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

Tim Canty

Class Web Sites: **http://www.atmos.umd.edu/~rjs/class/spr2013/**

Goals for today:

- **Acid rain: sources and problems**
- **Aerosols:**
  - **Physical processes**
  - **Health problems**

Lecture 13
14 March 2013

History

Mid **1600s** John Evelyn: "Hellish and dismall cloud of sea-coale."

1948 Donora, PA – four-day episode, 20 deaths, 6000 people ill

1952 London – weeklong episode, 4000 excess deaths.
Re-analysis- month long episode, 12,000 deaths.

"The fog was thicker on that Friday morning than many people could ever remember. Through the day it steadily grew even thicker and people were already experiencing discomfort, and noticing the choking smell in the air…On (Saturday and) Sunday the fog continued and so did the deaths. The emergency services were no longer able to respond in any effective way. It is doubtful that many people perceived the nature of the calamity that had befallen them."
- Peter Brimblecombe, *The Big Smoke*

1956 London – 1000 excess deaths

http://www.nickelinthemachine.com/wordpress/wp-content/uploads/smog-d.jpg

History continued:

Each episode was the result of SO_2 and particulate matter emissions from burning coal.

Air Pollution Control Act (1955) – provided funding for research ($5M/yr for 5 years, later extended)

Clean Air Act (1963) – Sought to control air pollution.

- Amendments in 1965,66,67,and 69: focused on auto emission standards
- Expanded local air pollution control programs
- Authorized research on low emission fuels, encouraged sulfur removal from fuels ($95M/3years)

Clean Air Act (1970) – Initially set unrealistic goals (amended in 1977)

- Set NAAQS to protect public welfare
- New Source Performance Standards (NSPS) regulated new sources
- Standards for hazardous emissions
- Vehicle emission standards

History continued:

Clean Air Act (1990) – Drastically overhauled previous Acts.

- States responsible for attainment. Allowed states to establish deadlines for sources.
- Tightened auto emission standards, introduced reformulated gasoline in 9 cities with worst ozone problem (1995)
- Addressed acid rain (cap and trade system for SO_2)
- CFC's (phased out production by 2000, non-essential use prohibited)
- Reduced the amount of air toxics.

Why is legislation still being passed?

When Clean Air Act first passed, companies argued that controls shouldn't apply to old technology. Too expensive to replace with state of the art facilities. **Congress agreed.** Currently, hundreds of power plants are exempt from emission controls

Present Day

Record Beijing air pollution forces warning from China officials to keep kids indoors – January 14, 2013

"Levels of PM2.5 particle pollution over the weekend reached the highest levels since the Beijing government began publicly releasing figures following a public outcry. In separate monitoring by the U.S. Embassy, **levels were at 886 micrograms per cubic meter** in a reading that was labeled "beyond index."

http://www.cbsnews.com/8301-202_162-57563772/record-beijing-air-pollution-forces-warning-from-china-officials-to-keep-kids-indoors/

NAAQS

"Levels of PM2.5 particle pollution over the weekend reached the highest levels since the Beijing government began publicly releasing figures following a public outcry. In separate monitoring by the U.S. Embassy, **levels were at 886 micrograms per cubic meter** in a reading that was labeled "beyond index."

Table 1.5 National Ambient Air Quality Standards (NAAQS), 1999

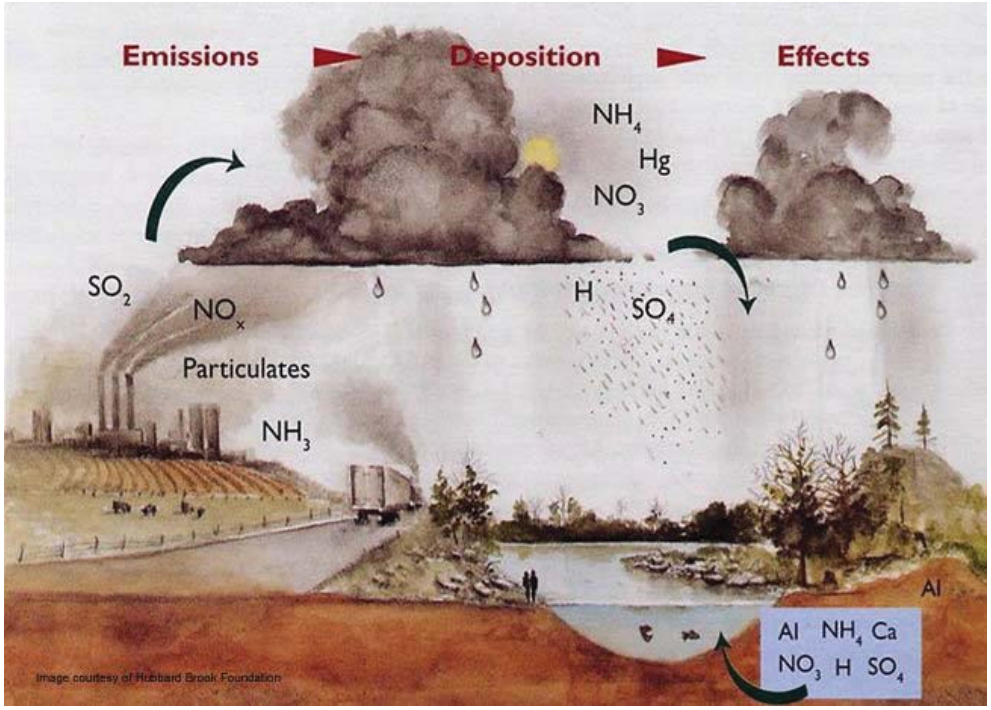
Pollutant	Standard (ppm)	Approximate Equivalent Concentration ($\mu g/m^3$)
Carbon monoxide		
8-hr average	9	1×10^4
1-hr average	35	4×10^4
Nitrogen dioxide		
Annual average	0.053	100
Ozone		
8-hr average	0.08	157
1-hr average	0.12	235
Lead		
Quarterly average	…	1.5
Particulates*		
PM_{10}, annual average	…	50
PM_{10}, 24-hr average	…	150
$PM_{2.5}$, annual average	…	15
$PM_{2.5}$, 24-hr average	…	65
Sulfur dioxide		
Annual average	0.03	80
24-hr average	0.14	365
3-hr average	0.50	1300

… Data not available

*PM_{10} refers to airborne particles 10 μm in diameter or less. $PM_{2.5}$ refers to particles less than 2.5 μm in diameter.

