

Sources, Emissions & Exposure— Flame Retardants & Other SVOCs

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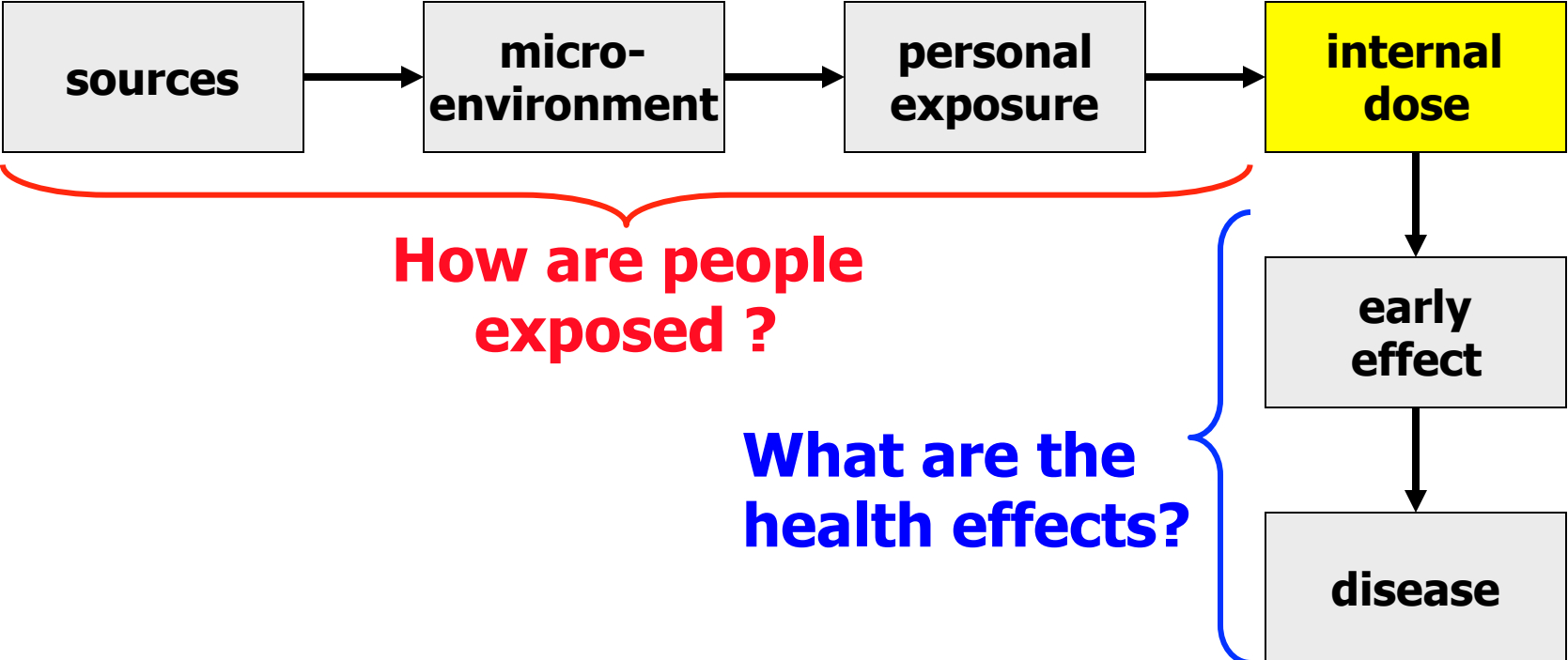


***SVOCs in the Indoor
Environment***

RTP

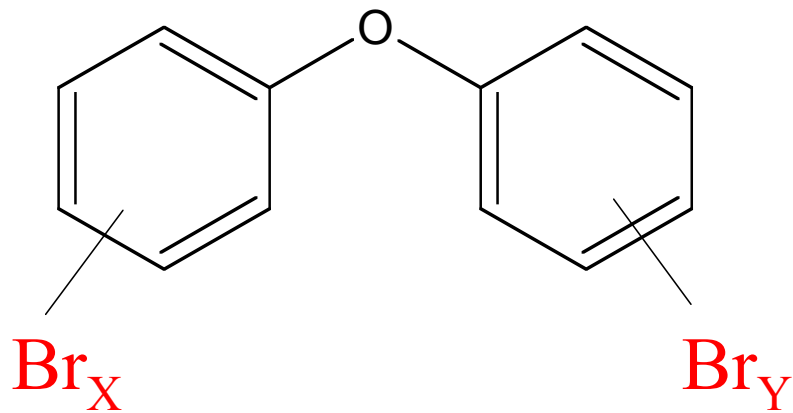
5-7 January 2011

Exposure Assessment Paradigm: Source to Disease



The PBDE story begins in the middle

Polybrominated diphenyl ethers (PBDEs)



- **209 possible congeners**
- **structurally related to PCBs...**
- **persistent, bioaccumulative, toxic**
- **semivolatile to nonvolatile**

Use of PBDEs as flame retardants

Penta **furniture (polyurethane foam)**
mainly used in N. America



Octa **electrical hard plastic**
(minor)

Deca **TV/computer plastic,**
textiles (carpets, draperies)



up to ~10 % by weight

***not* chemically bound to the plastic**

Penta & Octa manufacturing phase-out 2005;

