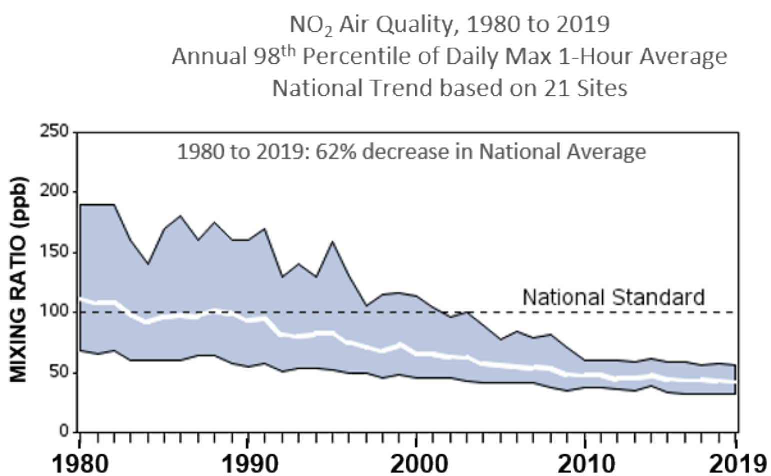
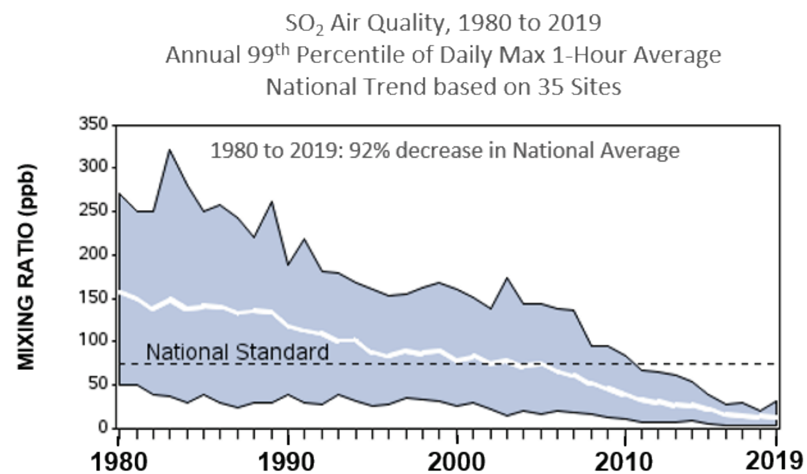
Pollution of Earth's Troposphere: Acid Rain & Aerosols
AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2020
https://myelms.umd.edu/courses/1291919





Lecture 14

29 October 2020

Announcements: Outside of Class

1) Today, 29 Oct : AOSC Weekly Seminar (3:30 pm)

Dr. Kevin Reed, School of Marine & Atmospheric Sciences, Stony Brook University, NY
Detecting climate change impacts on tropical cyclones

The next century will see unprecedented changes to the climate system with direct consequences for society. As stated in the National Climate Assessment, “changes in extreme weather events are the primary way that most people experience climate change.” In this sense, the characteristics of extreme weather are key indicators of climate change impacts, at both local and regional scales. Understanding potential changes in the location, intensity and structure of such extremes (e.g., tropical cyclones, severe thunderstorms and flooding) is crucial in planning for future adaptation as these events have large economic and social costs. The goal of this work is to better understand climate impacts on tropical cyclones in various high-resolution configurations of the Community Atmosphere Model (CAM) run at horizontal grid spacings of approximately 28 km and forced with prescribed sea-surface temperatures and greenhouse gas concentrations for past, present, and future climates. This analysis will include the evaluation of conventional (AMIP-style) decadal simulations typical of climate models, short 7-day ensemble hindcasts of recent devastating events, and reduced complexity simulations of idealized states of the climate system. Through this hierarchical modeling approach the impact of climate change on the characteristics (frequency, intensity, rainfall, etc.) of tropical cyclones can be quantified.

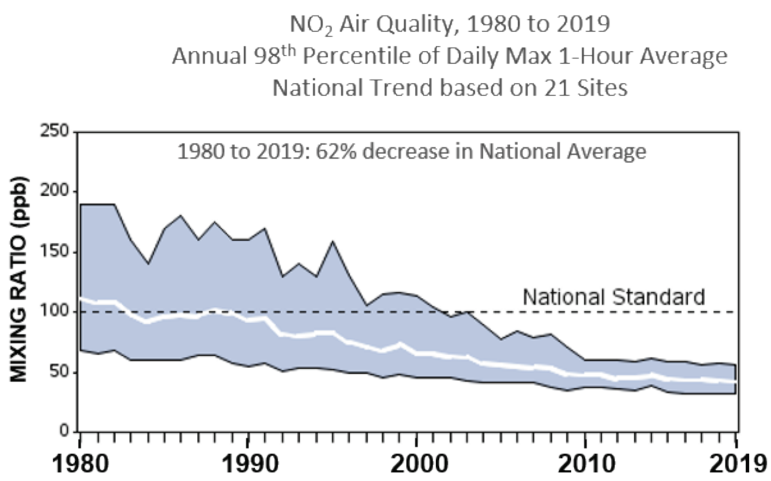
https://aosc.umd.edu/seminars/department-seminar

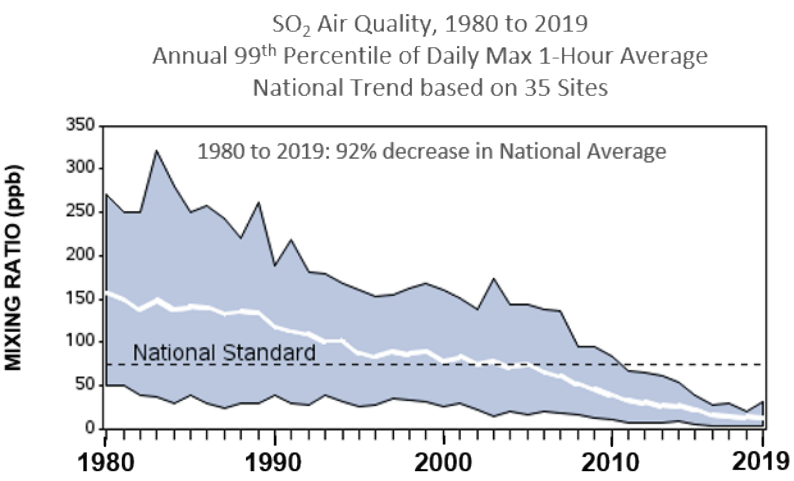
Email Joseph Knisely at jknisely@umd.edu for Zoom connection info

What two pollutants were responsible for the enhanced acidity of rain samples for the portion of the U.S. that experienced pH of rain that was more acidic than normal in 2008?

What two pollutants were responsible for the enhanced acidity of rain samples for the portion of the U.S. that experienced pH of rain that was more acidic than normal in 2008?

These compounds are “affectionately” known as NO_x and SO_x
Chemically, we write NO_x and SO_x, where $NO_x = NO + NO_2$ & $SO_x = SO_2 + SO_3$





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)

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

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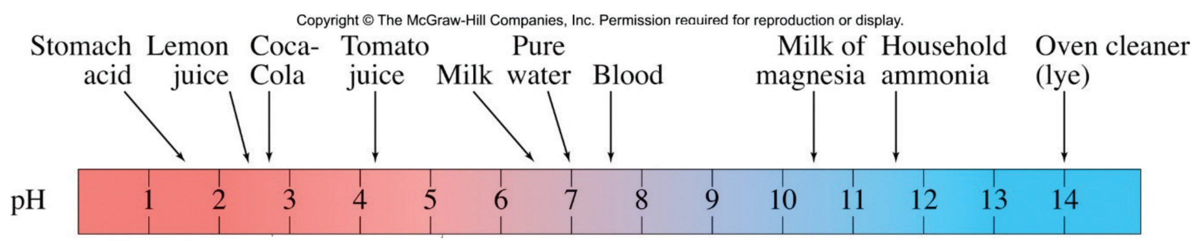

Figure 6.4, Chemistry in Context.

pH for 200

My pH is 5.6

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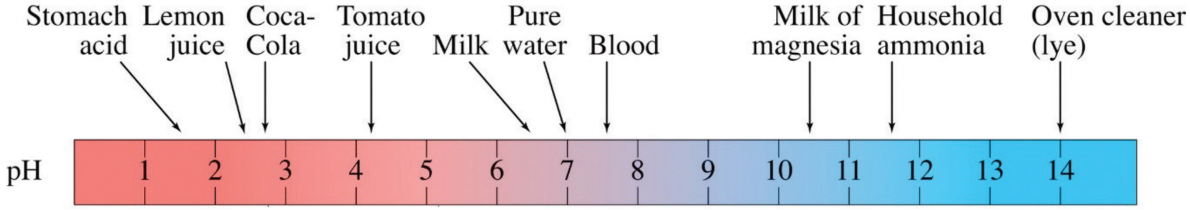

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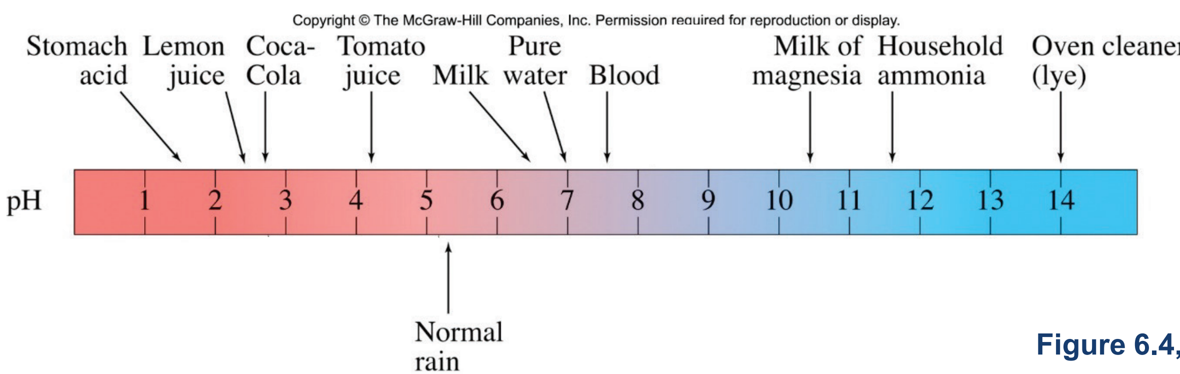


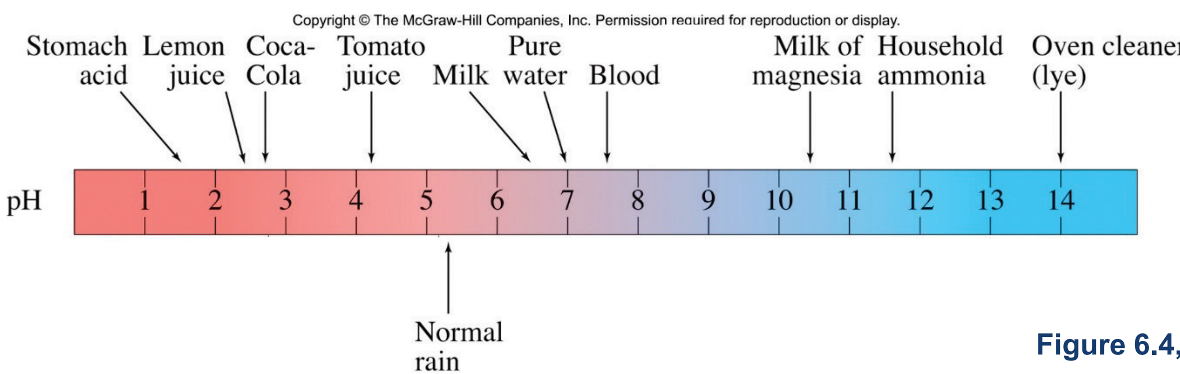
Figure 6.4, Chemistry in Context.

pH for 400

My pH is 5.6

What is water in equilibrium with atmospheric CO_2 of 400 ppm, or "normal rain" ?

My pH is approximately 8.2



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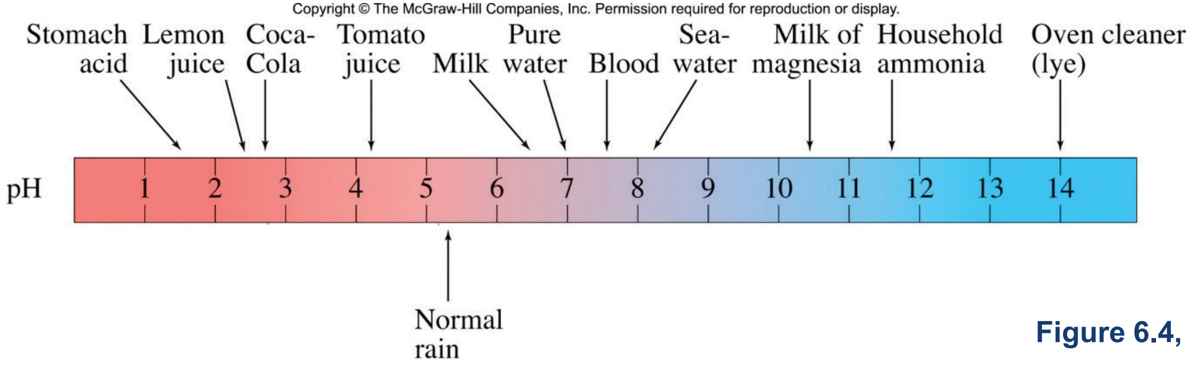


Figure 6.4, Chemistry in Context.

pH for 600

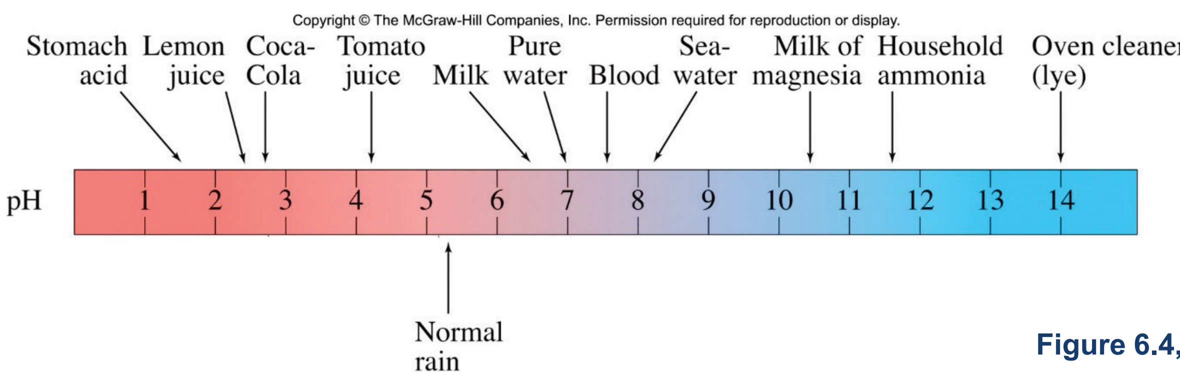
My pH is 5.6

What is water in equilibrium with atmospheric CO_2 of 400 ppm, or "normal rain" ?

My pH is approximately 8.2

What is ocean water?

Dissolution of these types of rocks tends to maintain the world's oceans in a slightly basic state



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What are carbonates?

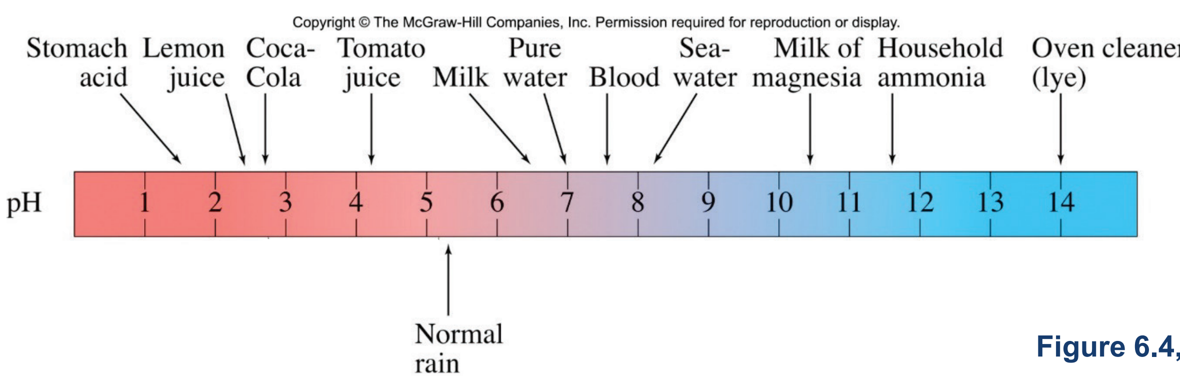


Figure 6.4, Chemistry in Context.

pH for 600

Limestone https://en.wikipedia.org/wiki/Limestone

From Wikipedia, the free encyclopedia

For other uses, see Limestone (disambiguation).

Limestone is a carbonate sedimentary rock that is often composed of the skeletal fragments of marine organisms such as coral, foraminifera, and molluscs. Its major materials are the minerals calcite and aragonite, which are different crystal forms of calcium carbonate ($CaCO_3$). A closely related rock is dolostone, which contains a high percentage of the mineral dolomite, $CaMg(CO_3)_2$. In fact, in old USGS publications, dolostone was referred to as *magnesian* ***limestone***, a term now reserved for magnesium-deficient dolostones or magnesium-rich limestones.

About 10% of sedimentary rocks are limestones. The solubility of limestone in water and weak acid solutions leads to karst landscapes, in which water erodes the limestone over thousands to millions of years. Most cave systems are through limestone bedrock.

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$
$$H^+ + CO_3^{2-} \rightarrow HCO_3^-$$

Magnesium carbonates ($MgCO_3$) and potassium carbonates (K_2CO_3) also contribute

Dissolution of these types of rocks tends to maintain the world's oceans in a slightly basic state

What are carbonates?

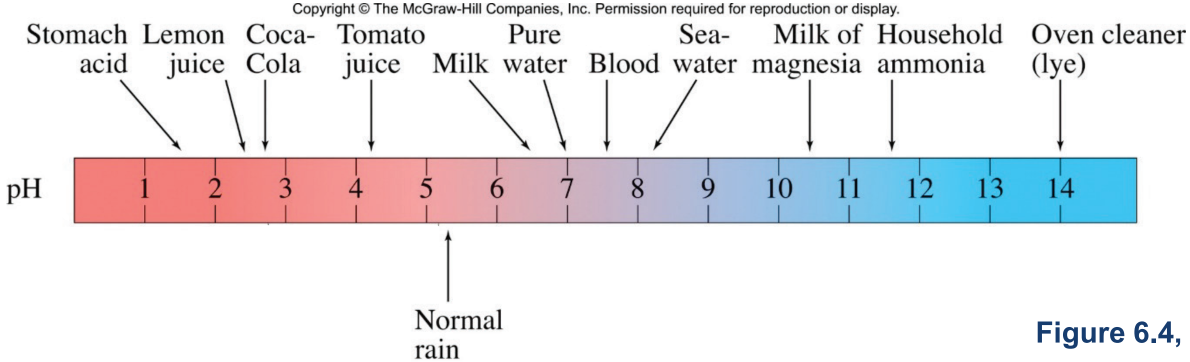


Figure 6.4, Chemistry in Context.

