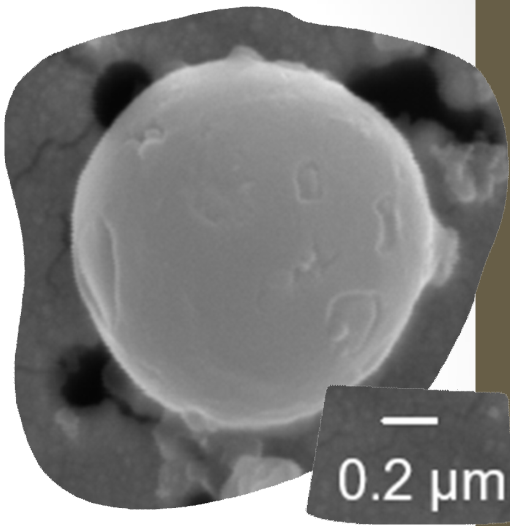
Particulate Matter (1 of 3)

- Complex mixture of solid and liquid particles
- Composed of many different compounds
- Both a primary and secondary pollutant
- Sizes vary tremendously
- Forms in many ways
- Clean-air levels are < 5 μg/m^3 *
- Background concentrations can be higher due to dust and smoke
- Concentrations range from 0 to 500+ μg/m^3 *
- Health concerns
  - Can aggravate heart diseases
  - Associated with cardiac arrhythmias and heart attacks
  - Can aggravate lung diseases such as asthma and bronchitis
  - Can increase susceptibility to respiratory infection

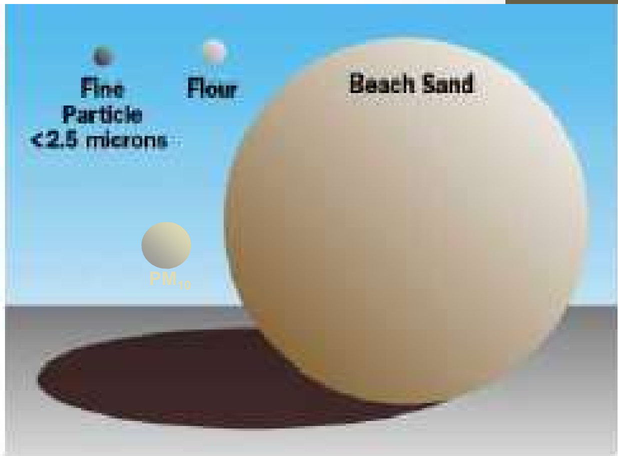


Ultra-fine fly-ash or carbon soot

* 24-hour average

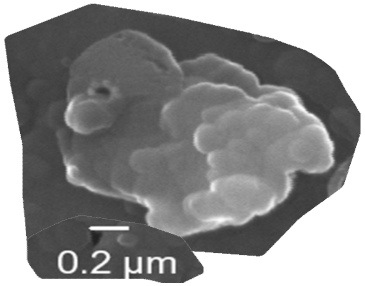
Particulate Matter (2 of 3)

Particles come in different shapes and sizes

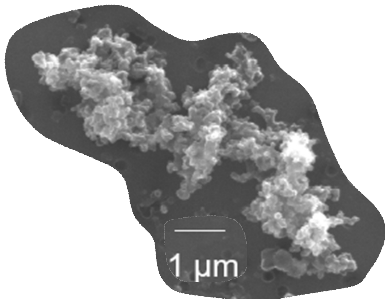


Particle sizes

- Ultra-fine particles (<0.1 µm)
- Fine particles (0.1 to 2.5 µm)
- Coarse particles (2.5 to 10 µm)