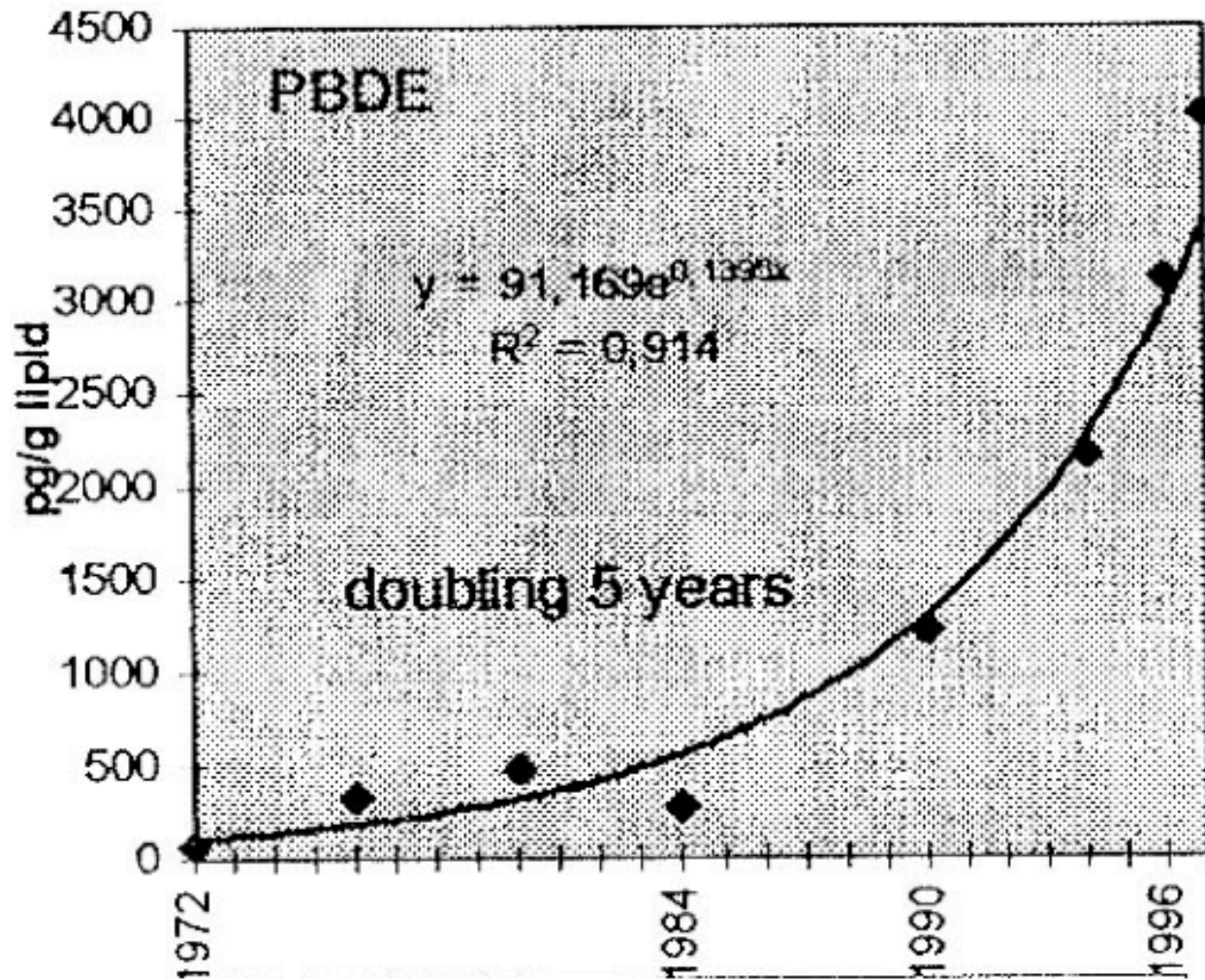
added to Stockholm Convention 2009

Deca phase-out in USA 2013

Large reservoir for years to decades

The graph that launched a thousand papers...

PentaBDE levels in human milk in Sweden (1998)



Norén and Meironyté 1998

- **How are people being exposed? (initial idea)**

food*

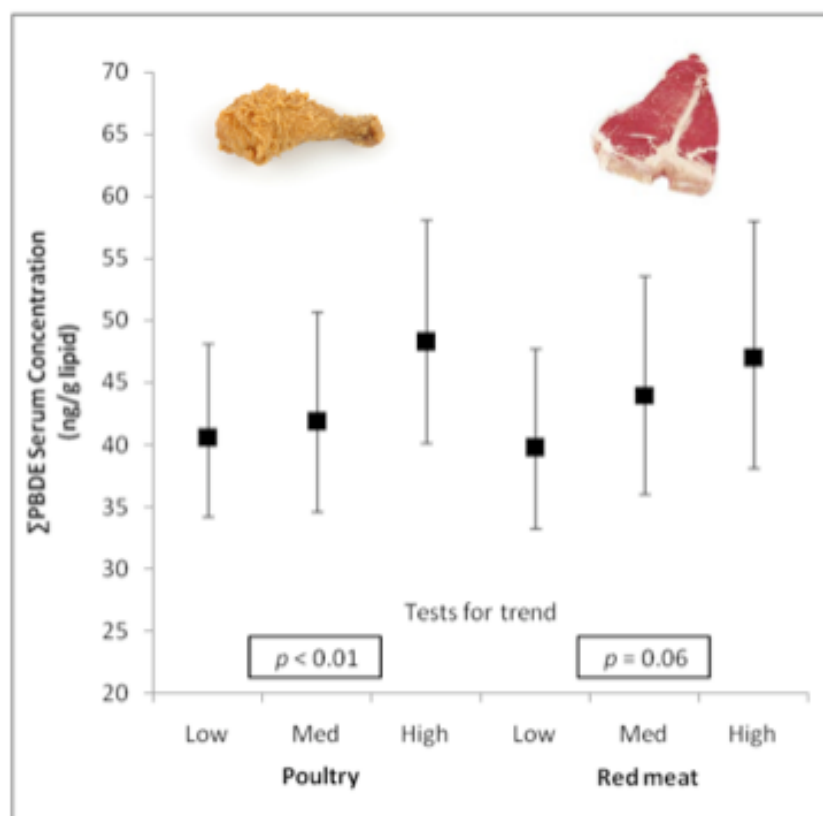


occupational

- * **by analogy with PCBs & dioxin, logKow research in Scandinavia (fish consumption)**

Clear US evidence for diet as exposure route for PentaBDE

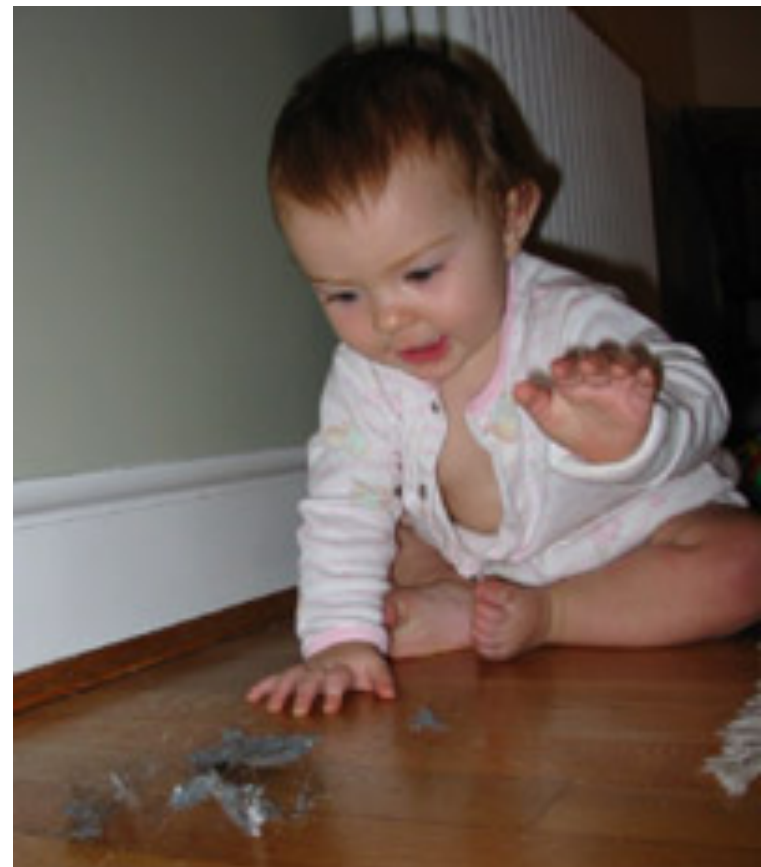
- 2003-4 data
- Particularly for meat
- How is food getting contaminated?

