Hand back Midterm Exams (average = 84)

Interaction of atmospheric constituents with light

Haze and Visibility

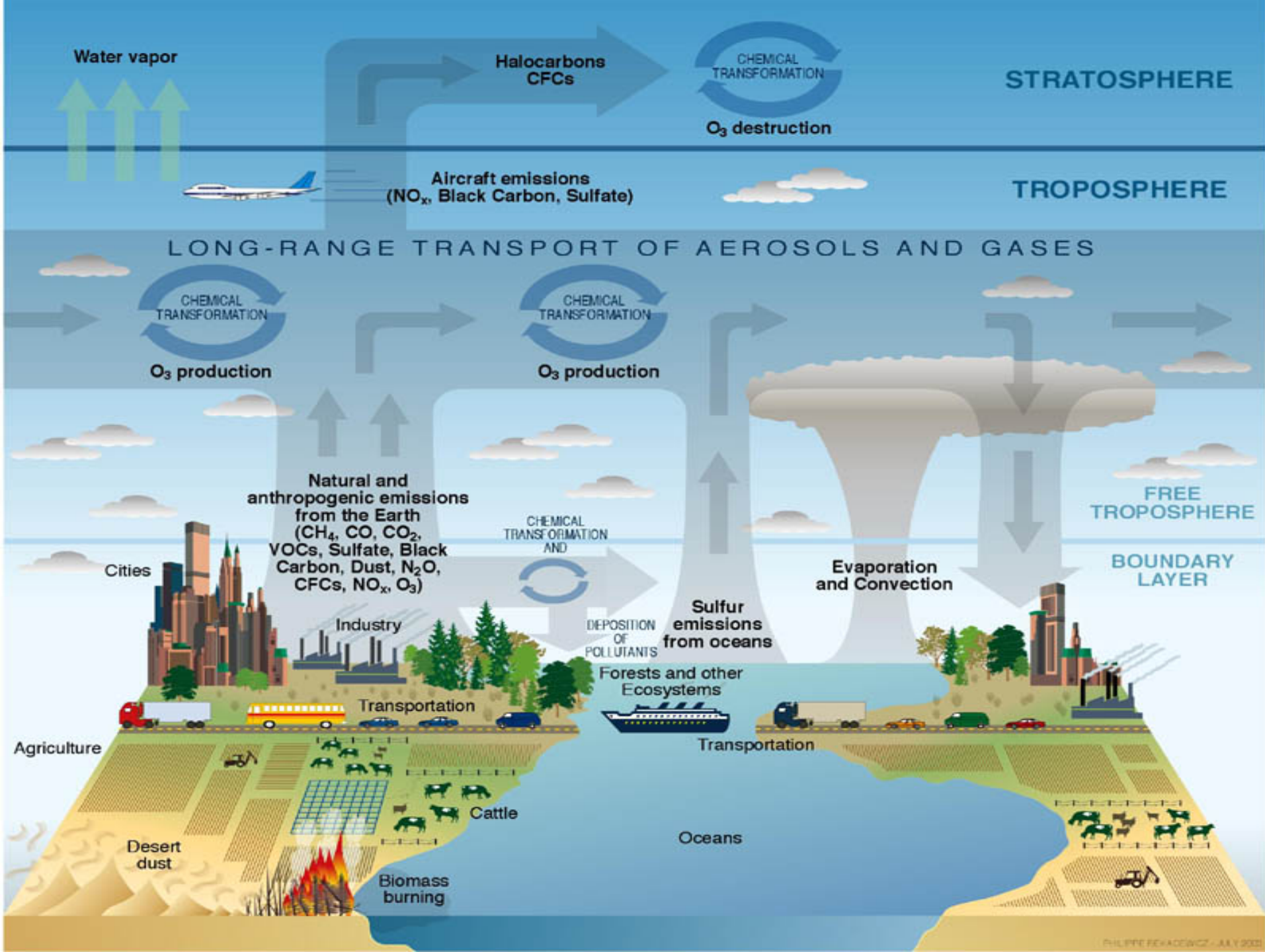Aerosol formation processes (more detail)