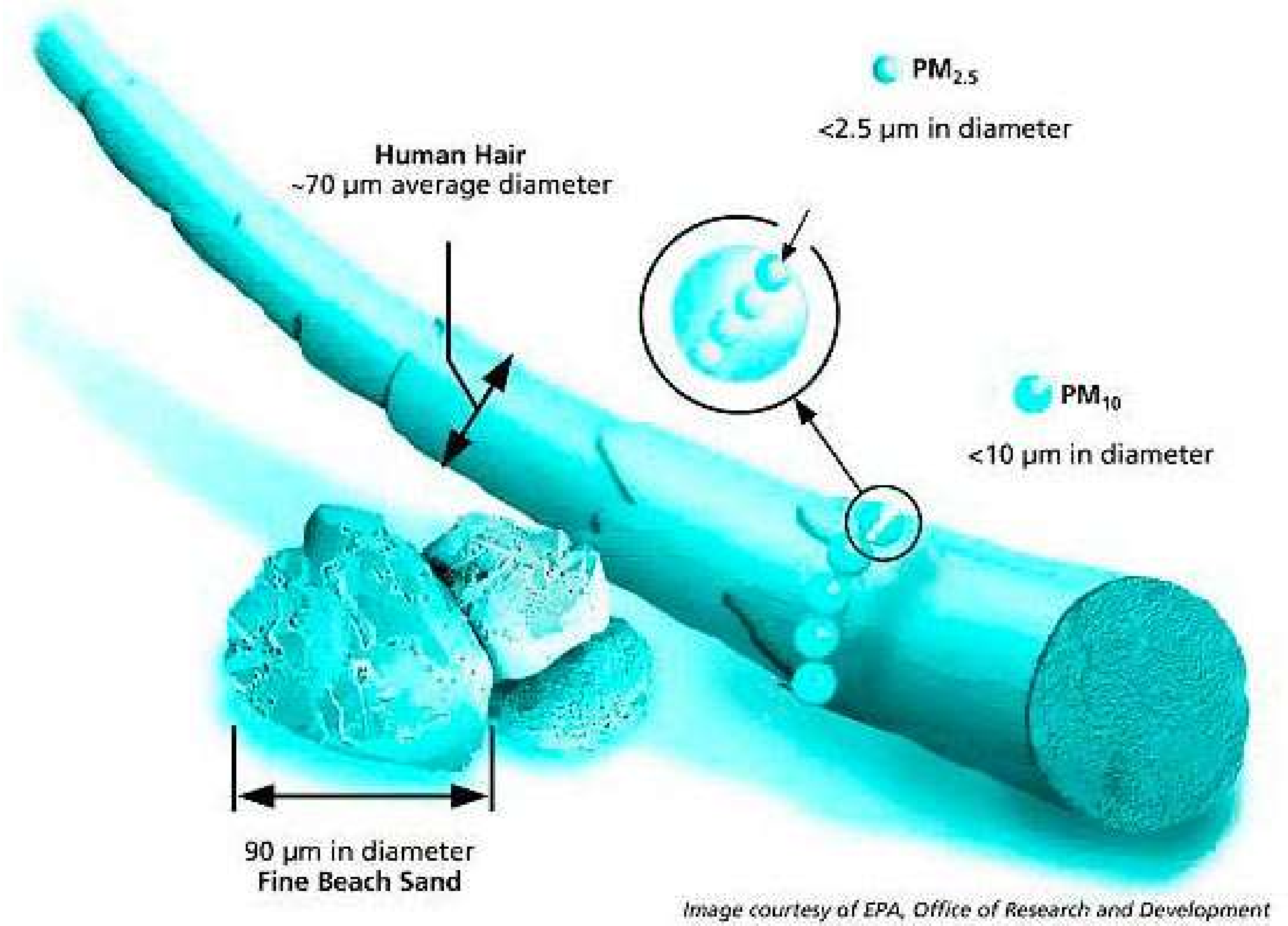


Crustal material

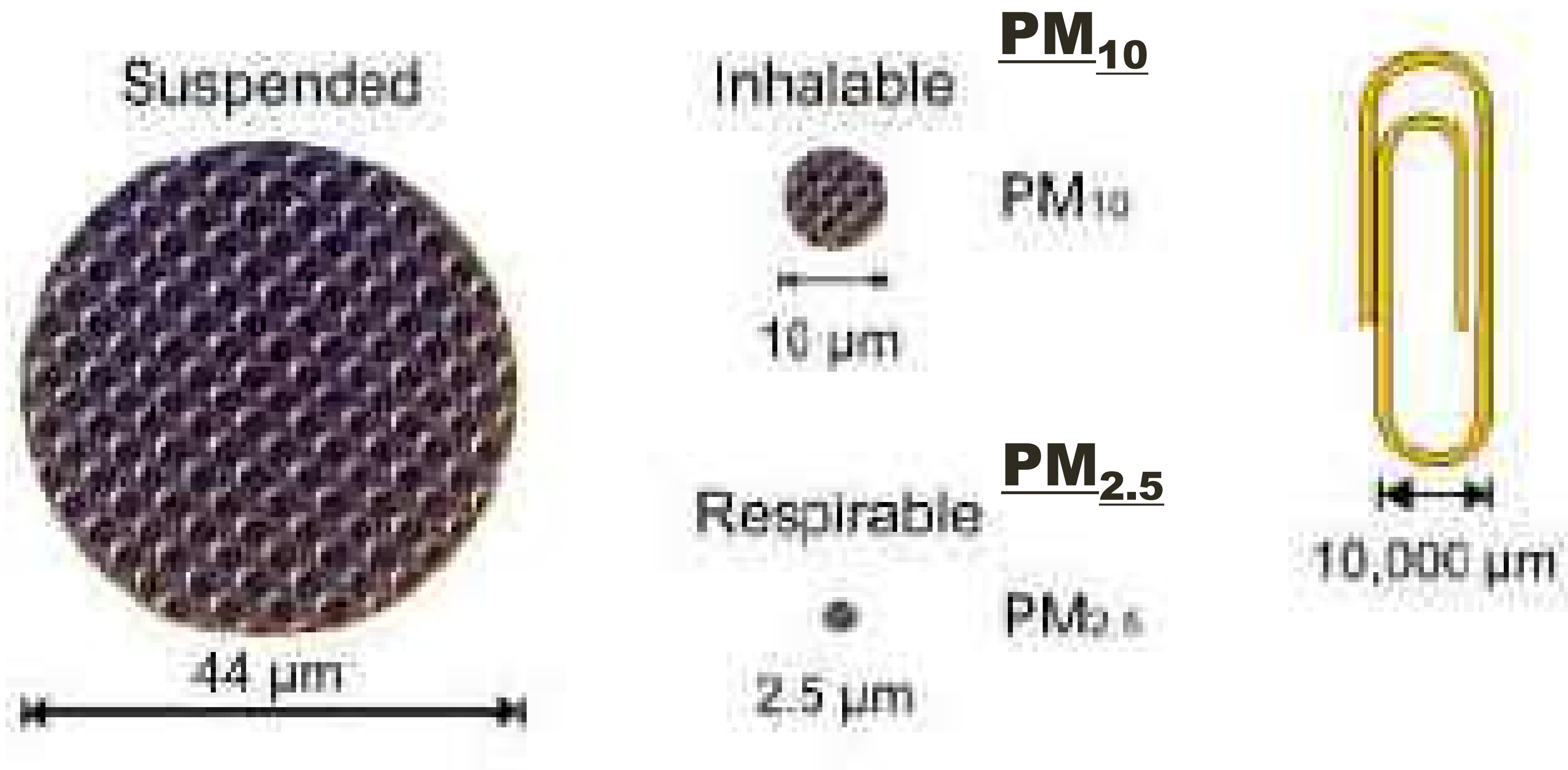


Carbon chain agglomerates

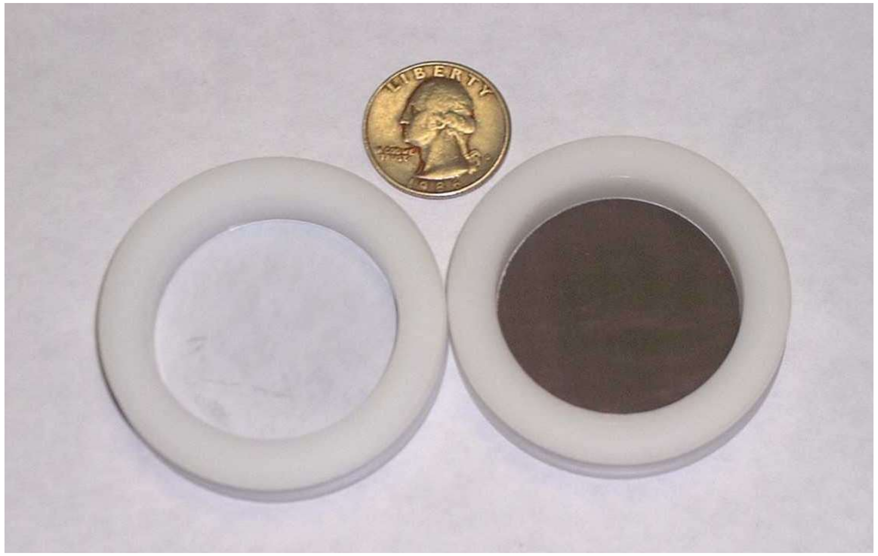
Relative sizes of particles in air



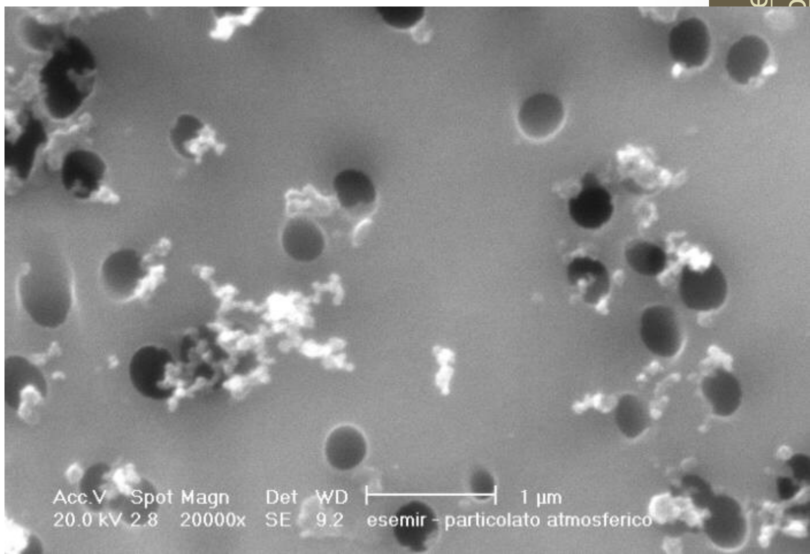
Relative sizes of particles in air



Particulate Matter (3 of 3)



A clear (left) and dirty (right) PM filter



Particulate Matter Composition
(1 of 3)

PM is composed of a mixture of primary and secondary compounds.

- Primary PM (directly emitted)
  - Suspended dust
  - Sea salt
  - Organic carbon
  - Elemental carbon
  - Metals from combustion
  - Small amounts of sulfate and nitrate
- Secondary PM (precursor gases that form PM in the atmosphere)
  - Sulfur dioxide (SO_2): forms sulfates
  - Nitrogen oxides (NO_x): forms nitrates
  - Ammonia (NH_3): forms ammonium compounds
  - Volatile organic compounds (VOCs): form organic carbon compounds

Particulate Matter Composition

(3 of 3)

Most PM mass in urban and nonurban areas is composed of a combination of the following chemical components

- **Geological Material –** suspended dust consists mainly of oxides of Al, Si, Ca, Ti, Fe, and other metal oxides
- **Ammonium –** ammonium bisulfate, sulfate, and nitrate are most common
- **Sulfate –** results from conversion of SO_2 gas to sulfate-containing particles
- **Nitrate –** results from a reversible gas/particle equilibrium between ammonia (NH_3), nitric acid (HNO_3), and particulate ammonium nitrate
- **NaCl –** salt is found in PM near sea coasts and after de-icing materials are applied
- **Organic Carbon (OC) –** consists of hundreds of separate compounds containing mainly carbon, hydrogen, and oxygen
- **Elemental Carbon (EC) –** composed of carbon without much hydrocarbon or oxygen. EC is black, often called soot.
- **Liquid Water –** soluble nitrates, sulfates, ammonium, sodium, other inorganic ions, and some organic material absorb water vapor from the atmosphere

Chow and Watson (1997)

Physiochemical Properties

- **Physical Characteristics**

  particle surface area, particle number, particle mass, particle size distribution, surface chemistry, surface charge

Chemical Components

biological components (e.g., pollen, microbes)

ions (sulfates, nitrates, ammonium)

strong acidity (H^+)

transition metals (water soluble, bioavailable, oxidant generation)

elemental carbon

organic carbon (total, nonvolatile, and semivolatile, functional groups and individual species)

PM Emissions Sources (1 of 4)

Point – generally a major facility emitting pollutants from identifiable sources (pipe or smoke stack). Facilities are typically permitted.