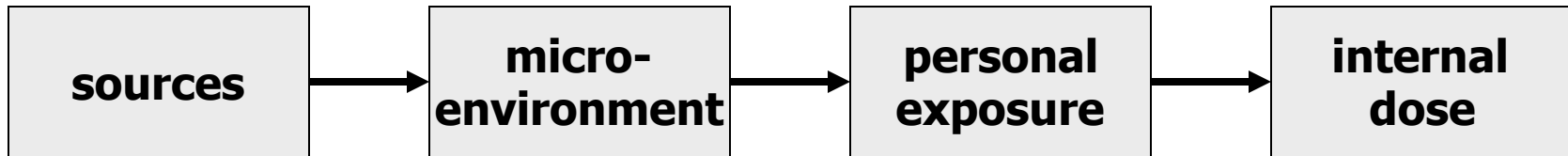


**But PBDEs used in consumer products...
and show up in house dust**

**e.g., Stapleton et al 2005
Rudel et al 2003**

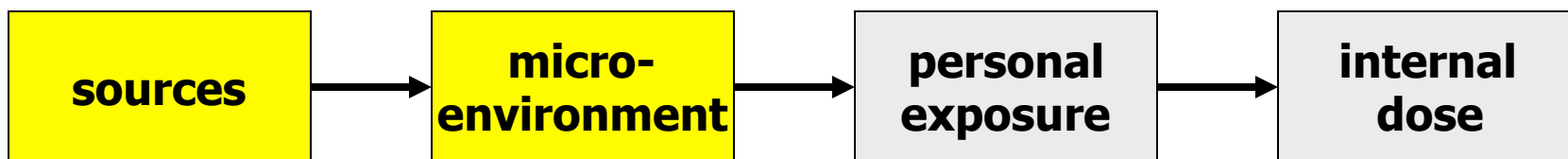
**Hypothesis: House dust may be
important route of exposure
(But exposure factors VERY
uncertain, especially for adults)**





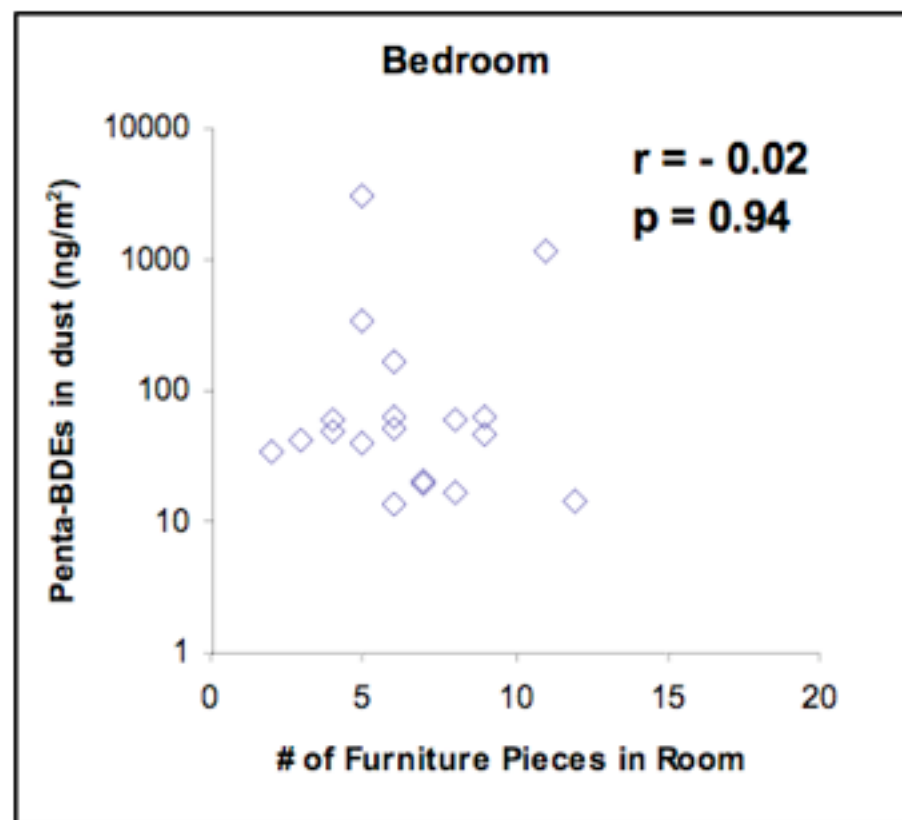
- **Exposure factor approach:**
e.g., $\underbrace{\text{media concentration}}_{\text{representative? methods?}} \times \underbrace{\text{exposure factor}}_{\text{how well known?}}$
- **Empirical studies linking boxes:**
e.g., **association of dust concentrations & body burden**

1. Sources to Microenvironment (Dust)



dust

NO or weak association between dust/air PBDE and counts of putative sources (foam furniture, electronics)



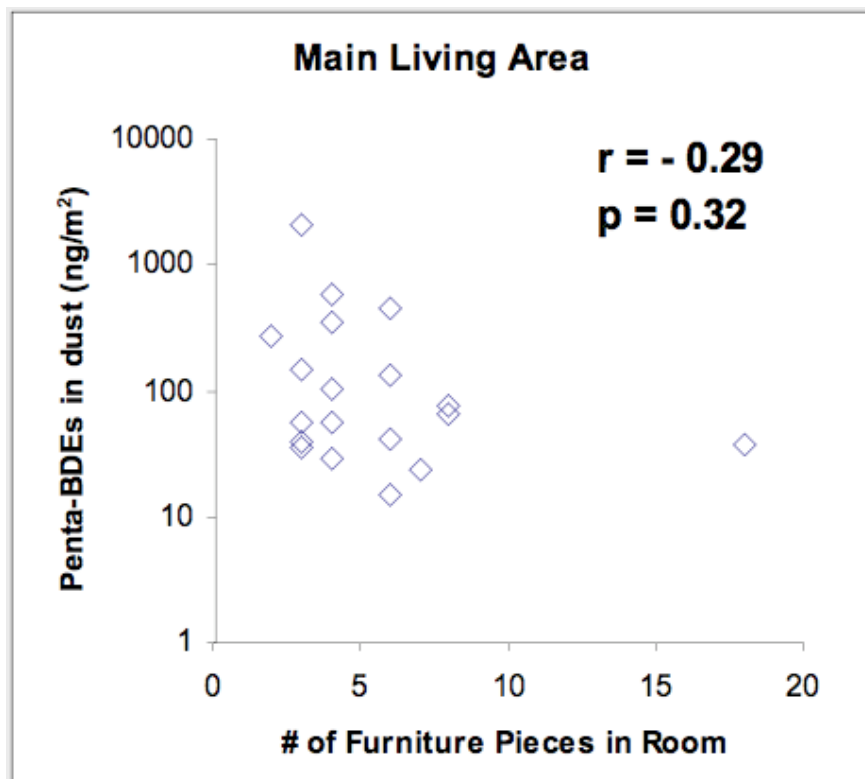
Hypothesis: Counts of furniture (or electronics) may not work if there are large differences in PBDE concentrations between products, i.e., exposure measurement error