From Chapter 1
Chemistry in Context

Acid Rain



http://www.maine.gov/dep/air/acidrain/images/ARAIN1.jpg

Acid Rain: SO_x Sources

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

Burning sulfur in presence of oxygen leads sulfur dioxide

$$S(s) + O_2(g) \rightarrow SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

SO_2 can also react with O_2 to form sulfur trioxide

$$2SO_2 + O_2 \rightarrow 2SO_3 + H_2O(l) \rightarrow H_2SO_4\ (aq)$$

Followed by the reactions:

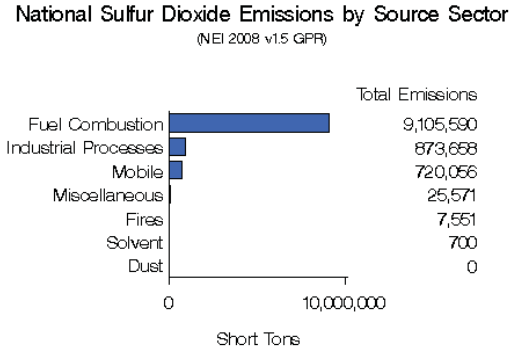
$$H_2SO_3\ (aq) \leftrightarrow H^+ + HSO_3^-$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$$

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

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

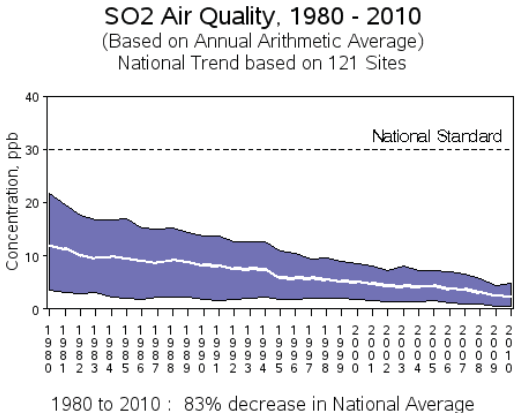
SO_2 Sources



http://www.epa.gov/air/emissions/so2.htm

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

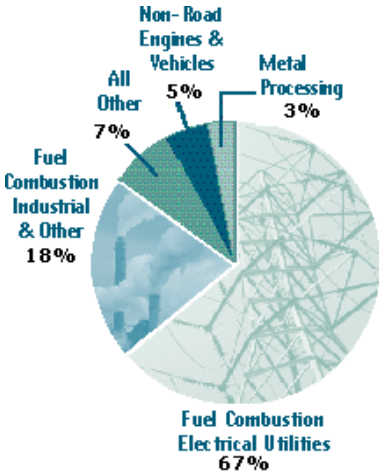
Emissions from transportation are largely unchanged.



http://www.epa.gov/airtrends/sulfur.html#soloc

SO_2 well below national standard (based on observations from ~121 sites)

SO_2 Sources



Since cap and trading program began, sulfur emissions are falling ahead of predictions.

Also, new rail system bringing low sulfur coal from western states

In mid to late 90's, cost of SO_2 allowances were in low $100s. Cheaper for utility to buy allowances

At 2008 auction, prices ~$600. Total auction proceeds ~$66 million. Companies began investing more into scrubbing technology.

http://www.epa.gov/airmarkets/trading/auction.html

2003 congressional report estimates the program cost $1.7 billion/yr but yields as much as $77 billion/yr in benefits including fewer deaths and illnesses

http://www.electricityforum.com/news/mar05/sulfurdioxideallowancescosts.html

Acid Rain: NO_x Sources

NO_x plays major role in ozone formation. How will it affect water?

Nitric acid formed through different processes:

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

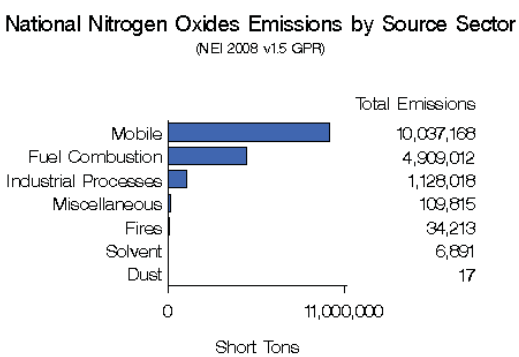
NO_2 can also react in moist air

$$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$$

Nitric acid dissociates in water

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

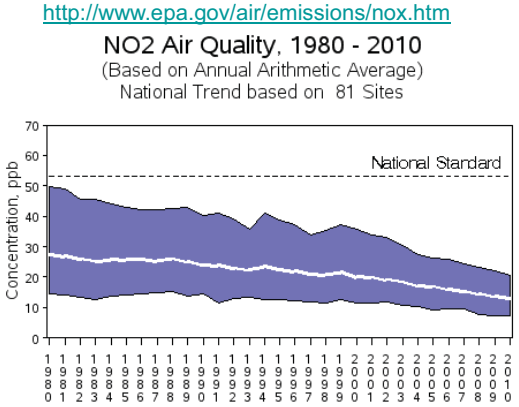
NO_2 Sources



http://www.epa.gov/air/emissions/nox.htm

Primary source of NO_2 is transportation; emissions from transportation sector are largely unchanged though cars are more efficient.

Why?

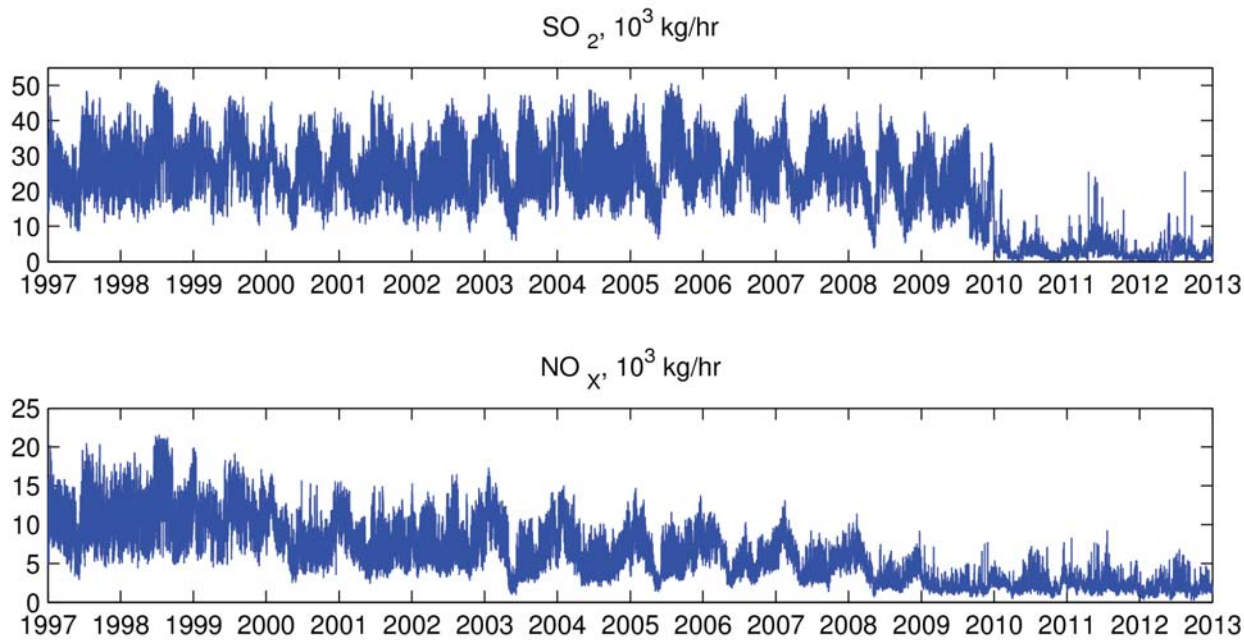


1980 to 2010 : 52% decrease in National Average

NO_2 measured at 80 sites indicates emissions are below the national standard. However, local emissions can still be quite high.