Origin of the term pH

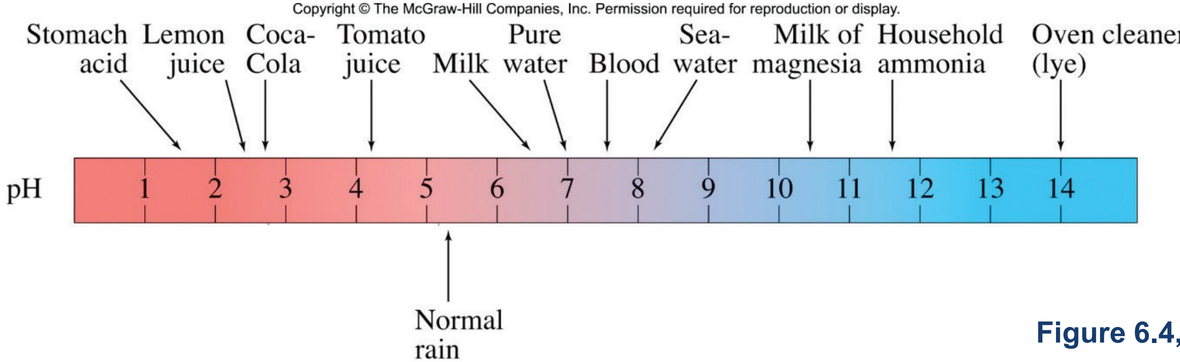


Figure 6.4, Chemistry in Context.

pH for 800

Origin of the term pH

What is power of hydrogen?

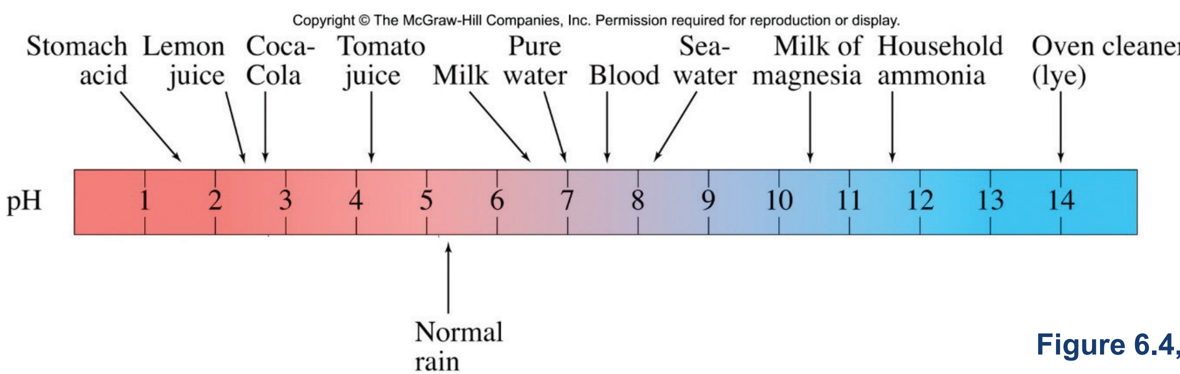


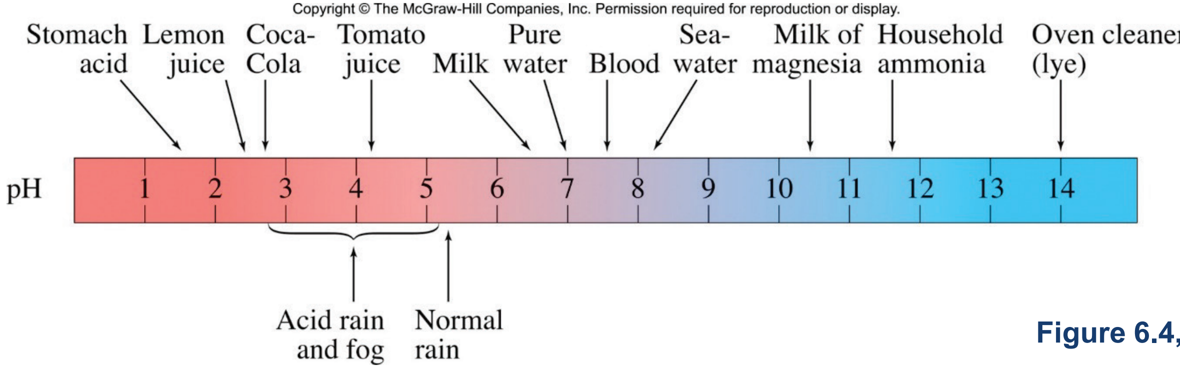
Figure 6.4, Chemistry in Context.

pH for 1000

Origin of the term pH

What is power of hydrogen?

Metropolitan area with the most acidic measurement of fog or rain



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What is Los Angeles?

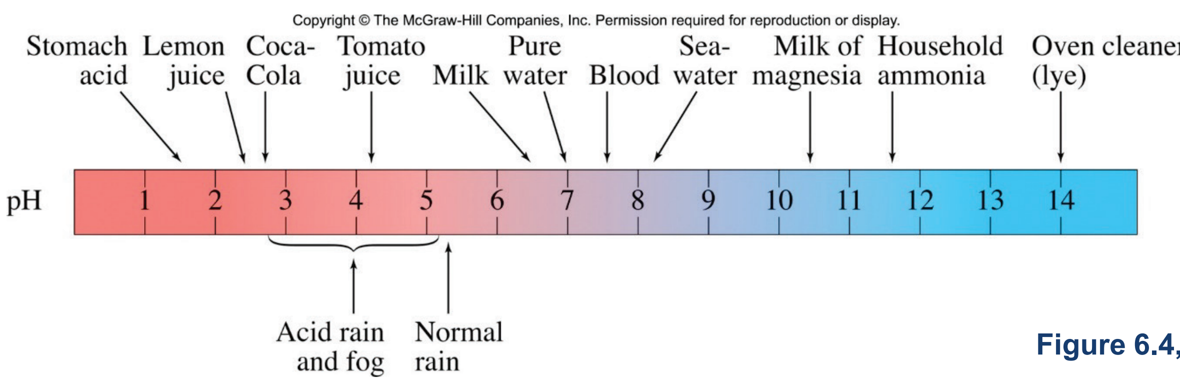


Figure 6.4, Chemistry in Context.

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

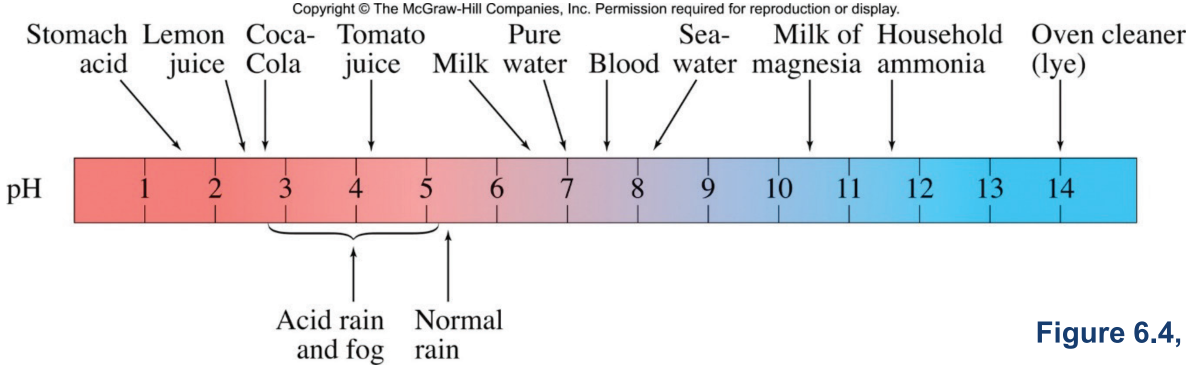


Figure 6.4, Chemistry in Context.

Acid Rain

Concentration of H^+ for rain with a pH of 5

$[H^+] = 10^{-5}$ M (moles of solute / liter of solution)

Concentration of H^+ for rain with a pH of 4

$[H^+] = 10^{-4}$ M (moles of solute / liter of solution)

Concentration of H^+ for rain with a pH of 3

$[H^+] = 10^{-3}$ M (moles of solute / liter of solution)

Concentration of H^+ for rain with a pH of 2

$[H^+] = 10^{-2}$ M (moles of solute / liter of solution)

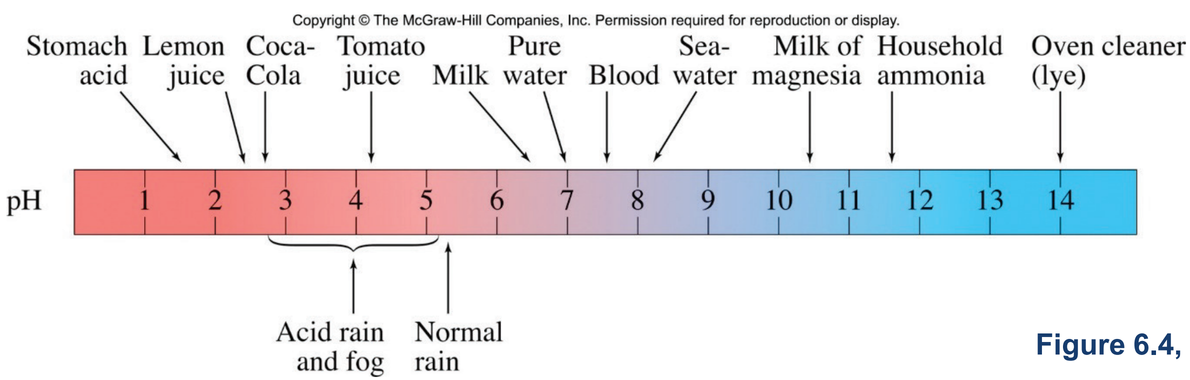
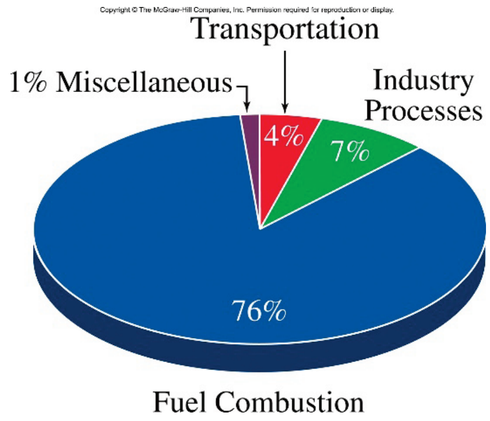


Figure 6.4, Chemistry in Context.

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

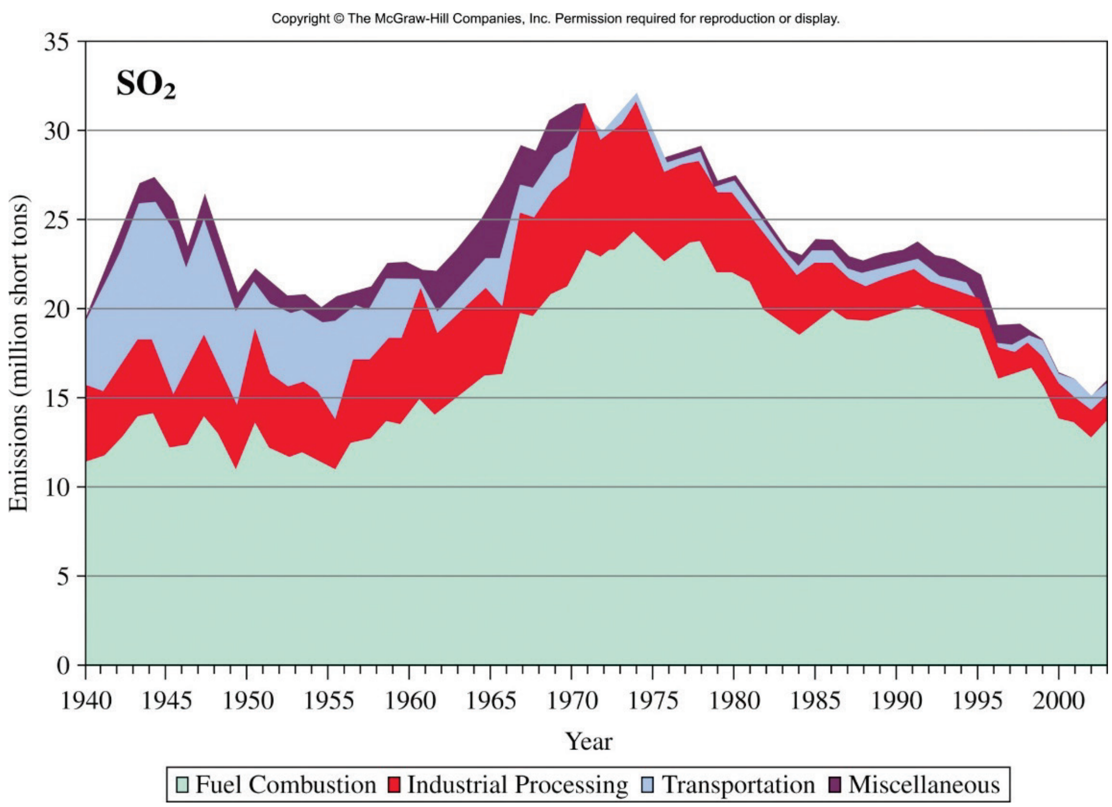
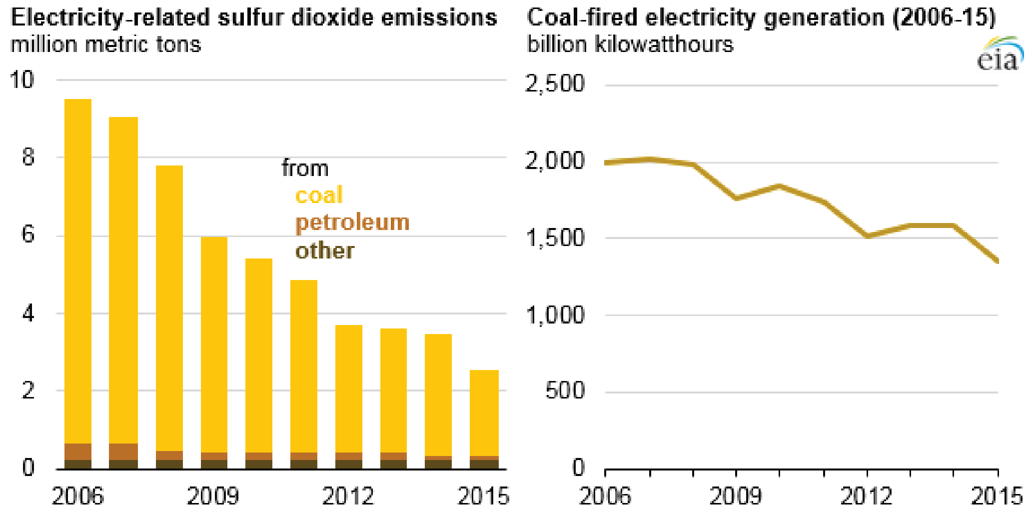


Figure 6.21, Chemistry in Context.
U.S. SO_2 emissions, 1940 to 2003

SO_2 Sources (U.S.)



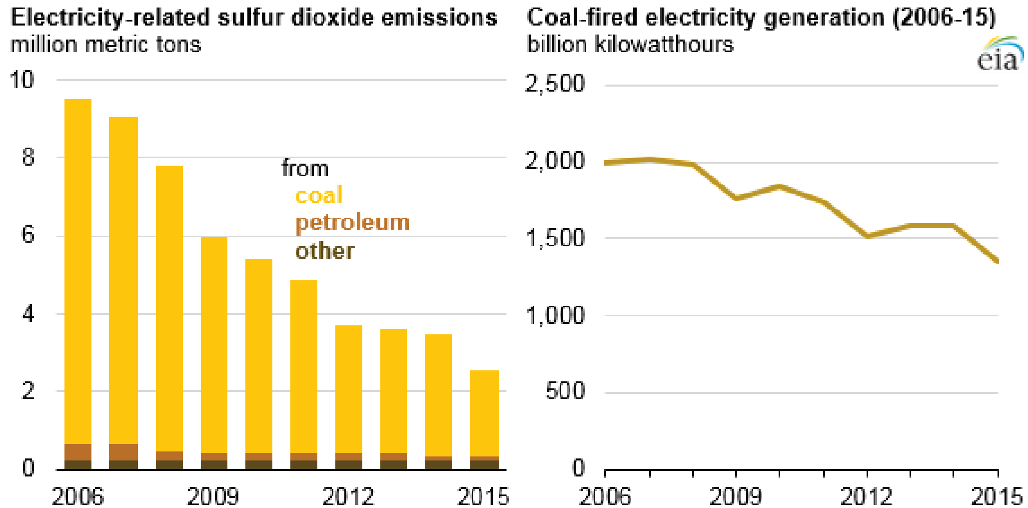
SO_2 emissions from U.S. power plants in the United States declined by 73% from 2006 to 2015, a much larger reduction than the 32% decrease in coal-fired electricity generation over that period.

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.

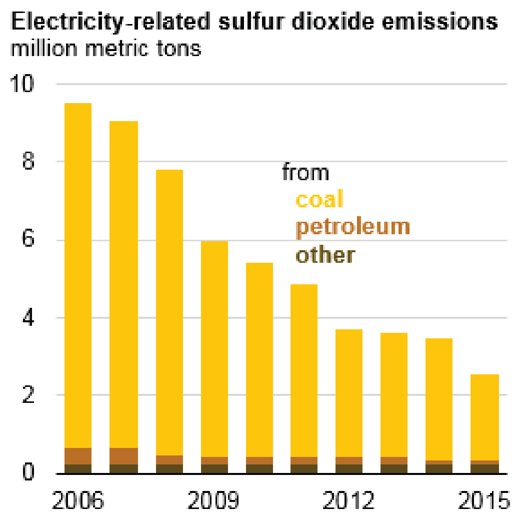
To comply with the federal Mercury and Air Toxics (MATS) rule, coal plants had to install pollution control equipment. Plants had to comply by April 15, 2015, or for some plants that received one-year extensions, by April 15, 2016. Two types of pollution control technologies installed for compliance 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.

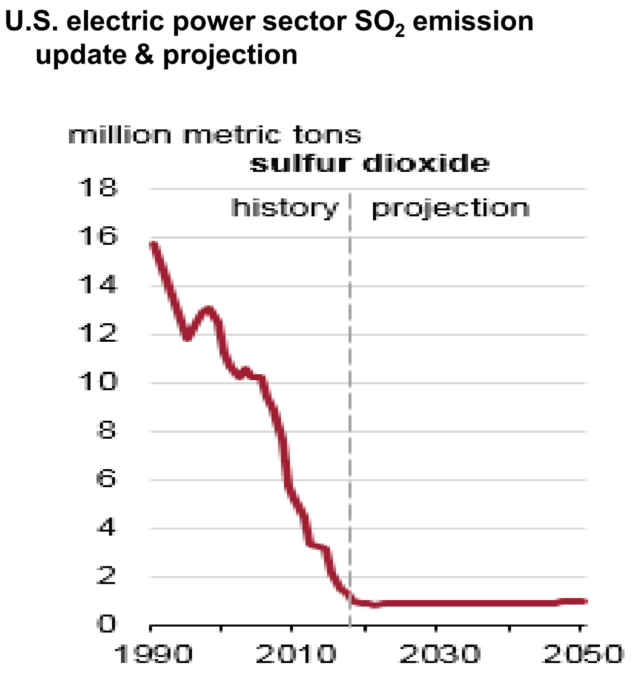
3) Lower utilization of the most-polluting plants

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

SO_2 Sources (U.S.)





