# ENVE 576
# Indoor Air Pollution
Fall 2015

## Week 3: September 8, 2015
Overview of indoor pollutants

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

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# Schedule update

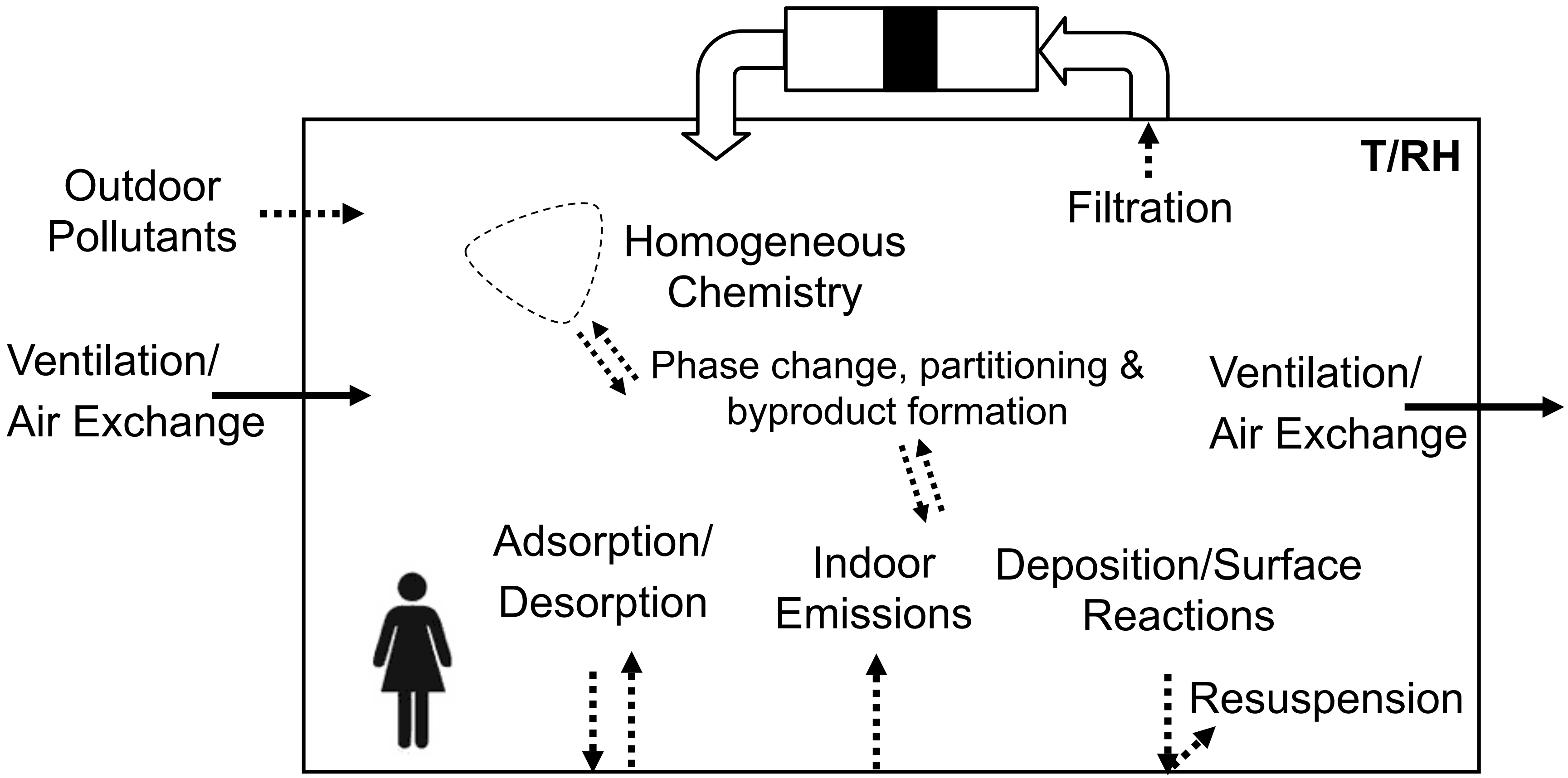
- Next Tuesday's class (Sep 15) has been rescheduled:
  - Friday September 18, 12:00-2:49 pm in E1 032

# Review from last time

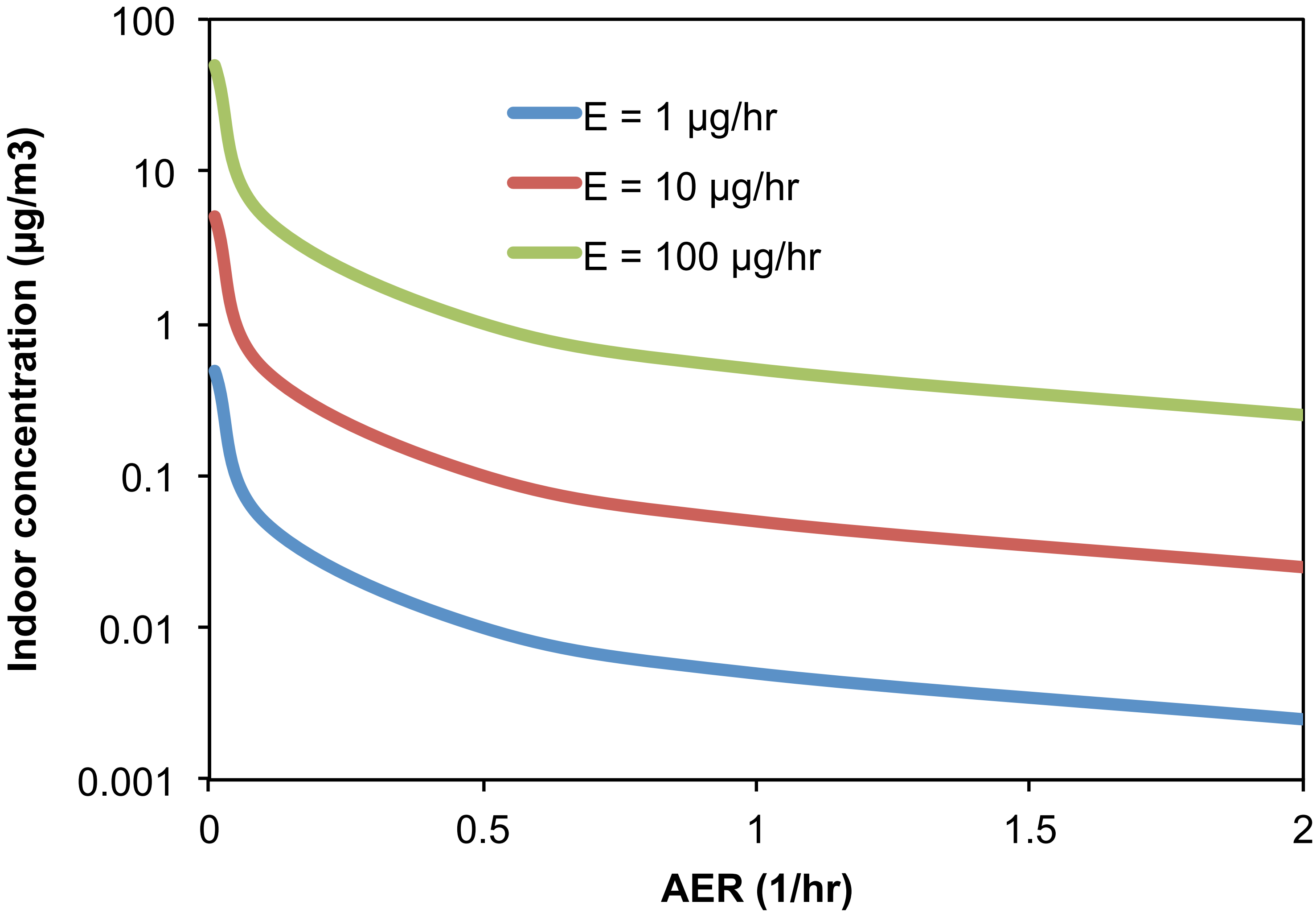
- Last time we covered:
  - Human exposure patterns
    - Where do people spend their time?
  - Well-mixed reactor models
    - Steady-state
    - Dynamic
  - Ventilation rates
    - i.e., air exchange rates

- HW1 is due today
- First blog post is due next week: www.iitindoorair.wordpress.com

# Indoor environment: Mass balance



# Indoor environment: Mass balance & AER



# Review from last time

- Well-mixed mass balances

**General steady-state solution:** $C_{ss} = \frac{S}{L}$

**General dynamic solution:** $C(t) = C_0 e^{-Lt} + \frac{S}{L}\left(1 - e^{-Lt}\right)$

- Q: What are typical units for $S$ and $L$?

- Where do we stand now?
  - We know that indoor air is important for human exposures
  - But what concentrations of which pollutants are we exposed to?

# Today's objectives

- Now that we understand a little bit about what governs indoor pollutant concentrations ($S$ and $L$)
  - I would like to provide a general overview of indoor pollutants
  - How $S$ and $L$ work to influence $C$

- The purpose is to become familiar with the kinds of pollutants that have been measured in a variety of spaces
  - And understand whether those are predominantly indoor or outdoor generated, or both

# TYPES OF INDOOR POLLUTANTS

# Types of indoor emission sources

- Building materials
  - Wood and composite wood
  - Gypsum wallboard
  - Concrete
  - Carpet
  - Vinyl flooring
- Furnishings
  - Bedding
  - Tables
  - Couches/chairs
  - Drapes
- Architectural coatings
  - Paints
  - Stains
  - Varnishes

\+ Outdoor-to-indoor transport

- Consumer products
  - Cleaners
  - Fragrances
  - Personal care products
- Combustion
  - Cigarettes, cigars, pipes
  - Gas stoves
  - Space heaters
  - Candles
  - Incense
- Electronic equipment
  - Laser printers
  - Computers
  - Photocopiers
- Volatilization from water
- Soil vapor intrusion
- People, pets, insects

# Some important classes of indoor pollutants

- Inorganic gases
  - Combustion products: CO, $NO_x$, $SO_2$, $H_2O$, (and PM)
  - $NH_3$, $O_3$, $H_2S$, radon, metals
- Organic gases
  - Volatile organic compounds (VOCs)
    - Hundreds of these
  - Aldehydes
  - Semi-volatile organic compounds (SVOCs)
    - Polycyclic aromatic hydrocarbons (PAHs), phthalates, pesticides, BFRs
- Particulate matter (PM)
  - Solid and liquid aerosols; fibers/asbestos
  - Biological: viruses, bacteria, fungi, endotoxins, allergens (pollen, dander)
  - Metals; organics, inorganics
- Environmental tobacco smoke (ETS) [PM + VOCs]



Godish 2001 *Indoor Environmental Quality*; Spengler et al. 2001 *Indoor Air Quality Handbook*

# Inorganic gases: Combustion products

- Combustion for heating, cooking and lighting is a major source of indoor air pollution throughout the world
  - Sources vary greatly by country/region
- Principal combustion products
  - Smoke: mixture of airborne particles (solids + liquids) and gases
    - Composition varies by combustion source and combustion efficiency
  - Water vapor ($H_2O$) and carbon dioxide ($CO_2$)
  - Products of incomplete combustion:
    - Carbon monoxide (CO)
    - Oxides of nitrogen ($NO_x$, NO, $NO_2$)
- Major sources
  - Gas cooking and heating
    - Particularly heating with unvented appliances
  - Backdraft of vented appliances
  - Vehicles in garages (and transport indoors)

# Inorganic gases: Combustion products

- Products of complete combustion
  - Example: combustion of methane ($CH_4$) in oxygen ($O_2$)

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + \text{heat energy}$$

- Products of incomplete combustion
  - Example: combustion of $CH_4$ in oxygen-deprived environment

$$2\ CH_4 + 3\ O_2 \rightarrow 2\ CO + 4\ H_2O$$

$$N_2 + O_2 \rightarrow 2\ NO\ (\textit{at high } T)$$

$$N_2 + 2\ O_2 \rightarrow 2\ NO_2\ (\textit{at high } T)$$

# Inorganic gases: Products of incomplete combustion

- Carbon monoxide (CO)
  - Colorless, odorless, poisonous gas
  - Both indoor and outdoor sources (regulated outdoors in U.S.)

- Health effects
  - Combines with hemoglobin (oxygen carrier in red blood cells) in bloodstream to produce carboxyhemoglobin (COHb)
    - COHb hinders delivery of oxygen to the body
    - Combines with hemoglobin with about 250x affinity of $O_2$
  - Acute: Headache, nausea, vomiting, dizziness, fatigue, and death
  - Chronic: Similar with additional neurological and psychiatric effects

- Typical concentrations
  - Natural outdoors ~0.1-1.0 ppm
  - Average level in homes ~0.5-5 ppm
  - Exhaust from a residential wood fire ~5000 ppm

# Inorganic gases: Products of incomplete combustion

- Oxides of nitrogen ($NO_x = NO + NO_2$)
  - Nitric oxide (NO)
  - Nitrogen dioxide ($NO_2$)
    - NO converted to $NO_2$ in air
  - Rate of formation depends on:
    - Amount of oxygen; flame temperature

- Health effects
  - $NO_2$ causes oxidative damage to lining of airways
  - Reduced clearance of respiratory pathogens
    - Increased respiratory illness

- Typical concentrations
  - Average level in homes ~5-20 ppb
  - Peak from gas burner ~500 ppb

# Inorganic gases: Others

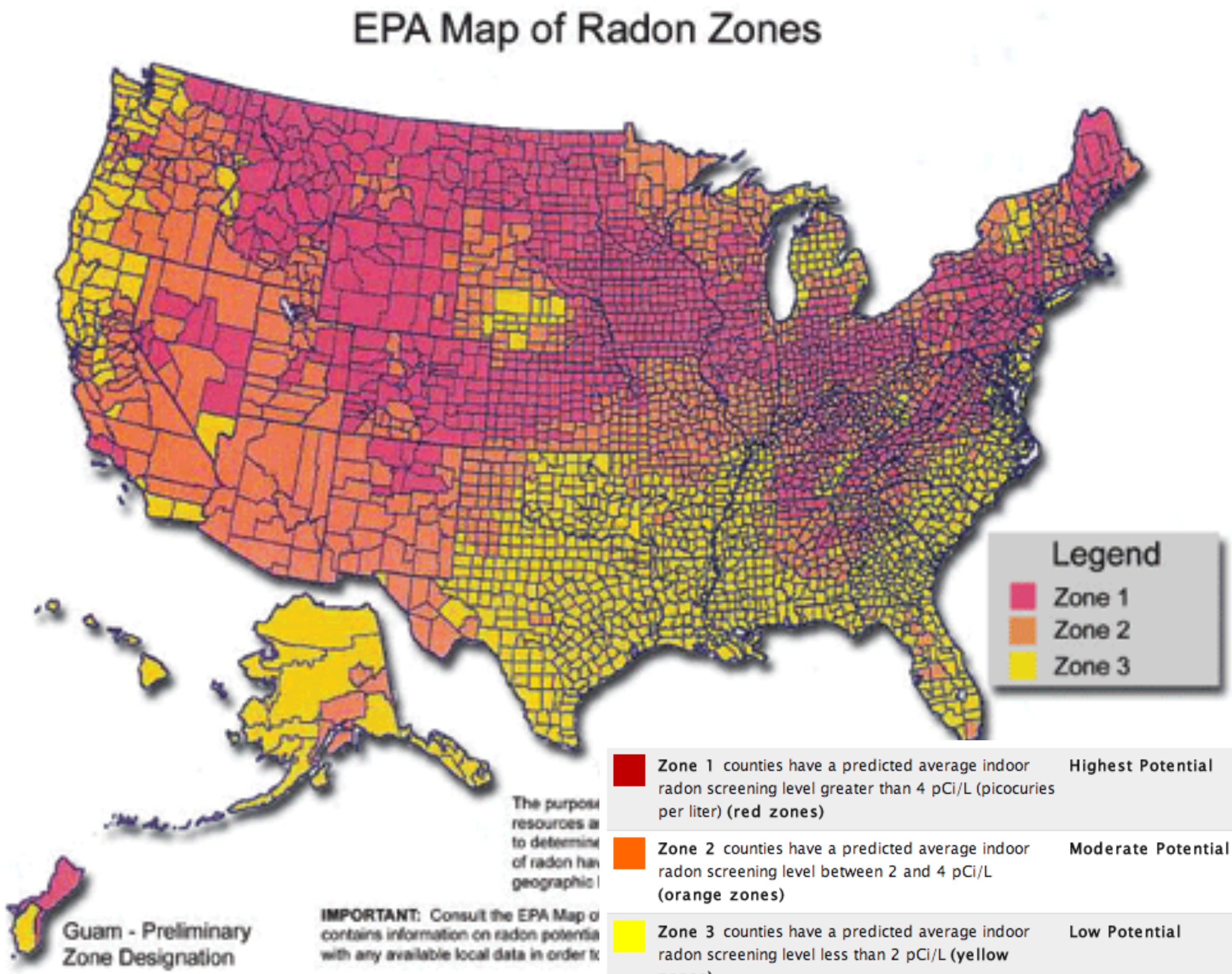
- Hydrogen sulfide ($H_2S$)
  - Colorless, poisonous, flammable gas with rotten egg odor
  - Sources: Landfills; volatilization from water; infiltration of sewer gas
- Ozone ($O_3$)
  - Very reactive, powerful oxidant; causes lung damage
  - Sources: Outdoor photochemistry; indoor electronic “air cleaners”
    - Driver of indoor chemistry
- Ammonia ($NH_3$)
  - Colorless, corrosive gas with sharp odor; causes irritation
  - Sources: Household cleaners; animal waste and fertilizers (outdoors)
- Radon (Rn-222)
  - Noble, inert gas resulting from decay of naturally occurring uranium (U238); radioactive alpha particle emitter; carcinogen responsible for ~20k lung cancer deaths per year in U.S.
  - Diffuses through rock and soil and enters indoor environments as gas

# Notes on radon

- Uranium-238 is universally present in the earth
  - Radon is a ubiquitous gaseous indoor pollutant, varying by region
- Radon has a half life of ~3.5 days
  - Once inhaled as a gas, radon progeny (alpha emissions) cause cancer
  - Progeny are solid, forming clusters or attaching to aerosols (particles)

- Units are very different from other pollutants
  - Becquerels
    - Bq is a unit of radioactivity (Bq = 1/s = 1 nucleus decay per second)
  - Picocuries
    - 1 Curie (Ci) = $3.7\times10^{10}$ decays per second = $3.7\times10^{10}$ Bq
    - 1 pico-Curie = $10^{-12}$ Curies
    - 1 pCi/L = 37 Bq/$m^3$ ← either of these are used as Rn measures

# Radon map of U.S.




| | | |
|---|---|---|
| | **Zone 1** counties have a predicted average indoor radon screening level greater than 4 pCi/L (picocuries per liter) **(red zones)** | **Highest Potential** |
| | **Zone 2** counties have a predicted average indoor radon screening level between 2 and 4 pCi/L **(orange zones)** | **Moderate Potential** |
| | **Zone 3** counties have a predicted average indoor radon screening level less than 2 pCi/L **(yellow zones)** | **Low Potential** |

# Organic gases: VOCs

- Volatile Organic Compounds (VOCs)
  - Original definition of VOC referred to a class of carbon-containing chemicals that participate in photochemical reactions in outdoor air
    - Excluding CO, $CO_2$, $H_2CO_3$, and some others
  - VOCs are also defined according to analytical methods

- Indoor air literature:
  - VOC commonly refers to all organic vapor-phase compounds
    - TVOC = total volatile organic compounds
  - Also:
  - VVOC = very-volatile organic compounds
  - SVOC = semi-volatile organic compounds
  - POM = particulate organic matter
    - Organic compounds associated with particulate matter

# 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.

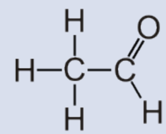
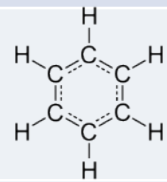
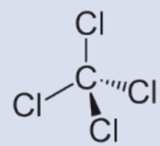
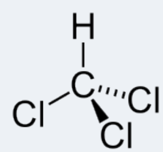
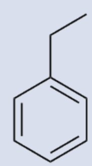
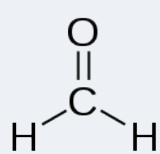
# Organic gases: VOCs

- Some VOCs have strong odors, cause sensory irritation (primarily to mucus membranes), or are classified as hazardous air pollutants with carcinogenic or other effects

- VOCs are some of the most prevalent indoor pollutants
  - Also some of the most studied
  - Often dozens if not hundreds of individual compounds present at 1-5 ppb over long periods and can reach hundreds of ppb during peak events

