Atmospheric Chemistry

Chem 245 website

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Grading and Textbooks

Grading Thresholds:
• "B-" threshold is 70% of the maximum total score for graduate students.
• "A" threshold is 90% of the maximum total score for graduate students.
• These requirements are somewhat relaxed for undergraduate students.

Weights of Assignments:
• Homework 35%
• Midterm 25%
• Final 25%
• Term Paper 15%

Note: assignments and term paper missing deadline will incur a 10% penalty


Atmospheric Chemistry

• Broad, new field of both fundamental and applied nature:
  – Photochemistry ⇔ atomic and molecular physics, quantum mechanics
  – Aerosols ⇔ surface chemistry, material science, colloids
  – Instrumentation ⇔ analytical chemistry, mass spectrometry, optics
  – Air pollution ⇔ toxicology, organic chemistry, biochemistry
  – Reaction modeling ⇔ chemical reaction dynamics and kinetics
  – Global modeling ⇔ meteorology, fluid dynamics, biogeochemistry
  – Global observations ⇔ aeronautics, space research
  – Air quality standards ⇔ political and social sciences

• Comparatively new field:
  – 1961: First dedicated textbook written by P.A. Leighton (“Photochemistry of Air Pollution”)
  – 1985: Ozone hole discovered by British scientists, and later by NASA
  – 1995: Nobel price awarded to Paul Crutzen, Mario Molina, Sherwood Rowland for their research on stratospheric ozone chemistry
Earth's Atmosphere Today

- Strongly oxidizing atmosphere
- Distinct temperature layers
- Exponential pressure decrease with elevation: 99.9% mass contained below stratopause ⇒ atmosphere is very thin
- Atmospheric mass = $5.14 \times 10^{18}$ kg
  (Mass of the Earth = $5.98 \times 10^{24}$ kg)
  (Mass of all humans ~ $5 \times 10^{11}$ kg)

Table 1-1 Mixing Ratios of Gases in Dry Air

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mixing ratio (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N₂)</td>
<td>0.78</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>0.21</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>0.0093</td>
</tr>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>$365 \times 10^{-6}$</td>
</tr>
<tr>
<td>Neon (Ne)</td>
<td>$18 \times 10^{-6}$</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>$(0.01-10) \times 10^{-6}$</td>
</tr>
<tr>
<td>Helium (He)</td>
<td>$5.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>$1.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Krypton (Kr)</td>
<td>$1.1 \times 10^{-6}$</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>$500 \times 10^{-9}$</td>
</tr>
<tr>
<td>Nitrous oxide (N₂O)</td>
<td>$310 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

FIGURE 1.1 Typical variation of temperature with altitude at mid-latitudes as a basis for the divisions of the atmosphere into various regions. Also shown is the variation of total pressure (in Torr) with altitude (top scale, base 10 logarithms) where 1 standard atmosphere = 760 Torr.
Earth’s Atmosphere in Perspective

How about other planets?

All major planets (except Pluto and Mercury) as well as some large moons (such as Saturn's moon Titan) have atmospheres.

Properties of atmospheres on the neighboring Mars, Venus, and Earth are amazingly different.

Earth is unique in:
- Very high O$_2$ content
- High H$_2$O content
- Occurrence of students and boring chemistry professors on its surface

