Atmospheric Aerosols I

Required reading: Jacob Chapter 8

Atmospheric chemistry
ATOC-5151 / CHEM-5151
Spring 2013
Prof. J.L. Jimenez

Some slides adapted from lectures from Qi Zhang, Daniel Jacob, and Sergey Nidkorodov

Business Items

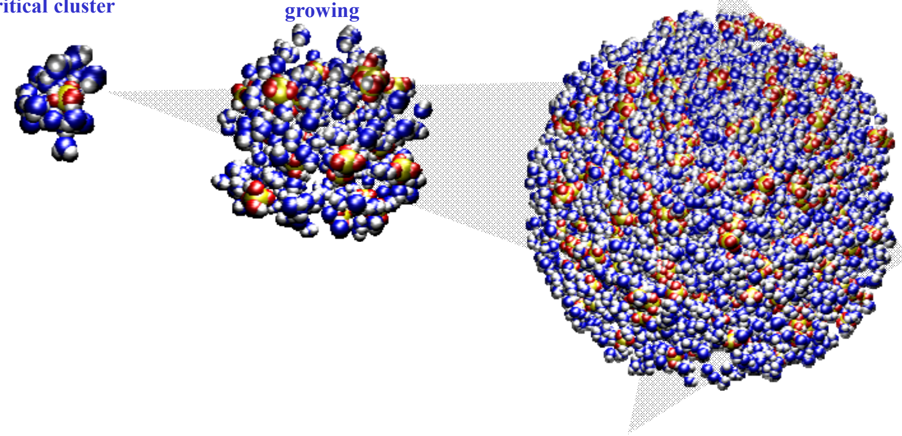
- HW#6 will be assigned later today
  - Due in 2 weeks
  - 2 problems + 1 bonus problem
- Final will be cumulative
- HW4 and 5 to be sent back soon
- Midterm not graded yet, hopefully this week
- Other questions?

From molecules to particles: nucleation

$H_2SO_4\ (H_2O)_{20}$
a typical critical cluster

$(H_2SO_4)_{25}\ (H_2O)_{250}$
a nucleated particle that is growing

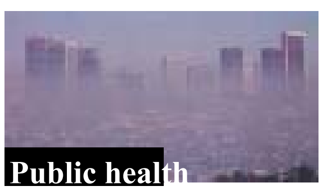
4nm + 6 nm
$(H_2SO_4)_{500}\ (H_2O)_{4000}$
a nanodroplet of aqueous sulfuric acid

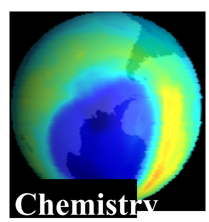


- Nucleation creates new atmospheric aerosol
- Fundamental understanding of nucleation is limited
- Binary nucleation of H_2SO_4 and H_2O is important in free troposphere

Slide courtesy of Shawn Katzman (PNNL)

Why care about atmospheric aerosols?

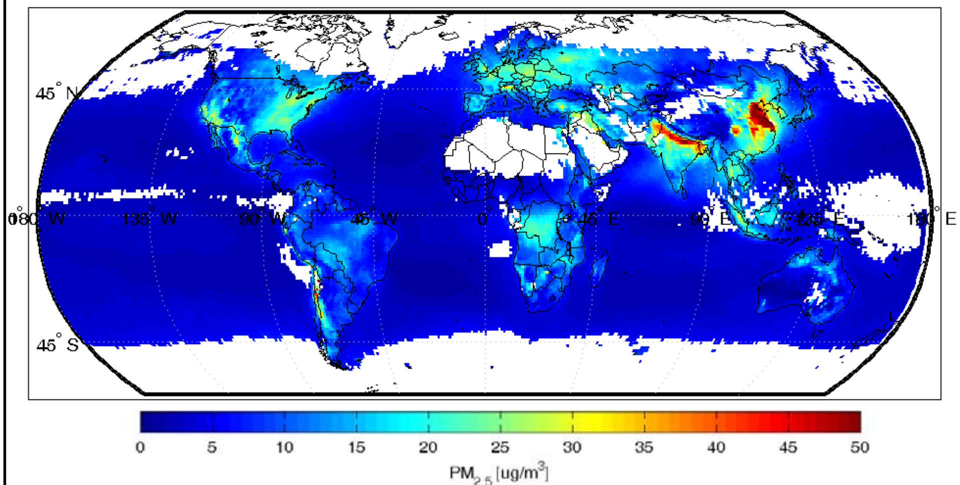




From Jacob

ANNUAL MEAN $PM_{2.5}$ CONCENTRATIONS (2002)

derived from MODIS satellite instrument data



Clicker Q: How does the mass conc. of PM compare to other species?

A. Similar to CO_2

B. Similar to CH_4

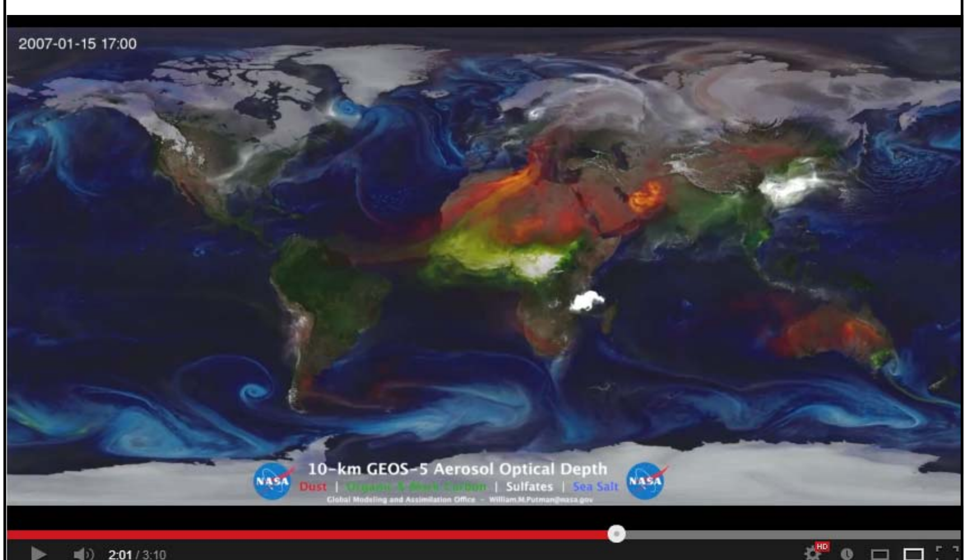
C. Similar to O_3

D. Similar to OH

E.I don't know

Adapted from Jacob

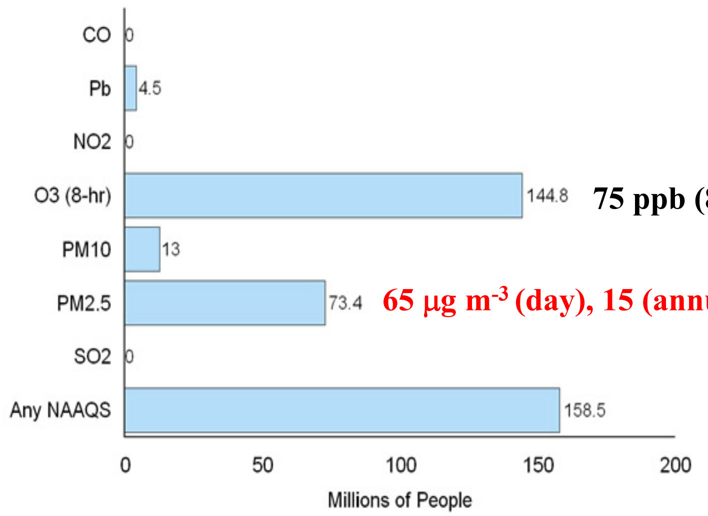
Global Hi-Res Aerosol Simulation



https://www.youtube.com/watch?v=zgFSpHL2k8I

Ozone and Particulate Matter (PM)

 # millions of people living in areas exceeding national ambient air quality standards (NAAQS) in 2007



75 ppb (8-h average)

65 µg m^{-3} (day), 15 (annual)

From Jacob

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

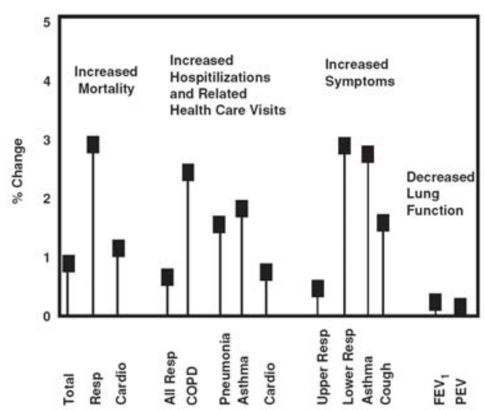


Figure 2.5. Stylized summary of acute exposure studies, percent change in health endpoint per 10 µg/m³ increase in PM_{10}. (Adapted from Pope and Dockery, 1999).

2003 NARSTO Assessment

From Zhang

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)

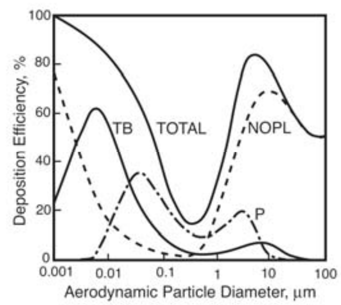


Figure 2.3. Particle deposition in the major regions of the human respiratory tract during normal respiration corrected for size dependent inhalability. (NOPL, naso-oro-pharyngo-laryngea) region; TB, tracheo-bronchial region; and P, pulmonary region). Developed from the National Council on Radiation Protection Model (NCRP, 1997) by Phalen (2002).
2003 NARSTO Assessment

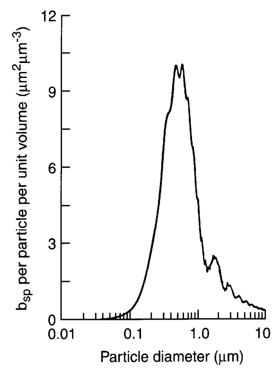
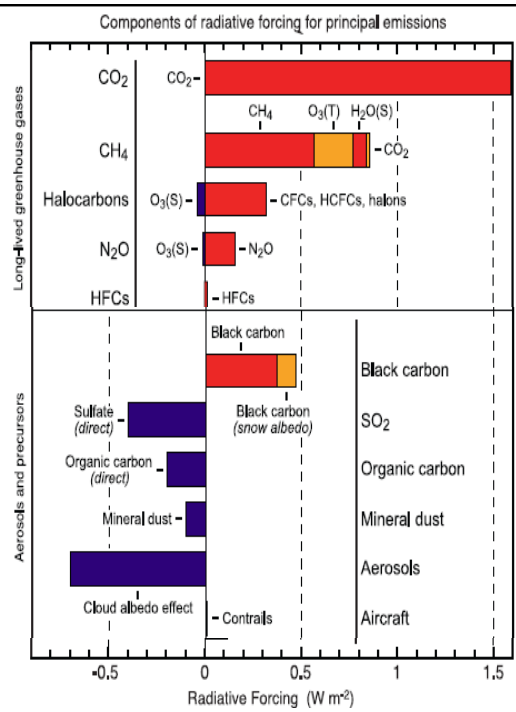


FIGURE 9.22 Scattering coefficient per particle divided by particle volume plotted as a function of diameter. The particles are assumed to be spheres of refractive index 1.50 and the light has λ = 550 nm (adapted from Waggoner and Charlson, 1976).
Finlayson-Pitts & Pitts

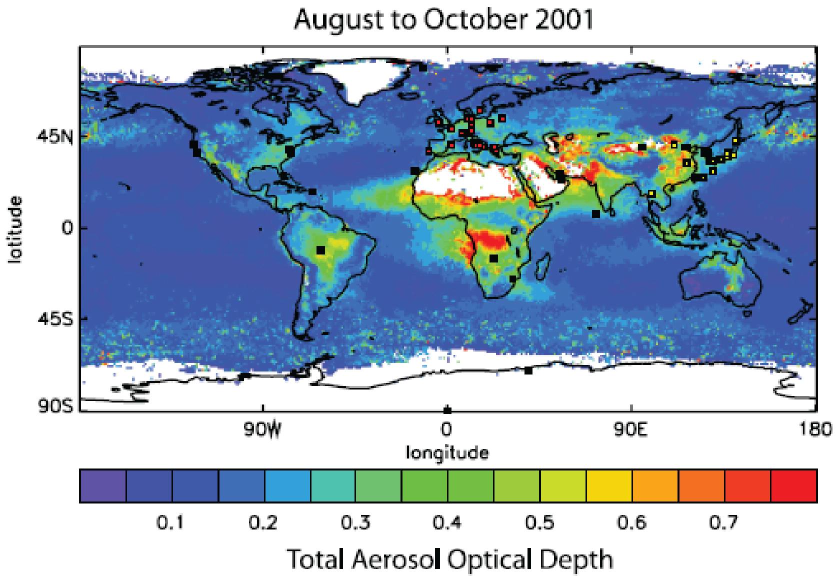
From Zhang



RADIATIVE FORCING From IPCC

IPCC [2007]

