ENVE 576
Indoor Air Pollution
Fall 2015

Week 11: November 3, 2015
1. SVOCs
2. Aerosol sampling techniques

Dr. Brent Stephens, Ph.D.
Department of Civil, Architectural and Environmental Engineering
Illinois Institute of Technology
brent@iit.edu

Built Environment Research @ IIT

Advancing energy, environmental, and sustainability research within the built environment

Built Environment Research Group
www.built-envi.com

Updates

Last time:

- Particle filtration and stand-alone air cleaners

Today:

- SVOCs
- Aerosol sampling techniques

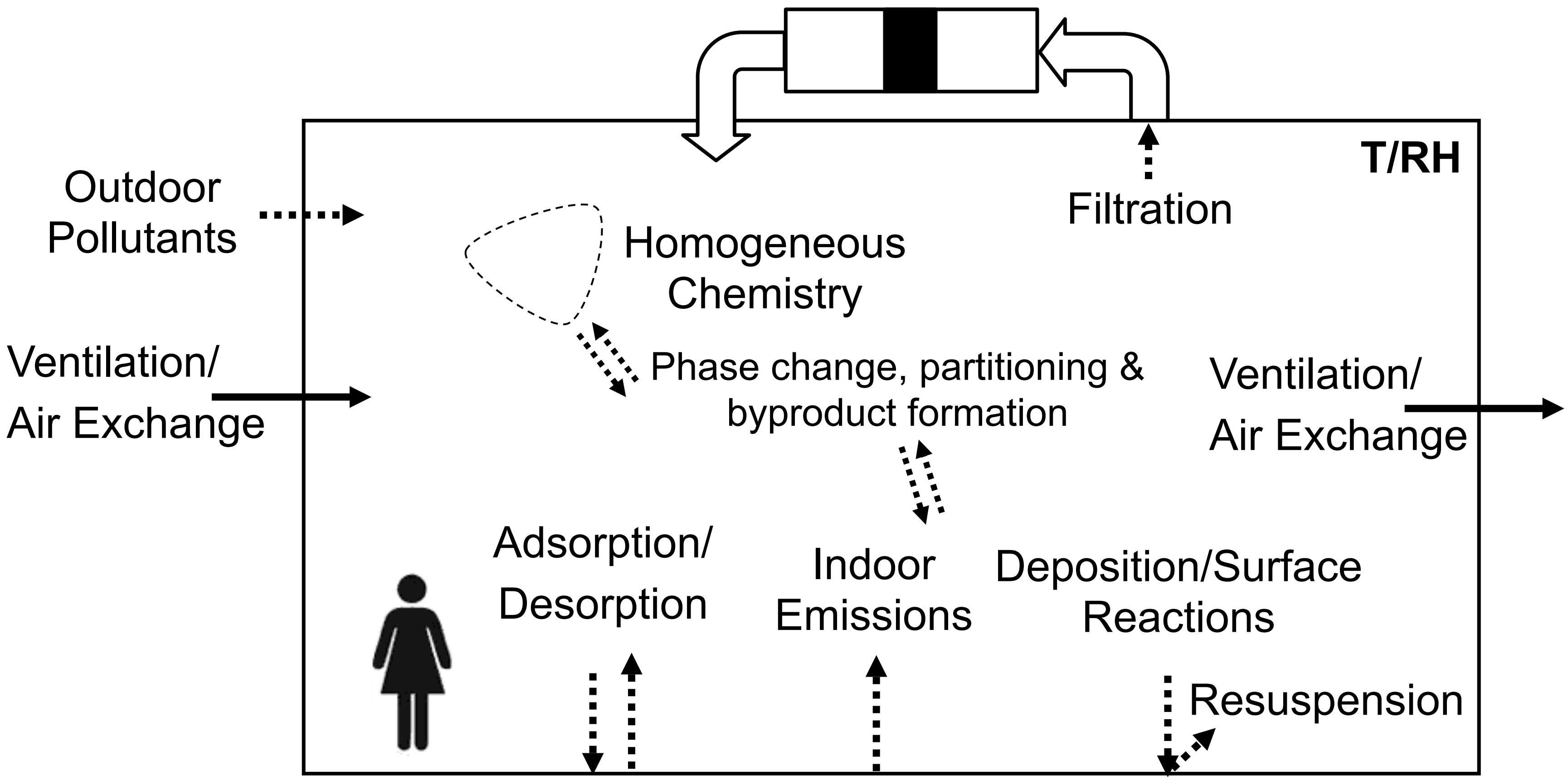
Take home-exam released today

- Due Tuesday November 10

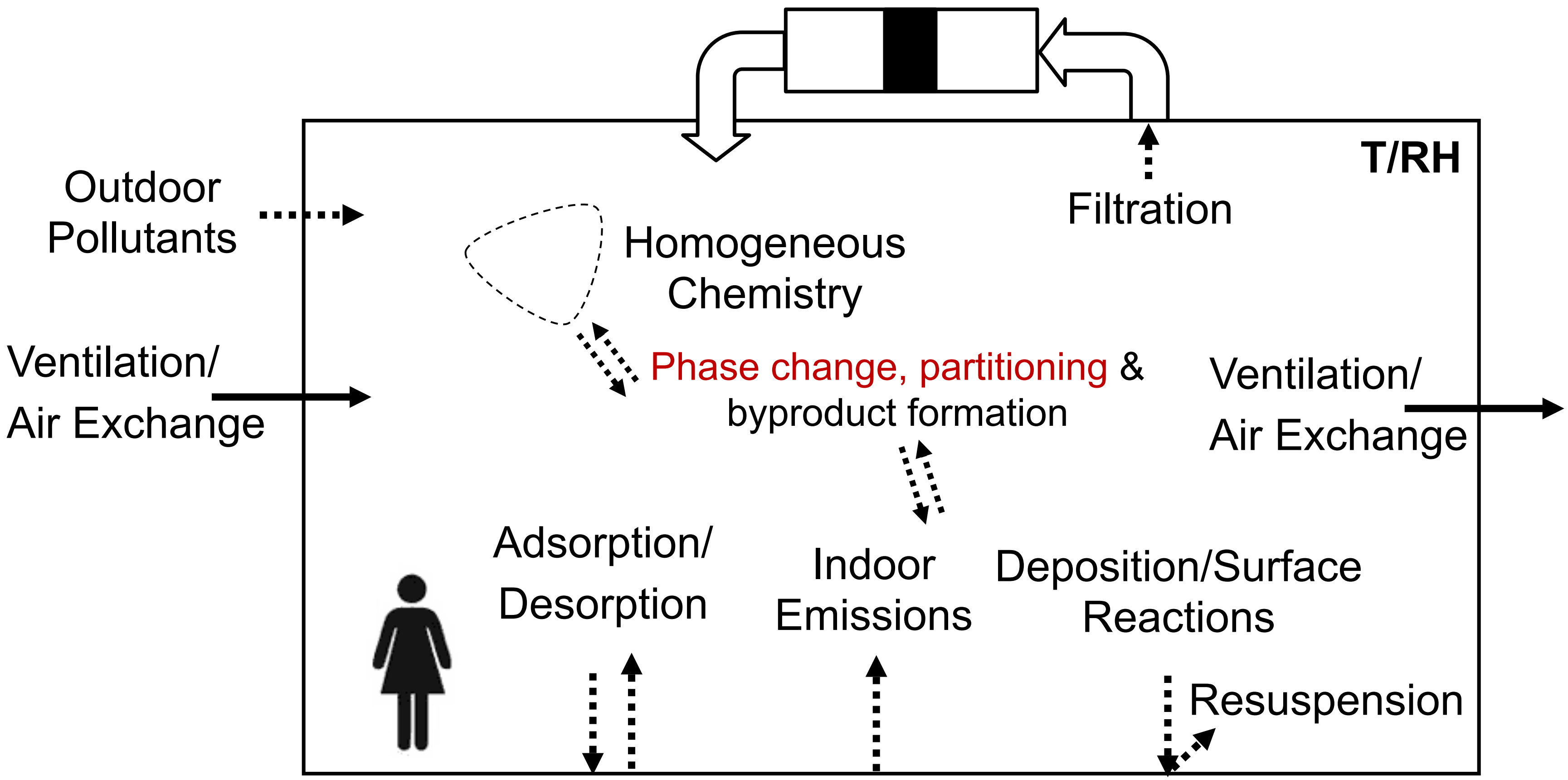
Revisiting the question about final paper/presentation

- Our final presentations are scheduled for Tuesday night, December 8, 5-7 PM
- I have to be in Washington, DC on December 8-9
- We have a few options:
  1. Reschedule our presentations and keep them as 25% of your grade
     - The week before (canceling a class and presenting December 1)
     - During exam week (perhaps Monday)
  2. Cancel our presentations and count only the final paper

Indoor environment: Mass balance



Indoor environment: Mass balance



SEMI-VOLATILE ORGANIC COMPOUNDS

What are semi-volatile organic compounds?

- Semi-volatile organic compounds (SVOCs) are organic molecules that can have meaningful abundances in both the gas phase and condensed (particle) phases
  - Sometimes called particulate organic matter (POM)
  - Compounds with boiling points from 240 to 400°C
  - Compounds with saturation vapor pressures from 10^{-2} to 10^{-7} kPa

  Generally: as $p_{vap,sat}$ ↑ BP ↓ → More likely to be in gas phase than solid phase
- SVOCs are generally under-studied relative to VOCs and aerosols
  - Doesn't mean they're not important → largely due to analytical limitations
- We've already touched on some of these
  - e.g., polycyclic aromatic hydrocarbons (PAHs) originating from combustion
- SVOCs also occur as active ingredients in pesticides, cleaning agents, and personal care products
  - And as major additives in materials such as floor coverings, furnishings, and electronics components

Weschler and Nazaroff, 2008 *Atmospheric Environment*

What are semi-volatile organic compounds?

- Most SVOCs have a slow rate of release from sources
- Exposures can occur via inhalation
  - Both gases and SVOCs adsorbed onto particles
- Exposures can also occur via dermal and ingestion pathways
- Some are known to be toxic
  - Dioxins, benzo[a]pyrene, pentachlorophenol
    - Many have been removed from production over the years
- Others have emerging indicators of concern
  - More than 100 SVOCs have been found in the US population’s blood in large biomonitoring studies

Some SVOCs of emerging concern

- Phthalate esters (BBzP, DEHP) (often used as plasticizers)
  - Allergic symptoms in children
  - Slowed male reproductive development
  - Altered semen quality

- Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA)
  - Was a key ingredient in Scotchgard
  - Low birth weight, chronic kidney disease

- Polychlorinated biphenyl (PCBs), brominated flame retardants (BFRs), di-2-ethylhexyl phthalate (DEHP), bisphenol A, and some pesticides
  - Have been linked to endocrine disrupting (ED) activity
  - SVOCs that have chemical structures similar to those of human hormones and can either mimic or block endocrine (hormonal) activity
  - EDs may be important contributors to neurodevelopment and behavioral problems ranging from autism to attention deficit disorder
    - Incomplete and sometimes controversial evidence

SVOC classifications, sources, and potential health effects

SVOC Compounds	Uses	Sources	Potential Health Effects
Alkylphenols *Example:* *4-nonylphenol, 4-octylphenol*	Nonionic Surfactants	Detergents, Disinfectants, Surface Cleaners	May Interfere With, Mimic or Block Hormones
Organochlorines *Example:* *DDT, Chlordane*	Pesticides, Termiticide, Bactericide (Some Have Been Banned or Restricted in the 1980s)	Outdoor and Indoor Air, Tracked-In Dust, Disinfecting Products	Neurotoxicity, Effects on Developing Reproductive Systems And on Lactation, Cancer
Organophosphorus Compounds *Example:* *Tris(2-chloroethy)phosphate (TCEP), Tris(chloropropyl)phosphate (TCPP)*	Plasticizers, Antifoaming Agents, Flame Retardants, Pesticides	Polymeric Materials, Fabrics, Polyurethane Foams, Electronics (Cable Sheathing and Casings), Outdoor and Indoor Air, Dust	Effects on Neurodevelopment and Growth in Developing Tissue, Relate To Respiratory Disease in Children Through Dysregulation of the Autonomic Nervous System
Phthalates *Example:* *Di(2-ethylhexyl)-phthalate (DEHP), Di-iso-nonyl-phthalate (DINP)*	Plasticizers, Solvents, Fixing Fragrances (Use of DEHP And BBP Reduced Due to the Concern on Health Effects)	Flexible PVC, PVC Flooring, Wall Covering, Electrical Cable and Casings, Personal Care Products	Effects on the Development of Male Reproductive Tract, Prenatal Mortality, Reduced Growth and Birth Weight, May Relate to Asthma and Allergies in Children
Polybrominated Diphenyl Ethers (PBDEs) *Example:* *Hexabromodiphenyl ether (BDE-153), Tetrabromodiphenyl ether (BDE-47)*	Flame Retardants (Use of Penta- and Octa-BDEs Have Been Restricted)	Carpet Padding, Wall Coverings, Electronics (Casings), Furniture (Foam Cushioning and Mattress)	Effects on the Development of Brain And Nerve Tissues, Permanent Learning and Memory Impairment, Behavioral Changes, Delayed Puberty Onset, Fetal Malformations, Thyroid Hormone Disruption

Xu and Zhang **2011** *ASHRAE Journal*

SVOC classifications, sources, and potential health effects

SVOC Compounds	Uses	Sources	Potential Health Effects
PolychlorinatedBiphenyls (PCBs) *Example:* *2,2′,5,5′-tetrachloro-1,1′-biphenyl (PCB 52), 2,2′,4,4′,5,5′-hexachloro-1,1′-biphenyl (PCB 153)*	Heat Transfer Fluids, Stabilizers, Flame Retardants, (Have Been Banned or Restricted in the 1970s)	Floor Finishes, Foam Cushioning and Mattresses, Oil-Filled Transformers, Capacitors	Developmental Neurotoxicants, Effects on Immune, Reproductive, Nervous, and Endocrine Systems, Cancer (Including Breast Cancer)
Polycyclic Aromatic Hydrocar-bons (PAHs) *Example:* *Benzo(a)pyrene, Pyrene*	Combustion Byproducts	Outdoor Air, Cooking, Smoking	Cataracts, Kidney and Liver Damage, Jaundice, Increased Risk Of Skin, Lung, Bladder, and Gastrointestinal Cancers
Pyrethroids *Example:* *Cyfluthrin, Permethrin*	Insecticides	Outdoor and Indoor Air, Tracked-In Dust, Cleaning Products	Weak Anti-Androgenic, Anti-Estrogenic, or Estrogenic Effect
Parabens *Example:* *Butyl paraben, Methyl paraben*	Bactericides, Antimicrobial Agents, Preservatives	Personal Care Products, Canned Food, Fabrics	Weak Environmental Estrogens

Xu and Zhang **2011** *ASHRAE Journal*

Semi-volatile organic compounds found indoors

Table 1
Selected semivolatile organic compounds observed or expected in indoor environments, organized by product class and chemical class, with examples.

