AIR POLLUTION

CE 326 Principles of Environmental Engineering
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Seven Major Pollutants of Concern

1. Particulates
2. Sulfur Oxides ($SO_x$)
3. Ozone
4. Nitrous Oxides ($NO_x$)
5. Carbon Monoxide
6. Volatile Organic Compounds (VOCs)
7. Lead (& others: mercury, other inorganic metals, radon, HCl)
Particulates

• released directly into the air
• largely a result of stationary sources
• a nearly ubiquitous urban pollutant.

“Although particulate levels in North America and Western Europe rarely exceed 50 micrograms of particulate matter per cubic meter ($\mu g/m^3$) of air, levels in many Central and Eastern European cities and in many developing nations are much higher, often exceeding 100 $\mu g/m^3$ (http://www.wri.org/wr-98-99/urbanair.htm).”
Global distribution of urban PM$_{10}$ concentrations

Cumulative percentage of urban population

Population-weight PM$_{10}$ concentrations $\mu g/m^3$

Adapted from Reference
Size of Particulates

- **PM$_{2.5-100}$**: 2.5 to 100 μ in diameter, usually comprise soot and dust from industrial processes, agriculture, construction and road traffic, plant pollen, and other natural sources.
- **PM$_{2.5}$**: particles less than 2.5 μ in diameter generally come from combustion of fossil fuels.
- Vehicle exhaust soot which is often coated with various chemical contaminants
- Fine sulfate and nitrate aerosols that form when SO$_2$ and nitrogen oxides condense in the atmosphere.
- Largest source of fine particles is coal-fired power plants, but auto and diesel exhaust are also prime contributors, especially along busy transportation corridors.
Health Effects

- Small particulates most damaging (PM$_{2.5}$)
- PM$_{2.5}$ aggravate existing heart and lung diseases
- Changes the body's defenses against inhaled materials, and damages lung tissue.
- Elderly, children and those with chronic lung or heart disease are most sensitive
- Lung impairment can persist for 2-3 weeks after exposure to high levels of PM$_{2.5}$
- Chemicals carried by particulates can also be toxic
Science 307:1857-1861, News Focus, March 2005
Sulfur Oxides

- Sulfur Oxides ($SO_x$, mainly $SO_2$)
- emitted largely from burning coal, high-sulfur oil, and diesel fuel.
- usually found in association with particulates
- $SO_2$ is the precursor for fine sulfate particles (separating the health effects of these two pollutants is difficult)
- $SO_2$ and particulates make up a major portion of the pollutant load in many cities, acting both separately and in concert to damage health.
- concentrations are higher by a factor of 5-10 in a number of cities in Eastern Europe, Asia, and South America, where residential or industrial coal use is still prevalent and diesel traffic is heavy
- major component of acid rain
Health Effects

- SO₂ affects people quickly, usually within the first few minutes of exposure.
- SO₂ exposure can lead to the kind of acute health effects typical of particulate pollution.
- Exposure is linked to an increase in hospitalizations and deaths from respiratory and cardiovascular causes, especially among asthmatics and those with preexisting respiratory diseases.
- Severity of these effects increases with rising SO₂ levels, and exercise enhances the severity by increasing the volume of SO₂ inhaled and allowing SO₂ to penetrate deeper into the respiratory tract.
- Asthmatics may experience wheezing and other symptoms at much lower SO₂ levels than those without asthma.
- When ozone is also present, asthmatics become even more sensitive to SO₂ indicating the potential for synergistic effects among pollutants.
Ozone (ground level)

- major component of photochemical smog
- formed when NO$_x$ from fuel combustion react with VOCs
- Sunlight and heat stimulate ozone formation, peak levels occur in the summer.
- Widespread in cities in Europe, North America, and Japan as auto and industrial emissions have increased. Many cities in developing countries also suffer from high ozone levels, although few monitoring data exist.
- powerful oxidant, can react with nearly any biological tissue.
Photochemical smog

- Mexico City and many of the world’s cities suffer from the brownish haze of photochemical smog.
- Inversion layers and mountains can trap smog over certain cities.
Photochemical smog

- Chemistry of photochemical smog:
  - Nitric oxide starts a chain reaction.
  - Reaction with sunlight, water vapor, hydrocarbons, results in over 100 secondary pollutants.