AEROSOL OPTICAL DEPTH

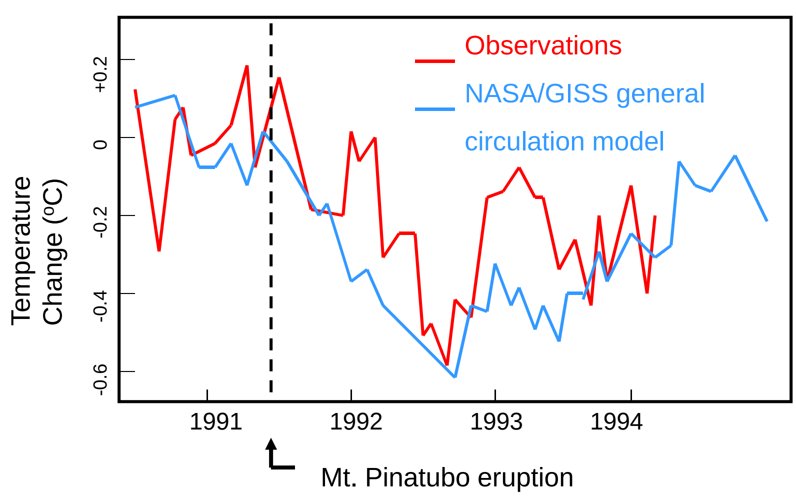


Global mean AOD is about 0.1, with 25% of that anthropogenic

From Jacob *IPCC [2007]*

Evidence of Aerosol Effects on Climate

Temperature decrease following large volcanic eruptions

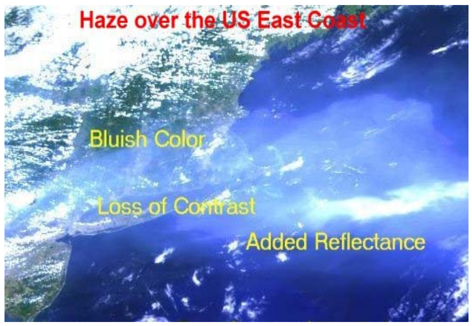


From Jacob

Scattering vs. Absorbing Aerosols

Scattering sulfate and organic aerosol over Massachusetts

Partly absorbing dust aerosol downwind of Sahara

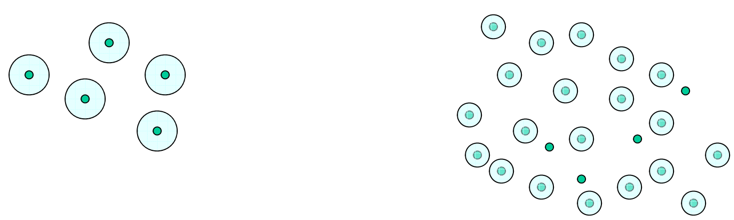


Absorbing aerosols (black carbon, dust) warm the climate by absorbing solar radiation

From Jacob

Aerosol "Indirect Effect" from Cloud Changes

Clouds form by condensation on preexisting aerosol particles ("cloud condensation nuclei")when RH>100%



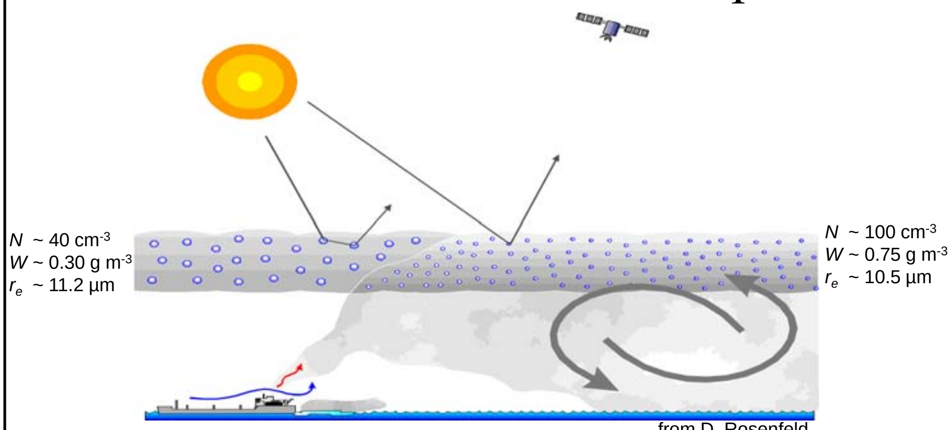
clean cloud (few particles):
- large cloud droplets
- efficient precipitation

polluted cloud (many particles):
- small cloud droplets
- suppressed precipitation

Adapted from Jacob

Clicker Q: Based on slide 7, the clean cloud will be:
A. More efficient in reflecting visible radiation back to space
B. Less efficient
C. Same efficiency
D. It depends on additiona information
E.I don't know

Evidence of Indirect Effect: Ship Tracks



from D. Rosenfeld

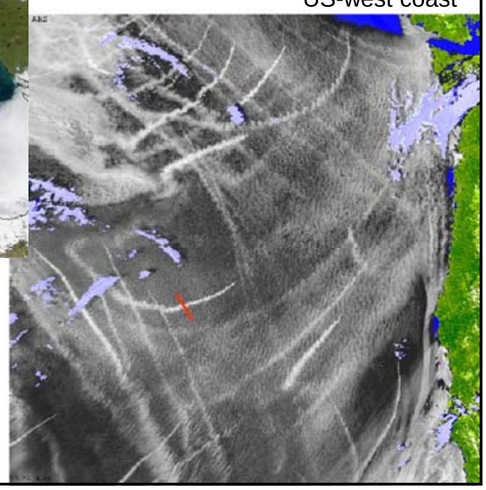
- Particles emitted by ships increase concentration of cloud condensation nuclei (CCN)
- Increased CCN increase concentration of cloud droplets and reduce their avg. size
- Increased concentration and smaller particles reduce production of drizzle
- Liquid water content increases because loss of drizzle particles is suppressed
- Clouds are *optically thicker* and brighter along ship track

From Jacob

Satellite Images of Ship Tracks

NASA, 2002
Atlantic, France, Spain

AVHRR, 27. Sept. 1987, 22:45 GMT
US-west coast

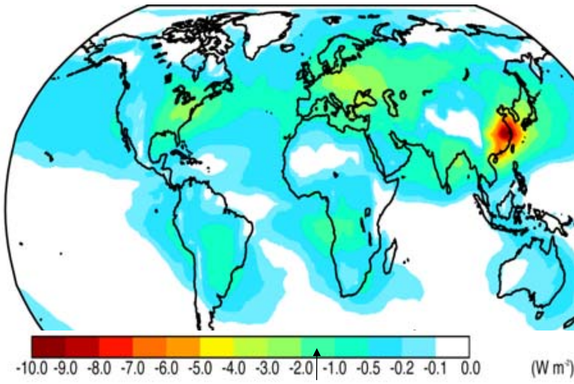


From Jacob

Radiative forcing by aerosols is very inhomogeneous

…in contrast to the long-lived greenhouse gases

Present-day annual direct radiative forcing from anthopogenic aerosols



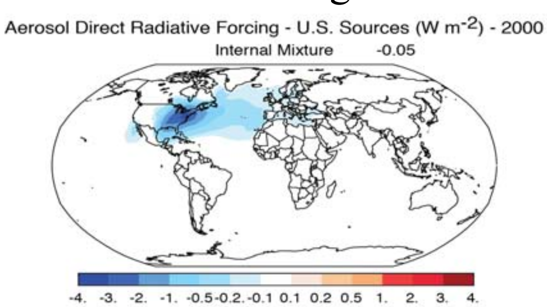
global radiative forcing from CO_2

Leibensperger et al., 2011

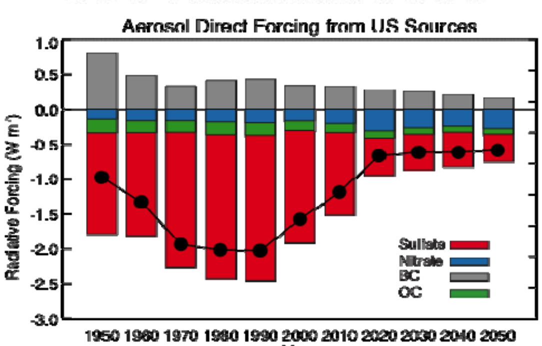
- Aerosol radiative forcing over polluted continents can more than offset forcing from greenhouse gases
- The extent to which this regional radiative forcing translates into regional climate response is not understood

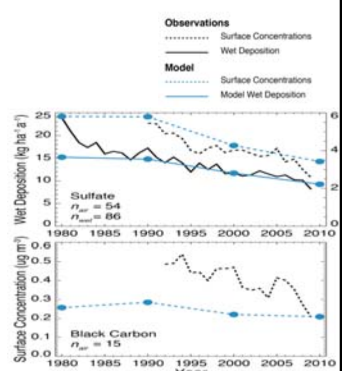
From Jacob

Radiative forcing from US anthropogenic aerosol



- Forcing is mostly from sulfate, peaked in 1970-1990
- Little leverage to be had from BC control





Leibensperger et al., 2011

From Jacob

Knudsen Number (Kn)

$$Kn = \frac{\lambda_{gas}}{R_p} = \frac{2\lambda_{gas}}{D_p}$$

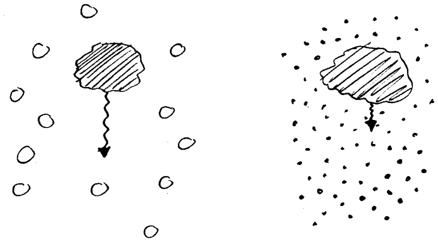
If a particle is sufficiently large, the gas surrounding it can be regarded as a continuous medium with a certain viscosity

A good figure of merit is Knudsen number (= mean free path, λ_{gas}, relative to the particle radius, R_p):

- ✓ Kn >>1 ⇒ kinetic regime (or free-molecular regime)
- ✓ Kn <<1 ⇒ continuum regime (or viscous regime)

In a continuum regime, moving particle experiences friction against gas all the time, whereas in kinetic regime the particle can slip past molecules as if it is in vacuum

Solve in class: calculate Knudsen number for a particle with 2 μm diameter in air at 1 atm



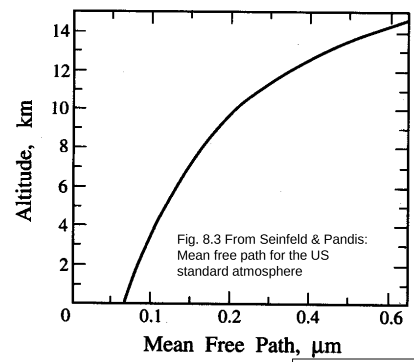


Fig. 8.3 From Seinfeld & Pandis: Mean free path for the US standard atmosphere

From Nidkorodov

Stokes' Law

Particle moving with speed υ in a continuous medium (Kn << 1) with viscosity η experiences a drag force given by Stokes law

In molecular regime, Stokes law can still be applied with a slip correction factor, C_c (also known as Cunningham factor)

Stokes law can be used to predict the terminal speed of motion of a particle under the influence of a constant force (e.g., gravity)

Continuum regime:

$$F_{drag} = 6\pi\eta R_p \upsilon$$

Molecular regime:

$$F_{drag} = \frac{6\pi\eta R_p \upsilon}{C_c}$$

η: gas viscosity
= 2 x 10^{-5} kg / m/s (air @ 300K)
v: speed

TABLE 8.3 Slip Correction Factor C_c for Spherical Particles in Air at 298 K and 1 atm

D_p (μm)	C_c
0.001	216
0.002	108
0.005	43.6
0.01	22.2
0.02	11.4
0.05	4.95
0.1	2.85
0.2	1.865
0.5	1.326
1.0	1.164
2.0	1.082
5.0	1.032
10.0	1.016
20.0	1.008
50.0	1.003
100.0	1.0016

Solve in class: Calculate sedimentation velocity of a 2 μm diameter particle with a unit density at STP

From Nidkorodov

Atmospheric Aerosols II

Required reading: Jacob Chapter 8

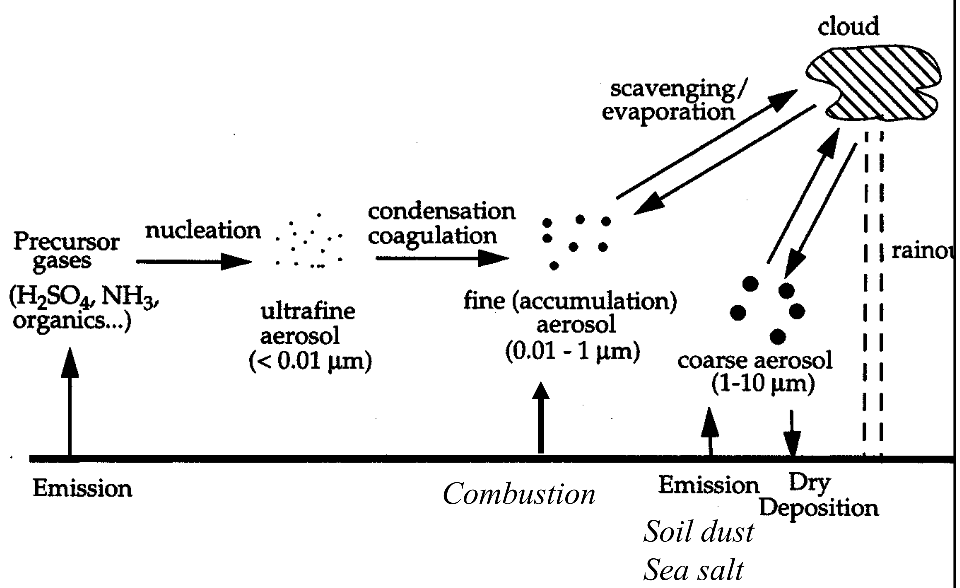
Atmospheric chemistry
ATOC-5151 / CHEM-5151
Spring 2013
Prof. J.L. Jimenez

Some slides adapted from lectures from Qi Zhang, Daniel Jacob, and Sergey Nidkorodov

Review Question

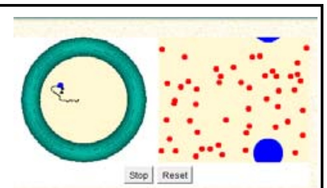
- If an organic molecule with an IR absorption spectrum similar to that of methane partitions to the aerosol, its impact on radiative forcing will be on average:
  A. The same as if it stayed in the gas phase
  B. x1000 smaller
  C. x3 larger
  D. x1000 larger
  E. I don't know

Origin of the atmospheric aerosol



Adapted from Jacob

Brownian Diffusion



http://www.aip.org/history/einstein/brownian.htm

- Small enough particles start to behave like gases and diffuse
- Fick's law: $J = -D\frac{dN}{dx}$
  - J: flux of particles
  - D: diffusion coefficient
  - N: number of particles
- Diffusion coefficient for particles: $D = \frac{kTC}{3\pi\eta d}$
  - k: Boltzmann constant T: temperature
  - C: Cunningham slip correction factor
  - η: gas viscosity d: particle diameter
- Time scale for diffusion (D has units of m2/s): $\tau_d \sim = \frac{L^2}{D}$
- Clicker Q: D = 6.9 x 10^{-10} m^2/s for a 100 nm particle. How quickly will it diffuse to the ground if it starts 1m above it?