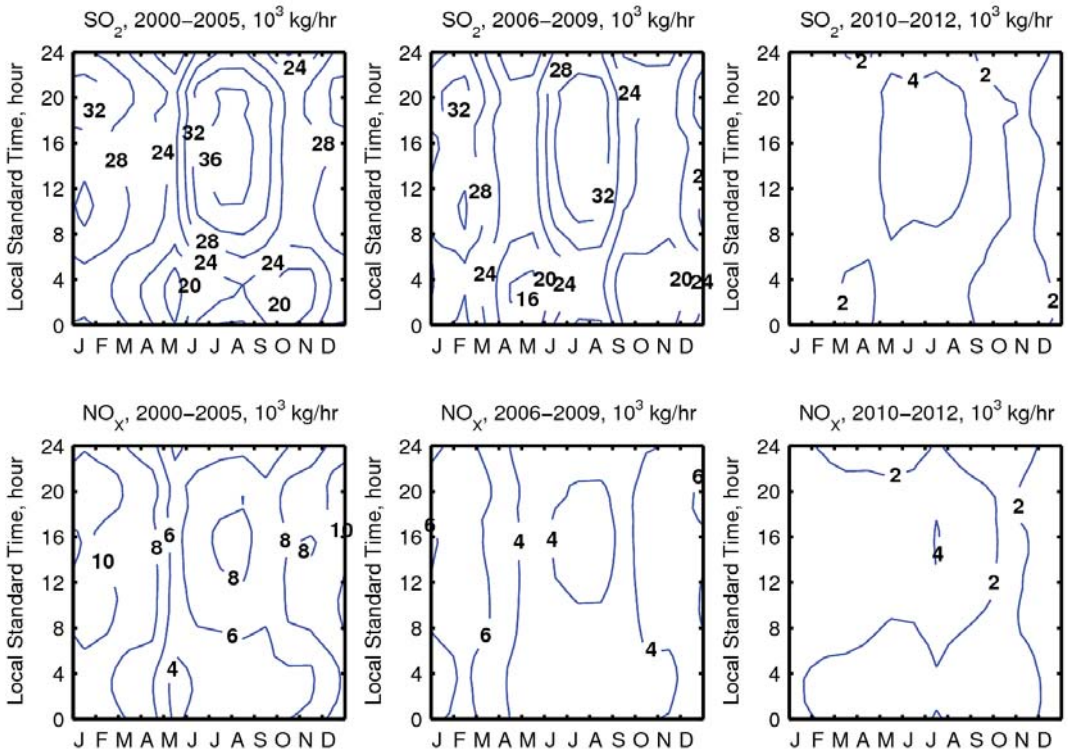
http://www.epa.gov/airtrends/nitrogen.html

Maryland Trends



Courtesy: K. Vinnikov

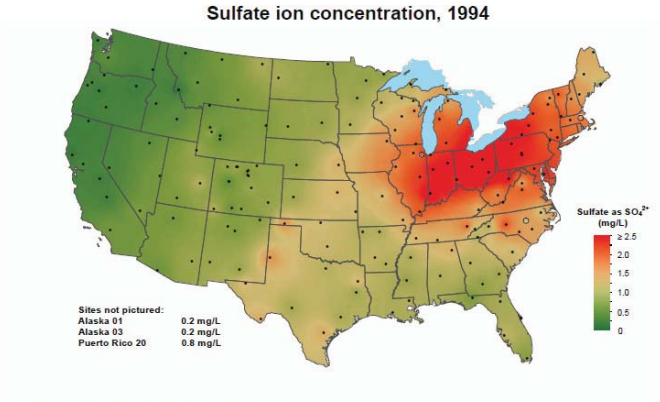
Maryland Trends



Courtesy: K. Vinnikov

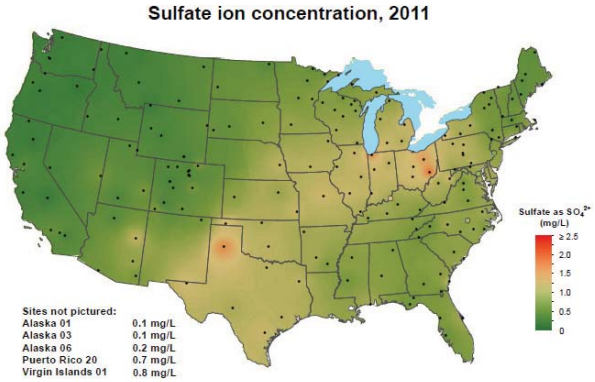
Deposition

1994



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

2009



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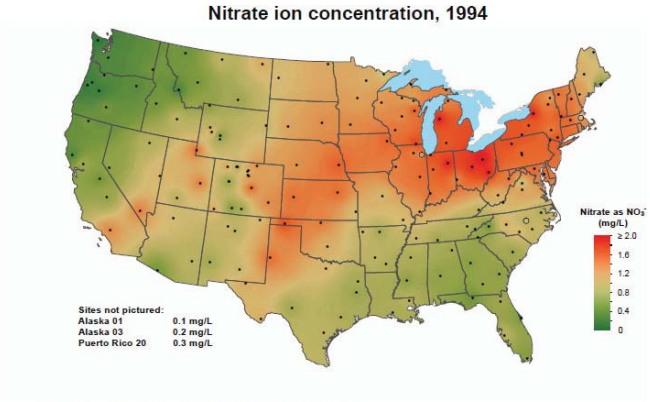
http://nadp.sws.uiuc.edu/

Deposition

1994



National Atmospheric Deposition Program/National Trends Network
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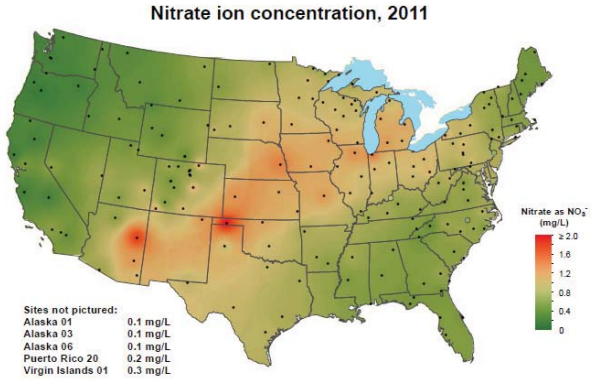
2011



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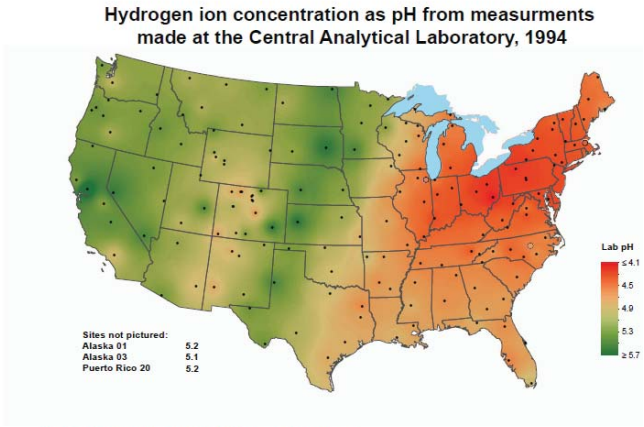
http://nadp.sws.uiuc.edu/

