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

Ross Salawitch

Class Web Sites: http://www.atmos.umd.edu/~rjs/class/spr2015

Lecture 13
26 March 2015
Overview of Aerosols

- Aerosols aka particulate matter (PM)
- Size generally ranges from 0.005 \( \mu \text{m} \) to 100 \( \mu \text{m} \) diameter
- Can be liquid or solid
- Dust: solid, produced by grinding or crushing operation
- Fumes: formed by condensation of gases
- Smoke or soot: carbon particles resulting from incomplete combustion
- SOA: secondary organic aerosol, formed by condensation of decomposition products of VOCs (volatile organic compounds) including isoprene (\( \text{C}_5\text{H}_8 \)) which is mainly biogenic and benzene (\( \text{C}_6\text{H}_6 \)) 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 \( \text{SO}_2 \), \( \text{NO}_x \), and \( \text{NH}_3 \)

  Eastern US: sulfates dominate due to greater reliance on coal-fired power plants
  Western US: carbon and nitrates dominate due to agriculture & transportation
Overview of Aerosols

• Health effects driven by size and chemical composition
• Smaller particles most hazardous
• Benzene-like compounds called polycyclic aromatic hydrocarbons (PAH) most hazardous

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

• Fall speed of aerosols varies as \((\text{diameter})^2\)
  
  2 \(\mu\)m diameter particle has residence time in 1 km of atmosphere of 2 months, if removed by only gravitational settling
  
  \(\Rightarrow\) small particles are suspended in the atmosphere until removed by _____ ?
Air pollution — even for just one day — significantly increases the risk of stroke, a large review of studies has found.

Researchers pooled data from 123 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

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 Aerosols

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

PM10 may fill alveola
PM2.5 can inhibit oxygen exchange within alveola

Alveoli radius ≈ 50 to 100 µm
Health Effects of Aerosols
Assessment of Public Health Risks Associated with Atmospheric Exposure to PM$_{2.5}$ in Washington, DC, USA

Natasha A. Greene$^{1}$, and Vernon R. Morris$^{1,2}$

$^1$Program in Atmospheric Sciences, Howard University, Washington, DC 20059, USA
$^2$Department of Chemistry, Howard University, Washington, DC 20059, USA

Our findings show that there are significant risks of ward-specific pediatric asthma emergency room visits (ERV). Results also illustrate lifetime excess lung cancer risks, exceeding the 1x10$^{-6}$ threshold for the measured levels of particulate matter and heavy metals (chromium and arsenic) on behalf of numerous subpopulations in the DC selected wards.

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

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

Lake Acidification

Adirondack Park, New York

- Largest American park outside of Alaska (9,300 square miles)
- Suffered worse damage due to acid rain than any other region in the U.S.
- 700 lakes had become too acidic to support native aquatic species
- Considerable recent progress after extensive legislative battles:

The EPA states that from 1990 to 2013, there was a seventy-seven percent decrease in sulfur dioxide emissions and a forty-nine percent decrease in total nitrogen oxide emissions.

Charles Driscoll is a professor at Syracuse University who has been studying acid rain in the Adirondacks for decades. Driscoll noted that because of the reductions that many lakes are now once again supporting species like brook trout. However, he also said that some lakes will take centuries to recover.

“We’ve seen a partial recovery, but there is still quite a bit of damage, particularly on soils and streams,” Driscoll said. “I think that we’re part way there … but we need additional reductions to more fully recover.”

See also http://www.adirondackalmanack.com
Cultural Degradation

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 (CaCO₃), slowly dissolves in the presence of hydrogen ion:

\[
\text{CaCO}_3 (s) + \text{H}^+ (aq) \rightarrow \text{Ca}^{2+} (aq) + \text{HCO}_3^- (aq)
\]

\[
\text{HCO}_3^- (aq) + \text{H}^+ (aq) \rightarrow \text{H}_2\text{CO}_3 (aq) \rightarrow \text{CO}_2 (g) + \text{H}_2\text{O} (l)
\]

or:

\[
\text{CaCO}_3(s) + 2 \text{H}^+ (aq) \rightarrow \text{Ca}^{2+} (aq) + \text{CO}_2 (g) + \text{H}_2\text{O} (l)
\]
Acid Rain: SO₂

Chemical formula of coal: $C_{135}H_{96}O_{9}NS$ (S varies with coal type)

Combustion of leads to release of sulfur dioxide (SO₂)

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

$SO_2$ reacts with $O_2$ to form sulfur trioxide (SO₃)

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

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

Followed by:

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

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$$
SO$_2$ Sources (US)

Primary source of SO$_2$ is fuel combustion; emissions from this sector are decreasing.

Emissions from transportation are small and largely unchanged.

Figure 6.14, Chemistry in Context. US SO$_2$ emission sources, 2007

Figure 6.21, Chemistry in Context. US SO$_2$ emissions, 1940 to 2003
SO$_2$ Sources (US)

Primary source of SO$_2$ is fuel combustion; emissions from this sector are decreasing.

Emissions from transportation are small and largely unchanged.