Chemical class	Specific chemical	CAS No.	Formula	log P_s[a]
Biocides and preservatives				
Antimicrobials	Triclosan	3380-34-5	$C_{12}H_7Cl_3O_2$	−8.9
Antioxidants	Butylated hydroxytoluene (BHT)	128-37-0	$C_{15}H_{24}O$	−6.7
Fungicides	Tributyltin oxide (TBTO)	56-35-9	$C_{24}H_{54}OSn_2$	−10.9
Wood preservatives	Pentachlorophenol (PCP)	87-86-5	C_6HCl_5O	−7.4
Combustion byproducts				
Environmental tobacco smoke	Nicotine	54-11-5	$C_{10}H_{14}N_2$	−4.7
Polychlorinated dibenzo-*p*-dioxins	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	1746-01-6	$C_{12}H_4Cl_4O_2$	−11.4
Polycyclic aromatic hydrocarbons	Benzo[*a*]pyrene (B*a*P)	50-32-8	$C_{20}H_{12}$	−10.5
Polycyclic aromatic hydrocarbons	Phenanthrene	85-01-8	$C_{14}H_{10}$	−6.6
Polycyclic aromatic hydrocarbons	Pyrene	129-00-0	$C_{16}H_{10}$	−7.5
Degradation products/residual monomers				
Phenols	Bisphenol A	80-05-7	$C_{15}H_{16}O_2$	−10.5
Flame retardants				
Brominated flame retardants	2,2′,4,4′,5,5′-Hexabromodiphenyl ether (BDE-153)	68631-49-2	$C_{12}H_4Br_6O$	−13.8
Brominated flame retardants	2,2′,4,4′,5-Pentabromodiphenyl ether (BDE-99)	60348-60-9	$C_{12}H_5Br_5O$	−12.0
Brominated flame retardants	2,2′,4,4′-Tetrabromodiphenyl ether (BDE-47)	5436-43-1	$C_{12}H_6Br_4O$	−10.5
Chlorinated flame retardants	Perchloropentacyclodecane (mirex)	2385-85-5	$C_{10}Cl_{12}$	−10.6
Phosphate esters	Tris(chloropropyl) phosphate	13674-84-5	$C_9H_{18}Cl_3O_4P$	−6.3
Heat-transfer fluids				
Polychlorinated biphenyls (PCBs)	2,2′,5,5′-tetrachloro-1,1′-biphenyl (PCB 52)	35693-99-3	$C_{12}H_6Cl_4$	−7.8
Polychlorinated biphenyls (PCBs)	2,2′,4,4′,5,5′-hexachloro-1,1′-biphenyl (PCB 153)	35065-27-1	$C_{12}H_4Cl_6$	−9.8
Microbial emissions				
Sesquiterpenes	Geosmin	23333-91-7	$C_{12}H_{22}O$	−5.3
Personal care products				
Musk compounds	Galaxolide	1222-05-5	$C_{18}H_{26}O$	−7.5
Petrolatum constituents	*n*-Pentacosane	629-99-2	$C_{25}H_{52}$	−10.2

Weschler and Nazaroff **2008** *Atmos Environ*

Semi-volatile organic compounds found indoors

Table 1
Selected semivolatile organic compounds observed or expected in indoor environments, organized by product class and chemical class, with examples.

Chemical class	Specific chemical	CAS No.	Formula	log P_s[a]
Pesticides/termiticides/herbicides				
Carbamates	Propoxur	114-26-1	$C_{11}H_{15}NO_3$	−6.8
Organochlorine pesticides	Chlordane	57-74-9	$C_{10}H_6Cl_8$	−7.8
Organochlorine pesticides	*p,p'*-DDT	50-29-3	$C_{14}H_9Cl_5$	−9.7
Organophosphate pesticides	Chlorpyrifos	2921-88-2	$C_9H_{11}Cl_3NO_3PS$	−7.9
Organophosphate pesticides	Diazinon	333-41-5	$C_{12}H_{21}N_2O_3PS$	−8.0
Organophosphate pesticides	Methyl parathion	298-00-0	$C_8H_{10}NO_5PS$	−6.6
Pyrethroids	Cyfluthrin	68359-37-5	$C_{22}H_{18}Cl_2FNO_3$	−12.4
Pyrethroids	Cypermethrin	52315-07-8	$C_{22}H_{19}Cl_2NO_3$	−12.4
Pyrethroids	Permethrin	52645-53-1	$C_{21}H_{20}Cl_2O_3$	−10.7
Synergist	Piperonyl butoxide	51-03-6	$C_{19}H_{30}O_5$	−10.1
Plasticizers				
Adipate esters	Di(2-ethylhexyl) adipate (DEHA)	103-23-1	$C_{22}H_{42}O_4$	−9.9
Phosphate esters	Triphenylphosphate (TPP)	115-86-6	$C_{18}H_{15}O_4P$	−9.2
Phthalate esters	Butylbenzyl phthalate (BBzP)	85-68-7	$C_{19}H_{20}O_4$	−10.0
Phthalate esters	Dibutyl phthalate (DBP)	84-74-2	$C_{16}H_{22}O_4$	−8.0
Phthalate esters	Di(2-ethylhexyl) phthalate (DEHP)	117-81-7	$C_{24}H_{38}O_4$	−11.5
Sealants				
Silicones	Tetradecamethylcycloheptasiloxane (D7)	107-50-6	$C_{14}H_{42}O_7Si_7$	–
Stain repellents, oil and water repellents				
Perfluorinated surfactants	*N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE)	1691-99-2	$C_{12}H_{10}F_{17}NO_3S$	−6.8
Perfluorinated surfactants	*N*-methylperfluorooctane sulfonamidoethanol (MeFOSE)	24448-09-7	$C_{11}H_8F_{17}NO_3S$	−6.4
Surfactants (nonionic), emulsifiers, coalescing agents				
Alkylphenol ethoxylates	4-Nonylphenol	104-40-5	$C_{15}H_{24}O$	−7.1
Coalescing agents	3-Hydroxy-2,2,4-Trimethylpentyl-1-Isobutyrate (Texanol)	25625-77-4	$C_{12}H_{24}O_3$	−5.6
Terpene oxidation products				
	Pinonaldehyde	2704-78-1	$C_{10}H_{16}O_2$	−4.1
Water disinfection products				
	3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX)	77439-76-0	$C_5H_3Cl_3O_3$	−9.3
Waxes, polishes and essential oils				
Fatty acids	Stearic acid (octadecanoic acid)	57-11-4	$C_{18}H_{36}O_2$	−11.0
Fatty acids	Linoleic acid	60-33-3	$C_{18}H_{32}O_2$	−10.2
Sesquiterpenes	Caryophyllene	87-44-5	$C_{15}H_{24}$	−4.6

Weschler and Nazaroff **2008** *Atmos Environ*

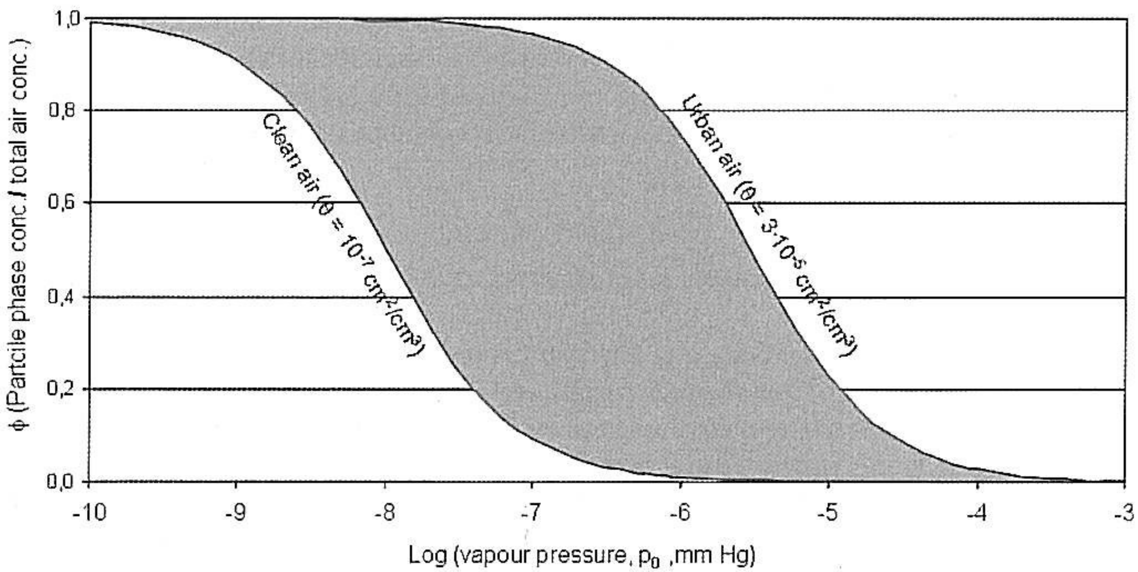
SVOC 'partitioning'

SVOCs can exist in both gas and particle phases

$$\phi = \frac{\text{particle phase concentration}}{\text{total gas} + \text{particle phase concentration}} = \frac{k * SA_{particles}}{p_{vap,sat} + k * SA_{particles}}$$

ϕ = concentration of a compound in the particle phase relative to the total air concentration (gas + particle) [dimensionless]
k = constant that depends on MW of compound
$SA_{particles}$ = aerosol surface area per volume [cm²/cm³]
$p_{vap,sat}$ = saturation vapor pressure of compound (mm Hg)

Generally: as VP ↑ BP ↓ → More likely to be in gas phase than solid phase



And: the more PM there is to adsorb/ partition on to, the more you'll have in the particle phase

Organic gases: VOCs

- VOCs, VVOCs, SVOCs, and POM are all categorized by their boiling points
  - Lower molecular weight (and low boiling point) compounds are more likely in the gas-phase

Table 1. Classification of indoor organic pollutants

Category	Description	Abbreviation	Boiling-point range (°C)[a]	Sampling methods typically used in field studies
1	Very volatile (gaseous) organic compounds	VVOC	<0 to 50–100	Batch sampling: adsorption on charcoal
2	Volatile organic compounds	VOC	50–100 to 240–260	Adsorption on Tenax, carbon molecular black or charcoal
3	Semivolatile organic compounds	SVOC	240–260 to 380–400	Adsorption on polyurethane foam or XAD-2
4	Organic compounds associated with particulate matter or particulate organic matter	POM	>380	Collection on filters

[a] Polar compounds appear at the higher end of the range.

SVOC 'partitioning'

We can also describe particle/gas partitioning as a function of the total aerosol mass concentration suspended in the air (TSP):

$$K_p = \frac{(F / TSP)}{c_g} = \frac{c_p}{c_g}$$

K_p = thermodynamic particle-gas partition coefficient [m^3/µg]
F = equilibrium particle phase concentration of a compound [ng/m^3]
TSP = concentration of total suspended particles [µg/m^3]
c_g = equilibrium gas phase concentration (ng/m^3)
c_p = concentration within the particle phase (ng/m^3)

$$\frac{F}{c_g} = K_p (TSP)$$

How do we get K_p?

Remember: as VP ↑ BP ↓ → More likely to be in gas phase than solid phase

Weschler **2003** *Atmos Environ*

SVOC 'partitioning'

- Ratio between organic compound's particle phase concentration and its gas phase concentration:

$$\frac{F}{c_g} = K_p(TSP)$$

K_p = thermodynamic particle-gas partition coefficient [$m^3/\mu g$]
F = equilibrium particle concentration of a compound [ng/m^3]
TSP = concentration of total suspended particles [$\mu g/m^3$]
c_g = equilibrium gas phase concentration (ng/m^3)

log(K_p) is higher for lower log($p_{vap,sat}$)

K_p is therefore higher for lower $p_{vap,sat}$

Higher K_p means greater fraction F in the particle phase

Lower vapor pressure more likely to be in solid phase… makes sense, right?

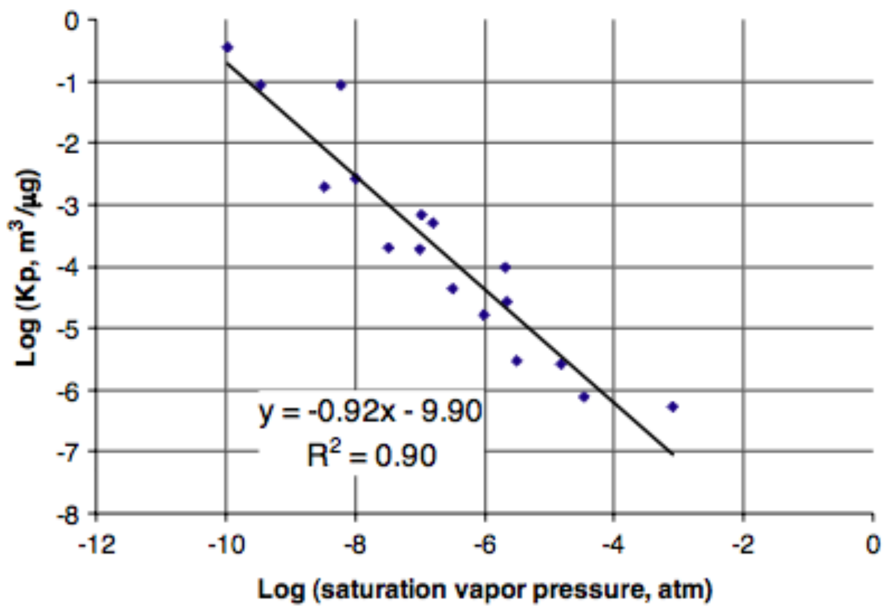


Fig. 1. Log(K_p) versus log (saturation vapor pressure at 31°C) for a series on *n*-alkanes and PAHs sorbed to particles generated from gasoline vapors. Data taken from Liang et al. (1997).

