Atmospheric Aerosols:
The Role of Vehicles

presented to the

Metropolitan Washington Council of Governments

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

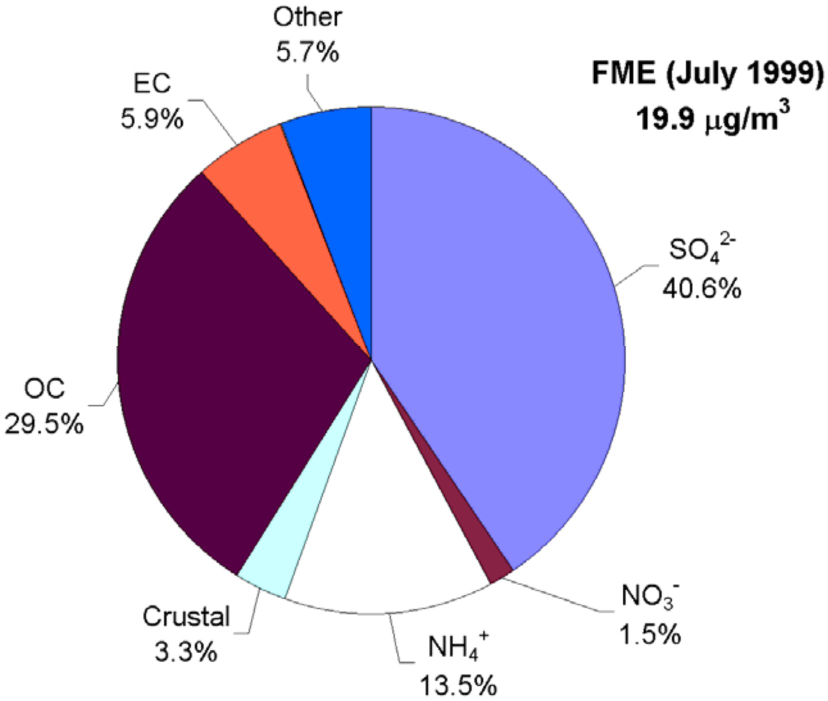
…will require essentially total elimination of anthropogenic aerosols!

clean day

moderately polluted day

Acadia National Park

http://www.hazecam.net/

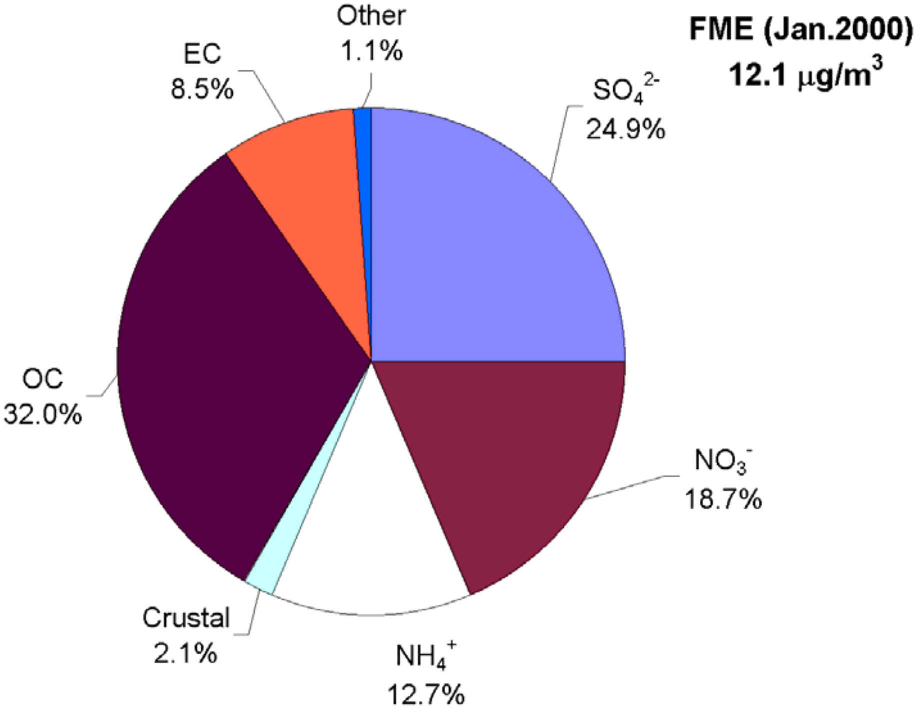


Inorganic compounds ~50% (by mass)

Carbonaceous material ~40% (by mass)

Summer: Sulfate dominates.

Winter: Nitrate/carbonaceous particles play bigger roles.



Particles, like gases, are characterized by chemical content, usually expressed in μg m^{-3}, but unlike gases, particles also have a characteristic size. We may want to start discussion the characteristics of atmospheric aerosols by addressing the question "What is the mean diameter of the particles?" The answer to this question changes with your point of view.

A. Size Number Distribution

If your concern is the **mass** of some pollutant that is being transported through the air for biogeochemical cycles, then you want to know the mean diameter of the particles with the mass or **volume**. In other words, "What size particles carry the most mass?”

If your concern loss of **visibility** then you want to know the diameter of the particles that have the largest cross section or **surface area**. In other words, "What size particles cover the largest surface area?"

If your concern is **cloud formation or microphysics** then you want to know the range of diameters with the largest **number** of particles. In other words, "What is the size of the most abundant particles?"

If your concern is **human health** then you need to know about both the **mass and number** of the particles, because only a certain size particle can enter the lungs.

Chemical Composition

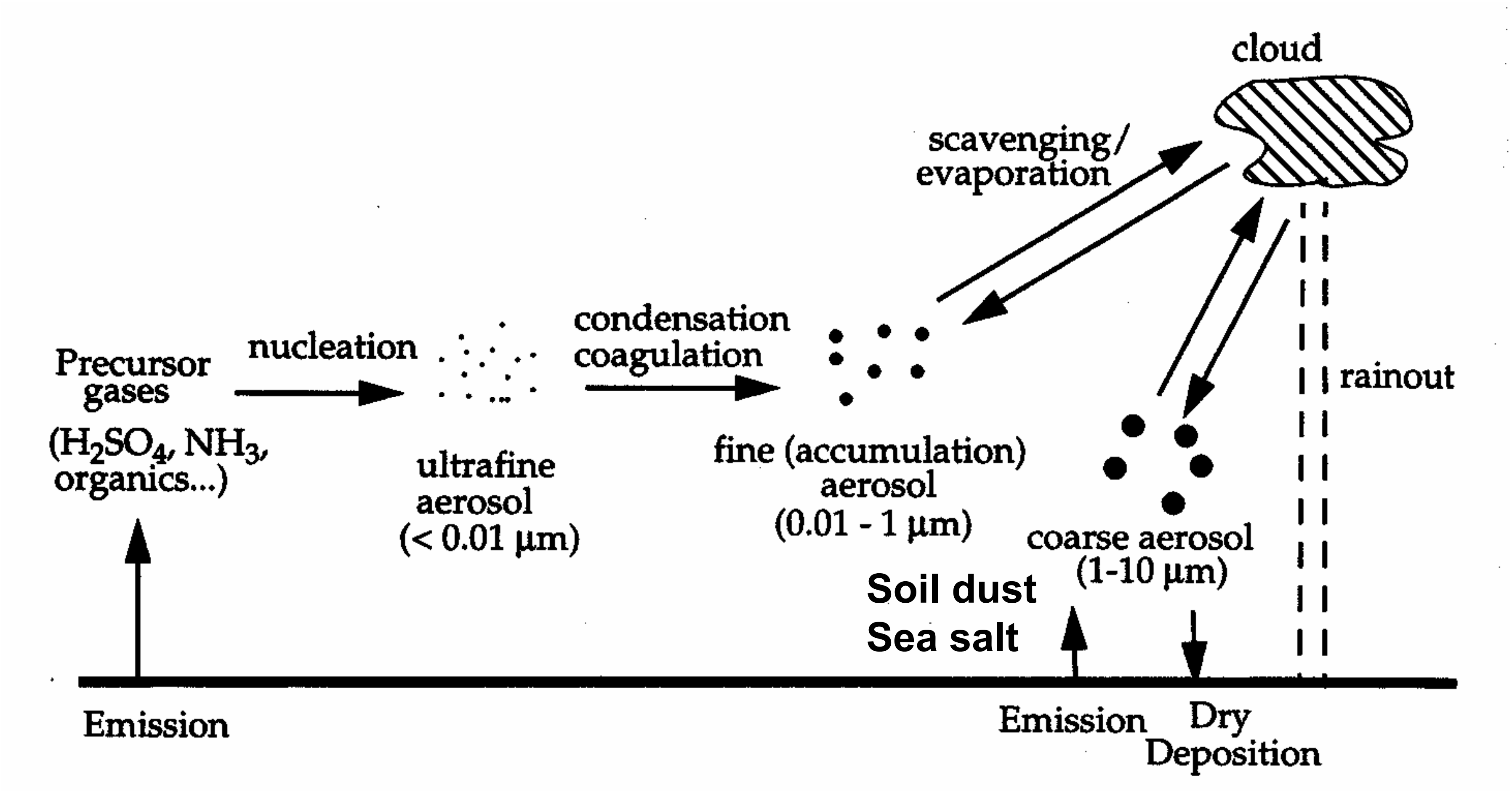
The bimodal nature of the size-number distribution of atmospheric particles suggests at least two distinct mechanisms of formation, and the chemical composition of the particles reflects their origins.

Fine particles have a diameter smaller than about 2.5 μm, and are produced by the condensation of vapors, accumulation, and coagulation. They have a chemical composition that reflects the condensable trace gases in the atmosphere: SO_2, NH_3, HNO_3, VOC's, and H_2O. The chemical composition is water with SO_4^{-2}, NO_3^-, NH_4^+, Pb, Cl^-, Br^-, C(soot), and organic matter; where biomass burning is prevalent, K^+.

Coarse Particles have a diameter greater than about 2.5 μm, are produced by mechanical weathering of surface materials. Their lifetimes, controlled by fallout and washout, are generally short. The composition of particles in this size range reflects that of the earth's surface - silicate (SiO_2), iron and aluminum oxides, $CaCO_3$ and $MgCO_{3;}$ over the oceans , NaCl.