Figure 6.14, Chemistry in Context. US SO$_2$ emission sources, 2007

http://www.eia.gov/todayinenergy/detail.cfm?id=10151
SO$_2$ Sources (US)

Observed SO$_2$ dropping, largely in compliance with NAAQS 1 hr standard of 75 ppb

http://www.epa.gov/airtrends

http://www.eia.gov/todayinenergy/detail.cfm?id=10151
Removal of SO₂ from Power Plants

SO₂ Control: Flue Gas Desulphurization

Pulverized limestone (CaCO₃) is mixed with water to make a slurry sprayed into flue gas, resulting in:

\[
\text{CaCO}_3 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot \text{H}_2\text{O} + \text{CO}_2
\]

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
## Md Coal Plants with Capacity over 400 Mw

<table>
<thead>
<tr>
<th>Plant</th>
<th>County</th>
<th>Capacity, MW</th>
<th>Year Built</th>
<th>SCR</th>
<th>FGD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brandon Shores</td>
<td>Anne Arundel</td>
<td>1273</td>
<td>1984, 1991</td>
<td>Partial</td>
<td>Yes</td>
</tr>
<tr>
<td>Morgantown</td>
<td>Charles</td>
<td>1252</td>
<td>1970, 1971</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Chalk Point</td>
<td>Prince Georges</td>
<td>728</td>
<td>1964, 1965</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Dickerson</td>
<td>Montgomery</td>
<td>588</td>
<td>1959, 1960, 1962</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Herbert Wagner</td>
<td>Anne Arundel</td>
<td>977</td>
<td>1959, 1966</td>
<td>Partial</td>
<td>No</td>
</tr>
<tr>
<td>Crane</td>
<td>Baltimore</td>
<td>400</td>
<td>1961, 1963</td>
<td>Partial</td>
<td>No</td>
</tr>
</tbody>
</table>

Note: A 7th coal plant, R. Paul Smith Power Station in Williamsport (near Hagerstown), closed on 1 Sept 2012

Sources:  
http://www.sourcewatch.org/index.php/Maryland_and_coal  
http://raven-power.com/plants/brandonshores  
Maryland Trends

SO$_2$, $10^3$ kg/hr

NO$_x$, $10^3$ kg/hr

Courtesy: K. Vinnikov
Trends in power plant NO$_x$ emission, region

H. He et al.: Trends in emissions and concentrations of air pollutants

He et al., *ACP*, 2013
SO$_2$ From Space (US)

Fig. 4. Mean SO$_2$ burdens over the Ohio River Basin for 2005–2007 (left) and 2008–2010 (right) measured by OMI, confirming a substantial reduction in SO$_2$ pollution around the largest coal-fired power plants, as a result of the implementation of SO$_2$ emission control measures (adapted from NASA Earth Observatory, as reported in Fioletov et al., 2011).

Streets et al., Atmos. Envir., 2013
SO$_2$ From Space (Global)

OMI, 2005-2010

SCIAMACHY, 2005-2009

GOME 2 DLR, 2007-2010

Fioletov et al., JGR, 2013
Copper and nickel smelters in Norilsk, Russia are largest anthropogenic point source of SO$_2$

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

Enhanced SO$_2$ in this region readily apparent from space

http://earthobservatory.nasa.gov/IOTD/view.php?id=36063
Acid Rain: NO\textsubscript{x}

NO\textsubscript{x} plays major role in tropospheric O\textsubscript{3} formation.

In Lecture 12, we emphasize the critical importance of radical termination:

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

Nitric acid, HNO\textsubscript{3}, is soluble. Hence, in the presence of droplets, HNO\textsubscript{3} \text{(g)} can become HNO\textsubscript{3} \text{(aq)}

HNO\textsubscript{3} \text{(aq)} then dissociate:

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

and well “oops, we did it again”
**NO$_x$ Sources (US)**

Primary source of NO$_2$ is transportation; EPA inventory suggests emissions from this sector are holding steady, whereas the UMd Atmos Chem group believes emission in the mid-Atlantic have fallen dramatically (Anderson et al., Atmos Envor, 2014)

Emissions from fuel combustion primary driver of inventory decline

---

Figure 6.16, Chemistry in Context. US NO$_x$ emission sources, 2007

Figure 6.21, Chemistry in Context. US NO$_x$ emissions, 1940 to 2003
Primary source of NO$_2$ is transportation; EPA inventory suggests emissions from this sector are holding steady, whereas the UMd Atmos Chem group believes emission in the mid-Atlantic have fallen dramatically (Anderson et al., Atmos Envor, 2014)

Emissions from fuel combustion primary driver of inventory decline

Figure 6.16, Chemistry in Context. US NO$_x$ emission sources, 2007

http://www.eia.gov/todayinenergy/detail.cfm?id=10151
Observed NO$_2$ dropping, largely in compliance with NAAQS 1 hr standard of 100 ppb

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

1994

Sulfate ion concentration, 1994

Sites not pictured:
- Alaska 01: 0.2 mg/L
- Alaska 03: 0.2 mg/L
- Puerto Rico 20: 0.8 mg/L

2013

Sulfate ion concentration, 2013

Sites not pictured:
- Alaska 01: 0.1 mg/L
- Alaska 02: 0.2 mg/L
- Alaska 03: 0.1 mg/L
- Alaska 97: 0.3 mg/L
- Puerto Rico 20: 0.7 mg/L
- British Columbia 22: 1.0 mg/L
- Saskatchewan 21: 0.4 mg/L

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

1994

Nitrate ion concentration, 1994

2013

Nitrate ion concentration, 2013

http://nadp.sws.uiuc.edu/
1994

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1994

2013

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2013

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

**PM2.5 Air Quality, 2000 - 2013**
(Seasonally-Weighted Annual Average)
National Trend based on 537 Sites

**PM10 Air Quality, 2000 - 2013**
(Annual 2nd Maximum 24-Hour Average)
National Trend based on 449 Sites

2000 to 2013: 34% decrease

2000 to 2013: 30% decrease

http://www.epa.gov/airtrends/
Uncertainty of Aerosol RF Effects Future Climate

If tropospheric aerosols have offset a large fraction of GHG induced warming, then the actual warming that may occur could be considerably larger than “best estimate”

If tropospheric aerosols have offset only a tiny fraction of GHG induced warming, then the actual warming that may occur could be considerably smaller larger “best estimate”