Indoor Air Changes, Chemicals and Tighter Homes

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Large changes in indoor pollutants over the past 60 years

These changes have been amplified by tighter homes, which often have reduced air exchange rates

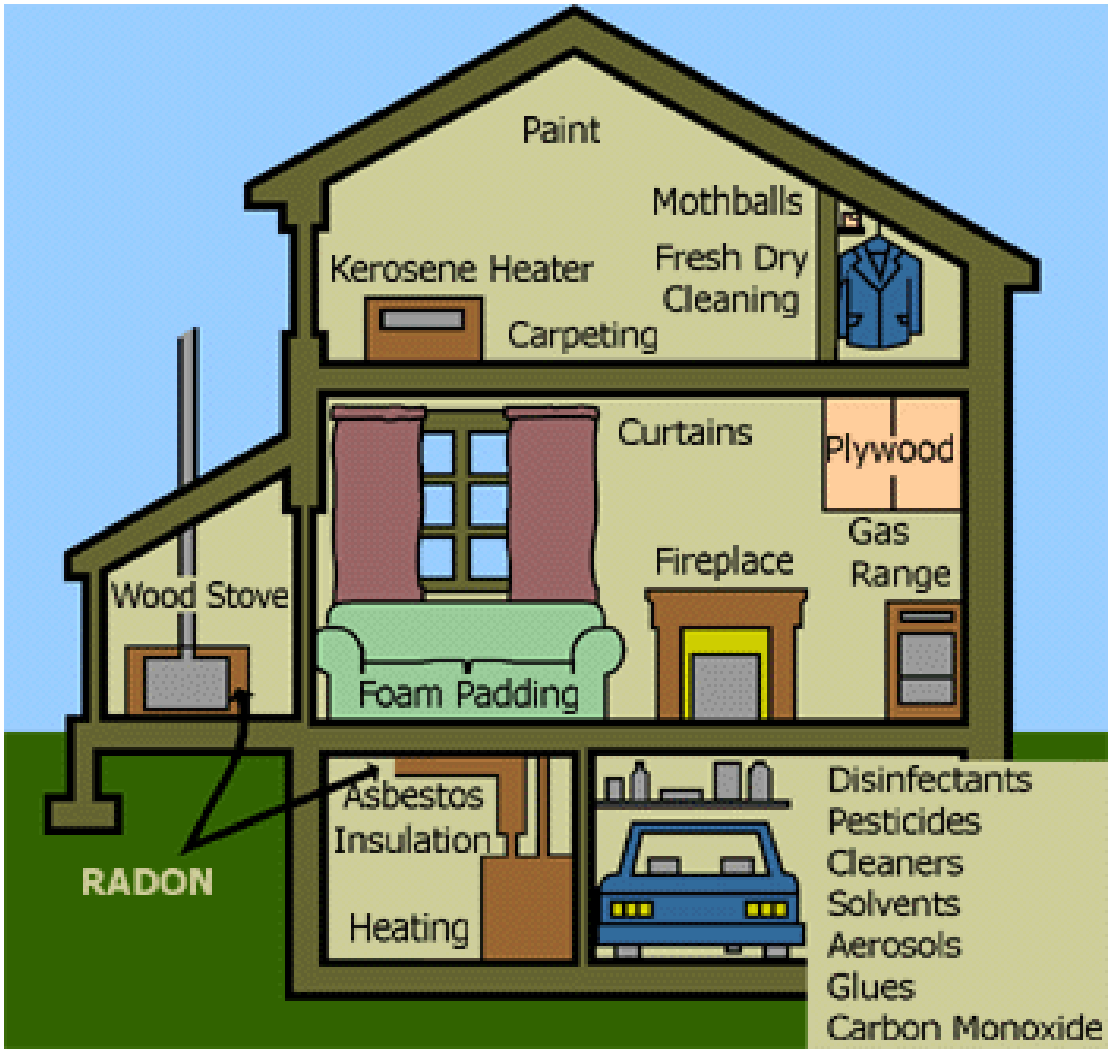
Chemicals in indoor environments in early 1950s quite different from those found indoors in 2010

Different:

- Consumer products
- Building materials
- Building construction
- Building operation
- Personal habits

Major sources of indoor chemicals

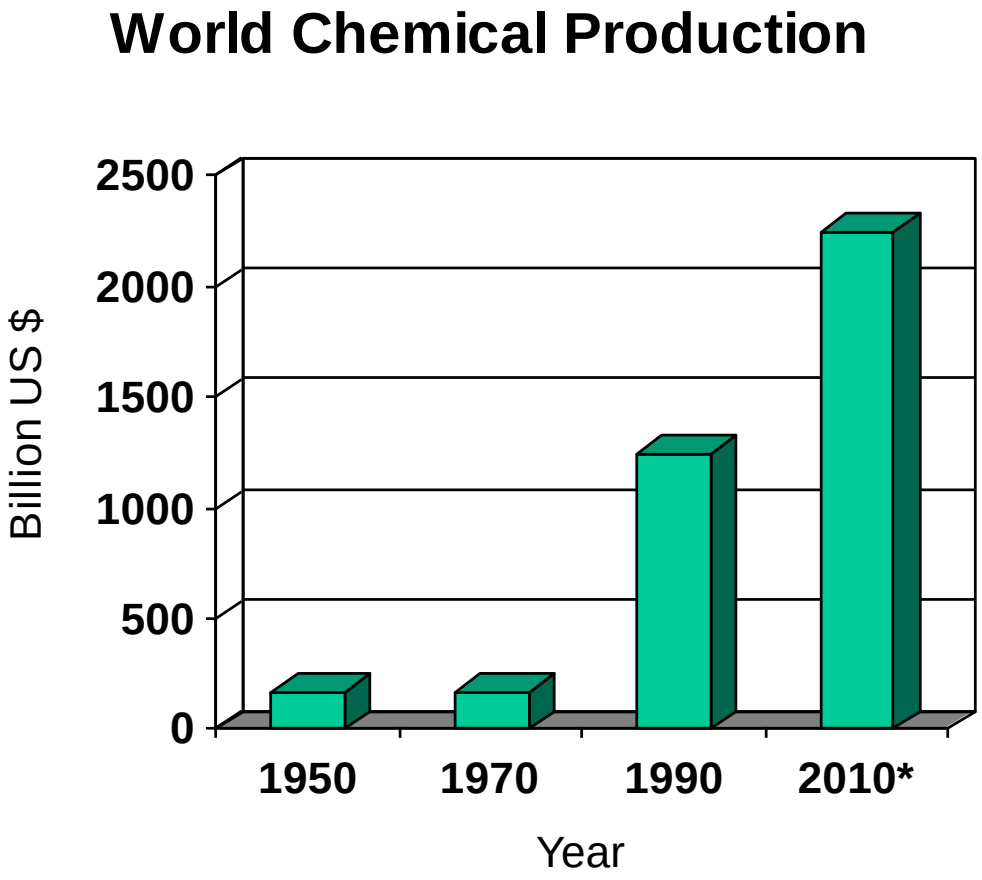
- Occupants & pets
- Cooking & heating
- Smoking (tobacco)
- Building materials
- Paint, floor and wall coverings
- Furnishings
- Cleaning products
- Pesticides
- Mold/Fungi



Major sinks for indoor chemicals

- Ventilation
- Surface removal
- Chemical reactions
- Filtration

World chemical production has increased dramatically since 1970



Commercial chemicals currently in use:

- ~ 143,000 in Europe
- ~ 100,000 in US
- ~ ?? In China
- ~ 30,000 produced at > 1 tonne/year