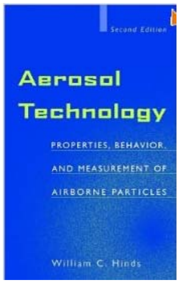
A. 1 s B. 1 hr C. 1 month

D. 1 century E. Dunno

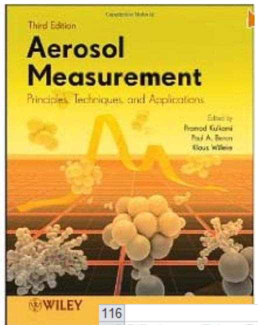
$D_{air} \sim 10^{-5}$ m^2/s

Practical Aerosol Resources

Great intro to medium book



Measurement "bible"



- For practical aerosol calculations
  - Aerosol calculator from Willeke and Baron
  - Linked on course page

116				
117	Diffusion coefficient (B&W 4-12; W&B 3-12; Hinds 2-35, 7-7), mechanical mobility (B&W 4-14; W&B 3-14;			
118	Temperature	293.15	Kelvin	
119	Pressure	101.3	kPa	
120	Molecular weight	0.02896	kg/mole	= 0.02896 for air
121	Particle/molecule diameter	4	μm	
122	Particle density	1000	kg/m^3	
123	------------------------------------	------------------	------------------	
124	Air viscosity =	1.80711E-05	Pa*s	
125	Slip correction factor =	1.04148201		
126	Diffusion coefficient =	1.51E-13	m^2/s	molecular range
127	Diffusion coefficient =	6.18E-12	m^2/s	particle range
128	Mechanical mobility =	1.53E+09	m/(N*s)	
129	Mean thermal velocity =	0.000554454	m/s	
130				
131	********************************	*****************	*****************	

Sedimentation vs. Brownian Diffusion

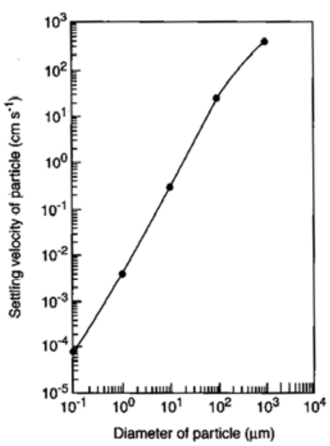


FIGURE 9.16 Settling velocities in still air at 0°C and 760 Torr pressure for particles having a density of 1 g cm^{-3} as a function of particle diameter. For spherical particles of unit density suspended in air near sea level, the Stokes law applies over a considerable range of particle sizes, where the line is straight, but a correction is required at the particle size extremes (adapted from LBL, 1979).

TABLE 9.5 Cumulative Deposition of Unit Density Particles onto a Horizontal Surface from Unit Aerosol Concentrations[a] during 100 s by Diffusion and Gravitational Settling[b]

	Cumulative deposition		
Diameter (μm)	Diffusion (number cm^{-2})	Settling (number cm^{-2})	Ratio diffusion / settling
0.001	2.5	6.5×10^{-5}	3.8×10^{4}
0.01	0.26	6.7×10^{-4}	390
0.1	2.9×10^{-2}	8.5×10^{-3}	3.4
1.0	5.9×10^{-3}	0.35	1.7×10^{-2}
10	1.7×10^{-3}	31	5.5×10^{-5}
100	5.5×10^{-4}	2500	2.2×10^{-7}

[a] This assumes an aerosol concentration of 1 particle cm^{-3} outside the gradient region.
[b] From Hinds (1982).

- ✓ Collisions with molecules exert randomly oriented forces on the particle resulting in its chaotic Brownian motion that competes with sedimentation under gravity
- ✓ Brownian motion wins for particles < 0.1 μm
- ✓ In the absence of convection, particles larger than 100 μm will quickly sediment from the troposphere (they drop like rocks!)

Question: size of maximum lifetime is the size as max effect on climate and human health. Is this a coincidence or is there a reason why they are the same? A. Coincidence B. Reason C. I don't know

From Nidkorodov

Dry Deposition Velocity


ATMOSPHERIC ENVIRONMENT

Parameterization of size-dependent particle dry deposition velocities for global modeling

E.-Y. Nho-Kim, M. Michou, V.-H. Peuch

$$\boxed{J_{dd} = v_{dep} C}$$

J_{dd}: dry deposition flux of particles (p/cm^2 s^{-1})
v_{dep}: "deposition velocity" (cm/s)
C: particle concentration (cm^{-3})

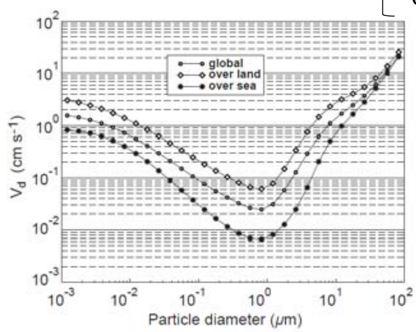


Fig. 1. Annual mean deposition velocities by particle size and surface type (particle density 1000 kg m^{-3}).

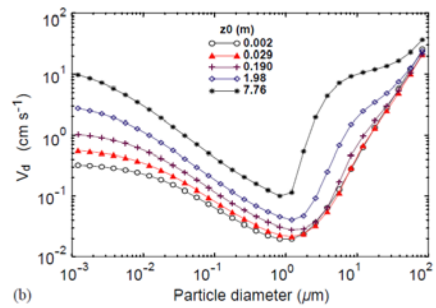


Fig. 6. Effect of surface roughness on deposition velocity: (a) unstable and (b) stable and neutral cases (particle density 1000 kg m^{-3}).

Clicker Q: timescale of loss of 100 nm from a 1 km boundary layer over a forest? A. 100 s B. 1 hr C. 1 day D. 1 century E. I don't know

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

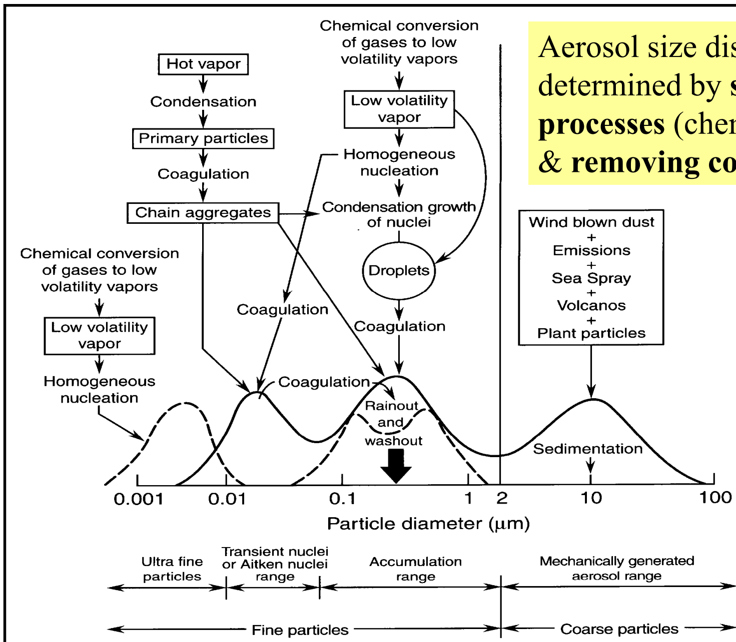


FIGURE 9.7 Schematic of an atmospheric aerosol size distribution showing four modes. The original hypothesis of Whitby and co-workers is shown by the solid, trimodal curves, and the fourth, ultrafine particle mode, as well as the two peaks sometimes observed in the accumulation mode are shown by the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

Finlayson-Pitts &Pitts (Slide from Zhang)

Mathematical Description of Size Distributions

Normal distribution (bell shaped)

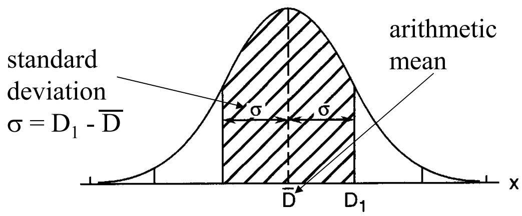


FIGURE 9.12 Meaning of standard deviation for a normal distribution. The hatched area represents 68% of total area under curve.

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).

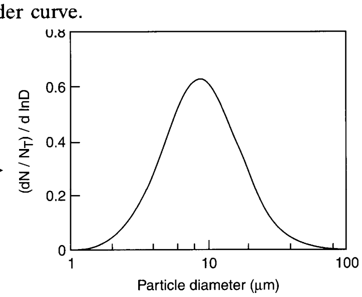
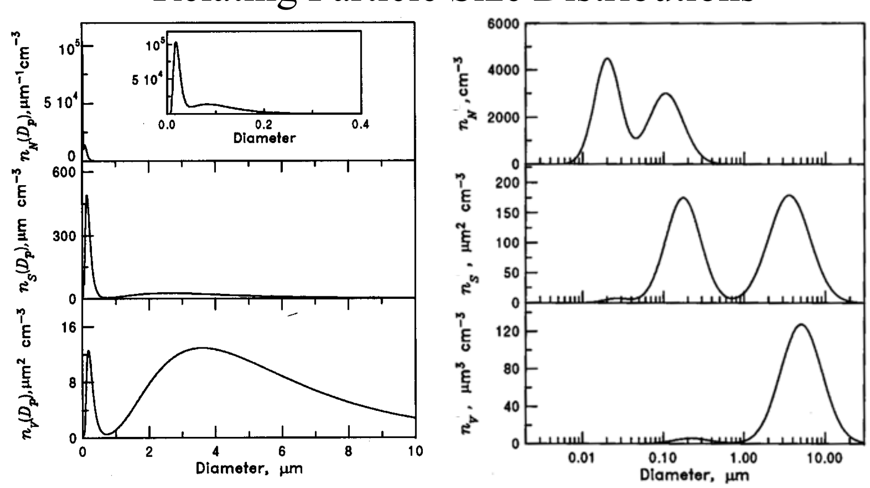


FIGURE 9.13 Frequency distribution curve (logarithmic size scale) (adapted from Hinds, 1982). *Finlayson-Pitts & Pitts*

Relating Particle Size Distributions



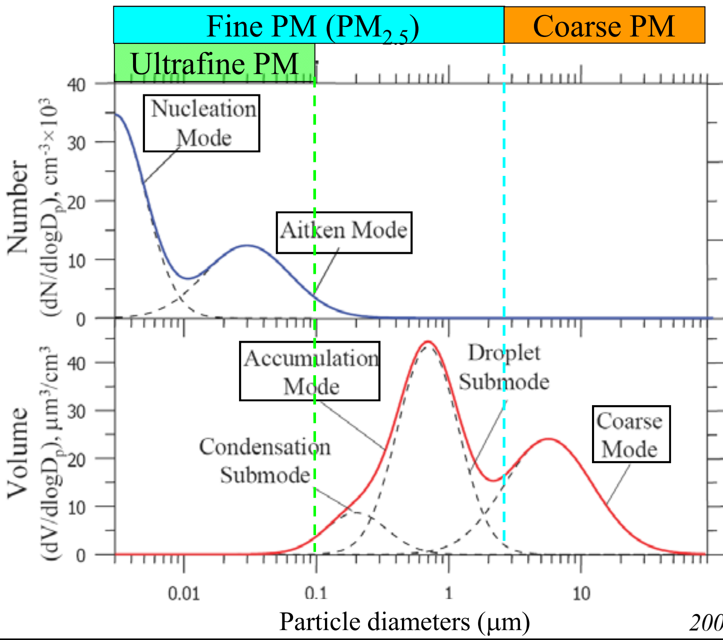
Note: these are several representations of one and the same distribution!

log x/y = log x – log y

Solve in class: Based on the distributions shown above, how many particles have diameter = 0.1 μm? How many particles have diameters in the range 0.1 to 0.11 μm? Use both $n_N(D_p)$ and $n_N^e(D_p)$ to find your answers.

