Air Pollution

Chapter 18
April 23, 2009
A Brief History of Air Pollution

• Smoke problems:
  – 1273 King Edward I forbid use of sea coal
  – 1873 London, 700 deaths
  – 1911 London, 1150 deaths
  – 1930 Meuse Valley Belgium, 63 deaths
  – 1948 Donora, PA episode, 20 deaths
  – 1952 London episode, 4000 deaths
Types and Sources of Air Pollutants

• Air Pollution: Trends and Patterns
  – Clean Air Act 1970 has decreased air pollution in the US, greatest reduction in lead (Unleaded gasoline)
  – Increase in number of autos negates impact of Act is some areas
  – Air quality index (AQI)
  – Primary and Secondary National Ambient Air Quality Standards (NAAQS)
Major Groups of Pollutants

- **Sulfur containing compounds**
  - $\text{SO}_2$, $\text{H}_2\text{S}$, $\text{H}_2\text{SO}_4$, etc.

- **Nitrogen containing compounds**
  - $\text{NO}_x$ ($\text{NO}_2+\text{NO}$), $\text{HNO}_3$, $\text{NH}_3$, etc.

- **Carbon containing compounds**
  - $\text{CO}_2$, CO, hydrocarbons, etc.

- **Halogen containing compounds**
  - CFCs, etc.

- **Toxic substances**
  - Heavy metals, benzene, toluene, etc.

- **Radioactive compounds**
  - Radon, $^{238}\text{U}$, $^{90}\text{Sr}$, $^{137}\text{Cs}$, Pu, etc.
Types and Sources of Air Pollutants

• Primary and secondary pollutants
• Point, area, mobile and biogenic sources
• Regulated Pollutants
  – Aerosols: PM-10, PM-2.5 (NAAQS)
  – Carbon Monoxide (NAAQS)
  – Sulfur Dioxide (NAAQS)
  – VOCs (hydrocarbons)
  – Nitrogen dioxide (NAAQS)
  – Lead (NAAQS)
  – Ozone (NAAQS)
Sulfur Dioxide (SO$_2$)

- 90% from fossil fuel burning, of which 85% comes from power plants (~75% of total)
- Other sources are oil refining, copper smelting, autos
- coal > oil (less than 1 ppm after refining) > gas
- $\text{SO}_2 (g) + \text{OH} \rightarrow \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$ (acid rain)
- $\text{SO}_2 (aq) \rightarrow \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$
- SO$_4$ also forms fine particulates $(\text{NH}_4)_2\text{SO}_4$
Nitrogen Oxides (NOx = NO + NO₂)

- NO is colorless, non-toxic, oxidizes to NO₂
- NO₂ is red-brown, lung irritant, bronchitis, pneumonia
- Sources: ~50% industrial, ~50% mobile
- Important for ozone generation
  \[ \text{NOx + VOCs + hν} \rightarrow \text{O}_3 \]
- NOx + OH \rightarrow \text{HNO}_3 (acid precipitation)
- NO₃ also forms fine particulate (NH₄NO₃)
Carbon monoxide (CO)

- Colorless, odorless, tasteless gas
- From incomplete combustion of carbonaceous fuels
- Cars and light truck tailpipe emissions
- Also from biomass burning (wildfires, fireplaces, etc.)
- Roughly 78% of CO emissions are related to transportation in US
- In an urban area, mobile sources contributes as much as 95% of the total CO
Lead (Pb)

- Industrial sources such as smelters
- Manufacturing lead acid batteries, ammunition, cable covering, plumbing materials
- Other sources include paint, soil around highways, burning used motor oil
- Wheel weights use Pb (1.6 million lb lost)
- Most common exposure through inhalation of Pb particles
- Phase out of Pb from gasoline from 1975 to 1995
- Gasoline no longer sold after 1995 with Pb (requirement of 1990 CAAA)
Particulate Matter (aerosols)

