ENVE 576
Indoor Air Pollution
Fall 2016

Week 3: September 6, 2016
Overview of indoor pollutants

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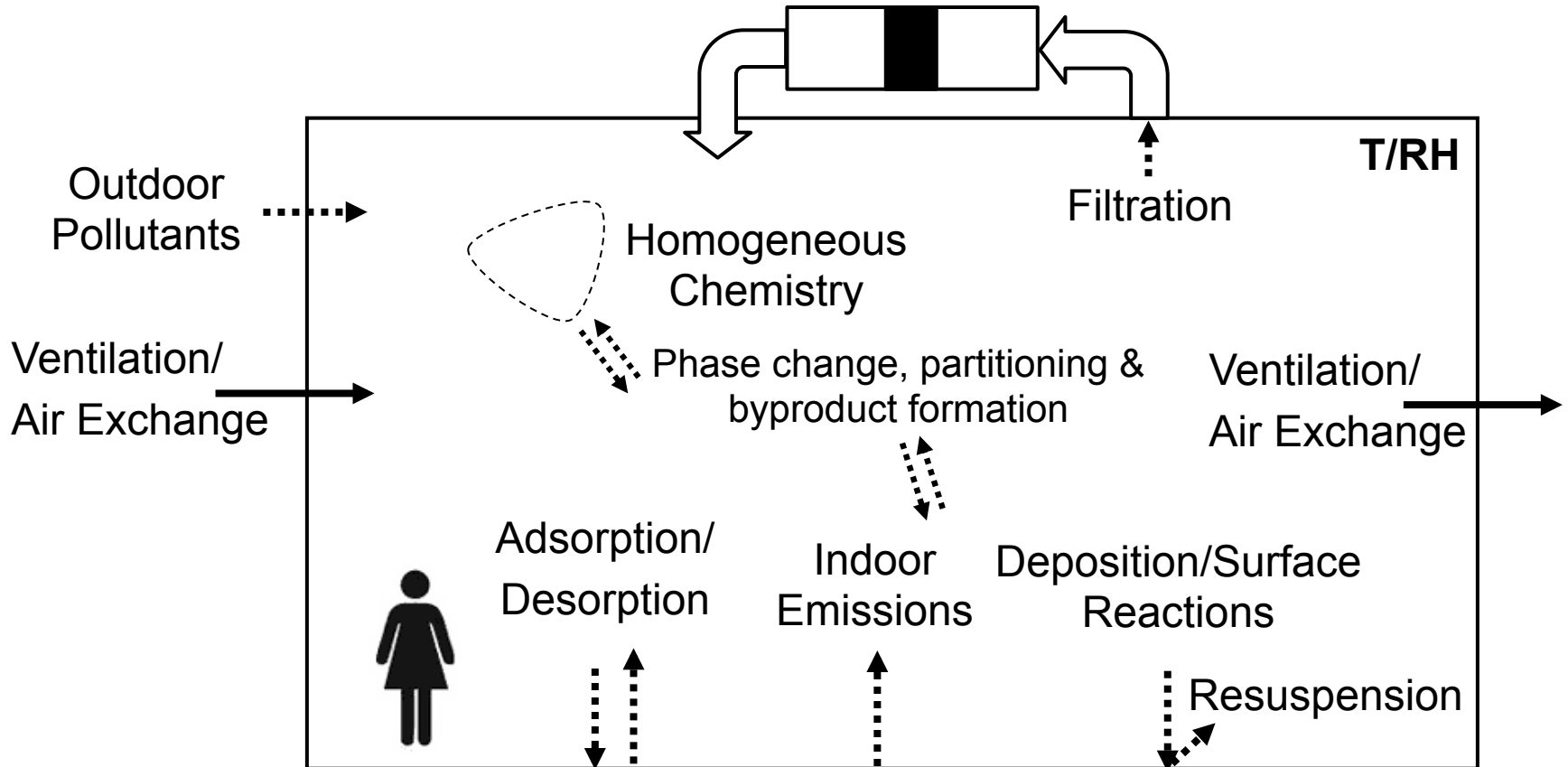Illinois Institute of Technology
brent@iit.edu

Built
Environment
Research
@ IIT

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

Built Environment Research Group
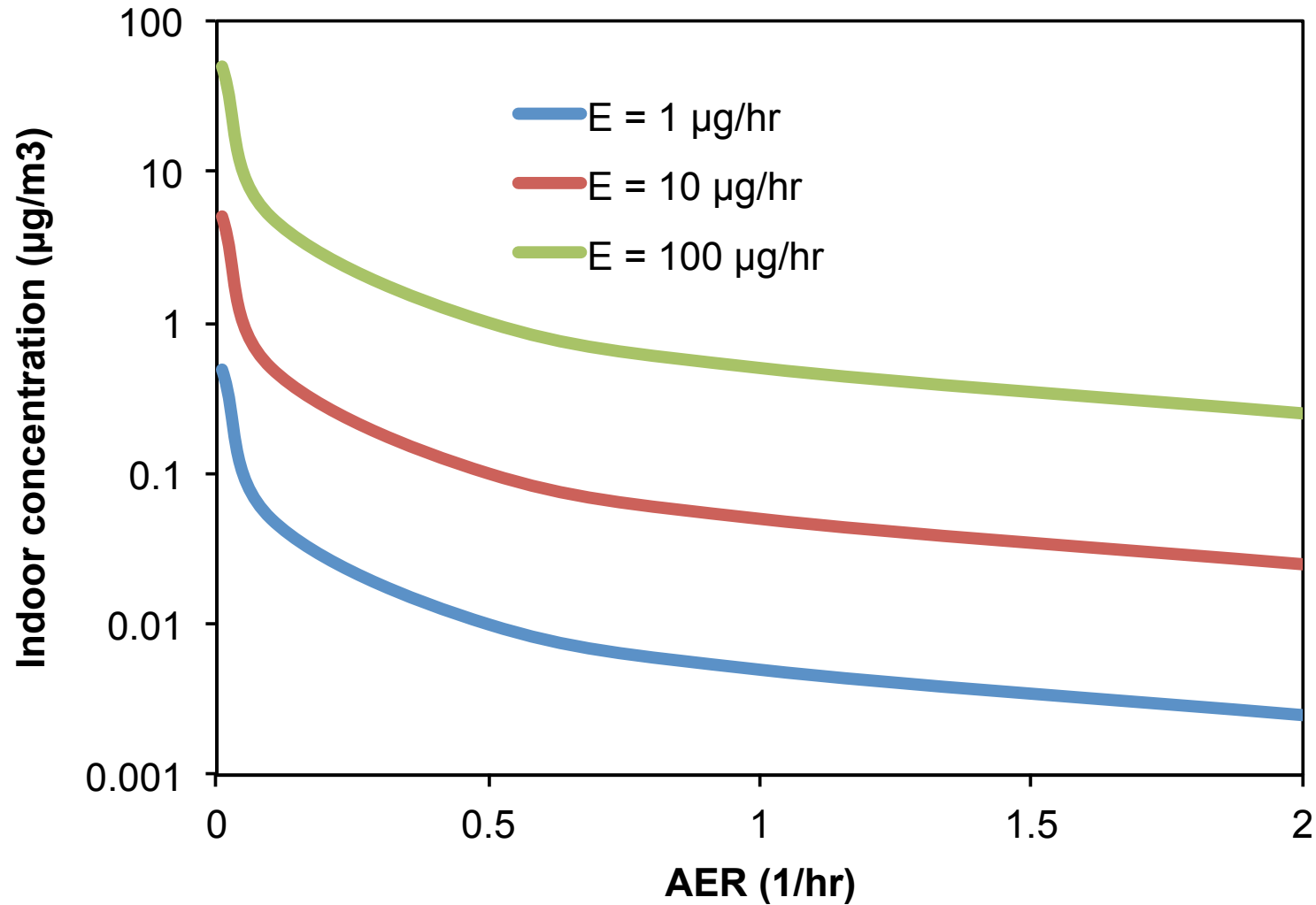www.built-envi.com

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

- Blog post #1 graded
- HW #1 is due today

Indoor environment: Mass balance

Outdoor Pollutants

Ventilation/ Air Exchange

Filtration

T/RH

Homogeneous Chemistry

Phase change, partitioning & byproduct formation

Ventilation/ Air Exchange

Adsorption/ Desorption

Indoor Emissions

Deposition/Surface Reactions

Resuspension

Indoor environment: Mass balance & AER

Review from last time

- Well-mixed mass balances

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

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

- 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*
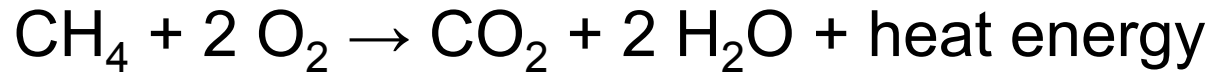
Inorganic gases: Combustion products

- 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)
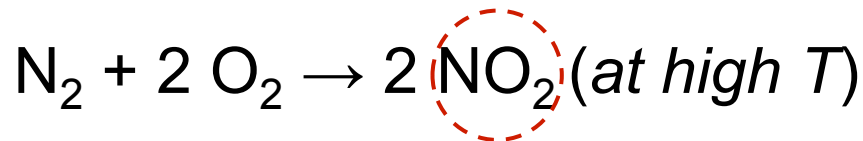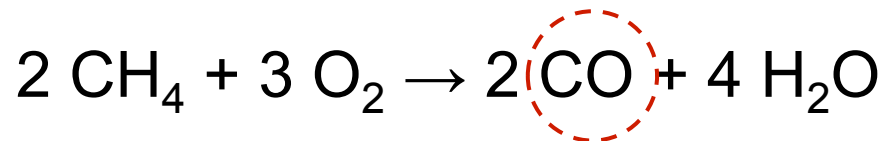
Inorganic gases: Combustion products

- 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

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

$$N_2 + O_2 \rightarrow 2\, NO\ (at\ high\ T)$$

$$N_2 + 2\, O_2 \rightarrow 2\, NO_2\ (at\ high\ T)$$

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

A few notes on radon

- Radon has a half life of ~3.5 days
  - Once inhaled as a gas, radon progeny (alpha emissions) cause cancer
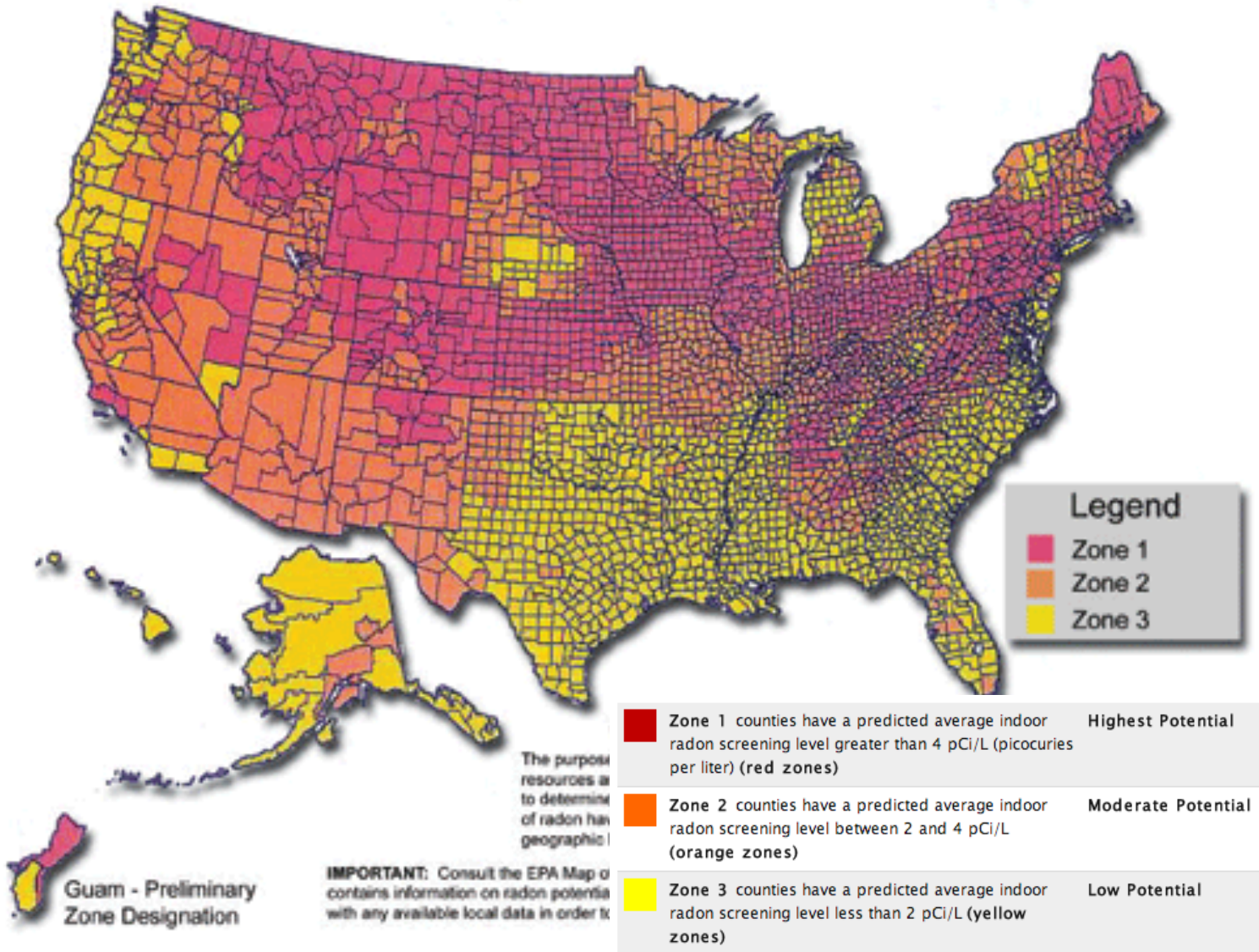 - Progeny are solid, forming clusters or attaching to aerosols (particles)

Half-life		Element
4.5×10^9 years	α	Uranium-238
24.5 day	β	Thorium-234
1.14 minutes	β	Protactinium-234
2.33×10^5 years	α	Uranium-234
8.3×10^4 years	α	Thorium-230
1,590 years	α	Radium-226
3.83 days	α	Radon-222
3.05 minutes	α	Polonium-218
26.8 minutes	β	Lead-214
19.7 minutes	β	Bismuth-214
1.5×10^{-4} seconds	α	Polonium-214
22 years	β	Lead-210
5 days	β	Bismuth-210
140 days	α	Polonium-210
Stable		Lead-206

α : Alpha radiation

β : Beta radiation

15

A few notes on radon

- Units for radon 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) = 3.7×10^{10} decays per second = 3.7×10^{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.

EPA Map of Radon Zones

Legend
- Zone 1
- Zone 2
- Zone 3

Guam - Preliminary
Zone Designation

The purpos...
resources a...
to determin...
of radon ha...
geographic...

IMPORTANT: Consult the EPA Map o...
contains information on radon potentia...
with any available local data in order t...