### Comparison between Venus, Mars, and the Earth

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Venus</th>
<th>Earth</th>
<th>Mars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mass (10$^{27}$ g)</td>
<td>5</td>
<td>6</td>
<td>0.6</td>
</tr>
<tr>
<td>Radius (km)</td>
<td>6049</td>
<td>6371</td>
<td>3390</td>
</tr>
<tr>
<td>Atmospheric mass (ratio)</td>
<td>100</td>
<td>1</td>
<td>0.06</td>
</tr>
<tr>
<td>Distance from Sun (10$^6$ km)</td>
<td>108</td>
<td>150</td>
<td>228</td>
</tr>
<tr>
<td>Solar constant (W m$^{-2}$)$^a$</td>
<td>2613</td>
<td>1367</td>
<td>589</td>
</tr>
<tr>
<td>Albedo (%)</td>
<td>75</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>Cloud cover (%)</td>
<td>100</td>
<td>50</td>
<td>Variable</td>
</tr>
<tr>
<td>Effective radiative (°C)</td>
<td>-39</td>
<td>-18</td>
<td>-56</td>
</tr>
<tr>
<td>Surface temperature (°C)</td>
<td>427</td>
<td>15</td>
<td>-53</td>
</tr>
<tr>
<td>Greenhouse warming (°C)</td>
<td>466</td>
<td>33</td>
<td>3</td>
</tr>
<tr>
<td>N$_2$ (%)</td>
<td>&lt;2</td>
<td>78</td>
<td>&lt;2.5</td>
</tr>
<tr>
<td>O$_2$ (%)</td>
<td>&lt;1 ppmv</td>
<td>21</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>CO$_2$ (%)</td>
<td>98</td>
<td>0.035</td>
<td>&gt;96</td>
</tr>
<tr>
<td>H$_2$O (range %)</td>
<td>$1 \times 10^{-4}$ - 0.3</td>
<td>$3 \times 10^{-4}$ - 4</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>SO$_2$ (fraction)</td>
<td>150 ppmv</td>
<td>&lt;1 ppbv</td>
<td>Nil</td>
</tr>
<tr>
<td>Cloud composition</td>
<td>H$_2$SO$_4$</td>
<td>H$_2$O</td>
<td>Dust, H$_2$O, CO$_2$</td>
</tr>
</tbody>
</table>

$^a$The intensity of the solar radiation over a square meter of surface at a distance equal to that from the Sun to the planet’s orbit.

From Graedel and Crutzen, 1995.
Stability of Planetary Atmospheres

- Molecules in the high velocity tail of the Maxwell-Boltzmann distribution can escape the atmosphere.
- The molecules are held back by the gravitational pull of the planet. The critical parameter is the ratio of their gravitational and thermal energy \((r = \text{planet radius}; \ G = 6.675 \times 10^{-11} \text{ m}^3/(\text{kg s}^2) = \text{gravitational constant}; \ M = \text{planet mass}; \ m = \text{mass of the molecule}; \ k = \text{Boltzmann constant})\)
- Escape rate per unit area per second can be estimated as \((n_c = \text{density at the critical level})\). This is known as the Jeans escape formula.
- Escape velocity is the ratio of the escape rate and the gas concentration.

\[
P_{\text{Max-Boltz}}(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \times \exp\left(-\frac{mv^2}{2kT}\right)
\]

\[
\lambda = \frac{E_{\text{potential}}}{E_{\text{thermal}}} = \frac{GMm}{rkT}
\]

\[
\text{Rate} = \frac{n_c \overline{v}}{2\sqrt{\pi}} (1 + \lambda) \times e^{-\lambda}
\]

\[
\overline{v} = \sqrt{\frac{2kT}{m}}
\]

\[
V_{\text{escape}} = \frac{\text{Rate}}{n_c} = \frac{\overline{v}}{2\sqrt{\pi}} (1 + \lambda) \times e^{-\lambda}
\]

<table>
<thead>
<tr>
<th>Planet</th>
<th>Exospheric Temperature (K)</th>
<th>(\lambda_H)</th>
<th>(V_{\text{escape}}) (cm/s)</th>
<th>Has atmosphere?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranus</td>
<td>810</td>
<td>33</td>
<td>1.6\times10^{-8}</td>
<td>Yes</td>
</tr>
<tr>
<td>Venus</td>
<td>400</td>
<td>16.2</td>
<td>0.11</td>
<td>Yes</td>
</tr>
<tr>
<td>Earth</td>
<td>1200</td>
<td>6.3</td>
<td>1700</td>
<td>Yes</td>
</tr>
<tr>
<td>Moon</td>
<td>390</td>
<td>0.9</td>
<td>550000</td>
<td>No</td>
</tr>
<tr>
<td>Io</td>
<td>700</td>
<td>0.8</td>
<td>660000</td>
<td>No</td>
</tr>
</tbody>
</table>

Solve in class: Calculate \(\lambda_O\) and \(V_{\text{escape}}\) for the oxygen atom on Earth. The mass of the Earth is \(5.98\times10^{24}\) kg, and its radius is 6371 km. Do a similar calculation for the Moon, \(M = 7.35\times10^{22}\) kg, \(r = 1738\) km.

- Earth answer: \(\lambda_O = 100\); \(V_{\text{escape}} = 0.00\) cm/s
- Moon answer: \(\lambda_O = 13.9\); \(V_{\text{escape}} = 0.24\) cm/s
The evolution of Earth’s atmosphere is intricately tied to the evolution of life. Biological processes are responsible for many disequilibria in today’s atmosphere (e.g., unusually high O2 content). In the past, the atmosphere was not anywhere close to what it is now.