• Tiny solid or liquid particles suspended in air
• Is not just one chemical compound...it’s usually many compounds
• The smaller the particle the further they deposit in your lungs
• Aerosols are assumed spherical but not always
• PM$_{10}$ (less than 10 µm in aerodynamic diameter)
• PM$_{2.5}$ (less than 2.5 µm in aerodynamic diameter)
  – Also called fine particles
• Ultrafine (<0.1 µm or 100 nm)
• Nanoparticles (<10 nm)
Typical Aerosol Particles

a) Saharan Dust in the US

b) Smoldering phase Smoke from Amazon

c) Smoke Cluster from Amazon

d) China pollution

http://alg.umbc.edu/usaq/archives/2005_06.html
Relative Particle Sizes

Particulate Matter with an aerodynamic diameter less than 10 or 2.5 microns, respectively

Human hair
Wildfires

PM2.5
CO
VOC
NOx

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Dust Storms

Dust Storms

Nov 27, 2005, 19:50 UTC

El Paso

PM10

PM2.5

Big Bend NP

Ozone ($O_3$)

- Formed in the troposphere though chemical reaction
- Not talking about stratospheric ozone here
- $\text{NO}_x + \text{VOCs} + h\nu \rightarrow$ photochemical smog ($O_3$, formaldehyde, peroxyacetyl nitrate, other oxidants)
- $\text{NO}_x$ and VOCs from automobiles, industry, power plants are precursor emission sources
- Biogenic VOCs are important precursors in vegetated parts of country
- Urban $[O_3]$ peaks in afternoon, after NO & NO$_2$
Photochemical Reactions

Precursor Gases

Hydrocarbons

NO \quad NO_2

SO_2

+ SUNLIGHT \rightarrow

Oxygenated Hydrocarbons

NO_2 \quad O_3

PAN \quad HNO_3

“Photochemical Smog”
Influence of VOCs: generates the excess NO$_2$
Needed to make ozone
Urban/Rural Ozone

Urban/Ozone concentration

Urban site

Rural site

Urban O$_3$ destroyed at night by the reaction:
O$_3$ + NO $\rightarrow$ NO$_2$ + O$_2$

Hour of day

midnight sunrise noon sunset midnight
Trends in Emissions

- Almost all of the pollutants show a decline since 1990
- Lead is only one down to nearly zero
- NOx shows a decline in late 1990s
Factors that Affect Air Pollution

• The Role of Wind
  – Dilution of pollution dependent upon wind speed

• The Role of Stability and Inversions
  – Vertical mixing
  – Radiation inversion
  – Mixing layer
  – Mixing depth
The Role of Topography

- Mountains, valleys, and coasts and the orientation to prevailing winds can exacerbate air pollution
Valley Inversion Example: Smoke

- Wildfires in Idaho, morning of 11 Sept 2007
- Estimated boundary layer at 1000m
Factors that Affect Air Pollution

• Severe Air Pollution Ingredients
  – Many sources of pollution
  – Stationary high pressure
  – Light surface winds
  – Subsidence inversion
  – Shallow mixing layer
  – Valley
  – Clear night
Urban Heat Island Circulation

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National Inventory of SO$_2$ Sources in 2002
Regional Scale Effects

Distribution of fine sulfate aerosol across US

http://vista.cira.colostate.edu/views/
More Regional Scale Effects

Distribution of fine nitrate aerosol across US

http://vista.cira.colostate.edu/views/
Global scale transport of pollutants

Example of Asian dust transported east

Saharan dust transported west across Atlantic Ocean
Deposition

- Deposition is the removal of pollutants from the atmosphere either through falling to the ground and sticking to some surface or falling to the surface through precipitation.
- Dry deposition (gas or aerosols)
- Wet deposition (rain, snow, fog)
Acid Deposition

- Rain combines with sulfur dioxide and nitrogen oxides to create sulfuric and nitric acid
- Acidic deposition damages ecosystems, particularly lakes, and buildings
- Coal burning plants in Ohio Valley are source, greatest damage in Adirondacks
Acid Deposition

- Acidic deposition (Acid rain) occurs when emissions of SO$_2$ and NOx in the atmosphere react with H$_2$O, O$_2$ and oxidants to form acidic compounds.
- These compounds fall to surface through dry and wet deposition
- Major acidic products include HNO$_3$, HCl, H$_2$SO$_4$, etc.
- Addressed in Title IV 1990 CAAA
2005 Precipitation pH
Effects of Acid Rain