Exposure to PBDEs from Product to Person (or…Wash Your Hands!)

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SCHOOL OF
PUBLIC HEALTH

California Dept. Toxic Substances Control
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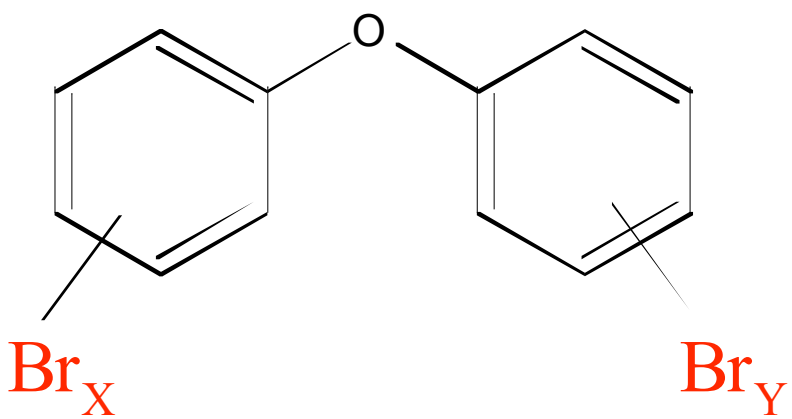
Polybrominated diphenyl ethers (PBDEs)



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

Use of PBDEs as flame retardants

Penta furniture (polyurethane foam) mainly used in N. America, CA & similar regulations

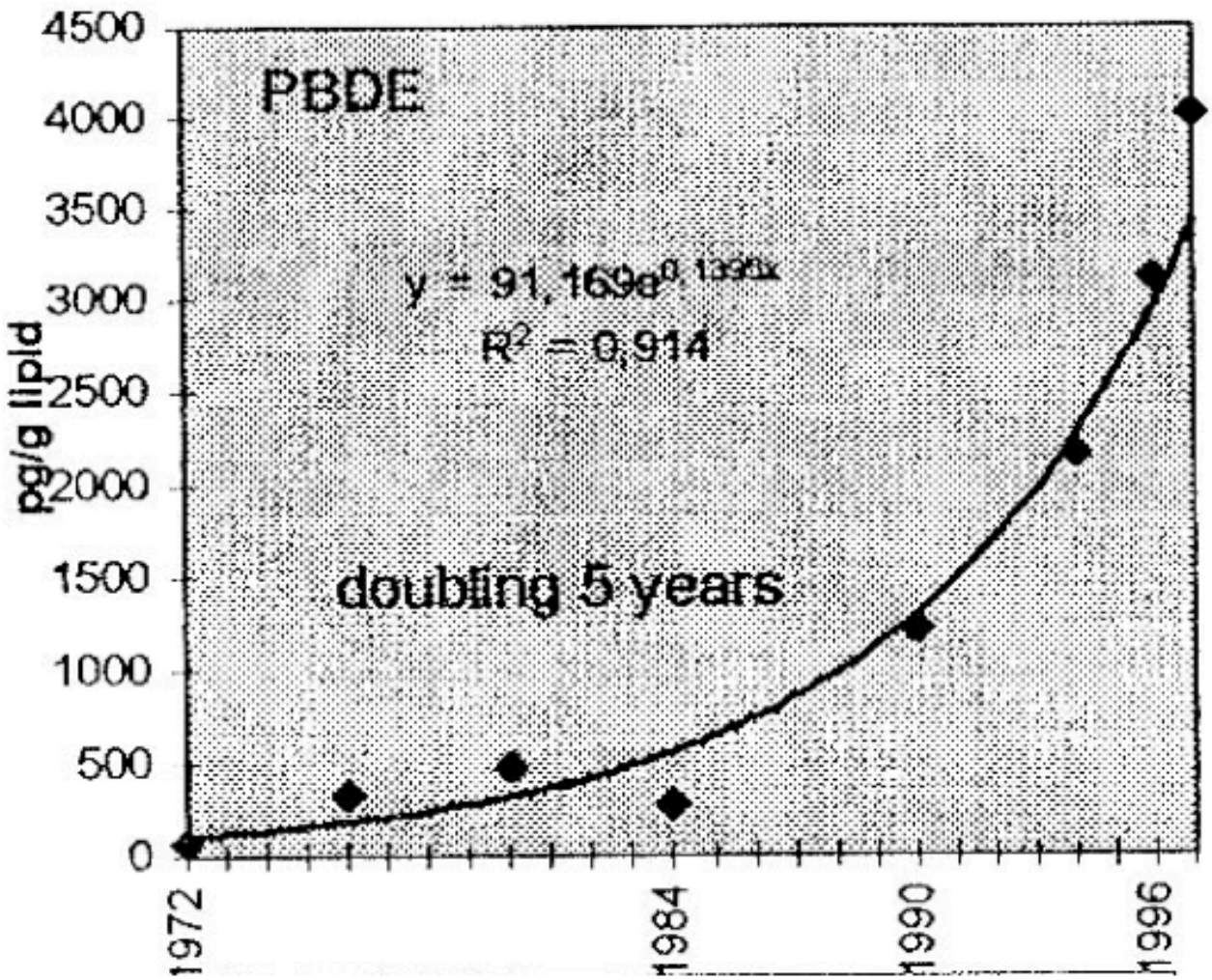
Octa electrical hard plastic (minor)

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

% levels by weight
***not* chemically bound to the plastic**
Penta & Octa manufacturing: US phase-out 2005; added to Stockholm Convention 2009
Deca phase-out in USA 2013
Large reservoir: continuing exposure

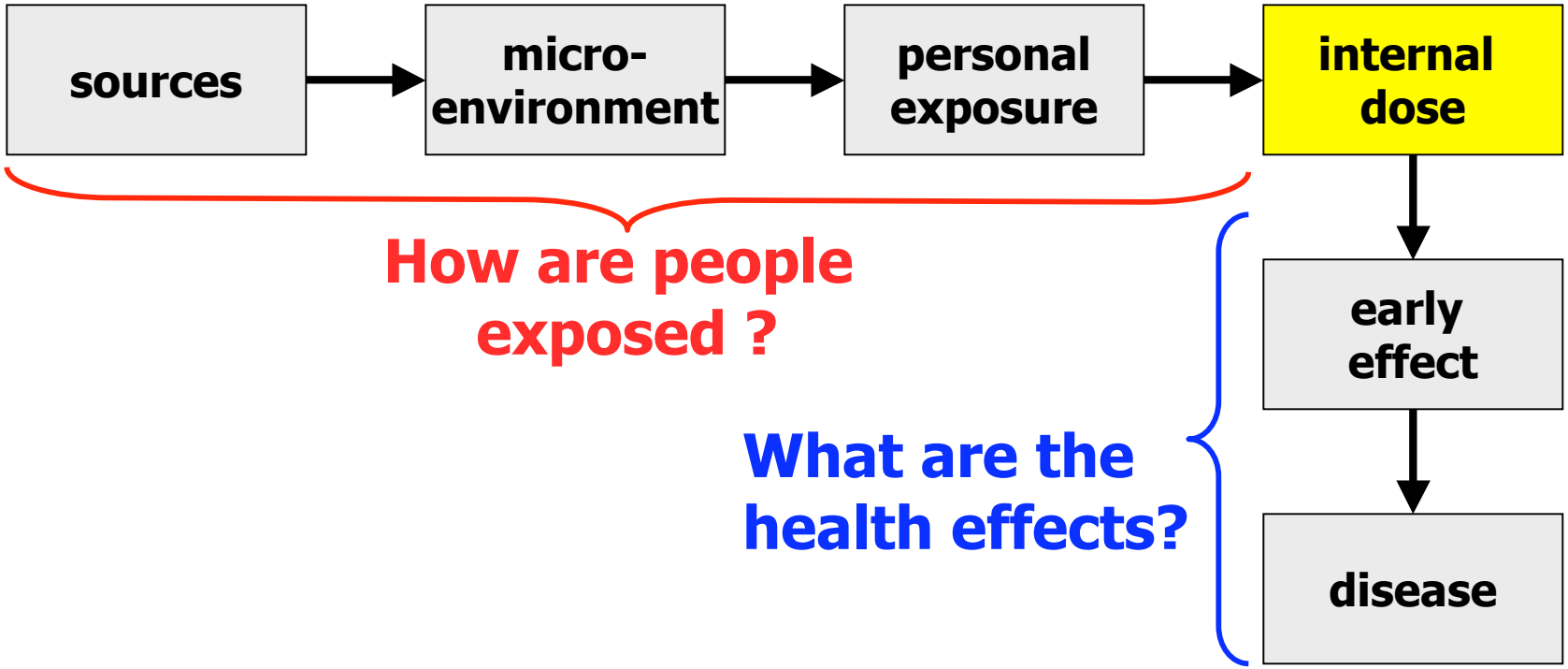
The graph that launched a thousand papers…

