

The Fate of PBDEs in the (Indoor) Environment

Tom Webster, DSc
Associate Professor & Associate Chair
Department of Environmental Health
Boston University School of Public Health

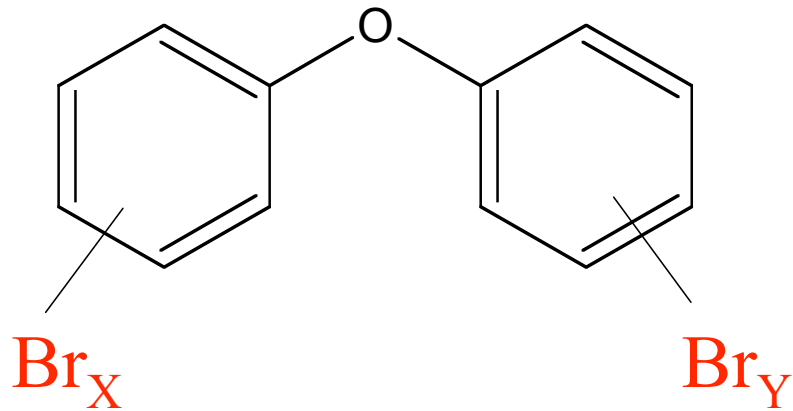


***Fire Retardants & their Potential
Impact on Fire Fighter Health***

NIST

30 September 2009

PBDEs: Polybrominated diphenyl ethers



- **209 possible congeners**
- **structurally related to PCBs & PBBs...**
- **persistent, bioaccumulative, toxic**

Use of PBDEs as fire retardants

penta **furniture (polyurethane foam)**



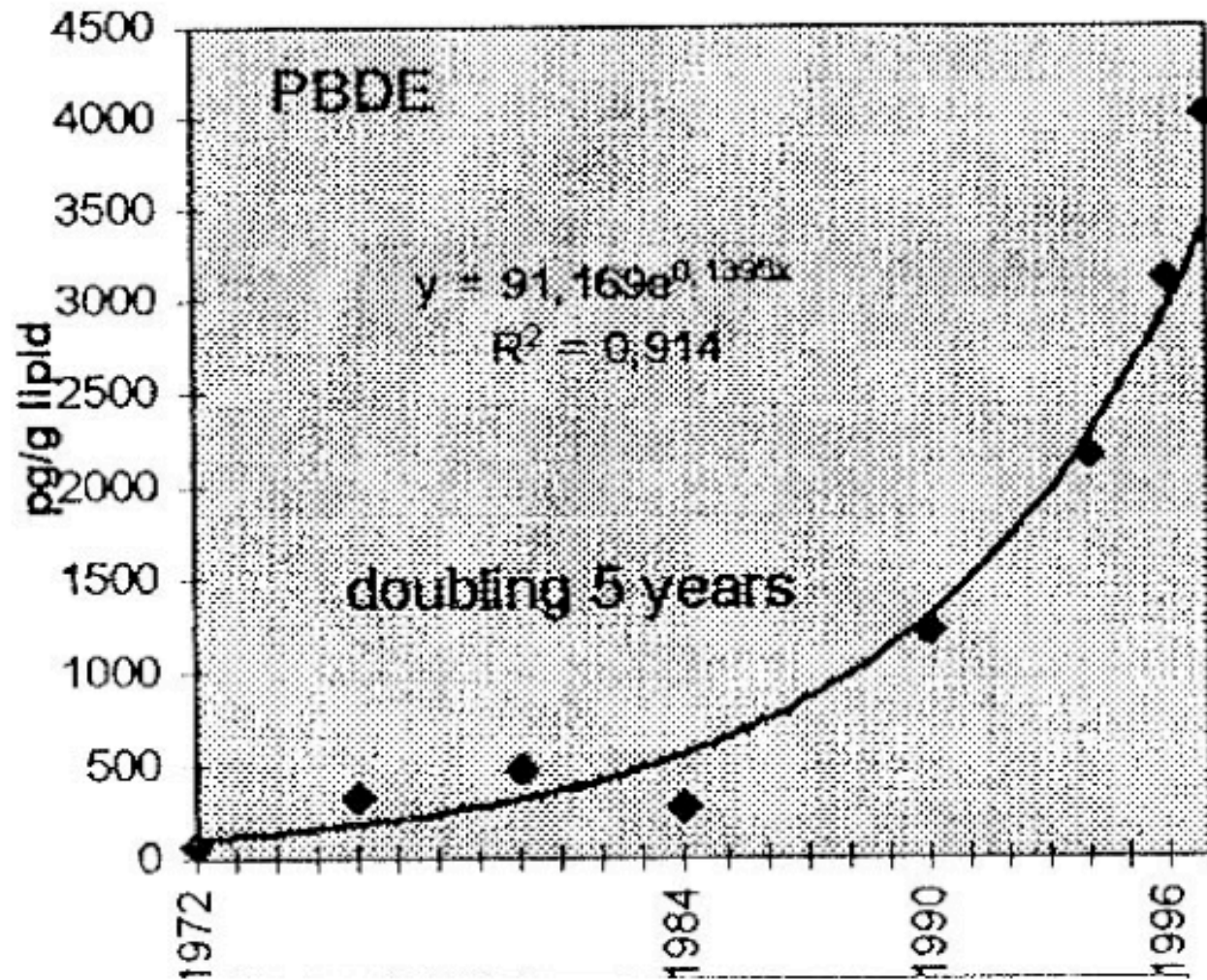
octa **electrical hard plastic**

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



- up to 10-20 % by weight
- *not* chemically bound to the plastic
- penta and octa added to Stockholm Convention 2009
- No longer manufactured but still present: lbs/home?
also recycled foam?

PBDE levels in human milk in Sweden (1998)



Norén and Meironyté 1998

U.S./Canadian > 10 times higher than Europe human levels & increased since 1970s

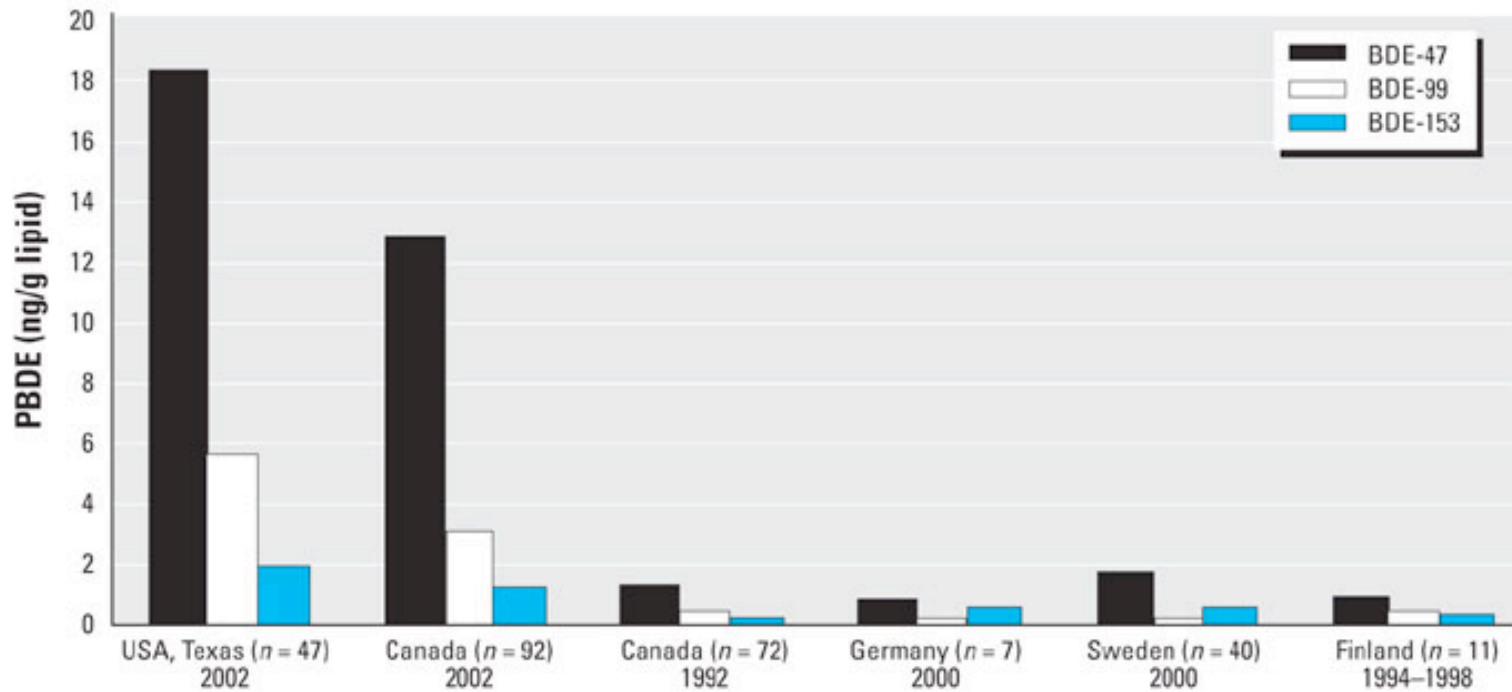


Figure 3. Median concentrations (ng/g lipid) of BDE-47, BDE-99, and BDE-153 in human milk from different countries. Data from Ryan et al. (2002) and Ryan and Patry (2001) for Canada, from Schroeter-Kermani et al. (2000) for Germany, from Noren and Merionyte (2000) for Sweden, and from Strandman et al. (2000) for Finland.

