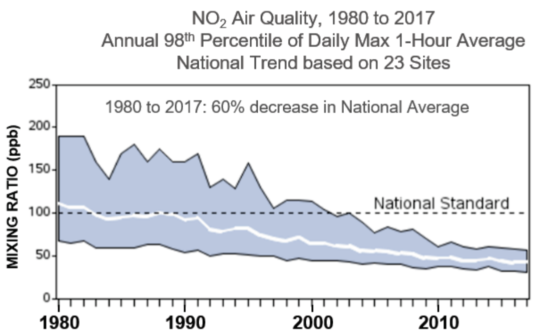
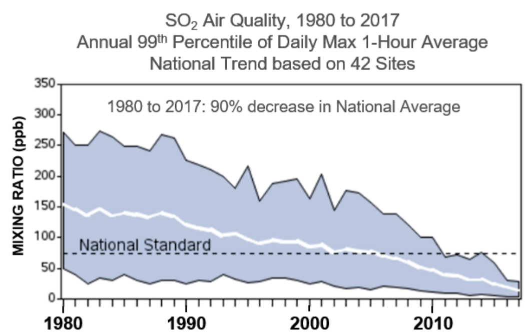
Pollution of Earth's Troposphere: Acid Rain & Aerosols
AOSC/ CHEM 433 & AOSC 633

Ross Salawitch & Walt Tribett

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





Lecture 13
28 March 2019

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:

$$H_2SO_4\,(aq) \rightarrow 2\,H^+ + HSO_4^{2-}$$

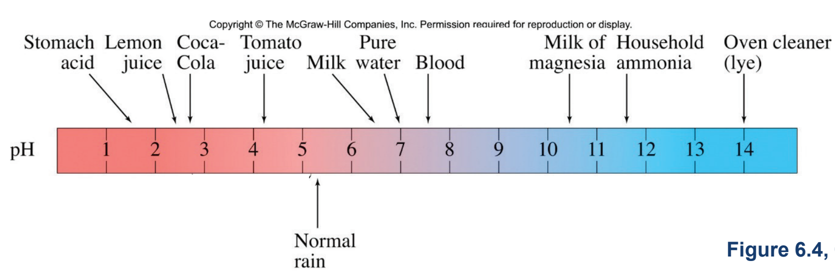


Figure 6.4, Chemistry in Context.

Acid Fog

The Role of Ground-based Pollutants

Based on these findings, Hoffmann and his students speculate that the preexisting smog aerosol forms the seed for the formation of acid fog. Furthermore, SO_2 and NO_x are converted to sulfuric and nitric acids within the fog droplets.

Their hypothesis explains the greater acidity of fog as compared to cloud and rain water, for fog forms close to the ground where concentrations of pollutants are higher than they are further aloft. To document this concentration gradient, the research team simultaneously sampled fog and cloud water at the same site. At ground level, fog was pH 2.8. At the top of the cloud bank, 600 meters up, the pH was 3.6.

Further sampling around the state supports the hypothesis that acid fog is related to ground-based pollution sources, particularly power plant and automobile emissions. In Bakersfield, near an oil recovery plant, the researchers measured fog with a pH of 2.9. In Upland, east of Los Angeles and in the direct line of the wind trajectory away from the city, they found their lowest reading to date: pH 2. In nearby Fontana, the site of a steel mill, they measured cloud water with a pH 2.5. Not even San Francisco's celebrated fogs escaped; they routinely were pH 3.5 to 4.

Bioscience,1982

https://academic.oup.com/bioscience/article-pdf/32/10/778/636513/32-10-778.pdf

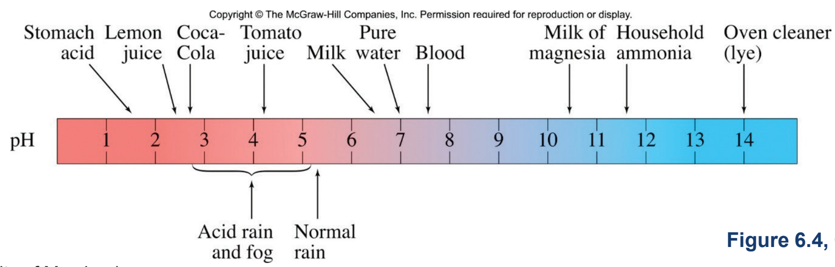
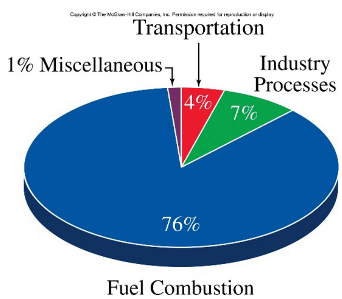


Figure 6.4, Chemistry in Context.

SO_2 Sources (U.S.)



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.
U.S. SO_2 emission sources, year 2007

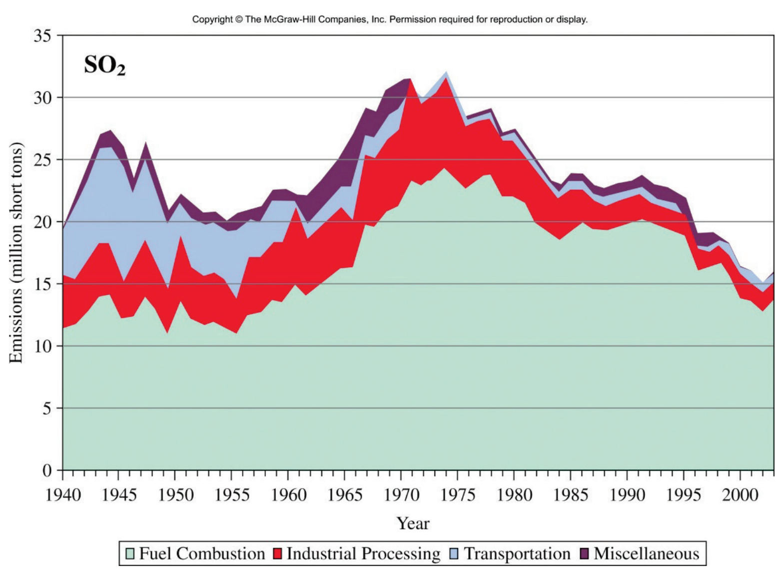
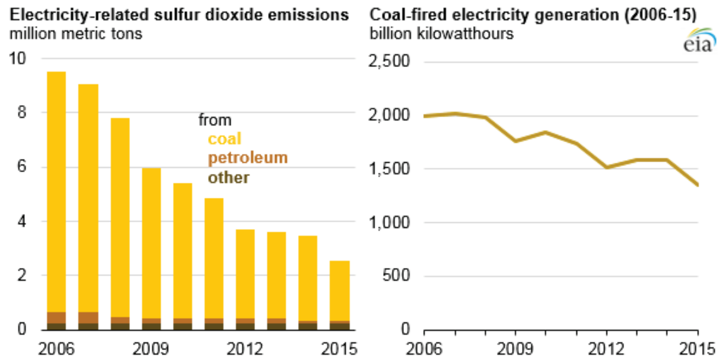


Figure 6.21, Chemistry in Context.
U.S. SO_2 emissions, 1940 to 2003

SO_2 Sources (U.S.)



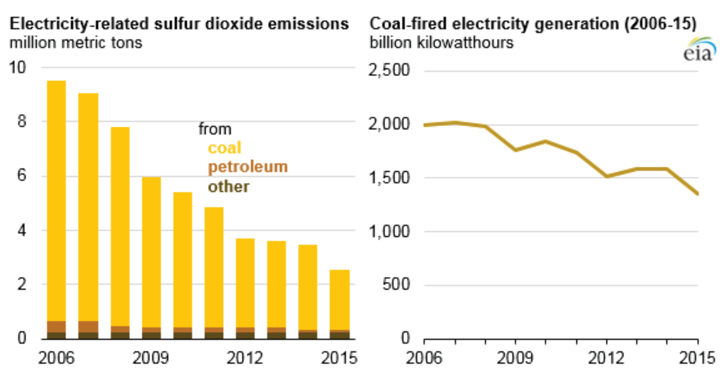
SO_2 emissions from U.S. power plants in the United States declined by 73% from 2006 to 2015, a much larger reduction than the 32% decrease in coal-fired electricity generation over that period.

From 2014 to 2015, SO_2 emissions fell 26%—the largest annual percentage drop in the previous decade.

Nearly all electricity-related SO_2 emissions are associated with coal-fired generation.

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

SO_2 Sources (U.S.)



Factors that have contributed to lower SO_2 emissions:

1) Changes in the electricity generation mix.

Electricity generation from coal fell 14% from 2014 to 2015; mostly offset by an increase in electricity generation from natural gas.

