Air Pollution

Atmospheric Chemistry Cycles and Residence Times

- Atmosphere composition mostly Nitrogen (76.6 %), Oxygen (23.1 %), and other gases
- Chemical materials cycle through the atmosphere as they do in other reservoirs
  - Residence Times (Table 17.1)
  - Influenced by amounts present in a given reservoir
    - $\text{CO}_2$ – 4 years
    - $\text{O}_2$ - 7 million years
    - $\text{N}_2$ – 44 million years

Types of Air Pollution

- Gaseous
  - CO and $\text{CO}_2$
  - S and N
  - Ozone and CFCs
- Particulates
  - Soot, smoke, ash (from coal/wood burning)
  - Dust (released from industrial processes)
  - Other solids release by burning

### Abundances and Residence Times of Some Elements and Gases in the Atmosphere

<table>
<thead>
<tr>
<th>Substance</th>
<th>Average Concentration (ppm)</th>
<th>Estimated Residence Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen</td>
<td>76.6%</td>
<td>44 million years</td>
</tr>
<tr>
<td>ammonia (NH₃)</td>
<td>6 ppm</td>
<td>2-4 months</td>
</tr>
<tr>
<td>nitrous oxide (N₂O)</td>
<td>295 ppm</td>
<td>12-13 years</td>
</tr>
<tr>
<td>nitrogen dioxide (NO₂)</td>
<td>2 ppm</td>
<td>1-2 months</td>
</tr>
<tr>
<td>nitric acid (HNO₃)</td>
<td>unknown, low</td>
<td>2-3 weeks</td>
</tr>
<tr>
<td>oxygen (as O₂)</td>
<td>28.1%</td>
<td>5 million years</td>
</tr>
<tr>
<td>carbon</td>
<td>1.6 ppm</td>
<td>3.6 years</td>
</tr>
<tr>
<td>carbon dioxide (CO₂)</td>
<td>390 ppm</td>
<td>4 years</td>
</tr>
<tr>
<td>carbon monoxide (CO)</td>
<td>0.1 ppm</td>
<td>1-2 months</td>
</tr>
<tr>
<td>sulfur</td>
<td>0.2 ppm</td>
<td>hours or days</td>
</tr>
<tr>
<td>sulfur dioxide (SO₂)</td>
<td>0.2 ppm</td>
<td>hours</td>
</tr>
<tr>
<td>hydrogen sulfide (H₂S)</td>
<td>0.1 ppm</td>
<td>several days</td>
</tr>
<tr>
<td>sulfuric acid (H₂SO₄)</td>
<td>0 ppm</td>
<td>60 days</td>
</tr>
<tr>
<td>mercury</td>
<td>0.001 ppm</td>
<td>60 days</td>
</tr>
<tr>
<td>lead</td>
<td>0.003 ppm</td>
<td>2 weeks</td>
</tr>
<tr>
<td>CFCs (chlorofluorocarbons)</td>
<td>0.1-0.2 ppm</td>
<td>years to decades</td>
</tr>
</tbody>
</table>

Impact of Atmospheric Layering on Pollutants

- Layering inhibits vertical transport of material between stratosphere and troposphere.
- Concentration of water vapor in atmosphere declines with elevation. Almost all water is confined to troposphere.
- In troposphere: pollutants more easily removed by raindrops.
- In stratosphere: pollutants may linger for longer periods of time.

Carbon Gases

- CO – carbon monoxide
  - Not very abundant in the atmosphere but deadly
  - Odorless, tasteless and invisible – toxic to animals
  - Very short residence time but easily added to the atmosphere by common anthropogenic sources (automobiles)
- CO$_2$ - carbon dioxide
  - Essential for life of plants (photosynthesis)
  - Product of plant respiration, combustion, and volcanic eruptions
  - Short residence time and easily fluxes between oceans and atmosphere

The Global Carbon Cycle

Numbers are billions of tons of carbon
Sulfur and Nitrogen Gases

- **SO₂** - sulfur dioxide forms acid rain
  - very short residence time (days or hours)
  - By product from combusting coal
  - \( \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 = \text{H}_2\text{SO}_4 \) (sulfuric acid) and will lower the pH scale for rain

- **NO₂** - nitrogen dioxide forms acid rain
  - residence time (1-2 months)
  - By product from fossil fuel combustion
  - \( 2\text{NO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 = 2\text{HNO}_2 \) (nitric acid) and will lower the pH scale for rain

Anthropogenic Sources

Acid Rain or Deposition

- Includes rain, snow, fog, humidity, and dust with acidity lower than pH 5.6

Most falls between 4.5 and 5.6, but some as low as 1.6 has been recorded. (This is 80,000 times more acidic than pure water!)