Schechter et al (2003)

Much higher North American use of penta

PBDE levels vary considerably in populations

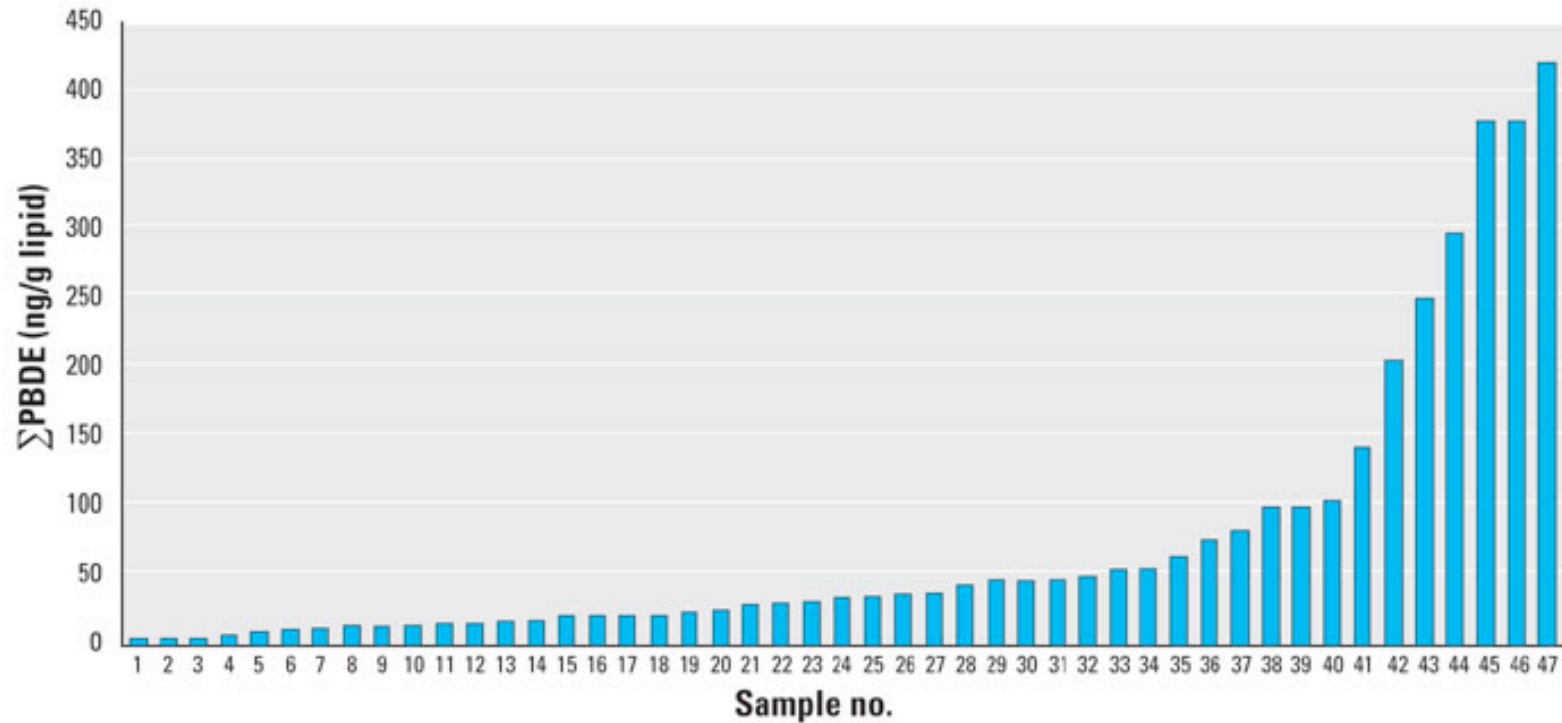
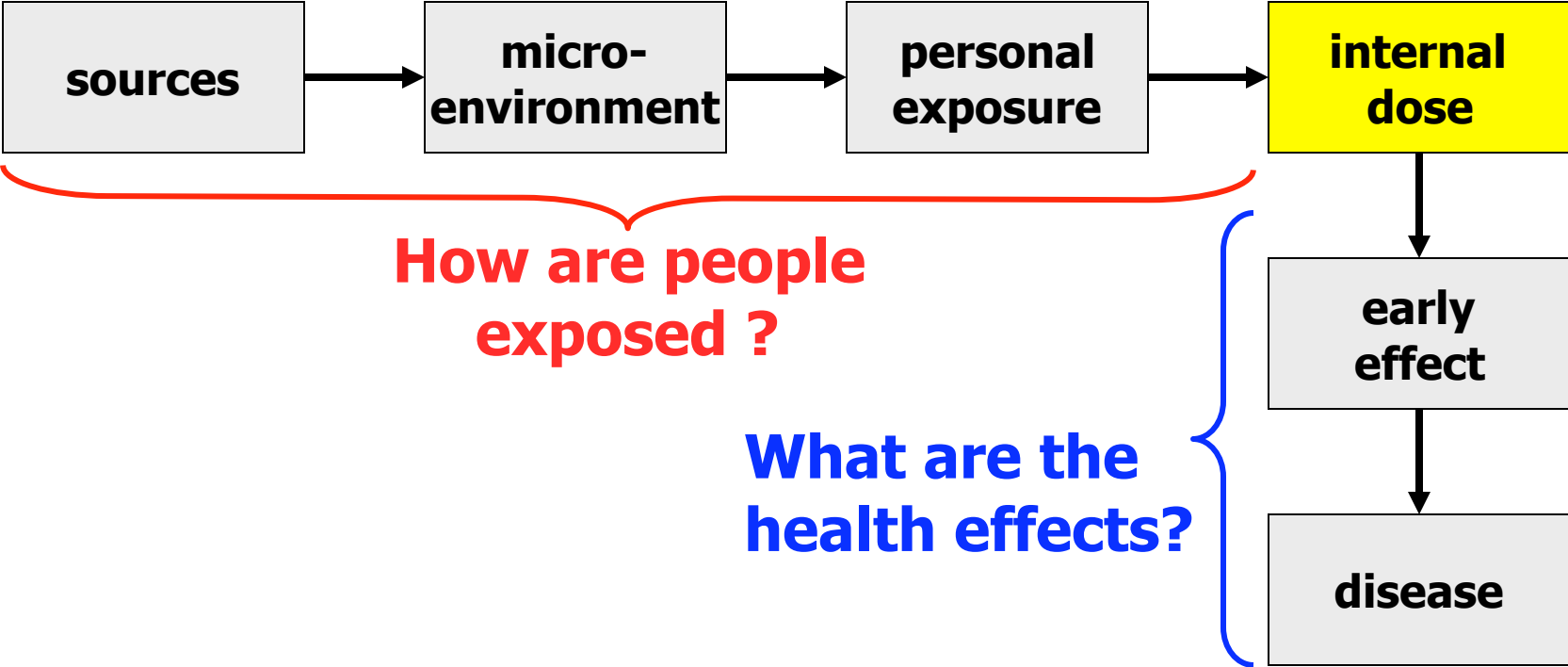


Figure 2. PBDE concentrations in individual U.S. human milk samples from 2002 (ng/g lipid).