ORIGIN OF THE ATMOSPHERIC AEROSOL

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



Soil dust
Sea salt

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

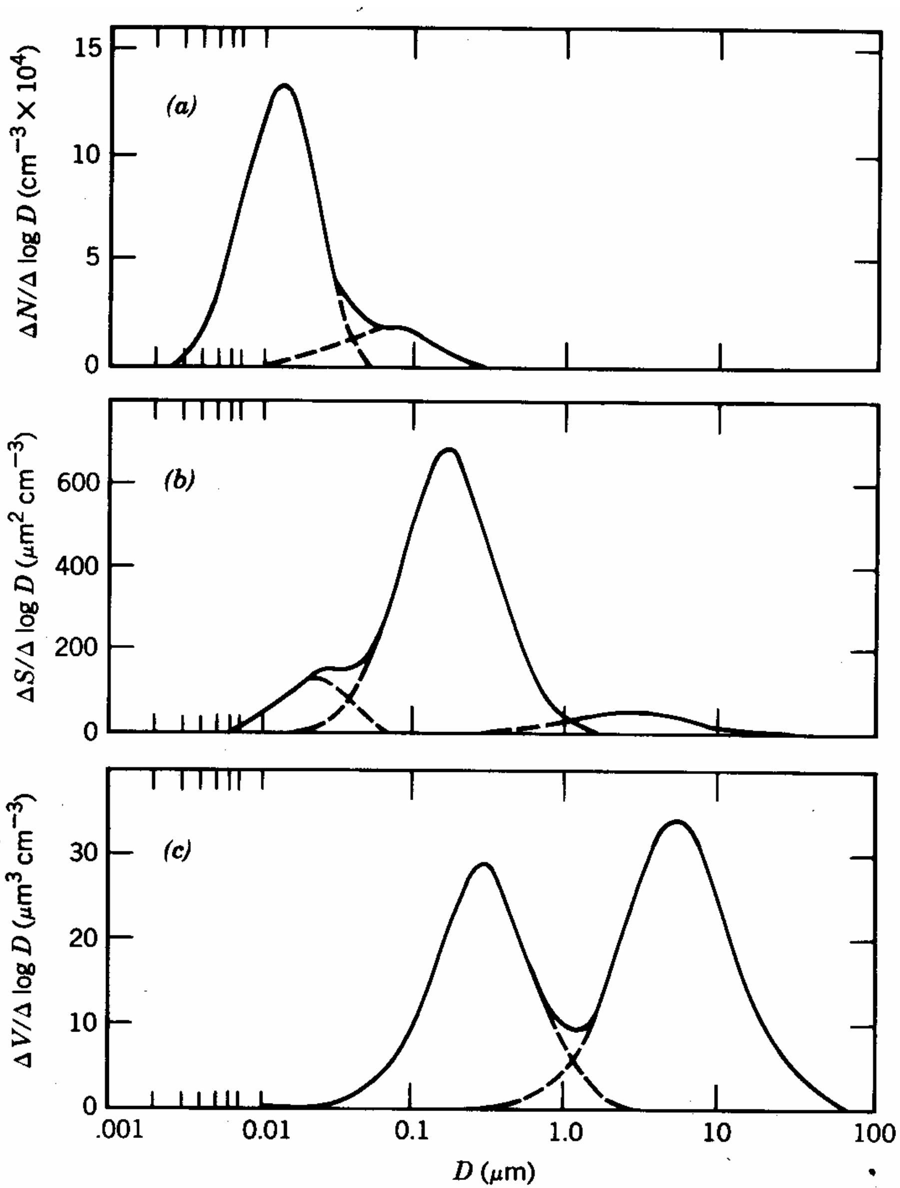
Aerosol Distributions

Number
- cloud formation

Surface
- visibility

Volume
- mass

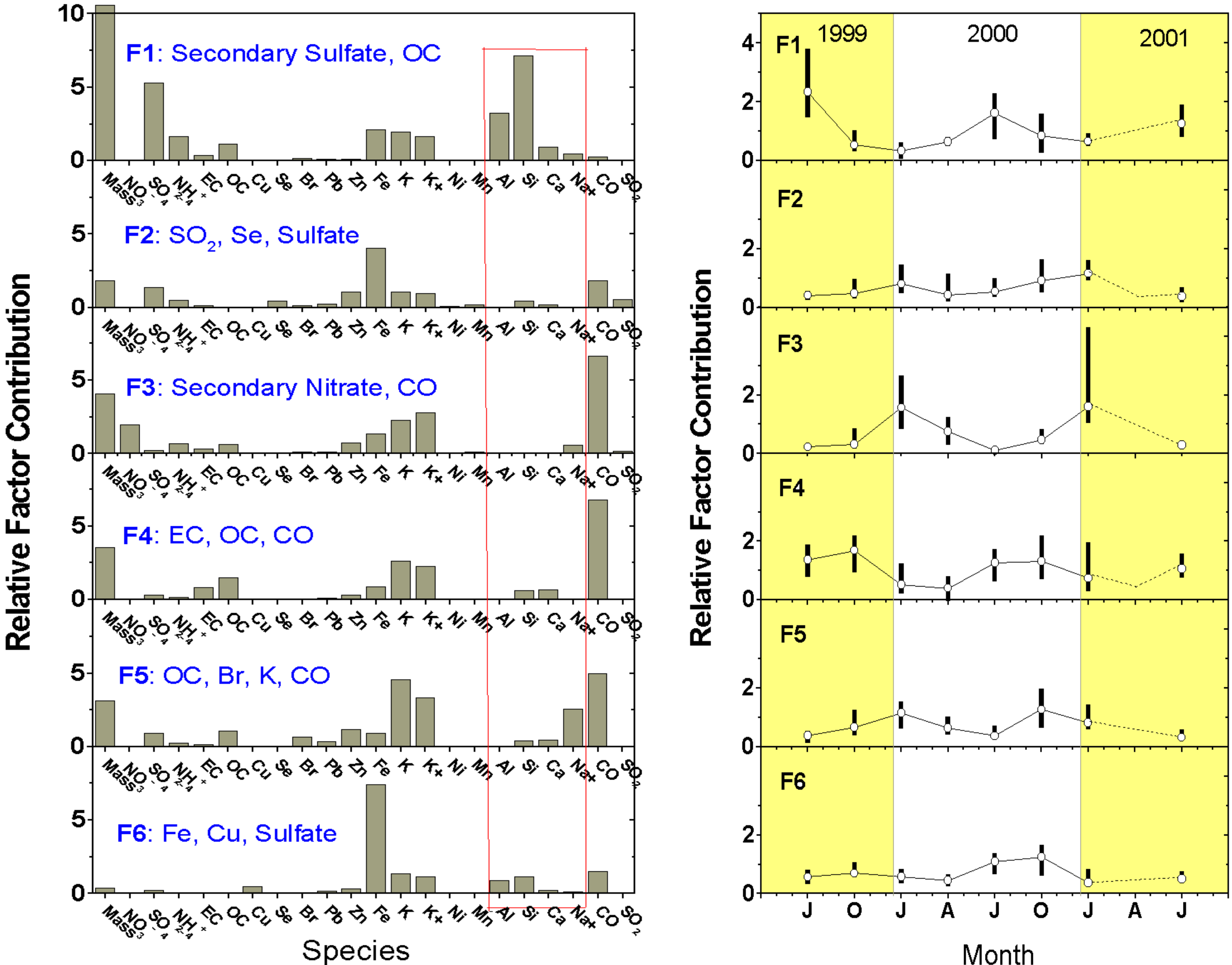
Mass & Number
- human health

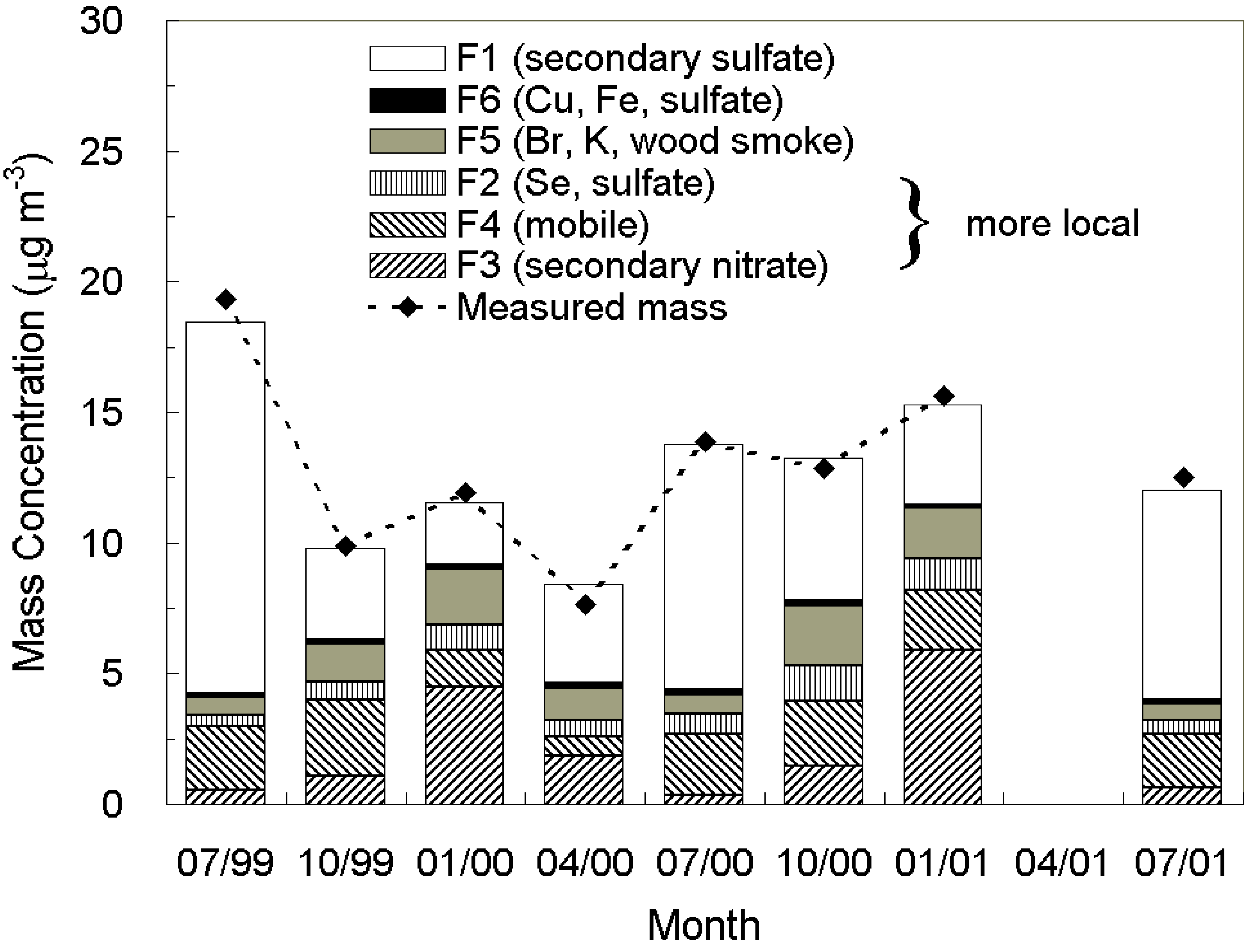


Fort Meade, MD

Aerosol speciation, analysis with UNMIX (Factor Analysis)

1999 – 2001 Antony Chen
2002 Jennifer Hains & Brett Taubman


Relative Factor Contribution
F1: Secondary Sulfate, OC
F2: SO$_2$, Se, Sulfate
F3: Secondary Nitrate, CO
F4: EC, OC, CO
F5: OC, Br, K, CO
F6: Fe, Cu, Sulfate
10
5
0
Mass
NO$_3$
SO$_4$
NH$_4$
EC
OC
Cu
Se
Br
Pb
Zn
Fe
K
K+
Ni
Mn
Al
Si
Ca
Na+
CO
SO$_2$
Species
Relative Factor Contribution
F1
F2
F3
F4
F5
F6
1999
2000
2001
4
2
0
J
O
J
A
J
O
J
A
J
Month



- Monthly contribution of six factors from UNMIX to the $PM_{2.5}$ mass at FME.