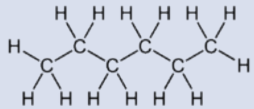
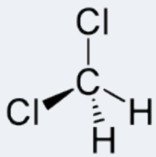
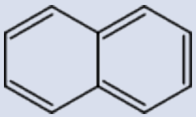
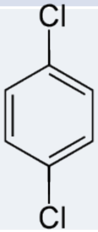
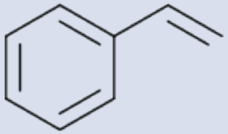
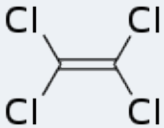
- Concentrations result from a wide variety of synthetic and natural products, and people and their activities
  - Highest concentrations tend to result from solvent application or use of certain personal care products, hobby materials, or cleaning agents

# **Hazardous** VOCs found indoors

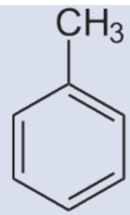
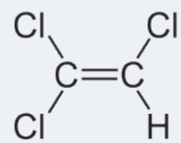
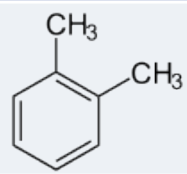
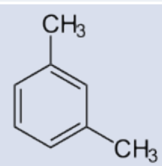
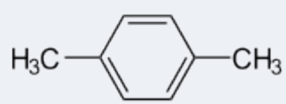
| Compound | Formula | Structure | Categories of indoor sources |
|---|---|---|---|
| Acetaldehyde* | $C_2H_4O$ |  | Floor materials, HVAC systems and components, machines, wood products |
| Benzene | $C_6H_6$ |  | Furnishings, paints and coatings, wood products |
| Carbon tetrachloride | $CCl_4$ |  | Pesticides |
| Chloroform | $CHCl_3$ |  | Furnishings, pesticides |
| Ethylbenzene | $C_6H_5CH_2CH_3$ |  | Floor materials, insulation products, machines, paints and coatings |
| Formaldehyde* | $CH_2O$ |  | Cabinetry, floor materials, furnishings, indoor reactions, insulation products, paints and coatings, space heating and cooking equipment, wall and ceiling materials, wood products |

*Also classified as aldehydes

# Hazardous VOCs found indoors

| Compound | Formula | Structure | Categories of indoor sources |
|---|---|---|---|
| Hexane | $C_6H_{14}$ |  | Floor materials, furnishings, paints and coatings, wood products |
| Methylene chloride | $CH_2Cl_2$ |  | Furnishings |
| Naphthalene | $C_{10}H_8$ |  | Pesticides (moth crystals) |
| *p*-dichlorobenzene | $C_6H_4Cl_2$ |  | Pesticides, floor materials |
| Styrene | $C_8H_8$ |  | Cabinetry, floor materials, insulation products, machines, paints and coatings, wood products |
| Tetrachloroethylene | $C_2Cl_4$ |  | Caulks and sealants |

# Hazardous VOCs found indoors

| Compound | Formula | Structure | Categories of indoor sources |
|---|---|---|---|
| Toluene | $C_7H_8$ |  | Adhesives, caulks and sealants, floor materials, furnishings, machines, paints and coatings, wall and ceiling materials, wood products |
| Trichloroethylene | $C_2HCl_3$ |  | Furnishings |
| Xylenes (*o*, *m*, *p*) | | | |
| *o*-xylene (1,2-dimethylbenzne) | $C_8H_{10}$ |  | |
| *m*-xylene (1,3-dimethylbenzne) | $C_6H_4(CH_3)_2$ |  | Floor materials, furnishings, machines, paints and coatings, wall and ceiling materials |
| *p*-xylene (1,4-dimethylbenzne) | $C_6H_4C_2H_6$ |  | |

# VOCs found indoors

- Many other VOCs also found indoors but not necessarily classified as hazardous
  - Can still engage in chemistry
  - Can still have other irritating effects

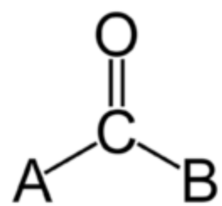
How do we know what is hazardous and what is not?

TOXNET: Toxicology Data Network
http://toxnet.nlm.nih.gov/

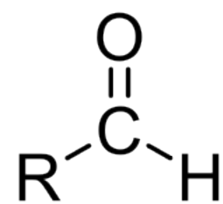
*Look for HSDB in particular

# Organic gases: Aldehydes

- Aldehydes belong to a class of organic compounds called carbonyls
  - Carbonyls are composed of a carbon atom double-bonded to an oxygen atom (C=O)




**General carbonyl**




**General aldehyde (functional group)**

- Many aldehydes are potent sensory (mucus membrane) irritants
  - Some are skin sensitizers, and a few may be human carcinogens
  - Reactive and soluble

# Organic gases: Aldehydes

| Compound | Formula | Categories of sources |
|---|---|---|
| Formaldehyde | $CH_2O$ | Cabinetry, floor materials, furnishings, indoor reactions, insulation products, paints and coatings, space heating and cooking equipment, wall and ceiling materials, wood products (and cigarette smoke) |
| Acetaldehyde | $C_2H_4O$ | Floor materials, HVAC systems and components, machines, wood products, auto and diesel exhaust |
| Acrolein | $C_3H_4O$ | Cooking of oils and fats, wood combustion, cigarette smoke, auto and diesel exhaust |
| Crotonaldehyde | $C_4H_6O$ | Cooking of oils |
| Benzaldehyde | $C_7H_6O$ | Cooking (almond flavor!) |

Aldehydes are also generated as secondary byproducts of reactions between ozone ($O_3$) and unsaturated hydrocarbons (VOCs) such as d-limonene, α-pinene, α-terpenine, styrene, and isoprene

# Organic gases (and particle phase): SVOCs

- Semi-volatile organic compounds (SVOCs) are higher molecular weight VOCs
  - Usually exist partially in gas-phase and partially in particle-phase
  - Includes:
    - Polycyclic aromatic hydrocarbons (PAHs)
    - Phthalates
    - Pesticides
    - Brominated flame retardants (BFRs)

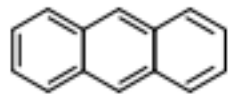
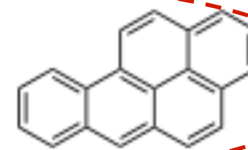
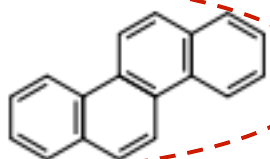
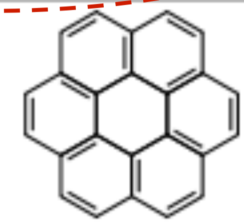
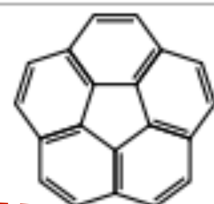
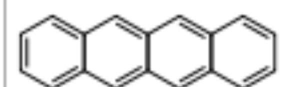
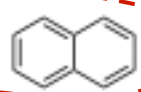
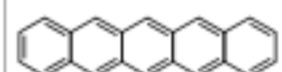
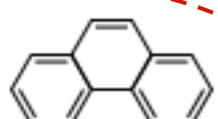
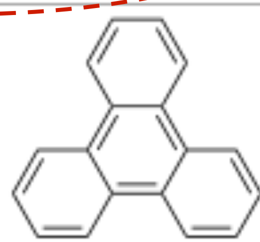
- PAHs are products of incomplete combustion
  - Typical health effect: carcinogenic
- Phthalates are plasticizers used in PVC resins
  - Typical health effect: hormone signaling systems disruptors

# Organic gases (and particle phase): SVOCs

- PAHs
  - Multiple benzene rings that share a pair of carbon atoms
  - Three- and four-ringed PAHs (smaller MW) are more volatile and typically exist in the gas-phase
  - Larger five- to seven-ring PAHs occur in the particulate phase

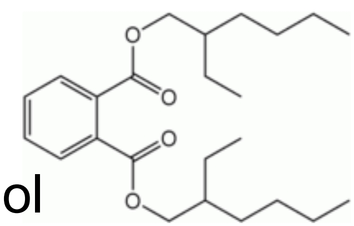
- Major PAH sources
  - Emissions from combustion of wood or other fuel (e.g., kerosene), unvented gas appliances, ETS, and cooking, grilling, and frying
  - Major outdoor sources as well
  - Typically at ng/m$^3$ levels

# Organic gases (and particle phase): PAHs

| Chemical compound | | Chemical compound | |
|---|---|---|---|
| Anthracene |  | Benzo[*a*]pyrene |  |
| Chrysene |  | Coronene |  |
| Corannulene |  | Tetracene |  |
| Naphthalene |  | Pentacene |  |
| Phenanthrene |  | Pyrene |  |
| Triphenylene |  | Ovalene |  |

# Organic gases (and particle phase): SVOCs

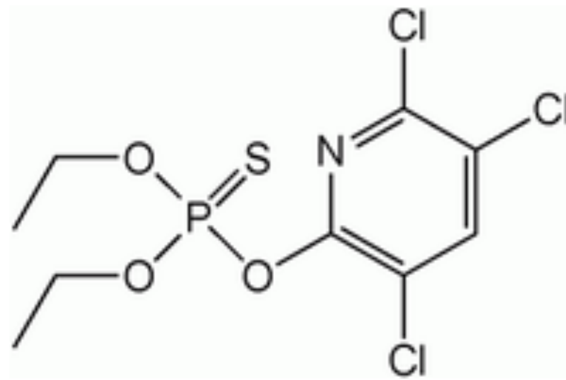
- Phthalates
  - Plasticizers in polyvinyl chloride (PVC) resins used to make building materials and consumer products
    - Vinyl upholstery, shower curtains, food containers, toys, floor tiles, automobile interiors, lubricants, sealers, and adhesives
  - Much higher concentrations indoors than outdoors
    - Although typically at ng/m$^3$ levels
  - Particle and gas phases → relative fraction depends on MW
- Some common phthalates
  - Diethyl phthalate (DEP) | MW = 222 g/mol
  - Butyl benzyl phthalate (BBP or BBzP) | MW = 312 g/mol
  - Di(2-ethylhexyl) phthalate (DEHP) | MW = 390 g/mol




- Health effects (or at least *associations*)
  - Some cancer evidence; some endocrine disrupting evidence; others
    - e.g. reproductive effects, obesity, diabetes, and allergies

# Organic gases (and particle phase): SVOCs

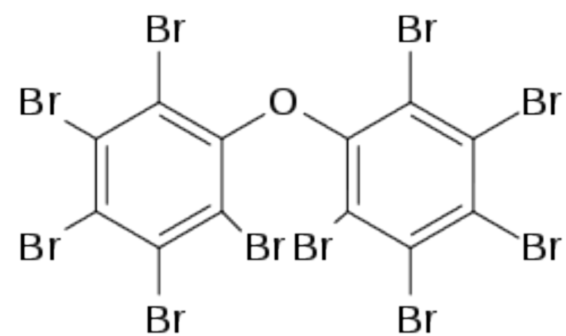
- Pesticides
  - Common pesticides (found in more than ~50% of homes) include:
    - Chlorpyrifos
    - Propoxur
    - *o*-phenylphenol
    - Diazinon
    - Dieldrin
    - Chlordane




- Health effects
  - Acute poisoning
  - Chronic and long-term effects
    - Cancers (many)
    - Neurological development, including Parkinson's
    - Reproductive effects, including birth defects and fetal death
    - Fertility reductions

# Organic gases (and particle phase): SVOCs

- Brominated flame retardants (BFRs)
  - Organobromide compounds that inhibit combustion
- Several groups:
  - Polybrominated diphenyl ethers (PBDEs)
    - DecaBDE
    - OctaBDE (not manufactured anymore)
    - PentaBDE (not manufactured anymore)
  - Polybrominated biphenyl (PBB)
    - Also not manufactured anymore



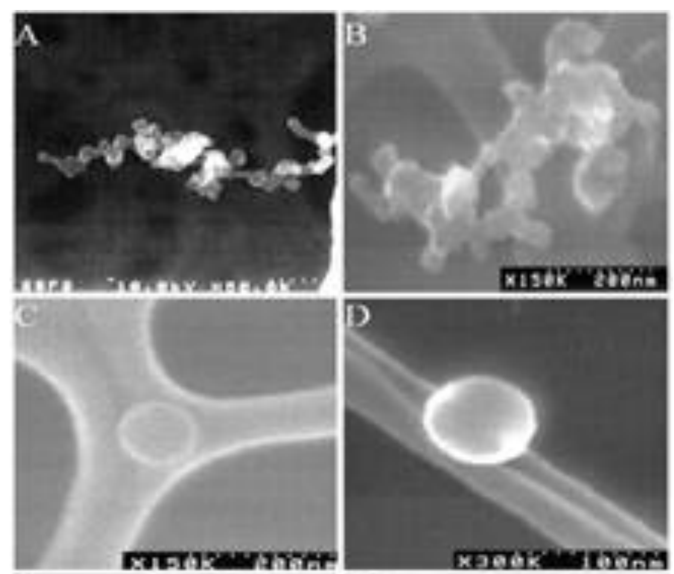

- Health effects (or associations)
  - More endocrine (hormone) disrupting effects
    - Estrogen and thyroid hormones
    - Reproductive and metabolism effects

# 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

- Health effects
  - Respiratory, cardiovascular

- Visibility effects outdoors

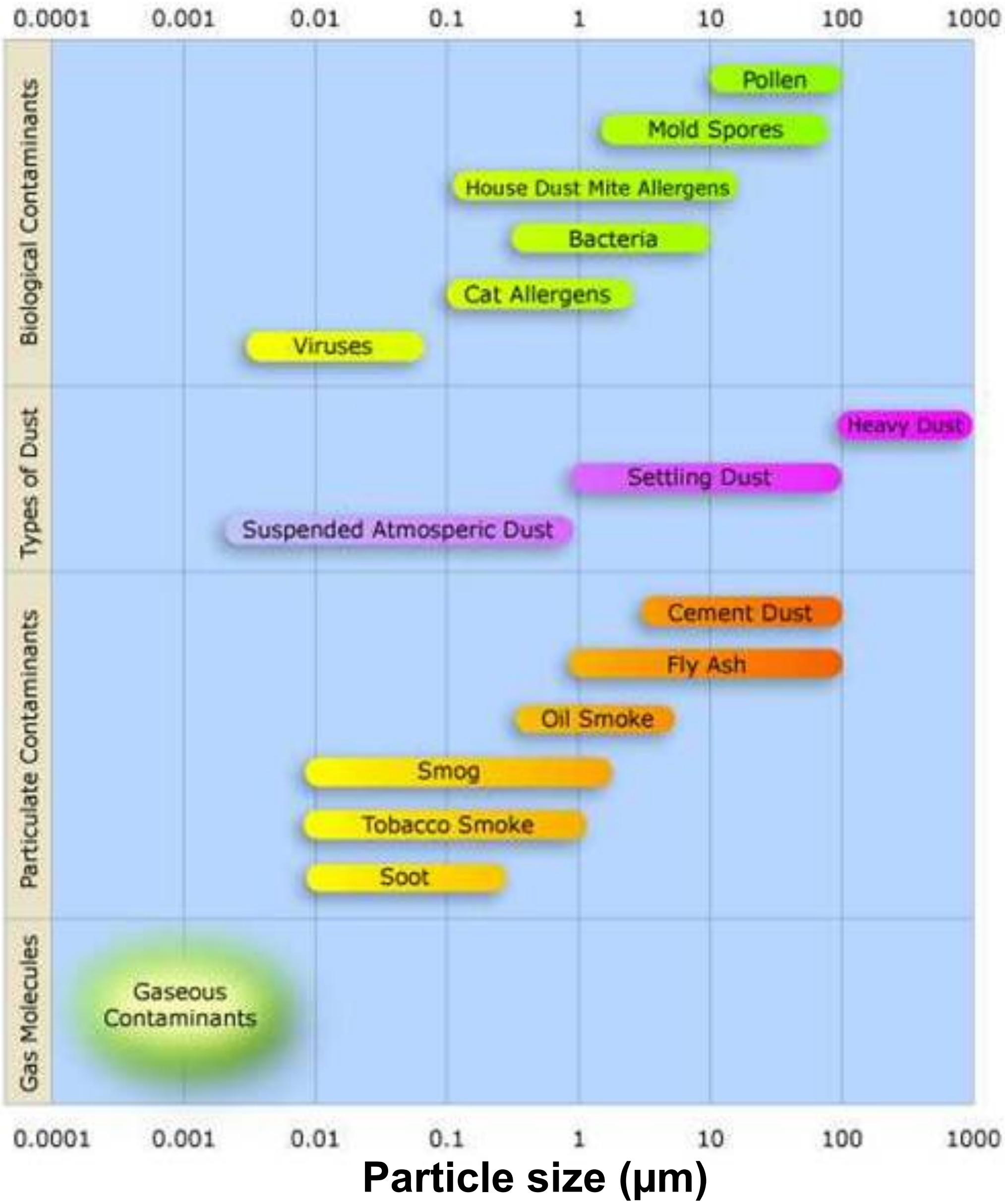


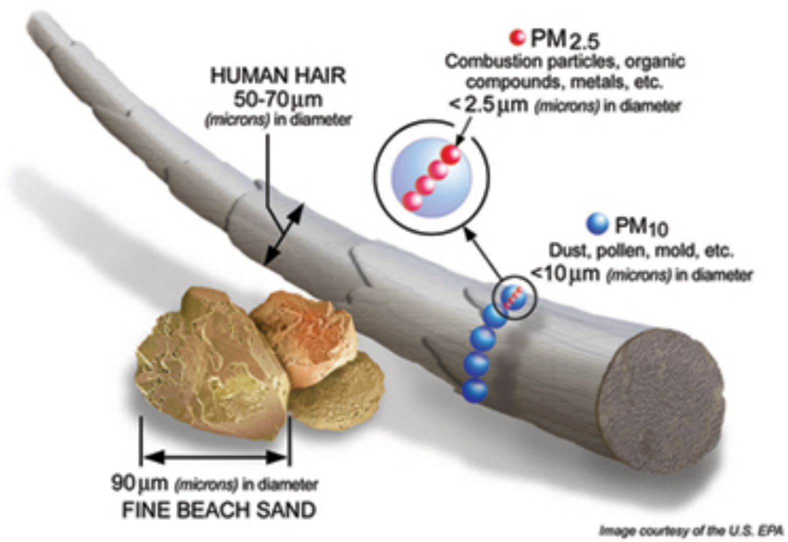

http://www.aerosols.wustl.edu/education/AerosolBasics/What%20is%20an%20aerosol.htm

# Particulate matter (PM)

- **Some key definitions for PM**
  - **Aerosol**: Mostly stable particles suspended in a gas
    - Refers to both gas and particles
  - **Bioaerosol:** Aerosol of biological origin
    - Fungi, bacteria, viruses
    - Fungal spores, dust mite parts, pollen
  - **Cloud**: Visible aerosol with defined boundaries
  - **Dust**: Irregular, solid phase produced by mechanical processes
  - **Fume**: Solid phase chains or clusters of small primary particles
    - Produced by condensation of vapors or gaseous combustion products
  - **Haze**: Atmospheric aerosol that affects visibility
  - **Mist and Fog**: Spherical liquid-particle aerosols
    - Formed by condensation and atomization
  - **Smoke**: Results from incomplete combustion
  - **Spray:** Liquid particle analog to dust

# Particulate matter (PM)



# 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

- More on shapes and particle physics in a few lectures
  - Just need to know some basic sizes for now
  - Composition is also important