PM Emissions Sources (2 of 4)

Area – any low-level source of air pollution released over a diffuse area (not a point) such as consumer products, architectural coatings, waste treatment facilities, animal feeding operations, construction, open burning, residential wood burning, swimming pools, and charbroilers

PM Emissions Sources (3 of 4)

Mobile

- On-road is any moving source of air pollution such as cars, trucks, motorcycles, and buses
- Non-road sources include pollutants emitted by combustion engines on farm and construction equipment, locomotives, commercial marine vessels, recreational watercraft, airplanes, snow mobiles, agricultural equipment, and lawn and garden equipment



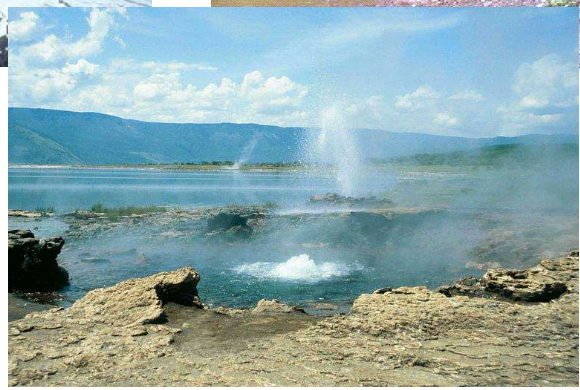


PM Emissions Sources (4 of 4)

Natural – biogenic and geogenic emissions from wildfires, wind blown dust, plants, trees, grasses, volcanoes, geysers, seeps, soil, and lightning

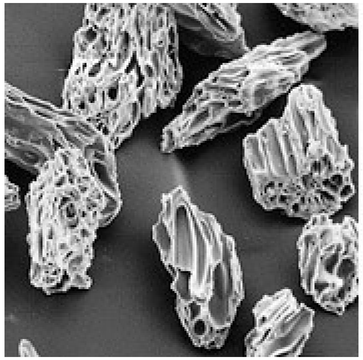




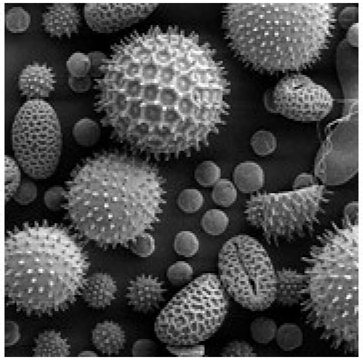


What are aerosols?

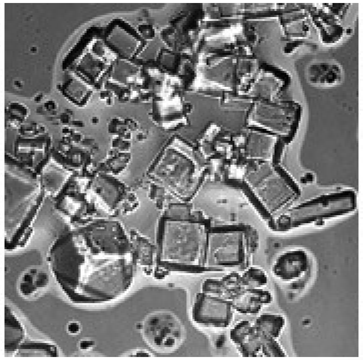
- Types
  - Dust
  - Sea salt
  - Sulfates
  - Black carbon
  - Organic matter
  - Nitrates