▉	**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**

Radon in U.S. homes

- Indoor radon concentration distribution

No. points	10251
Arithmetic mean	4.26
Geometric mean	1.74
Median	1.65
Highest value	691.31

Alter and Oswald 1987 *JAPCA*
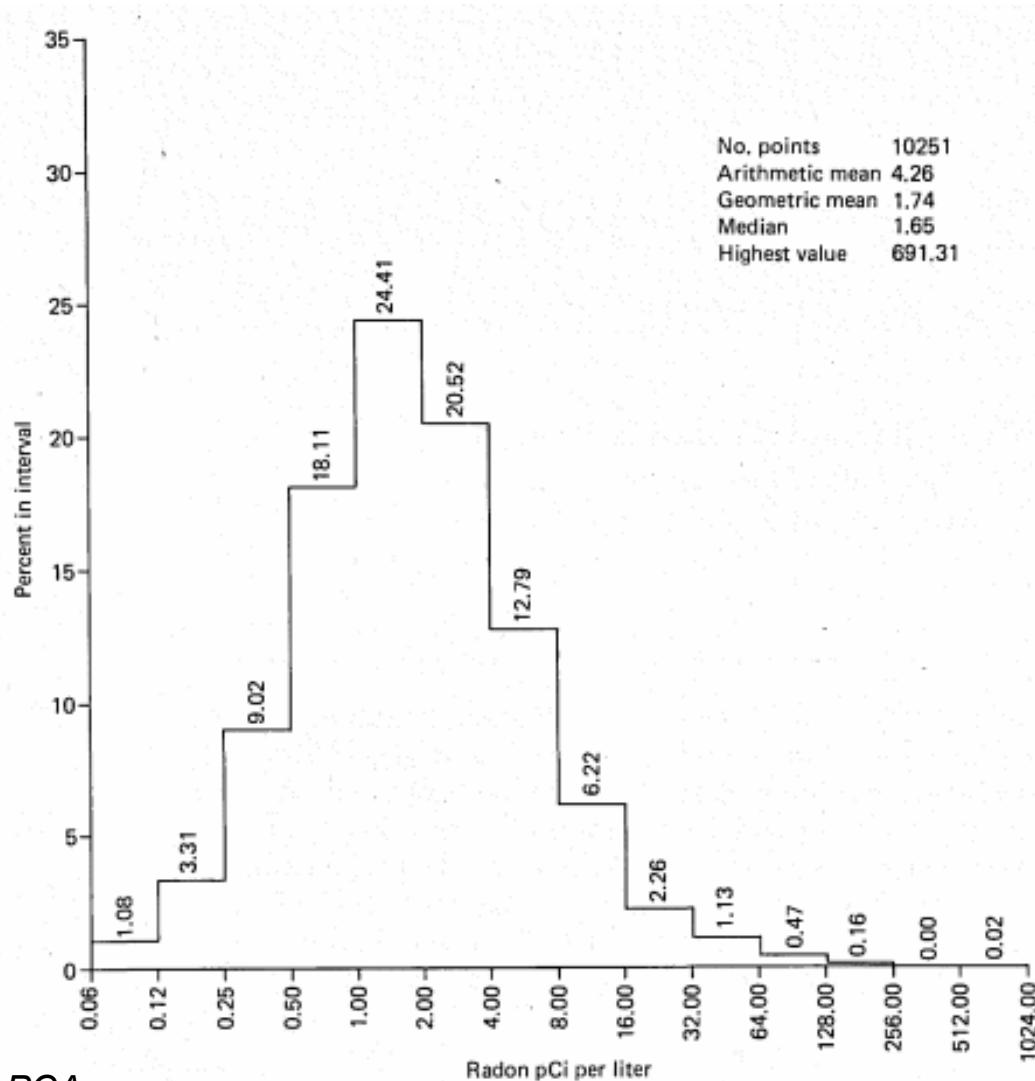
Organic gases: VOCs

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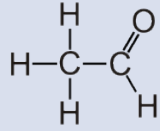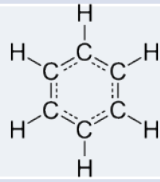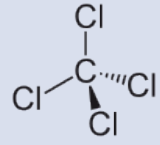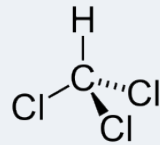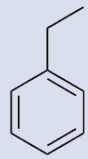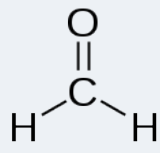
- Some VOCs have strong odors, cause sensory irritation (primarily to mucus membranes), or are classified as hazardous air pollutants with carcinogenic or other effects

- 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
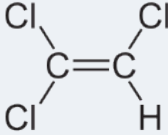
Mean VOC concentrations in U.S. residences
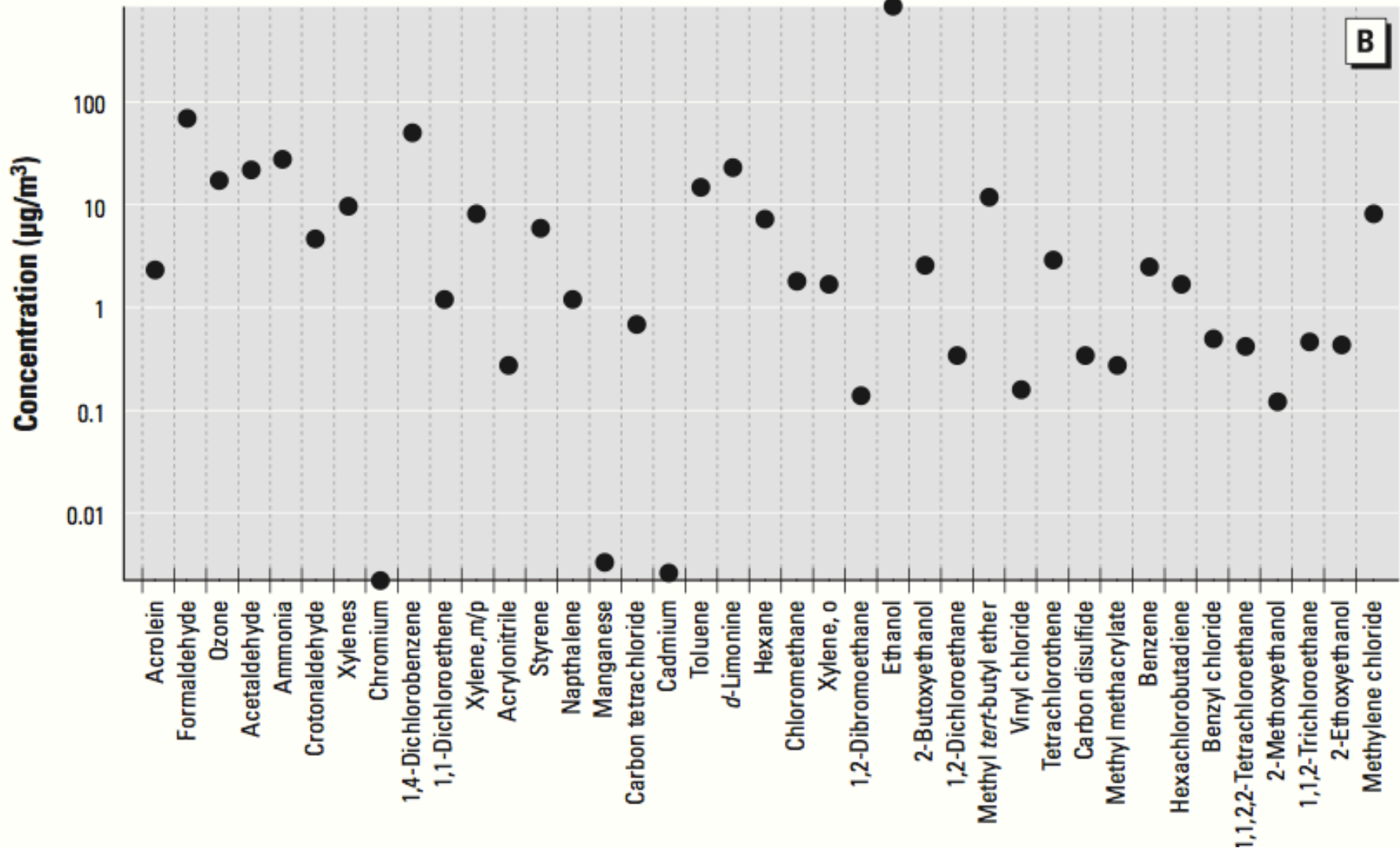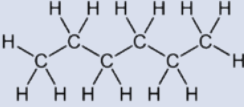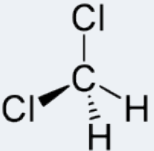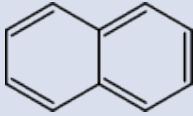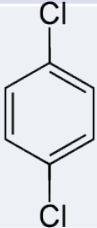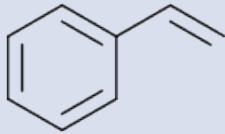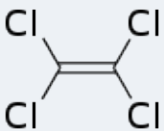
Hazardous VOCs found indoors

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
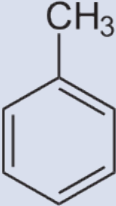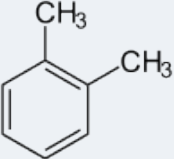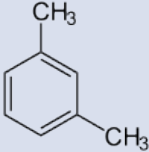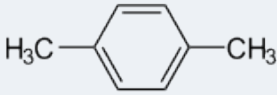
Hazardous VOCs found indoors

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

24

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
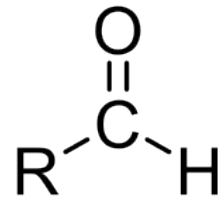http://toxnet.nlm.nih.gov/

*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)
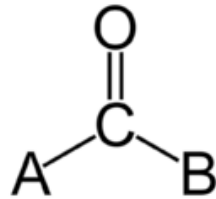
General carbonyl **General aldehyde (functional group)**

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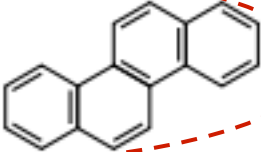
Organic gases (and particle phase): SVOCs
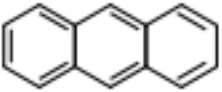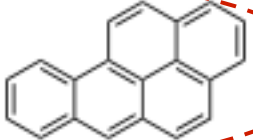
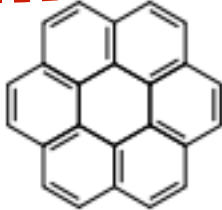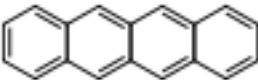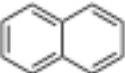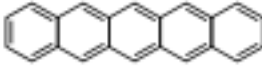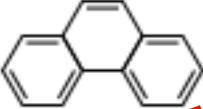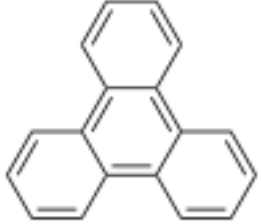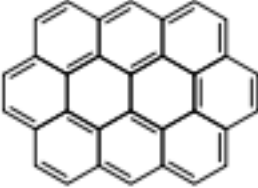- **Semi-volatile organic compounds** (**SVOCs**) are higher molecular weight VOCs
  - Usually exist partially in gas-phase and partially in particle-phase
  - Includes:
    - Polycyclic aromatic hydrocarbons (PAHs)
    - Phthalates
    - Pesticides
    - Brominated flame retardants (BFRs)

- 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
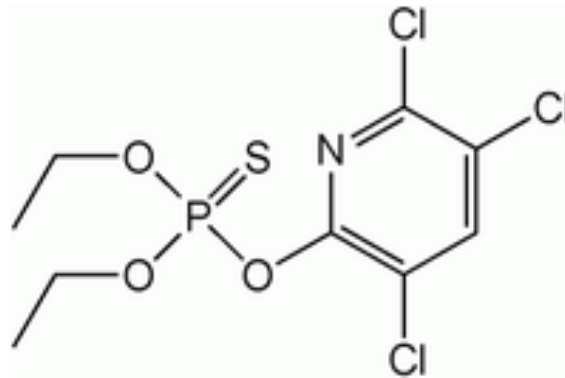   - e.g. reproductive effects, obesity, diabetes, and allergies
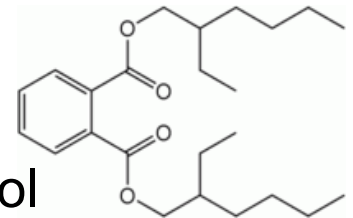
Organic gases (and particle phase): SVOCs

- 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
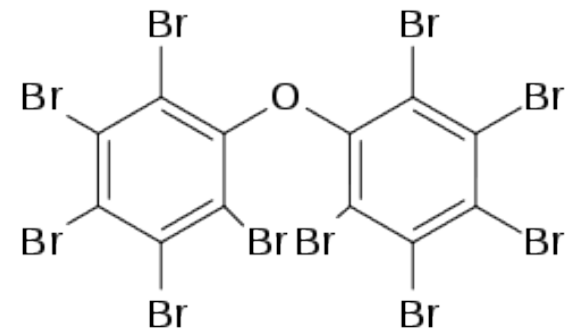
Particulate matter (PM)

- 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
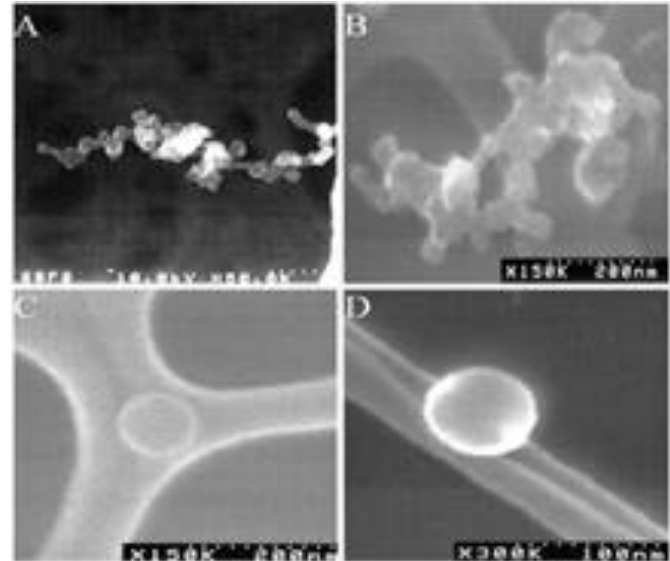
Particulate matter (PM)

- **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)
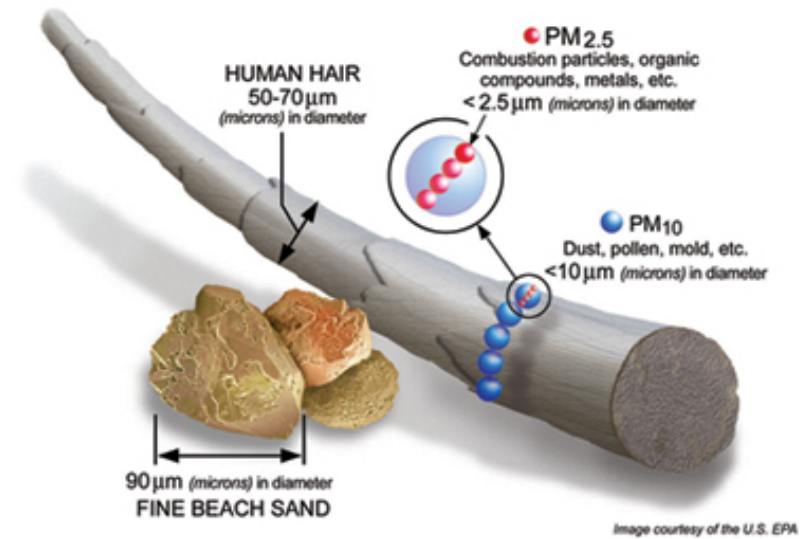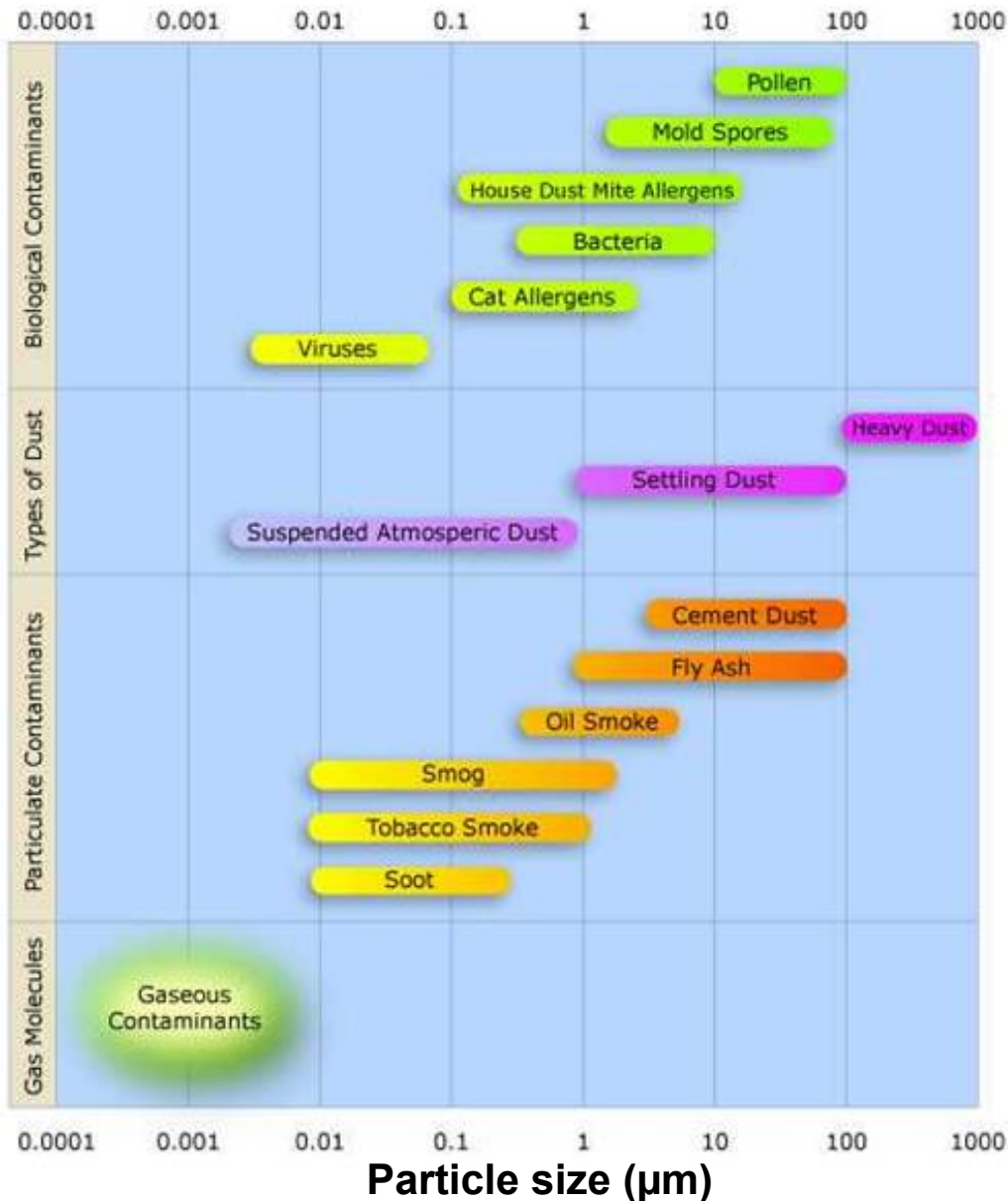
Particle sizes