Black Carbon (soot) and Organic Carbon Aerosols

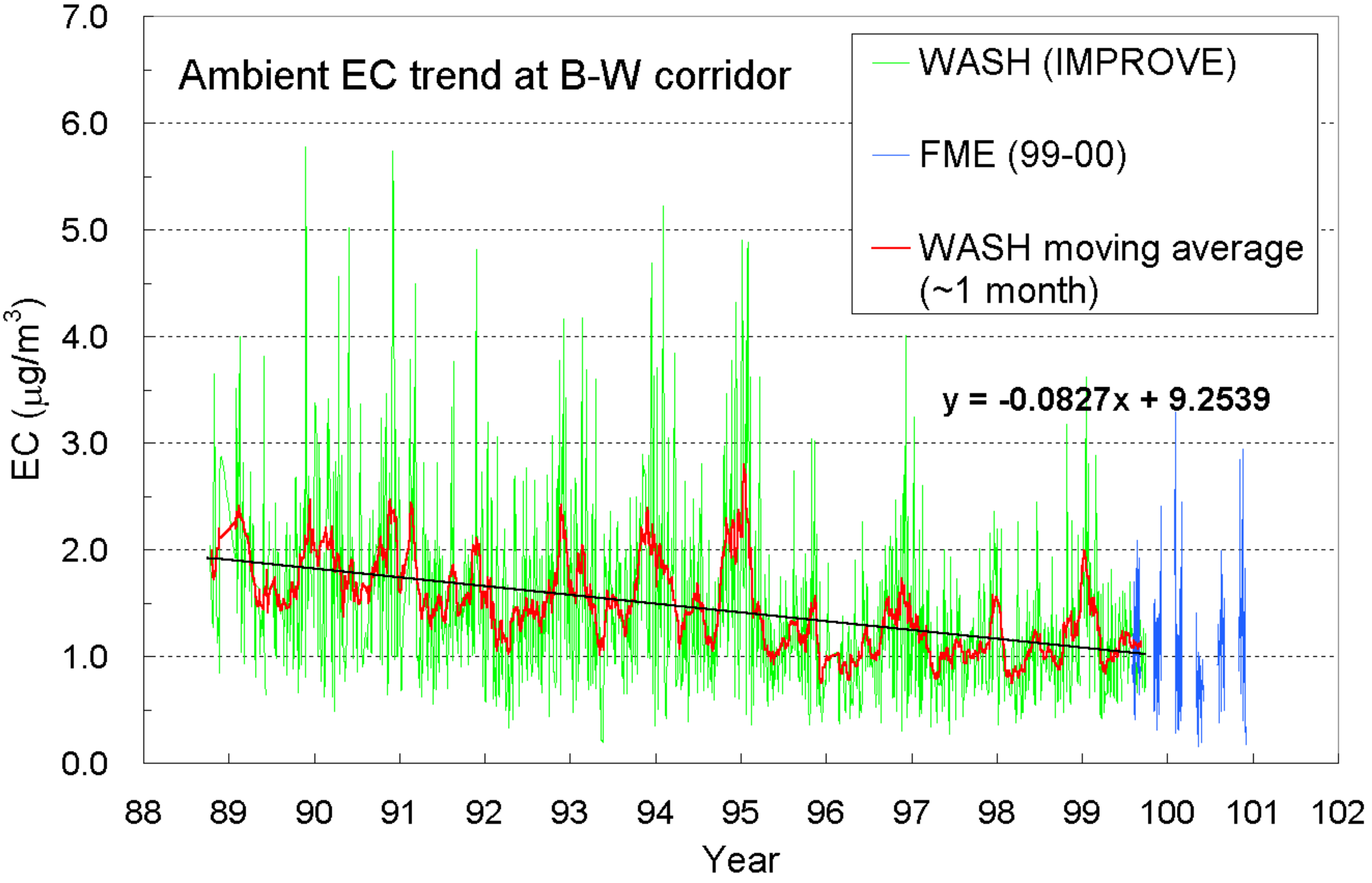
From Bond et al. (*J. Geophys. Res.*, 2004)

North America: The sources of **Black Carbon**

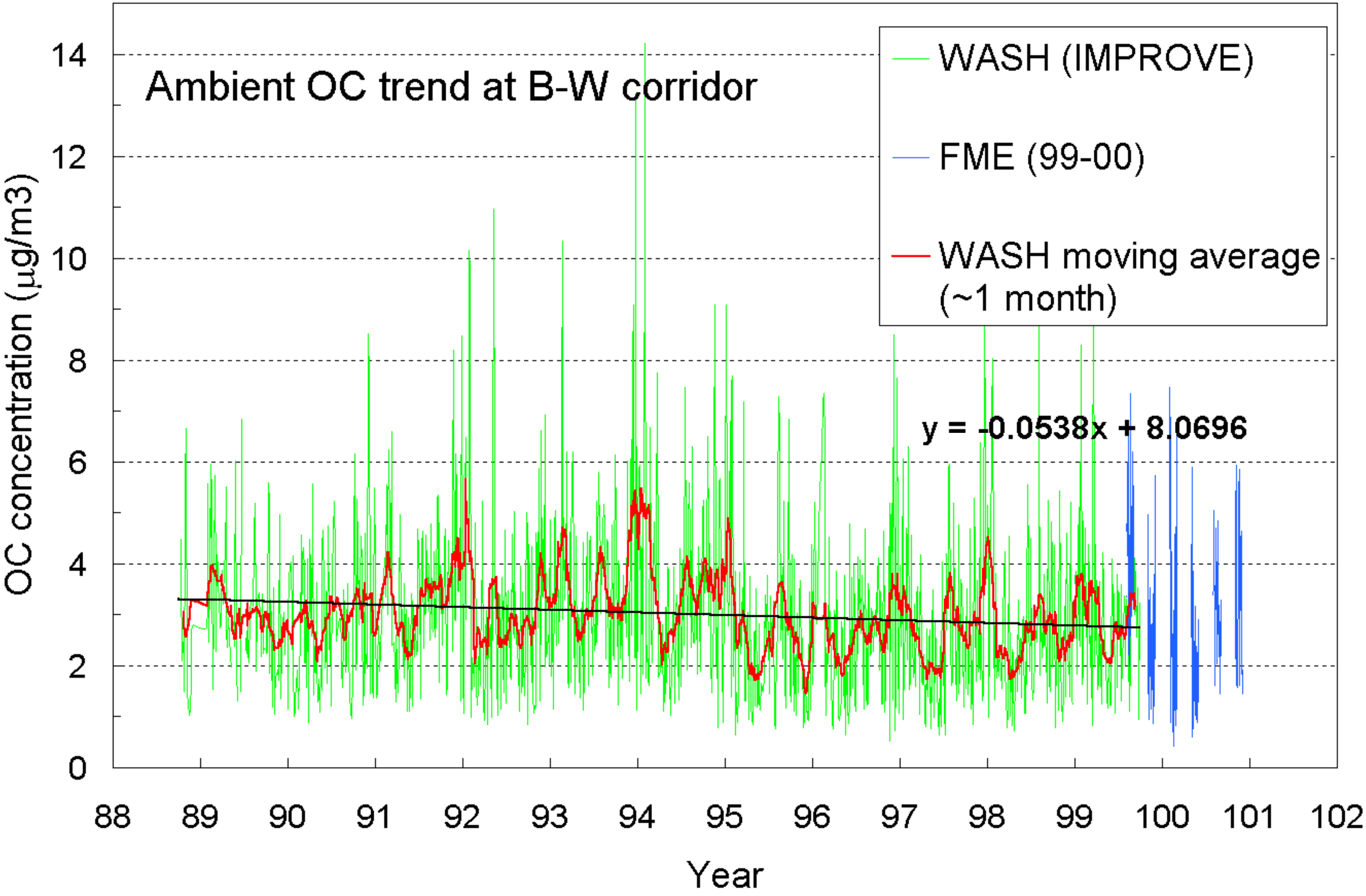
Electrical power	2%,
Industry	4%
On-road Vehicle	39%
Off-Road vehicles	32%
Other	23%

Sources of **Organic Carbon**

Electrical power	2%,
Industry	4%
On-road Vehicle	28%
Off-Road vehicles	9%
Other	57%



- The ambient EC concentration decreases ~50% in the recent 11 years.



- The ambient OC concentration decreases ~10% in the recent 11 years.

From Ron Siefert UMCES, CBL
Ammonia Sources

- **Urban Sources Baltimore (EPA Supersite)**
- **Chamber Studies at LESREC**
- **Tunnel Studies (vehicle emissions)**

EPA PM 2.5 Supersite (Baltimore)

Fort McHenry Tunnel (Baltimore)

Vehicle Emissions

Catalyst Reactions

Water-gas shift reaction

$$CO + H_2O \text{ R } CO_2 + H_2$$

Then …

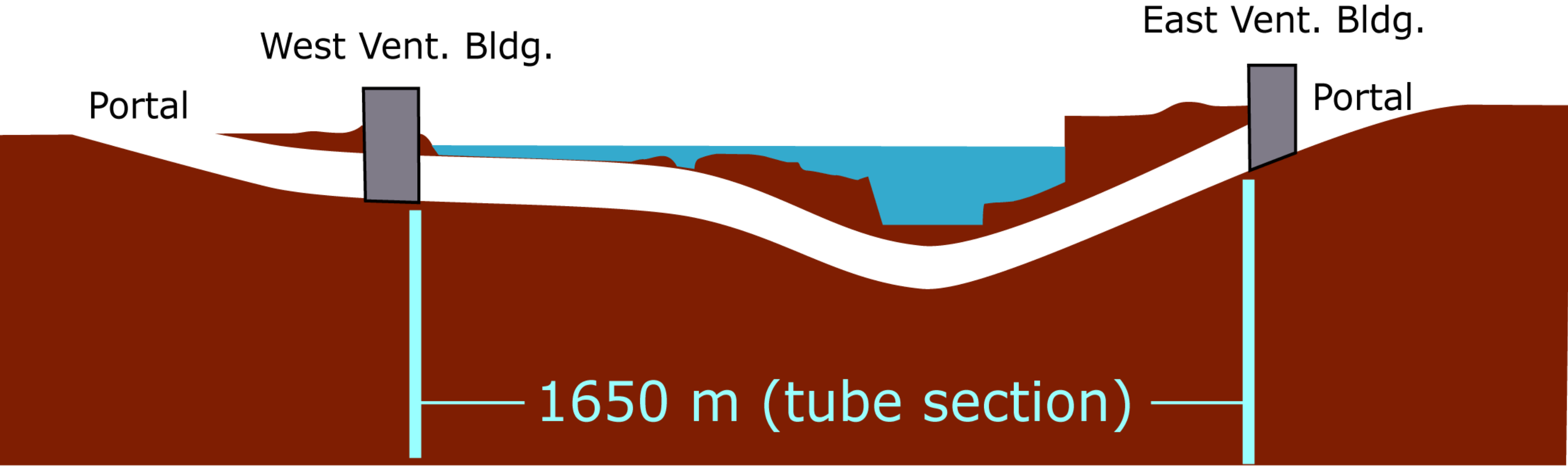
$$2NO + 2CO + 3H_2 \rightarrow 2NH_3 + 2CO_2$$

Or

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$$

Battye et al. *Atmos. Environ.* (2003) said ¾ of NH_3 in Fresno, CA and Charlotte, NC from vehicles.