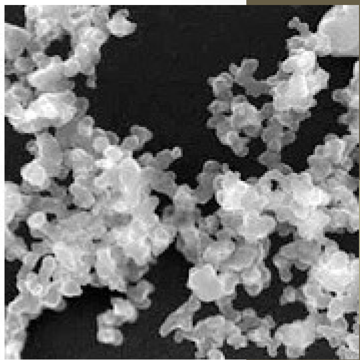
Volcanic ash



Pollen

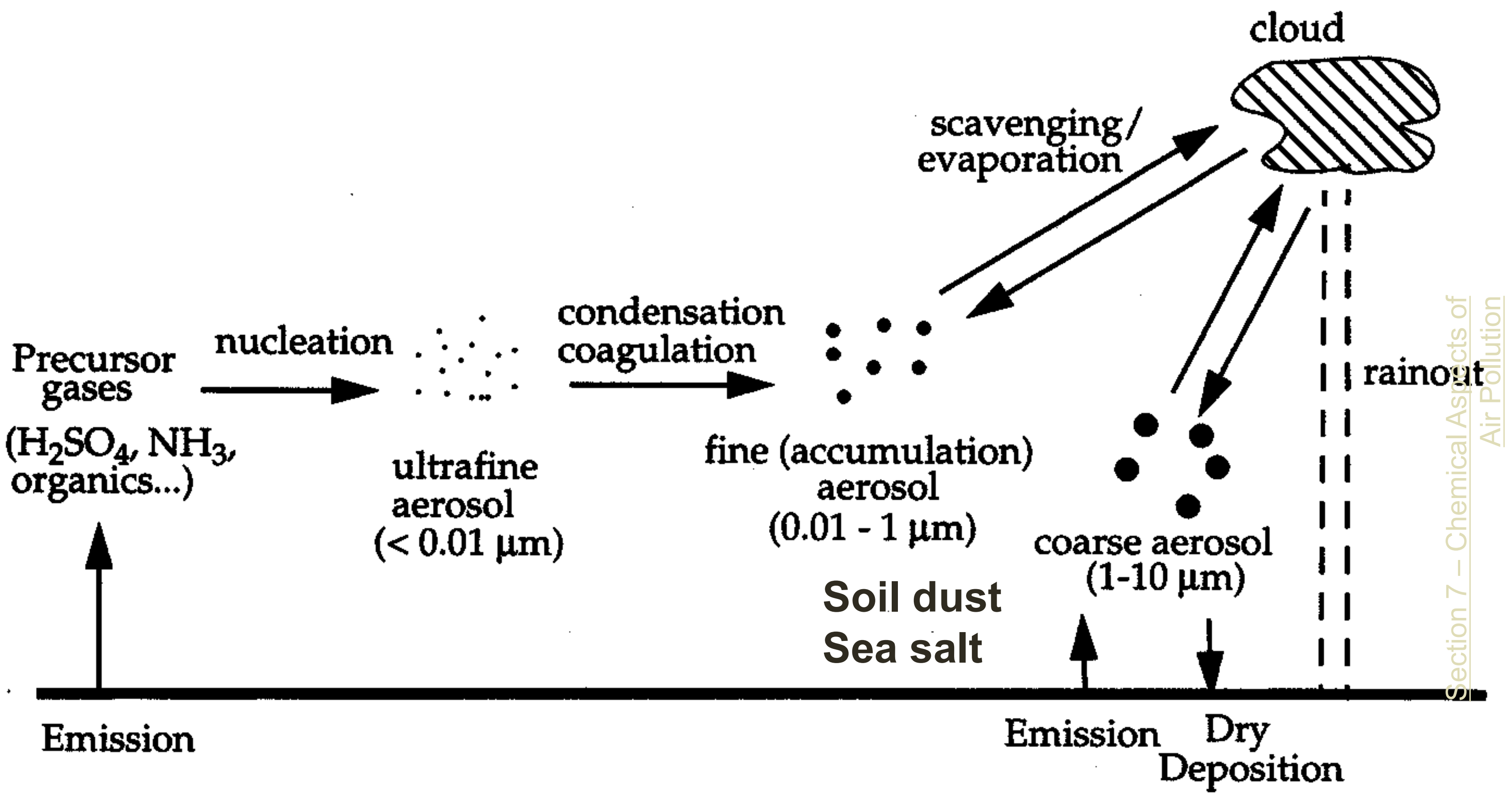


Sea salt



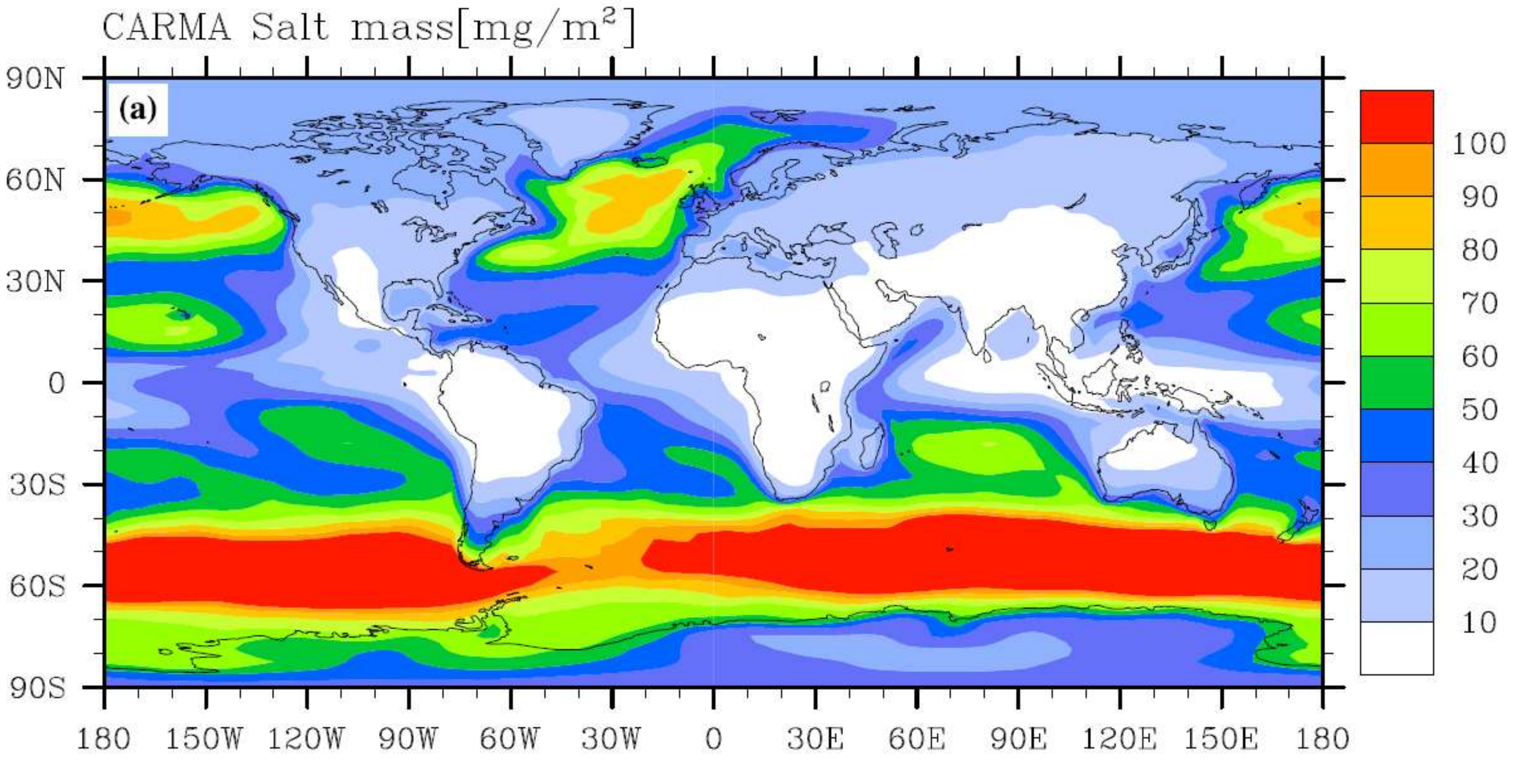
Soot

Aerosol: dispersed condensed matter suspended in a gas
Size range: 0.001 μm (molecular cluster) to 100 μm (small raindrop)



Environmental importance: health (respiration), visibility, radiative balance, cloud formation, heterogeneous reactions, delivery of nutrients…

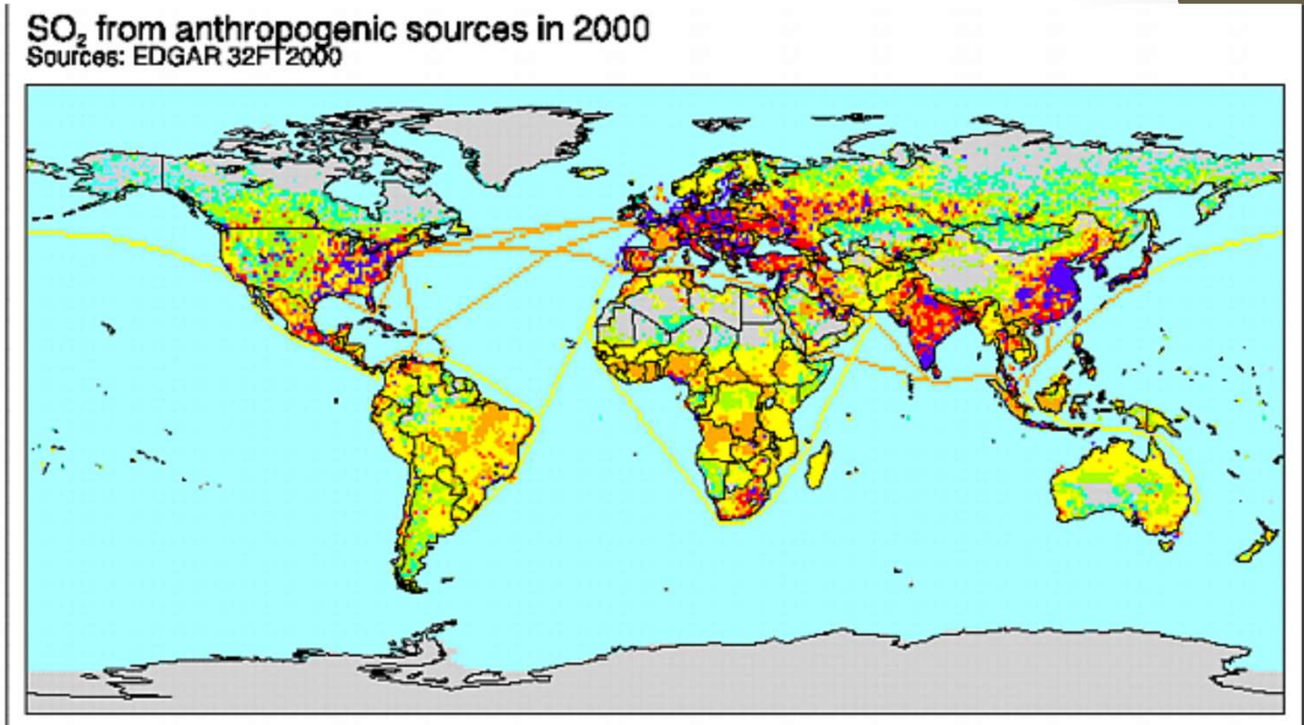
Sea Salt



- Mainly from the oceans
- Solid particles unless hydrated with water
- Mostly natural
- Causes cooling

Sulfates (nitrates are similar)

- Secondary emission
  - Produced from SO_2 or DMS
- Mostly from humans
  - Fossil fuel combustion
- Albedo of 0.99
  - Does this cause warming or cooling?
    - Cooling