Figure 16.1. Probable evolution of the relative abundance (in percent) of chemical composition of the atmosphere during the Earth’s history (Alègre and Schneider, 1994).

Figure 16.2. Vertical distribution of major atmospheric constituents in a weakly reduced, prebiotic atmosphere. The major gases are N2 and CO2. Photochemical destruction of CO2 leads to the production of O and O2 in the upper atmosphere (Kasting, 1990).
Atmospheric Chemistry Units

- **Temperature** (usually measured in Kelvin)
- **Pressure** (has many different units)
- **Density and mixing ratio** (many different units)

  - ppm = ppmv = part per million by volume (mixing ratio)
  - ppb = ppbv = part per billion by volume (mixing ratio)
  - ppt = pptv = part per trillion by volume (mixing ratio)
  - molec/cm³ = molecules per cubic centimeter
  - µg/m³ = partial weight per cubic meter of air

\[
T_{[K]} = T_{[°C]} + 273.15 \\
T_{[K]} = T_{[°F]}*5/9 + 255.37
\]

\[
1 \text{ atm} = 760 \text{ Torr} = 101325 \text{ Pa} \\
1013.25 \text{ hPa} = 1.01325 \text{ bar} = 14.696 \text{ psi}
\]

At 298.15 K (25°C):
- 1 Torr = \(3.239 \times 10^{16}\) #/cm³
- 1 atm = \(2.461 \times 10^{19}\) #/cm³
- 1 ppt = \(2.461 \times 10^{7}\) #/cm³

Solve in class: Dr. Evil accidentally spilled one hundred thousands 55-gallon drums of tetrachloromethane in Nevada (MW = 154 g/mole; \(\rho = 1.59 \text{ g/cm}^3\), 1 gallon = 3.785 liters). Assuming that CCl₄ all evaporates and that it does not react with anything, calculate its mixing ratio after it gets uniformly distributed through the entire atmosphere. Mass of the atmosphere is \(5.14 \times 10^{18}\) kg (home assignment). Did his Evilness accomplish much given that the present day CCl₄ mixing ratio is roughly 100 ppt? (A: 1.2ppt)

![Fig. 1.2. Variation of atmospheric ozone concentration with altitude, expressed as an absolute number density and as a mixing ratio. From Stratospheric Ozone 1988, UK Stratospheric Ozone Research Group, HMSO, London, 1988.](image-url)
More on Units

Solve in class: What is wrong with these two pictures?

Einstein discovers that time is actually money (Gary Larson)

“Now that desk looks better. Everything’s squared away, yessir, squaaaaaared away.”
Barometric Law
(dependence of pressure on altitude)

Newton's laws:
\[ \rho g Adz = [P(z) - P(z + dz)] A \]
\[ \frac{dP}{dz} = -\rho \cdot g \]
Ideal gas law (\( MW = \) mol. weight):
\[ \rho = \frac{P \cdot MW}{R \cdot T} \]

Combining these two we get:
\[ \frac{dP}{P} = -\frac{g \cdot MW}{R \cdot T} \cdot \frac{dz}{dz} \]

Assuming that \( T \) and \( M \) are independent of \( z \):
\[ P(z) = P(0) \cdot e^{-z/H} \]

where \( H = \frac{R \cdot T}{g \cdot MW} \) is "scale height"

Conclusion: Pressure drops exponentially with altitude

Solve in class: What is the scale height for Earth for \( T = 250 \text{K} \)?
(A: 7.3 km) What is its physical meaning? Derive an equation for the height under which a fraction \( f \) of the atmospheric mass is contained. Calculate it for \( f = 0.99 \) (99%). (A: 34 km).

Answer: \( z_f = -H \cdot \ln(1 - f) \)
For adiabatically expanding gas:

\[ nc_v dT \text{ (internal energy)} = -P dV \text{ (work)} \]

where \( c_v \) is molar heat capacity of air at constant \( V \).