Ammonia Emissions From Vehicles: Fort McHenry Tunnel Study



Mass Balance: $F_{NH_3,IN} + G_{NH_3} = F_{NH_3,OUT}$

$F_{NH_3,IN}$ => Flow of NH_3 into the tunnel

$F_{NH_3,OUT}$ => Flow of NH_3 out of the tunnel

G_{NH_3} => Amount of NH_3 produced by vehicles

Results

- **Fraser & Cass (ES&T, 1998)**
  61 mg NH_3-N km^{-1}
- **Emmenegger et al. (IJEP, 2004) in Zurich tunnel study.**
  31 mg NH_3-N km^{-1} for light duty vehicles.
  14 mg NH_3-N km^{-1} for heavy duty vehicles.
- **Durbin et al. (Atmos. Environ., 2004) California-cert low-emission vehicles.**
  11 mg NH_3-N km^{-1} for light duty vehicles.
- **Haui et al. (ES&T 2003)**
  High NH_3 emission occurred during high vehicle specific power events under rich operating conditions.

Fort McHenry Tunnel Study (29 September 2003) Slefert et al.

Emission Rate ≈ 12 mg NH_3-N km^{-1} (Sep 2003)

Emission Rate ≈ 12 mg NH_3-N km^{-1} (Nov 2003)

Emission Rate ≈ 2 mg NH_3-N km^{-1} (Mar 2004)

Some Comparisons
(based on Siefert's study)

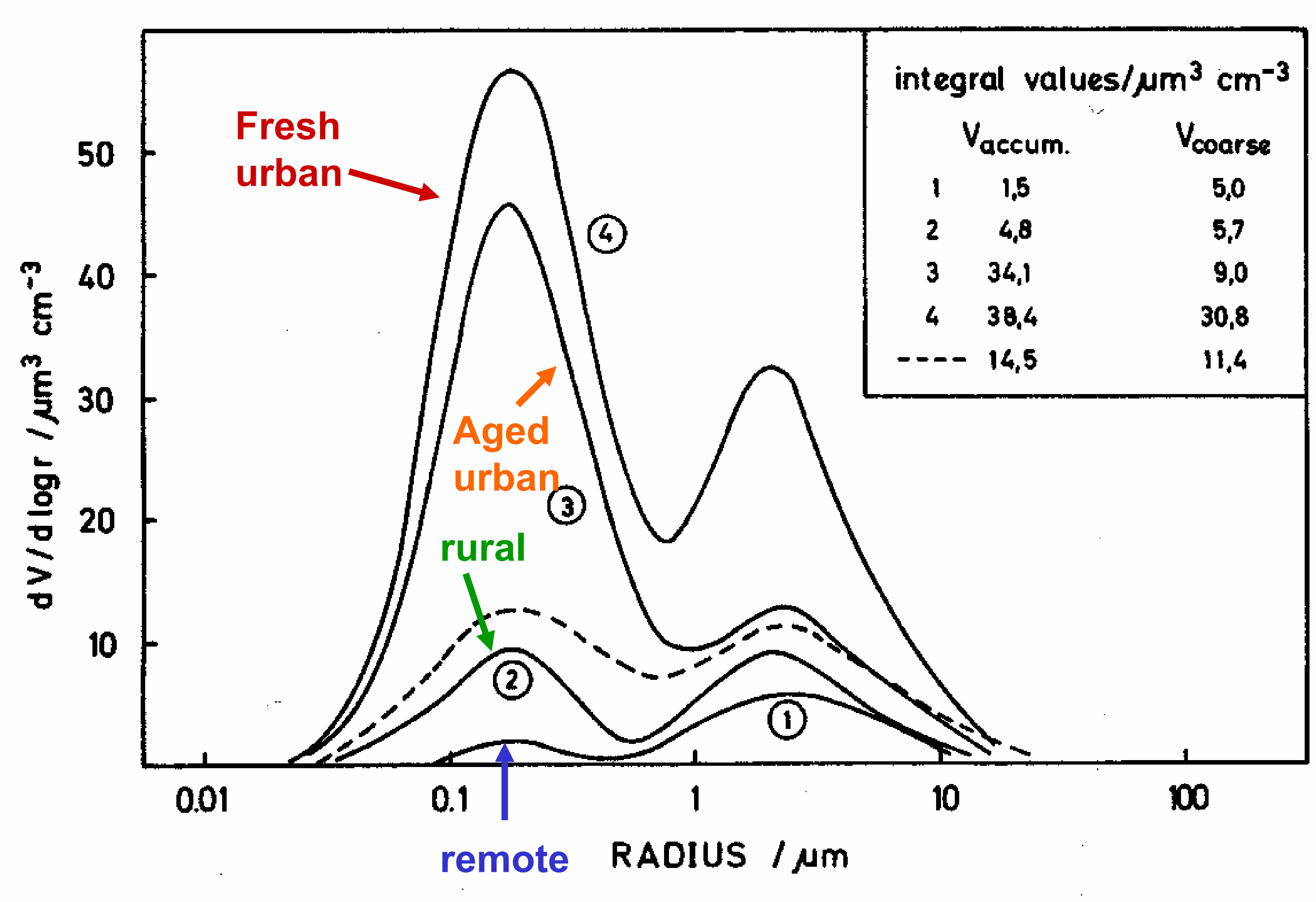
- Vehicles in Baltimore
  - Traffic: 5 x 10^9 km yr^{-1}
    - For 12 mg NH_3-N km^{-1} → 0.6 x 10^5 kg NH_3 yr^{-1}
    - For 2 mg NH_3-N km^{-1} → 0.1 x 10^5 kg NH_3 yr^{-1}
- EPA Toxic Release Inventory for MD
  - 1.5 x 10^5 NH_3-N yr^{-1}
    - 75% occurs in Baltimore
- Chickens on Delmarva
  - 180 x 10^5 kg NH_3-N yr^{-1}

Conclusions

- Major source of aerosol mass in Washington is Sulfate from coal combustion.
- Vehicles are a major source of organic aerosols and NOx.
- Secondary organic aerosol from vegetation is important.
- Vehicles are a dominant source of soot.
- Vehicles are probably a minor source of ammonia.

EXTRA SLIDES FOLLOW

TYPICAL U.S. AEROSOL SIZE DISTRIBUTIONS



integral values/$\mu m^3\ cm^{-3}$

	$V_{accum.}$	V_{coarse}
1	1,5	5,0
2	4,8	5,7
3	34,1	9,0
4	38,4	30,8
----	14,5	11,4

Fresh urban

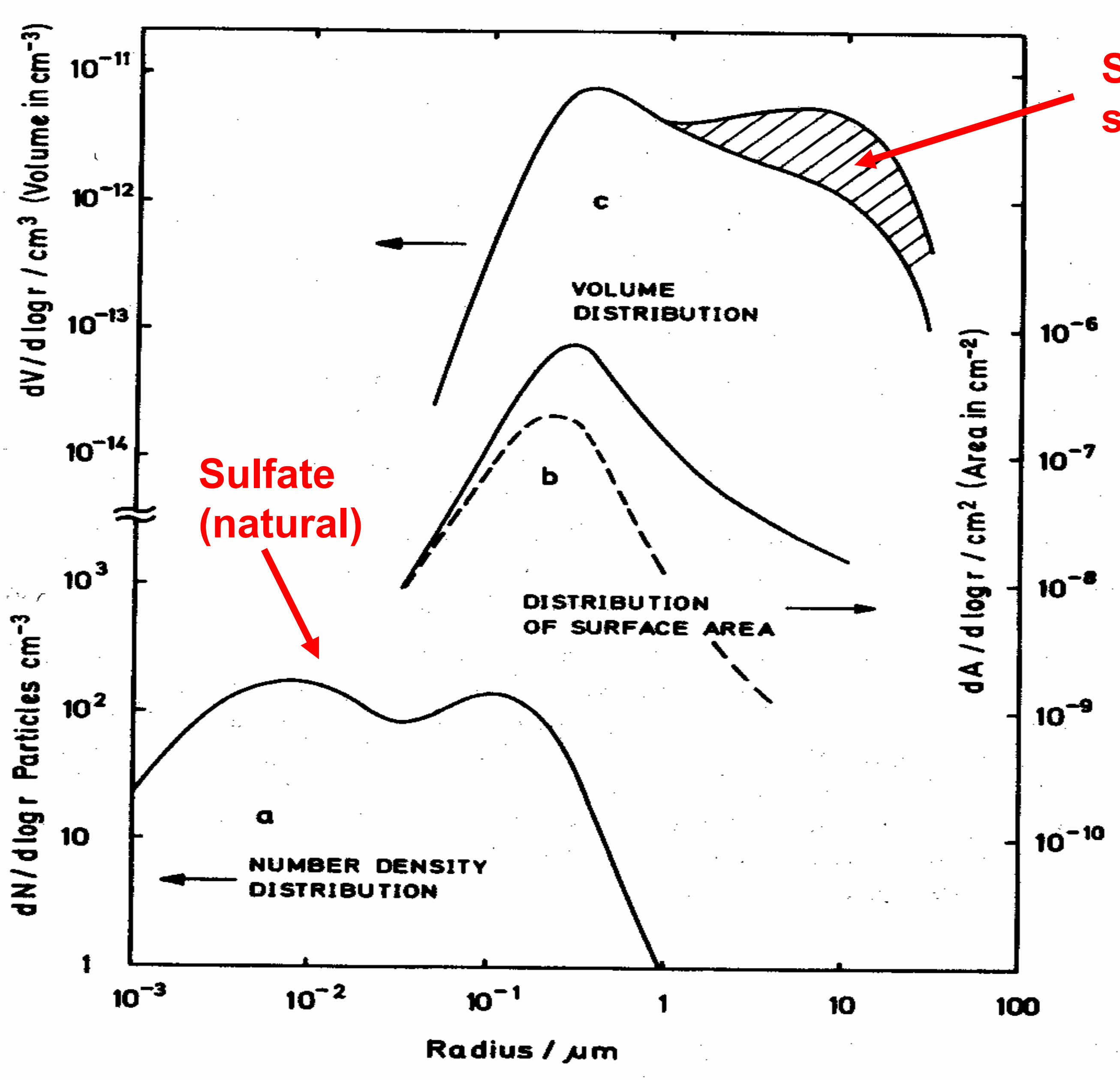
Aged urban

rural

remote

Warneck [1999]