Weschler **2003** *Atmos Environ*

SVOC 'partitioning'

- Rule of thumb: higher MW compounds will have lower vapor pressures and thus be more likely to be in the particle phase (higher K_p, F, and c_p)

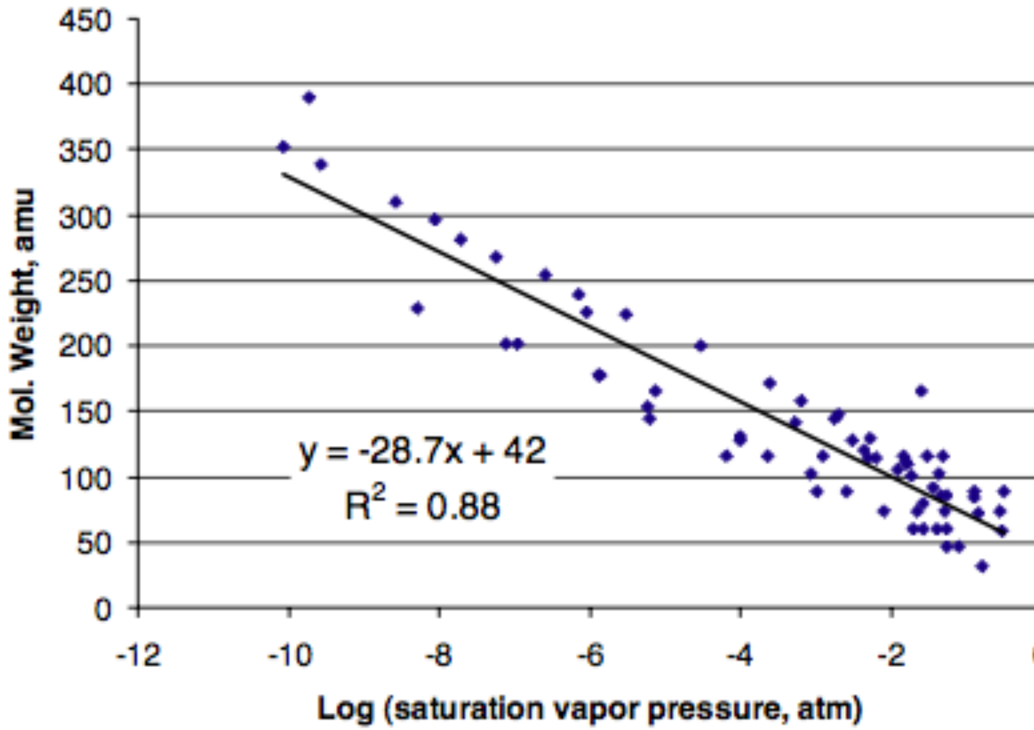


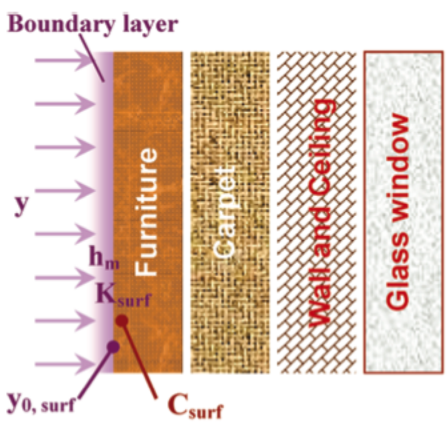
Fig. 6. Log (molecular weight, amu) versus log (saturation vapor pressure at 25°C) for compounds plotted in Figs. 1–3 and 5, as well as DEHP.

Weschler **2003** *Atmos Environ*

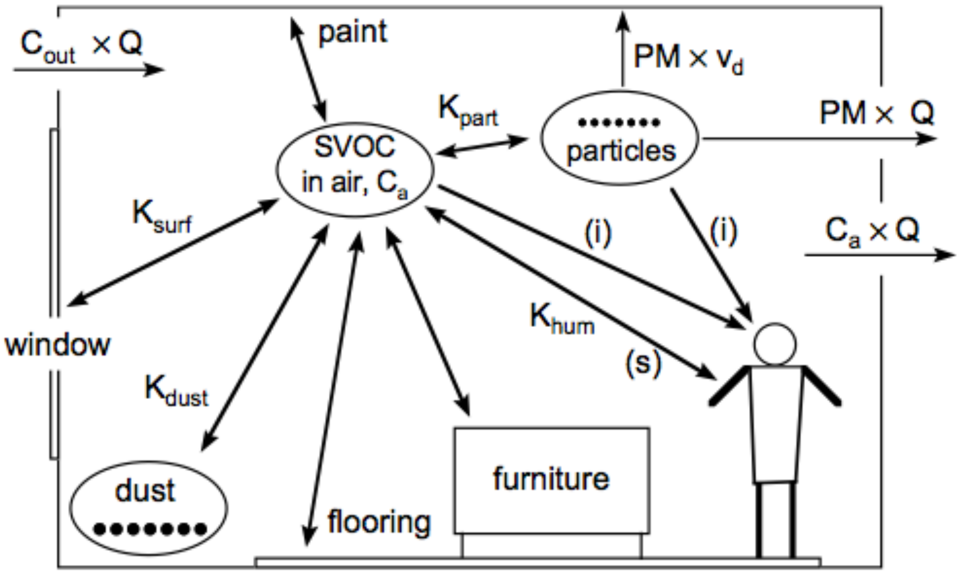
SVOCs in indoor environments

Mass balance. SVOCs emitted from indoor materials exist as:

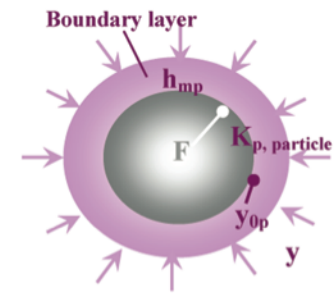
- Gases
- Attached to particles
- Adsorbed to surfaces



a. Adsorption to interior surfaces



(i) - inhalation intake; (s) - skin permeation



b. Adsorption to airborne particles

Fig. 3. Schematic illustration of some key aspects of indoor SVOC dynamics. The figure emphasizes the partitioning of an SVOC between the gas phase and different indoor sorptive compartments (airborne particles, settled dust, fixed surfaces, and human surfaces). Also shown are SVOC exchanges with outdoor air associated with ventilation. Important, but not illustrated, are emissions from indoor sources.

Weschler and Nazaroff **2008** *Atmos Environ*; Xu et al. **2009** *Environ Sci Technol*

Predicted gas, particle, and surface concentrations of different SVOCs

Distribution of selected organic compounds between the gas phase and the surfaces of airborne particles, a carpet and walls within a typical room

Compound	Mol. weight (amu)	Vapor pressure at 25°C (atm)	Assumed gas phase concentration ($\mu g\,m^{-3}$)	Mass in gas phase (μg)	Mass on particles (μg)	Mass on carpet (μg)	Mass on walls (μg)
MTBE	88	3.2E−01	10	400	2.3E−5	17	19
Toluene	92	3.7E−02	10	400	1.4E−4	100	70
Ethylbenzene	106	1.3E−02	10	400	3.6E−4	260	140
Propylbenzene	120	4.5E−03	10	400	8.9E−4	610	260
Naphthalene	128	1.0E−04	5	200	1.2E−2	7400	1390
Acenaphthene	154	5.9E−06	5	200	0.13	8.0E+4	8000
Hexadecane	226	9.1E−07	5	200	0.66	3.8E+5	2.6E+4
Phenanthrene	178	1.4E−06	1	40	0.093	5.4E+4	4000
Octadecane	254	2.5E−07	1	40	0.40	2.3E+5	1.1E+4
Pyrene	202	7.6E−08	1	40	1.1	6.2E+5	2.4E+4
Heneicosane	296	8.7E−09	0.5	20	3.6	1.9E+6	4.6E+4
Chrysene	228	5.0E−09	0.5	20	5.8	3.0E+6	6.4E+4
Tetracosane	338	2.8E−10	0.01	0.4	1.4	6.9E+5	7800
DEHP	390	1.9E−10	0.07	3.0	14	6.7E+6	6.9E+4
Pentacosane	352	8.7E−11	0.01	0.4	3.8	1.8E+6	1.6E+4

Values derived for a $3 \times 3.65 \times 3.65\,m^3$ room containing $20\,\mu g\,m^{-3}$ of airborne particles (TSP), a $10\,m^2$ carpet with pad, and painted gypsum board walls. See text for further details.

Weschler **2003** *Atmos Environ*

What are typical indoor SVOC concentrations?

Indoor concentrations and body burden of selected semivolatile organic compounds.

Chemical	Typical reported concentrations in indoor environments				US body burdens (95%ile)[a] – blood (ng g^{-1} serum); urine (μg g^{-1} creatinine)
	Air (ng m^{-3})	References	Dust (μg g^{-1})	References	
Biocides and preservatives					
Triclosan	–	–	0.2–2	Canosa et al., 2007	360 (urine)[b]
Tributyltin oxide (TBTO)	–	–	0.01–0.1	Fromme et al., 2005	–
Pentachlorophenol (PCP)	0.4–4	Rudel et al., 2003; Morgan et al., 2004	0.2–2	Rudel et al., 2003	2.3 (urine)
Combustion byproducts					
Nicotine	200–2000	Leaderer and Hammond, 1991; Gehring et al., 2006	10–100	Hein et al., 1991; Matt et al., 2004	2.2 (blood)[c]
Benzo[*a*]pyrene (BaP)	0.02–0.2	Naumova et al., 2002; Morgan et al., 2004	0.2–2	Rudel et al., 2003; Mannino and Orecchio, 2008	0.18 (urine)
Phenanthrene	10–100	Naumova et al., 2002	0.2–2	Mannino and Orecchio, 2008	1.7 (urine)[d]
Pyrene	1–10	Naumova et al., 2002; Rudel et al., 2003	0.2–2	Mannino and Orecchio, 2008	0.24 (urine)
Degradation products/residual monomers					
Bisphenol A	0.5–5	Morgan et al., 2004	0.2–2	Rudel et al., 2003	11 (urine)[e]
Flame retardants					
2,2′,4,4′,5,5′-Hexabromodiphenyl ether (BDE-153, hexa BDE)	0.002–0.02	Wilford et al., 2004; Shoeib et al., 2004; Allen et al., 2007	0.03–0.3	Stapleton et al., 2005; Wilford et al., 2005; Wu et al., 2007	0.44 (blood)[f]
2,2′,4,4′,5-Pentabromodiphenyl ether (BDE-99, pentaBDE)	0.03–0.3	Wilford et al., 2004; Shoeib et al., 2004; Allen et al., 2007	0.4–4	Rudel et al., 2003; Stapleton et al., 2005; Wilford et al., 2005; Wu et al., 2007	0.28 (blood)[f]
2,2′,4,4′-Tetrabromodiphenyl ether (BDE-47, tetra BDE)	0.06–0.6	Wilford et al., 2004; Shoeib et al., 2004; Allen et al., 2007	0.3–3	Stapleton et al., 2005; Wilford et al., 2005; Wu et al., 2007	1.1 (blood)[f]
Perchloropentacyclodecane (Mirex)	–	–	–	–	0.41 (blood)
Tris(chloropropyl) phosphate	6–60	Wensing et al., 2005	0.3–3	Wensing et al., 2005	–

Weschler and Nazaroff **2008** *Atmos Environ*

What are typical indoor SVOC concentrations?

Indoor concentrations and body burden of selected semivolatile organic compounds.

Chemical	Typical reported concentrations in indoor environments				US body burdens (95%ile)[a] – blood (ng g^{-1} serum); urine (μg g^{-1} creatinine)
	Air (ng m^{-3})	References	Dust (μg g^{-1})	References	
Personal care products					
Galaxolide	25–250	Fromme et al., 2004	0.5–5	Fromme et al., 2004	–
Pesticides/termiticides/herbicides					
Propoxur	0.8–8	Rudel et al., 2003	0.05–0.5	Rudel et al., 2003	<1 (urine)
Chlordane	0.5–5	Morgan et al., 2004; Offenberg et al., 2004	0.04–0.4	Rudel et al., 2003	0.35 (blood)
p,p′-DDT	0.2–2	Rudel et al., 2003	0.1–1	Rudel et al., 2003	0.18 (blood)
Chlorpyrifos	1–10	Morgan et al., 2004	0.08–0.8	Julien et al., 2008; Morgan et al., 2004	9.2 (urine)
Diazinon	1–5	Morgan et al., 2004	0.02–0.2	Julien et al., 2008	<1 (urine)
Methyl parathion	0.05–0.5	Rudel et al., 2003	0.01–0.1	Rudel et al., 2003	2.9 (urine)
Cyfluthrin	0.1–1.0	Morgan et al., 2004	0.08–0.8	Julien et al., 2008; Morgan et al., 2004	} Common metabolite: 2.6 (urine)
Cypermethrin	–	–	0.08–0.8	Julien et al., 2008; Rudel et al., 2003	}
Permethrin	0.1–0.7	Rudel et al., 2003; Morgan et al., 2004	0.2–2	Rudel et al., 2003; Julien et al., 2008	3.8 (urine)
Piperonyl butoxide	0.1–1.0	Rudel et al., 2003	0.1–1.0	Rudel et al., 2003	–
Plasticizers					
Di(2-ethylhexyl) adipate (DEHA)	5–15	Rudel et al., 2003	2–10	Rudel et al., 2003	–
Triphenylphosphate (TPP)	0.1–1	Wensing et al., 2005	2–20	Wensing et al., 2005	–

Weschler and Nazaroff **2008** *Atmos Environ*

Indoor SVOC behavior

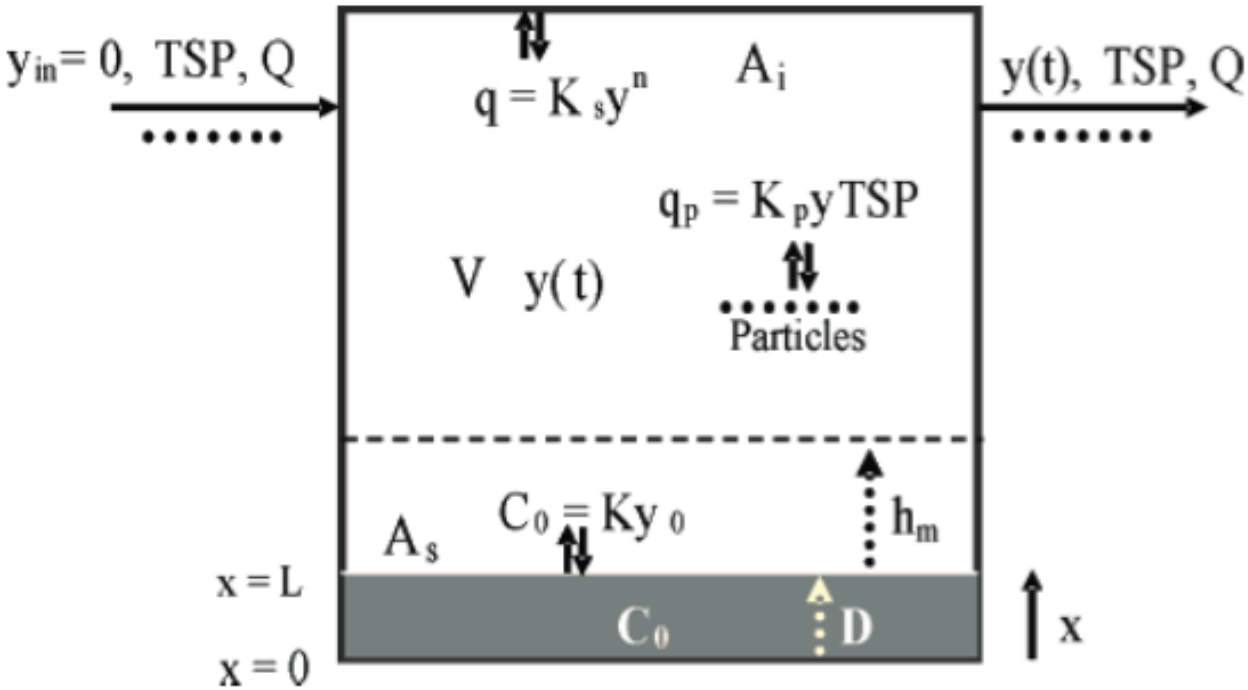


FIGURE 1. Schematic representation of vinyl flooring in experimental chamber.