From Nidkorodov

Size Distribution of Ambient Aerosols: Modes



Nucleation mode: < 0.01 µm

Ultrafine mode: < 0.1 µm

Accumulation mode: 0.1 – 2.5 µm

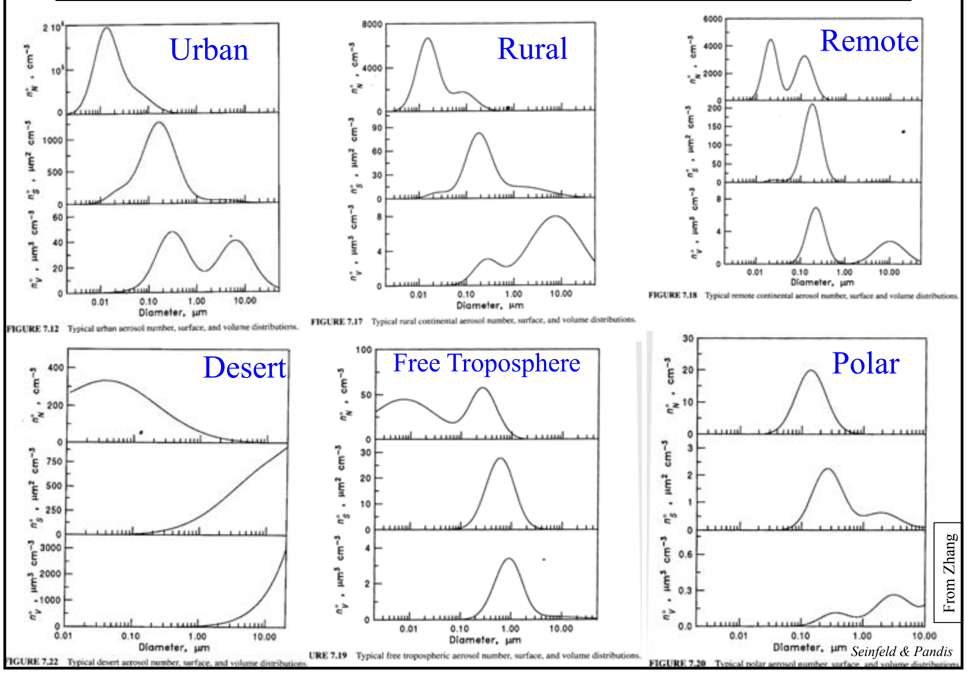
Fine mode: < 2.5 µm

Coarse mode: > 2.5 µm

From Zhang

2003 NARSTO Assessment

Typical PM Size Distributions in Various Atmospheres



From Zhang

Seinfeld & Pandis

Clicker Questions

- The number of particles in the polar atmosphere below 1 micron is
  A. 2 cm^{-2}
  B. 2 cm^{-3}
  C. 20 cm^{-3}
  D. 2000 cm^{-3}
  E. I don't know

- The typical mass of particles in the free troposphere below 200 nm is
  A. 0.02 $\mu m^3\ cm^{-3}$
  B. 0.2 $\mu m^3\ cm^{-3}$
  C. 20 $\mu m^3\ cm^{-3}$
  D. 200 $\mu m^3\ cm^{-3}$
  E. I don't know

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).

$$J_{12}=K_{12}N_1N_2$$

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

From Seinfeld and Pandis

	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}

Adapted from Zhang

Particle ~ Particle Interaction (Coagulation)

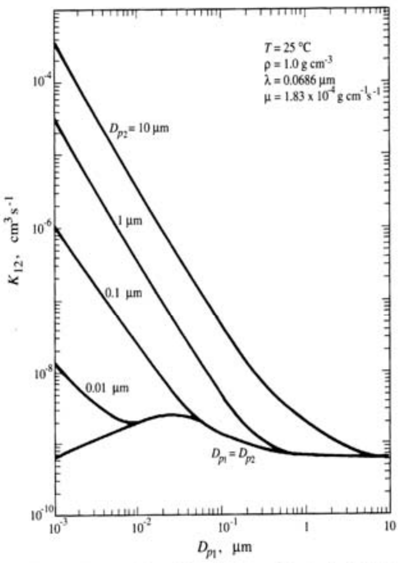


FIGURE 12.5 Brownian coagulation coefficient K_{12} for coagulation in air at 25°C of particles of diameters D_{p1} and D_{p2}. The curves were calculated using the correlation of Fuchs in Table 12.1. To use this figure find the *smaller* of the two particles as the abscissa and then locate the line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

From Seinfeld and Pandis

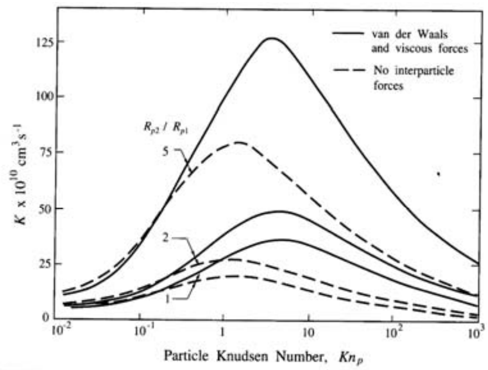


FIGURE 12.10 Coagulation coefficient at 300 K, $\rho_p = 1$ g cm^{-3}, $A/kT = 20$ as a function of Knudsen number (Kn_p) for particle radii ratios of 1, 2, and 5 both in the presence and in the absence of interparticle forces.

From Seinfeld & Pandis

Bigger size ratio (D_{p1}/D_{p2}), higher coagulation rates
(Pandis' "The elefant and the ant")

Adapted from Zhang

Clicker Q on Coagulation

- $N_{100nm} = 1000$ cm^{-3} and $N_{1nm} = 10^6$ cm^{-3}
- This is typical of new particle formation events in the atmosphere
- What is the timescale for loss of 1 nm particles to coagulation to 100 nm particles?

A. 1 s
B. 1000 s
C. 1 hr
D. 3.2 days
E. I don't know

Followup: what is the timescale for the 100 nm particles?

How Does Coagulation Affect Size Distribution?

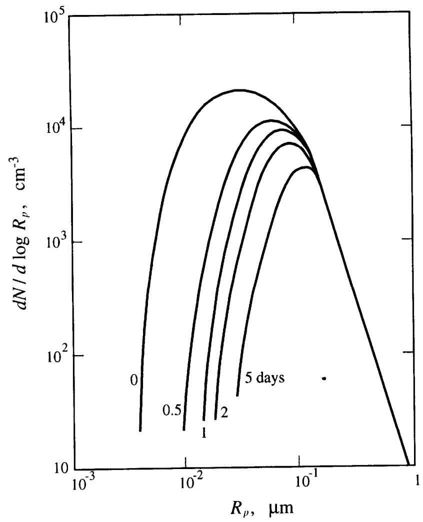


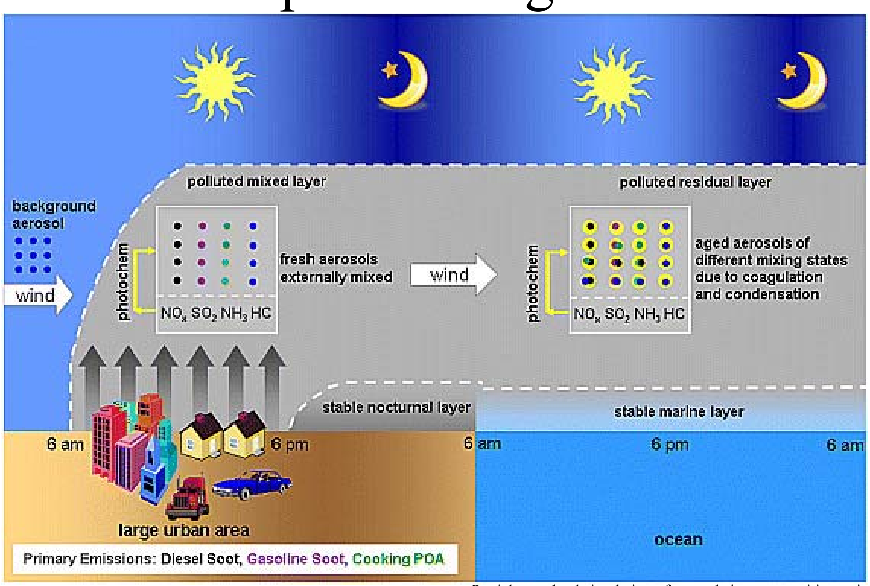
FIGURE 12.13 Evolution of a coagulating particle population size distribution during a period of 5 days (Butcher and Charlson, 1972).

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

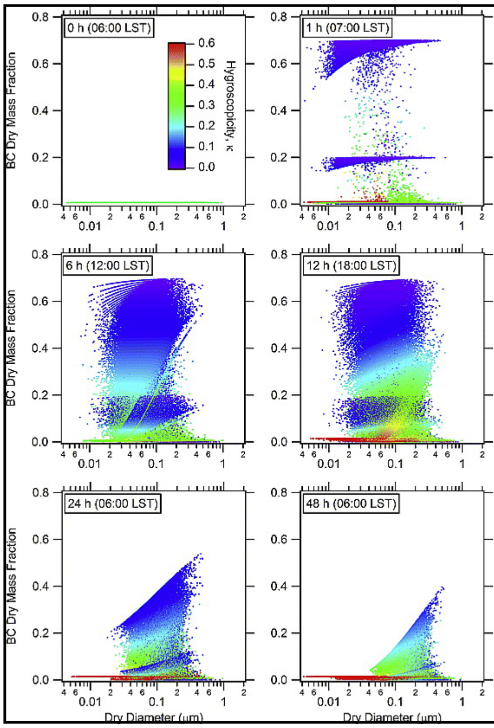
From Zhang

Example of Coagulation I



Journal of Geophysical Research: Atmospheres
Volume 115, Issue D17, D17210, 11 SEP 2010 DOI: 10.1029/2009JD013616
http://onlinelibrary.wiley.com/doi/10.1029/2009JD013616/full#jgrd16283-fig-0001

Particle-resolved simulation of aerosol size, composition, mixing state, and the associated optical and cloud condensation nuclei activation properties in an evolving urban plume



Example of Coagulation II

Journal of Geophysical Research: Atmospheres
Volume 115, Issue D17, D17210, 11 SEP 2010 DOI: 10.1029/2009JD013616
http://onlinelibrary.wiley.com/doi/10.1029/2009JD013616/full

Particle-resolved simulation of aerosol size, composition, mixing state, and the associated optical and cloud condensation nuclei activation properties in an evolving urban plume

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)
2. The free molecular (kinetic regime): $\lambda >> D_p$ (ambient, $D_p < 0.01$ μm)
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

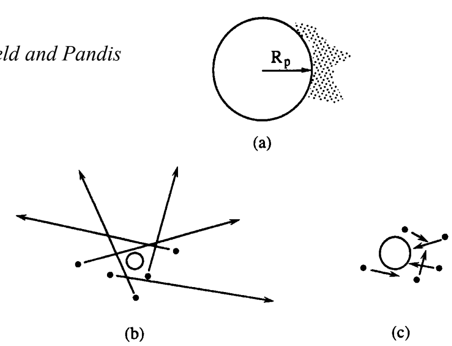


FIGURE 8.1 Schematic of the three regimes of suspending fluid–particle interactions: (a) continuum regime ($Kn \to 0$), (b) free molecule (kinetic) regime ($Kn \to \infty$), and (c) transition regime ($Kn \approx 1$)

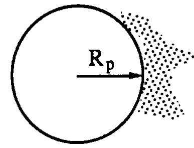
From Zhang

Gas to Particle Conversions

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**

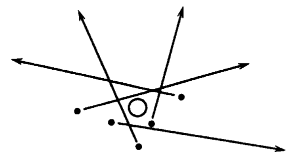
$$J_c = 4\pi R_p D_g (c_\infty - c_s)$$



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)**

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



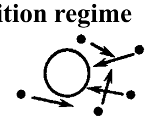
$\bar{c}_A$: Mean speed of the molecules
α: Molecular accommodation coefficient, i.e., probability of A to stick on particle. $0 \le \alpha \le 1$

From Zhang

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



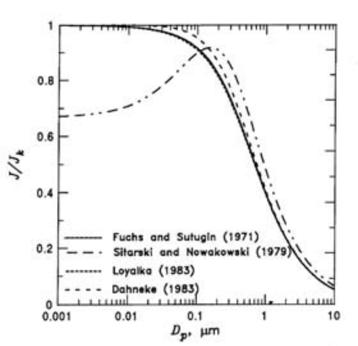


FIGURE 11.2 Mass transfer rate predictions for the transition regime by the approaches of (a) Fuchs and Sutugin, (b) Dahneke, (c) Loyalka and (d) Sitarski and Nowakowski ($z = 15$) as a function of particle diameter. Accommodation coefficient $\alpha = 1$.

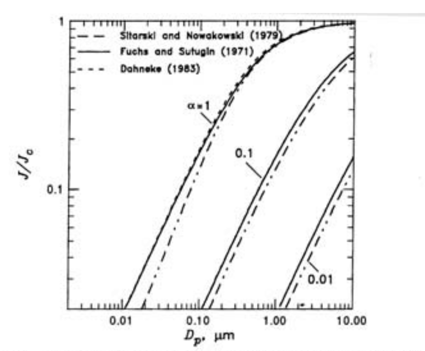


FIGURE 11.4 Mass transfer rates as a function of particle diameter for accommodation coefficient values 1.0, 0.1, and 0.01 for the approaches of Sitarski and Nowakowski (1979), Fuchs and Sutugin (1970), and Dahneke (1983).

From Seinfeld and Pandis

From Zhang

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

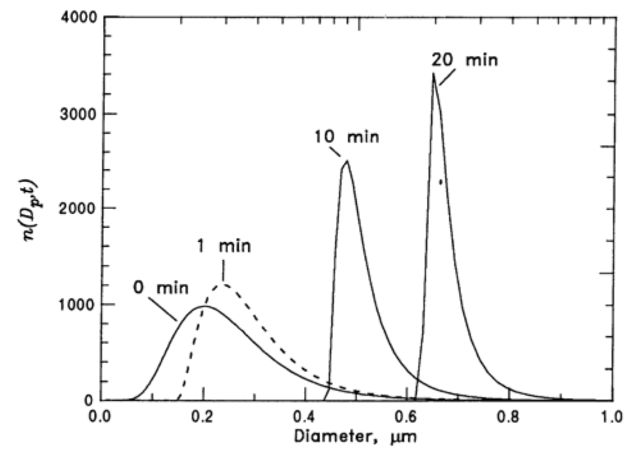


FIGURE 12.3 Evolution of a log-normal distribution (initially $\bar{D}_p = 0.2\ \mu m$, $\sigma_g = 1.5$) assuming $D_i = 0.1\ cm^2\ s^{-1}$, $M_i = 100\ g\ mol^{-1}$, $(p_i - p_{eq,i}) = 10^{-9}$ atm(1 ppb), $T = 298$ K and $\rho_p = 1\ g\ cm^{-3}$.