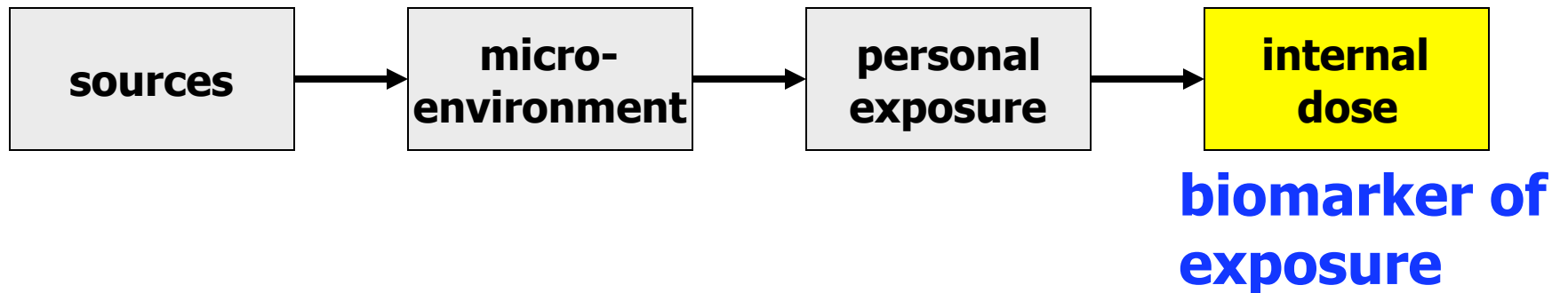
Schechter et al (2003)

**In everybody, but large variation.
Small number of people have very high levels—why?**

Exposure Assessment Paradigm: Source to Disease



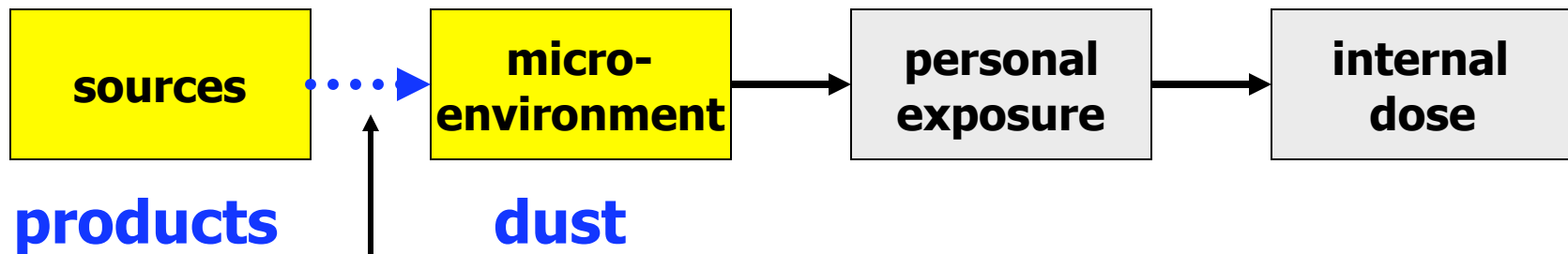
How are people exposed?



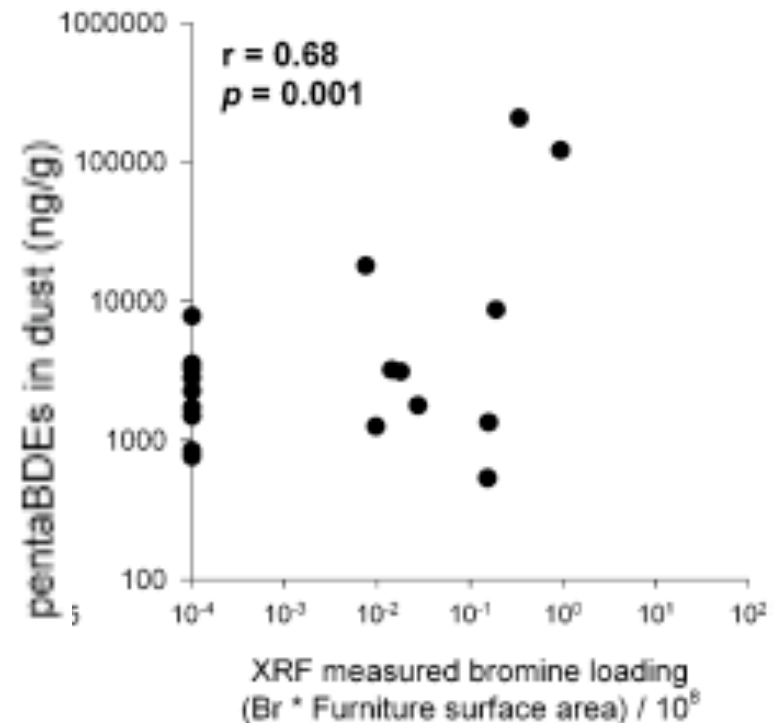
Goal: Understand how people are exposed to PBDEs along complete pathway from product to person

**focus on our research:
North America, non-occupational**

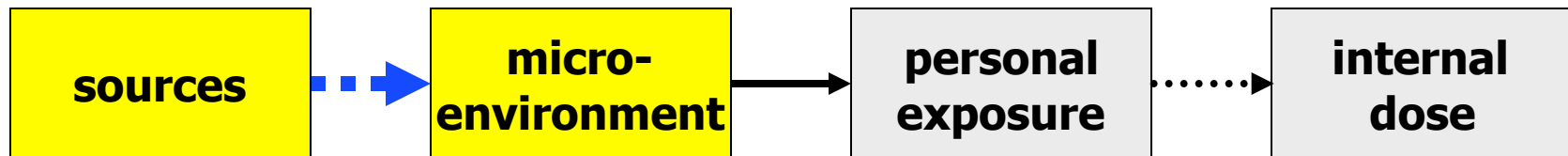
1. PBDEs in dust are associated with products



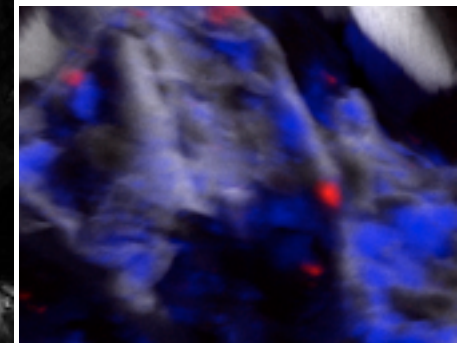
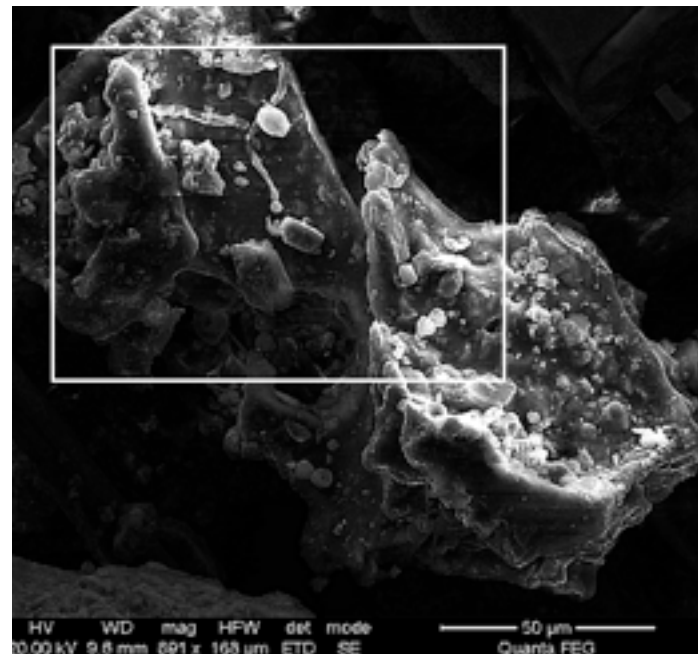
Dust concentrations doesn't correlate with product counts, but with Br via XRF (X-ray fluorescence), a surrogate for PBDEs (BFRs) in products.