Egeghy, US EPA, 2010

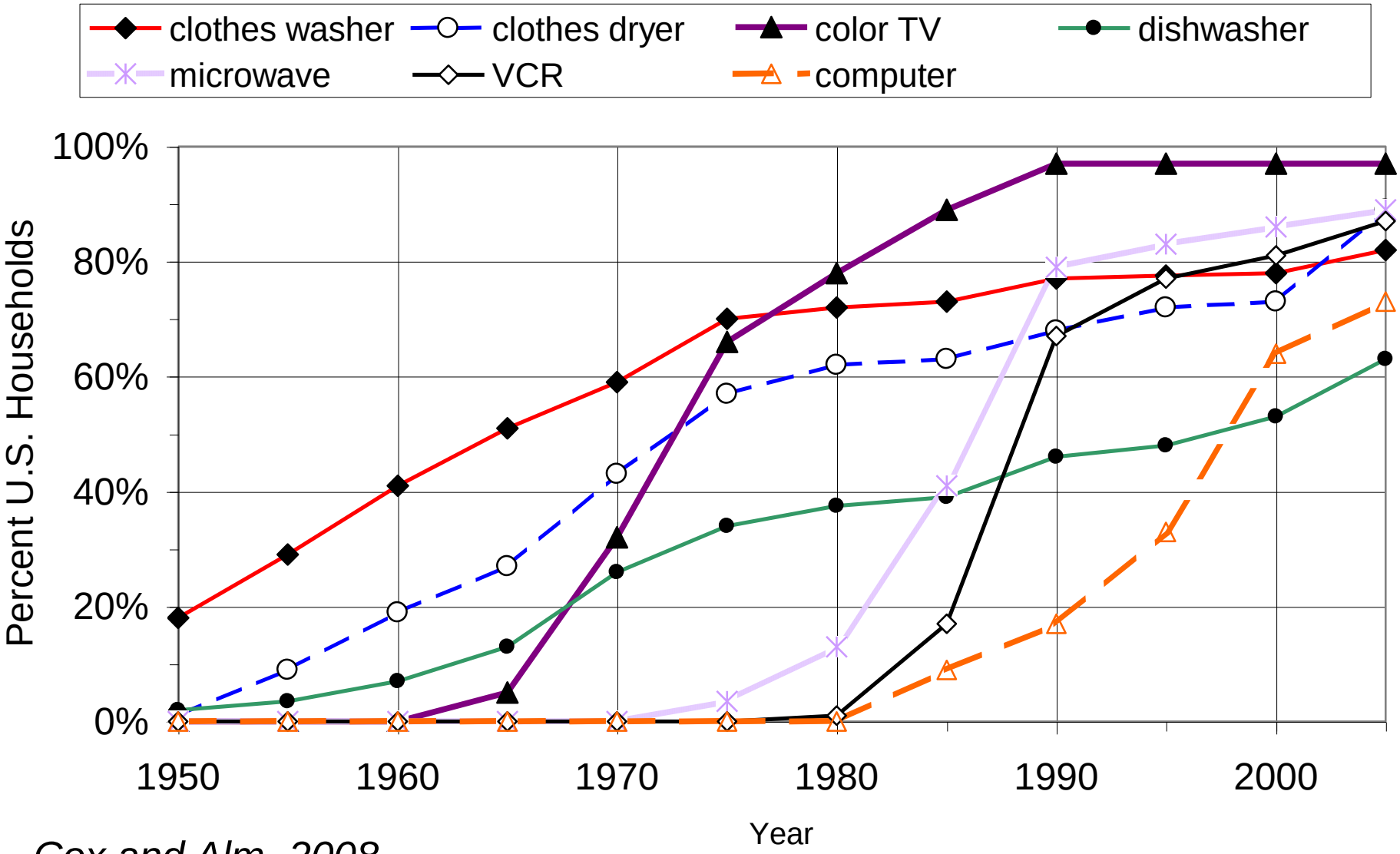
"A Scientific Milestone"

- Chemical Abstract Services (CAS) registry: a data base of chemicals – assigns unique number to each chemical
- "On Sept. 7, CAS scientists recorded the 50-millionth chemical substance into the *CAS Registry*."
  - *Chemical & Engineering News, Sept. 14, 2009, p. 3*
- *CAS registry* began more than 40 years ago
- It took **33 years to record the first 10 million** substances
- It took **nine months to register last 10 million** substances
- More than 80,000 new chemicals have been developed since World War II

Materials and products used indoors

- Increased use of pressed wood products
  - Resins emit formaldehyde, …
- Synthetics have replaced wool & cotton in carpets
  - Flame retardants, anti-stain agents, antioxidants
- Permanent-press fabrics introduced
  - Resins emit formaldehyde, …
- Plastics and polymers have become common
  - Plasticizers, flame retardants, antioxidiants
- Increased use of scenting agents
  - Some are readily oxidized to undesirable products
- Rapid growth in ownership of mechanical & electronic appliances
  - Flame retardants, heat transfer fluids, particles

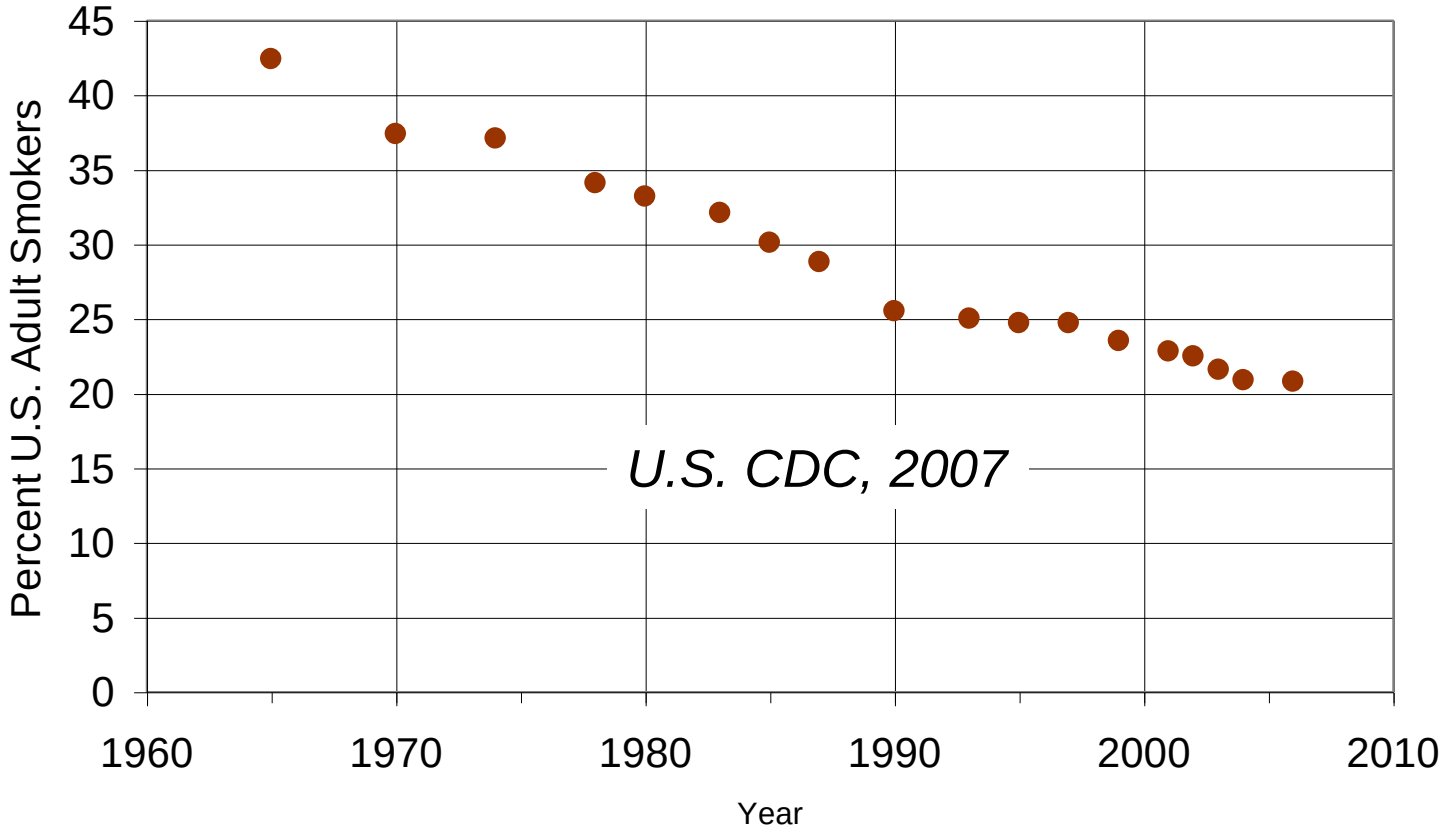
Percent U.S. houses with selected appliances: 1950-2005