- 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
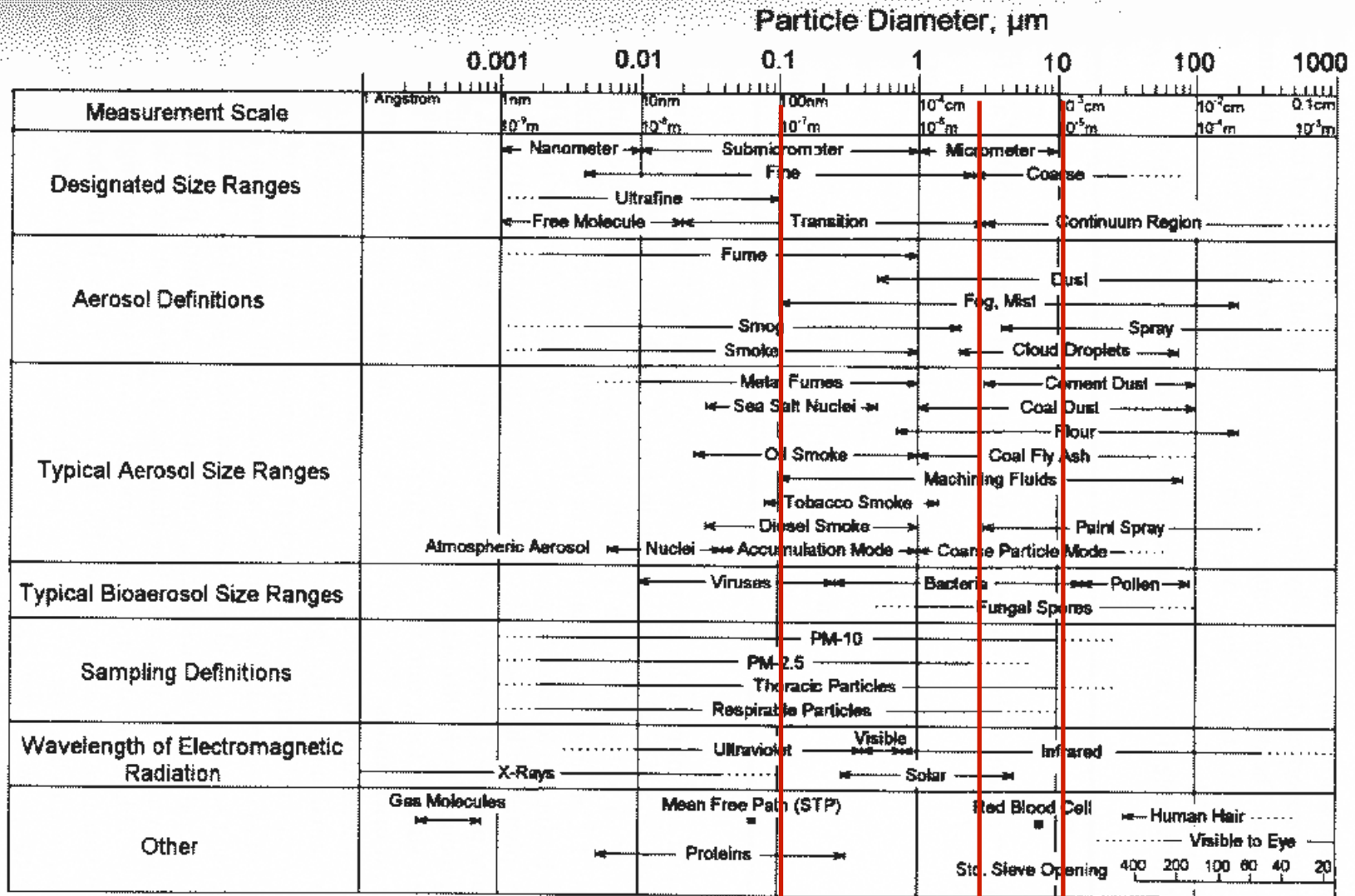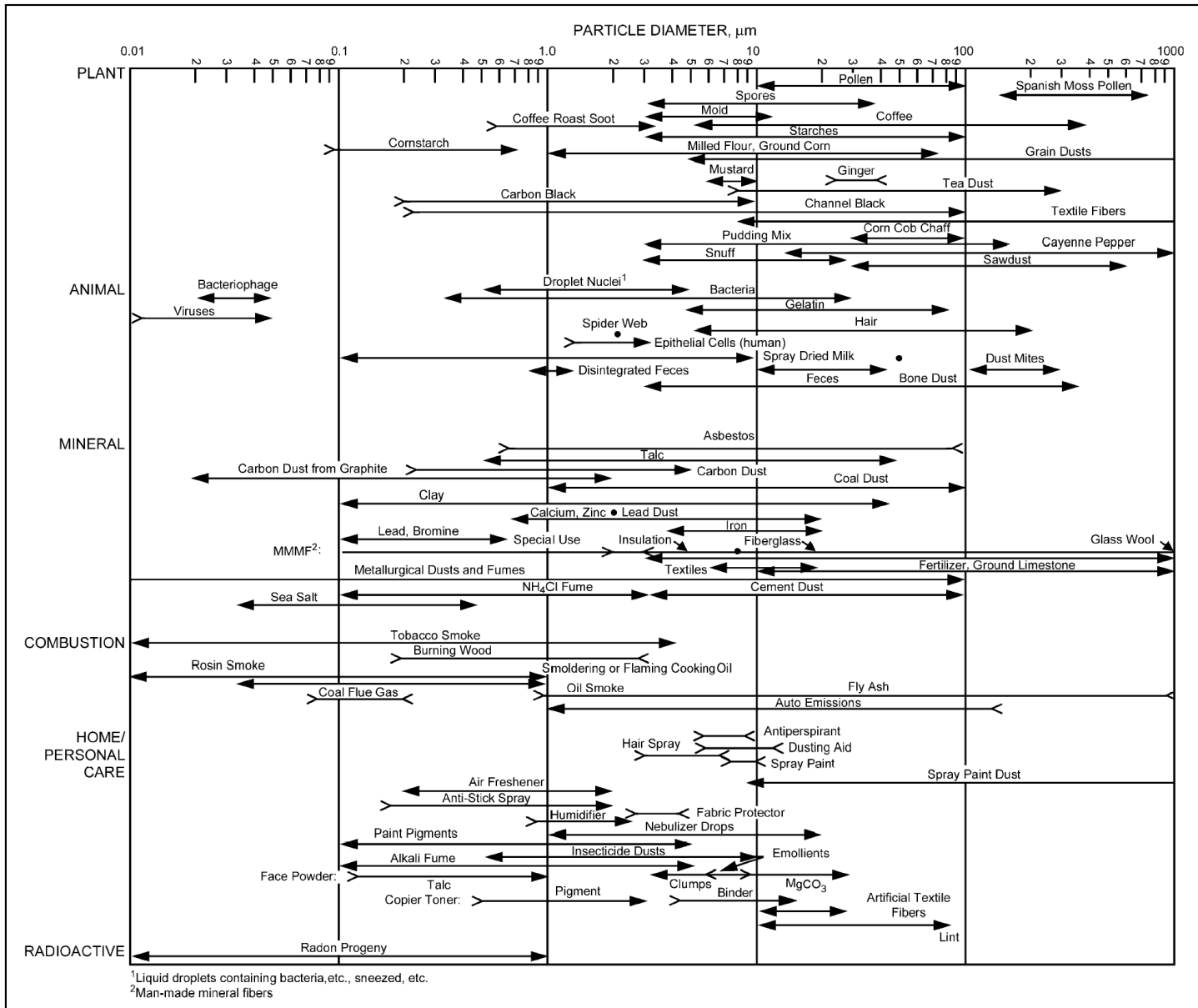 - Composition is also important

Particle sizes

FIGURE 1.6   Particle size ranges and definitions for aerosols.

Hinds 1999

← UFP   ← PM$_{2.5}$ ← PM$_{10}$

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$_{2.5-10}$
  - TSP
  - RSP

Figure 2. Ambient Particulate Matter Size Distributions
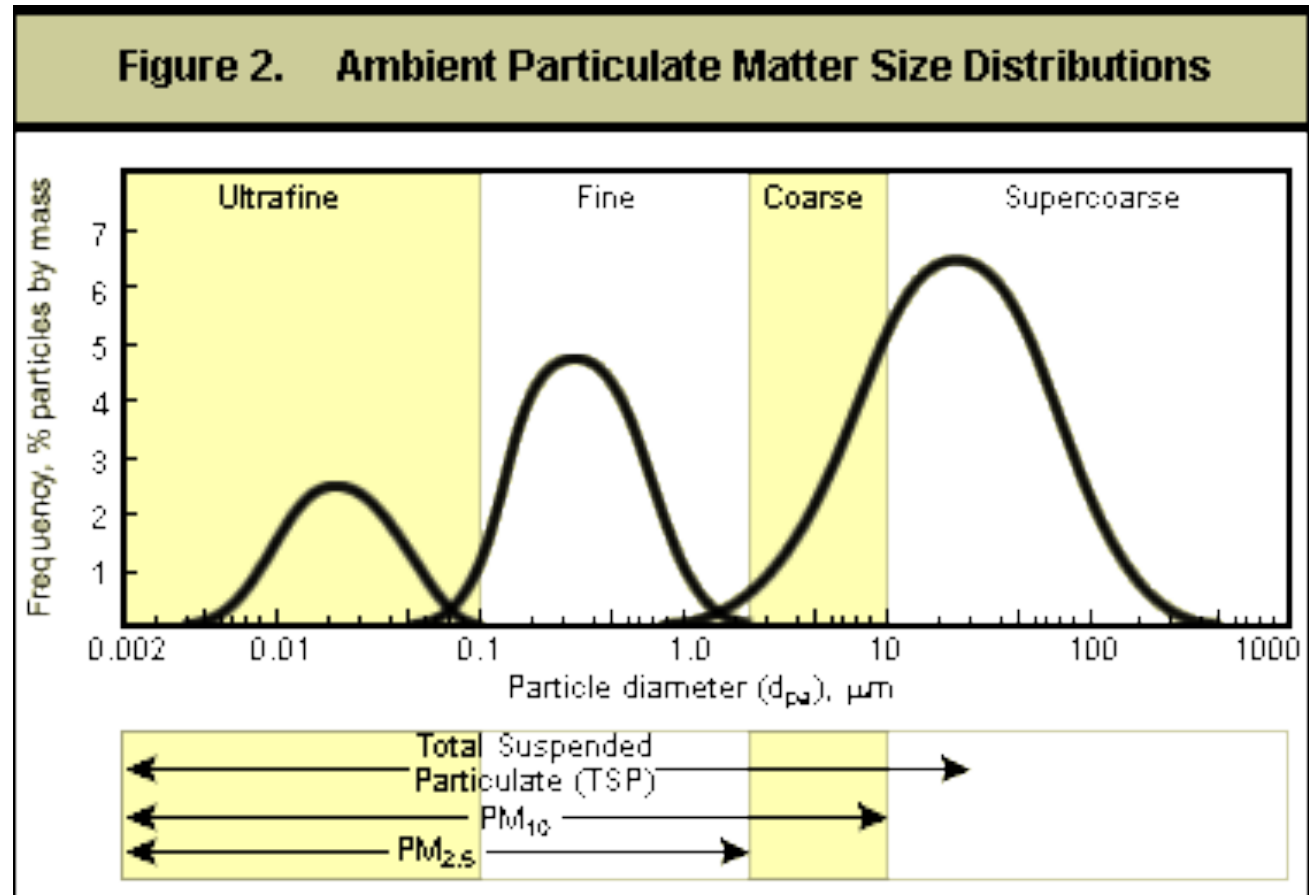
Typical urban distributions

- Number distributions

Morawska and Salthammer 2003 *Indoor Environment*
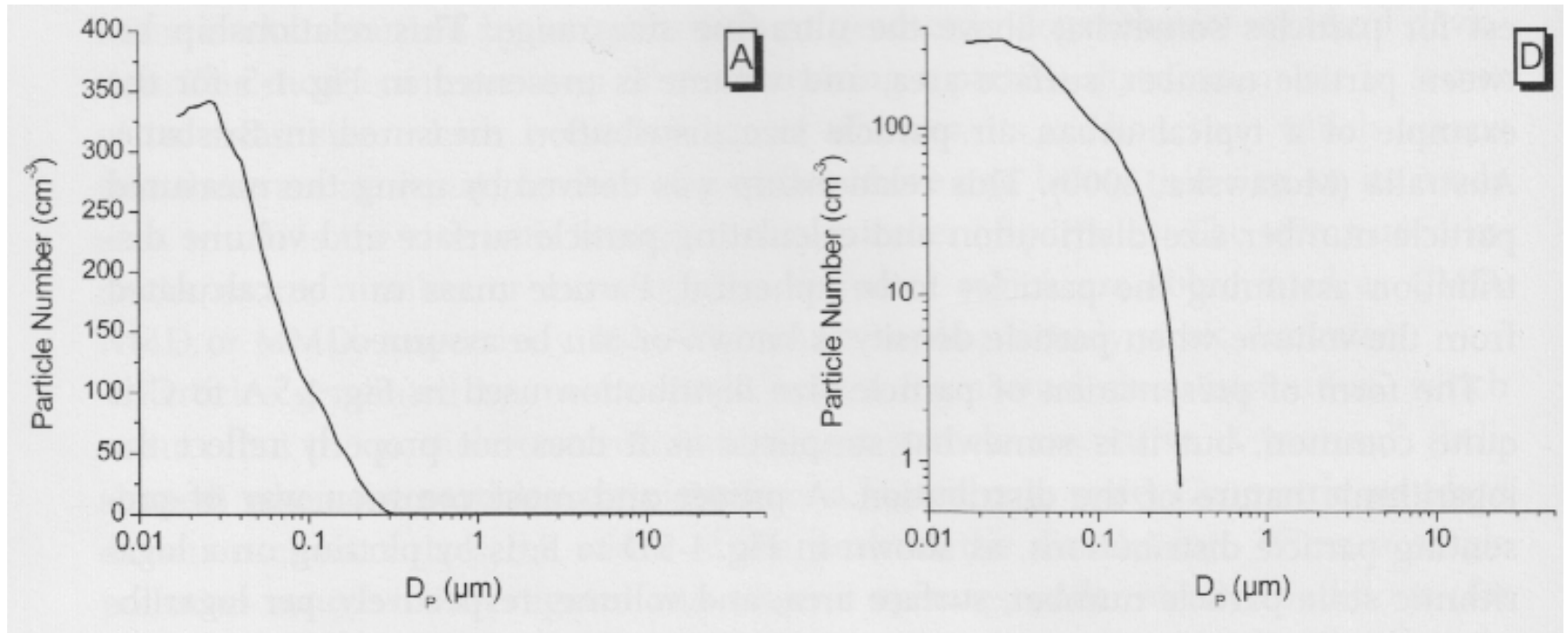
Typical urban distributions

- Surface area distributions

Morawska and Salthammer 2003 *Indoor Environment*
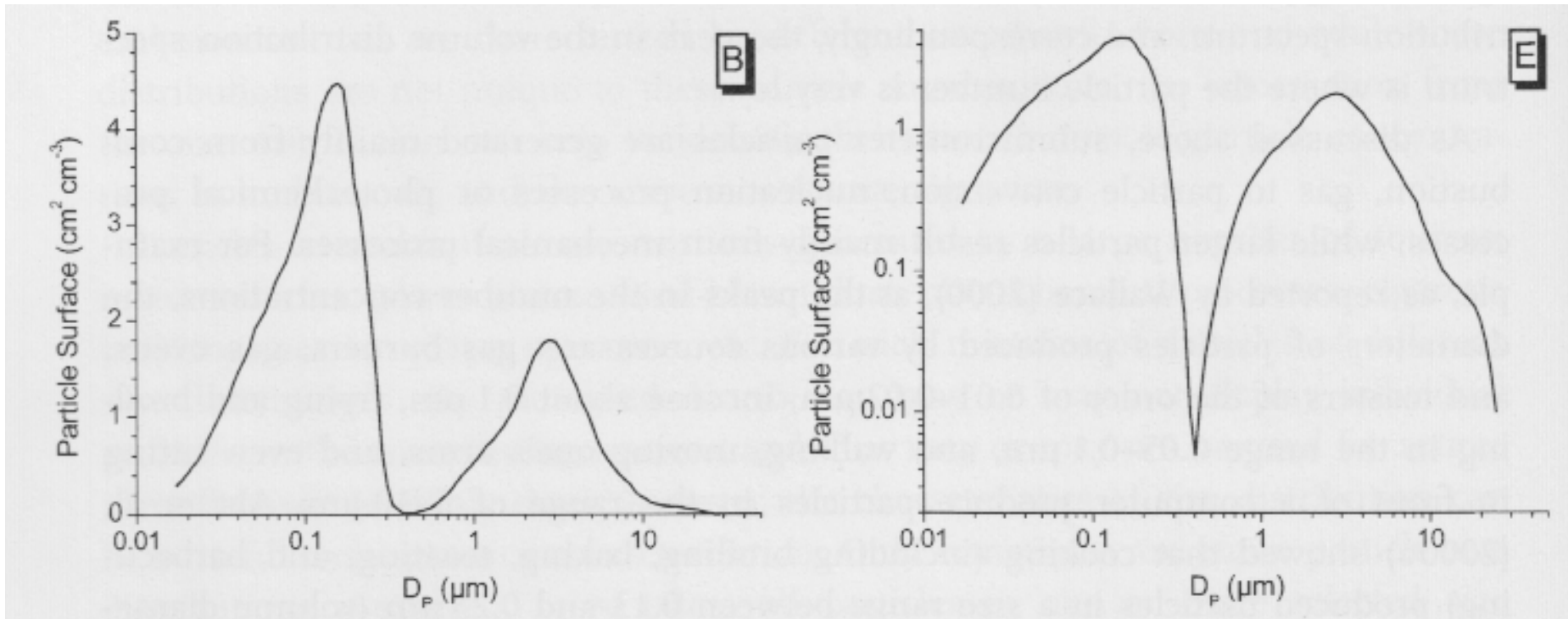
Typical urban distributions