Combining this with ideal gas law,

\[ PV = nRT \]

we get:

\[ \frac{dT}{dP} = \frac{RT}{c_p P} \]

where \( c_p \) is molar heat capacity of air at constant \( P \).

\[ \Gamma_d = -\frac{dT}{dz} = -\frac{RT}{c_p P} \frac{dP}{dz} = \frac{MW \cdot g}{c_p} \]

is called "dry adiabatic lapse rate"

\[ -\frac{dT}{dz} > \Gamma_d \quad \text{unstable} \]

\[ -\frac{dT}{dz} < \Gamma_d \quad \text{stable (including T inversions)} \]

**DEVIATIONS**

- Stratospheric ozone absorbs solar radiation ⇒ adiabatic assumption no longer applies (\( T \) actually rises with \( z \) in the stratosphere).
- Moist air can condense as it rises causing release of latent heat ⇒ lapse rate is reduced (to 2-7 K/km).
- Temperature inversions are common in the troposphere (air cannot possibly be adiabatically rising everywhere).
**DEFINITION**

Condition under which temperature increases with altitude (negative lapse rate) instead of decreasing.

**CONSEQUENCE**

Air in the inversion layer is not mixed efficiently, which results in local trapping of pollutants.

**Atmospheric Boundary Layer**

Air contained below the inversion layer, where mixing is rapid. This layer is directly affected by the surface. Air pollutants emitted on the ground rapidly distribute through the boundary layer and accumulate in the inversion layer.

**FIGURE 2.18** Variation of temperature with altitude within the troposphere: (a) normal lapse rate; (b) change in lapse rate from positive to negative, characteristic of a thermal inversion.
Subsidence inversion is produced by descending air masses, which compress and may become warmer than air beneath them (inversion heights of $\geq 500$ m).

Such inversions are very common in the atmosphere.

Lateral distance between the point of ascent and descent for the air mass can be as short as several kilometers and as large as thousands of kilometers leading to the formation of stable air circulation patterns around the globe ($\rightarrow$ ESS courses).
Potential Temperature

DEFINITION
- Potential temperature, $\theta$, is the temperature an air parcel would assume if it were adiabatically compressed from its initial pressure $P$ to some reference pressure $P_0$ (usually 1 atm).

USEFULNESS
- Air parcels approximately conserves its potential temperature and tend to move along lines of constant $\theta$.
- Air parcels with constant $\theta$ can be assumed to be well mixed.
- In other words, potential temperature is a convenient indicator of atmospheric stability:

$$\frac{d\theta}{dz} = 0 \text{ when } \frac{dT}{dz} = -\Gamma_d = -\frac{MW \cdot g}{c_p}$$

$\Rightarrow$ well mixed atmosphere

$$\frac{d\theta}{dz} > 0$$

$\Rightarrow$ poorly mixed atmosphere

If the adiabatic approximation applies, we have

$$T^\gamma P^{1-\gamma} = \text{constant} = \theta^\gamma P_0^{1-\gamma}$$

where $P_0$ is reference pressure (= 1 atm)

$$\gamma = \frac{C_p}{C_v} \approx \frac{7}{5}$$

The quantity

$$\theta = T \times \left(\frac{P}{P_0}\right)^{\frac{1-\gamma}{\gamma}} = T \times \left(\frac{P}{P_0}\right)^{\frac{2}{7}}$$

is known as the "potential temperature".

Solve in class: An air parcel has a temperature of 70 F and a pressure of 450 Torr. What is its potential temperature? Is this parcel likely to have the same composition as the air at the ground level below it? (A. 341.8 K)

Fig. 4-19 Vertical profiles of temperature $T$, potential temperature $\theta$, water vapor (dew point), and ozone measured by aircraft in early afternoon in August over eastern Canada.
Air Pollution

• Different types of air pollution exist:
  – Sulfurous smog (London)
  – Photochemical smog (Los Angeles, Mexico City)
  – Acid rain and fog
  – Particulate air pollution
  – Long-lived greenhouse gases

• Air pollution poses serious environmental concerns worldwide

<table>
<thead>
<tr>
<th>TABLE 1.2 Historical Aspects of Sulfurous (London) and Photochemical (Los Angeles) Air Pollution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristics</td>
</tr>
<tr>
<td>First recognized</td>
</tr>
<tr>
<td>Primary pollutants</td>
</tr>
<tr>
<td>Secondary pollutants</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Relative humidity</td>
</tr>
<tr>
<td>Type of inversion</td>
</tr>
<tr>
<td>Time air pollution peaks</td>
</tr>
</tbody>
</table>