From Seinfeld and Pandis

From Zhang

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

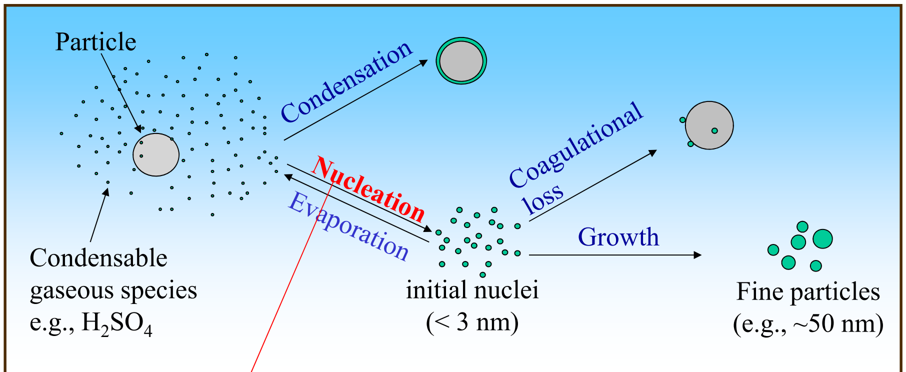
[a] From Pandis *et al.* (1995).

From Finlayson-Pitts and Pitts

- At ambient conditions, condensation faster than coagulation, except during new particle formation events

Adapted from Zhang

Gas to Particle Conversions (Particle Nucleation)

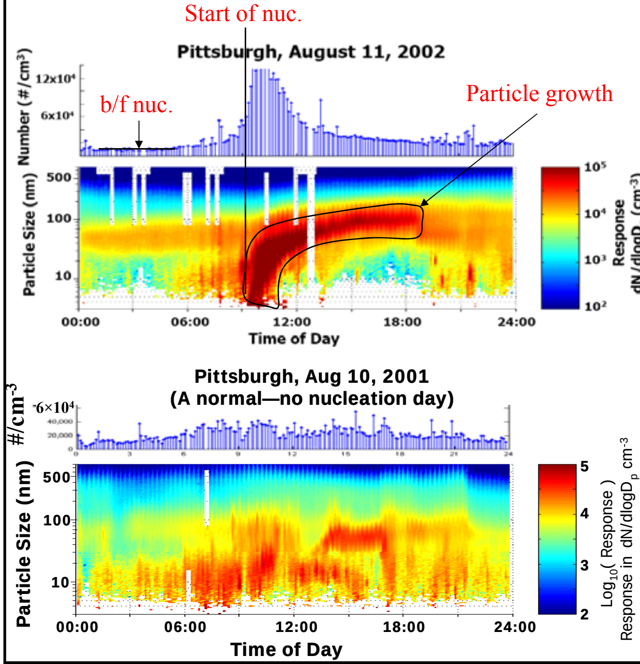


- Nucleation
- Condensation and nucleation are competing processes.
- Nucleation dominate when PM condensational sink is low.

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

From Zhang

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)

From Zhang

Chemical Reactions of Particles

- Chemistry
  - Solid aerosol provide surfaces upon which trace gases can be absorbed and then react
  - Liquid aerosols absorb gases which may then react together in solution

  e.g. $SO_2 \rightarrow H_2SO_4$

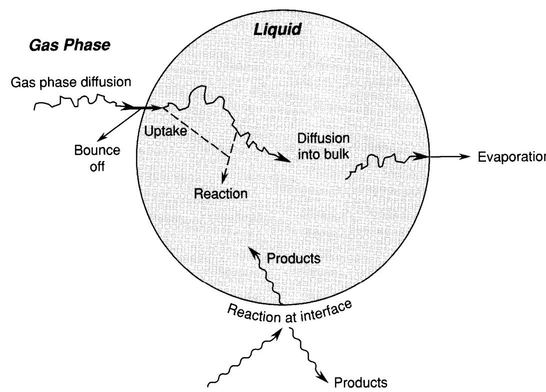
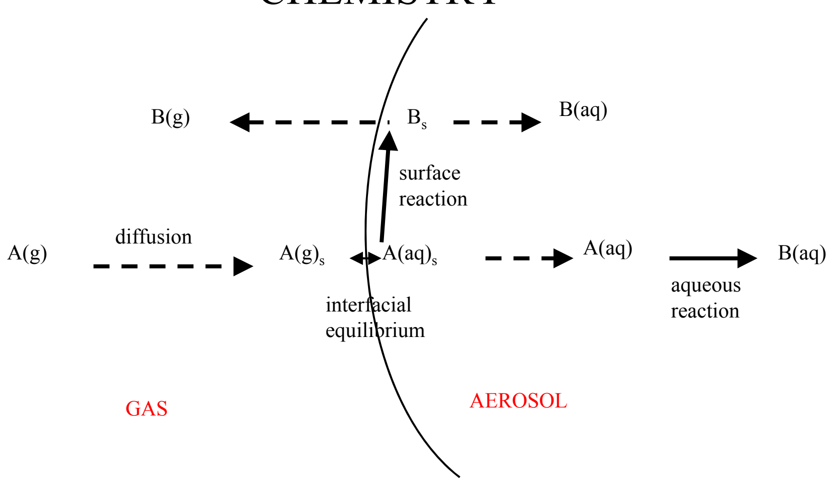


FIGURE 5.12 Schematic diagram of uptake and reaction of gases in liquids.

From Finlayson-Pitts and Pitts

GENERAL SCHEMATIC FOR HETEROGENEOUS CHEMISTRY



Aerosols enable surface and ionic reactions that would not happen in the gas phase; also concentrate low-volatility species in condensed phase

From Jacob

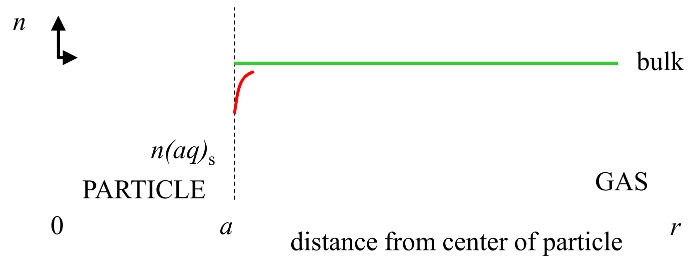
FLUX AT THE GAS-PARTICLE INTERFACE

A(g) $\xrightarrow{\text{diffusion}}$ $A(g)_s \leftrightarrow A(aq)_s$

interfacial equilibrium

l = mean free path of air (0.18 μm at STP)
a = particle radius
Knudsen number Kn = a/l

Kn >>1: continuum (diffusion-limited) regime
Kn<<1: free molecular (collision-limited) regime



From Jacob

SOLUTION FOR THE CONTINUUM REGIME

Continuity equation:

$$D\nabla^2 n_g(r) = 0 \quad \text{with BCs } n_g(\infty) = n_{bulk}\ ,\ n_g(a) = n_{aq}(a)/K_H$$

D = molecular diffusion coefficient in gas phase
K_H = Henry's law equilibrium constant

In spherical coordinates,

$$D\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dn_g}{dr}\right) = 0$$

Solve for the transfer flux at gas-particle interface:

$$F = -D\left.\frac{dn}{dr}\right|_{r=a} = \frac{D}{a}\left(n_g(\infty) - \frac{n_{aq}(a)}{K_H}\right)$$

From Jacob

SOLUTION FOR THE FREE MOLECULAR REGIME

Collision flux with surface from random motion of molecules:

$$F = \frac{v}{4}(n_g - \frac{n_{aq}(a)}{K_H})$$

where v is the mean molecular speed. Only a fraction α (mass accommodation coefficient) of collisions results in bulk uptake by the particle, so the uptake flux is

$$F = \frac{\alpha v}{4}(n_g - \frac{n_{aq}(a)}{K_H})$$

From Jacob

APPROXIMATE SOLUTION FOR TRANSITION REGIME:

$$-\frac{dn_g(\infty)}{dt} = kA(n_g(\infty) - \frac{n_{aq}(a)}{K_H})$$

where A is the aerosol surface area per unit volume of air (cm^2 cm^{-3}), and k is a first-order gas-particle transfer rate constant:

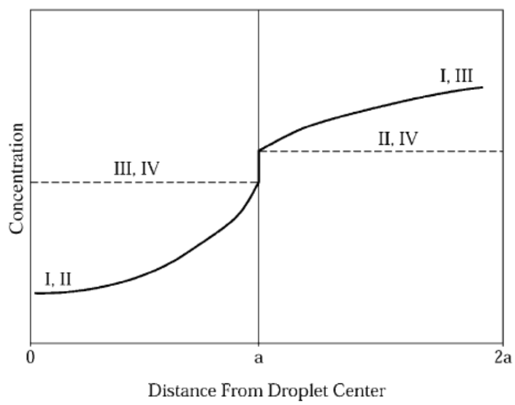
$$k = (\frac{a}{D} + \frac{4}{\alpha v})^{-1}$$

From Jacob

TIME SCALES FOR GAS-PARTICLE TRANSFER

$$A(g) \xrightarrow[\text{diffusion}]{} A(g)_s \xleftrightarrow[\text{interfacial equilibrium}]{} A(aq)_s \xrightarrow[\text{mixing}]{} A(aq) \xrightarrow[\text{chemical reaction } (k_c)]{} B(aq)$$

$$\tau_{diff} = f(\frac{K_H}{A}) \qquad \tau_{mix} = \frac{a^2}{\pi^2 D_{aq}} \qquad \tau_{chem} = \frac{1}{k_c}$$



In cloud:

CASE I:
$\tau_{chem} < \tau_{mix}$, $\tau_{chem} < \tau_{diff}$ — **OH**

CASE II:
$\tau_{chem} < \tau_{mix}$, $\tau_{chem} > \tau_{diff}$ — **O_3 , NO_3**

CASE III:
$\tau_{chem} > \tau_{mix}$, $\tau_{chem} < \tau_{diff}$ — **HO_2**

CASE IV:
$\tau_{chem} > \tau_{mix}$, $\tau_{chem} > \tau_{diff}$ — **most others; bulk equilibrium**

Jacob, Atmos. Environ. 2000

From Jacob

REACTION **PROBABILITY** γ: simplified representation of aerosol chemistry

γ = probability that a gas molecule impacting the surface undergoes reaction

GAS PHASE | *AEROSOL AQUEOUS PHASE*

$$A(g)_{bulk} \xrightarrow[\text{diffusion}]{} A(g)_{surf} \underset{\text{equilibrium}}{\overset{K_H}{\rightleftarrows}} A(aq)_{surf} \xrightarrow[\text{diffusion}]{D_a} A(aq)_{bulk} \xrightarrow[\text{reaction}]{k_c} B(aq)_{bulk}$$

γ

γ convolves all transfer/reaction processes:

$$\gamma = \left[\frac{1}{\alpha} + \frac{v}{4K_H RT\sqrt{D_a k_c}} \cdot \frac{1}{\coth(q) - \frac{1}{q}}\right]^{-1} \qquad q = a\sqrt{\frac{k_c}{D_a}}$$

so that one can write

$$\frac{-d[A(g)]}{dt} = k[A]$$

with

$$k = \frac{A}{\frac{a}{D_g} + \frac{4}{v\gamma}}$$

Jacob, Atmos. Environ. 2000

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)

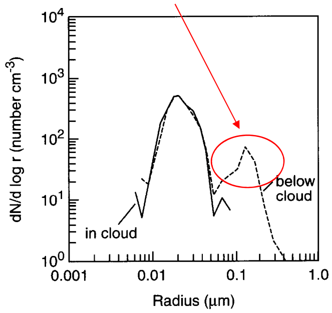
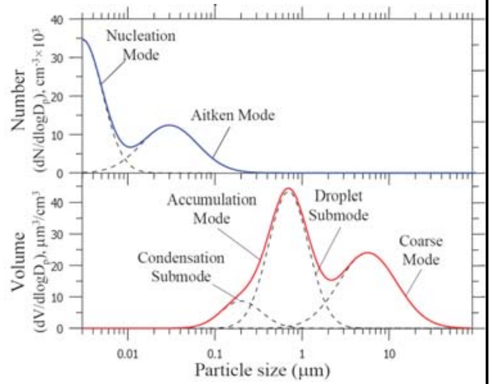


FIGURE 9.33 Size distribution of particles in clouds (solid line) and below the clouds (dashed line), showing two modes (adapted from Hoppel *et al.*, 1994). *From Finlayson-Pitts & Pitts*



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

Vertical Variation

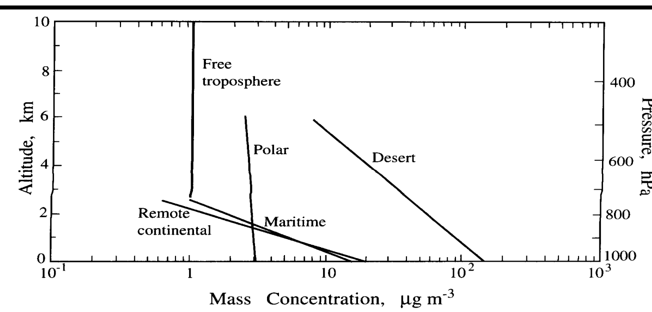
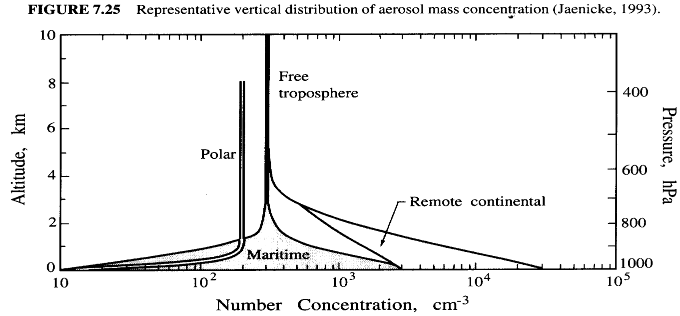


FIGURE 7.25 Representative vertical distribution of aerosol mass concentration (Jaenicke, 1993).



From Zhang

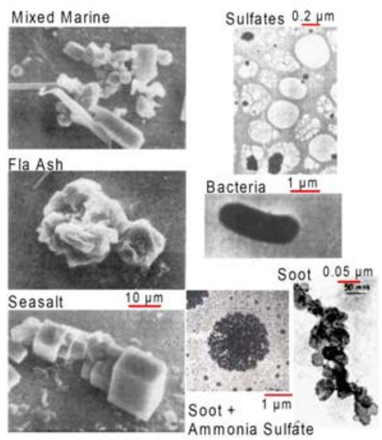
FIGURE 7.26 Representative vertical distribution of aerosol number concentration (Jaenicke, 1993). A range of concentrations is shown for marine and remote continental aerosols.