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

STRATOSPHERE

Water vapor

Halocarbons
CFCs

CHEMICAL TRANSFORMATION

O_3 destruction

Aircraft emissions
(NO_x, Black Carbon, Sulfate)

TROPOSPHERE

LONG-RANGE TRANSPORT OF AEROSOLS AND GASES

CHEMICAL TRANSFORMATION

O_3 production

CHEMICAL TRANSFORMATION

O_3 production

FREE TROPOSPHERE

Natural and anthropogenic emissions from the Earth (CH_4, CO, CO_2, VOCs, Sulfate, Black Carbon, Dust, N_2O, CFCs, NO_x, O_3)

CHEMICAL TRANSFORMATION AND

DEPOSITION OF POLLUTANTS

Sulfur emissions from oceans

Evaporation and Convection

BOUNDARY LAYER

Cities

Industry

Forests and other Ecosystems

Transportation

Transportation

Agriculture

Cattle

Desert dust

Oceans

Biomass burning

PHILIPPE REKACEWICZ / JULY 2005

Aerosol Formation Processes

We will talk about primary and secondary particles, in a sense, reflecting two key ways that particles are generated in the atmosphere. While there is some discussion in the aerosol community over semantics, for practical purposes we can assume that if a particle forms within a few seconds of being released from a source that it is a primary particle. Whereas a particle that forms downwind of a source of pollution can be considered a secondary particle.

Common examples of primary particles include
- Breaking waves and bubbles
- Manufacturing
- Volcanic eruption
- Combustion, biomass burning

It is important to note that these sources also produce gaseous compounds that are precursors to particles, so that the total particle production by each of these sources is likely to be larger than simply the amount of primary particles that are initially produced.

It is important to note that particles typically grow over their lifetimes – meaning that they accumulate mass. They can do this by acquiring mass from atmospheric vapors ("condensation" or uptake) or by collisions with other particles. In the case of condensation, the total number of particles will remain constant, but the average diameter of the particles will increase.

Uptake of water by a particle often involves a process where a water-soluble material will aid the condensation process by reducing the vapor pressure over the particle relative to a droplet of pure water. This process is called "deliquescence" ("the action or process of dissolving or becoming liquid especially by a deliquescent substance")

The opposite of deliquescence is called "efflorescence"