PBDE levels in human milk in Sweden (1998)



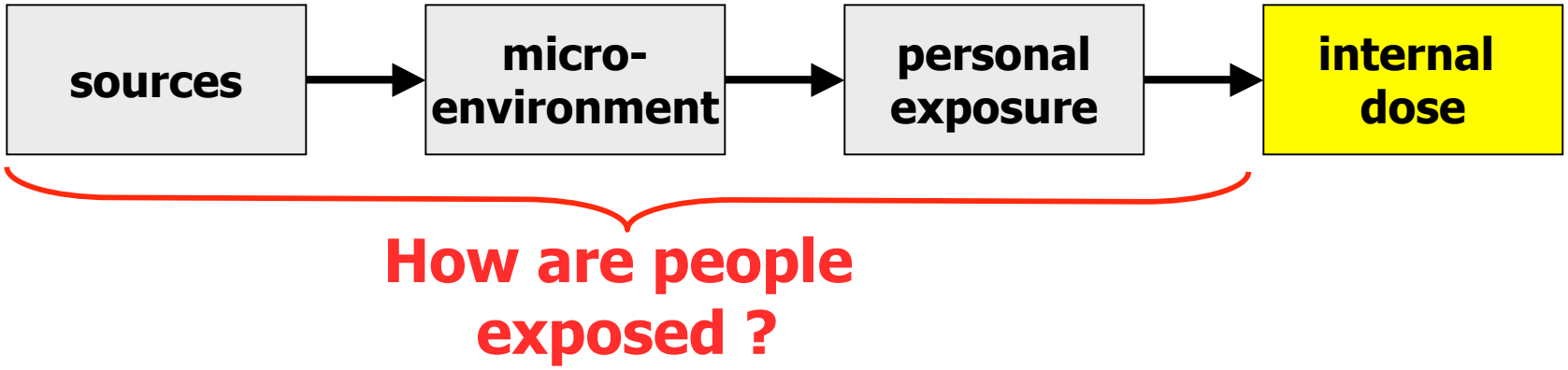
Norén and Meironyté 1998

Exposure Assessment Paradigm: Source to Disease



The PBDE story begins in the middle

Exposure Assessment Paradigm: Source to Disease



Today: North American context

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

food*

occupational

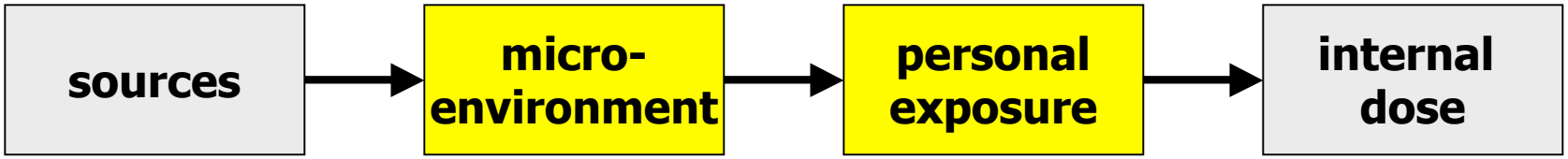
*** by analogy with PCBs & dioxin, logKow**
→ numerous studies of food; Wu et al 2007; Fraser et al 2009

PBDEs are used in consumer products… and show up in house dust

e.g., Stapleton et al 2005

Hypothesis: Indoor environment --e.g., house dust--may be an important source of exposure

Indoor environment as an exposure route for PBDEs



- **Exposure factor approach:**

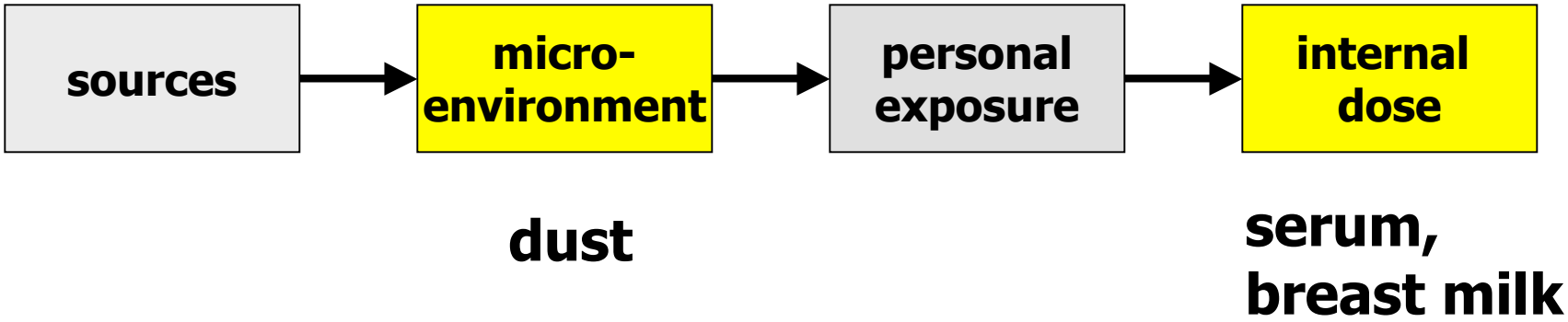
  media concentration X exposure factor

  dust concentration X dust ingestion

Representative? How & where should we sample dust?

<u>Very</u> poorly known, especially for adults

Indoor environment as an exposure route for PBDEs

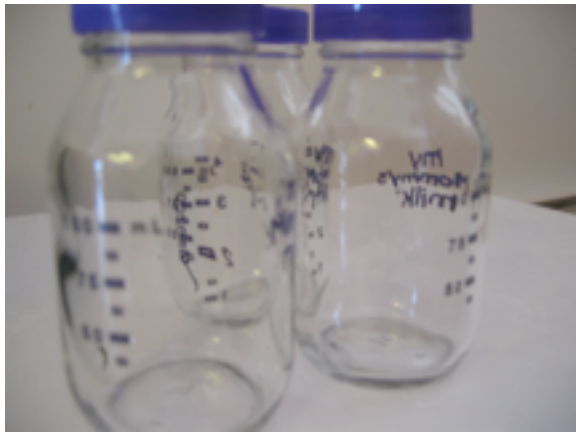


- **Empirical (epidemiologic) studies linking boxes:**
  association of dust concentration & body burden

  How & where should we sample dust? --poses a potential exposure misclassification problem

Indoor environment as an exposure route for PBDEs

- **epidemiologic approach:**



PBDEs in breast milk (measures mother's body burden)