Deposition

1994



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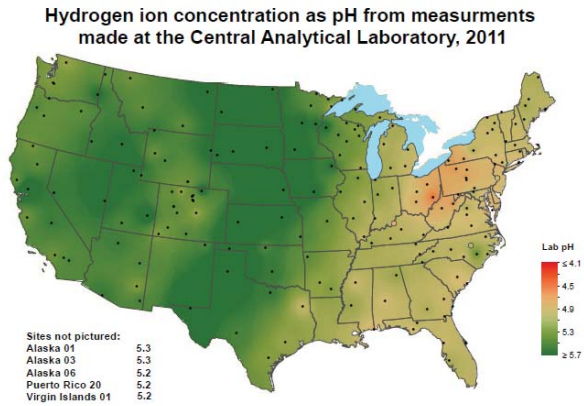
2011



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

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

Acidification

From Lecture 5,

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

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

We're are now adding,

$$HNO_3 \leftrightarrow H^+ + NO_3^-$$

$$H_2SO_3 \leftrightarrow H^+ + HSO_3^-$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$$

$$H_2SO_4 \leftrightarrow H^+ + HSO_4^-$$

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

Acidification can be mitigated by the addition of a buffering agent

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

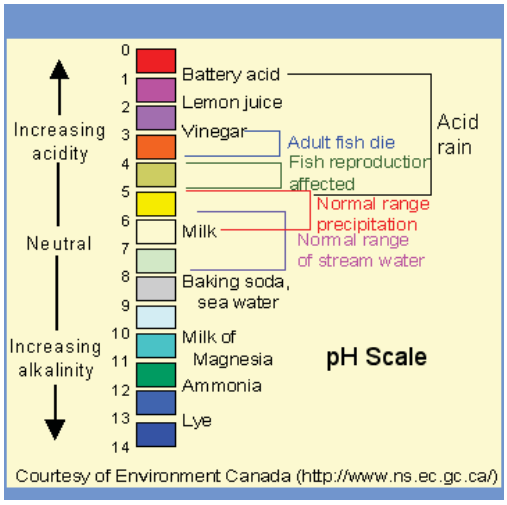
$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O$$

Acidification

Acidic water may fall in the form of rain or remain suspended as a fog. Dry deposition leads to acidification when water interacts with what has been deposited

pH of acid rain has been measured as low as 4.5. pH of acid fog has been measured as low as 2!

In January 1982, the fog at the Rose Bowl in Pasadena had a pH of 2.5.

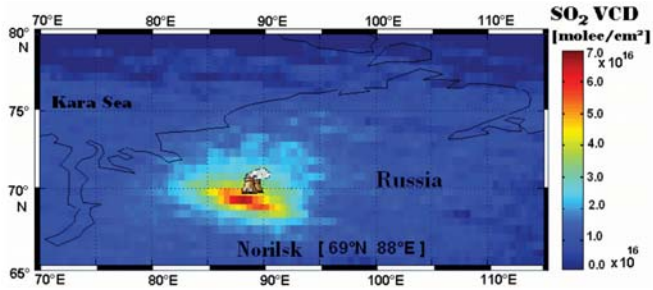


Effects of Acidification

Environmental affects often spoken about more than health affects. Acid deposition over long term (or short term depending on pH) leads to increase in respiratory problems

Industrial complex in Norilsk believed to be worlds largest producer of acid rain.

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



7-year mean (1996–2002) SO_2 vertical column over Norilsk, Russia measured by GOME satellite instrument.

Norilsk copper smelters indicated by smoke-stack symbol

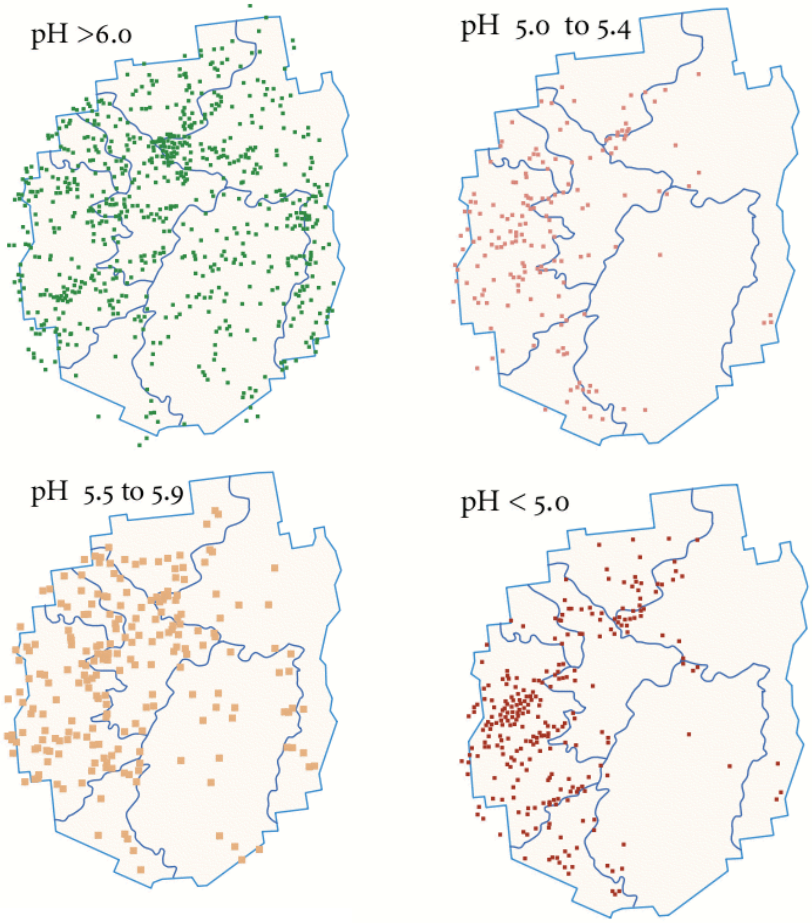
Khokhar *et al.*, *Atmos. Chem. Phys.*, 2008

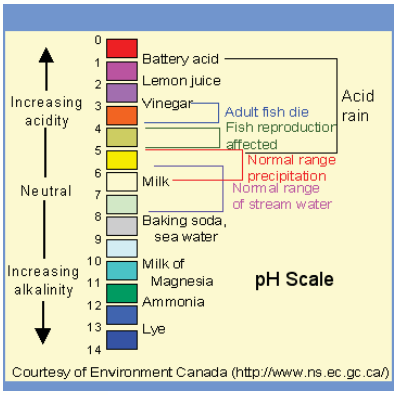
Effects of Acidification

Main cause of crop damage is difficult to determine. Damage may mimic that produced by pathogens, drought, phytotoxicity, or damage from pesticides.

Often, acid rain weakens local flora enough that other stressors (insect, air pollutants, weather, etc.) are able to kill off trees, crops, etc.

