ATOC 3500 **October 6, 2006**

Haze and Visibility

Recap of Aerosols

- Know there is a variety of particles present in the atmosphere and their importance to many phenomena
- Many sources of particulate matter; anthropogenic generally much less than natural
- Classification of particles by size (and, to some extent, sources)

Objectives

- Review aerosol formation processes
- Learn about the interaction of light with particles
- Discuss the concept of visibility

Aerosol Formation Processes

- Primary particles - mechanical processes and natural emissions
  - Breaking waves and bubbles
  - Manufacturing
  - Volcanic eruption
  - Combustion, biomass burning

Secondary particles - chemical transformation of gases

- Sulfate particles

$$SO_2 + OH + M \rightarrow HSO_3 + M$$

$$HSO_3 + O_2 \rightarrow HO_2 + SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$H_2SO_{4(g)} \rightarrow H_2SO_{4(aq)}$$

Or

$$SO_2 + \text{particles} \rightarrow\rightarrow H_2SO_4$$

- Nitrate particles

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

$$HNO_{3(g)} \rightarrow HNO_{3(aq)}$$

- Hydrocarbon particles

$$RH + O_3 \rightarrow\rightarrow\rightarrow \text{particles}$$

The Denver "Brown Cloud"

Two things contribute to the brown color of the sky:

(1) Absorption of light by nitrogen dioxide (NO_2)

(2) Scattering of light by particles

Small particles are typically secondary - generated from ammonia and sulfates, nitrates: $(NH_4)_2SO_4$; NH_4NO

Large particles tend to be dust and airborne dirt (why roads aren't "sanded" here!)

Haze and Visibility

- What is haze?

Particulate pollution (mostly small particles)

Haze (particulates) ≠ PHOTOCHEMICAL Smog (ozone, NO_2, PAN), although they often occur at the same time.

- Why should we care about haze?

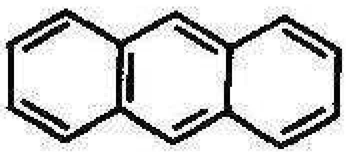
<u>Aesthetics</u>: it affects visibility - our ability to see objects in the distance.

<u>Health</u>: small particles can be inhaled and can lodge in lung tissue or deposit hazardous substances there.

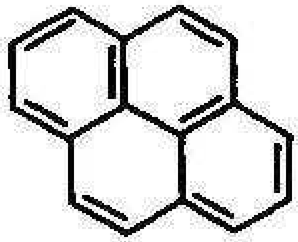
For example: Soot - mostly elemental carbon, comes from combustion

Contain (or have on surface) small amounts of other combustion by-products, especially polycyclic aromatic hydrocarbons (PAHs)

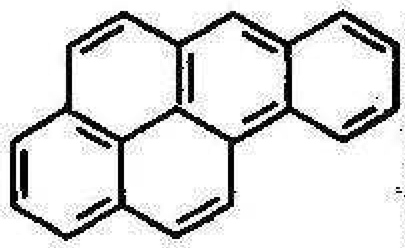
PAHs are known to be carcinogenic or mutagenic! Studies have shown high incidence of lung cancer among urban residents, probably related to PAHs



Anthracene



Pyrene

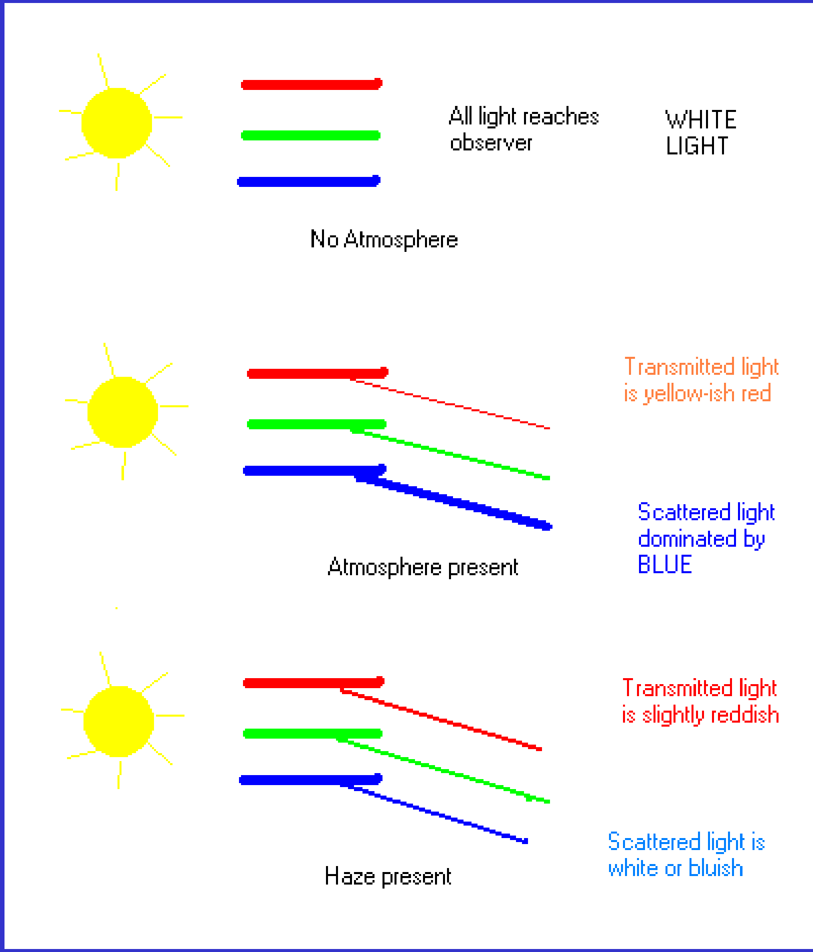


Benzo(a)pyrene

Interaction of Visible Light and Particles

The effect of this interaction depends on the nature and size of the particles present.