2. PBDEs are likely getting out of products via both volatilization & weathering of plastics



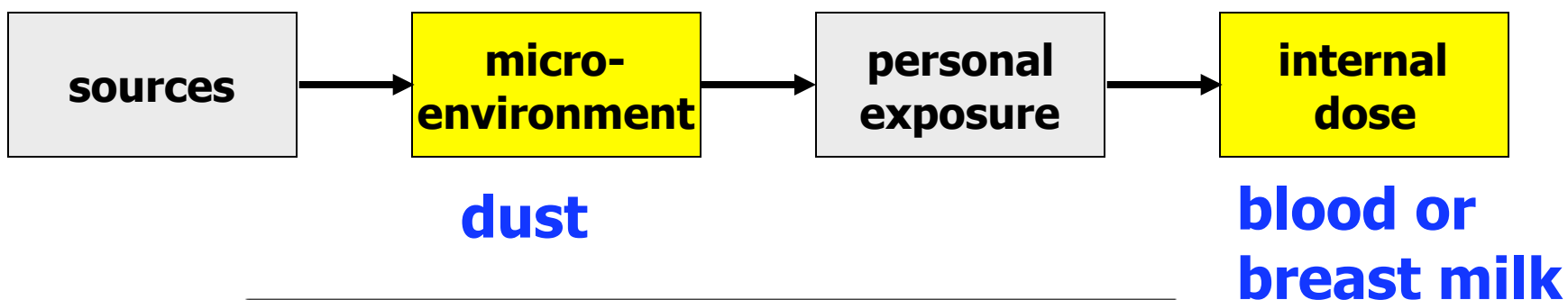
- penta via volatilization: limited chamber experiments
- deca via weathering: initial work with scanning electron microscopy



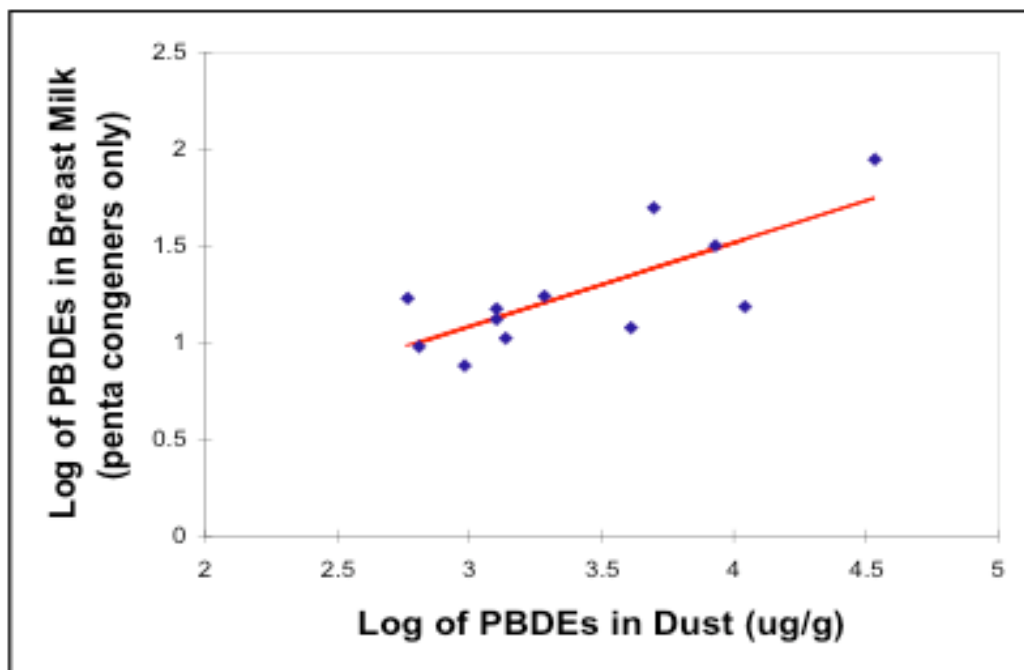
C
Br
Ca

CaCO₃=plastic additive

3. Dust is an important route of exposure



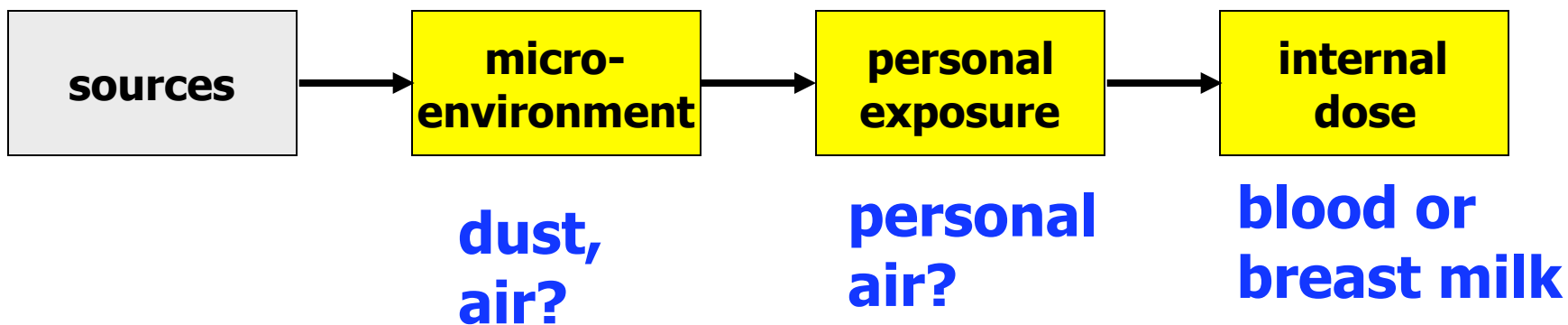
Penta



$R = 0.76$
 $p = 0.006$

Consistent with exposure factor approach

4. Dust exposure > air (in homes)

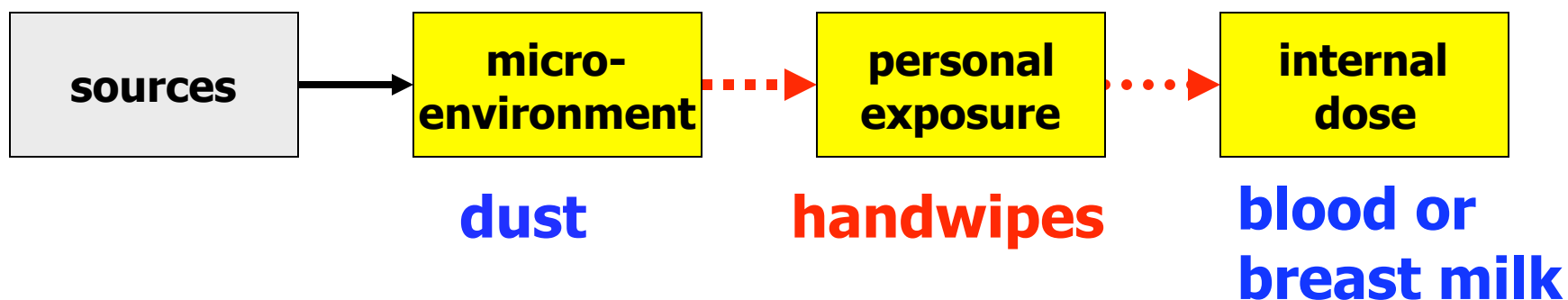


- Inhalation appears minor except occupational?
- Personal air > room air

“personal cloud”