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

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

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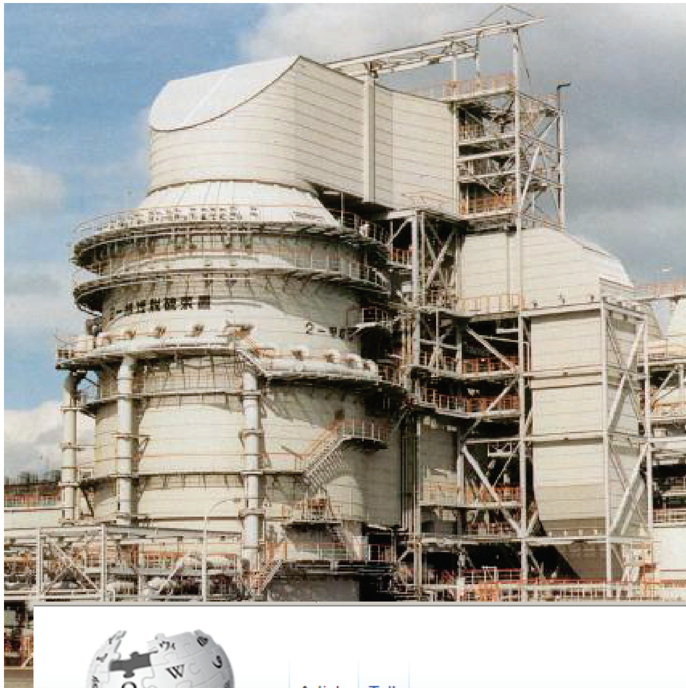

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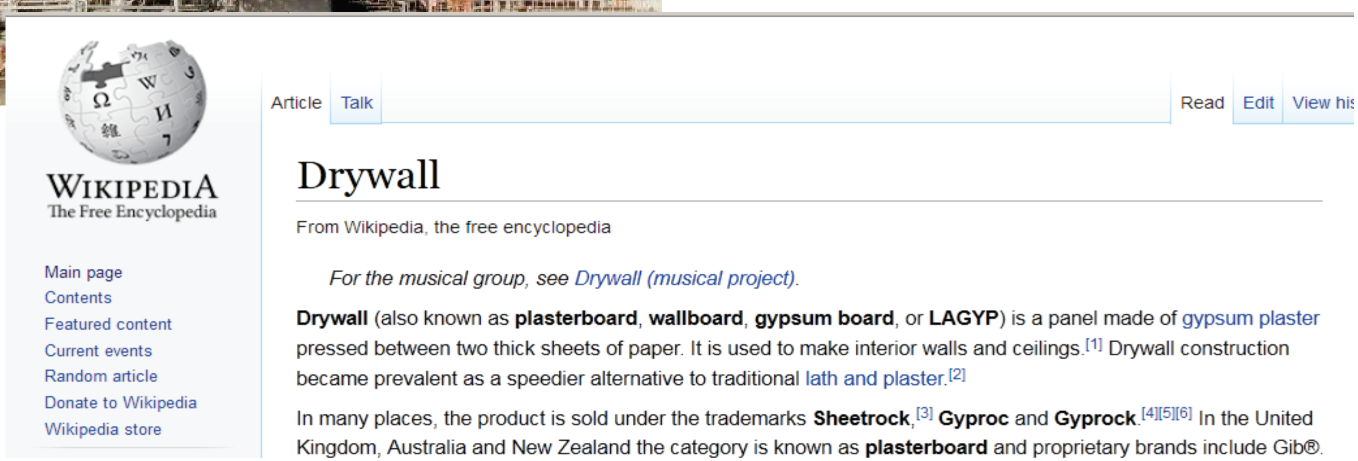

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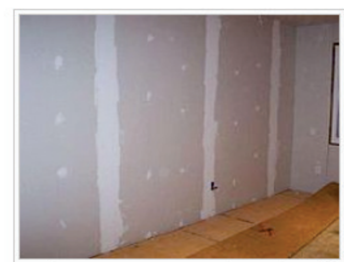
Drywall

From Wikipedia, the free encyclopedia

For the musical group, see Drywall (musical project).

Drywall (also known as **plasterboard**, **wallboard**, **gypsum board**, or **LAGYP**) is a panel made of gypsum plaster pressed between two thick sheets of paper. It is used to make interior walls and ceilings.[1] Drywall construction became prevalent as a speedier alternative to traditional lath and plaster.[2]

In many places, the product is sold under the trademarks **Sheetrock**,[3] **Gyproc** and **Gyprock**.[4][5][6] In the United Kingdom, Australia and New Zealand the category is known as **plasterboard** and proprietary brands include Gib®.



Vertically hung drywall with joint

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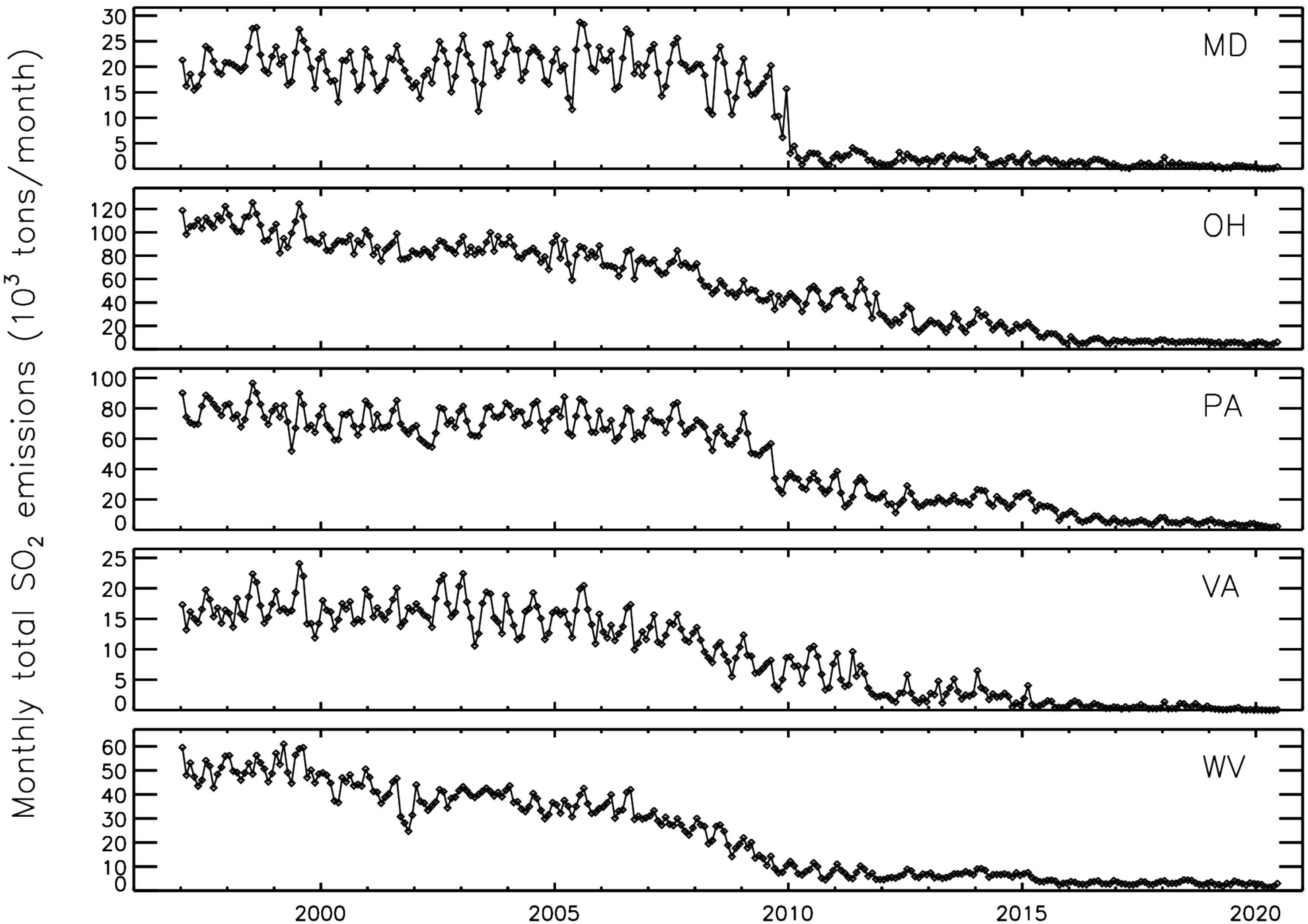
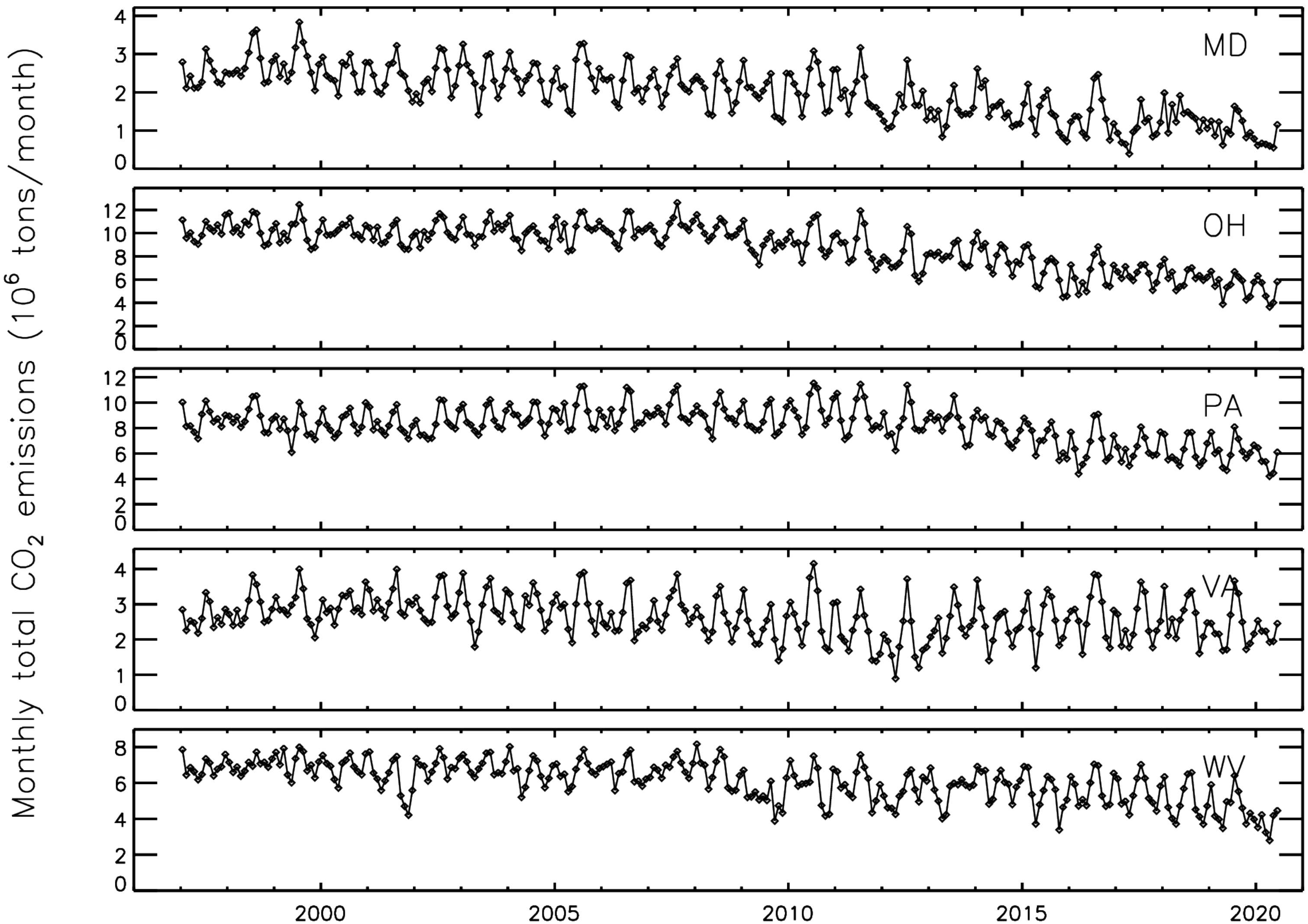
What happens to the CO_2 ?

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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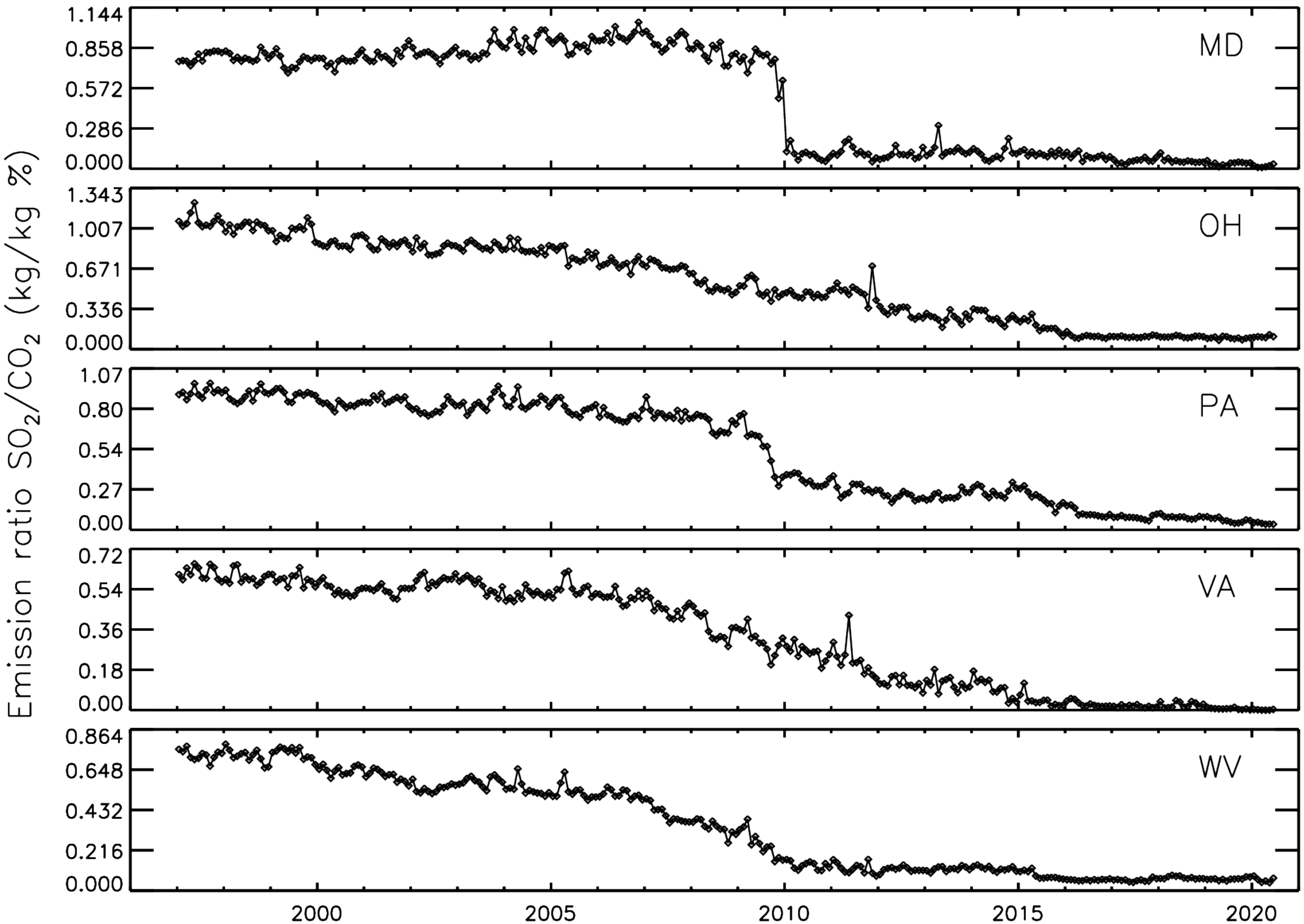

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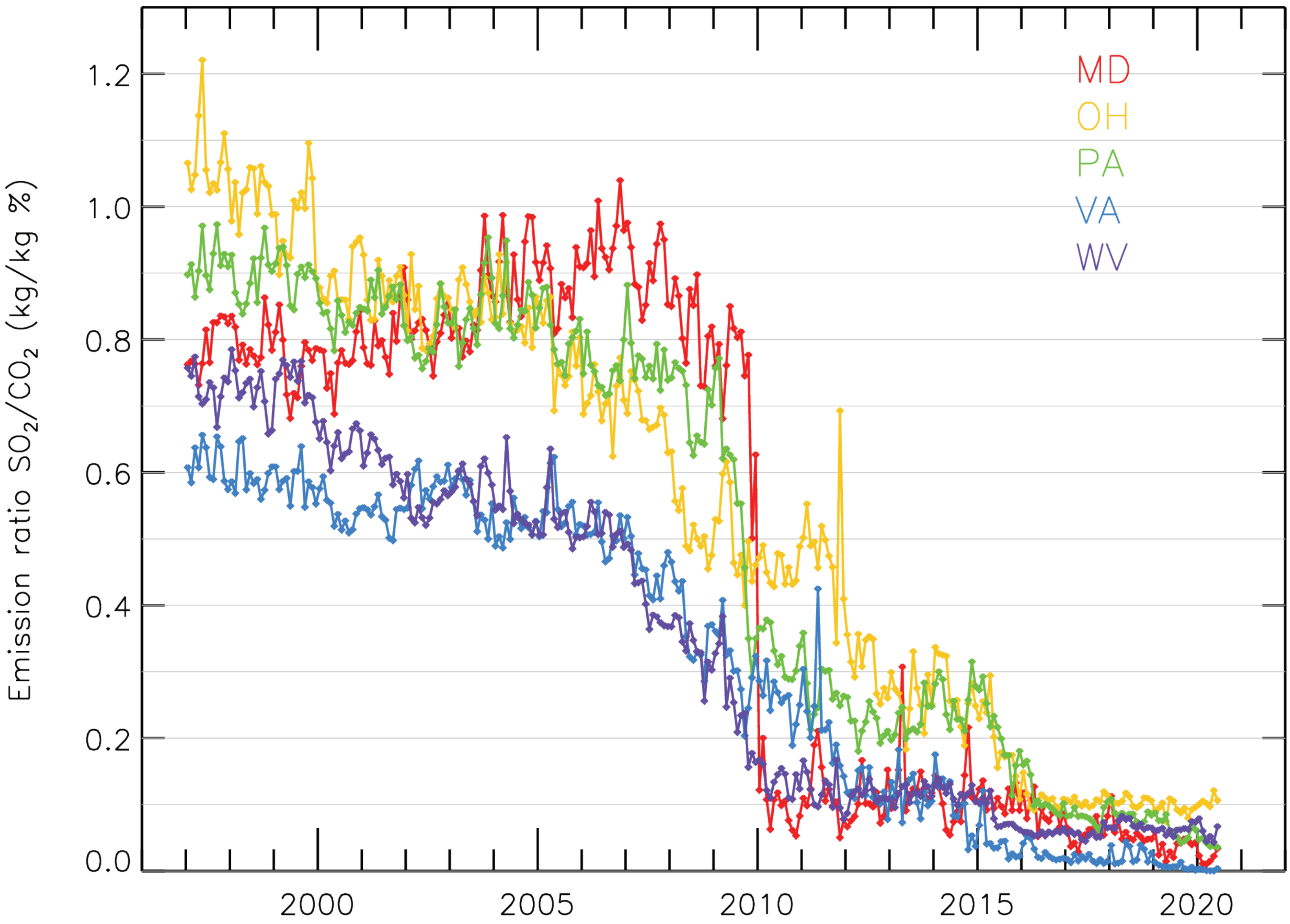