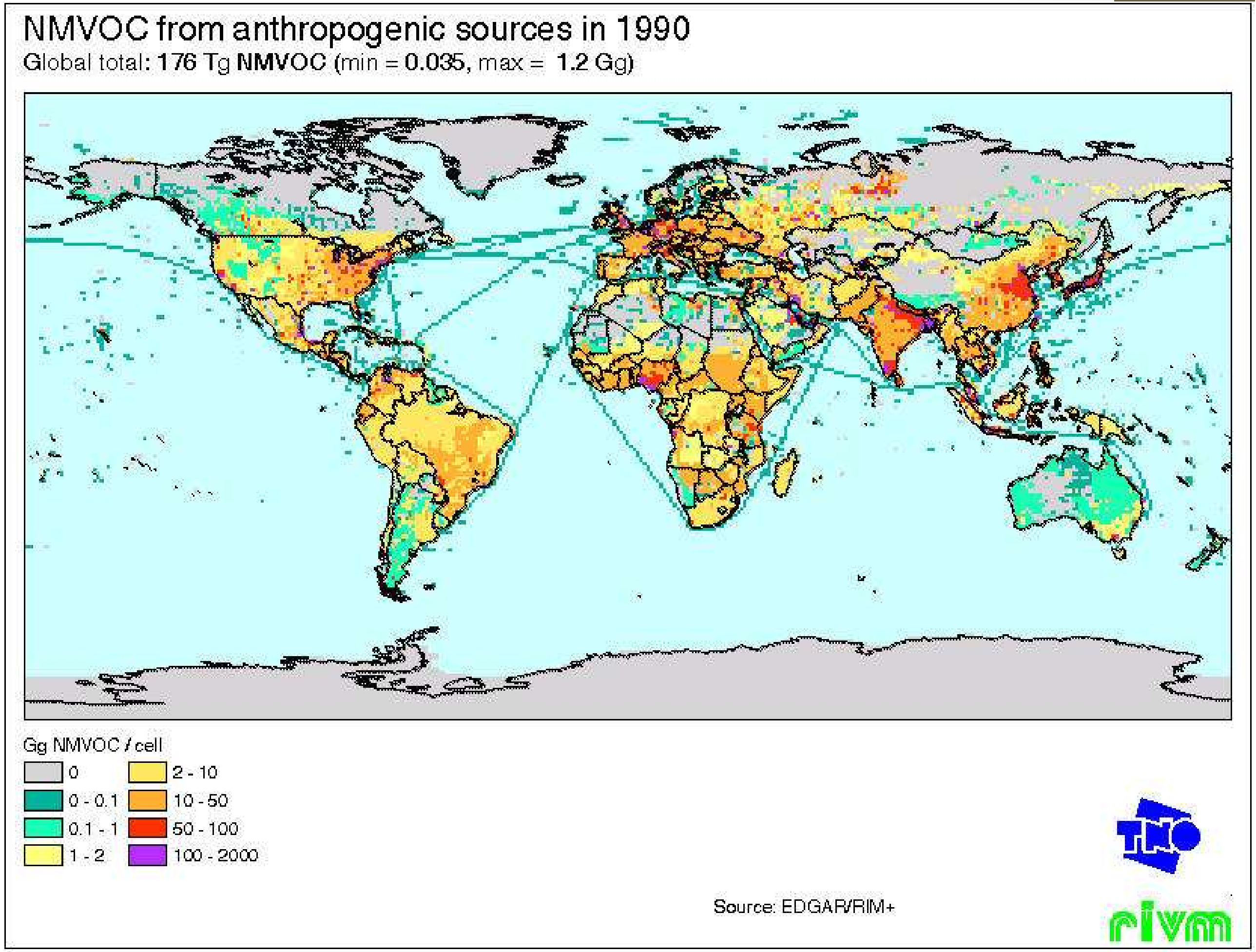


Black carbon

- Mostly from biomass burning and fossil fuel combustion
- Appears black to the naked eye
  - What would it's albedo be?
    - Close to 0
  - Does this cause warming or cooling?
    - Warming over snow/ice especially!

Organic Matter

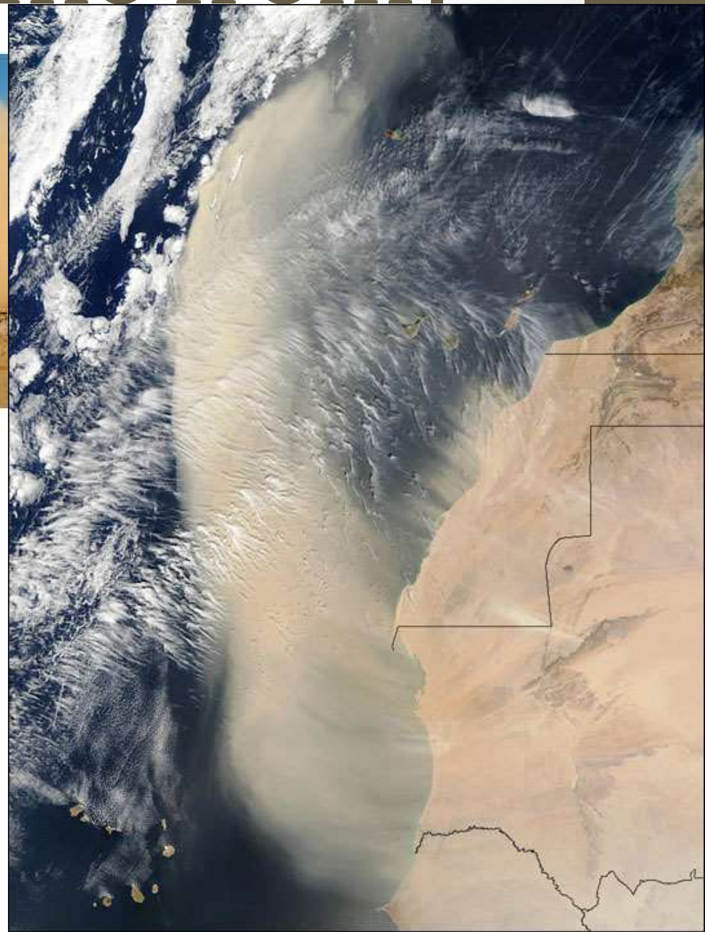
- Variety of compounds
- Natural or from humans
  - Terpenes from trees, vegetation
  - Fossil fuel and biomass burning
- Can be primary or secondary emissions



Where do aerosols come from?

- Dust
  - Deserts
  - Agriculture
- Sea salt
  - Oceans
- Sulfates
  - Chemical reaction of sulfur dioxide
    - Volcanoes
    - Fossil fuel burning
    - Marine plankton

Desert dust

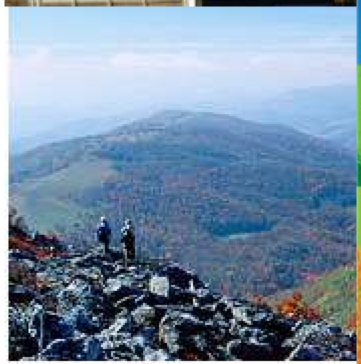


Saharan dust storm off West African coas

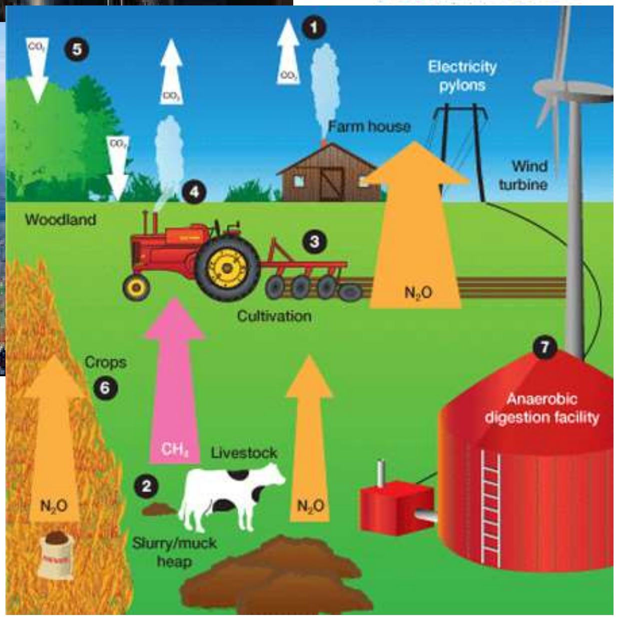
Volcanic ash

Where do aerosols come from?