Cox and Alm, 2008

Smoking habits have changed

- Percent of US adults who smoke has decreased



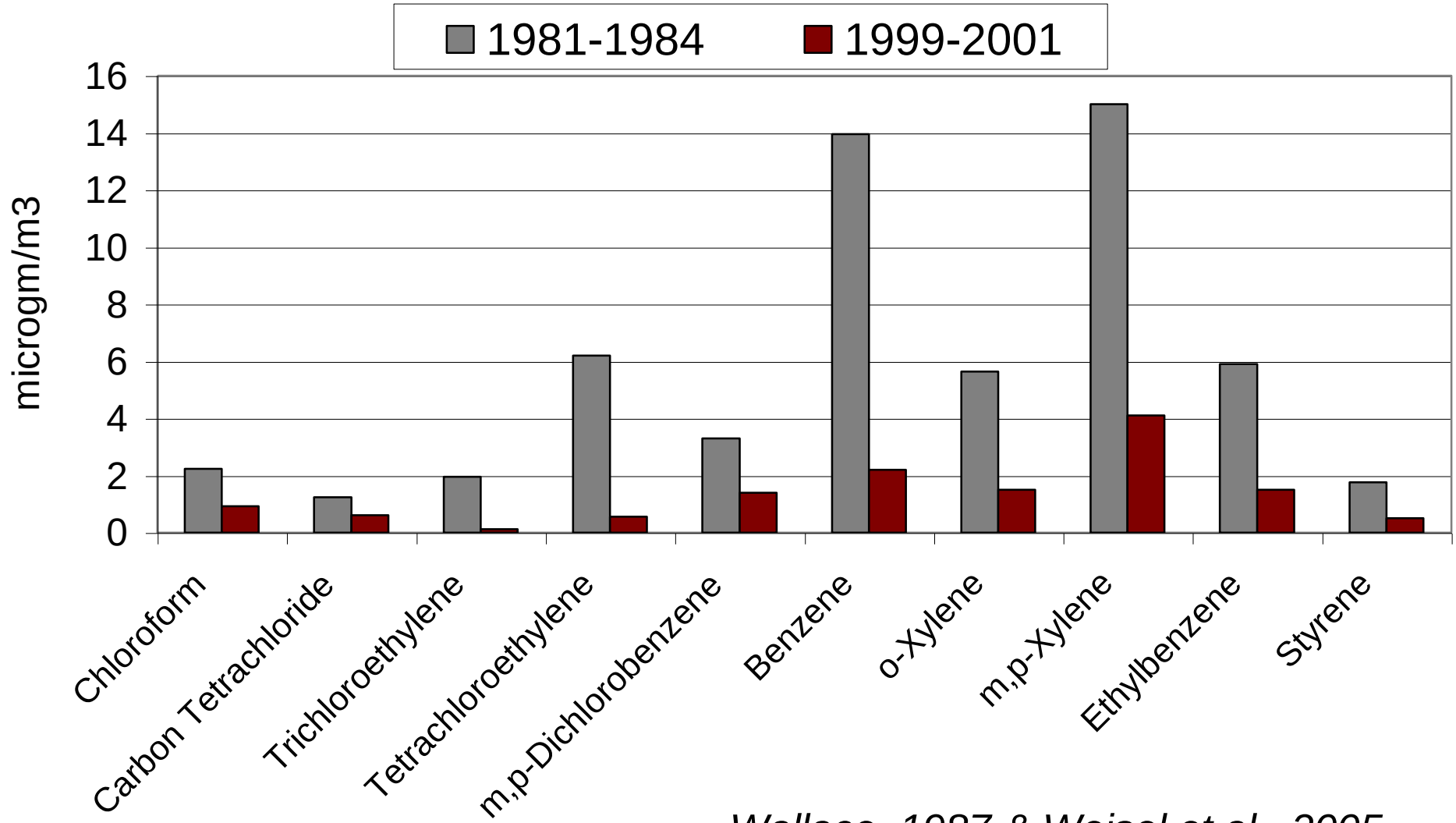
- In China, smoking is now banned in many public buildings

Good news: solvents in materials and products used indoors have changed

- Carbon tetrachloride and benzene no longer used as solvents in indoor products
- The use of other chlorocarbons and aromatic solvents (e.g., toluene, xylene isomers, ethyl benzene) in indoor products has decreased

Chlorocarbons and aromatics have decreased

`81-`84 (n = 715) `99-`01 (n = 553)