# Particle sizes

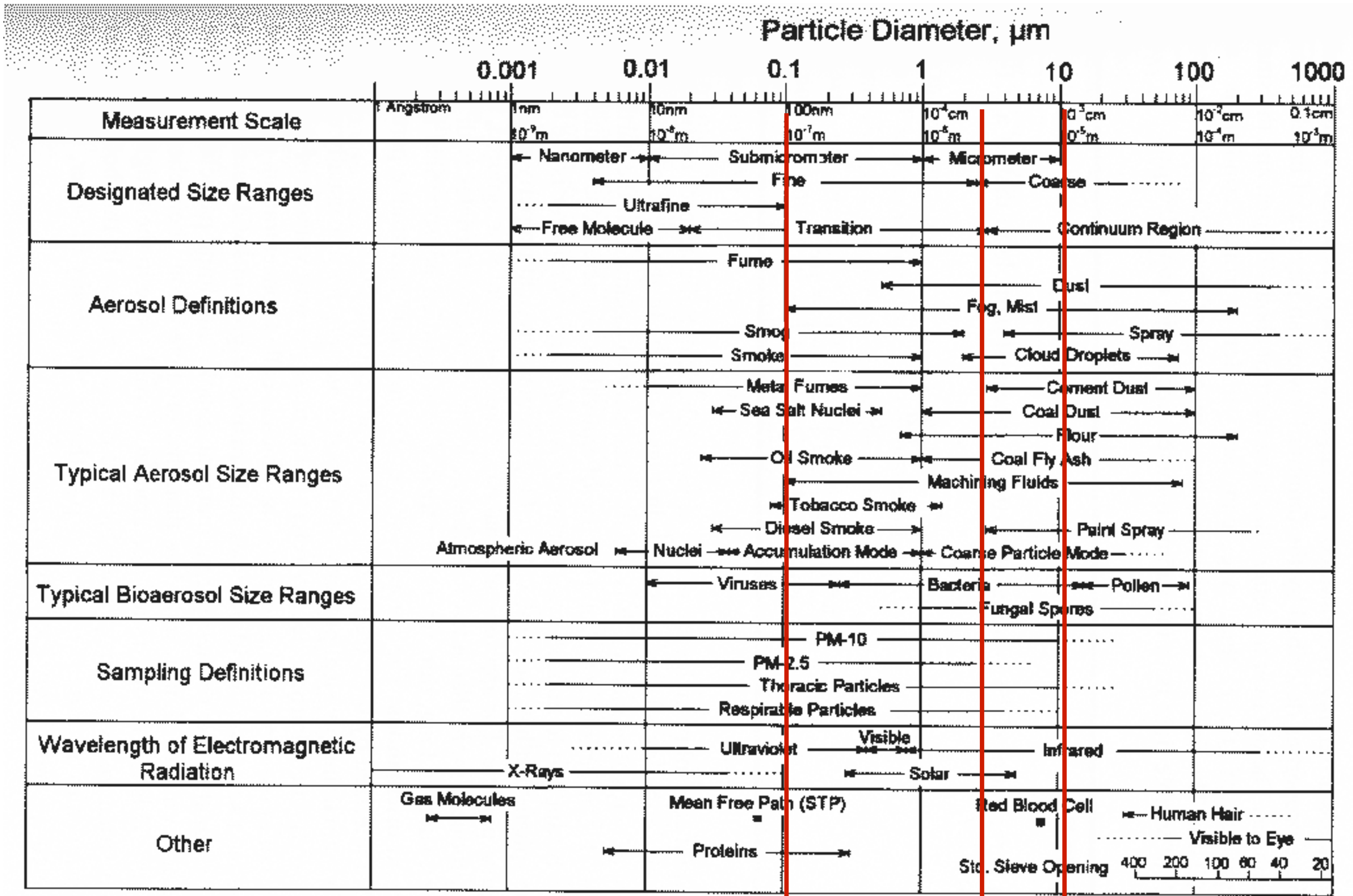
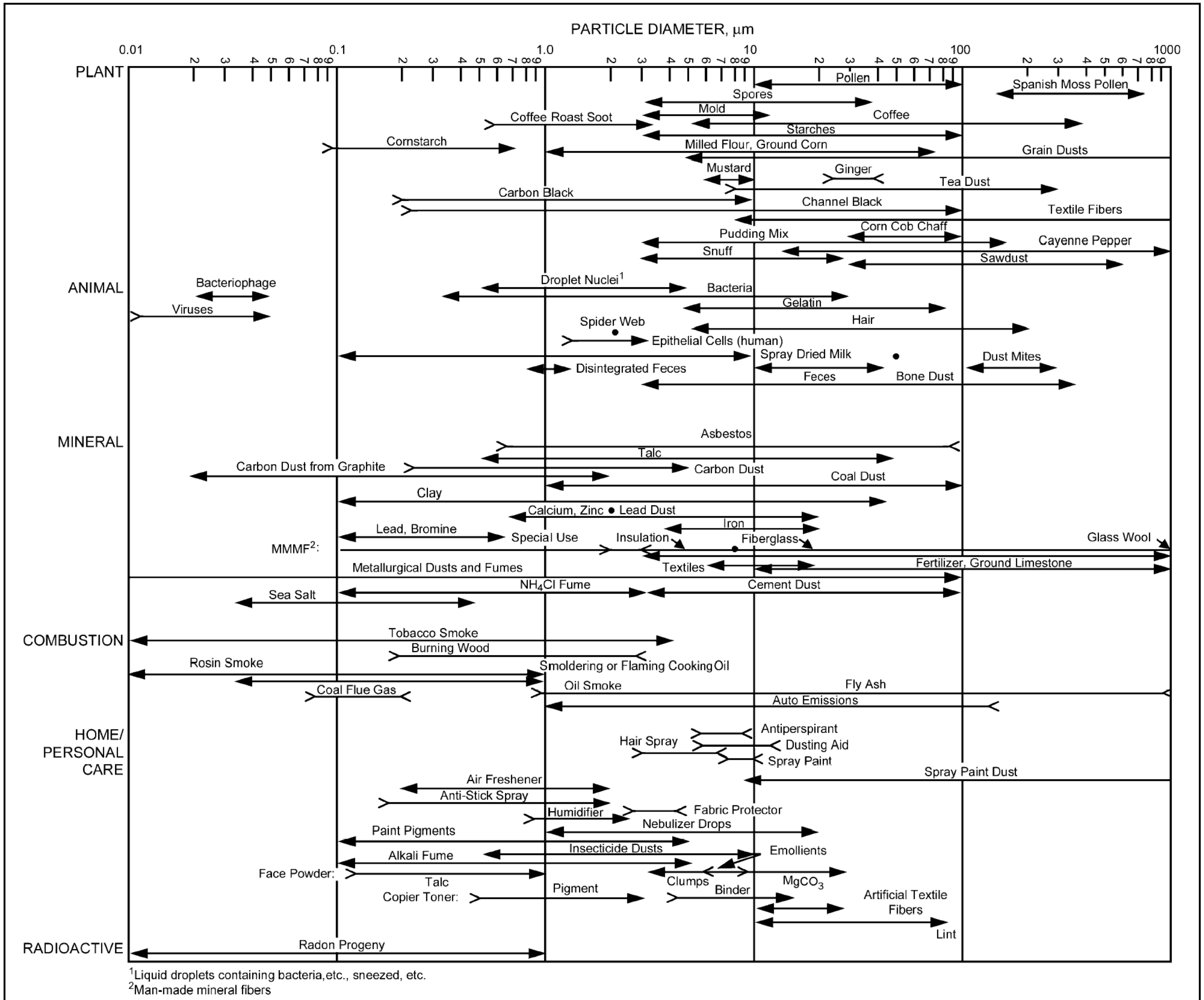



**FIGURE 1.6** Particle size ranges and definitions for aerosols.

Hinds 1999

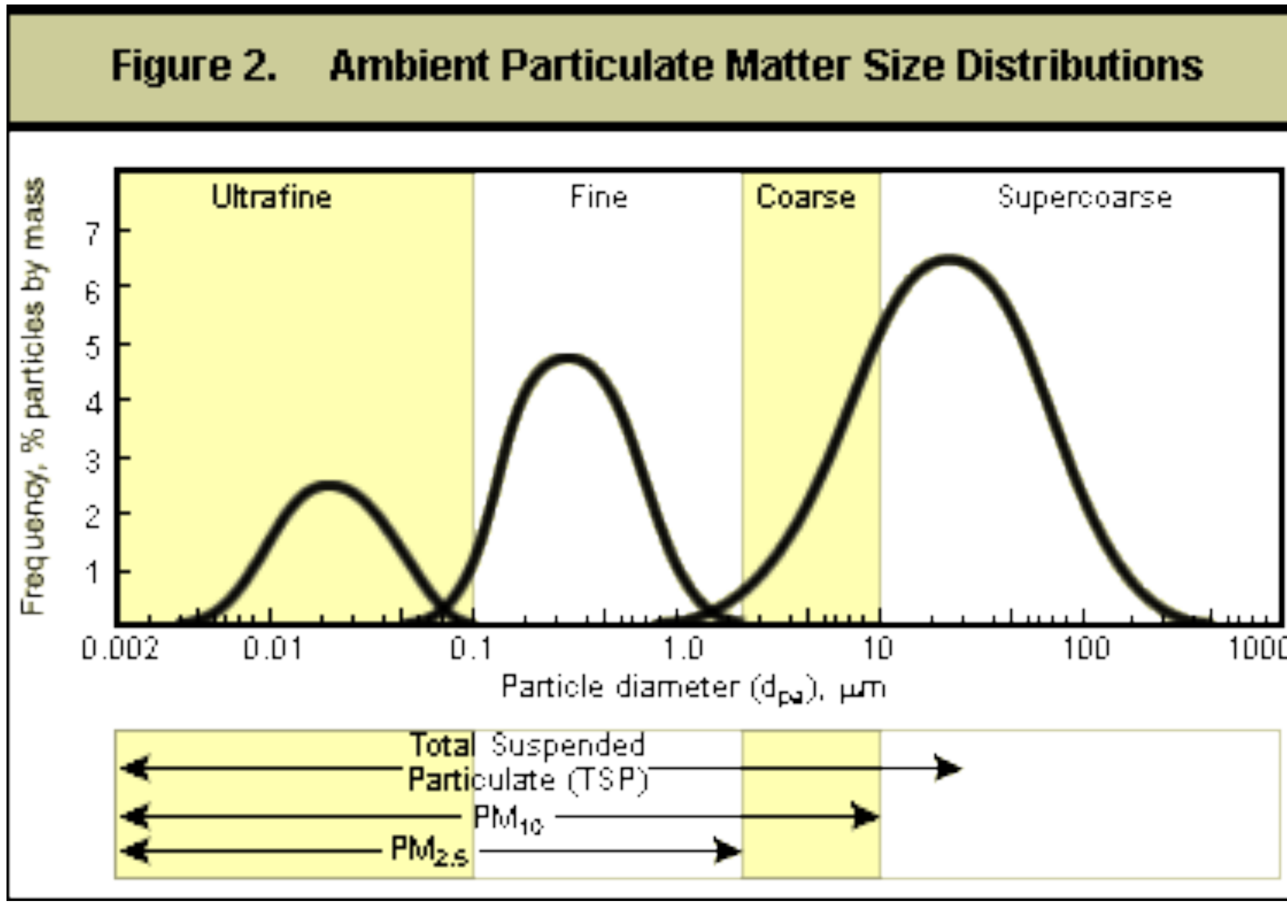
# Indoor particle source sizes




ASHRAE HoF

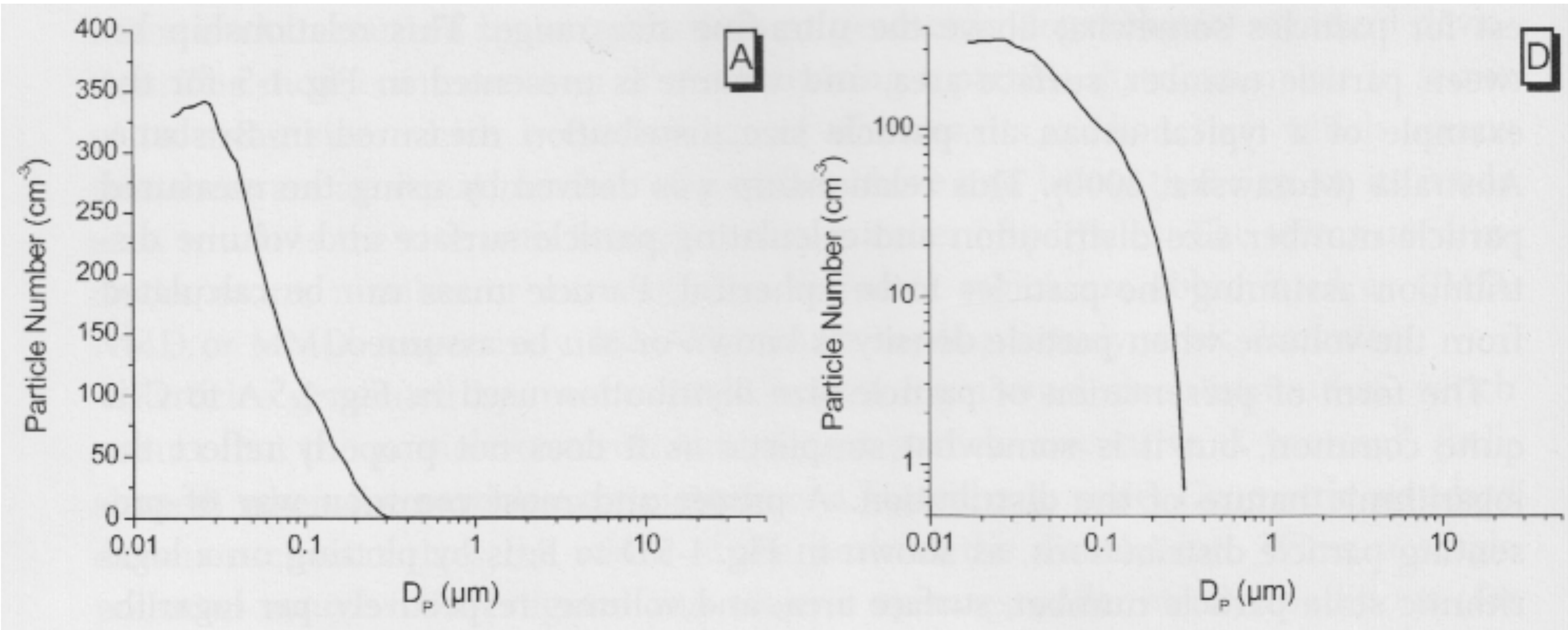
# How are particles measured?