Major organizations dealing with air pollution problems:
  • **IPCC** – Intergovernmental Panel on Climate Change ([http://www.ipcc.ch/](http://www.ipcc.ch/))
  • In USA: **EPA** – Environmental Protection Agency ([http://www.epa.gov/](http://www.epa.gov/))
  • In California: **CARB** – California Air Resources Board ([http://www.arb.ca.gov/](http://www.arb.ca.gov/))
Air Quality Standards: Criteria Pollutants

EPA uses six "criteria pollutants" as indicators of air quality, and has established for each of them a maximum concentration above which adverse effects on human health may occur. These threshold concentrations are called National Ambient Air Quality Standards (NAAQS). Only primary values, which are aimed at protecting public health, are listed in the table below.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Primary Standards (protect public health)</th>
<th>Averaging Time</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide</td>
<td>9 ppm 8 hour</td>
<td>8 hour</td>
<td>Not to be exceeded more than once per year</td>
</tr>
<tr>
<td></td>
<td>35 ppm 1 hour</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>0.15 µg/m³ 3 months rolling average</td>
<td></td>
<td>Not to be exceeded</td>
</tr>
<tr>
<td>Nitrogen Dioxide</td>
<td>53 ppb 1 year</td>
<td></td>
<td>Annual mean</td>
</tr>
<tr>
<td></td>
<td>100 ppb 1 hour</td>
<td></td>
<td>98th percentile, averaged over 3 years</td>
</tr>
<tr>
<td>Particulate Matter (PM₁₀)</td>
<td>150 µg/m³ 24 hour</td>
<td></td>
<td>Not to be exceeded more than once per year on average over 3 years</td>
</tr>
<tr>
<td>Particulate Matter (PM₂₅)</td>
<td>12 µg/m³ 1 year</td>
<td></td>
<td>Annual mean, averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td>35 µg/m³ 24 hour</td>
<td></td>
<td>98th percentile, averaged over 3 years</td>
</tr>
<tr>
<td>Ozone</td>
<td>75 ppb 8-hour</td>
<td></td>
<td>Annual fourth-highest daily maximum 8-hr concentration, averaged over 3 years</td>
</tr>
<tr>
<td>Sulfur Oxides</td>
<td>75 ppb 1 hour</td>
<td></td>
<td>99th percentile of 1-hour daily maximum concentrations, averaged over 3 years</td>
</tr>
</tbody>
</table>
Keeping up with NAAQS

Non-attainment Area: A geographic area that violates the National Ambient Air Quality Standards (Source: EPA Green Book)

As the most populated state with unique geographical conditions that favor easy generation of photochemical smog, California has struggled to keep up with NAAQS for particulate matter, and ozone.

Solve in class: The PM$_{2.5}$ concentration remained at 50 µg/m$^3$ level for several days in the Los Angeles basin. Which NAAQS was likely violated? The LA basin is approximately 35 miles long and 15 miles wide. Assuming that the pollutants were uniformly mixed in the planetary boundary layer, which was 1000 feet tall, calculate the total mass of particulate matter suspended over Los Angeles during these two days? Further assume that PM is removed from the basin by 0.2 m/s winds blowing from the ocean towards the mountains. Calculate the production rate of PM$_{2.5}$ (in tons/day) required to sustain PM$_{2.5}$ at the 50 µg/m$^3$ level. (A: 20.7 tons; 15 tons/day)
Non-criteria and Hazardous Air Pollutants

**Non-criteria pollutants** are any recognized and otherwise regulated air pollutants that are not listed as criteria pollutants. These pollutants include VOCs, carbon dioxide and chlorofluorocarbons. Some of them can be quite nasty, and taken all together they can form a substantial fraction of the air pollution.

In addition, EPA defines and requires to control a subset of non-criteria pollutants called **hazardous air pollutants** (HAPs). These are also known as toxic air pollutants or air toxics, and they cause or may cause cancer or other serious health effects.

**Examples of HAPs:**
- Benzene (component of gasoline)
- Perchloroethlyene (emitted from some dry cleaning facilities)
- Methylene chloride (solvent and paint stripper)
- Asbestos
- Mercury
- Over 180 others

**PAN** is a very strong irritant but it is not regarded as a HAP

**FIGURE 2.22** Maximum concentrations of some trace pollutants and the percentage of the peak ozone they form when summed. Also shown is the California Air Quality Standard for O3 and the various alert levels (from Tuazon et al., 1981).
Example 1: Photochemical Air Pollution

Organics + $\text{NO}_x$ + sunlight $\rightarrow$ $\text{O}_3$ + aerosols + PAN + ...

