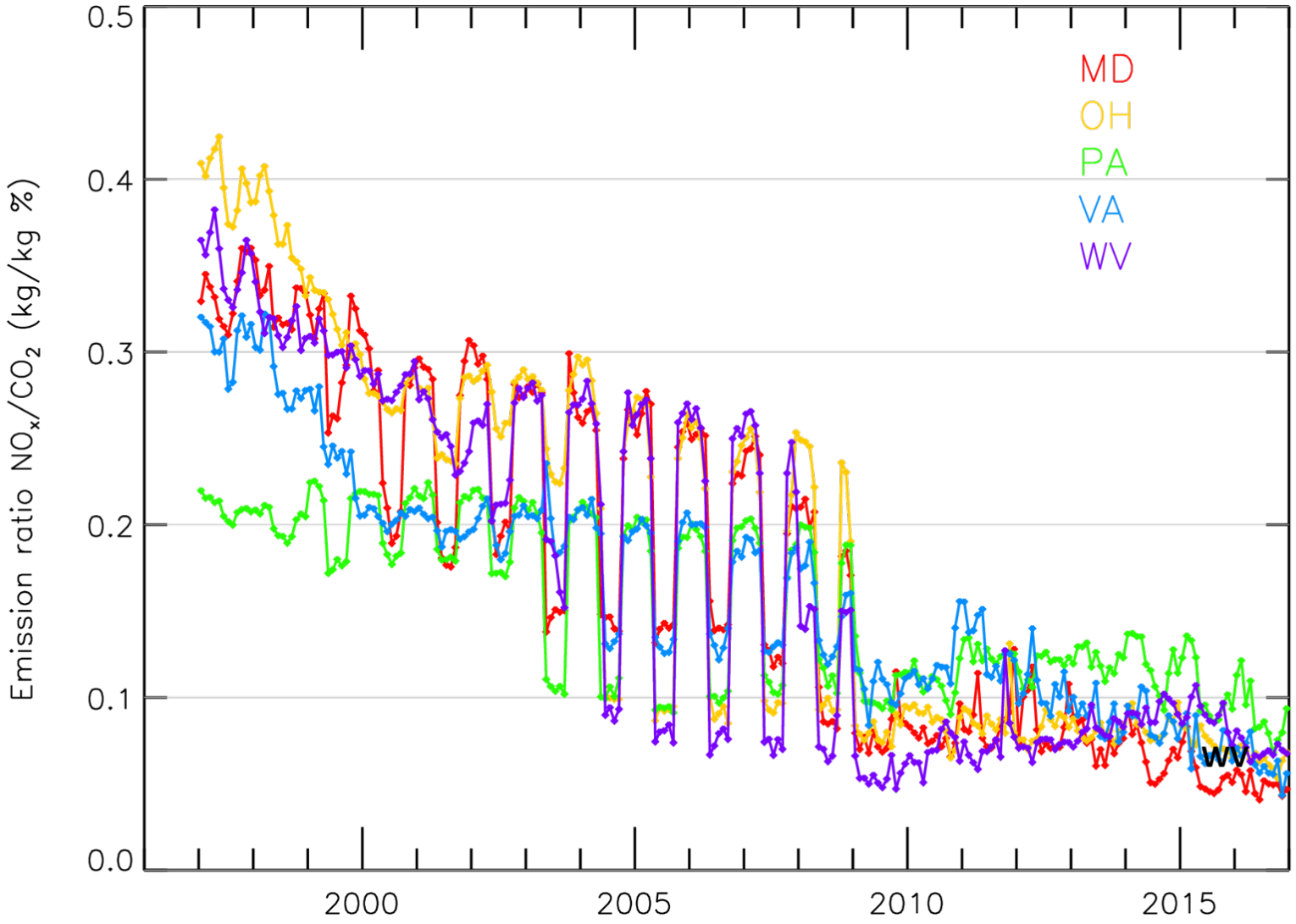