Figure 11.15b
PHOTOCHEMICAL SMOG

STAGE I
Accumulation of Pollutants

Inversion

Emissions:
NO + CO + VOC

Breeze

NO → NO₂

STAGE II
Oxidant Formation

Haze

NO₂ + NO → NO₃

NO₂ + VOC → HHO₂

NO₂ + HHO₂ → NO₃

H₂O

Ethene

O₂

OH

Light (PAR / UV)

atmosphere

DOM

photofragmentation
direct

higher plants

anthropogenic

automobiles and fossil-fired power plants

Nitrogen Oxides

Volatile Organic Compounds

Sunlight

Pollutants "bake" together in direct sunlight forming ozone.
Preventable health effects due to a 10% reduction of environmental levels of PM$_{10}$ and ozone between 2000 and 2020

Source: Cifuentes et al., 2001
Nitrogen Oxides

- principal precursor component of photochemical smog
- component of acid rain (NO\textsubscript{x} is oxidized to NO\textsubscript{3} in the atmosphere, NO\textsubscript{3} reacts with moisture to form nitric acid H\textsubscript{2}NO\textsubscript{4})
- formed inadvertently due to high temperature of combustion of atmospheric nitrogen
Carbon Monoxide

- Hemoglobin has an affinity for CO that is 200 to 250 times its affinity for oxygen
  - this reduces its affinity for oxygen, disrupts release of oxygen.
- Blood level of 0.4% is maintained by CO produced by blood.
- Blood is cleared of 50% of CO in 3-4 hours after exposure.
- Global emissions of CO are 350 million tons per year, 20% from mobile sources.
- CO concentration in cigarette smoke is ~400 ppm.
- 24% of emergency room patients complaining of flu-like symptoms in one study showed carbon monoxide poisoning.
Carbon Monoxide health effects

- CO blocks the oxygen transport in your blood.
- CO is 200 times better at binding in the oxygen site.
- CO poisoning is like suffocating.
Volatile Organic Compounds (VOCs)

- contribute to ozone generation
- many are subject to NESHAPS (benzene from gasoline vapors)
- significant industrial emissions (e.g., perchloroethylene from dry cleaners)
- many are carcinogens or suspected carcinogens
Other Air Pollutants

- Lead
- Mercury
- other inorganic metals
- Indoor air pollution
  - Second hand smoke
  - Radon
“Pyramid of Effects”

- Death
- Hospital Admissions
- Doctor visits
- Asthma attacks, medication use, symptoms
- Lung function changes, immune cell responses, heart rate or heart rate variability responses
What is acid rain?

- More accurate term may be acid deposition
- Occurs in two forms
  - Wet deposition (acidic rain, fog, and snow)
  - Dry deposition (acidic gases and particles)
- Principal components are \( \text{SO}_x \) and \( \text{NO}_x \)
- About 2/3 of \( \text{SO}_x \) and ¼ of \( \text{NO}_x \) comes from power plants (most are coal burning)
How do we measure?

• What is pH of “natural” rain water (pK\textsubscript{a1} of carbonic acid is 6.35)?

• Monitored by two networks, both supported by EPA
  – The National Atmospheric Deposition Program measures wet deposition, and its Web site (http://nadp.sws.uiuc.edu/) features maps of rainfall pH
  – The Clean Air Status and Trends Network (CASTNET) measures dry deposition. Its features information about the data it collects, the measuring sites, and the kinds of equipment it uses - http://www.epa.gov/castnet/
Effects of acid rain

- damage to forests and soils, fish and other living things, materials, and human health.
- acidification of lakes and streams
- In a National Surface Water Survey (NSWS)
  - effects of acidic deposition in over 1,000 lakes larger than 10 acres and in thousands of miles of streams believed to be sensitive to acidification
  - acid rain caused acidity in 75 percent of the acidic lakes
  - acid rain caused acidity in about 50 percent of the acidic streams
Effects of acid rain