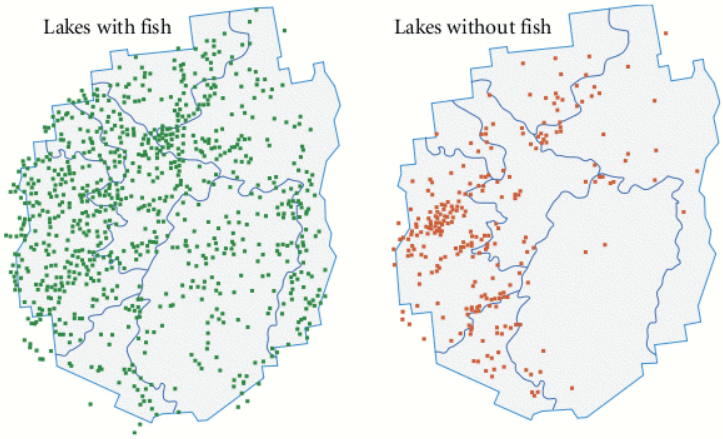
Nelson and Sewake, *Plant Disease*, 2008





Maps from Gallagher and Baker, "Current status of fish communities in Adirondack lakes," in Baker et al., *Adirondack Lakes Survey: An Interpretive Analysis of Fish Communities and Water Chemistry, 1984–1987*, 1990. Circumneutral

Lake Acidification

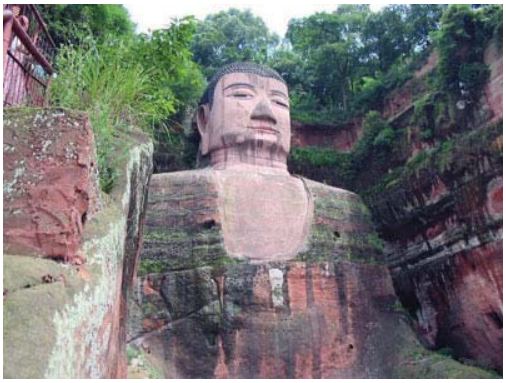


Maps from Gallagher and Baker, "Current status of fish communities in Adirondack lakes," in Baker et al., *Adirondack Lakes Survey: An Interpretive Analysis of Fish Communities and Water Chemistry, 1984–1987*, 1990. Circumneutral

New York's 9,300-square-mile Adirondack Park is the largest American park outside of Alaska. It is larger than Massachusetts. The Adirondack Park has suffered worse damage from acid rain than any other region of the United States. **More than 700 lakes and ponds have become too acidic to support their native aquatic wildlife.** Heritage strains of brook trout have gone extinct. Thousands of acres of high-elevation forests have been killed. Mercury pollution from the same coal-fired power plant smokestacks is poisoning fish, birds and mammals. The Catskill Mountains, Hudson Highlands, Long Island's eastern Pine Barrens and the Finger Lakes are also suffering long-term damage from acid rain. Acid rain damages East Coast ecosystems from the Florida Everglades to the forests of Maine.

http://www.adirondackalmanack.com/2008/07/court-guts-acid-rain-clean-air-rules.html

Cultural Degradation



http://www.china.org.cn/english/photo/231197.htm

The same reactions that buffer lakes destroy statues, monuments, buildings, etc.

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

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O$$

http://www.geocities.com/kamil_pollutionpage/AcidRain.htm

http://www.windows.ucar.edu/tour/link=/milagro/images/property_big_jpg_image.html&edu=elem

Aerosols

Table 1.5 National Ambient Air Quality Standards (NAAQS), 1999

Pollutant	Standard (ppm)	Approximate Equivalent Concentration ($\mu g/m^3$)	Proposed changes
Carbon monoxide			
8-hr average	9	1×10^4	
1-hr average	35	4×10^4	
Nitrogen dioxide			
Annual average	0.053	100	
Ozone			
8-hr average	0.08	157	
1-hr average	0.12	235	
Lead			
Quarterly average	...	1.5	
Particulates*			
PM_{10}, annual average	...	50	NA
PM_{10}, 24-hr average	...	150	70
$PM_{2.5}$, annual average	...	15	15
$PM_{2.5}$, 24-hr average	...	65	35
Sulfur dioxide			
Annual average	0.03	80	
24-hr average	0.14	365	
3-hr average	0.50	1300	

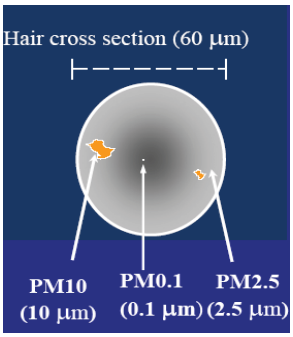
... Data not available

*PM_{10} refers to airborne particles 10 μm in diameter or less. $PM_{2.5}$ refers to particles less than 2.5 μm in diameter.

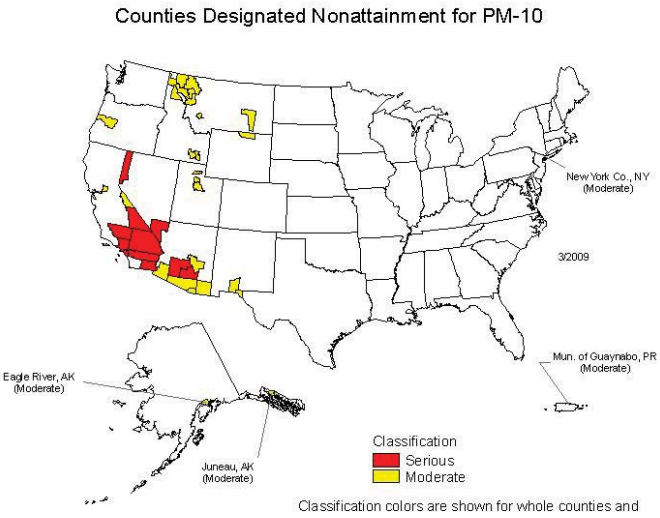
This will be a new category "PM10-2.5"

From Chapter 1
Chemistry in Context

Aerosol Size (PM10)



http://www.epa.gov/oar/oaqps/greenbk/mappm10.html



Original NAAQS did not take into account particle size. Larger particles may dominate mass per volume but smaller particles can be more harmful to human health.

PM10 standard introduced in 1987. Emissions tracked by the EPA are associated with:

Fuel combustion	**45%**
Industrial Processing	**33%**
Transportation	**22%**

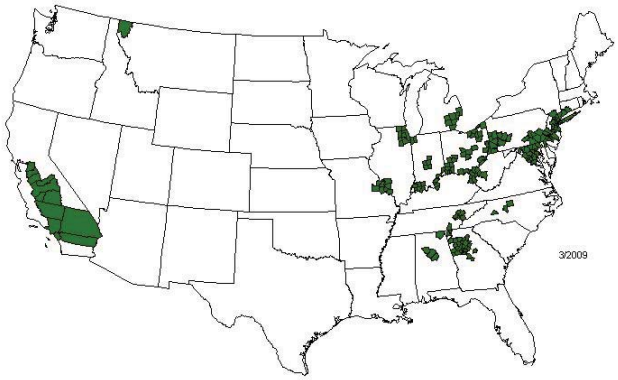
Regions of the country that do not meet standards are primarily in the southwest.

Aerosol Size (PM2.5)

http://airnow.gov/

http://www.epa.gov/oar/oaqps/greenbk/mappm25.html

Counties Designated Nonattainment for PM-2.5



Partial Counties are shown as whole counties

Original NAAQS did not take into account particle size. Larger particles may dominate mass per volume but are not that important to human health.