Xu and Little **2006** *Environ Sci Technol*

Indoor SVOC behavior w/ different sample areas

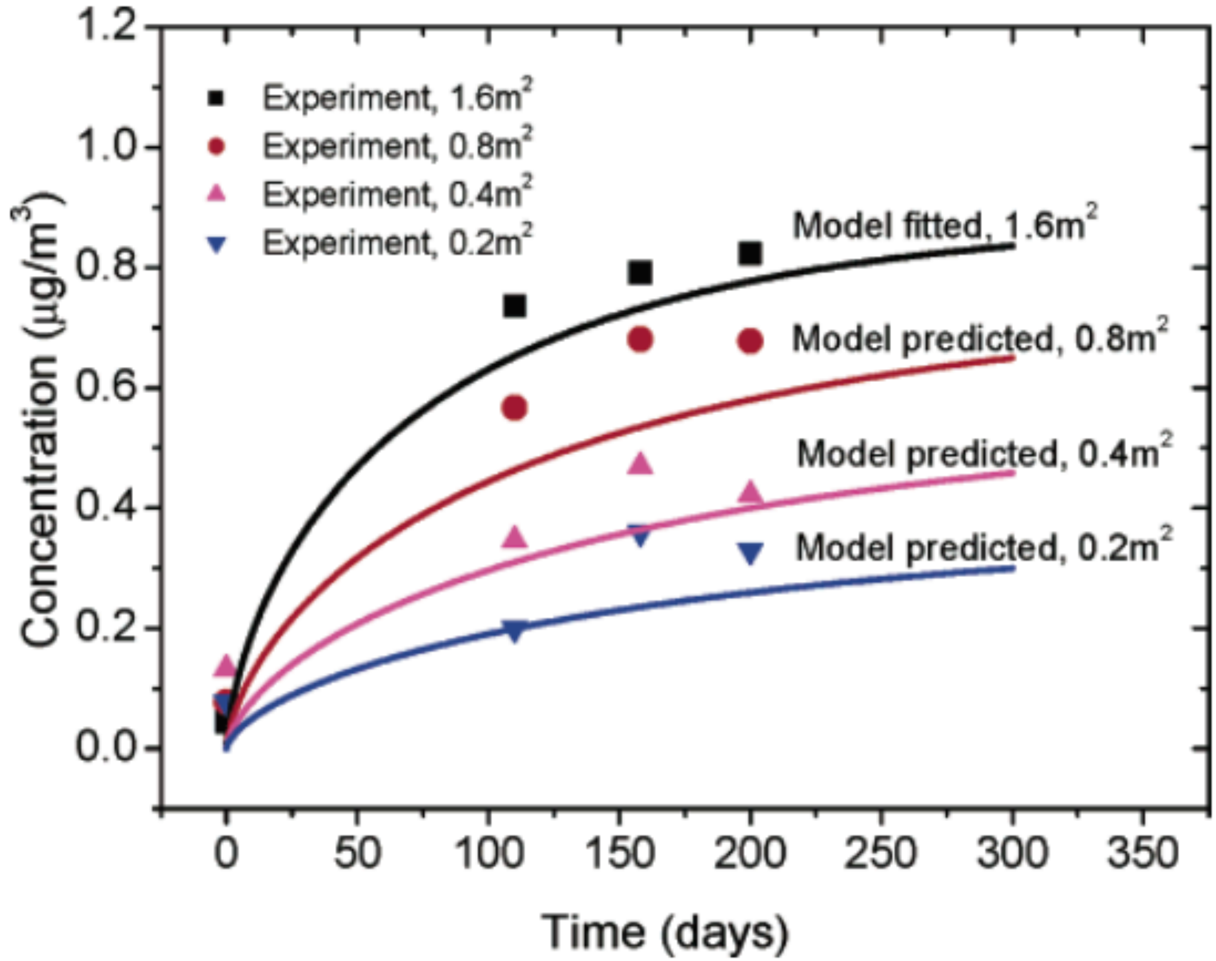


FIGURE 2. Comparison of fitted and predicted gas-phase DEHP concentrations with data measured in CLIMPAQ.

Xu and Little **2006** *Environ Sci Technol*

Indoor SVOC behavior w/ material/air partitioning

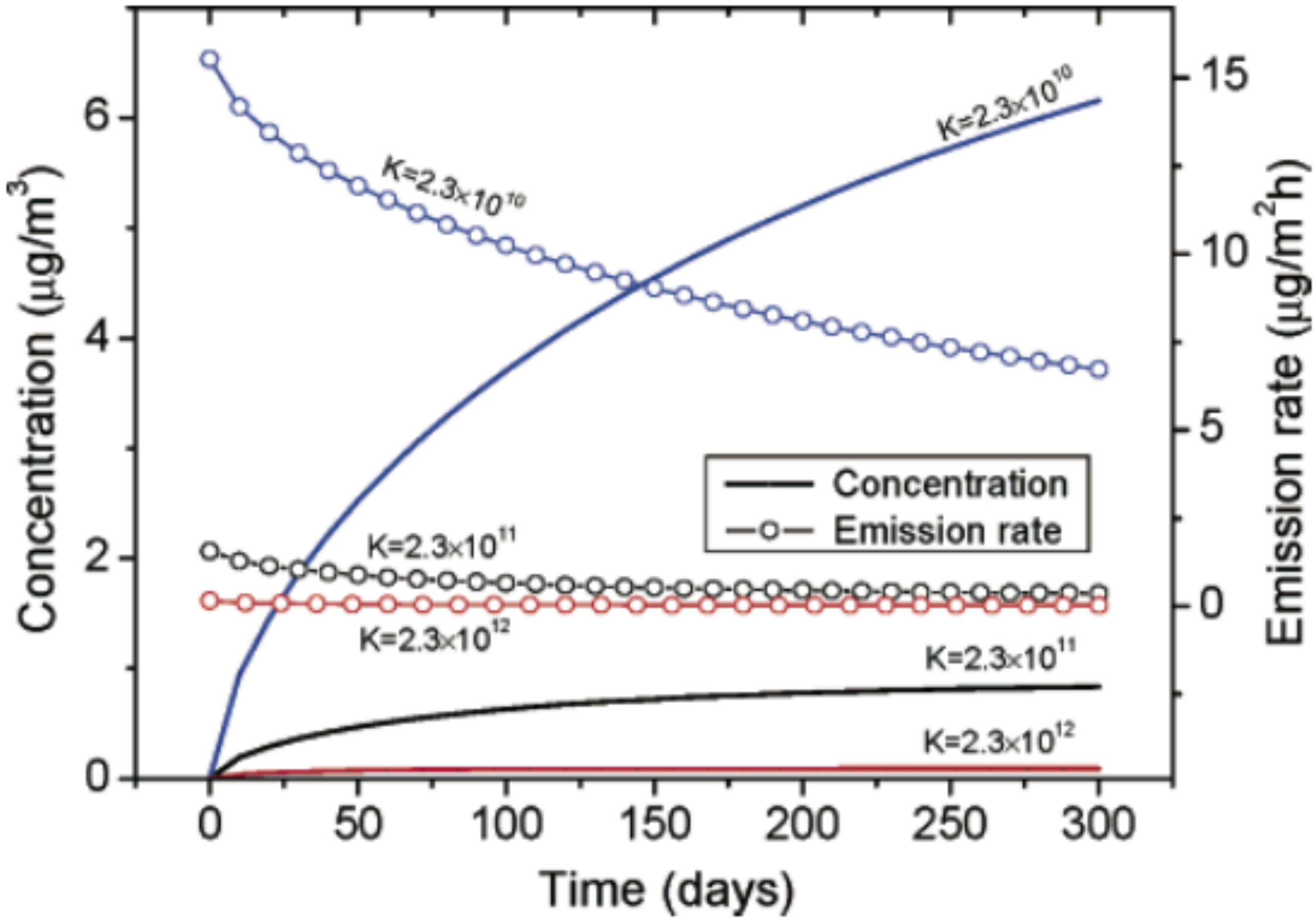


FIGURE 5. Influence of the material/air partition coefficient (*K*) on SVOC emission rate and gas-phase concentration.

Xu and Little **2006** *Environ Sci Technol*

Indoor SVOC behavior w/ surface area

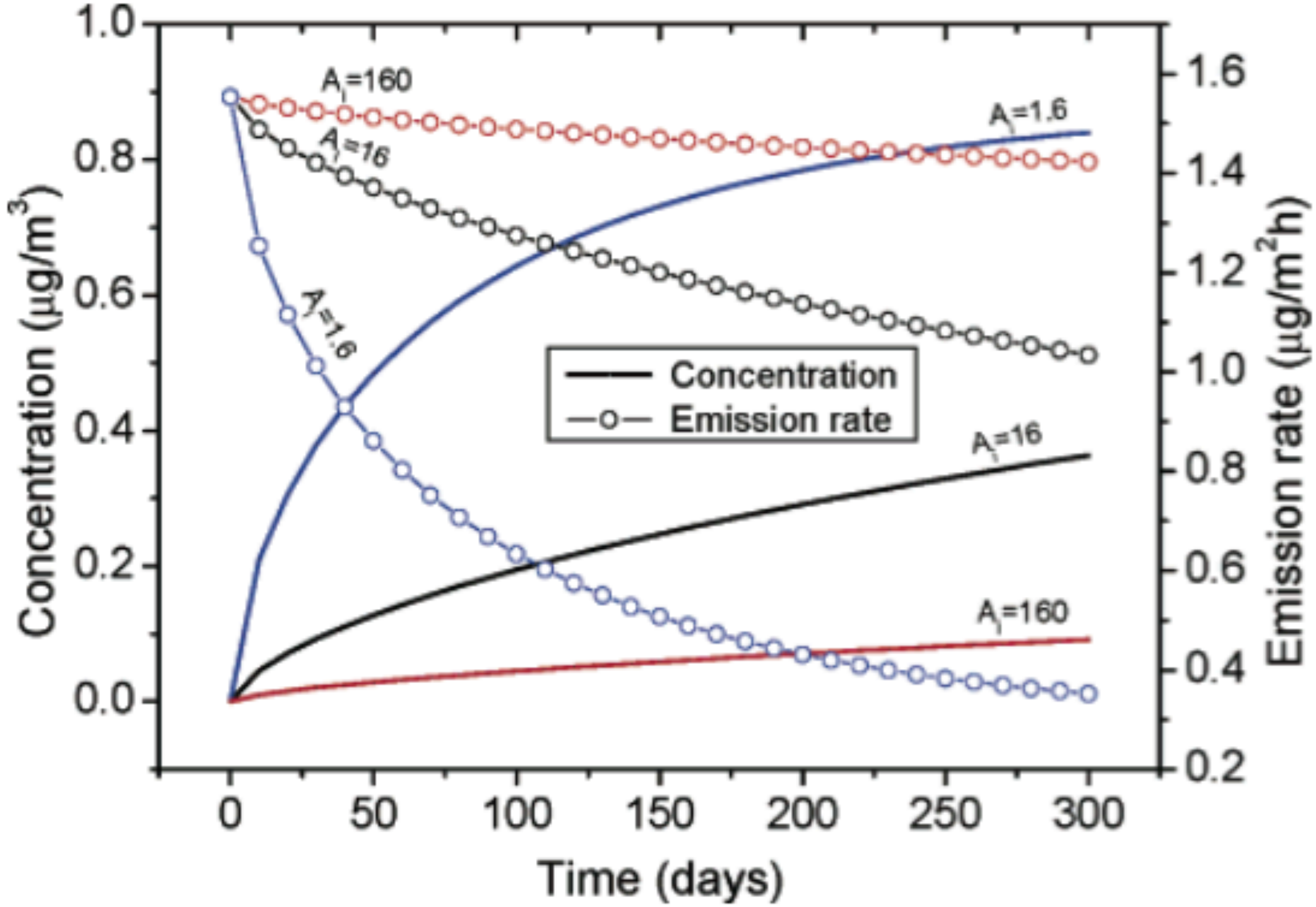


FIGURE 7. Influence of internal surface area (A_i) on SVOC emission rate and gas-phase concentration.

Xu and Little **2006** *Environ Sci Technol*

Indoor SVOC behavior w/ suspended particles

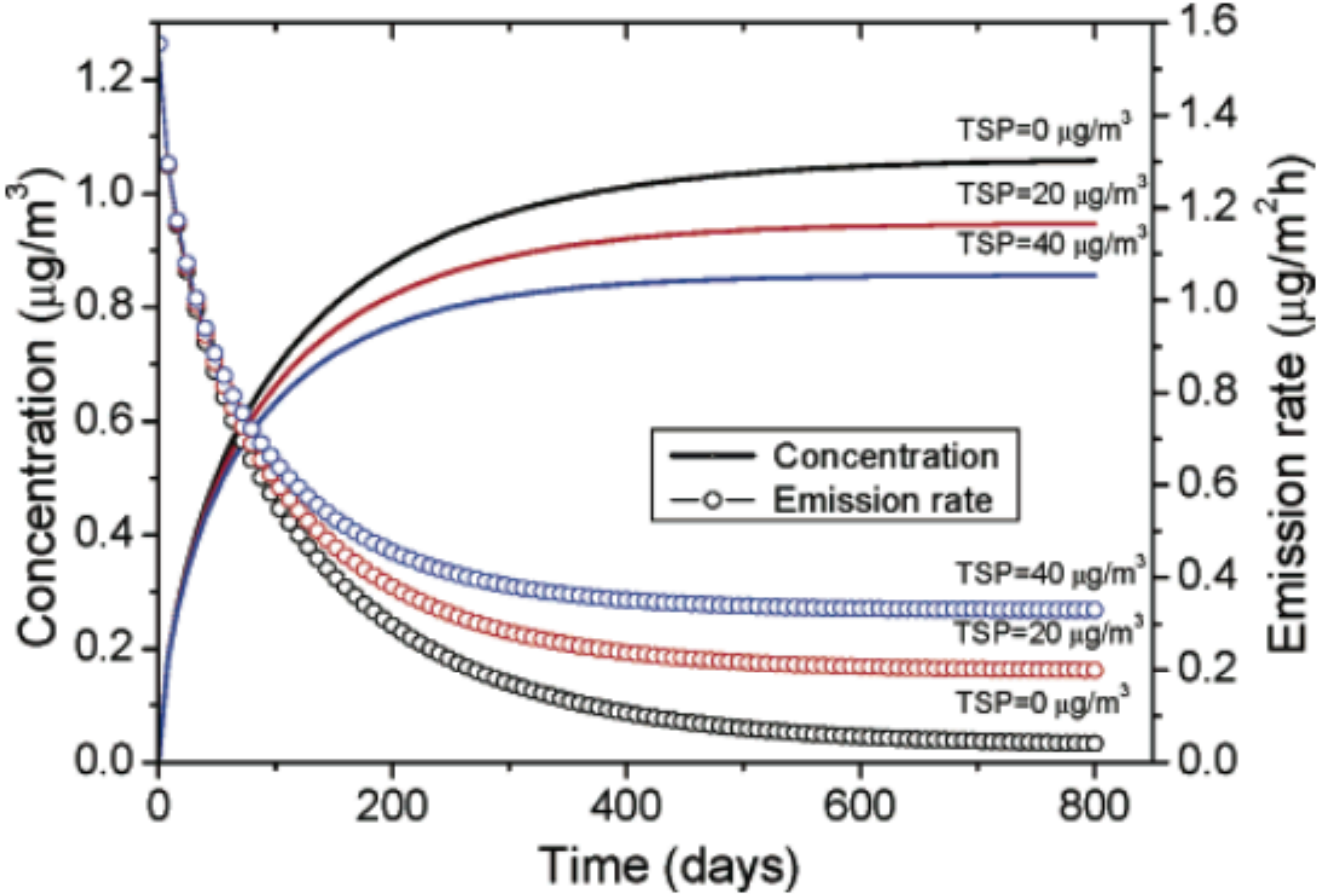


FIGURE 9. Influence of total suspended particle concentration on DEHP emission rate and gas-phase DEHP concentration.