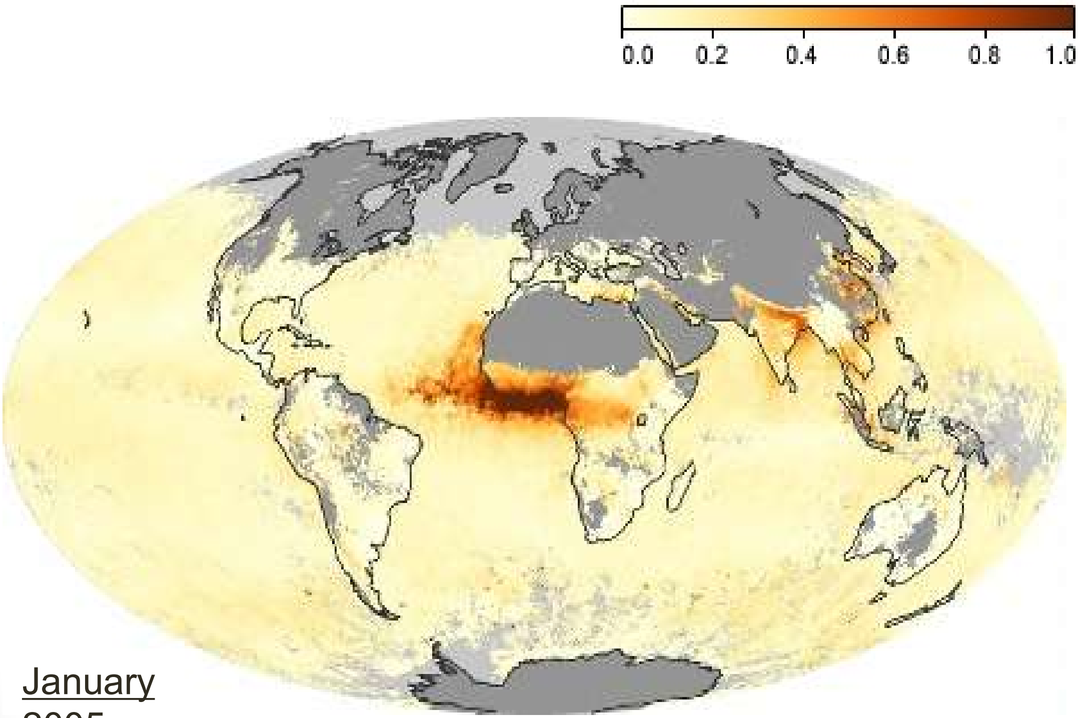
Smoke from forest fires



VOCs from vegetation



Where do aerosols come from?



January 2005

- Pale yellow
  - Clear sky
  - Maximum visibility
- Dark red-brown
  - Very hazy conditions
- Video of aerosol optical depth over time (1/05 - 6/12)

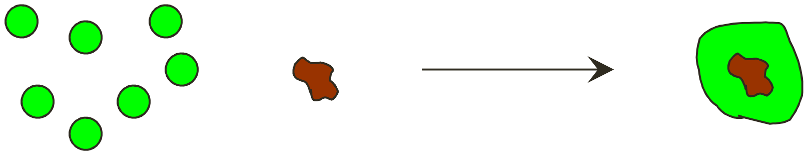
Where do aerosols come from?

- High concentrations due to land clearing and agricultural fires (dry seasons)
  - South America
    - July – Sept
  - Central America
    - March – May
  - Central and south Africa
    - June – Sept
  - Southeast Asia
    - January – April
- High concentrations due to dust storms
  - Arabian Peninsula
    - May – August
- High concentrations due to human-produced air pollution
  - Northern India and Himalayas region
    - Many months
  - Eastern China
    - Most of the year

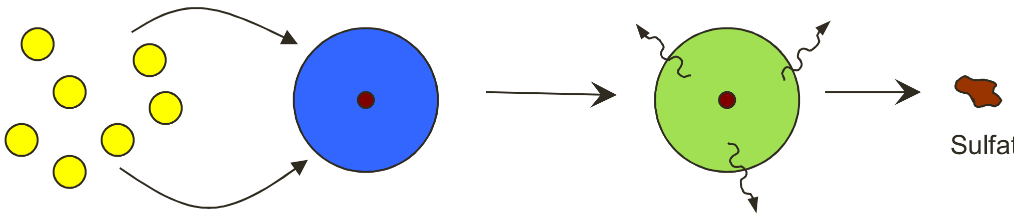
Particulate Matter Chemistry (1 of 4)

Coagulation: Particles collide and stick together.

Condensation: Gases condense onto a small solid particle to form a liquid droplet.



Cloud/Fog Processes: Gases dissolve in a water droplet and chemically react. A particle exists when the water evaporates.



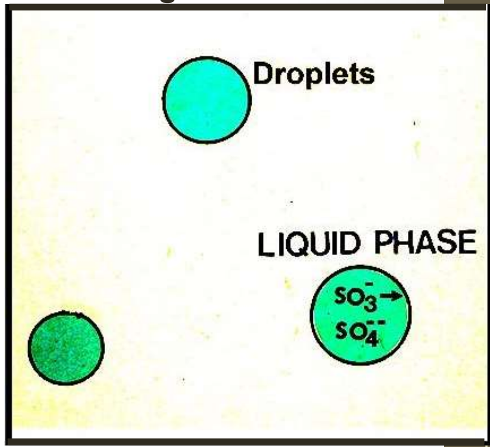
Chemical Reaction: Gases react to form particles.

Particulate Matter Chemistry (2 of 4

Sulfate Chemistry

- Virtually all ambient sulfate (99%) is secondary, formed within the atmosphere from SO_2 during the summer.
- About half of SO_2 oxidation to sulfate occurs in the gas phase through photochemical oxidation in the daytime. NO_x and hydrocarbon emissions tend to enhance the photochemical oxidation rate.
- At least half of SO_2 oxidation takes place in cloud droplets as air molecules react in clouds.
- Within clouds, soluble pollutant gases, such as SO_2, are scavenged by water droplets and rapidly oxidize to sulfate.
- Only a small fraction of cloud droplets deposit out as rain; most droplets evaporate and leave a sulfate residue or "convective debris".
- Typical conversion rate 1-10% per hour

Heterogeneous Oxidation



Husar (1999)

Particulate Matter Chemistry (3 of 4)

Nitrate Chemistry

- NO_2 can be converted to nitric acid (HNO_3) by reaction with hydroxyl radicals (OH) during the day.
  - The reaction of OH with NO_2 is about 10 times faster than the OH reaction with SO_2.
  - The peak daytime conversion rate of NO_2 to HNO_3 in the gas phase is about 10% to 50% per hour.
- During the nighttime, NO_2 is converted into HNO_3 by a series of reactions involving ozone and the nitrate radical.
- HNO_3 reacts with ammonia to form particulate ammonium nitrate (NH_4NO_3).
- Thus, PM nitrate can be formed at night and during the day; daytime photochemistry also forms ozone.