- Volume distributions

Morawska and Salthammer 2003 *Indoor Environment*
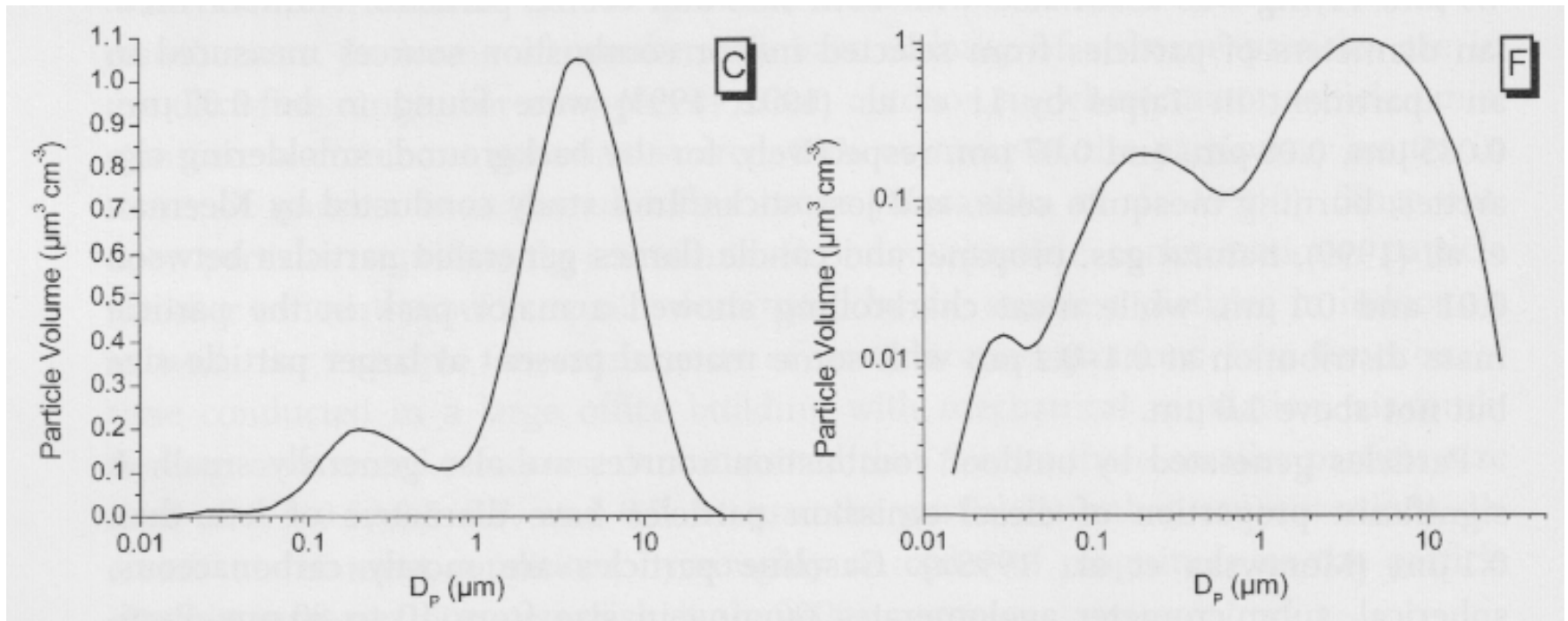
Composition of outdoor PM$_{2.5}$

Davidson 2005 *Aerosol Sci Technol*
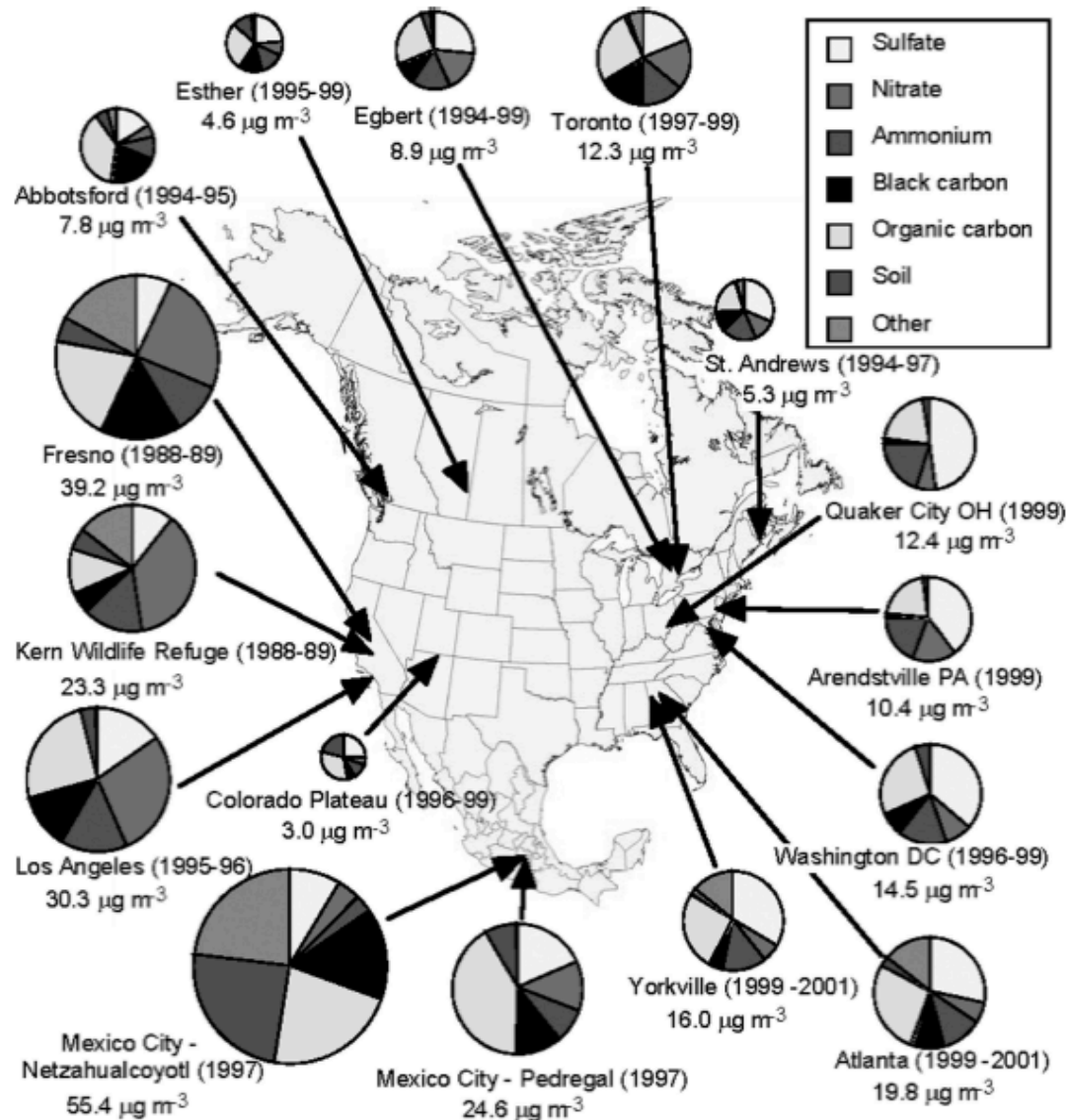
Particulate matter: ETS

- 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
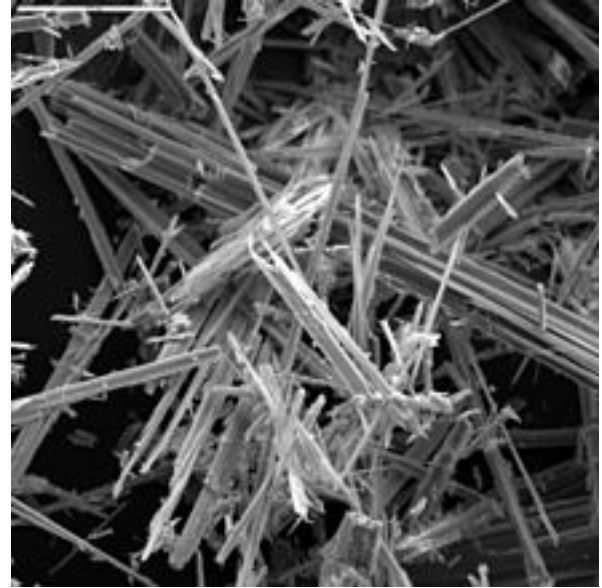
Particulate matter: Biological

- 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*
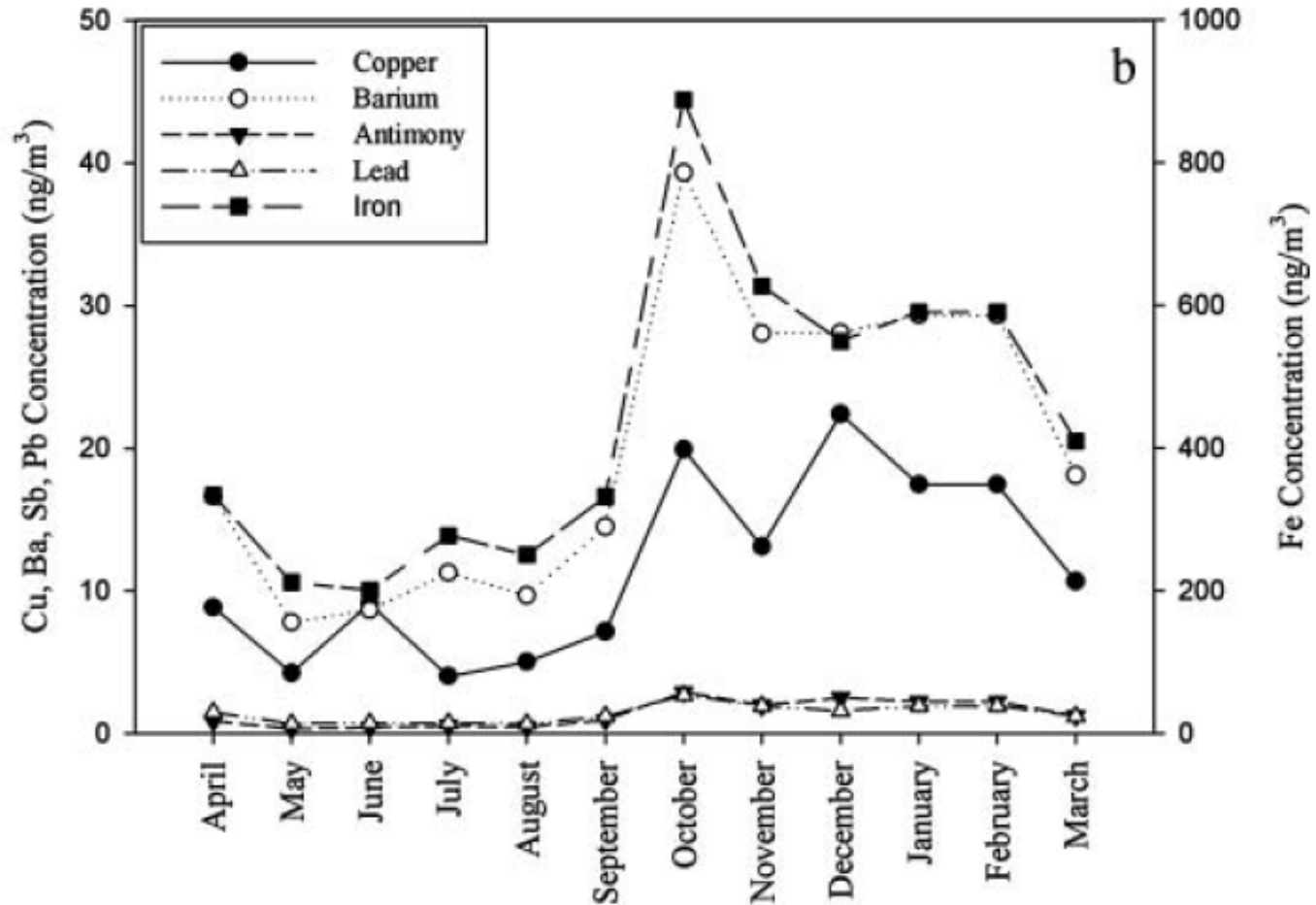
Metals