2) Installation of environmental equipment.

To comply with the federal Mercury and Air Toxics (MATS) rule, coal plants had to install pollution control equipment. Plants had to comply by April 15, 2015, or for some plants that received one-year extensions, by April 15, 2016. Two types of pollution control technologies installed for compliance that also reduce SO_2 emissions are dry sorbet injection systems (DSI) and flue gas desulfurization (FGDS) systems. Between December 2014 and April 2016, DSI systems were installed on 15 gigawatts of coal capacity and FGDS scrubbers were installed on 12 GW of coal capacity.

3) Lower utilization of the most-polluting plants.

Coal-fired plants produce SO_2 at different rates. Plants that produce more than two metric tons of SO_2 per million kilowatthours of electricity generation were used less often in 2015.

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:

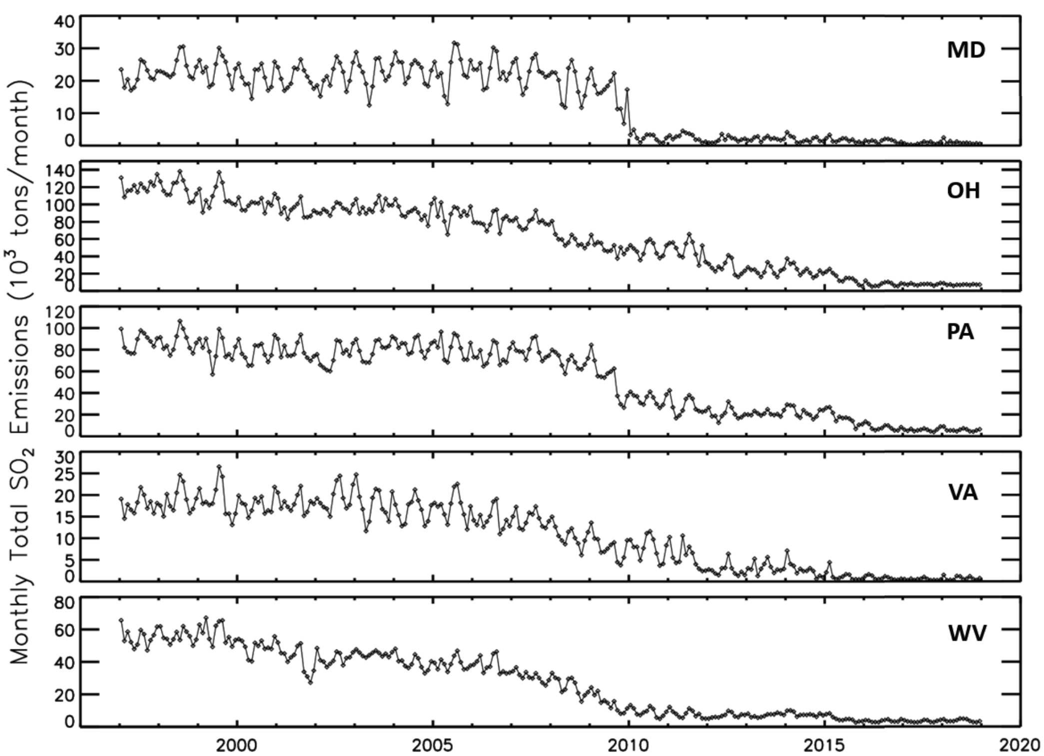
$$CaCO_3 + SO_2 + 2H_2O \rightarrow CaSO_3 \cdot H_2O + CO_2$$

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

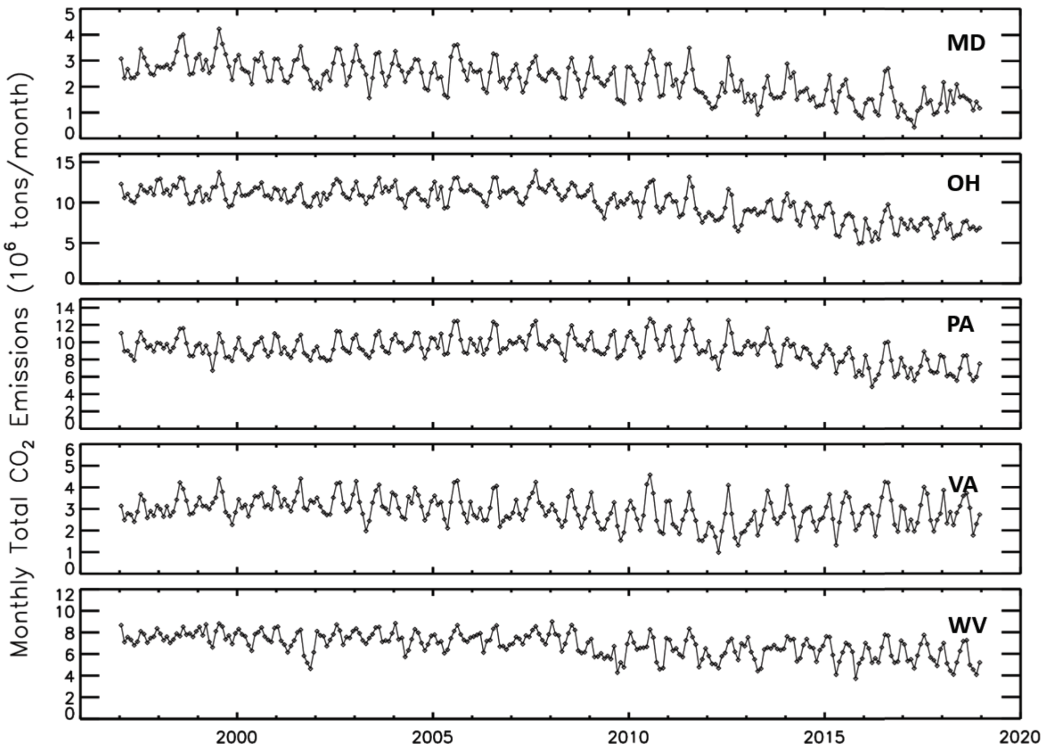
What happens to the $CaSO_3 \cdot H_2O$?

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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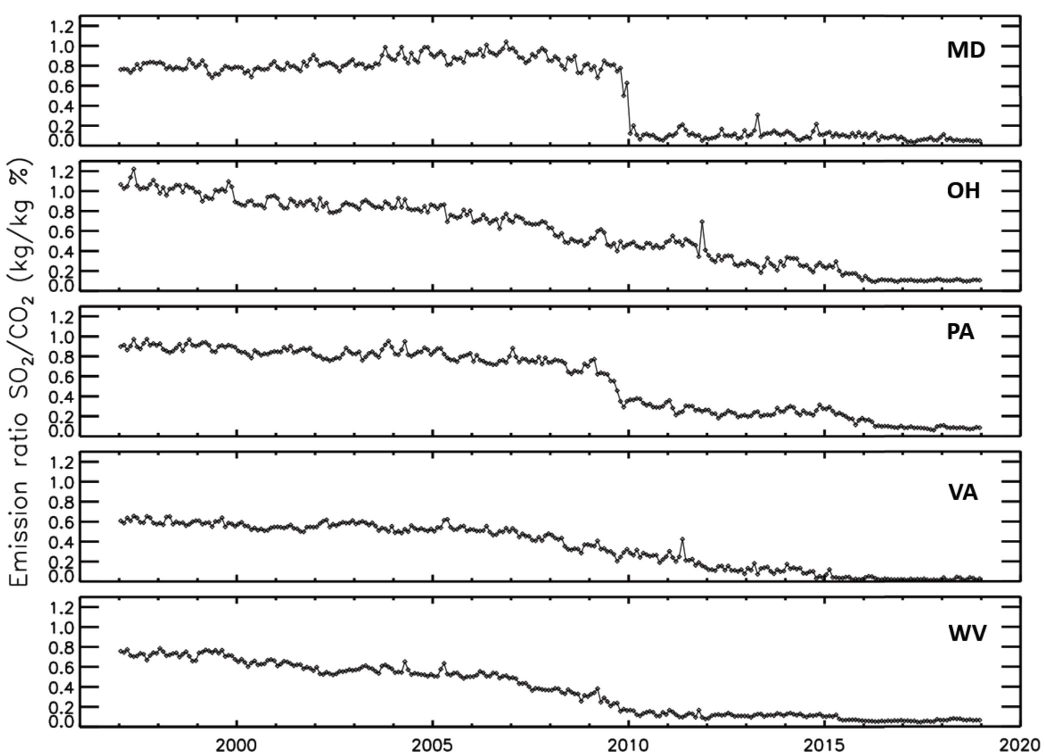
Trends in power plant emission, region