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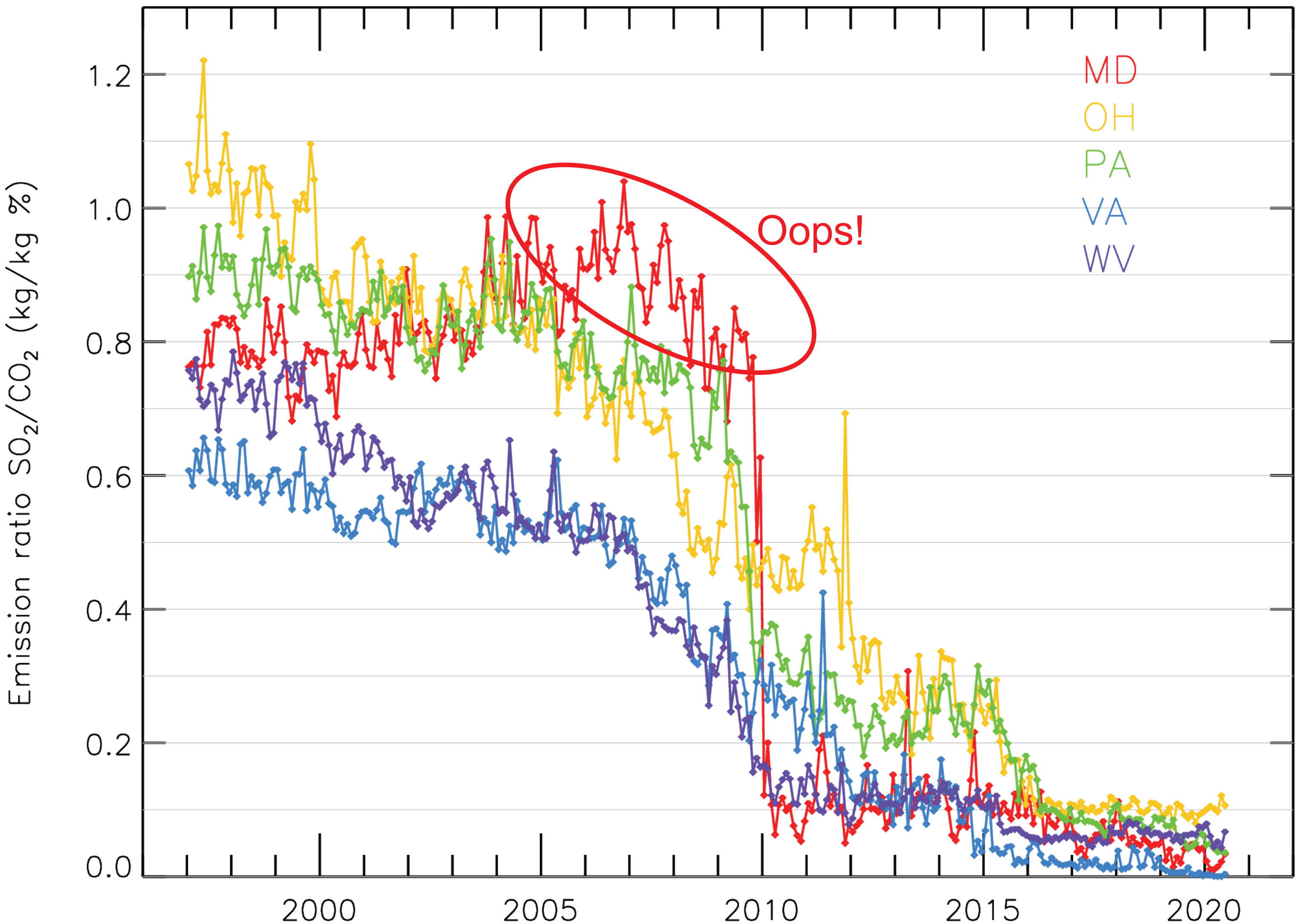

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Maryland Healthy Air Act

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

Maryland Department of the Environment
Air Quality Control Advisory Council

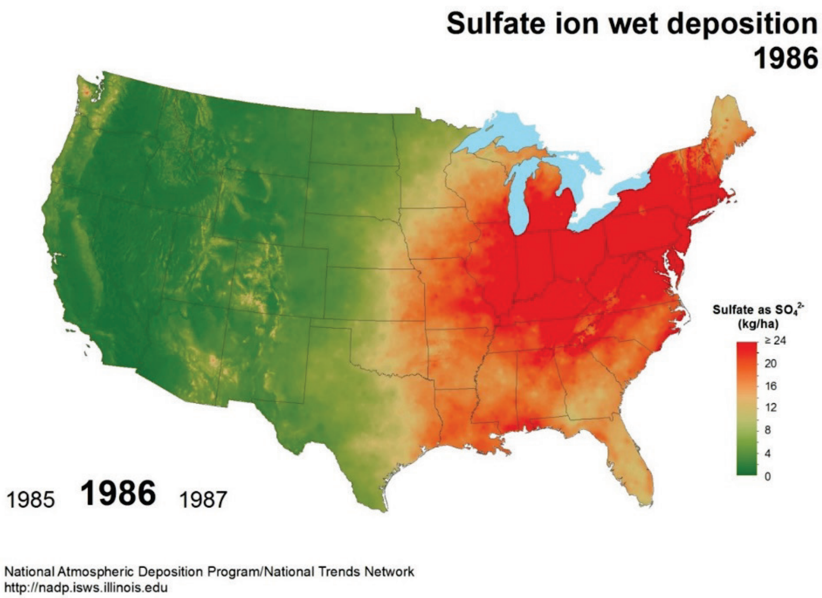
Current Membership

- Maryland Chamber of Commerce (Public Utility) - John Quinn, ***Chair***
- American Institute of Chemical Engineers - John Kumm, ***Vice Chair***
- American Society of Mechanical Engineers - Lawrence J. ("Larry") Schoen, P.E.
- Maryland Chamber of Commerce (Manufacturing Industry) - Todd Chason
- MD/DC AFL-CIO - Thomas Killeen
- University of Maryland - Ross Salawitch
- Johns Hopkins University - Benjamin F. Hobbs, PhD
- Physician - Sania Amr, M.D.
- Children's Environmental Health and Protection Advisory Council (CEHPAC) - Julian Levy
- Maryland Association of Counties - Weston Young, PE
- Regional Planning Council (BMC) - Sara Tomlinson
- Metropolitan Washington Council of Governments (COG) - Leta Mach
- Farming - Jonathan S. Kays
- General Public - Stephen Bunker
- General Public - Robert Wright

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

Sulfate Deposition (see Fig 6.12)

1986



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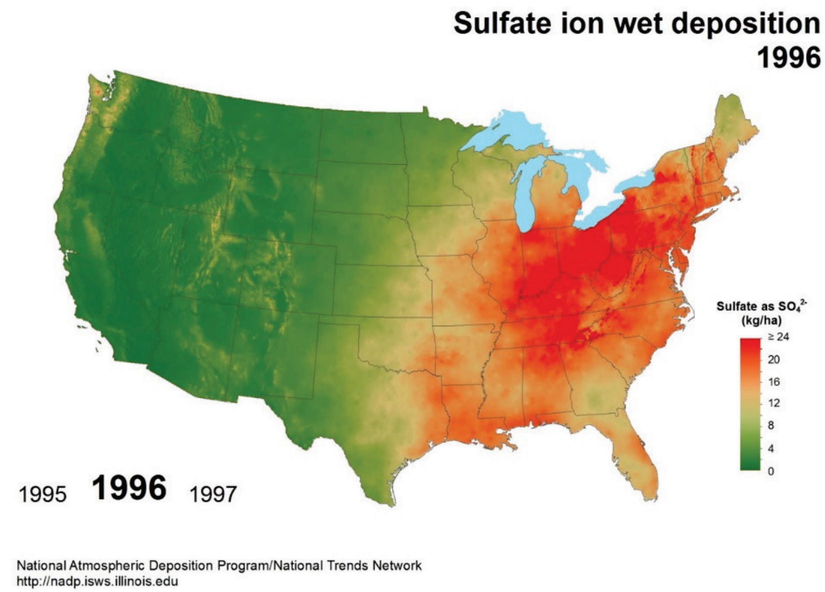

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Sulfate Deposition (see Fig 6.12)

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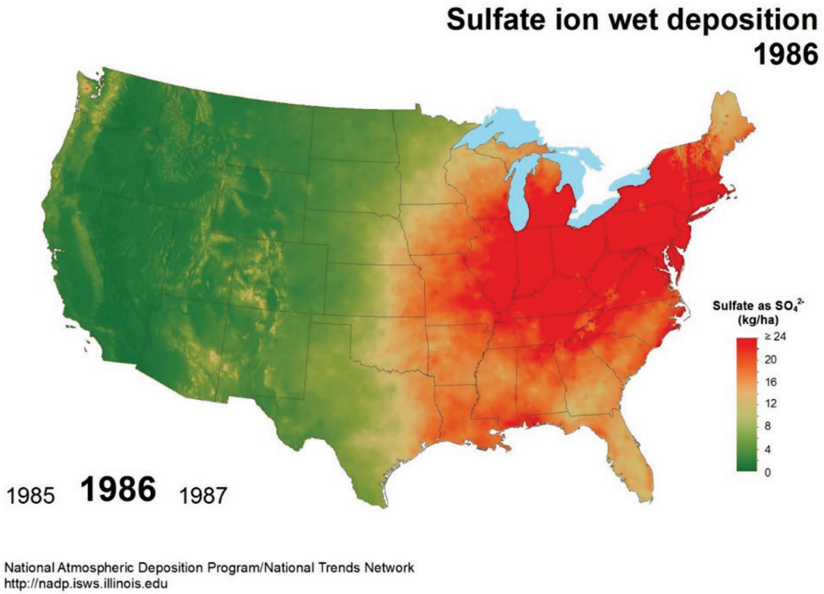

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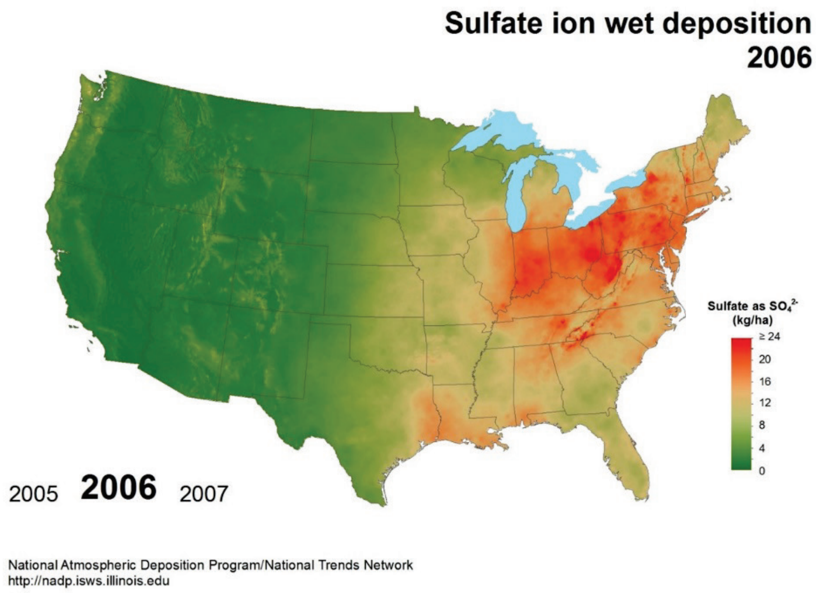

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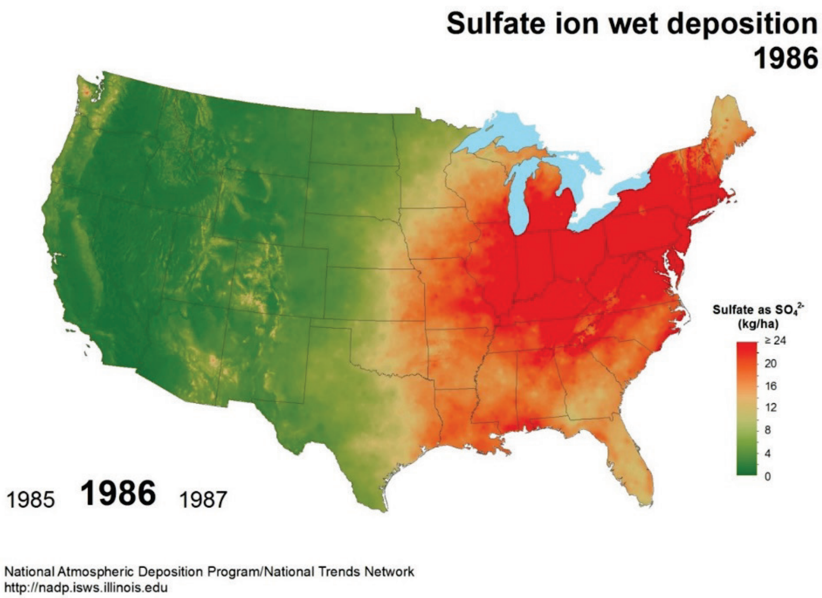
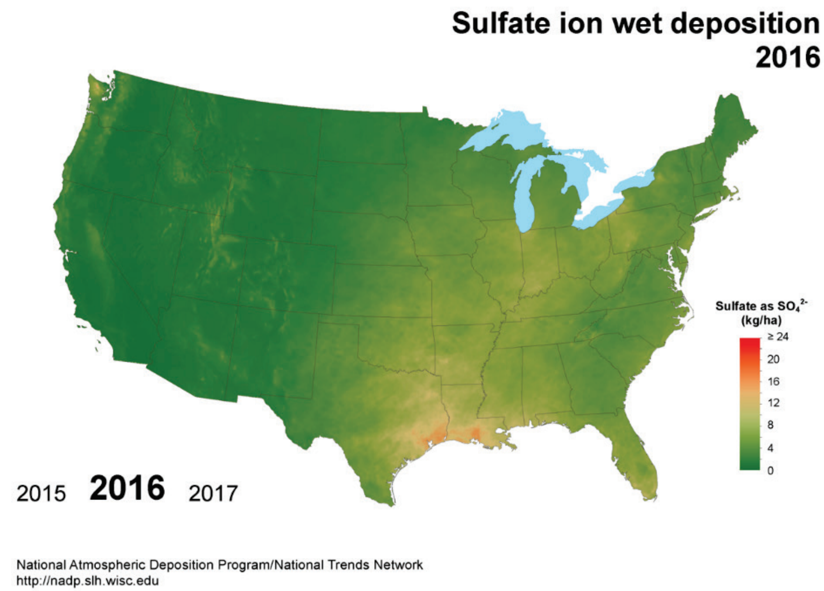
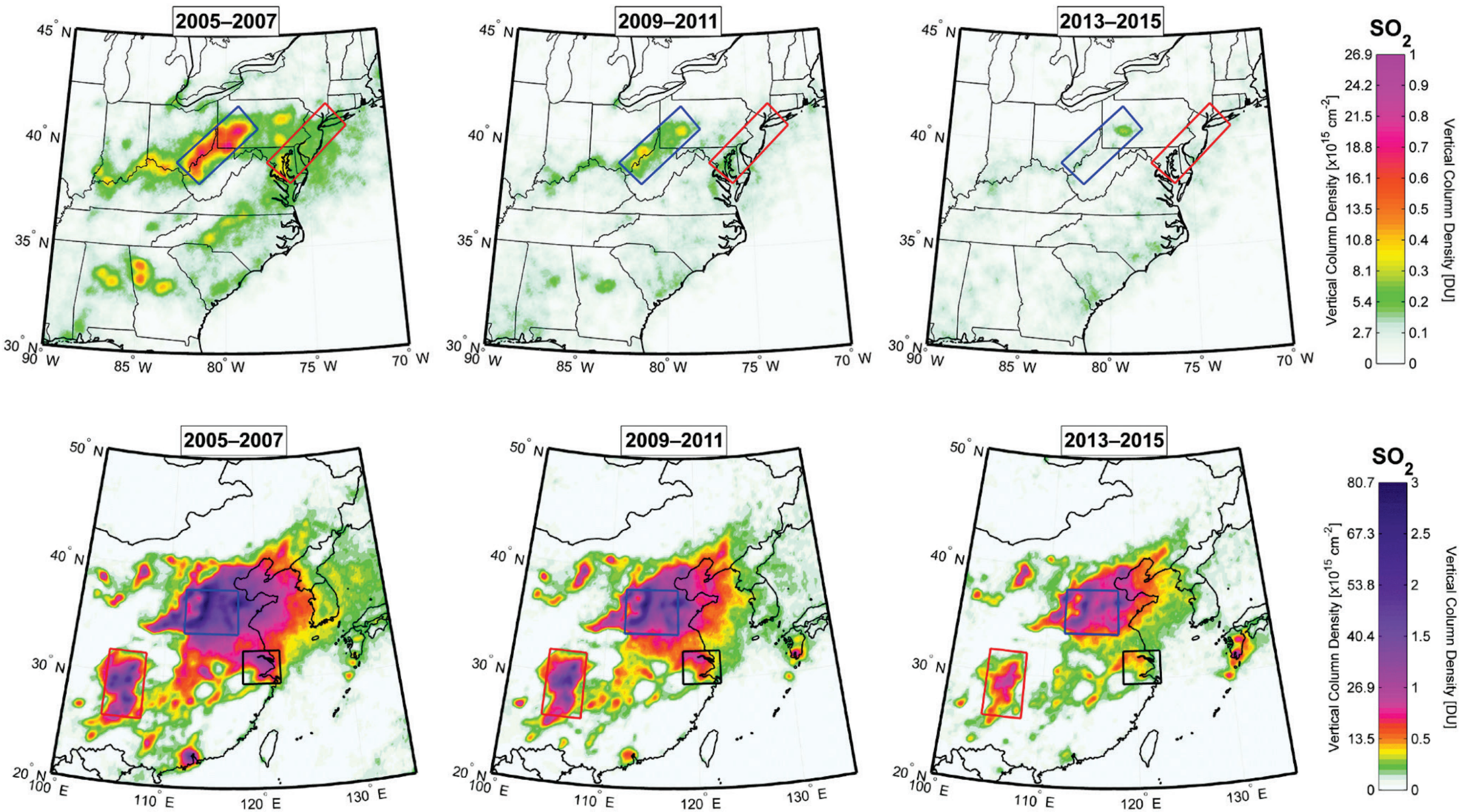


2016



http://nadp.slh.wisc.edu/data/animaps.aspx

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 13, 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!