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



# Typical urban distributions

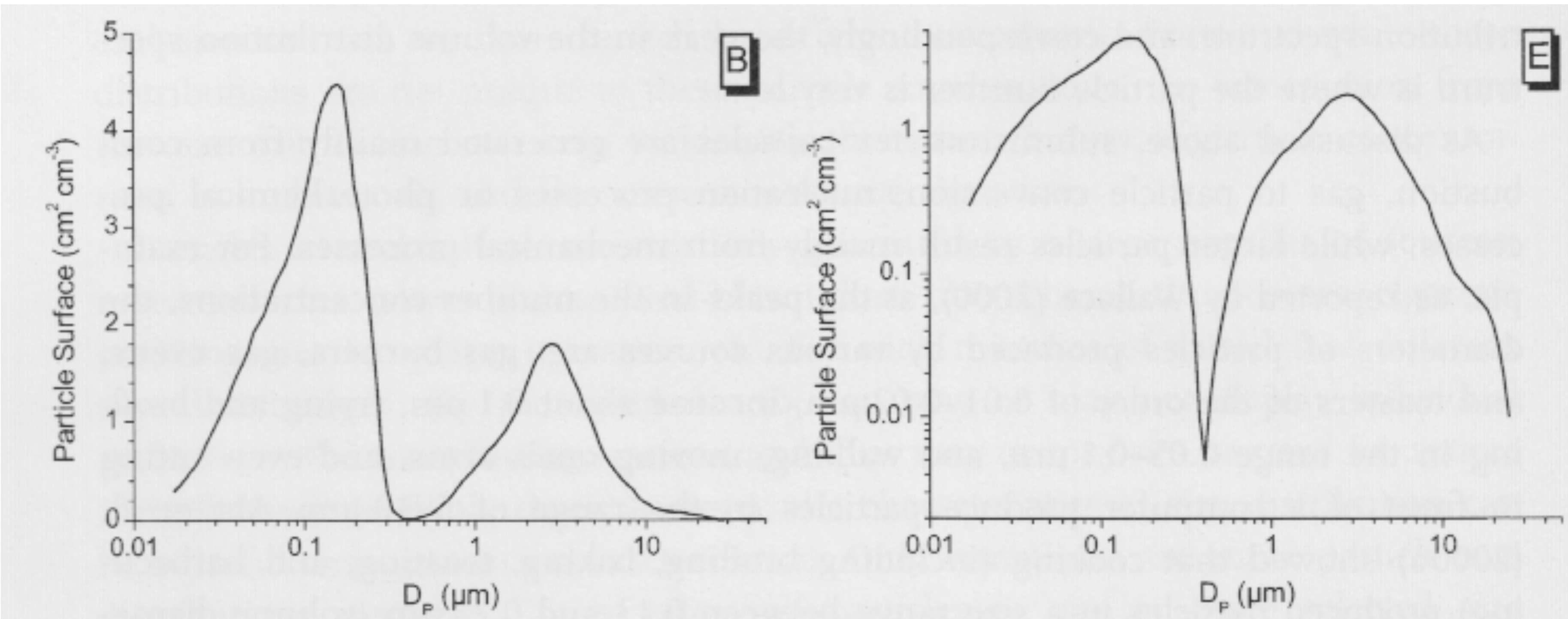
- Number distributions




Morawska and Salthammer 2003 *Indoor Environment*

# Typical urban distributions

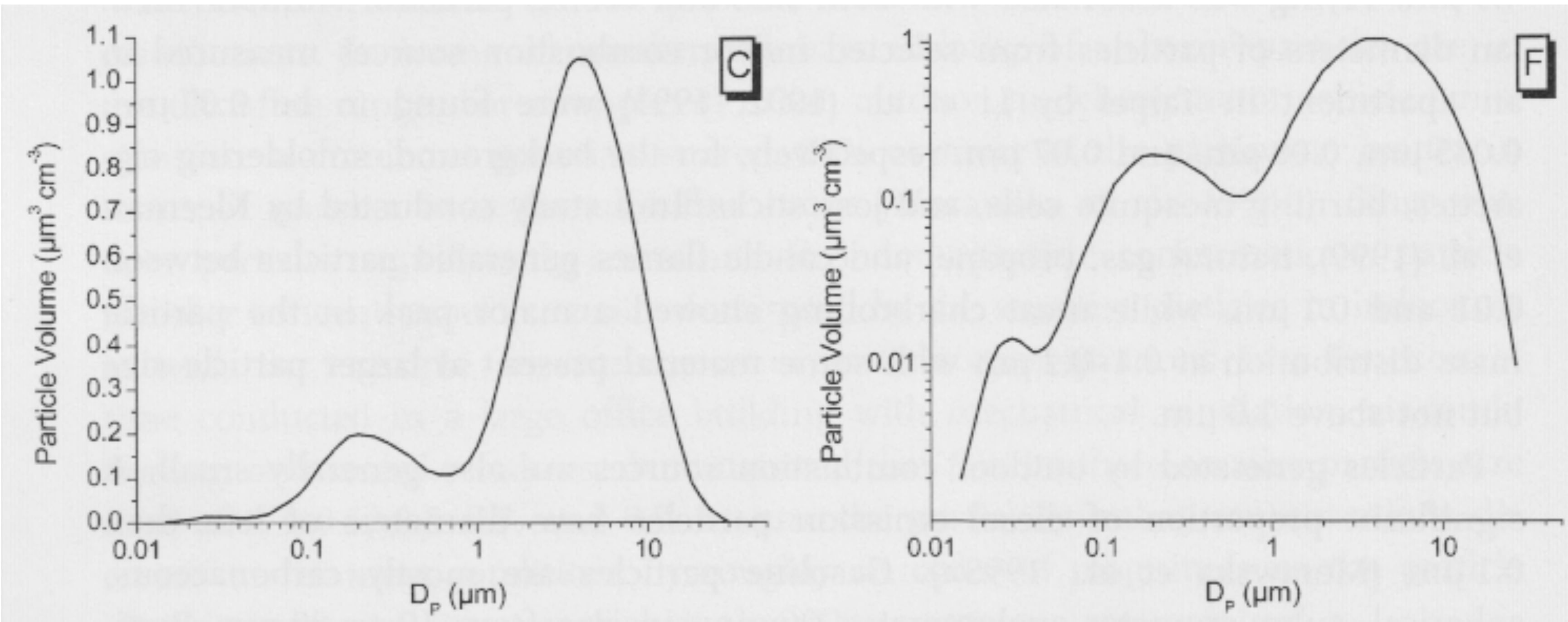
- Surface area distributions




Morawska and Salthammer 2003 *Indoor Environment*

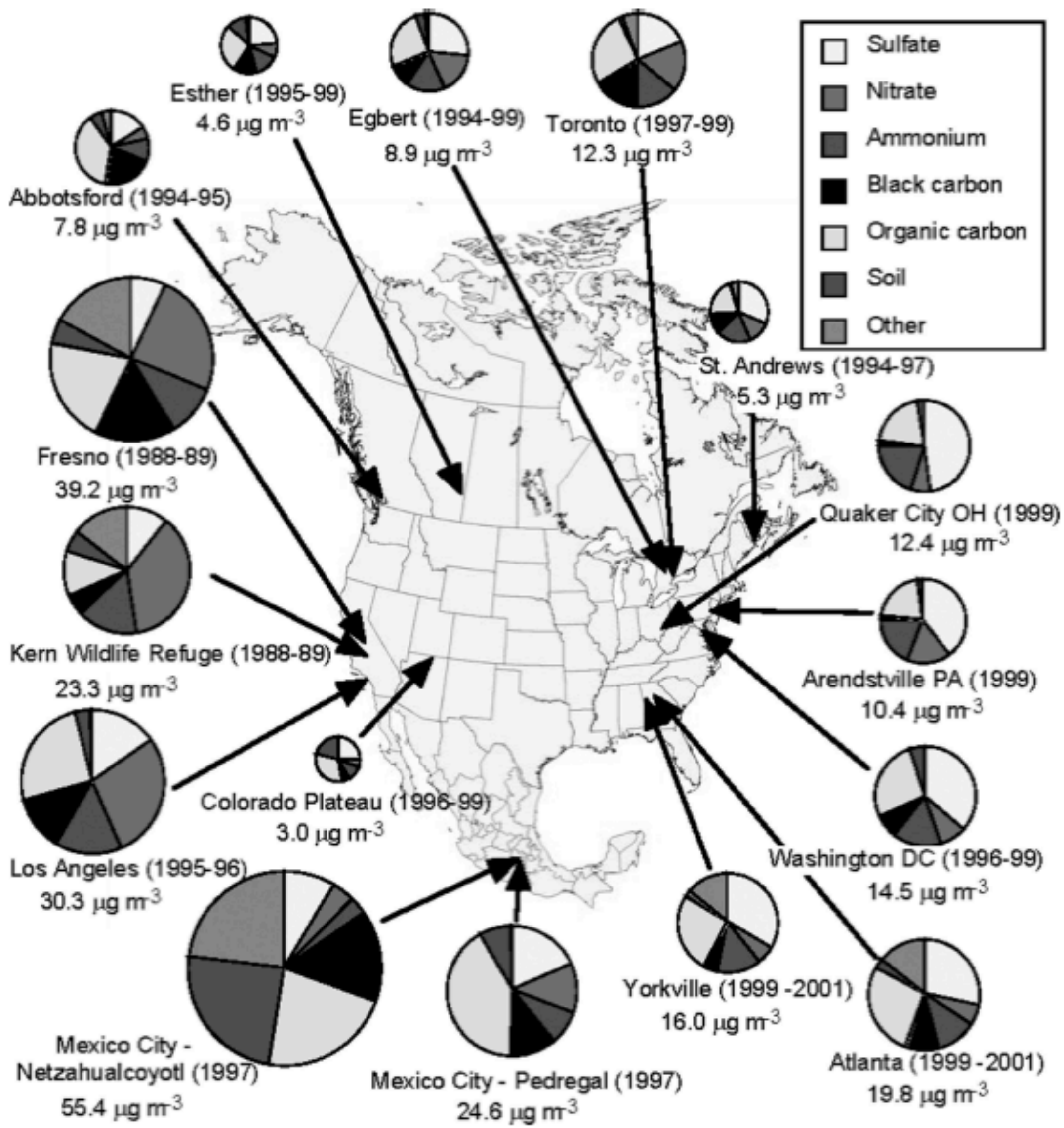
# Typical urban distributions

- Volume distributions




Morawska and Salthammer 2003 *Indoor Environment*

# Composition of outdoor $PM_{2.5}$



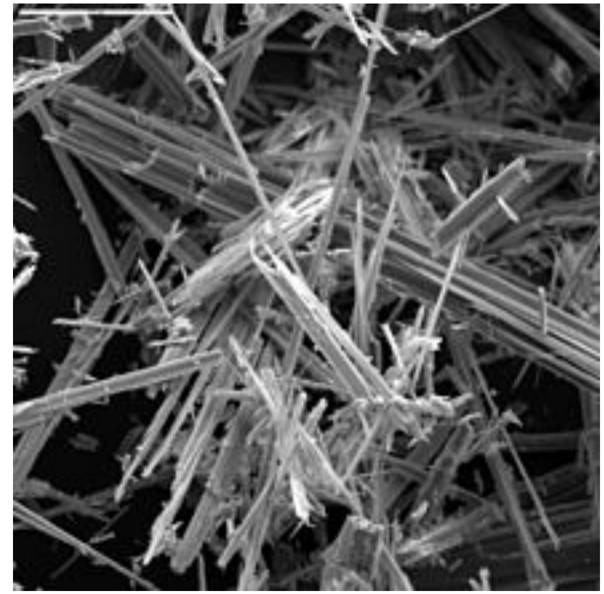

Davidson 2005 *Aerosol Sci Technol*

# Particulate matter: ETS

- Environmental tobacco smoke (ETS) is a combination of many of the pollutants we've already mentioned
  - Particles, VOCs, SVOCs, aldehydes, inorganic gases, and metals
- Health effects of involuntary smoking
  - Reduced fetal growth
  - Sudden infant death syndrome
  - Cancer
  - Lower respiratory tract illness
  - Asthma
  - Reduced lung growth
  - Heart disease
  - Odor and irritation

# Particulate matter: Fibers/asbestos

- Fibrous products are ubiquitous in buildings
  - Insulating products, ceiling tiles, wall panels, duct linings, etc.
  - L:W ratios of 3:1 or more
- Prior to 1980, these were made with asbestos fibers
  - Asbestos refers to fibrous silicate materials
- Now they are typically cellulose fibers and other less harmful materials
  - Old buildings will still contain asbestos
- Health effects
  - Lung scarring and fibrosis
  - Increased incidences of lung cancer

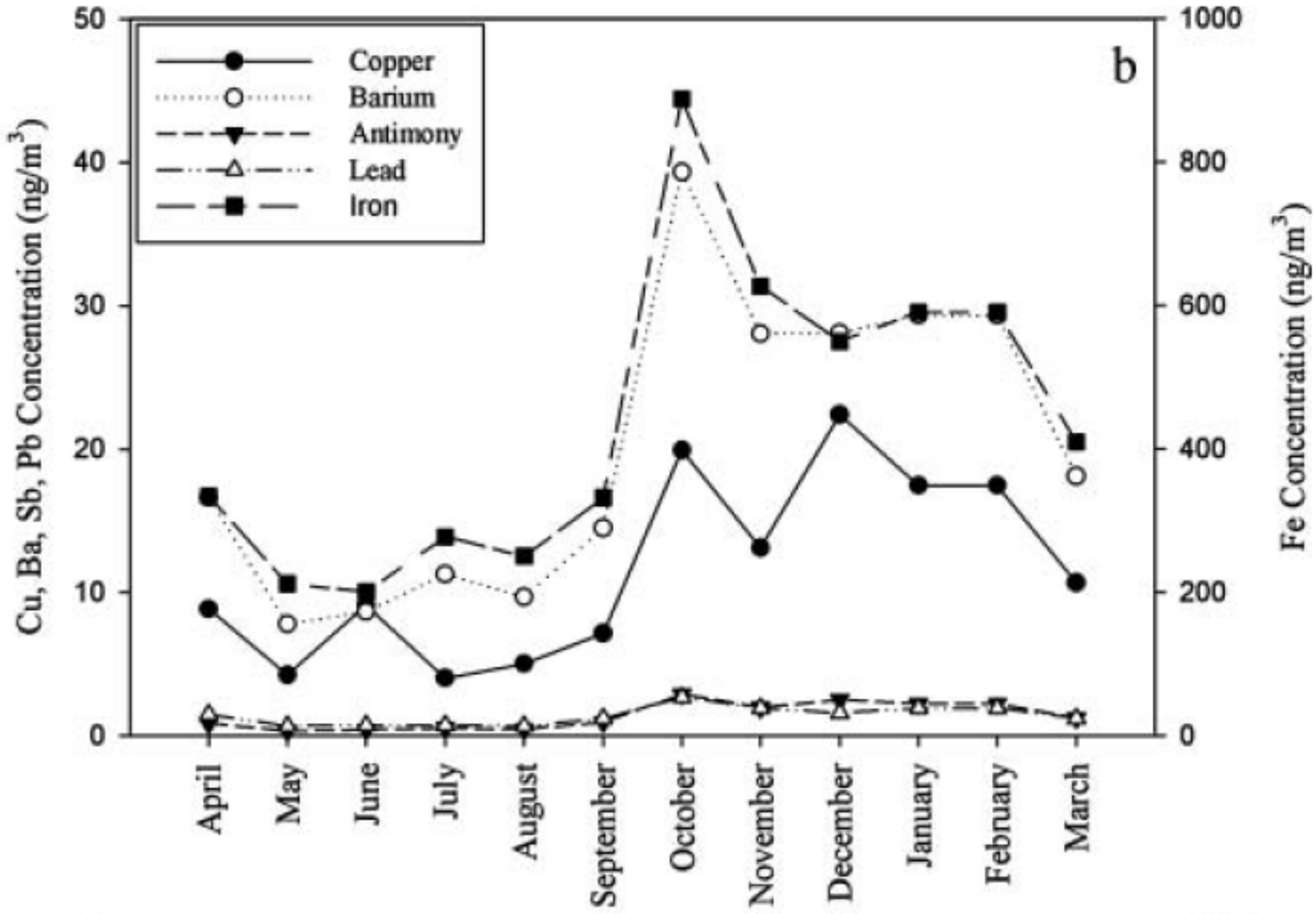


# Particulate matter: Biological

- Biological sampling in indoor environments is an ongoing field of research
  - New analytical techniques are advancing capabilities (DNA)
- Most of the previous biological work involves:
  - Endotoxin: inflammatory substances present in some bacteria
  - Allergens
    - From insects: mice, cats, dogs, cockroaches, dust mites
    - From plants: pollen, certain fungi
      - Existing as complete spores or attached to other aerosols
  - Fungi/molds
    - Can grow on building substrates with the right T/RH/light conditions
  - Viruses and bacterial pathogens
    - Influenza, rhinovirus, tuberculosis, legionella, etc.
- New sampling techniques focus on the many organisms that are probably harmless, potentially protective

# Metals

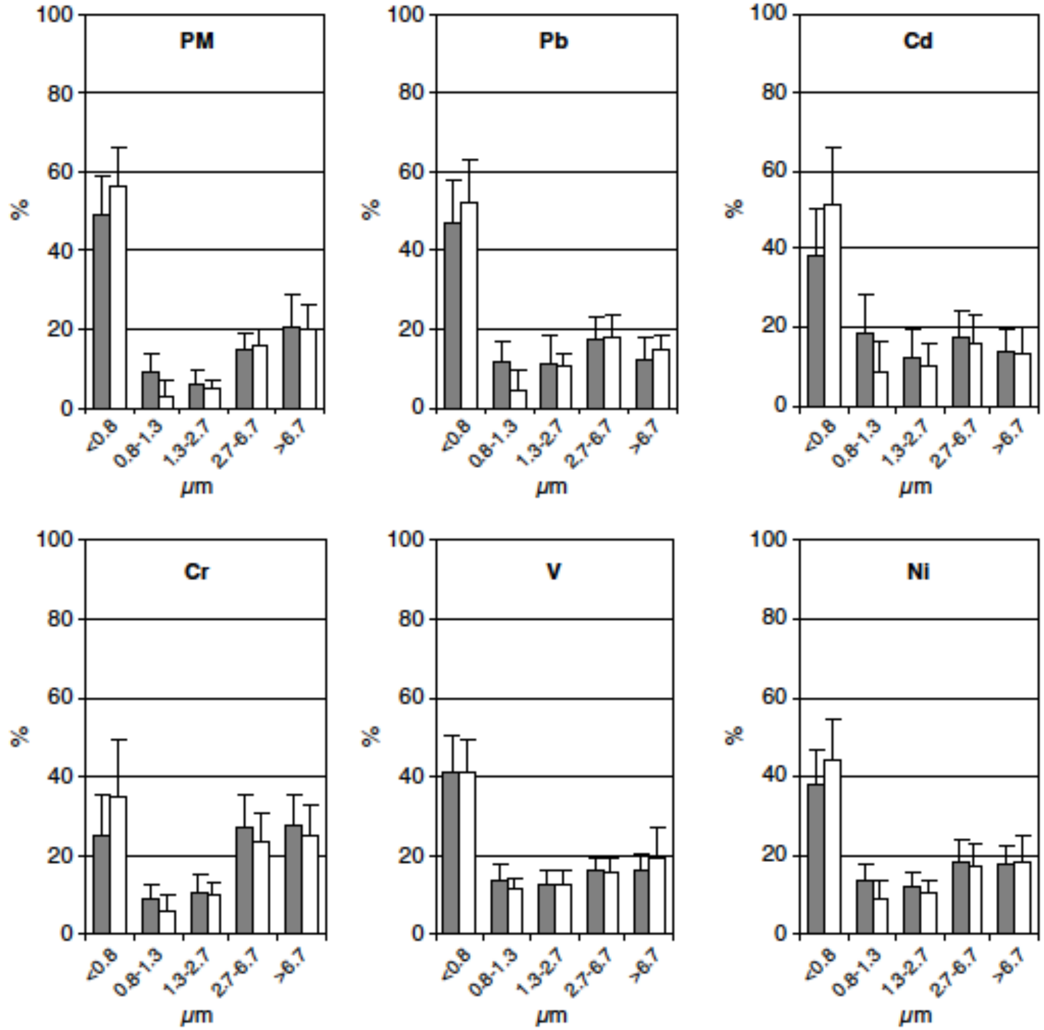
- Particle-bound metals (outdoors)




Pakbin et al., 2011 *Aerosol Sci Technol*

# Metals

- Particle-bound metals (outdoors, size-resolved)




Samara and Voutsa, 2005 *Chemosphere*

Enough about what pollutants are out there…

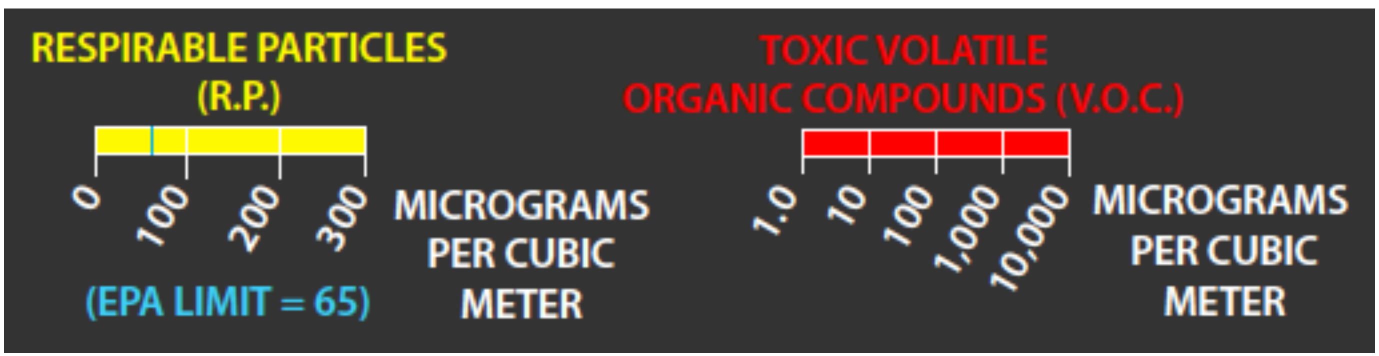
# MEASURED INDOOR EXPOSURES

# Large exposure studies

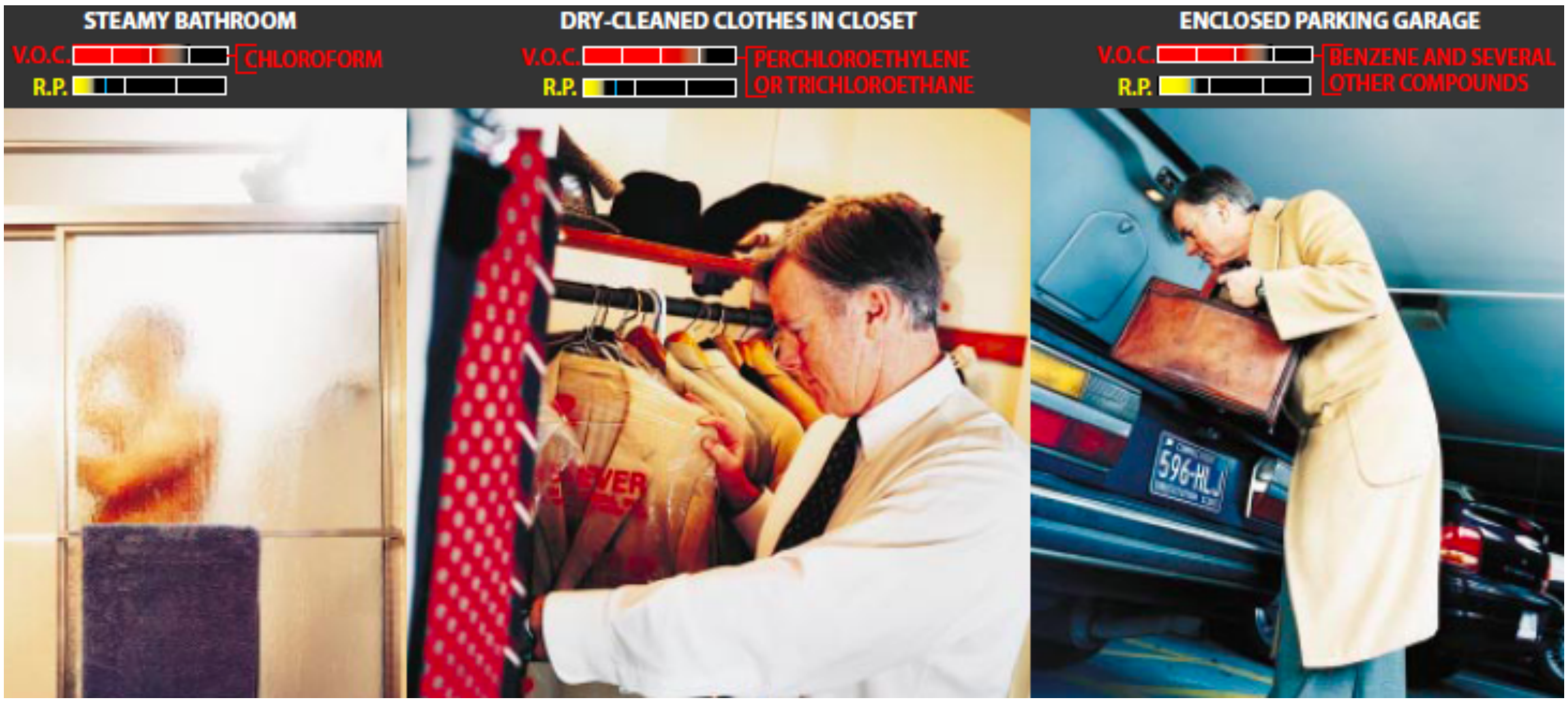
- There have been several large exposure studies in the U.S. that have focused on indoor, outdoor, and "personal" measurements
  - Typically "large" means 100 or more people or buildings
  - "Personal" meaning samplers affixed to people
  - Captures indoors, outdoors, home, work, transport, etc.
- Some of the larger studies:
  - TEAM and PTEAM in US
    - Ott and Roberts paper reported on some of these findings
  - BASE study of office buildings in US
  - RIOPA study of people + homes in 3 US cities
  - EXPOLIS in Europe
  - SHIELD in US
- These studies help us identify indoor and outdoor environments as being more or less important for exposure

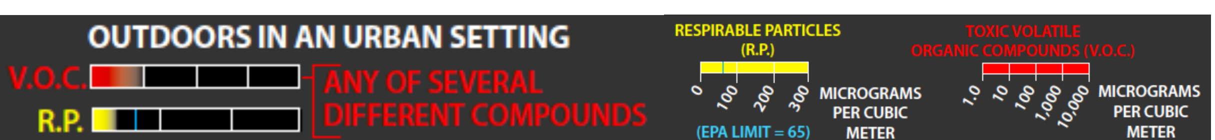
# Ott and Roberts (1998) *Sci Am*

# Everyday Exposure to Toxic Pollutants

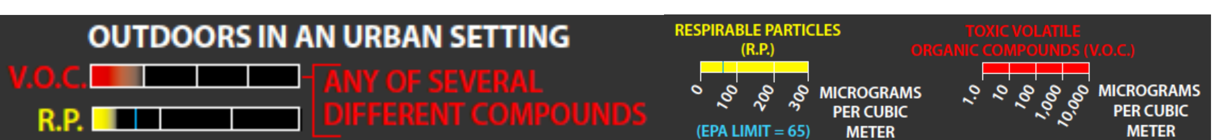


# Ott and Roberts (1998)

# Ott and Roberts (1998)

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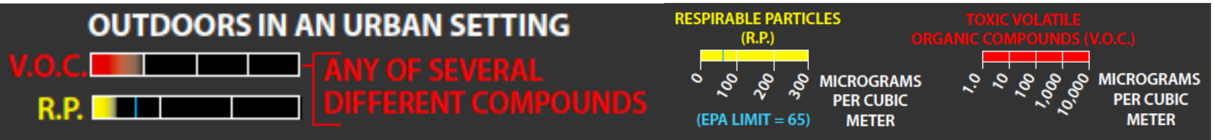