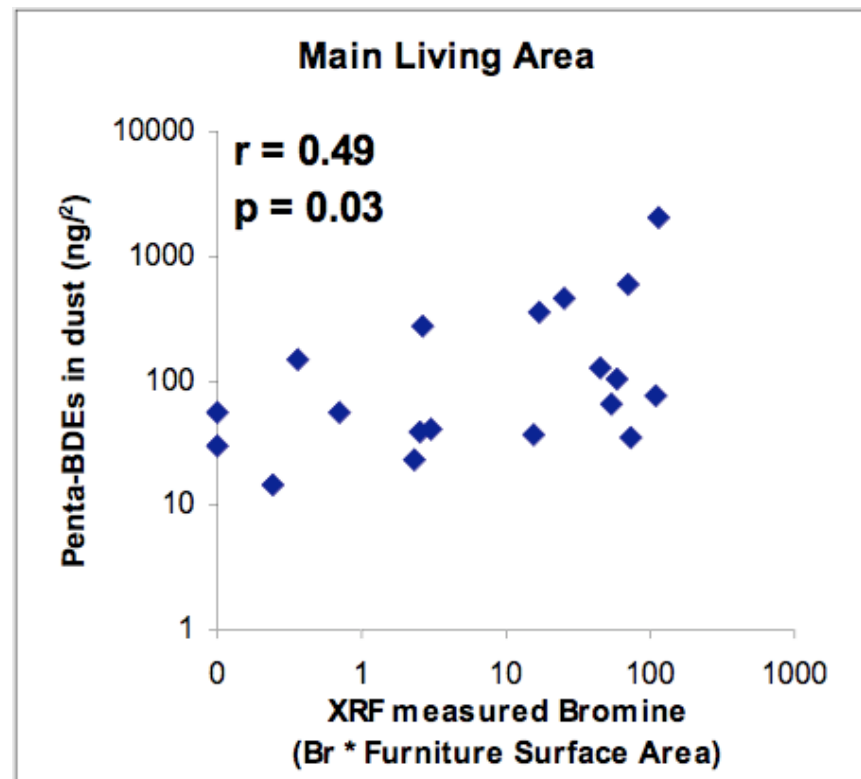
Limitation: Can't generally do furniture "biopsies"

XRF of Br as surrogate for PBDEs: greatly improves ability to predict Penta in dust

counts

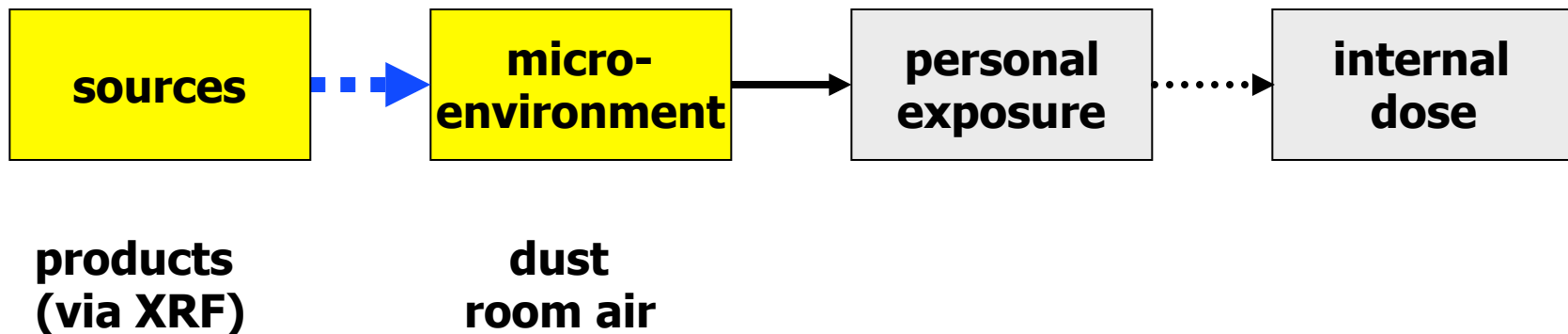


XRF



also for Deca vs. electronics

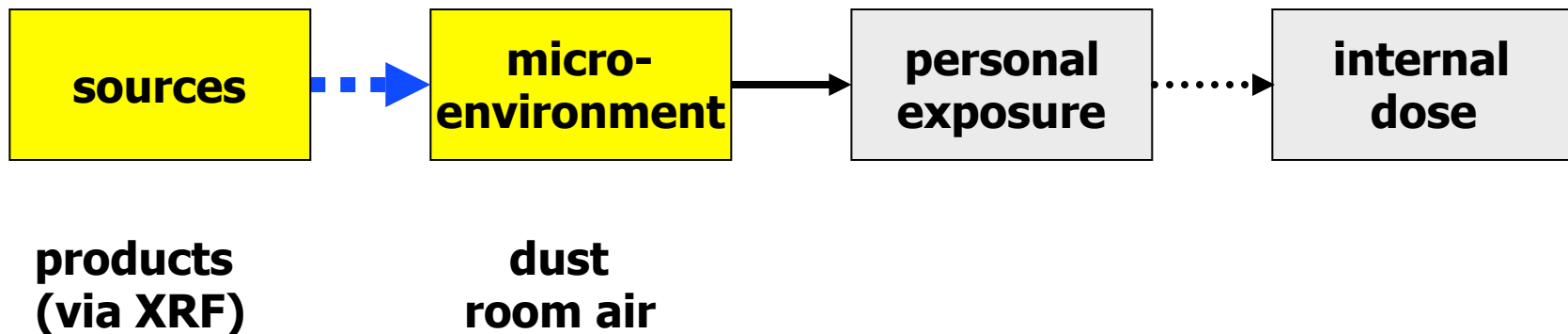
2. How are PBDEs getting out of products?



- volatilization?
- partitioning from plastic to dust ?
- physical weathering (e.g., microfragmentation) ?

Chamber experiments (difficult!) have so far provided limited results for PentaBDE, very little data for DecaBDE

2. How are PBDEs getting out of products?



- volatilization?

- partitioning from plastic to dust ?