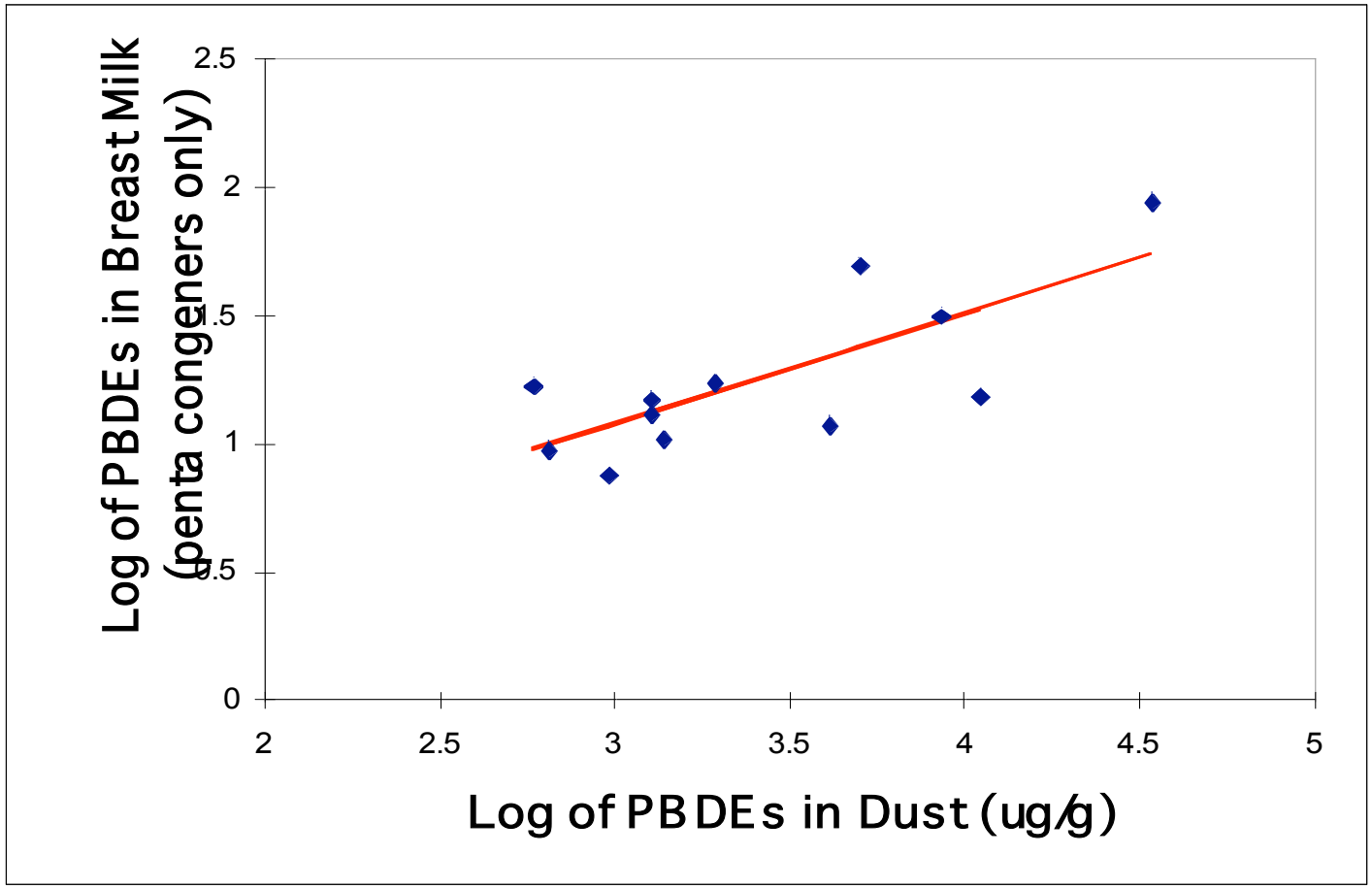
PBDEs in house dust

Diet questionnaire

	Never	Less than 1x/week	1x/week	2-3 x/ week	4-6x/ week	1x/day	More than 1x/day
Dairy							
D1. Milk (one 8 oz. glass)							
D1a. What kind of milk did you usually drink?	_____ skim _____ 1% _____ 2% _____ whole						
D2. Cheese (one ounce – 1 inch square) (This can be in any form – in sandwiches, pizza, etc.)							
D2a. How often do you choose low-fat cheese options?	_____never _____not normally _____usually _____always						
D3. Eggs (one egg)							
D4. Ice cream (1/2 cup)							
D5. Frozen Yogurt (1/2 cup)							
D6. Yogurt (1 cup)							
D6a. What is the fat content of the yogurt you usually eat?	_____ fat free _____low fat _____regular						
	Never	Less than 1x/week	1x/week	2-3 x/ week	4-6x/ week	1x/day	More than 1x/day
Meat							
D7. Beef (1 burger or 2-3 ounces of uncooked steak meat)							

Wu et al *ES&T* 2007

Association of PentaBDE in breast milk & dust
Implies exposure via the indoor environment

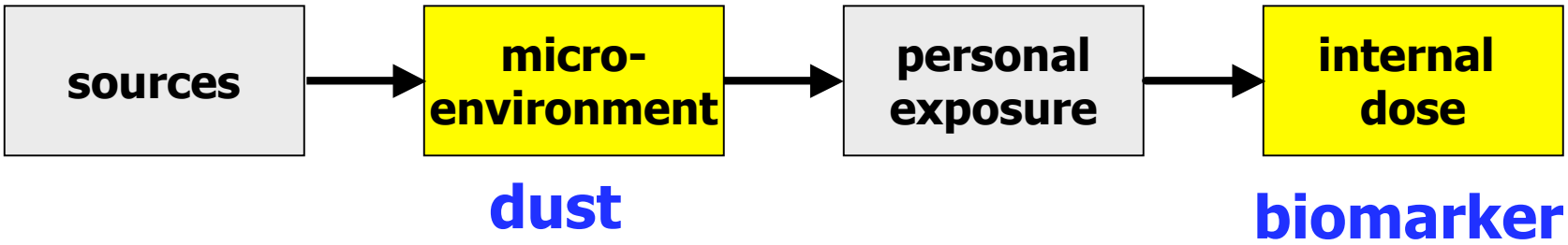


R = 0.76
p = 0.006

Small; appears not confounded by diet (replicated in other studies)

Wu et al *ES&T* 2007

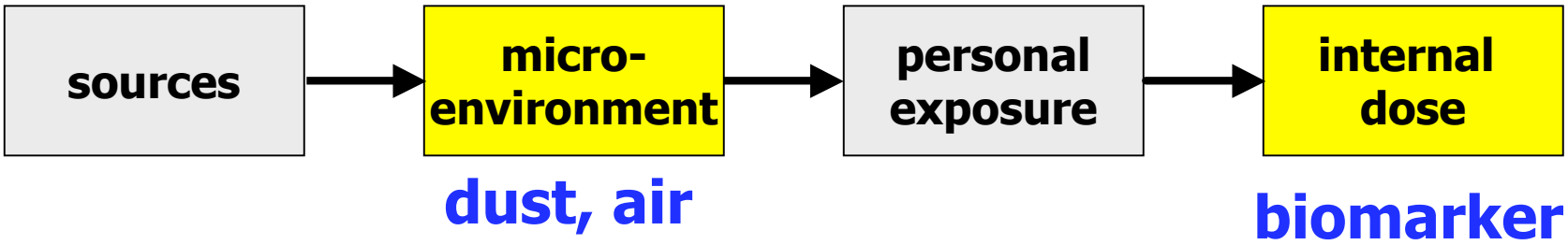
How are we exposed indoors?



Association with dust could be confounded if air and dust are correlated

- **air - inhalation**
- **air - dermal exposure**
- **dust - ingestion**
- **dust - dermal**

How are we exposed indoors?

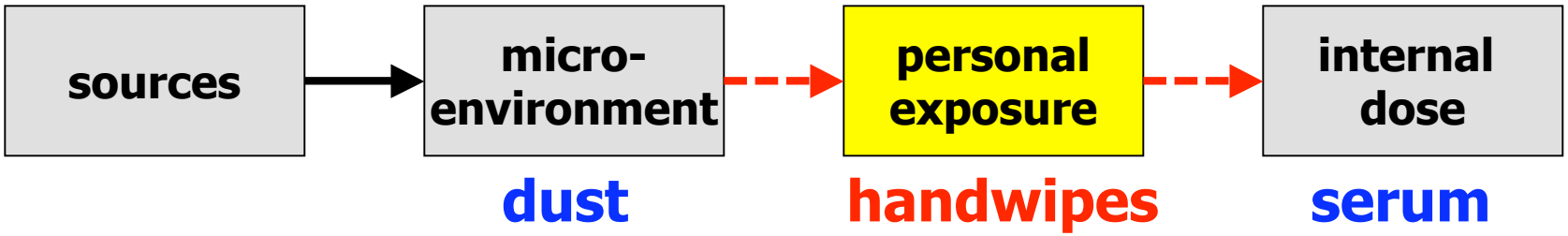


- air - inhalation
- air - dermal exposure
- dust - ingestion
- dust - dermal

Allen et al *ES&T* 2007

How are we exposed indoors?

Examine another (potential) intermediate step



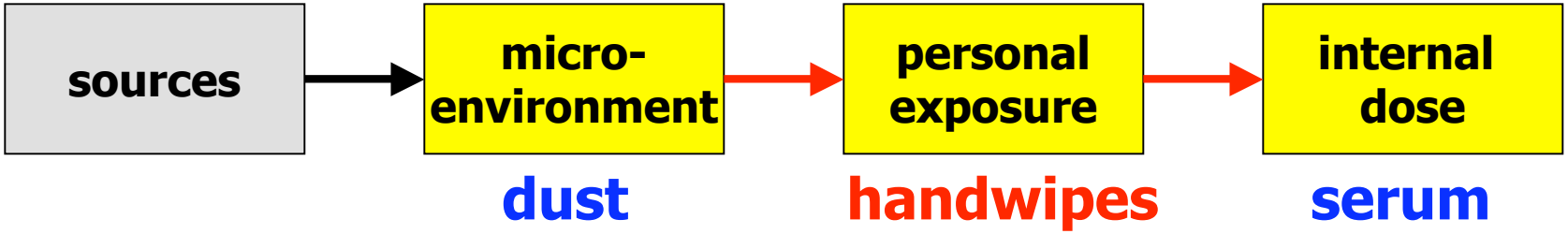
N=33	PBDE
detected	100%
median	129 ng
mean	225 ng
range	3-1982 ng

Stapleton et al *ES&T* 2008

- **Can measure PBDEs on hands? (gause+isopropanol)**
- **Exposure may also depend on behavior**
- **Can we link handwipes to dust & biomarker?**

How are we exposed indoors?