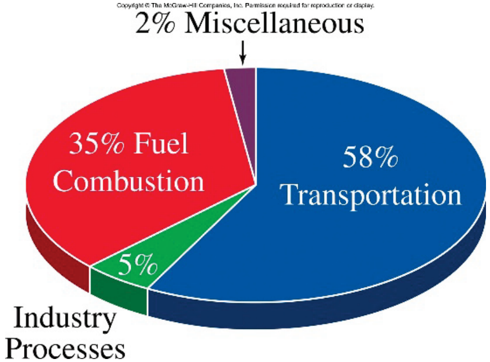
Hence, in the presence of liquid water, HNO_3 (g), can become HNO_3 (aq)

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

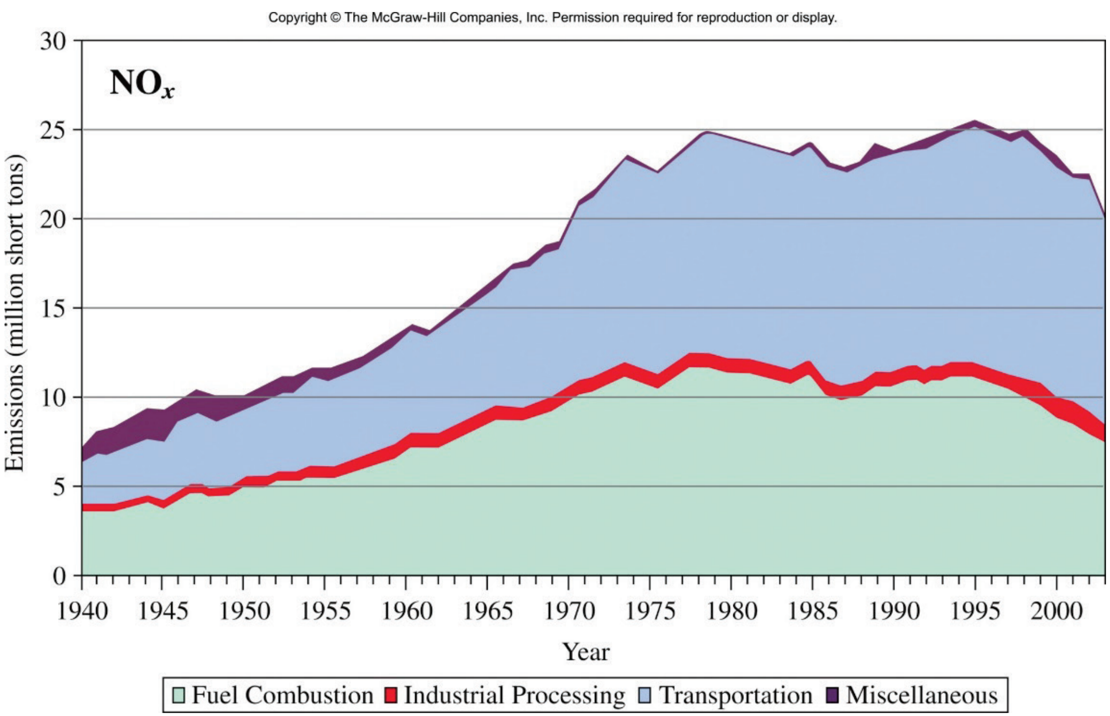
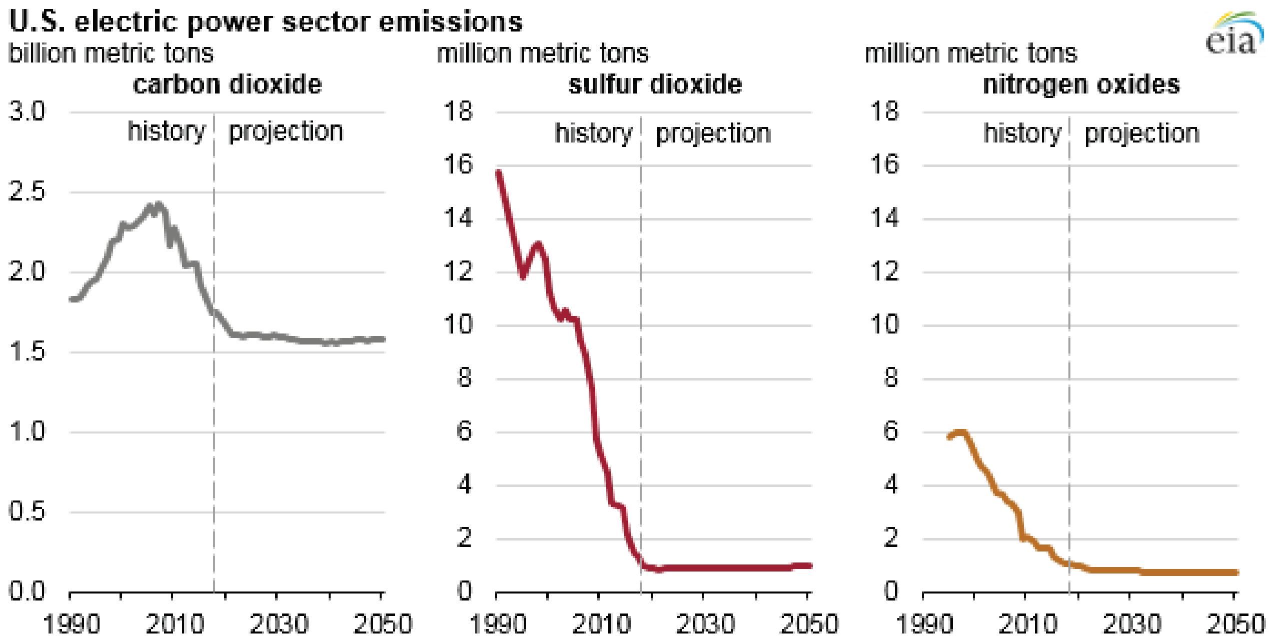


Figure 6.21, Chemistry in Context.
U.S. NO_x emission sources, 1940 to 2003.

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***.

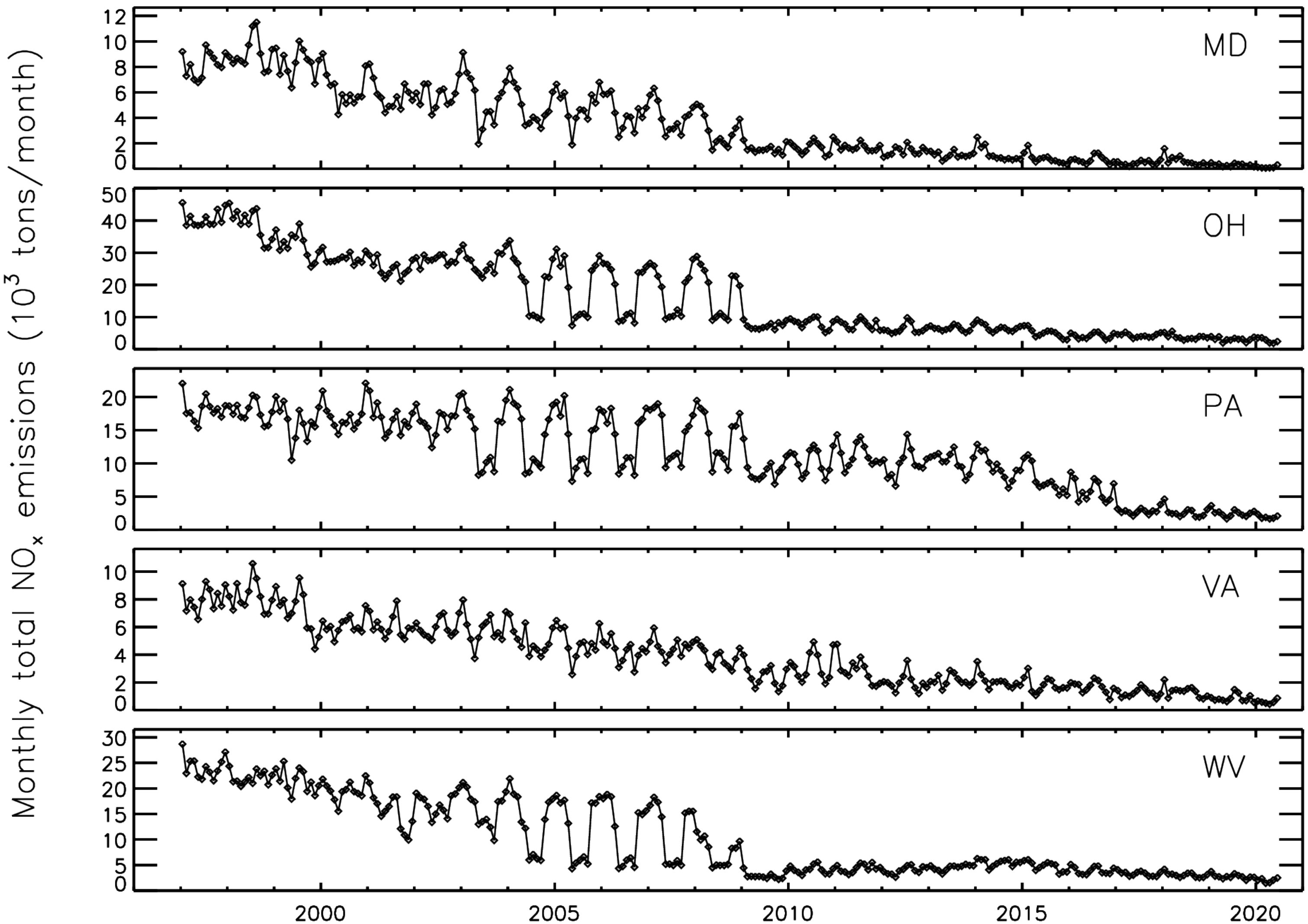
SO_2 and **NO_x** emissions from the electric power sector have declined over the past several decades, largely because of the phased implementation of regulations under the Clean Air Act Amendments of 1990. For SO_2, these regulations include acid rain cap-and-trade program deadlines in 1995 and 2000. 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.

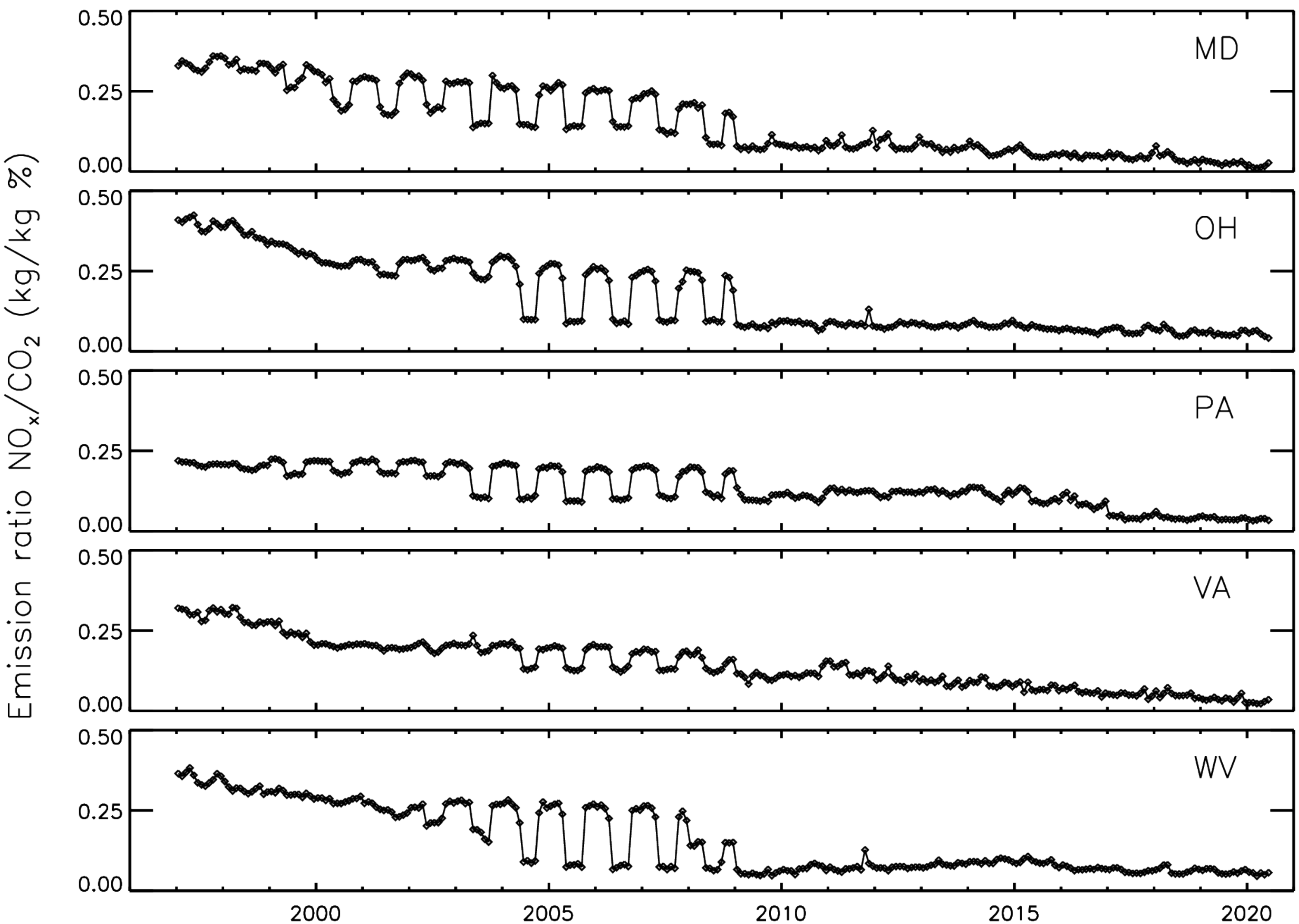
https://www.eia.gov/todayinenergy/detail.php?id=38293

Trends in power plant emission, region



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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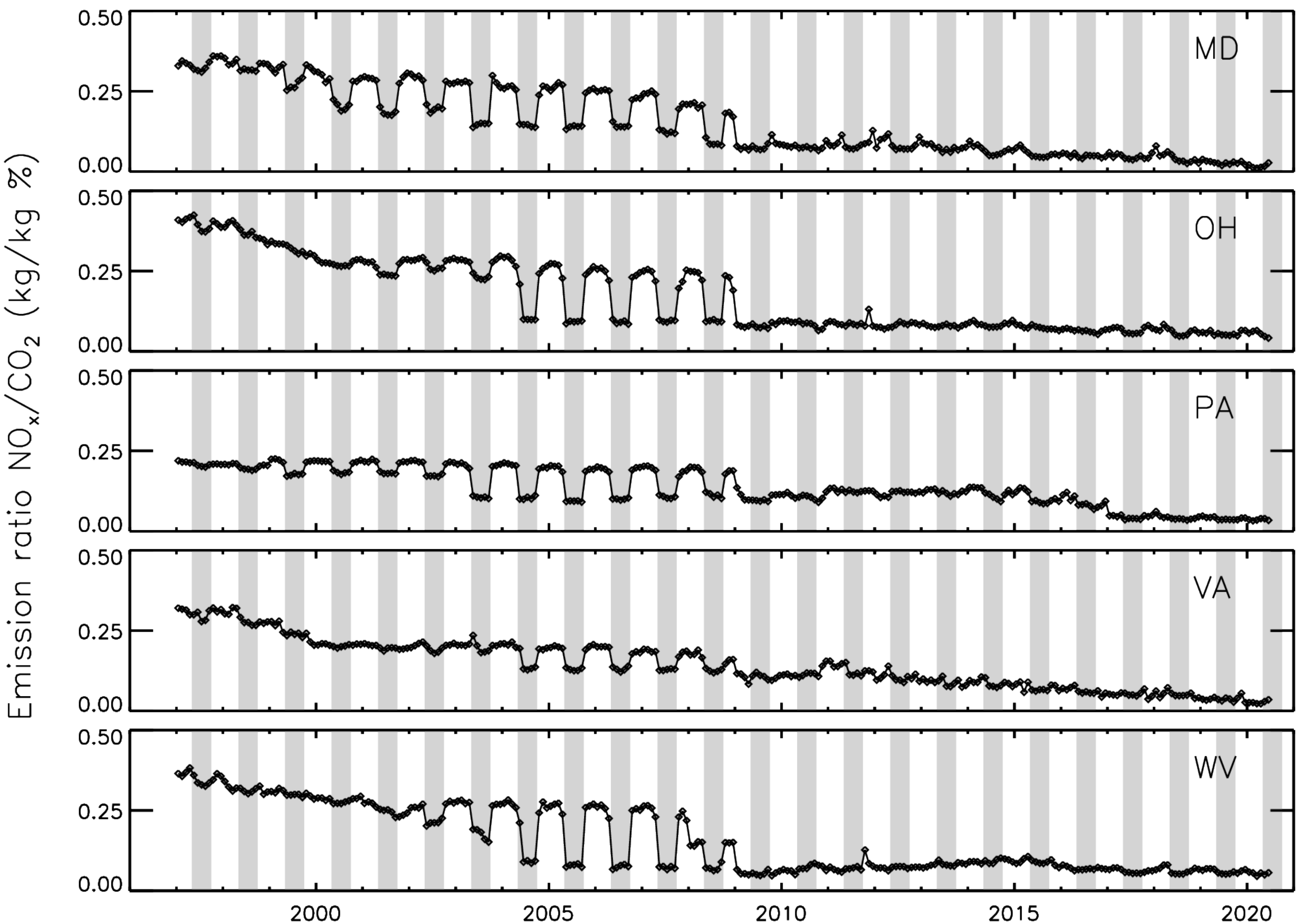
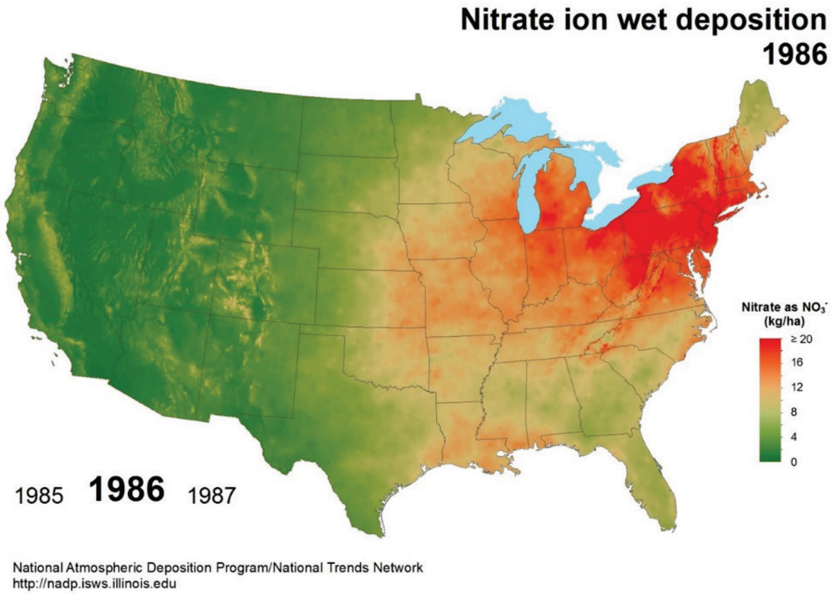
Trends in power plant emission, region



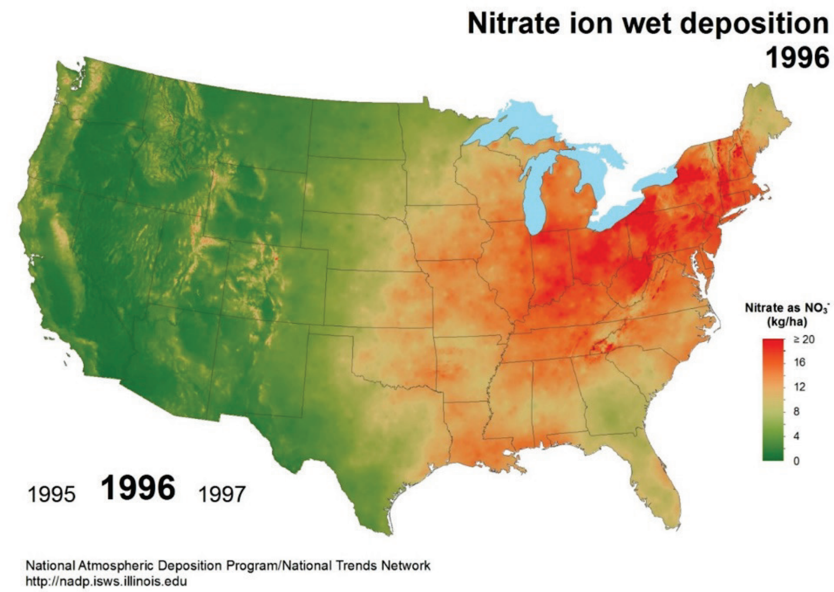
Shading denotes "ozone season", April to Sept

Nitrate Deposition (see Fig 6.12)

1986



1996



http://nadp.slh.wisc.edu/data/animaps.aspx

Nitrate Deposition (see Fig 6.12)