Often, deliquescence and efflorescence equate to a change in state from solid to liquid as the relative humidity (RH) changes. RH can change due to an increase in the mixing ratio of water vapor – (equating to more collisions of water molecules with the surface, so a net exchange of mass from the vapor phase to the condensed phase).
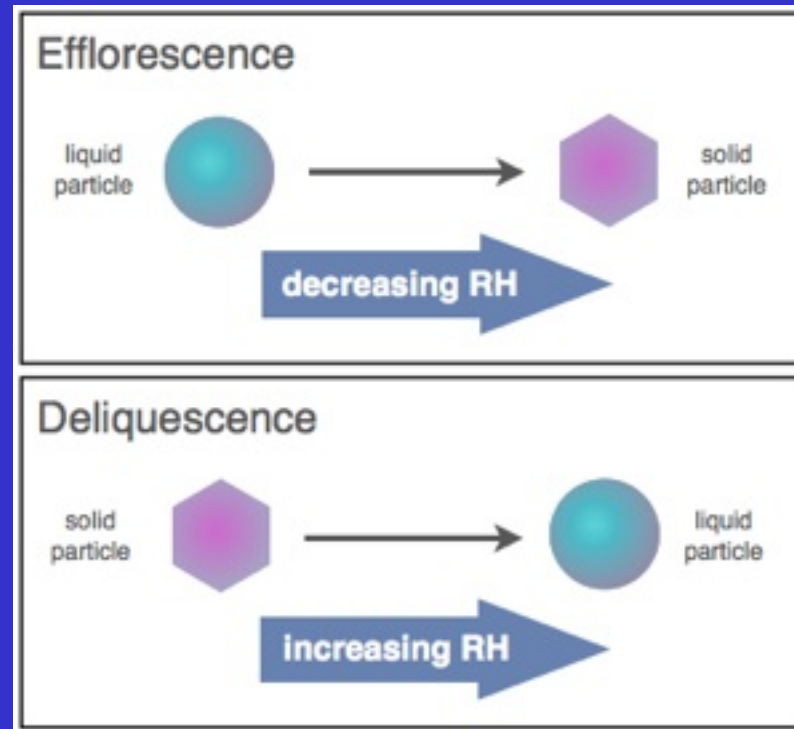
Alternatively, cooling of an airmass with constant water vapor can increase RH by reducing the saturation vapor pressure (a cooler air mass will hold less water vapor than a warm air mass)
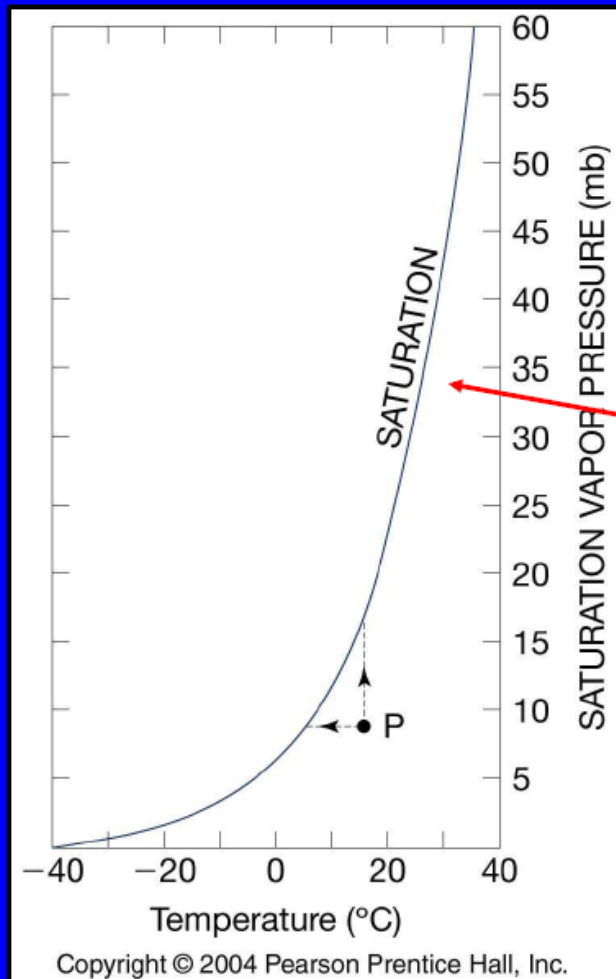

Water vapor pressure

(Clausius Clapeyron curve)