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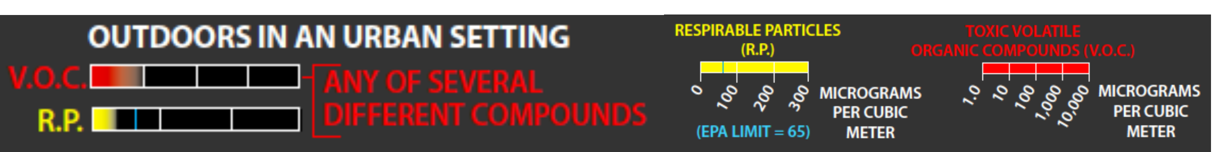

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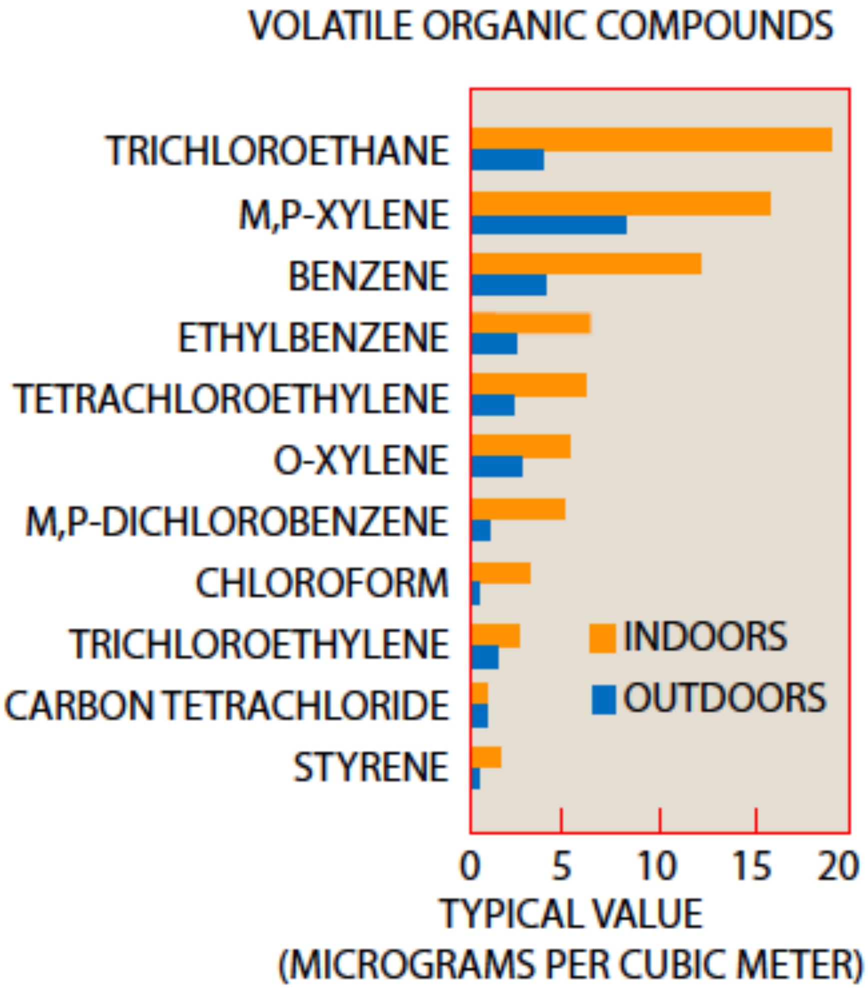
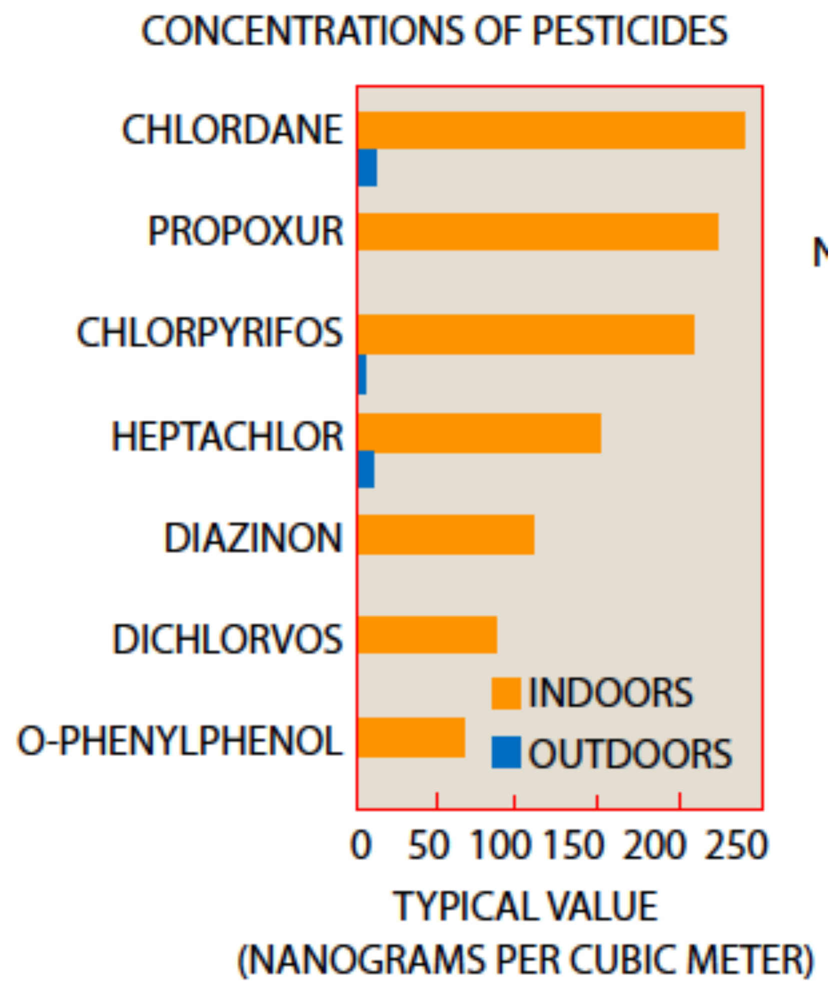
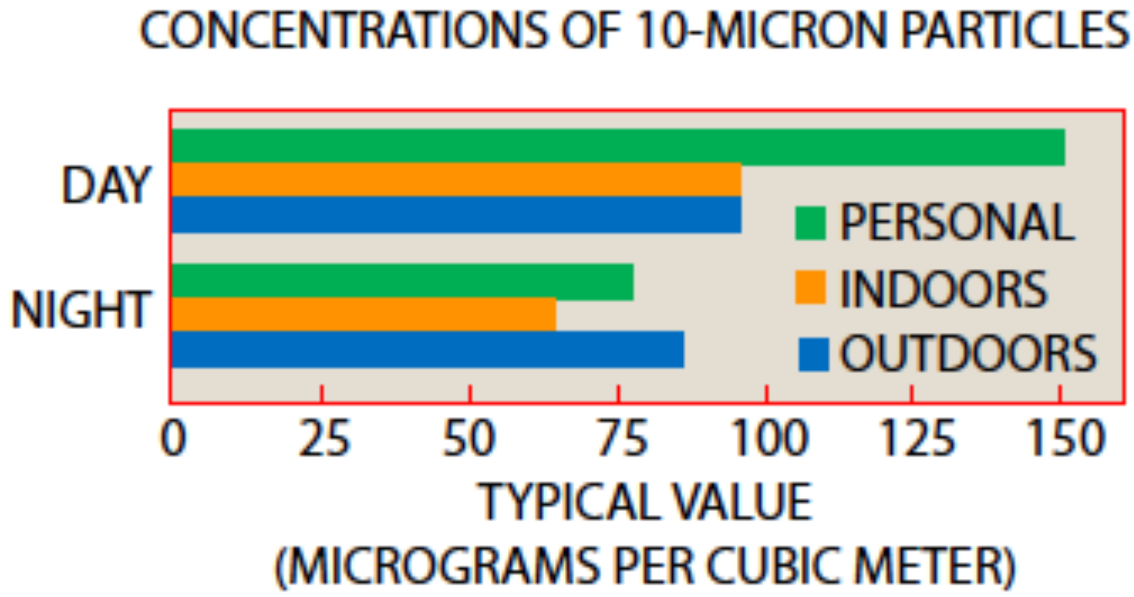


# Ott and Roberts (1998)



# SHIELD study: Children’s VOC exposures

- Children’s VOC exposures in many microenvironments
  - Children attended two inner-city schools in Minneapolis, MN
  - 100+ subjects

**Measurements**

- Outdoors (O)
- Indoors at home (H)
- Indoors at school (S)
- Personal samplers on children (P)

Adgate et al., 2004 *EHP*

# SHIELD study: Children's VOC exposures

- SHIELD study details
  - Winter and spring measurements
  - Fifteen VOCs using organic vapor monitors (3M 3520)
    - Passive samplers
  - P and H were 48-hour continuous measurements
  - S was measured during weekly daytime periods
    - Cap on monitor overnight to disregard non-exposure periods
    - 31 hours over 5 days
  - O measured at each school from Mon-Fri (100 hours)


Adgate et al., 2004 *EHP*

# SHIELD study: Children's VOC exposures

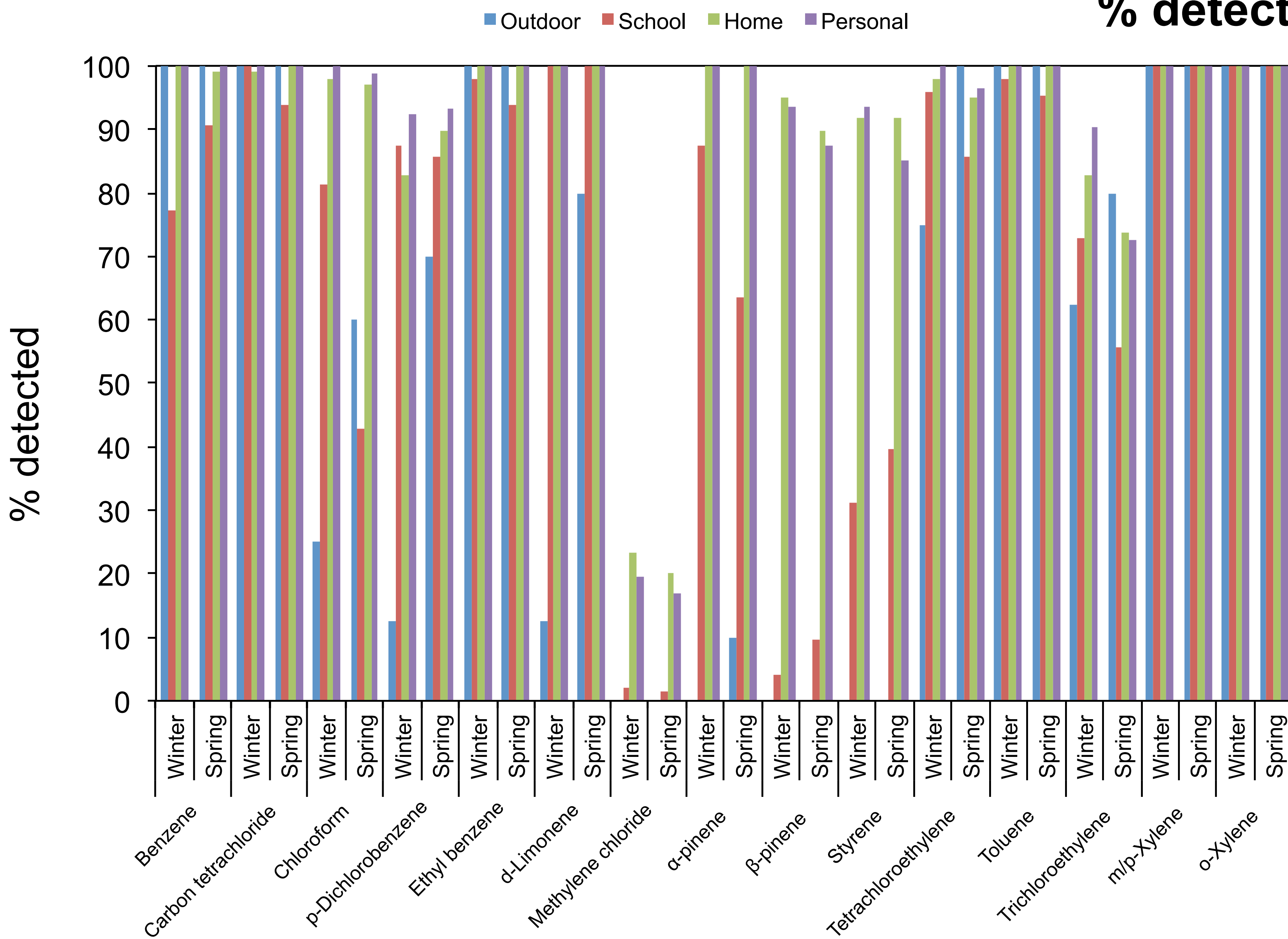
**Table 2.** Summary of VOC concentration (μg/m³) distributions for 15 VOCs in matched P, S, H, and O samples from 113 subjects in winter and spring 2000.

| | | O[a] | | | | S[b] | | | | H[c] | | | | P[c] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| VOC | Season | %Det | Median | Q10 | Q90 | %Det | Median | Q10 | Q90 | %Det | Median | Q10 | Q90 | %Det | Median | Q10 | Q90 |
| Benzene | Winter | 100.0 | 1.3 | 0.4 | 2.2 | 77.1 | 0.6 | 0.1 | 1.6 | 100.0 | 2.2 | 0.8 | 6.2 | 100.0 | 2.1 | 0.7 | 6.5 |
| | Spring | 100.0 | 1.1 | 0.7 | 1.6 | 90.5 | 0.6 | 0.2 | 1.0 | 99.0 | 2.1 | 0.6 | 7.2 | 100.0 | 1.5 | 0.7 | 4.2 |
| Carbon tetrachloride | Winter | 100.0 | 0.5 | 0.5 | 0.7 | 100.0 | 0.6 | 0.5 | 0.7 | 99.0 | 0.6 | 0.5 | 0.6 | 100.0 | 0.5 | 0.4 | 0.6 |
| | Spring | 100.0 | 0.5 | 0.4 | 0.7 | 93.7 | 0.5 | 0.2 | 0.9 | 100.0 | 0.5 | 0.4 | 0.8 | 100.0 | 0.5 | 0.4 | 0.6 |
| Chloroform | Winter | 25.0 | 0.1 | 0.1 | 0.1 | 81.3 | 0.2 | 0.1 | 0.3 | 98.0 | 0.8 | 0.3 | 2.6 | 100.0 | 0.7 | 0.3 | 2.1 |
| | Spring | 60.0 | 0.1 | 0.1 | 0.3 | 42.9 | 0.1 | 0.1 | 0.4 | 97.0 | 1.5 | 0.5 | 3.4 | 98.9 | 1.2 | 0.5 | 2.9 |
| *p*-Dichlorobenzene | Winter | 12.5 | 0.1 | 0.0 | 0.2 | 87.5 | 0.5 | 0.1 | 1.1 | 82.8 | 0.7 | 0.1 | 344.6 | 92.5 | 1.0 | 0.2 | 167.2 |
| | Spring | 70.0 | 0.2 | 0.1 | 0.4 | 85.7 | 0.5 | 0.1 | 1.1 | 89.9 | 0.9 | 0.2 | 429.0 | 93.2 | 1.3 | 0.2 | 87.2 |
| Ethylbenzene | Winter | 100.0 | 0.6 | 0.2 | 0.8 | 97.9 | 0.6 | 0.2 | 1.0 | 100.0 | 1.0 | 0.6 | 2.8 | 100.0 | 1.0 | 0.6 | 2.4 |
| | Spring | 100.0 | 0.5 | 0.3 | 0.7 | 93.7 | 0.3 | 0.2 | 0.5 | 100.0 | 1.0 | 0.5 | 3.8 | 100.0 | 0.9 | 0.5 | 2.0 |
| *d*-Limonene | Winter | 12.5 | 0.1 | 0.0 | 0.3 | 100.0 | 4.6 | 1.8 | 12.1 | 100.0 | 28.6 | 6.4 | 122.3 | 100.0 | 24.7 | 7.5 | 159.5 |
| | Spring | 80.0 | 0.4 | 0.1 | 0.6 | 100.0 | 1.9 | 0.9 | 7.9 | 100.0 | 21.2 | 7.2 | 124.8 | 100.0 | 22.2 | 8.3 | 110.0 |
| Methylene chloride | Winter | 0.0 | 0.3 | 0.2 | 0.6 | 2.1 | 0.4 | 0.1 | 0.6 | 23.2 | 0.4 | 0.2 | 1.3 | 19.4 | 0.4 | 0.2 | 1.3 |
| | Spring | 0.0 | 0.2 | 0.1 | 0.6 | 1.6 | 0.3 | 0.1 | 0.5 | 20.2 | 0.3 | 0.2 | 1.2 | 17.0 | 0.3 | 0.2 | 1.3 |
| α-Pinene | Winter | 0.0 | 0.0 | 0.0 | 0.1 | 87.5 | 0.2 | 0.1 | 0.3 | 100.0 | 2.4 | 0.7 | 6.5 | 100.0 | 1.9 | 0.7 | 5.1 |
| | Spring | 10.0 | 0.1 | 0.1 | 0.1 | 63.5 | 0.2 | 0.1 | 0.4 | 100.0 | 2.4 | 0.7 | 8.6 | 100.0 | 1.8 | 0.6 | 5.4 |
| β-Pinene | Winter | 0.0 | 0.1 | 0.1 | 0.1 | 4.2 | 0.1 | 0.1 | 0.1 | 94.9 | 2.5 | 0.5 | 11.7 | 93.5 | 1.7 | 0.4 | 11.5 |
| | Spring | 0.0 | 0.1 | 0.1 | 0.1 | 9.5 | 0.1 | 0.1 | 0.2 | 89.9 | 1.5 | 0.1 | 7.4 | 87.5 | 1.1 | 0.1 | 5.3 |
| Styrene | Winter | 0.0 | 0.1 | 0.0 | 0.1 | 31.3 | 0.1 | 0.0 | 0.4 | 91.9 | 0.7 | 0.2 | 1.5 | 93.5 | 0.5 | 0.2 | 1.2 |
| | Spring | 0.0 | 0.0 | 0.0 | 0.1 | 39.7 | 0.1 | 0.1 | 0.3 | 91.9 | 0.8 | 0.3 | 2.1 | 85.2 | 0.5 | 0.1 | 1.2 |
| Tetrachloroethylene | Winter | 75.0 | 0.2 | 0.1 | 0.4 | 95.8 | 0.3 | 0.2 | 0.4 | 98.0 | 0.5 | 0.2 | 1.3 | 100.0 | 0.4 | 0.2 | 1.3 |
| | Spring | 100.0 | 0.3 | 0.2 | 0.4 | 85.7 | 0.3 | 0.1 | 0.6 | 94.9 | 0.4 | 0.2 | 1.0 | 96.6 | 0.4 | 0.2 | 0.9 |
| Toluene | Winter | 100.0 | 2.6 | 0.9 | 4.2 | 97.9 | 2.9 | 1.4 | 5.6 | 100.0 | 8.2 | 3.5 | 19.2 | 100.0 | 7.7 | 3.4 | 17.7 |
| | Spring | 100.0 | 2.7 | 1.1 | 3.6 | 95.2 | 1.6 | 0.2 | 3.2 | 100.0 | 8.9 | 4.2 | 25.1 | 100.0 | 7.7 | 3.1 | 18.0 |
| Trichloroethylene | Winter | 62.5 | 0.3 | 0.0 | 1.0 | 72.9 | 0.2 | 0.1 | 0.8 | 82.8 | 0.3 | 0.1 | 0.9 | 90.3 | 0.3 | 0.1 | 0.8 |
| | Spring | 80.0 | 0.2 | 0.1 | 0.7 | 55.6 | 0.1 | 0.0 | 0.3 | 73.7 | 0.2 | 0.1 | 1.7 | 72.7 | 0.2 | 0.1 | 0.8 |
| *m/p*-Xylene | Winter | 100.0 | 2.3 | 0.9 | 3.3 | 100.0 | 2.3 | 1.1 | 3.6 | 100.0 | 3.7 | 2.2 | 10.4 | 100.0 | 3.5 | 2.1 | 8.0 |
| | Spring | 100.0 | 2.0 | 1.1 | 2.8 | 100.0 | 1.2 | 0.7 | 1.5 | 100.0 | 3.3 | 1.5 | 13.2 | 100.0 | 2.9 | 1.4 | 6.9 |
| *o*-Xylene | Winter | 100.0 | 0.8 | 0.3 | 1.1 | 100.0 | 0.8 | 0.3 | 1.2 | 100.0 | 1.2 | 0.7 | 3.2 | 100.0 | 1.1 | 0.7 | 2.6 |
| | Spring | 100.0 | 0.7 | 0.4 | 0.9 | 100.0 | 0.4 | 0.3 | 0.5 | 100.0 | 1.1 | 0.5 | 4.1 | 100.0 | 1.0 | 0.5 | 2.7 |