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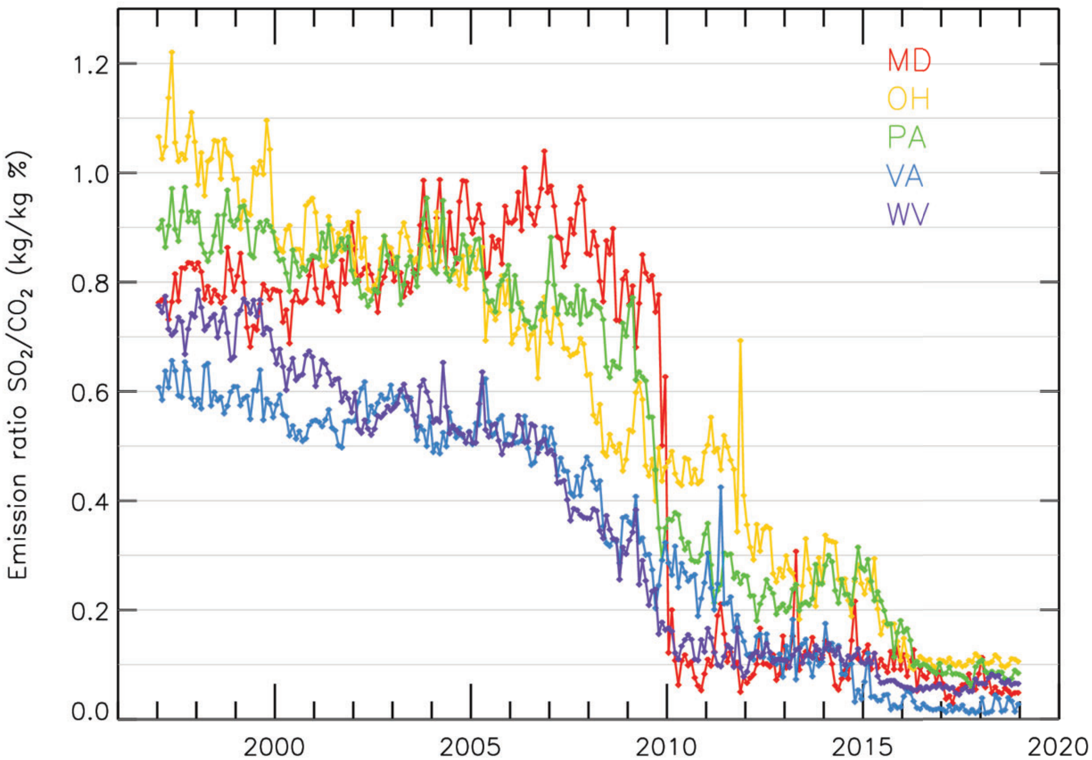
Trends in power plant emission, region



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Maryland Healthy Air Act

The Maryland Healthy Air Act 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 (**NO_x**), sulfur dioxide (**SO_2**), 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.

Which pollutants are covered by this rule and how much pollution will be reduced?

The Healthy Air Act requires year-round emission controls that will significantly reduce nitrogen oxides (**NO_x**), sulfur dioxide (**SO_2**), and **mercury** from power plants located in Maryland. NO_x emissions in Maryland will be reduced almost 70% in 2009. A second phase of NO_x control will reduce emissions by a total of 75% by 2012. SO_2 emissions will be reduced by 80% in 2010 with a second phase of controls in 2013, which will increase the emission reduction to 85%. When the rule is adopted, mercury emissions will be reduced by 80% in 2010. A second phase of controls will reduce mercury emissions by 90% by 2013. All of the above emission reductions are based on a comparison to a 2002 emissions baseline.

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

Maryland Department of the Environment
Air Quality Control Advisory Council

History, Charge and Term

The Air Quality Control Advisory Council (AQCAC) was established pursuant to the Annotated Code of Maryland, § 2-201 et seq. in 1967. The duties of the Council include:

- Reviewing and advising the Department on draft air quality rules and regulations which are being considered for adoption in order to achieve air quality and public health goals and protect the environment, and
- Evaluating, as requested by the Department, state-level measures to meet air quality standards, legislation proposed by the General Assembly or the Department and strategic plans created by the Department's Air and Radiation Management Administration.

AQCAC gives the Department its advice on proposals by recommending adoption, rejection or modification of the draft regulations or other matters brought before it.

The Council consists of 15 members appointed by the Secretary of the Department. Members include representatives from industry, labor, professional associations, local and regional government organizations, academia, farming, the medical community and the general public.

Member terms are for 5 years. At the end of term, a member continues to serve until a successor is appointed and qualifies. A member appointed after a term has begun serves only for the rest of the term and until a successor is appointed and qualifies.

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

Sulfate Deposition

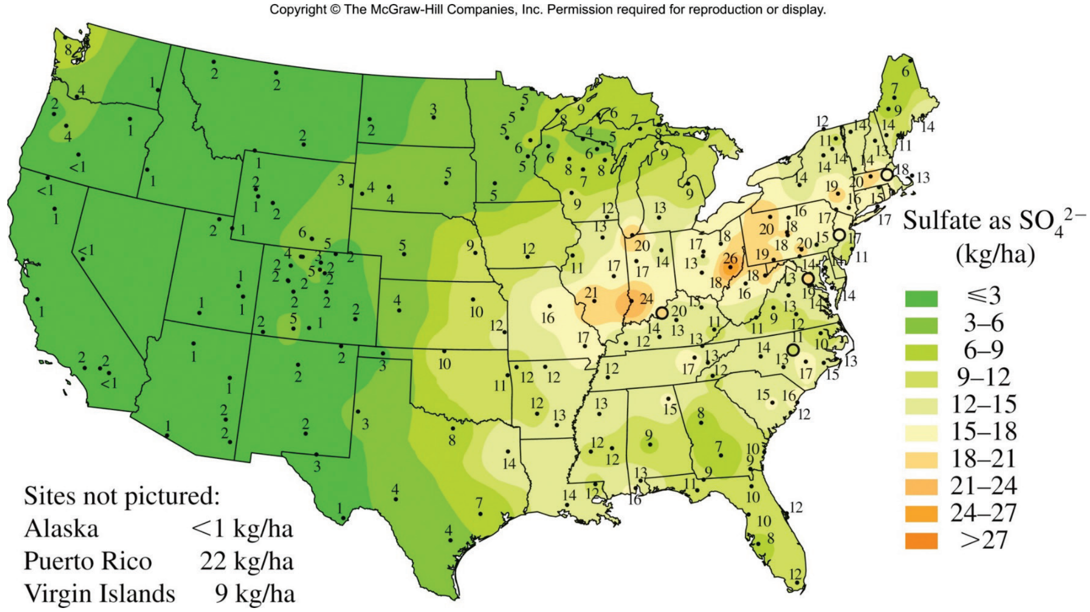
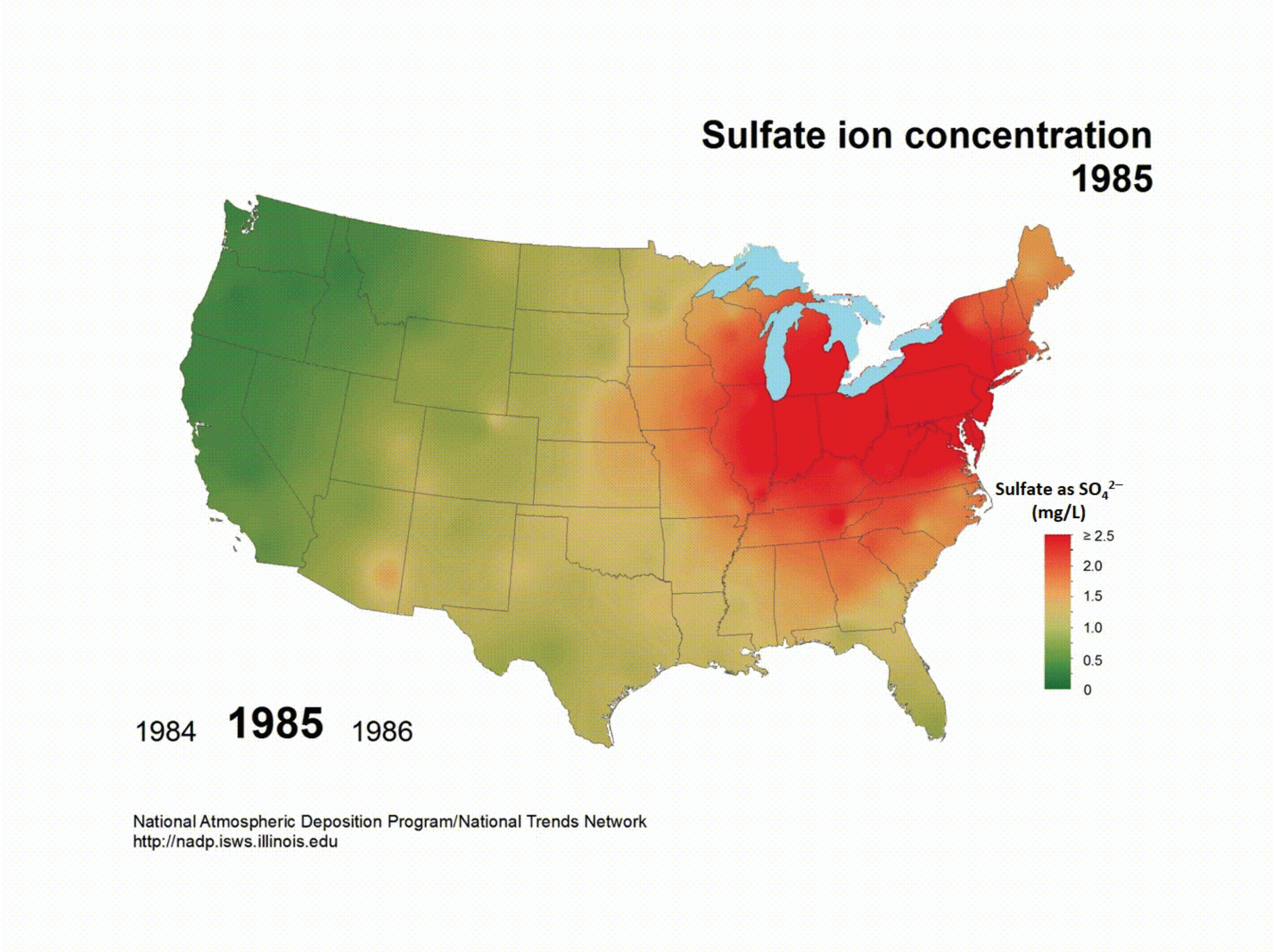