Xu and Little **2006** *Environ Sci Technol*

Transdermal uptake of DEHP and DnBP

Transdermal Uptake of Diethyl Phthalate and Di(*n*-butyl) Phthalate Directly from Air: Experimental Verification

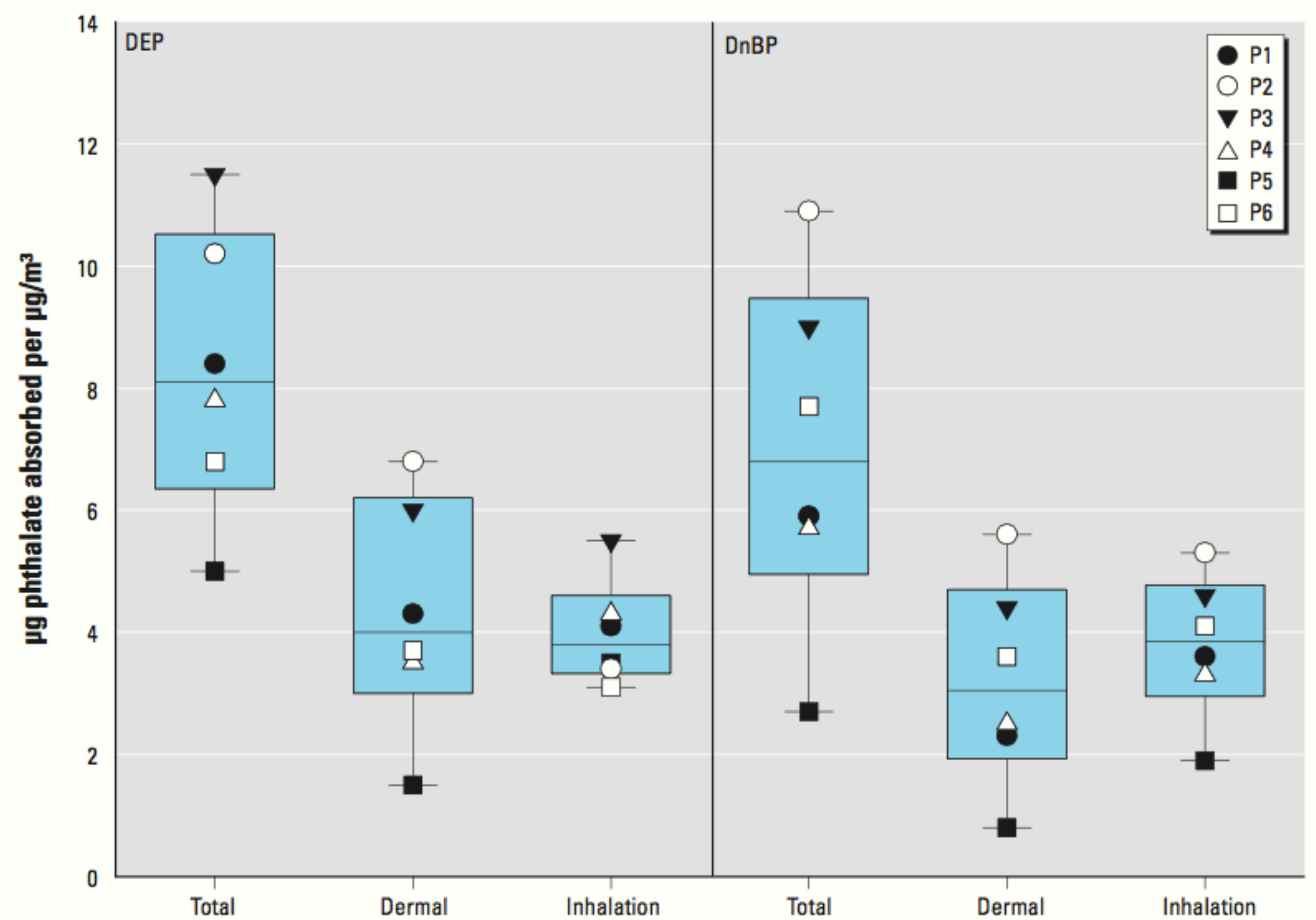
OBJECTIVES: This study investigated transdermal uptake, directly from air, of diethyl phthalate (DEP) and di(*n*-butyl) phthalate (DnBP) in humans.

METHODS: In a series of experiments, six human participants were exposed for 6 hr in a chamber containing deliberately elevated air concentrations of DEP and DnBP. The participants either wore a hood and breathed air with phthalate concentrations substantially below those in the chamber or did not wear a hood and breathed chamber air. All urinations were collected from initiation of exposure until 54 hr later. Metabolites of DEP and DnBP were measured in these samples and extrapolated to parent phthalate intakes, corrected for background and hood air exposures.

Weschler et al **2015** *Environ Health Persp*

Transdermal uptake of DEHP and DnBP

Transdermal Uptake of Diethyl Phthalate and Di(*n*-butyl) Phthalate Directly from Air: Experimental Verification

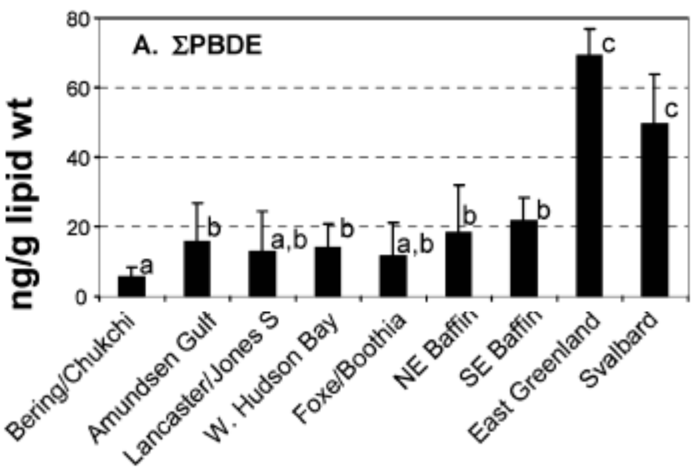


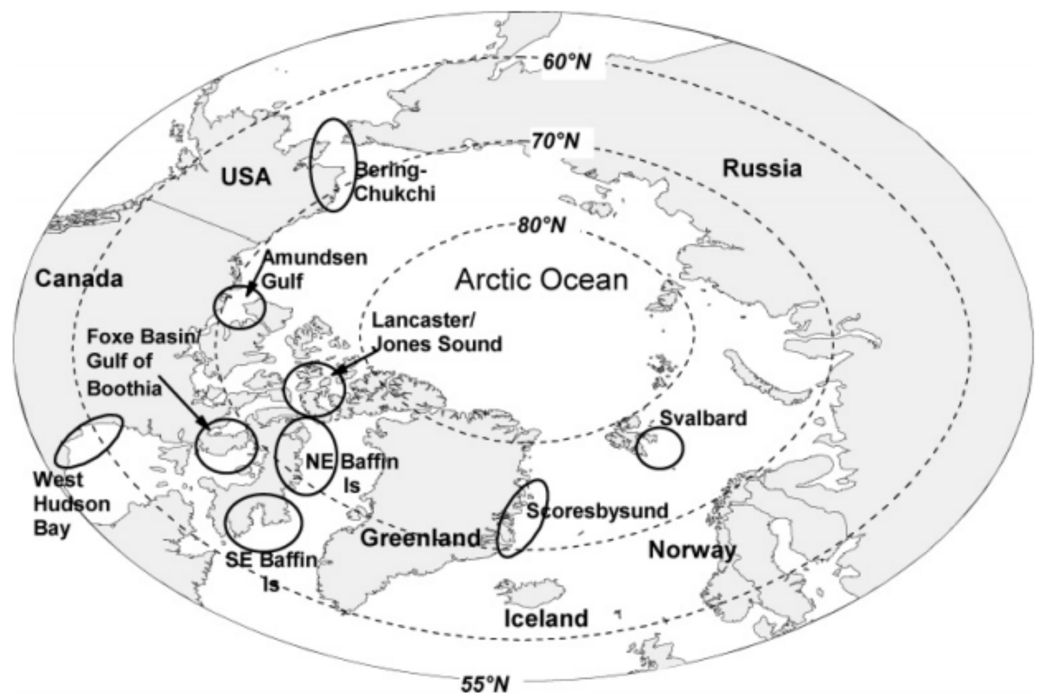
Weschler et al **2015** *Environ Health Persp*

Indoor and outdoor connections

Brominated Flame Retardants in Polar Bears (*Ursus maritimus)* from Alaska, the Canadian Arctic East Greenland, and Svalbard

Muir et al., **2006** *Environ Sci Technol*





- What do flame retardants in polar bears have to do with indoor air pollution??

Indoor and outdoor connections

Indoor Air Is a Significant Source of Tri-decabrominated Diphenyl Ethers to Outdoor Air via Ventilation Systems

Björklund et al., **2012** *Environ Sci Technol*

Table 4. Estimated Emissions of PentaBDE to Outdoor Air in Sweden (See SI for Full Description of Calculations and References)

source	emission factor	activity (kg/year)	annual emission (kg/year)	comment
metals manufacturing	35−716 μg/tonne product	1.7×10^9	0.06−1	concerns the sum of 20 congeners (di-octaBDEs), with BDE-47 and -99 being the most predominant
municipal incineration	no information	0.8−18	not possible to estimate	
electronics recycling	no information	$9 \times 10^4 - 5.6 \times 10^5$	not possible to estimate	
e-waste fires	8.4−50.2 μg/kg burnt material, assuming no extinguishing water	1.48×10^6	0.01−0.07	concerns sum of BDEs (47,85,99,100,138,153,154). nondetected congeners were assigned a value of 0 (d.l. = 1.5 μg/kg burnt)
landfill fires	4.96 − 394 μg/kg C burned	$7 \times 10^4 - 7 \times 10^5$	3.5×10^{-4}−0.028	concerns BDE-47 only
indoor environment - households	*10−260 pg/m³*	*$1.7 \times 10^{12} - 9.4 \times 10^{12}$ m³/year*	*0.024−0.92*	*concerns BDE-28, -47, -99, -153*
indoor environment— public buildings	*84−1600 pg/m³*	*$2.7 \times 10^{12} - 8.7 \times 10^{12}$ m³/year*	*0.26−8.7*	*concerns BDE-28, -47, -99, -153*
total			**0.35−11**	
percentage total contribution of indoor air			81−82	

For one of the first times we're aware of, indoor air pollution in modern countries is linked strongly to outdoor air pollution in remote regions of the world!

- Potential effects go beyond human beings

AEROSOL SAMPLING TECHNIQUES

Measuring particulate matter

- Sampling methods distinguish between:
  - Particle counting
    - No sizing
  - Particle sizing
    - Count + size information
  - Particle mass
  - Particle composition

For biological particles:

- Viable and non-viable bioaerosols

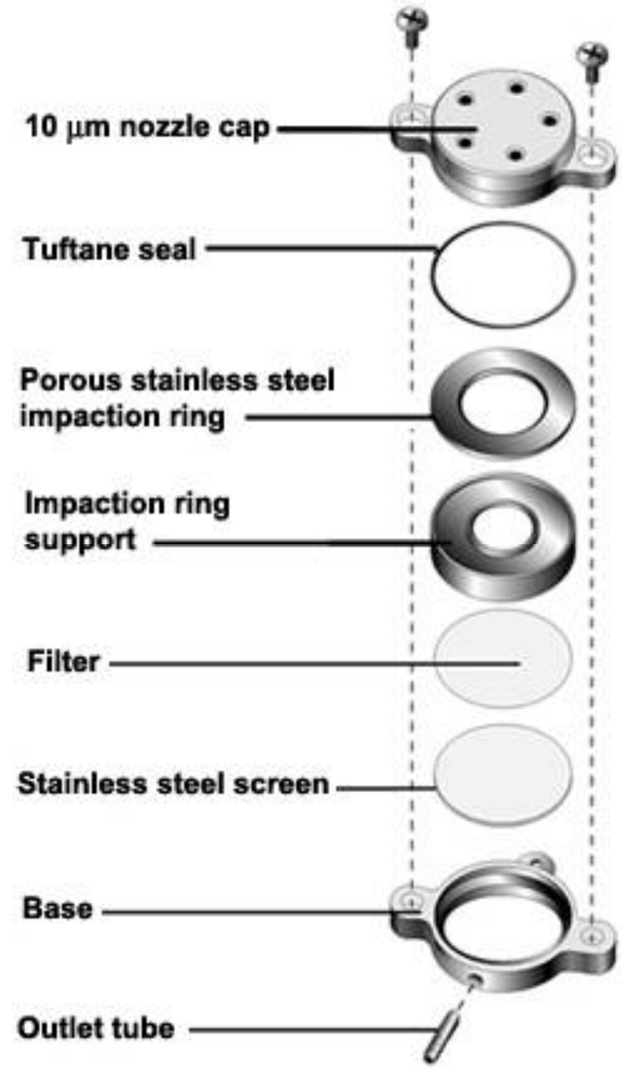
Gravimetric (mass-based) particle sampling

- Particles have very low masses
- Need to collect many particles to have measureable mass
- Most mass-based techniques are integrated samples
  - Sample onto filters at known airflow rate for known period of time
  - Weigh filters before and after
  - Calculate concentration
  - Correct for RH