- regions in the U.S. identified as containing many of the surface waters sensitive to acidification include:
  - the Adirondacks and Catskill Mountains in New York state,
  - the mid-Appalachian highlands along the east coast
  - the upper Midwest, and mountainous areas of the Western United States.
- In areas like the Northeastern United States, where soil buffering capacity is poor, some lakes now have a pH value of less than 5.
- One of the most acidic lakes reported is Little Echo Pond in Franklin, New York. Little Echo Pond has a pH of 4.2.
- also a problem in lakes smaller than 10 acres that were not included in the NSWS (may increase the number up to four-fold).
Acid Rain and Ecological Effects

Anc

% Species Loss

pH


http://ncaswcd.org/Programs/Education/High%20School%20Envirothon/Current%20Environmental%20Issues_files/image018.gif

http://ncaswcd.org/Programs/Education/High%20School%20Envirothon/Current%20Environmental%20Issues_files/image016.gif
Tree and Forest Damage

- damage of trees at high elevations (for example, red spruce trees above 2,000 feet) and many sensitive forest soils.
Water Quality Impacts

- Nitrogen impacts on water quality due to eutrophication (oxygen depletion, algal blooms, declines in the health of fish and shellfish, loss of seagrass beds and coral reefs, and ecological changes in food webs):
  - 10-45 percent of the nitrogen produced by various human activities that reaches estuaries and coastal ecosystems is transported and deposited via the atmosphere.
  - For example, about 30 percent of the nitrogen in the Chesapeake Bay comes from atmospheric deposition.
Materials and Building Decay

• Accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation's cultural heritage.

• Acid rain can scar automotive coatings.

• Acid rain and the dry deposition of acidic particles contributes to the corrosion of metals (such as bronze) and the deterioration of paint and stone (such as marble and limestone).

• Some manufacturers use acid-resistant paints, at an average cost of $5 for each new vehicle (or a total of $61 million per year for all new cars and trucks sold in the U.S.).
A marble column at the Merchants' Exchange in Philadelphia shows loss of material where the stone is exposed to rain and blackening of the stone surface where the stone is sheltered from rain.
How acid rain affects stonework.
The picture on the left was taken in 1908.
The picture on the right was taken in 1968.
Affects visibility

- visibility affected from photochemical smog resulting from $SO_x, VOC's$ and $NO_x$
- Sulfate particles account for 50-70 percent of the visibility reduction in the eastern part of the United States

http://www.mwhazecam.net/stpaul.html
Ozone Depletion

- 90% of the planet's ozone is in the ozone layer in the stratosphere (10-50 kilometers above the Earth's surface).
- Stratospheric ozone is a naturally-occurring gas that filters the sun's ultraviolet (UV) radiation.
- Diminished ozone layer allows more radiation to reach the Earth's surface.
Ozone Depletion

- Overexposure to UV rays can lead to skin cancer, cataracts, and weakened immune systems.
- Increased UV can also lead to reduced crop yield and disruptions in the marine food chain.
- Ozone destruction occurs when the release of chlorofluorocarbons (CFCs) and other ozone-depleting substances (ODS), widely used as refrigerants, insulating foams, and solvents.
- CFCs are heavier than air, can take as long as 2-5 years to reach the stratosphere.
- Measurements of CFCs in the stratosphere are made from balloons, aircraft, and satellites.
When CFCs reach the stratosphere, the ultraviolet radiation from the sun causes them to break apart and release chlorine atoms which react with ozone, starting chemical cycles of ozone destruction that deplete the ozone layer.

One chlorine atom can break apart more than 100,000 ozone molecules.

Other chemicals that damage the ozone layer include:

- Methyl bromide (used as a pesticide)
- Halons (used in fire extinguishers), and
- Methyl chloroform (used as a solvent in industrial processes).
Ozone Depletion

- As methyl bromide and halons are broken apart, they release bromine atoms, which are 40 times more destructive to ozone molecules than chlorine atoms.
- Halon-1301 has 10 times depleting potential as CFC-11
- Total chlorine is decreasing, while bromine from industrial halons is increasing
- Volcanoes and oceans release large amounts of chlorine, the chlorine from these sources is easily dissolved in water and washes out of the atmosphere in rain.
- CFCs are not broken down in the lower atmosphere and do not dissolve in water.
Ozone Depletion

- The increase in stratospheric chlorine since 1985 matches the amount released from CFCs and other ozone-depleting substances produced and released by human activities.
- In 1978, the use of CFC propellants in spray cans was banned in the U.S.
- In the 1980s, the Antarctic "ozone hole" appeared and an international science assessment more strongly linked the release of CFCs and ozone depletion.
Ozone Depletion

• 1987, the Montreal Protocol was signed and the signatory nations committed themselves to a reduction in the use of CFCs and other ozone-depleting substances.