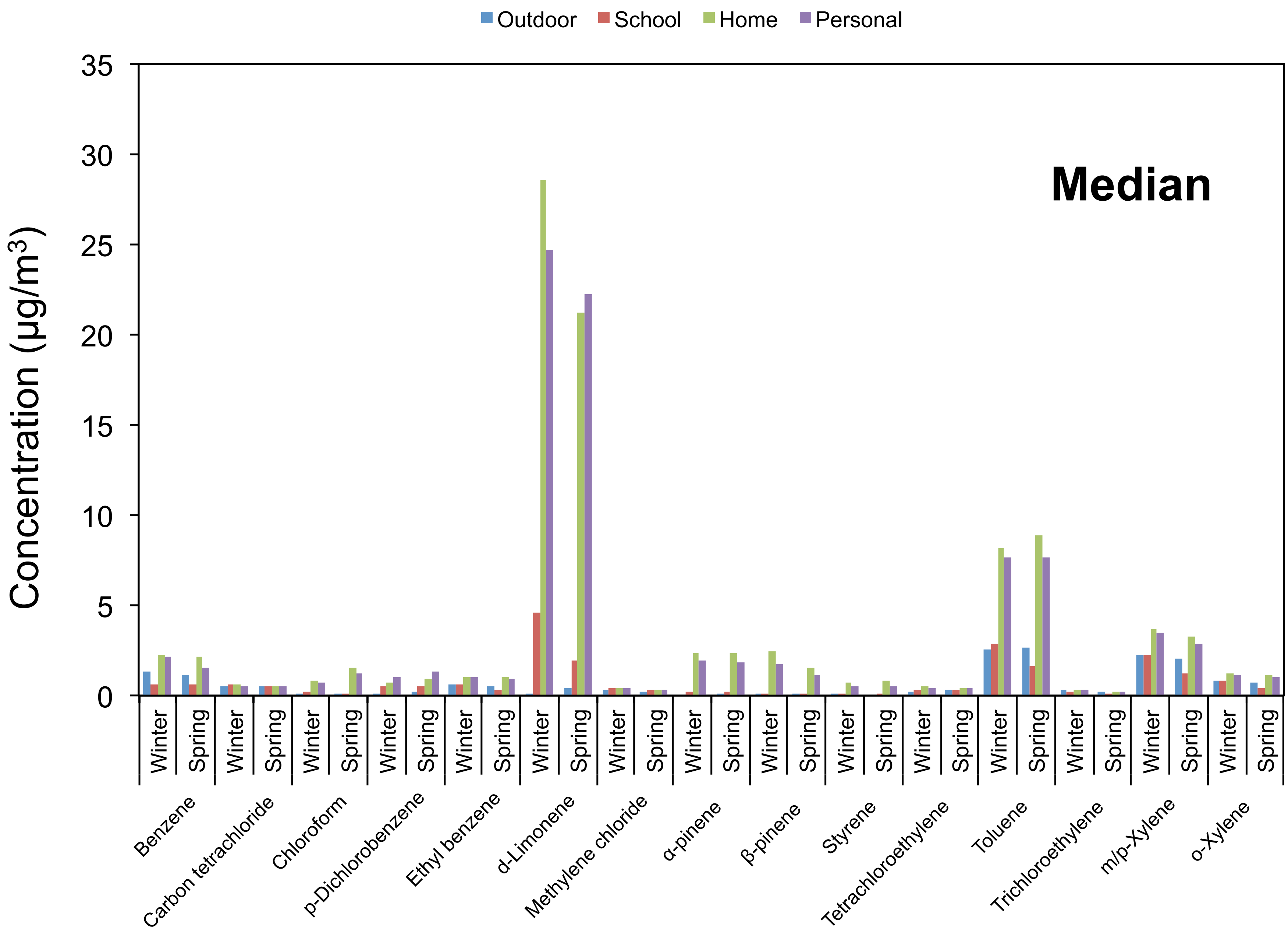


Adgate et al., 2004 *EHP*

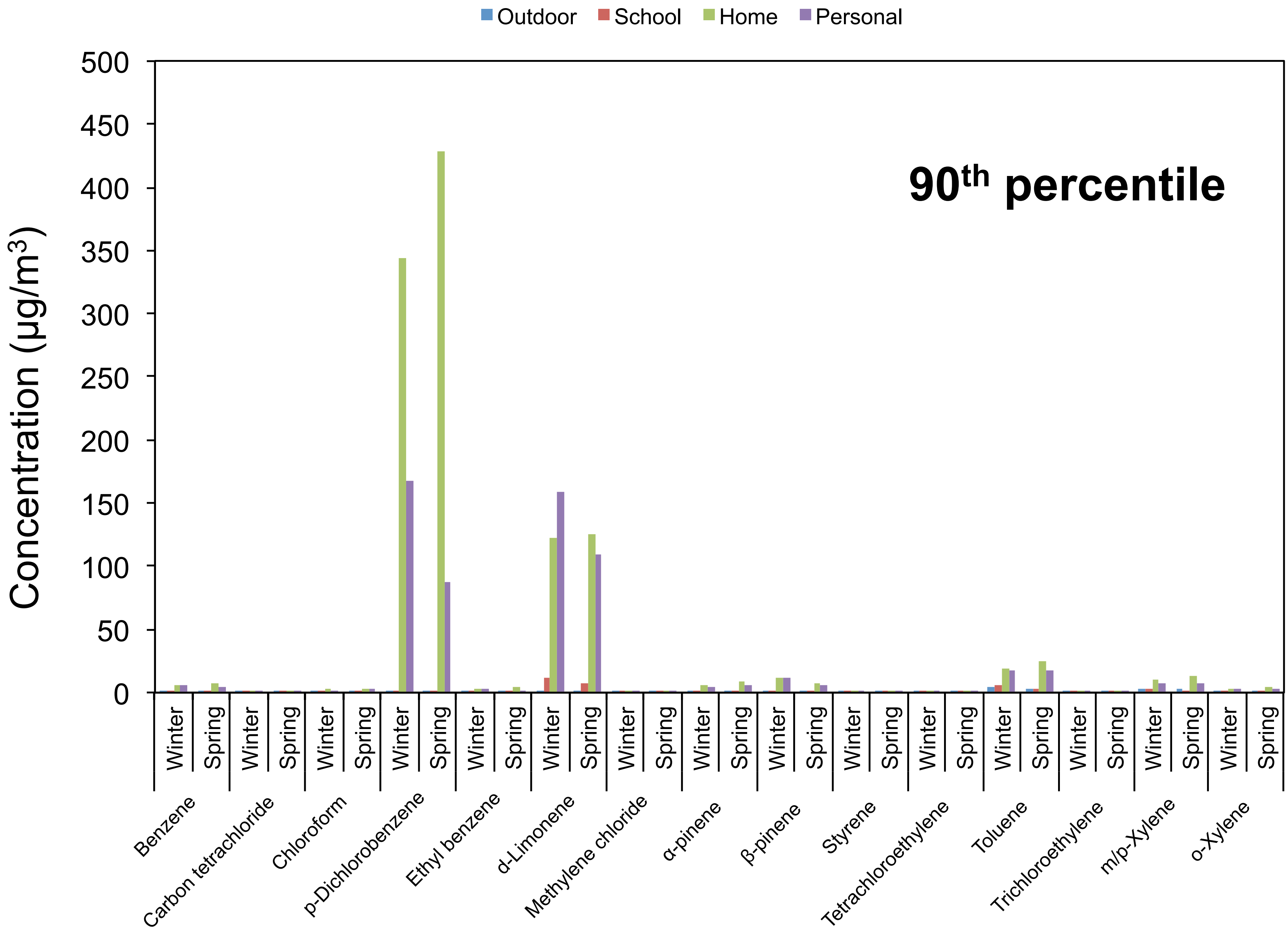
# % detected




Adgate et al., 2004 *EHP*




Adgate et al., 2004 *EHP*




Adgate et al., 2004 *EHP*

# SHIELD study: Children's VOC exposures

- Most VOCs followed the pattern:
- Home >= Personal > School ~ Outdoor
  - Getting the home measurement alone predicted most of the personal exposure

- What do these relationships say about building characteristics and activity patterns?

Adgate et al., 2004 *EHP*

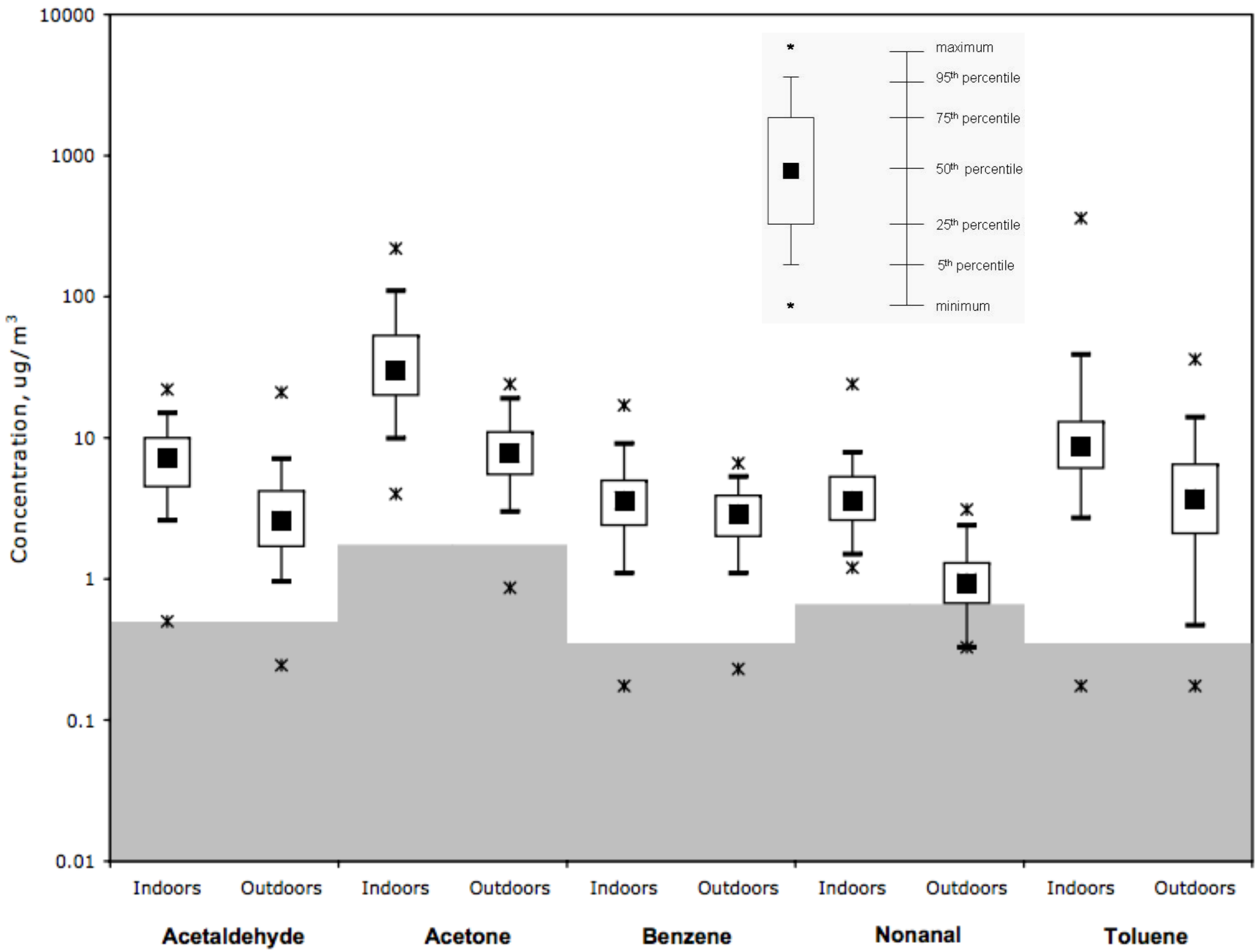
# EPA BASE Study of office buildings

- Building Assessment Survey and Evaluation (BASE) Study
  - Between 1994 and 1998 data and samples were collect in 100 office building using a standardized protocol
  - The protocol included not only indoor and outdoor air samples but building characterizations, environmental parameters, HVAC measurements, and occupant questionnaires



