

Exposure to Polybrominated Diphenyl Ethers (PBDEs): From Product to Person

Tom Webster, DSc
Department of Environmental Health
Boston University School of Public Health



Green Science Policy Institute
The Fire Retardant Dilemma VII
U.C. Berkeley
30 January 2009

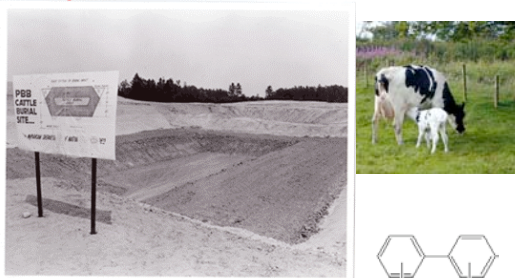
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Overview

- Background
- Review of our studies over the last 6 years
- Summary & thoughts

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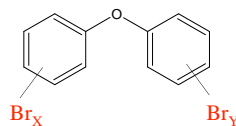
Michigan 1973-4



Polybrominated Biphenyls (PBBS)

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Polybrominated diphenyl ethers (PBDEs)



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

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Use of PBDEs as fire retardants

penta furniture (polyurethane foam)



octa electrical hard plastic

deca TV/computer plastic, textiles

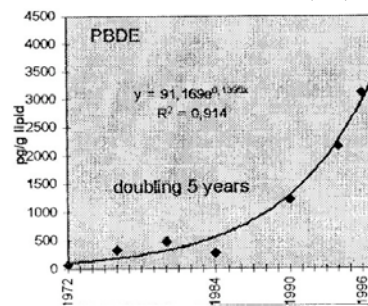


up to 10-30 % by weight
not chemically bound to the plastic

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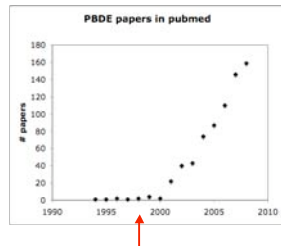
The graph that launched a thousand papers...

PBDE levels in human milk in Sweden (1998)



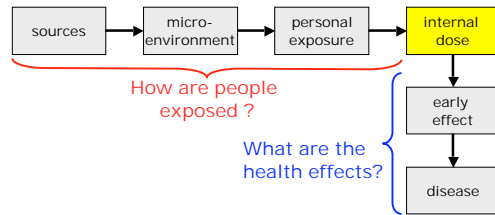
Norén and Meironyté 1998 6

the scientific feeding frenzy begins



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Exposure Assessment Paradigm: Source to Disease



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- How are people being exposed? (initial idea)

food*



occupational

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

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

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

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

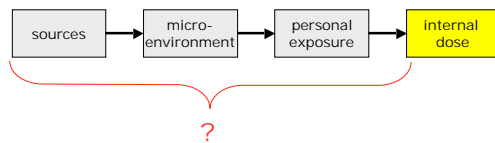
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Goal: Understand how people are exposed to PBDEs along complete pathway *from product to person*



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```


    graph LR
    A[sources] --> B[micro-environment]
    B --> C[personal exposure]
    C --> D[internal dose]
  
```

- Exposure factor approach:
e.g., media concentration X exposure factor
 representative? how well known?
- Empirical (epidemiologic) studies linking boxes:
e.g., association of dust concentrations & body burden


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PBDEs in house dust



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





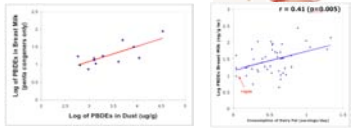
Diet questionnaire

PentaBDE body burden associated with both diet and dust

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    graph LR
    A[sources] --> B[micro-environment]
    B -.-> C[personal exposure]
    C --> D[internal dose]
  
```

dust diet biomarker


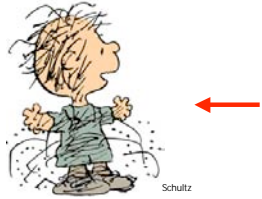
Wu et al 2007

Dust or air? May be correlated.
Measuring inhalation exposure is easier than for dust.