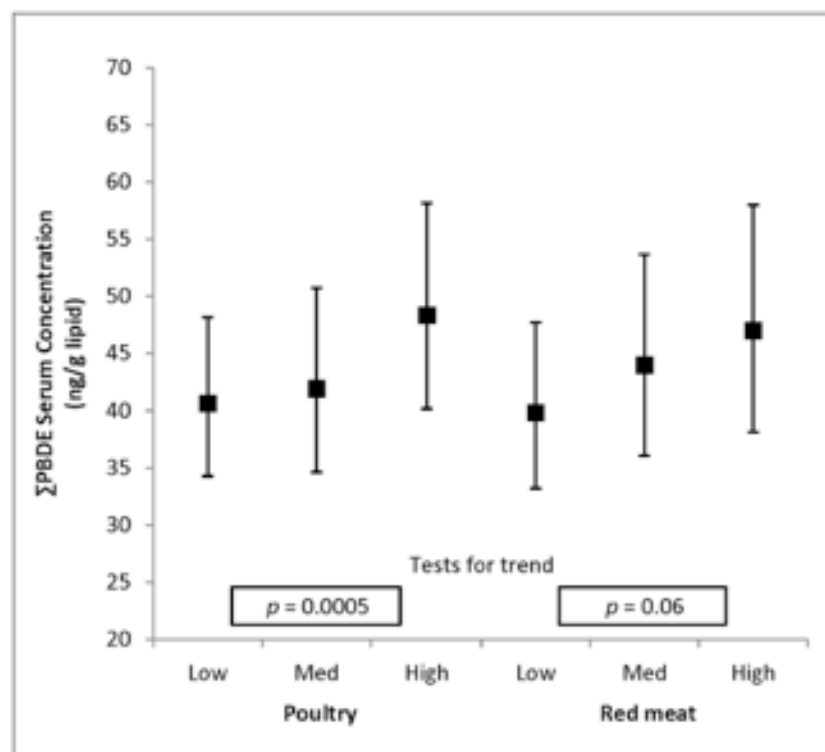
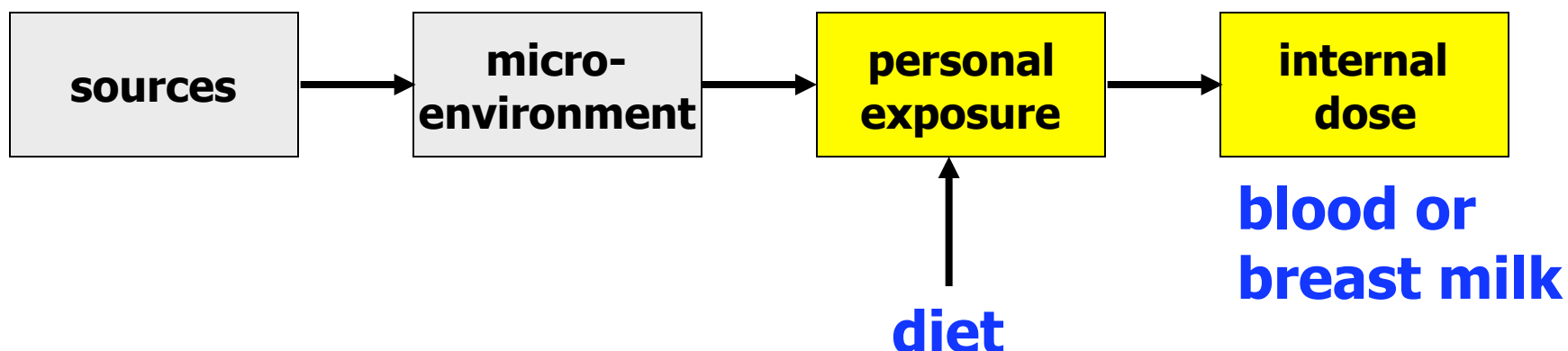
5. Dust exposure: Hand-to-mouth, dermal?



N=33	PBDE
detected	100%
median	129 ng
range	3-1982 ng

- **Can measure PBDEs on hands**
- **Next steps: Link handwipes to dust & biomarker**

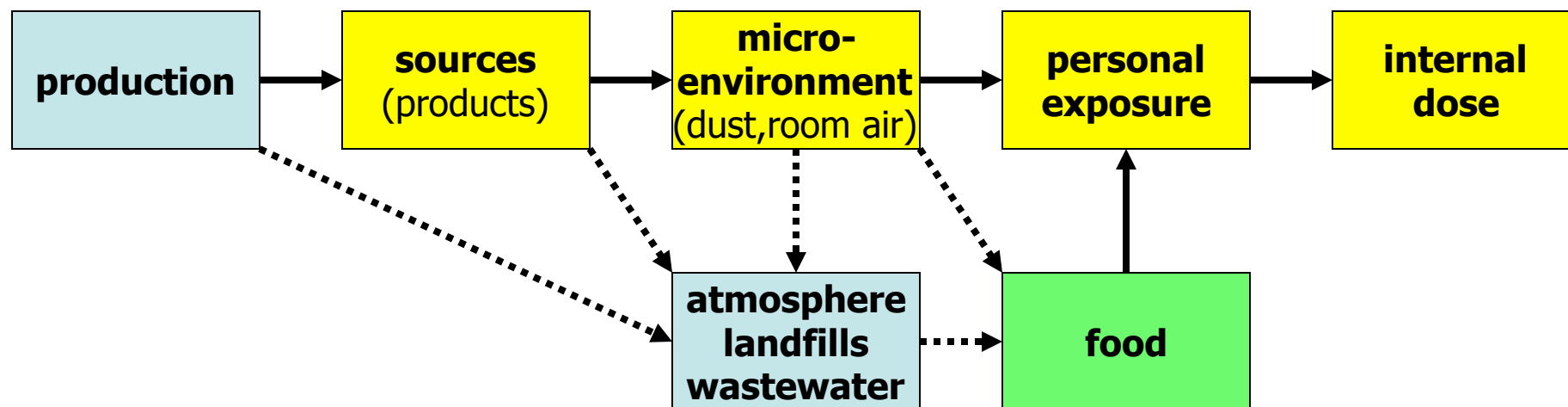
6. Diet is also an important route of exposure



Penta in serum associated with meat consumption in general US population

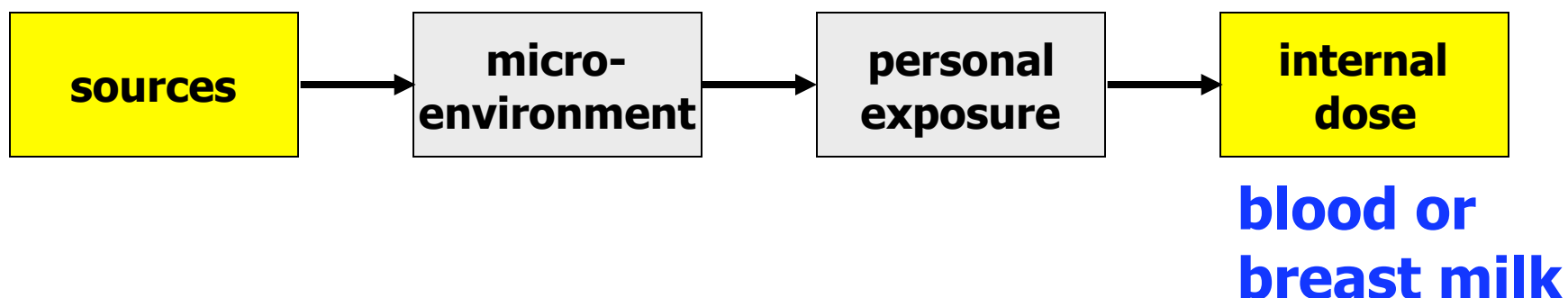
Dairy, fish: weaker

Bigger picture & food contamination



- **Main pathways of food contamination?**
- **Urban environment as source to wider environment?**

7. PBDE exposure and fire regulations



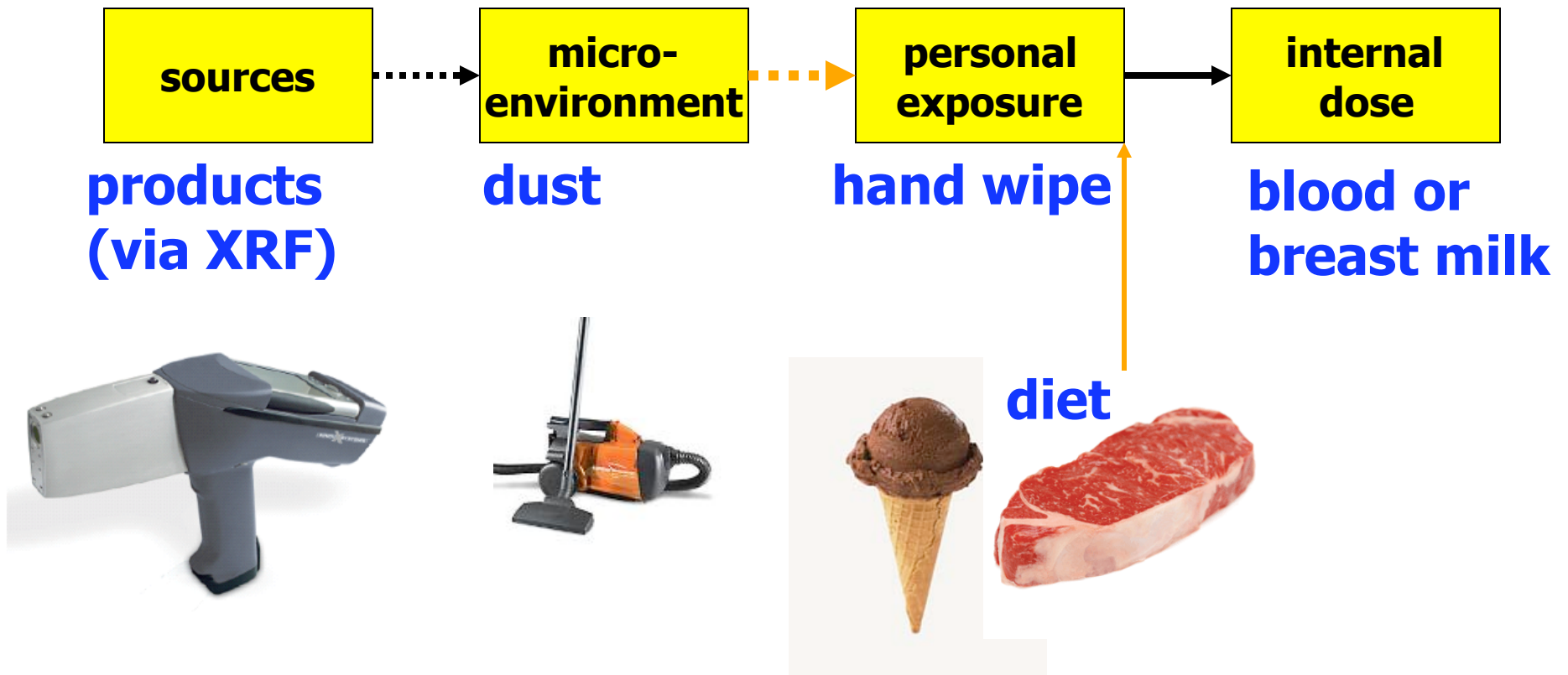
Penta exposure higher where furniture FR regs stricter?