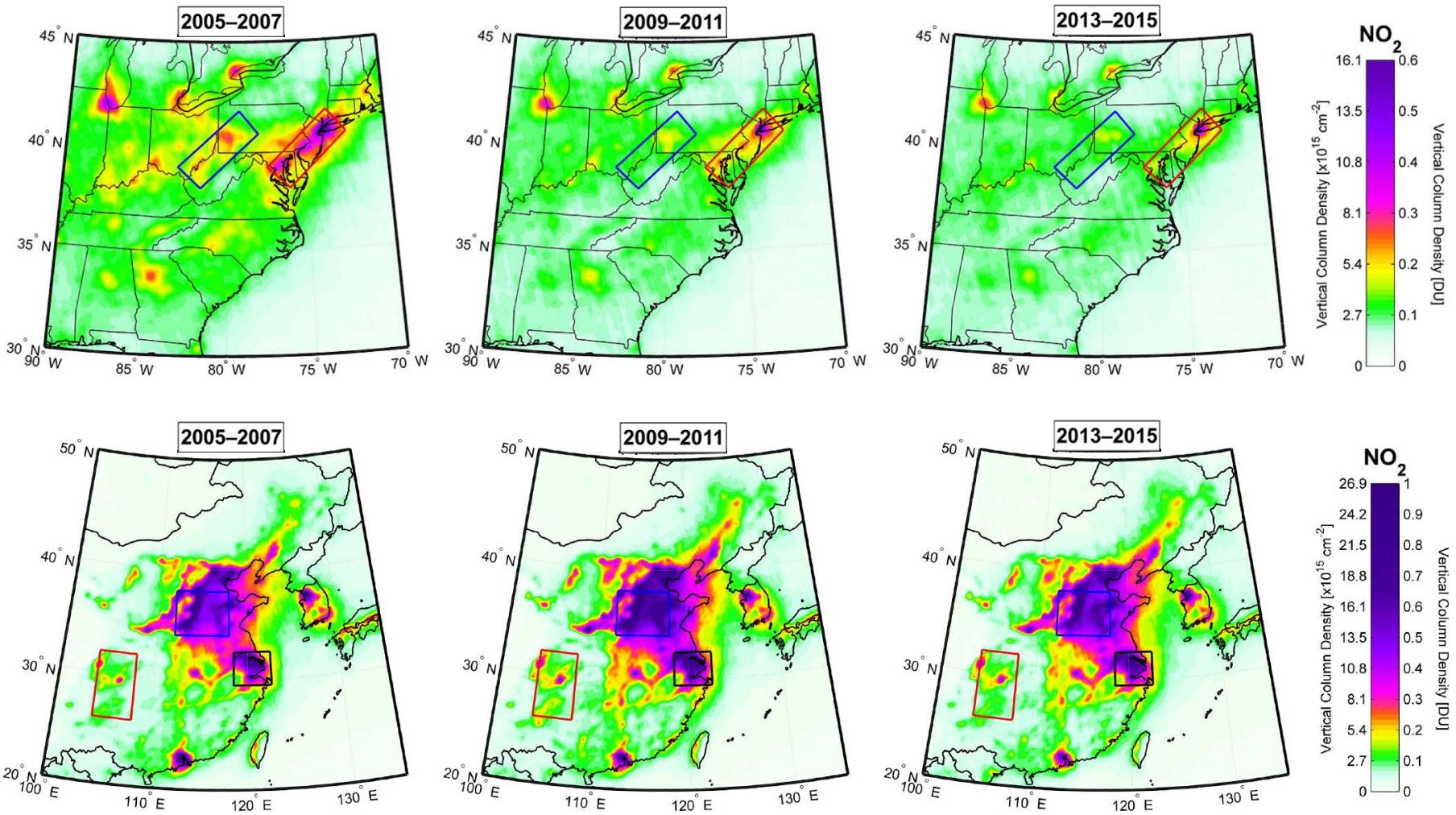