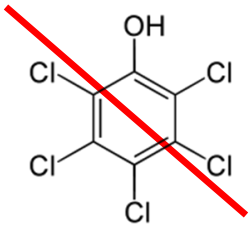
Wallace, 1987 & Weisel et al., 2005

Good news: materials and products used indoors

- Lead and mercury no longer added to indoor paints

- Gas appliances emit less nitrogen oxides and particles

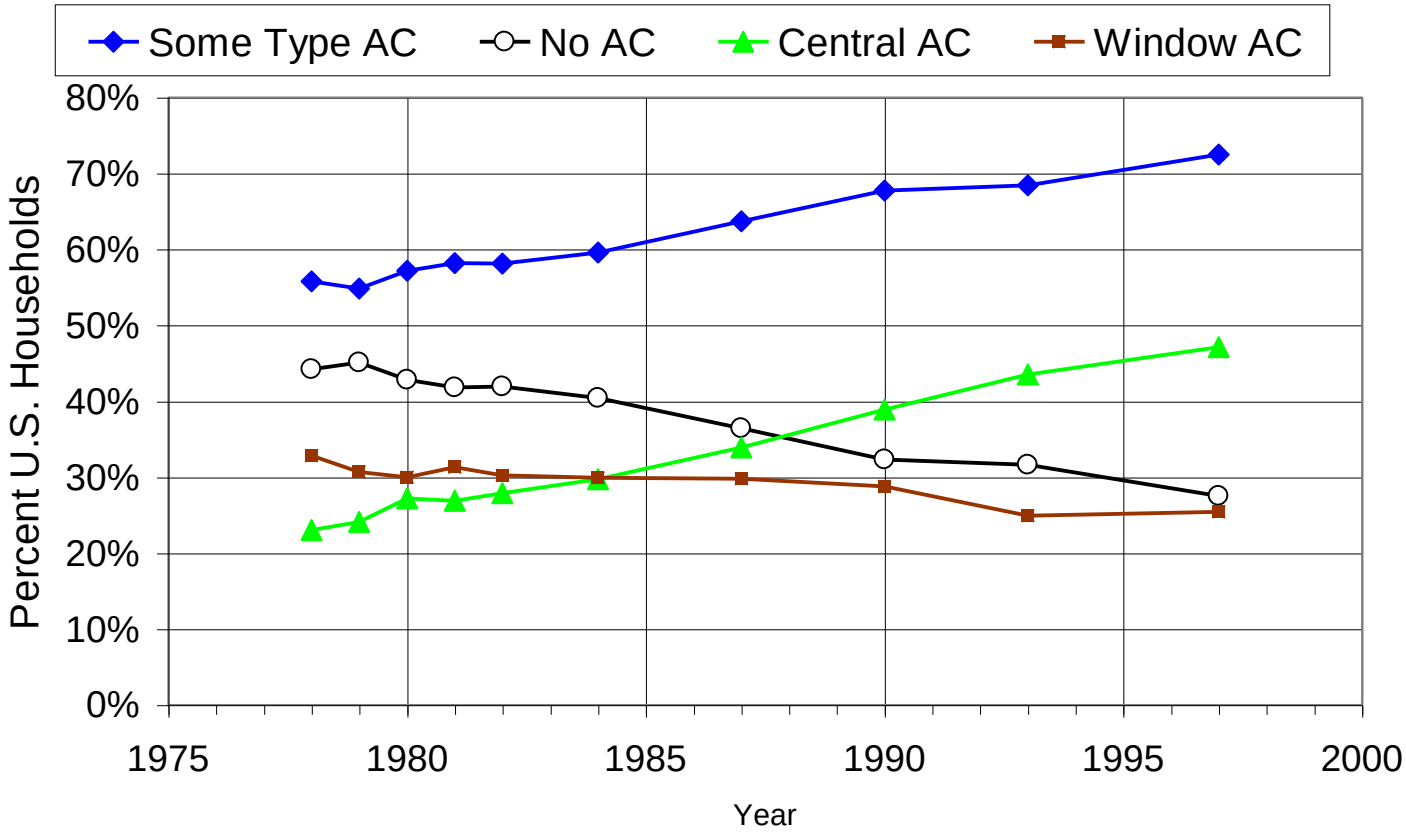
- Indoor use of certain pesticides eliminated (e.g., DDT, chlordane, chlorpyrifos)
- Indoor use of pentachlorophenol eliminated



Building operation: more U.S. homes air conditioned

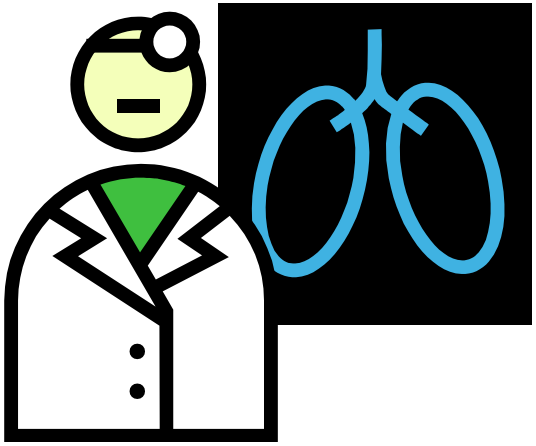
- 1950: few homes had air conditioning (AC)
- 1979: 25% had central AC; 55% some type of AC
- 1997: 50% had central AC; 72% some type of AC

Air conditioned buildings tend to have lower air exchange rates

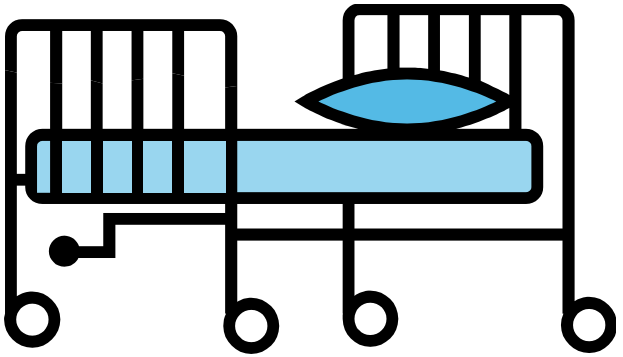


Building construction & location

- Newer buildings tend to be tighter than older buildings (better windows, better doors, better barrier materials)
- Damp buildings more common than in the 1950s
  - More buildings; more construction on “wetlands”
  - More homes in hot, humid regions; made possible by air conditioning, but in humid regions this can lead to condensation in wall cavities
  - Modern materials (e.g., plastics, wall board) buffer moisture less than materials used 60 years ago (e.g., lumber, plaster)



Is the indoor environment healthier today than it was 60 years ago?



Indoor exposures to a number of known or suspected carcinogens have decreased

- Benzene
- Formaldehyde
- Asbestos
- Environmental tobacco smoke
- Radon

→ Known carcinogens

- Chloroflorm
- Tricloroethylene
- Carbon tetrachloride
- Napthalene
- Polybrominated biphenyls (PBBs)
- Tris(2,3-dibromopropyl)phosphate

→ Suspected carcinogens

Indoor exposures to a number of gas phase and heavy metal toxicants have decreased

