ENVE 576
Indoor Air Pollution
Summer 2020

Lecture 6 – Finish gas-phase reaction chemistry
Particulate matter: physics, size distributions, respiratory deposition

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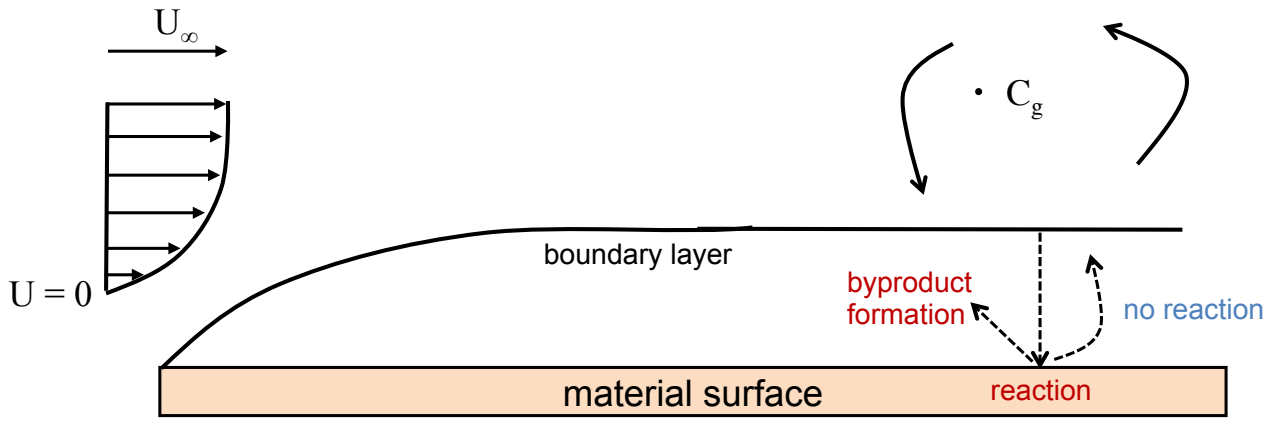
Schedule updates

- HW 1 graded; HW 2 due today
  - Final project ideas also due today
- Two classes this week
  - Today June 23 (8 am) and Friday June 26 (11:30 am)
- Last time we covered:
  - Reactions of gas-phase compounds
    - Heterogeneous (reactive deposition)
    - Homogeneous (gas-phase chemistry) ← Finish today
- Next up: 3+ weeks of lectures on particulate matter
  - Starting with:
    - Single particle physics
    - Particle size distributions
    - Respiratory deposition

Final project topics

Name	Project topic (initial ideas)
Beke, Marina	1. Desktop computer emissions (see Scot Waye) 2. Particulates from make-up (and personal care) products (cosmetics)
Chen, Lingzhou	Dust accumulation modeling
Kang, Insung	Healthcare settings (modular airborne infection room), CFD modeling (see Mohammad H)
Lee, Jongki	
Manoharan, Monika	Smart residential ventilation/IAQ
Manorom, Thammanoon	Novel materials for air filtration
Orts Costa, Enrique	Parametric design and IAQ (*working on it*)
Salimian Rizi, Behzad	ML approaches to estimating air exchange rates
Zhu, Tingli	

Reactive deposition: summary



- For reactive gas-phase pollutants, we will have an additional loss rate to account for reactive losses to material surfaces

$$\frac{dC}{dt} = P\lambda C_{out} + \frac{E}{V} - \lambda C - \frac{v_d A}{V} C \qquad k_{dep} = \frac{v_d A}{V}$$

$$v_d = \frac{v_s v_t}{v_s + v_t}$$

$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{1}{v_s} = \frac{1}{v_t} + \frac{4}{\gamma \langle v \rangle}$$

v_s = surface-limited deposition velocity (m/hr)
v_t = transport-limited deposition velocity (m/hr)
γ = reaction probability (-)
$\langle v \rangle$ = Boltzmann velocity (m/hr)

Reactive deposition: byproduct formation

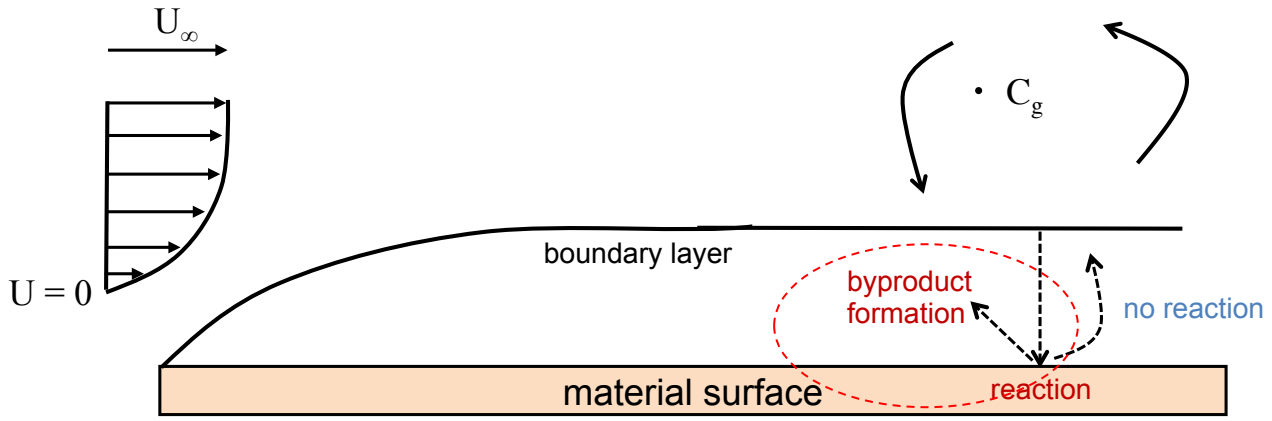
- Reactive deposition to surfaces removes indoor pollutants
  - Can also generate others in the form of reaction by-products

$$R_{byproduct} = (v_d AC) Y_i f_{conversion}$$

$R_{byproduct,i}$ = by-product i production rate (moles/hr)

Y_i = molar yield of i (moles i per moles of gas consumed)

$f_{conversion}$ = conversion factor (e.g., $\frac{10^{-6}}{MW}$ to convert from $\frac{\mu g}{m^3}$ to $\frac{moles}{hour}$)



Byproduct formation: mass balance

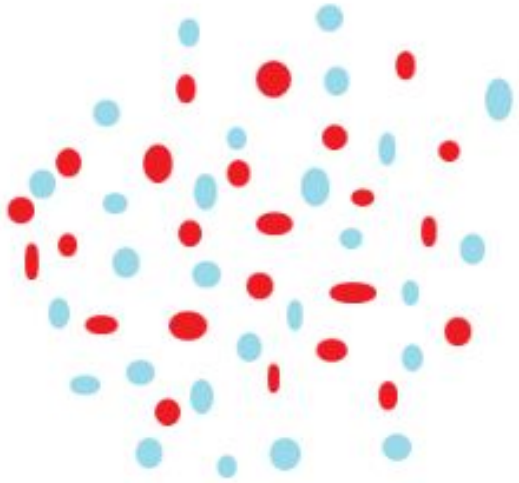
- Mass balance on reactive pollutant (e.g., ozone)

$$\frac{dC}{dt} = P\lambda C_{O_3,out} - \lambda C_{O_3} - \frac{v_d A}{V} C_{O_3}$$

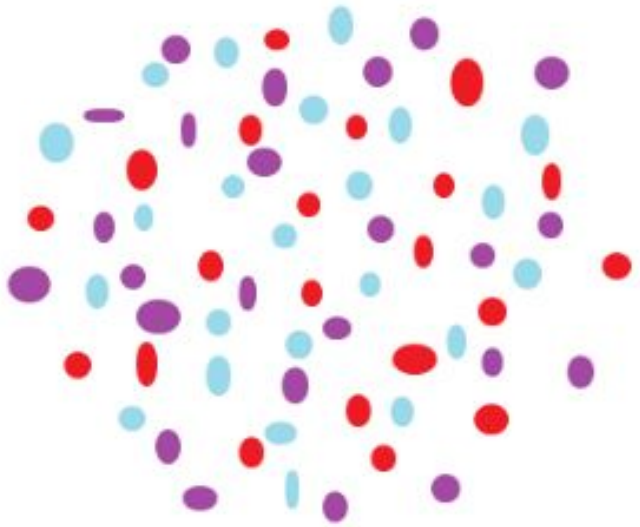
- Mass balance on byproduct i

$$\frac{dC_i}{dt} = P\lambda C_{i,out} - \lambda C_i + Y_i \frac{v_{d,O_3} A}{V} f_{conversion} C_{O_3}$$

Tracking two species, need two mass balances…



Initial: Reactants A and B



Equilibrium: Reactants A and B. Product AB

HOMOGENEOUS CHEMISTRY

Gas-phase to gas-phase reactions

Homogeneous chemistry

- Homogeneous reactions also occur in indoor environments
  - Gas *i* + Gas *j* → Byproduct *k*

$$R_{\text{homogeneous}} = -k_{ij} C_i C_j V$$

$R_{\text{homogeneous}}$ = loss rate due to homogenerous reactions between i and j (moles/hr or μg/hr)

k_{ij} = reaction rate constant ($\text{ppb}^{-1}\ \text{hr}^{-1}$)

$k_{ij} C_j$ = reaction rate (1/hr)

- Need at least 3 mass balances:
  - Two reactants + product(s) $\quad R_{byproduct,k} = (k_{ij} C_i C_j) Y_k f_{conversion}$
- For a reaction to be relevant indoors, it must occur on a relevant time scale
  - $k_j C_j$ (1/hr) needs to be on the same order as λ (1/hr)
    - Reaction must be reasonably fast

Homogenous chemistry: Mass balance

- Summary of mass balance terms:

$$\frac{dC}{dt} = P\lambda C_{out} + \frac{E}{V} - \lambda C - \sum k_j C C_j$$

C = concentration in air inside space of interest (mg/m^3)

C_{out} = concentration outside of space (mg/m^3)

V = chamber volume (m^3)

λ = air exchange rate through space (1/hr)

C_j = concentration of species j in indoor air (mg/m^3)

k_j = reaction rate constant ($\frac{m^3}{mg\ hr}$ or $\frac{1}{ppb\ hr}$)

$k_j = f$(temperature, reactants)

Homogenous chemistry: Mass balance

- Summary of mass balance terms (steady-state):

$$C_{ss} = \frac{P\lambda C_{out} + E/V}{\lambda + \sum k_j C_j} \qquad k_j = f(\text{temperature, reactants})$$

If: $\sum k_j C_j << \lambda$

Then: reactions are <u>not</u> important

If: $\sum k_j C_j \approx \lambda$

Then: reactions **<u>are important</u>**

(reaction must occur reasonably fast)

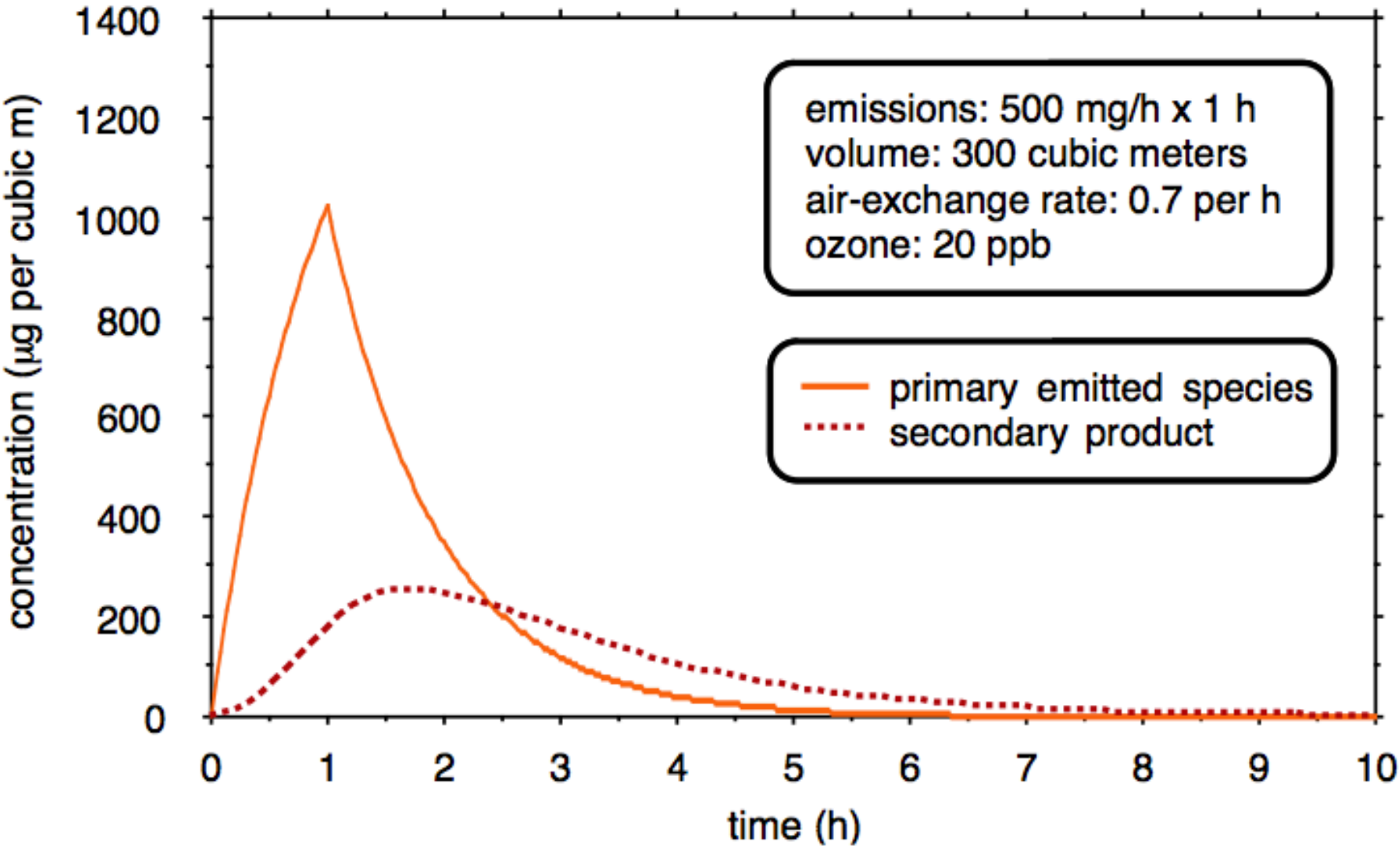
- Mass balance for estimating by-production formation:

$$C_{byproduct,ss} = \frac{\sum y_p k_j C_j C}{\lambda} \qquad y_p = \text{byproduct yield}$$

Homogeneous chemistry

- **Ozone (O_3)** is an important driver of homogeneous chemistry
  - Oxidation chemistry with unsaturated (C=C double bond) VOCs
  - Weschler (2000) *Indoor Air* provides great review of ozone chemistry
    - Including what reactants are important
  - Important reactants include:
    - Terpenes (limonene, pinene, and others)
      - Household cleaners, scented products
    - Fatty acids (oleic acid, linoleic acid)
    - Squalene
  - Important byproducts include:
    - Gas phase: aldehydes (including HCHO), carbonyls
    - Particle phase: secondary organic aerosols (low-vapor pressure species that self-nucleate to form small particles or condense on and increase the mass of existing particles)
  - Byproducts from indoor chemistry can be respiratory or skin irritants

Reaction byproducts: O_3 + VOCs from cleaning products



Nazaroff and Weschler 2004 *Atmos Environ*

Gas phase reaction byproducts (O_3 + VOCs)

Products (reported or inferred for indoor settings) derived from reactions between unsaturated organic compounds and ozone, hydroxyl radicals or nitrate radicals

Product	Product of reaction with			Refs[a]
	O_3	OH	NO_3	
Primary ozonides	✓			a, d
Stabilized Crigee biradicals	✓			d, p, q
Hydroxyl radical	✓			l, o t, u
Alkyl radicals		✓	✓	a, d
Hydroxyalkyl radicals		✓		a
Nitrooxyalkyl radicals			✓	a
Hydroperoxy radical	✓	✓	✓	l, n, v
Alkoxy radicals	✓	✓	✓	a, d, n
Unidentified radical	✓			b
α-Hydroxyhydroperoxides	✓	✓		a, c
Hydrogen Peroxide	✓			h, i
Hydroperoxides	✓			a, h, i, p, q
Peroxy-hemiacetals	✓			p, q
Secondary ozonides	✓			k, p, q
Epoxides	✓			a
Hydroxy carbonyls		✓		a
Dihydroxy carbonyls		✓		a
Hydroxy nitrates			✓	a
Carbonyl nitrates			✓	a
Formaldehyde	✓	✓		a, d
Other aldehydes	✓	✓	✓	a, d
Acetone	✓	✓		a, d
Other ketones	✓	✓	✓	a, d
Formic acid	✓	✓		a
Other carboxylic acids	✓	✓		a
Organic nitrates		✓	✓	a
Multifunctional oxidation products with carbonyl, carboxylate and/or hydroxyl groups	✓	✓	✓	d, e, f, r, x
Secondary organic aerosols via gas/particle partitioning of low volatility products	✓	✓	✓	i, l, s, v, w

Nazaroff and Weschler 2004 *Atmos Environ*

O_3 chemistry: Typical VOC concentrations + rate constants indoors

Table 4 Volatile organic compounds commonly found indoors: typical indoor concentrations and rate constants for their reaction with ozone. N. B.: units of concentration are "μg/m³" rather than "ppb", reflecting units used by Brown et al. (1994) in their review of the literature

Common indoor organic	Brown et al., 1994; weighted average[a]	Daisey et al., 1994; geo. mean[b]	Shields et al., 1996; median[c]	Girman et al., 1999; range, median[d]	Rate constant[e]
	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	
Ethanol	50–100	36	–	–	2.46×10^{-10}
Acetone	20–50	10.2	–	7.1–220, 29	2.46×10^{-10}
2-Propanol	–	5.6	–	–	2.46×10^{-10}
Toluene	20–50	9.8	6	1.6–360, 9	3.69×10^{-12}
1,1,1-Trichloroethane	20–50	24.3	–	0.6–450, 3.6	2.46×10^{-11}
m- & p-Xylene	10–20	9.1	5	0.8–96, 5.2	1.48×10^{-11}
Dichloromethane	10–20	1.4	–	0.5–360	2.46×10^{-11}
Decamethylcyclopentasiloxane	–	–	40	–	2.46×10^{-13}
p-Dichlorobenzene	5–10	–	0.2	0.3–85	1.72×10^{-12}
Ethyl acetate	5–10	1.1	–	0.2–65	2.46×10^{-10}
n-Decane	5–10	2.9	6	0.3–50	2.46×10^{-13}
Branched C10	–	–	5	–	2.46×10^{-13}
n-Undecane	1–5	7	9	0.6–58, 3.7	2.46×10^{-13}
n-Dodecane	1–5	10.4	7	0.5–72, 3.5	2.46×10^{-13}
n-Pentadecane	1–5	–	13	–	2.46×10^{-13}
n-Hexadecane	<1	–	11	–	2.46×10^{-13}
n-Tetradecane	1–5	–	11	–	2.46×10^{-13}
1,2,4-Trimethylbenzene	5–10	3.9	5	0.3–25	3.20×10^{-11}
Octamethylcyclotetrasiloxane	–	–	10	–	2.46×10^{-13}
Ethylbenzene	5–10	2.2	2	0.3–30	3.69×10^{-12}
Nonanal	5–10	–	–	1.2–7.9, 3.1	2.46×10^{-10}
2-Butanone	1–5	–	–	0.7–18	2.46×10^{-10}
Benzene	5–10	3.2	–	0.6–17, 3.7	1.72×10^{-12}
Tetrachloroethylene	5–10	2.7	4	0.3–50	2.46×10^{-11}
o-Xylene	5–10	3	2	0.3–38	2.46×10^{-10}
n-Hexane	1–5	1.8	–	0.6–21, 2.9	2.46×10^{-13}
Camphene	10–20	–	–	–	2.21×10^{-8}
1,2-Dichloroethylene	10–20	–	–	–	6.05×10^{-9}
Isoprene	–	–	–	–	2.95×10^{-7}
d-Limonene	20–50	6.7	6	0.3–140, 7.1	5.14×10^{-6}
a-Pinene	1–5	–	0.2	0.3–8.4	2.14×10^{-6}
Styrene	1–5	1.7	1.5	0.2–6.7	5.31×10^{-7}

Weschler 2000 *Indoor Air*

O_3 chemistry: Typical VOC concentrations + half-lives indoors

Table 5 Half-lives for the reaction of ozone with volatile organic compounds commonly found in indoor air

Common indoor organics	50 ppb O3 half-life	50 ppb O3 half-life	100 ppb O3 half-life	100 ppb O3 half-life
	hours	days	hours	days
Ethanol	15700	650	7850	325
Acetone	15700	650	7850	325
2-Propanol	15700	650	7850	325
Toluene	1040000	43500	522000	21700
1,1,1-Trichloroethane	157000	6500	78300	3250
m-p-Xylene	260840	10868	130420	5434
Dichloromethane	156504	6521	78252	3261
Decamethylcyclopentasiloxane	15700000	652000	7820000	326000
p-Dichlorobenzene	2240000	93000	1120000	46500
Ethyl acetate	15700	650	7850	325
n-Decane	15700000	652000	7820000	326000
Branched C10	15700000	652000	7820000	326000
n-Undecane	15700000	652000	7820000	326000
n-Dodecane	15700000	652000	7820000	326000
n-Pentadecane	15700000	652000	7820000	326000
n-Hexadecane	15700000	652000	7820000	326000
n-Tetradecane	15700000	652000	7820000	326000
1,2,4-Trimethylbenzene	120000	5020	60200	2510
Octamethylcyclotetrasiloxane	15700000	652000	7820000	326000
Ethylbenzene	1040000	44000	520000	22000
Nonanal	15700	650	7850	325
2-Butanone	15700	650	7850	325
Benzene	2230000	93000	1120000	46500
Tetrachloroethylene	157000	6500	78300	3250
o-Xylene	15700	650	7850	325
n-Hexane	15700000	652000	7820000	326000
1,2-Dichloroethylene	636	27	318	13
Camphene	174	7.2	87	3.6
Isoprene	13	0.54	6.5	0.27
d-Limonene	0.75	0.03	0.37	0.02
a-Pinene	1.80	0.08	0.90	0.04
Styrene	7.25	0.30	3.62	0.15

Weschler 2000 *Indoor Air*

Other homogeneous chemistry

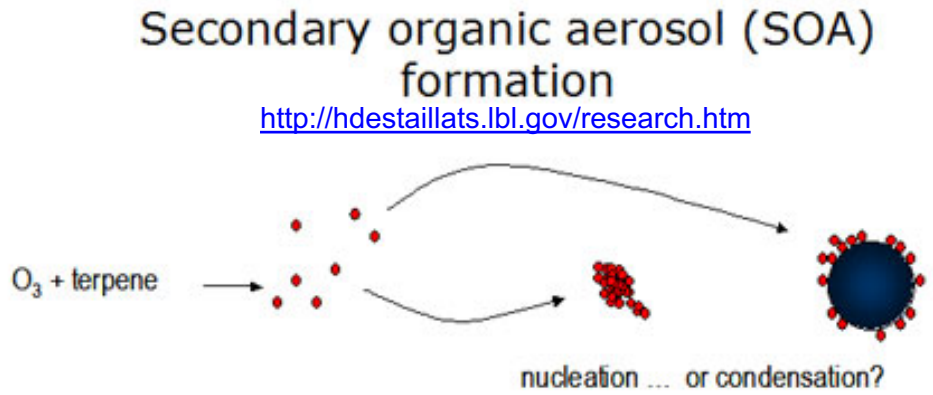
- Hydroxyl radical ($\cdot OH$)
  - Formed during ozone-terpene chemistry
  - Strong oxidant and reacts with almost any hydrocarbon (very fast)
  - Concentrations typically ppt
  - Byproducts from oxidation are expected to be more irritating and corrosive than their precursors

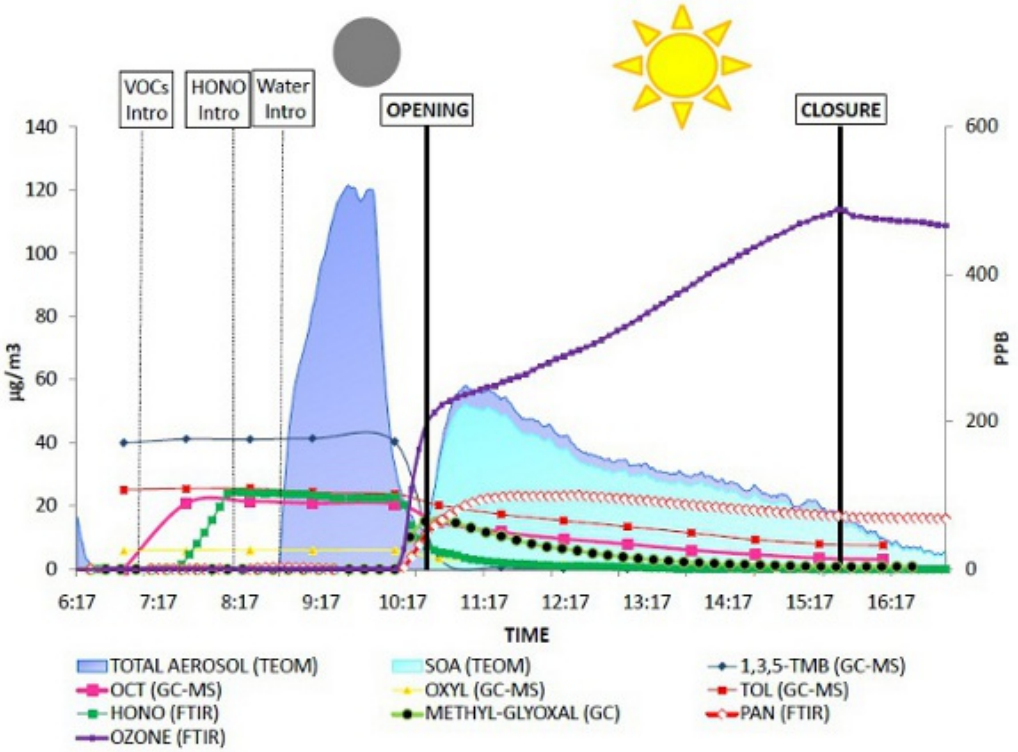
Weschler and Shields 1996 *Environ Sci Technol*

