Lectures 15 - 17: Atmospheric Aerosols

<u>Required</u> reading: S&P chapters 2.7 & 7-13
Recommended reading: F-P & P chapter 9

Other readings: NARSTO, Particulate Matter Science for Policy Makers: A NARSTO Assessment, 2003

Atmospheric chemistry
CHEM-5151/ATOC-5151
Spring 2005
Qi Zhang

General Outline

I. Introduction and Fundamentals
- Effects
- Size distribution
- Chemical composition
- Morphology and shape
- Temporal & spatial variations
- Vertical variation
- Sources

II.1. Aerosol Dynamics & Thermodynamics
- Diffusion
- Condensation
- Coagulation
- Evaporation
- Scavenging

Will be discussed in Aerosol IV
- *Deliquescence*
- *Cloud nucleation*
- *Light scattering*
- *Crystallization*

II.2. Formation & Transformation
- Nucleation
- Gas to particle conversion
- Surface rxn (e.g., acid replacement)
- Bulk rxn

Concerning aerosols …
- Why do we care?
- Physical and chemical properties
- Sources, processes, and removal

Atmospheric aerosols

III. Organic Aerosols
- Elemental & organic carbon (EC/OC)
- Chemical nature
- Primary sources
- Secondary organic aerosol formation
- Photolysis and oxidation

Part I: Introduction and Fundamentals

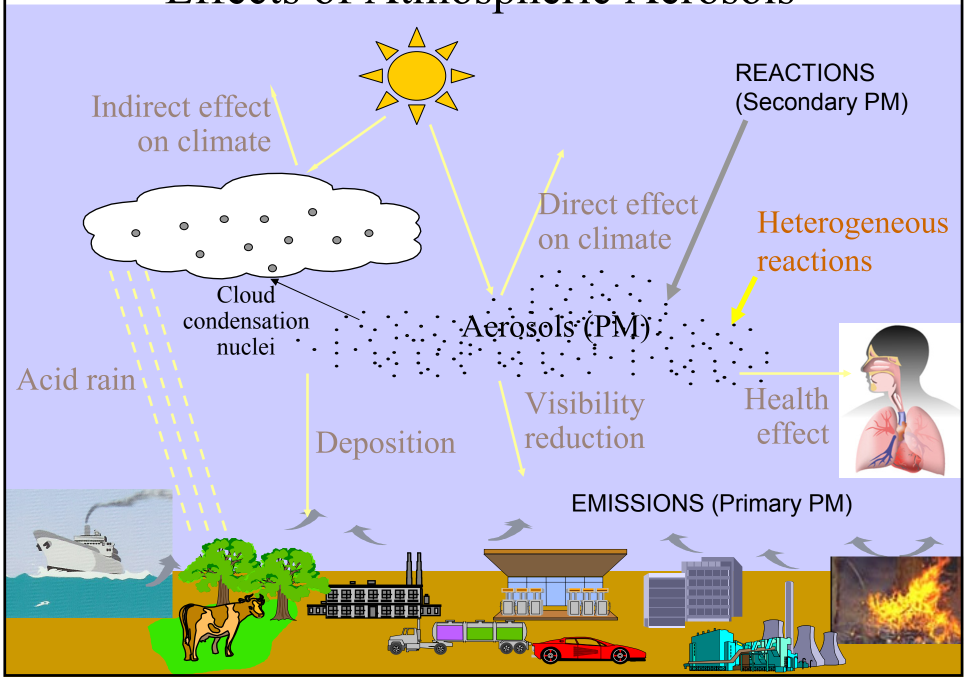
Definition: An aerosol is a relatively stable suspensions of fine solid or liquid particle in a gas. (Commonly refer to the particulate component only)
Aerosol = Particles = Particulate Matter (PM)
PM$_x$: particles with diameters smaller than x µm (e.g., PM$_{2.5}$, PM$_{10}$)

Outline

- Effects
- Size distribution
- Chemical composition
- *Morphology and Shape (briefly mention)*
- Sources
- Temporal & spatial variations
- Vertical variation

<u>Required</u> reading: S&P chapters 2.7 & 7
Recommended reading: 1) F-P & P chapters 9.A.1, 9.A.2, & 9.C
2) NARSTO Assessment 2003, chapters 1 & 6

Effects of Atmospheric Aerosols



Effects of Atmospheric Aerosols

- Visibility reduction:
  - Form haze under high RH conditions that reduces visibility
  - Economical concerns (tourism)

Pittsburgh

$PM_{2.5}$=45 µg m^{-3}

July 2, 2001

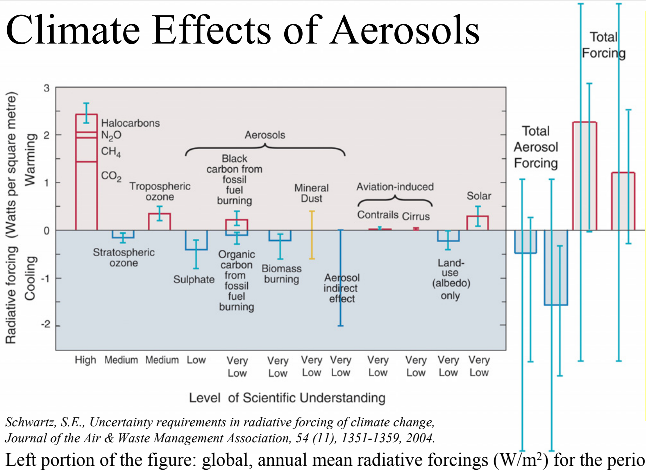
$PM_{2.5}$=4 µg m^{-3}

July 18, 2001

Pictures taken from a same location at same time of day, on two different days

- Climate effects:
  - Absorb and scatter solar radiation and outgoing IR radiation
  - Act as CCN (cloud condensation nuclei), affecting cloud formation and properties
  - LARGEST sources of uncertainty in assessments of anthropogenic climate change (IPCC, Intergovernmental Panel on Climate Change).
  - Uncertain whether aerosol increase cause a net increase or decrease in average global T.

Climate Effects of Aerosols



- For mineral dust and the aerosol indirect effect, no estimates of the forcing, only uncertainty ranges.
- The dominant effect of atmospheric particles is a negative forcing (cooling).
- Uncertainty in aerosol forcing must be reduced at least 3-fold for uncertainty in climate sensitivity to be meaningfully reduced and bounded!

Schwartz, S.E., Uncertainty requirements in radiative forcing of climate change, Journal of the Air & Waste Management Association, 54 (11), 1351-1359, 2004.

Left portion of the figure: global, annual mean radiative forcings (W/m^2) for the period from pre-industrial (1750) as given by the IPCC. The height of each rectangular bar denotes a best estimate value while its absence denotes no best estimate is possible. I-beams denote estimated uncertainties. Level of scientific understanding represents the subjective judgment of the IPCC working group on radiative forcing of the reliability of the forcing estimate. Bars and I-beams at right denote estimates of total aerosol forcing, total forcing, and associated uncertainties. First bar denotes total aerosol forcing evaluated as algebraic sum of IPCC aerosol forcings, with mineral dust and aerosol indirect forcings taken as 0; for second bar, these forcings are taken as the midpoints of the IPCC uncertainty ranges. Third and fourth bars denote total forcing evaluated in the same way, again with mineral dust and aerosol indirect forcings taken as 0 and as the midpoints of the IPCC uncertainty ranges, respectively. For each bar, two uncertainty estimates are provided. Upper and lower limits of the first (larger) uncertainty range are calculated as algebraic sum of upper and lower limits, respectively, of the uncertainties of the several forcings. Upper and lower limits of the second (smaller) uncertainty range are calculated as the square root of the sum of the squares, respectively, of the of the upper and lower uncertainty ranges relative to the estimated forcings denoted by the bars.

Effects of Atmospheric Aerosols

- Health effects:
  - Epidemiological evidence: affect cardiorespiratory system, cause cancer, impair lung development of children
  - More deadly than car accidents (est. kills ~ 60,000 people / year in US)
- Ecological hazards:
  - Acid and nutrient deposition: damage ecosystems and ecological components, disturb nutrient balance
- Influence atmospheric chemistry:
  - Reaction media
  - Heterogeneous & surface rxns (e.g., *polar stratospheric clouds and the ozone*)
  - Transport media

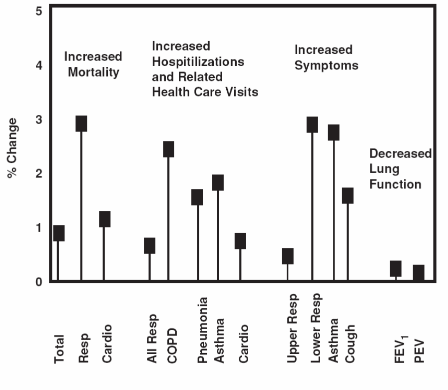


Figure 2.5. Stylized summary of acute exposure studies, percent change in health endpoint per 10 μg/m^3 increase in PM_{10}. (Adapted from Pope

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Size Distributions of Atmospheric Aerosols

Why PM size matters?

- Particle toxicity (deposition efficiency are size dependent)
- Light scattering (0.1 – 1 μm most efficient for scattering solar radiation)
- Surface rxns (w/ same PM mass, smaller particles higher total surface area)
- PM life time (coagulational loss of small PM, faster sedimentation of bigger PM)

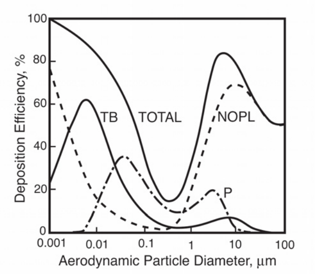

Figure 2.3. Particle deposition in the major regions of the human respiratory tract during normal respiration corrected for size dependent inhalability. (NOPL, naso-oro-pharyngo-laryngea) region; TB, tracheo-bronchial region; and P, pulmonary region). Developed from the National Council on Radiation Protection Model (NCRP, 1997) by Phalen (2002).

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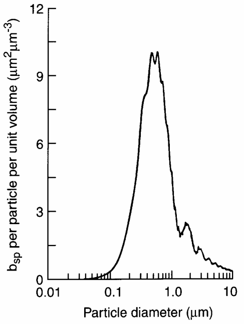
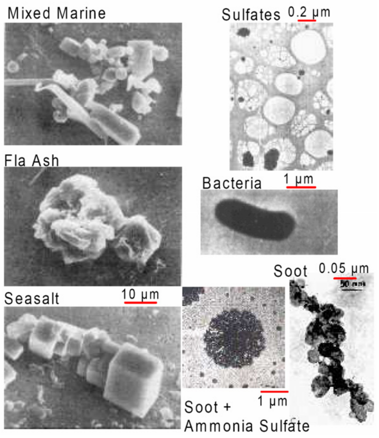


FIGURE 9.22 Scattering coefficient per particle divided by particle volume plotted as a function of diameter. The particles are assumed to be spheres of refractive index 1.50 and the light has λ = 550 nm (adapted from Waggoner and Charlson, 1976).

Finlayson-Pitts & Pitts

Aerosol Sizes (Diameters)

- Aerosol sizes are usually reported as diameters.
- Yet many atmospheric particles have irregular shapes → have to use equivalent / effective diameter that depends on a physical property.



Details on PM diameters and shapes see:
DeCarlo et al., Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory, Aerosol Science & Technology, 38, 1185-1205, 2004.

Commonly used effective diameters:

Aerodynamic diameter, D_a: the diameter of a sphere of unit density (1 g cm^{-3}) that has the same terminal falling speed in air as the particle under consideration. Measured by inertial methods such as impactors and cyclones, depends on particle shape, density & size

Electrical mobility diameter, D_m: the diameter of a charged sphere with the same migration velocity of the charged particle under consideration in a constant electric field at atmospheric pressure. Obtained by electrostatic mobility analyzers (e.g., DMA) depends on particle shape and size.

Vacuum aerodynamic diameter, D_{va}: the diameter of a sphere, in the free molecular regime, with unit density (1 g/cm^3) and the same terminal velocity as the particle under consideration. Measured by e.g., Aerodyne AMS, under high vacuum, depends on particle shape, density & size.

Optical diameter, D_o: obtained by light scattering detectors, depends on particle refractive index, shape, and size.

Aerosol Diameters

- Particle diameters are operationally defined
- Different measurement techniques may report enormously different numbers
- Be aware of the measurement technique!

C. Van Gulijk et al. / Aerosol Science 35 (2004) 633–655 647

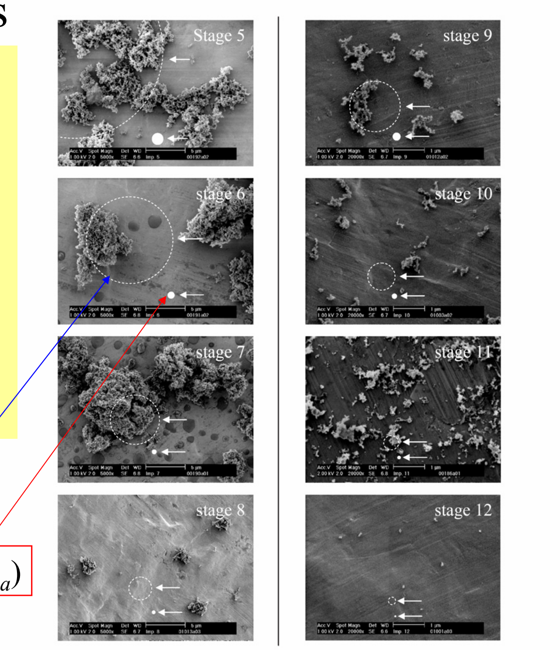


Fig. 5. Diesel soot on the ELPI-impactor stages 5–8 (5000×) and stages 9–12 (20,000×). White spots indicate aerodynamic upper size limit (previous impactor cutoff-size), white circles indicate corresponding mobility diameter (Table 3).