Chain reaction mechanism

**FIGURE 1.3** Diurnal variation of NO, NO$_2$, and total oxidant in Pasadena, California, on July 25, 1973 (adapted from Finlayson-Pitts and Pitts, 1977).
Experiments on the effects of ozone on living organisms and on the origin of photochemical smog formation by a Caltech scientist Arie Haagen-Smit (1900-1977) were of key importance in the difficult battle for US air pollution regulations. (This week's discussion paper).
Air quality record from 1976 clearly shows that strict pollution prevention measures do work.
Example 2: Acid Deposition

\[
\text{OH} + \text{SO}_2 (+ \text{M}) \rightarrow \text{HOSO}_2 \\
\text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4 \text{ in water droplets and aerosols}
\]

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

- pH as low as 1.69 were reported in southern California in 1983.
- As of the year 2000, the most acidic rain falling in the US had a pH of about 4.3.
- \(\text{SO}_2\) and \(\text{NO}_2\) are the primary sources of acidity in rains and fogs. Organic acids contribute as well.
Example 3: Halogen Containing Species and Depletion of Global Mean Stratospheric Ozone

Stratospheric ozone depletion is not limited to the polar regions; the effect is also detectable on a global scale!
Reasons for CFC Level Increase

- Air Conditioners
- Refrigerators
- Solvents
- Aerosol cans

Graph showing the increase in CFC-11 levels from 1975 to 2010, with CCl₃F labeled on the graph.

NOAA/ESRL halocarbons program
May 11, 2011
Much of the appreciation that air particles are bad for health came from extreme air pollution episodes. In the United States, the best known examples include:

- **St. Louis - 1939**, lanterns needed during daytime for one week
- **Los Angeles - 1943**, visibility reduced to three blocks
- **Donora, Pennsylvania - 1948**, 20 dead and 6000 seriously sick
- **Los Angeles - 1954**, heavy smog shut down industry & schools for most of October
- **New York - 1953**, about 200 dead; **1963**, 405 dead

Donora, PA at noon on October 29, 1948 as deadly smog envelops the town.
London Killer Fogs

"Night at Noon", midday, Sunday, January 16, 1955

December 1952, London "Killer Fog"
Particulate Matter and Mortality

INITIAL 6-city study
An Association between Air Pollution and Mortality in Six U.S. Cities

FOLLOW-UP 6-city study

From a number of similar studies:
In US, 10 $\mu$g/m$^3$ increase in PM results in:
- 4% increase in general morbidity
- 6% increase in cardio-pulmonary mortality
- 8% increase in cancer mortality

See review by Dockery and Pope on the website
Example 5: Greenhouse Effect

- **Greenhouse effect**: CO₂, CH₄, N₂O, H₂O, O₃, and CFCs strongly absorb infrared radiation while transmitting visible radiation ⇒ **surface heating**
- **Whitehouse effect**: Clouds and aerosol particles reflect (on average) solar radiation back to space ⇒ **surface cooling**

Adopted from: IPCC 2007 Report (Frequently Asked Questions)
http://ipcc-wg1.ucar.edu/wg1/wg1-report.html
Unprecedented rate of change in CH₄, N₂O, and CO₂ concentration occurring in the industrial era (Image taken from the IPCC FAR Summary for Policy Makers)
Increase in the CO₂ atmospheric level is linked to the increased fossil fuel consumption

Reasons for CO₂ Level Increase

- Power plants
- Transportation

Typical emission units
- \( \text{Pg/yr} = 10^{15} \text{ gram/year} \)
- \( \text{Tg/yr} = 10^{12} \text{ gram/year} \)
- \( \text{Gt/yr} \) (gigaton per year) = same as \( \text{Pg/yr} \)

Solve in class: According to this graph, the fossil fuel emission rate was about 6 PgC/year in year 2000. Assuming that 50% of it ends up in the atmosphere (and the rest is taken up by ocean and biosphere) estimate the rate of atmospheric CO₂ increase due to the fossil fuel burning in ppm/year. (A: 1.4 ppm/year).

Is your answer consistent with the recent atmospheric observations? (see next page)

From "Biological oceanography" by Charles B. Miller (arrows indicate El Nino years)