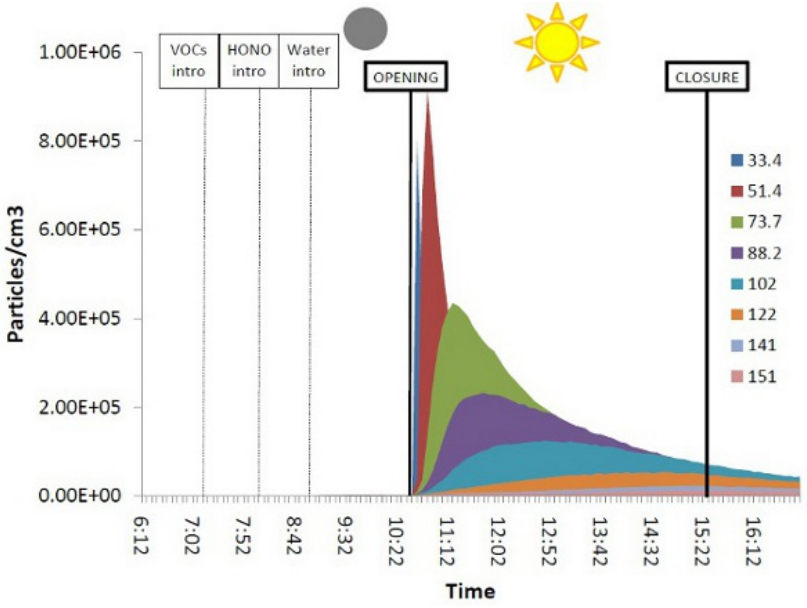
- Nitrate radical ($NO_3\cdot$)
  - Forms as product of reaction between O_3 and NO_2
  - Targets reactions with terpenes
  - Concentrations typically ppt

Weschler et al. 1992 *Environ Sci Technol*

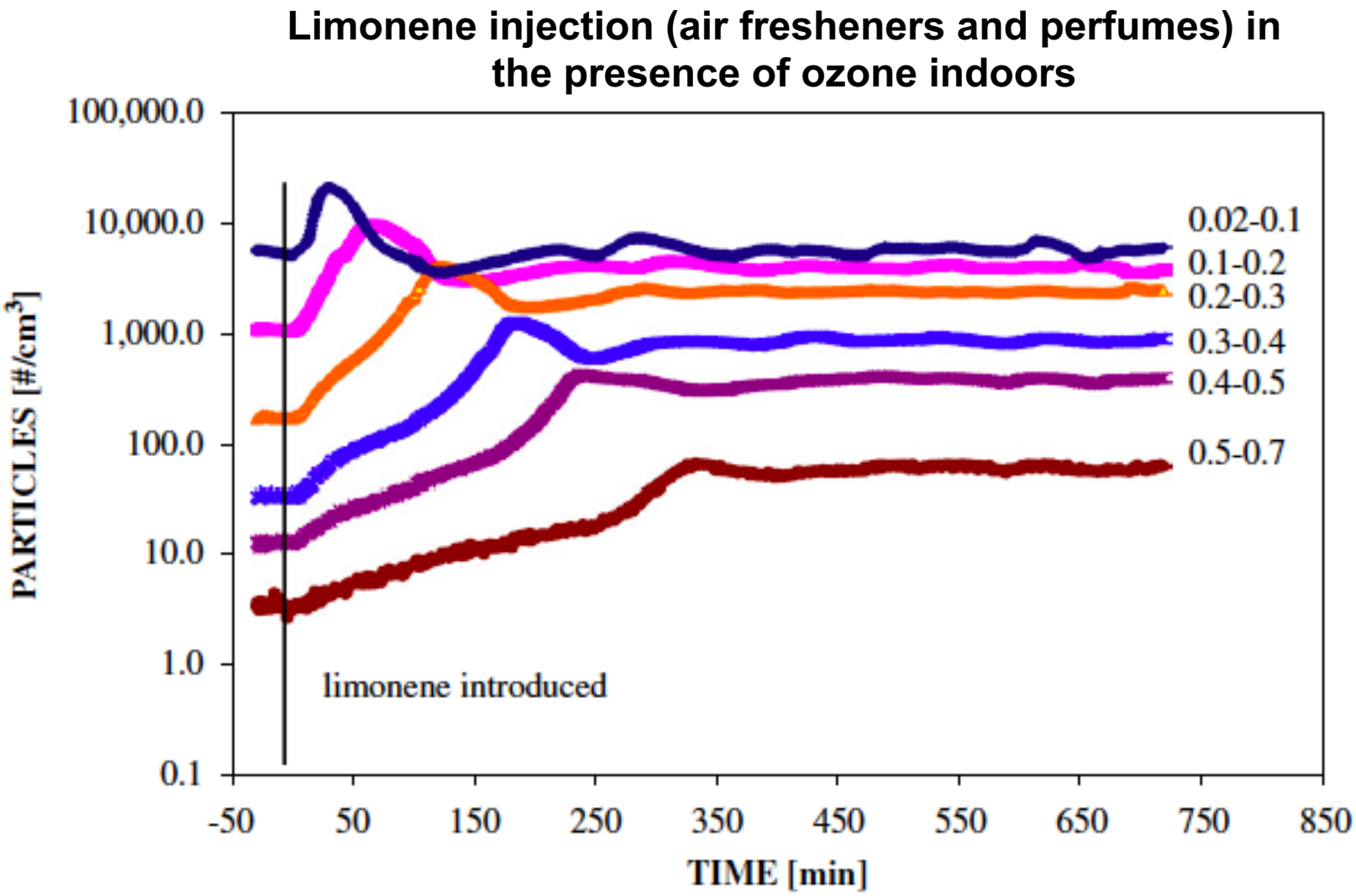
SOA: Secondary organic aerosols







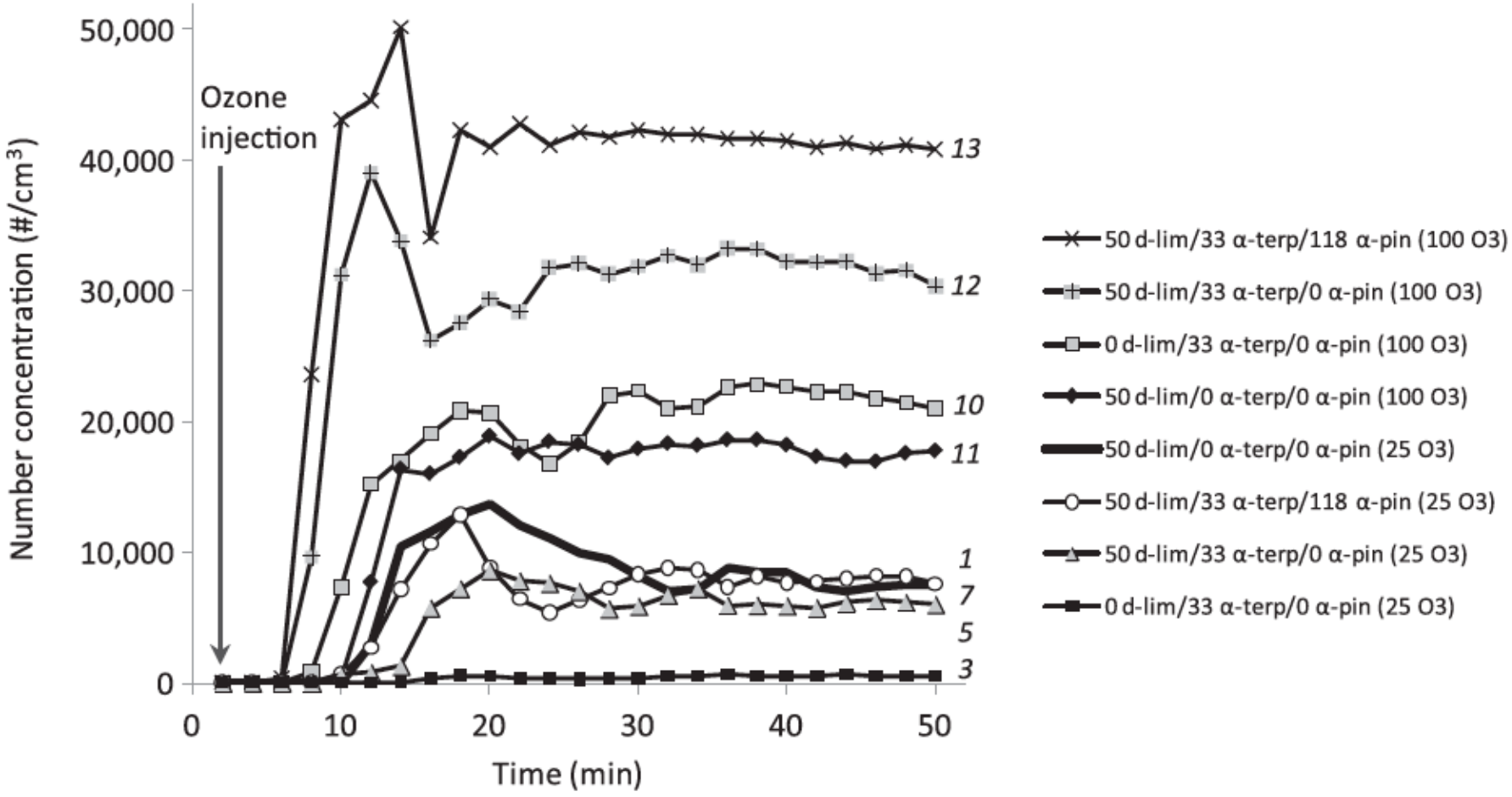
SOA formation from homogeneous chemistry



Sarwar et al., 2004 *Atmospheric Environment*

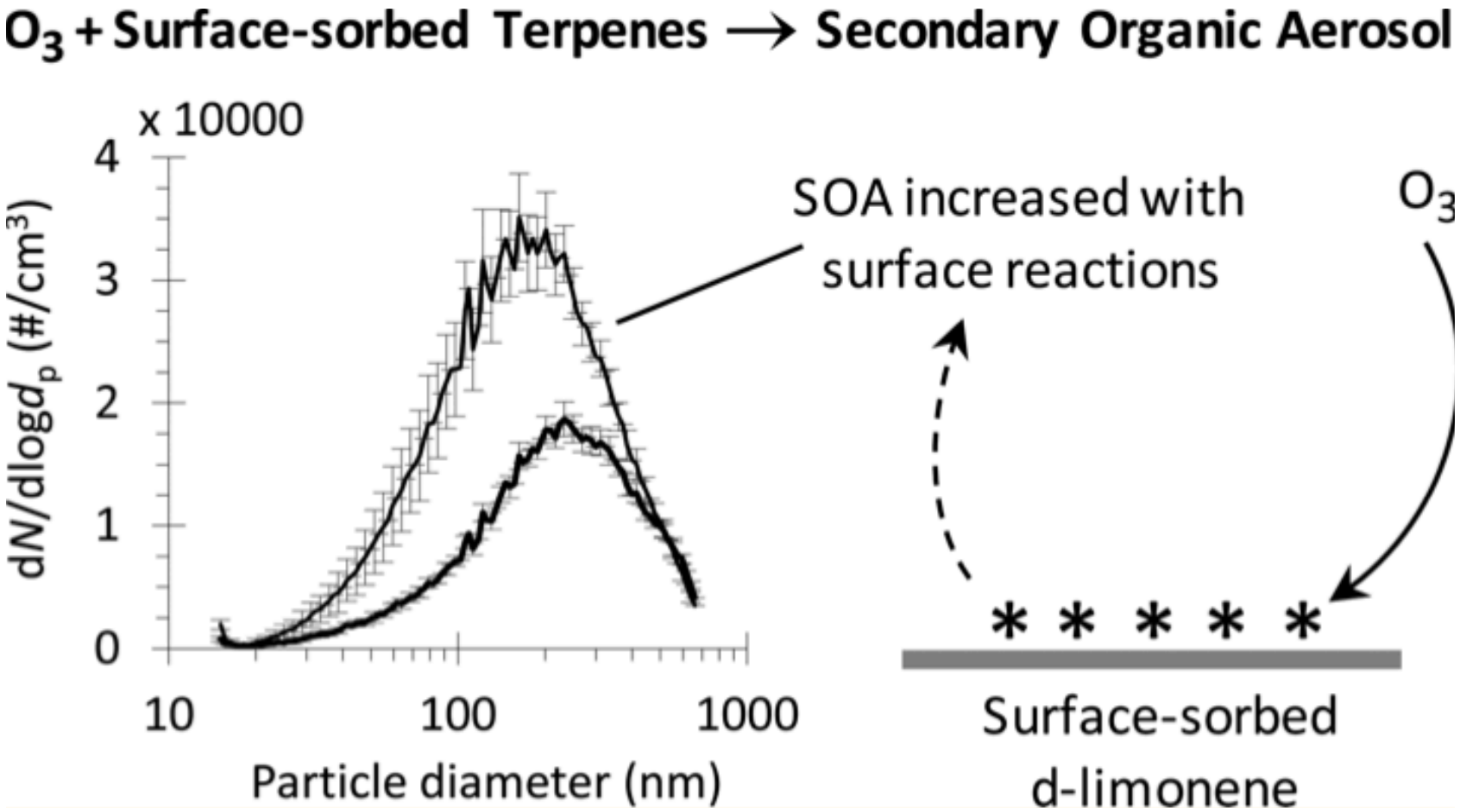
SOA formation from homogeneous chemistry

Chamber experiments with <u>mixtures</u> of terpenes and more realistic O_3 conc.
(10-500 nm particles)



Waring et al., 2011 *Atmospheric Environment*

We can also have heterogeneous SOA formation



Waring and Siegel, 2013 *Environ Sci Technol*

Indoor chemistry in residences

Volatile organic compound conversion by ozone, hydroxyl radicals, and nitrate radicals in residential indoor air: Magnitudes and impacts of oxidant sources

- Monte Carlo modeling to predict O_3, OH, and NO_3 concentrations and their impacts on reactions with common indoor VOCs in residences

$$C_i = \frac{p_i \lambda C_{i,o} + E_i/(V\Gamma_i) + R_{S,i}}{\lambda + \beta_i + R_{L,i}}$$

$$\text{Total VOC conversion rate by each oxidant} = C_{ox} \sum_j (k_{j\cdot ox} C_j)$$

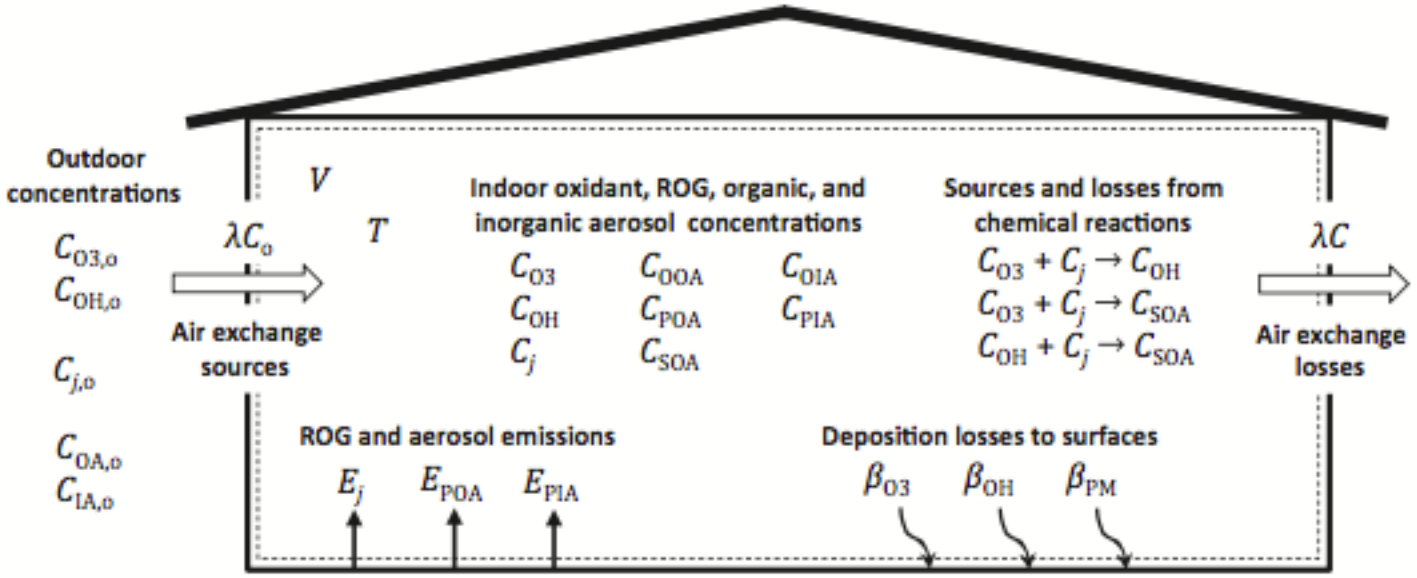
- Results suggest that total VOC conversion is dominated by reactions with O_3 (reacting mostly with d-limonene) AND with OH (which reacted with d-limonene, other terpenes, alcohols, aldehydes, and aromatics)

Waring and Wells, 2014 *Atmospheric Environment*

SOA in residences

Secondary organic aerosol in residences: predicting its fraction of fine particle mass and determinants of formation strength

- **Methods:** Monte Carlo modeling to predict indoor SOA mass formed in residences due to the oxidation of 66 reactive organic compounds by ozone or the hydroxyl radical
  - Used the RIOPA data set

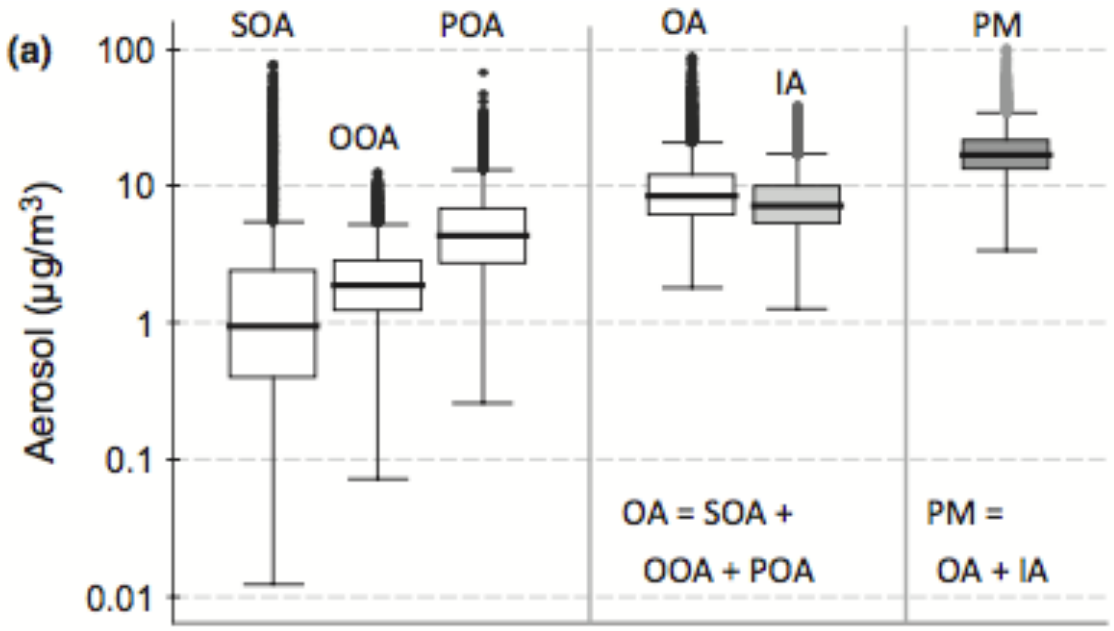


Waring, 2014 *Indoor Air*

SOA in residences

Secondary organic aerosol in residences: predicting its fraction of fine particle mass and determinants of formation strength

- **Results:** SOA typically a small fraction of total indoor $PM_{2.5}$ mass conc.
  - Except in about 10% of the cases, SOA contributed to >30% of total indoor $PM_{2.5}$
  - Highest in homes with high terpene emissions (mostly d-limonene) and high outdoor ozone



SOA = secondary organic aerosol
OOA = outdoor OA
POA = primary OA
OA = total organic aerosol (OOA + POA + SOA)
IA = total inorganic aerosol

Waring, 2014 *Indoor Air*

A few notes on:

CONTROL OF GAS PHASE COMPOUNDS

Control of VOCs and inorganic gases

- There are a few important ways to control (i.e., remove) VOCs and inorganic gases:
  1. Source control
  2. Adsorption-based air-cleaning (e.g., activated carbon)
  3. Photocatalytic air-cleaning (e.g., UV/PCO)
  4. Do plants clean air?

- We won't spend much time on these, but we need to know they exist
  - You may want to incorporate into your final project too

Source control/substitution

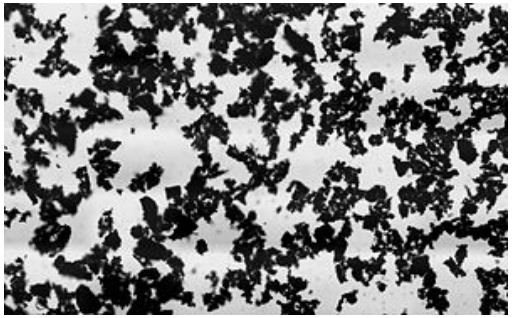
- Simple enough: this involves switching to low-emitting materials
  - We've discussed this already in some form

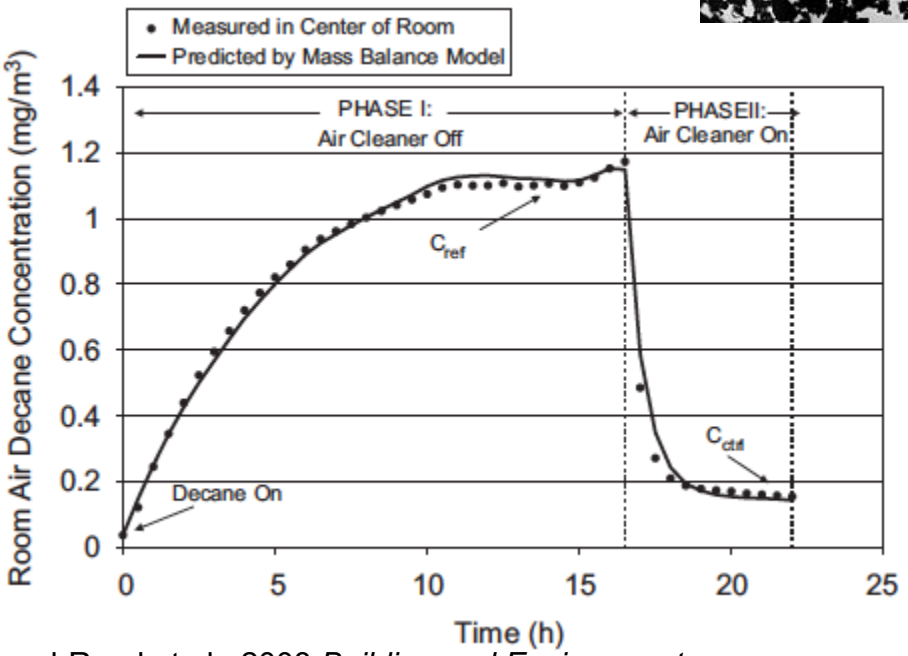
GREEN SEAL

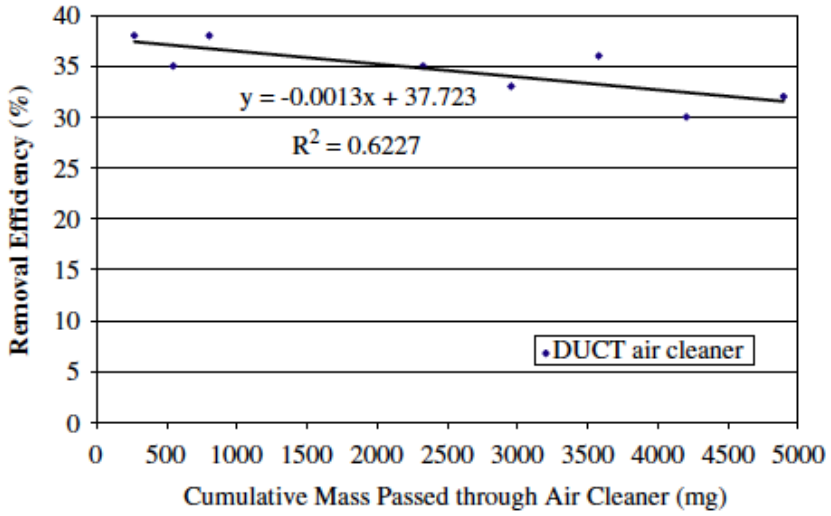
GREENGUARD CERTIFICATION
FROM UL ENVIRONMENT

Air cleaning: Adsorption (e.g. activated carbon)

- Microporous activated carbon adsorbents
  - Very high surface areas
    - e.g., 800-2000 m^2/g



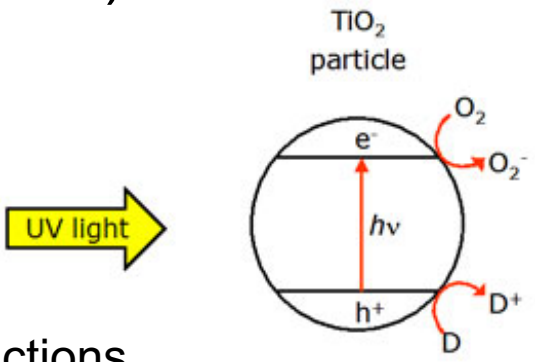




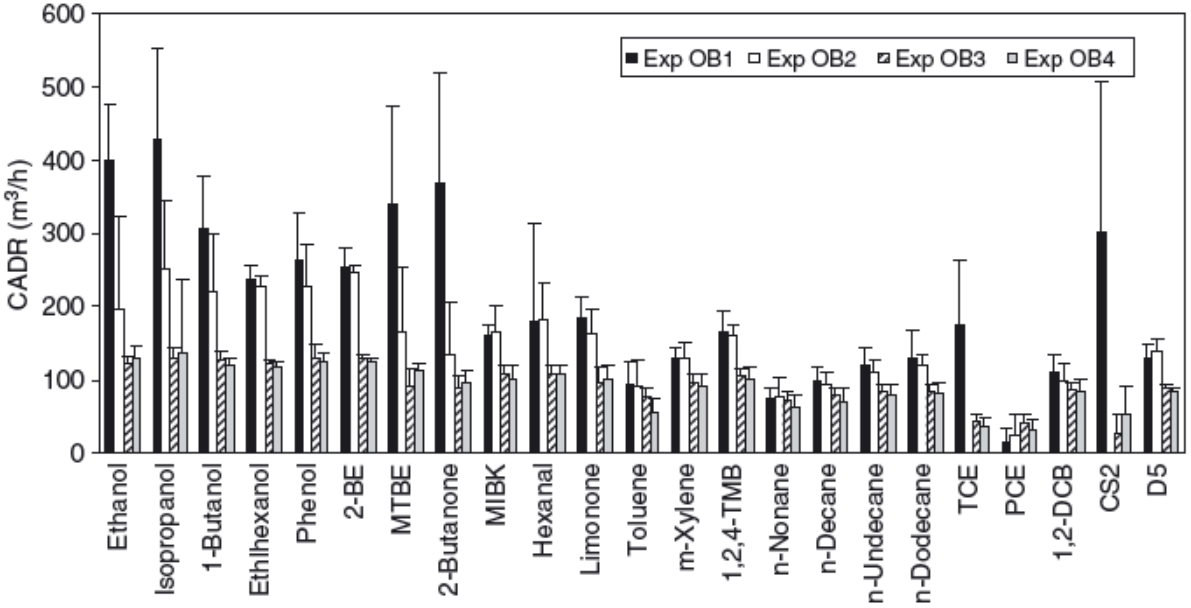
Howard-Reed et al., 2008 *Building and Environment*

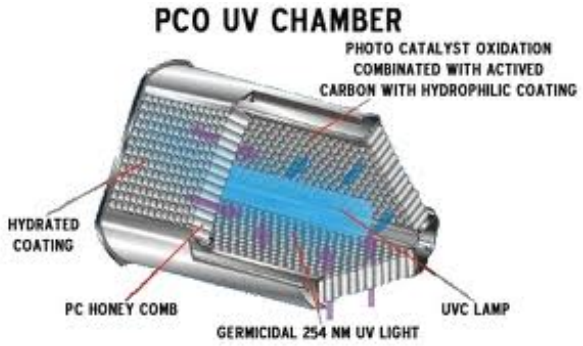
Air cleaning: UV+PCO

- Ultraviolet (UV) photocatalytic oxidation (PCO)
  - Honeycomb reactor coated with TiO_2
  - Structure is irradiated with UV light
  - VOCs adsorb reversibly on the catalyst
  - React to form CO_2 and water
    - TiO_2 semi-conductor sensitizes light-induced reactions



http://hdestaillats.lbl.gov/research.htm





Hodgson et al., 2007 *Indoor Air*

Do plants clean the air?