Gases

- Carbon monoxide
- Sulfur dioxide
- Nitrogen oxides

Heavy Metals

- Lead
- Mercury
- Cadmium

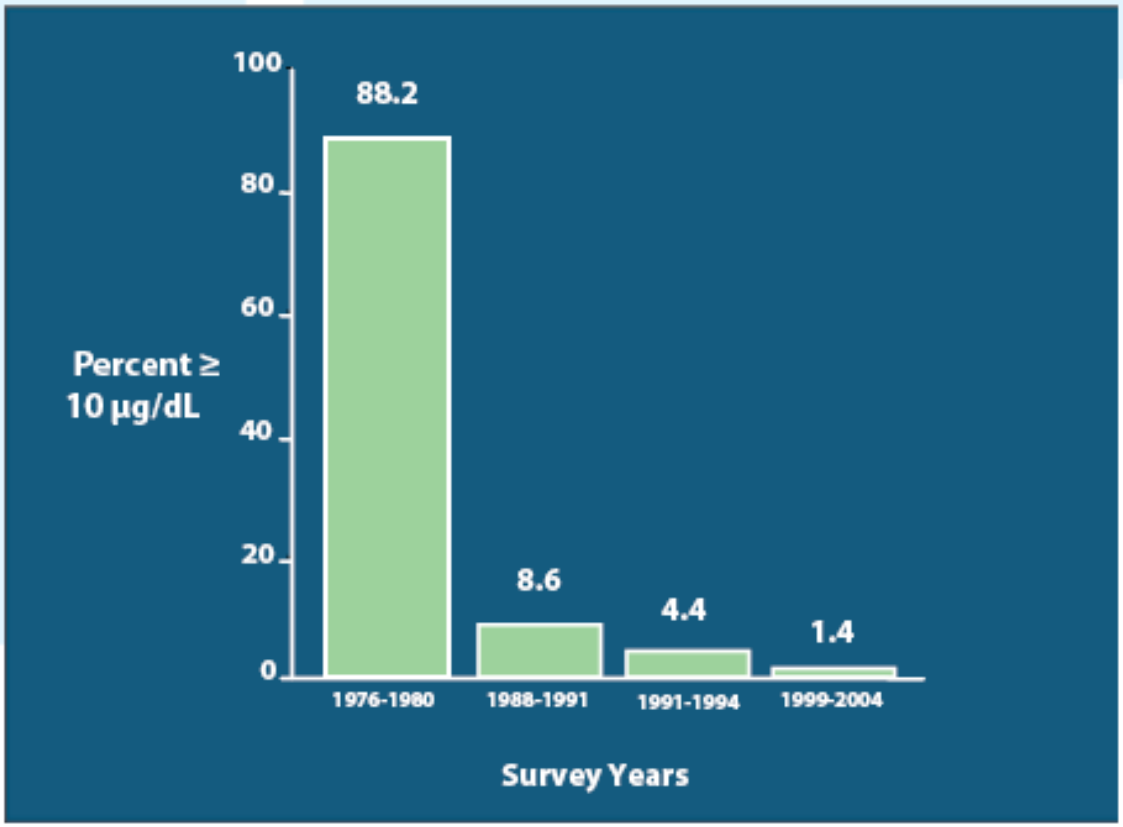


Figure 1. Percentage of children 1-5 years old in the U.S. population with elevated blood lead levels (≥ 10 µg/dL).[1]

Jones et al., Pediatrics, e376, 2009

Pesticide exposures have changed (hopefully for the better)

- Sequentially phased out and replaced:
  - DDT
  - Chlordane
  - Chlorpyrifos
  - Mirex
- Dominant current pesticides
  - Pyrethroids

Exposures to oxidation products have increased

- Indoor levels of unsaturated organic compounds, especially terpenoids, have increased
  - 1950: < 20% of homes used air fresheners
  - 2007: ~ 70% of homes use air fresheners

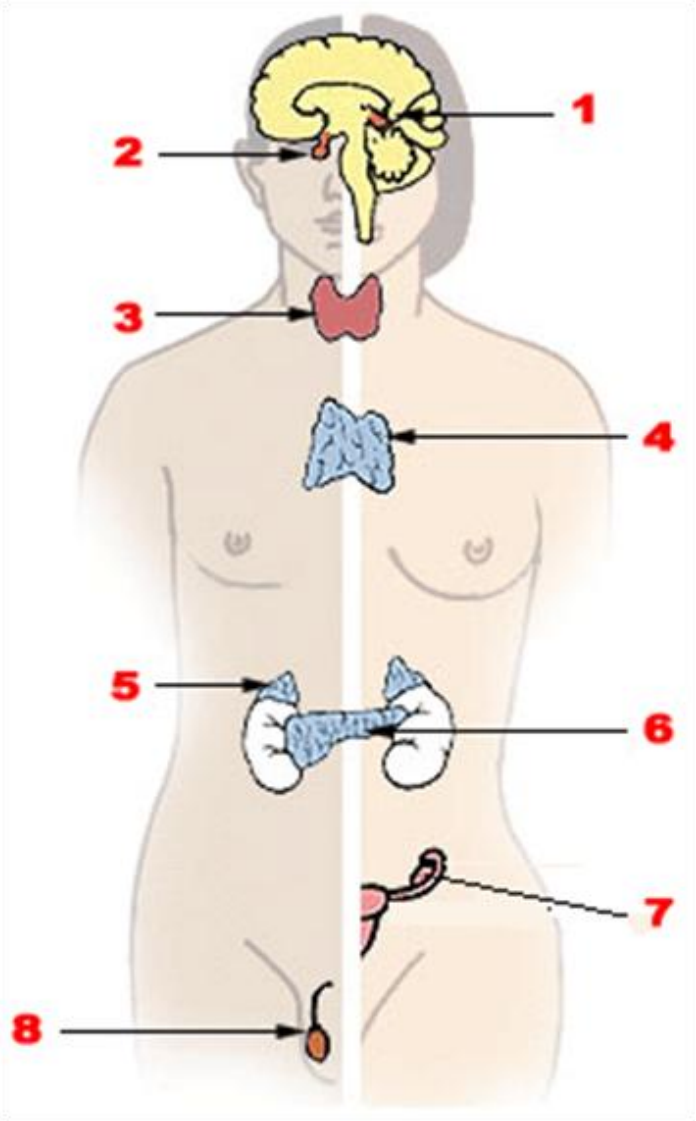
U.S. "Air Freshener" Sales

2000	$0.9 billion
2005	$1.5 billion

- Outdoor ozone levels have increased
- Air exchange rates have decreased (more time for gas phase chemistry)

Endocrine disruptors

- *Endocrine disruptors*: chemicals that can mimic hormones
- Whiles some of these chemicals are poor mimics …
- even a poor mimic can have an adverse health effect if its concentration in the body is high



Exposures to endocrine disruptors have increased

- More plastics in use today
  - Plasticizers used in certain plastics (e.g., flexible PVC)
  - Flame retardants used in certain plastics
  - Residual monomers & degradation products often present (e.g., BPA)
- More electronic equipment in homes and offices
  - Flame retardants (e.g., PBDEs) in polymeric housings, wiring and circuit boards
- More synthetic carpets and foam cushioning in use today
  - Flame retardants used in carpet backing and foam
- Increased use of polyethoxylate detergents
  - Nonylphenol produced during degradation

Many plastics, plasticizers and flame-retardants produced in *extremely large* amounts

- Worldwide production of PVC:

  20×10^{12} g/y ~ 3000 g/y per person
- Worldwide production of phthalate ester plasticizers:

  3.5×10^{12} g/y ~ 500 g/y per person
- Worldwide production of brominated flame retardants:

  0.2×10^{12} g/y ~ 30 g/y per person
- High percentage of plastics, plasticizers and flame retardants used indoors

Many plasticizers and flame-retardants present in large amounts indoors

- 20 m^2 vinyl flooring contains ~ 20 kg DEHP
- Foam “queen size” mattress contains ~ 3 kg PBDEs
- **These are “legacy” pollutants.** Removing the product that was the original indoor source does not remove the pollutant from indoors *Weschler & Nazaroff, Atmos. Environ., 2008*

Body burdens

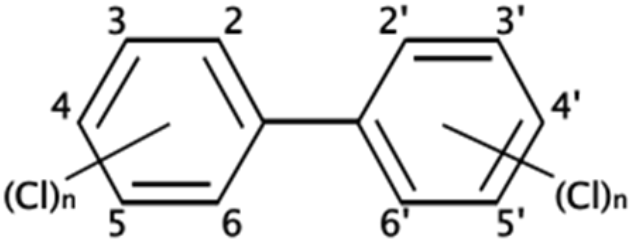
- Numerous manmade chemicals are present in our bodies, as evident from blood and urine samples
- Many of these were not produced in commercial amounts in the 1950s
- Solid and liquid foods contribute to body burdens
- *Indoor exposures* **also** contribute to body burdens
  - Inhalation of airborne species
  - Direct contact with indoor surfaces & air-to-skin transport followed by dermal absorption
  - Ingestion of “settled dust”

PCBs in blood of U.S. residents sampled from 2001-04

Heat transfer fluids, plasticizers, sealants, etc.