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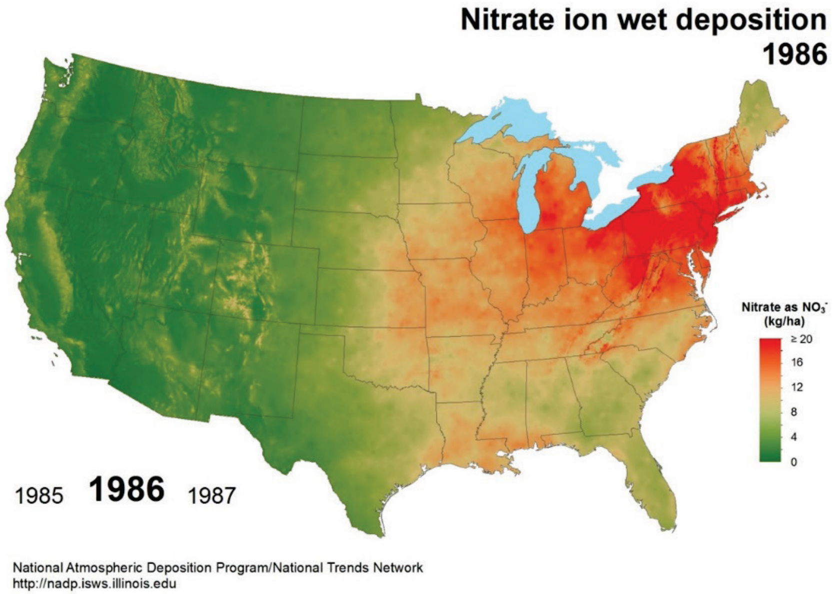
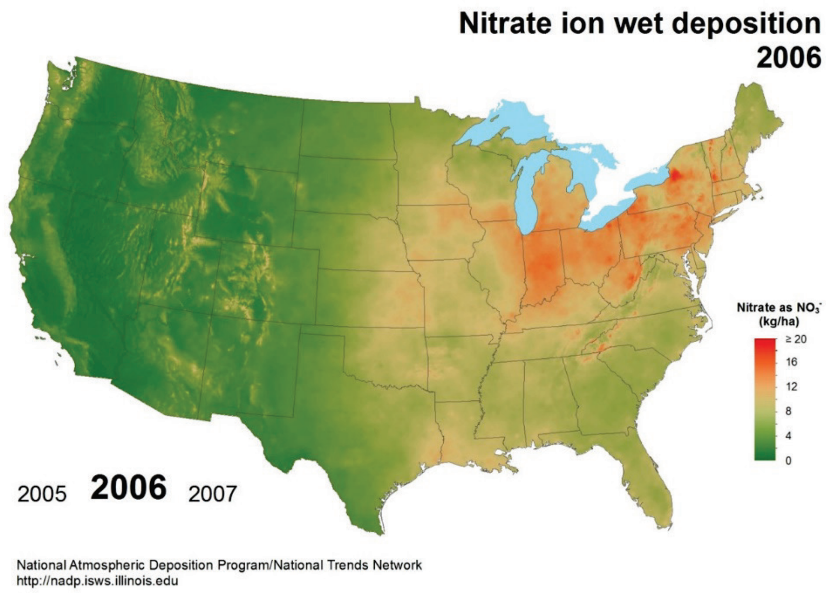


2006



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Nitrate Deposition (see Fig 6.12)

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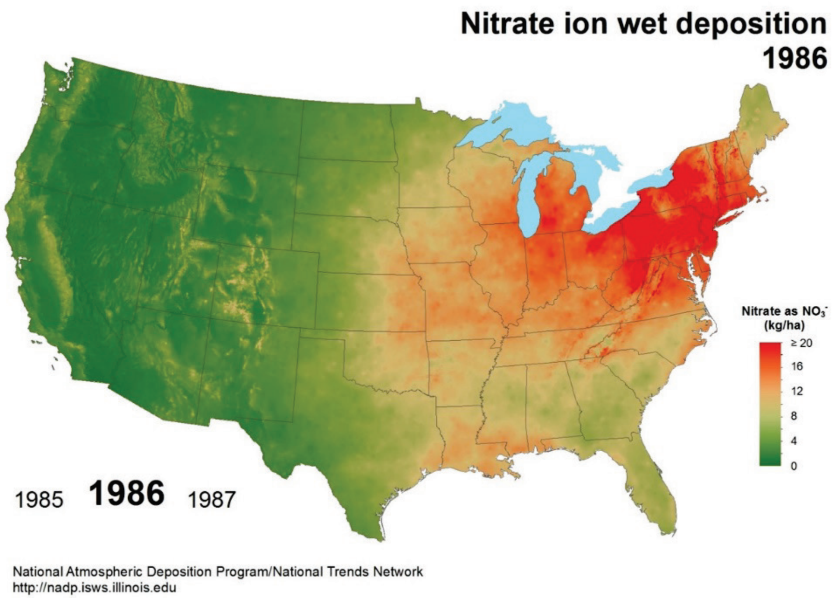
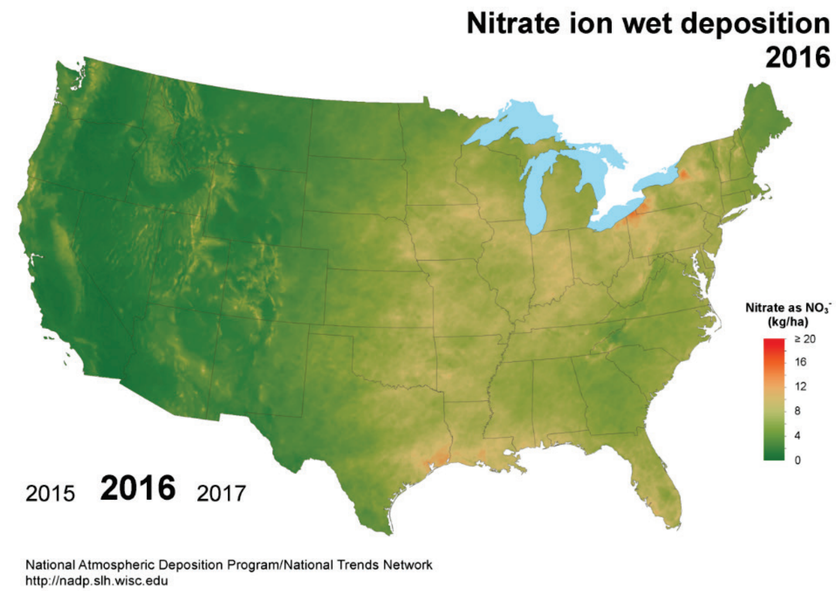


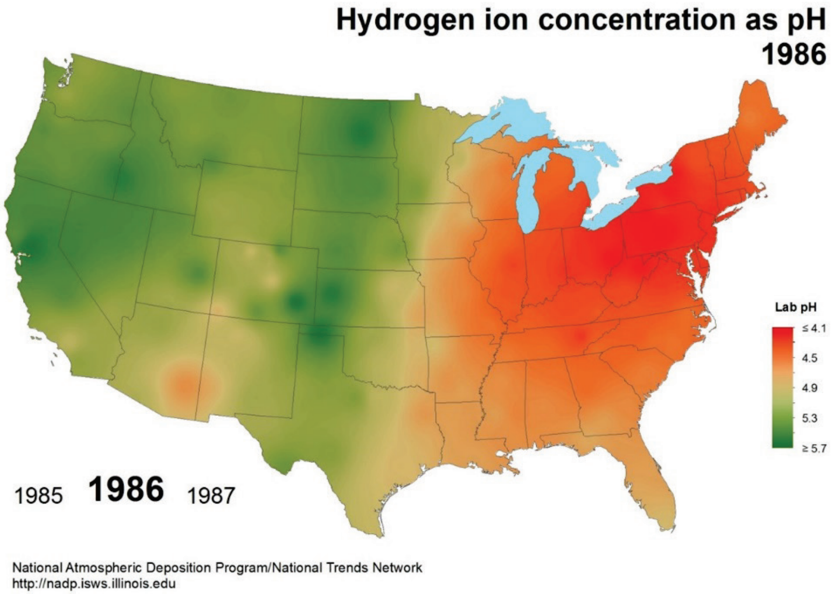
2016



http://nadp.slh.wisc.edu/data/animaps.aspx

pH of rain samples (see Fig 6.11)

1986



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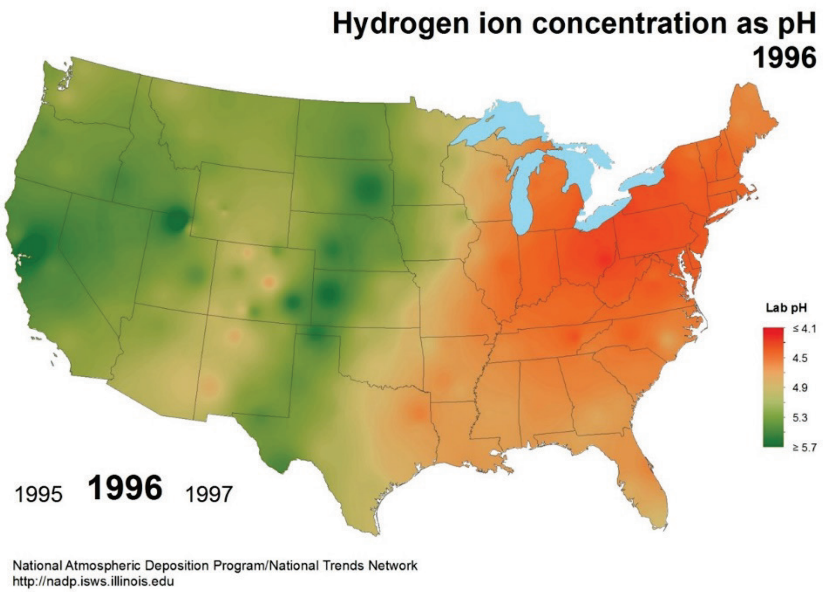

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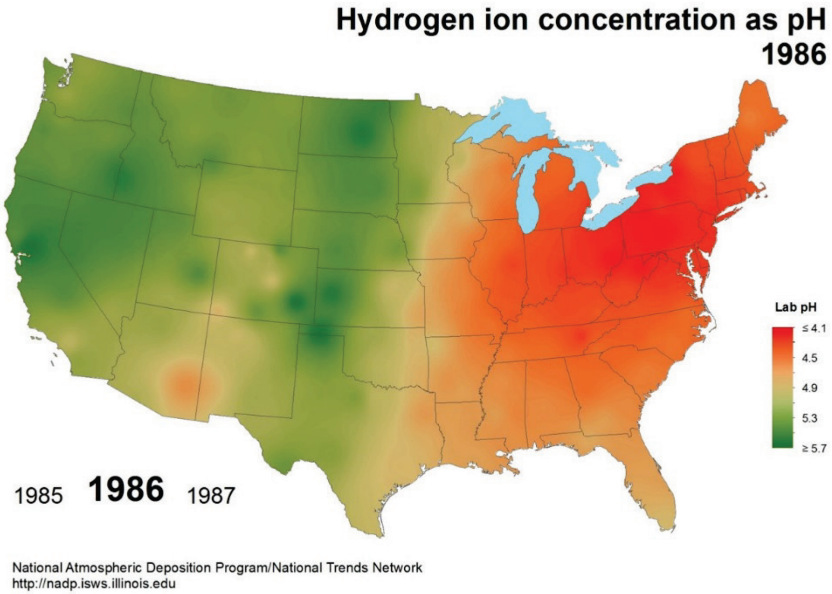
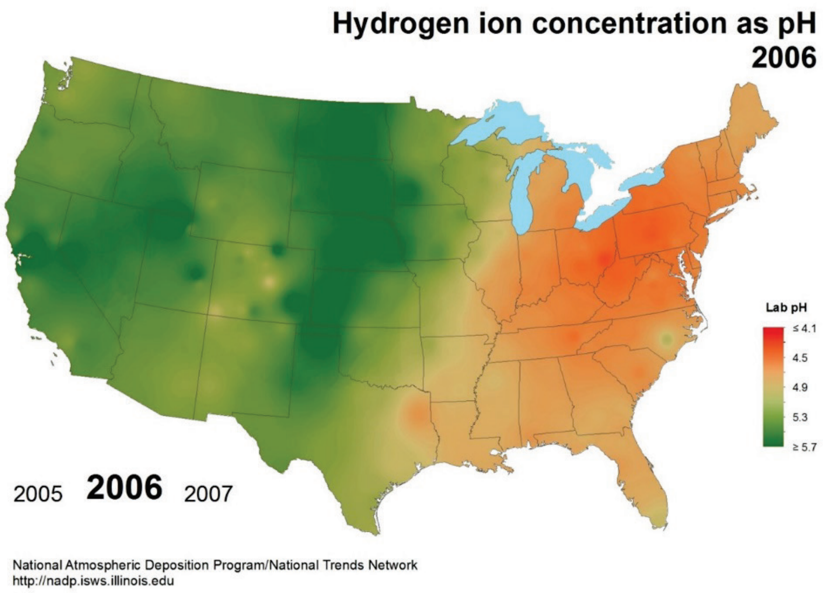
pH of rain samples (see Fig 6.11)

1986



2006



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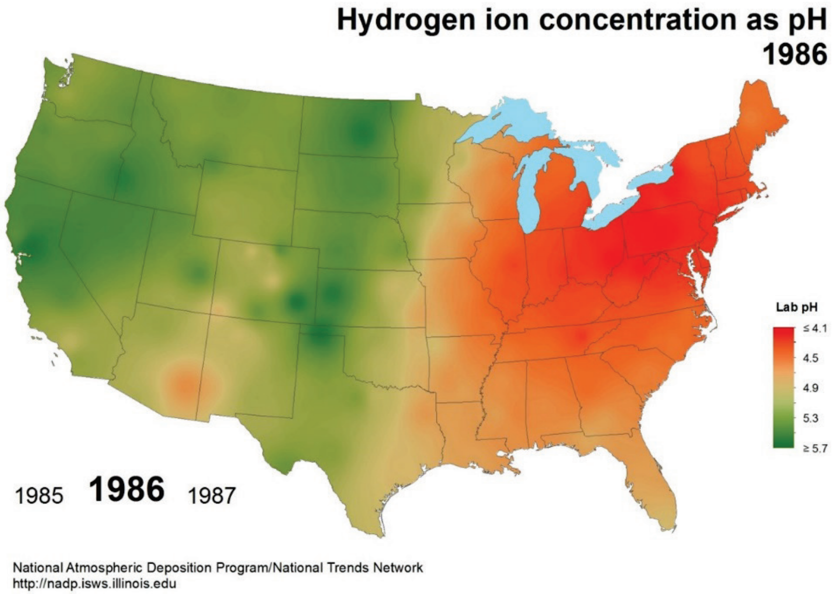
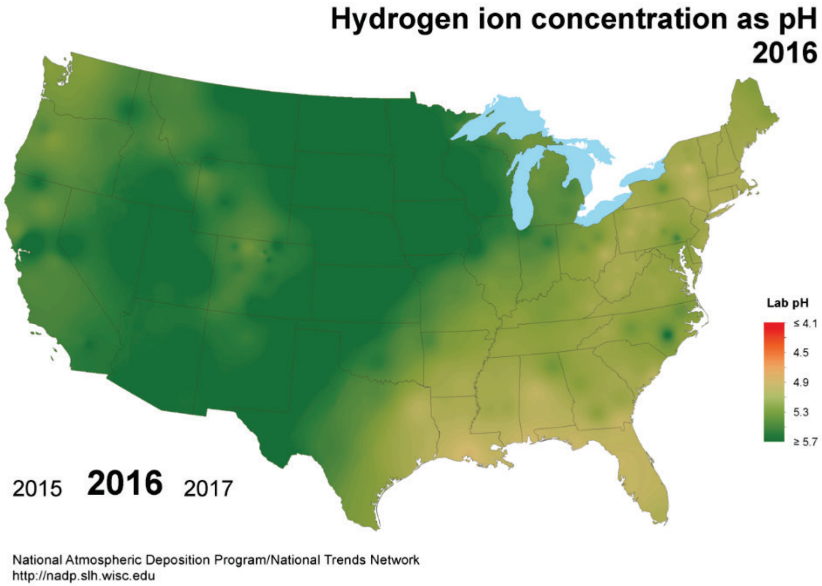


2016



http://nadp.slh.wisc.edu/data/animaps.aspx

Cultural Degradation

In 1944 | At present

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

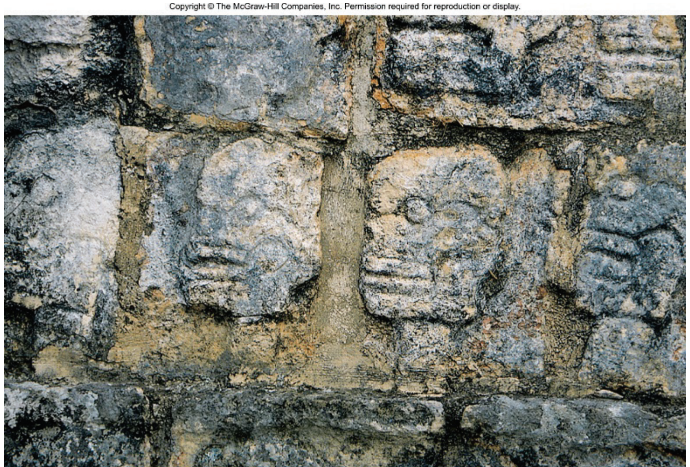


Figure 6.24, Chemistry in Context.
Mayan art, Mexico.

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:

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

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?

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?

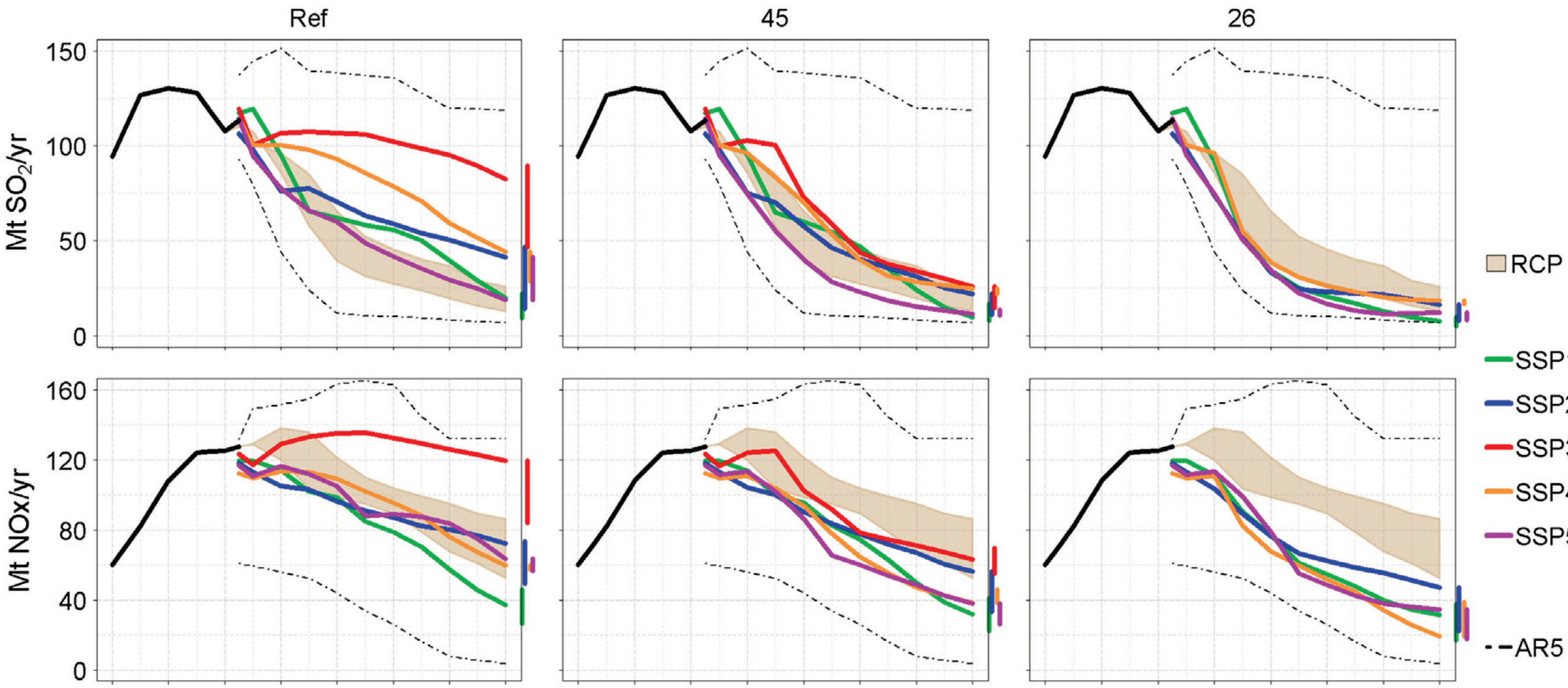
Least sensitive lakes are in the Midwest, because these lakes are lined with limestone.