Figure 6.12, Chemistry in Context.
Wet deposition of sulfate ion, year 2008



SO_2 From Space (U.S.)

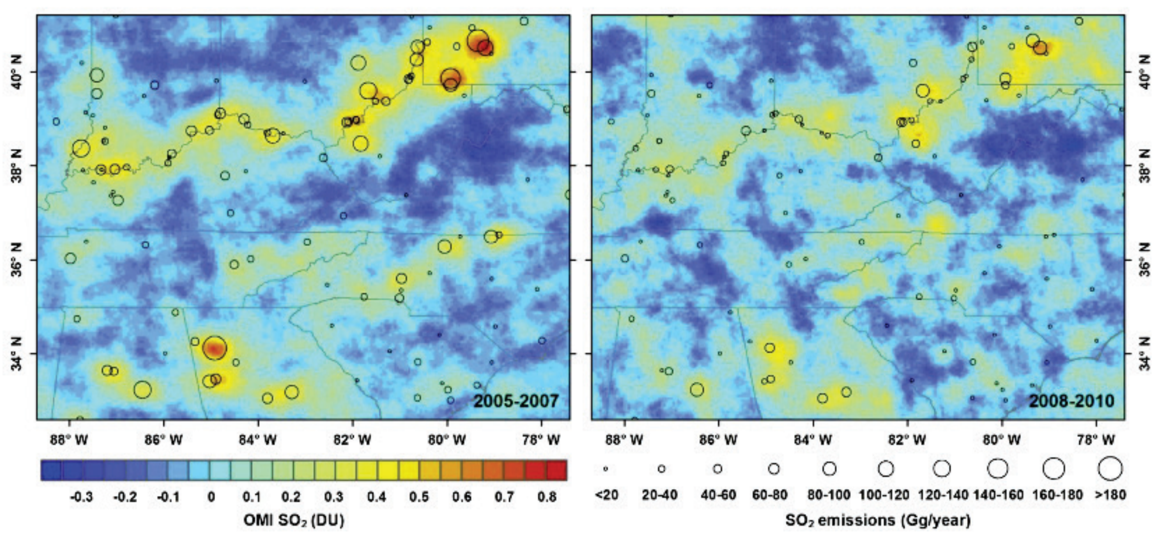
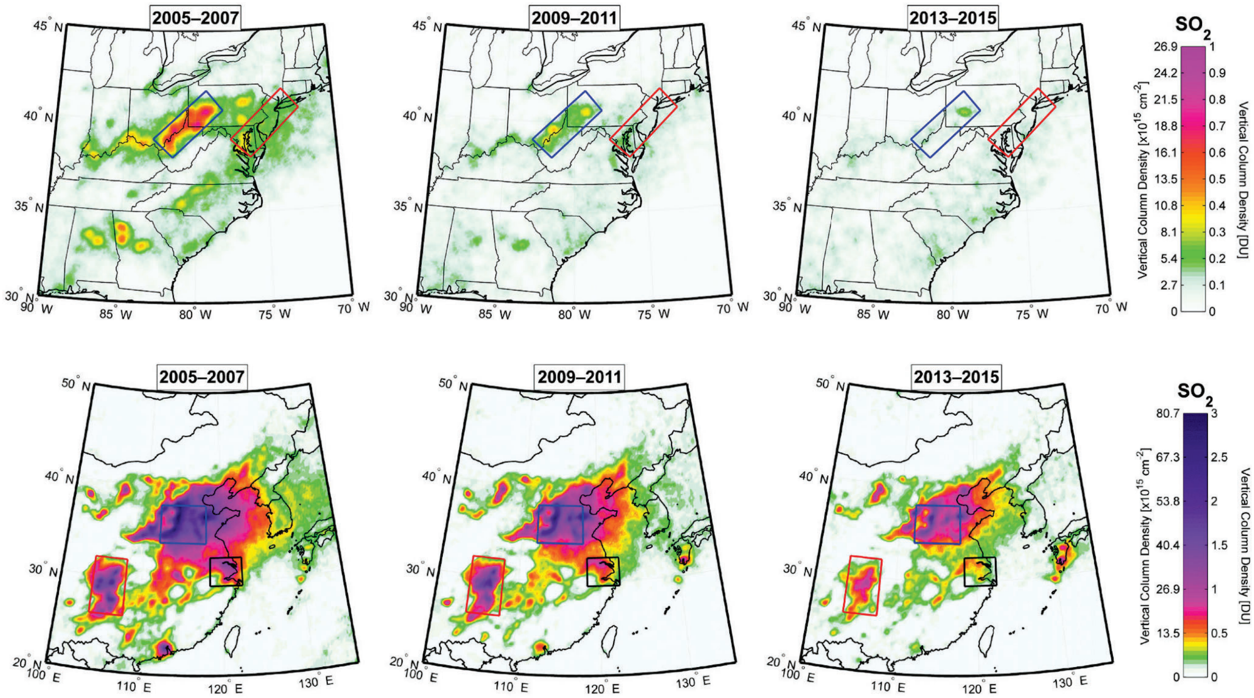


Fig. 4. Mean SO_2 burdens over the Ohio River Basin for 2005–2007 (left) and 2008–2010 (right) measured by OMI, confirming a substantial reduction in SO_2 pollution around the largest coal-fired power plants, as a result of the implementation of SO_2 emission control measures (adapted from NASA Earth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

Streets *et al.*, *Atmos. Envir.*, 2013

SO_2 Trends from Space



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

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!

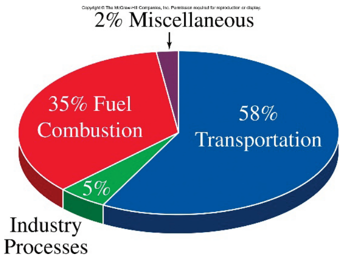
Hence, in the presence of liquid water, HNO_3 (g), can become HNO_3 (aq)

HNO_3 (aq) will then dissociate:

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

and well “oops, we did it again”

NO_x Sources (U.S.)



Primary source of NO_2 is transportation.