Examine another (potential) intermediate step

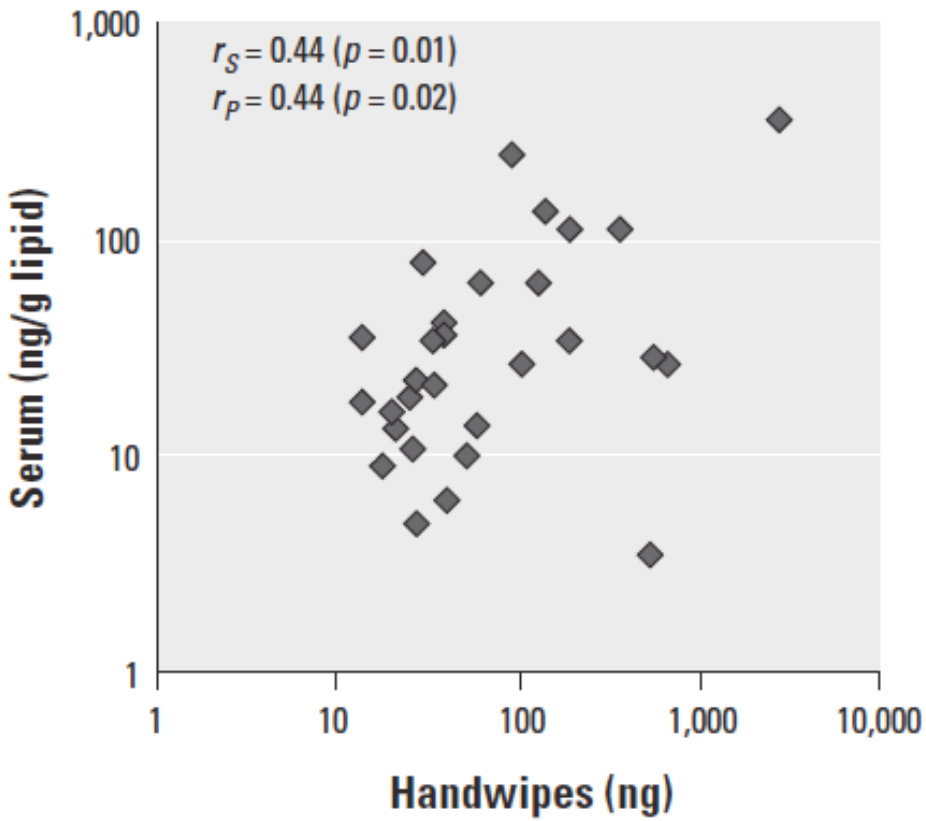


31 adults in Boston, MA who work in offices sampled winter 2009

Collected office dust, handwipe, serum

Watkins et al. EHP 2011

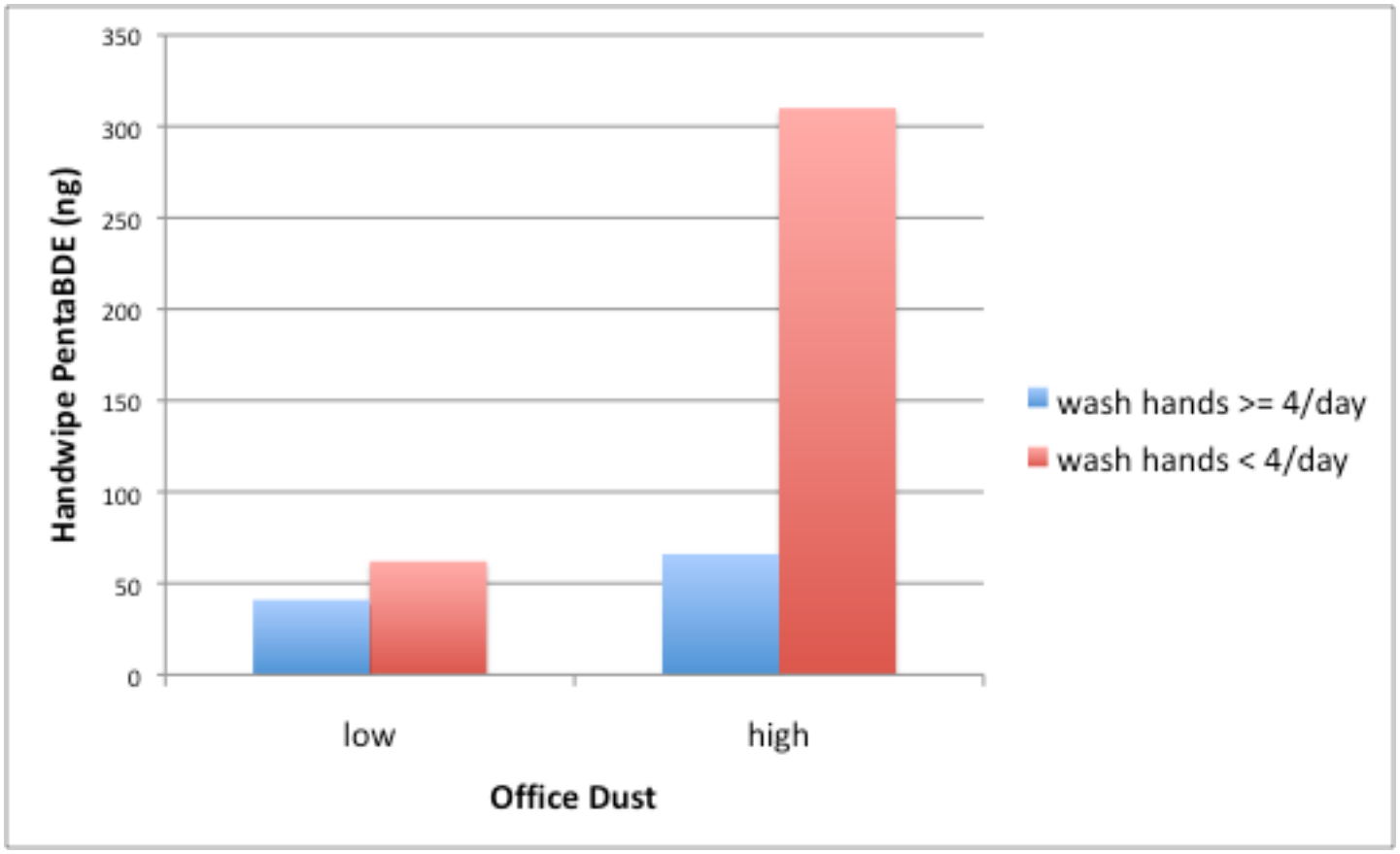
PentaBDE in serum associated with amounts in handwipes



Watkins et al. EHP 2011

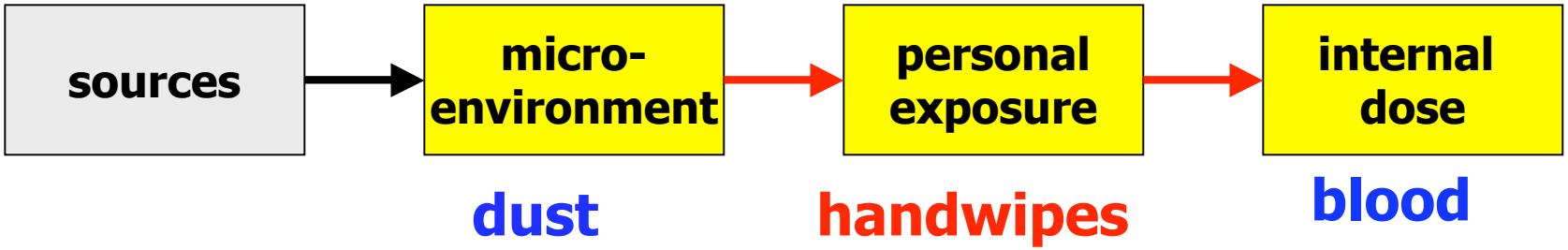
PentaBDE on handwipes are related to:

- **concentrations of PentaBDE in dust**
- **frequency of handwashing**



Watkins et al. EHP 2011

Dust <-> Handwipes <-> Biomarker



air - inhalation

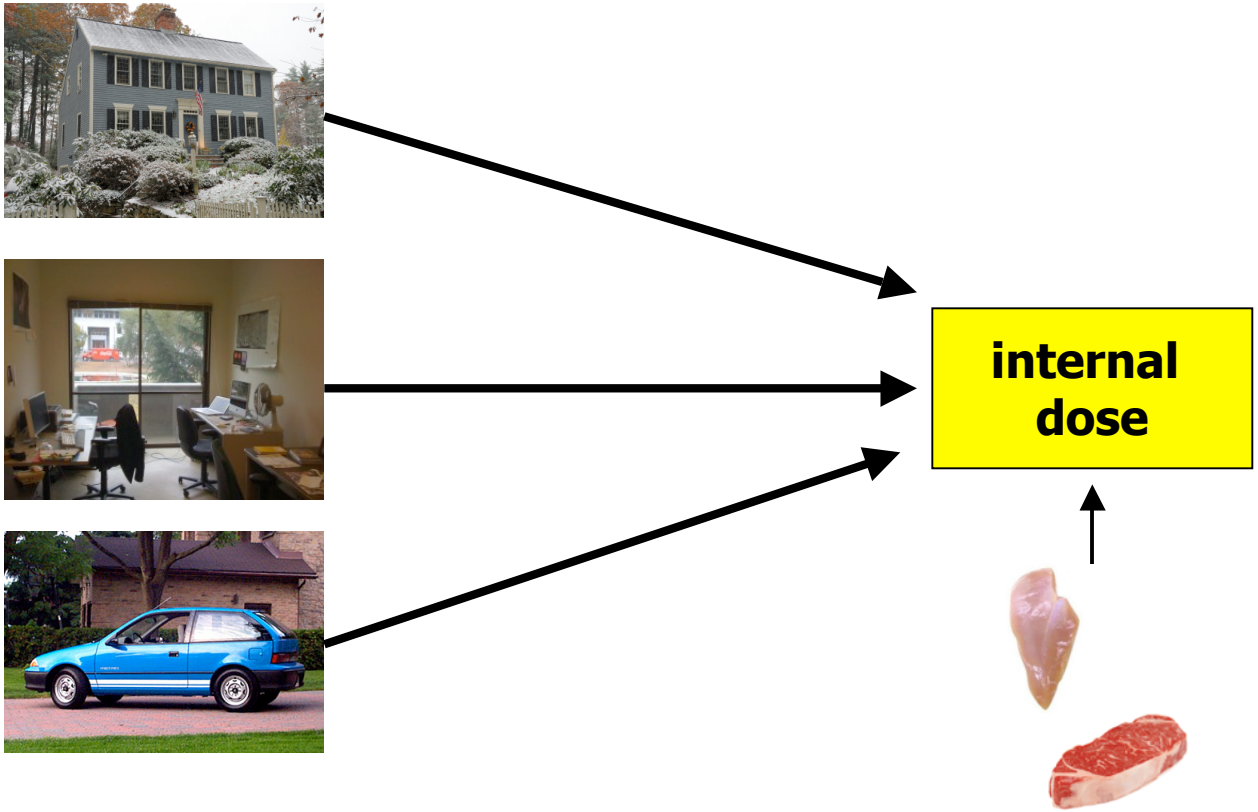
air - dermal exposure

dust - ingestion

dust – dermal

reverse causation?

Which is the most important for exposure?

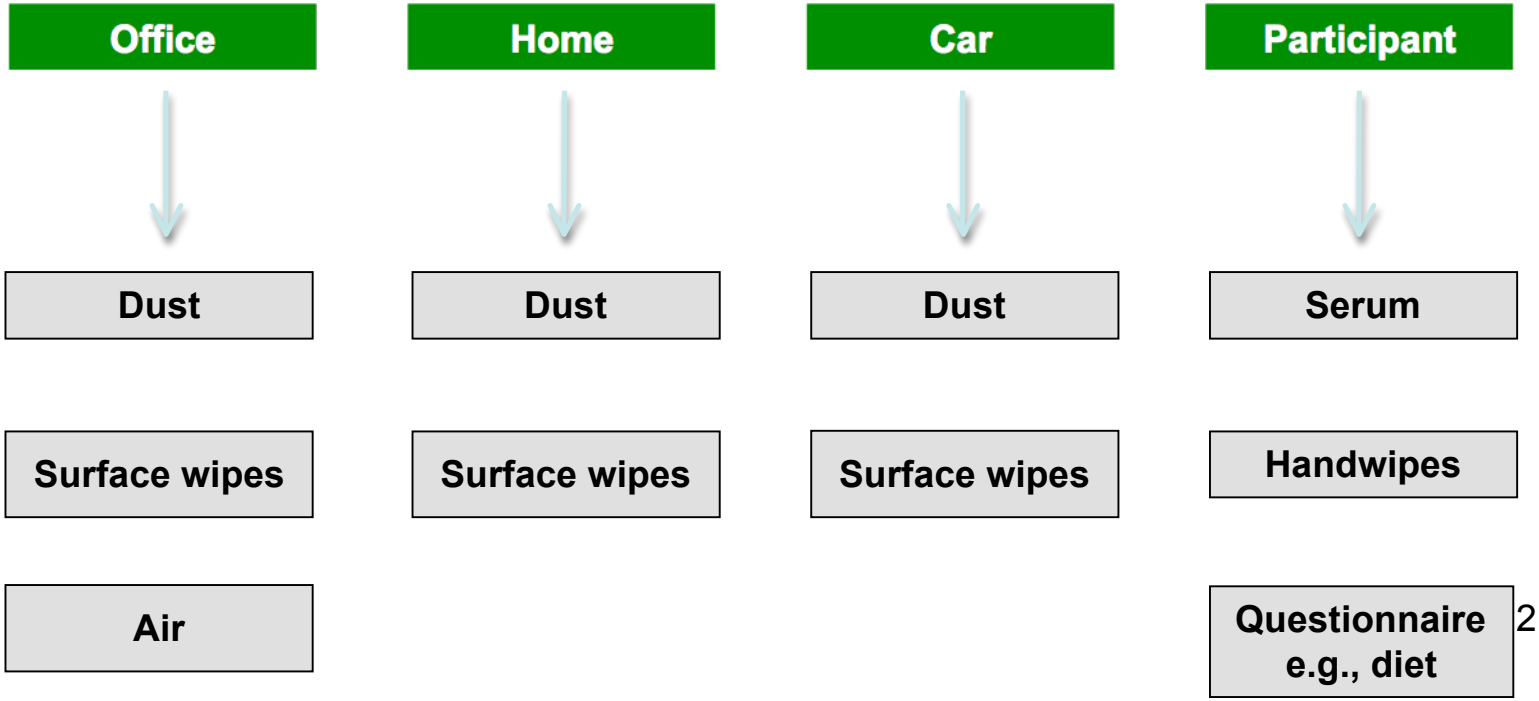


Watkins et al. *ES&T* 2012

Study Design

- **What microenvironment is most important: office, home or car?**
- **How does indoor environment compare with diet?**
- **How do dust, surface wipes & air compare?**

- Convenience sample of 31 adults, Boston MA, USA
- Data collected during the winter of 2009
- Healthy non-smokers who worked at least 20 hours/week in office environment



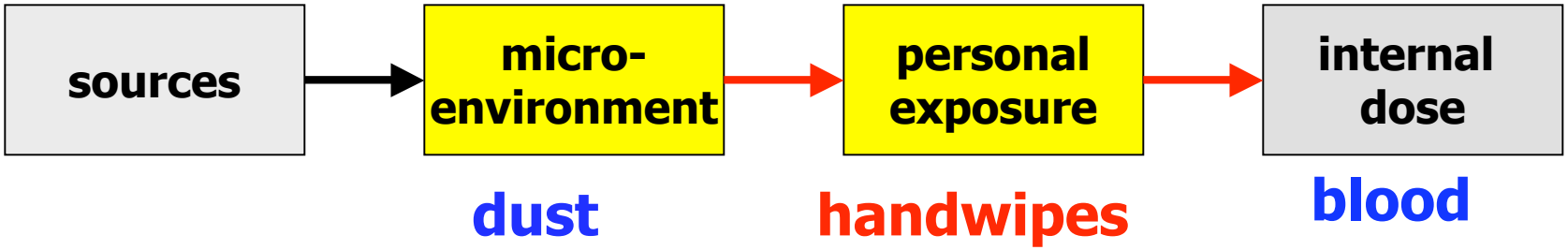
PentaBDEs in Dust (GM, ng/g)