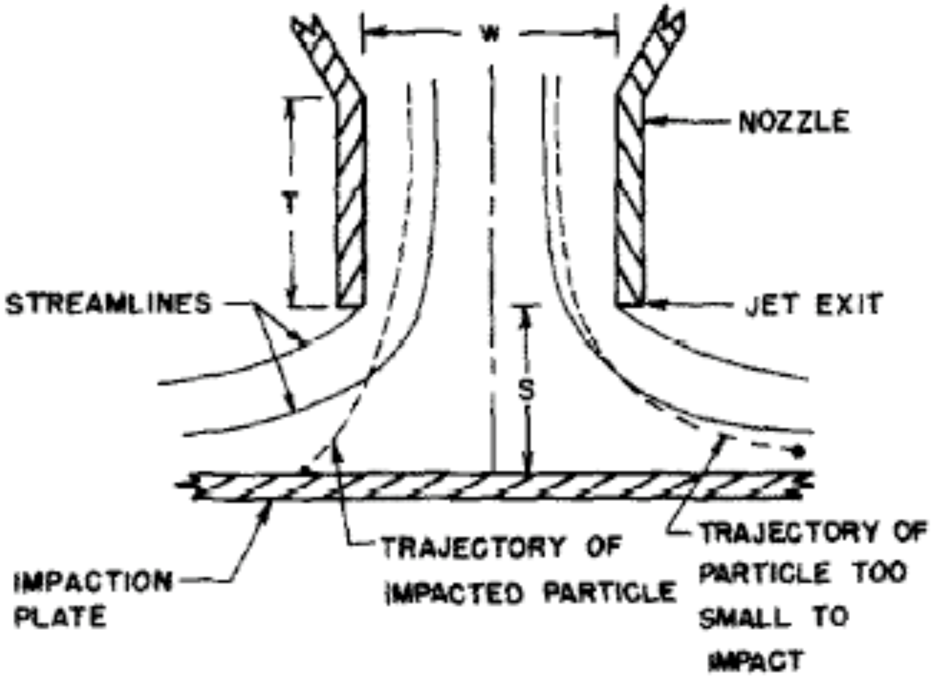
Particle Diameter [μm]	Particle Mass [g]
0.01	$5 \cdot 10^{-19}$
0.1	$5 \cdot 10^{-16}$
1	$5 \cdot 10^{-13}$
10	$5 \cdot 10^{-10}$

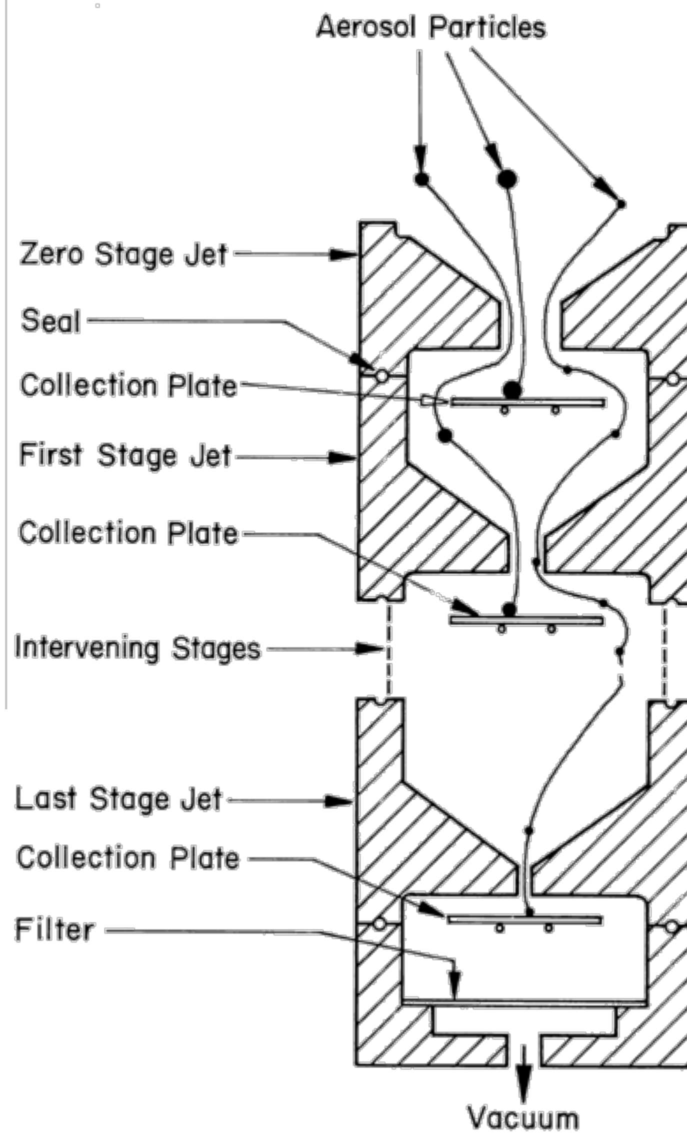
Gravimetric (mass-based) particle sampling

SKC PEM sampler

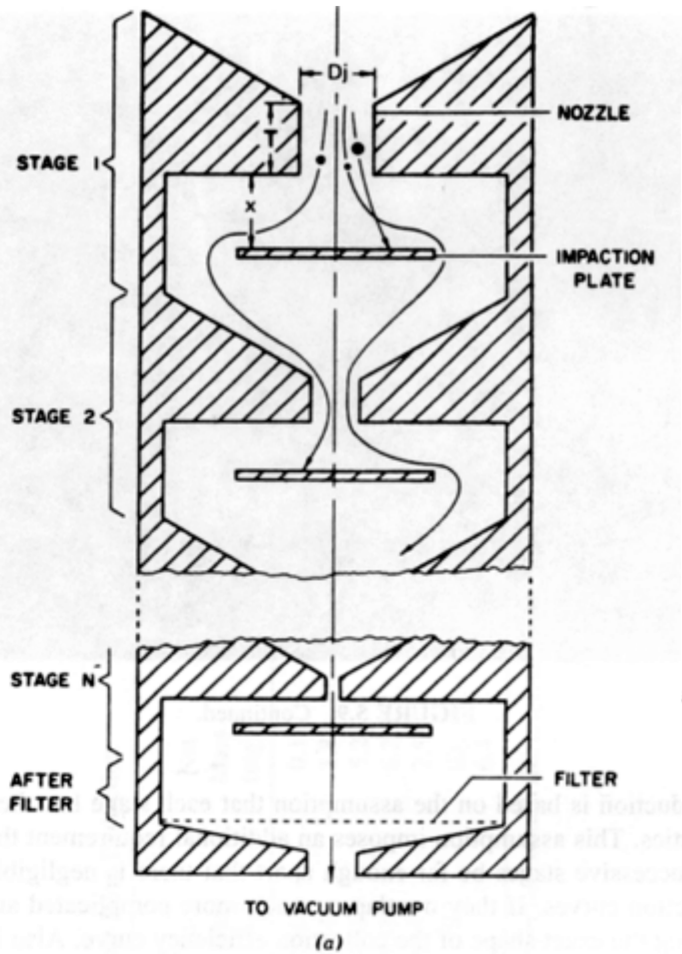


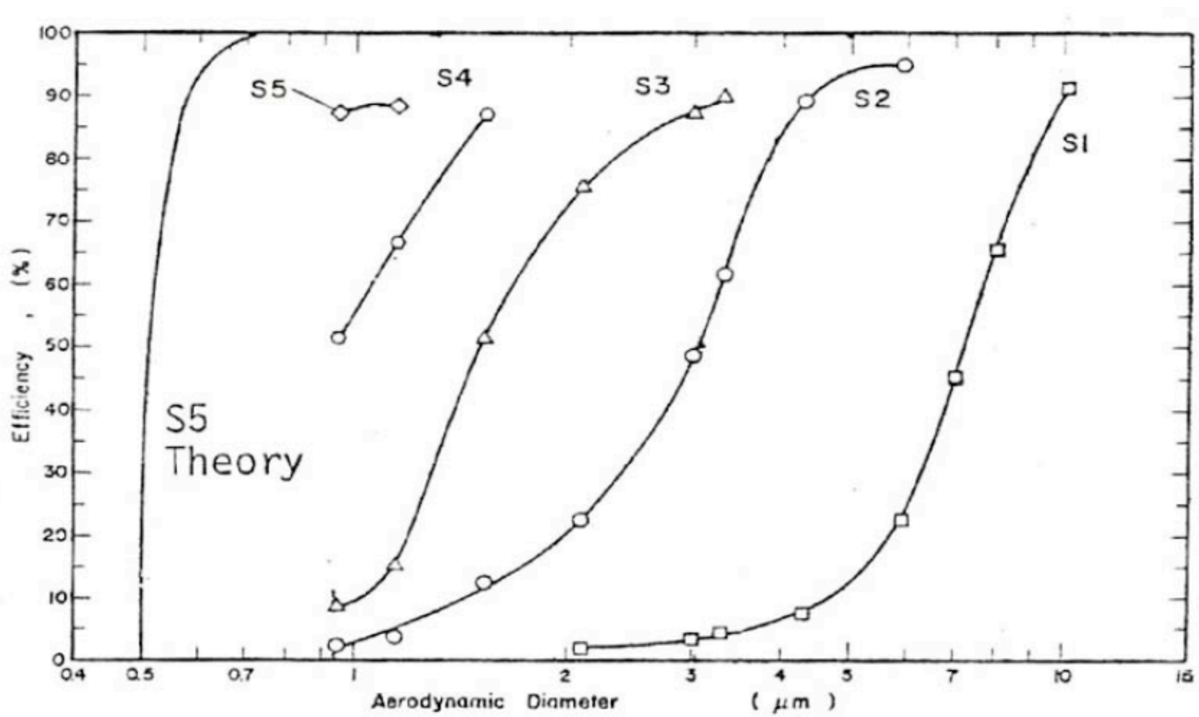
Gravimetric particle sampling: Cascade impactor





Gravimetric particle sampling: Cascade impactor





Optical measurements

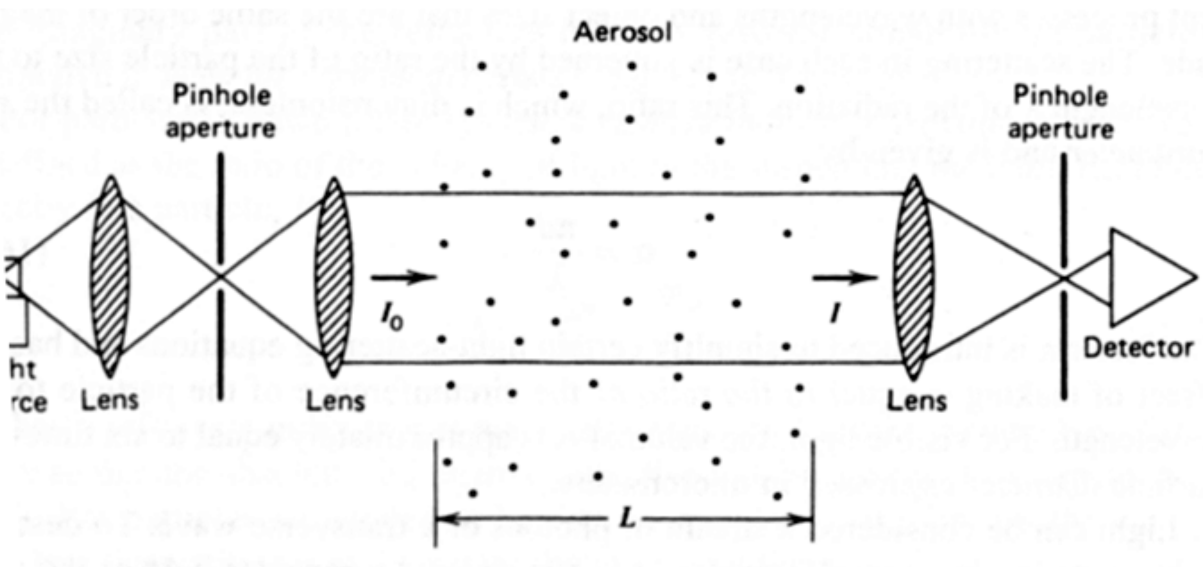


FIGURE 16.1 Schematic diagram of an extinction-measuring apparatus.

Extinction: $$\frac{I}{I_0} = e^{-\sigma_e L}$$

Optical measurements: Mie/Rayleigh Theory for Scattering

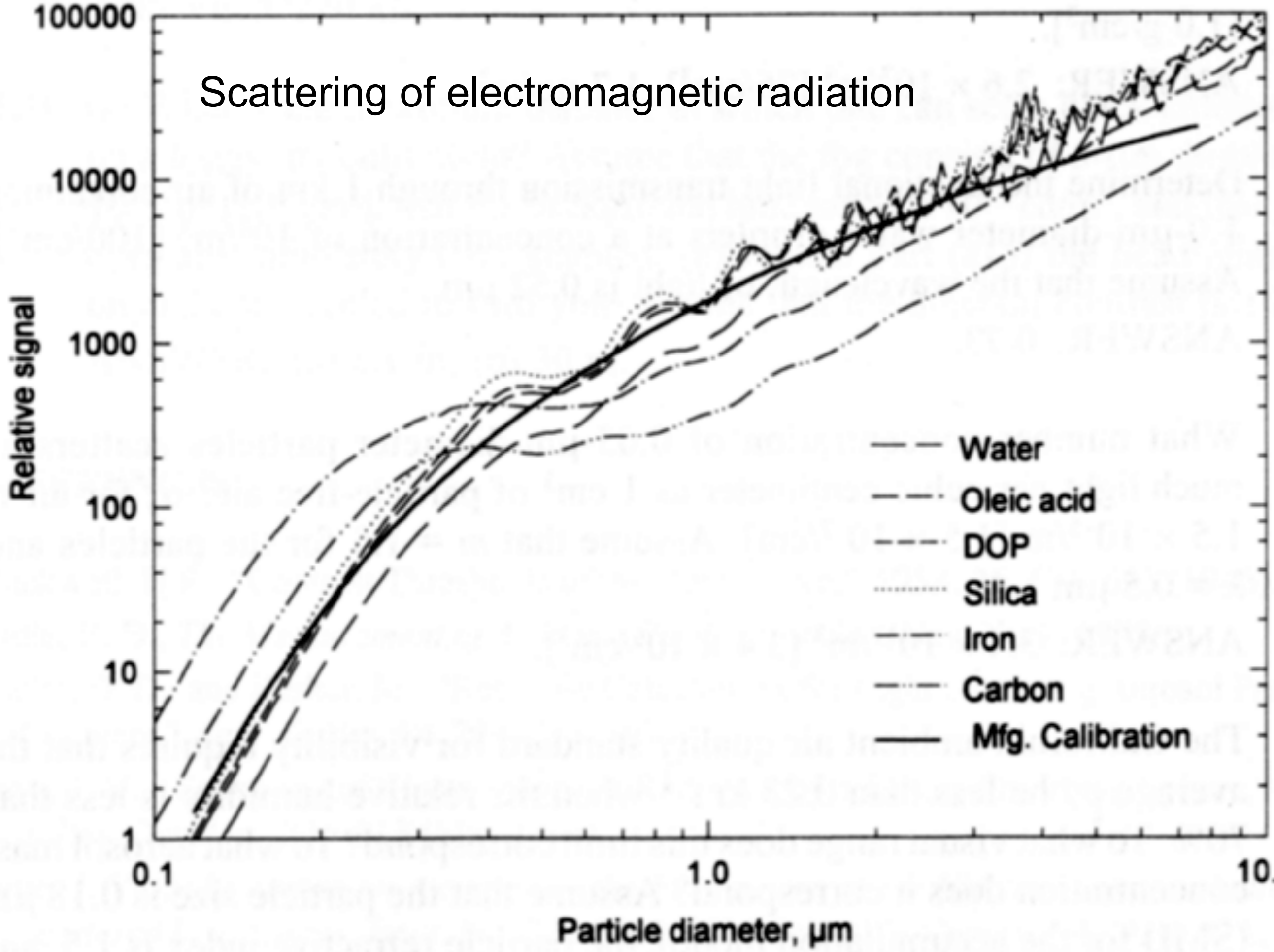


FIGURE 16.16 Calculated response curves for six materials and manufacturer's calibration curve for model LAS-X® (PMS, Inc., Boulder, CO) optical particle counter.