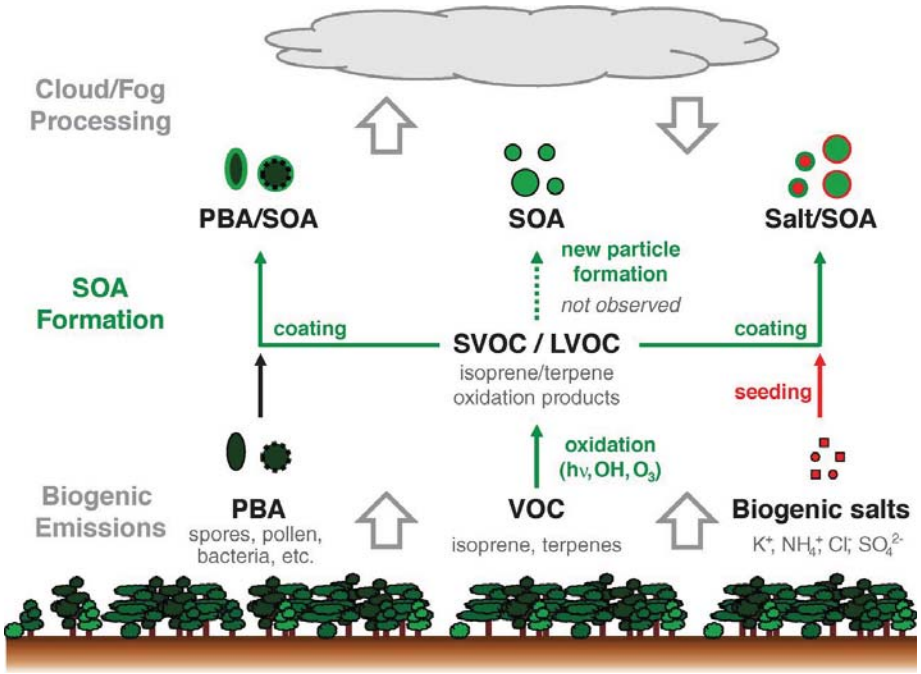
PM2.5 standard introduced in 1997. Hard to attribute sources – formation may occur through gas phase reactions

$$HNO_3\,(g) + NH_3\,(g) \rightarrow NH_4NO_3\,(s)$$

Regions of the country that do not meet standards are primarily in the southwest and throughout the east.

Secondary Organic Aerosol

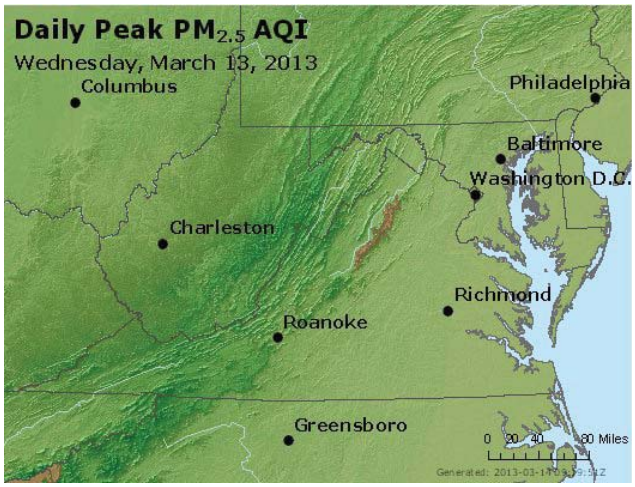
Produced from a variety of sources, difficult to quantify

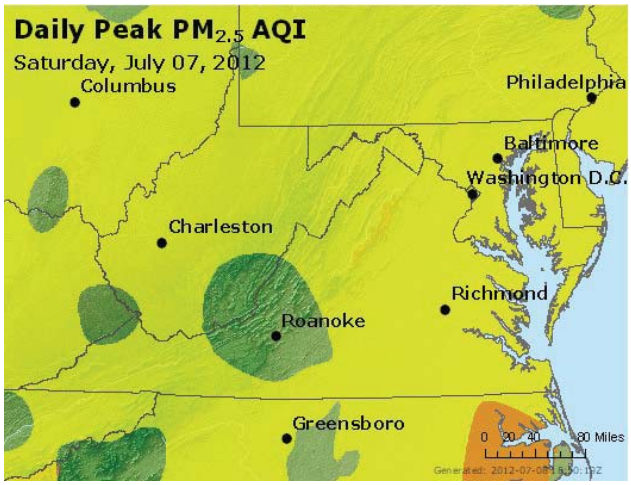


Pöhlker et al., Science 2012

Aerosol Size (PM2.5)

Yesterday… not bad



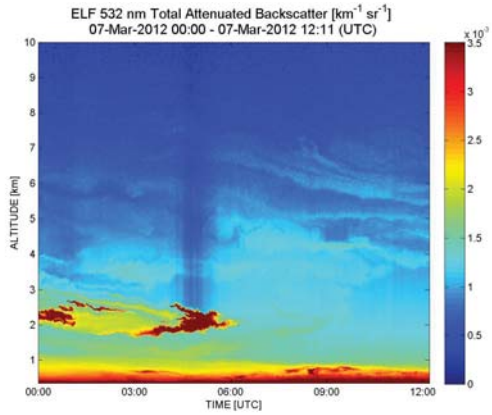


Not always this clean!

http://airnow.gov/

Aerosol Observations – Ground Based

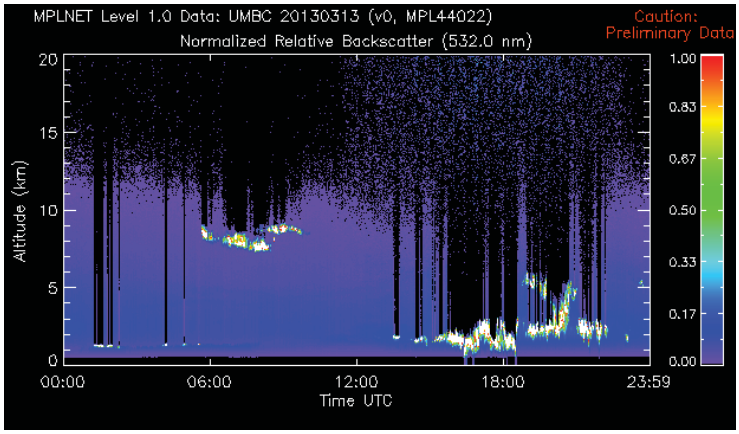
Elastic Lidar Facility (ELF)



http://alg.umbc.edu/umap/elf_index.html

Lidar (Light Detection and Ranging): Measures backscattered light emitted from laser source. Can measure cloud, aerosol optical properties.