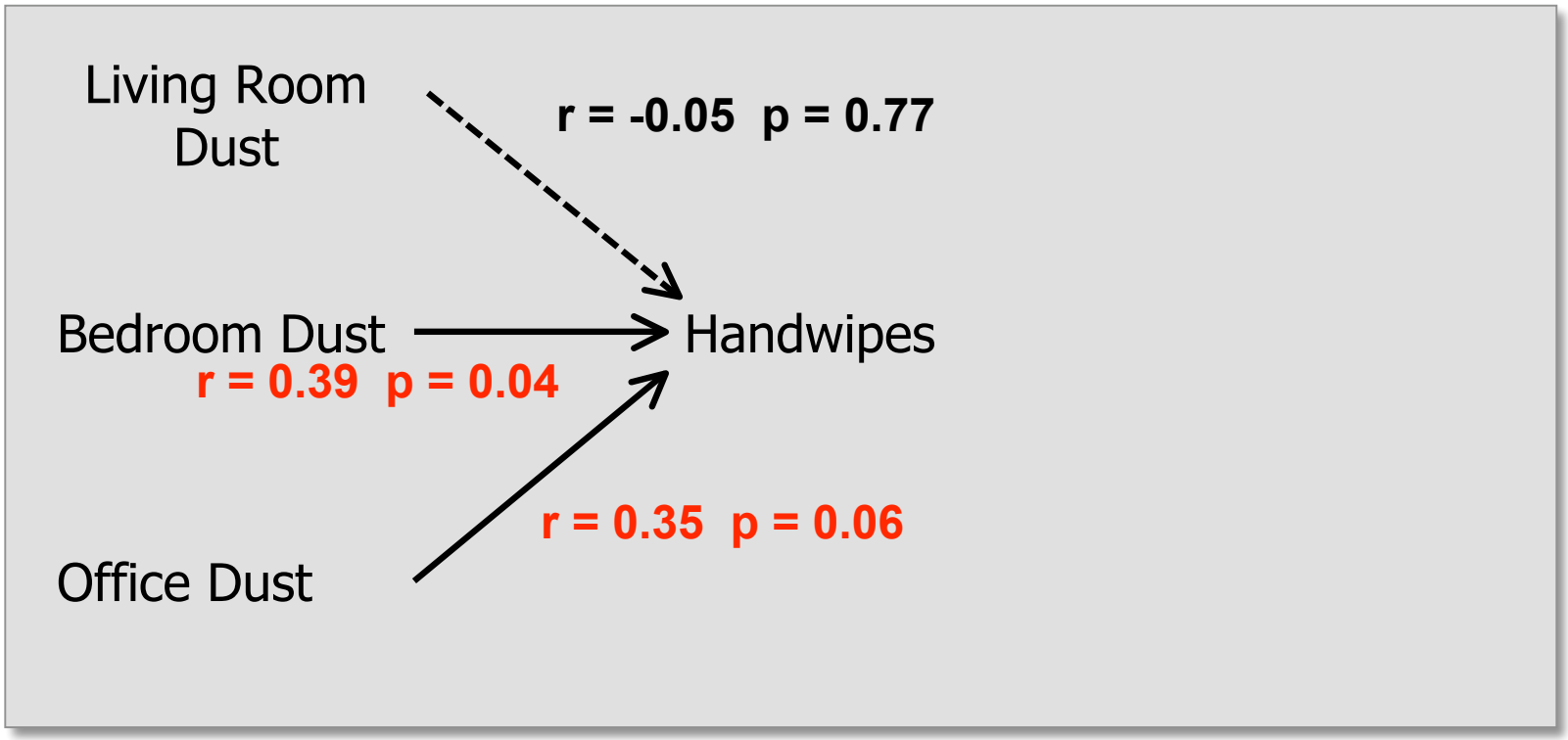
Congener	Office (n = 31)	Living Room (n = 31)	Bedroom (n = 29)	Car (n = 20)
BDE28/33	8	14	10	11
BDE47	697	671	454	765
BDE99	915	647	696	1377
BDE100	195	135	115	189
BDE153	138	65.7	59.0	125
Σ PentaBDEs	**2167**	**1691**	**1378**	**2607**

Consistent with more stringent fire regs for offices than homes in Boston
Possible upward bias in car sampling

Watkins et al. *ES&T* 2012

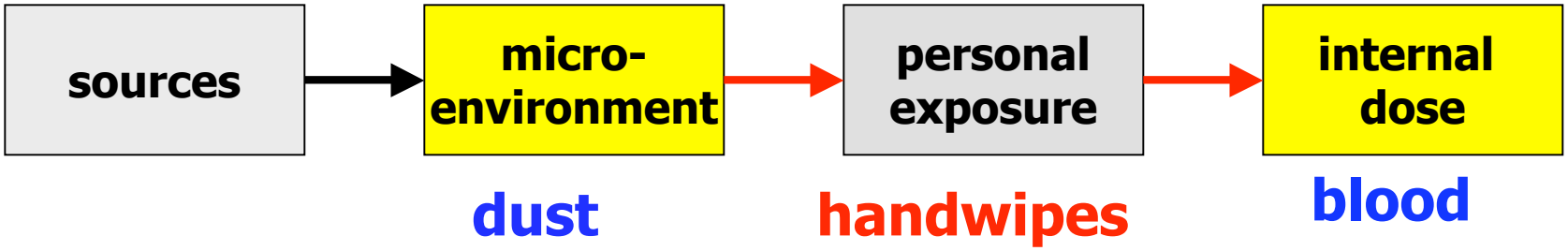
Handwipes collected in office, integrate recent exposure?