Measuring particle "mass" optically

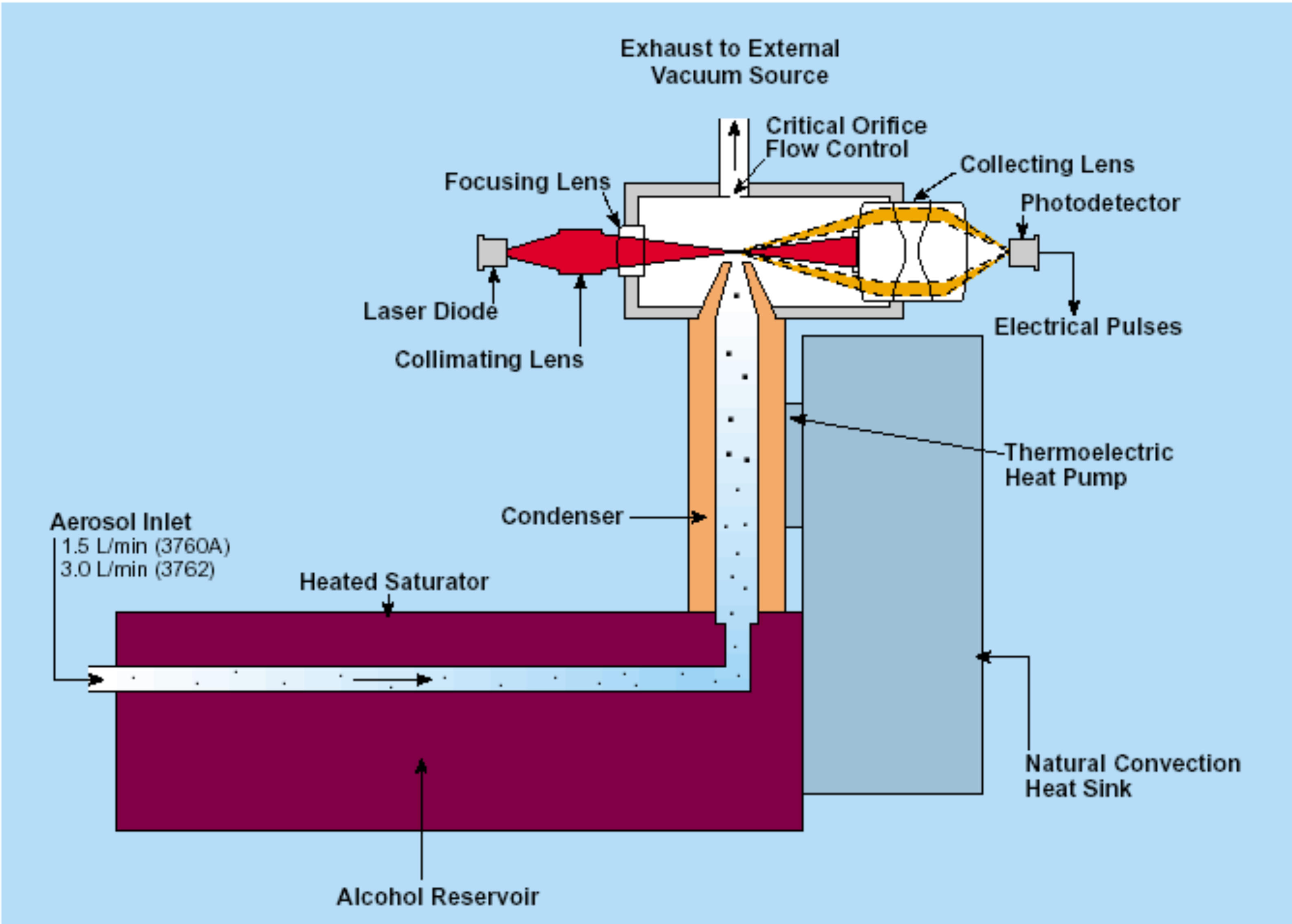
- Photometers
  - Typically **relative** instruments
  - Sensitive to particle speed
- Nephelometer
  - Measure scattering for aerosol sample (~ 1L) over wide range of angles (θ)
    - Particle density is function of the light reflected into the detector
      - Scattered light depends on properties of the particles such as their shape, color, and reflectivity
  - Determines mass concentration much more accurately than photometer
  - Often calibrated to single particle composition

Condensation nuclei counter (CNC)

- Subject aerosol stream to alcohol (or water) vapor
- Cool air stream to cause condensation
- Count particles with an optical particle counter

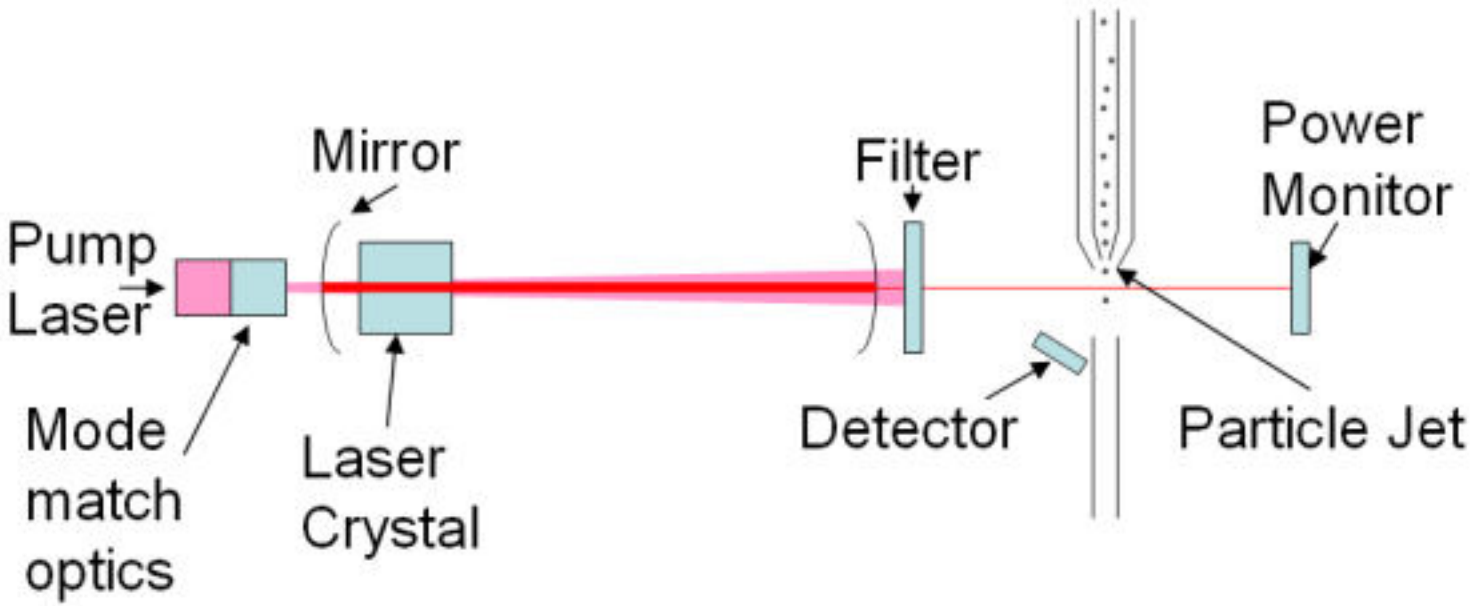
- Closely related to a condensation particle counter (CPC)

Condensation nuclei counter (CNC)



Optical particle counter

- Similar to photometer, but particles are isolated
  - May require dilution
- 0.065 – 20 µm
  - Practically 0.1 – 5 µm
- Some devices just count and don't size



Optical particle counter

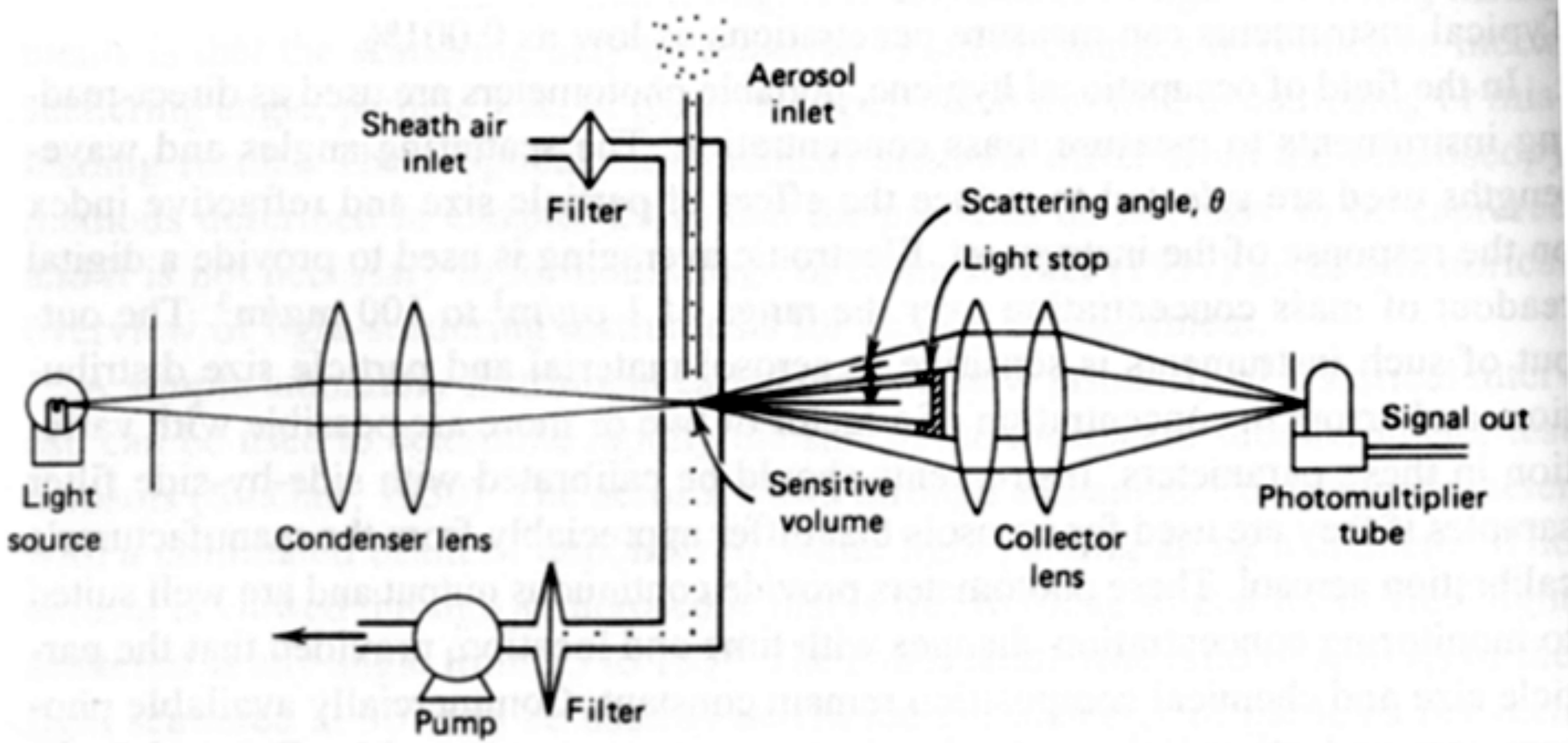


FIGURE 16.15 Diagram of a forward-scattering optical particle counter.

Aerodynamic particle sizer

- One of many **time-of-flight** instruments
  - Two laser beams separated by known distance
  - Particle is accelerated between beams
  - Time between beams being broken is calibrated to a test aerosol
  - Particles exiting the jet have a velocity related to their aerodynamic diameter (assume spherical particles and unit density)
- Measures 0.5 - 20 μm

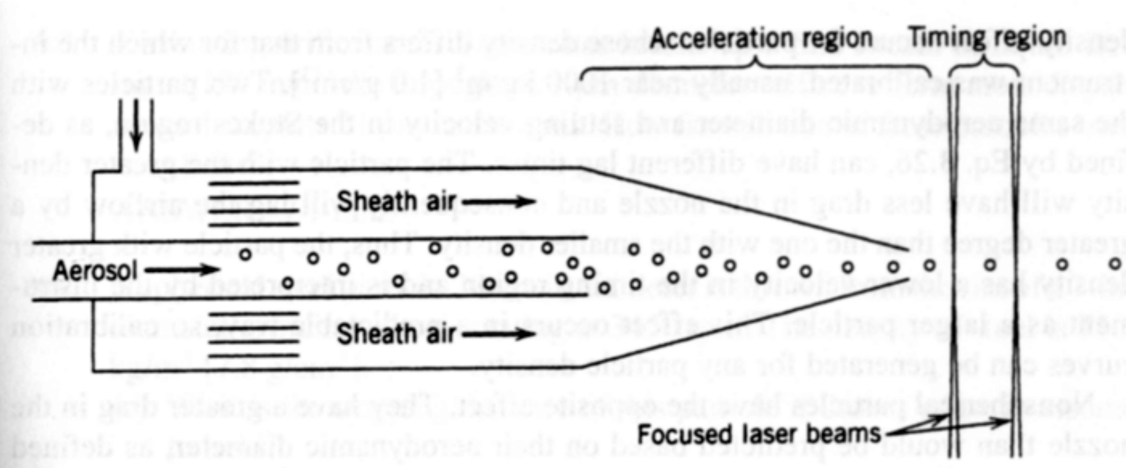
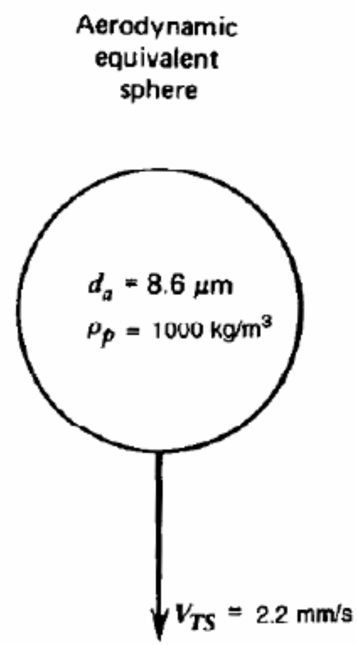


FIGURE 5.13 Schematic diagram of time-of-flight instrument.