The EPA inventory suggests emissions from this sector are holding steady. However, UMd researchers believe mobile NO_x emission in the mid-Atlantic are much lower than estimated by EPA (Anderson *et al*., Atmos. Envir., 2014)

Figure 6.16, Chemistry in Context.
U.S. NO_x emission sources, year 2007

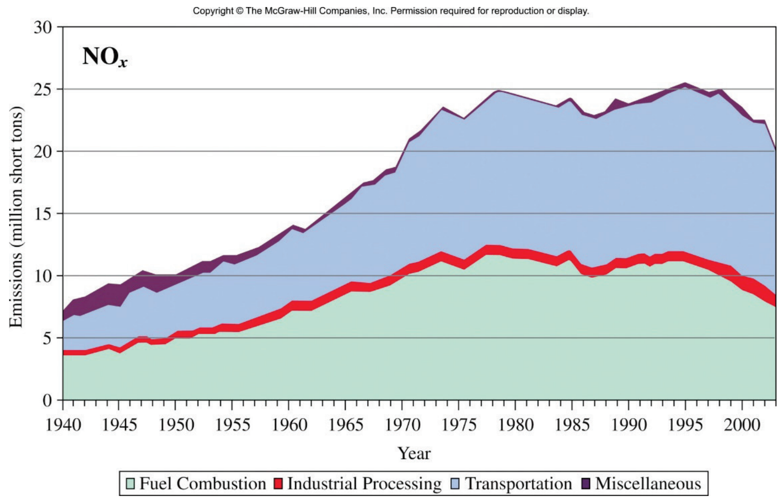
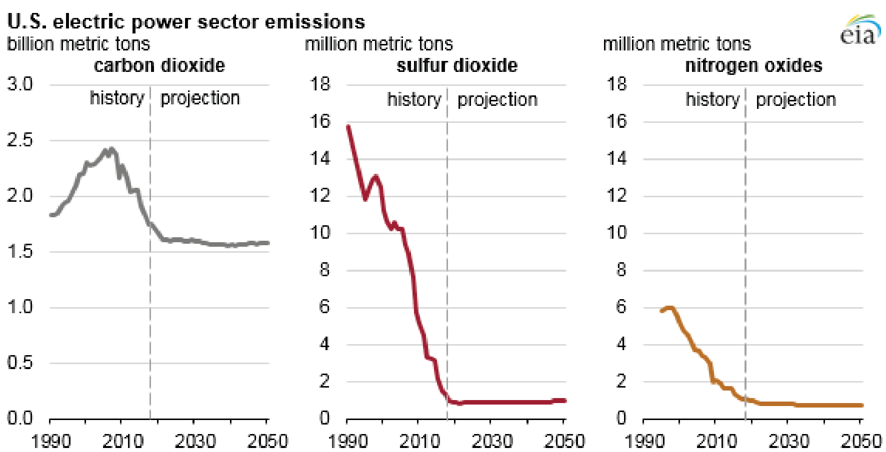


Figure 6.21, Chemistry in Context.
U.S. NO_x emission sources, 1940 to 2003.

NO_x Sources (U.S.)



EIA Annual Energy Outlook 2019 projects U.S. electric power sector emissions of **SO_2**, **NO_x** and **CO_2** will remain mostly flat through 2050 ***assuming no changes to current laws and regulations***.

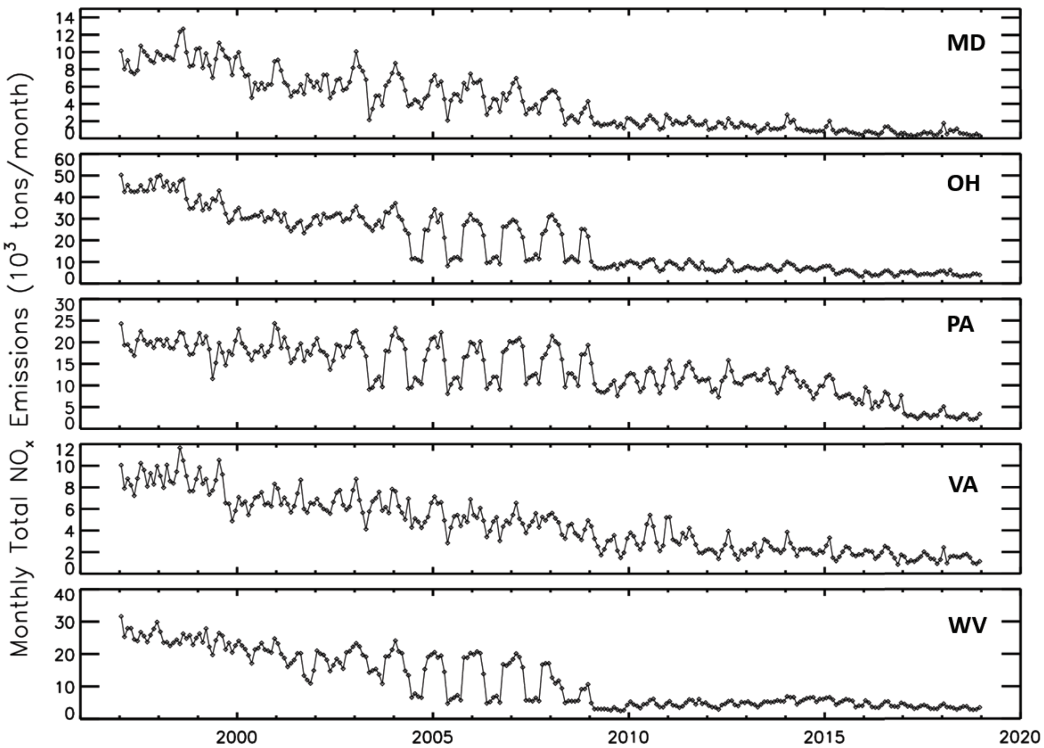
SO_2 and **NO_x** emissions from the electric power sector have declined over the past several decades, largely because of the phased implementation of regulations under the Clean Air Act Amendments of 1990. For SO_2, these regulations include acid rain cap-and-trade program deadlines in 1995 and 2000. One of the main regulations affecting NO_x emissions was the 2003 expansion of the Environmental Protection Agency's (EPA) NO_x Budget Trading Program (Title I) to include most states east of the Mississippi River.

In addition, the EPA's *Mercury* and Air Toxics Standards (MATS), announced in 2011 and implemented in 2015, required power generators to comply with emissions limits for toxic air pollutants that … also decreased emissions of **SO_2** and **NO_x**.

These programs did not directly target emissions of **CO_2** but they did affect the economics of power plant operation cost as well as retirement decisions. Emissions of CO_2 in the U.S. power sector have been declining since a peak in 2007.

https://www.eia.gov/todayinenergy/detail.php?id=38293

Trends in power plant emission, region



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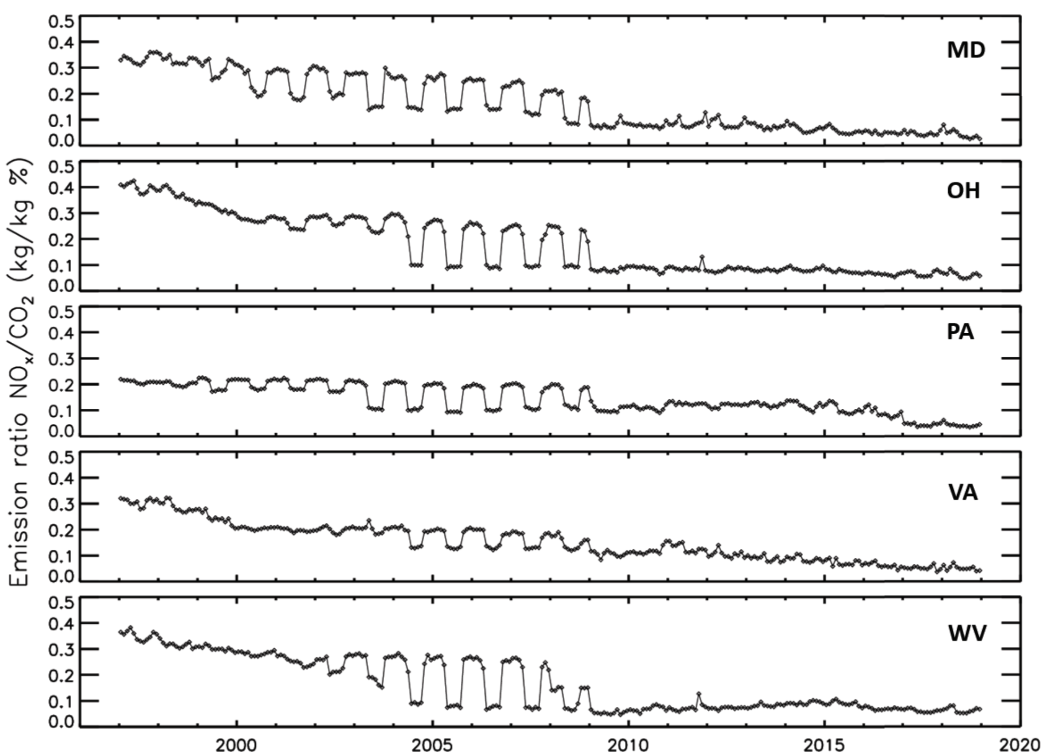
Trends in power plant emission, region