Thanks to Doyeon Ahn for this wonderful analysis of CEMS (Continuous Emission Monitoring System) Data provided by EPA

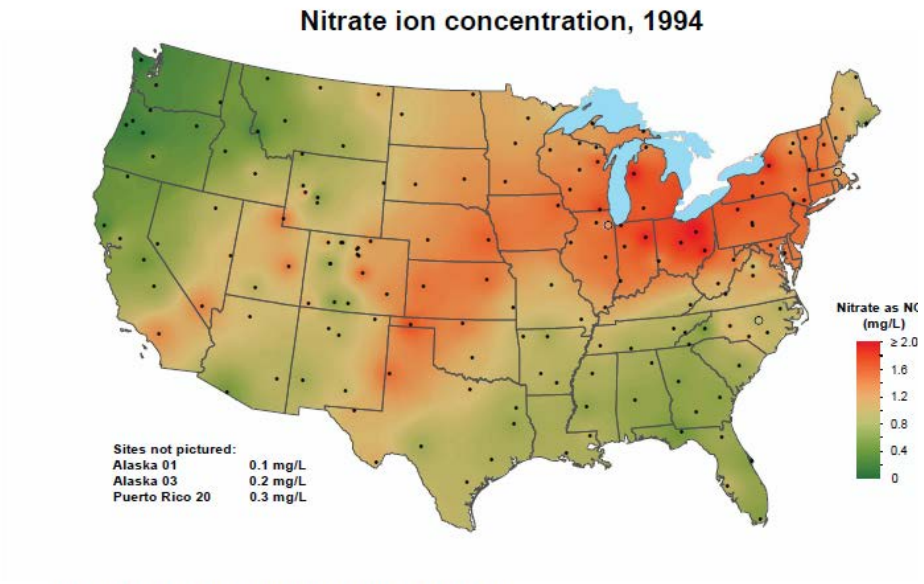
NO_2 Trends from Space



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

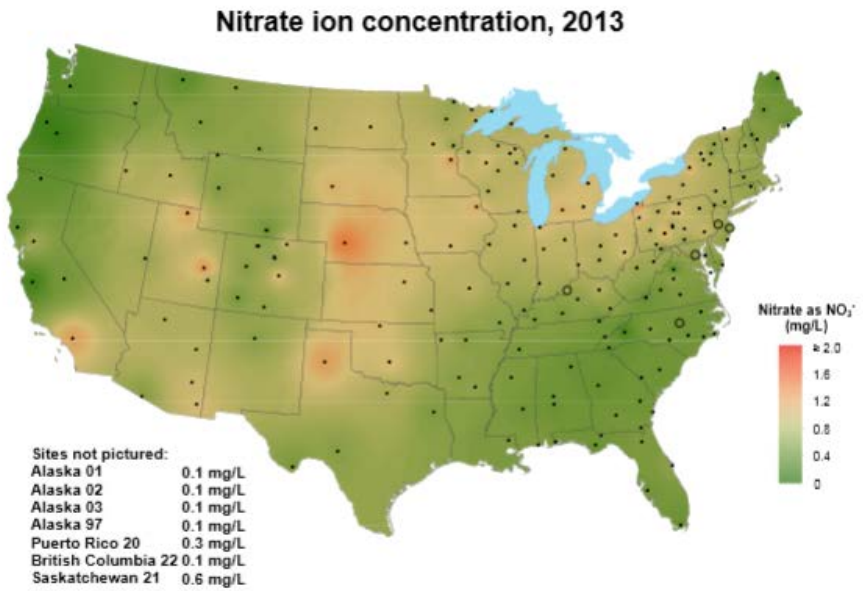
Nitrate Deposition

1994



National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

2013



National Atmospheric Deposition Program/National Trends Network
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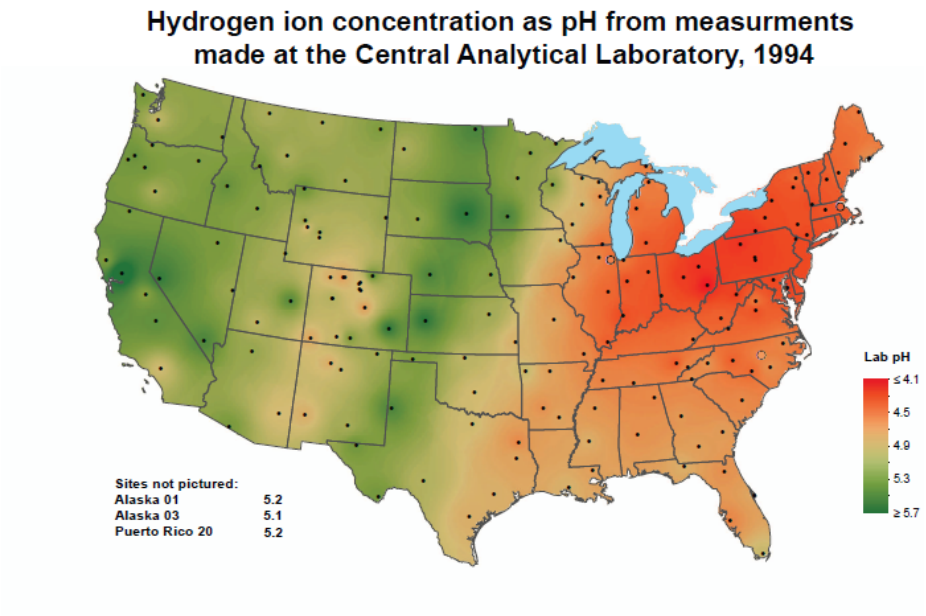
http://nadp.sws.uiuc.edu/