Micro-pulse Lidar Network (MPLNET)

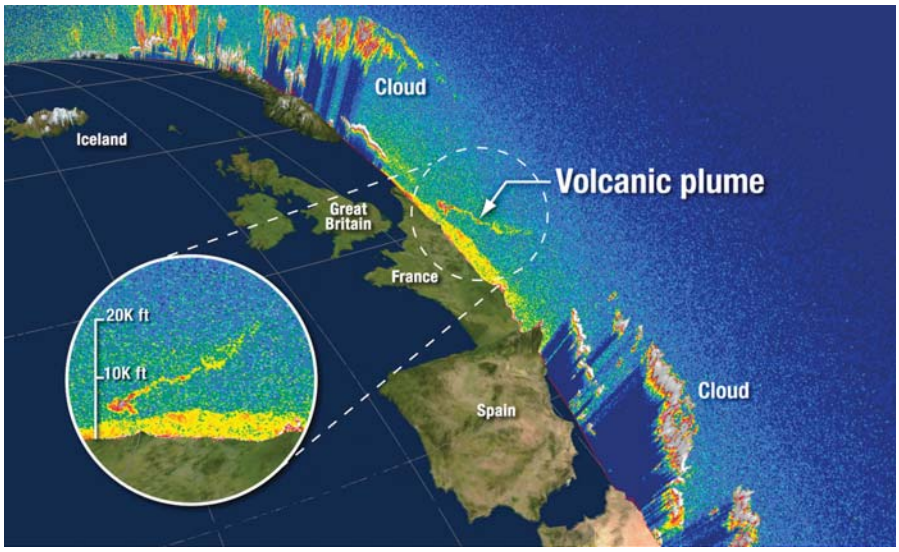


Observations from 2 different Lidar instruments over UMBC

http://mplnet.gsfc.nasa.gov/cgibin/Mplnet/site_page_direct.cgi/site=UMBC

Aerosol Observations – Satellite

Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO)



April 17, 2010, CALIPSO captured this image of the Eyjafjallajökull ash cloud.

http://eosweb.larc.nasa.gov/PRODOCS/calipso/featured_imagery/iceland_volcano_ash_cloud.html

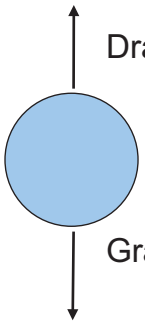
Aerosol Removal – Dry Deposition

Diffusion—Brownian motion applies to particles. Inversely proportional to diameter, D_p or D_p^2 (i.e. smaller the particle, faster the removal rate).

Diffusion completely negligible for particles larger than ~10μm

Gravitational Settling—speed of removal proportional to $D_p^2 \times m$; most important for larger particles, negligible for 0.01μm particles.

Rate at which particles settle due to gravity is derived by balancing gravitational pull with frictional drag force provided by air



Drag force=$3\pi\eta vd$

Gravitational force =$mg=\pi d^3\rho g/6$

d = diameter
g = gravitational acceleration
v = settling velocity
ρ = density
m= mass
η = viscosity of air

Aerosol Removal – Dry Deposition

Diffusion—Brownian motion applies to particles. Inversely proportional to diameter, D_p or D_p^2 (i.e. smaller the particle, faster the removal rate).

Diffusion completely negligible for particles larger than ~10μm

Gravitational Settling—speed of removal proportional to $D_p^2 \times m$; most important for larger particles, negligible for 0.01μm particles.

Deposition Velocity

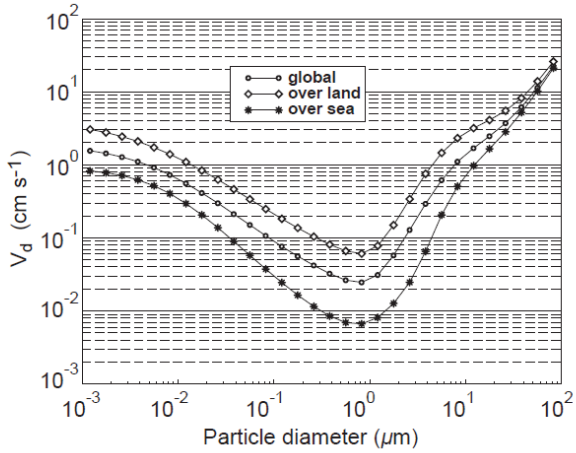


Fig. 1. Annual mean deposition velocities by particle size and surface type (particle density 1000 kg m^{-3}).

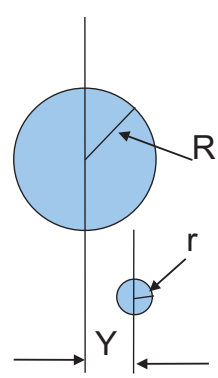
Nho-Kim et al., 2004

Aerosol Removal – Wet Deposition

Rainout—aerosols act as condensation surfaces (Cloud Condensation Nuclei). If enough water collects and forms a drop, drop will fall carrying any aerosols with it

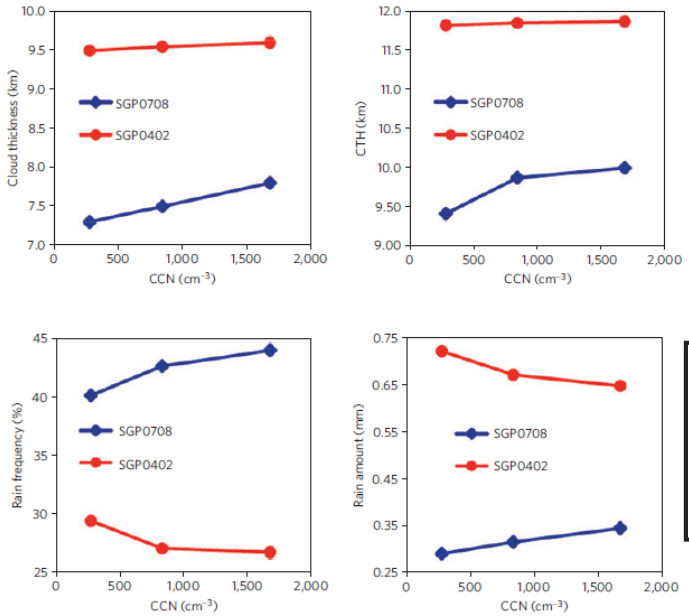
Washout—aerosols incorporated into a water droplet. Note: different from rainout because water drop already exists. If droplet grows large enough, it will fall carrying any aerosols with it

Sweepout— if there is an aerosol in the way of a falling drop, it can be incorporated into the drop and be deposited