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

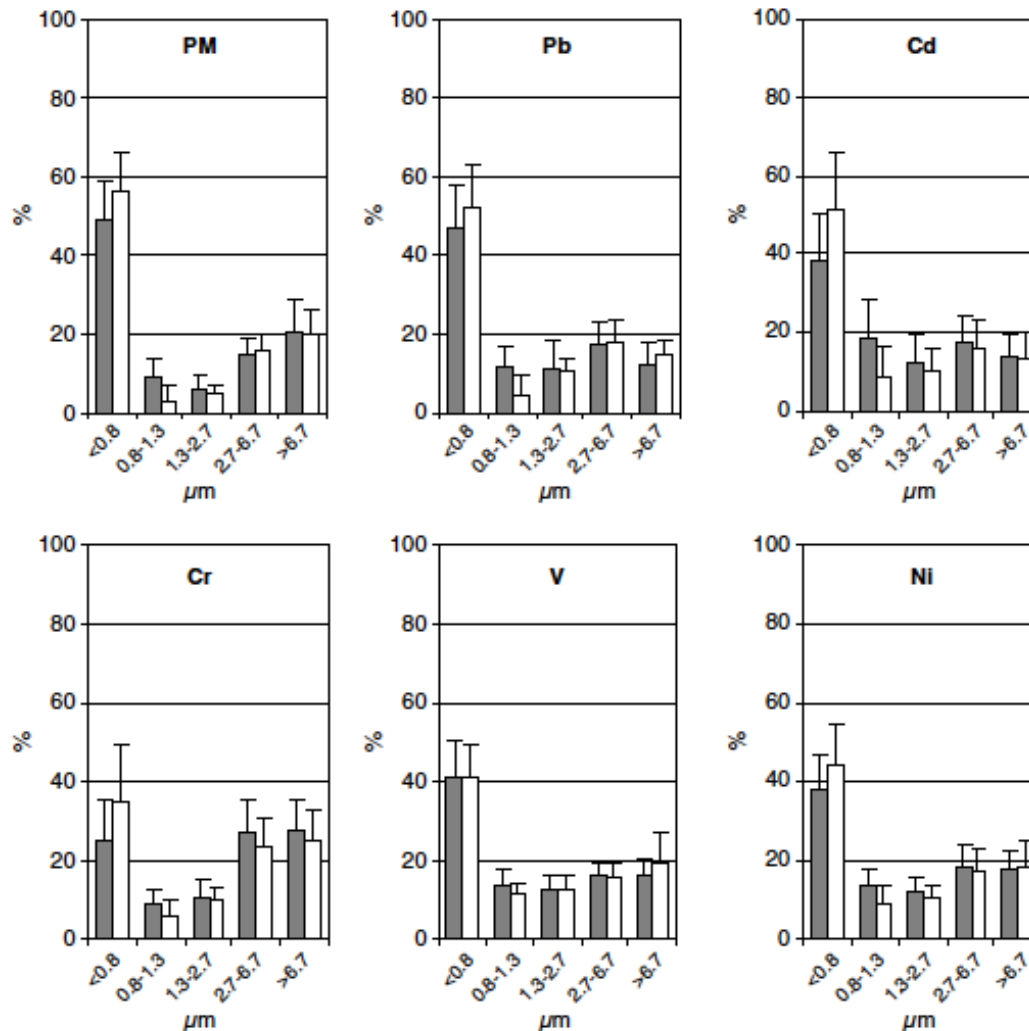Samara and Voutsa, 2005 *Chemosphere*

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

Everyday Exposure to Toxic Pollutants
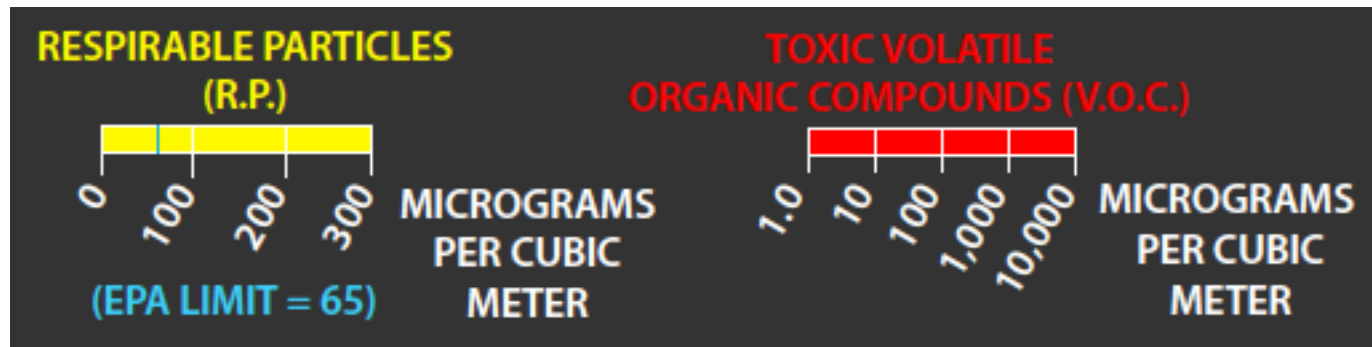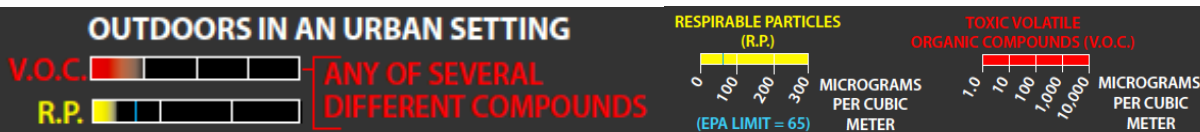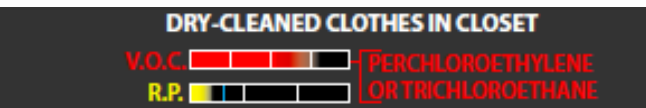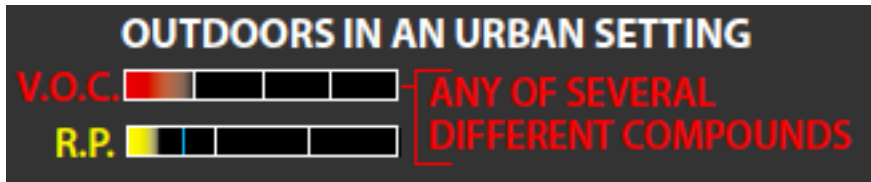
RESPIRABLE PARTICLES (R.P.)	TOXIC VOLATILE ORGANIC COMPOUNDS (V.O.C.)
0 100 200 300 MICROGRAMS PER CUBIC METER (EPA LIMIT = 65)	1.0 10 100 1,000 10,000 MICROGRAMS PER CUBIC METER
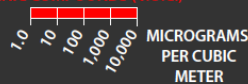
Ott and Roberts (1998)

Ott and Roberts (1998)

Ott and Roberts (1998)

Ott and Roberts (1998)

Ott and Roberts (1998)

Ott and Roberts (1998)

CONCENTRATIONS OF 10-MICRON PARTICLES

TYPICAL VALUE (MICROGRAMS PER CUBIC METER)
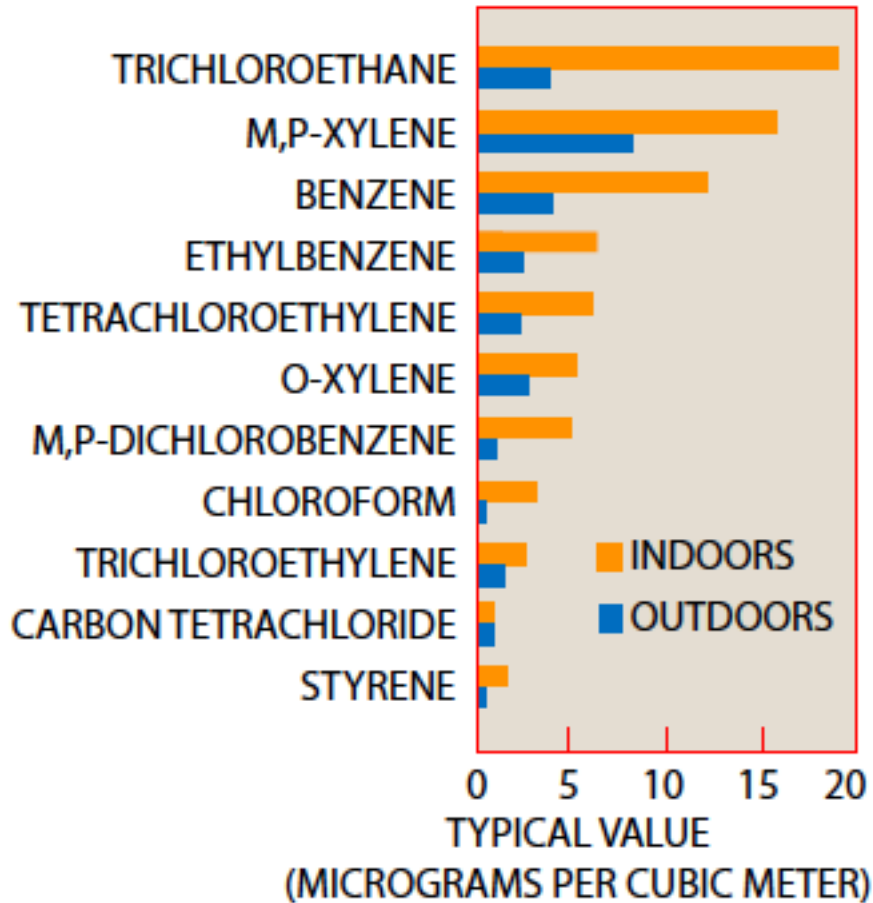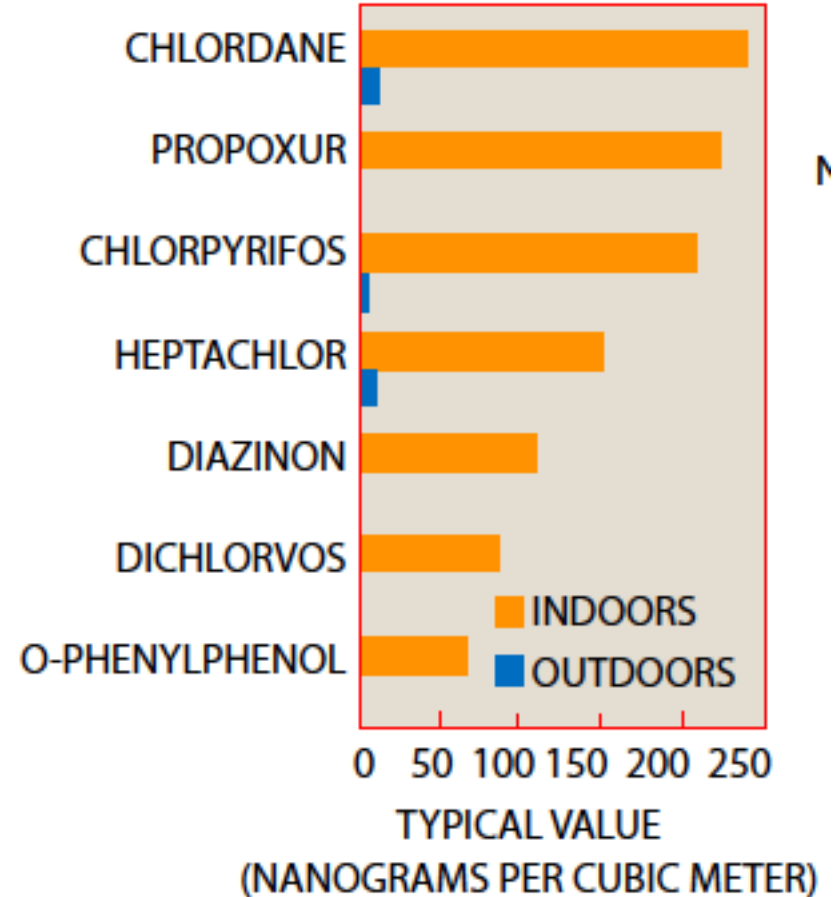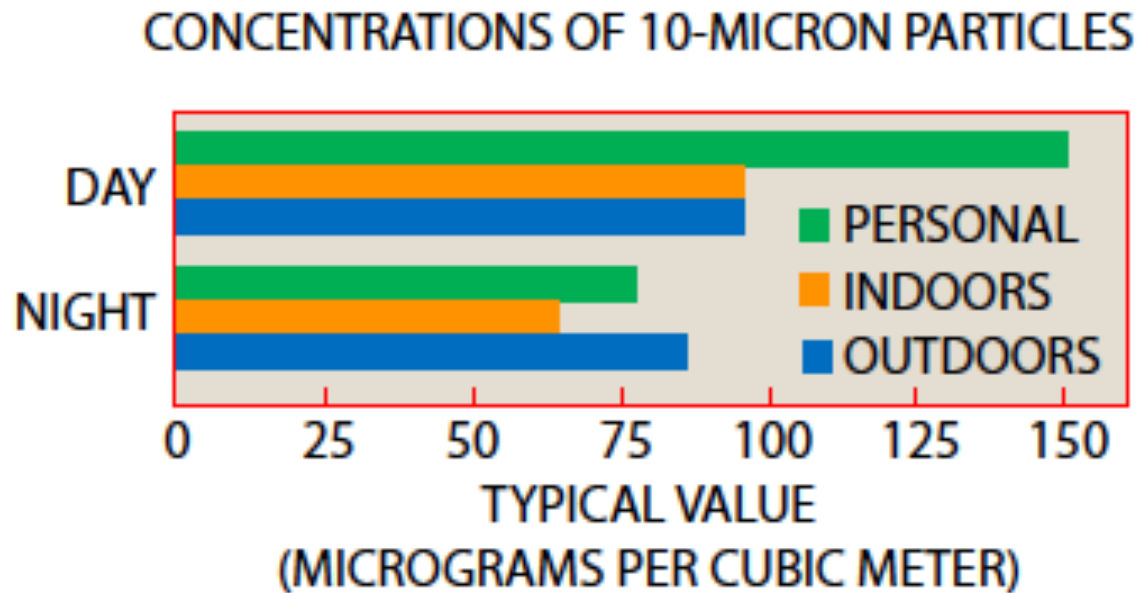
Personal > Indoor > Outdoor

- Several large field studies have shown the importance of personal and indoor measurements
  - SHIELD
  - BASE
  - RIOPA

- A smaller number of field studies have also shown the importance of measuring other parameters relevant to the mass balance on indoor pollutants
  - P/I/O concentrations are helpful, but additional measurements can tease out much more information
  - e.g., RIOPA

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)

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/m^3) distributions for 15 VOCs in matched P, S, H, and O samples from 113 subjects in winter and spring 2000.

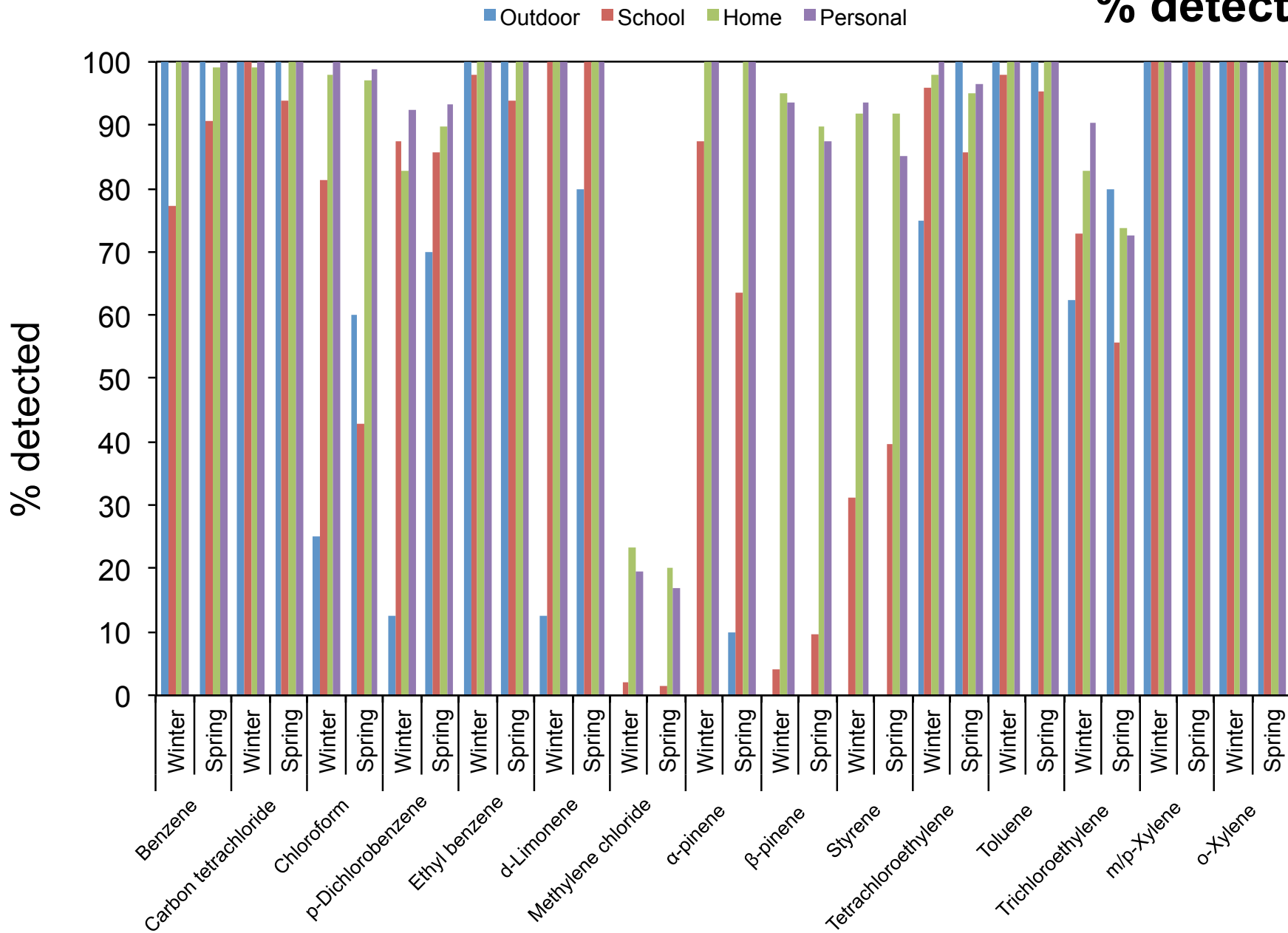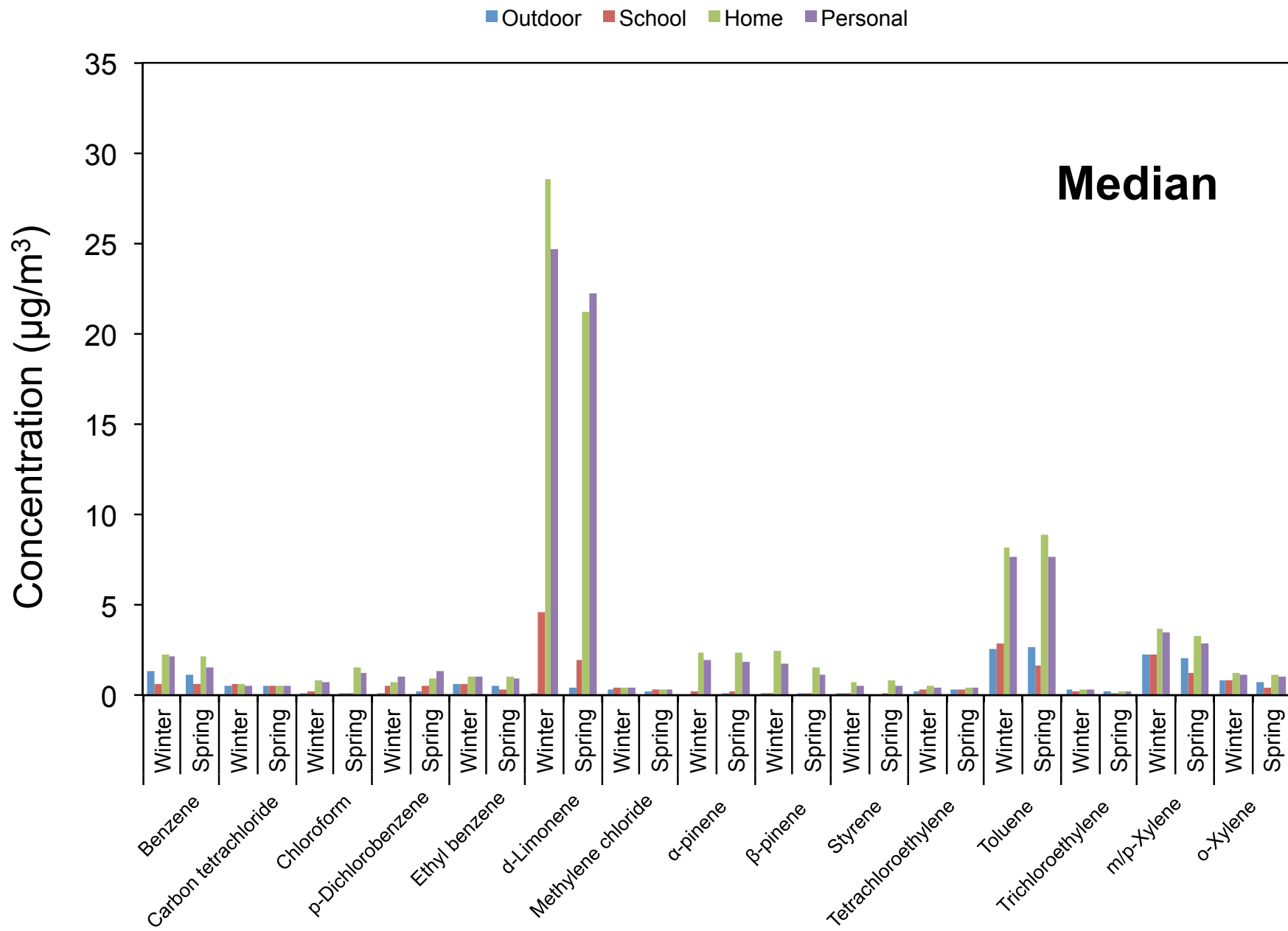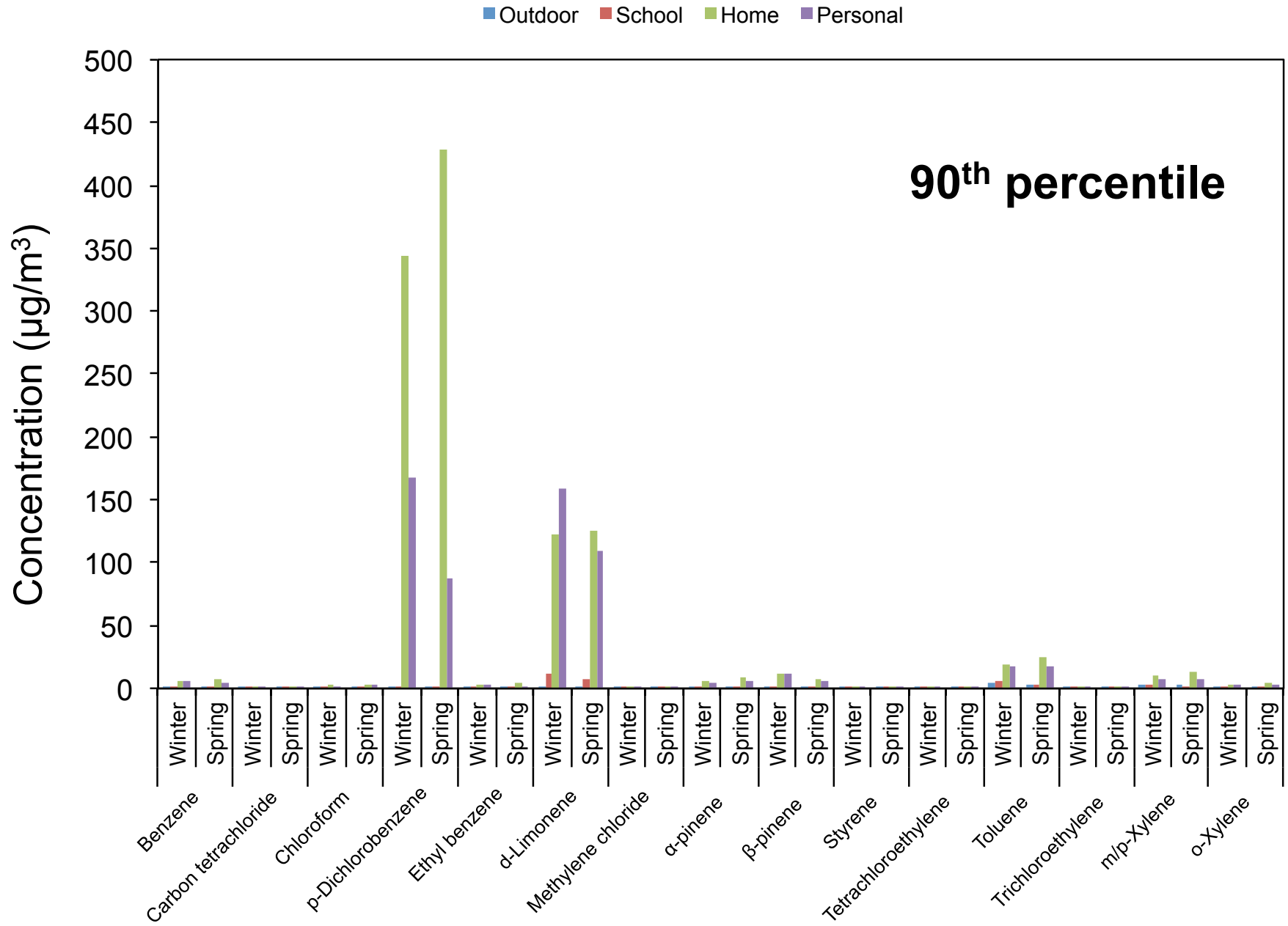| VOC	Season	O[a] %Det	Median	Q10	Q90	S[b] %Det	Median	Q10	Q90	H[c] %Det	Median	Q10	Q90	P[c] %Det	Median	Q10	Q90
Benzene	Winter	100.0	1.3	0.4	2.2	77.1	0.6	0.1	1.6	100.0	2.2	0.8	6.2	100.0	2.1	0.7	6.5
	Spring	100.0	1.1	0.7	1.6	90.5	0.6	0.2	1.0	99.0	2.1	0.6	7.2	100.0	1.5	0.7	4.2
Carbon tetrachloride	Winter	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*