NHANES, 2005 & 2008

Compound	Blood Levels
PCB 180	0.61 ng/g serum
PCB 153	0.85 ng/g serum
PCB 118	0.29 ng/g serum
PCB 74	0.21 ng/g serum



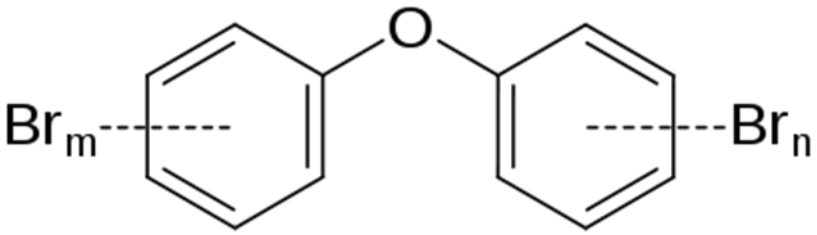
- Production peaked in 1960s; **manufacture and use of PCBs was halted in the United States in August 1977**
- These compounds are **still commonly found in indoor air and dust samples** (e.g., PCB 153: typically 0.1 to 1 ng/m^3 air; typically 7 to 70 ng/g dust)
- Remediation has proven to be difficult & expensive

PBDEs in blood of U.S. residents sampled from 2001-04

Flame retardants

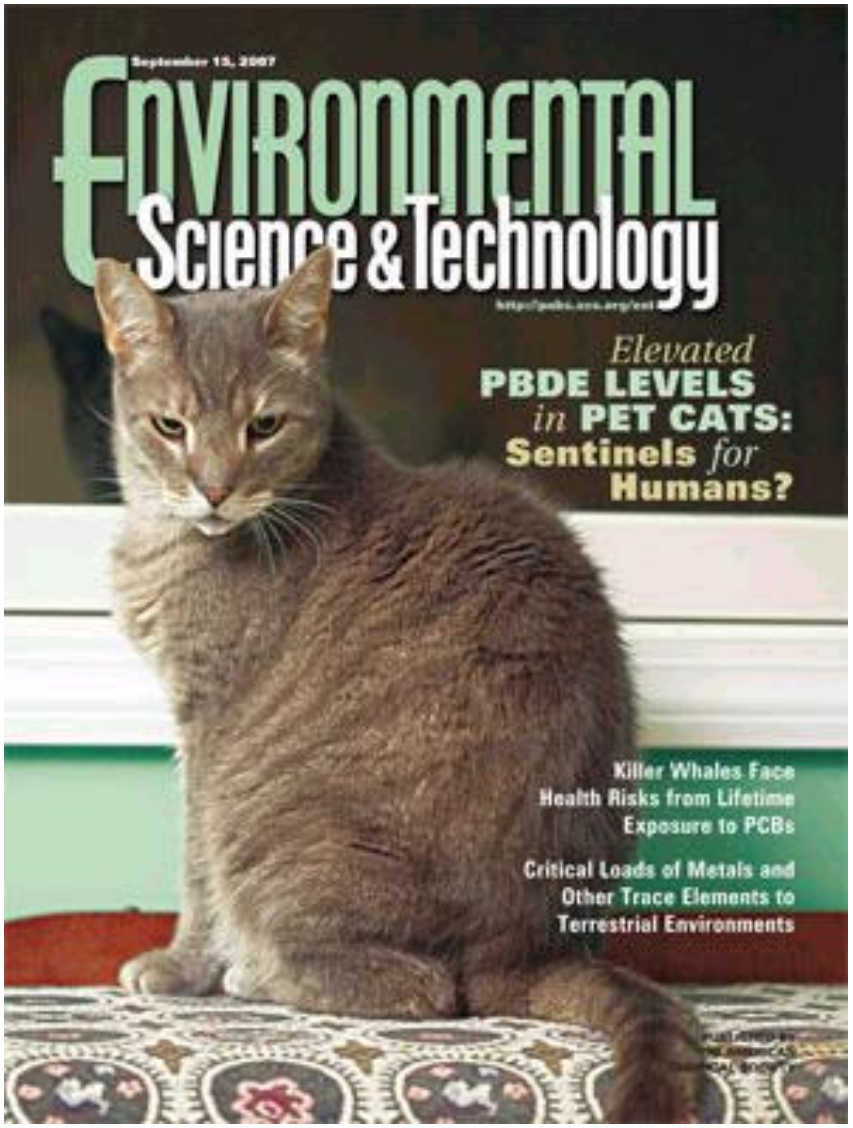
NHANES, 2005 & 2008

Compound	**Blood Levels**
BDE-47	1.05 ng/g serum
BDE-99	0.28 ng/g serum
BDE-100	0.24 ng/g serum
BDE-153	0.44 ng/g serum



- Use began to rise in the early 1980s
- Have become common in indoor air and settled dust (e.g., BDE 47: typically 0.06 - 0.6 ng/m^3 air; 300 - 3000 ng/g dust)

Flame retardants & feline hyperthyroidism



Coincident with the introduction of PBDEs into household materials nearly 30 years ago, feline hyperthyroidism has increased.

Blood levels indicate that cats are highly exposed to PBDEs. Cats may serve as sentinels for human exposures.

Dye et al., ES&T, 41, 6350, 2007

Perfluorocarbons in blood of U.S. residents: 2001-04

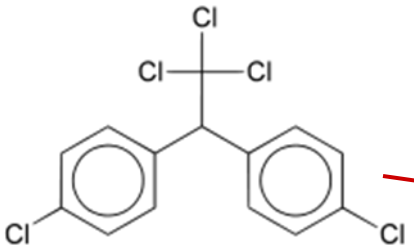
Surfactants, anti-stain- anti-stick-agents

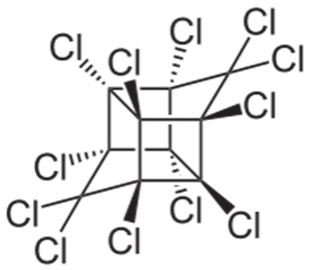
NHANES, 2005 & 2008

Compound	**Blood Levels**
Perfluorooctanesulfonic acid (PFOS)	55 ng/g serum
Perfluorooctanoic acid (PFOA)	9.8 ng/g serum
Perfluorohexanesulfonate (PFHxS)	8.3 ng/g serum
Perfluorononanoate (PFNA)	3.2 ng/g serum

- Use began to rise in mid-1970s
- May, 2000: 3M announced phase-out of production of PFOS, PFOA, and PFOS-related products
- Still common in indoor air and settled dust (e.g., PFOS: typically 0.011 – 2.5 µg/g dust; PFOA: 0.069 – 3.7 µg/g dust)

Pesticides in blood of U.S. residents sampled from 2001-04





Insecticides/termiticides/herbicides

NHANES, 2005 & 2008

Compound	Blood Levels
p,p'-DDT	0.18 ng/g serum
p,p'-DDE	15 ng/g serum
Mirex	0.41 ng/g serum
Dieldrin	0.15 ng/g serum
Chlordane	0.35 ng/g serum

- DDT banned in 1972; still common in indoor air & dust (typically 0.2 - 2 ng/m^3 air; 100 - 1000 ng/g dust)
- Mirex banned as a pesticide in 1978
- Dieldrin banned as a termiticide in 1987
- Chlordane banned in 1988
- Mirex, Dieldrin & Chlordane still common in older homes