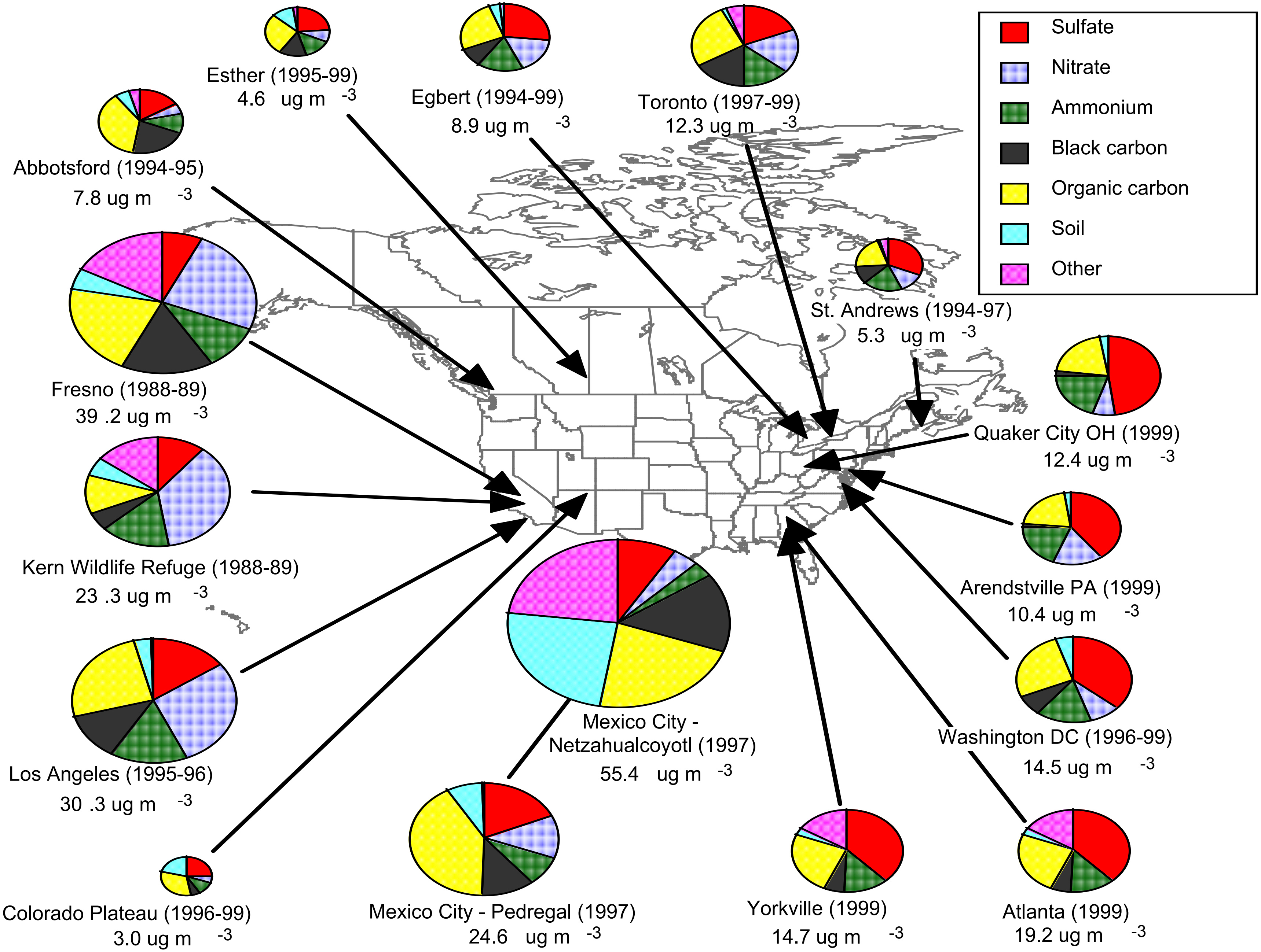
SAMPLE AEROSOL SIZE DISTRIBUTION (MARINE AIR)



Sea salt

Sulfate (natural)

COMPOSITION OF PM2.5 (NARSTO PM ASSESSMENT)



Radiation and fine particles

Seinfeld & Pandis (1998)

1116 RADIATIVE EFFECTS OF ATMOSPHERIC AEROSOLS: VISIBILITY AND CLIMATE

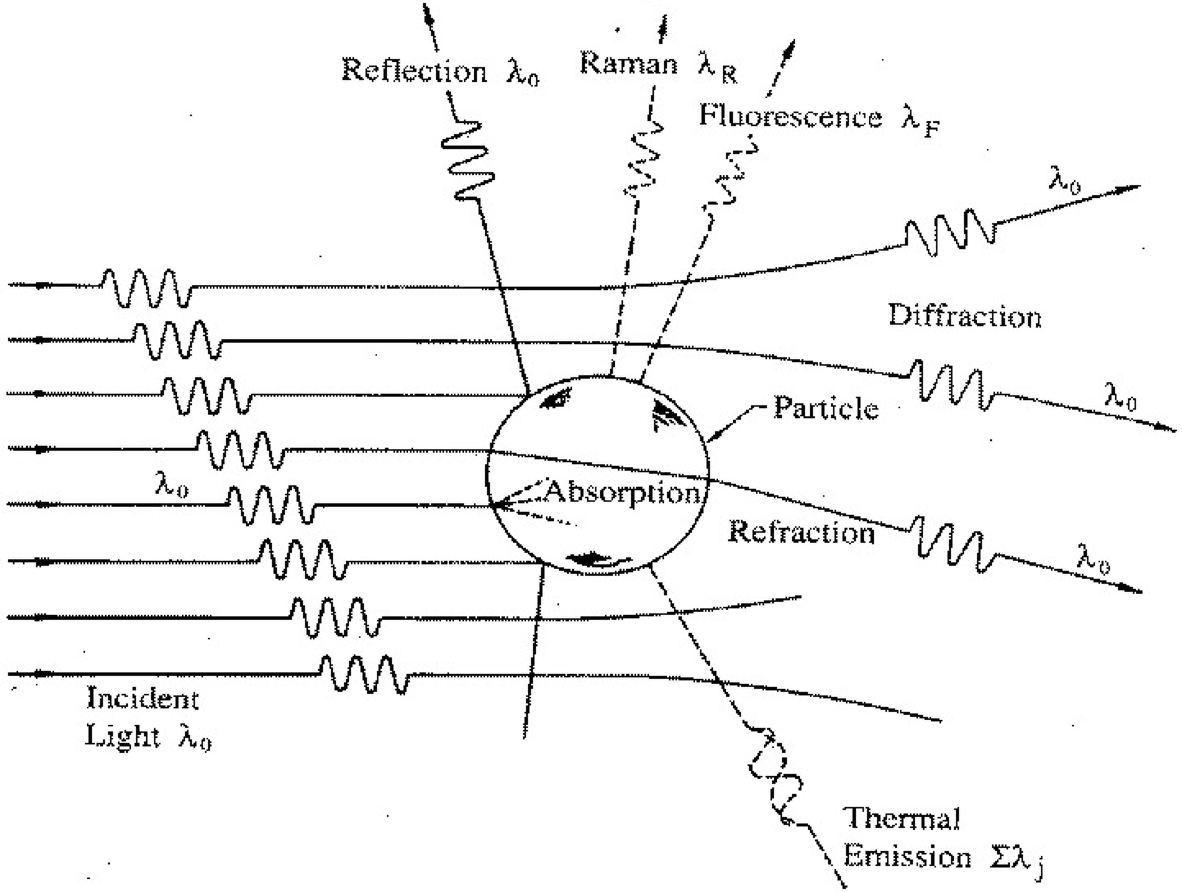
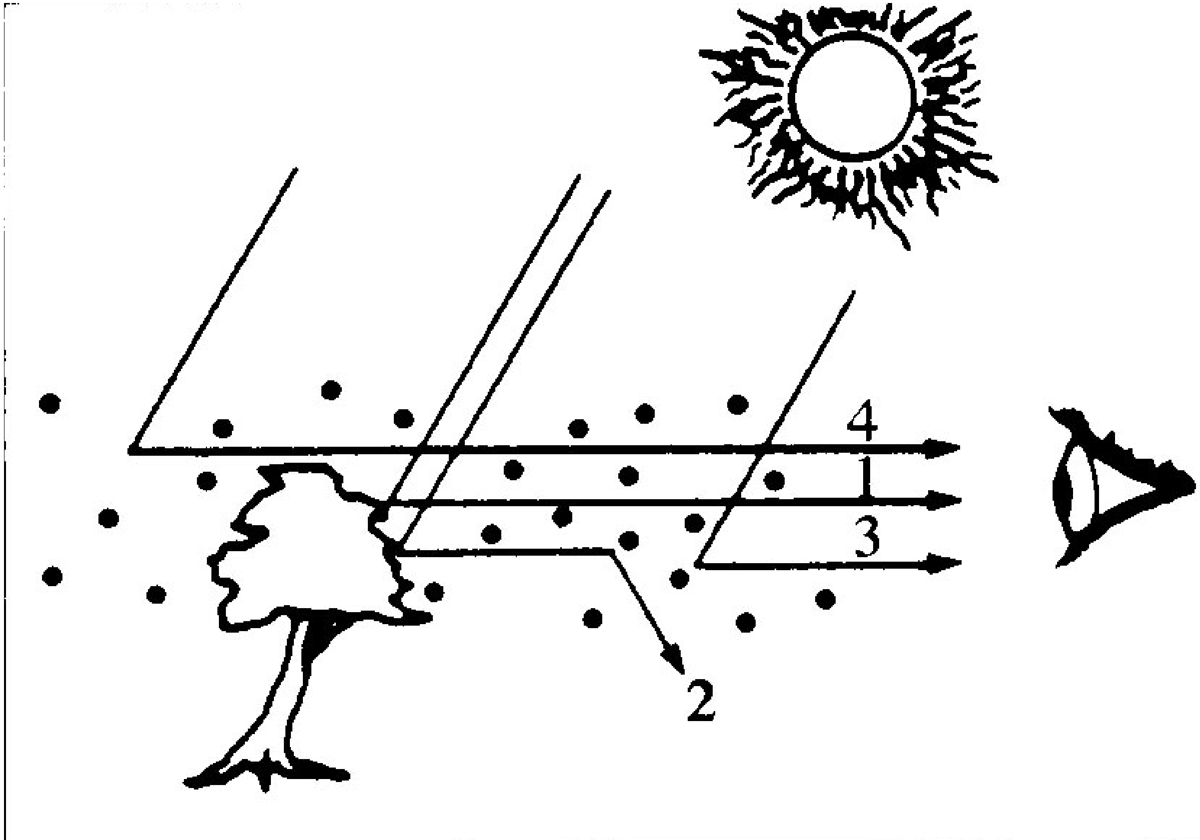


FIGURE 22.1 Mechanisms of interaction between incident radiation and a particle.