10 best air purifying plants for the home

CountryLiving

Carefully selecting and positioning the right house plants can ultimately make your home a healthier place to relax.

BY SAMANTHA PRATTEY APR 11, 2019

12 NASA recommended air-purifying plants that you must have in your house

20 Best Plants for Cleaning Indoor Air

Discover the top 20 plants that aid in the removal of pollutants.

February 26, 2020

HGTV

Air cleaning: Plants?

SCIENCE

A Popular Benefit of Houseplants Is a Myth

The science is clear: Indoor vegetation doesn't significantly remove pollutants from the air.

ROBINSON MEYER MARCH 9, 2019

https://drexel.edu/now/archive/2019/November/potted-plants-do-not-improve-air-quality/

The *Atlantic*: https://www.theatlantic.com/science/archive/2019/03/indoor-plants-clean-air-best-none-them/584509/

Air cleaning: Plants?

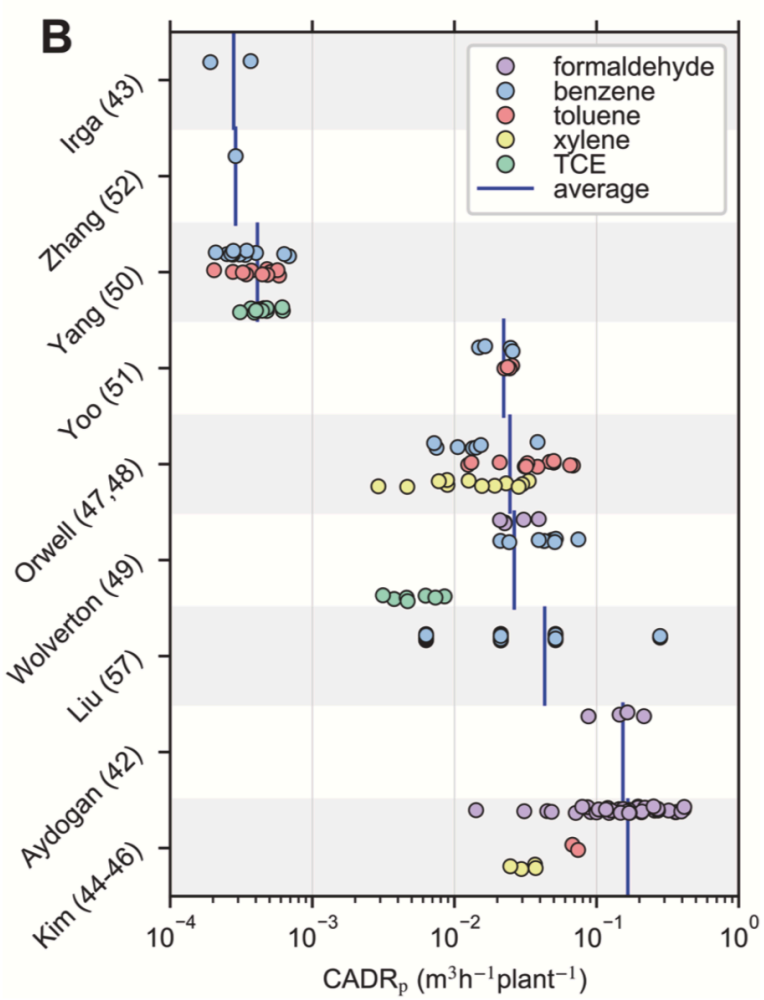


Fig. 1 a Histogram of the $CADR_p$ dataset assembled from the reviewed chamber studies outlined in Table 1. $CADR_p$ computations are detailed in the SI. **b** The $CADR_p$ data resolved by publication (labeled by first author and reference number) and measured VOC

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https://doi.org/10.1038/s41370-019-0175-9

ARTICLE

Potted plants do not improve indoor air quality: a review and analysis of reported VOC removal efficiencies

Bryan E. Cummings[1] · Michael S. Waring[1]

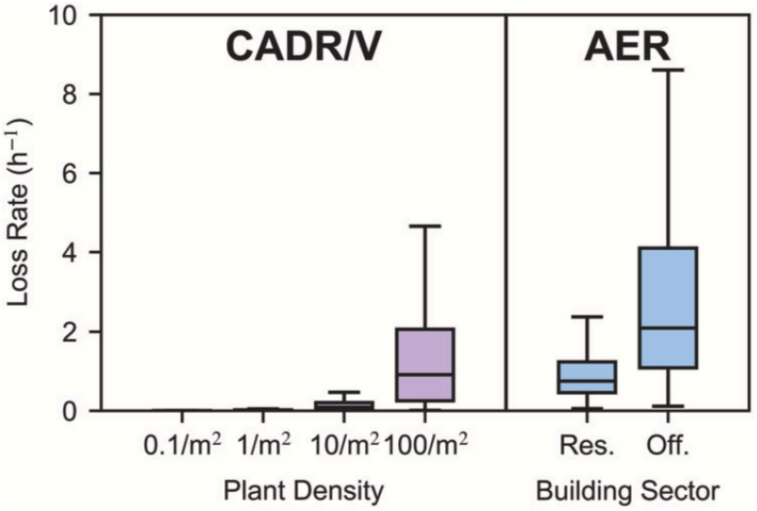


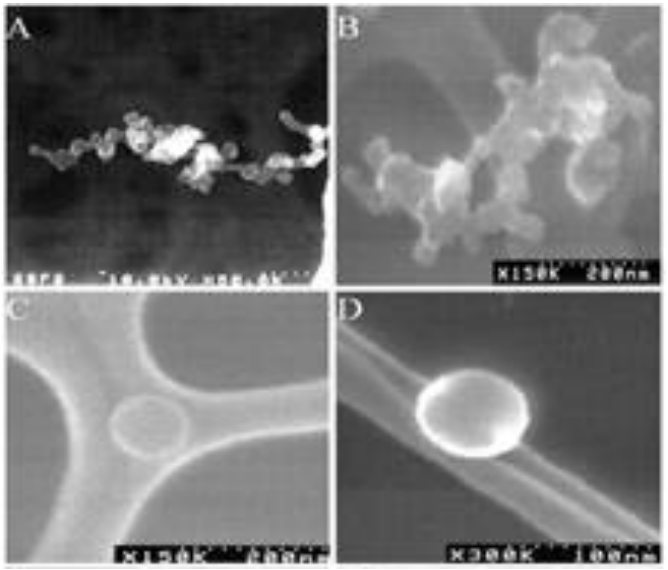
Fig. 2 Boxplots of VOC loss rates due to: (left) CADR/*V* over four cases of plant density (ρ_p); compared to (right) the VOC loss rates due to air exchange rates (AER, λ) in residences (Res.) or offices (Off.)

PARTICULATE MATTER

Overview, physics, size distributions, respiratory deposition

Particulate matter (PM)

- Particulate matter (PM) is its own class of pollutant
  - PM consists of a mixture of solid particles and liquid droplets suspended in air
  - Primary emissions are emitted directly by sources
    - Outdoors: Industry, construction, roads, smokestacks, fires, vehicles
    - Indoors: Smoking, cooking, resuspension of dust, transport from outdoors
  - Secondary emissions are formed in atmospheric reactions and some indoor reactions
- Health effects
  - Respiratory, cardiovascular, others
- Visibility effects outdoors

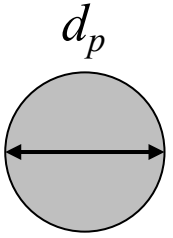


http://www.aerosols.wustl.edu/education/AerosolBasics/What%20is%20an%20aerosol.htm

Particle sizes

- Usually referring to a characteristic dimension
  - Diameter for sphere
  - Diameter for fibers (e.g. asbestos)
  - Equivalent diameter for non-spherical
- Micrometer (μm)
  - 1 μm = 10^{-6} m
- Nanometer (nm)
  - 1 nm = 10^{-9} m

- We usually treat particles as spherical:
  - Or 'equivalent' spheres



$$V = \frac{\pi}{6} d_p^3$$

Particle sizes

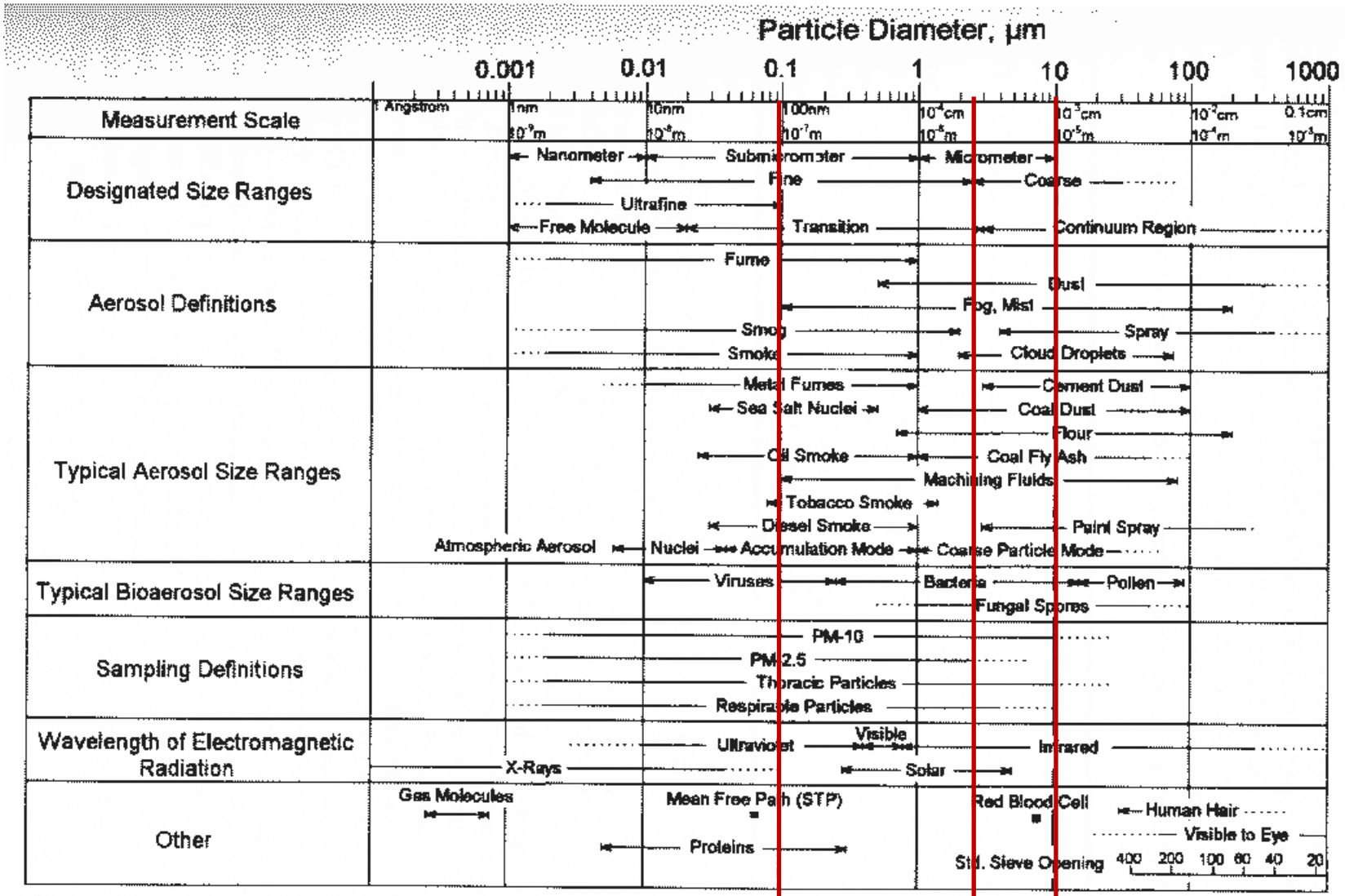
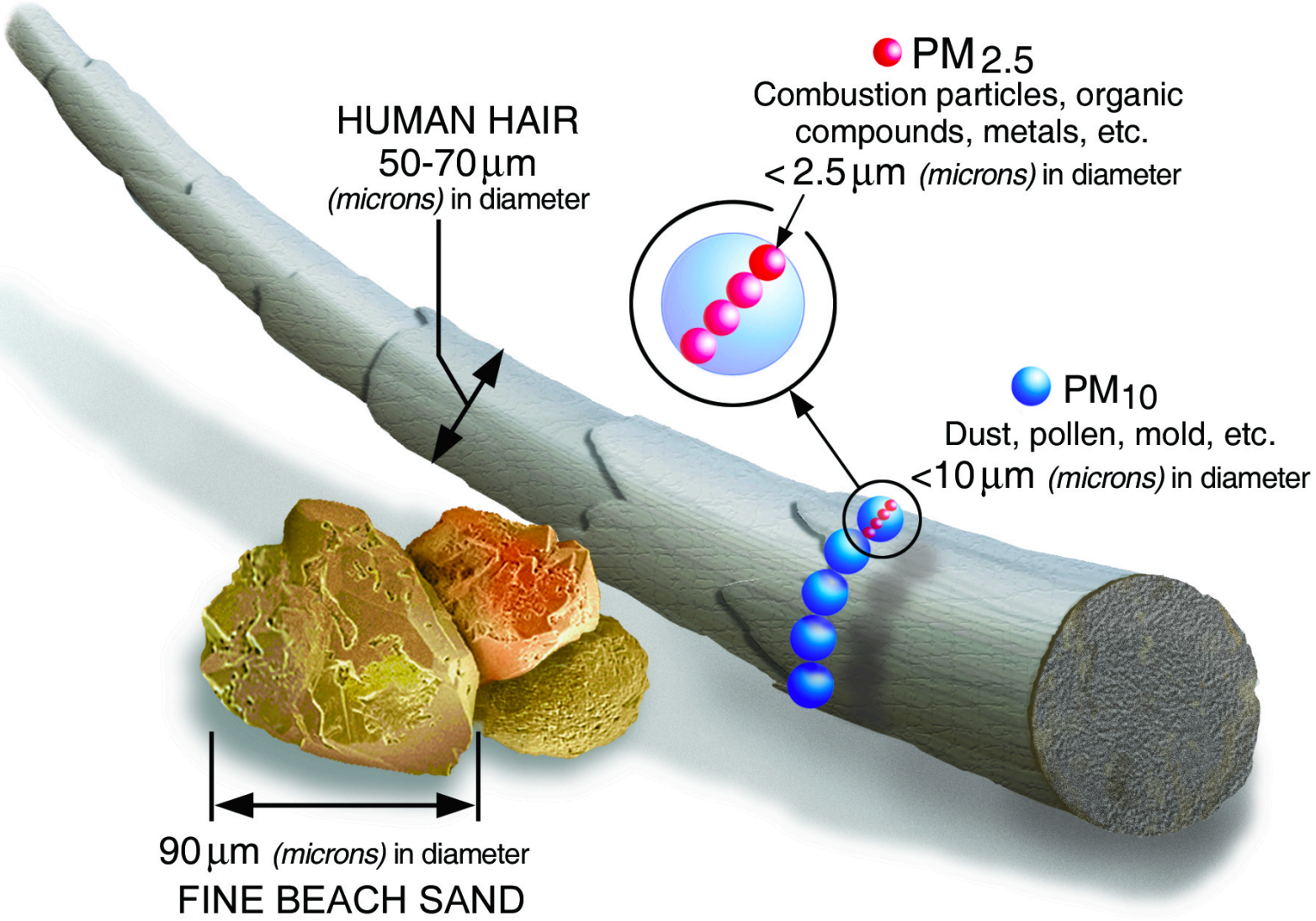


FIGURE 1.6 Particle size ranges and definitions for aerosols.

← UFP ← $PM_{2.5}$ ← PM_{10}

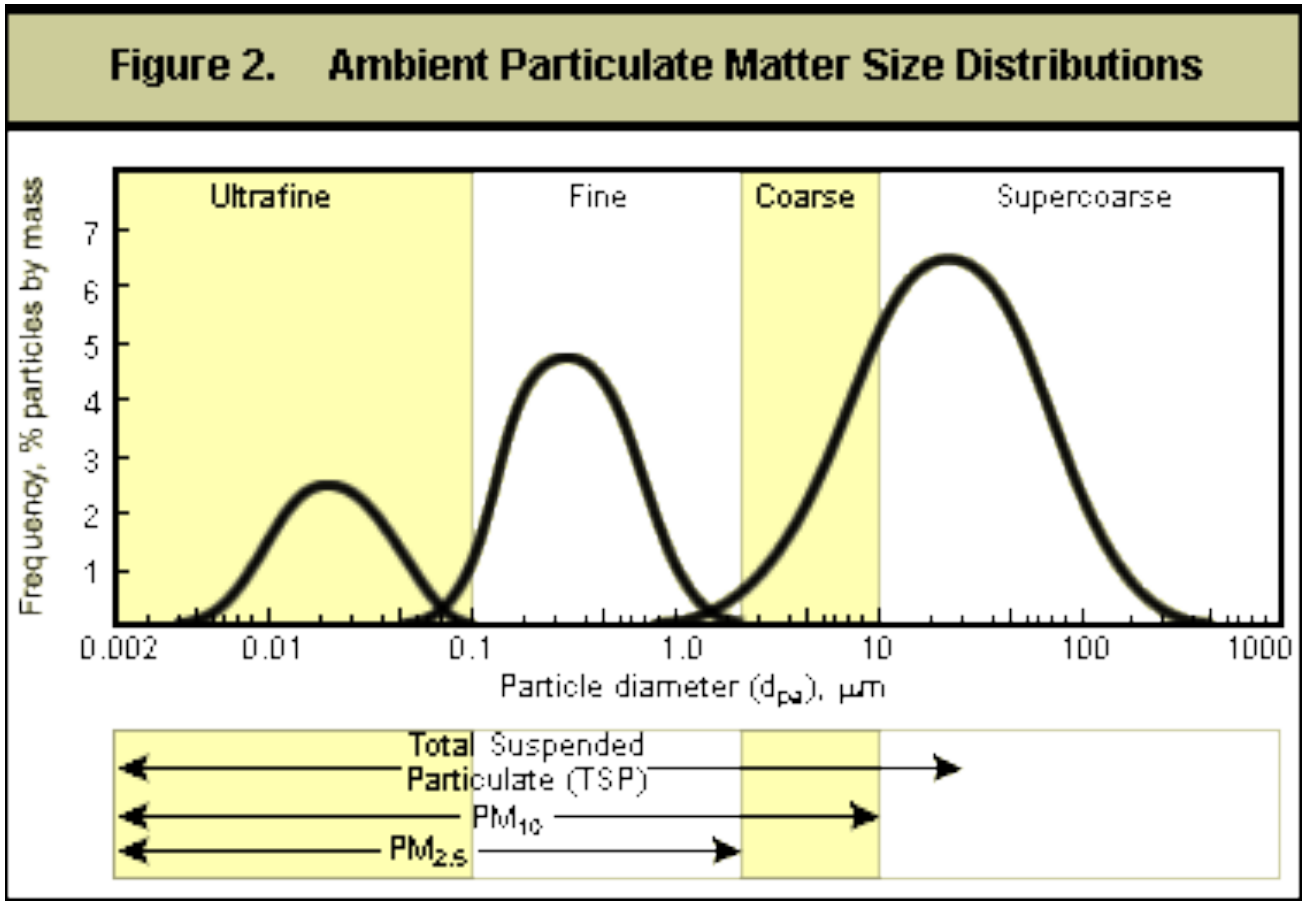
Hinds 1999

Particle sizes

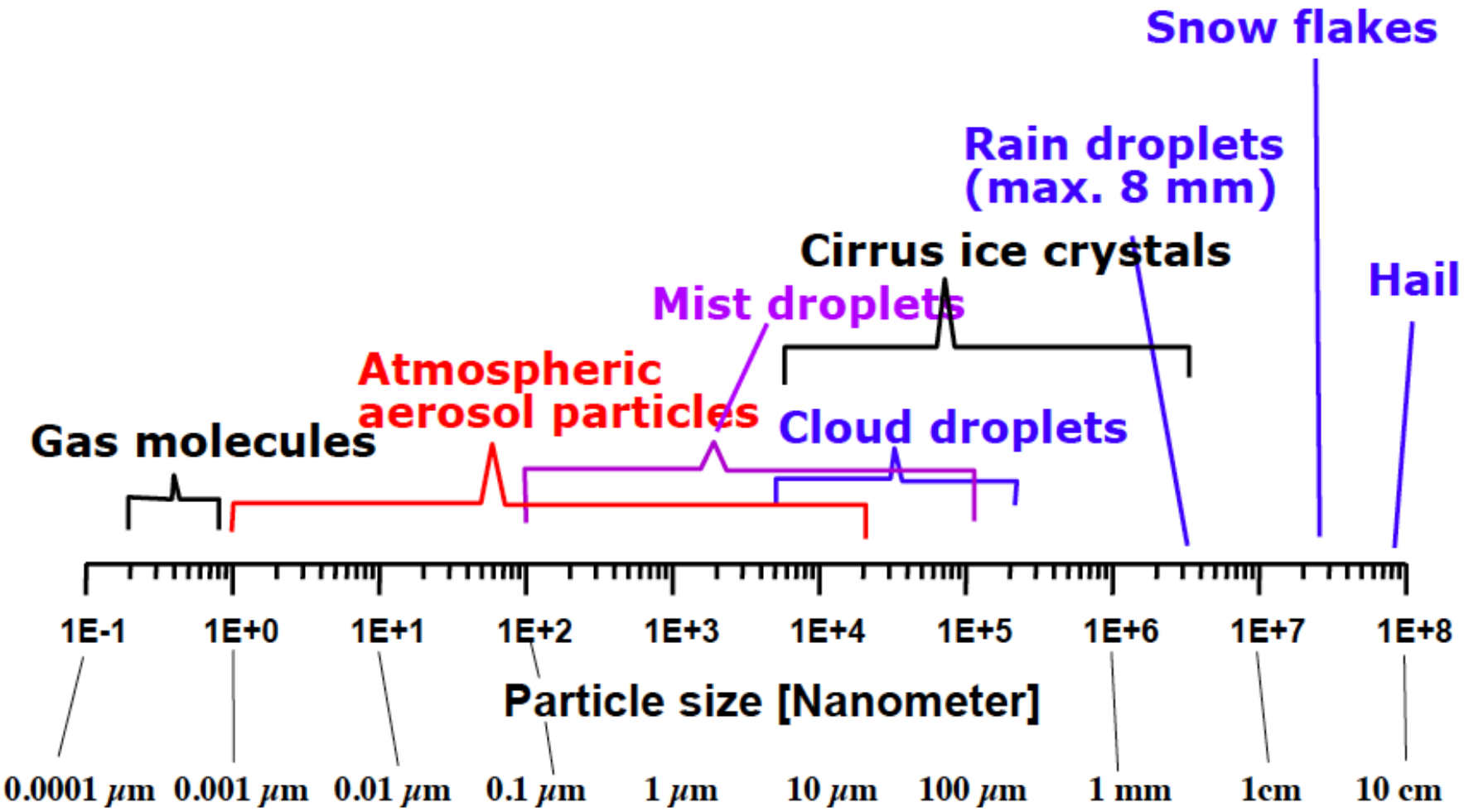


How are particle concentrations reported?