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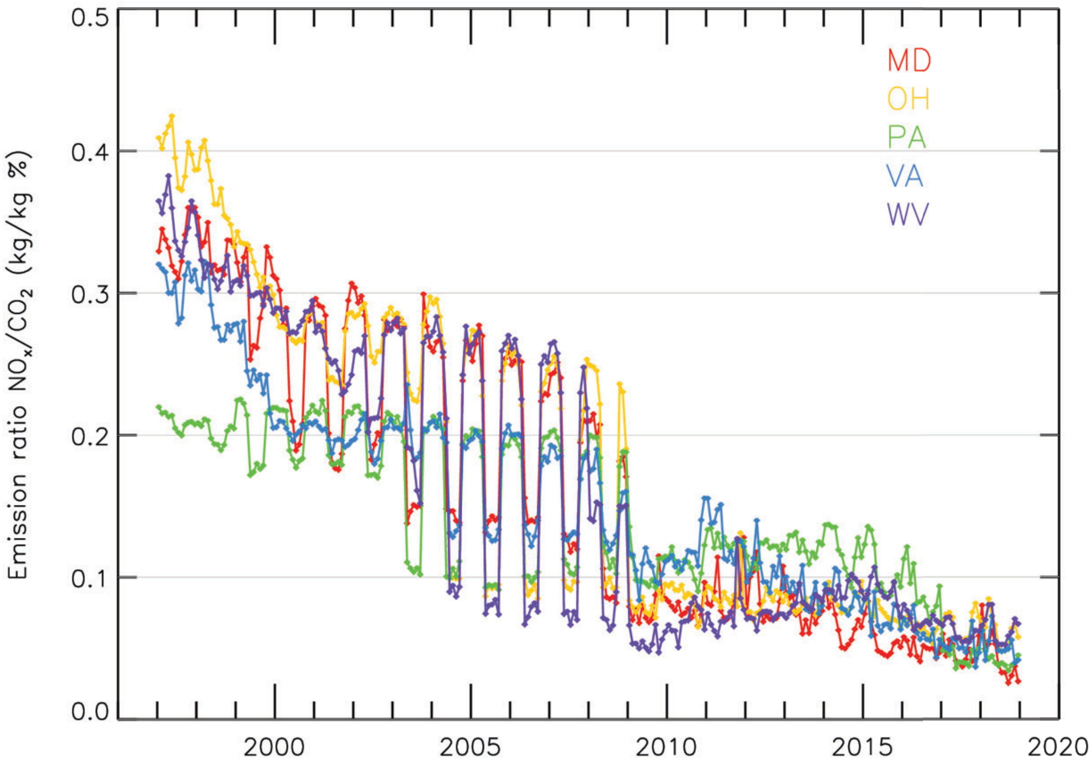
Trends in power plant emission, region



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Nitrate Deposition

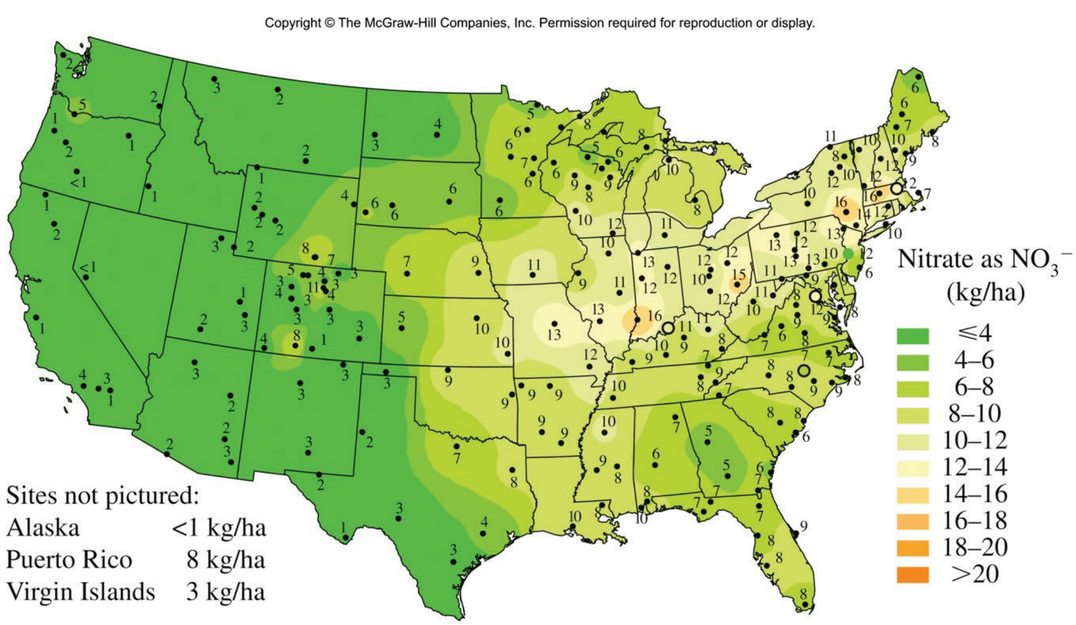
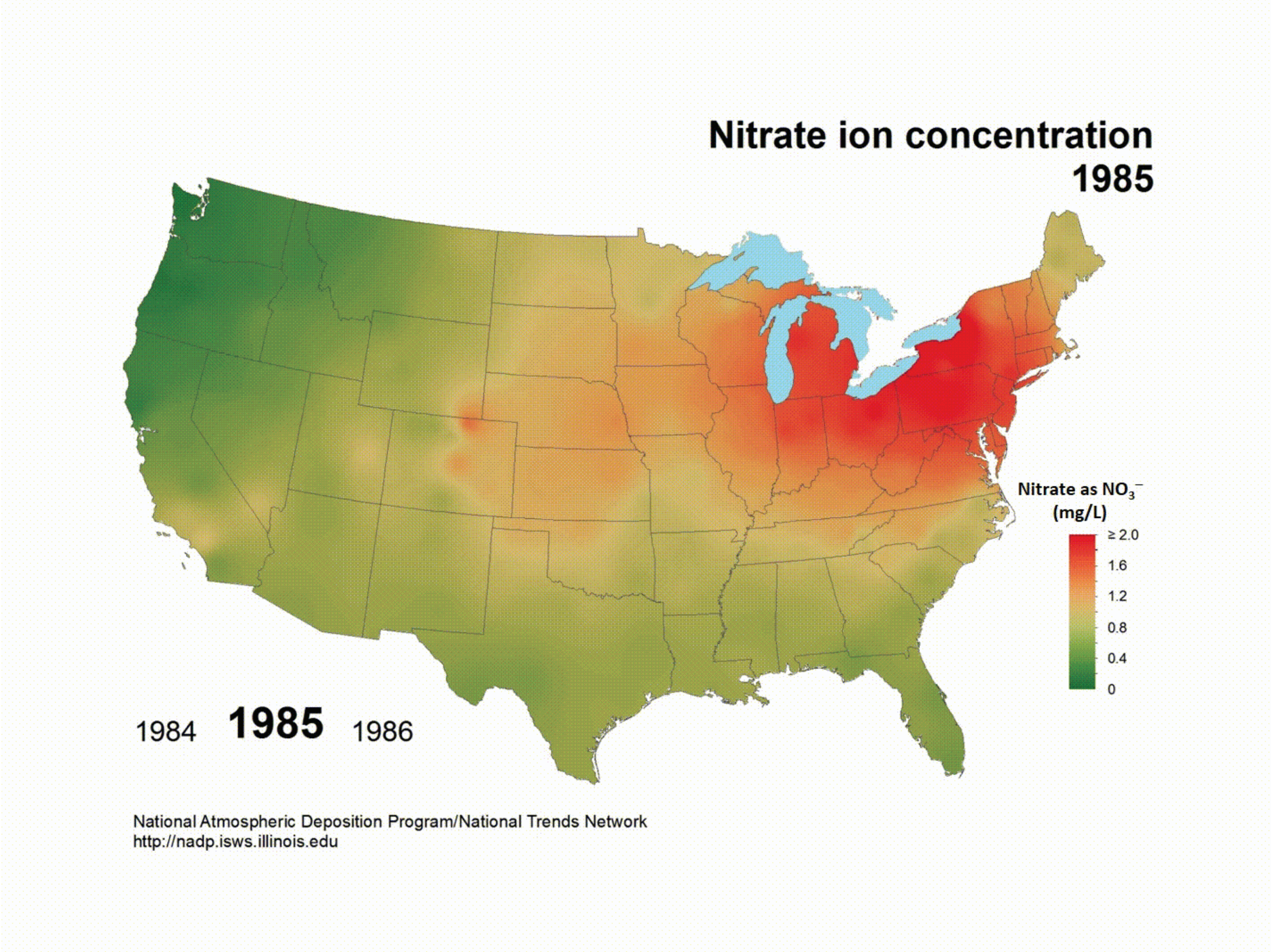