Median

Adgate et al., 2004 *EHP*

90th percentile

Concentration (μg/m³)

Benzene, Carbon tetrachloride, Chloroform, p-Dichlorobenzene, Ethyl benzene, d-Limonene, Methylene chloride, α-pinene, β-pinene, Styrene, Tetrachloroethylene, Toluene, Trichloroethylene, m/p-Xylene, o-Xylene

Outdoor School Home Personal

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
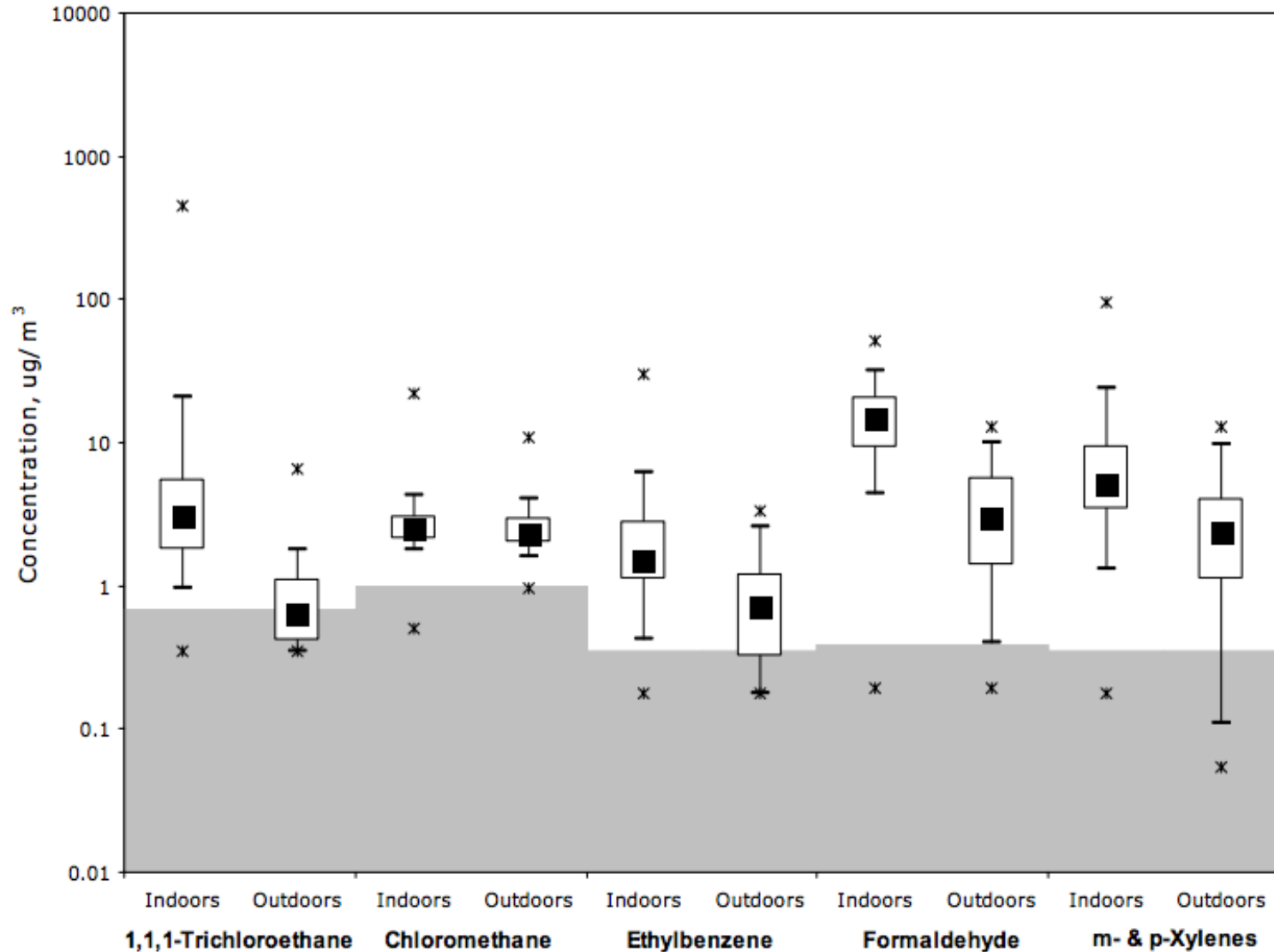
- Building Assessment Survey and Evaluation (BASE) Study
  - Between 1994 and 1998 data and samples were collect in 100 office building using a standardized protocol

  - The protocol included not only indoor and outdoor air samples but building characterizations, environmental parameters, HVAC measurements, and occupant questionnaires
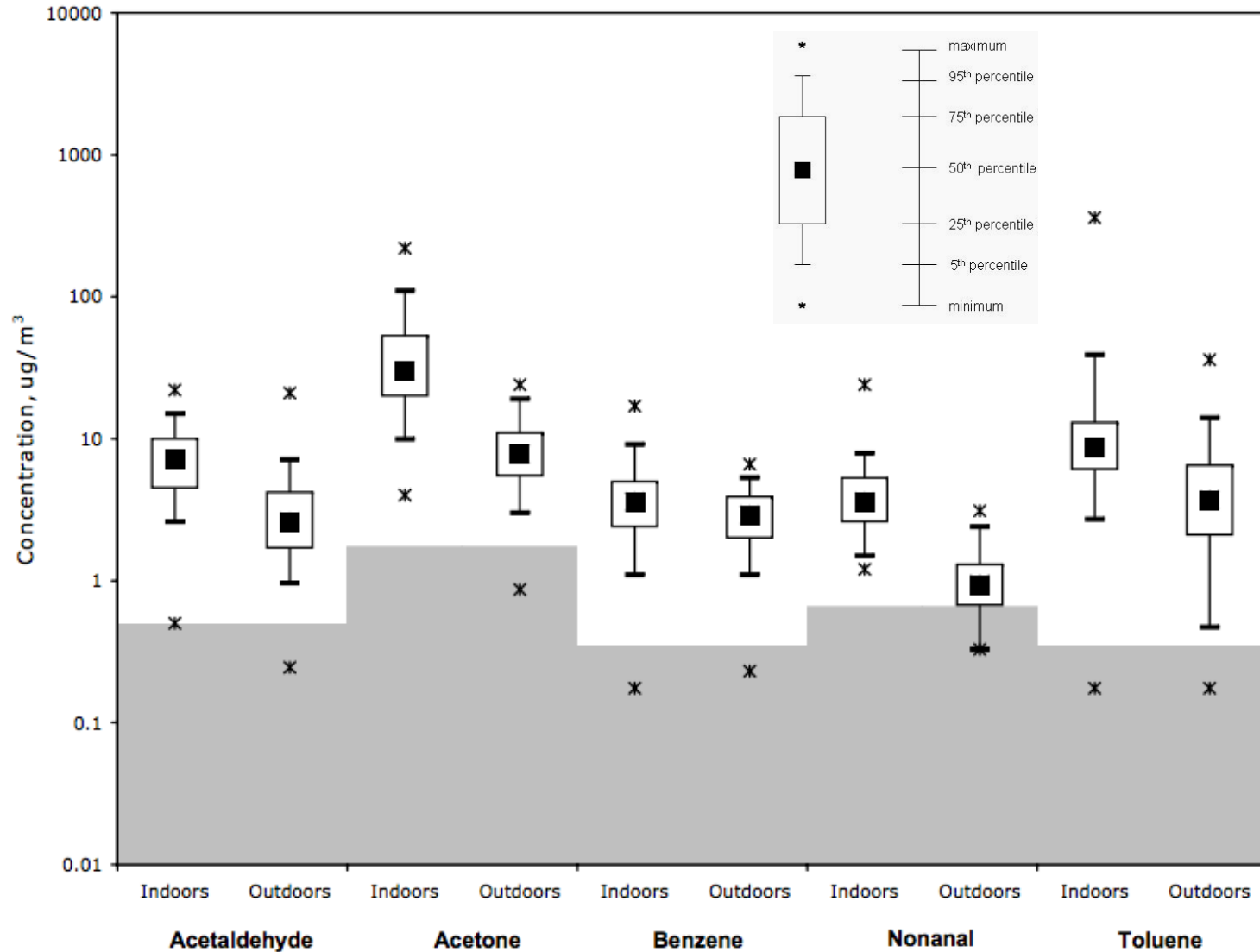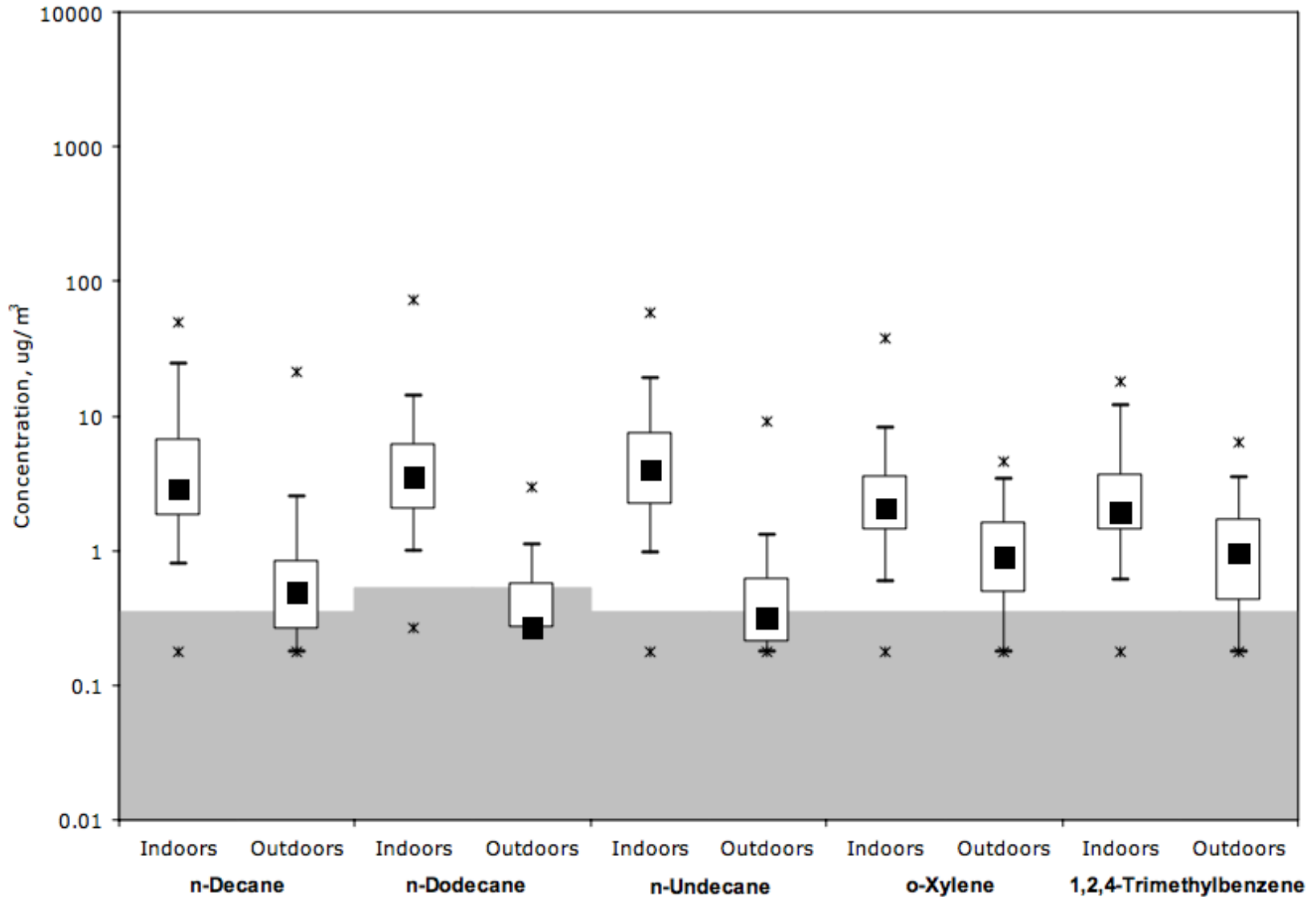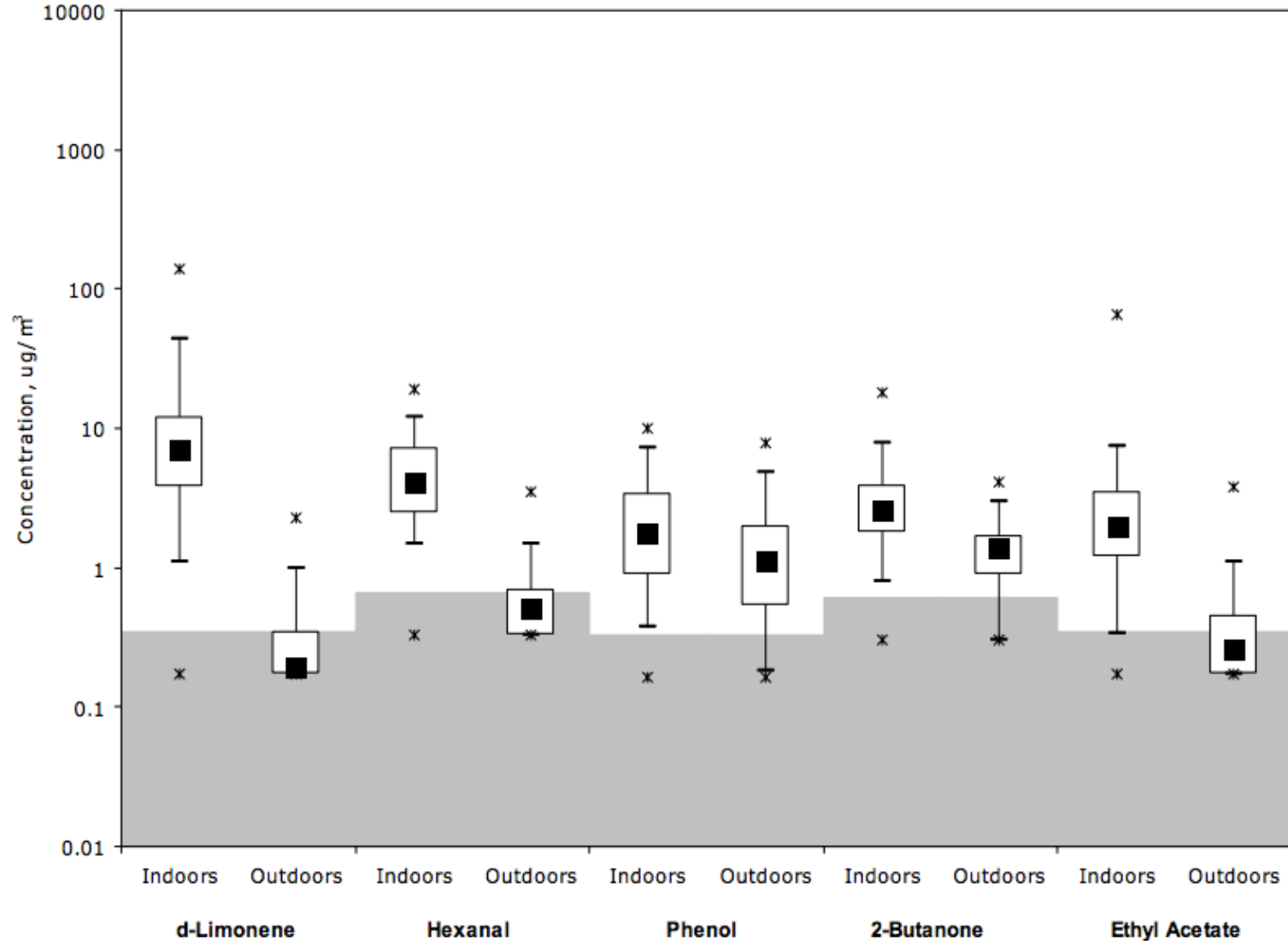
http://www.epa.gov/iaq/base/