Seinfeld & Pandis

Aerosol Sizes (Diameters)

From Zhang

- 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.

Effective Particle Diameters

Depending on the circumstance, different metrics are used for the particle size:

- ✓ Classical aerodynamic diameter: diameter of a sphere with density = 1 g/cm^3 that has the same terminal velocity in a gravitational field as the particle under consideration
- ✓ Stokes diameter: same as above except that density of the reference spherical particle is the same as for the particle in question
- ✓ Volume equivalent diameter: diameter of a sphere with the same density that has the same volume as the non-spherical particle in question
- ✓ Electrical mobility equivalent diameter: diameter of a sphere with density = 1 g/cm^3 that has the same mobility in electrostatic field as the particle under consideration.

Particle in an E-field:

F_{drag} ← q^+ → $F = qE$

E →

$$qE = \frac{6\pi\eta\vartheta R_p}{C_c}$$

Stokes radius

$$\vartheta = \boxed{\frac{C_c}{6\pi\eta R_p}} \cdot qE$$

electric mobility

Solve in class: Find volume equivalent diameter of a rod-like virus, which is 1 µm long and 0.1 µm wide. The effective density of the virus is 1.1 g/cm^3

Solve in class: Find a relationship between aerodynamic and Stokes diameters

From Nidkorodov

Aerosol Diameters

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

Mobility diameter (D_m)

Aerodynamic diameter (D_a)

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

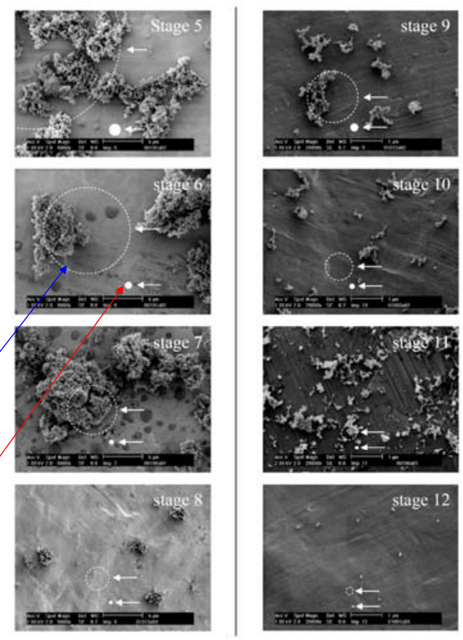
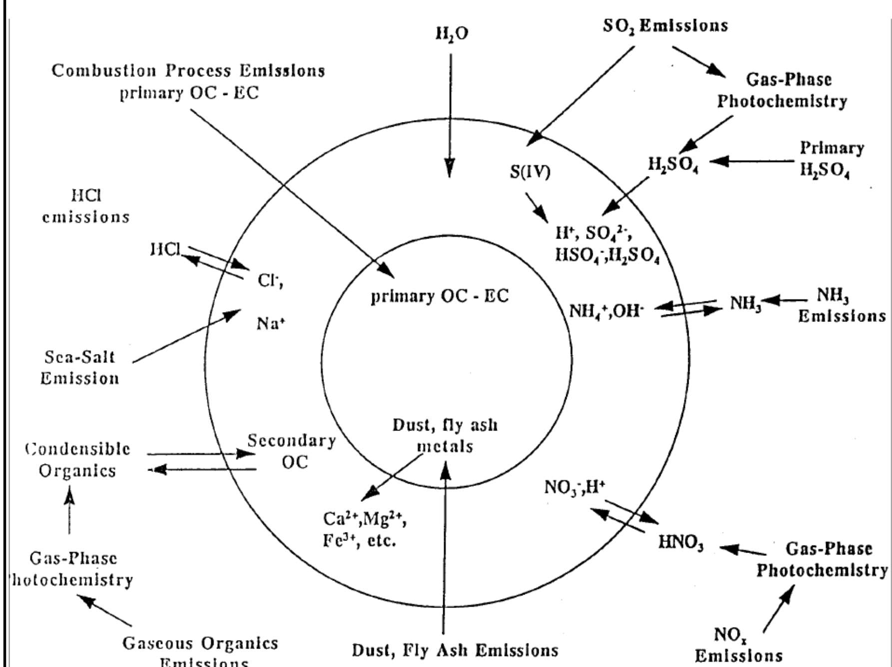


Fig. 5. Diesel soot on the ELPI-impactor stages 5–8 (5000×) and stages 9–12 (20,000×). White spots indicate aerodynamic upper size limit (previous impactor cutoff-size), white circles indicate corresponding mobility diameter (Table 3).

From Zhang

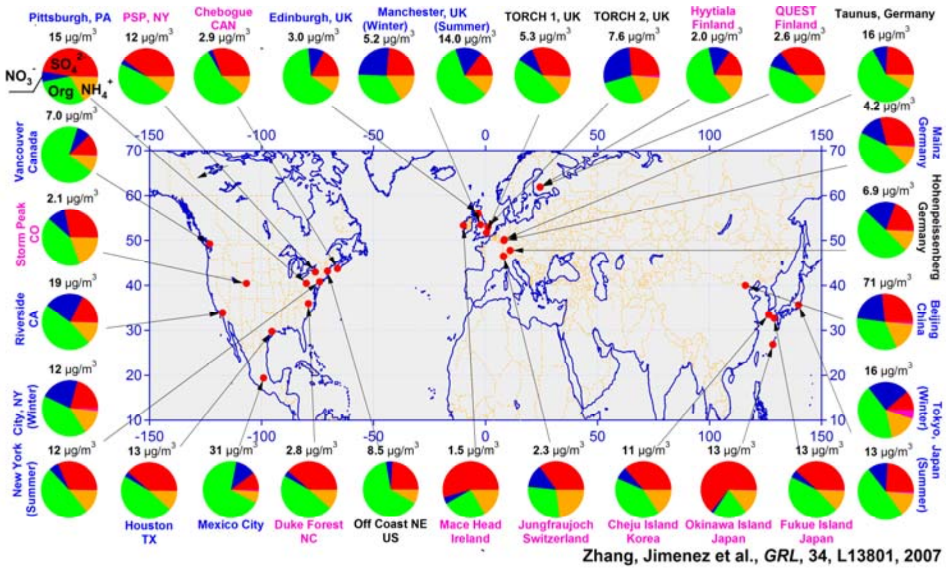
Typical Chemical Composition of Atmospheric Aerosols



Adapted from Zhang

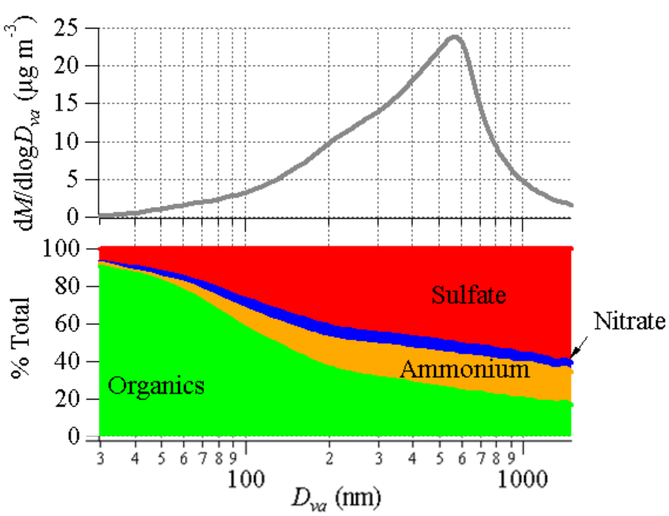
2003 NARSTO Assessment

Submicron aerosol Composition in Northern Hemisphere



Does not include black carbon and other minor components (metals etc.)

Size Resolved Composition of Pittsburgh Fine PM

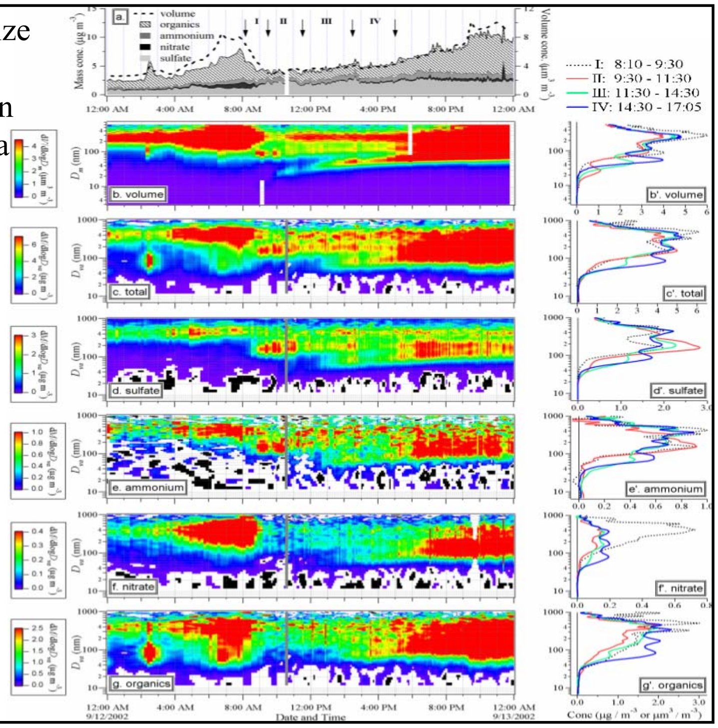


Zhang et al., Time and size-resolved chemical composition of submicron particles in Pittsburgh - Implications for aerosol sources and processes, J. Geophys. Res., 110 (D07S09), 2005.

Size dependent composition of ambient aerosols

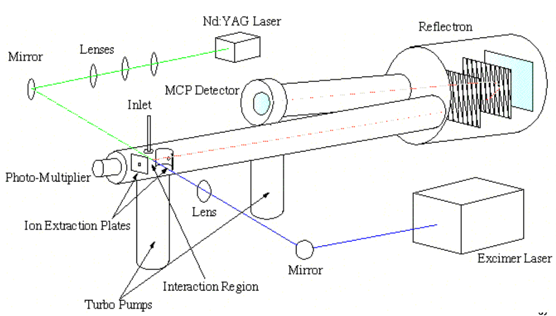
From Zhang

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.

Single Particle Composition by Mass Spectrometry



PALMS designed by Dan Murphy at Aeronomy Lab
http://www.al.noaa.gov/PALMS/.

Particle mass-spectrometers use lasers or heat to vaporize individual particles and analyze their compositions with either quadrupole or TOF MS. They provide valuable information about size distribution and composition of atmospheric aerosols. Jose-Luis Jimenez (CU Boulder) created an excellent compilation of existing aerosol mass spectrometers at http://cires.colorado.edu/jimenez/ams.html

From Nidkorodov

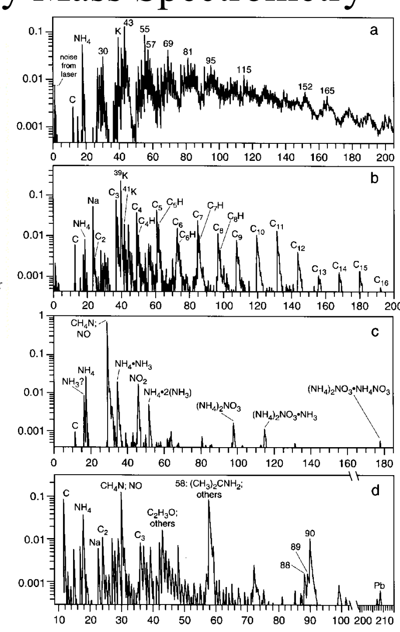


FIGURE 11.71 Typical laser ionization positive ion mass spectra of single particles in rural Colorado (adapted from Murphy and Thomson, 1997a,b).