Mobility diameter (D_m)

Aerodynamic diameter (D_a)

Aerosol size distributions are determined by **source**, **processes** (chemical, physical), & **removing conditions**.

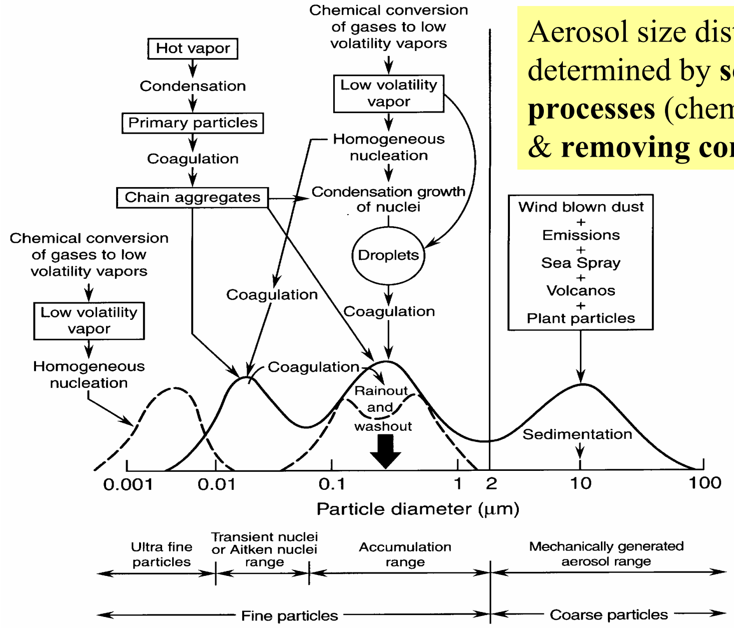


FIGURE 9.7 Schematic of an atmospheric aerosol size distribution showing four modes. The original hypothesis of Whitby and co-workers is shown by the solid, trimodal curves, and the fourth, ultrafine particle mode, as well as the two peaks sometimes observed in the accumulation mode are shown by the dashed lines (adapted from Whitby and Sverdrup, 1980). *Finlayson-Pitts &Pitts*

Aerosol Sources

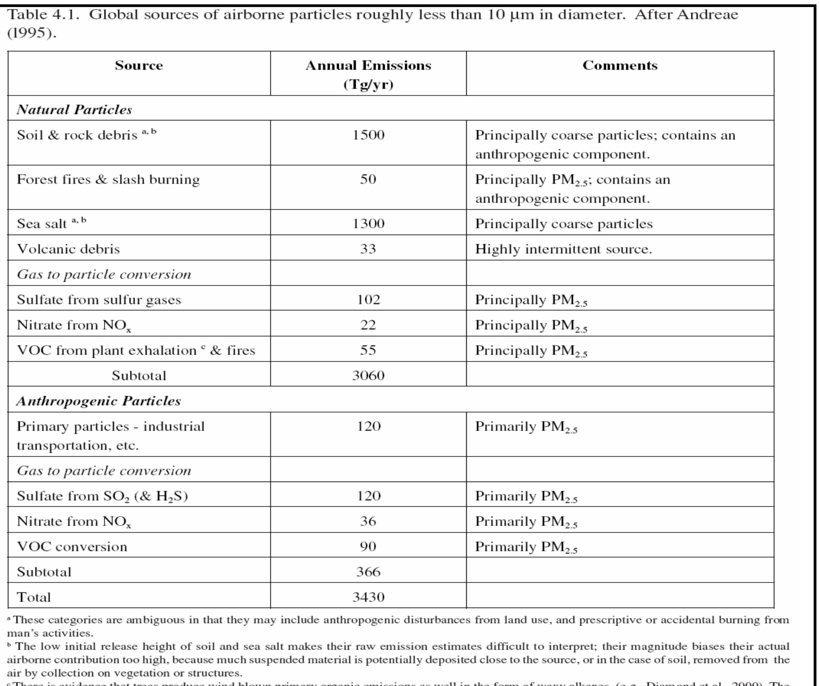


Table 4.1. Global sources of airborne particles roughly less than 10 μm in diameter. After Andreae (1995).

Source	Annual Emissions (Tg/yr)	Comments
Natural Particles		
Soil & rock debris [a, b]	1500	Principally coarse particles; contains an anthropogenic component.
Forest fires & slash burning	50	Principally $PM_{2.5}$; contains an anthropogenic component.
Sea salt [a, b]	1300	Principally coarse particles
Volcanic debris	33	Highly intermittent source.
Gas to particle conversion		
Sulfate from sulfur gases	102	Principally $PM_{2.5}$
Nitrate from NO_x	22	Principally $PM_{2.5}$
VOC from plant exhalation [c] & fires	55	Principally $PM_{2.5}$
Subtotal	3060	
Anthropogenic Particles		
Primary particles - industrial transportation, etc.	120	Primarily $PM_{2.5}$
Gas to particle conversion		
Sulfate from SO_2 (& H_2S)	120	Primarily $PM_{2.5}$
Nitrate from NO_x	36	Primarily $PM_{2.5}$
VOC conversion	90	Primarily $PM_{2.5}$
Subtotal	366	
Total	3430	

[a] These categories are ambiguous in that they may include anthropogenic disturbances from land use, and prescriptive or accidental burning from man's activities.

[b] The low initial release height of soil and sea salt makes their raw emission estimates difficult to interpret; their magnitude biases their actual airborne contribution too high, because much suspended material is potentially deposited close to the source, or in the case of soil, removed from the air by collection on vegetation or structures.

[c] There is evidence that trees produce wind blown primary organic emissions as well in the form of waxy alkanes. (e.g., Diamond et al., 2000). The magnitude of these emissions is essentially not known.

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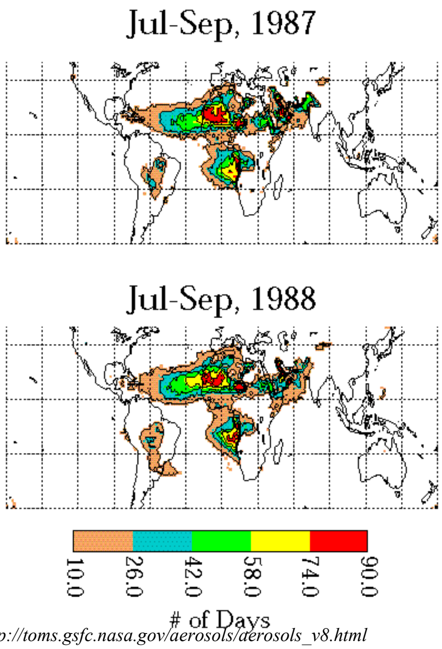
TOMS Smoke and Dust Detection


Jul-Sep, 1987

Jul-Sep, 1988

http://toms.gsfc.nasa.gov/aerosols/aerosols_v8.html

Satellite image of aerosol index detected in the presence of UV-absorbing tropospheric aerosols over each region of the Earth during July, August, and September of 1987 and 1988.

TOMS: **T**otal **O**zone **M**apping **S**pectrometer

Aerosol Index (AI): A measure of how much the wavelength dependence of backscattered UV radiation from an atmosphere containing aerosols (Mie scattering, Rayleigh scattering, and absorption) differs from that of a pure molecular atmosphere (pure Rayleigh scattering). Under most conditions, the AI is positive for absorbing aerosols and negative for on-absorbing aerosols (pure scattering).

- The areas in South America and Africa south of the equator indicate smoke produced by biomass burning.
- A large amount of the smoke from Africa can be seen to collect just off the coast in the Atlantic.
- North of the equator, most of the aerosol is due to dust blowing off of desert regions.

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lnD_p Based Size Distribution

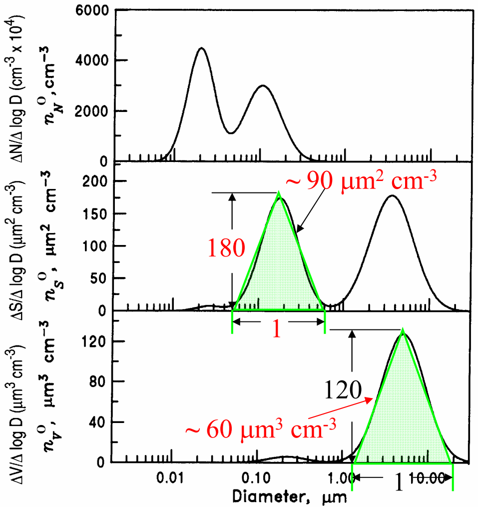


Figure 7-6 (S&P) The aerosol number, surface, and volume distributions expressed as a function of log Dp and plotted vs. log Dp. **The areas below the three curved correspond to the total aerosol number, surface, and volume, respectively.**

Number distribution

$$N = \int_{-\infty}^{\infty} n_N^o (\log D_{p)} d \log D_p$$

Surface area distribution

$$S = \pi \int_{-\infty}^{\infty} D_p^2 n_N^o (\log D_{p)} d \log D_p$$

$$\int_{-\infty}^{\infty} D_S^2 (\log D_{p)} d \log D_p$$

Volume distribution

$$V = \frac{\pi}{6} \int_{-\infty}^{\infty} D_p^3 n_N^o (\log D_{p)} d \log D_p$$

$$\int_{-\infty}^{\infty} n_V^o (\log D_p) d \log D_p$$

Exercise:
Estimate the number, surface, and volume concentrations of each mode.

Why Describe PM Size Distribution Based on ln D_p & log D_p

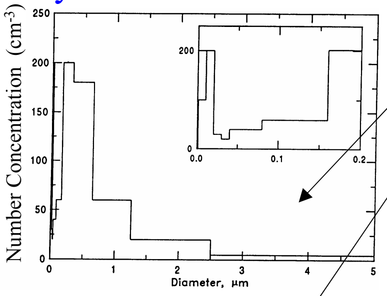


Figure 7.1 Histogram of aerosol number conc. v.s. the diameter. Inset: 0–0.2 μm. *Seinfeld & Pandis*

Ambient PM size dist. can be described by:

1) **ΔN (cm^{-3}) ~ D_p** (describe size dist. by size bins)

loss info. about the distribution structure inside each bin.
ΔN depend on definition of size bin.

2) dN/dD_p (μm^{-1} cm^{-3}) ~ D_p

Inconvenient b/c PM sizes range over orders of magnitude.

3) dN/dD_p (μm^{-1} cm^{-3}) ~ logD_p

Hard to interpret physically (area ≠ number conc.)

4) $dN/d\log D_p$ (cm^{-3}) ~ logD_p

The area below the curve corresponds to the # conc.

$$N_{a-b\mu m} = \int_{\log a}^{\log b} n_N^o(\log D_p)\, d\log D_p \qquad (\mathrm{cm}^{-3})$$

$$n_N^o(\log D_p) = dN/d\log D_p$$

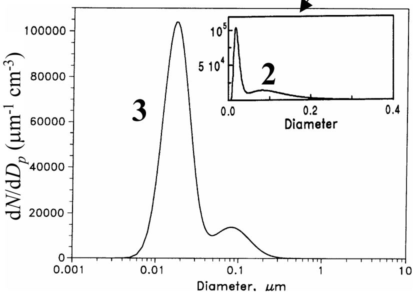


Figure 7.5 Aerosol number continuous distribution vs. the diameter. *Seinfeld & Pandis*

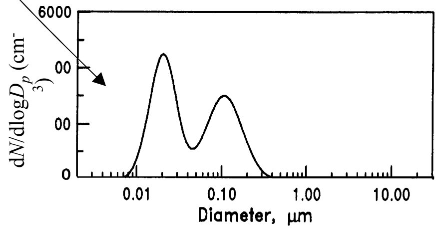


Figure 7.6 The same aerosol number distribution as in Fig.7.5 expressed as a function of log D_p and plotted vs. log D_p.

