Human Exposure to Brominated Flame Retardants

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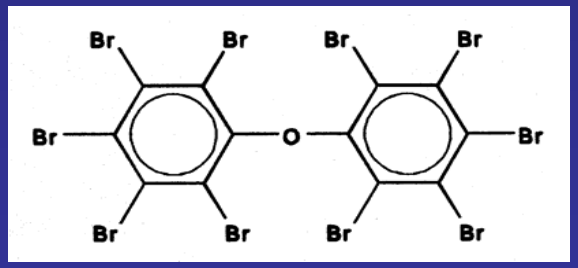


Presentation Outline:

1. Background on brominated flame retardants with a focus on polybrominated diphenyl ethers (PBDEs)

    - types, use, commercial formulations
    - toxicology
    - trends in human body burdens in US

2. Exposure to PBDEs (current collaborative project)

    - dietary exposure vs. indoor exposure
    - estimating exposure to PBDEs from air and dust
    - identifying sources of PBDEs in indoor environments

3. Exposure to New/Alternate BFRs

4. Summary and Conclusions

Statistics:

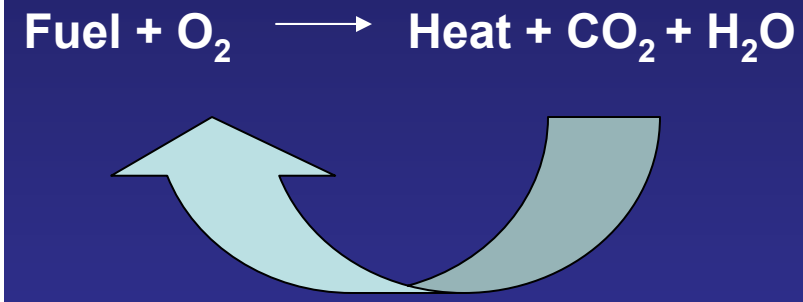
- Every year in the U.S. there are over a million fires reported
- Direct losses account for billions in damages

Flame Retardants:

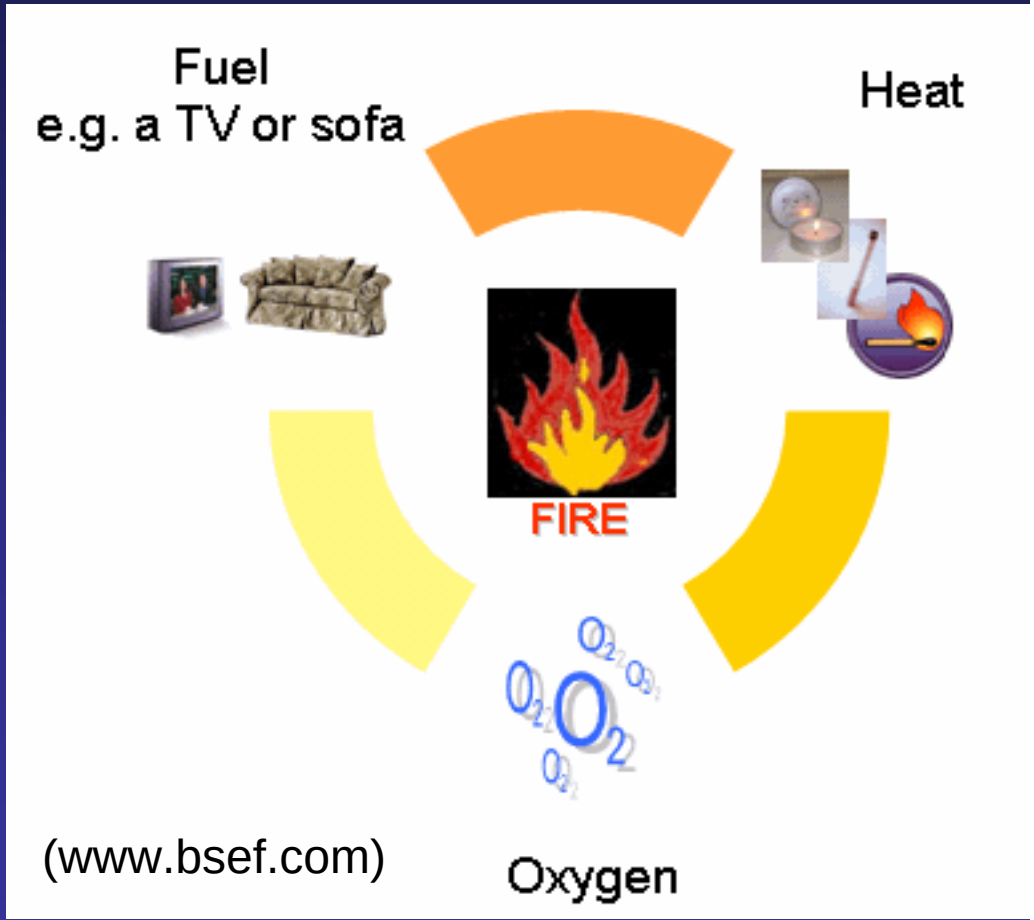
Definition:

"A substance added or a treatment applied to a material in order to suppress, significantly reduce or delay the combustion of the material" *EHC:192, WHO 1997*

How do Flame Retardants Work?



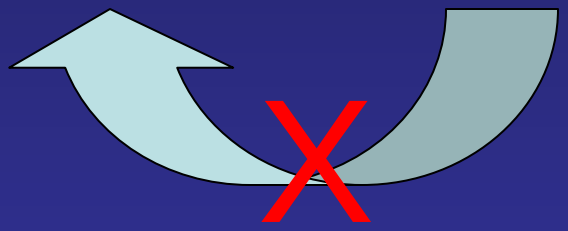
*Formation of radical species



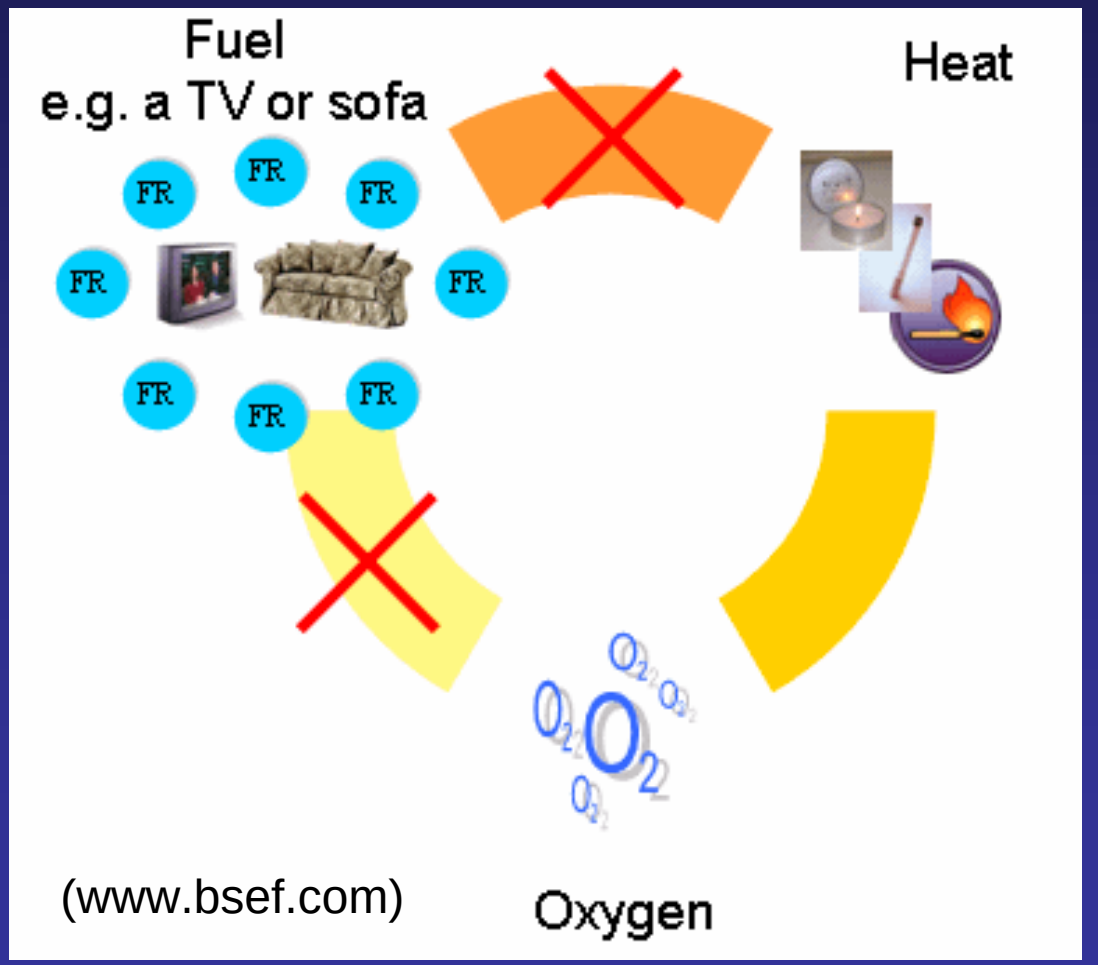
How do Flame Retardants Work?