- Number
  - #/cm^3
  - UFP <100 nm
- Surface area
  - cm^2/cm^3
- Volume
  - m^3/m^3
- Mass
  - $\mu g/m^3$
  - $PM_{2.5}$
  - PM_{10}
  - $PM_{2.5-10}$
  - TSP
  - RSP

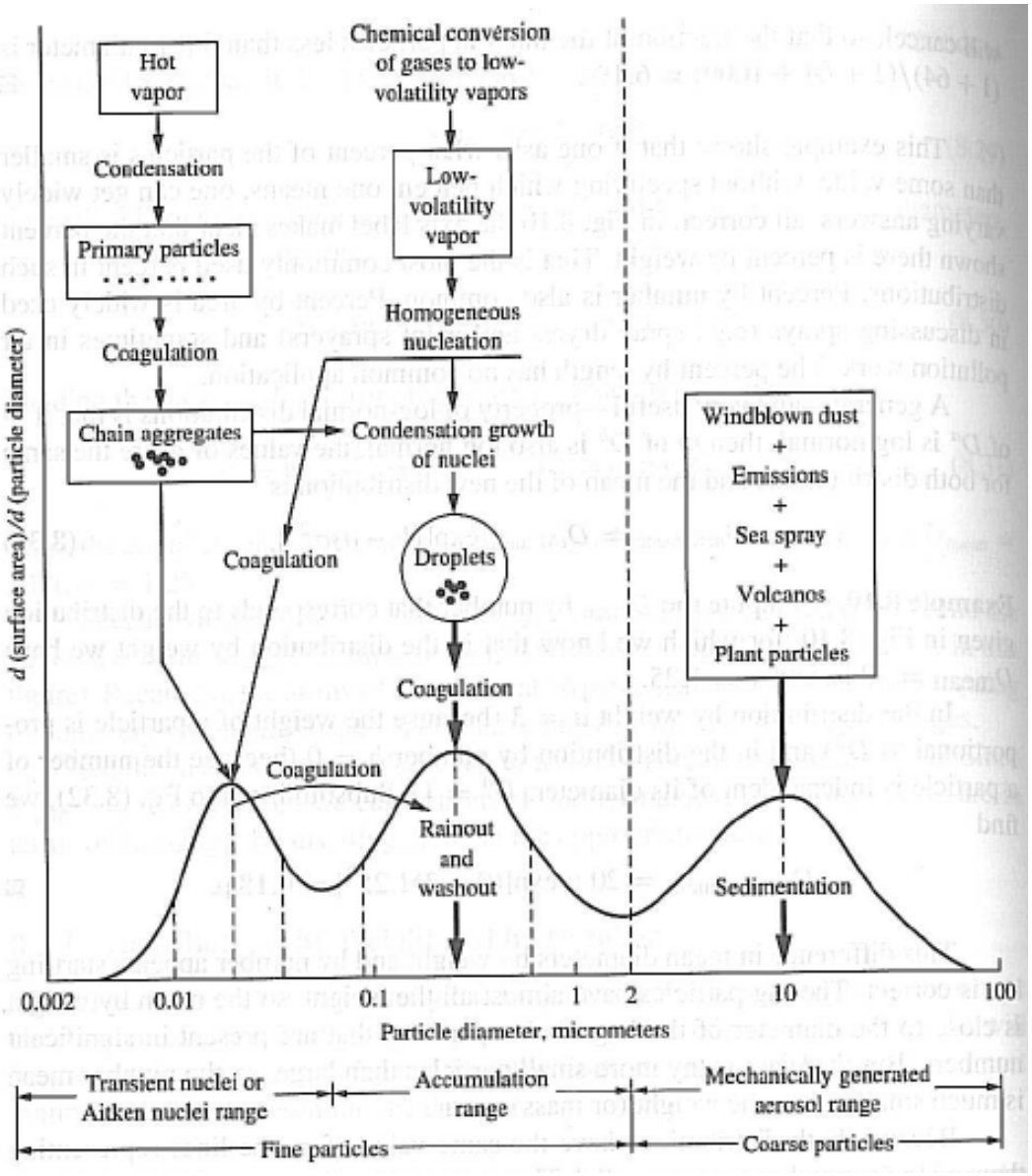


Particle sizes



Schneider, 2010

Particle formation mechanisms, surface area, and size



Seinfeld and Pandis, 2006

FUNDAMENTALS: PARTICLE MOTION

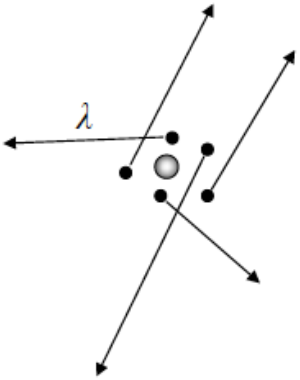
What affects the movement of particles?

Particle motion in gases: Size regime

- Continuum regime and free molecular regime
  - Behavior of a particle in a gas is characterized by the ratio of the mean free path of the gas molecules to the diameter of the particle
  - Ratio is called the Knudsen number (*Kn*):

$$Kn = \frac{2\lambda}{d_p}$$

d_p = particle diameter (μm)
λ = mean free path of air (0.066 μm @ STP)

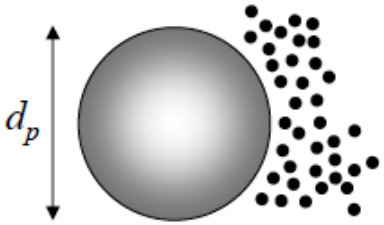


Free molecular regime
$Kn \rightarrow \infty$

$d_p < \sim 10$ nm

Transition regime
$Kn \approx 1$

10 nm < d_p < 1 µm



Continuum regime
$Kn << 1$

$d_p > \sim 1$ µm

Seinfeld and Pandis, 2006; Schneider, 2010

Particle motion in gases: Flow regime

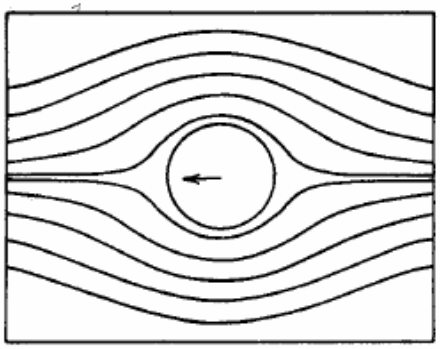
- Reynolds number:
  - Re is the ratio of inertial forces to frictional forces for fluid flow through a pipe or around an obstacle
  - For flow around a particle:

$$\mathrm{Re} = \frac{\rho_{air} V d_p}{\mu}$$

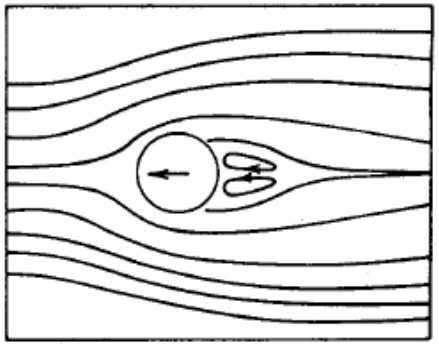
ρ_{air} = air density ($\mathrm{kg/m^3}$)
V = relative velocity between particle and air (m/s)
μ = dynamic viscosity of air (1.8×10^{-5} kg/(m-s) at STP)

  - For flow around a particle:
    - Re < 1: laminar flow (frictional forces dominate)
    - Re > 1: turbulent flow (inertial forces dominate)

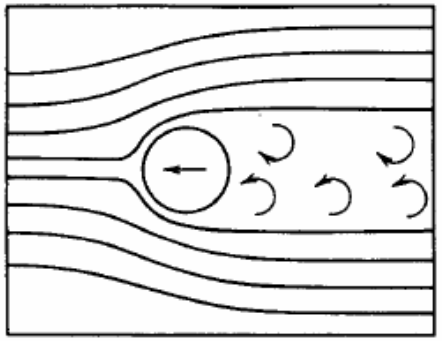
Hinds 1999



Re = 0.1 (a)



Re = 2 (b)



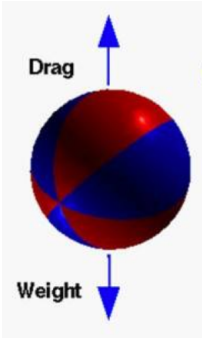
Re = 250 (c)

Particle motion in gases: Drag forces (large d_p)

- Newton's resistance law
  - Newton derived an equation for the force resisting the motion of a sphere passing through a gas:

$$F_D = C_D \frac{\pi}{8} \rho_{air} d_p^2 V^2$$

F_D = drag force (kg-m/s^2)
C_D = drag coefficient (-)



  - Assumes only inertia of air is important (not friction forces)
  - Therefore, this assumption is only valid for high Re (Re > 1000)
  - For smaller Re, the molecular viscous (friction) forces must be considered
    - Under laminar flow conditions (Re < 1), viscous forces dominate and inertial forces can be neglected
    - In this case, we use **Stokes' Law**

Particle motion in gases: Drag forces (small d_p)

- Stokes' law states that:

$$F_D = 3\pi\mu V d_p$$

V = particle velocity (m/s)

  - Valid for laminar flow around a solid sphere

- Comparing Newton's and Stokes' laws:

$$F_D = C_D \frac{\pi}{8} \rho_{air} d_p^2 V^2 = 3\pi\mu V d_p$$

$$C_D = \frac{24\mu}{\rho_{air} V d_p} = \frac{24}{\mathrm{Re}}$$

  - Therefore, in the Stokes' regime (Re < 1) the drag coefficient is 24/Re

Particle motion in gases

- Drag coefficient, C_D:

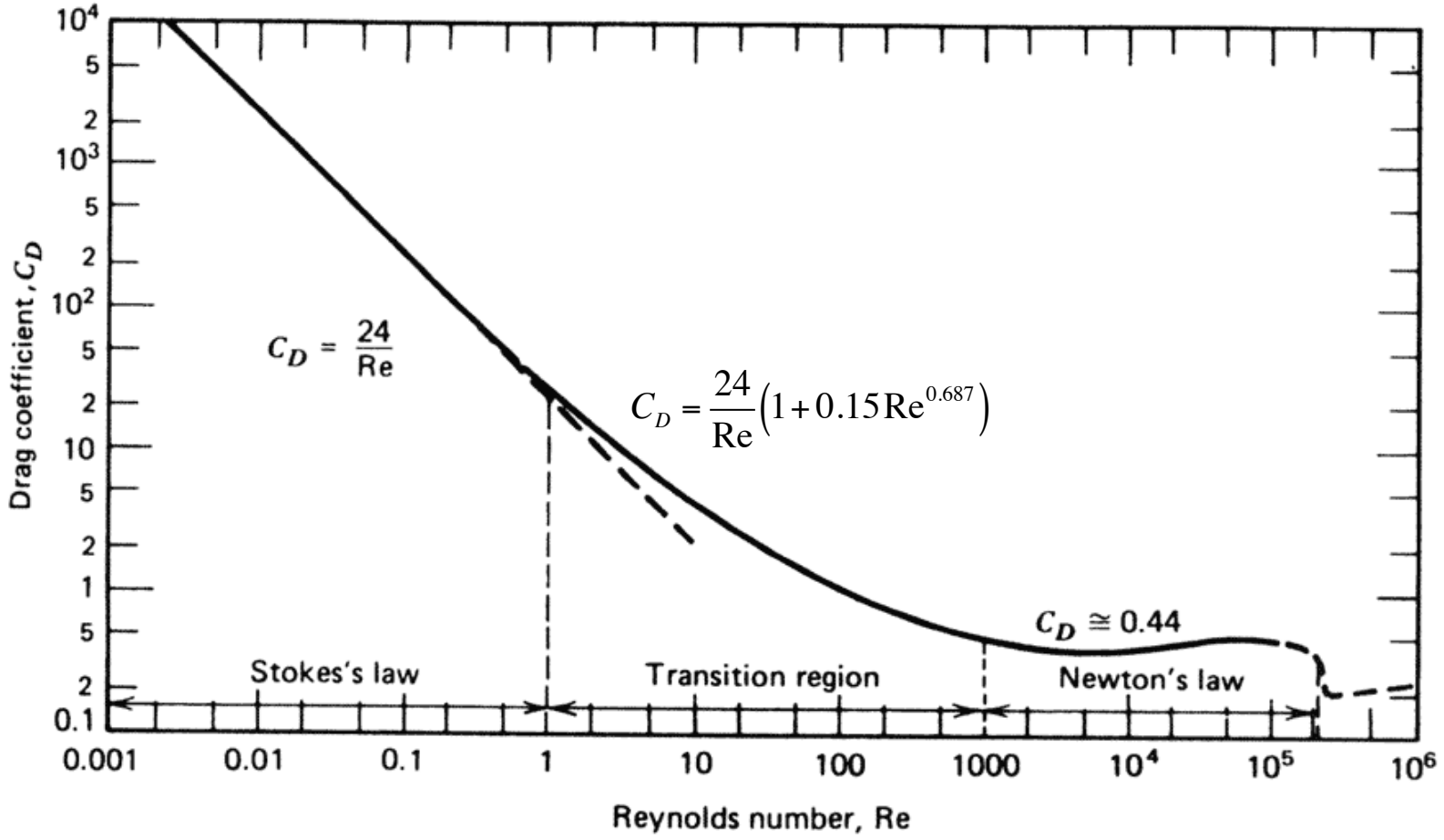


FIGURE 3.1 Drag coefficient versus Reynolds number for spheres.

Hinds 1999

Particle motion in gases: Typical Re values

- Re for various particle diameters at STP:
  - Reynolds numbers for particles in air falling at their terminal settling velocities at 298 K

Diameter (μm)	*Re*
0.1	7×10^{-9}
1	2.8×10^{-6}
10	2.5×10^{-3}
20	0.02
60	0.4
100	2
300	20

  - Almost all atmospheric aerosols are in the Stokes' regime and Stokes' law can be applied (i.e., d_p < ~80 μm)

Hinds 1999

Particle motion in gases: Stokes' regime

- Drag coefficient, C_D:

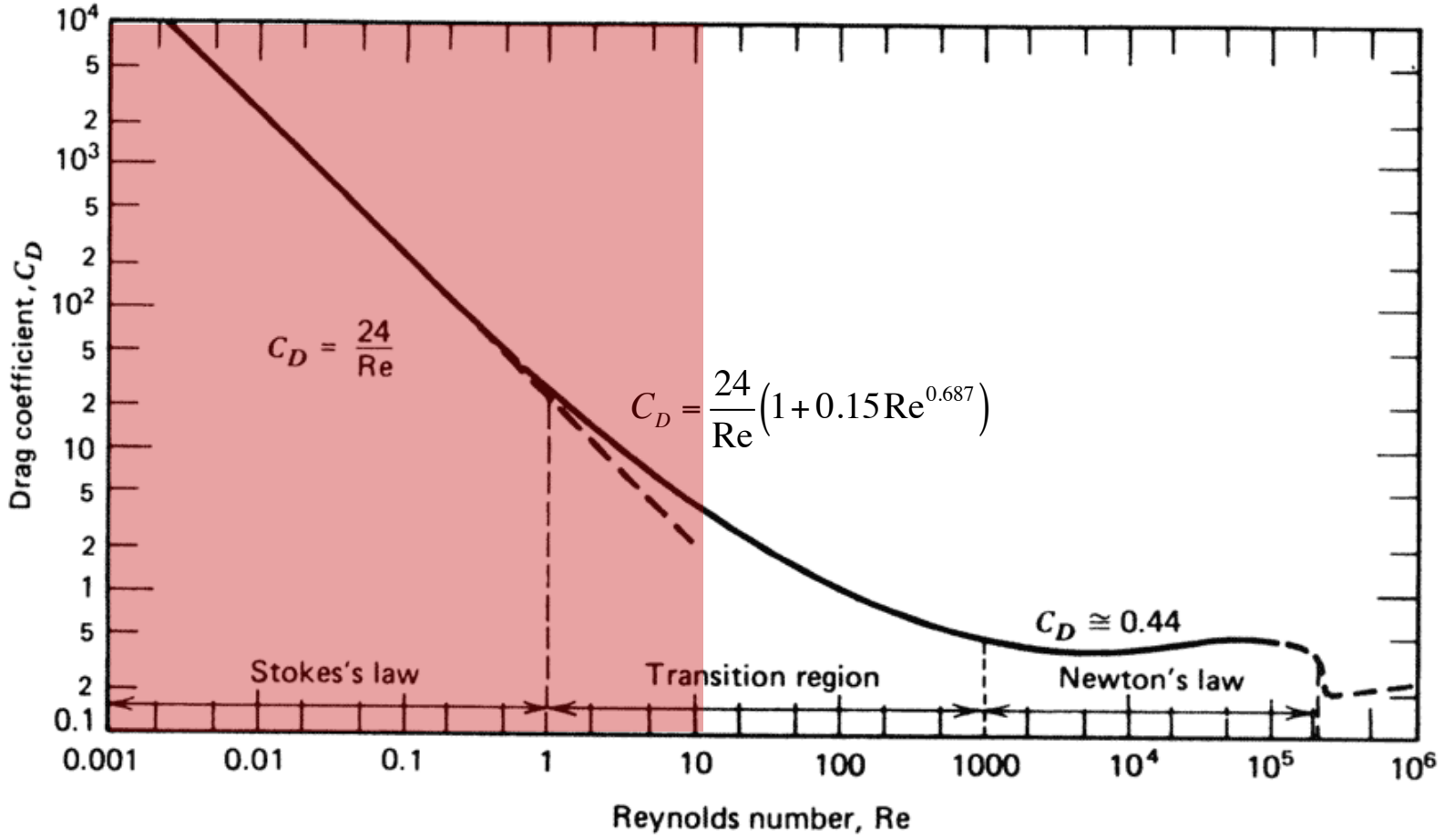


FIGURE 3.1 Drag coefficient versus Reynolds number for spheres.

Hinds 1999

Particle motion in gases: Newton's and Stokes' Laws

- When a particle is released into the air, it quickly reaches its "**terminal settling velocity**," V_{TS}
  - V_{TS} is a condition of constant velocity wherein the drag force of the air on the particle F_D is exactly equal but opposite to the force of gravity F_G

$$F_G = mg = \frac{\pi}{6}\rho_p d_p^3 g \qquad F_D = 3\pi\mu V d_p$$

$$\frac{\pi}{6}\rho_p d_p^3 g = 3\pi\mu V d_p$$

$$V_{TS} = \frac{\rho_p d_p^2 g}{18\mu}$$

Particle motion in gases

- In the derivation of Stokes' law, it is assumed that the relative velocity of the gas (air) at the surface of the particle is zero
- This doesn't hold for small particles whose size approaches the mean free path of air (Kn ≤ 1)
  - Particles less than about 1 μm
- Stokes' law must be corrected for "slip" conditions:
  - Cunningham slip correction factor, C_C:

$$F_D = \frac{3\pi\mu V d_p}{C_C}$$

$$C_C = 1 + \frac{\lambda}{d_p}\left(2.34 + 1.05e^{-0.39\frac{d_p}{\lambda}}\right)$$

Based on Kn → lets you use Stokes' law for all regimes

Particle motion in gases: V_{TS} with slip correction

$$F_G = mg = \frac{\pi}{6}\rho_p d_p^3 g \qquad F_D = \frac{3\pi\mu V d_p}{C_C}$$

$$\frac{\pi}{6}\rho_p d_p^3 g = \frac{3\pi\mu V d_p}{C_C}$$

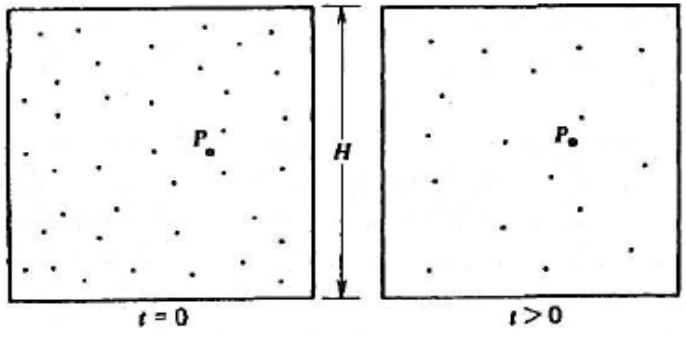
$$\boxed{V_{TS} = \frac{\rho_p d_p^2 g C_C}{18\mu}}$$

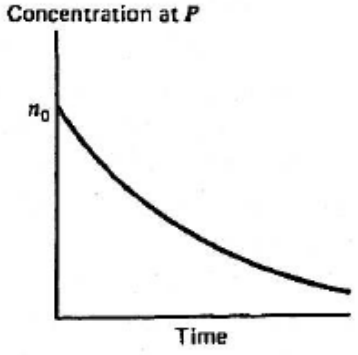
For Re < 1, which is true for most d_p < 100 μm

Particle motion in gases

- Terminal settling velocity for particles at STP

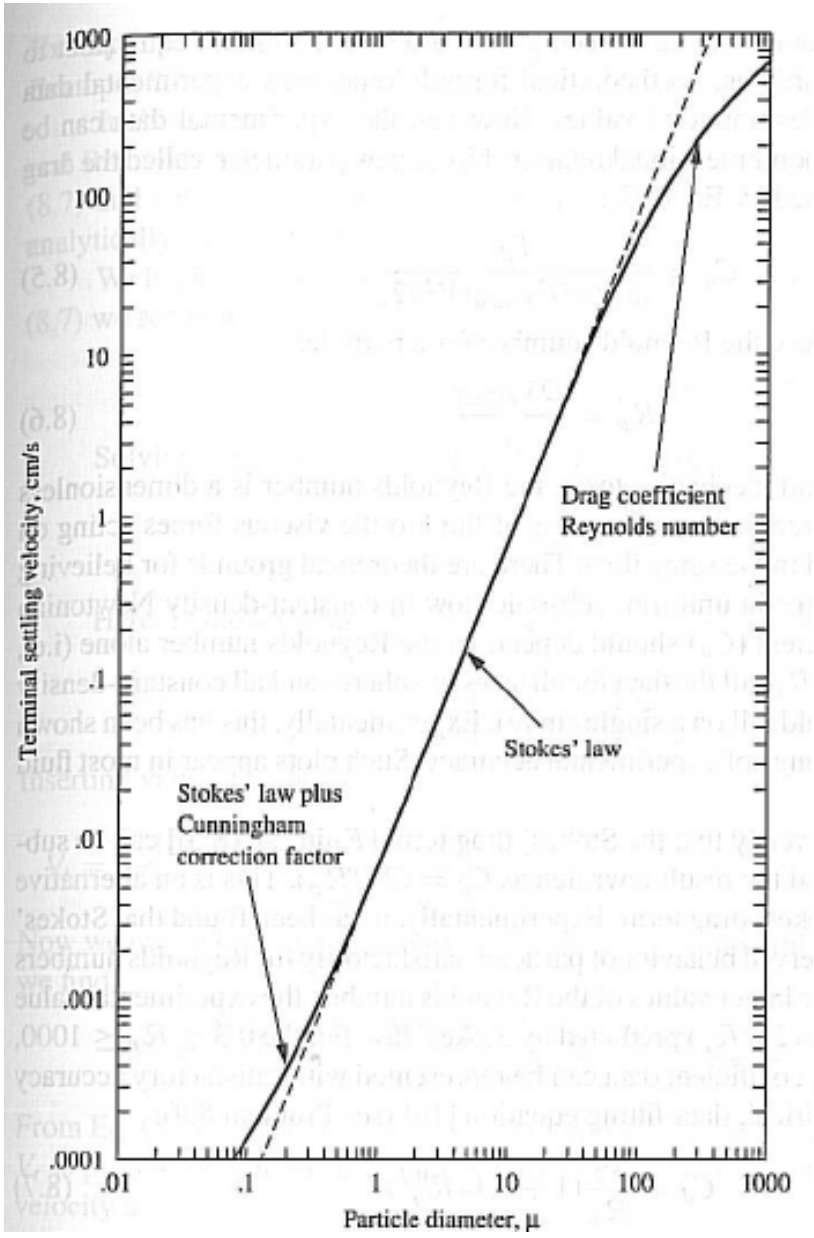
- What can we use V_{TS} for?
- Imagine "stirred settling"





$$N(t) = N_{t=0} e^{-\frac{V_{TS}}{H}t}$$

Larger particles settle out of the air faster



Particle motion in gases

- A few other important particle properties also exist:
  - Equivalent diameters
  - Aerodynamic diameters
  - Stokes diameters

Non-spherical particles: Equivalent diameters

- Many aerosol particles are not spherical
  - For example, soot particles, mineral dust, sea salt
- We can account for the effect of shape on particle motion by introducing a dynamic shape factor, χ:

Shape	Dynamic Shape Factor,[a] χ			
		Axial Ratio		
		2	5	10
Geometric Shapes				
Sphere	1.00			
Cube[b]	1.08			
Cylinder[b]				
Vertical axis		1.01	1.06	1.20
Horizontal axis		1.14	1.34	1.58
Orientation averaged		1.09	1.23	1.43
Straight chain[c]		1.10	1.35	1.68
Compact cluster				
Three spheres	1.15			
Four spheres	1.17			
Dusts				
Bituminous coal[d]	1.05–1.11			
Quartz[d]	1.36			
Sand[d]	1.57			
Talc[e]	1.88			

$$V_{TS} = \frac{\rho_p g C_C d_e^2}{18\mu\chi}$$

$$F_D = \frac{3\pi\mu V d_e}{C_C}\chi$$

d_e = volume equivalent diameter, or the diameter of a sphere having the same volume and density as the nonspherical particle

χ = ratio of the actual resisting force of the nonspherical particle to the resisting force a sphere of the same volume and density would have

Aerodynamic and Stokes diameters

Two other equivalent diameters are commonly used:

- The aerodynamic diameter (d_a) is the diameter of a spherical particle having the density of water (1 g/cm^3) and having the same settling velocity as the particle in question
- The Stokes diameter (d_s) is the diameter of a spherical particle having the same density and settling velocity as the particle in question

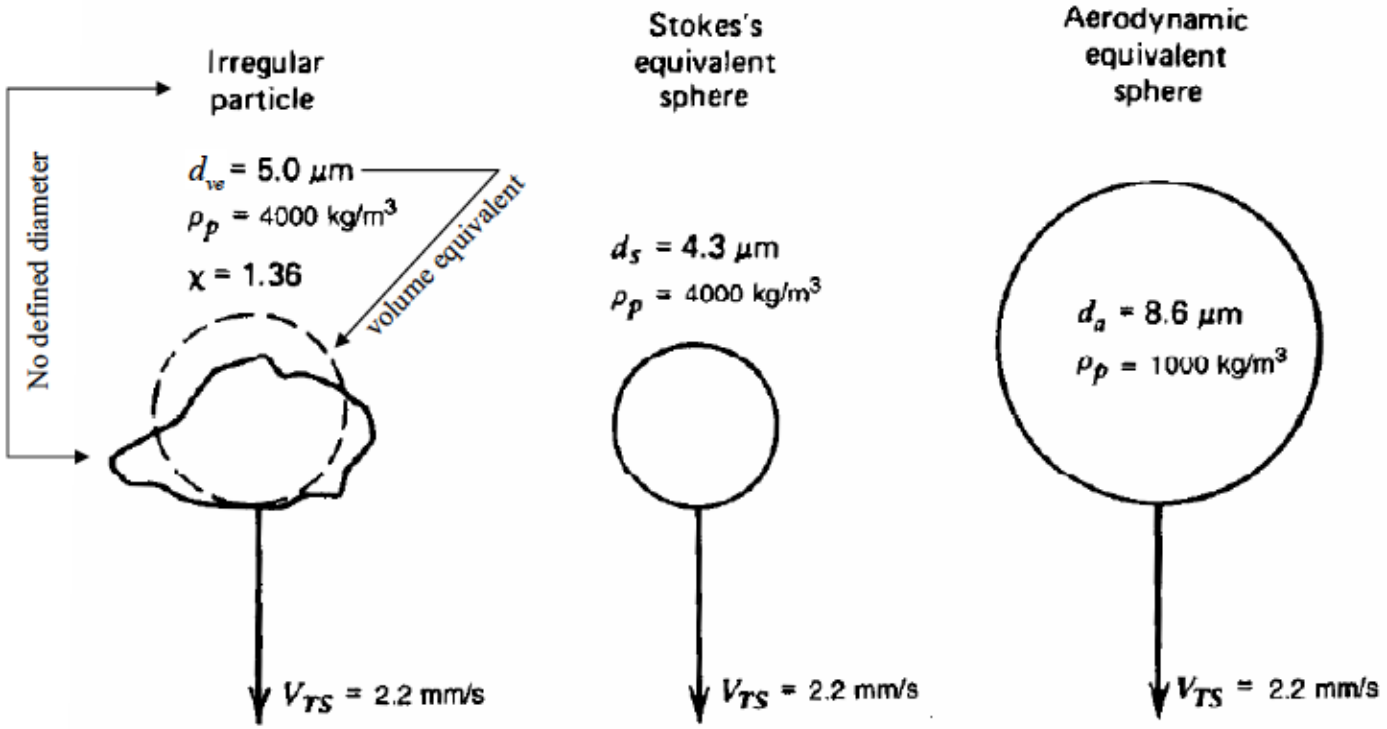
$$V_{TS} = \frac{\rho_p g C_C(d_e) d_e^2}{18\mu\chi} = \frac{\rho_0 g C_C(d_a) d_a^2}{18\mu} = \frac{\rho_p g C_C(d_s) d_s^2}{18\mu}$$