Properties of Size Distributions

TABLE 7.2 Mean Values Often Used in Characterizing an Aerosol Size Distribution

Property	Defining Relation	Description
Number mean diameter, $\overline{D}_p$	$\overline{D}_p = \int_0^\infty D_p n_N(D_p)\, dD_p$	Average diameter of the population
Median diameter, D_{med}	$\int_0^{D_{\mathrm{med}}} n_N(D_p)\, dD_p = \frac{1}{2}N$	Diameter below which one-half the particles lie and above which one-half the particles lie
Mean surface area, $\overline{S}$	$\overline{S} = \frac{1}{N}\int_0^\infty n_S(D_p)\, dD_p$	Average surface area of the population
Mean, volume, $\overline{V}$	$\overline{V} = \frac{1}{N}\int_0^\infty n_V(D_p)\, dD_p$	Average volume of the population
Surface area mean diameter, D_S	$N\pi D_S^2 = \int_0^\infty n_S(D_p)\, dD_p$	Diameter of the particle whose surface area equals the mean surface area of the population
Volume mean diameter, D_V	$N\frac{\pi}{6}D_V^3 = \int_0^\infty n_V(D_p)\, D_p$	Diameter of the particle whose volume equals the mean volume of the population
Surface area median diameter, D_{S_m}	$\int_0^{D_{Sm}} n_S(D_p)\, dD_p = \frac{1}{2}\int_0^\infty n_S(D_p)\, dD_p$	Diameter below which one-half the particle surface area lies and above which one-half the particle surface area lies
Volume median diameter, D_{V_m}	$\int_0^{D_{Vm}} n_V(D_p)\, dD_p = \frac{1}{2}\int_0^\infty n_V(D_p)\, dD_p$	Diameter below which one-half the particle volume lies and above which one-half the particle volume lies
Mode diameter, D_{mode}	$\left(\frac{dn_N(D_p)}{dD_p}\right)_{D_{\mathrm{mode}}} = 0$	Local maximum of the number distribution

Seinfeld & Pandis

Mathematical Description of Size Distributions

Normal distribution (bell shaped)

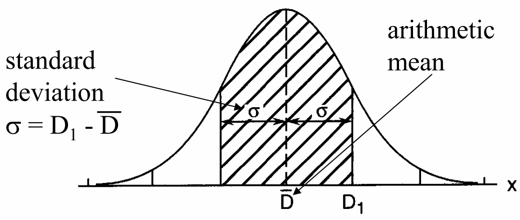


FIGURE 9.12 Meaning of standard deviation for a normal distribution. The hatched area represents 68% of total area under curve.

Finlayson-Pitts & Pitts

- A normal distribution is fully characterized by the $\overline{D}$ and the σ
- 68% of the particles have sizes in the range of $\overline{D} \pm \sigma$

The size distributions of atmospheric aerosols are best described by lognormal distributions (i.e., the logarithm of particle sizes is normally distributed).

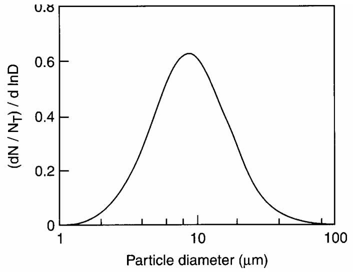


FIGURE 9.13 Frequency distribution curve (logarithmic size scale) (adapted from Hinds, 1982). *Finlayson-Pitts & Pitts*

Lognormal Distribution

- Describe ambient aerosol sizes by a lognormal distribution function → use 2 parameters (σ_g, and $\overline{D}_{pg}$) to describe the size dependency of key aerosol parameters (e.g., number, surface area, volume, mass)

$$n_N^e(\ln D_p) = \frac{dN}{d\ln D_p} = \frac{N}{(2\pi)^{1/2}\ln\sigma_g}\exp\left(-\frac{(\ln D_p - \ln\overline{D}_{pg})^2}{2\ln^2\sigma_g}\right) \quad \text{(S\&P eqn. 7.42)}$$

$$n_N(D_p) = \frac{dN}{dD_p} = \frac{N}{(2\pi)^{1/2}D_p\ln\sigma_g}\exp\left(-\frac{(\ln D_p - \ln\overline{D}_{pg})^2}{2\ln^2\sigma_g}\right) \quad \text{(S\&P eqn. 7.43)}$$

N: Number of particles having logarithmic diameters between ln$D$ and ln$D$ + dln$D$
σ_g: Geometric standard deviation. It is the ratio of the diameter below which 84.1% of the particles lie to the median diameter.
$\overline{D}_{pg}$: the median diameter

Lognormal Distribution

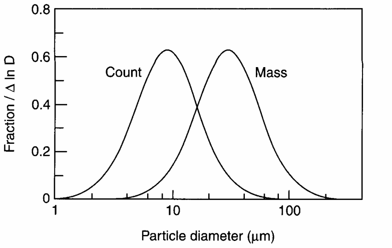


FIGURE 9.14 Count and mass distributions for a hypothetical log-normal sample. The spread, σ_g, of the two curves is seen to be the same, but the mean diameters associated with each are different (adapted from Hinds, 1982). *Finlayson-Pitts & Pitts*

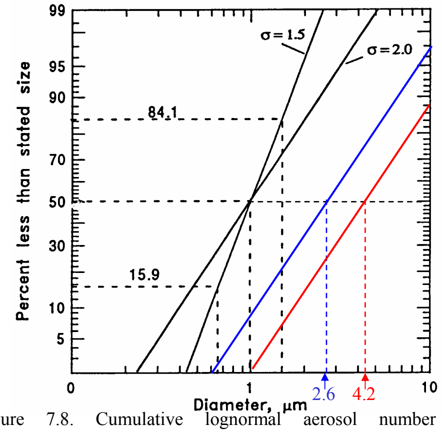


Figure 7.8. Cumulative lognormal aerosol number distributions. The distributions have mean diameter of 1 μm and σ_g =2 & 1.5, respectively. *Seinfeld & Pandis*

σ_g is the same for a given sample for all types of distributions – #, mass, S, & V.

Surface mean diameter:

$$\ln \overline{D}_{pgS} = \ln \overline{D}_{pg} + 2\ln^2 \sigma_g$$

Volume mean diameter:

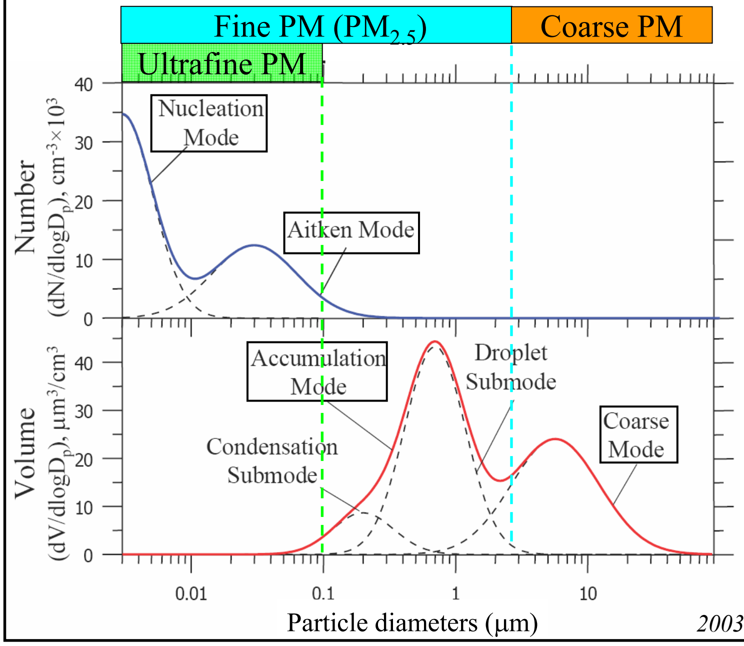
$$\ln \overline{D}_{pgV} = \ln \overline{D}_{pg} + 3\ln^2 \sigma_g$$

Exercise:

Know $\sigma_g = 2$, $\overline{D}_{pg} = 1\,\mu\text{m}$, determine $\overline{D}_{pgS}$ and $\overline{D}_{pgV}$

$\overline{D}_{pgS} = 2.6\ \mu\text{m}$ $\overline{D}_{pgV} = 4.2\ \mu\text{m}$

Size Distribution of Ambient Aerosols: Modes



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Nucleation mode:
< 0.01 μm

Ultrafine mode:
< 0.1 μm

Accumulation mode:
0.1 – 2.5 μm

Fine mode:
< 2.5 μm

Coarse mode:
> 2.5 μm

Size Distribution of Ambient Aerosols

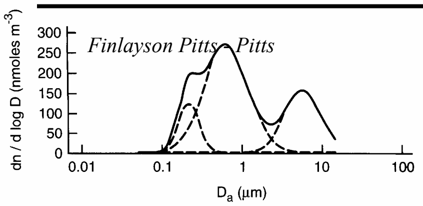


FIGURE 9.8 Typical size distribution of nitrate in southern California in 1987 fitted by the sum of three log-normal distributions with peaks at 0.2, 0.7, and 4.4 μm (adapted from John *et al.*, 1990).

$$\frac{dN}{d\ln D_p}=\sum_{i=1}^{l}\frac{N_i}{(2\pi)^{1/2}\ln\sigma_{g,i}}\exp\left(-\frac{(\ln D_p-\ln\overline{D}_{pg,i})^2}{2\ln^2\sigma_{g,i}}\right)$$

l – number of modes

$\overline{D}_{pg,i}$ – the median diameter of mode *i*

$\sigma_{g,i}$ – geometric standard deviation of mode *i*

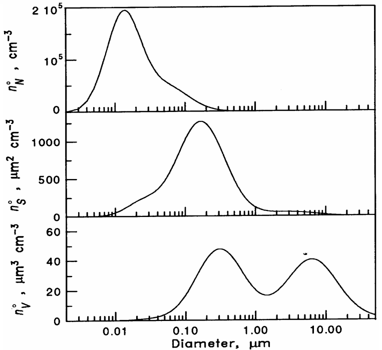


Figure 7.12. Typical urban aerosol #, S, & V distributions. *Seinfeld & Pandis*

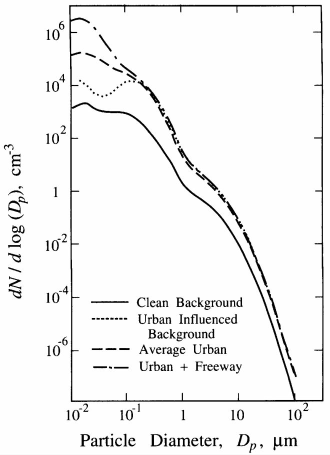


Figure 7.13. Aerosol number distributions next to a source (freeway), for average urban, for urban influences background, and for background conditions. *Seinfeld & Pandis*

Typical PM Size Distributions in Various Atmospheres

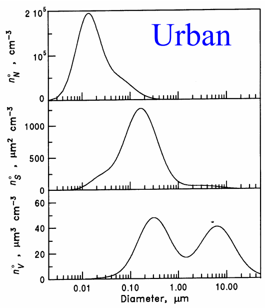


FIGURE 7.12 Typical urban aerosol number, surface, and volume distributions.

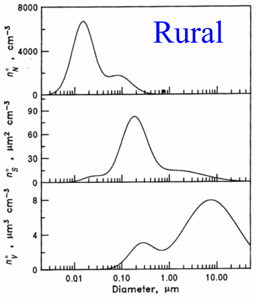


FIGURE 7.17 Typical rural continental aerosol number, surface, and volume distributions.

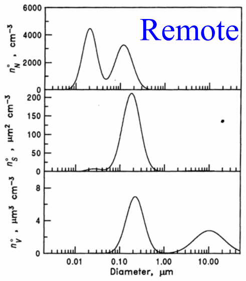


FIGURE 7.18 Typical remote continental aerosol number, surface and volume distributions.

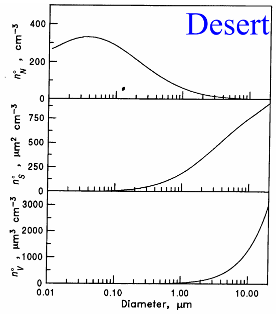
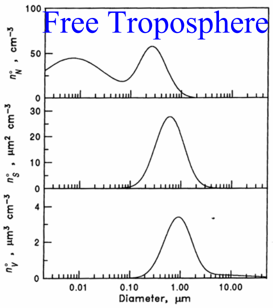


FIGURE 7.22 Typical desert aerosol number, surface, and volume distributions.



URE 7.19 Typical free tropospheric aerosol number, surface, and volume distributions.

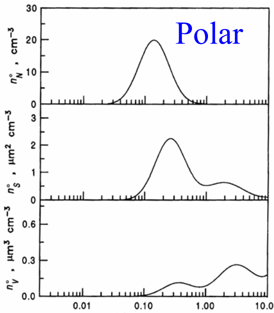


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FIGURE 7.20 Typical polar aerosol number, surface, and volume distributions.

Atmospheric Aerosol Composition

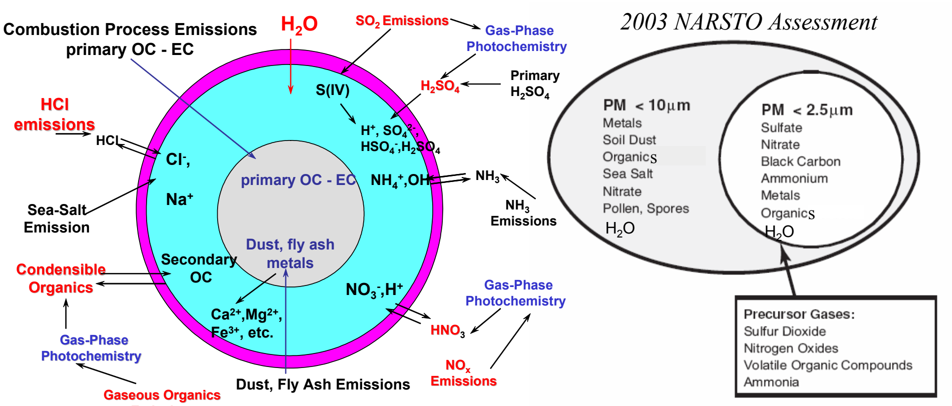


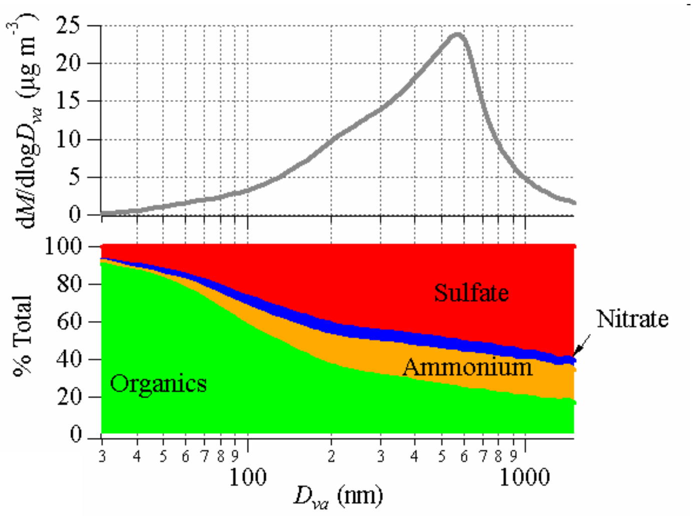
Figure 1.2. Representative Composition of PM.