Again, limestone (i.e., calcium carbonate, $CaCO_3$) dissolves in the presence of H^+

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

Lakes with granite beds are much more susceptible to the dire effects of acid rain.

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.

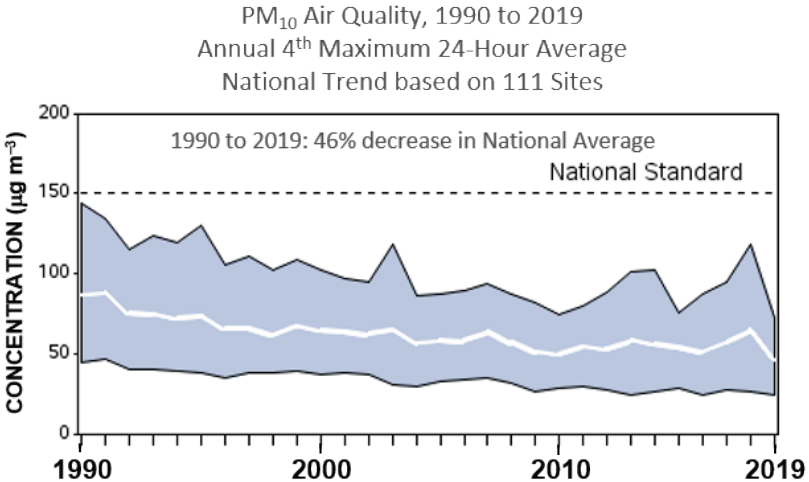
Rao *et al.*, *Glob. Envir. Change*, 2017

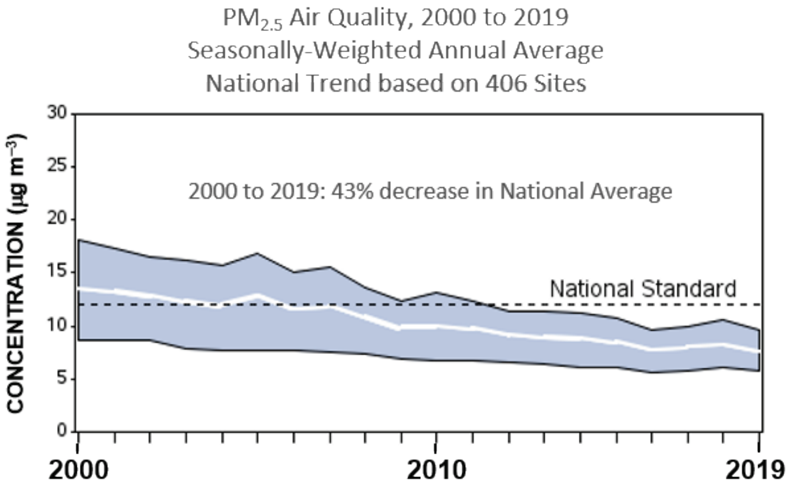
Overview of Aerosols

- 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

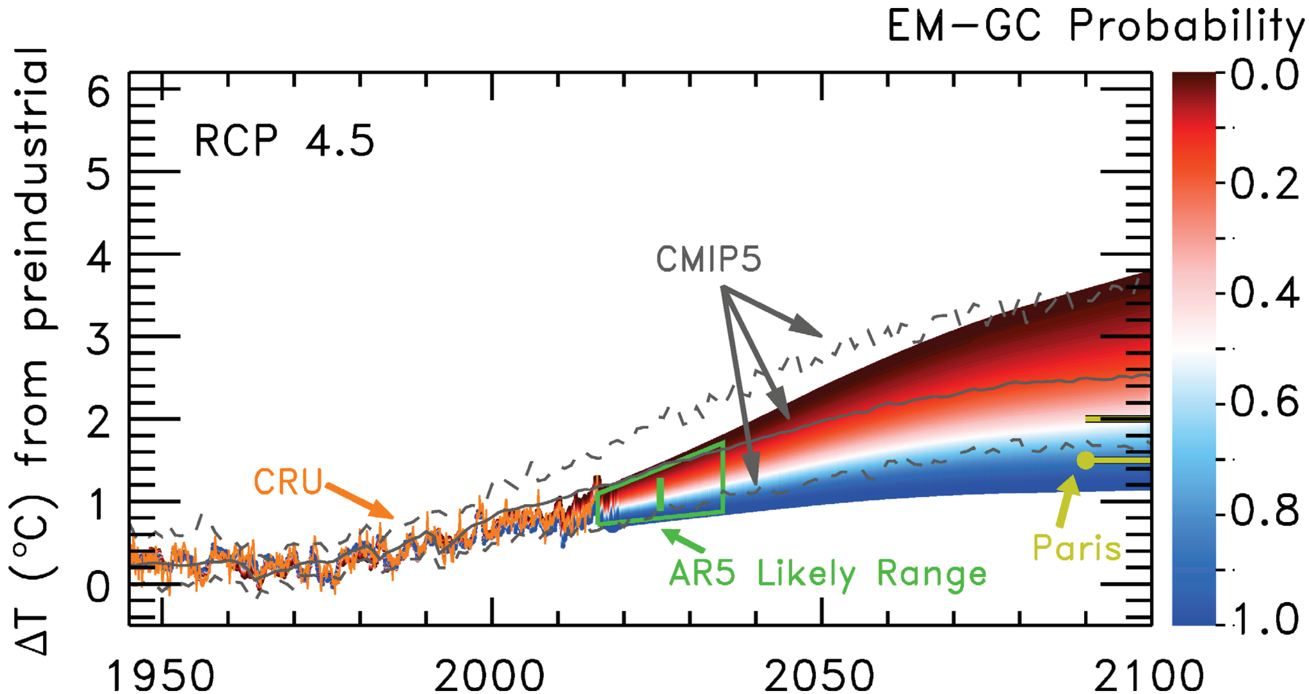
PM Trends





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

Uncertainty of Aerosol RF Effects Future Climate



If GHGs follow RCP 4.5, 10% chance rise GMST stays below 1.5°C and 50% chance stays below 2.0°C

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* than "best estimate"

Lecture 8, Slide 63

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

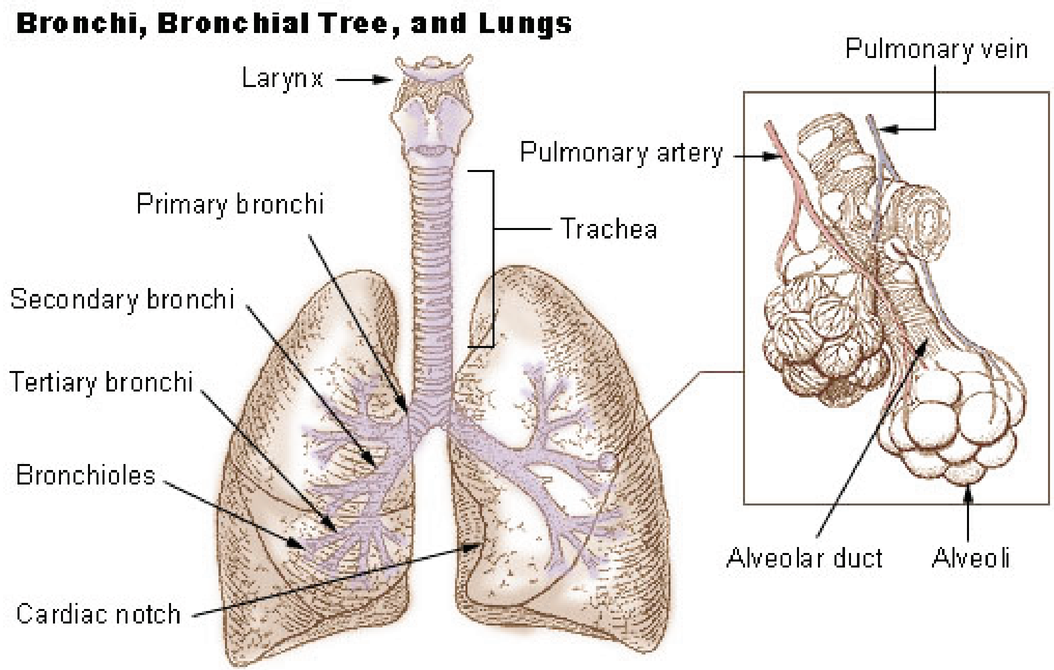
http://www.barnesandnoble.com/w/polycyclic-aromatic-hydrocarbons-pierre-a-haines

- 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

Terminal Velocity as a Function of Particle Diameter

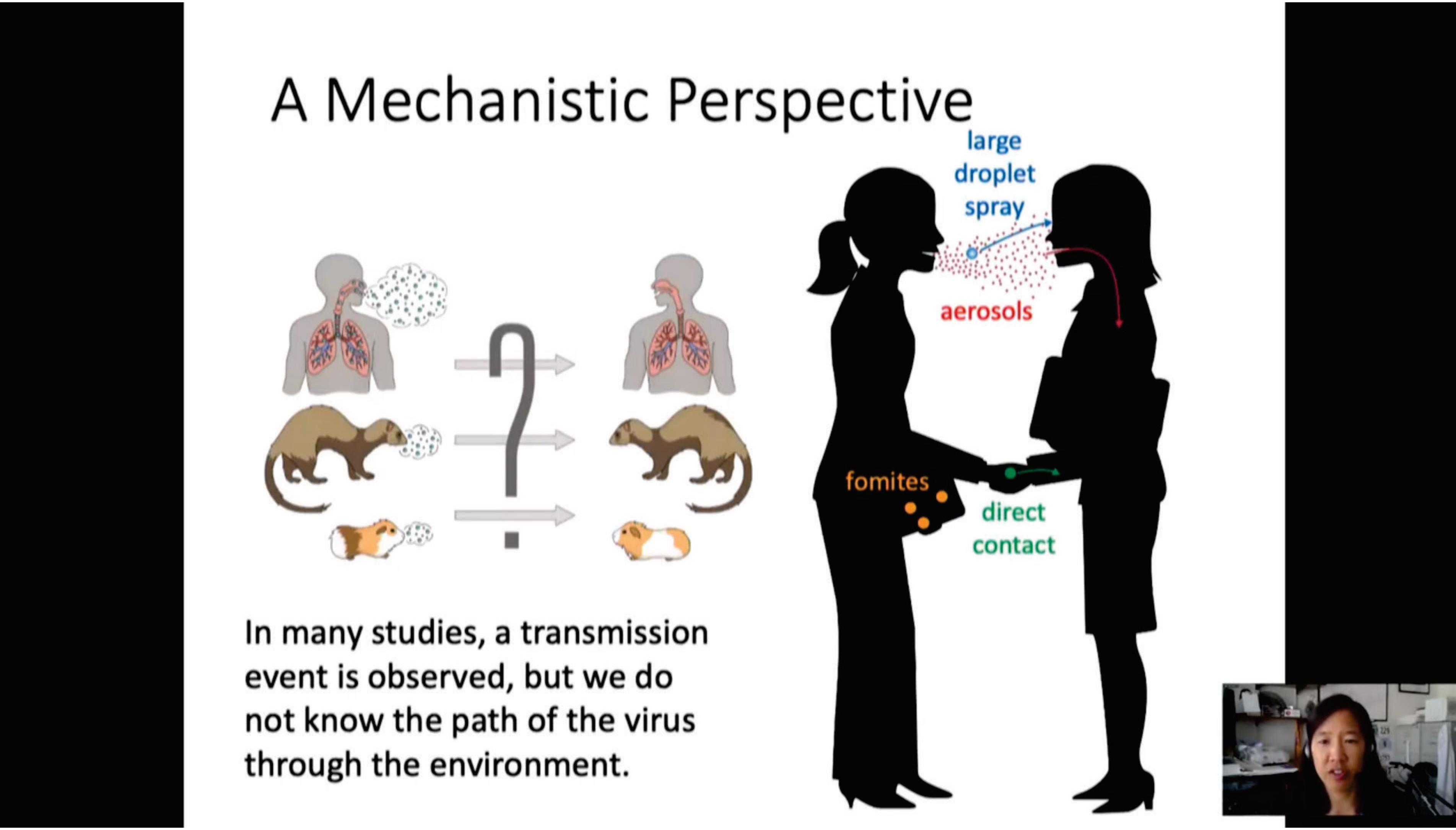
D_p	v_t (cm/s)
100 μm	32
10 μm	0.32
1 μm	0.0032
100 nm	0.000032

← Falls 1 m within ~3 s

- Large droplets deposit pathogens on surfaces (fomites)
- SARS-CoV 2 can survive 9 DAYS on non-porous surfaces
- Inactivated within ~1 minute by
  - Dilute bleach
  - Dilute hydrogen peroxide
  - 62-71% ethanol

Kampf et al. *J. Hosp. Infect.* 2020 **104**(3) 246-251

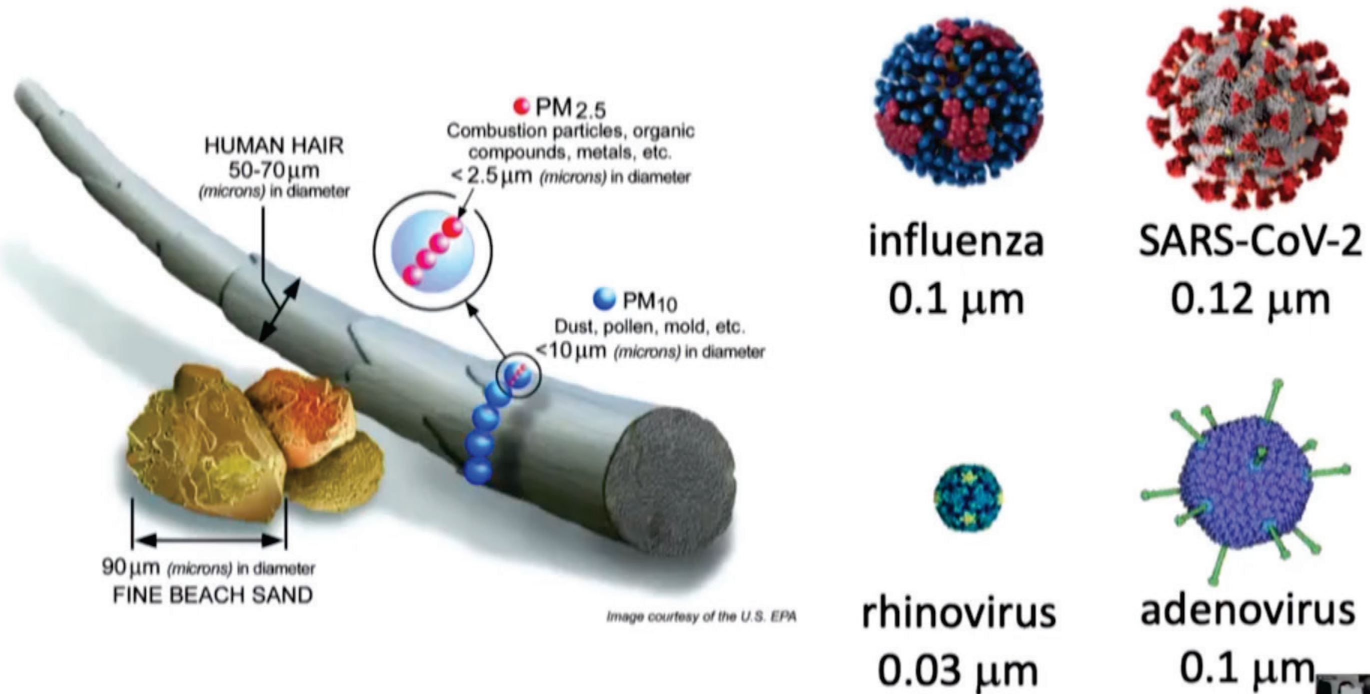
https://www.youtube.com/watch?v=9V9LgdE4W8c



Prof. Linsey Marr, Virginia Tech

https://www.nationalacademies.org/event/08-26-2020/airborne-transmission-of-sars-cov-2-a-virtual-workshop

Virus Size



https://www.cdc.gov/flu/resource-center/freeresources/graphics/images.htm, http://solutionsdesignedforhealthcare.com/rhinovirus, https://phil.cdc.gov/Details.aspx?pid=23312, https://pdb101.rcsb.org/motm/132

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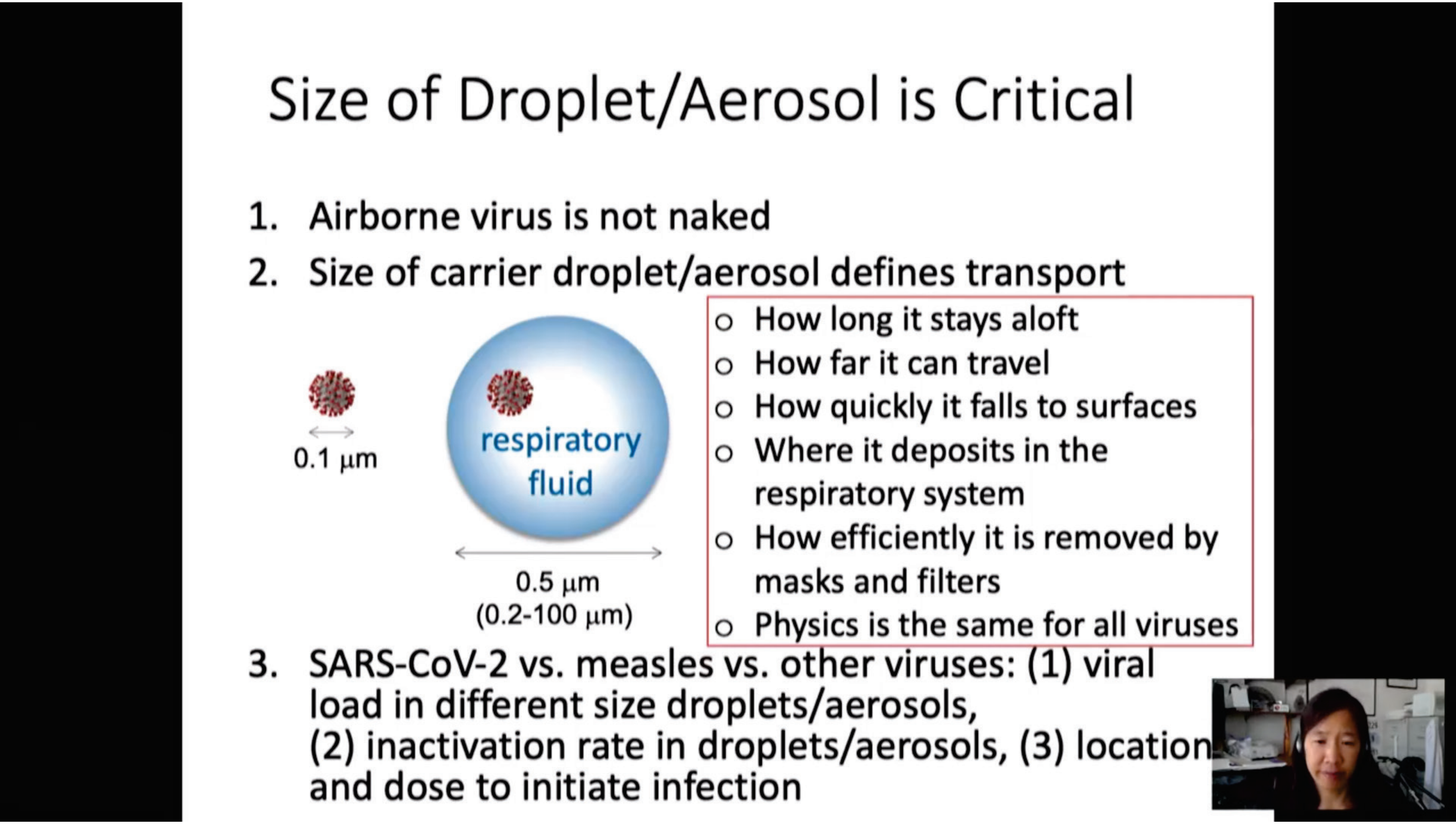