Particulate Matter Chemistry (4 o

Sources	Emissions	PM Formation	PM Transport/Loss	Sample Collection

Chemical Processes

Mechanical → **Particles**
- Sea salt
- Dust

Particles
- NaCl
- Crustal

Combustion → **Particles**, **Gases**
- Motor vehicles
- Industrial
- Fires

Particles
- Soot
- Metals
- OC

Gases
- NO_x
- SO_2
- VOCs
- NH_3

Other gaseous → **Gases**
- Biogenic
- Anthropogenic

Gases
- VOCs
- NH_3
- NO_x

PM Formation:

gases condense onto particles

cloud/fog processes

condensation and coagulation

photochemical production

cloud/fog processes

PM Transport/Loss:

transport

sedimentation (dry deposition)

wet deposition

Sample Collection:

Measurement Issues
- Inlet cut points
- Vaporization of nitrate, H_2O, VOCs
- Adsorption of VOCs
- Absorption of H_2O

Meteorological Processes

Emissions	PM Formation	PM Transport/Loss	Sample Collection
Winds	Clouds, fog	Winds	Temperature
Temperature	Temperature	Precipitation	Relative humidity
Solar radiation	Relative humidity		Winds
Vertical mixing	Solar radiation		

Particulate Matter Meteorology

How weather affects PM emissions, formation, and transport

Phenomena	Emissions	PM Formation	PM Transport/Loss
Aloft Pressure Pattern	No direct impact.	No direct impact.	Ridges tend to produce conditions conducive for accumulation of $PM_{2.5}$. Troughs tend to produce conditions conducive for dispersion and removal of PM and ozone. In mountain-valley regions, strong wintertime inversions and high $PM_{2.5}$ levels may not be altered by weak troughs. High $PM_{2.5}$ concentrations often occur during the approach of a trough from the west.
Winds and Transport	No direct impact.	In general, stronger winds disperse pollutants, resulting in a less ideal mixture of pollutants for chemical reactions that produce $PM_{2.5}$.	Strong surface winds tend to disperse $PM_{2.5}$ regardless of season. Strong winds can create dust which can increase $PM_{2.5}$ concentrations.
Temperature Inversions	No direct impact.	Inversions reduce vertical mixing and therefore increase chemical concentrations of precursors. Higher concentrations of precursors can produce faster, more efficient chemical reactions that produce $PM_{2.5}$.	A strong inversion acts to limit vertical mixing allowing for the accumulation of $PM_{2.5}$.
Rain	Reduces soil and fire emissions	Rain can remove precursors of $PM_{2.5}$.	Rain can remove $PM_{2.5}$.
Moisture	No direct impact.	Moisture acts to increase the production of secondary $PM_{2.5}$ including sulfates and nitrates.	No direct impact.
Temperature	Warm temperatures are associated with increased evaporative, biogenic, and power plant emissions, which act to increase $PM_{2.5}$. Cold temperatures can also indirectly influence $PM_{2.5}$ concentrations (i.e., home heating on winter nights).	Photochemical reaction rates increase with temperature.	Although warm surface temperatures are generally associated with poor air quality conditions, very warm temperatures can increase vertical mixing and dispersion of pollutants. Warm temperatures may volatize Nitrates from a solid to a gas. Very cold surface temperatures during the winter may produce strong surface-based inversions that confine pollutants to a shallow layer.
Clouds/Fog	No direct impact.	Water droplets can enhance the formation of secondary $PM_{2.5}$. Clouds can limit photochemistry, which limits photochemical production.	Convective clouds are an indication of strong vertical mixing, which disperses pollutants.
Season	Forest fires, wood burning, agriculture burning, field tilling, windblown dust, road dust, and construction vary by season.	The sun angle changes with season, which changes the amount of solar radiation available for photochemistry.	No direct impact.

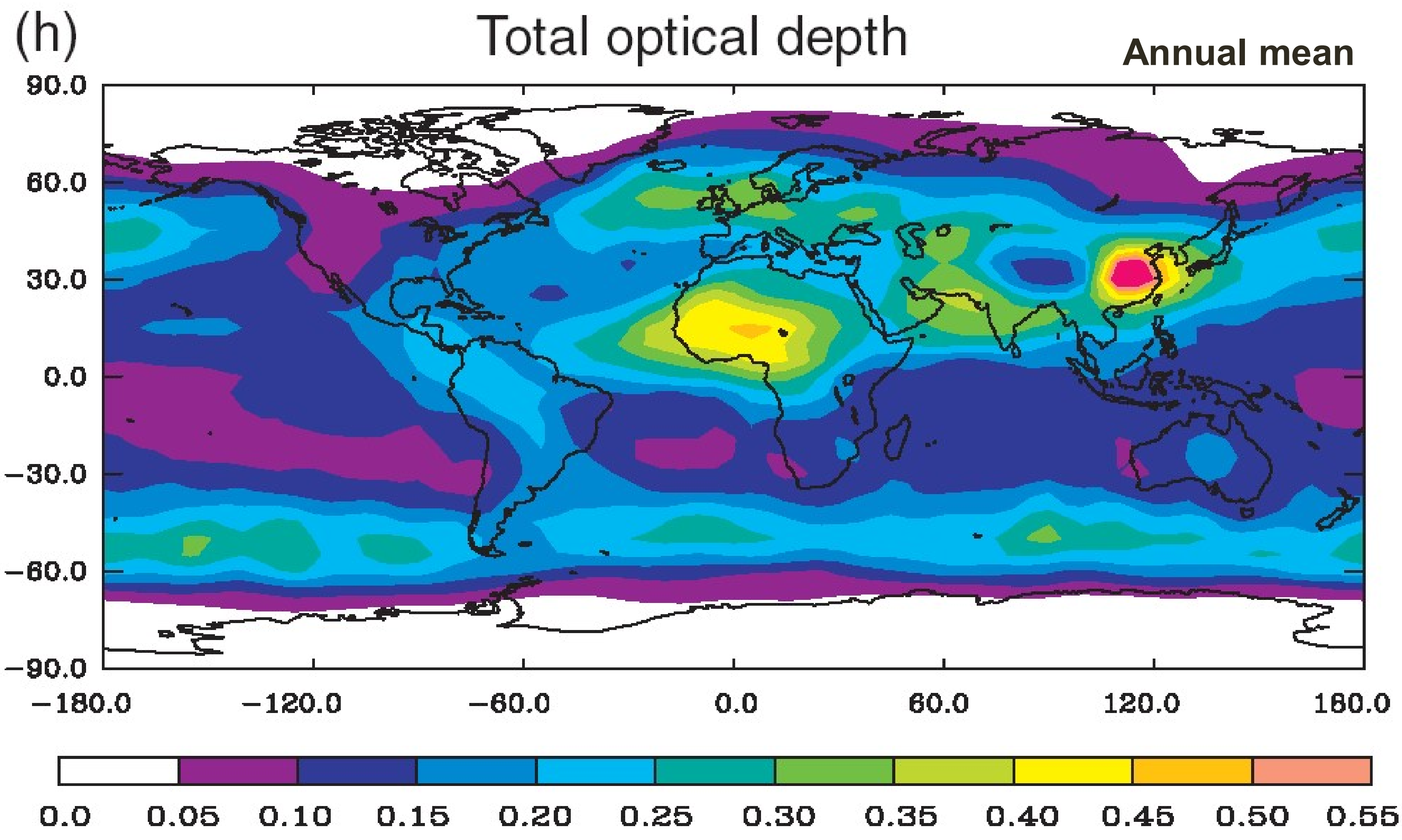
Particulate Matter Standards

- High-volume samplers measured PM by Total Suspended Particulate Matter (TSP). TSP usually less than 25-50 µg/m^3. Concentrations measured usually around 260 µg/m^3 .

- Based on research in the 1960s and 1970s, the human respiratory system was found to be affected by PM that was finer than what high-volume samplers measured.

- A new standard based on PM_{10} was established using a 24-hour concentration of 150 µg/m^3.