Chemical composition reflects the sources and processes of particles:

- Metals/crustal materials (e.g., Al, Fe, Ca, Si): soil erosion, dust
- Na, Cl^-: Sea-salt
- Black carbon: Fusil fuel / biomass combustion
- Sulfate, nitrate, ammonium: secondary formation
- Organics: a complex mixture of many individual organic compounds
- H_2O

Size Resolved Composition of Pittsburgh Fine PM

Only the non-refractory components



Size dependent composition of ambient aerosols

Zhang et al., Time and size-resolved chemical composition of submicron particles in Pittsburgh - Implications for aerosol sources and processes, J. Geophys. Res., 110 (D07S09), 2005.

Atmospheric Aerosol Composition

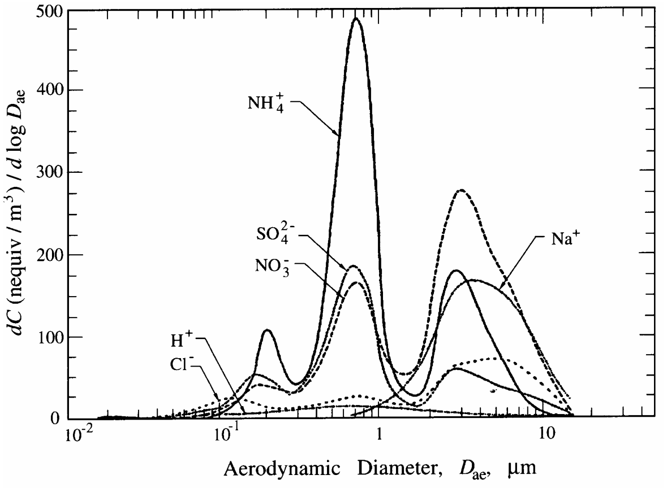
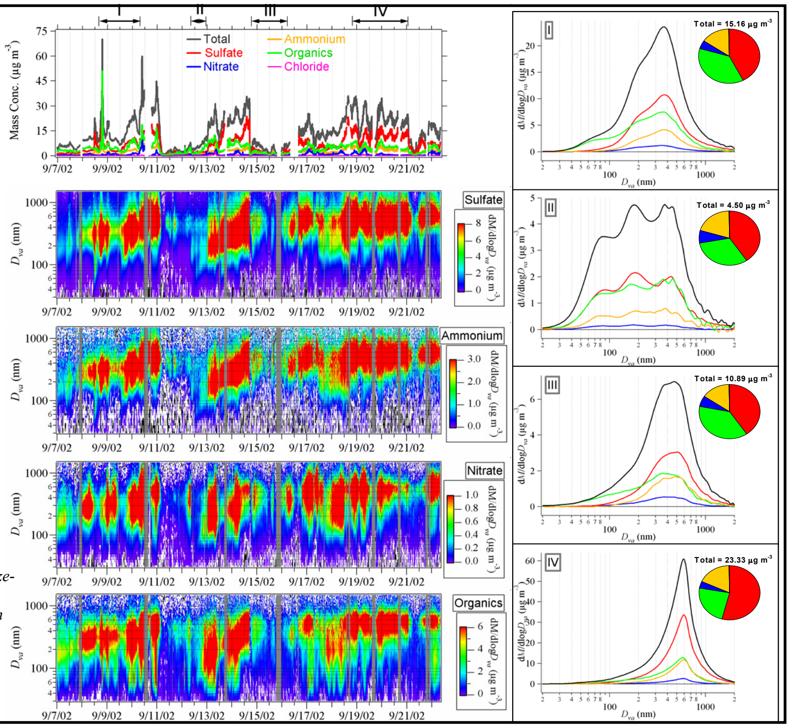


FIGURE 7.23 Measured size distributions of aerosol sulfate, nitrate, ammonium, chloride, sodium, and hydrogen ion in Claremont, CA (Wall et al., 1988).

Size dependent composition of ambient aerosols

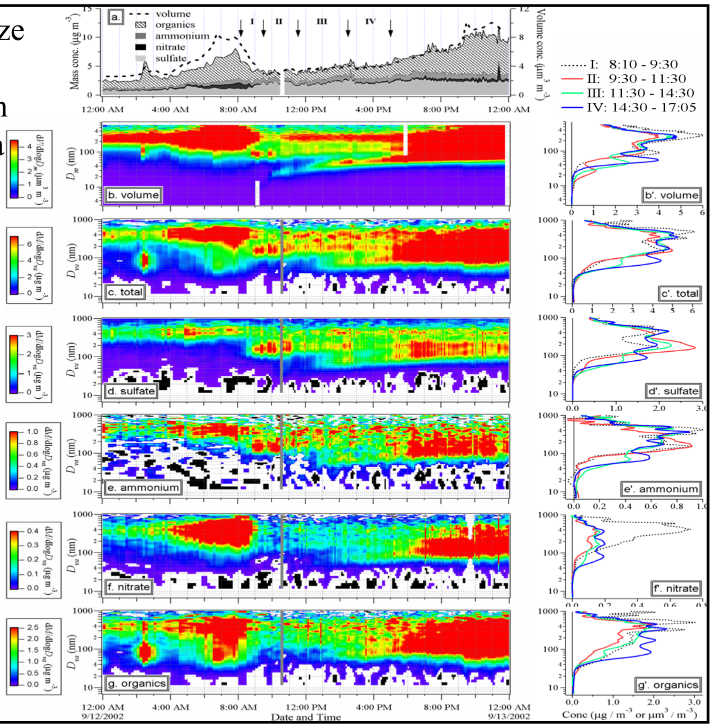
Seinfeld & Pandis

Size distributions of ambient fine PM in Pittsburgh



Zhang et al., Time and size-resolved chemical composition of submicron particles in Pittsburgh - Implications for aerosol sources and processes, J. Geophys. Res., 110 (D07S09), 2005.

Evolution of the size distributions of ambient aerosols in Pittsburgh during a nucleation day



Zhang et al., Insights into the chemistry of new particle formation and growth events in Pittsburgh based on Aerosol Mass Spectrometry, Environmental Science & Technology, 38 (18), 4797-4809, 2004.

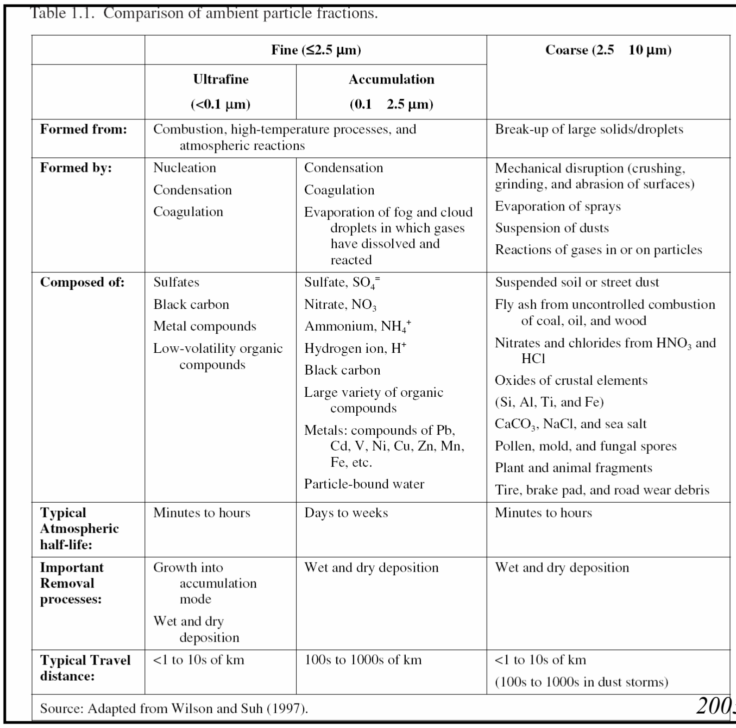


Table 1.1. Comparison of ambient particle fractions.

	Fine (≤2.5 µm)		**Coarse (2.5 10 µm)**
	Ultrafine (<0.1 µm)	**Accumulation (0.1 2.5 µm)**	
Formed from:	Combustion, high-temperature processes, and atmospheric reactions		Break-up of large solids/droplets
Formed by:	Nucleation Condensation Coagulation	Condensation Coagulation Evaporation of fog and cloud droplets in which gases have dissolved and reacted	Mechanical disruption (crushing, grinding, and abrasion of surfaces) Evaporation of sprays Suspension of dusts Reactions of gases in or on particles
Composed of:	Sulfates Black carbon Metal compounds Low-volatility organic compounds	Sulfate, $SO_4^{=}$ Nitrate, NO_3 Ammonium, NH_4^+ Hydrogen ion, H^+ Black carbon Large variety of organic compounds Metals: compounds of Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc. Particle-bound water	Suspended soil or street dust Fly ash from uncontrolled combustion of coal, oil, and wood Nitrates and chlorides from HNO_3 and HCl Oxides of crustal elements (Si, Al, Ti, and Fe) $CaCO_3$, NaCl, and sea salt Pollen, mold, and fungal spores Plant and animal fragments Tire, brake pad, and road wear debris
Typical Atmospheric half-life:	Minutes to hours	Days to weeks	Minutes to hours
Important Removal processes:	Growth into accumulation mode Wet and dry deposition	Wet and dry deposition	Wet and dry deposition
Typical Travel distance:	<1 to 10s of km	100s to 1000s of km	<1 to 10s of km (100s to 1000s in dust storms)

Source: Adapted from Wilson and Suh (1997).

2003 NARSTO Assessment

$PM_{2.5}$ Concentration & Composition in US

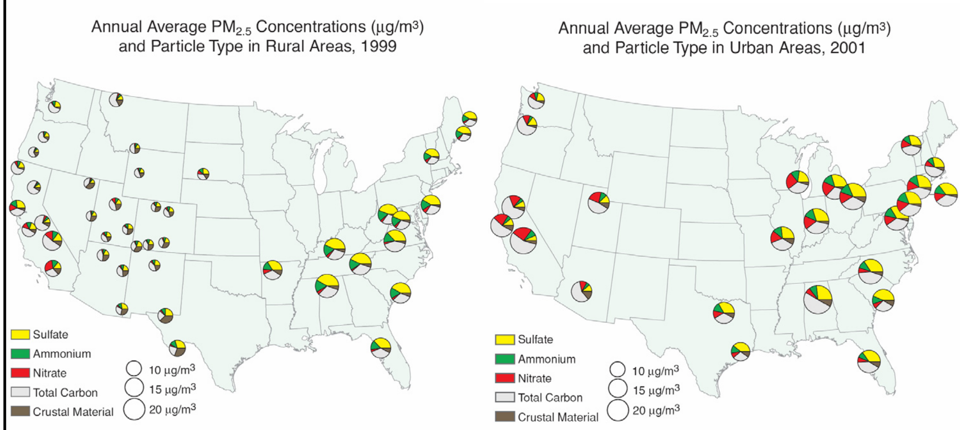


Figure 6.16. Comparisons of average $PM_{2.5}$ mass and species concentrations at urban and rural locations. The rural data are from the IMPROVE network, while the urban data are from the EPA Speciation Trends Network. Note that urban nitrate concentrations are distinctly higher than rural levels. Direct comparison of the information in these two maps should take into consideration: the fact that they represent different years; that one is an urban network and the other is a rural network; and that there are also differences in instruments and measurement methods (Source: U.S. EPA, 2002). *2003 NARSTO Assessment*

Atmospheric PM vary greatly in concentration & composition

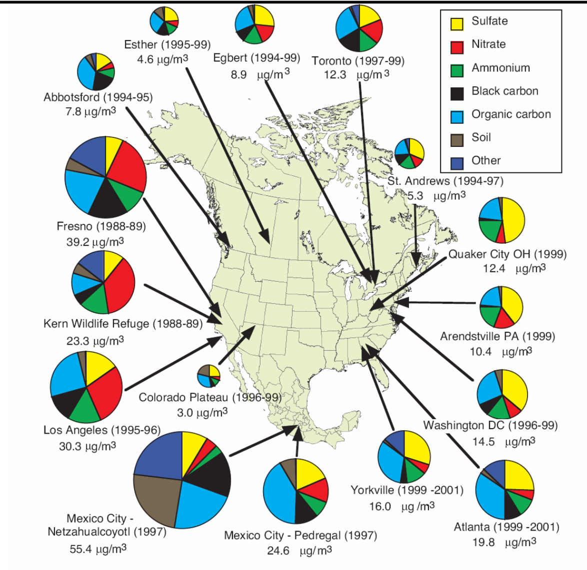


Figure 6.12. Composition of $PM_{2.5}$ at representative urban and rural locations. The urban sites are Toronto, Washington DC, Atlanta, Mexico City, Los Angeles, and Fresno. Averaging periods and average $PM_{2.5}$ mass are indicated. All sites have at least one year of sampling except Mexico City, for which the average was determined from one month (14 days). More recent short-term measurements from December 1995 and January 1996 at Fresno and Kern Wildlife refuge show lower $PM_{2.5}$ mass concentrations but similar composition to the data displayed here. The Colorado Plateau data are the averages of the IMPROVE sites located at Bryce Canyon, Canyonlands, Grand Canyon, Petrified Forest, Mesa Verde, and Zion National Parks. (Source: Vet et al., 2001; Malm, 2000; Hansen et al., 2003; Chow et al., 1993; U.S. EPA, 2000; Kim et al., 2000).