Summary: blood of U.S. residents sampled from 2001-04

Compound	Blood Levels
Heat transfer fluids	
2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB 180)	0.61 ng/g serum
2,2',4,4',5,5'-Hexachlorobiphenyl (PCB 153)	0.85 ng/g serum
2,3',4,4',5-Pentachlorobiphenyl (PCB 118)	0.29 ng/g serum
2,4,4',5-Tetrachlorobiphenyl (PCB 74)	0.21 ng/g serum
Flame retardants	
BDE-47	1.05 ng/g serum
BDE-99	0.28 ng/g serum
BDE-100	0.24 ng/g serum
BDE-153	0.44 ng/g serum
Anti-stain; anti-stick agents	
Perfluorooctanesulfonic acid (PFOS)	55 ng/g serum
Perfluorooctanoic acid (PFOA)	9.8 ng/g serum
Perfluorohaxanesulfonate (PFHxS)	8.3 ng/g serum
Perfluorononanoate (PFNA)	3.2 ng/g serum
Pesticides/herbicides	
p,p'-DDT	0.18 ng/g serum
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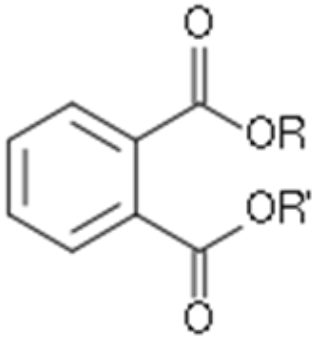
Chlordane	0.35 ng/g serum
Mirex	0.41 ng/g serum
Dieldrin	0.15 ng/g serum

NHANES, 2005 & 2008

Phthalates in urine of U.S. residents sampled from 2001-04

Plasticizers, solvents in personal care products



Compound	**Urine Levels**
Diethyl phthalate	1860 μg/g creatinine
Di(n-butyl) phthalate (DnBP)	81 μg/g creatinine
Butylbenzyl phthalate	90 μg/g creatinine
DEHP	267 μg/g creatinine

NHANES, 2005 & 2008

- Use began to rise sharply in the early 1950s
- Among the most commonly found chemicals in indoor air and settled dust

  DnBP: typically 200 - 1200 ng/m^3 air; 20 - 200 µg/g dust

  DEHP: typically 50 - 500 ng/m^3 air; 300 - 900 µg/g dust

Body burdens of DEHP and other phthalates have started to decrease

- Phthalates are currently being phased out of many products in the U.S. and Europe over health concerns
- As of February 2009, unlawful to manufacture, distribute or import into the US any children's toy or childcare article that contains concentrations > 0.1 % DnBP, BBzP or DEHP
- Evidence of this shift -- Värmland vs. Odense (next slide)

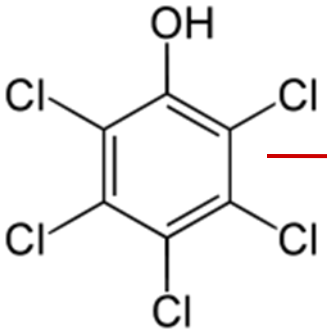
Levels of phthalates appear to be decreasing in Scandinavia

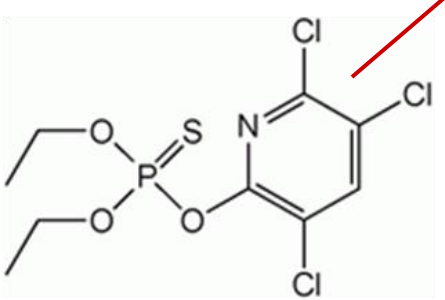
Mass fractions of selected phthalates measured in dust samples					
		DnBP	DiBP	BBzP	DEHP
		Median (µg/g)	Median (µg/g)	Median (µg/g)	Median (µg/g)
Värmland, Sweden 2000-2001	346 children's bedrooms	150	45	135	770
Odense, Denmark 2008	500 children's bedrooms	15	27	4	212

However, higher molecular weight phthalates are "legacy pollutants" and will remain in homes & offices for years after primary sources have been removed

Pesticides in urine of U.S. residents sampled from 2001-04

Insecticides/termiticides/antimicrobials





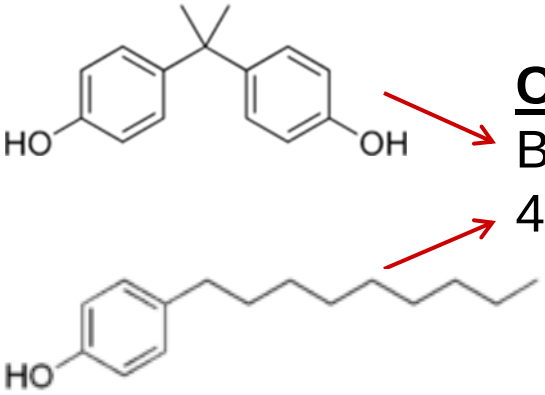
Compound	**Urine Levels**
Pentachlorophenol	2.3 μg/g creatinine
cis-Permethrin	3.8 μg/g creatinine
Methyl parathion	2.9 μg/g creatinine
Chlorpyrifos	9.2 μg/g creatinine

NHANES, 2005 & 2008

- Pentachlorophenol was widely used for wood treatment; elevated indoor levels tied to health problems; EPA restricted indoor use in 1984
- Chlorpyrifos banned for indoor use in 2001; still common in indoor air and dust

Bisphenol A (BPA) and nonylphenol in urine of U.S. residents sampled from 2001-04

Residual monomers & degradation products



Compound	Urine Levels
Bisphenol A	11.2 μg/g creatinine
4-Nonylphenol	1.4 μg/g creatinine

NHANES, 2005 & 2008

- BPA present in polycarbonate and certain epoxy resins as both residual monomer and degradation product
- **BPA not just in food/drink; also common in indoor air and settled dust -- typically 0.5 - 5 ng/m^3 air; 0.2 - 2 μg/g dust**
- 4-nonyl phenol common degradation product of polyethoxylate detergents; typically 40 - 400 ng/m^3 air; 0.8 - 8 μg/g dust