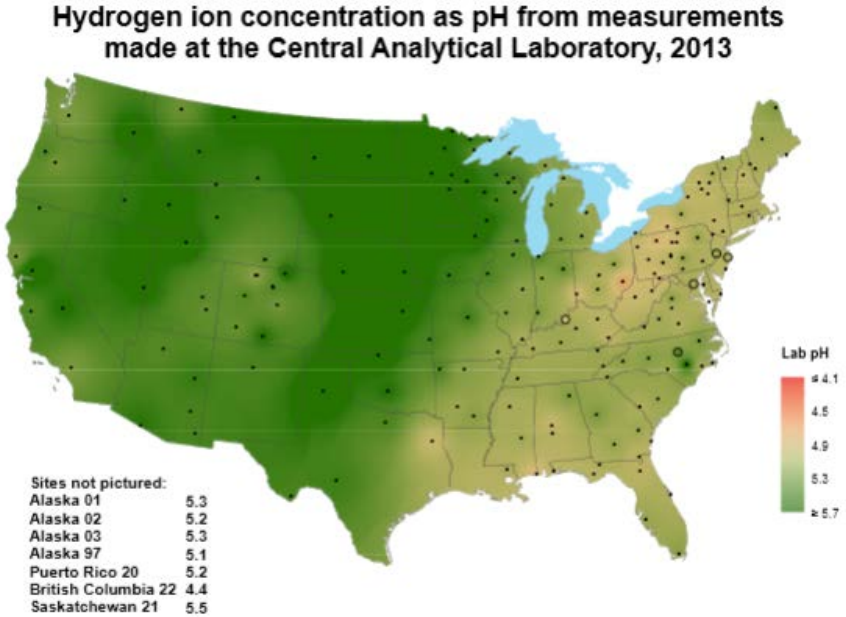
pH

1994



National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

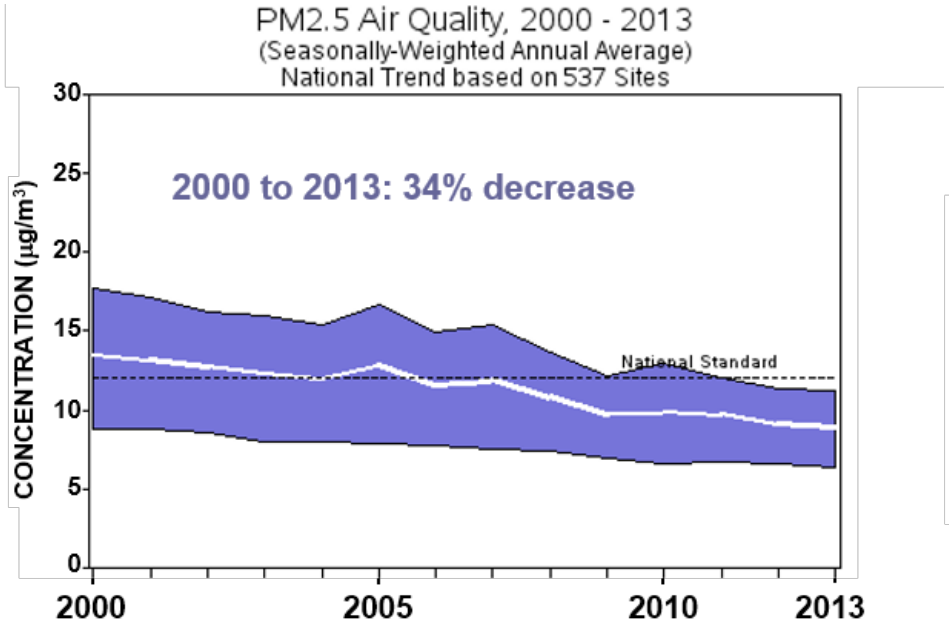
2013

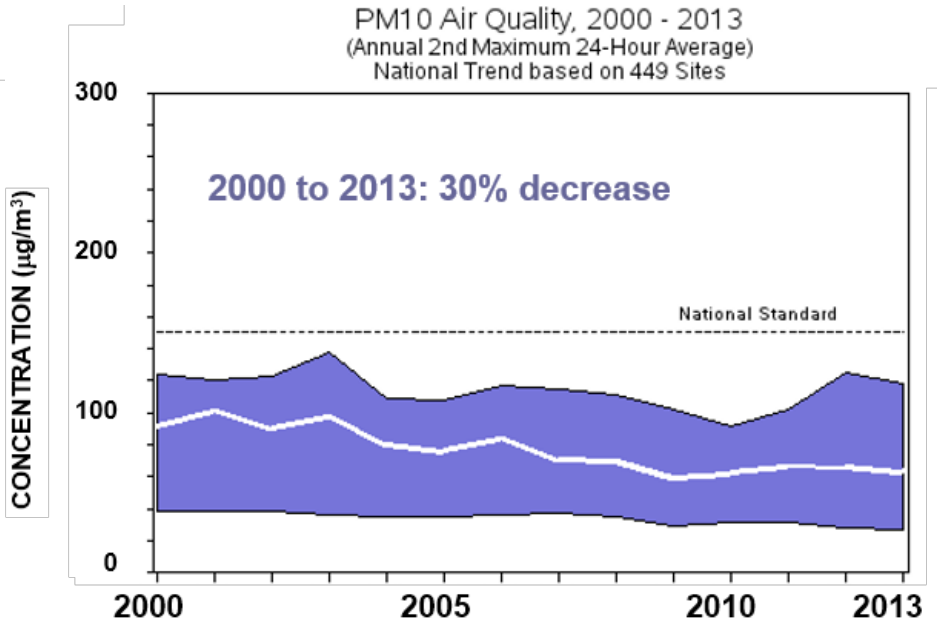


National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