2003 NARSTO Assessment

Seasonal Variations of PM_{10} Mass Concentration

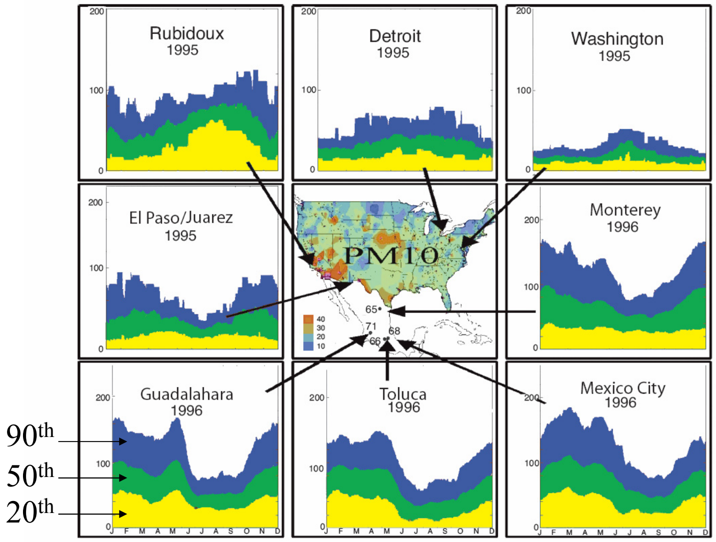
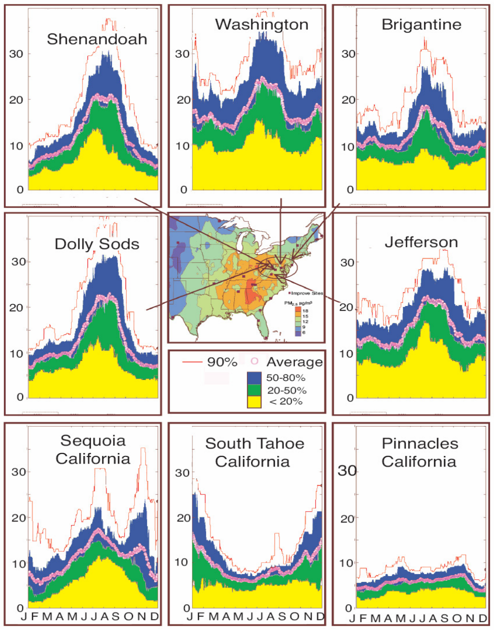


Figure 6.4. Seasonal variation of PM_{10} mass concentrations at selected monitors in the United States and Mexico. The graphs indicate the estimated 20th percentile (yellow), average (green), and 90th percentile (blue) on each date beginning in 1995 or 1996. Data for U.S. locations represent one site; data for Mexican locations include five to eight sites per location. Statistical smoothing procedures were applied to each time series in estimating the percentiles (Source: R. Husar, pers. comm.).

2003 NARSTO Assessment

Seasonal Variations of $PM_{2.5}$ Mass Concentration



2003 NARSTO Assessment

Figure 6.11. Seasonal variations of $PM_{2.5}$ mass concentrations at selected IMPROVE monitoring locations (1992-1999) for the cleanest (20 percent), moderate (20-50 percent), and highest PM (50-80 percent and 90 percent) days. The units of measurement are $\mu g/m^3$. (R. Husar, pers. comm.).

Vertical Variation

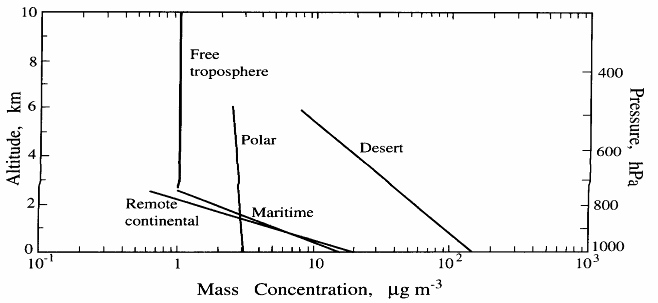


FIGURE 7.25 Representative vertical distribution of aerosol mass concentration (Jaenicke, 1993).

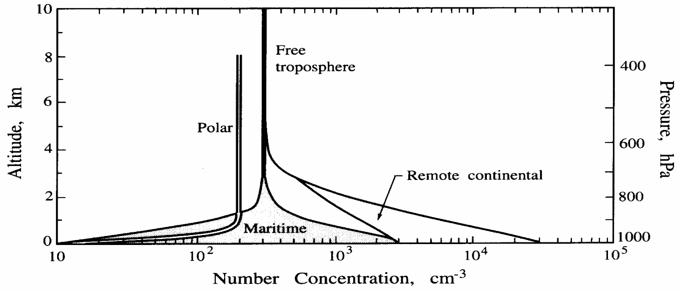


FIGURE 7.26 Representative vertical distribution of aerosol number concentration (Jaenicke, 1993). A range of concentrations is shown for marine and remote continental aerosols

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Part II: Aerosol Processes and Dynamics

II.1. Aerosol Dynamics
- Diffusion
- Condensation
- Coagulation
- Evaporation
- Scavenging

II.2. Formation & Transformation
- Nucleation
- Gas to particle conversion
- Surface rxn (e.g., acid replacement)
- Bulk rxn

To understand physical and chemical processes that are important for aerosol production, growth, and removal.

Required reading: F-P & P chapters 9.B. & S&P chapter 11.1.
Recommended reading: S&P chapters 8, 10, 12

Gas – Particle Interactions

Regimes of gas-particle interactions:

- Knudsen number (*Kn*) defines the nature of the suspending particle relative to the particle: **$Kn = 2\lambda/D_p$**

  λ – Mean free path: the average distance traveled by a molecule btw collisions with other molecules. $\lambda_{air} \approx 65$ nm

  D_p – Particle diameter

1. The continuum regime: $\lambda << D_p$ (ambient, $D_p > 0.2$ µm). The gas behave as to the particle as a continuous fluid.
2. The free molecular (kinetic regime): $\lambda >> D_p$ (ambient, $D_p < 0.01$ µm). The particle is small enough that looks like another gas molecule.
3. The transition regime: $\lambda \approx D_p$ (ambient, $0.01 < D_p < 0.2$ µm).

Mass transfer processes (i.e., condensation & coagulation) are function of *Kn*.

From Seinfeld and Pandis

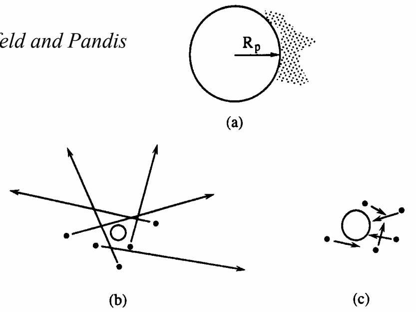


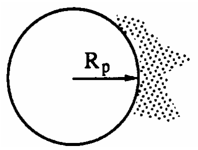
FIGURE 8.1 Schematic of the three regimes of suspending fluid–particle interactions: (a) continuum regime ($Kn \to 0$), (b) free molecule (kinetic) regime ($Kn \to \infty$), and (c) transition regime ($Kn \approx 1$)

Gas to Particle Conversion

Mass transfer of gas molecules to particles (i.e., condensation):

- J_c: the total flow of $A_{(g)}$ (moles time^{-1}) toward the particle in **continuum regime**

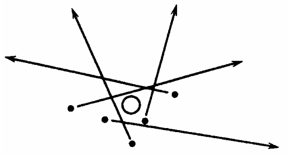
$$J_c = 4\pi R_p D_g (c_\infty - c_s)$$



R_p: Particle radius
D_g: Diffusivity of gas A
c_∞ : Conc. of A far from the particle
c_s: Vapor phase conc. of A at the particle surface

- J_k: the total flow of $A_{(g)}$ (moles time^{-1}) toward the particle in **free molecular (kinetic regime)**

$$J_k = \pi R_p^2 \bar{c}_A \alpha (c_\infty - c_s); \quad \bar{c}_A = \left(\frac{8kT}{\pi m_A}\right)^{1/2}$$

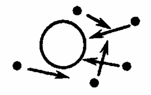


$\bar{c}_A$: Mean speed of the molecules
α: Molecular accommodation coefficient, i.e., probability of A to stick on particle. $0 \le \alpha \le 1$

Gas to Particle Conversions (Mass Transfer)

Mass transfer of gas molecules to particles (i.e., condensation):

- J: the total flow of A(g) (moles time^{-1}) toward the particle in **transition regime**
  - J_c & J_k eqns are not valid when $\lambda \approx D_p$ (or $Kn \approx 1$)
  - No general solution exists from solving distribution of gas molecules
  - ➔ Use flux matching to determine J



This curve does not match the experimental data

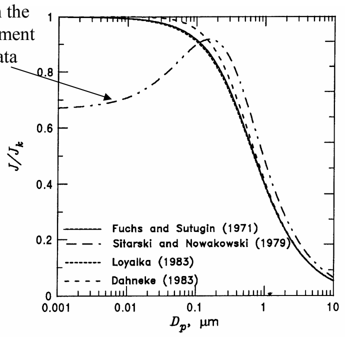


FIGURE 11.2 Mass transfer rate predictions for the transition regime by the approaches of (a) Fuchs and Sutugin, (b) Dahneke, (c) Loyalka and (d) Sitarski and Nowakowski ($z = 15$) as a function of particle diameter. Accommodation coefficient $\alpha = 1$.

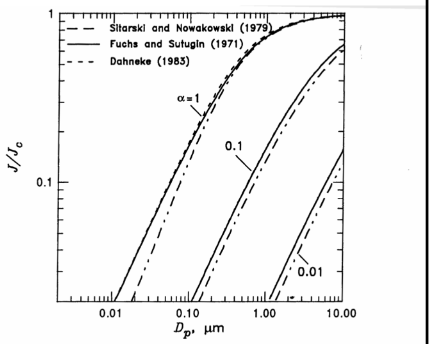


FIGURE 11.4 Mass transfer rates as a function of particle diameter for accommodation coefficient values 1.0, 0.1, and 0.01 for the approaches of Sitarski and Nowakowski (1979), Fuchs and Sutugin (1970), and Dahneke (1983).

From Seinfeld and Pandis

How Does Condensation Affect Size Distribution?

- Condensation/Evaporation → D_p change & size dist. change shape.
- Under condensation, smaller particles grow much faster than larger ones → The size distribution becomes much narrower

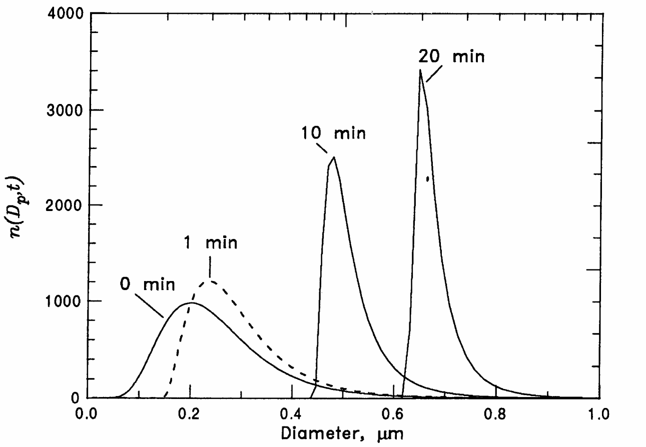
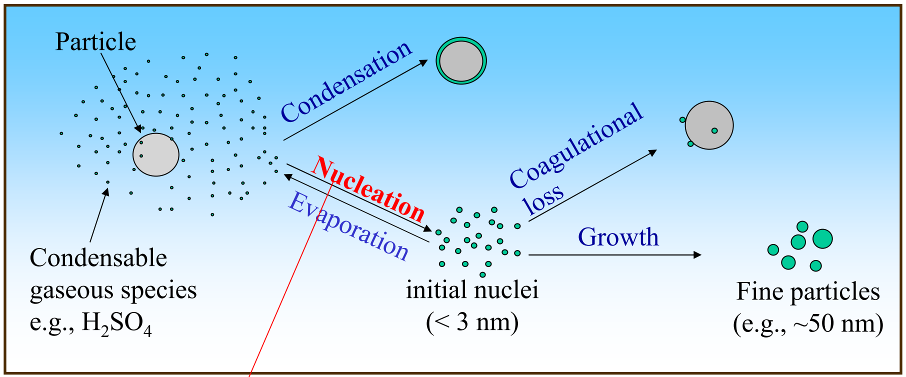


FIGURE 12.3 Evolution of a log-normal distribution (initially $\bar{D}_p = 0.2\ \mu$m, $\sigma_g = 1.5$) assuming $D_i = 0.1\ \mathrm{cm^2\,s^{-1}}, M_i = 100\ \mathrm{g\,mol^{-1}}, (p_i - p_{eq,i}) = 10^{-9}$ atm(1 ppb), $T = 298$ K and $\rho_p = 1\ \mathrm{g\,cm^{-3}}$.