Atmospheric Aerosols III

Required reading: Jacob Chapter 8

Atmospheric chemistry
ATOC-5151 / CHEM-5151
Spring 2013
Prof. J.L. Jimenez

Some slides adapted from lectures from Qi Zhang, Daniel Jacob, and Sergey Nidkorodov

Formation of Ammonium / Nitrate / Sulfate Aerosols

Thermodynamic rules:

$$H_2SO_4(g) \xrightarrow{H_2O} SO_4^{2-} + 2H^+$$

Sulfate always forms an aqueous aerosol

$$NH_3(g) \xrightarrow{H_2O} NH_4^+ + OH^-$$

Ammonia dissolves in the sulfate aerosol totally or until titration of acidity, whichever happens first

$$HNO_3(g) \xrightarrow{H_2O} NO_3^- + H^+$$

Nitrate is taken up by aerosol if (and only if) excess NH_3 is available after sulfate titration

$$NH_3(g) + HNO_3(g) \longrightarrow NH_4NO_3(aerosol)$$

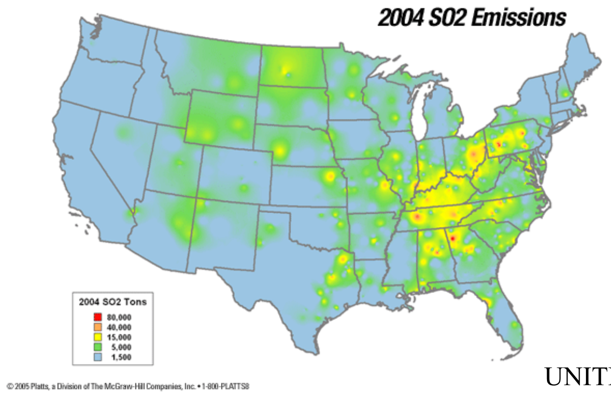
HNO_3 and excess NH_3 can also form a solid aerosol if RH is low

Condition	aerosol pH	Low RH	High RH
[S(VI)] > 2[N(-III)]	acid	$H_2SO_4 \bullet nH_2O$, NH_4HSO_4, $(NH_4)_2SO_4$	(NH_4^+, H^+, SO_4^{2-}) solution
[S(VI)] ≤ 2[N(-III)]	neutral	$(NH_4)_2SO_4$, NH_4NO_3	(NH_4^+, NO_3^-) solution

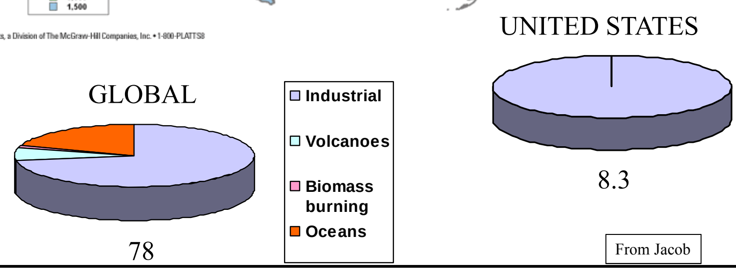
E.g. AIM model: http://www.aim.env.uea.ac.uk/aim/aim.php

From Jacob

U.S. SO_2

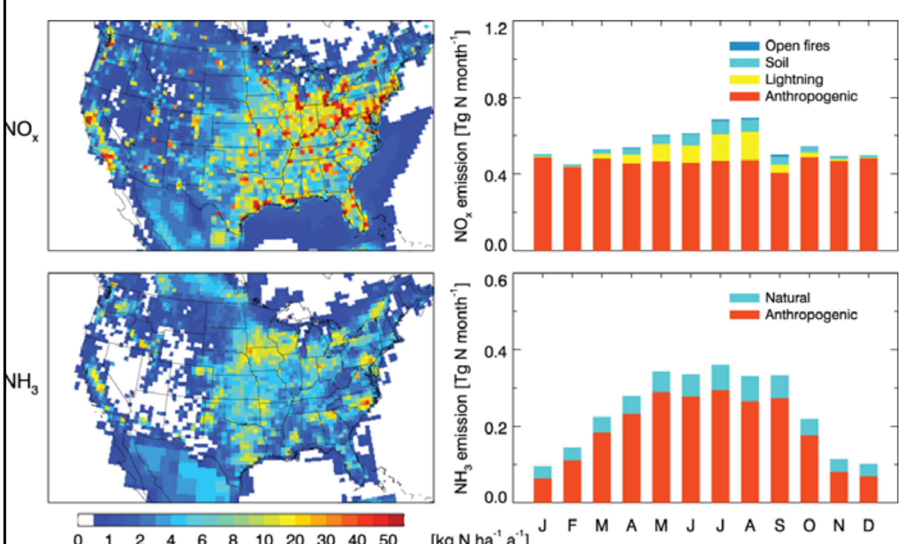


Sulfur emissions, Tg a^{-1}



From Jacob

Ammonia and NO_x emissions in the US (2006)



Zhang et al. [2011]

From Jacob

Natural pH of Rain

- $H_2O(l) \leftrightarrow H^+(aq) + OH^-(aq)$ $K_w = [H^+][OH^-] = 1.01 \times 10^{-14}$ at 25 °C
- In pure water $[H^+] = [OH^-]$ $K_w = [H^+][OH^-] = (x)(x) = 1.01 \times 10^{-14}$
  $x = [H^+] = [OH^-] = 1.01 \times 10^{-7}$ M
- $pH = -\log_{10}([H^+]) = 7$
- *for further reference see e.g. http://preparatorychemistry.com/Bishop_pH_Equilibrium.htm*

- Equilibrium with natural CO_2 (280 ppmv) results in a rain pH of 5.7:

$$CO_2(g) \overset{H_2O}{\rightleftarrows} CO_2 \bullet H_2O \qquad K_H = 3\times10^{-2}\ \text{M atm}^{-1}$$

$$CO_2 \bullet H_2O \rightleftarrows HCO_3^- + H^+ \qquad K_1 = 9\times10^{-7}\ \text{M}$$

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+ \qquad K_2 = 7\times10^{-10}\ \text{M}$$

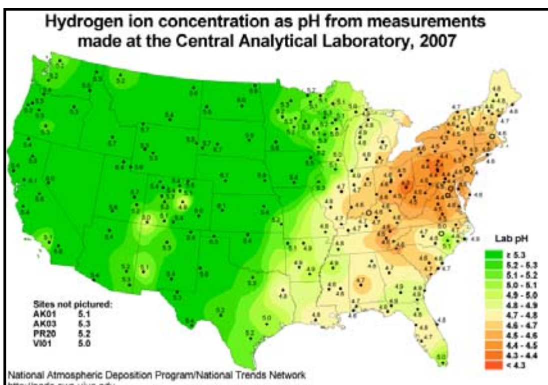
$$\Rightarrow [H^+] = (K_1 K_H P_{CO_2})^{1/2}$$

- This pH can be modified by natural acids (H_2SO_4, HNO_3, RCOOH…) and bases (NH_3, $CaCO_3$) ⇨ natural rain has a pH in range 5-7

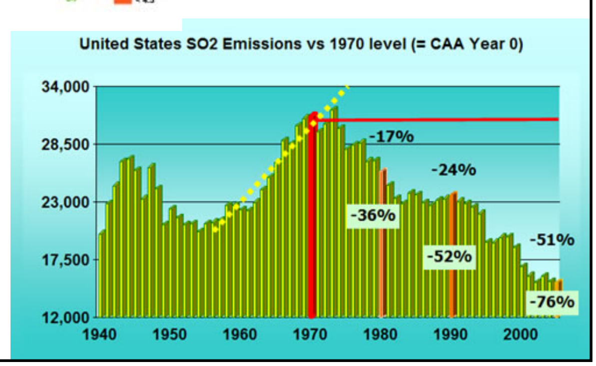
"Acid rain" refers to rain with pH < 5 ⇨ damage to ecosystems

From Jacob

Precipitation pH

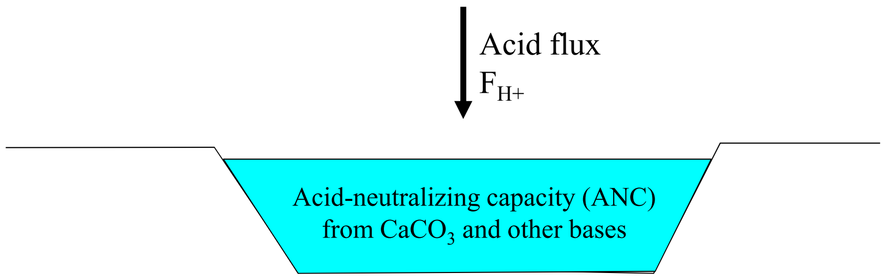


Long Term Trend of US SO_2 Emissions



Adapted from Jacob

But ecosystem acidicification is partly a titration problem from acid input over many years



$$\int_0^t F_{H^+}\,dt > ANC \Rightarrow \text{ acidification}$$

From Jacob

Elemental & Organic Carbon (EC/OC)

EC: elemental carbon
OC: organic carbon
Soot: a by product of the combustion, contain both EC and OC. Present as chain agglomerate of small roughly spherical elementary carbonaceous particles.
$\rho \approx 1.8$ g /cm^3

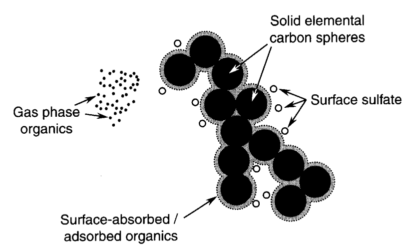
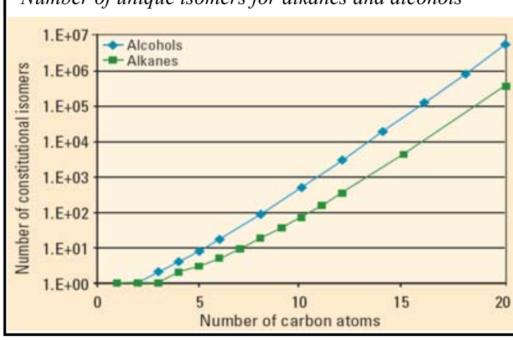


FIGURE 10.1 Schematic of a diesel soot particle consisting of an agglomeration of elemental carbon spheres (0.01- to 0.08-μm diameter). Its surface is covered with absorbed/adsorbed particle-phase organics, including 5-ring (e.g., BaP) and 6-ring PAHs. Gas-phase organics include all of the highly volatile 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

OC: thousands of compounds, extremely complex

Number of unique isomers for alkanes and alcohols



← Goldstein & Galbally, ES&T 2007

Adapted from Zhang

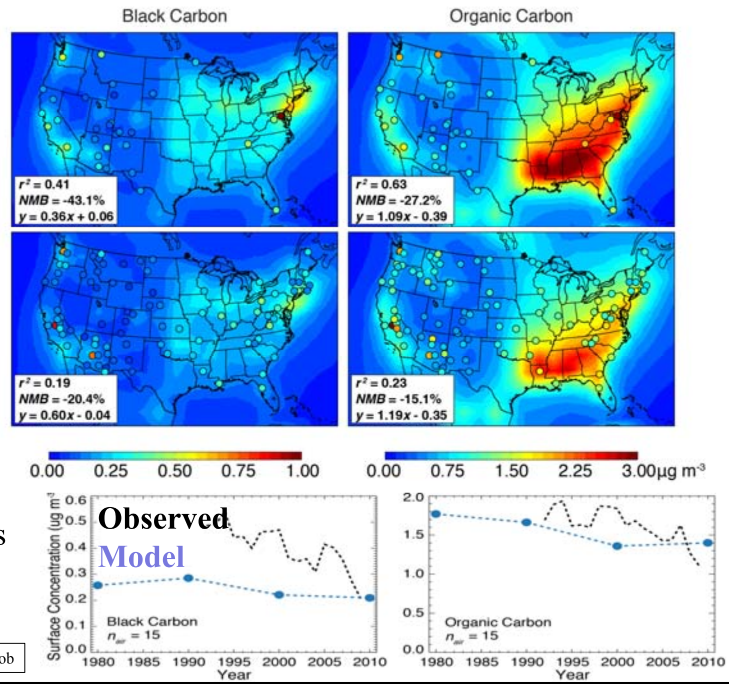
Long-term trends in BC and OC aerosol over the US

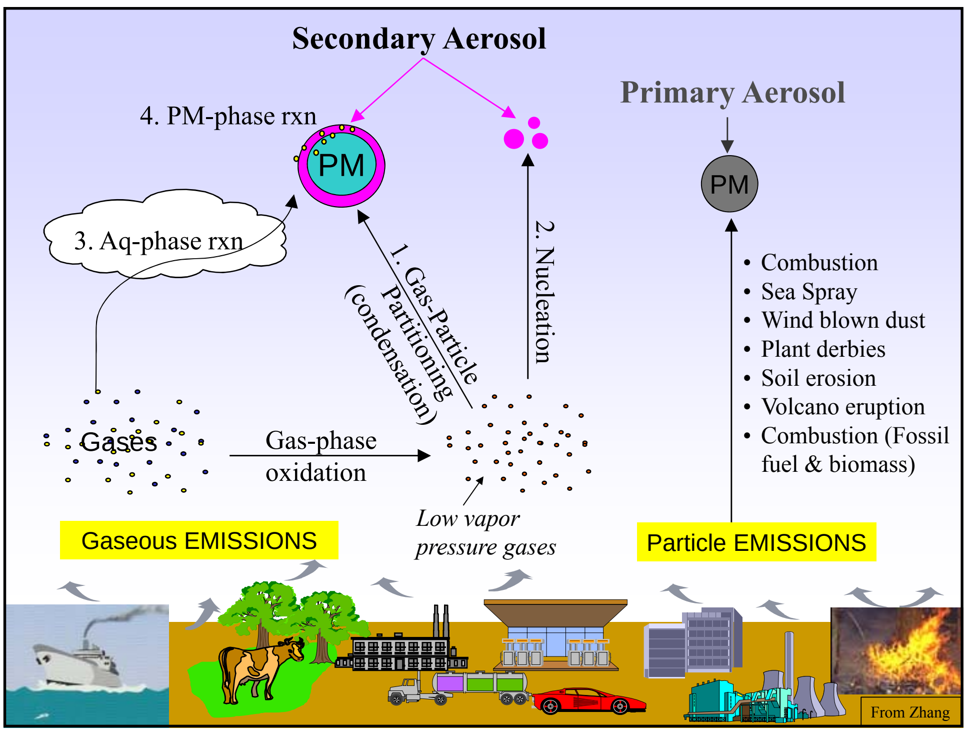
Annual mean concentrations

National trends

Leibensperger et al. [2011]

From Jacob





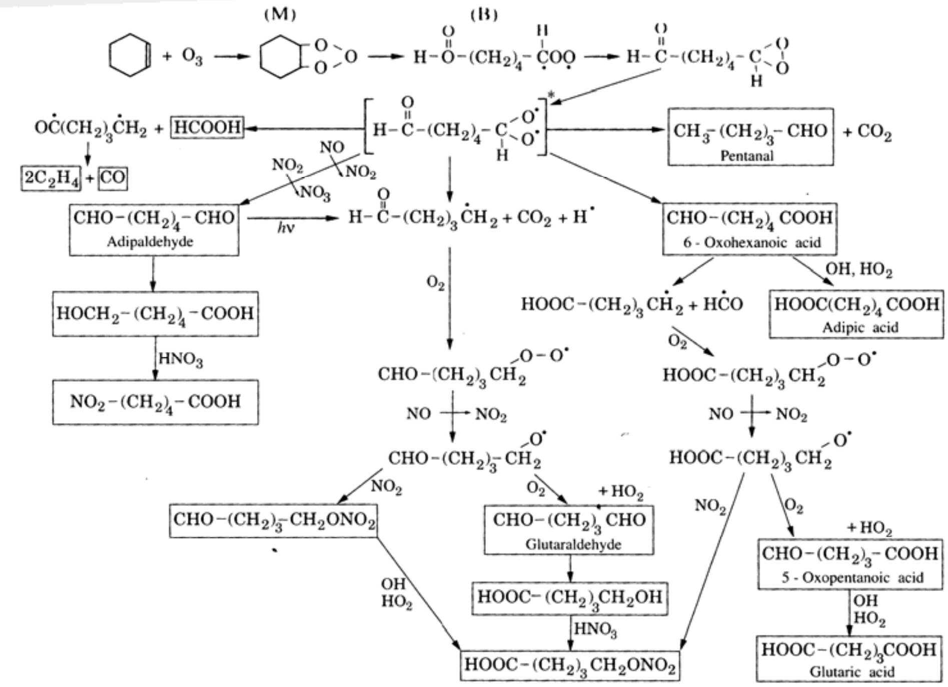


FIGURE 13.9 Proposed gas-phase reaction mechanism for the cyclohexene–ozone reaction. *Seinfeld & Pandis*

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.