• Since that time, the treaty has been amended to ban CFC production after 1995 in the developed countries, and later in developing countries.
Today, over 160 countries have signed the treaty. Since January 1, 1996, only recycled and stockpiled CFCs are available for use in developed countries like the US. This production phaseout is possible because of efforts to ensure that there will be substitute chemicals for all CFC uses.

but provided that we stop producing ozone-depleting substances, natural ozone production reactions should return the ozone layer to normal levels by about 2050.
Stratospheric ozone depletion

- In 1985, the “ozone hole” was detected over Antarctica.
- Ozone levels had declined 40–60% over the previous decade.
Stratospheric ozone depletion

- Scientists worried about the effects of extra cancer-causing UV on people, organisms, ecosystems.

*The ozone hole (blue) reached its greatest extent in September 2000 (satellite imagery).*
## National Ambient Air Quality Standards (NAAQS)

<table>
<thead>
<tr>
<th>Criteria Pollutants</th>
<th>Standard Type</th>
<th>Avg. Time</th>
<th>Conc.</th>
<th>Health Risks and Concerns</th>
<th>Anthropogenic Sources</th>
<th>Natural Sources</th>
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<tbody>
<tr>
<td>Carbon monoxide</td>
<td>Primary</td>
<td>8 h</td>
<td>9 ppm</td>
<td>carboxy-hemoglobin (blood)</td>
<td>incomplete combustion from mobile and stationary sources</td>
<td>intermediate in breakdown of methane by hydroxyl radicals (OH⁻)</td>
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<td></td>
<td></td>
<td>1 h</td>
<td>35 ppm</td>
<td></td>
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<tr>
<td>Hydrocarbons (measured as CH₄)</td>
<td>Primary</td>
<td>3 h</td>
<td>240 ppb</td>
<td>photochemical smog</td>
<td>incomplete combustion from mobile and stationary sources</td>
<td>see graph</td>
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<tr>
<td>Lead</td>
<td>Primary</td>
<td>24 h</td>
<td>18 ppb</td>
<td>CNS</td>
<td>leaded gasoline (obsolete?), smelters and refineries</td>
<td>volcanic activity and soils</td>
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<td>3 month</td>
<td>6 ppb</td>
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<tr>
<td>Nitrogen dioxide</td>
<td>Primary</td>
<td>annual</td>
<td>53 ppb</td>
<td>health risks, visibility (NO₂ has a brown color)</td>
<td>high temperature combustion</td>
<td>bacterial processes in soil release nitrous oxide N₂O</td>
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<td>1 h</td>
<td>250 ppb</td>
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<td>Ozone</td>
<td>Primary</td>
<td>1 h</td>
<td>120 ppb</td>
<td>eye irritation, breathing difficulties</td>
<td>formed in nitrogen oxide photolytic cycle (NOₓ + sunlight)</td>
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<td></td>
<td>8 h</td>
<td>80 ppb</td>
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<td>Sulfur dioxide</td>
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<td>30 ppb</td>
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<td>24 h</td>
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<td>Sulfur dioxide</td>
<td>Secondary</td>
<td>3 h</td>
<td>500 ppb</td>
<td>plant damage, material damage</td>
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<td>Total suspended particulates (TSP)</td>
<td>Primary</td>
<td>annual</td>
<td>75 µg/m³</td>
<td>visibility and respiratory effects</td>
<td>combustion of fossil fuels and industrial activity</td>
<td>soil, sea salt, sand, forest fires, volcanoes</td>
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<td></td>
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<td>24 h</td>
<td>150 µg/m³</td>
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