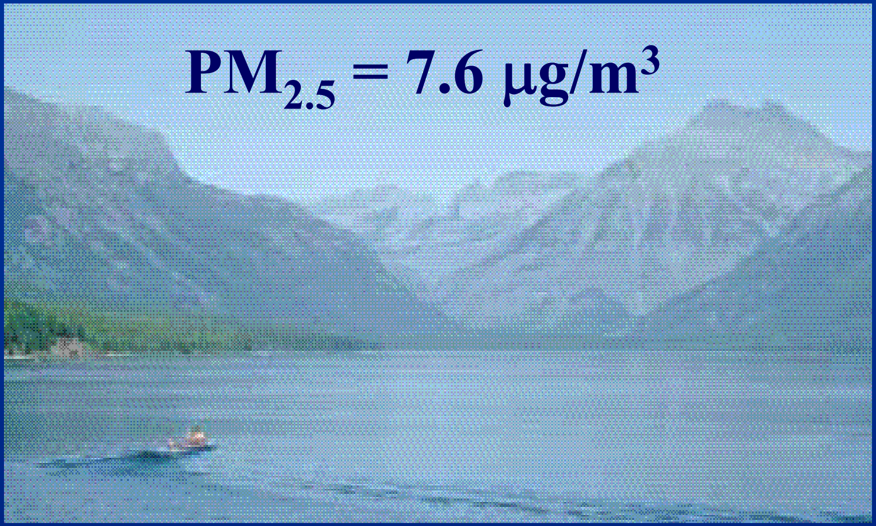
Atmospheric Visibility

(absorption & scattering)

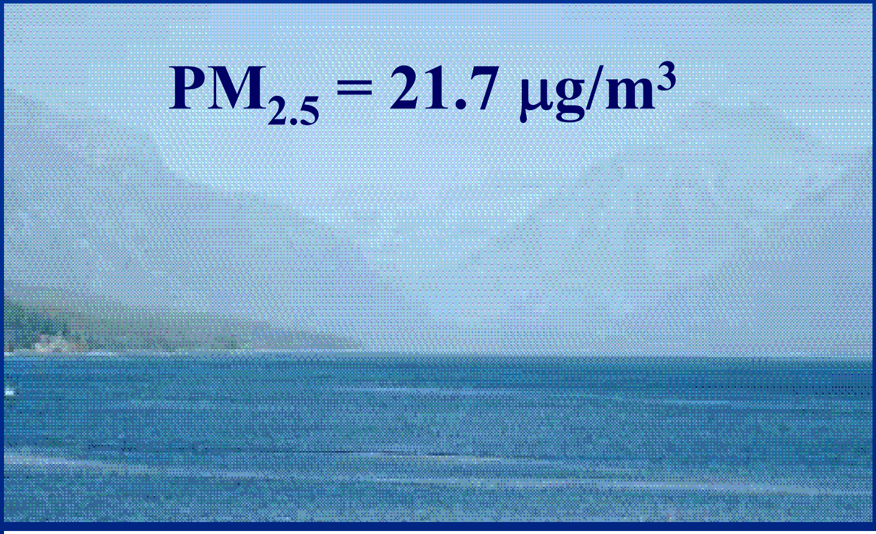
1. **Residual**
2. **Scattered away**
3. **Scattered into**
4. **Airlight**



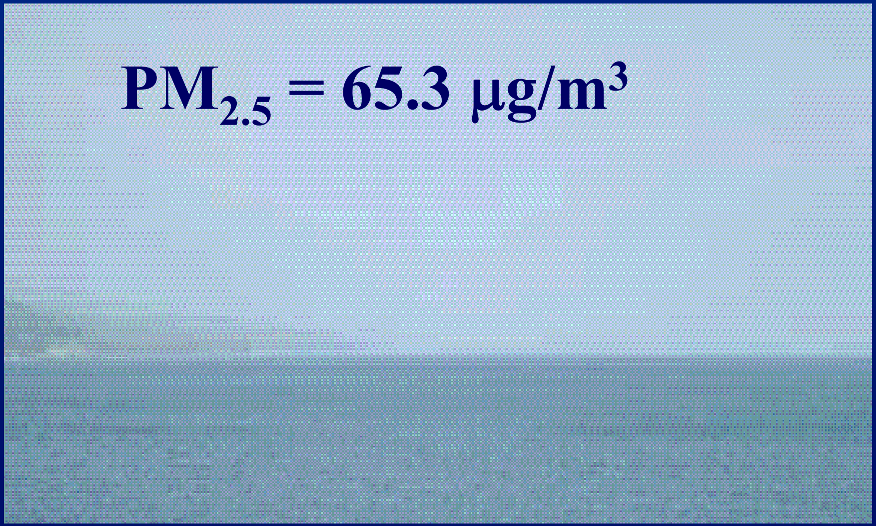
Extinction Coefficient as a PM2.5 Surrogate



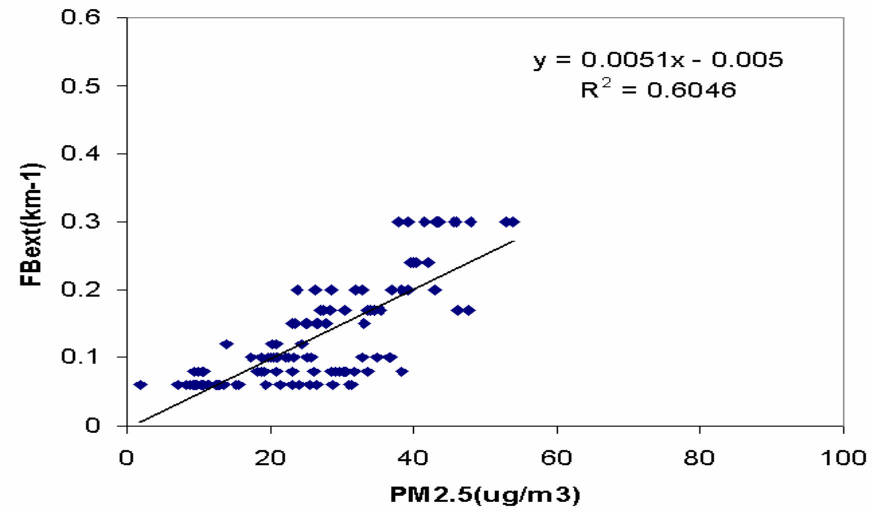
$PM_{2.5} = 7.6\ \mu g/m^3$



$PM_{2.5} = 21.7\ \mu g/m^3$



$PM_{2.5} = 65.3\ \mu g/m^3$

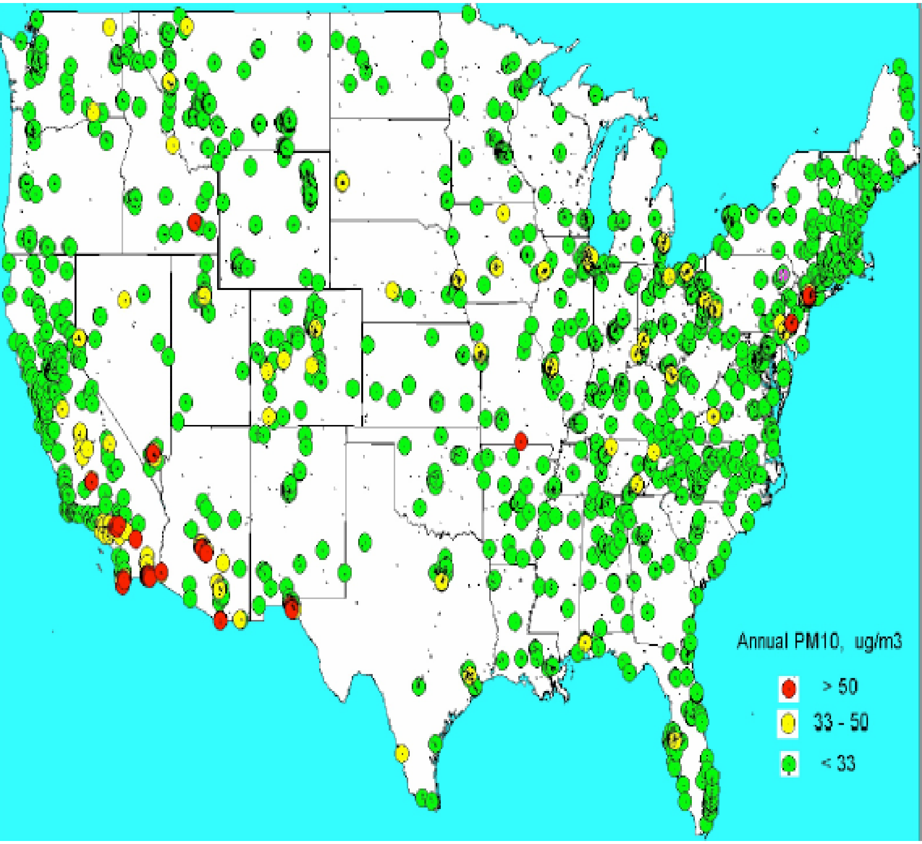


Glacier National Park images are adapted from Malm, *An Introduction to Visibility* (1999) http://webcam.srs.fs.fed.us/intropdf.htm