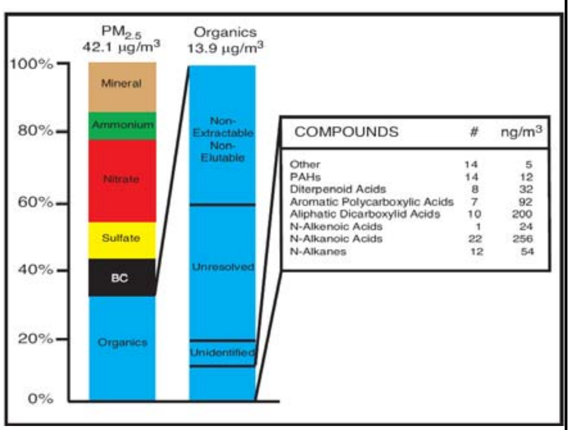


Figure 3.10. Speciation results for organic aerosol in Southern California (Rogge et al., 1993). Even if a hundred or so individual organic compounds were identified and quantified they represented only 15 percent or so of the total organic mass. *2003 NARSTO Assessment*

From Zhang

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

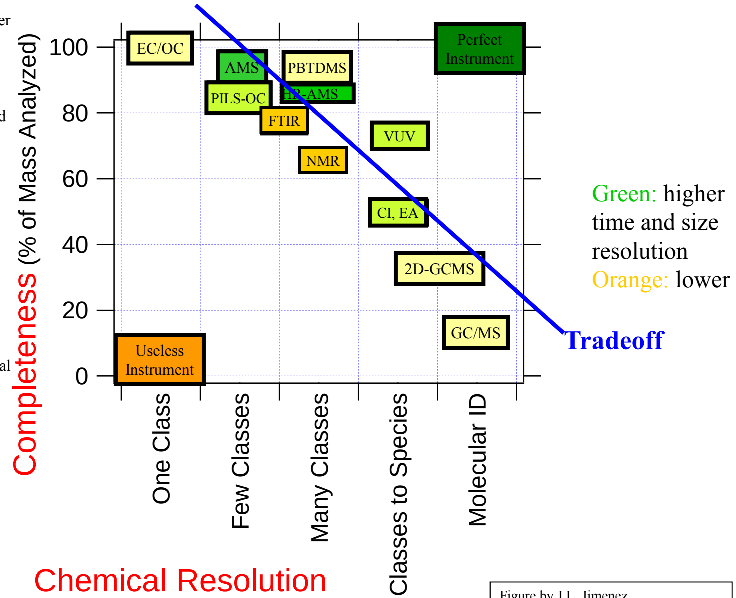
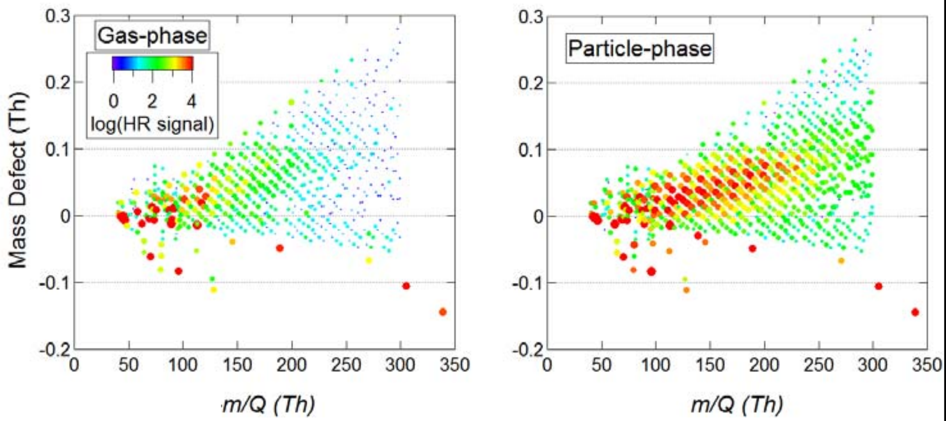


Figure by J.L. Jimenez
Published in Hallquist et al., ACP 2009

Diversity of Acids during RoMBAS 2011

Gas-phase

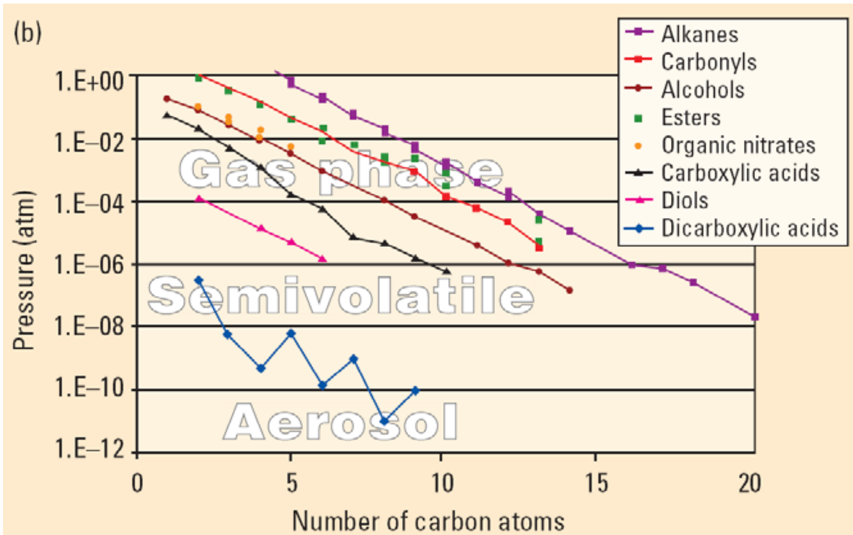
Particle-phase



- Large diversity of acids in gas and particle-phase
- Acids of higher *m/z* more in the particle phase

Slide courtesy of Harald Stark

Gas-Phase vs Aerosol Compounds



- For monofunctional compounds, alkanes beyond C_{20} and acids beyond C_3 will partition to aerosols

Goldstein & Galbally, ES&T 2007

Gas/particle partitioning Theory

Data: Fraction in particle-phase, F_p

$$F_p = \frac{Particle}{Gas + Particle}$$

Model: Absorptive partitioning theory using effective saturation concentration (C_i^*)

$$F_{p,i} = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

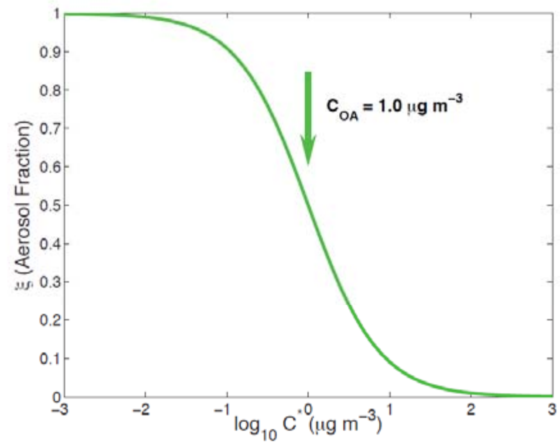
$$C_i^* = \frac{M_i 10^6 \zeta_i P_{L,i}^o}{760\ RT}$$

Model Inputs: T (K) = Ambient temperature
C_{OA} (μg m^{-3}) = Organic aerosol mass concentration
$P_{L,i}^o$ (torr) = Vapor pressures of compound i (at T)
ζ_i = Activity coefficient of compound i = 1
M_i (g mol^{-1}) = Molecular weight of compound i

(Pankow, AE 1994; Donahue et al., ES&T 2006)

Partitioning of an individual species vs c*

$$\xi_i = \frac{1}{1 + \frac{C_i^*}{C_{OA}}}$$

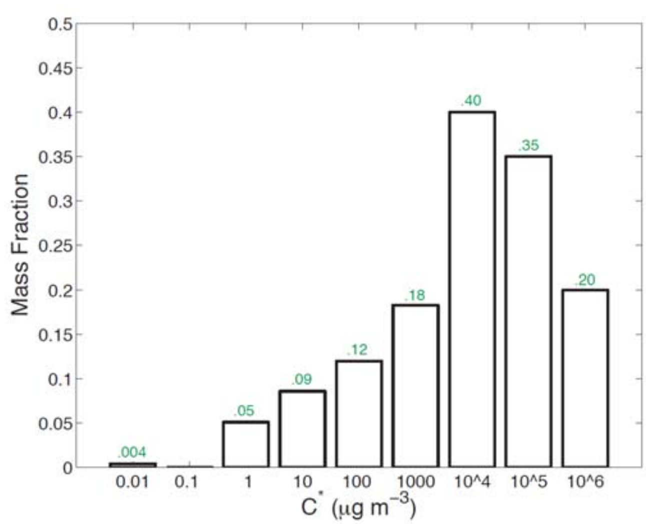


The bottom line is that an individual component only 'cares' about the *total* mass of the solution compared to its saturation concentration. For example, a 1 $\mu g\ m^{-3}$ C^* component will be 50-50 partitioned if there is 1 $\mu g\ m^{-3}$ total organic aerosol, no matter what its composition.

Donahue et al., ES&T 2006. Slide courtesy of Neil Donahue

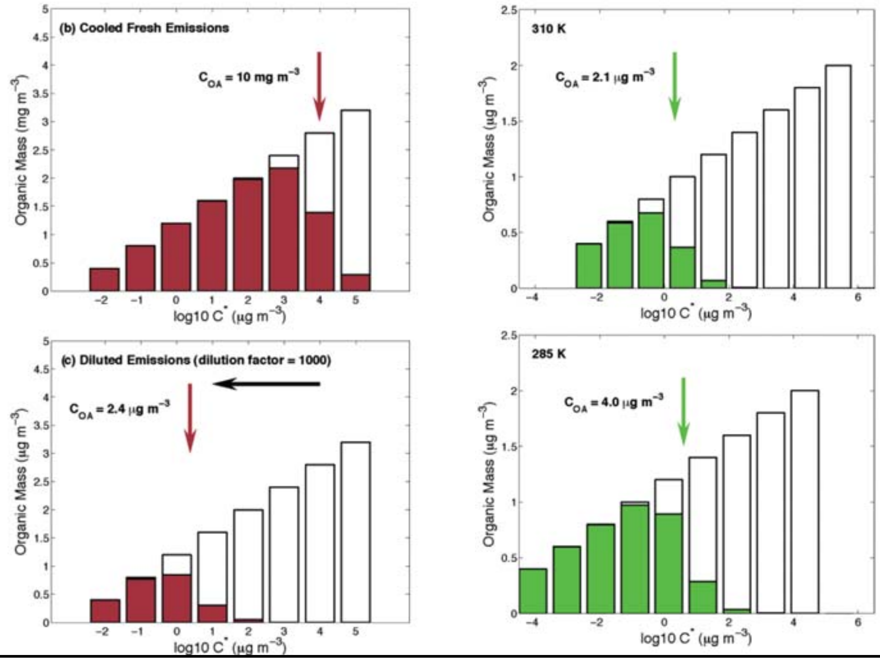
Basis Set 101: Calculate % Partitioning of α-pinene SOA when $C_{OA} = 10\ \mu g\ m^{-3}$

- α-pinene + O_3 → 0.004 $P_{0.01}$ + 0.1 $P_{0.1}$ + …



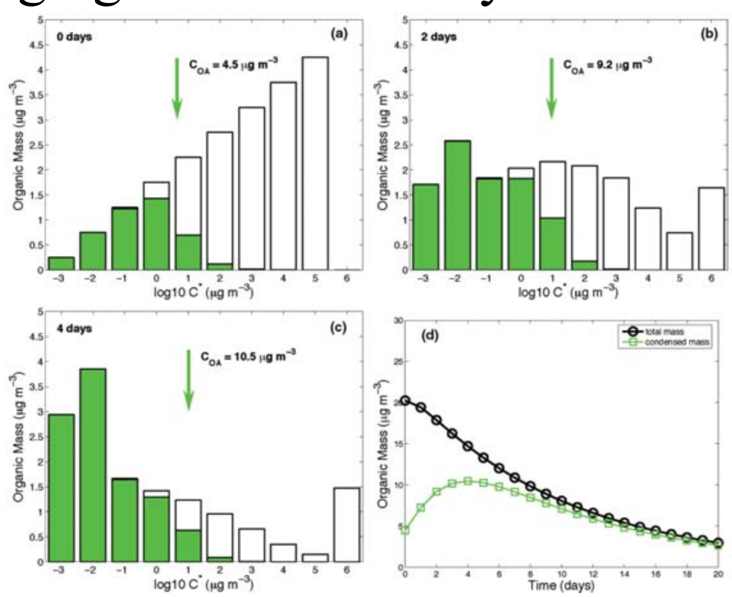
Adapted from Neil Donahue

Cooling & Dilution in VBS



Donahue et al. 2006

Aging in the Volatility Basis Set



As VOCs go through successive oxidation steps, products become more oxygenated and less volatile, but eventually smaller and more volatile

Donahue et al. 2006; Jimenez et al. 2009