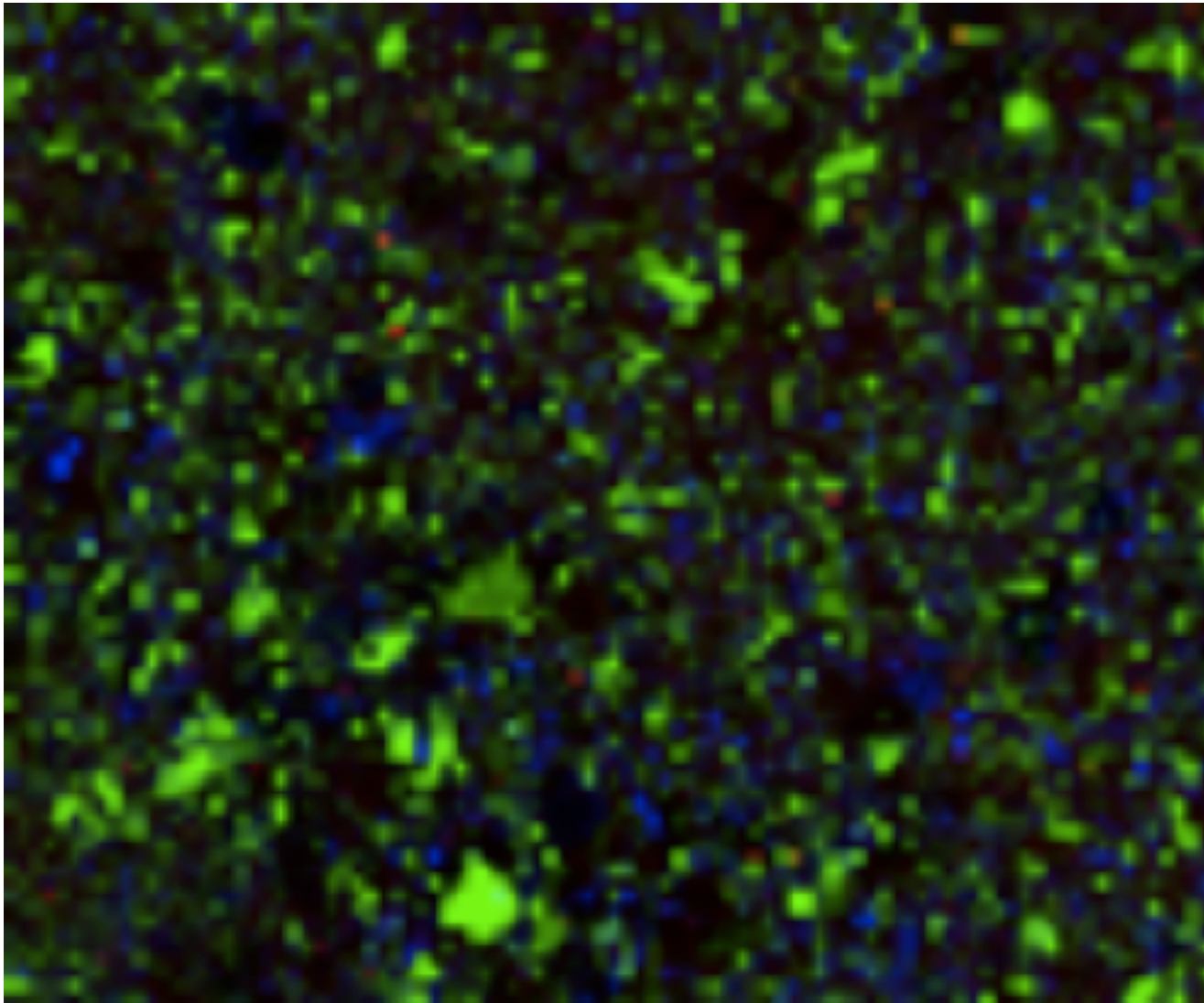
- physical weathering (e.g., microfragmentation) ?

Expect widely distributed

Expect high levels in discrete pieces of original matrix

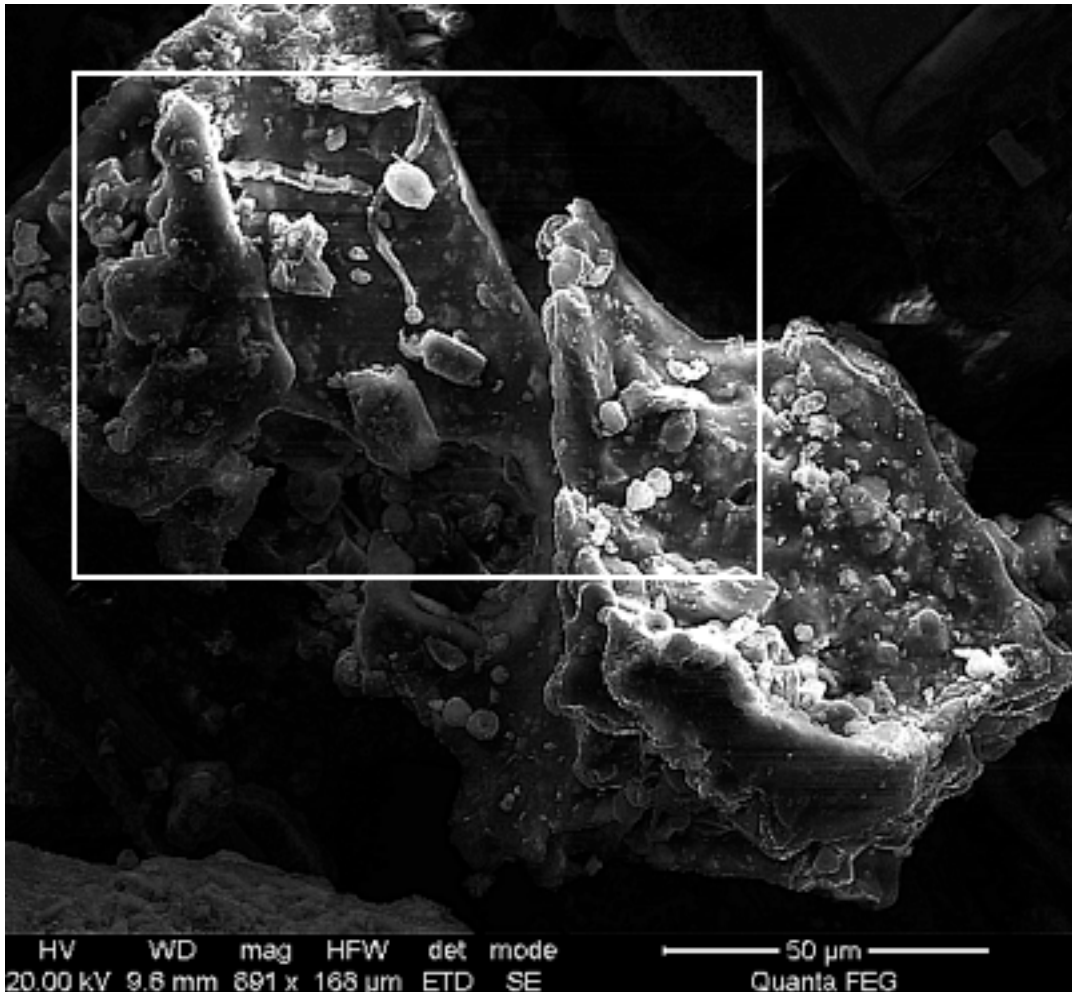
Boston house dust with high BDE209 concentrations
Micro-XRF: Bromine-containing particles widely scattered