  - Note that C_C must be calculated as a function of the diameter you're using

Aerodynamic and Stokes diameters

- For particles with d_p > 1 μm we can assume C_C = 1:

$$\frac{\rho_p d_{ve}^2}{\chi} = \rho_p d_S^2 = \rho_0 d_a^2$$



Non-spherical particle and its equivalent diameters

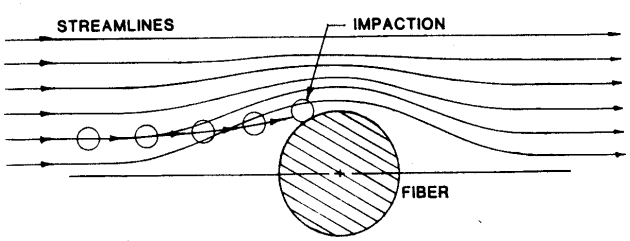
Other forces

- Other forces governing particle motion:
  - Gravity (already covered)
  - Inertial impaction
  - Brownian diffusion
  - Electrophoretic
  - Thermophoretic

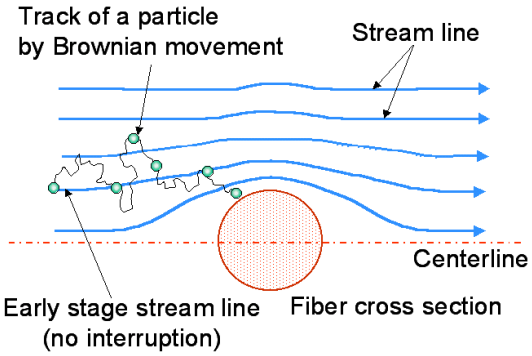
- We don't have time to cover these in full detail
  - But I will provide basic concepts and equations so we can understand what forces act to remove particles of various d_p from air

Other important forces

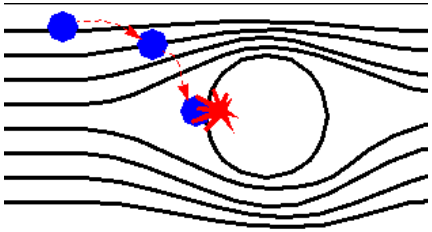
- **Inertial impaction**
  - Inertial transfer of particles onto surfaces
  - Important for larger particles: scales with d_p^2



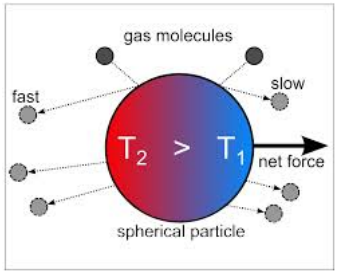
- **Brownian diffusion**
  - Movement by random molecular motion across a concentration gradient
  - Important for smaller particles: scales with $1/d_p$



- **Electrophoretic/electrostatic forces**
  - Particles can and do acquire charges and can be attracted to oppositely charged surfaces
  - Important for smaller particles: scales with $1/d_p$



- **Thermophoretic forces**
  - Particle movement driven by a temperature gradient
  - Weak function of d_p (but nearly constant for all d_p)



All forces combine to impact particle deposition

- More on this later, but these effects combine to influence particle deposition rates and rate constants
  - Particle deposition rate coefficient onto surfaces (1/hr): $k_{dep} = \frac{v_d A}{V}$

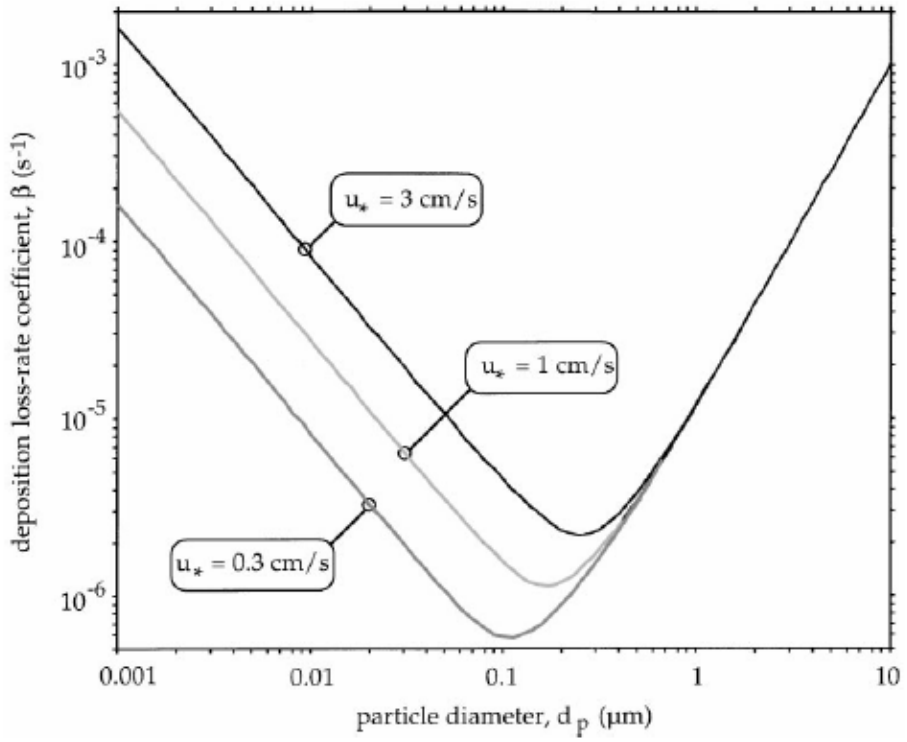


Fig. 5. Particle deposition loss-rate coefficient, β, for typical room dimensions (3 m high $\times$ 4 m $\times$ 5 m) according to the current model. Friction velocities of 0.3–3 cm s^{-1} approximately span the range expected for mechanically ventilated indoor spaces. Predictions assume air pressure is 1 atm, temperature is 293 K and particle density is 1.0 g cm^{-3}.

*Note that 'friction velocity' is a function of the ratio of shear stress at a surface to air density

Lai and Nazaroff 2000 *J Aerosol Sci*

PARTICLE SIZE DISTRIBUTIONS

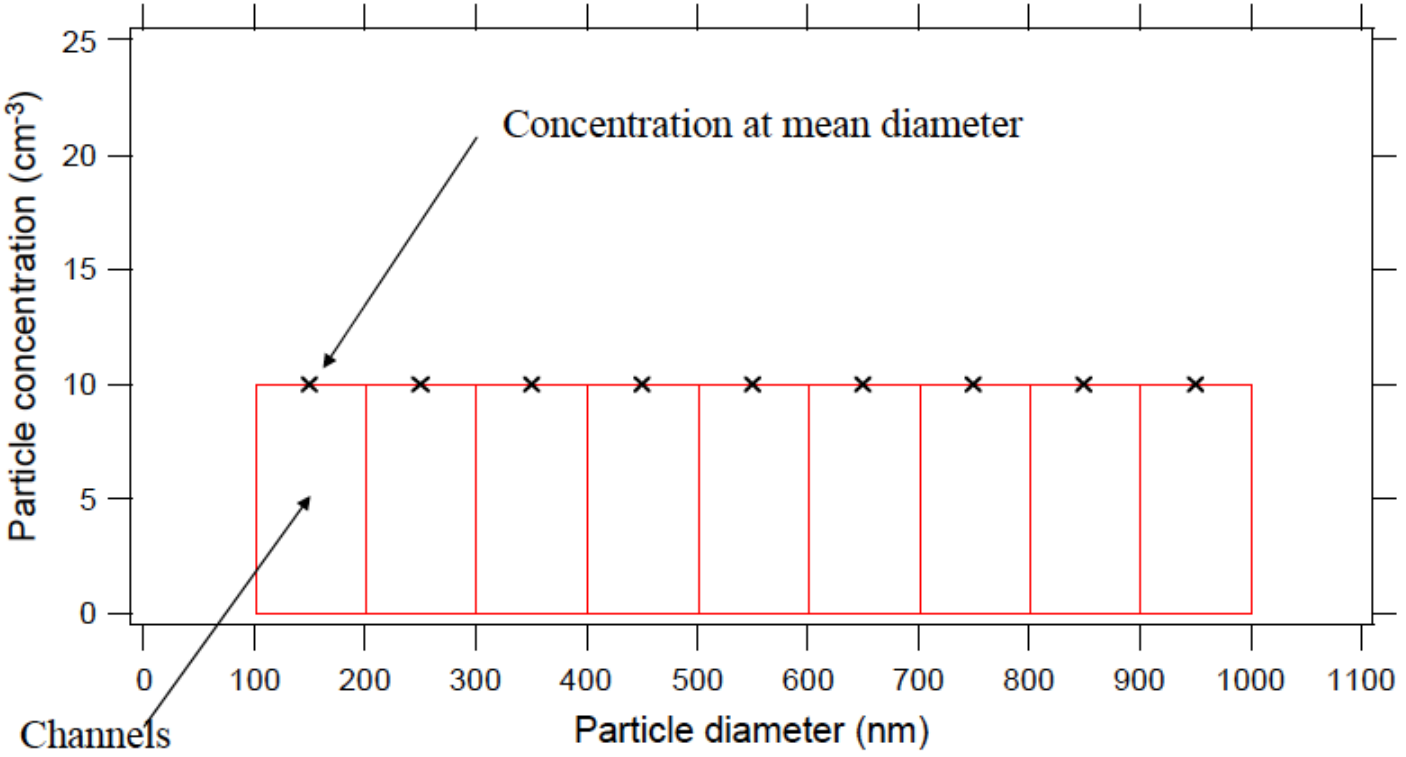
Size distributions

- A monodisperse aerosol (i.e., all particles have the same size) does not exist in the ambient atmosphere
  - Not indoors or outdoors

- What we have are polydispersed aerosols
  - So we need to describe the sizes of aerosol particles with a particle size distribution (PSD), which gives the concentration of particles as a function of particle diameter
  - Practically, a number concentration is determined between ranges of particle sizes: e.g., in the range $d_{p2} - d_{p1}$ or Δd_p or $\mathrm{d}d_p$
    - Number of particles with diameters between d_{p2} and d_{p1}

Size distributions

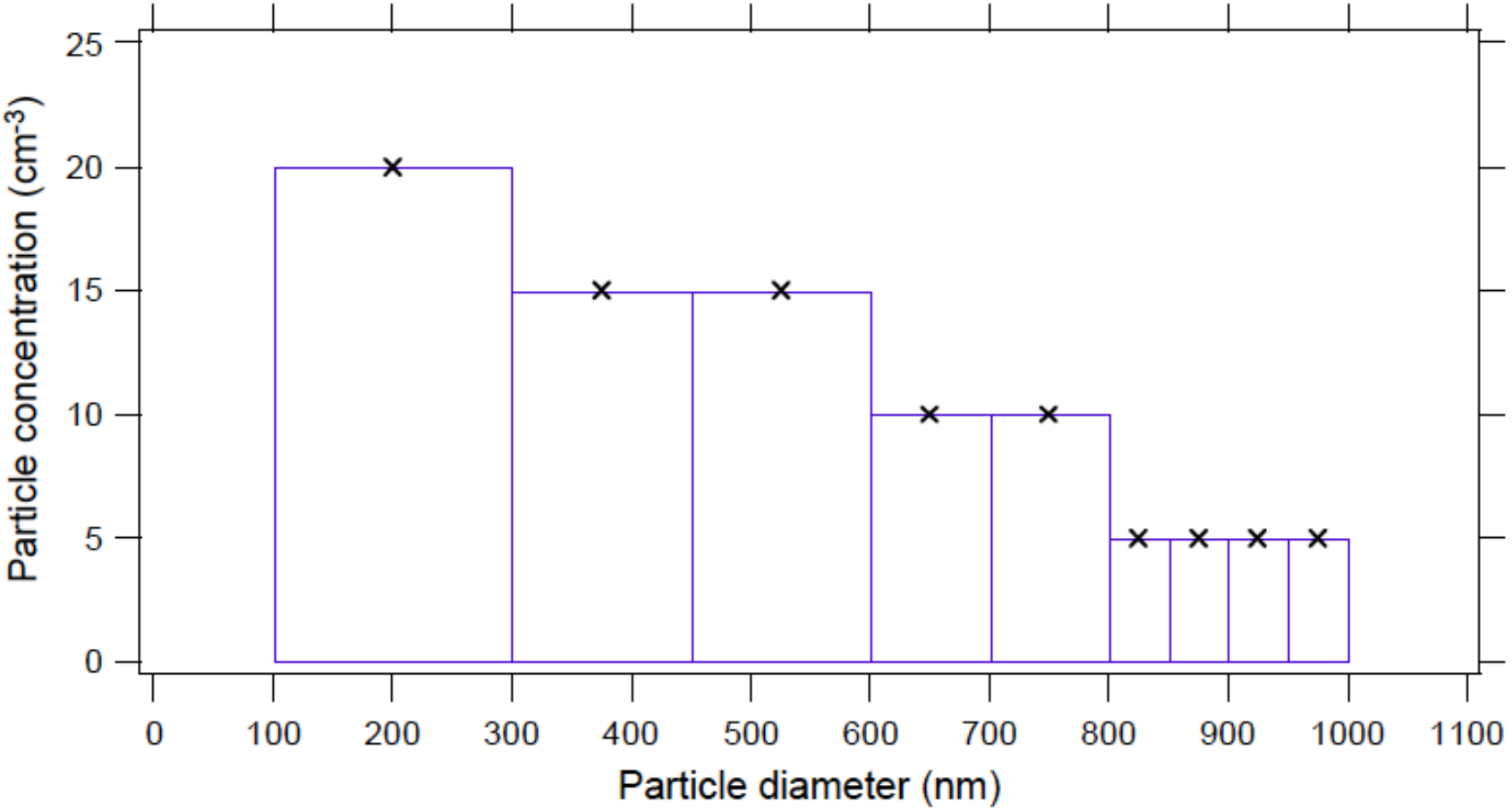
- Example instrument: 9 size channels, width of 100 nm each, each with 10 particles per cm^3
- We consider the measured concentration as dN in each channel



Schneider, 2010

Size distributions

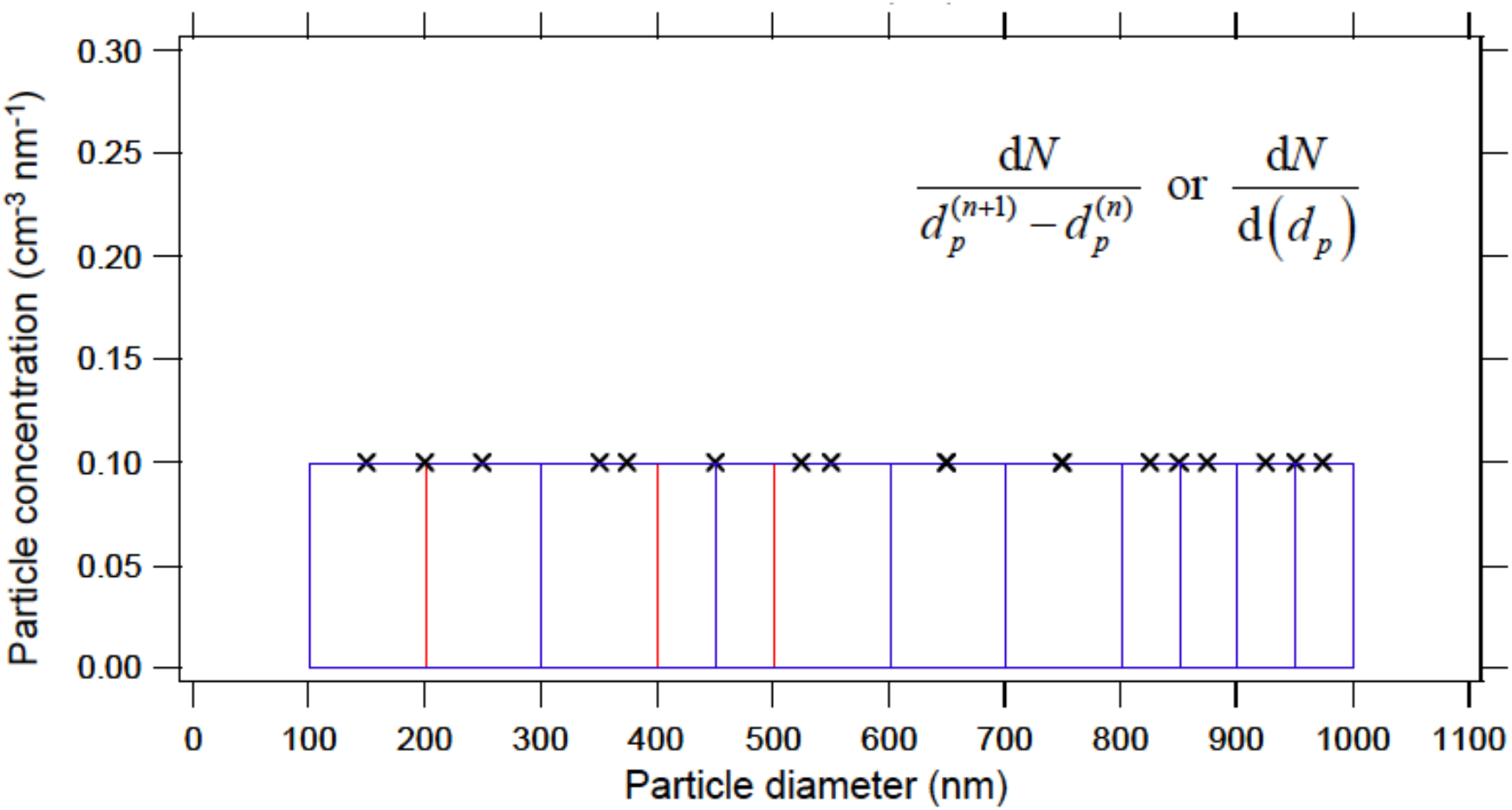
- If we use a different instrument with different channel widths, the shape of the distribution changes:



Schneider, 2010

Size distributions

- To avoid this sizing effect, we divide the measured concentrations (dN) by the width of the size channels



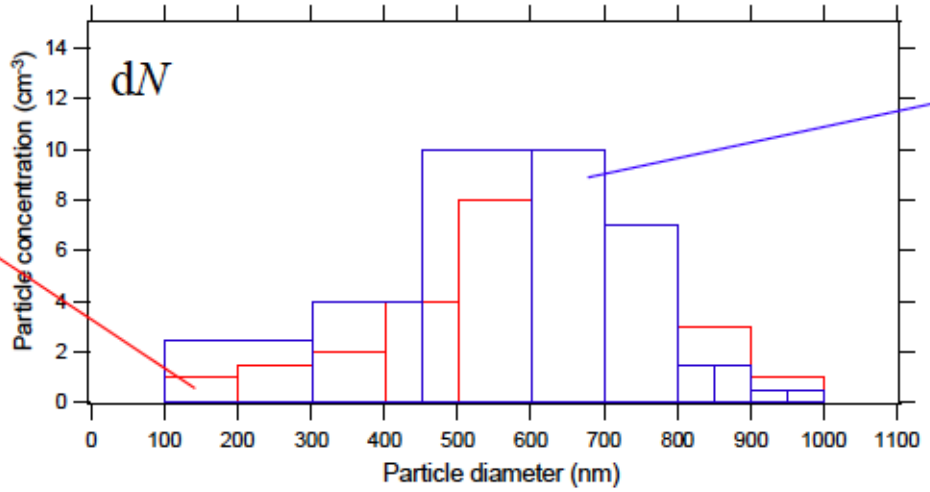
Schneider, 2010

Size distributions

- Similar example but for a more realistic size distribution

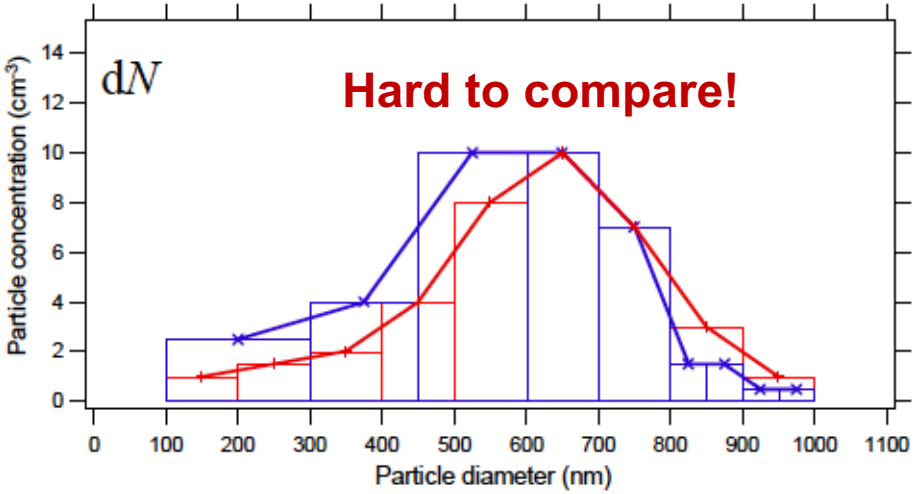
"Instrument 1"

Channel	N (cm^{-3})
100-200	1
200-300	1.5
300-400	2
400-500	4
500-600	8
600-700	10
700-800	7
800-900	3
900-1000	1



"Instrument 2"

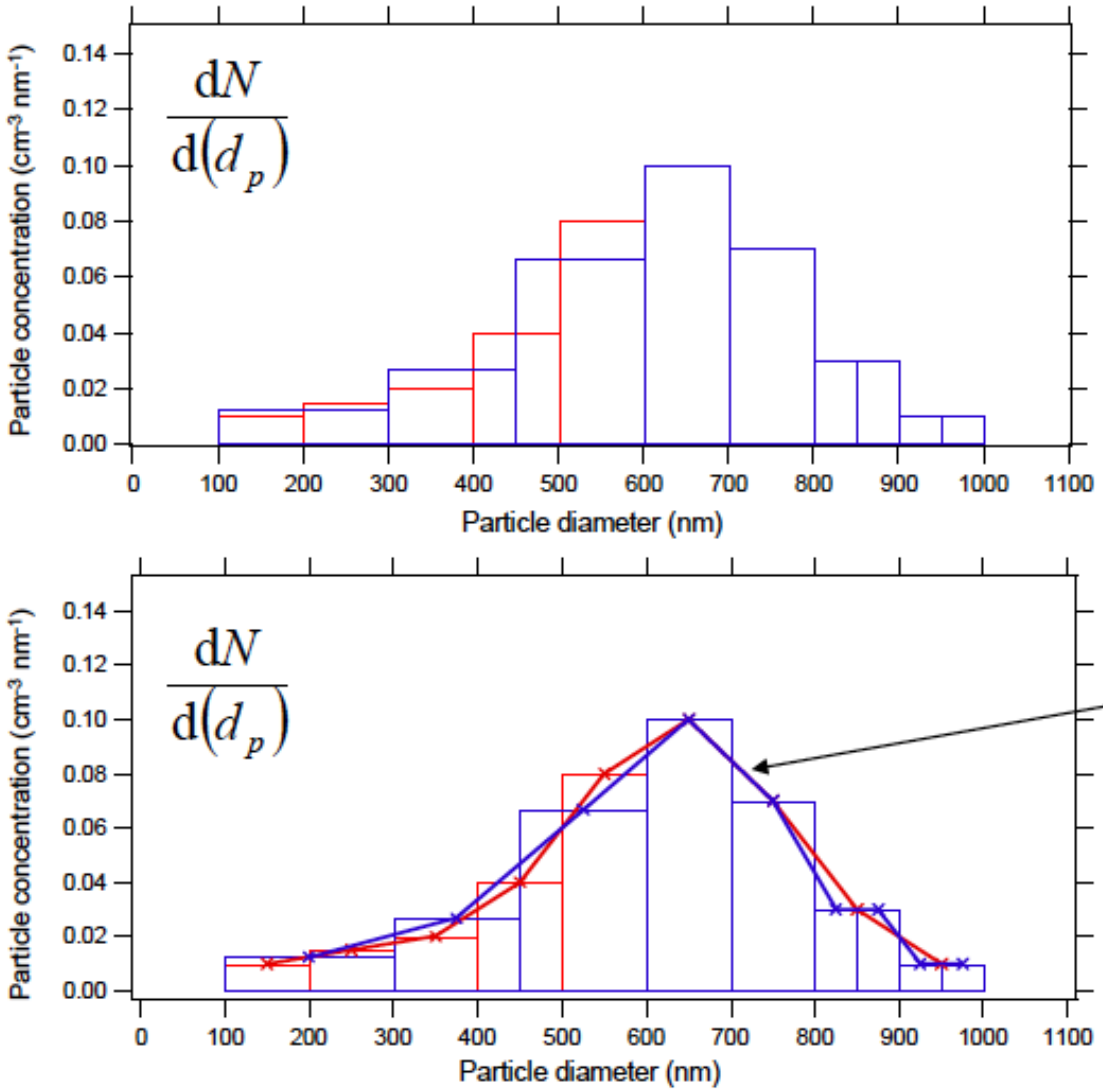
Channel	N (cm^{-3})
100-300	2.5
300-450	4
450-600	10
600-700	10
700-800	7
800-850	1.5
850-900	1.5
900-950	0.5
950-1000	0.5



Schneider, 2010

Size distributions

- Divide by the channel widths… (better)