Penta in serum higher in CA (Zota et al 2008)

not control for diet

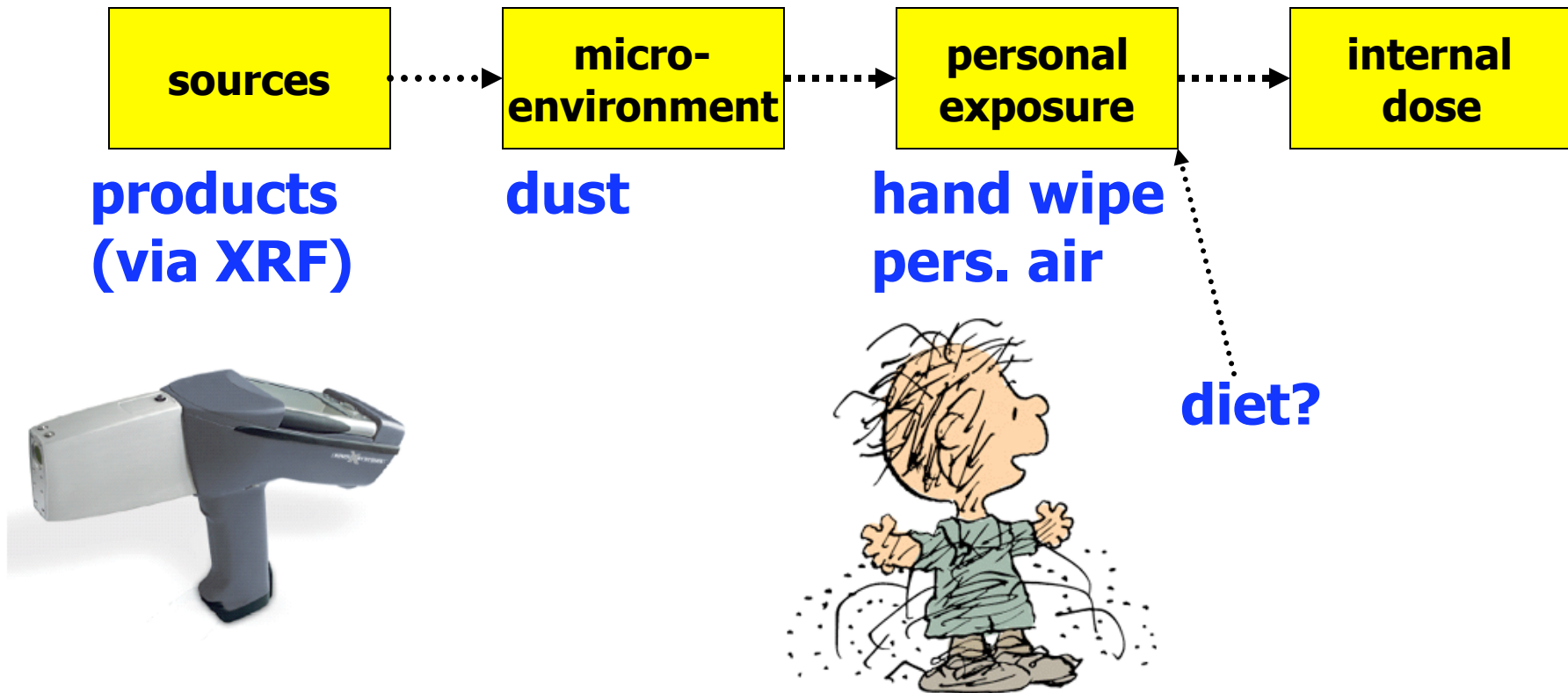
some evidence that CA dust levels are elevated

Penta: levels in dust related to products exposure via diet and indoor environment (dust)



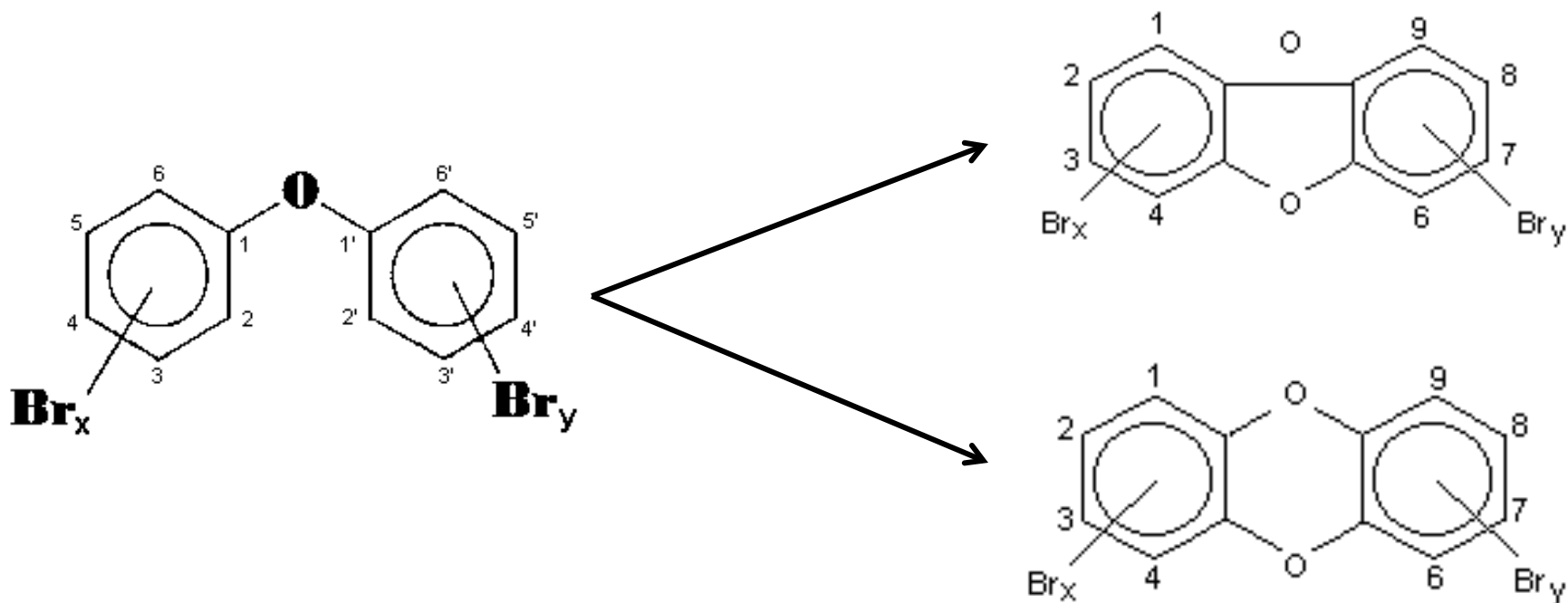
Need to better understand personal exposure to dust
Dust vs. diet: relative importance
Replicate in other groups