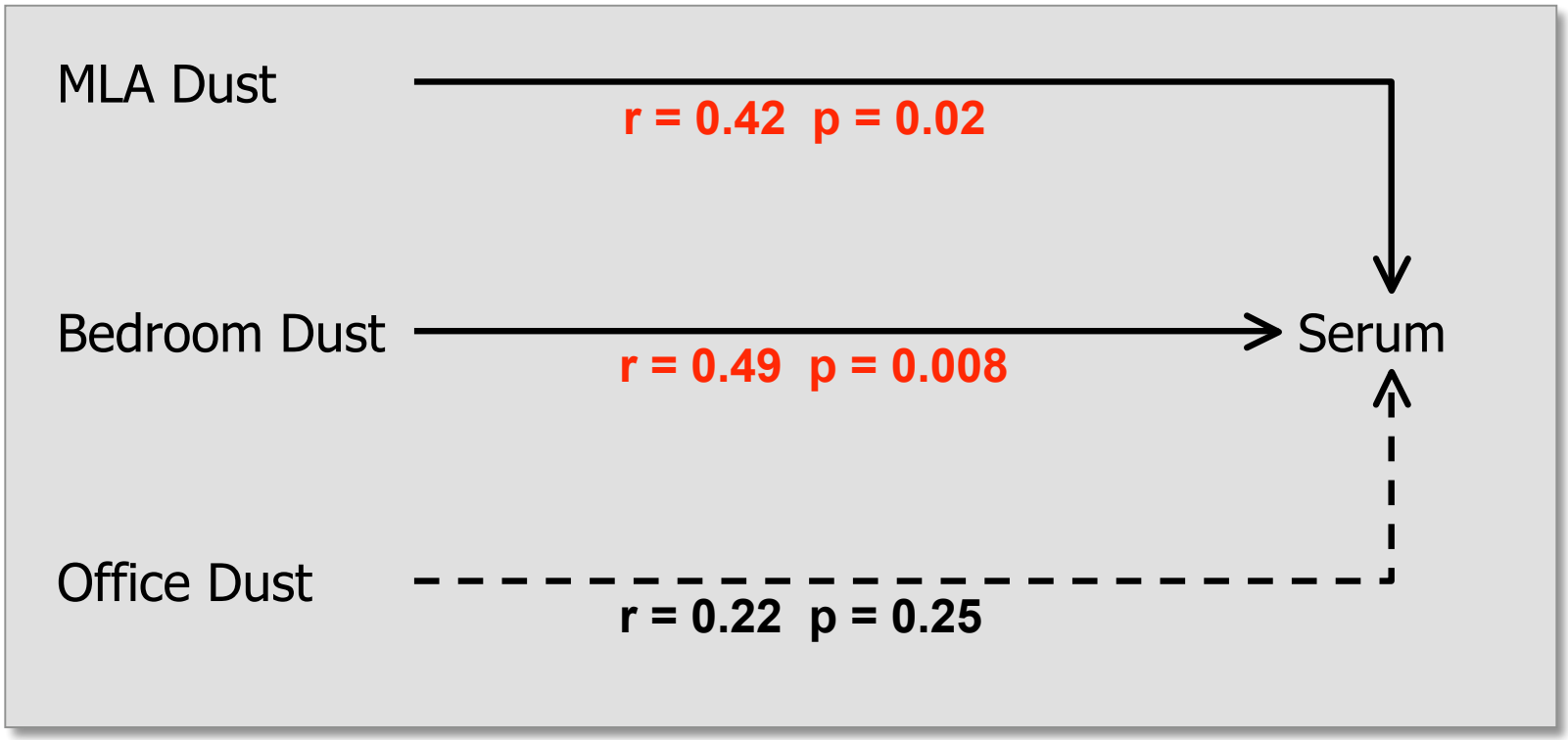




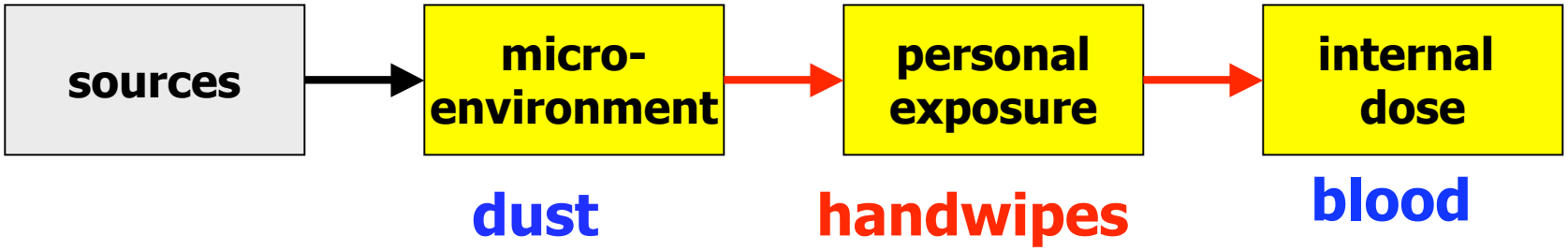
Watkins et al. *ES&T* 2012

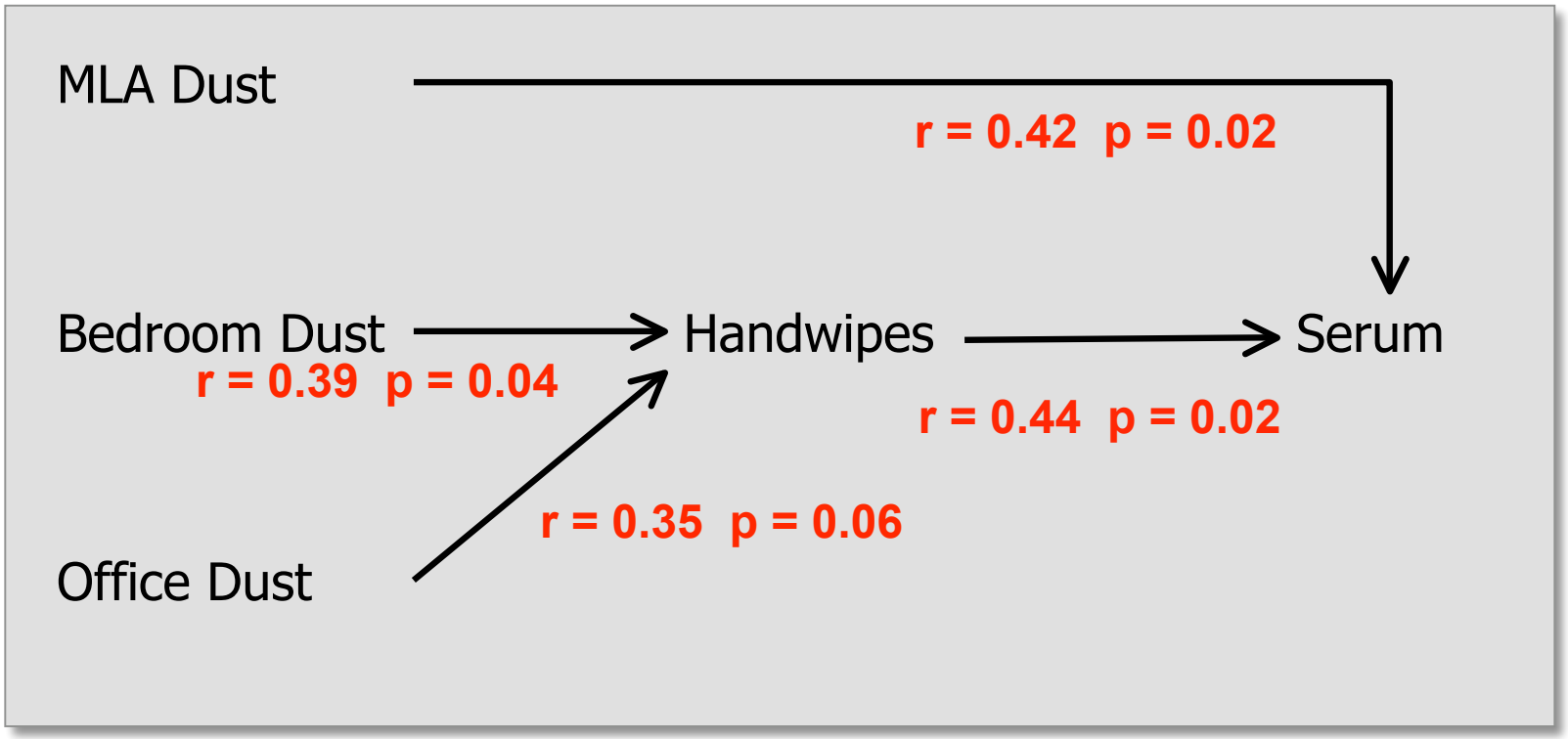
Home > Office: time spent at home, activities?





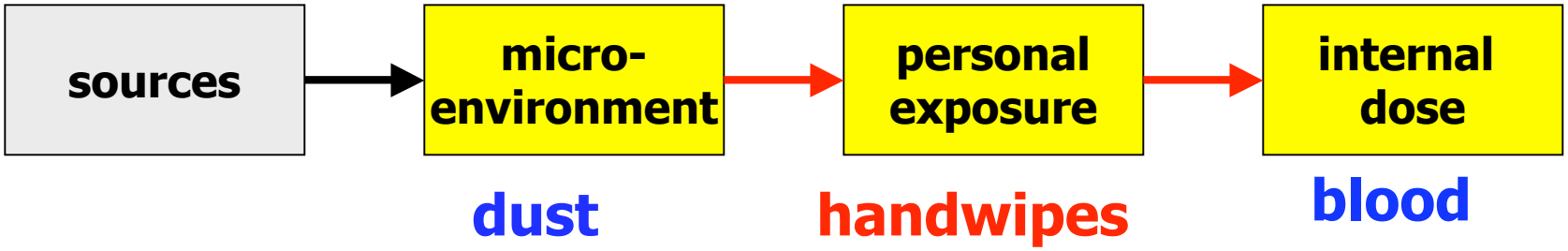
Watkins et al. *ES&T* 2012

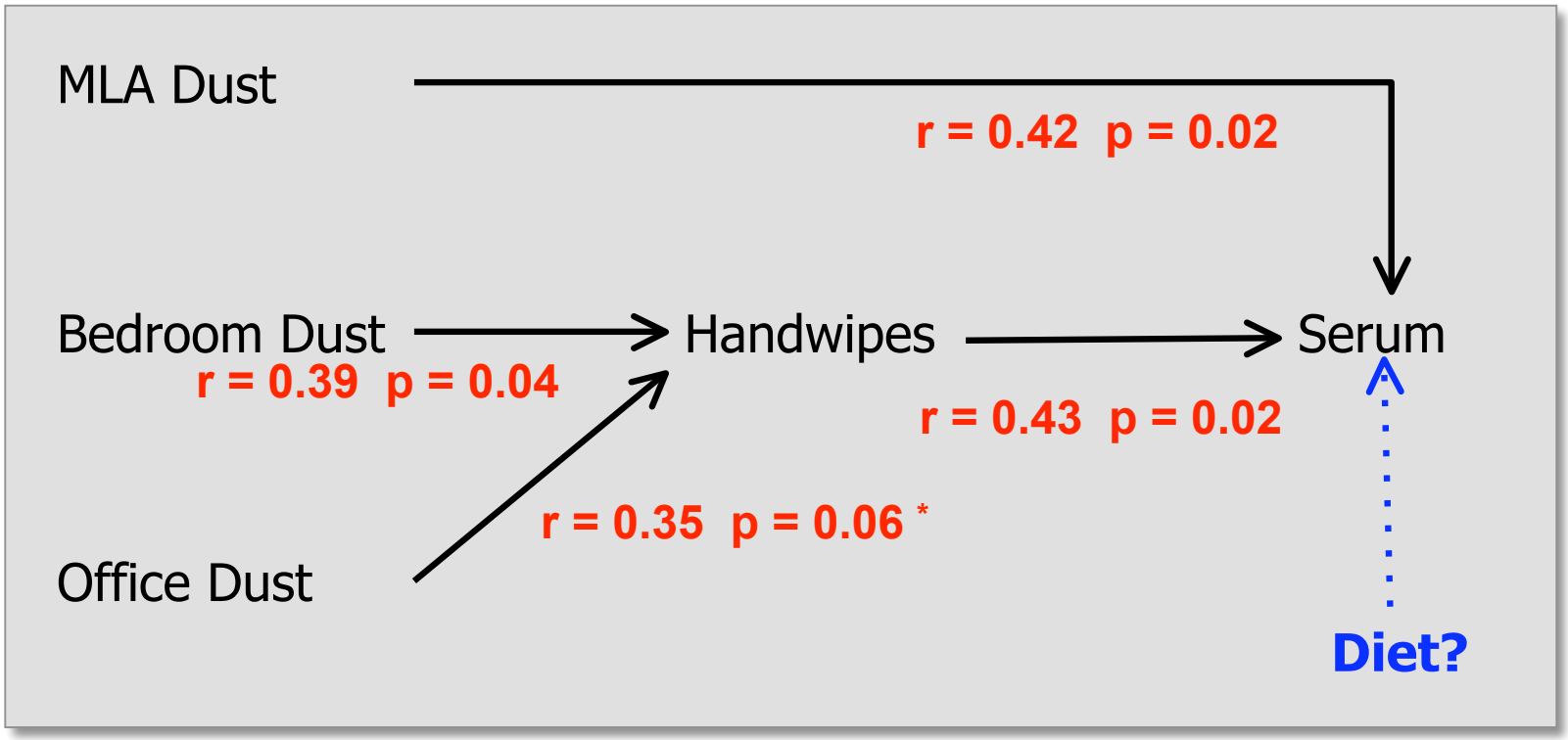




Suggests doing handwipes in the home (too)

No association between serum & diet (although same questionnaire as before): Chance? Population? Trend?