Why would the rain in the Eastern United States be more acidic than in the Western US?
Acid Rain

Effects of Acid Rain

- Harmful to plants, health of rivers and lakes, and animals
- Acid rain causes increases in the build up of heavy metals (lead, zinc, selenium, copper, and aluminum) leached from rocks and soils
- Toxic levels are then found in our waterways, fish, and fish eaters
- High mortality in birds and mammals that depend on insects for food.
- Alteration of soil chemistry, nutrient availability and plant growth.
- Trees/shrubs become vulnerable to insects, diseases, and fungus.

Regional Variations in Rainfall Acidity and Impacts

- Rain down wind of an industrial or populated areas have greater acidic conditions
  - Generally, industrial areas have notably higher sulfur dioxide emissions than non-industrial areas
  - Urban areas, with automobiles, generally have higher nitrogen oxide emissions than areas without autos
- Local geology can reduce the acidity of waterways that receive acid rain.
  - Limestone can neutralize acidic water; granite can not

Effects of Increasing Acidity on Fish

<table>
<thead>
<tr>
<th>pH</th>
<th>Effects on Fish</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0 - 6.5</td>
<td>Harmless of most fish</td>
</tr>
<tr>
<td>6.5-6.0</td>
<td>Significant reductions in egg hatchings and growth in brook trout</td>
</tr>
<tr>
<td>6.0 - 5.0</td>
<td>Rainbow trout do not occur; small populations of few fish are found; declines in salmon</td>
</tr>
<tr>
<td>4.5 - 4.0</td>
<td>Harmful to salmon eggs and fry</td>
</tr>
<tr>
<td>4.0 - 3.5</td>
<td>Lethal to salmon</td>
</tr>
<tr>
<td>3.5-3.0</td>
<td>Toxic to most fish</td>
</tr>
</tbody>
</table>
Nitrogen Gases and “Smog Ozone”

- Complex geochemistry
  - oxygen and nitrogen are very abundant in the atmosphere
  - high temperatures cause nitrogen and oxygen to form nitrogen oxide compounds
- $\text{NO}_2 + \text{strong sun light} \rightarrow \text{photochemical smog}$
- $\text{NO}_2$ can breakdown in sunlight to NO and will react with common oxygen ($\text{O}_2$) to form ozone ($\text{O}_3$)

Photochemical Smog

- Smog is a complex mixture of ground-level ozone, nitrogen oxides, and hydrocarbons.

\[
\text{NO}_2 + \text{SR} \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 \rightarrow \text{O}_3
\]
Photochemical Smog

- Smog can injure health: difficulty breathing, asthma, reduced resistance to lung infections and colds, eye irritation.
- Smog inhibits photosynthesis in plants and causes damage to crops and forests.

Weather and Air Pollution

Warm pollutant-bearing gases rise through cooler, dense air.

Thermal Inversions trap pollutants under unstable layers of warmer air

Trapped gases caught below warmer air layer

Smog near oil field near San Francisco Bay
Ozone

- Triatomic form of oxygen: \( \text{O}_3 \)
- Unstable molecule; releases an oxygen easily. (Oxidant)

Usefulness:
- Ozone gas bubbling through water can purify it.
- Absorbs harmful ultraviolet radiation.

The Ozone Layer

- Highest concentration is 20-25 km above the surface.
- Prevents transmission of harmful amounts of UV to Earth.

- Total amount: Small!
  - If all of it were brought down to the surface, it would form a layer only 4 mm thick!
Removal of Stratospheric Ozone

- Ozone layer naturally fragile.
- Constant formation and removal of ozone.
- Absorption of UV radiation destroys the ozone.
- Anything that changes the balance between formation and renewal has potential to disrupt ozone layer.