Deca: less well understood



- **Dust a likely route of exposure, not yet tied to body burden**

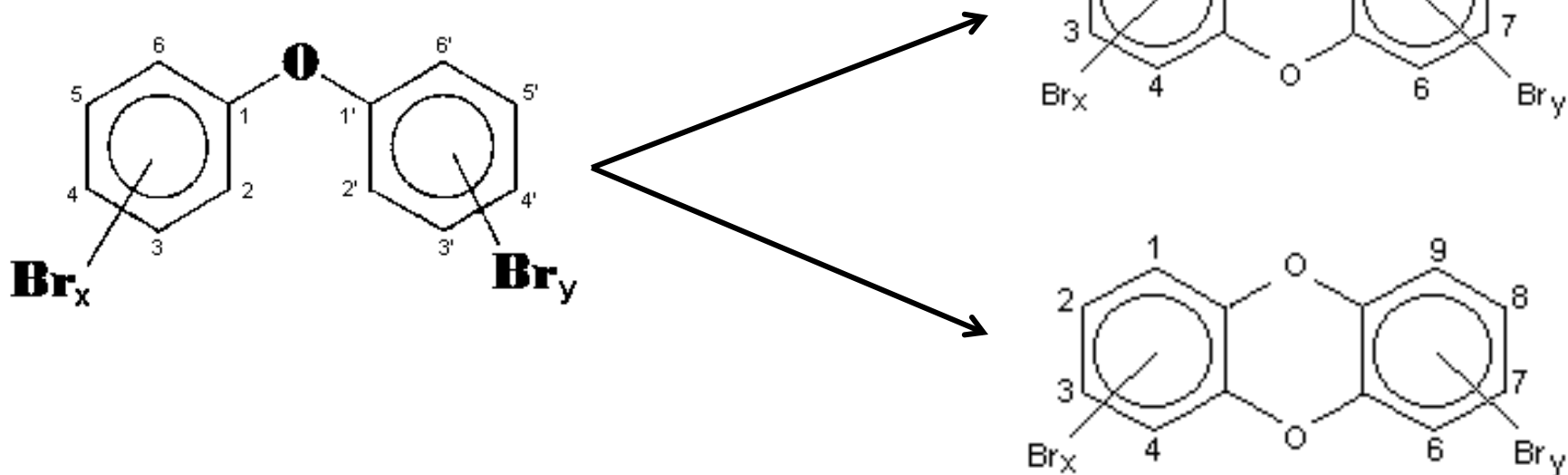
Combustion of PBDEs (& other BFRs) produces brominated dioxins and dibenzofurans



- Also bromo-chloro mixed versions
- Extremely high levels at ewaste sites in China

e.g., Weber 2003, 2009

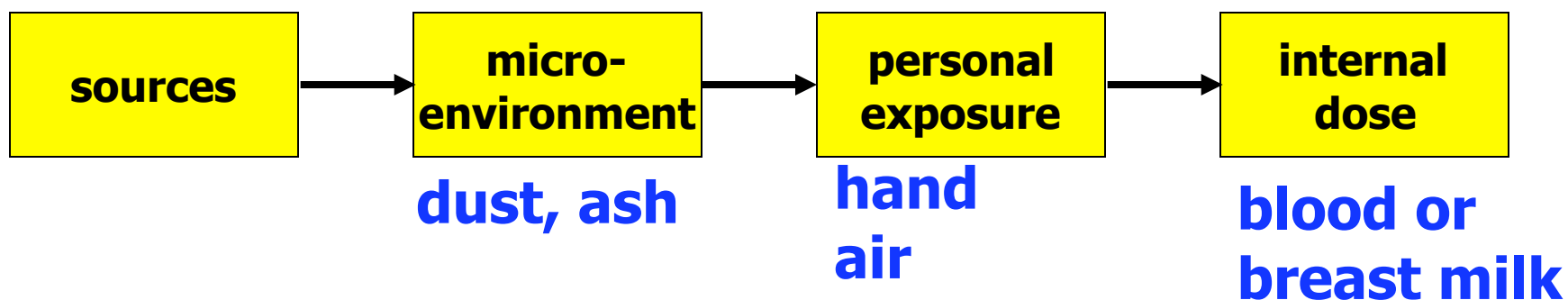
Fires: PBDEs (& other BFRs) produce brominated dioxins and dibenzofurans



- House fires
- Found on fire fighters clothing

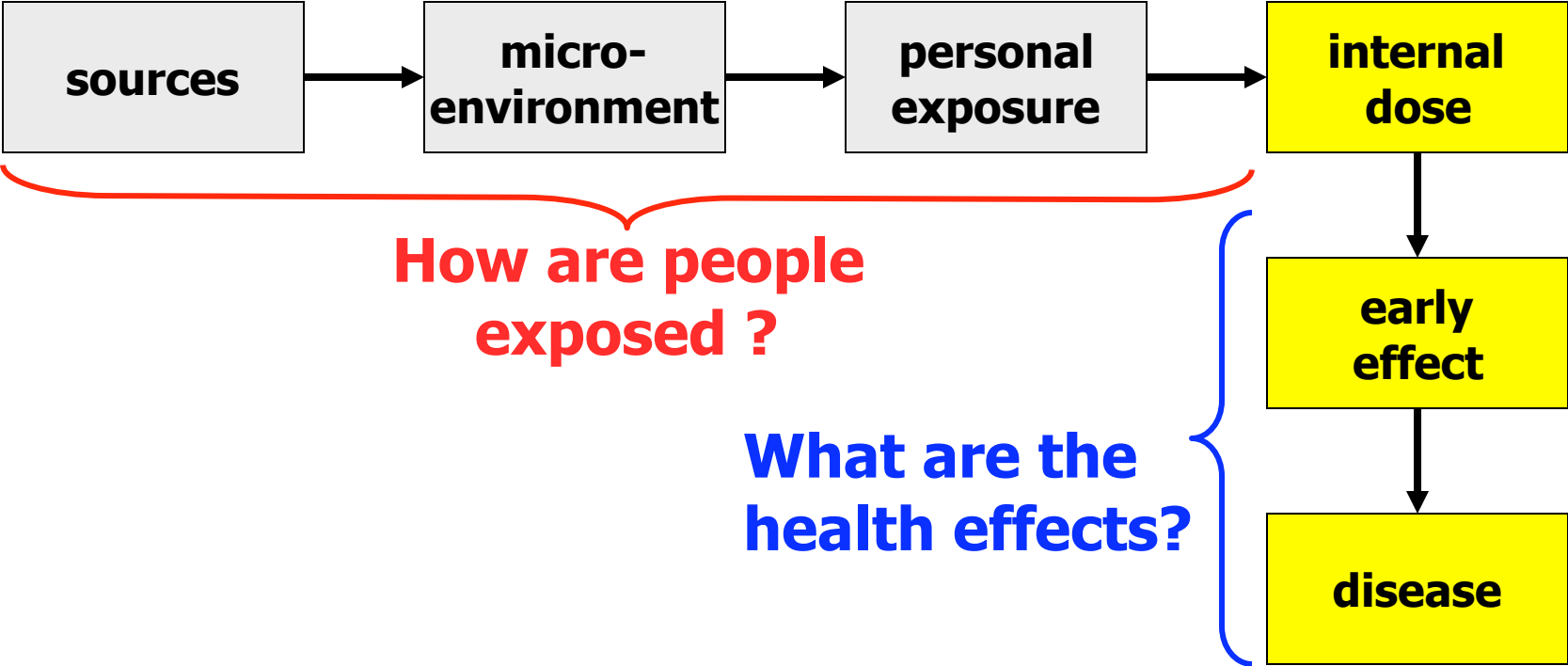
e.g., Weber 2003, Ebert 2003, Litten 2003, Takechi 2009

Exposure of Fire Fighters to PBDEs, brominated dioxins and dibenzofurans



- **Exposure likely via dust/ash, air**
- **Studies of fire fighter body burdens?**

Exposure Assessment Paradigm: Source to Disease



PBDE Toxicology

(selected, mostly rats & mice, depends on congener)

endocrine disruption

thyroid

anti-androgen (OH-metabolites?)

developmental neurotoxicology

reproductive effects

ovarian changes

decreased sperm, epididymis weight

delayed puberty

Some effects seen at levels not that different from those found in some people.