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Personal Air > Room Air Allen et al 2008

- closer to sources (e.g., foam mattresses)
- personal dust cloud ("Pigpen effect")

Schultz

But inhalation not enough to account for exposure?

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Dust Sampling




& participants vacuum cleaner bag

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Critical factors in assessing exposure to PBDEs via house dust
 Joseph G. Allen ^{1,2,3*}, Michael D. McClean ⁴, Heather M. Stapleton ⁴, Thomas F. Webster ⁴
Environ Intern 2008; 34: 1085-1091

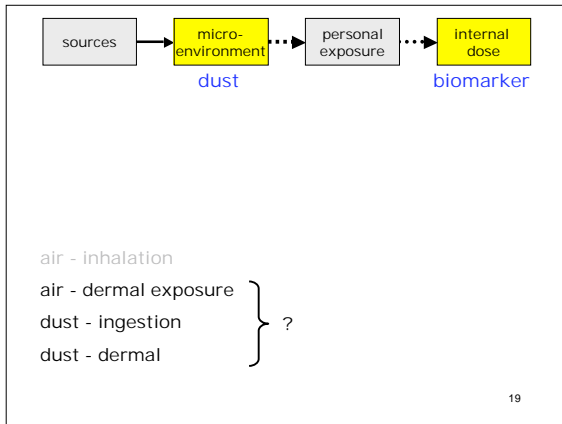
It matters how and where you sample dust in homes:

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

Dust concentrations significantly correlated when sampled 6-8 months apart

Deca very high in some dust ~ 1 mg/g
 Some evidence for breakdown of deca in dust

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

Stapleton et al 2008

- Can measure PBDEs on hands
- Exposure also depends on hand-to-mouth behavior, etc.

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

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

Limitation: Can't generally do furniture "biopsies"

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X-ray fluorescence (XRF) as surrogate for PBDEs

Strengths: rapid, noninvasive detection of bromine
 Weakness: can't distinguish PBDEs from other Br compounds, penetrates ~ 1 cm

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Validation: compare foam & electronics samples using XRF & GC-MS

Allen et al 2008

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XRF: Standardized sampling protocol



All foam furniture & electronics in rooms
 3 readings per sub-item (e.g., TV back)
 10 seconds per reading
 Measure surface area & volume of sub-items

Br Concentrations in Consumer Products (ppm)

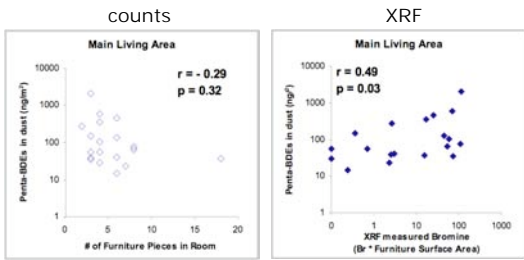
	n	mean	median
TVs	24	137206	144100
DVD,VCR...	36	31979	14584
computers	19	3324	268
couch	16	532	33
chair	45	3451	32
mattress	20	135	8

TVs: highest; backs least variable
 For many products, high variation
 Couches & mattresses generally low
 Boston (may be different in CA?)

Allen et al 2008

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XRF greatly improves ability to predict penta in dust



Allen et al 2008

also for deca vs. electronics 27

Statistical analysis indicates:

Penta in dust related primarily to foam furniture containing Br

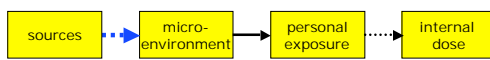


Deca in dust related primarily to TVs containing Br



The deca-TV association is strongest in homes with more residents, a possible indicator of use

How are PBDEs getting out of products?