warmer air can hold more water vapor

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Deliquescence and efflorescence are not reversible processes. That is, once a particle deliquesces, it is very difficult to remove the water that has condensed. Thus, in the atmosphere, it is common to see a threshold (called the "deliquescence point") that, once reached, is hard to return to. One usually has the dry a particle far below the original deliquescence point into to remove the condensed water.
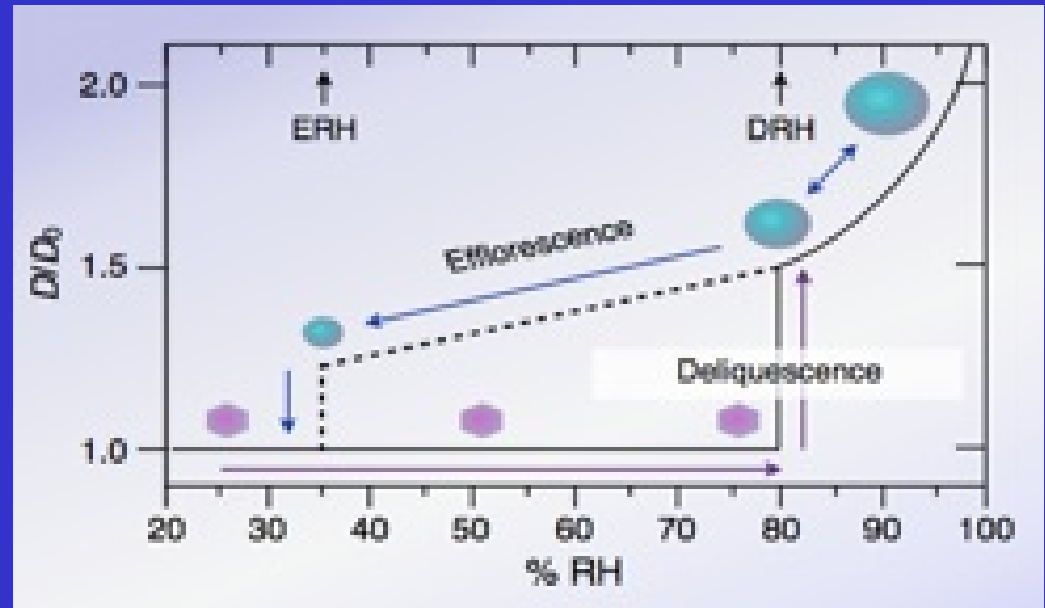
Example of a mocroscopic image of particles deliquescing
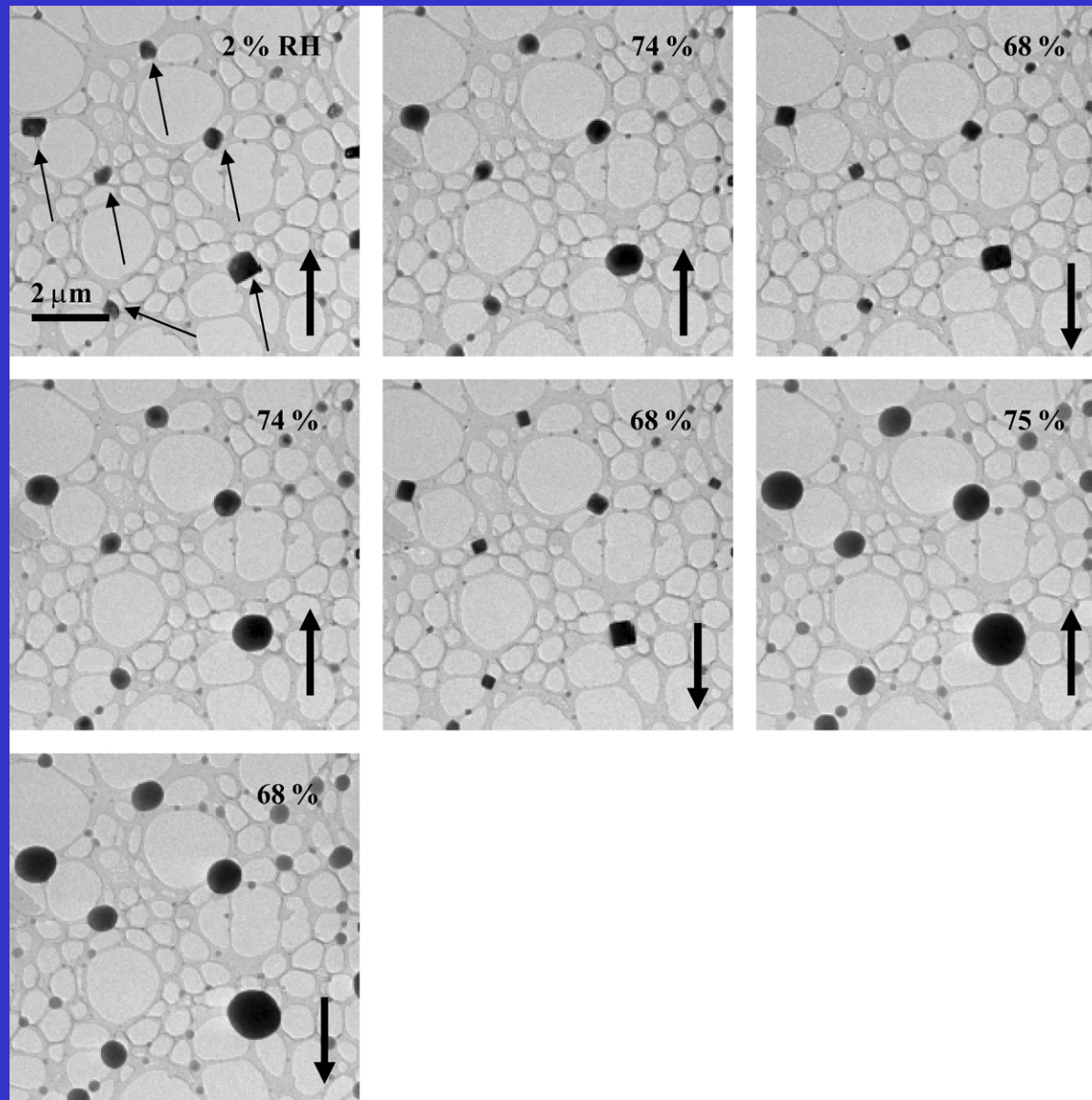
Examples of Secondary particle formation processes - chemical transformation of gases