The Story of the Ozone “Hole”

- Not a hole, but a thinning of the layer.
- “Hole” first detected in 1976 over Antarctica, but not widely recognized as a problem until 1985.
- Detection of increasing levels of chlorine in stratosphere through 1970-1990....
- Connection made to human-made chemicals.

CFCs

Chlorofluorocarbons are non-toxic, non-flammable molecules of carbon, chlorine, and fluorine.

Chemically stable, insoluble, and non-reactive = long residence time (100 yrs)

CFCs are used as blowing agents for foam, in aerosol sprays, to produce styrofoam, as cleaning fluids, fire retardants, and in refrigerants (Freon).

Used since the 1960's.
Increase in CFCs in atmosphere

- 1960s -- 100 ppt (parts per trillion)
- 1970s -- 200 ppt
- 1987 -- 400 ppt
- 1990 -- 750 ppt

How CFCs Destroy Ozone

- UV radiation breaks off a chlorine atom from a CFC molecule.
- The chlorine atom attacks an ozone (O_3) molecule, breaking it apart and destroying it.
- The result is an ordinary oxygen (O_2) molecule and a chlorine monoxide molecule (ClO).
- The chlorine monoxide (ClO) is attacked by a free oxygen atom (O), releasing the chlorine atom and forming an ordinary oxygen (O_2) molecule.
- The chlorine atom is now free to attack and destroy another ozone molecule!

Ozone Depletion

- During the average 1-2 year residence time of one chlorine atom in stratosphere, it could destroy 100,000 ozone molecules!!
Size of “hole” in 2003, about three times the size of U.S. -- 28 million km²

Ozone depletion is both seasonal and spatially controlled. Greatest in spring (Sept-Nov) in Southern Hemisphere. Most pronounced over poles, but stronger over Antarctica because of atmosphere circulation patterns there.

Environmental Effects of Increased UV

• Potential Effects of Crops
  – Decreased productivity of food plants such as soybeans
  – Plant damage (which may affect food supply)

• Marine biological processes
  – UV penetration in oceans could damage planktonic life
  – Plankton forms the base of food chain in marine water.
  – Disruption of plankton could affect entire food chain, including people who consume these resources.
    • In air masses beneath depleted layer in Antarctica, a reduction in planktonic life of 6 to 12% has been documented.

Potential Effects on Humans

Bigger, badder sunburns
Increases in all types of skin cancers

UN Environment Programme estimates that each 1% reduction in ozone could result in a 3% increase in non-melanoma and melanoma skin cancers.
Also: increase in blindness related to cataracts and gene mutations.
Environmental Effects of Increased UV

- Marine biological processes
  - Plankton are believed to be a major “sink” of carbon dioxide.
  - Their disruption could lead to increased CO₂ in atmosphere.
  - This could lead to more global warming!

The Good News

- Montreal Protocol, 1987
- Goal: elimination of CFC use by 1996.
- Signed by 70 countries, many in compliance.
- We are reducing the amount of CFCs up there, but it will take a long time for the ozone layer to respond.

Particulate Pollutants

- Fine particulate matter in suspension; solid or liquid droplets (aerosols)
- Volcanic ash, smoke from forest fires, heavy metals (arsenic, lead, zinc, mercury) from smelting, burning coal, mining dust.

Particulate Pollutants

- Lead - once a serious pollutant
  - Used in gasoline as an antiknock additive, tons of lead were released into the atmosphere by internal combustion engines
  - Unleaded fuels have reduced lead in air pollution
- High doses of lead can cause brain damage, depression, apathy, and other psychological disorders
A success story!!

Since the Clean Air Act of 1970, elimination of lead in gasoline, there has been a 96% reduction in lead emissions!

Air Pollution Management


- Set national ambient air quality standards (NAAQSs)

- Established maximum allowable concentrations for certain pollutants from point sources

Particulate Air Pollution Control

- Power plants/industrial sites now use settling chambers before emitting gases.

Scrubbers for power plant emissions of sulfur dioxide - effective but very costly.
The Good News

It appears to be working! After high levels in 1970's, increases in certain emissions seems to have stabilized, despite growing population.