From Seinfeld and Pandis

Gas to Particle Conversion (Particle Nucleation)



Particle

Condensation

Nucleation

Evaporation

Coagulational loss

Growth

Condensable gaseous species e.g., H_2SO_4

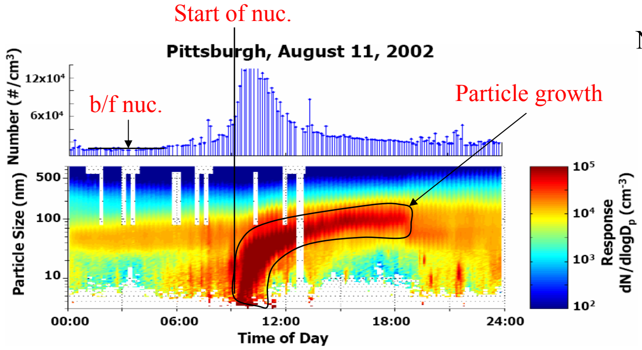
initial nuclei (< 3 nm)

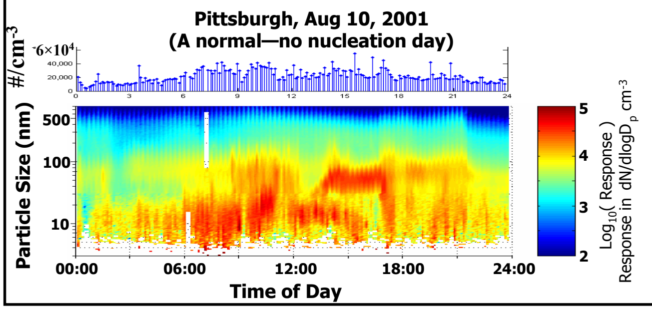
Fine particles (e.g., ~50 nm)

- Condensation and nucleation are competing processes.
- Nucleation dominate when PM condensational sink is low.

Possible nucleation mechanism
a) Binary nucleation ($H_2SO_4 + H_2O$)
b) Ternary nucleation ($H_2SO_4 + NH_3 + H_2O$)
c) Organic compounds nucleation
d) Ion-induced nucleation

How Does Nucleation Affect Size Distribution?

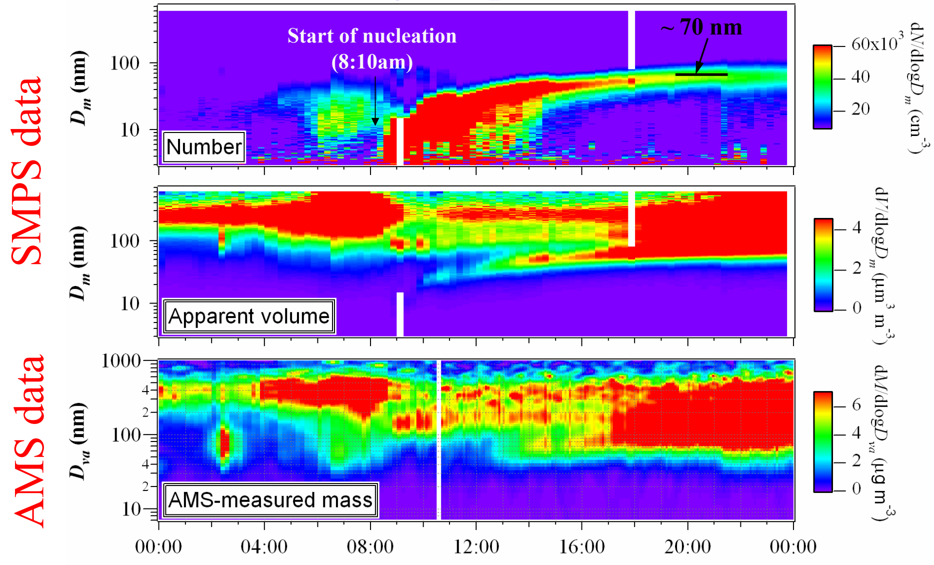




Nucleation + growth events:
- Frequent, ubiquitous
- Dramatically increase the number conc., change the size distribution and chemical composition of ambient particles.

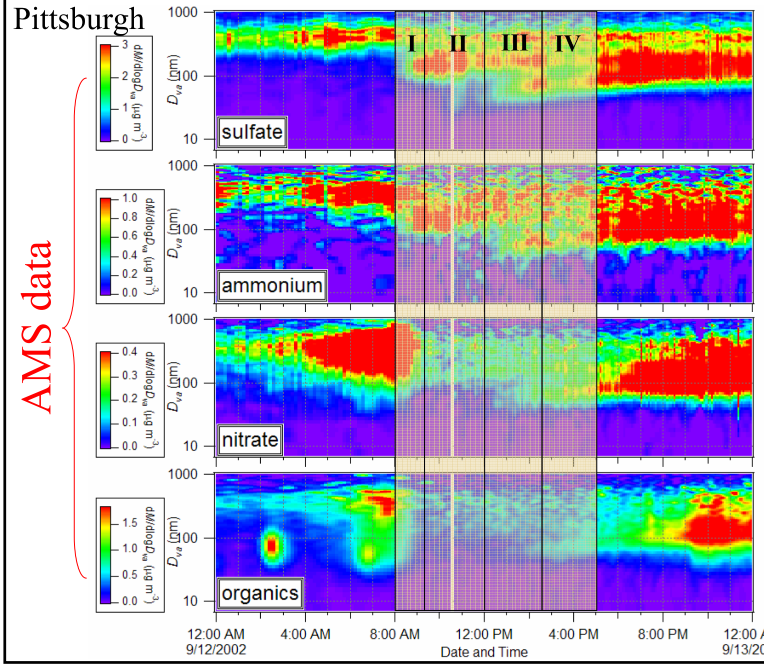
Particle number distribution data from Charlie Stanier, CMU (now at Univ. of Iowa)

Evolution of Number, Volume, & Mass distributions (Pittsburgh, Sept 12, 2002)



Zhang et al., Insights into the chemistry of new particle formation and growth events in Pittsburgh based on Aerosol Mass Spectrometry, Environmental Science & Technology, 38 (18), 4797-4809, 2004.

Evolution of Size-Resolved PM Comp. (Sept. 12, 2002)

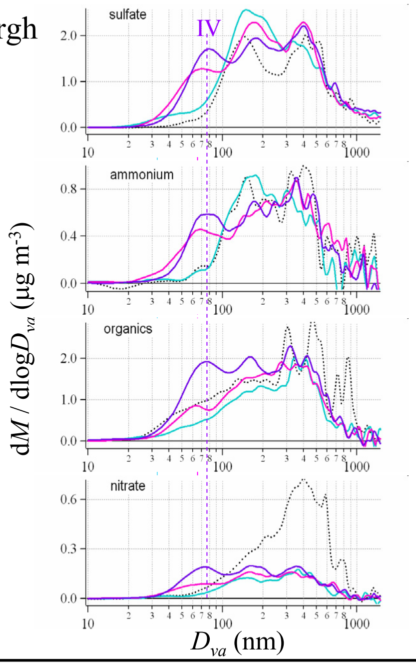


I:	Initial
II & III:	Growth
IV:	Final

Zhang et al., Insights into the chemistry of new particle formation and growth events in Pittsburgh based on Aerosol Mass Spectrometry, Environmental Science & Technology, 38 (18), 4797-4809, 2004.

Evolution of Size-Resolved PM Comp. (Sept. 12, 2002)

Pittsburgh



I: Size dist of SO_4^{2-} & NH_4^+ similar Org & NO_3^- different

II: SO_4^{2-} first to ↑; Org & NO_3^- ↓

III: Growth of the ultrafine mode.

IV: All developed into the same size dist. ➔ Extensive condensation

Zhang et al., Insights into the chemistry of new particle formation and growth events in Pittsburgh based on Aerosol Mass Spectrometry, Environmental Science & Technology, 38 (18), 4797-4809, 2004.

Particle ~ Particle Interaction (Coagulation)

Coagulation: formation of a single particle via collision and sticking of two smaller particles (e.g., Brownian coagulation)

- Need to consider in the context of different regimes.
- Coagulation rate depends on:
  - ➢ Diameter of the large particle
  - ➢ Diffusion rates of the smaller particle
  - ➢ Concentration of the particles
- Smallest coagulation rates b/w particles of same size (i.e., self-coagulation slowest).

TABLE 12.3 Coagulation Coefficients ($cm^3\ s^{-1}$) of Atmospheric Particles

	D_{p1} (μm)					
D_{p2} (μm)	0.002	0.01	0.1	1.0	10	20
0.002	4.5×10^{-10}	3×10^{-9}	1.6×10^{-7}	3.7×10^{-6}	4×10^{-5}	8×10^{-5}
0.01	3×10^{-9}	9×10^{-10}	1.2×10^{-8}	1.6×10^{-7}	1.6×10^{-6}	3×10^{-6}
0.1	1.6×10^{-7}	1.2×10^{-8}	7.2×10^{-10}	2.4×10^{-9}	2.2×10^{-8}	4.3×10^{-8}
1	3.7×10^{-6}	1.6×10^{-7}	2.4×10^{-9}	3.4×10^{-10}	1.0×10^{-9}	1.9×10^{-9}
10	4×10^{-5}	1.6×10^{-6}	2.2×10^{-8}	1.0×10^{-9}	3×10^{-10}	3.3×10^{-10}
20	8×10^{-5}	3.0×10^{-6}	4.3×10^{-8}	1.9×10^{-9}	3.3×10^{-10}	3×10^{-10}

From Seinfeld and Pandis

Particle ~ Particle Interaction (Coagulation)

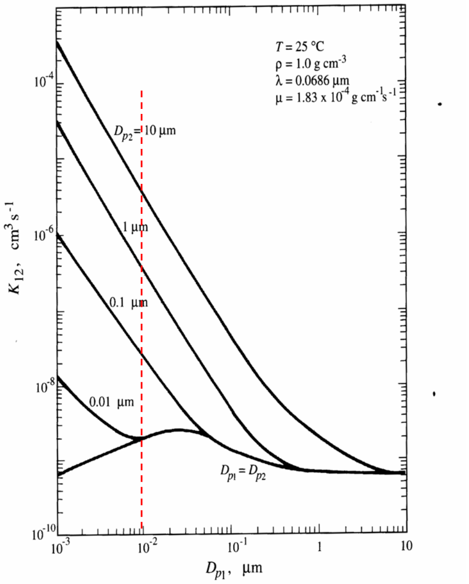


FIGURE 12.5 Brownian coagulation coefficient K_{12} for coagulation in air at 25°C of particles of diameters D_{p1} and D_{p2}. The curves were calculated using the correlation of Fuchs in Table 12.1. To use this figure find the *smaller* of the two particles as the abscissa and then locate the line corresponding to the larger particle.

From Seinfeld and Pandis

Bigger size ratio (D_{p1}/D_{p2}), higher coagulation rates

How Does Coagulation Affect Size Distribution?

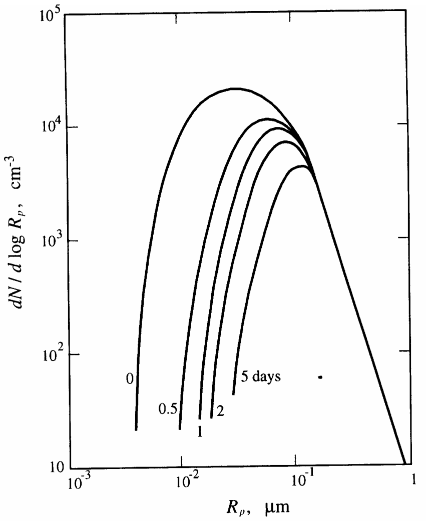


FIGURE 12.13 Evolution of a coagulating particle population size distribution during a period of 5 days (Butcher and Charlson, 1972).