• 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
$$SO_2 + particles \rightarrow\rightarrow H_2SO_4$$

• Nitrate particles

$$NO_2 + OH + M \rightarrow HNO_3 + M$$
$$HNO_{3(g)} \rightarrow HNO_{3(aq)}$$

• Hydrocarbon particles

$$RH + O_3 \rightarrow\rightarrow\rightarrow particles$$

Particles can also grow by collision, in which case the number of particles will decrease as the average particle diameter increases. This is an irreversible process (i.e., the bigger particles don't fall back apart into smaller ones). There no net exchange of mass between vapor and particulate phases. In this case, total mass will be conserved, but the number of particles in a given volume of air will decrease. This process is called "coalescence," "coagulation," or "aggregation."

The figure at right is of a group of smaller spherical particles that have coalesced into a larger, but non-spherical particle.
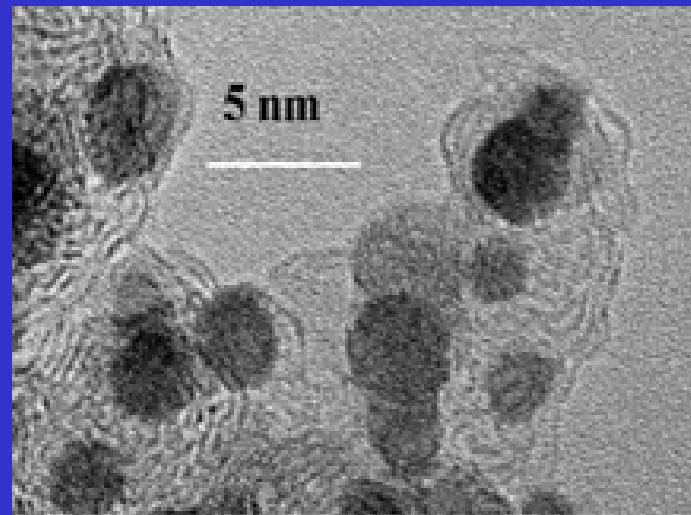
The Denver "Brown Cloud"
Two things contribute to the brown color of the sky:

(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) $\neq$ PHOTOCHEMICAL Smog (ozone, NO_2, PAN), although they often occur at the same time.

- Why should we care about haze?

Aesthetics: it affects visibility - our ability to see objects in the distance.