Collision efficiency= $Y^2/(R+r)^2$

Aerosol and Weather

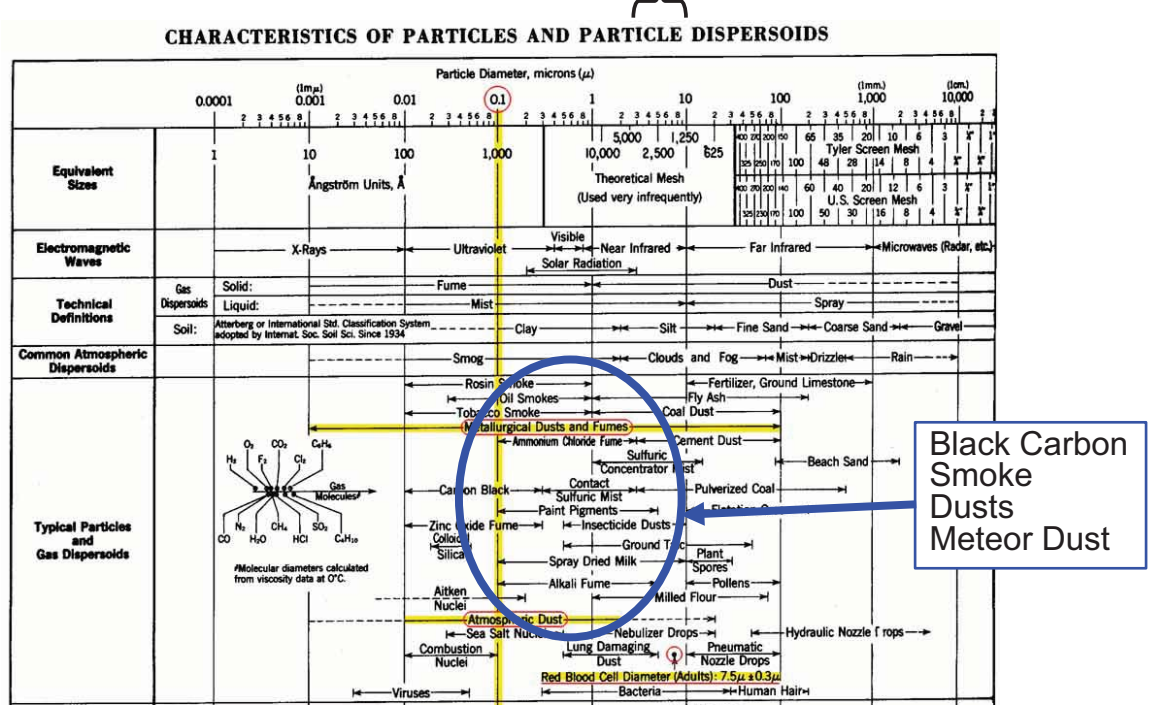


Li *et al., Nature*, 2011: 10 year study of clouds and aerosols over Southern Great Plains, US. In summer, ↑ aerosol correlated with ↑ cloud height and rainfall.

A strong aerosol invigoration effect on convection is observed in summer, leading to higher cloud tops for mixed-phase clouds with low bases. The precipitation frequency is found to increase with increasing concentration of condensation nuclei for clouds with high water contents but decreases for clouds with low water contents. The findings concerning the effects of aerosols on both clouds and precipitation have numerous implications for climate studies, and even have economic consequences.

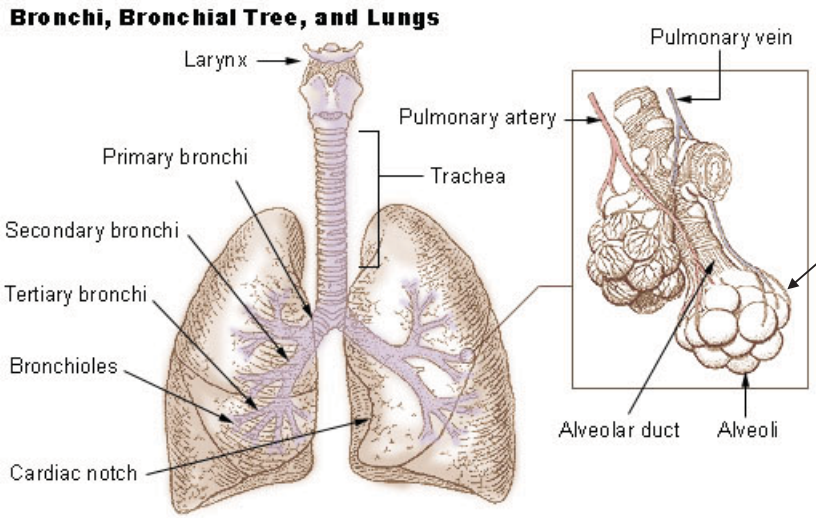
Characteristics of Particles

PM2.5 < Particle Size < PM10



C.E. Lapple, Stanford Research Institute Journal v.5, p.95 (Third Quarter, 1961)
http://www.mindfully.org/Nucs/Particle-Dispersoids-TableSep61.htm

Health Affects of Aerosols



Alveoli radius ≈ 0.05-0.1 mm

PM10 may fill alveola

PM2.5 can inhibit oxygen exchange within alveola

Leads to increase risk of respiratory illnesses, cardiopulmonary disease, ischemic heart disease, heart attack, etc.

This is without even considering chemical effects

Health Affects of Aerosols

Long-term exposure to air pollution is associated with survival following acute coronary syndrome

Cathryn Tonne and Paul Wilkinson – Feb 19, 2013

Table 4 **Sensitivity of the $PM_{2.5}$ associations with mortality following admission for acute coronary syndrome**

Hazard ratio (95% CI) per 10 μg/m³ $PM_{2.5}$	
Fully adjusted model	
Education in place of income	1.22 (1.06, 1.40)
Employment in place of income	1.20 (1.04, 1.38)
Income with random effect for hospital	1.17 (1.04, 1.33)
Income with time trend using 3 df	1.20 (1.04, 1.38)

"We found that for every 10μg/m³ increase in PM2.5 there was a 20% increase in the death rate. For example, over one year of follow-up after patients had been admitted to hospital with ACS, there would be 20% more deaths among patients exposed to PM2.5 levels of 20 μg/m³, compared to patients exposed to PM2.5 levels of 10μg/m³."

http://eurheartj.oxfordjournals.org/content/early/2013/02/18/eurheartj.ehs480.full

Health Affects of Aerosols

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

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temporally, and increased analysis of PM-related health effects. 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

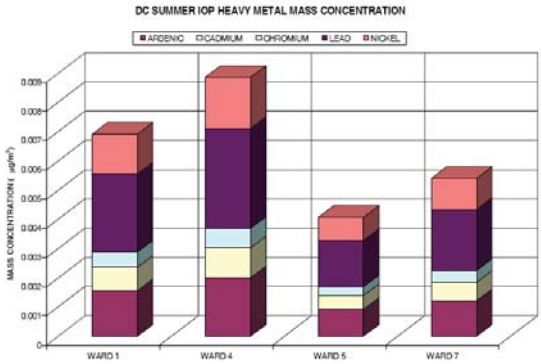

Figure 5: Heavy Metal Content of Fine PM for Summer IOP

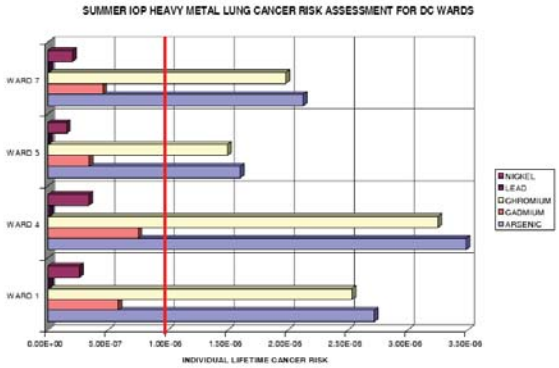

Figure 10: Summer IOP Lifetime Excess Lung Cancer Risk by DC Wards.

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

Overall, the air quality in the United States is getting better.

Much of this is due to the reduction in emissions by industry and utilities. This has been considered by some to be the “low hanging fruit”. More states are taking part in emission control strategies that seem to be working over all.

However, regional air quality in many parts of the country has not shown a great deal of improvement. Attainment of federal standards will be difficult in these areas mainly due to vehicle emissions.

The fact is that even though cars are cleaner, more people are driving.