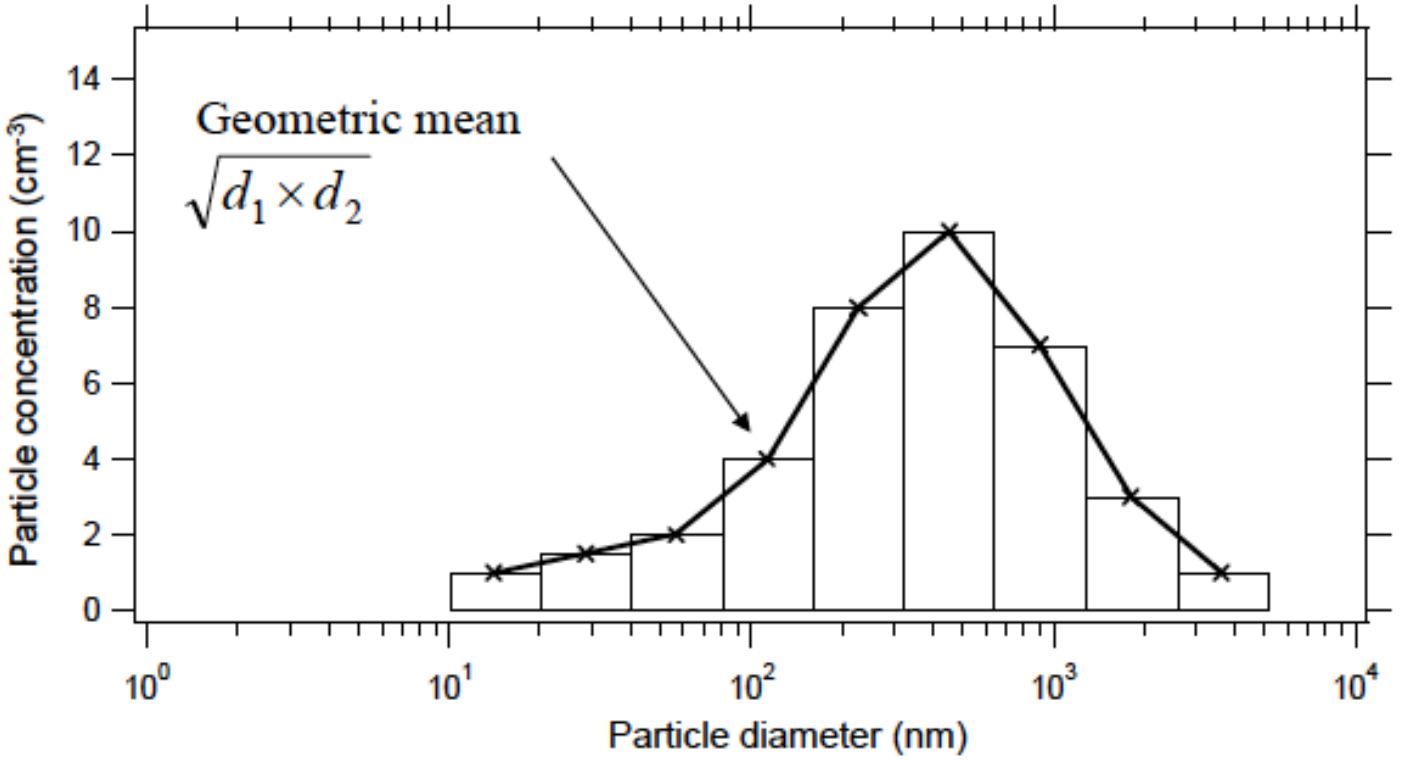
Almost the same distribution despite different measurement channels for the two instruments

Schneider, 2010

Size distributions

- Since the size of aerosol particles typically ranges over **several orders of magnitude**, we commonly use log scales for the x-axis (d_p) and refer to particle size bins by their geometric mean diameter

Channel	N (cm^{-3})
10-20	1
20-40	1.5
40-80	2
80-160	4
160-320	8
320-640	10
640-1280	7
1280-2560	3
2560-5120	1



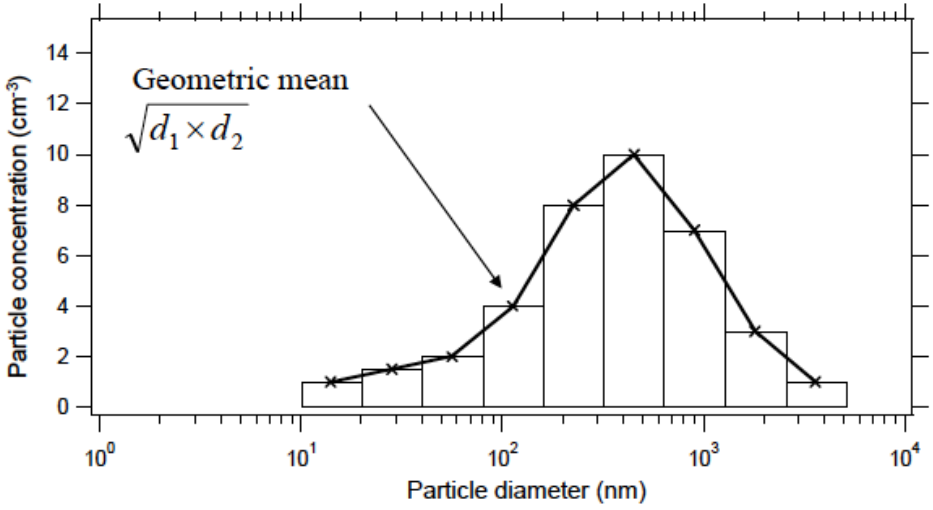
Schneider, 2010

Size distributions

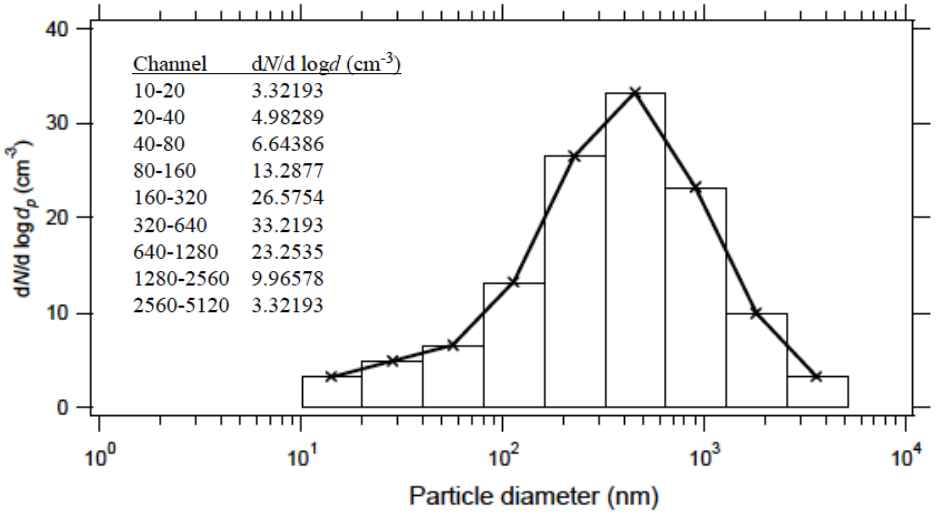
- For log scales we need to account for the channel width differently:

$$\frac{\mathrm{d}N}{\mathrm{d}\log d_p} = \frac{\mathrm{d}N}{\log(d_{p,upperbound}) - \log(d_{p,lowerbound})}$$

So this…



Becomes this…



We have transformed dN into dN/dlogd$_p$,
but the graphs **scale similarly**

Schneider, 2010

Number, surface area, volume, and mass distributions

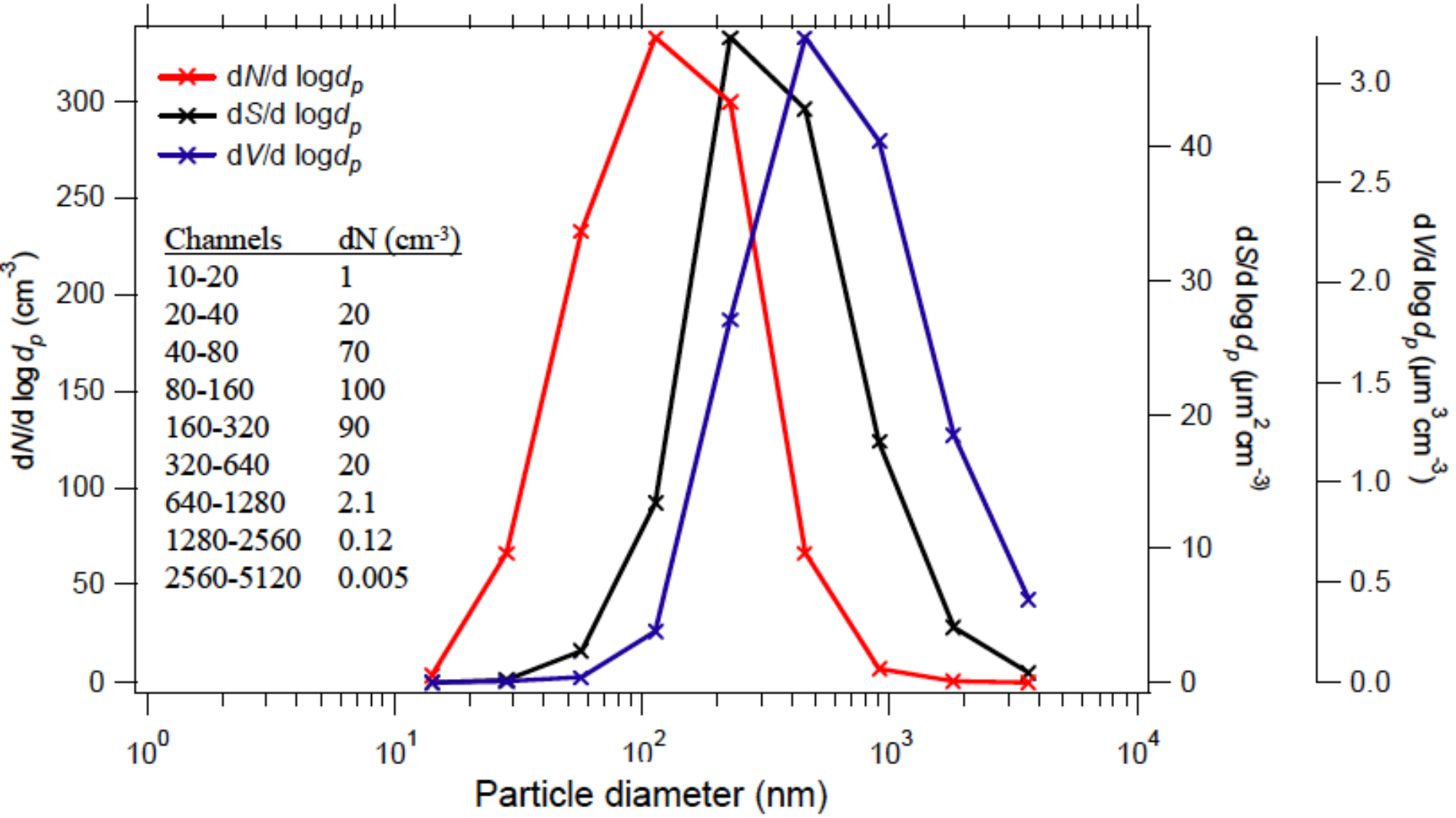
- Assuming spherical particles, the number concentration for each particle diameter can be converted to surface and volume concentrations:

- Surface area (μm2 per cm^3): $dS = \pi d_p^2 dN$

- Volume (μm^3 per cm^3): $dV = \frac{\pi}{6} d_p^3 dN$

- If we know particle density
  - We can estimate the mass distribution (μg per cm^3): $dM = \rho_p \frac{\pi}{6} d_p^3 dN$

Number, surface area, volume, and mass distributions



Schneider, 2010

Describing distributions mathematically

- Let $n(D_p)$ = size distribution function ($\mu m^{-1}\ cm^{-3}$)
- Let $dN = n(D_p)dD_p$ = number of particles per unit volume of air having diameters in the range D_p to $(D_p + dD_p)$
- Total number of particles per unit volume of air is:

$$N = \int_0^\infty n(D_p)dD_p \quad [\#/cm^3]$$

Describing distributions mathematically

- Because particle diameters in an aerosol often vary over several orders of magnitude, it is usually most convenient to express the size distribution in terms of the logarithm of the particle diameter
  - Either ln(Dp) or log(Dp)

- Define: $$dN = n(\log D_p)\, d\log D_p$$
  - Where dN = the number of particles per cm^3 of air in the size range of $\log D_p$ to $\log D_p + d\log D_p$
  - Note: $$n(\log D_p) \neq n(D_p)$$

Describing distributions mathematically

- Total number of particles is therefore:

$$N = \int_{-\infty}^{\infty} n(\log D_p)\, d\log D_p \quad [\#\ cm^{-3}]$$

- Normalized size distribution function with respect to $\log D_p$:

$$\tilde{n}(\log D_p) = \frac{n(\log D_p)}{N} \quad [\text{dimensionless}]$$

- Generic log-normal distributions:
  - If quantity u is log-normally distributed, the probability density function for u obeys a Gaussian distribution:

$$n(u) = \frac{N}{\sigma_u \sqrt{2\pi}} \exp\left[-\frac{(u - \bar{u})^2}{2\sigma_u^2} \right]$$

$\bar{u}$ = mean
σ^2 = variance
σ = std dev

Describing distributions mathematically

- For our purposes, replace $\bar{u}$ with the arithmetic mean of $\ln D_p$, which is defined as the geometric mean diameter D_g:

$$\ln D_g = \frac{\sum n_i \ln D_{p,i}}{N}$$

- And the standard deviation, σ, is replaced by the standard deviation of the logarithms, called the geometric standard deviation, σ_g:

$$\ln \sigma_g = \frac{\left[\sum n_i (\ln D_i - \ln Dg)^2\right]^{1/2}}{N-1}$$

Describing distributions mathematically

- The size distribution function, $n(D_p)$, can now be described following a log-normal distribution:

$$n(Dp) = \frac{N}{D_p \times (\ln \sigma_g)\sqrt{2\pi}} \exp\left[\frac{-(\ln D_p - \ln D_g)^2}{2(\ln \sigma_g)^2}\right]$$

  - Where the aerosol can be described with only 3 parameters:

N: Total particle number concentration
σ_g: Geometric standard deviation
$\bar{d}_g$: Geometric mean diameter

d_g is in units of μm
$\ln(d_g)$ or $\log(d_g)$ is dimensionless
σ_g is dimensionless with a value greater than or equal to 1.0

Schneider, 2010

Describing distributions mathematically

- Then, the cumulative distribution of an aerosol can then be characterized as follows:

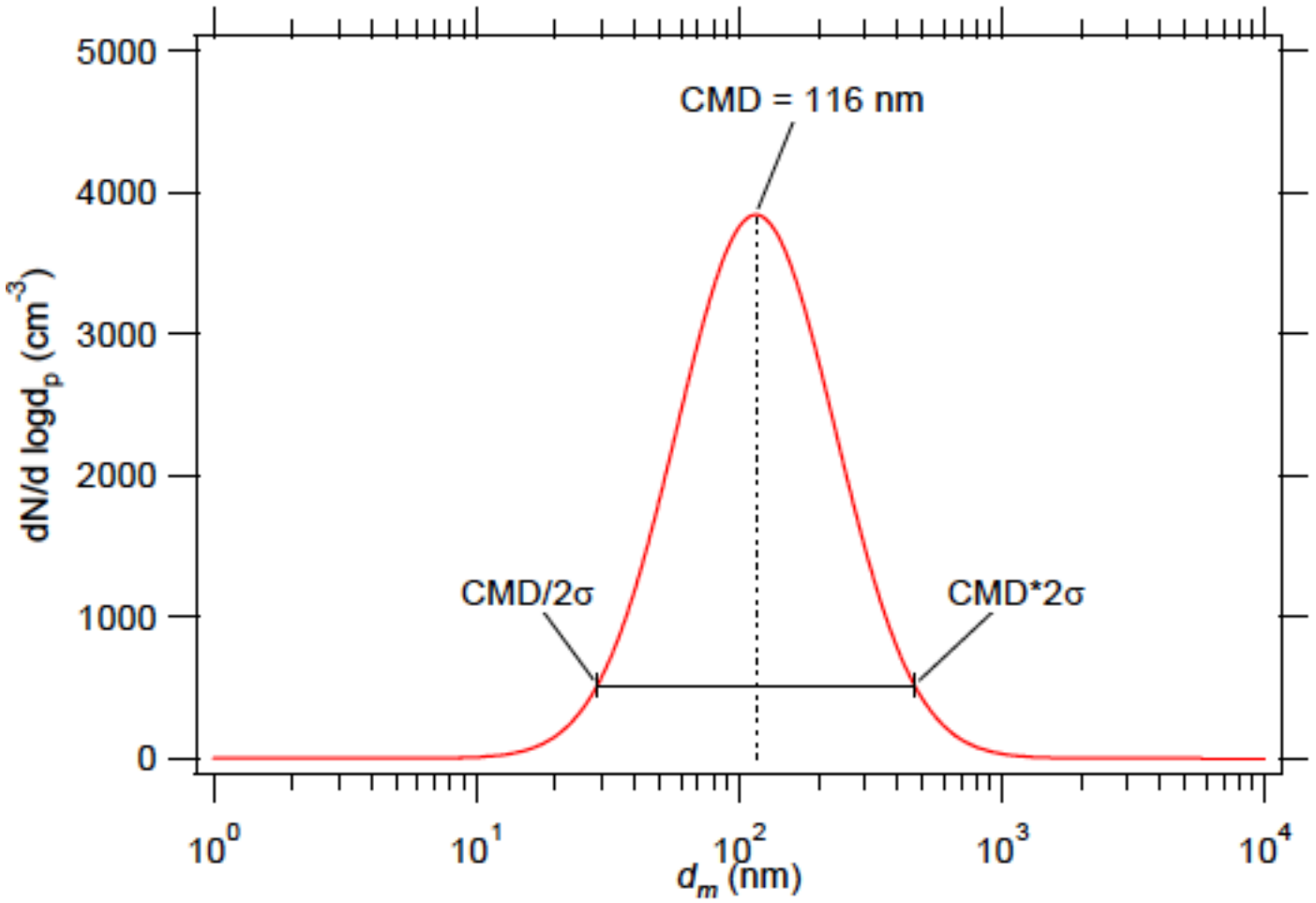
$$F(Dp) = \frac{N}{2} + \frac{N}{2} erf\left[\frac{\ln\left(D_p / D_g\right)}{\ln \sigma_g \times \sqrt{2}}\right]$$

$F(D_p)$ is in units of #/cm^3

- If a lognormal distribution based on number, then D_g is known as the count mean diameter (CMD), or the particle size for which half the total number of particles is larger and half is smaller
  - Mass median diameter (MMD) if distribution is based on mass

Lognormal distribution

- 95% of particles are in a size range given by: $e^{\ln \bar{d}_g \pm 2 \ln \sigma_g}$



Schneider, 2010

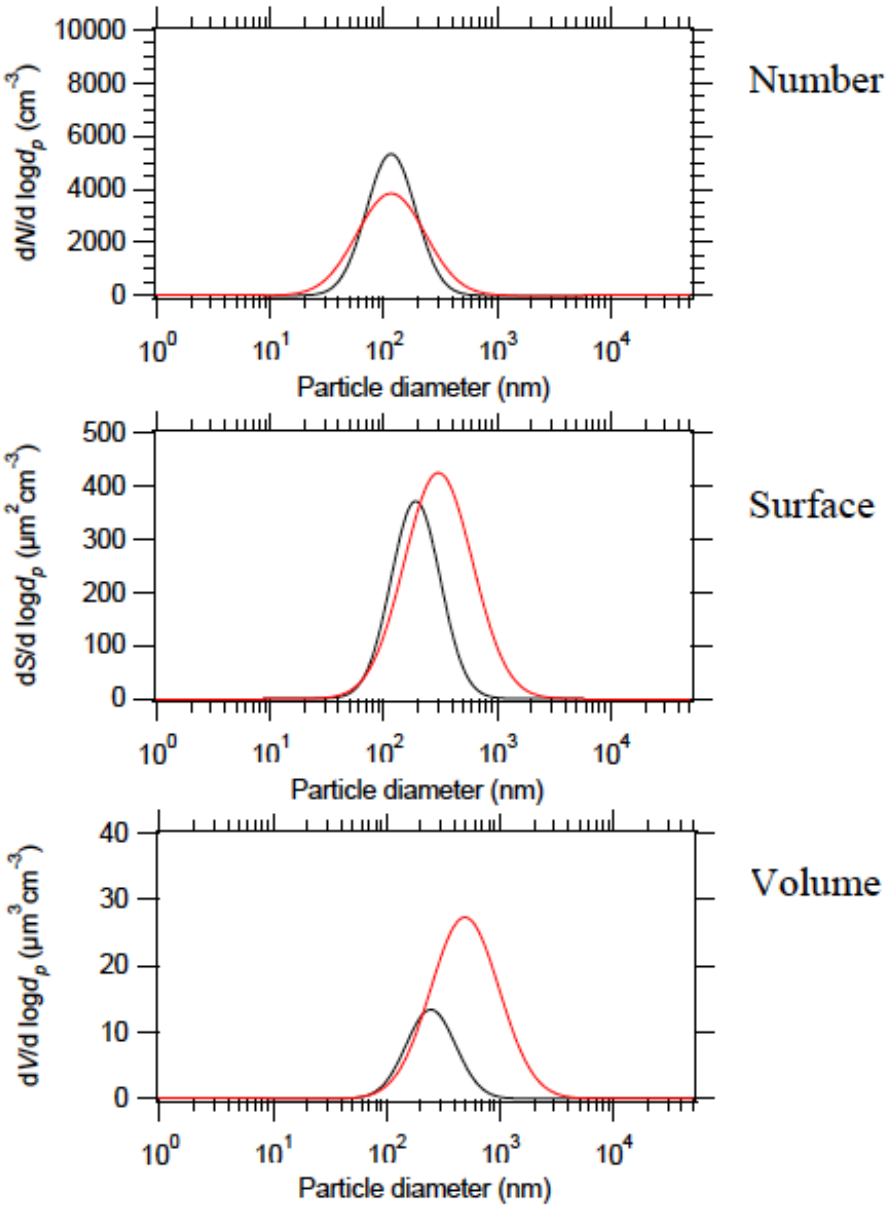
Lognormal distribution: dN, dS, and dV

- Example distribution for one ‘mode’:

$$N = 2900 \text{ cm}^{-3}$$

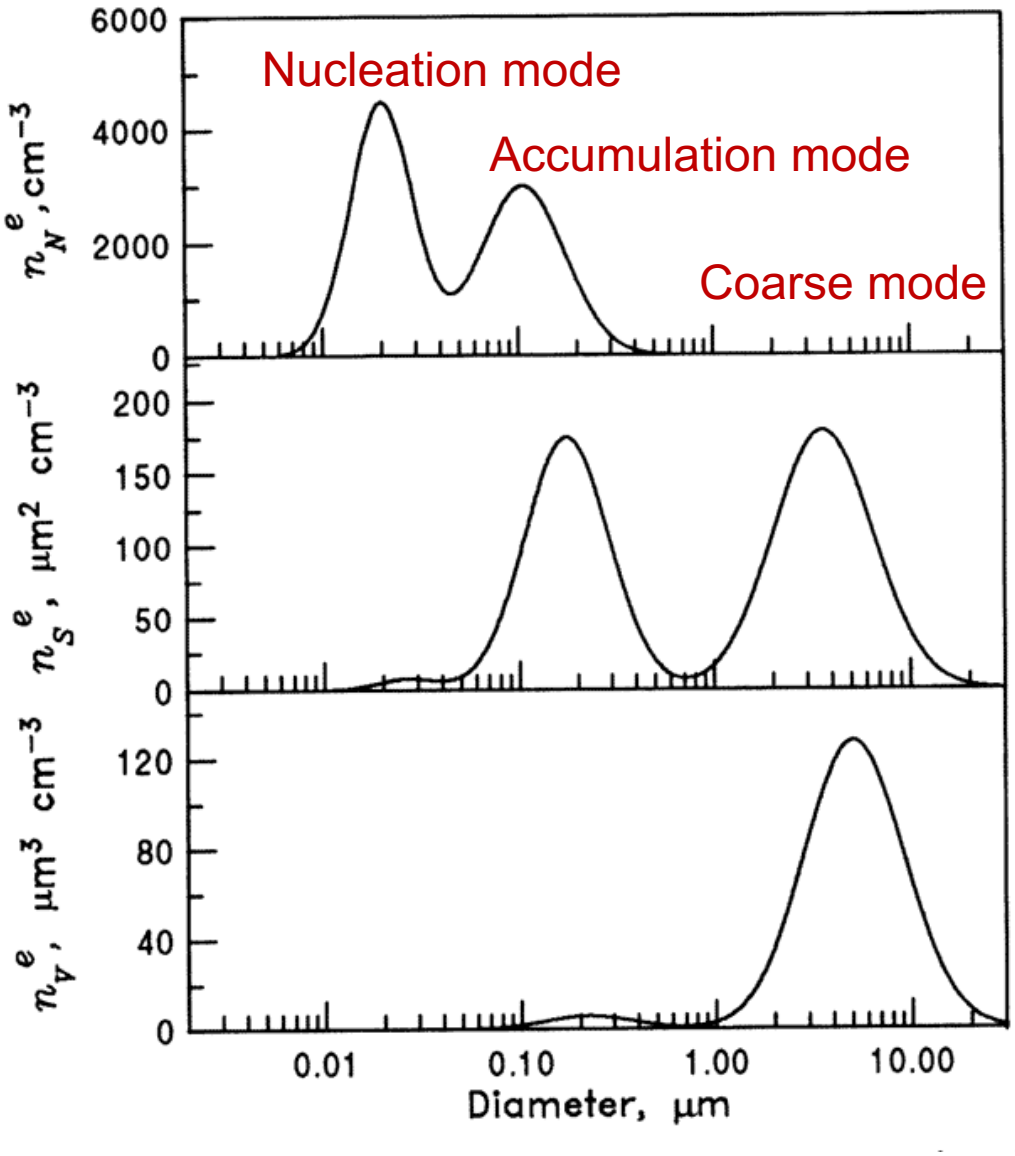
$$\sigma_g = 1.65 \quad \sigma_g = 2.0$$

$$\bar{d}_g = 116 \text{ nm}$$



Schneider, 2010

Typical aerosol distributions include multiple ‘modes’



Number

Surface area

Volume

Lognormal distributions: Summing across modes

$$\frac{dN}{d\log d_p} = \sum_{i=1}^{n} \frac{N_i}{\sqrt{2\pi}\log\sigma_i} e^{\left(-\frac{(\log d_p - \log \bar{d}_{g,i})^2}{2(\log\sigma_i)^2}\right)}$$

	Mode I			Mode II			Mode III		
Type	N (cm^{-3})	D_p (μm)	$\log\sigma$	N (cm^{-3})	D_p (μm)	$\log\sigma$	N (cm^{-3})	D_p (μm)	$\log\sigma$
Urban	9.93×10^4	0.013	0.245	1.11×10^3	0.014	0.666	3.64×10^4	0.05	0.337
Marine	133	0.008	0.657	66.6	0.266	0.210	3.1	0.58	0.396
Rural	6650	0.015	0.225	147	0.054	0.557	1990	0.084	0.266
Remote continental	3200	0.02	0.161	2900	0.116	0.217	0.3	1.8	0.380
Free troposphere	129	0.007	0.645	59.7	0.250	0.253	63.5	0.52	0.425
Polar	21.7	0.138	0.245	0.186	0.75	0.300	3×10^{-4}	8.6	0.291
Desert	726	0.002	0.247	114	0.038	0.770	0.178	21.6	0.438

Source: Jaenicke (1993).