General rule: Particles efficiently scatter light with a wavelength that is about the same size as the particle diameter. (Mie scattering)



Quantifying Visibility

Visibility: The ability to distinguish a black object against a white background. Practically speaking, it is the ease with which features along the skyline can be distinguished from the sky itself

Extinction: Removal of light from a path by absorption and/or scattering. It is not always possible or practical to separate out the two processes; ultimately we really only care about how much light reaches the observer.

Beer's Law:

$$I = I_o \, exp[-(\sigma_{scat} n l + \sigma_{abs} n l)]$$

Actual photo near Mexico City, March, 2006

Enhanced contast

"Dirty air"

Better?? - subjective

Since σ for absorption and scattering are likely to be different, we typically lump together these terms together:

$$I = I_o\, exp(-\varepsilon l)$$

ε is called the "extinction coefficient" and has units of cm^{-1}

Optical Depth: Another unit of measure; useful when the path length is not known or is ill-defined

$$I = I_o\, exp(-\tau)$$

Optical depth (τ) is a dimensionless number and can be thought of as the product of cross-section and column amount:

$$\tau = \sigma l n = \sigma N$$

Optical depth also describes the probability of removal of light:

$\tau < 0.1$	little attenuation
$0.1 < \tau < 0.5$	attenuation $\approx \tau$
$\tau > 1$	most light removed

Problem: The optical depth of the stratospheric aerosol layer is typically about 1×10^{-4} for wavelengths of 1 μm. Following the eruption of the Mt. Pinatubo volcano in 1991, the optical depth at 1 μm increased to 1×10^{-2}. How much more or less infrared light got through this layer? What do you think the consequences of this change might be?

Answer

From the restatement of Beer's Law above, we know that $I/I_o = e^{-\tau}$, where the ratio I/I_o represents the fraction of light getting to the detector or observer. We can make use of an approximation here: for small values of x, $e^{-x} \sim (1 - x)$. Both values for the optical depth are quite small, so we can approximate:

Typical: $I/I_o = e^{-(0.0001)} \sim (1 - 0.0001) \sim 1$

Post-volcano: $I/I_o = e^{-(0.01)} \sim (1 - 0.01) \sim 0.99$

The amount of light getting through the aerosol layer decreased following the volcanic eruption because the optical depth increased. Approximately 1% less light got through.

That "missing" 1% had to go somewhere - either be scattered by the particles or absorbed by them. In this case, it was likely absorbed. Evidence has shown that the enhanced aerosol layer following the Pinatubo eruption was responsible for slightly increasing the temperature of the lower stratosphere!

Quantifying Visibility (cont'd)

In clear air:

Visibility in the western US is typically 140 miles

Visibility in the eastern US is typically 90 miles

Why the difference? Related to relative humidity and particle composition

Commonly:

Visibility in the western US is 35 - 90 miles

Visibility in the eastern US is 15 - 25 miles

Differences between clear air and common values is related to total amount of particulate matter in air: Total Suspended Particulate (TSP)

Empirically, ε (km^{-1}) = TSP/250, where TSP is in $\mu g\ m^{-3}$.

Visibility Length: How far you can really see!

$$£ \text{ (km)} = 3.9/\varepsilon \approx 1000/TSP$$

For example:

PM_{10} standard (24-hr average) = 150 μg m^{-3}. Under those conditions, £ (km) $\approx$ 1000/TSP = 6.7 km (about 4 mi).

For average "bad" Denver/Boulder conditions of 65 μg m^{-3}, £ (km) $\approx$ 1000/TSP = 15 km (about 10 mi).

Problem: The visibility length in a certain fog is 0.5 km. Assuming that there are 100 spherical fog particles per cm^3 and that ρ_{H2O} is 1 g cm^{-3}, calculate the average radius of a fog droplet.

We learned above that visibility length is inversely related to the total suspended particulate mass. £ ~ 1000/TSP, so TSP ~ 1000/0.5 km = 2000 μg m^{-3}.

But how are we going to get from TSP to the radius of a fog droplet? What information are we given? We know the total mass of particles in a given volume, and the total number of particles in a given volume. So we can determine the mass of a single particle. Then, we are given the density of water (of which the particles are made). Recall that density is mass/volume; thus we can determine the volume of a single particle in this fog. Since we are told that the particles are spherical, we can then apply the relationship defining the volume of a sphere ($V = 4/3\pi r^3$) and calculate r!

First let's get everything in similar units:

$(2000\ \mu g/m^3) * (1\ g/1 \times 10^6\ \mu g) * (m/100\ cm)^3 = 2 \times 10^{-9}\ g\ cm^{-3}$

Then we can find the mass of a single particle:

$(2 \times 10^{-9}\ g\ cm^{-3}) * (cm^3/100\ particles) = 2 \times 10^{-11}\ g\ particle^{-1}$

Since the density of water is 1 g cm^{-3}, there must be $2 \times 10^{-11}\ cm^3\ particle^{-1}$

Then $r = (3V/4\pi)^{1/3} = (3 * 2 \times 10^{-11}\ cm^3 /4\pi)^{1/3} = 1.7 \times 10^{-4}$ cm (or about 1.7 μm)

For example:

The PM_{10} standard is 50 $\mu g\ m^{-3}$ (annual average), which corresponds to an extinction of $\varepsilon = 0.2\ km^{-1}$. Typical "bad" values for Denver/Boulder range from 60-70 $\mu g\ m^{-3}$ for $\varepsilon = 0.24 - 0.28\ km^{-1}$.