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

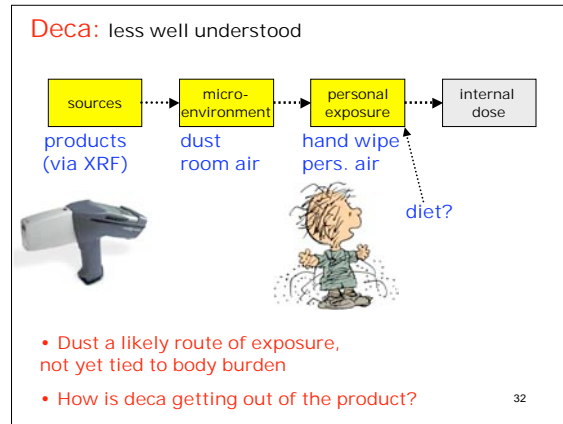
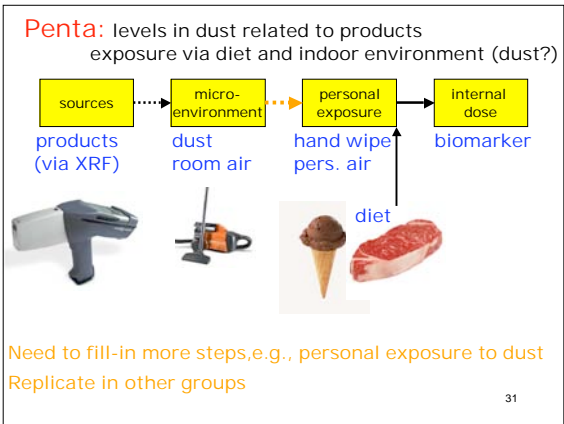
Chamber experiments have so far provided some results for penta, little data for deca

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Déjà vu all over again?

Use of PBDEs as fire retardants

penta* furniture (polyurethane foam)

octa* electrical hard plastic

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

* No longer manufactured in the US or EU, but still found everywhere. Deca under pressure.

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Decabromodiphenyl ethane

Stapleton et al 2008

Kellyn Betts--*Environ Sci Technol*
December 3, 2008

[Glut of data on "new" flame retardant documents its presence all over the world](#)

Now that DBDPE has been detected in more than a dozen species of animals in Asia and North America, scientists are calling for more research into its toxicology.

Unknown peaks in chromatographs of house dust...

After a lot of work:

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a main replacement for pentaBDE

Chemtura MATERIAL SAFETY DATA SHEET

MSDS Number: 00896 Effective Date: 05/20/2006
Product Name: FIREMASTER® 550 Page: 1 of 8

SECTION I - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product Name: FIREMASTER® 550
Supplier: Chemtura USA Corporation
Address: 199 Beacon Road City: Middletown Connecticut Zip: 06749
Emergency Telephone Number: 1-888-848-8187
Information Telephone Number: 1-765-497-6100 Fax: 1-765-497-6123
Chemture Phone: 1-800-424-8300; Internationally call 765-421-3887
Effective Date: 05/20/2006 Supersede Date: 11/28/2005
MSDS Prepared By: Chemtura Product Safety Group
Synonyms: ~~None~~

Product Use: Flame retardant in polystyrene matrices
Chemical Name: Mixture
Chemical Family: Halogenated aryl ester/Aromatic phosphorus blend

Manufacture: Great Lakes Chemical Corporation, A Chemtura Company
P.O. Box 2100 West Lafayette, Indiana 47996-2100

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SECTION II - COMPOSITION INFORMATION ON INGREDIENTS			
INGREDIENT NAME	CAS No.	%	EXPOSURE LIMITS
*Component B Triethyl phosphate, isopropylated	75	49-66 24-51	Y (Hazardous) Not established (OSHA PEL TWA) Not established (OSHA PEL STEL) Not established (OSHA PEL CEIL) Not established (ACGIH TLV TWA) Not established (ACGIH TLV STEL) Not established (ACGIH TLV CEIL) N (Hazardous)
Triphenyl phosphate	115966	6-24	3 mg/m ³ (OSHA PEL TWA) Not established (OSHA PEL STEL) Not established (OSHA PEL CEIL) 3 mg/m ³ , AA (ACGIH TLV TWA) Not established (ACGIH TLV STEL) Not established (ACGIH TLV CEIL) Y (Hazardous)
Component A	TS	40-60	Y (Hazardous) Not established (OSHA PEL TWA) Not established (OSHA PEL STEL) Not established (OSHA PEL CEIL) Not established (ACGIH TLV TWA) Not established (ACGIH TLV STEL) Not established (ACGIH TLV CEIL)