Seinfeld and Pandis, 2006

Typical outdoor PSDs

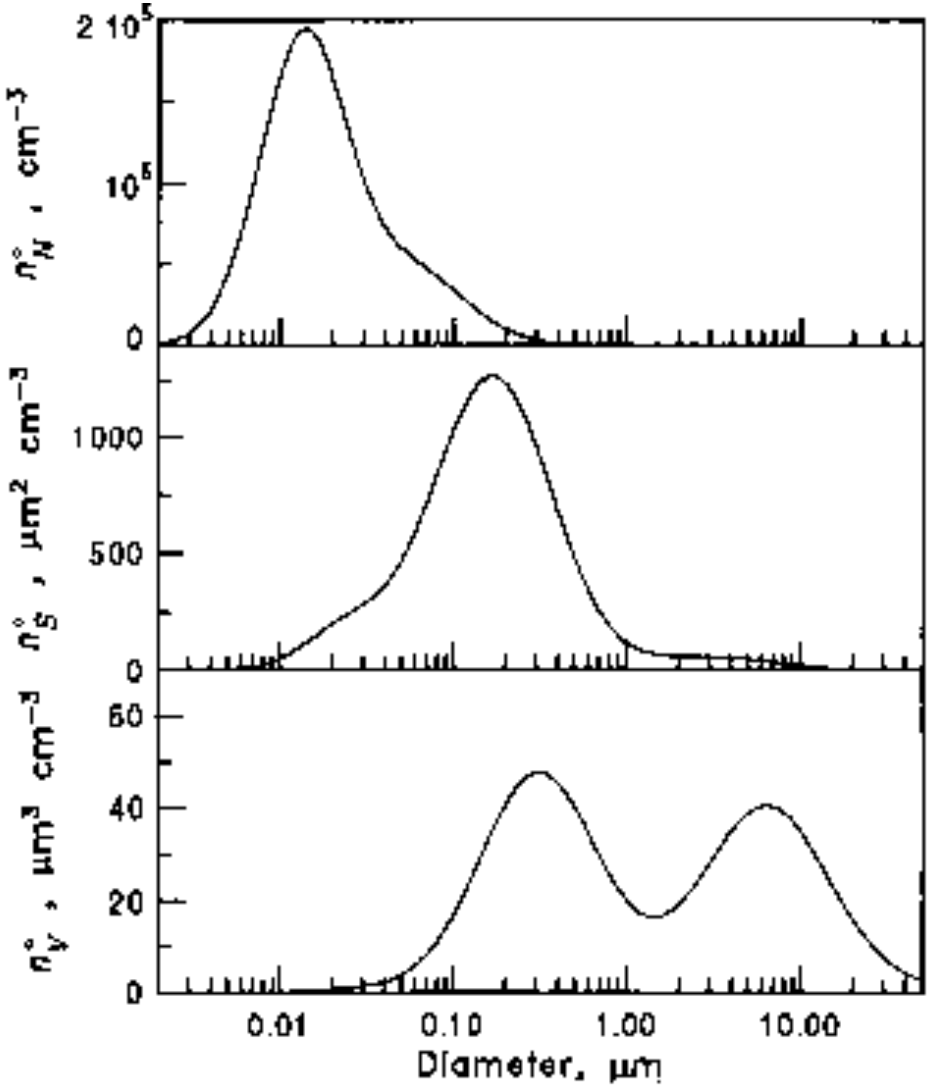
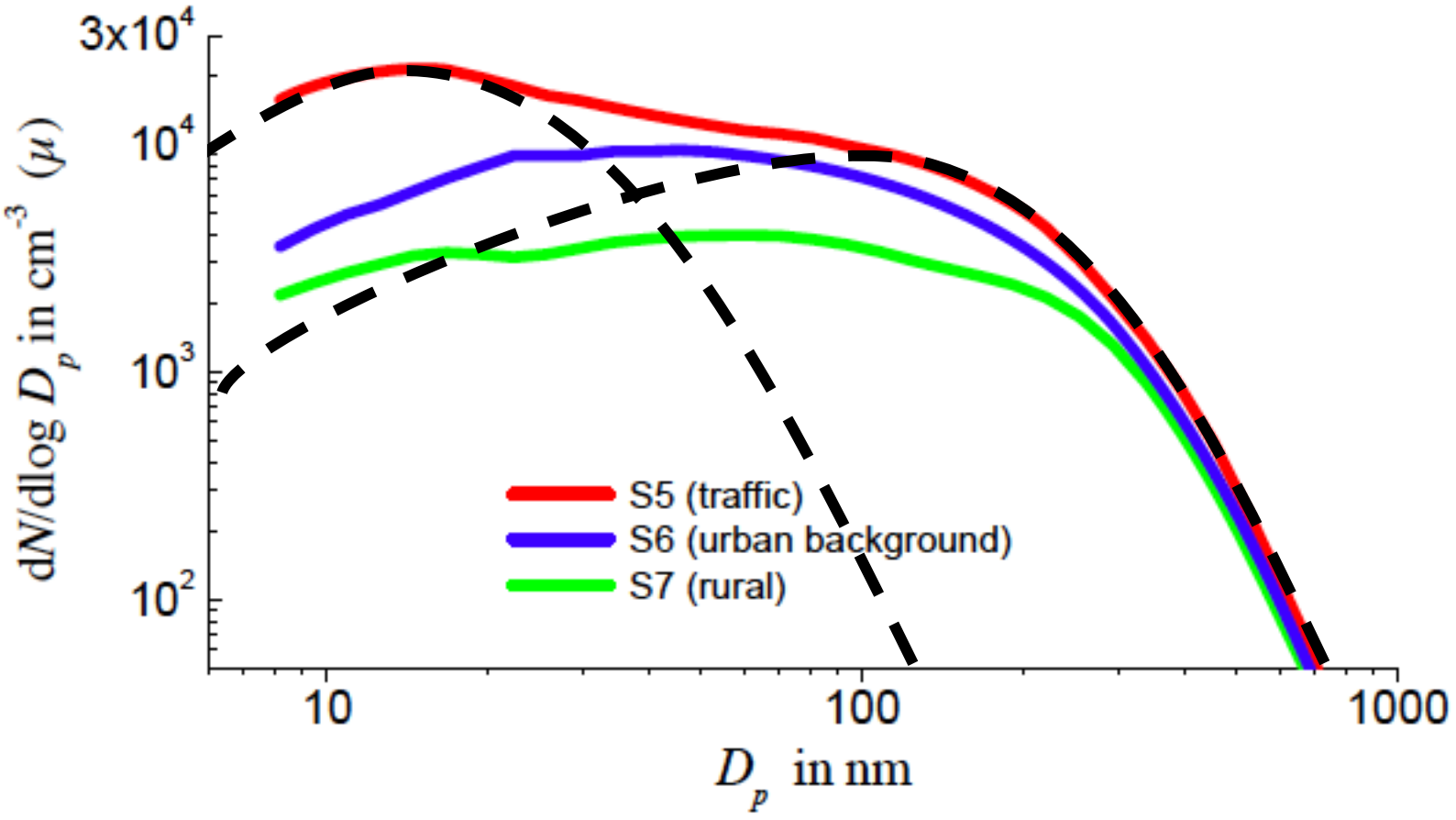


FIGURE 8.11 Typical urban aerosol number, surface, and volume distributions.

Seinfeld and Pandis, 2006

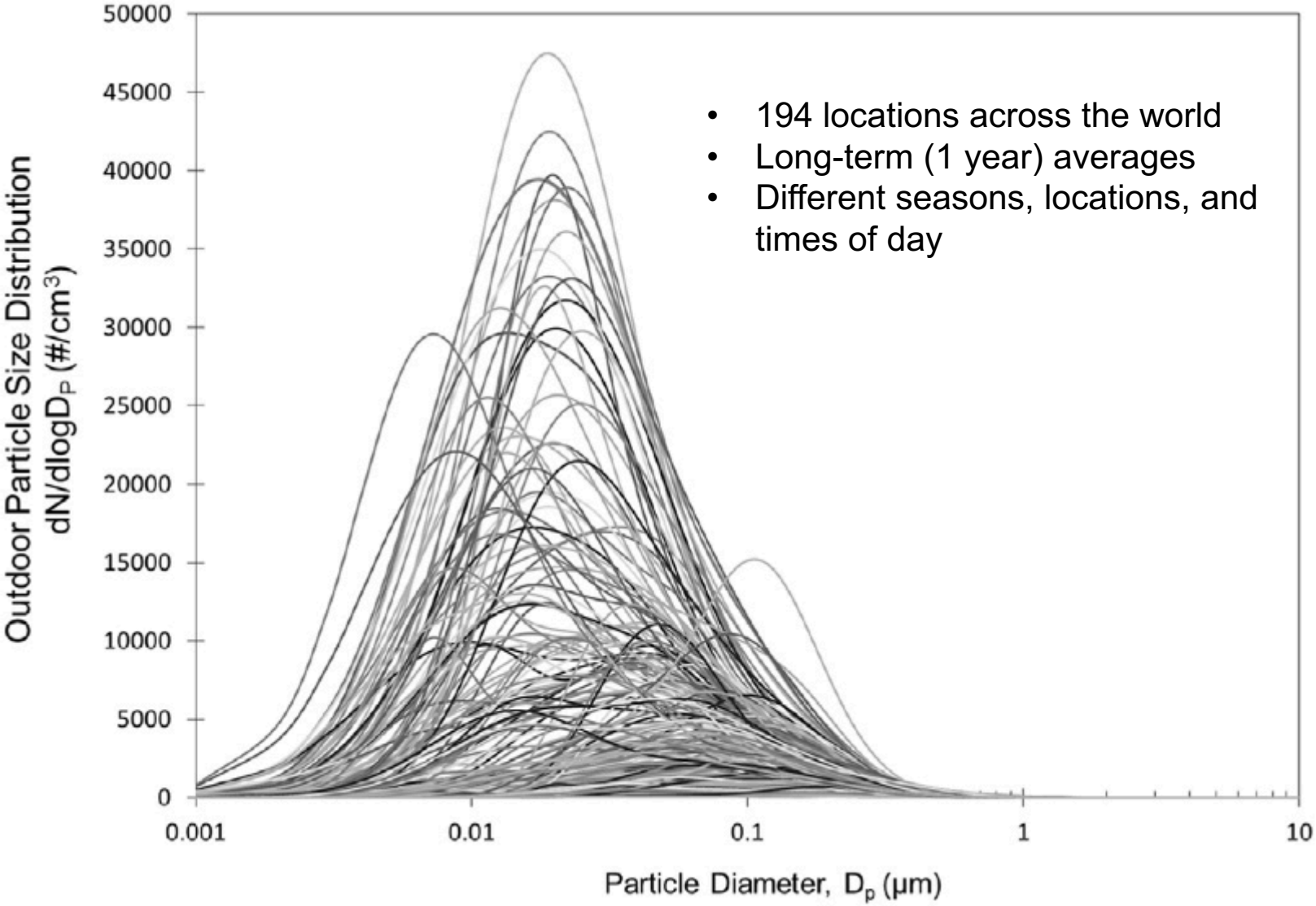
Typical outdoor PSDs

- Submicron particles outdoors in 3 locations in Germany



Costabile et al. 2009 *Atmos Chem Phys*

Typical outdoor PSDs



Azimi et al. 2014 *Atmos Environ*

Working with PSDs

- See Excel sheet

RESPIRATORY DEPOSITION

Why are we so concerned about particle size?

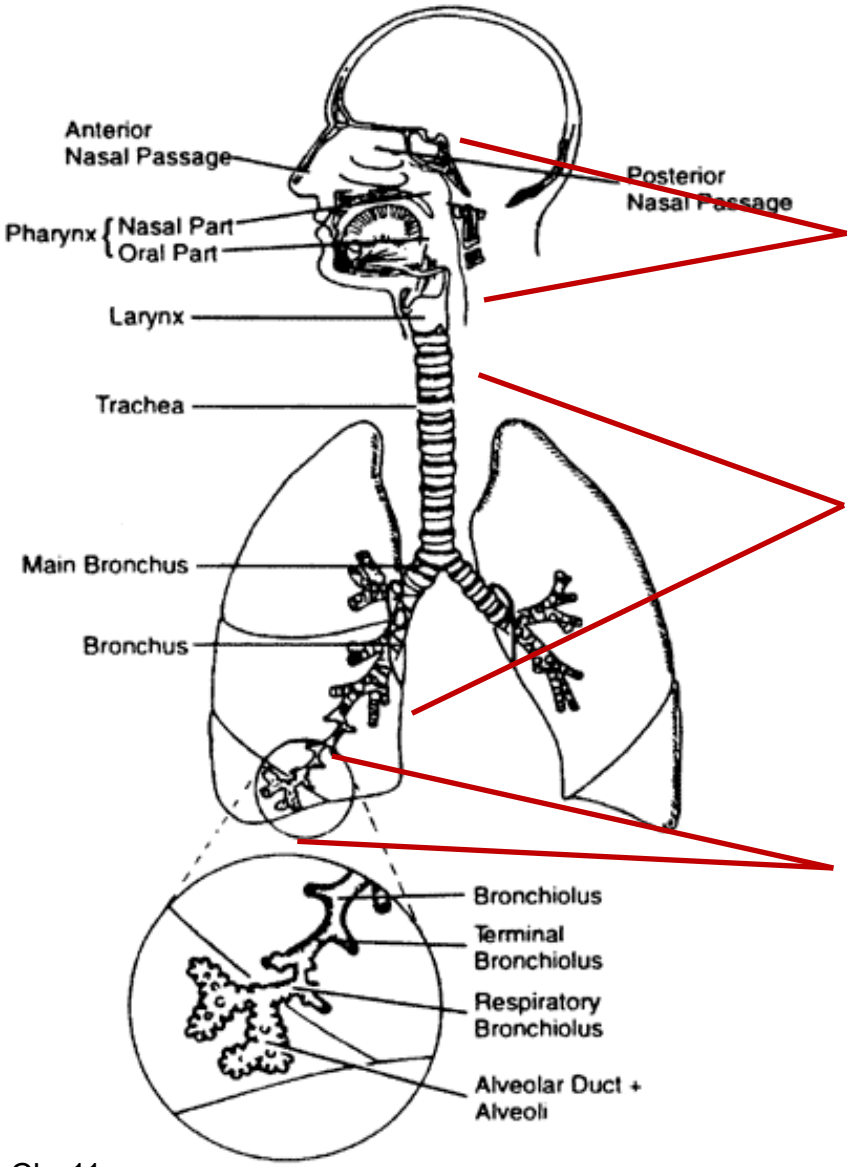
- One reason is because particles of different sizes deposit in different areas of our respiratory system with different efficiencies

- Humans breathe 10-25 m^3/day
  - ~0.5 L/breath at rest
  - ~12 breaths/minute at rest

- Surface area of lung devoted to gas exchange is ~75 m^2
  - ½ area of singles tennis court in alveolar region

- Velocities range from cm/s to mm/s

Human respiratory system



Nasopharyngeal

Tracheobronchial

(N&T regions "cleaned" by mucus)

Alveolar

Hinds, 1999 Ch. 11

Lung parameters

TABLE 11.1 Characteristics of Selected Regions of the Lung[a]

Airway	Generation	Number per Generation	Diameter (mm)	Length (mm)	Total Cross Section (cm^2)	Velocity[a] (mm/s)	Residence Time[b] (ms)
Trachea	0	1	18	120	2.5	3900	30
Main bronchus	1	2	12	48	2.3	4300	11
Lobar bronchus	2	4	8.3	19	2.1	4600	4.1
Segmental bronchus	4	16	4.5	13	2.5	3900	3.2
Bronchi with cartilage in wall	8	260	1.9	6.4	6.9	1400	4.4
Terminal bronchus	11	2000	1.1	3.9	20	520	7.4
Bronchioles with muscles in wall	14	16,000	0.74	2.3	69	140	16
Terminal bronchiole	16	66,000	0.60	1.6	180	54	31
Respiratory bronchiole	18	0.26×10^6	0.50	1.2	530	19	60
Alveolar duct	21	2×10^6	0.43	0.7	3200	3.2	210
Alveolar sac	23	8×10^6	0.41	0.5	72,000	0.9	550
Alveoli		300×10^6	0.28	0.2			

[a]Based on Weibel's model A; regular dichotomy average adult lung with volume. 0.0048 m^3 [4800 cm^3] at about three-fourths maximal inflation. Table adapted from Lippmann (1995).
[b]At a flow rate of 3.6 m^3/hr [1.0 L/s].

Note: based on steady flow

Hinds, 1999 Ch. 11

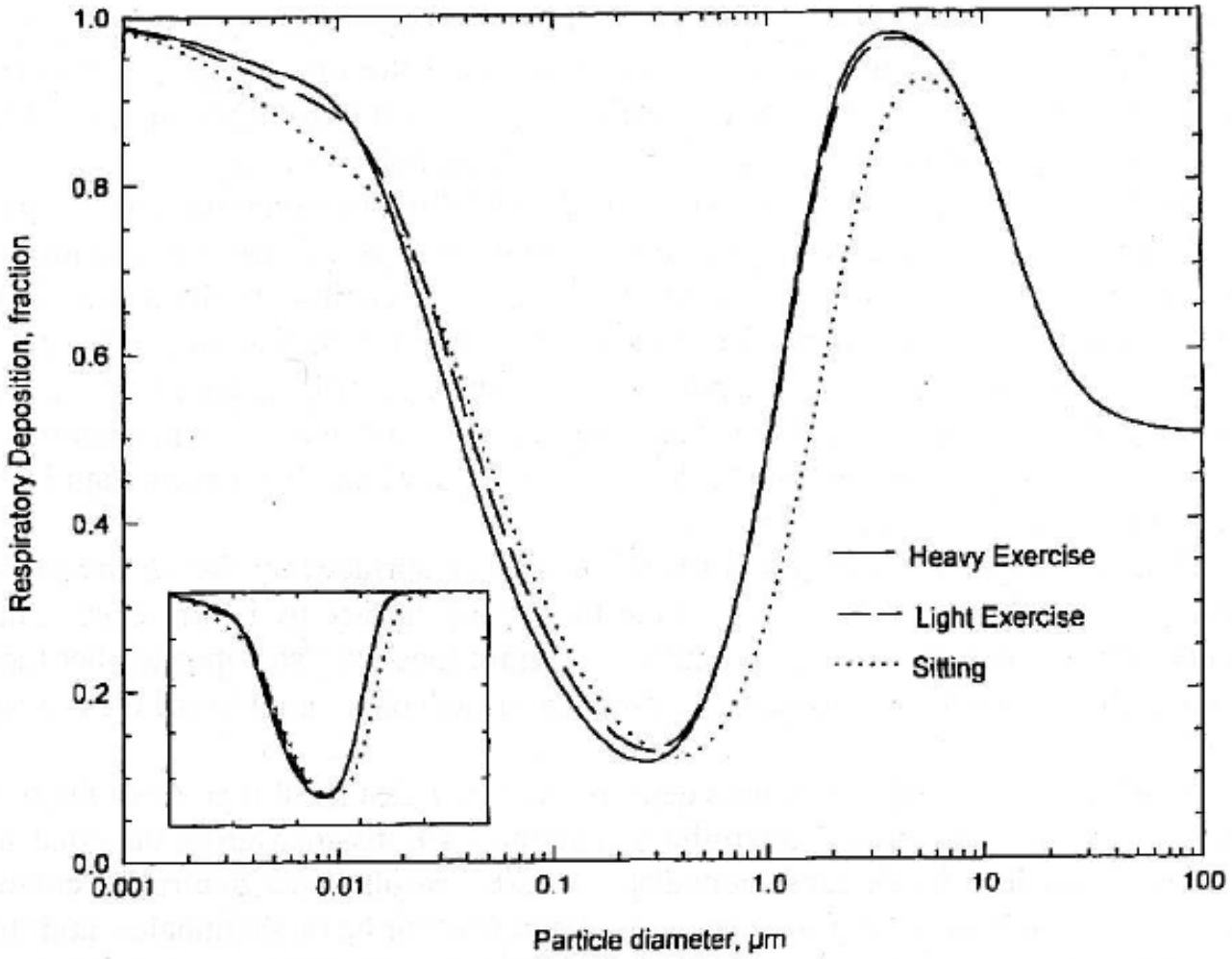
Particle deposition in lungs

- Similar to other systems:
  - Diffusion, settling, impaction are primary
  - Can neglect minor electrostatic forces

- Challenges:
  - Flow field is developing and unsteady
  - Particles are growing (humidification)

Total respiratory deposition

- Based on ICRP model, average for males/females
  - ICRP = International Commission on Radiological Protection



Hinds, 1999 Ch. 11

Respiratory deposition by region

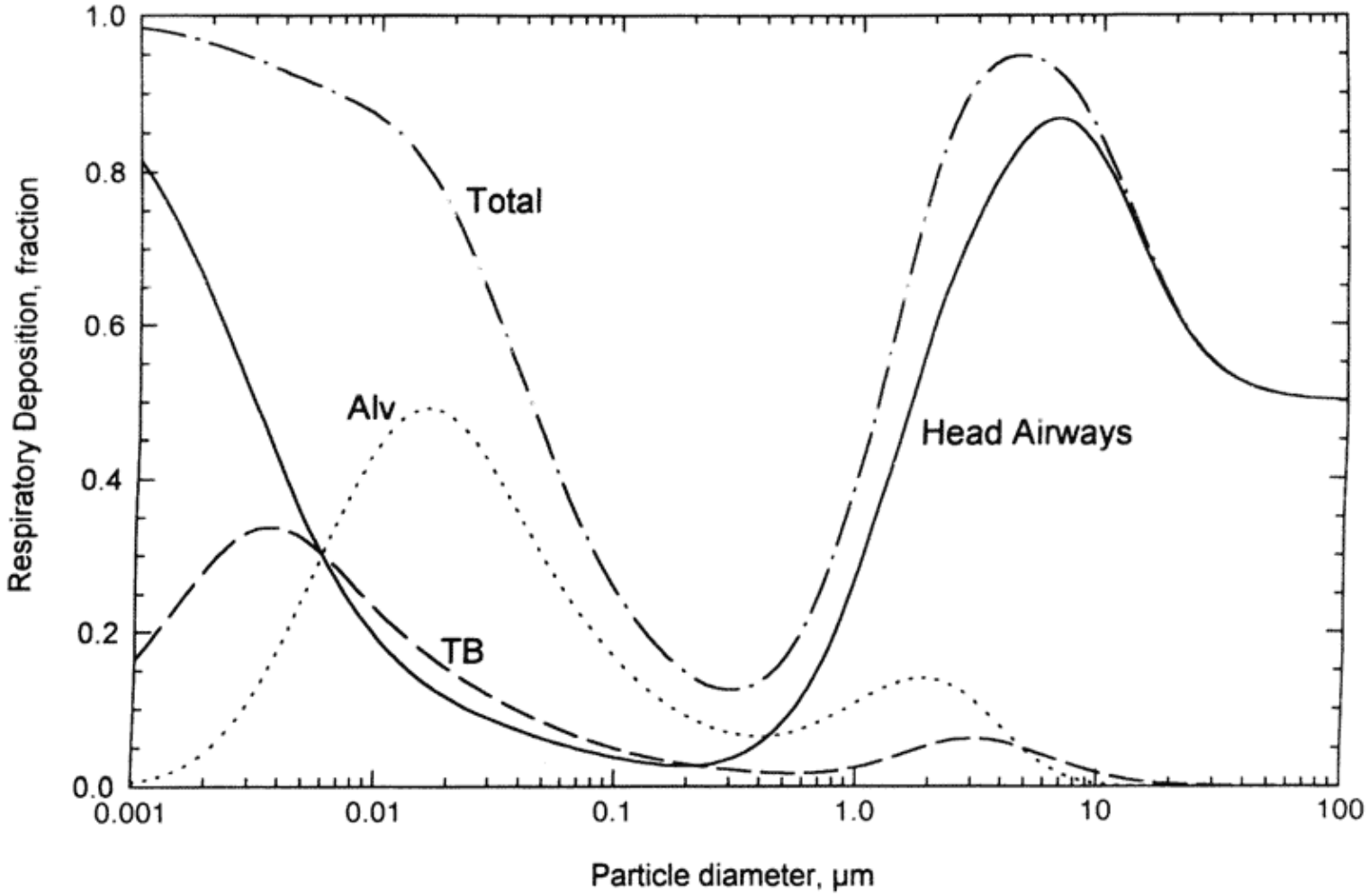


FIGURE 11.3 Predicted total and regional deposition for light exercise (nose breathing) based on ICRP deposition model. Average data for males and females.