e.g., Birnbaum & Staskal 2004, McDonald 2005

Health-related PBDE research on humans

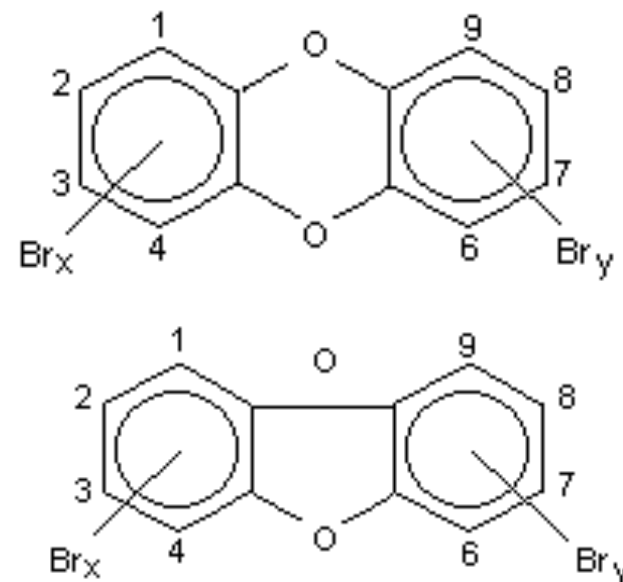
- testicular cancer (Sweden, Hardell et al 2005)
- decreased birthweight (Taiwan, Chao et al 2007)
- cryptorchidism (Scandinavia, Main et al 2007)
- infant thyroid (USA, Herbstmann et al 2008)
- developmental neurotoxicity (Netherlands, Roze 2009)

- adult thyroid (Sweden, Hagmar et al 2001)
- sperm, adult males (Japan, Akutsu et al 2008)
- thyroid, adult males (USA, Turyk et al 2008)
- hormones, adult males (USA, Meeker et al 2009)

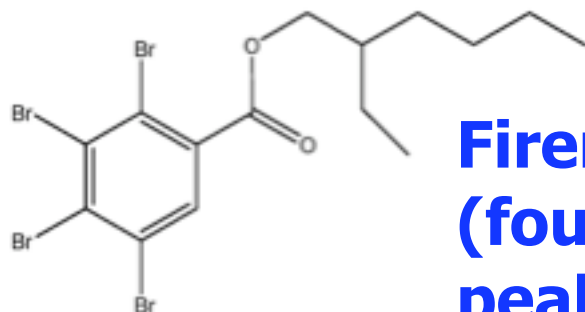
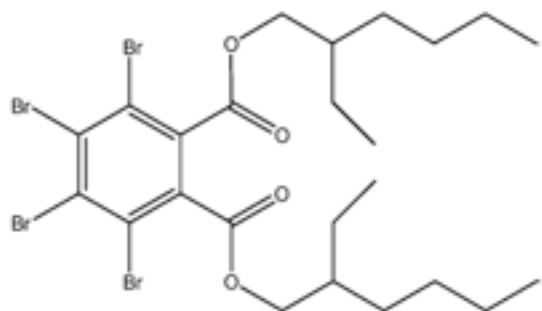
**Growing evidence for Penta effects in general population
More under way**

Brominated dioxins and dibenzofurans

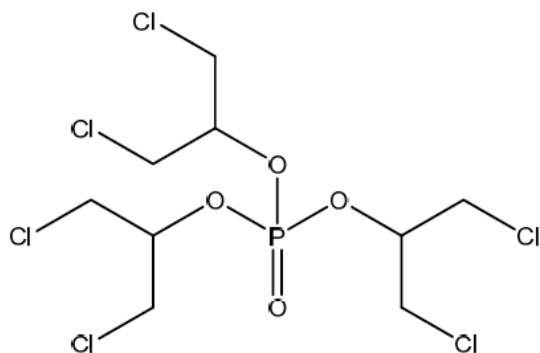
- Estimated as toxic as “regular” dioxins (chlorinated)
- All “dioxin-like” compounds thought to act via common mechanisms
- Dioxin-like toxicology:
 - endocrine disruption
 - reproductive system
 - immune system
 - developing organisms...
- TCDD considered a “known human carcinogen”



Replacements for PentaBDE: now found in dust



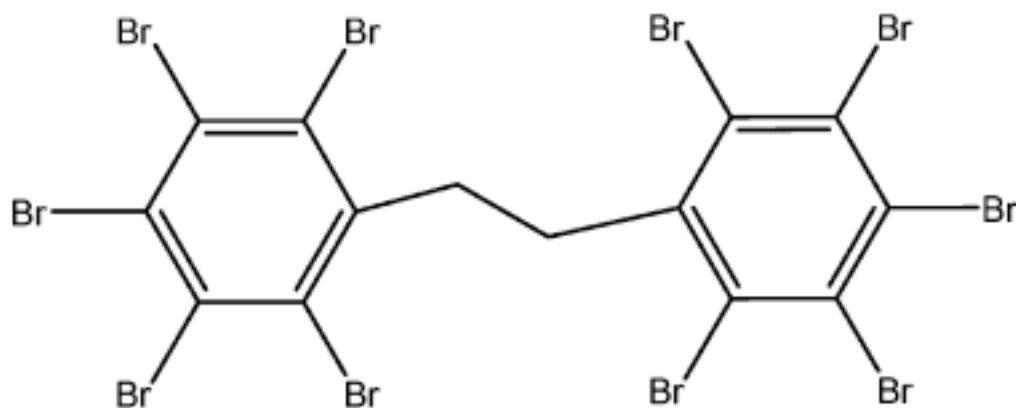
Firemaster 550
(found via unknown peaks on chromatogram)



Tris (1,3-dichloro-2-propyl) phosphate
"chlorinated tris"
used in children's sleepware in 1970s
weak mutagen
CPSC "probable human carcinogen"

Less understood than PBDEs

A replacement for deca:



**Decabromodiphenyl
ethane**

We found it in US house dust.

Others found it in wildlife from North America & Asia.

**What are the benefits
and risks of flame
retardants?**

Acknowledgements:

**Heather Stapleton (Duke University)
Mike McClean (Boston University SPH)**

Joe Allen, Nerissa Wu

**Deb Watkins, Alicia Fraser, Courtney Walker, Jessica Nelson
Stephanie Chan, Colleen Makey**

**David Holbrook (NIST), Jeff M. Davis (NIST), Olaf Pöpke (Ergo-
Eurofins), Rob Hale (VIMS), James Millette (MVA), Stuart Harrad
(U. Birmingham), Adrian Covaci (U. Antwerp), Susan Klosterhaus
(SFEI), Alex Konstantinov (Wellington), Arlene Blum (GSPI), John
Meeker (U. Michigan), Phil Brown (Brown U.), Cindy de Wit
(Stockholm U.)**

Study participants

National Institute of Environmental Health Sciences (NIEHS)

Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, La Guardia M, McClean MD, Webster TF. Human exposure to PBDEs: Associations of PBDE body burdens with food consumption and house dust concentrations. *Environ Sci Technol* 2007; 41(5): 1584-1589.

Allen JG, McClean MD, Stapleton HM, Nelson JW, Webster TF. Personal exposure to polybrominated diphenyl ethers (PBDEs) in residential indoor air. *Environ Sci Technol* 2007; 41(13): 4574-4579.

Stapleton HM, Kelly SM, Allen JG, McClean MD, Webster TF. Measurement of Polybrominated Diphenyl Ethers on Hand Wipes: Estimating Exposure from Hand to Mouth Contact. *Environ Sci Technol* 42(9): 3329-34.

Allen JG, McClean MD, Stapleton HM, Webster TF. Linking PBDEs in House Dust to Consumer Products using X-ray Fluorescence (XRF). *Environ Sci Technol* 2008; 42 (11): 4222-4228

Allen JG, McClean MD, Stapleton HM, Webster TF. Critical Factors in Assessing Exposure to PBDEs via House Dust. *Environ Intern* 2008; 34: 1085-1091.

Stapleton HM, Allen JG, Kelly S, Konstantinov A, Klosterhaus S, Watkins D, Mcclean MD, Webster TF. Alternate and New Brominated Flame Retardants Detected in US House Dust. *Environ Sci Technol* 2008; 42 (18), 6910-6.

Wu N, McClean MD, Brown P, Aschengrau A, Webster TF. Participant Experiences in a Breastmilk Biomonitoring Study. *Environmental Health*; 2009, 8:4

Webster TF, Harrad S, Millette JR, Holbrook RD, Davis JM, Stapleton HM, Allen JG, McClean MD, Ibarra C, Abdallah MA, Covaci A. Identifying transfer mechanisms and sources of decabrominodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. *Environ Sci Technol* 2009; 43(9): 3067-3072

Fraser AJ, Webster TF, McClean MD. Diet contributes significantly to the body burden of PBDEs in the general U.S. population. *Environ Health Perspect*. In press.

Stapleton HM, Klosterhaus S, Eagle S, Fuh J, Meeker JD, Blum A, Webster TF. Detection of organophosphate flame retardants in furniture foam and US house dust. *Environ Sci Technol* 2009. In press.