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
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.
- Expanded local air pollution control programs
- Authorized research on low emission fuels, encouraged sulfur removal from fuels ($95M/3 years)

**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.
- 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."


NAAQS

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Particulates

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Sulfur dioxide

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*PM₁₀ refers to airborne particles 10 µm in diameter or less. PM₂.₅ refers to particles less than 2.5 µm in diameter.

From Chapter 1
Chemistry in Context
Acid Rain: \( \text{SO}_x \) Sources

Chemical formula of coal: \( \text{C}_{135}\text{H}_{96}\text{O}_9\text{NS} \) (\( \text{S} \) varies with coal type)

Burning sulfur in presence of oxygen leads sulfur dioxide

\[
\text{S}(s) + \text{O}_2(g) \rightarrow \text{SO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_3(\text{aq})
\]

\( \text{SO}_2 \) can also react with \( \text{O}_2 \) to form sulfur trioxide

\[
2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4 (\text{aq})
\]

Followed by the reactions:

\[
\text{H}_2\text{SO}_3 (\text{aq}) \leftrightarrow \text{H}^+ + \text{HSO}_3^{-}
\]

\[
\text{HSO}_3^- \leftrightarrow \text{H}^+ + \text{SO}_3^{2-}
\]

\[
\text{H}_2\text{SO}_4 (\text{aq}) \leftrightarrow \text{H}^+ + \text{HSO}_4^- 
\]

\[
\text{HSO}_4^- \leftrightarrow \text{H}^+ + \text{SO}_4^{2-}
\]
**SO₂ Sources**

Primary source of SO₂ is fuel combustion; emissions from this sector are decreasing.

Emissions from transportation are largely unchanged.

SO₂ well below national standard (based on observations from ~121 sites)

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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 SO₂ 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.

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
Acid Rain: NO\textsubscript{x} Sources

NO\textsubscript{x} plays major role in ozone formation. How will it affect water?

Nitric acid formed through different processes:

\[ \text{NO}_2(g) + \text{OH}(g) \rightarrow \text{HNO}_3(l) \]

NO\textsubscript{2} can also react in moist air

\[ 4\text{NO}_2(g) + 2\text{H}_2\text{O}(l) + \text{O}_2(g) \rightarrow 4\text{HNO}_3(aq) \]

Nitric acid dissociates in water

\[ \text{HNO}_3(aq) \leftrightarrow \text{H}^+ + \text{NO}_3^- \]

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NO\textsubscript{2} Sources

Primary source of NO\textsubscript{2} is transportation; emissions from transportation sector are largely unchanged though cars are more efficient.

Why?

NO\textsubscript{2} measured at 80 sites indicates emissions are below the national standard. However, local emissions can still be quite high.
Maryland Trends

SO₂, 10³ kg/hr

NOₓ, 10³ kg/hr

Courtesy: K. Vinnikov
Acidification

From Lecture 5,

\[ \text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]
\[ \text{H}^+ + \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^- \]

We’re are now adding,

\[ \text{HNO}_3 \leftrightarrow \text{H}^+ + \text{NO}_3^- \]
\[ \text{H}_2\text{SO}_3 \leftrightarrow \text{H}^+ + \text{HSO}_3^- \]
\[ \text{HSO}_3^- \leftrightarrow \text{H}^+ + \text{SO}_3^{2-} \]
\[ \text{H}_2\text{SO}_4 \leftrightarrow \text{H}^+ + \text{HSO}_4^- \]
\[ \text{HSO}_4^- \leftrightarrow \text{H}^+ + \text{SO}_4^{2-} \]

Acidification can be mitigated by the addition of a buffering agent

\[ \text{H}^+ + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \]
\[ \text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]
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) SO₂ 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.


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.


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**Cultural Degradation**

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

\[
\begin{align*}
H^+ + CaCO_3 & \rightarrow Ca^{2+} + HCO_3^- \\
HCO_3^- + H^+ & \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O
\end{align*}
\]

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

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

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

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Proposed changes

This will be a new category "PM10-2.5"

From Chapter 1
Chemistry in Context

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.

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

Counties Designated Nonattainment for PM-10

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

\[
\text{HNO}_3 (g) + \text{NH}_3 (g) \rightarrow \text{NH}_4\text{NO}_3 (s)
\]

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.
Aerosol Size (PM2.5)

Yesterday… not bad

http://airnow.gov/

Aerosol Observations – Ground Based

Elastic Lidar Facility (ELF)


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

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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 $\sim 10\mu m$

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

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

\[
\text{Drag force} = 3\pi \eta v_d \\
\text{Gravitational force} = mg = \pi d^3 \rho g / 6
\]

\[
d = \text{diameter} \\
g = \text{gravitational acceleration} \\
v = \text{settling velocity} \\
\rho = \text{density} \\
m = \text{mass} \\
\eta = \text{viscosity of air}
\]
Aerosol Removal – Dry Deposition

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![Deposition Velocity](image)

**Figure 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.

\[
\text{Collision efficiency} = \frac{Y^2}{(R+r)^2}
\]
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

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

Cathryn Tonne and Paul Wilkinson – Feb 19, 2013

"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
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.