Fe
Ca
Br

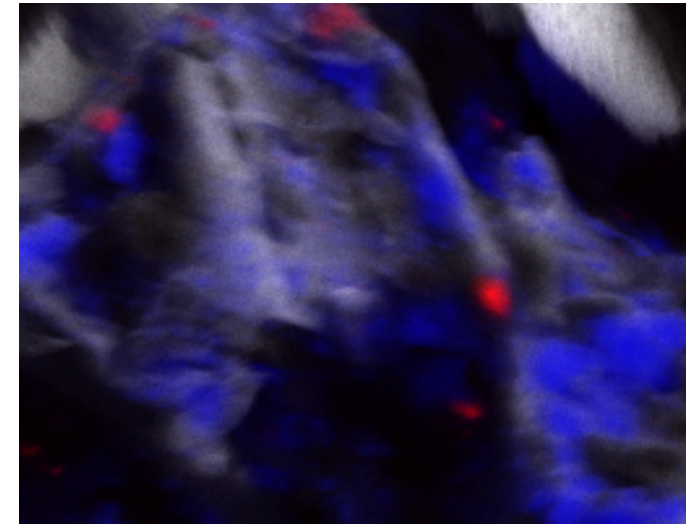


scanned size: 9.4 mm x 7.8 mm pixels: 100 um x 100 um

Bromine-containing particles are also heterogeneous

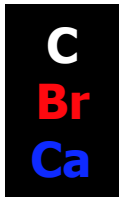


Scanning electron microscopy



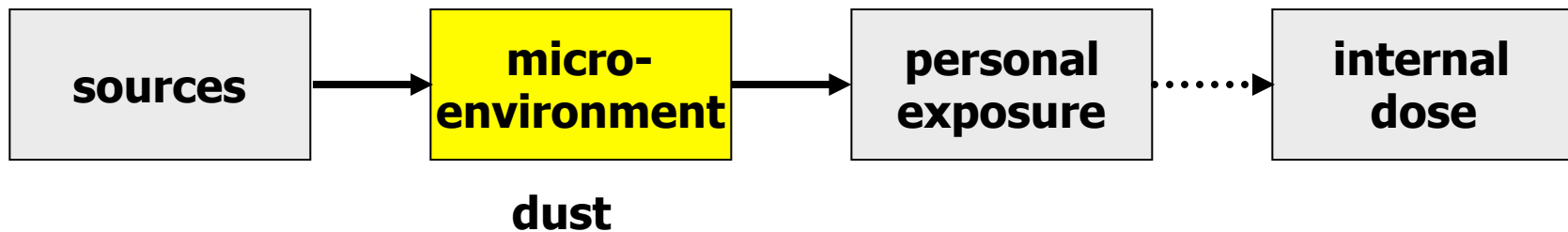
Elemental map via EDS

CaCO₃ = common plastics additive



Suggest microfragmentation, at least in this case

3. Methods for sampling dust to assess exposure



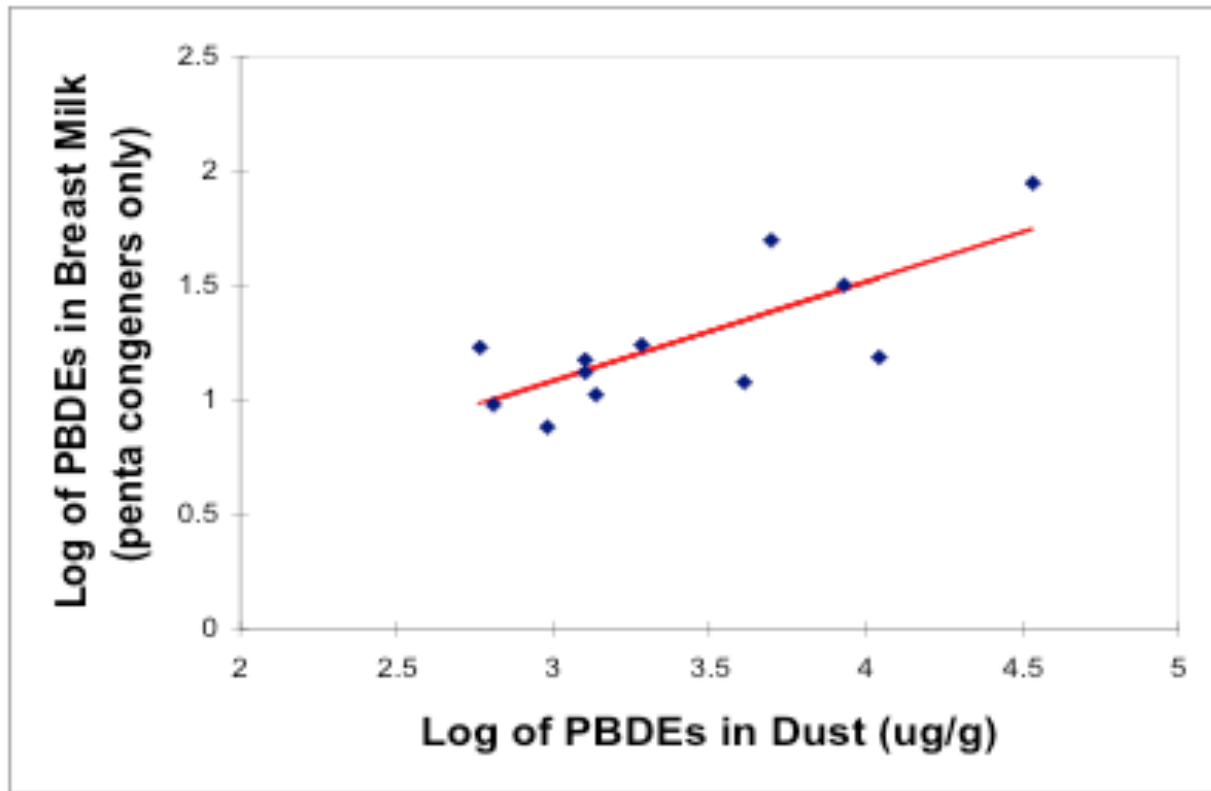
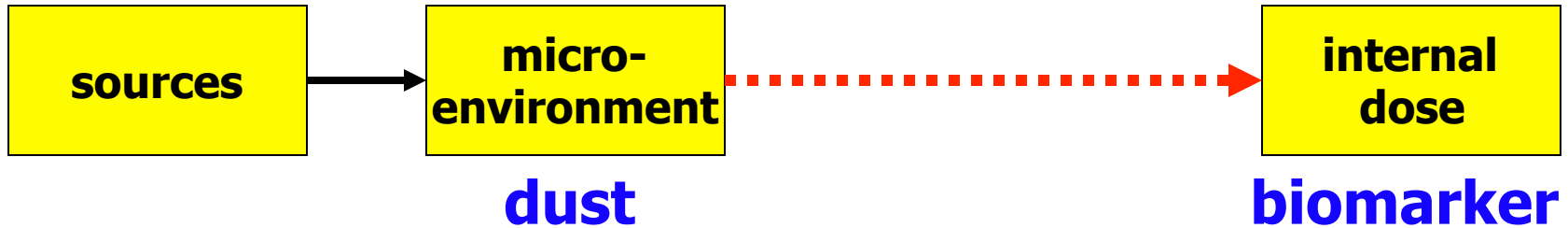
It matters how and where you sample dust in homes:

- differences between rooms
- differences between researcher-collected dust & vacuum cleaner bags

Dust concentrations significantly correlated when sampled 6-8 months apart

Best way? (depends on question)