Watkins et al. *ES&T* 2012

- How do dust, surface wipes & air compare?
- What's the best way to collect dust?

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

sources → micro-environment → personal exposure → internal dose

products (via XRF)

dust room air

hand wipe pers. air

diet

biomarker

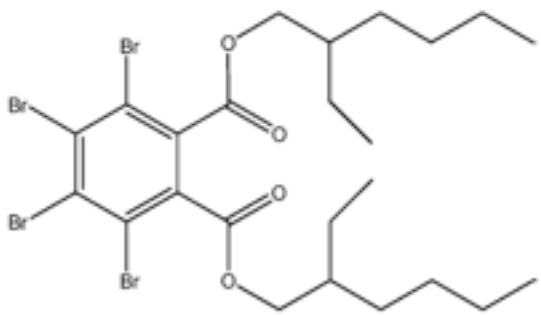
Phase out of PBDEs: Implications

Penta	**furniture (polyurethane foam) mainly used in N. America, CA & similar regulations**
Octa	**electrical hard plastic (minor)**
Deca	**TV/computer plastic, textiles (carpets, draperies)**

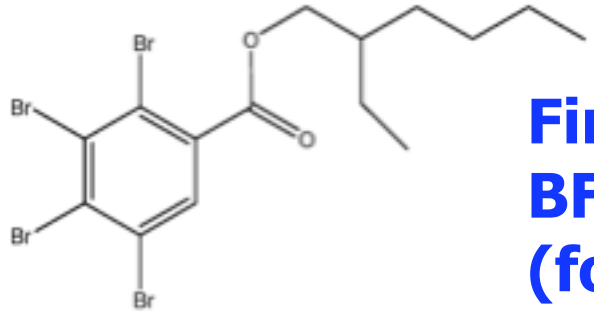
- **phase out manufacture of Penta, Octa in EU & USA: 2005**
  added to Stockholm Convention 2009
- **agreement to phase-out Deca manufacturing in US 2013**

- **Still large reservoir (exposure for years to decades?)**
- **What's being used instead?**

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

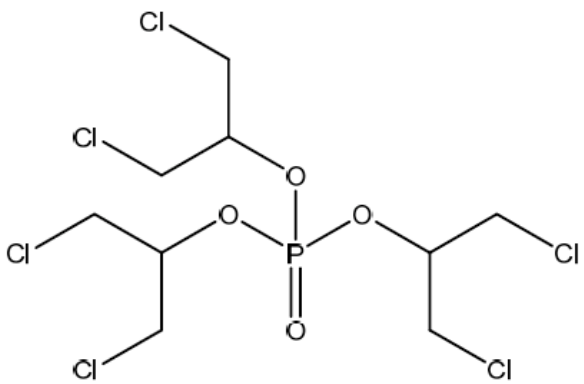


TBPH



TBB

Firemaster 550: BFRs+OPFRs (found via unknown peaks on chromatogram)



Tris (1,3-dichloro-2-propyl) phosphate TDCPP, "chlorinated tris" used in children's sleepware in 1970s

Both also found in consumer products, including baby products

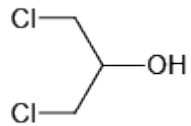
Stapleton et al. *ES&T* 2008,2009,2011

TDCPP: Metabolism/Elimination

- Short half-life (hours to days?)

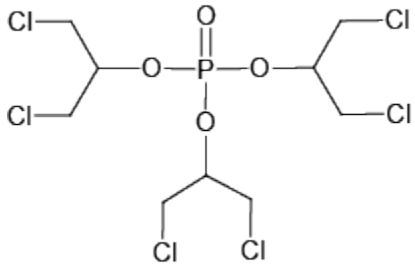
DCP

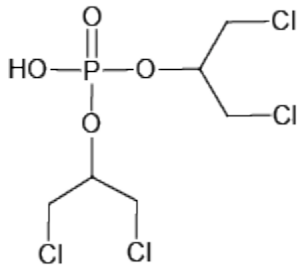
1,3-dichloro-2-propanol



TDCPP

tris(1,3-dichloro-2-propyl) phosphate



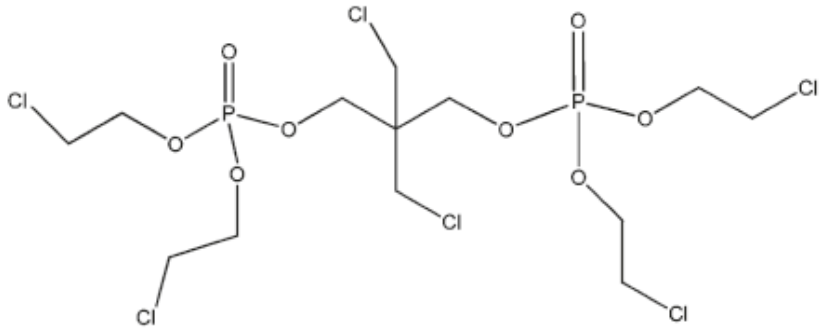


BDCPP

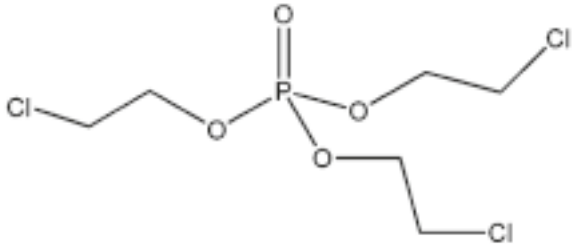
bis(1,3-dichloro-2-propyl) phosphate

Measure in urine (Cooper et al 2011)

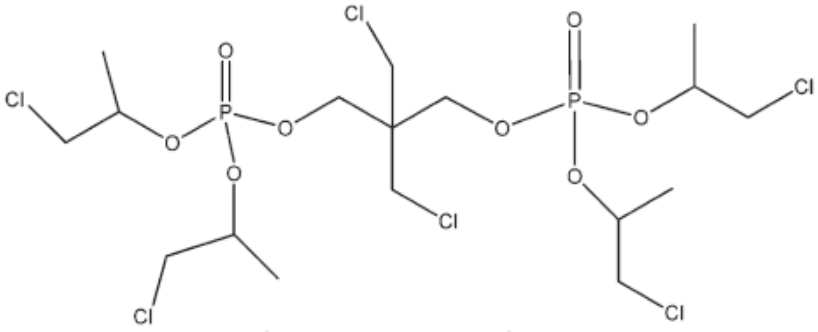
Some other OPFRs in baby products (Stapleton et al 2011):



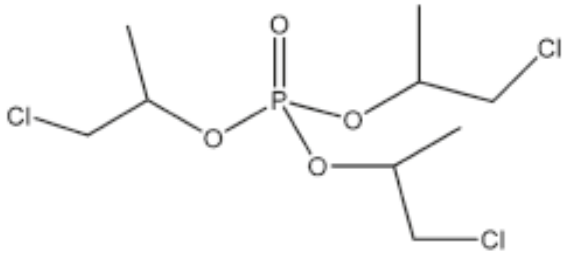
2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl)bis(phosphate)
"V6"



tris(2-chloroethyl) phosphate (TCEP)



2,2-bis(chloromethyl)propane-1,3-diyl tetrakis(1-chloropropan-2-yl) bis(phosphate).
"U-OPFR"



tris(1-chloro-2-propyl) phosphate (TCPP)

PentaBDE → FM550, TDCPP + more

New, poorly known FRs: is this good policy for fire safety / environmental health?

What are the benefits and risks of FRs?

What are we going to do with the PBDEs (& other FRs) already out there?

- **remediate homes & offices ?**
- **ewaste, foam furniture, recycling**
- **new hazardous waste sites?**

Indoor to Outdoor?

Conclusions:

- **Wash your hands!**
- **We need a better way to regulate introduction of new chemicals into commerce.**

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