Summary: urine of U.S. residents sampled from 2001-04

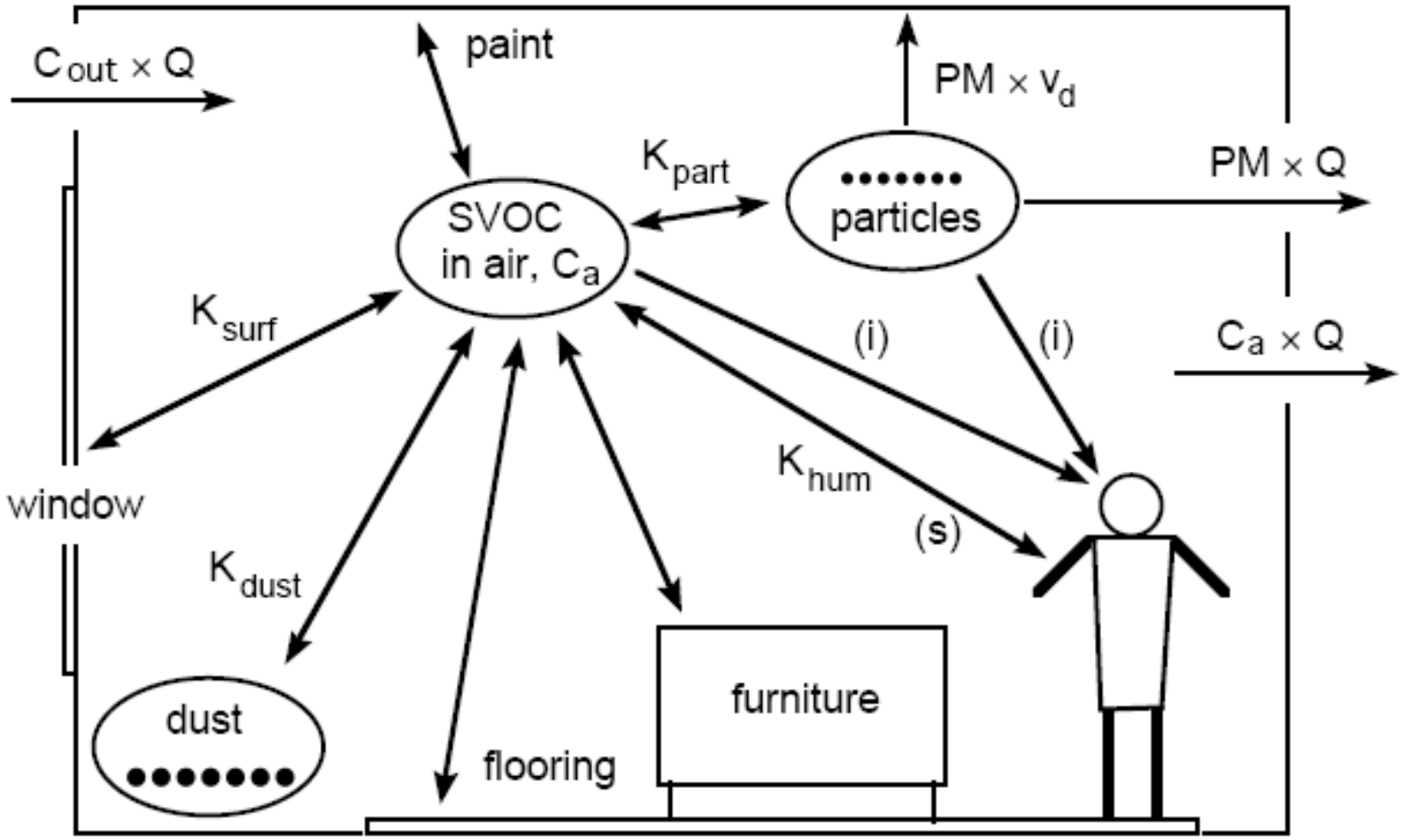
Compound	Urine Levels
Pesticides/herbicides/anti-microbials	
Pentachlorophenol	2.3 μg/g creatinine
Chlorpyrifos	9.2 μg/g creatinine
cis-Permethrin	3.8 μg/g creatinine
Methyl parathion	2.9 μg/g creatinine
Plasticizers	
Diethyl phthalate	1860 μg/g creatinine
Dibutyl phthalate	81 μg/g creatinine
Butylbenzyl phthalate	90 μg/g creatinine
DEHP	267 μg/g creatinine
Degradation products	
Bisphenol A	11.2 μg/g creatinine
4-Nonylphenol	1.4 μg/g creatinine
Combustion products	
Fluorene	~3.8 μg/g creatinine (Σ metabolites)
Phenanthrene	~1.7 μg/g creatinine (Σ metabolites)
Pyrene	0.243 μg/g creatinine
Benz[a]pyrene	0.184 μg/g creatinine
Naphthalene	34.5 μg/g creatinine (Σ metabolites)

NHANES, 2005 & 2008

Semi-volatile organic compounds (SVOCs)

- Many of the chemicals introduced since the 1950s (e.g., plasticizers, flame retardants, pesticides, surfactants, etc.) are semivolatile organic compounds (SVOCs)
- SVOCs have intermediate volatility; they simultaneously exist in both the gas phase and sorbed to airborne particles or other exposed surfaces

Indoor SVOC dynamics



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

Weschler & Nazaroff, Atmos. Environ., 2008

SVOC persistence

- VOCs disappear from indoor environments when their original sources disappear (witness decrease in benzene or CCl_4)
- Many SVOCs will remain in indoor environments long after the materials that contained them have been removed
- Indoor lifetime depends on volatility and the rate at which the SVOC is degraded by processes such as oxidation, hydrolysis, photolysis and microbial activity
- Examples of “legacy pollutants”:
  - pentachlorophenol, PCBs, chlordane, chlorpyrifos

Need for more toxicity information!

- Of the chemicals currently in commerce, ~ 3300 are produced or imported into the U.S. at levels > 1 million lbs/year (high production chemicals)
- No toxicity data for ~ 40% of the high production chemicals
- Full toxicity data available for only ~ 25% of the chemicals in consumer products

C. J. Mattingly, 2009

TSCA and *REACH:* *legislation addressing new chemicals*

USA

- Toxic Substances Control Act (TSCA)

European Union

- Registration, Evaluation and Authorization of CHemicals (REACH)

Different approaches to new chemicals

1976 U.S. TSCA

- New chemicals require testing only if evidence of toxic harm exists
- Government bears burden of proof of harm
- Chemicals in use before 1976 are assumed to be safe
- Limited public access to product formulations

2006 EU REACH:

- New chemicals have to be tested before being placed on the market
- Producers must demonstrate safety
- Chemicals in use before 1981 subject to same requirements as new ones
- Greater public access to product formulations

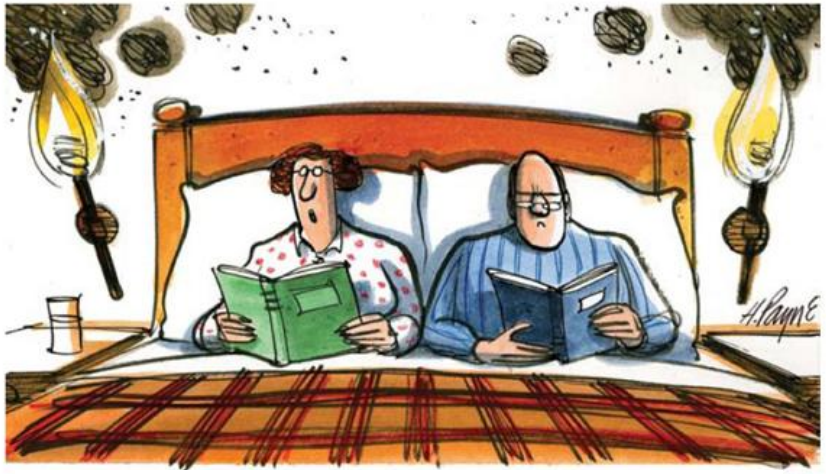
Schwarzman & Wilson, Science, 2009

REACH: It's impact

- It is estimated that around 27 000 chemical companies will fall under REACH regulation.
- It is estimated that around 30 000 chemicals will fall under REACH regulation
- Although REACH only applies to the European Union, it impacts both the USA and China, since companies in the USA and China want to be able to sell their products in Europe

Complex tradeoffs: long term effects?

- There are numerous chemicals in our indoor air that weren't there two generations ago
- We know why they are there
  - To make our plastics flexible
  - To reduce the risk of fire
  - To kill pests
  - To minimize mold growth
  - To make our paint spread easier
  - To repel dirt and stains



Torches?? Because light bulbs use too much energy and fluorescents contain mercury.

- They have become part of us
- Surprisingly, the long term health effects of most of these chemicals are unknown

Summary

- Chemicals in indoor environments change from month-to-month, year-to-year and decade-to-decade
- Most chemicals present in indoor environments are also in our bodies – some briefly, some for years
- Reduced ventilation translates to higher exposures to chemicals that originate indoors
- ??Are there links between these “new” chemicals and increases in certain health problems (e.g., allergies, asthma, autism, breast cancer, testicular cancer, male and female development abnormalities)??

For references to information presented in this talk, please see:

Weschler, C.J. (2009) "Changes in indoor pollutants since the 1950s", *Atmospheric Environment*, ***43, 153-169.***