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

RIOPA study

- 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 (μg/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*

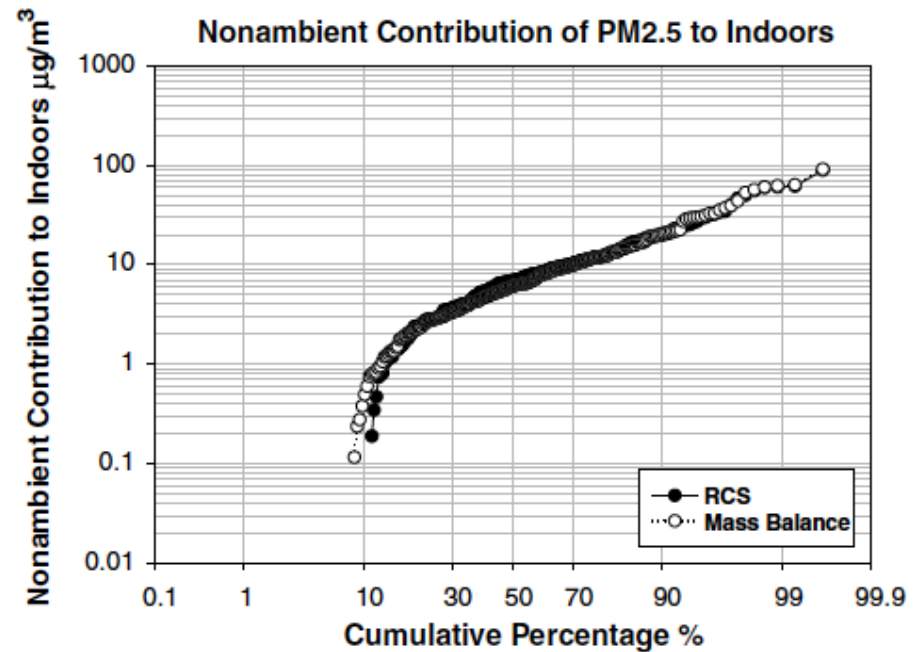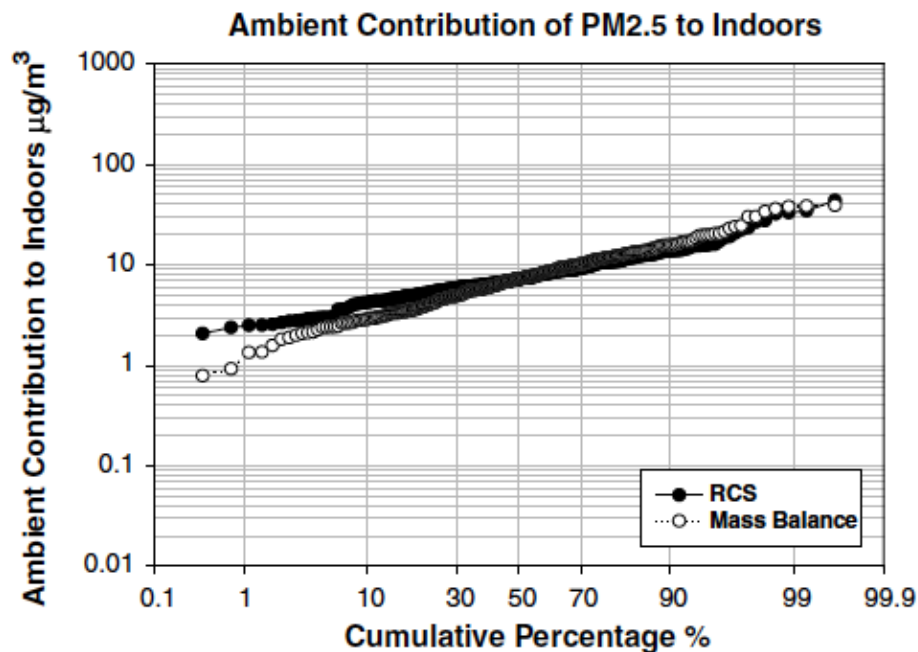# RIOPA I/O PM$_{2.5}$

Meng et al. 2005 *JESEE*
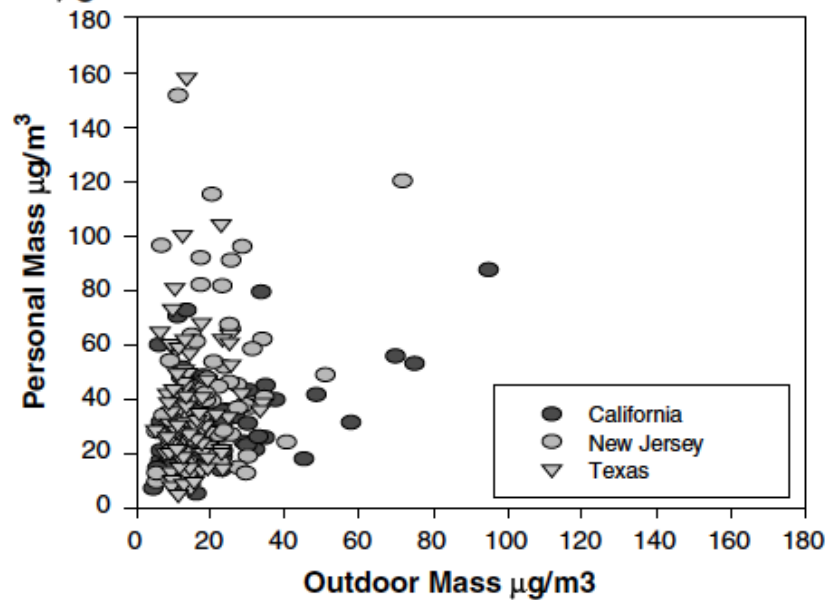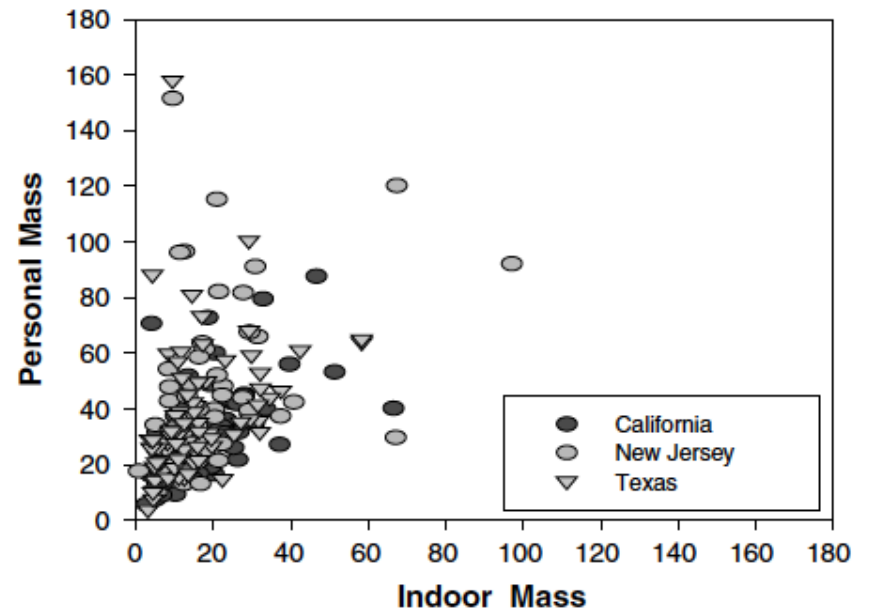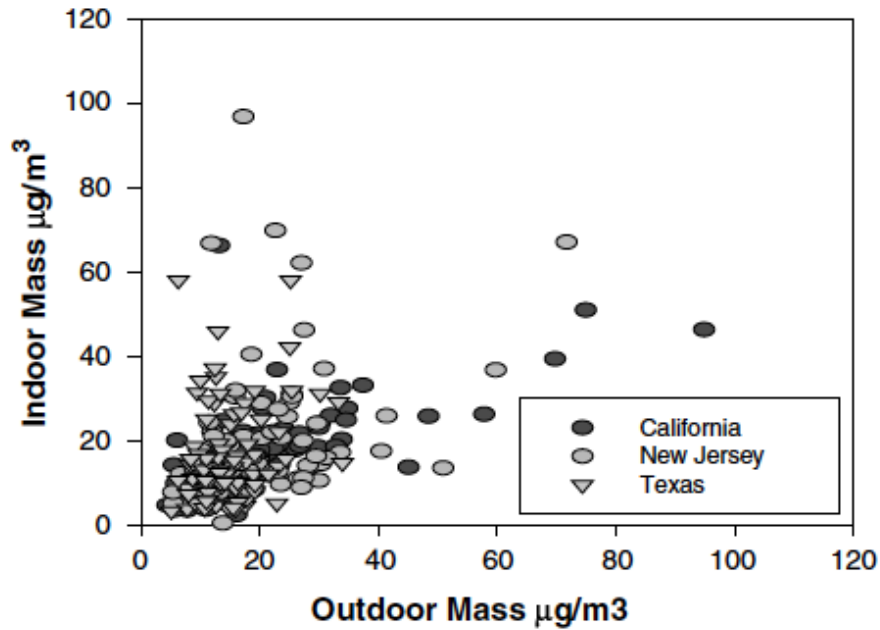
LEARNING FROM EXPOSURE STUDIES

How do we get at more fundamental parameters than just I/O concentration measurements?
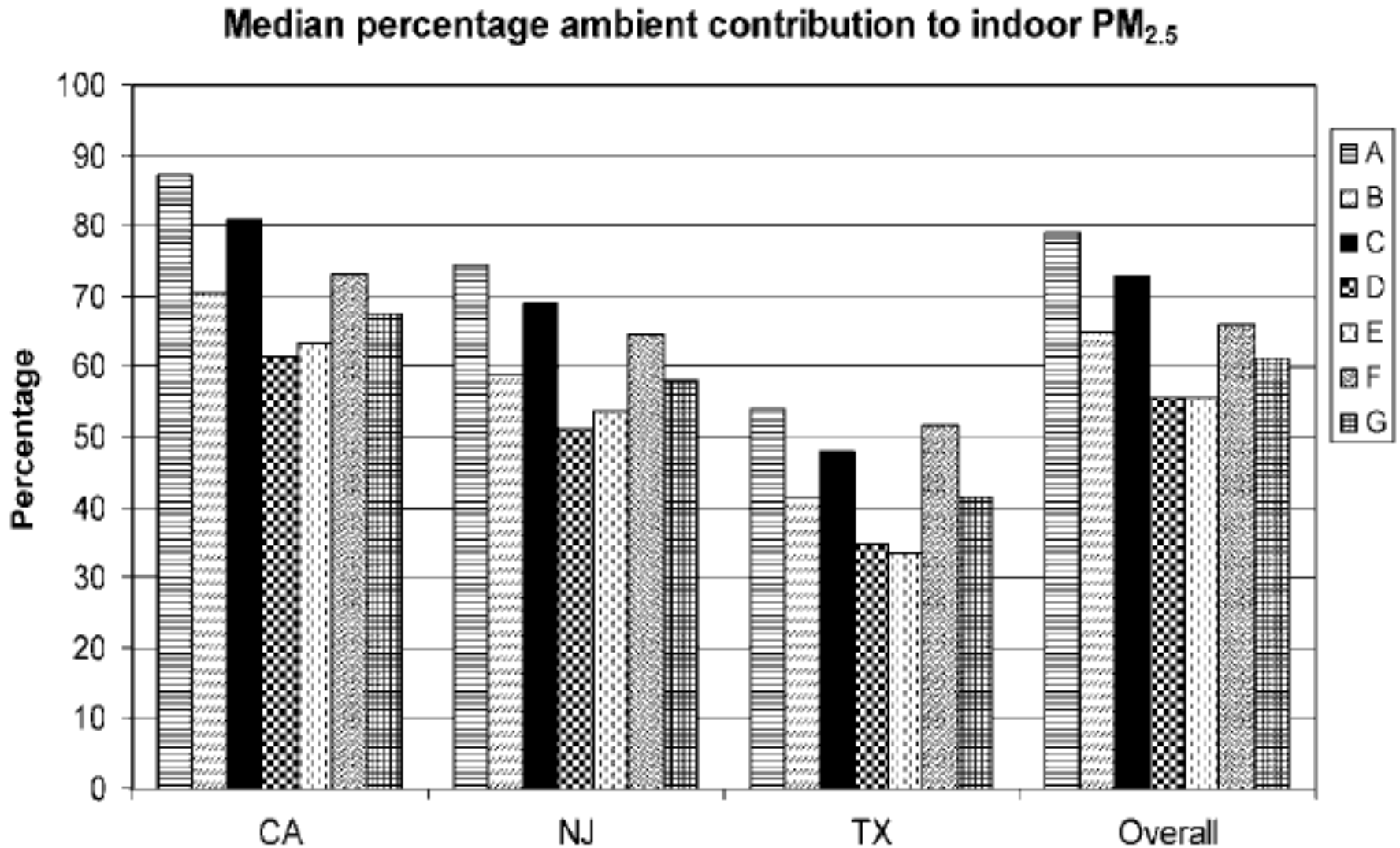
RIOPA I/O PM$_{2.5}$