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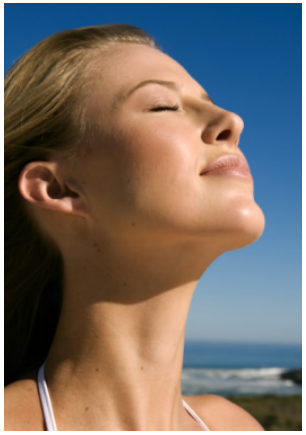
Alveolar deposition by breathing type

Depends on whether you're a nose breather or a mouth breather



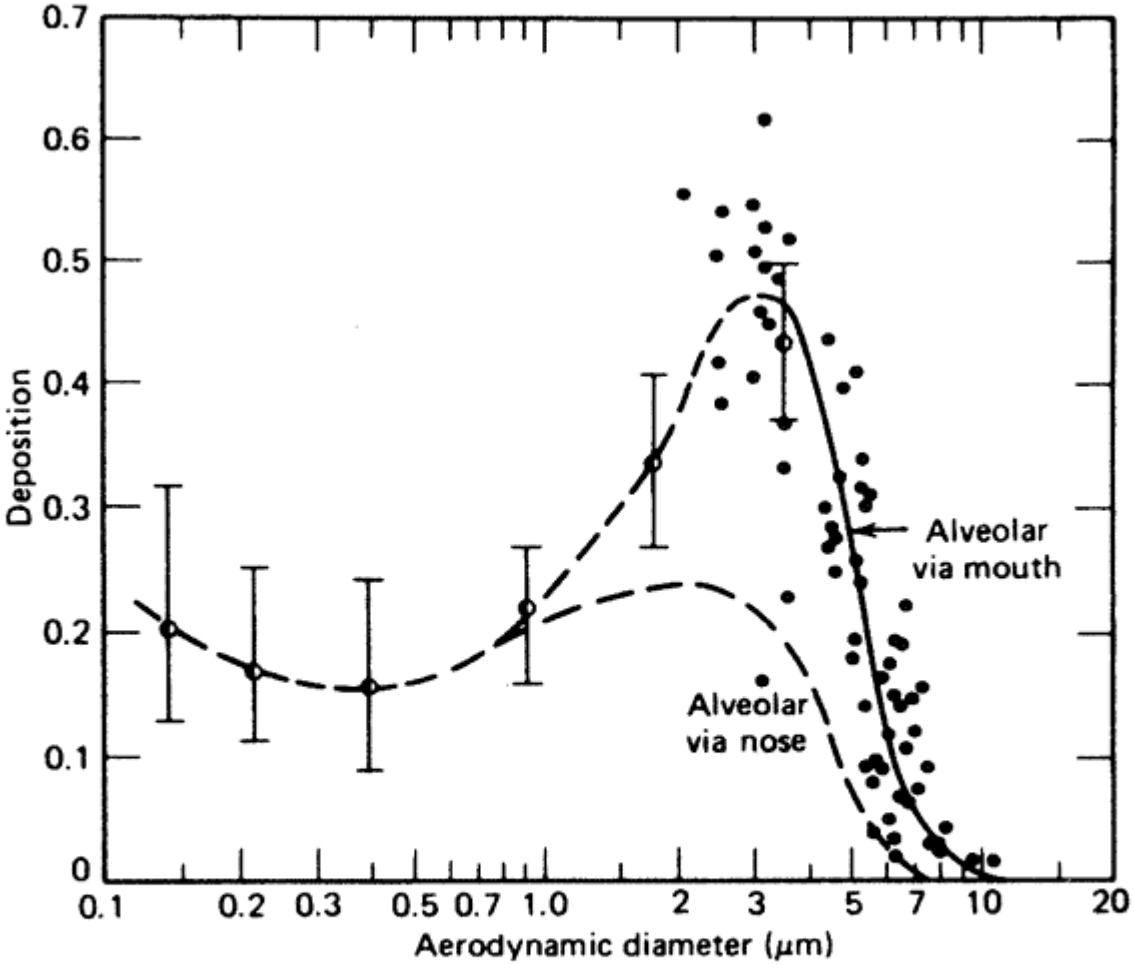


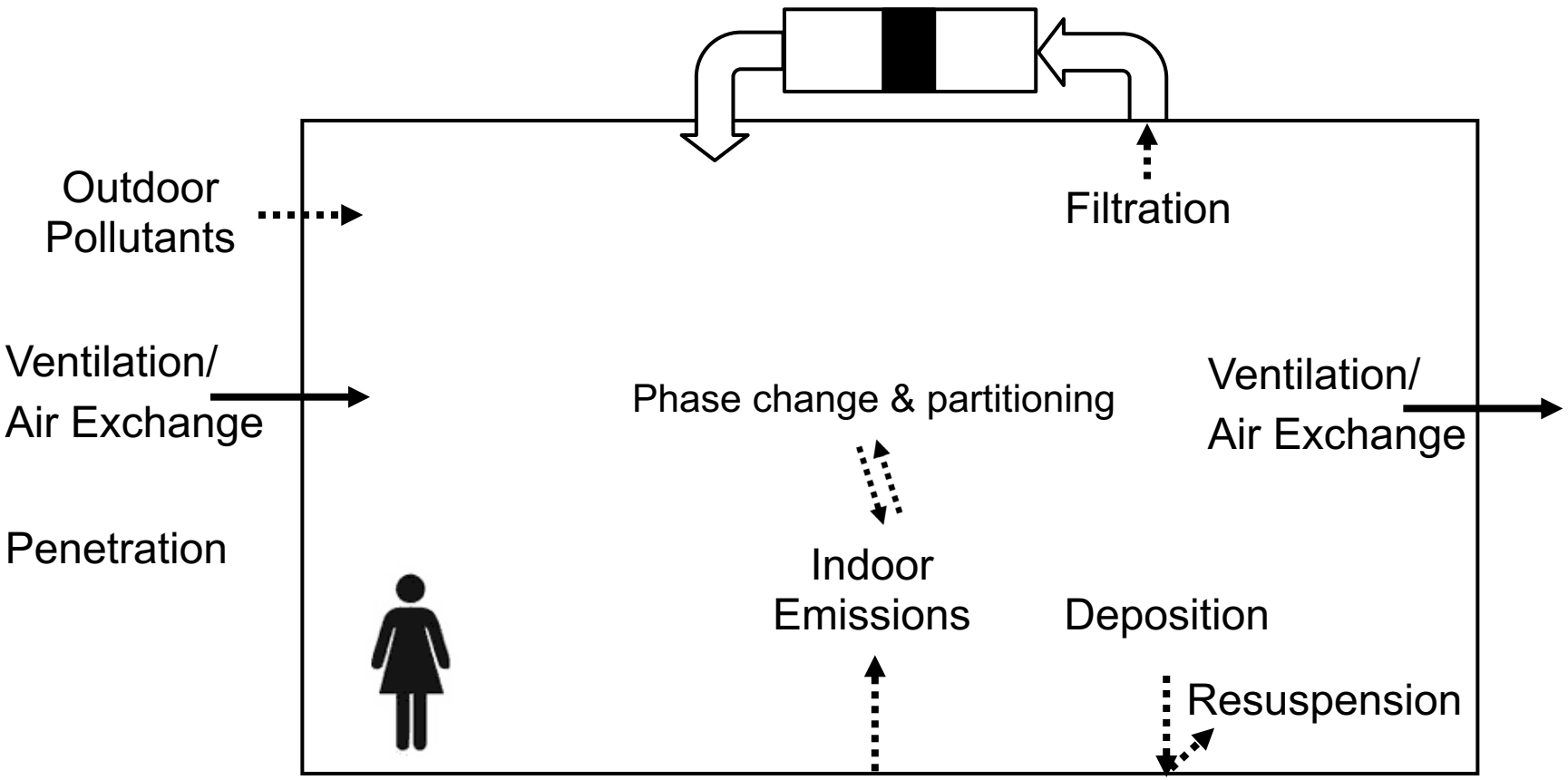
FIGURE 11.4 Experimental data for deposition in the alveolar region. Deposition is expressed as a fraction of mouthpiece inhalation versus aerodynamic diameter (geometric diameter used below 0.5 μm). Reprinted with permission from Lippmann (1977).

Hinds, 1999 Ch. 11

So what?

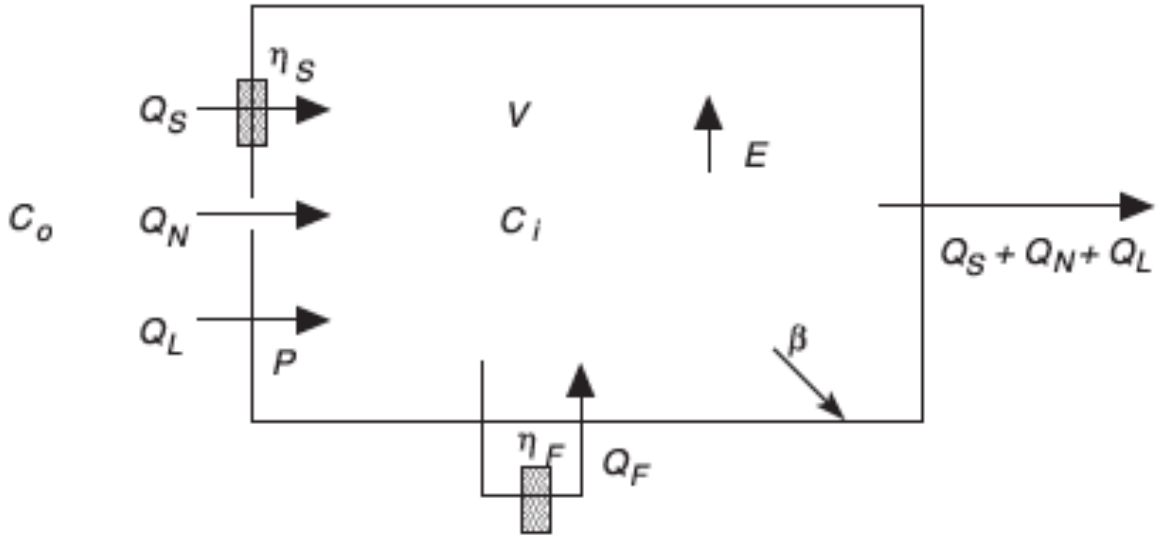
- We now understand more about particle sizes
  - And how different size particles deposit in different regions of our respiratory system
- We can examine different sources to determine their sizes
  - e.g., ETS or cooking particles
- And we can examine what particles will deposit in lungs?
  - And in which region?
- Helps elucidate health effects that may be observed

Mass (or number) balance approach for particles



Mass (or number) balance approach for particles

- Basic mass/number balance on particles of diameter i:



$$V\frac{dC_i}{dt} = E_i + C_{out,i}\left[Q_{vent}(1-\eta_{vent,i}) + Q_{nat} + Q_{inf}P_i\right] - C_i\left[Q_{vent} + Q_{nat} + Q_{inf} + v_{d,i}A + Q_{filt}\eta_{filt,i}\right]$$

$$\frac{dC_i}{dt} = \frac{E_i}{V} + C_{out,i}\left[\lambda_{vent}(1-\eta_{vent,i}) + \lambda_{nat} + \lambda_{inf}P_i\right] - C_i\left[\lambda_{vent} + \lambda_{nat} + \lambda_{inf} + k_{dep,i} + \lambda_{filt}\eta_{filt,i}\right]$$

Which parameters vary by particle size?

ETS lung penetration example

- Nazaroff, W. W., Hung, W. Y., Sasse, A. and Gadgil, A. J., 1993. Predicting regional lung deposition of environmental tobacco-smoke particles. *Aerosol Science and Technology* **19**, 243-254.

- Modeling exercise
  - Examine emissions from ETS
  - Used lung deposition model to examine where ETS particles end up

- Dynamic model
  - Assumed uniform cigarette smoking rate for first 16 hours of a day
  - Followed by 8 non-smoking hours

  - Varied smoking activity, age of exposed individuals

Emissions from ETS

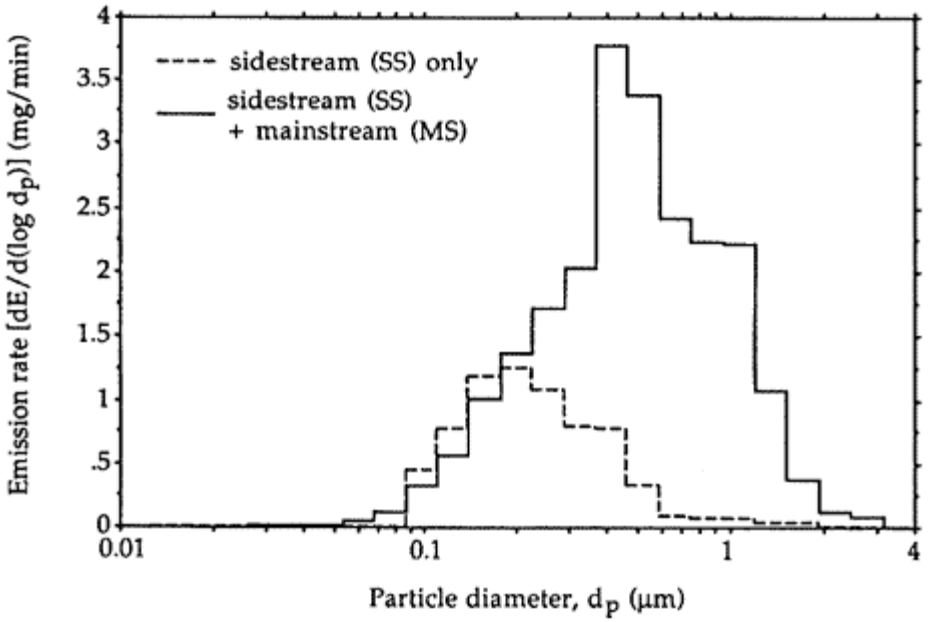
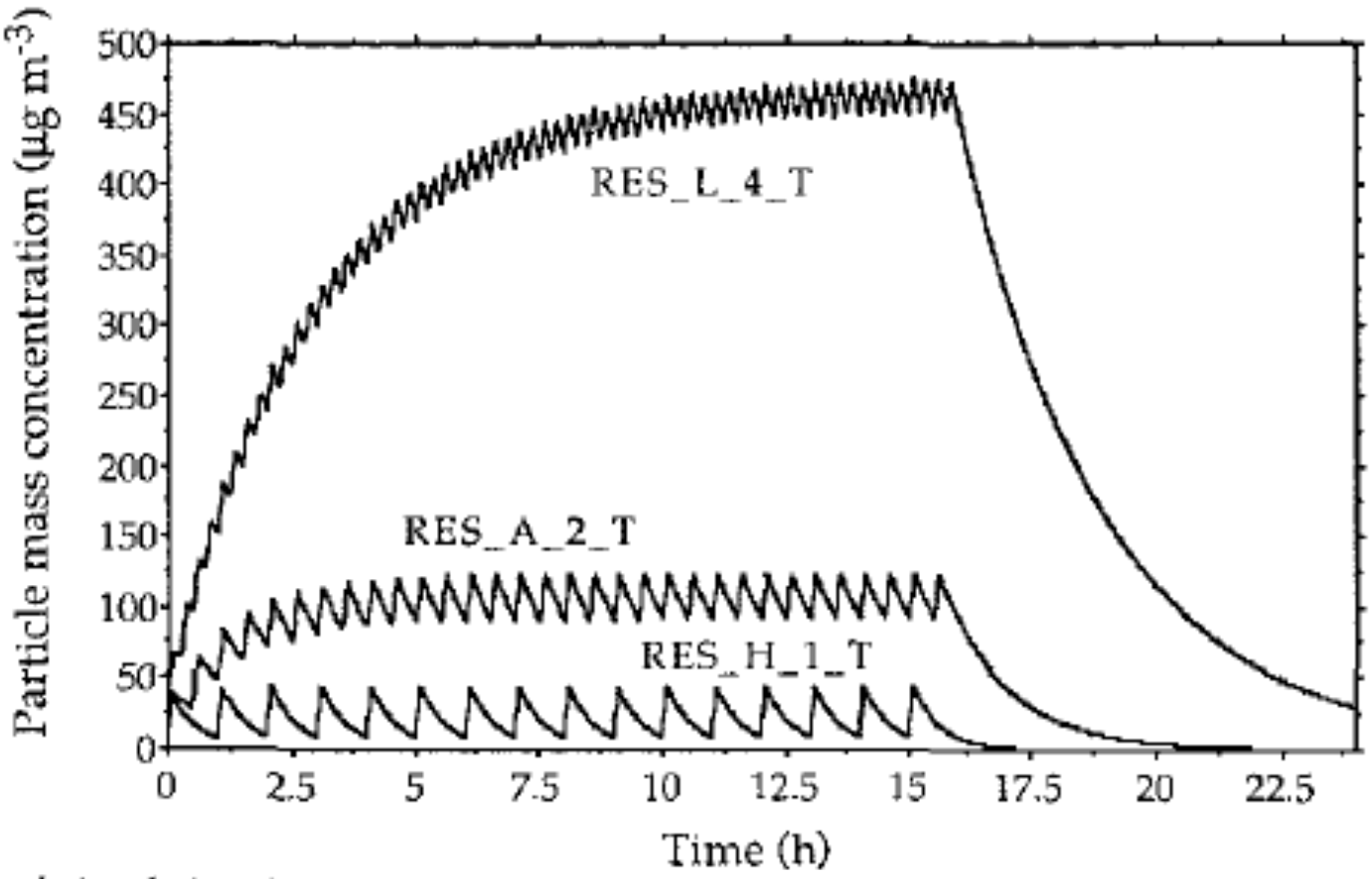


FIGURE 1. Effective particle emission rate from a burning cigarette as a function of particle diameter. The form of the figure is such that the area under a curve between two particle sizes is proportional to the mass emission rate of all particles within those size limits. These experiments were reported by Sextro et al. (1991). The emission profiles are based on a presumed particle density of 1.4 g cm^{-3}.

Nazaroff et al., 1993 *AS&T*

Indoor concentration profiles from ETS



Simulation designations

RES_H_1_S	**RES_A_2_S**	**RES_L_4_S**
RES_H_1_T	**RES_A_2_T**	**RES_L_4_T**

air-exchange rate: **H** = 1.7 h^{-1}; **A** = 0.68 h^{-1}; **L** = 0.28 h^{-1}

cigarette smoking frequency: **1**, **2**, or **4** per hour

Nazaroff et al., 1993 *AS&T*

Mean indoor concentrations from ETS

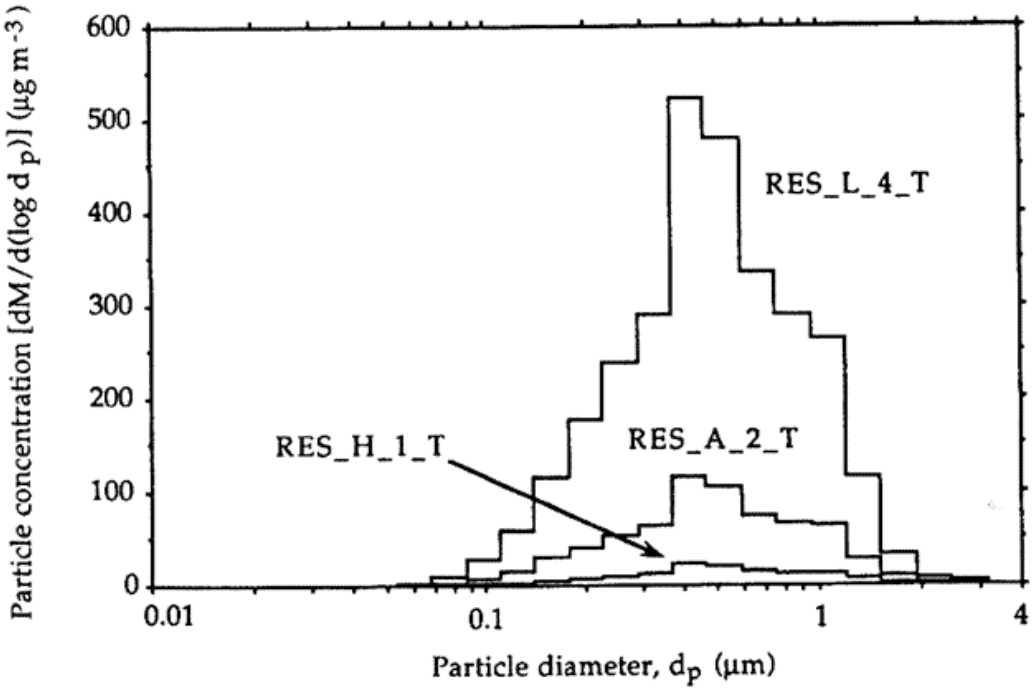


FIGURE 4. Average environmental tobacco smoke particle size distribution over 24-h period for three residential simulations corresponding

Simulation designations

RES_H_1_S	**RES_A_2_S**	**RES_L_4_S**
RES_H_1_T	**RES_A_2_T**	**RES_L_4_T**

air-exchange rate: **H** = 1.7 h^{-1}; **A** = 0.68 h^{-1}; **L** = 0.28 h^{-1}

cigarette smoking frequency: **1**, **2**, or **4** per hour

Nazaroff et al., 1993 *AS&T*

ETS lung deposition

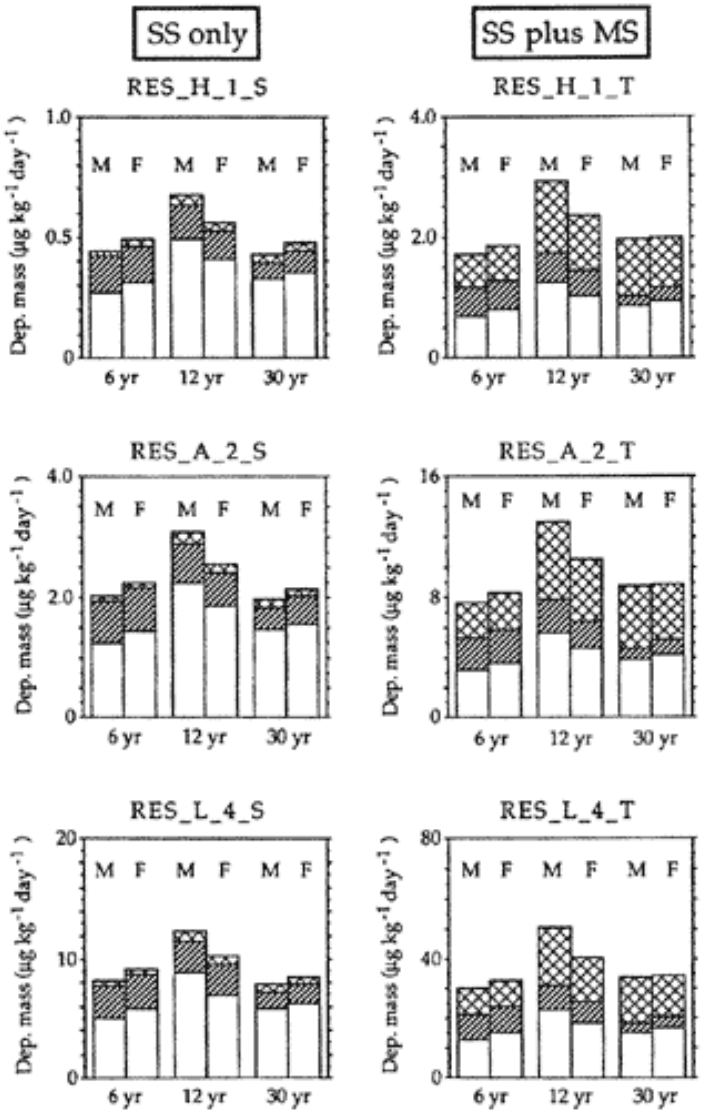
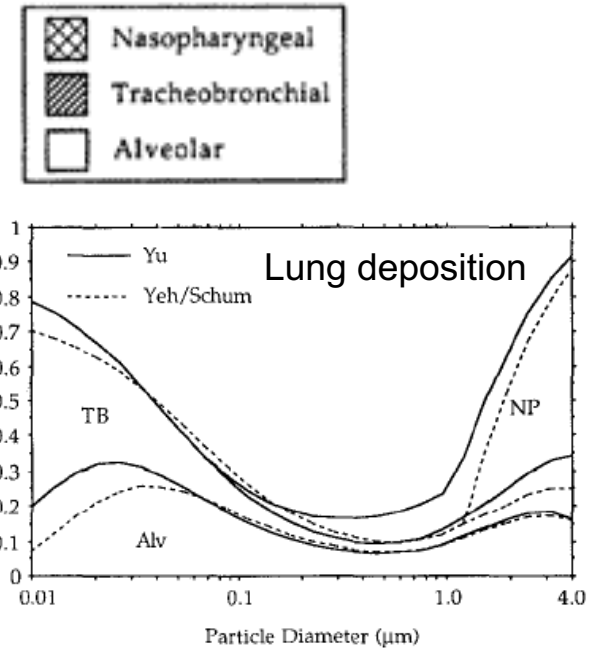


FIGURE 5. Regional lung deposition of environmental tobacco smoke particles from simulations of residential exposure. Each frame shows results for three age groups and each gender for one combination of smoking rate, particle emission profile, and building ventilation rate. The height of each bar gives the total respiratory deposition of particle mass per day per kg of body weight. Refer to Tables 1 and 2 for a description of simulation conditions. Note that the vertical scale varies from frame to frame.



Nazaroff et al., 1993 *AS&T*

ETS lung deposition

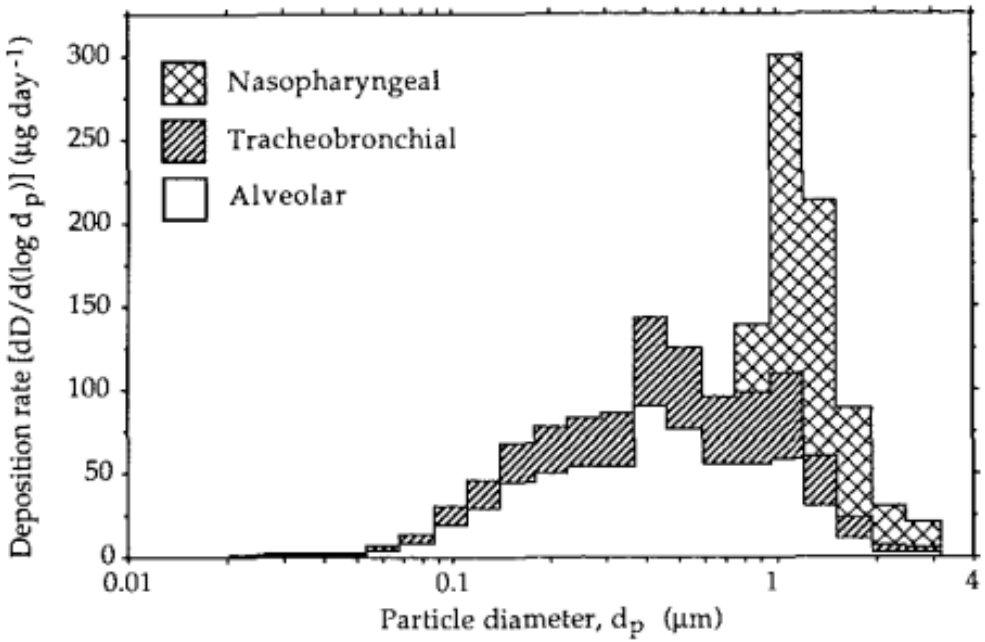
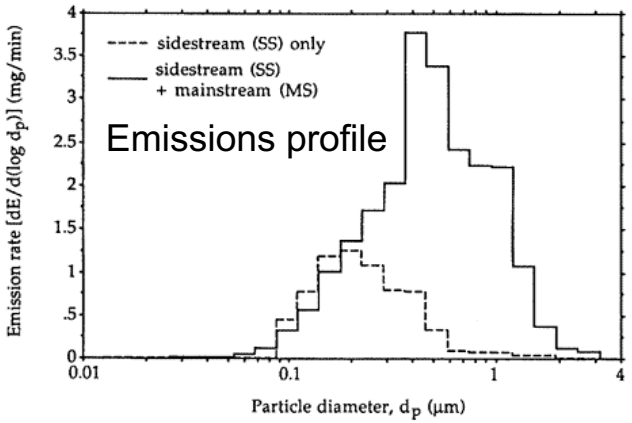
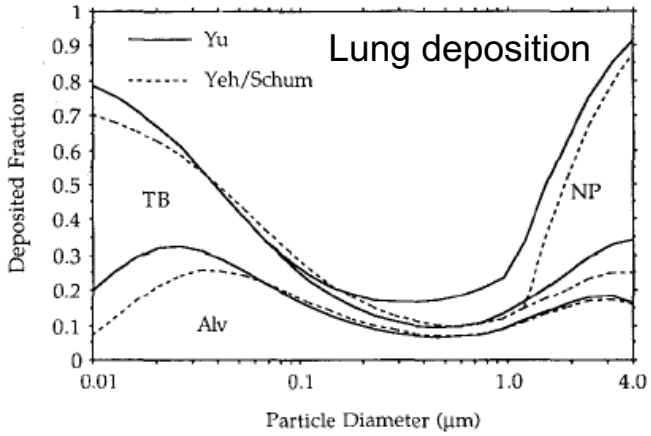


FIGURE 6. Size distribution of deposited mass of environmental tobacco smoke particles in 6-year-old boy for simulation RES_A_2_T. The form of the figure is such that the shaded area between two particle sizes is proportional to the average 24-h mass deposition rate of particles within those size limits. See Tables 1 and 2 for a description of simulation conditions.





Nazaroff et al., 1993 *AS&T*

Next time

- Particle emission source characteristics, deposition, resuspension, and penetration through cracks