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

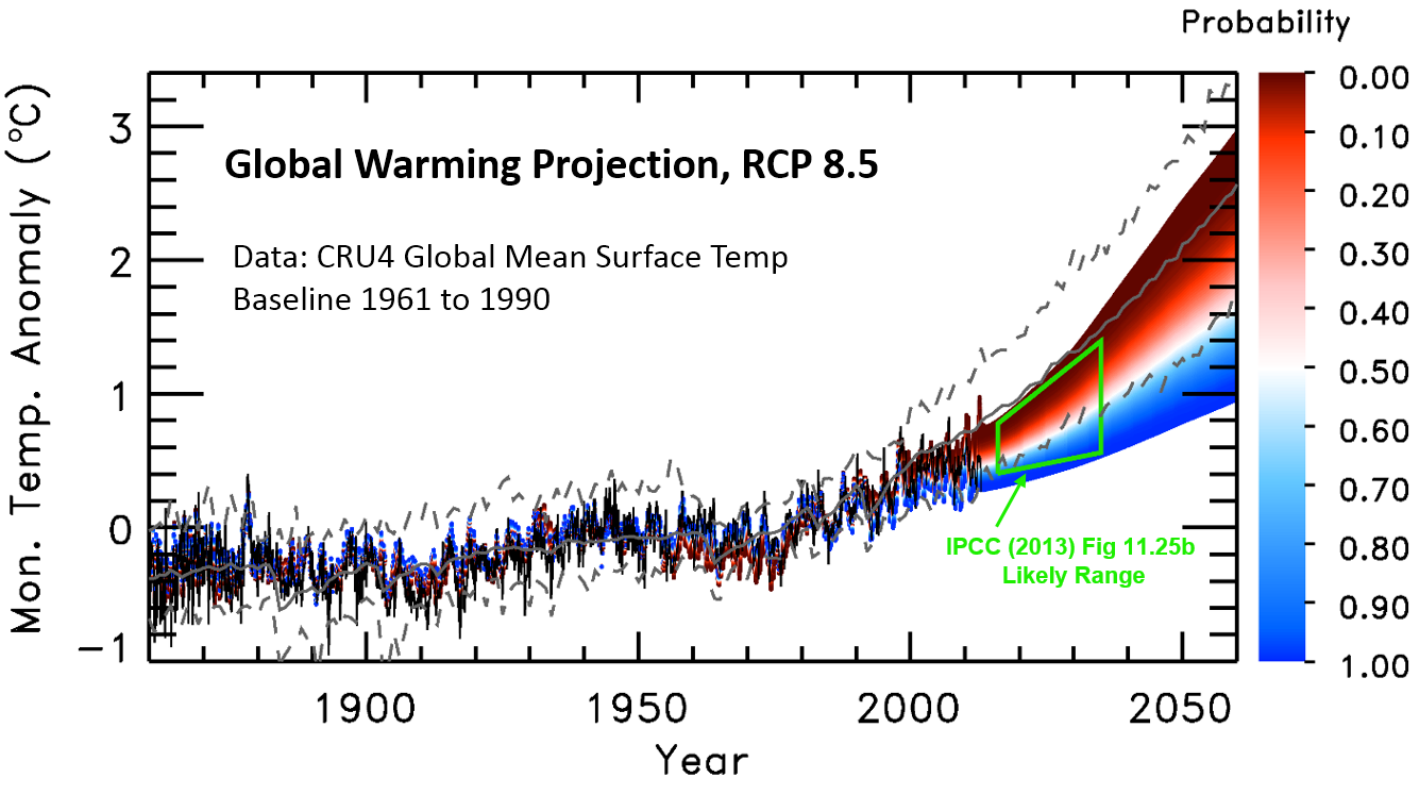
PM Trends





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

Uncertainty of Aerosol RF Effects Future Climate



If tropospheric aerosols have offset a large fraction 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 tiny fraction of GHG induced warming, then the actual warming that may occur could be considerably *smaller* than "best estimate"