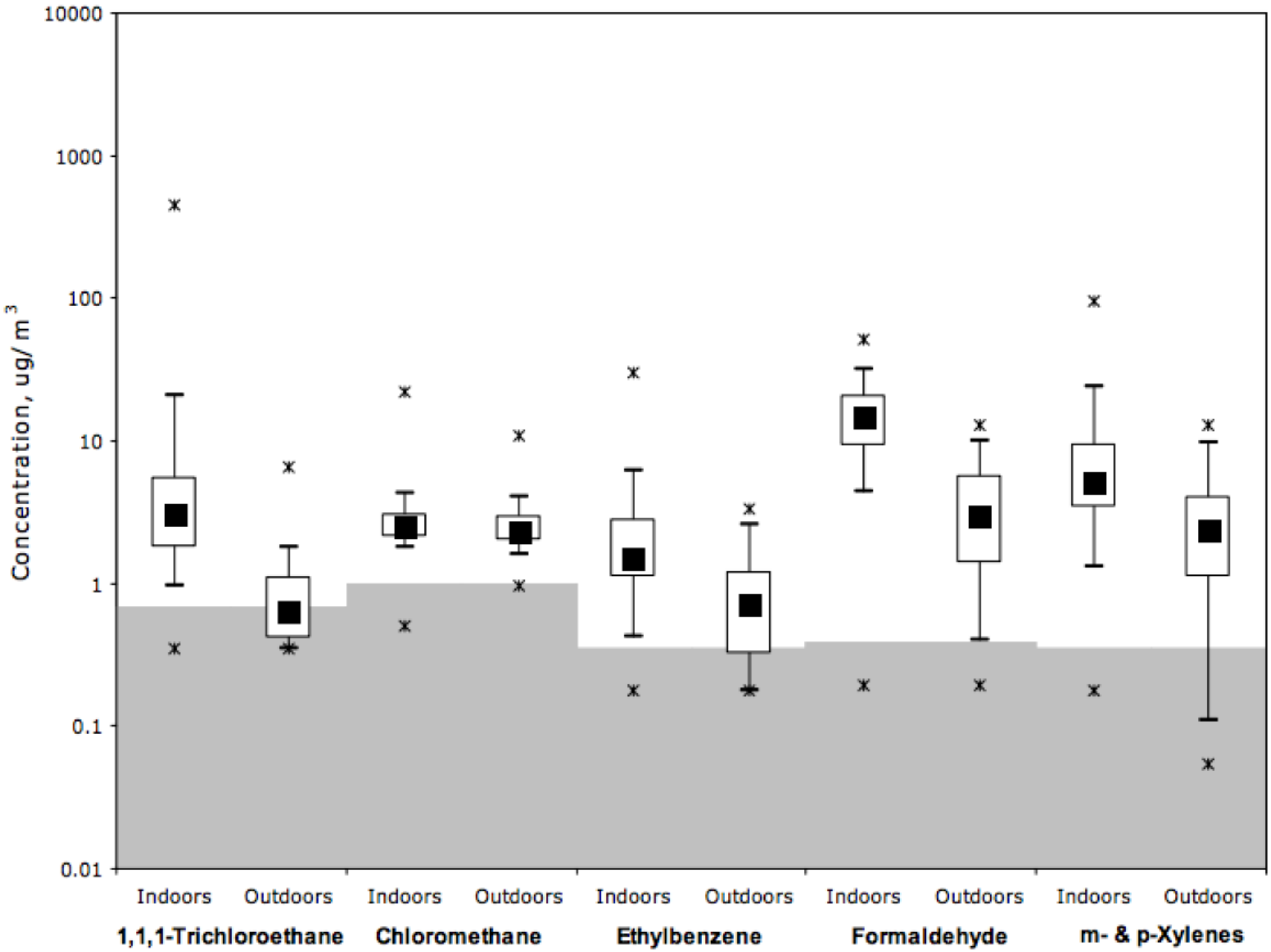
http://www.epa.gov/iaq/base/

# BASE study of ~100 office buildings



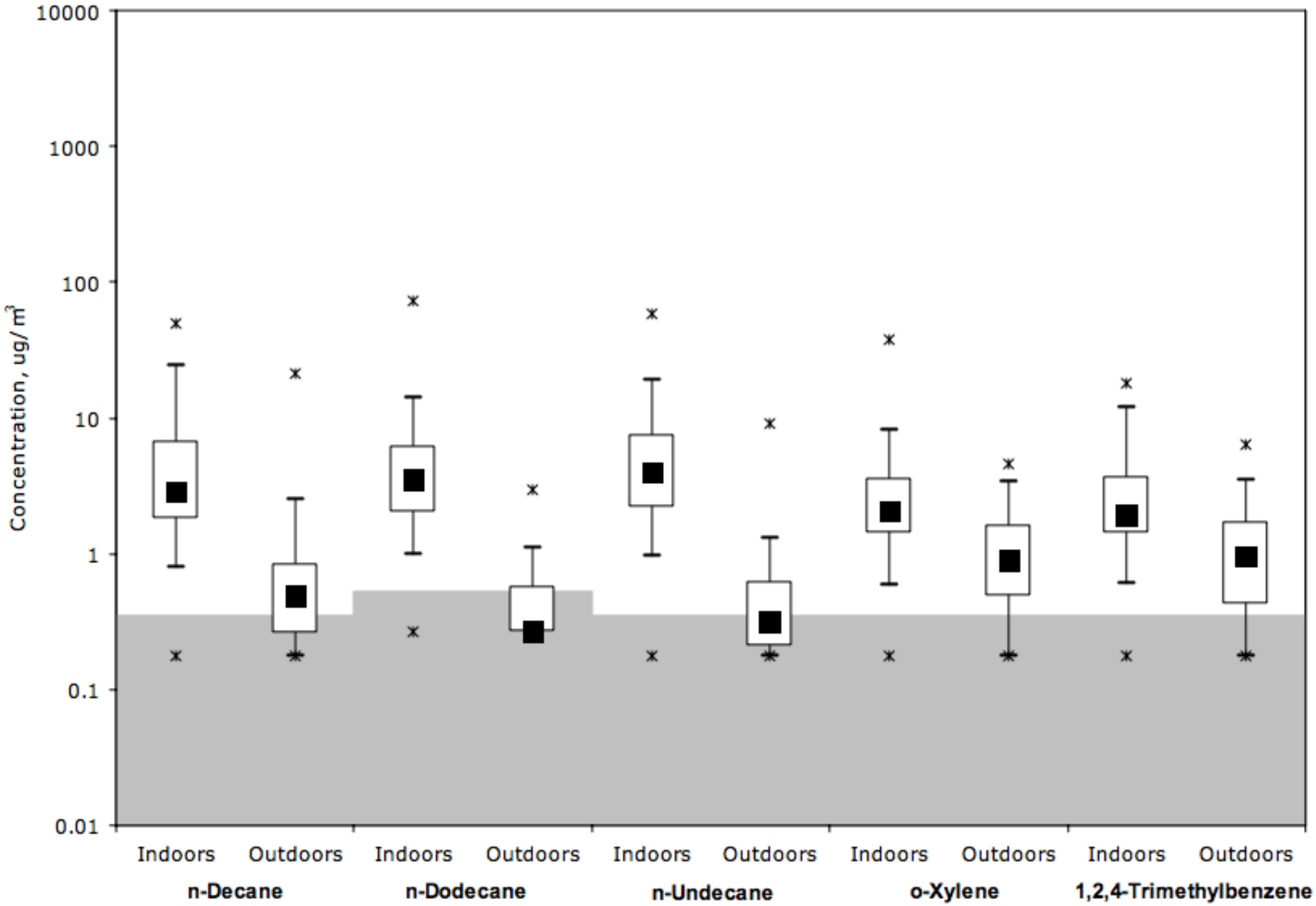

http://www.epa.gov/iaq/base/voc_master_list.html

# BASE study of ~100 office buildings




http://www.epa.gov/iaq/base/voc_master_list.html

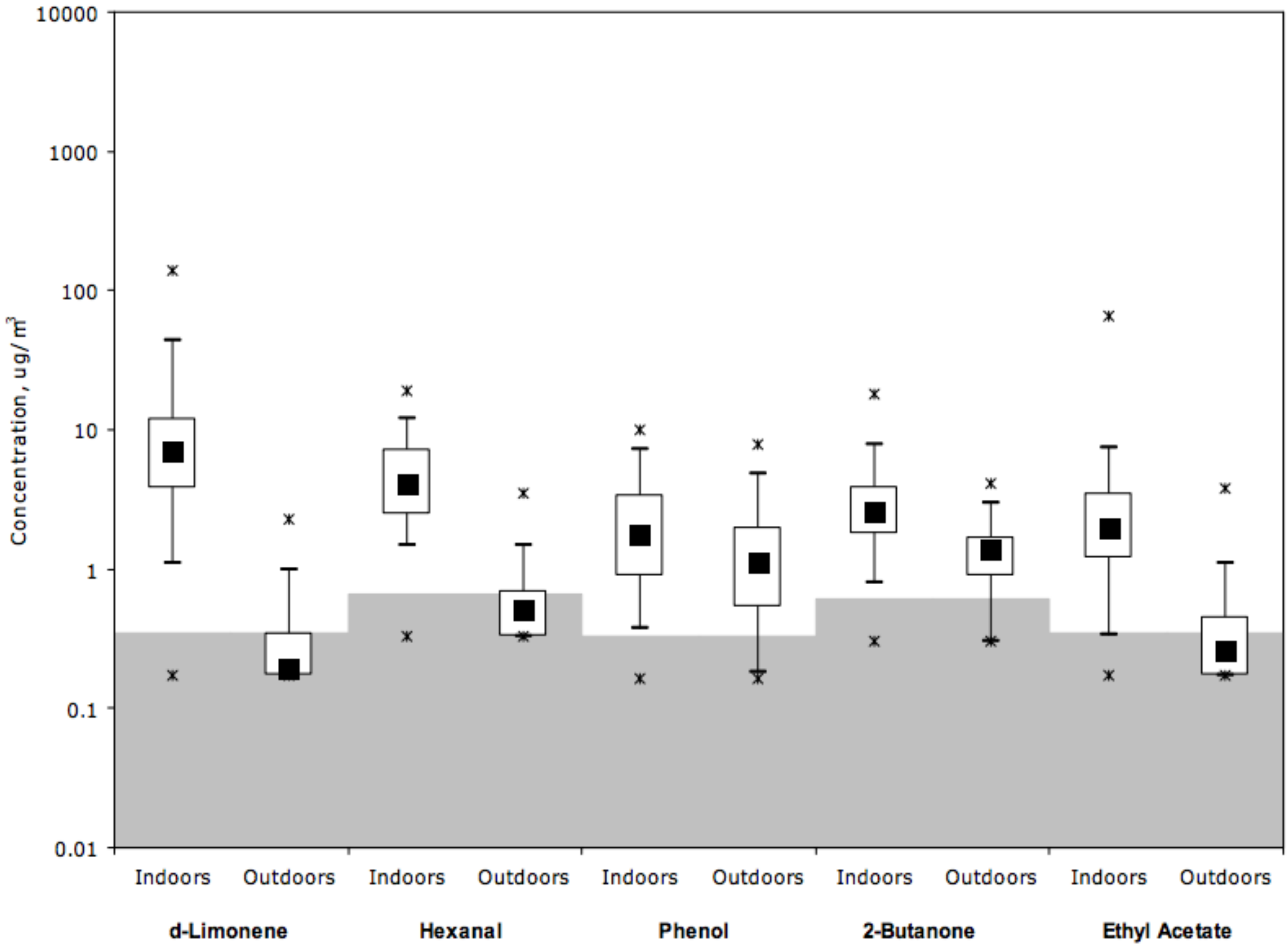
# BASE study of ~100 office buildings






http://www.epa.gov/iaq/base/voc_master_list.html

# BASE study of ~100 office buildings






http://www.epa.gov/iaq/base/voc_master_list.html

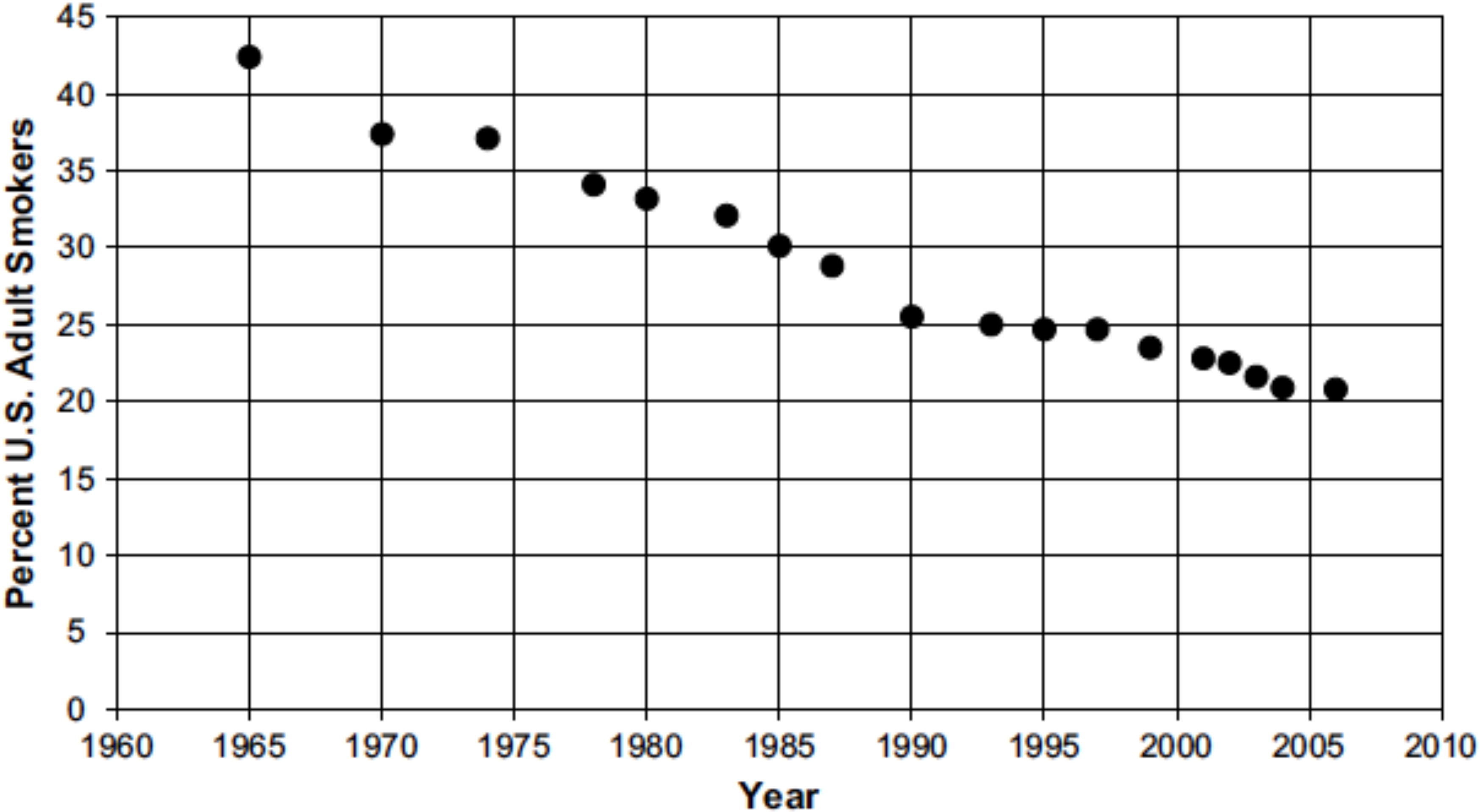
Changes in indoor pollutants since the 1950s

Charles J. Weschler [a,b]

- Major changes in building materials and consumer products used indoors
  - Composite wood, synthetic carpets, polymeric flooring, foam cushioning, plastic items, and scented cleaning agents have all become ubiquitous
  - Same as true for several electronics and appliances
    - Solvents, additives, and unreacted monomers
  - Homes are less ventilated
  - Levels of certain indoor pollutants have increased and then decreased
  - Levels of others have increased and remain high
  - Many chemicals found indoors now and in the blood and urine of occupants were not present 50 years ago

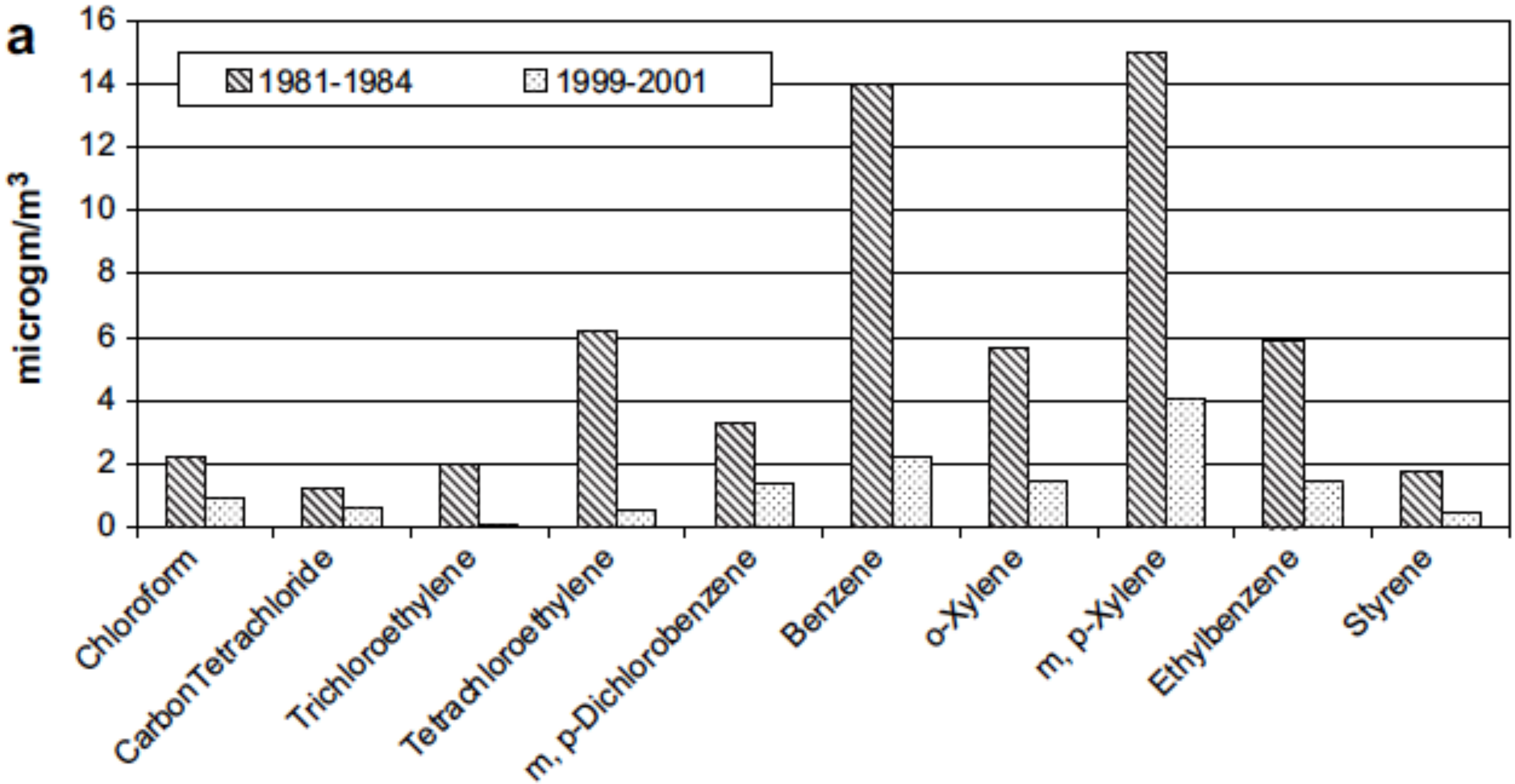
Weschler, 2009 *Atmos Environ*

# U.S. smokers




Weschler, 2009 *Atmos Environ*

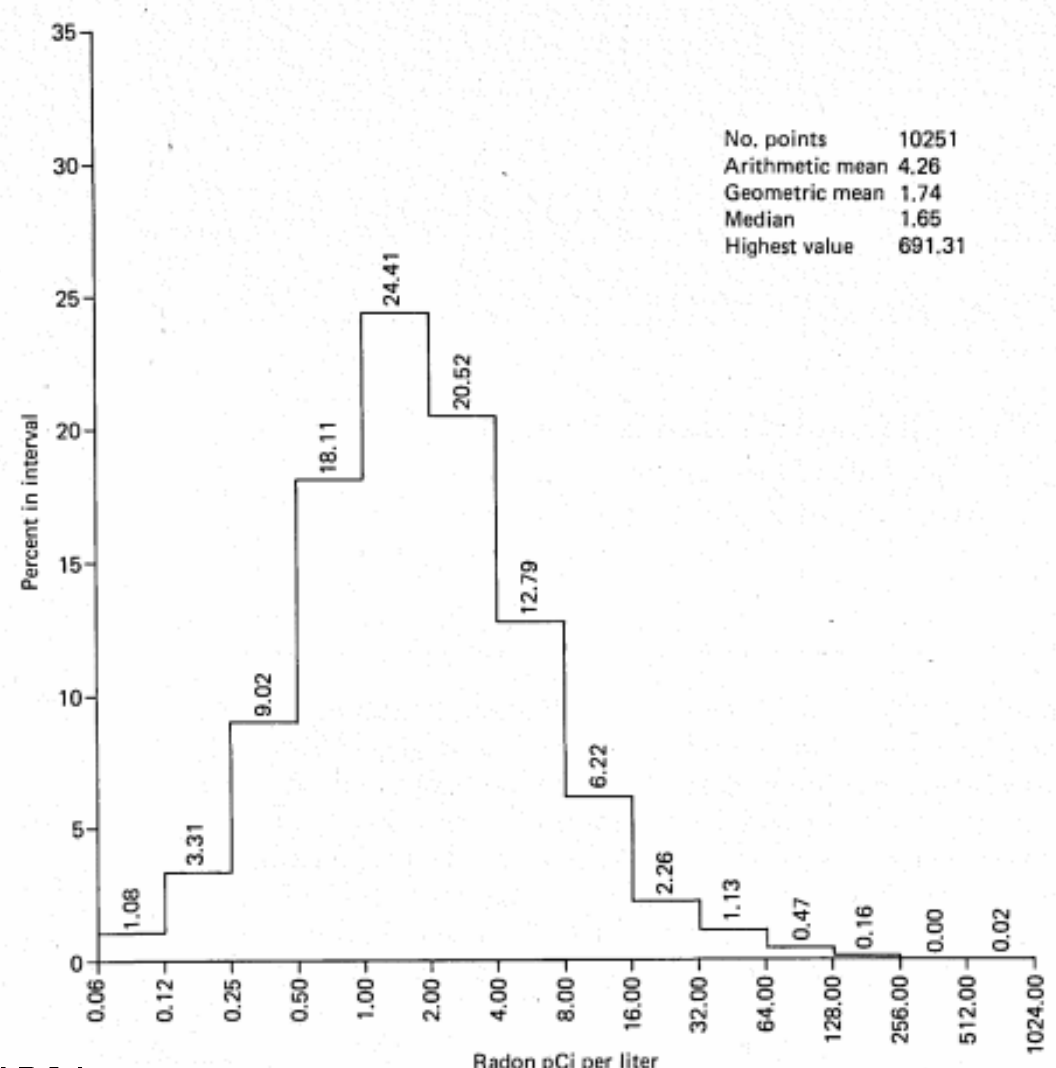
# Changes in indoor VOC concentrations




Weschler, 2009 *Atmos Environ*

# Radon in U.S. homes

- Indoor radon concentration distribution




Alter and Oswald 1987 *JAPCA*

# RIOPA

- Relationship of Indoor, Outdoor and Personal Air (RIOPA)
- I, O, and P sampling over 48-hours in approximately 100 non-smoking homes in each of Elizabeth, NJ, Houston, TX, and Los Angeles, CA
  - 18 VOCs
  - 17 carbonyls
  - Fine particulate matter ($PM_{2.5}$)
  - AER also measured in each home with PFT
  - Questionnaires were administered to characterize homes, neighborhoods, and personal activities

- I'm just going to show $PM_{2.5}$ data

# RIOPA I/O $PM_{2.5}$

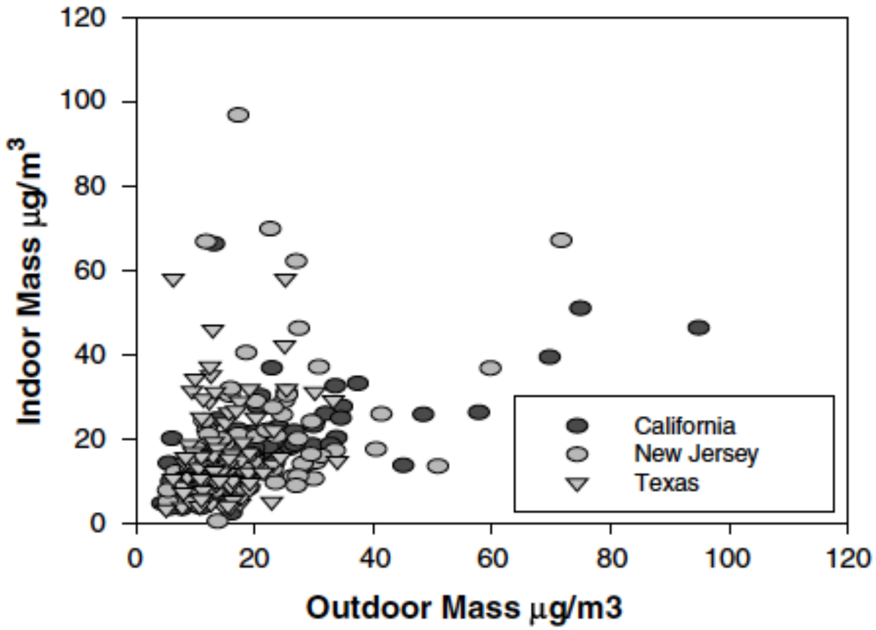
- ~300 homes in NJ, TX, and CA

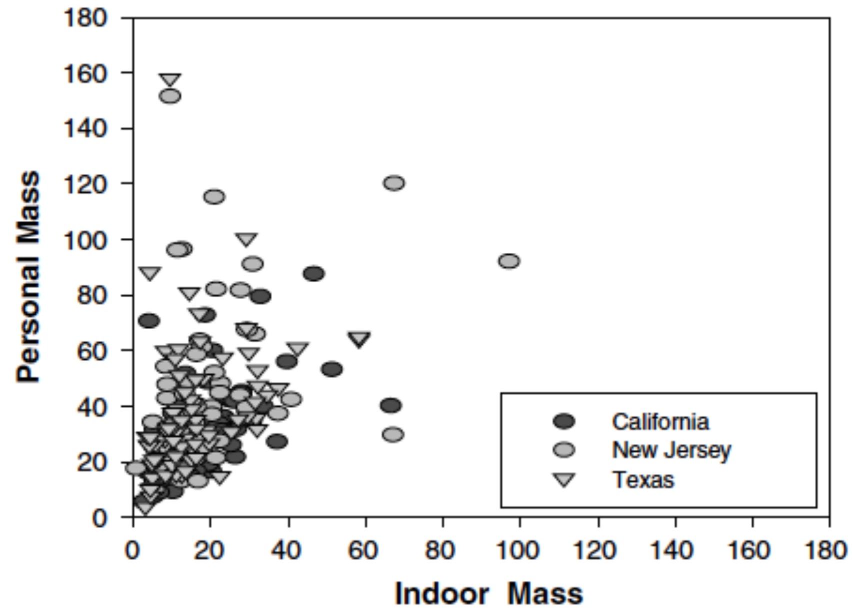
**Table 1.** Indoor, outdoor and personal $PM_{2.5}$ mass concentrations ($\mu g/m^3$) and air exchange rates (AER; $h^{-1}$).