- What can we learn about indoor vs. outdoor contributions to indoor PM$_{2.5}$ in RIOPA?
  - They fit a model that used measure C_i, C_a, AER (a), and estimated P and k

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

Ambient Contribution of PM2.5 to Indoors

Nonambient Contribution of PM2.5 to Indoors

Meng et al. 2005 *JESEE*

Median percentage ambient contribution to indoor 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:

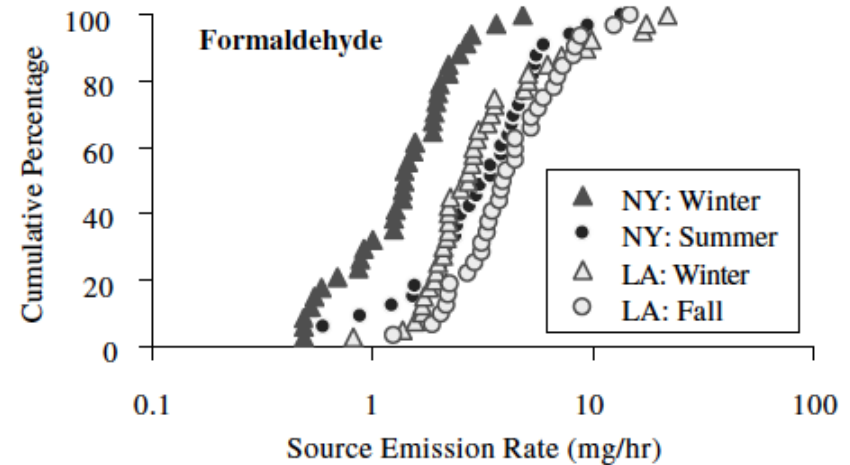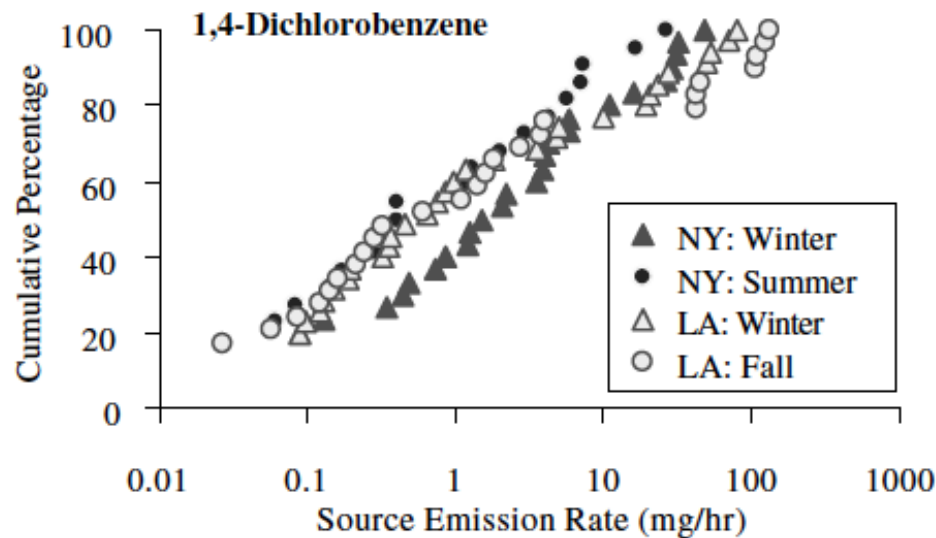$$\frac{E}{\lambda V} = C_{in} - PC_{out}$$
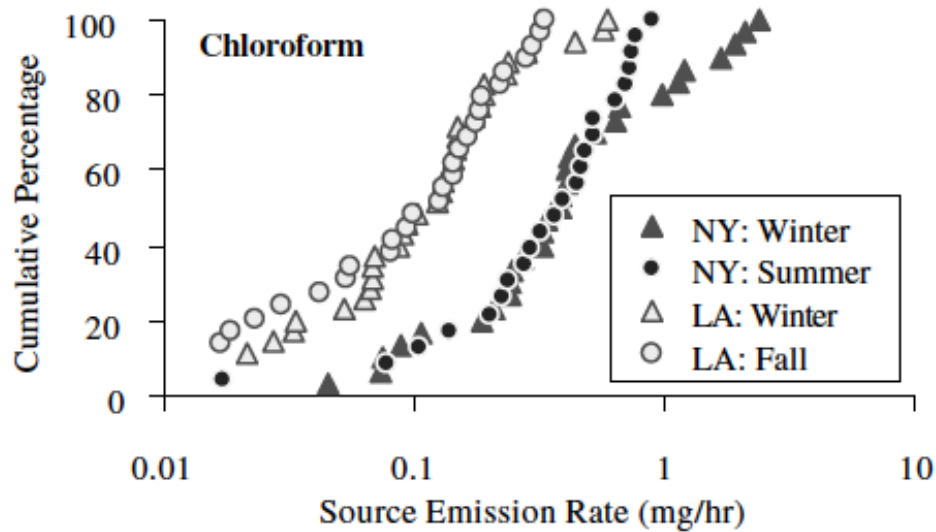
- Solve for E:

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

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

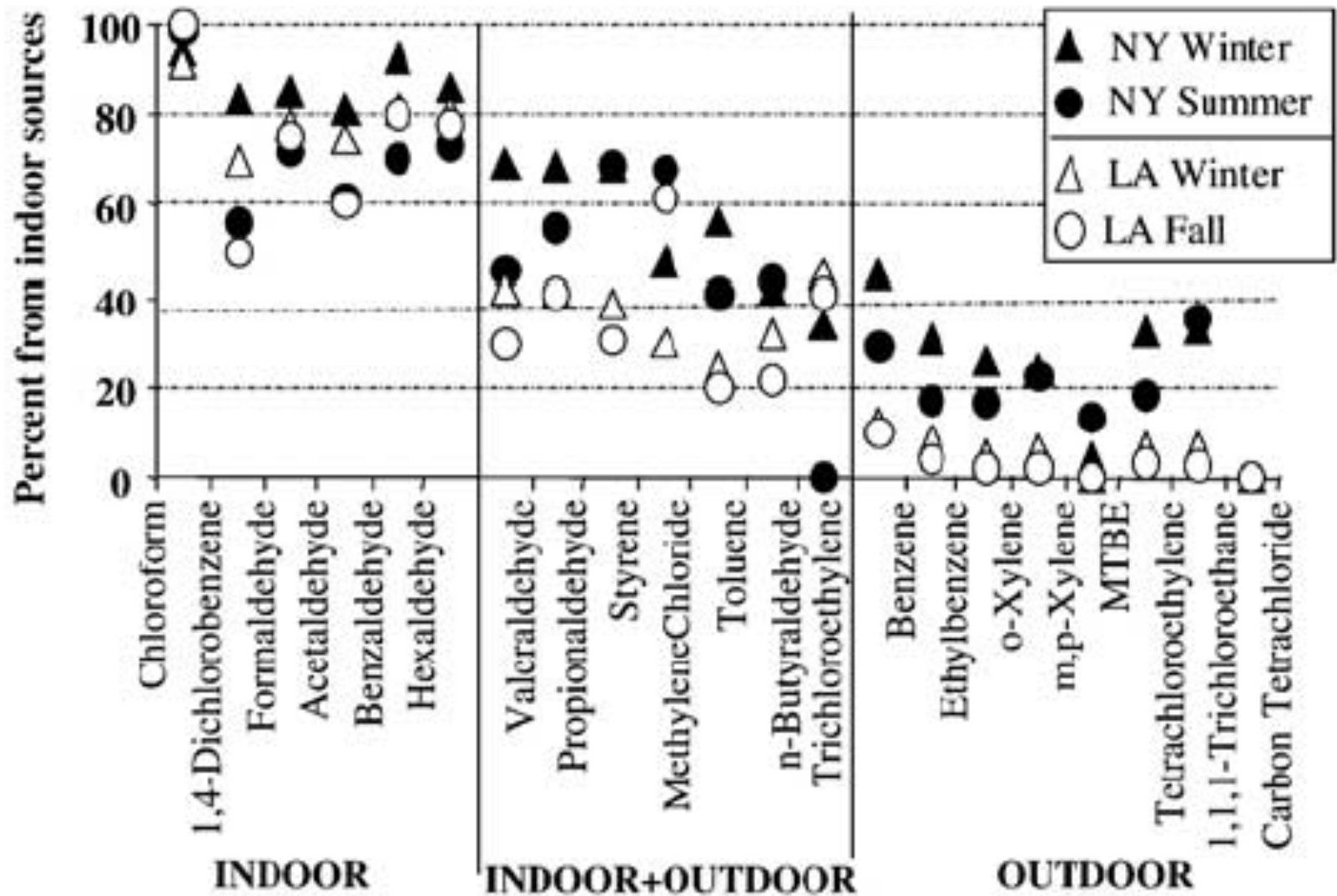- Or E/V to normalize for volume

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

Back-calculating E/V from RIOPA data

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

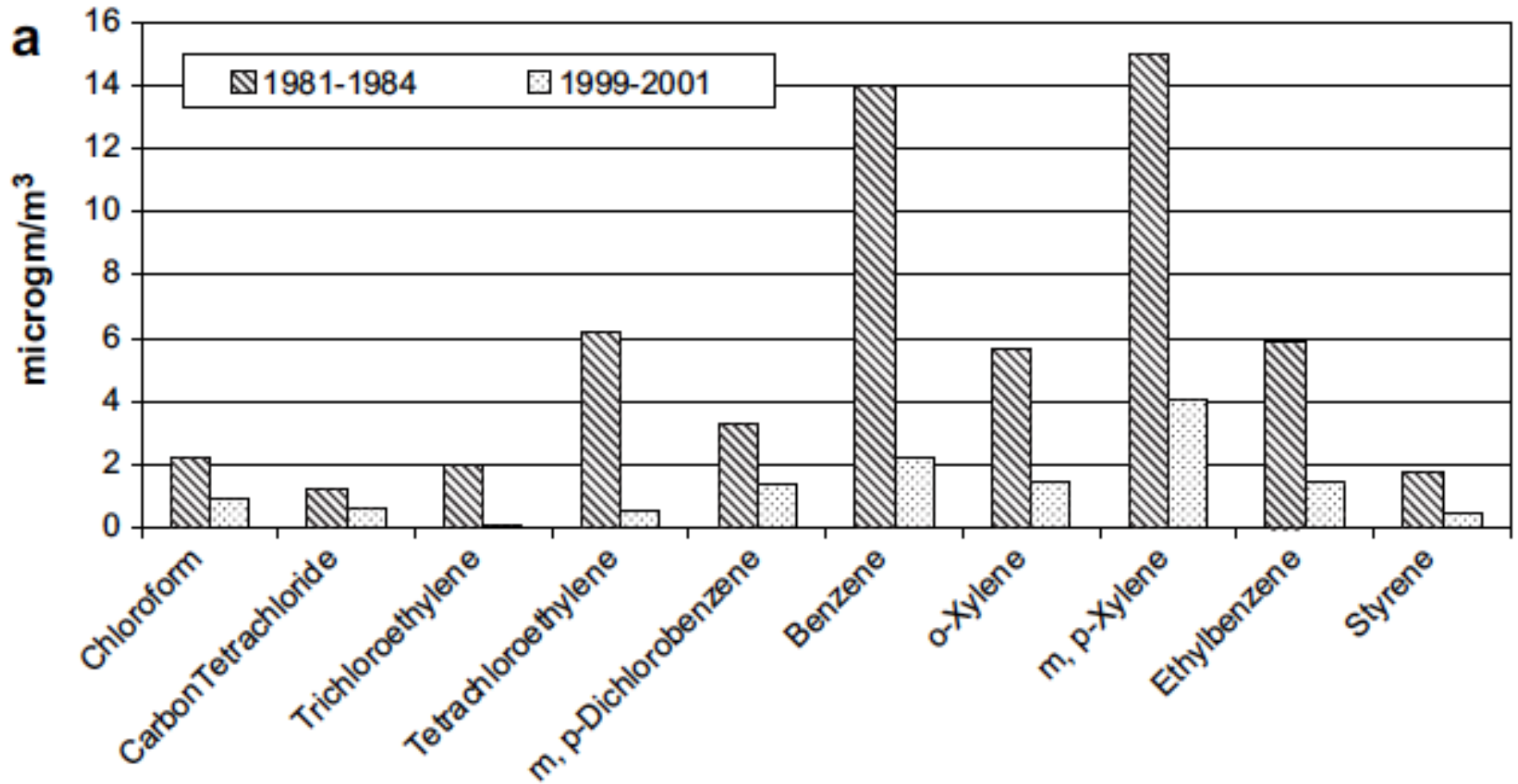# Changes in indoor pollutants since the 1950s

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*
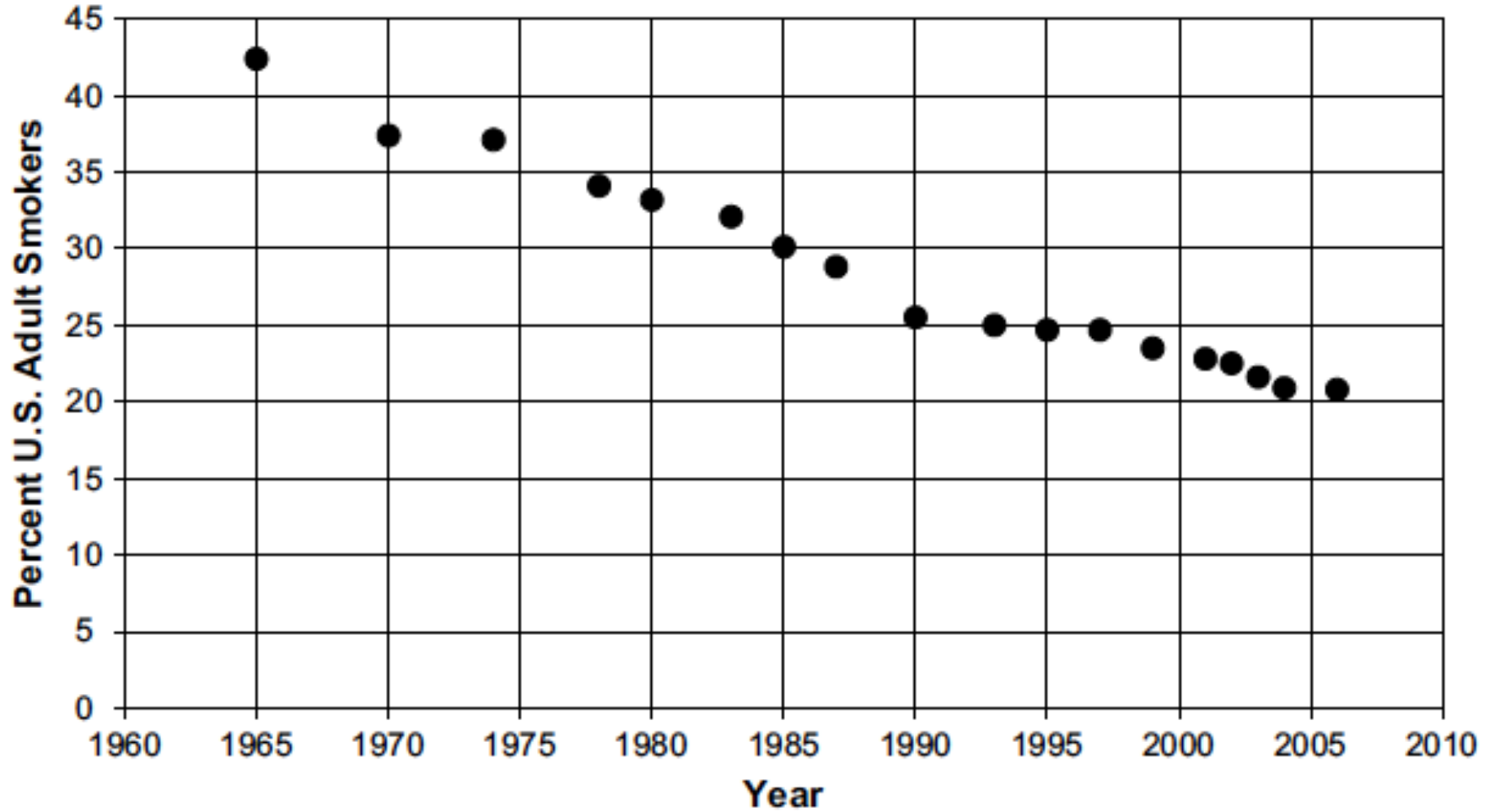
Changes in indoor VOC concentrations

Weschler, 2009 *Atmos Environ*

Next time

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

- No HW assigned this time