TS=Trade secret

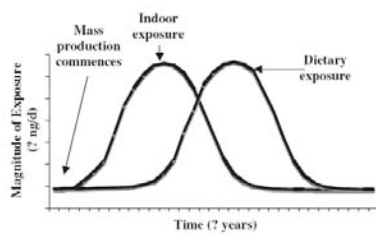
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Firemaster 550 -> Firemaster 600

A treadmill of new BFRs may help the careers of environmental scientists, but is this good policy for fire safety / environmental health?

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Penta & octa bans, but not "going away" ?



(Harrad & Diamond 2006)

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Acknowledgements:



Joe Allen Nerissa Wu Mike McClean Heather Stapleton

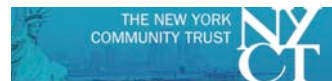
Deb Watkins, Alicia Fraser, Courtney Walker, Jess Nelson
Stephanie Chan
Veronica Vieira, Wendy Heiger-Bernays, Madeleine
Scammell, Tim Heeren
a number of former MPH students

Study participants!

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Joel Tickner (UMass Lowell)
David Holbrook (NIST)
Jeff M. Davis (NIST)
James Millette (MVA Scientific Consultants)
Stuart Harrad (University of Birmingham)
Adrian Covaci (University of Antwerp)
Susan Klosterhaus (San Francisco Estuary Institute)
Alex Konstantinov (Wellington Laboratories)

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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.

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Wu N, McClean MD, Brown P, Aschengrau A, Webster TF. Participant Experiences in a Breastmilk Biomonitoring Study. Submitted.

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 decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. Submitted.

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<http://www.cireeh.org/pmwiki.php/Main/ExposureToPBDEs>

Center for Interdisciplinary Research
in Environmental Exposures and Health

Main / Exposure to PBDEs—Research at Boston University View Edit History Attach Print

School of Public Health

The PBDE Research Group at Boston University School of Public Health, Dept. Environmental Health
Our principal focus is the investigation of human exposure to PBDEs in the indoor environment.

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Polybrominated diphenyl ethers (PBDEs)
PBDEs are a class of compounds commonly used as fire retardants in furniture containing polyurethane foam (PUF) and consumer products such as beverages. As shown by their generic **chemical structure** below, PBDEs are structurally related to their better known cousins: PCBs, polychlorinated biphenyls (PCBs), and polychlorinated dibenzodioxin/furans. Human body burdens and environmental concentrations of PBDEs have increased for several decades and vary geographically, with the highest values reported in the USA. Major questions include impacts on human health and the environment and major routes of human exposure.

Chemical Structure:
BrC1=CC=C(C=C1)OC2=CC=C(C=C2)Br

Exposure to PBDEs
PBDEs are persistent and bioaccumulative, suggesting exposure via diet, particularly animal products. Given their use in consumer products, it is very likely that the indoor environment also causes exposure. We found associations between PBDE concentrations in people and i) consumption of dairy products and meat, ii) house dust sampled from participant's homes (Wu et al 2005, 2007); see the figure below. The latter finding—in first time mothers from the Greater Boston area—is particularly important because of the very large uncertainty in adult exposure to dust. It supports the hypothesis that exposure to PBDEs in dust is an important route of exposure.

Figure:
PBDEs in Breast Milk as a Function of PBDEs in Breast Milk (parental consumption) (Wu et al. 2007)

People are exposed to PBDEs via dust and diet. See: 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. Web release date: 17 Jan 2007. Abstract and full text for EBST subscribers: [doi:10.1021/es060298r](http://dx.doi.org/10.1021/es060298r). See also the accompanying EBST News report by Kathy Bette.