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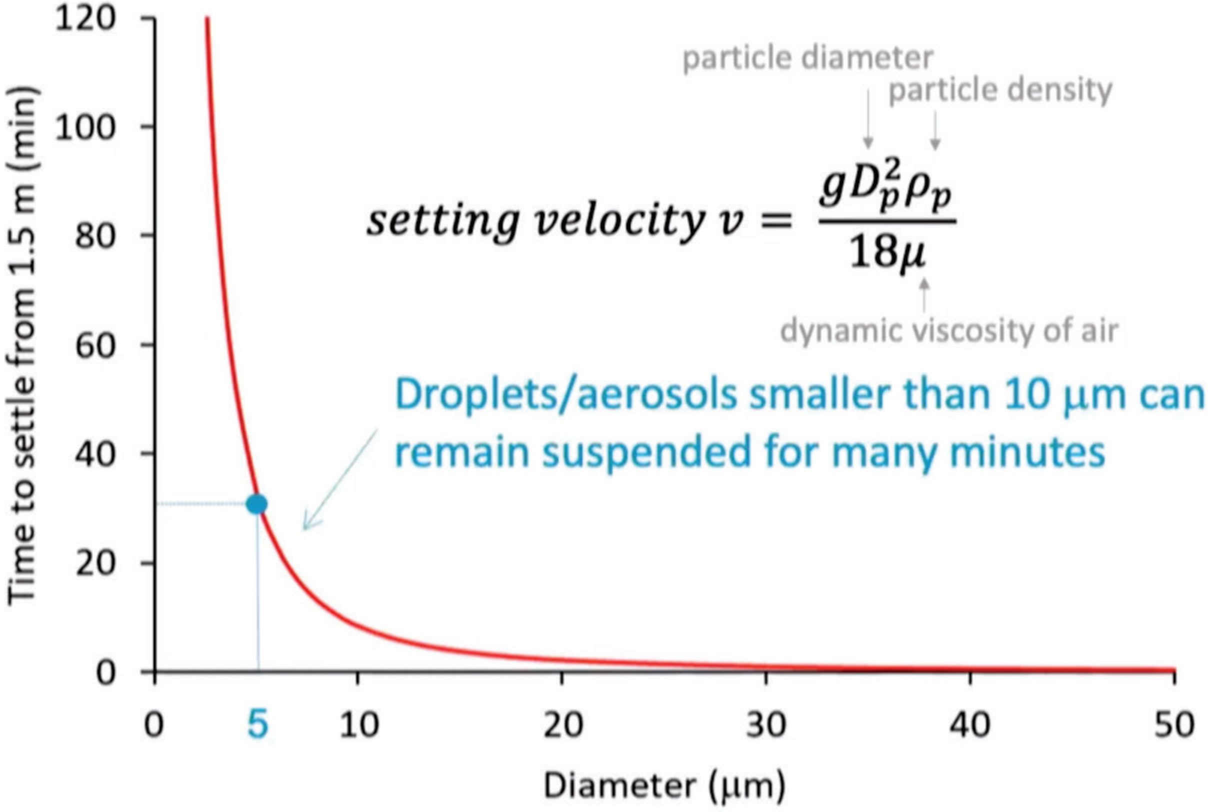
Settling Velocity and Time



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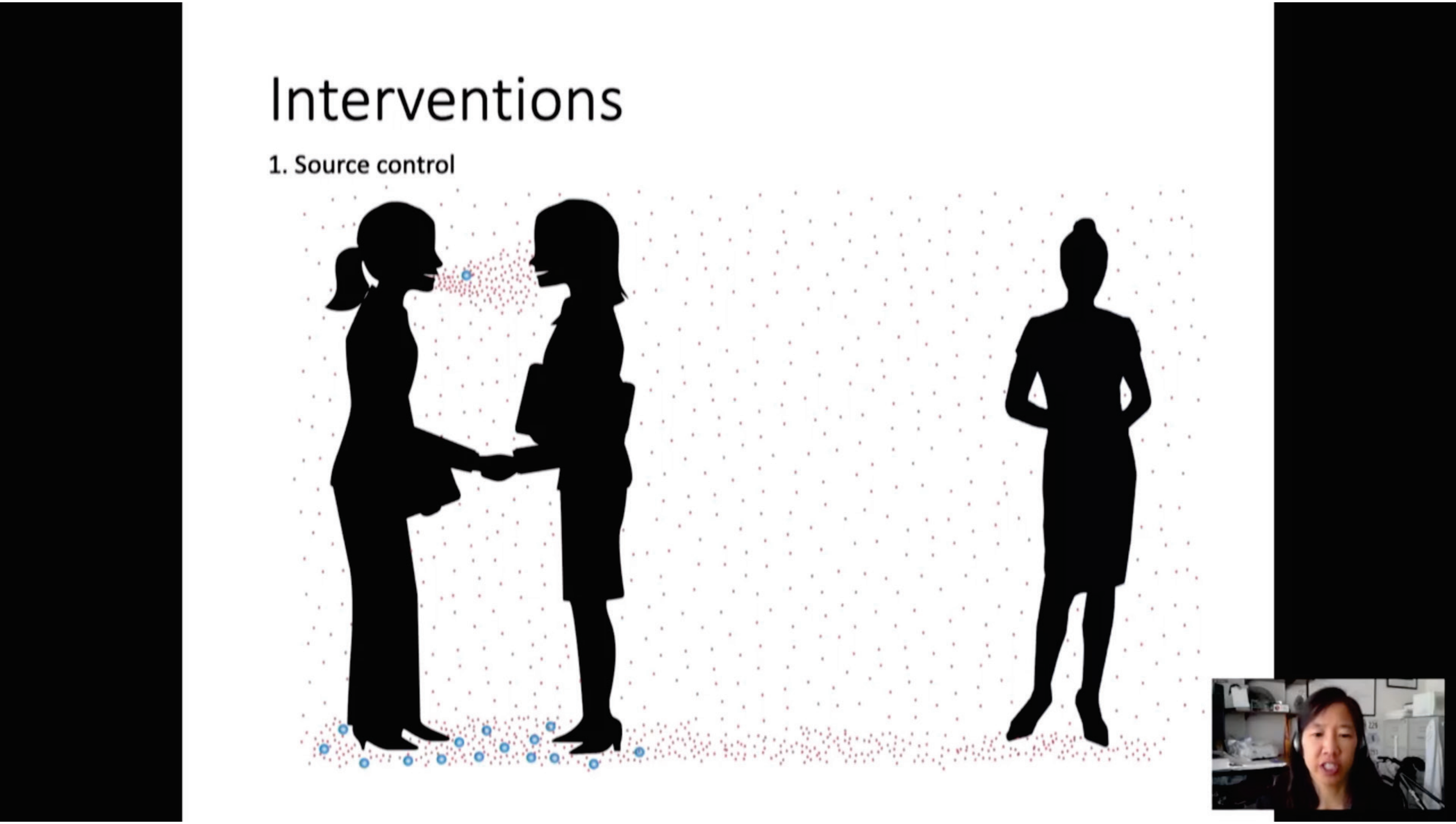

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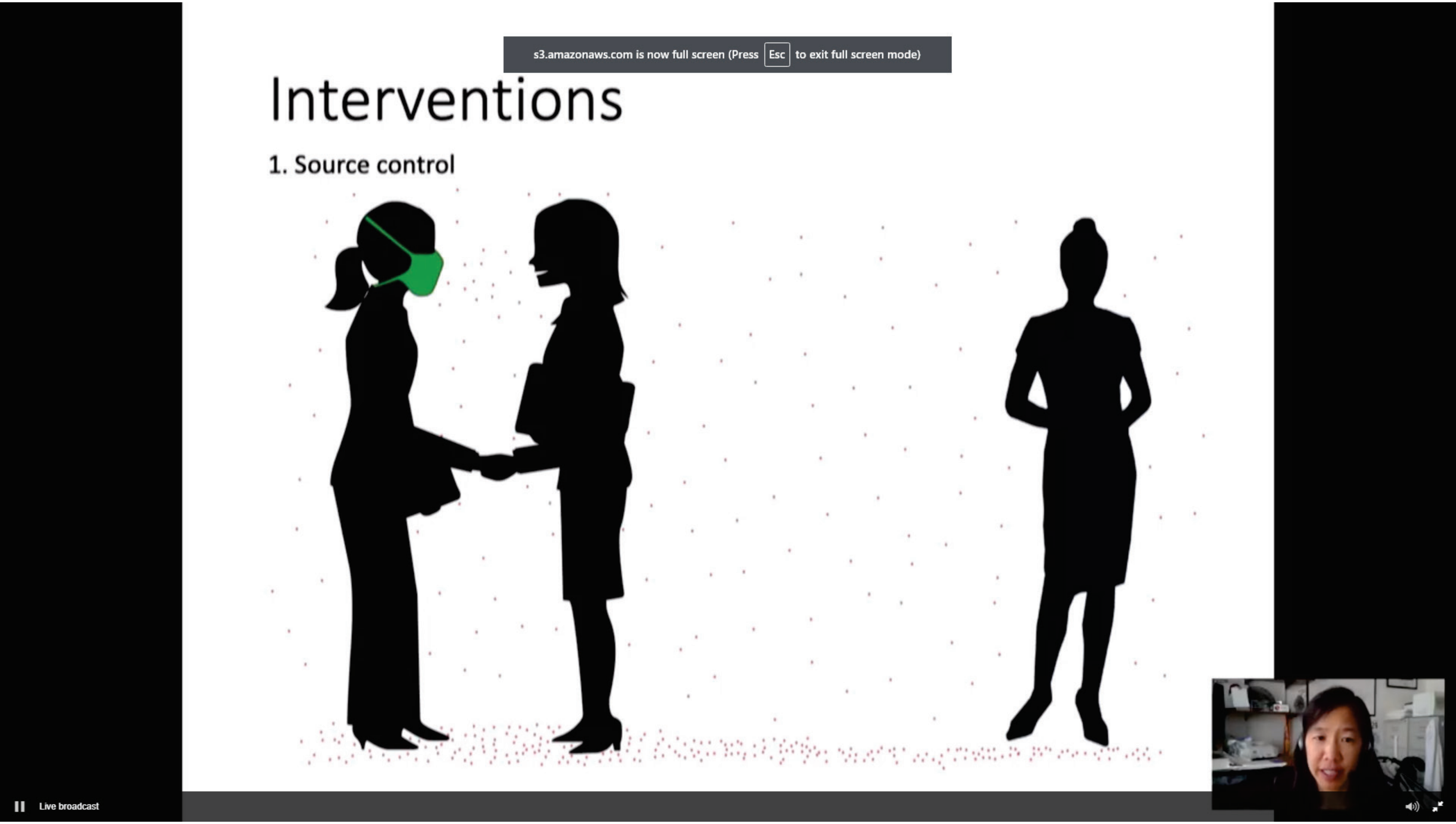

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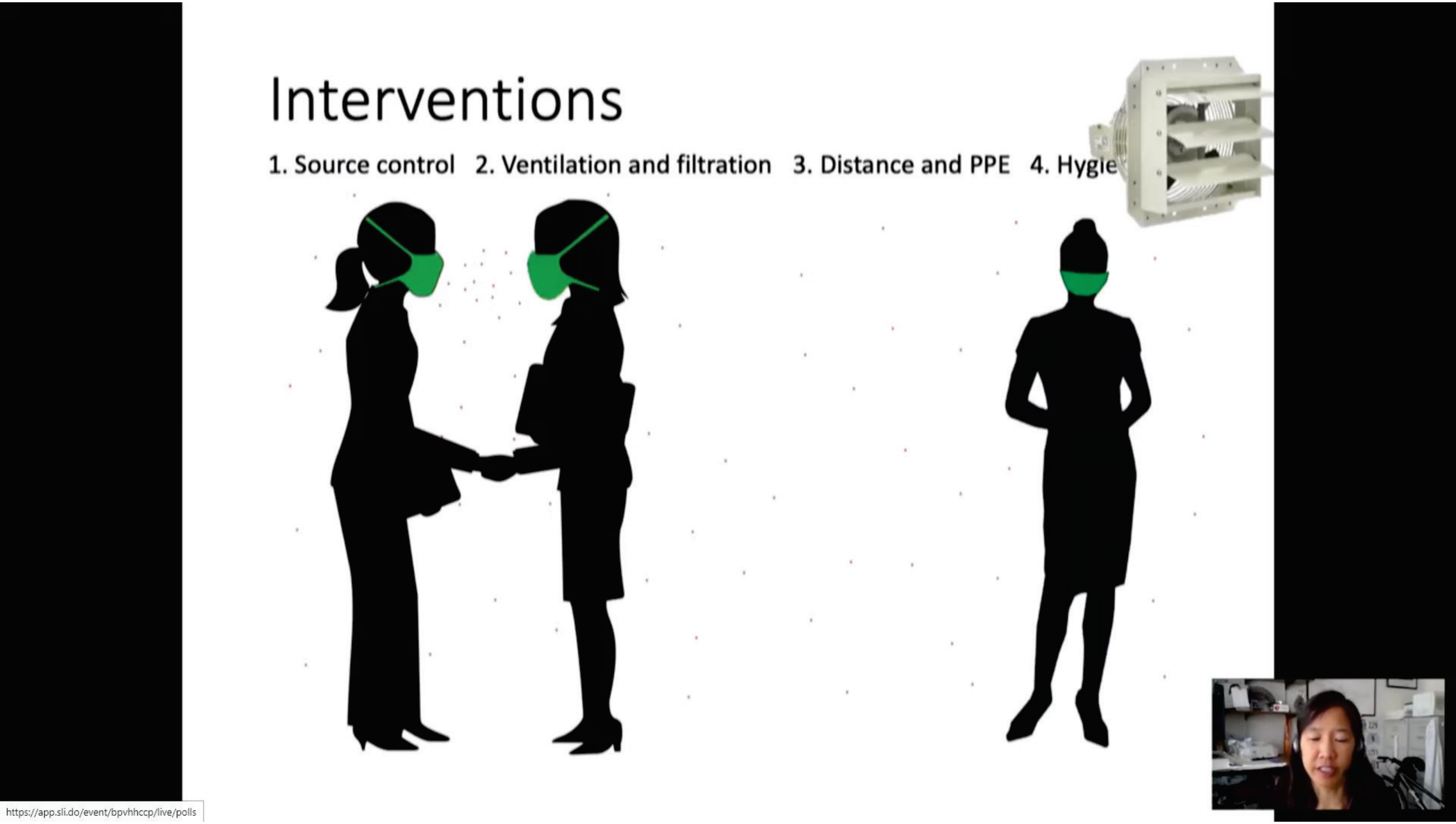

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https://www.nationalacademies.org/event/08-26-2020/airborne-transmission-of-sars-cov-2-a-virtual-workshop

Extra Slide 1

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

NOVA NEXT

HOME | STORYLINES | ARCHIVE | ABOUT

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/

Extra Slide 3

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

Carbon Water Chemistry

Acidity of pure water is 7. This means $[H^+] = 10^{-7}$ moles/liter or 10^{-7} M.

What is acidity of water in equilibrium with atmospheric CO_2 ?

$$[CO_2(aq)] = H_{CO2}\ p_{CO2} = 3.4 \times 10^{-2}\ M / atm\ p_{CO2}$$

For CO_2 = 400 ppm:

$$[CO_2(aq)] = 3.4 \times 10^{-2}\ M / atm \times 4.0 \times 10^{-4}\ atm = 1.36 \times 10^{-5}\ M$$

First equilibrium between CO_2, HCO_3^- (bicarbonate), and H^+

$$CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+$$

$$K_1 = \frac{[HCO_3^-]\,[H^+]}{[CO_2(aq)]} = 4.3 \times 10^{-7}\ M\ \ (at\ 298\ K)$$

Second equilibrium between CO_3^{2-} (carbonate), HCO_3^-, and H^+

$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$$

$$K_2 = \frac{[CO_3^{2-}]\,[H^+]}{[HCO_3^-]} = 4.7 \times 10^{-11}\ M\ \ (at\ 298\ K)$$

Can solve if we assume charge balance: $[H^+] = [HCO_3^-] + 2\,[CO_3^{2-}]$
- or – by taking a short-cut (see next slide)

Carbon Water Chemistry

Acidity of pure water is 7. What is acidity of water in equilibrium with atmospheric CO_2 ?

Shortcut:

$[CO_2(aq)] = 1.36 \times 10^{-5}$ M for present atmosphere

$[H^+]\,[HCO_3^-] = K_1\,[CO_2(aq)] = 4.3 \times 10^{-7}\text{ M} \times 1.36 \times 10^{-5}\text{ M} = 5.85 \times 10^{-12}\text{ M}^2$

Assume charge balance is primarily between $[H^+]$ and $[HCO_3^-]$:

i.e., that $[H^+] \approx [HCO_3^-]$ and that both are >> $[CO_3^{2-}]$

$[H^+]\,[H^+] = 5.85 \times 10^{-12}\text{ M}^2 \Rightarrow [H^+] = 2.418 \times 10^{-6}$ M

$pH = -\log_{10}[H+] = 5.6$ (400 ppm, 298 K)

Is the ***assumption*** justified? :

$[CO_3^{2-}] = K_2\,[HCO_3^-] / [H^+] \approx 4.7 \times 10^{-11}$ M

$[H^+]$ & $[HCO_3^-]$ are both ~ 2.4×10^{-6} M which is >> 4.7×10^{-11} M

Extra Slide 6

Ocean Acidity

As noted in class, the actual ocean is basic. The net charge from a series of **cations** (positively charged ions) and minor **anions** (negatively charged ions) is balanced by the total negative charge of the bicarbonate and carbonate ions. We write:

$$[\mathrm{Alk}] = [\mathrm{HCO_3^-}] + 2\,[\mathrm{CO_3^{2-}}] = [\mathrm{Na^+}]+[\mathrm{K^+}]+2[\mathrm{Mg^{2+}}]+2[\mathrm{Ca^{2+}}]-[\mathrm{Cl^-}]-[\mathrm{Br^-}]-2\,[\mathrm{SO_4^{2-}}] + \ldots$$

where Alk stands for Alkalinity

Henry's Law and the equations for the first and second dissociation constants yield:

$$\mathrm{pCO_2(vmr)} = \frac{[\mathrm{CO_2\,(aq)}]}{\alpha} \qquad \mathrm{K_1} = \frac{[\mathrm{HCO_3^-}]\,[\mathrm{H^+}]}{[\mathrm{CO_2(aq)}]} \qquad \mathrm{K_2} = \frac{[\mathrm{CO_3^{2-}}]\,[\mathrm{H^+}]}{[\mathrm{HCO_3^-}]}$$

The three equations above can be re-arranged to yield: $\mathrm{pCO_2(vmr)} = \left(\frac{\mathrm{K_2}}{\alpha \mathrm{K_1}}\right)\frac{[\mathrm{HCO_3^-}]^2}{[\mathrm{CO_3^{2-}}]}$

If we substitute $[HCO_3^-]$ = Alk – 2 $[CO_3^{2-}]$ into the eqn above, we arrive at a quadratic eqn for $[CO_3^{2-}]$ as a function of pCO_2 and Alk. Note that α, K_1, and K_2 vary as a function of temperature (T) and ocean salinity (S) (http://en.wikipedia.org/wiki/Salinity)

If T, Alk, & S are specified, it is straightforward to solve for $[CO_3^{2-}]$ from the quadratic eqn.

Values for $[CO_2(aq)]$, $[HCO_3^-]$, and [H+] are then found from Henry's law & the dissoc eqns.

Finally, Ocean Carbon is found from $[CO_2(aq)]+[HCO_3^-]+[CO_3^{2-}]$.

Numerical values on the slides entitled "Uptake of Atmospheric CO_2 by Oceans" were found in this manner, using Fortran program http://www.atmos.umd.edu/~rjs/class/code/ocean_carbon.f