Aerodynamic particle sizer

- Small particles move at the air velocity
- Large particles lag air velocity
- Problems
  - Small particles not-Stokesian
  - Larger density is sized as a larger particle
  - Shape also influences drag
  - Multiple particles in sizing chamber (same as other devices)

Particle mobility analyzer

- Particles entering the system are neutralized using a radioactive source
  - Yields equilibrium charge distribution
- Particles then enter a Differential Mobility Analyzer (DMA) where the aerosol is classified according to **electrical mobility**
  - Only particles of a narrow range of mobility exit through the output slit.
- This monodisperse distribution then goes to a Condensation Particle Counter which determines the particle concentration at that size
- Measures 0.001 – 1 μm
  - 0.002 – 0.4 μm most accurate

Electrical mobility: Ability of charged particles to move through medium in response to electric field (inversely proportional to diameter)

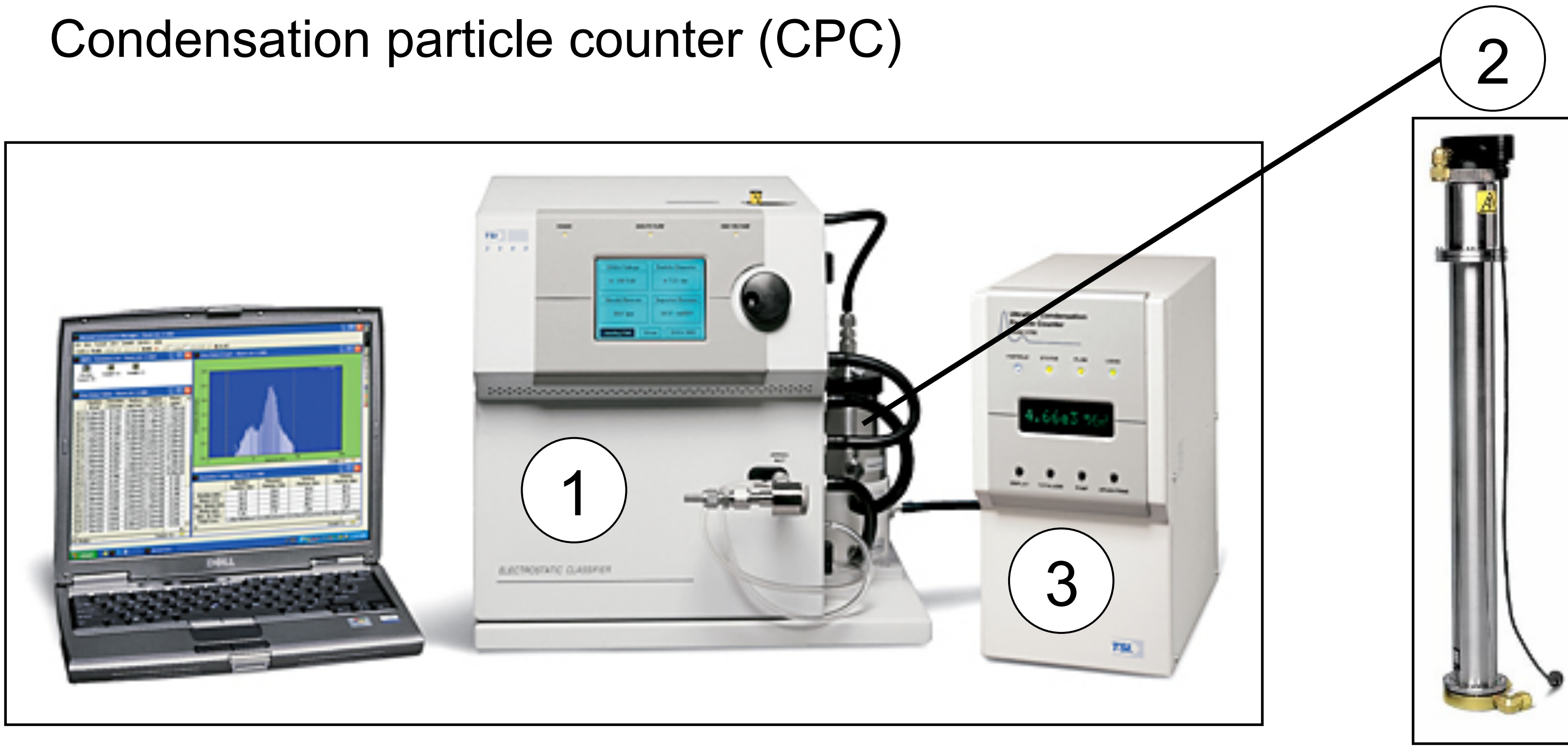
Particle mobility and charge distributions

TABLE 15.4 Distribution of Charge on Aerosol Particles at Boltzmann Equilibrium

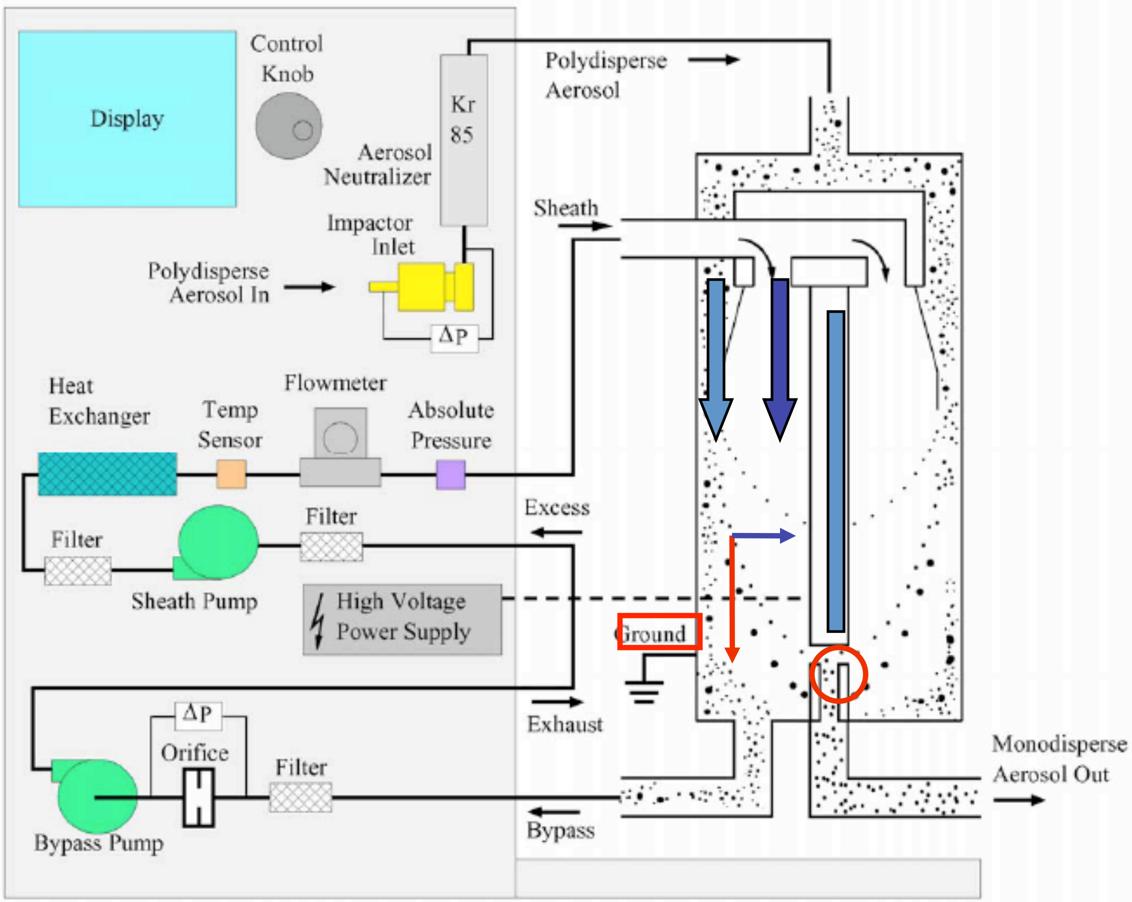
Particle Diameter (μm)	Average Number of Charges	Percentage of Particles Carrying the Indicated Number of Charges								
		< −3	−3	−2	−1	0	+1	+2	+3	>+3
0.01	0.007				0.3	99.3	0.3			
0.02	0.104				5.2	89.6	5.2			
0.05	0.411			0.6	19.3	60.2	19.3	0.6		
0.1	0.672		0.3	4.4	24.1	42.6	24.1	4.4	0.3	
0.2	1.00	0.3	2.3	9.6	22.6	30.1	22.6	9.6	2.3	0.3
0.5	1.64	4.6	6.8	12.1	17.0	19.0	17.0	12.1	6.8	4.6
1.0	2.34	11.8	8.1	10.7	12.7	13.5	12.7	10.7	8.1	11.8
2.0	3.33	20.1	7.4	8.5	9.3	9.5	9.3	8.5	7.4	20.1
5.0	5.28	29.8	5.4	5.8	6.0	6.0	6.0	5.8	5.4	29.8
10.0	7.47	35.4	4.0	4.2	4.2	4.3	4.2	4.2	4.0	35.4

Scanning Mobility Particle Sizer (SMPS)

1. Electrostatic classifier (EC)
2. Differential mobility analyzer (DMA)
3. Condensation particle counter (CPC)



SMPS: EC and DMA



EC

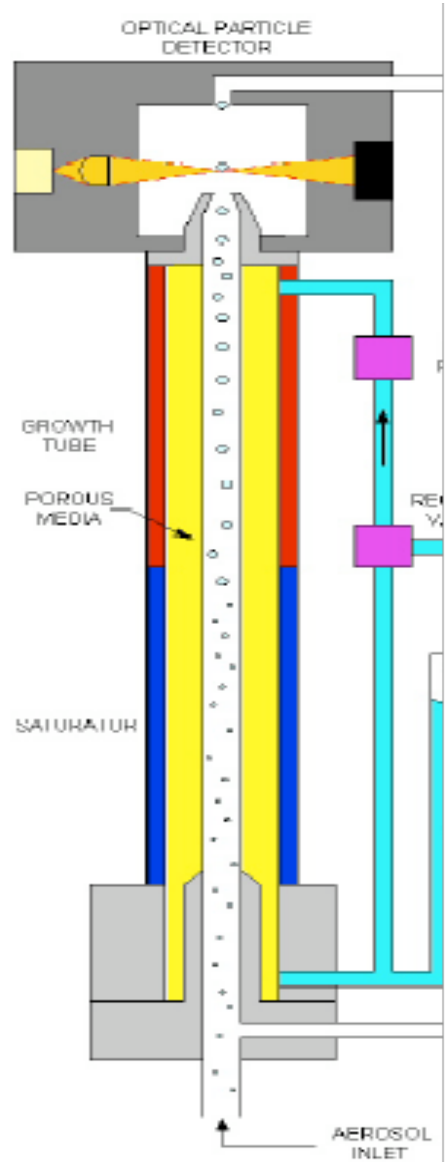
- Kr-85 bipolar charger

DMA

- 2 laminar flows
  - Sheath and aerosol
- 2 concentric cylinders
  - Center negative voltage
  - Electric field
- **Positive** particles attracted through sheath air
- Location depends on electrical mobility, flow rate, and geometry
  - Cycles through different voltages to capture different size particles

SMPS: CPC

- CPC interfaces with the EC and DMA to form the SMPS
- Particles are passed through a wick and grown with either water or butanol
  - Aerosol stream saturated and temperature equilibrated
  - Heterogeneous condensation on condensation nuclei (the particles)
  - Grown to 2 to 3 micrometers
  - Individual particles passed through light beam and scatter light onto a photodetector



Cost of particle sensors

- Relatively inexpensive
  - Gravimetric for particle mass
  - Light scattering for large particle mass
  - Condensation nucleus counter (CNC) for counting small particles
  - Cascade impactor for size-resolved mass
- Mid-range
  - Optical particle counters
- Expensive
  - Aerodynamic particle sizing for large particles
  - Differential mobility analyzer for small particles

Other issues with particle measurements

- Sampling line losses
  - Generally an issue for large (>1 μm) and small (< 0.05 μm) particles
- Sampling particles in moving air stream
  - Isokinetic and non-isokinetic sampling
- Particle composition
  - Collect sample of particles on filter
    - Analyze as you would for liquid or solid compounds
  - SMPS or APS w/ mass spec
    - Very expensive
- Bioaerosol sampling (*Dr. Kunkel*)
  - Fungi, bacteria, viruses
  - Quantitative or presence/absence
  - Culturable, viable, DNA-based
  - Inhibitors

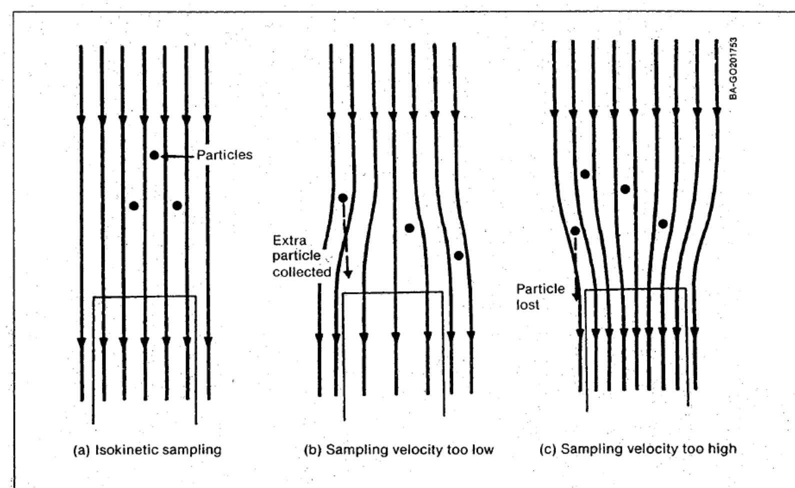


Fig. 7-10. Gas stream lines at the entrance to sampling probes (Source: Adapted from Strauss 1975, Fig. 2.12. © 1975. Used with permission of Pergamon Press)

Summary of particle measurements

- Wide variety of instruments available for particle measurement
  - What size of aerosol are you interested in?
  - Do you need sizing or is counting sufficient?
  - Do you need real-time data?
  - What type of aerosol are you trying to measure?
  - How much accuracy do you need?
  - How much money do you have?