From Seinfeld and Pandis

- Small particles faster Brownian motion → more collision → faster coagulational loss.
- Coagulation dramatically affects the # conc. of particles w/ $D_p < 0.05$ μm

Condensation vs. Coagulation Rates

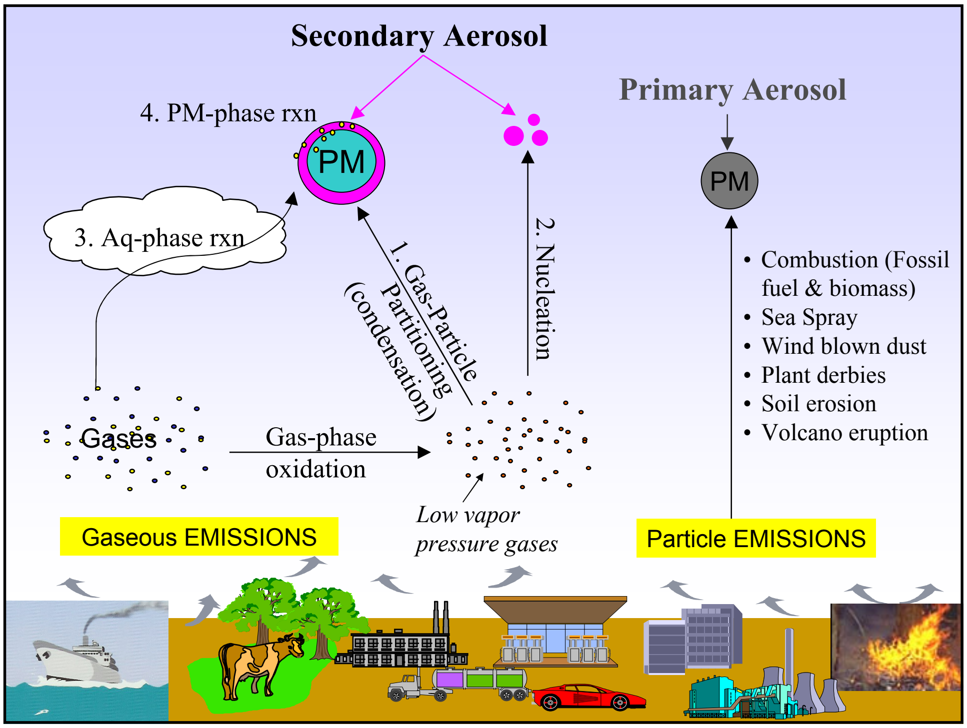
TABLE 9.10 Typical Time Scales for Various Aerosol Fates[a]

Fate	Type of air mass			
	Urban	Remote marine	Free troposphere	Nonurban continental
Condensation	0.01–1 h	1–10 h	2–20 h	0.5–20 h
Coagulation of 0.03-μm-particles with larger particles	0.1–2 days	10–30 days	~50 days	1–5 days
Deposition				
0.03-μm particles	0.5–10 days	0.5–10 days	—	~1 month
0.3-μm particles	~1 month	~1 month	—	~1 month
Transport	2–5 days	1–2 weeks	3 days to 2 weeks	1–2 weeks

[a] From Pandis *et al.* (1995).

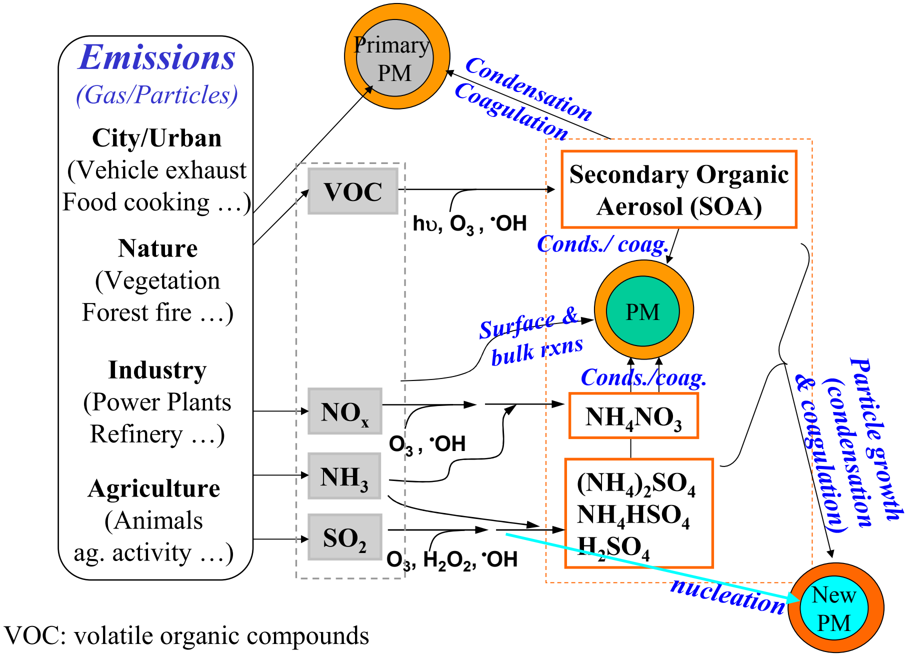
From Finlayson-Pitts and Pitts

- At ambient condition, condensation much faster than coagulation



- Combustion (Fossil fuel & biomass)
- Sea Spray
- Wind blown dust
- Plant derbies
- Soil erosion
- Volcano eruption

Secondary Aerosol Formation (i.e., Gas → PM Conversion)



Emissions

(Gas/Particles)

City/Urban
(Vehicle exhaust
Food cooking …)

Nature
(Vegetation
Forest fire …)

Industry
(Power Plants
Refinery …)

Agriculture
(Animals
ag. activity …)

VOC

NO_x

NH_3

SO_2

hυ, O_3 , ·OH

O_3 , ·OH

O_3, H_2O_2, ·OH

Primary PM

Condensation

Coagulation

Secondary Organic Aerosol (SOA)

Conds./ coag.

PM

Surface & bulk rxns

Conds./coag.

NH_4NO_3

$(NH_4)_2SO_4$
NH_4HSO_4
H_2SO_4

nucleation

New PM

Particle growth (condensation & coagulation)

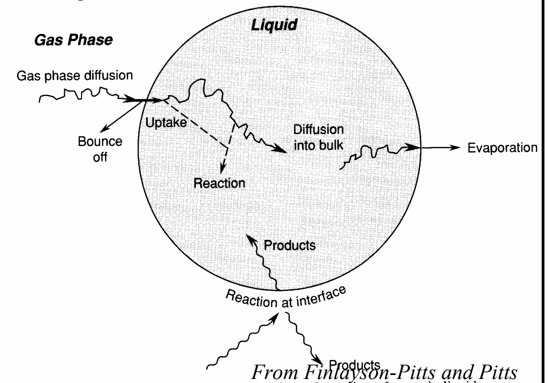
VOC: volatile organic compounds

Chemical Reactions of Particles

- Chemistry
  - Solid aerosol provide surfaces upon which trace gases can be absorbed and then react

    e.g., $NaCl_{(s)} + HNO_{3(g)} \rightarrow HCl_{(g)} + NaNO_{3(s)}$ (acid replacement on sea salt aerosols)
  - Liquid aerosols absorb gases which may then react together in solution

    e.g. $SO_{2(g)} \rightarrow H_2SO_{4(l)}$



From Finlayson-Pitts and Pitts

FIGURE 5.12 Schematic diagram of uptake and reaction of gases in liquids.

How Do Chemical Reactions Affect Size Distribution?

Due to cloud processing of small mode PM

1. Agglomeration of smaller PM
2. Gas → PM (e.g., SO_2 oxidation)

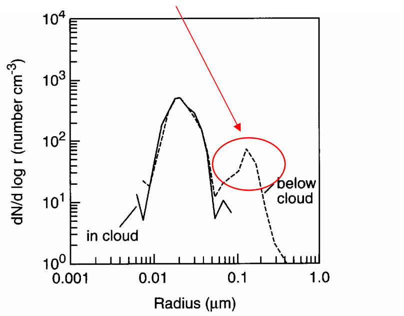
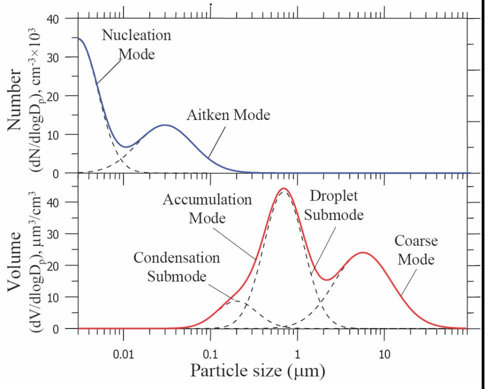


FIGURE 9.33 Size distribution of particles in clouds (solid line) and below the clouds (dashed line), showing two modes (adapted from Hoppel *et al.*, 1994). *From Finlayson-Pitts & Pitts*



Aqueous reactions (in fog/cloud droplets) responsible for the bimodal distribution of the accumulation mode.

Removal of Particles

- Dry deposition:
  - *Gravitational settling*: particle falling under gravity (settling velocity is directly proportional to particle mass). Only effective for larger particles.
  - *Turbulent deposition*: the most effective dry vertical transport mechanism in the boundary layer.
- Wet deposition
  - *Rainout*: aerosol → cloud condensation nucleus (CCN) → rain drops → deposit
  - *Washout*: the removal of aerosol by cloud droplets. An aerosol is incorporated into an already existing cloud drop, and that drop grows large enough to fall as rain, the particle is said to have been washed out.
    - The difference between washout and rainout is the required pre-existence of a collecting drop for washout.
  - *Sweepout*: Aerosol remaining below the cloudbase of a raining cloud can impact into falling raindrops. If the impact leads to incorporation of the aerosol into the drop, the aerosol is deposited with the raindrop, the condensation nucleus, and any other washed or swept out particles.
    - Although the final fate of rained, washed and swept out particles is the same, the three processes are distinct because the efficiency of each, and the size and amount of aerosol swept out by each process is calculated differently in modeling.
  - *Occult Deposition*: (deposition by way of fog and cloud droplets) Impaction efficiency is the likelihood that a particle will strike a surface feature encountered in a flow, rather than be deflected around the object. It is a strong function of size, with larger aerosol being more likely to impact on a surface feature than smaller particles.

Part III: Organic Aerosols

- Elemental carbon (EC) & organic carbon (OC)
- Chemical nature of organic aerosol compounds
- Primary sources
- Secondary organic aerosol formation
- Photolysis and oxidation

*<u>Required</u> reading: Seinfeld, J.H., and J.F. Pankow, **Organic atmospheric particulate material**, Annual Review of Physical Chemistry, 54, 121-140, 2003.*

Recommended reading:

1) S&P chapter 13

2) F-P & P chapters 9.C.2, 9.D

Elemental & Organic Carbon (EC/OC)

EC: elemental carbon, i.e., black carbon (BC)

OC: organic carbon

Soot: by-product of the combustion, contain both EC and OC. Present as chain agglomerate of small roughly spherical elementary carbonaceous particles. $\rho \approx 2$ g /cm^3

Atmospheric organic compound classes:

Aliphatics (e.g., alkanes, alkenes)

Aromatics

Aliphatic and aromatic acids

Aliphatic and aromatic carbonyls (i.e., aldehydes & ketones)

Aromatic polycarboxylic acids

Polycyclic aromatic hydrocarbons (PAH)

Peroxides

Nitrogen containing organic compounds (e.g., amines, amides, nitro compounds, nitrates, heterocyclics) …

Thousands of compounds, extremely complex

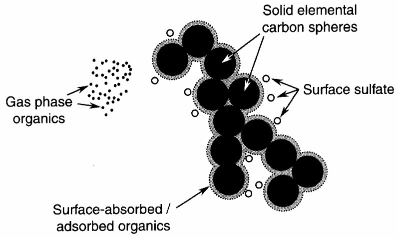


FIGURE 10.1 Schematic of a diesel soot particle consisting of an agglomeration of elemental carbon spheres (0.01- to 0.08-μm diameter). Its surface is covered with absorbed/adsorbed particle-phase organics, including 5-ring (e.g., BaP) and 6-ring PAHs. Gas-phase organics include all of the highly volatile 2-ring PAHs (e.g., naphthalene and methylnapthalenes). Semivolatile 3-ring (e.g., phenanthrene and anthracene) and 4-ring PAHs (e.g., pyrene (**II**) and fluoranthene (**V**)) are distributed between both phases. Sulfate is also associated with diesel particles. (Adapted with permission from Johnson *et al.*, 1994, SAE Paper 940233 © 940233 Society of Automotive Engineers, Inc.; see also Schauer *et al.*, 1999.) *Finlayson-Pitts & Pitts*

Primary and Secondary Organic Aerosols

Primary Organic Aerosol (POA)

Anthropogenic
- Gasoline
- Diesel
- Wood smoke
- Meat Cooking …

Biogenic
- *Plant debris*
- *Pollen*
- *Bacteria …*

Secondary Organic Aerosol (SOA)

Particulate products of anthropogenic & biogenic VOCs (volatile organic compounds)

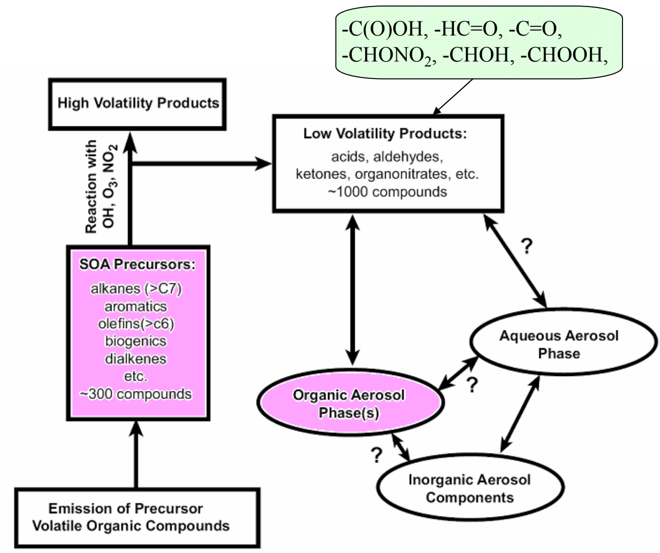


Figure 3.9. Schematic of the formation of secondary organic aerosol in the atmosphere. *2003 NARSTO Assessment*