AEROSOL OPTICAL DEPTH (GLOBAL MODEL)

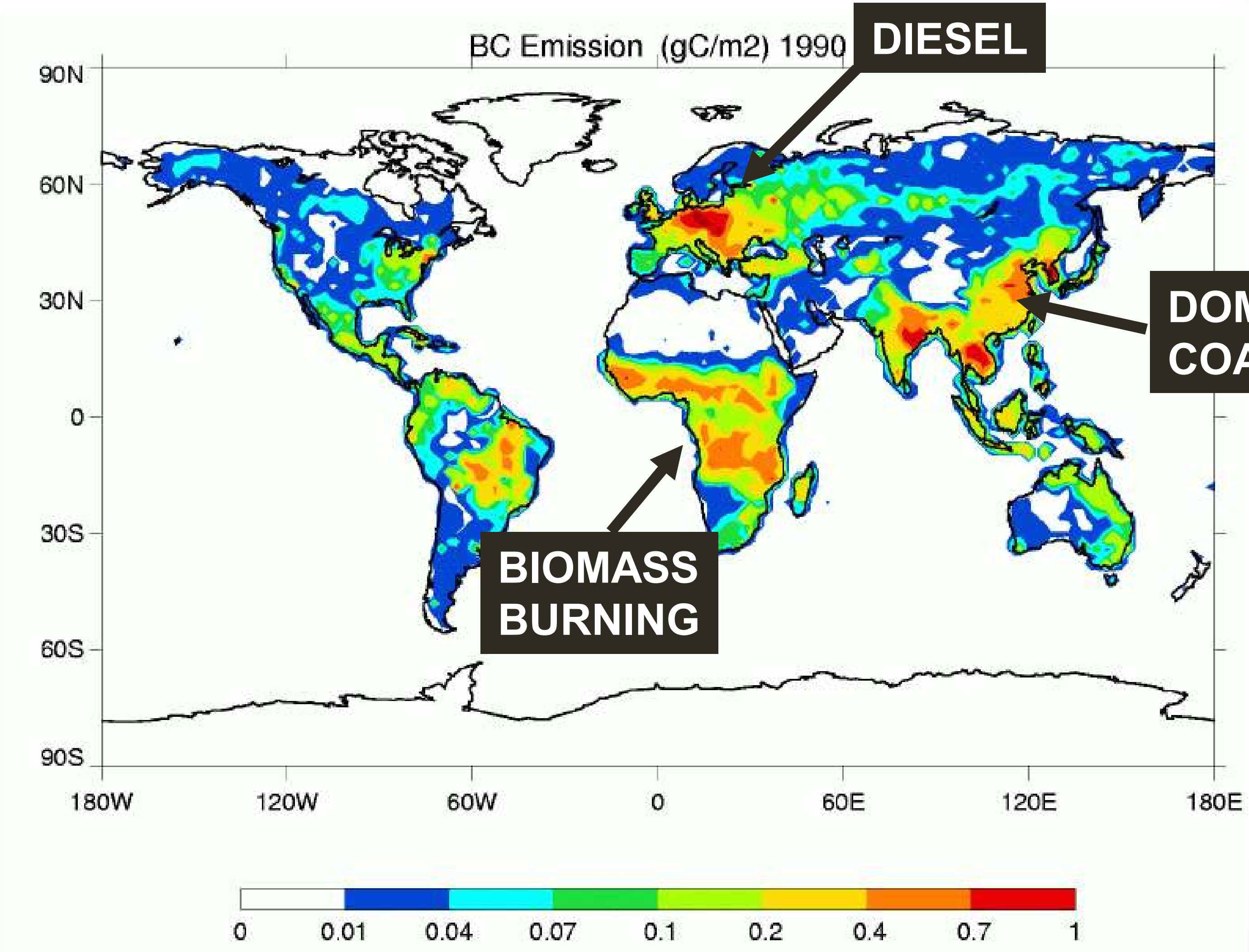


Biomass fire haze in central America yesterday (4/30/03)

Fire locations in red

Modis.gsfc.nasa.gov

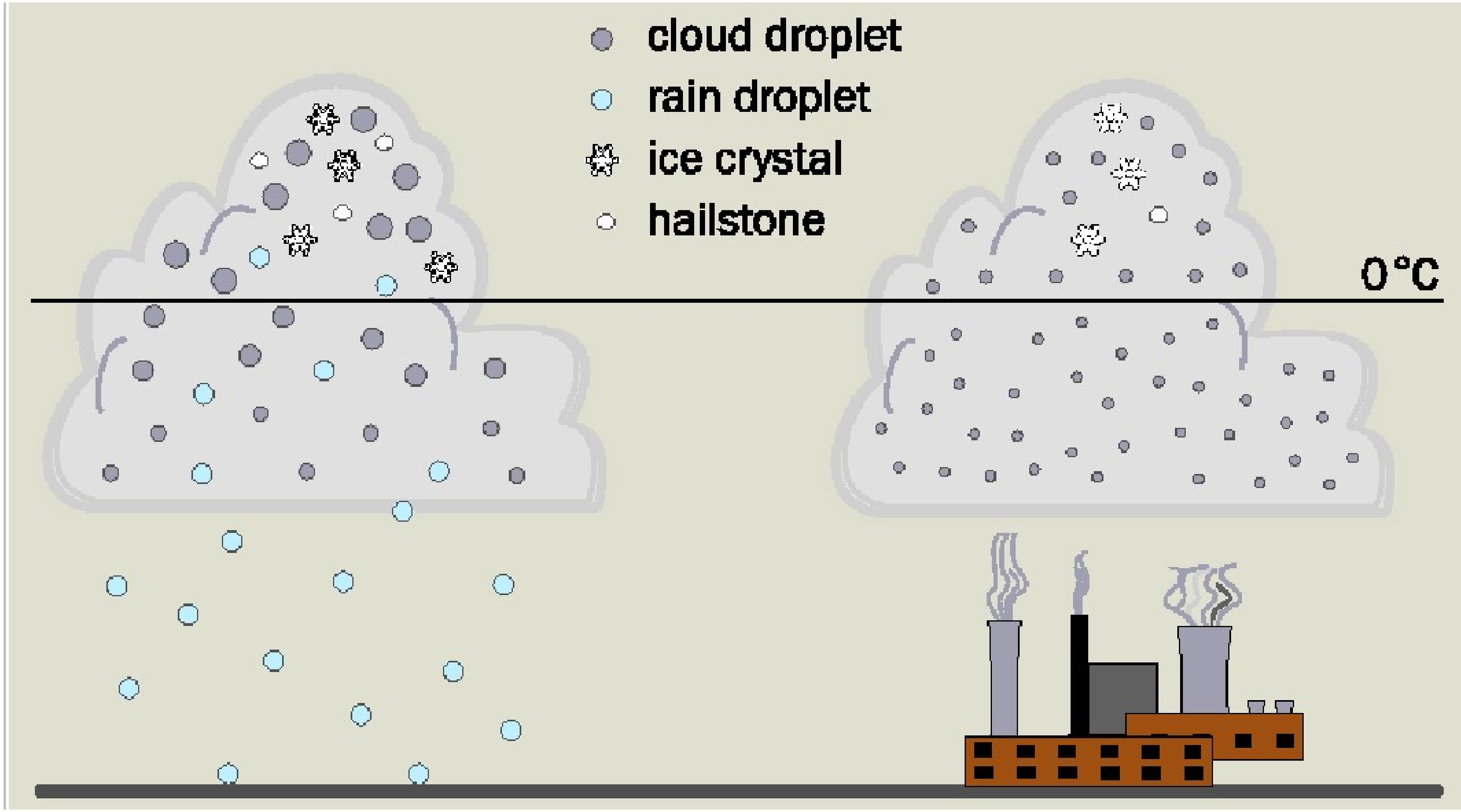
BLACK CARBON EMISSIONS



Chin et al. [2000]

Particles Impact Human Health and MORE

Suppression of Rain and Snow by Urban and Industrial Air Pollution



Courtesy of D. Rosenfeld.

EPA REGIONAL HAZE RULE: FEDERAL CLASS I AREAS TO RETURN TO "NATURAL" VISIBI LEVELS BY 2064

…will require essentially total elimination of anthropogenic aerosols!

clean day

moderately polluted day

Acadia National Park

http://www.hazecam.net/