4. Body Burden vs. Indoor Environment

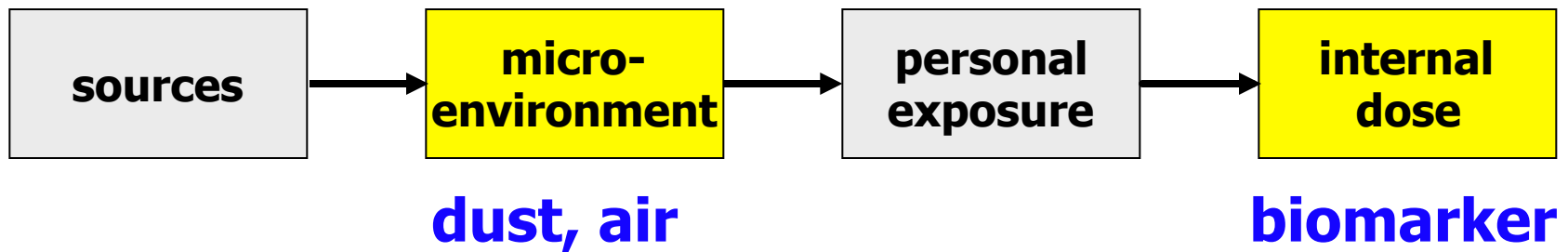


$R = 0.76$
 $p = 0.006$

**Association of penta congeners in breast milk & dust
(Boston first time mothers)**

Wu et al *ES&T* 2007

4a. *How are we exposed indoors?*



air - inhalation

air - dermal exposure

dust - ingestion

dust - dermal

Air Sampling - Area



Air Sampling - Personal



Pumps on simultaneously, after work until morning for 7 days
GFF + PUF, 2 L/min

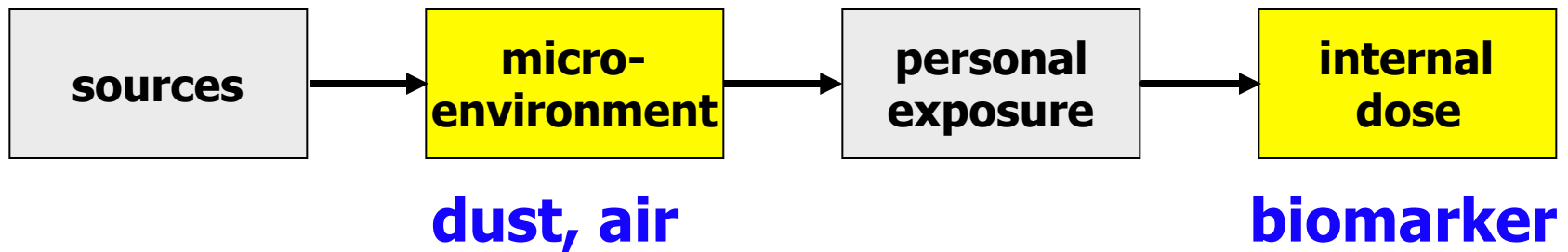
Personal Air > Room Air (primarily DecaBDE)

- **personal dust cloud?**
(“Pigpen effect”)



**But inhalation not enough to account for exposure
(based on exposure factor for inhalation)**

4b. *How are we exposed indoors?*



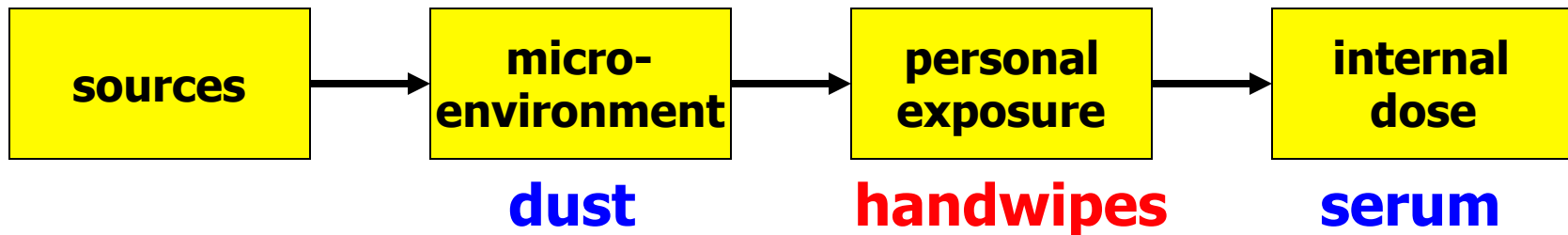
air - inhalation

air - dermal exposure

dust - ingestion

dust - dermal

Examine another (potential) intermediate step

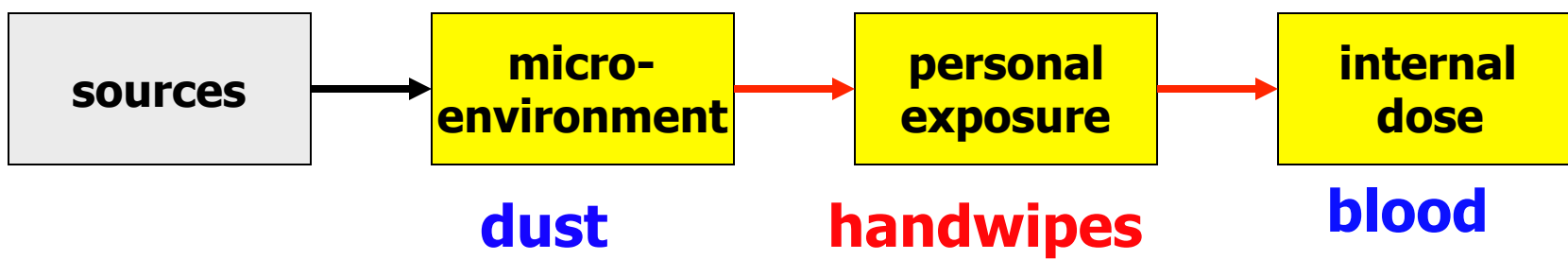


**31 people in Boston, MA
who work in offices
sampled winter 2009**

**Gauze pad +
isopropyl alcohol**



Dust <-> Handwipes <-> Biomarker



air - inhalation

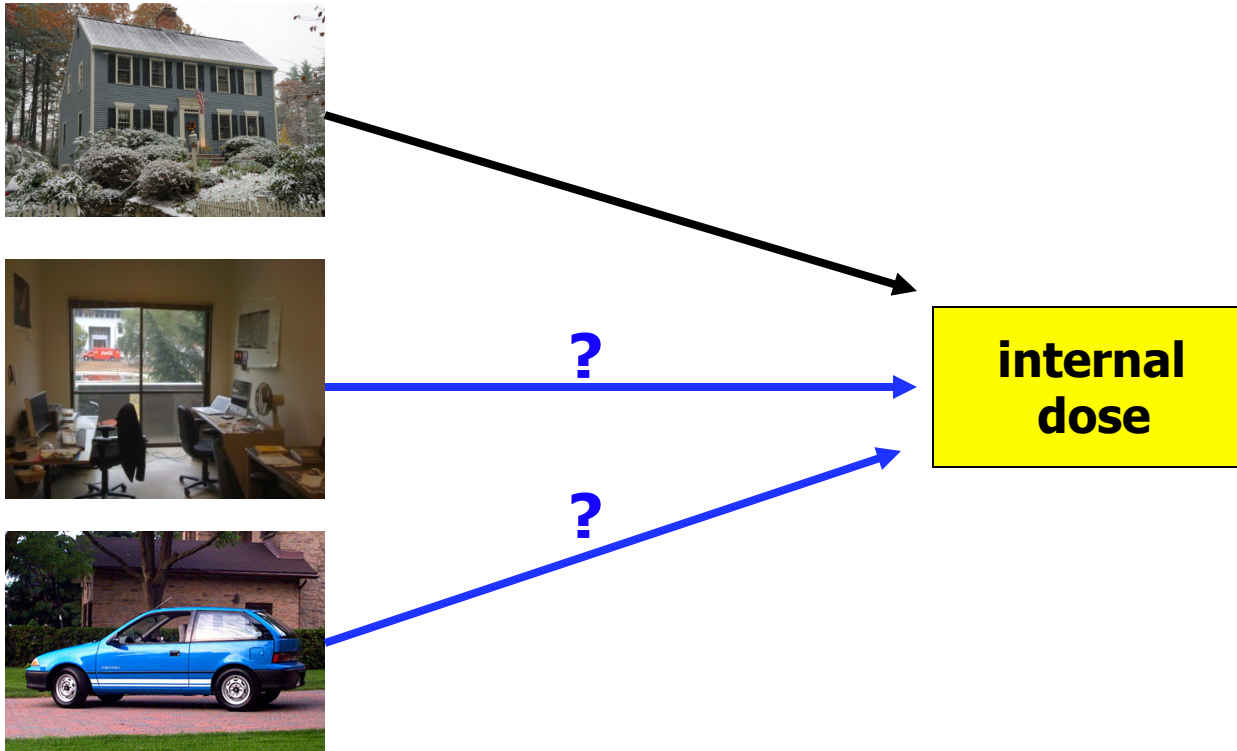
air - dermal exposure

dust - ingestion

dust - dermal

reverse causation?