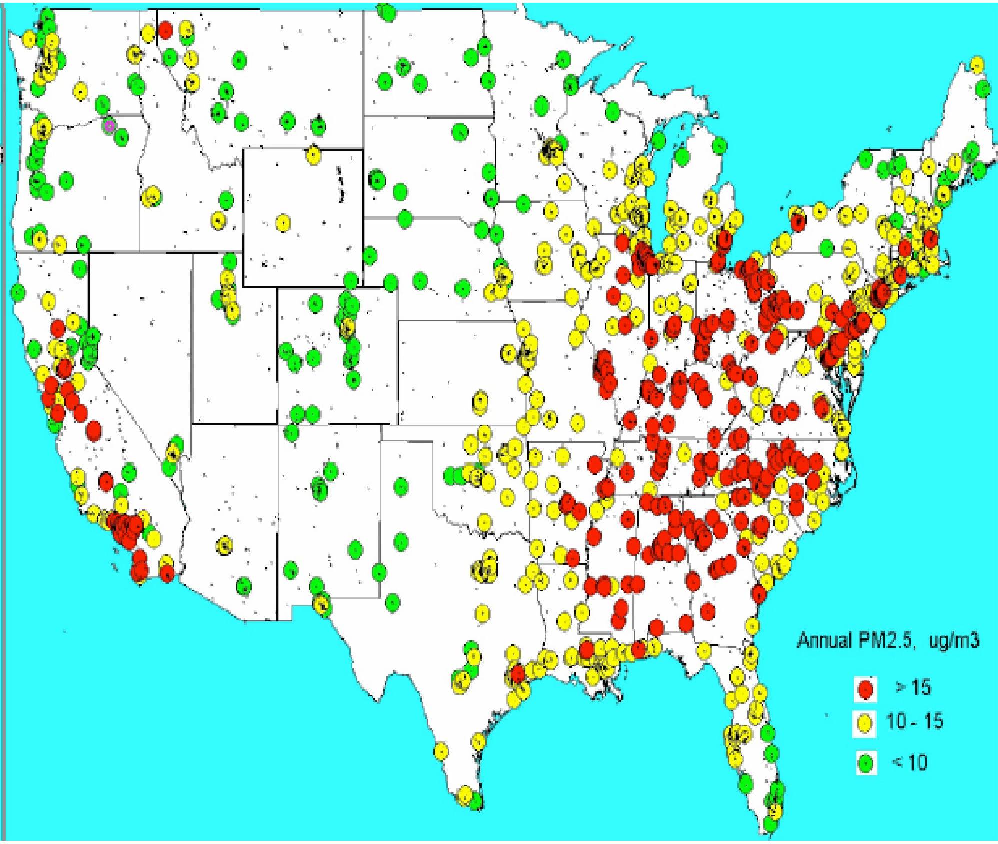
ANNUAL MEAN PARTICULATE MATTER (PM) CONCENTRATIONS AT U.S. SITES, 1995-2000

NARSTO PM Assessment, 2003

PM10 (particles > 10 μm)



PM2.5 (particles > 2.5 μm)



Red circles indicate violations of national air quality standard:
50 μg m^{-3} for PM10 **15 μg m^{-3} for PM2.5**

Aerosols in the Atmosphere

Abundance and size

- **Aerosol concentration is highly variable in space and time. Concentrations are usually highest near the ground and near sources.**
- **A concentration of 10^5 cm^{-3} is typical of polluted air near the ground, but values may range from 2 orders of magnitude higher in very polluted regions to several lower in very clean air.**
- **Radii range from ~ 10^{-7} cm for the for small ions to more than 10 μm (10^{-3} cm) for the largest salt and dust particles.**
- **Small ions play almost no role in atmospheric condensation because of the very high supersaturations required for condensation.**
- **The largest particles, however, are only able to remain airborne for a limited time**

Aerosol Size Naming Convention

Usually divided into three size groups (D - diameter)

1. Aitken Nuclei → $2 \times 10^{-3}\ \mu m < D \leq 0.2\ \mu m$

2. Large Nuclei → $0.2\ \mu m < D \leq 2.5\ \mu m$
   (also called the accumulation mode)

3. Giant Nuclei → $D > 2.5\ \mu m$

Other Naming Convention

- **Nucleation mode → D ≤ 0.1 μm**
- **Accumulation or coagulation mode → 0.1 μm < D ~ 1 μm**
  Thought to be most important in natural cloud formation
- **Coarse Particle Mode → D ~ 1 μm**

Origins of Atmospheric Aerosols

1. Condensation and sublimation of of vapors and the formation of smokes in natural and man-made combustion.

2. Reactions between trace gases in the atmosphere through the action of heat, radiation, or humidity.

3. The mechanical disruption and dispersal of matter at the earth’s surface, either as sea spray over the oceans, or as mineral dusts over the continents.

4. Coagulation of nuclei which tends to produce larger particles of mixed constitution

Aerosol Makeup

- Typical substances formed in large quantities by condensation following combustion include ashes, soot, tar products, oils as well as sulfuric acid and sulfates. These particles are primarily within the range of Aitken nuclei.

- Mechanical disintegration, by wind and water, of rocks and soil produces particles with diameters > 0.2 µm. These fall primarily in the large nuclei range.

- According to Jaenicke (*Science,* 308 p. 73, 2005) about 25% of the number of particles with diameter greater than 0.2 µm are biogenic. (remains to be verified).

Aerosol Makeup - continued

- Chemical reactions between nitrogen, oxygen, water vapor and various trace gases (e.g., sulfur dioxide, chlorine, ammonia, ozone, and oxides of nitrogen) primarily produce particles in the Aitken and Large range.

  Examples

  Formation of ammonium chloride from NH_3 and HCl

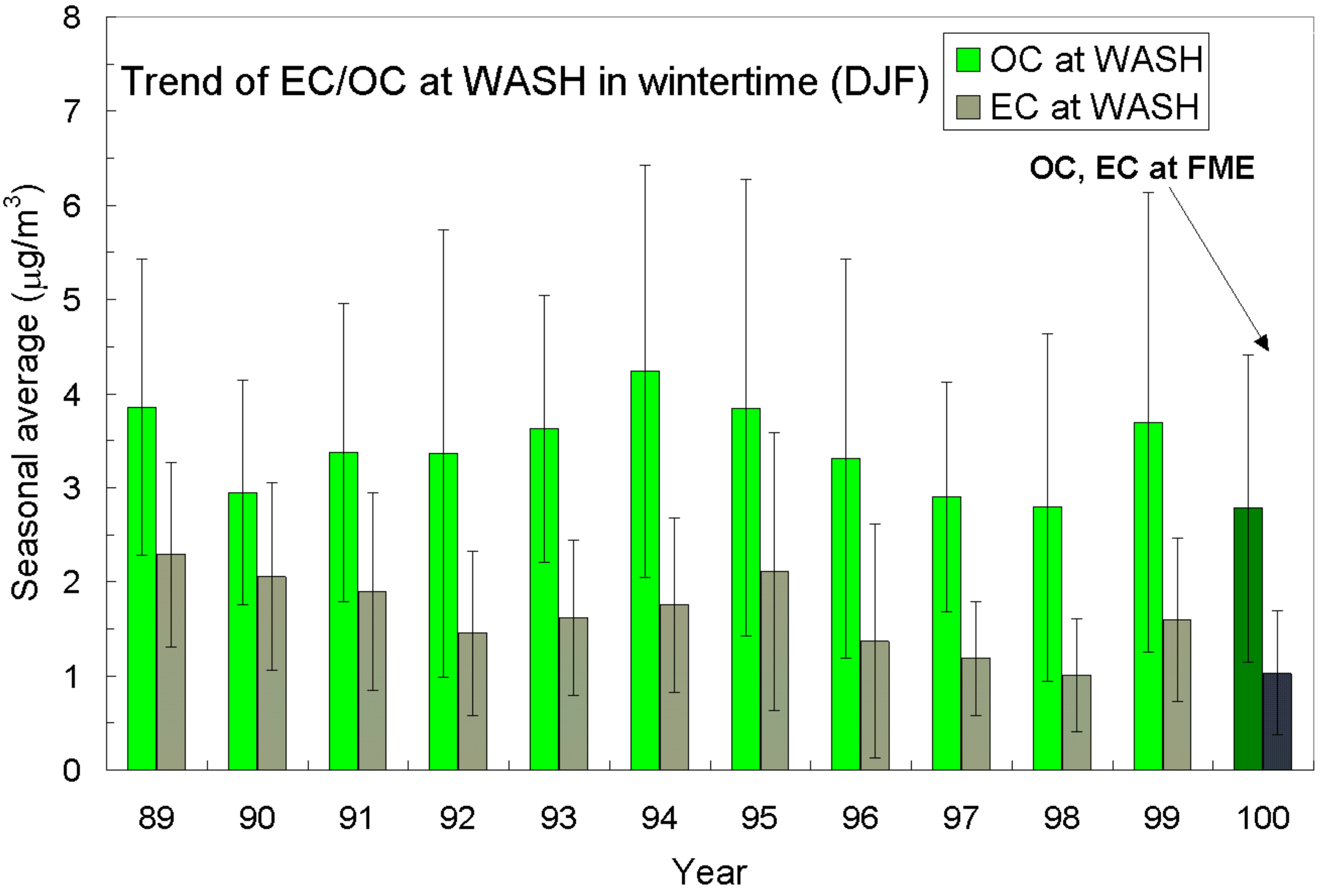
  Oxidation of SO_2 to H_2SO_4

  Reaction of sulfur dioxide, ammonia, and water to produce ammonium sulfate particles.

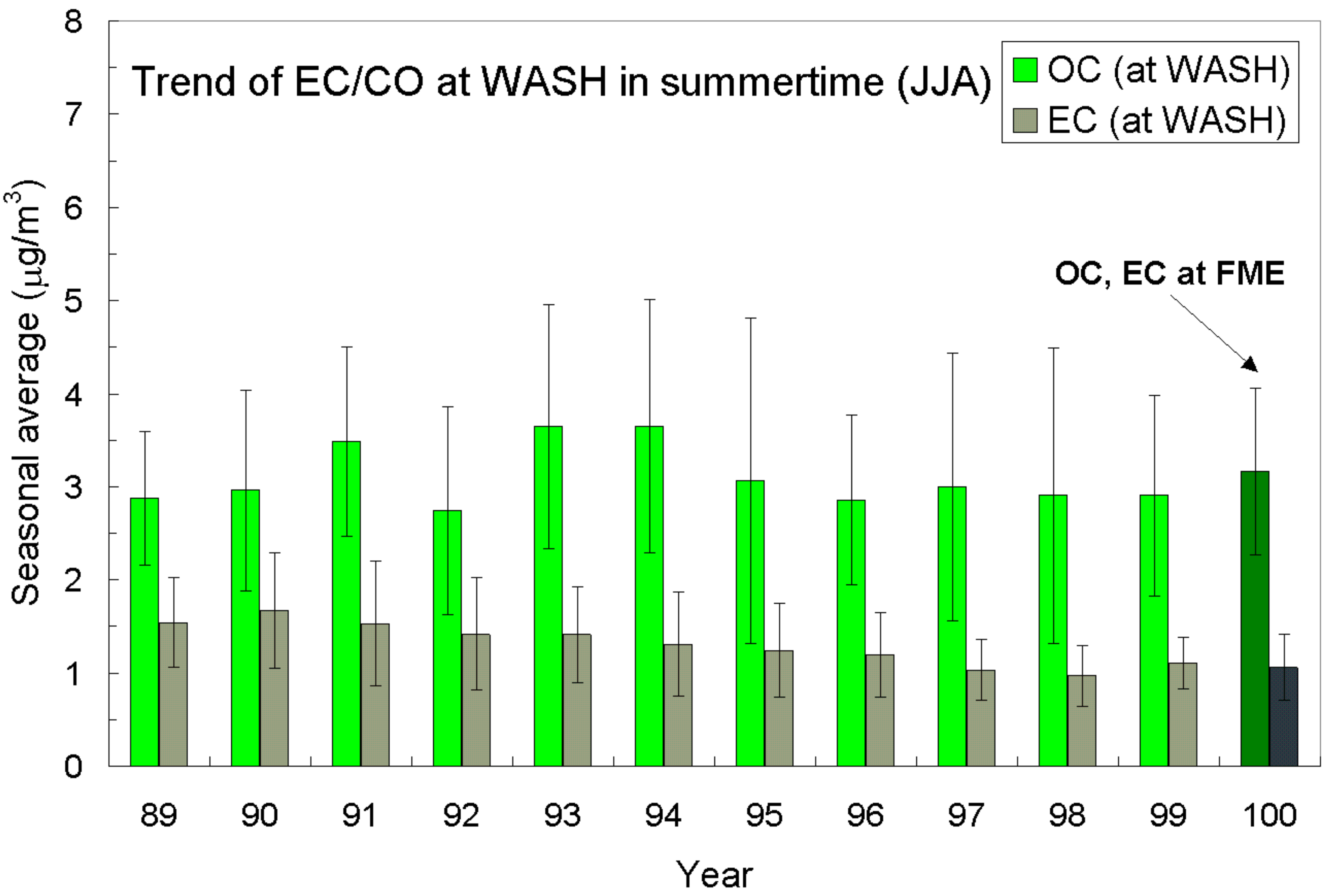
  Production of higher oxides of nitrogen through the action of heat, ozone or ultraviolet radiation