Health: small particles can be inhaled and can lodge in lung tissue or deposit hazardous substances there.
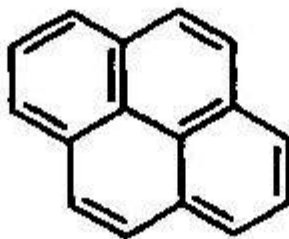
For example: Soot - mostly elemental carbon, comes from combustion

Contain (or have on surface) small amounts of other combustion by-products, especially polycyclic aromatic hydrocarbons (PAHs)
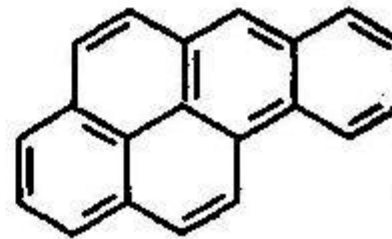
PAHs are known to be carcinogenic or mutagenic! Studies have shown high incidence of lung cancer among urban residents, probably related to PAHs
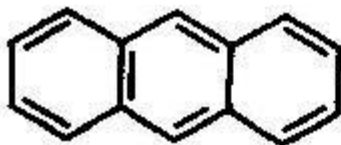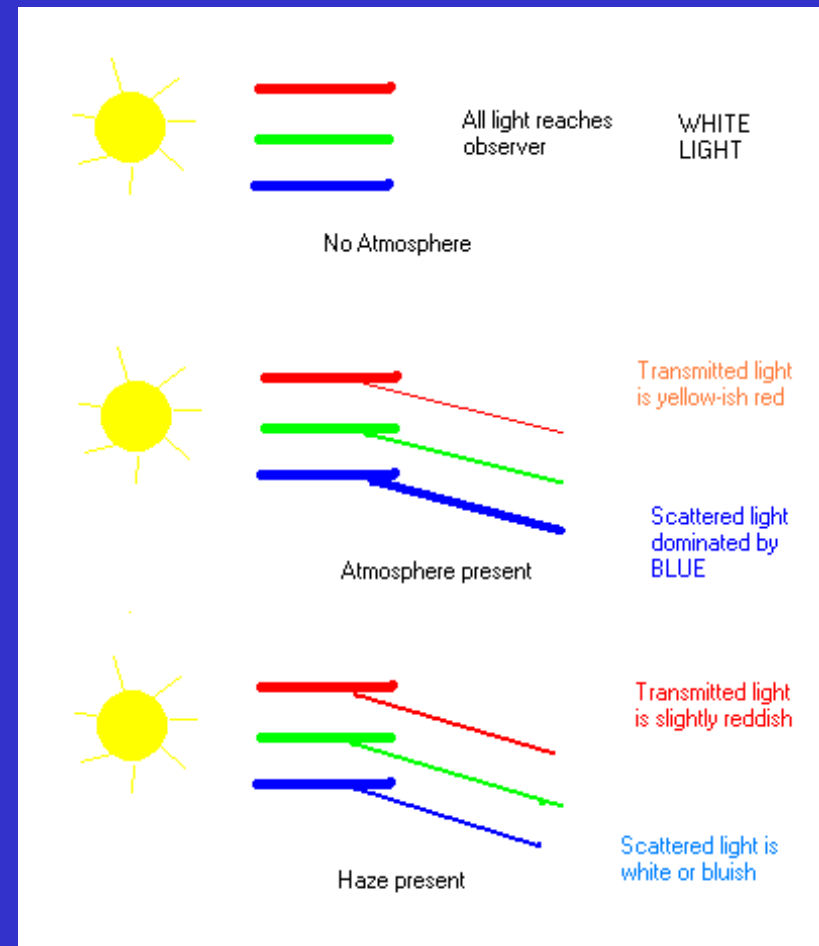

Anthracene   Pyrene   Benzo(a)pyrene

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)

All light reaches observer — WHITE LIGHT

No Atmosphere

Transmitted light is yellow-ish red

Atmosphere present

Scattered light dominated by BLUE

Transmitted light is slightly reddish

Haze present

Scattered light is white or bluish

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:

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

Actual photo near Mexico City,
March, 2006

Enhanced contrast

"Dirty air"

Better?? - subjective

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

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

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:

$$\tau = \sigma\ell n = \sigma N$$

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 x 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 x 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 μg m^{-3}.

<u>Visibility Length:</u> How far you can really see!

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

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:

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

Then we can find the mass of a single particle:

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

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

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

For example:

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