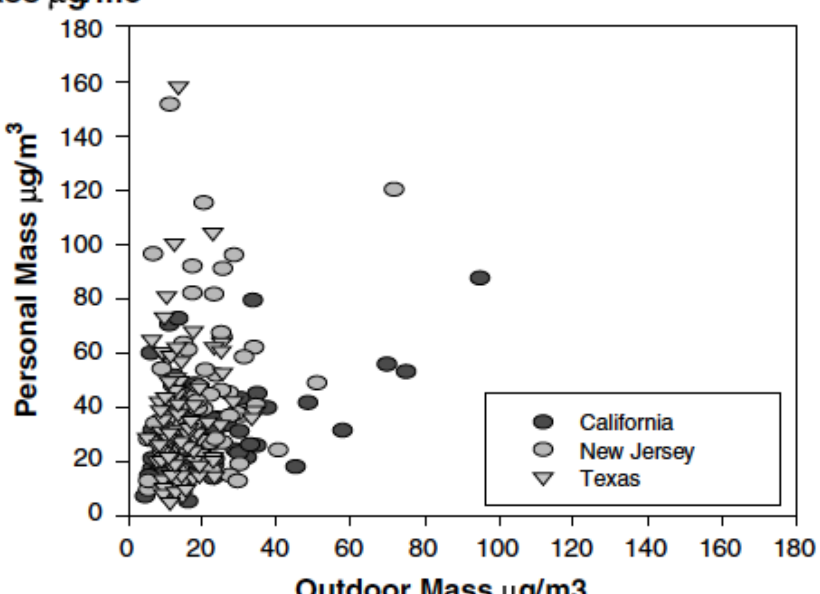
| Group | Category | Sample size | Mean | Median | STD |
|---|---|---|---|---|---|
| Overall study | Indoor | 326 | 17.6 | 14.4 | 12.6 |
| | Outdoor | 334 | 18.1 | 15.5 | 10.7 |
| | Personal | 307 | 37.6 | 31.4 | 24.6 |
| | AER | 349 | 1.06 | 0.78 | 0.89 |
| California | Indoor | 124 | 16.2 | 14.5 | 9.4 |
| | Outdoor | 121 | 19.2 | 16.1 | 13.3 |
| | Personal | 106 | 29.3 | 26.6 | 14.8 |
| | AER | 131 | 1.22 | 0.93 | 0.87 |
| New Jersey | Indoor | 96 | 20.1 | 15.7 | 15.5 |
| | Outdoor | 103 | 20.4 | 18.2 | 10.7 |
| | Personal | 100 | 46.9 | 38.6 | 30.5 |
| | AER | 111 | 1.22 | 0.88 | 0.97 |
| Texas | Indoor | 106 | 17.1 | 13.4 | 12.7 |
| | Outdoor | 110 | 14.7 | 13.2 | 5.7 |
| | Personal | 101 | 37.2 | 31.8 | 23.4 |
| | AER | 107 | 0.71 | 0.46 | 0.73 |

Meng et al. 2005 *JESEE*

# RIOPA I/O $PM_{2.5}$




Meng et al. 2005 *JESEE*

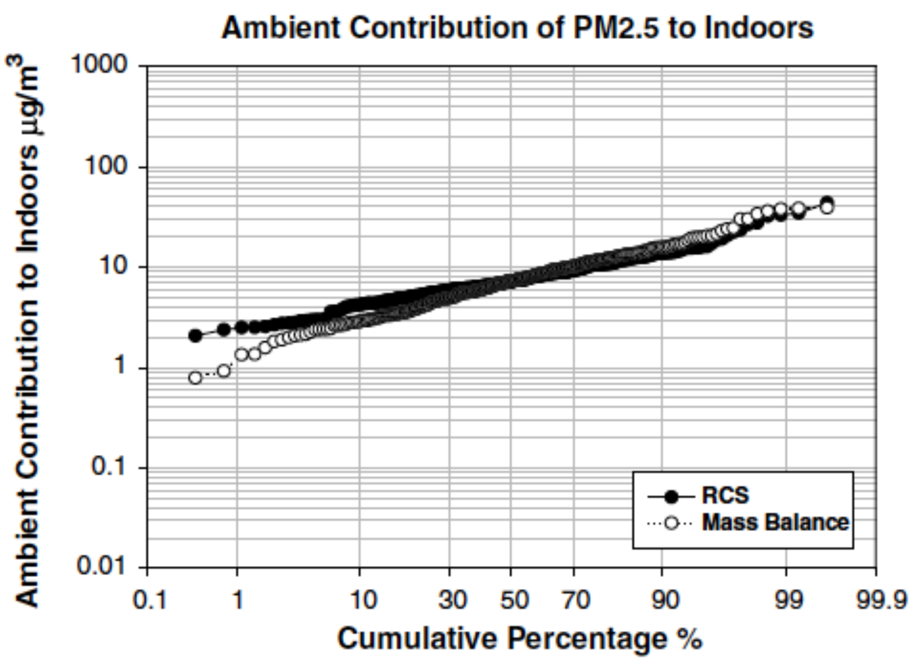
# LEARNING FROM EXPOSURE STUDIES

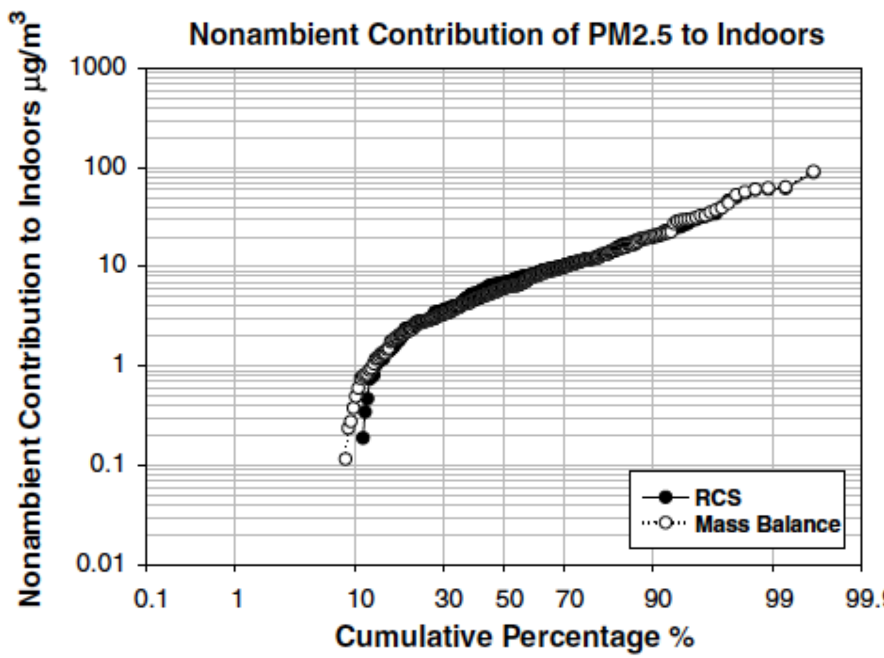
How do we get at more fundamental parameters than just I/O concentration measurements?

# RIOPA I/O $PM_{2.5}$

- What can we learn about indoor vs. outdoor contributions to indoor PM2.5 in RIOPA?
  - They fit a model that used measure $C_i$, $C_a$, AER ($a$), and estimated $P$ and $k$

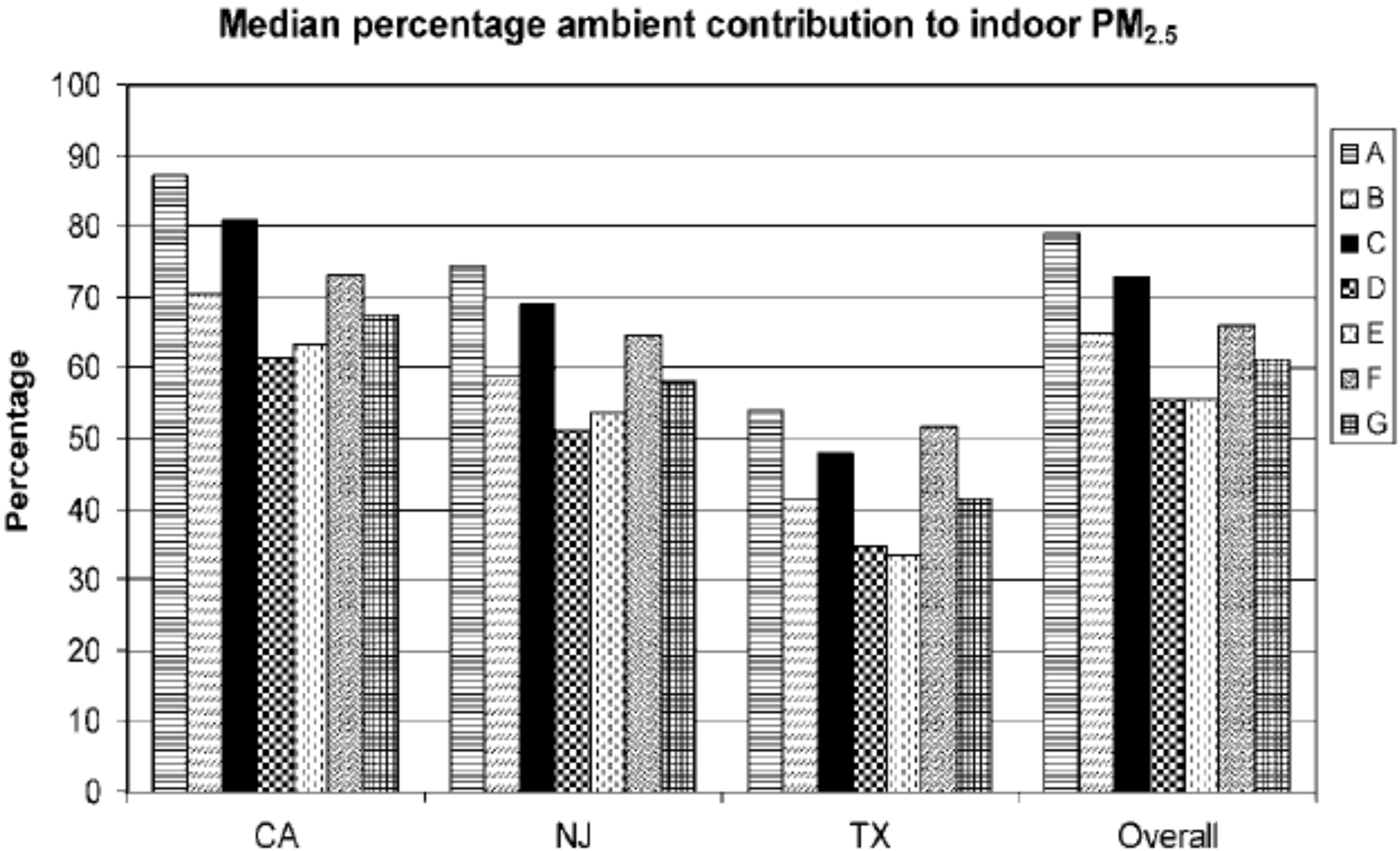
$$C_i = \frac{PaC_a}{a+k} + \frac{Q_i/V}{a+k} = F_{INF}C_a + C_{pig} = C_{ai} + C_{pig}$$




Meng et al. 2005 *JESEE*

# RIOPA I/O $PM_{2.5}$




Meng et al. 2005 *JESEE*

# Indoor and outdoor contributions

- If we go back to our mass balance, what is a fundamental parameter we need to determine concentrations of pollutants that are primarily emitted indoors?
  - Emission rates, $E$

$$C_{ss} = PC_{out} + \frac{E}{\lambda V}$$

- How do we get $E$?
  - Chamber testing
  - Back-calculated from I/O measurements

- We will discuss chamber testing later
  - Back-calculation of I/O measurements now

# Back-calculating E/V

$$C_{ss} = PC_{out} + \frac{E}{\lambda V}$$

- Rearrange: $$\frac{E}{\lambda V} = C_{in} - PC_{out}$$

- Solve for E: $$E = \lambda V (C_{in} - PC_{out})$$

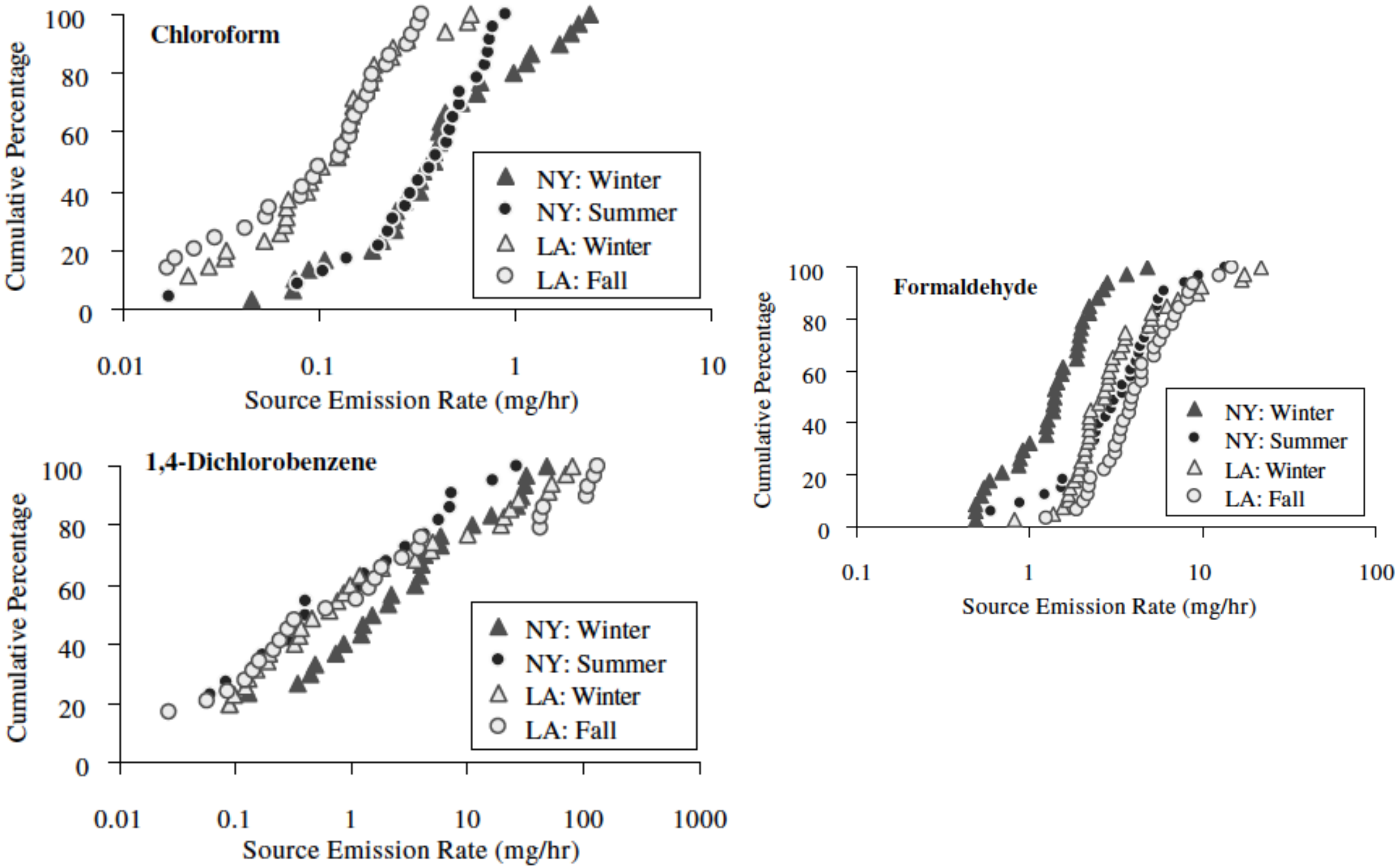
$$\frac{E}{V} = \lambda (C_{in} - PC_{out})$$

- Or E/V to normalize for volume

- These yield whole-building or whole-house emission rates

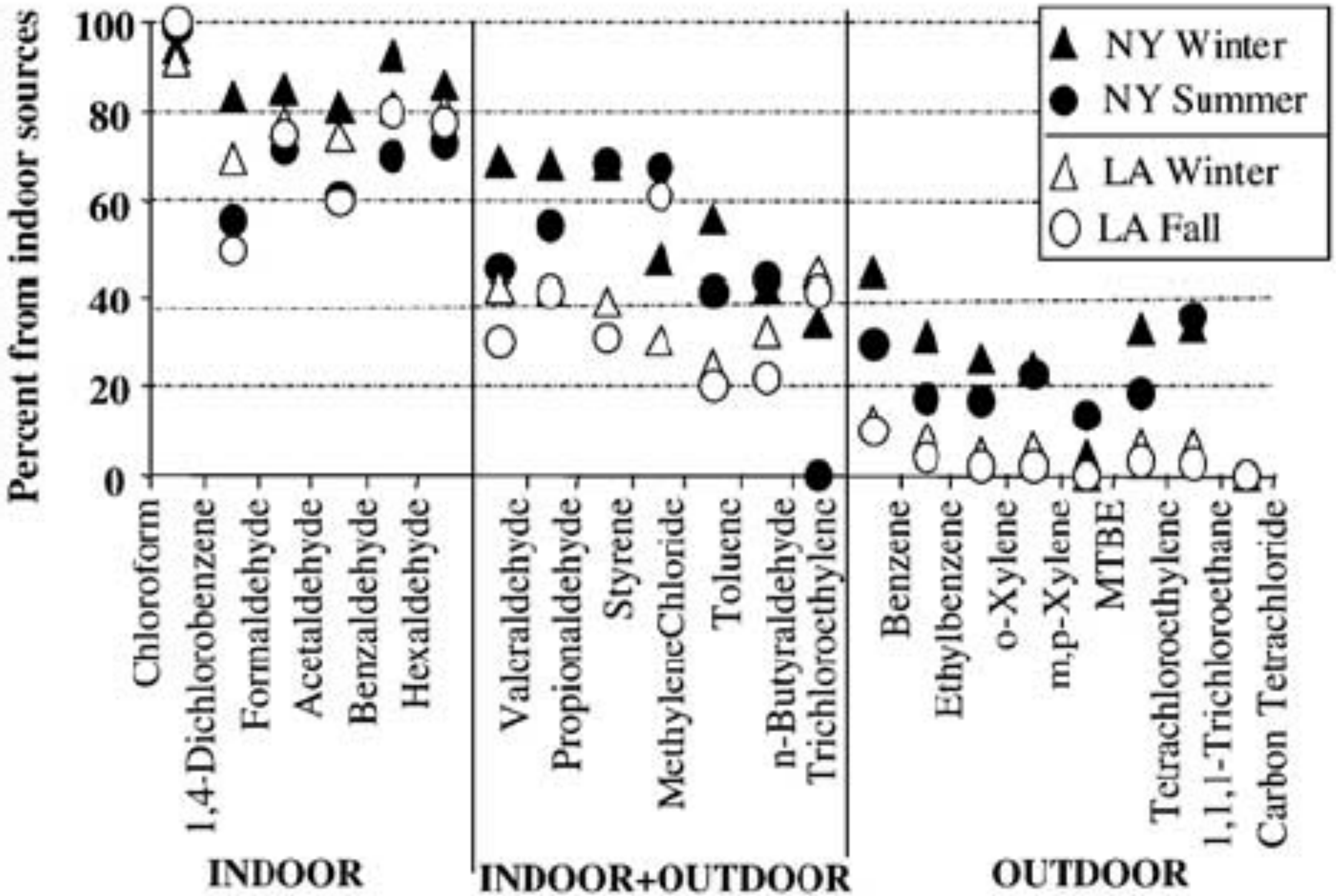
Sax et al. 2004 *JESEE*

# Back-calculating E/V




Sax et al. 2004 *JESEE*

# Using E/V and AER to estimate I/O contributions




Sax et al. 2004 *JESEE*

# A note on indoor emission rates

- Previous estimates of whole-house indoor emission rates

- Whole-building emission rate is just the sum of all emission rates from all materials in a building

$$E_{total} = \sum E_i$$

- These can be measured and simulated using basic mass transfer experiments or models
  - More on that next time

# Next time

- Gaseous pollutants
  - Individual sources
  - Adsorption/desorption
  - Emission models

- No HW assigned this time
- First blog post assigned and due next week