Figure 6.12, Chemistry in Context.
Wet deposition of nitrate ion, year 2008



power of Hydrogen

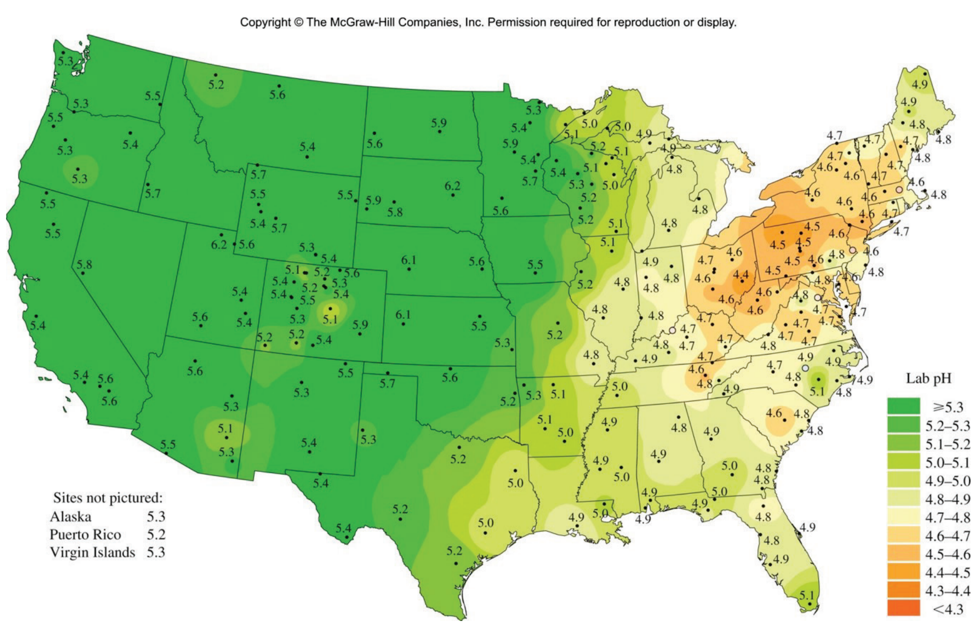
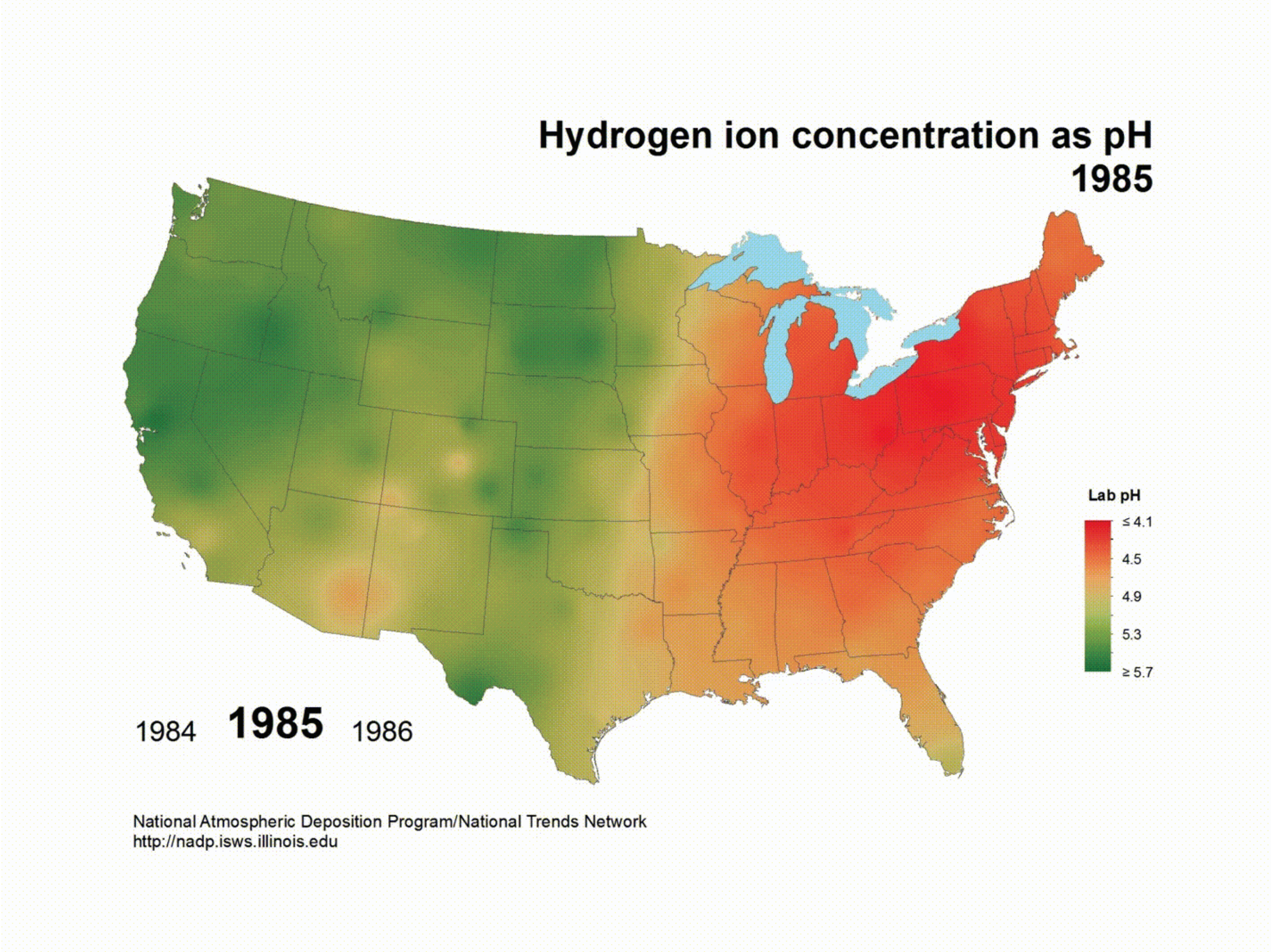


Figure 6.12, Chemistry in Context.
Wet deposition of nitrate ion, year 2008



Cultural Degradation

In 1944 At present

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

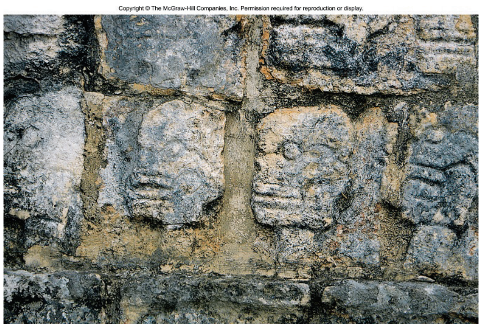


Figure 6.24, Chemistry in Context.
Mayan art, Mexico.

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

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

HCO_3^- (aq) + H^+ (aq) → H_2CO_3 (aq) → CO_2 (g) + H_2O (l)

or:

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

Cultural Degradation

$25 million dollar restoration of the Lincoln Memorial began in 2016

Will repair cracks in marble due to 2011 earthquake, install a new roof, and also patch a "baseball-size gouge of the penthouse's ornate outer wall caused by an errant antiaircraft bullet in 1942". During World War II, a gun was set up near a local bridge to defend D.C. against air attack. A soldier accidentally pulled the trigger, hitting the memorial's east side.

Work should be completed by 2022, in time for the memorial's centennial.

https://bangordailynews.com/2018/06/14/news/nation/battered-by-time-nature-and-antiaircraft-fire-lincoln-memorial-gets-facelift
https://www.youtube.com/watch?v=pBo2PSF2Pvg

Lake Acidification

Do all lakes respond to atmospheric transport of acidic substances in the same manner?

If so, what remarkable chemical process results in this property?

If not, where are the lakes that are least sensitive to the effects of acid rain located, and what is the process that allows these lakes to be less susceptible?