Secondary Organic Aerosol Formation

Mechanisms: **Volatility is the key!**

VOC $\xrightarrow{\text{rxn}}$ higher polarity, lower volatility products $\xrightarrow[\text{conversion}]{\text{G-P}}$ SOA material

- Typically VOC ≥ $C_{6\text{-}7}$ are effective SOA precursors
  - aromatic hydrocarbons (*e.g.* toluene, ethylbenzene, xylenes)
  - terpenic biogenic hydrocarbons (*e.g.* α-pinene, β-pinene)
- Oxidation mechanisms for large VOCs are very complex

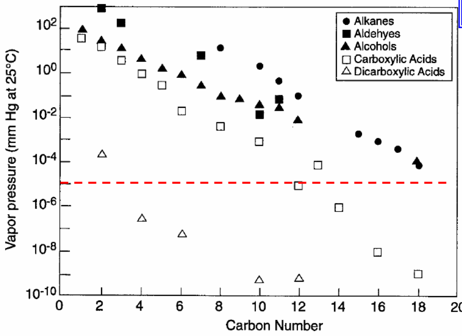
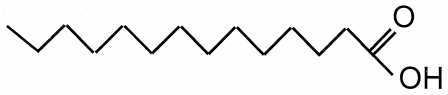


Figure 1. Vapor pressures of organic compounds as a function of carbon number and functionality. Data from *Grosjean* [1978]. *Jacobson, M.C., H.C. Hansson, K.J. Noone, and R.J. Charlson, Organic atmospheric aerosols: Review and state of the science, Reviews of Geophysics, 38 (2), 267-294, 2000.*

1 mmHg = 1 torr = 133 Pa = (1/760) atm

Vapor pressure depends on:
1) the number of carbon atoms in the molecule.
2) the number and type of polar functional groups.
3) Adding O and/or N atoms reduce volatility.

Effects of Oxidation on Compound Vapor Pressures

Compound	P^o_{25C} (torr)	Mass % in Particles*
 (C14)	2×10^{-2}	0.004
	3×10^{-3}	0.03
	8×10^{-4}	0.1
	2×10^{-4}	0.4
	7×10^{-6}	10
 (C15)	4×10^{-3}	0.02

TH
AL
PE

ACI
+ NI
MOST
IMPOR

*Assuming 10 μg m^{-3} organic matter in particles

From Ziemann, P. Tutorial on Secondary Organic Aerosol Formation.
American Association for Aerosol Research Annual Conference, Anaheim, CA 2003

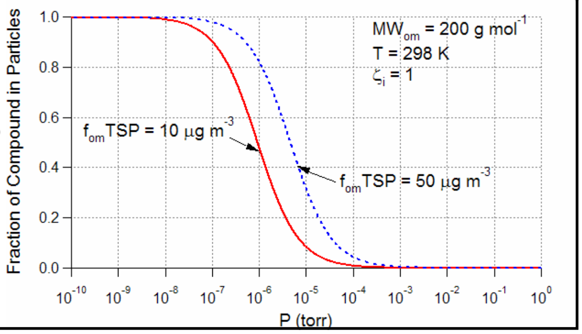
Secondary Organic Aerosol Formation

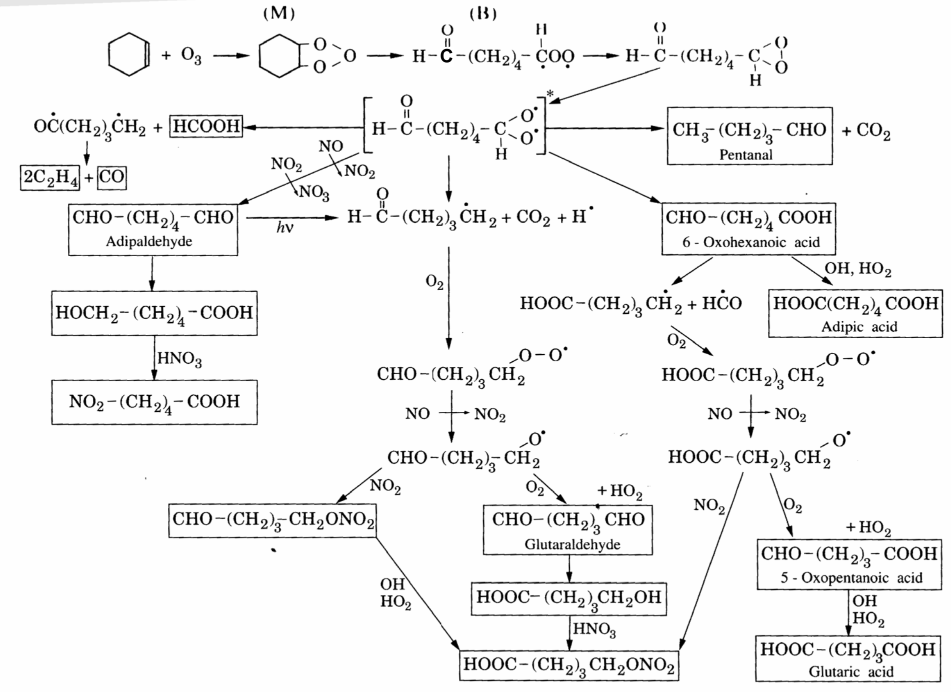
Once a multicomponent system contains enough condensable material to form aerosol, equilibrium G/P partitioning is governed by the equation for absorptive gas/liquid partitioning in a potentially nonideal system:

1) $p_i = X_i \zeta_i p^o_{L,i}$

2) $K_{p,i} = \dfrac{(ng/\mu g)_{ParticlePhase}}{(ng/m^3)_{GasPhase}} = \dfrac{F_i/TSP}{A_i} = \dfrac{760RTf_{om}}{10^6 \mathbf{MW_{om}} \zeta_i p^o_{L,i}}$

p_i (torr): the gas-phase partial pressure of species i
X_i: the mole fraction of i in the particle phase
ζ_i: the activity coefficient of species i in the particle phase typically lie in the range 0.3~ 3.
$p^o_{L,i}$ (torr): the compound's vapor pressure as a pure liquid (subcooled if necessary) at the temperature of interest.
A_i (ng m^{-3}): gas phase conc.
F_i (ng m^{-3}): OM phase conc.
TSP (μg m^{-3}): total suspended PM conc.
R : the ideal gas constant ($8.2E-5$ m^3 atm mol^{-1} K^{-1})
T (K): temperature
f_{om}: the weight fraction of the TSP that comprises the absorbing OM phase
MW_{om} (g mol^{-1}): the number-average molecular weight of the absorbing OM phase.

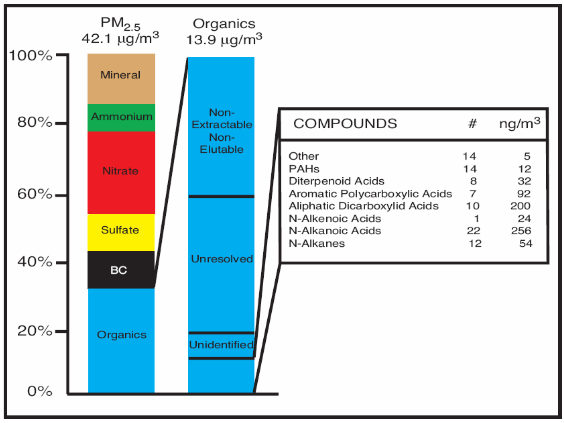




Seinfeld & Pandis **FIGURE 13.9** Proposed gas-phase reaction mechanism for the cyclohexene–ozone reaction.

Organic Aerosol Analysis

- Organic aerosols are composed of thousands of compounds.
- Chemical analysis is a significant challenge.
- Compound specific study can only explain a small fraction of total organic mass. Large fraction unidentified.
- A number of analytical methods are available, they are complementary.

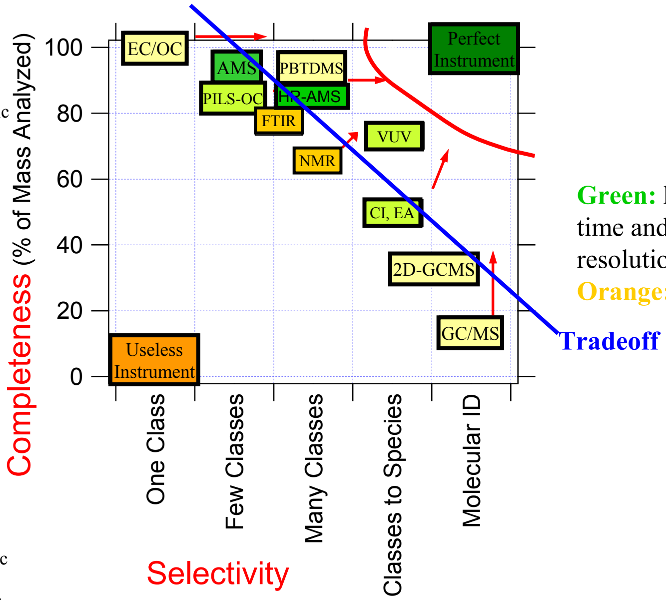


COMPOUNDS	#	ng/m^3
Other	14	5
PAHs	14	12
Diterpenoid Acids	8	32
Aromatic Polycarboxylic Acids	7	92
Aliphatic Dicarboxylid Acids	10	200
N-Alkenoic Acids	1	24
N-Alkanoic Acids	22	256
N-Alkanes	12	54

Figure 3.10. Speciation results for organic aerosol in Southern California (Rogge et al., 1993). Even if a hundred or so individual organic compounds were identified and quantified they represented only 15 percent or so of the total organic mass. *2003 NARSTO Assessment*

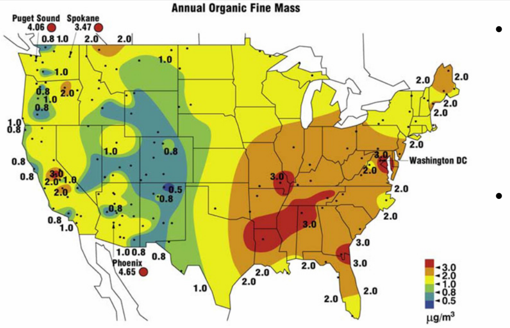
Organic Aerosol Analysis

AMS=Aerosol Mass Spectrometer
CI=Chemical Ionization
EA= Electron Attachment
EC/OC=Elemental/Organic Carbon
FTIR=Fourier Transform Infrared Spectroscopy
GC/MS=Gas Chromatography/Mass Spectrometry
2D-GCMS=Two-Dimensional Gas Chromatography/Mass Spectrometry
HR-ToFAMS=High-Resolution Time-of-Flight Mass Spectrometer
NMR=Nuclear Magnetic Resonance
PBTDMS=Particle Beam Thermal Desorption Mass Spectrometer
PILS-OC= Particle-Into-Liquid-Sampler for Organic Carbon
VUV= Vacuum Ultraviolet



Green: higher time and size resolution
Orange: lower

Produced by J. Jimenez



igure 4a. Isopleth map of organic mass concentrations. Phoenix, Seattle, and Spokane are shown as umerical insets and were not used for creating the contours.

- Estimated mass concentrations of OA:
  - Typical ~ 2.0 and 3.0 µg/m^3
  - Highest in the eastern US.
    (emissions of biogenic VOC are 2–10 times greater in the Southeast than much of the Northeast)
- Org% of total PM$_{2.5}$ mass:
  - Highest in the Northwest, typically > 40%.
  - ~ 30% in the Southeast.
  - Only a few sites < 20%

Data from 143 EPA IMPROVE (Interagency Monitoring of Protected Visual Environments) network sites in 2004.

Organic mass concentration = OC × 1.4

Malm, W.C., B.A. Schichtel, M.L. Pitchford, L.L. Ashbaugh, and R.A. Eldred, Spatial and monthly trends in speciated fine particle concentration in the United States, Journal of Geophysical Research-Atmospheres, 109, D03306, doi:10.1029/2003JD003739, 2004.

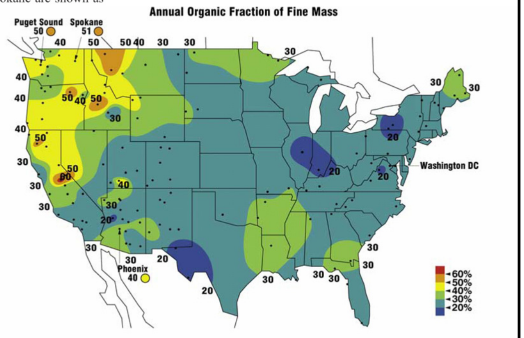


Figure 4b. Isopleth map of the percent that organic mass contributes to reconstructed fine mass. Phoenix, Seattle, and Spokane are shown as numerical insets and were not used for creating the contours.