Cloud Condensation Nuclei - CCN

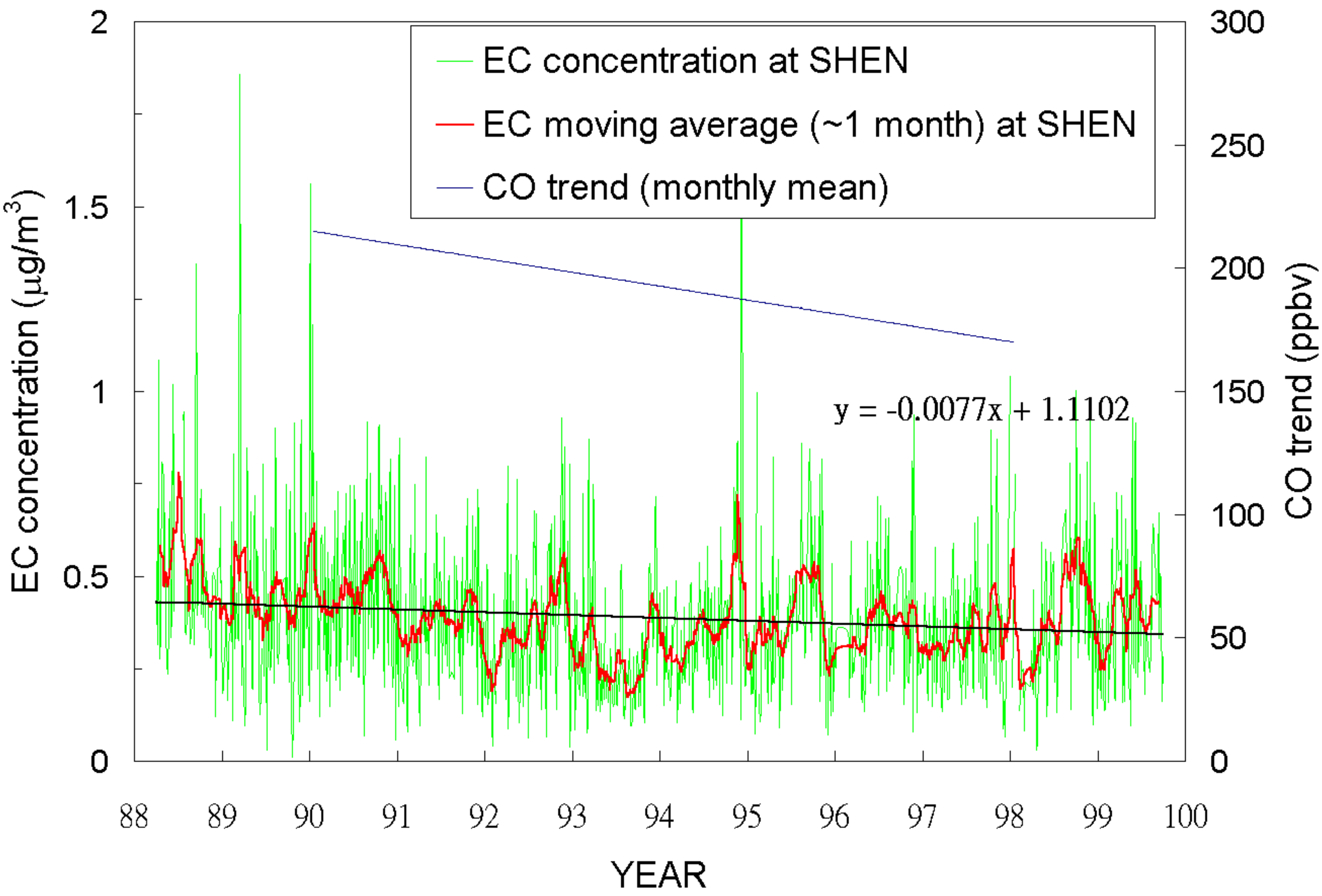
- **Comprises a small fraction of the total aerosol population**
- **Sea salt is the predominant constituent of CCN with D > 1µm**
- **For 0.1 µm < D < 1 µm, the main component is thought to be sulfate, which may be present as sulfuric acid, ammonium sulfate, or from phytoplankton produced dimethylsulfide (see Charlson et al.,** ***Nature*****,** 326, **655-661).**



- EC and OC are correlated (95-00) but show no obvious trend.



- EC shows a decreasing trend but no correlation with OC.



- At SHEN, EC decrease by ~15% in 8 years (1989-1997) while CO decrease by ~ 20% during the same period.

Black Carbon (soot) and Organic Carbon

Bond et al. (*J. Geophys. Res.*, 2004)

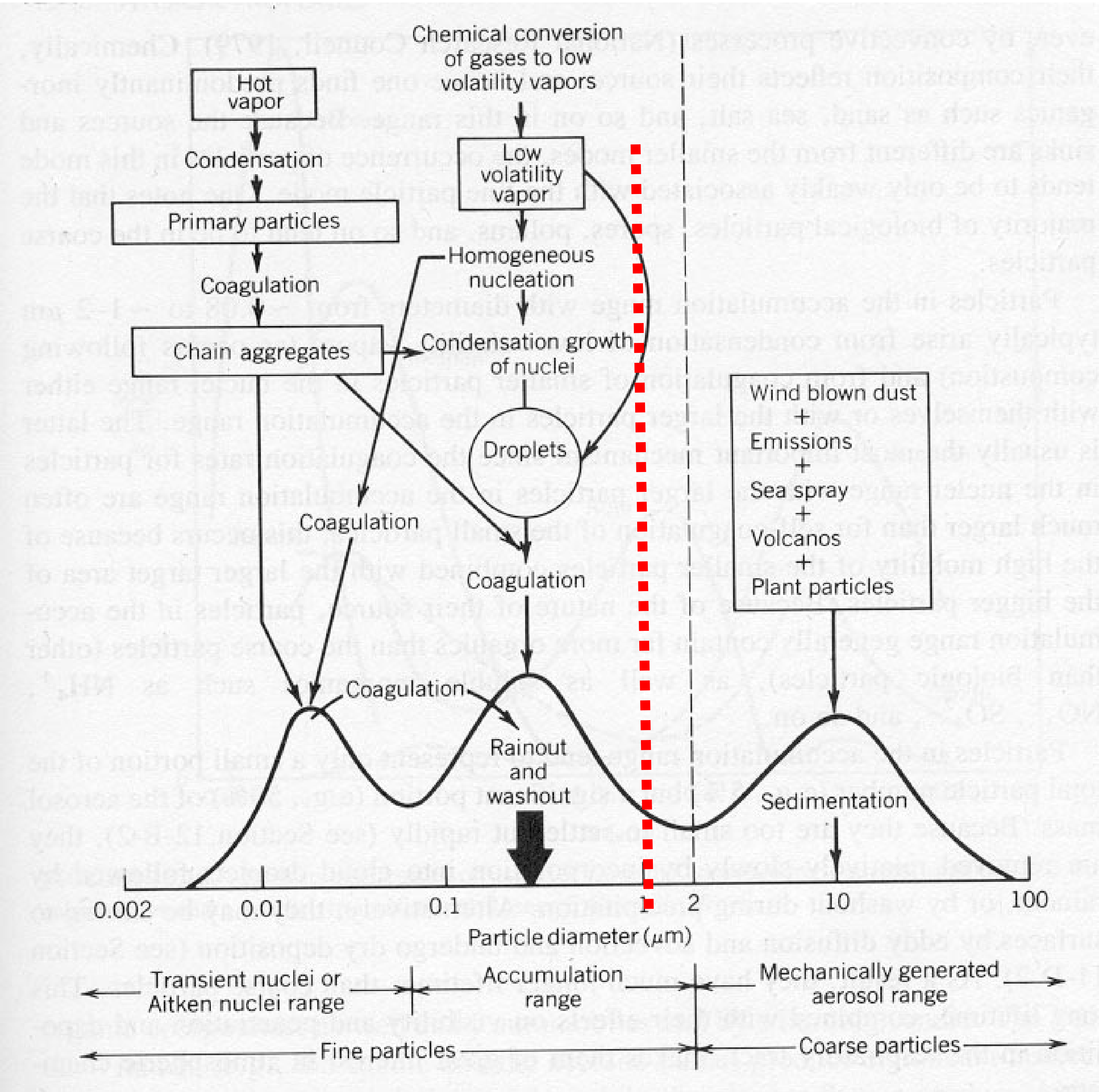
Globally: The source of Black Carbon

fossil fuel 38%,
biofuel 20%
open burning 42%

Sources of Organic Carbon

fossil fuel 7%,
biofuel 19%
open burning 74%

Atmospheric Aerosols



Example: Visibility improvement during the 2003 North American Blackout

Normal conditions over Eastern US during an air pollution episode:

$b_{sp} \approx 120\ \mathrm{Mm^{-1}} = 1.2 \times 10^{-4}\ \mathrm{m^{-1}}$ at 550 nm

$b_{ap} = 0.8 \times 10^{-5}\ \mathrm{m^{-1}}$

$b_{ext} = 1.28 \times 10^{-4}\ \mathrm{m^{-1}}$

Visual Range $\approx 3.9/b_{ext} = 30$ km

During blackout

$b_{sp} = 40\ \mathrm{Mm^{-1}} = 4.0 \times 10^{-5}\ \mathrm{m^{-1}}$

$b_{ap} = 1.2 \times 10^{-5}\ \mathrm{m^{-1}}$

$b_{ext} = 0.52 \times 10^{-4}\ \mathrm{m^{-1}}$

Visual Range $= 3.9/b_{ext} = 75$ km