**5. Most research has been done on homes.
Exposure may also occur in offices (and cars)**

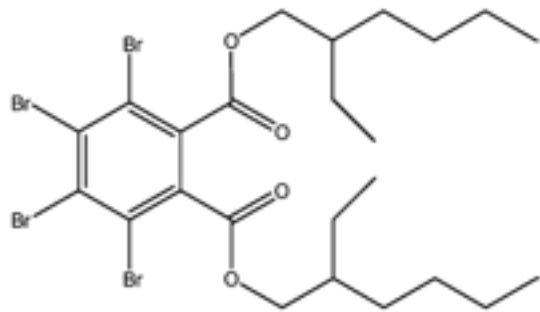


**Boston has much stricter
fire codes for furniture used
in public places (including
offices) than for homes**

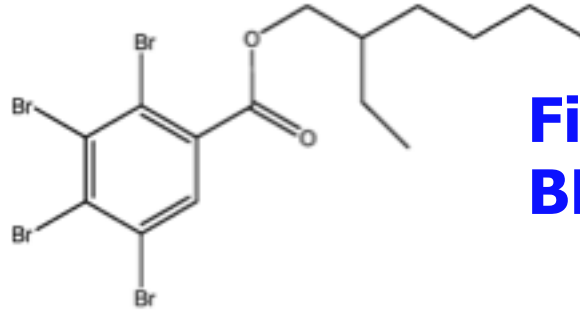


***California Technical
Bulletin 117***

Replacements for PentaBDE in USA: now found in dust at levels comparable to PBDEs

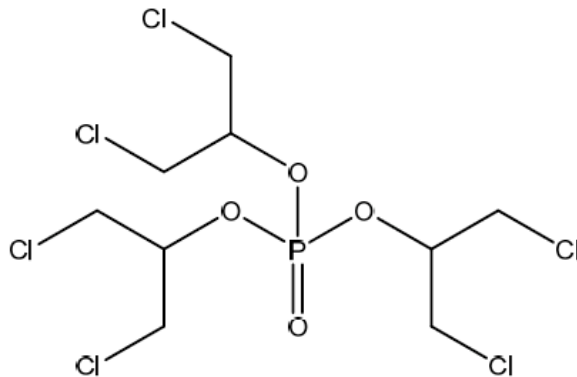


TBPH



TBB

**Firemaster 550:
BFR+OPFR**



**Tris (1,3-dichloro-2-propyl) phosphate
TDCPP, “chlorinated tris”
used in children’s sleepware in 1970s**

Stapleton et al. *ES&T* 2008,2009

Much less known about these compounds

6. Polyfluoroalkyl Compounds (PFCs)

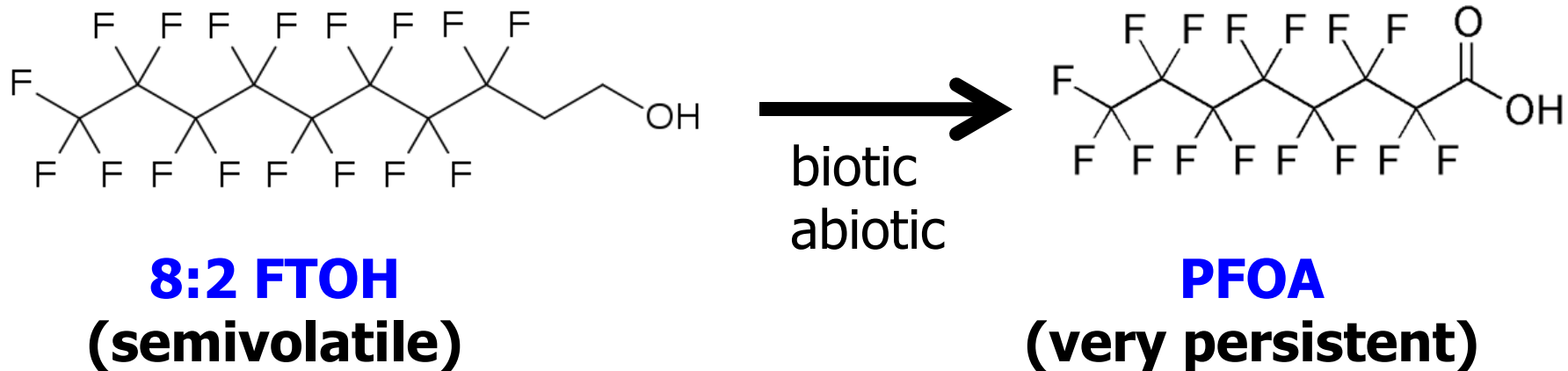
Use:

- * Used to repel water & stains (e.g., carpet & furniture)
- * Some food packaging

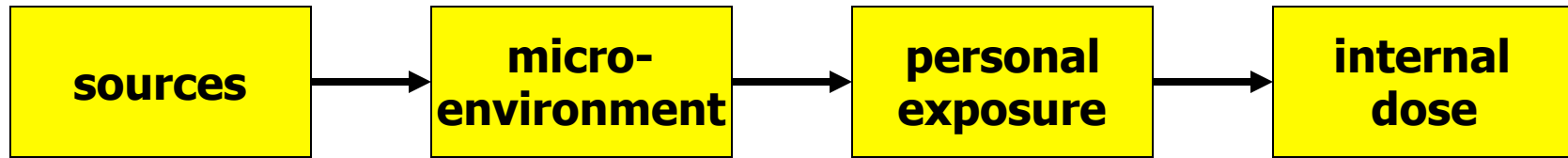
Exposure:

- Exposure hypothesized to be mainly via diet

Interconversions:



Summary



- **Useful framework**
- **Careful with exposure factors**
- **New flame retardant chemicals need screening**
- **Interconversions (8:2 FTOH->PFOA)**

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Study participants

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Antonia Calafat (CDC)
Adrian Covaci (University of Antwerp)
Jeff M. Davis (NIST)
Rob Hale (Virginia Institute of Marine Sciences)
Stuart Harrad (University of Birmingham)
Wendy Heiger-Bernays (Boston University)
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James Millette (MVA Scientific Consultants)
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Mahiba Shoeib (Environment Canada)
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Veronica Vieira (Boston University)
Cindy de Wit (Stockholm University)

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BFR 2011

12th Workshop on Brominated
and Other Flame Retardants

June 6-7, 2011
Boston University
Boston, MA USA

www.bfr2011.org