Recent SO_2 (left) and NO_2 (right) Trends from Space

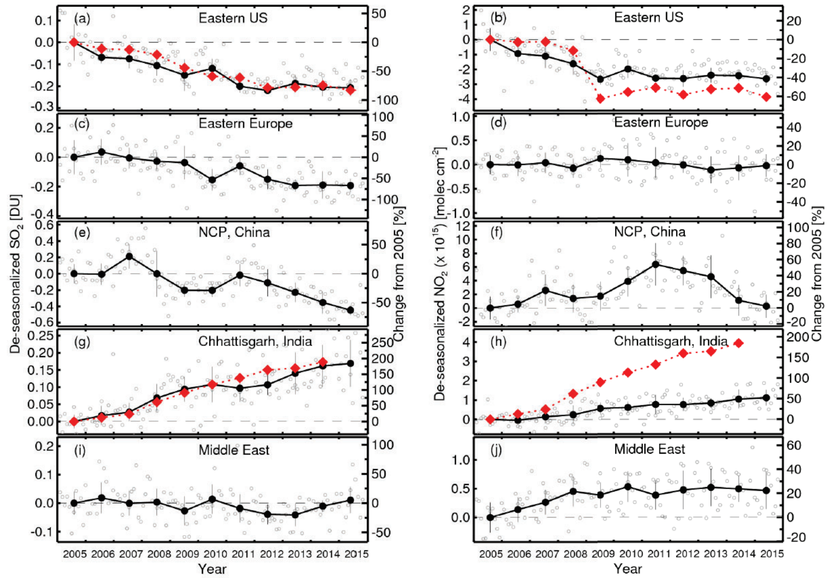
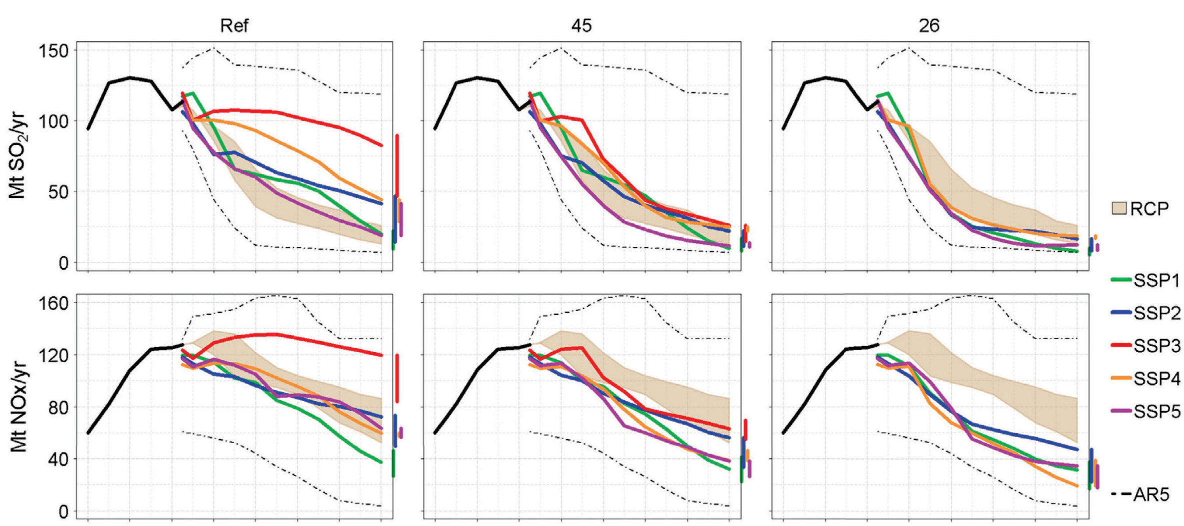


Figure 3. Relative changes (compared to 2005) in OMI PBL SO_2 columns (left) and tropospheric NO_2 columns (right) over the world's five most polluted regions: **(a)** and **(b)**: Ohio River valley and southwestern Pennsylvania (ORV) in the eastern US (ORV – blue box in Fig. 2); **(c)** and **(d)**: the Maritsa Iztok power plants in Bulgaria (blue box in Fig. 4); **(e)** and **(f)**: North China Plain (NCP – blue box in Fig. 5); **(g)** and **(h)**: NE India (blue box in Fig. 6); **(i)** and **(j)**: the Persian Gulf (blue box in Fig. 7). Gray circles show de-seasonalized monthly columns (see details in Appendix B). Black filled circles show annual means. Vertical bars show standard deviations. Red diamonds show bottom-up emission estimates for power plants in ORV and from coal-fired power plants in NE India (Chhattisgarh and Odisha region – blue box in Fig. 6).

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

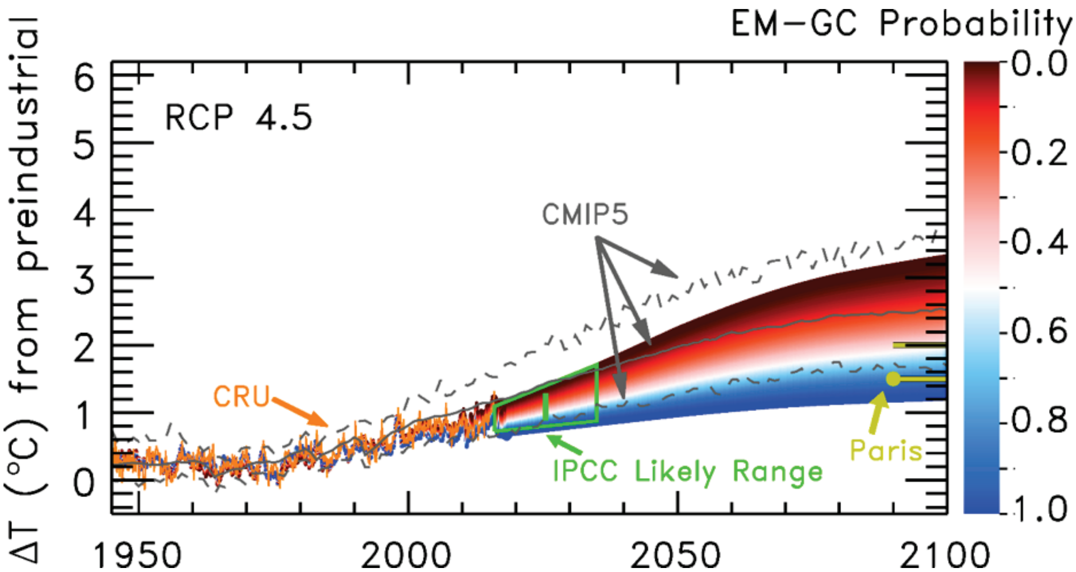
Future SO_2 (left) and NO_2 (right) Trends



Emissions of SO_2, NO_x in SSP baseline (Ref) and 4.5 (labeled as 45) and 2.6 (labeled as 26) W/m^2 climate mitigation cases. Shaded area indicates range of total emissions from the RCP scenarios. Assessment Report (AR5) range refers to the full range of scenarios reviewed in the Fifth Assessment Report (AR5) of Working Group III of the Intergovernmental Panel on Climate Change (IPCC) https://tntcat.iiasa.ac.at/AR5DB. Vertical colored bars indicate the range of uncertainty in 2100.

Rao *et al.*, *Glob. Envir. Change*, 2017

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"

Overview of Aerosols

- Aerosols aka particulate matter (PM)
- Size generally ranges from 0.005 μm to 100 μm diameter
- Can be liquid or solid
- Solids: produced by grinding or crushing operation
- Liquids: formed by condensation of gases on water droplets
- 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 had dominated due to greater reliance on coal
  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

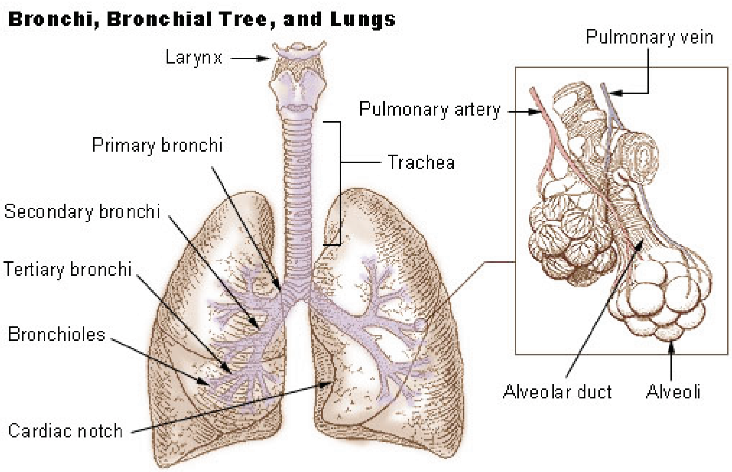
http://www.barnesandnoble.com/w/polycyclic-aromatic-hydrocarbons-pierre-a-haines

- 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 Aerosols



Our natural defenses help us to cough or sneeze larger particles out of our bodies.

These defenses don't work as well for particles smaller than about 10 microns (or micrometers) in diameter

Small particles get trapped in the lungs (bad) and some pass through the lungs into the bloodstream (really bad).

Exposure to elevated levels of PM leads to increase risk of respiratory illnesses, cardiopulmonary disease, heart disease, and heart attacks.

https://www.lung.org/our-initiatives/healthy-air/outdoor/air-pollution/particle-pollution.html

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]

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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

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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/