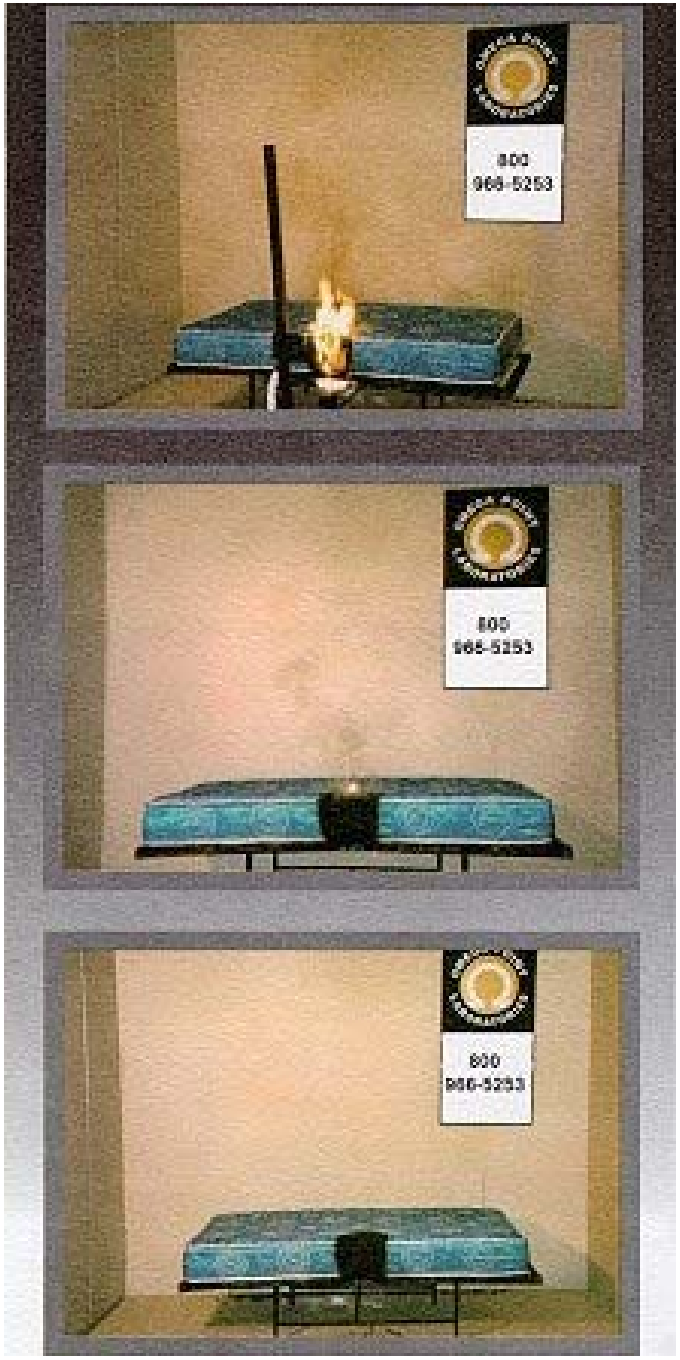
- Most common method for retarding fire is to quench the radical species formed in the fire reaction

$$\text{Fuel} + O_2 \longrightarrow \text{Heat} + CO_2 + H_2O$$



*Stop the formation of radical species

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Types of Brominated Flame Retardants (BFRs)

REACTIVE BFRs:

- Chemically bound to the product they are flame retarding….less likely to leach out into the environment

ADDITIVE BFRs:

-Mixed in with the resin during extrusion process…..more likely to leach out of products over time

Examples: PentaBDE
OctaBDE
DecaBDE
} Commercial Mixture Names

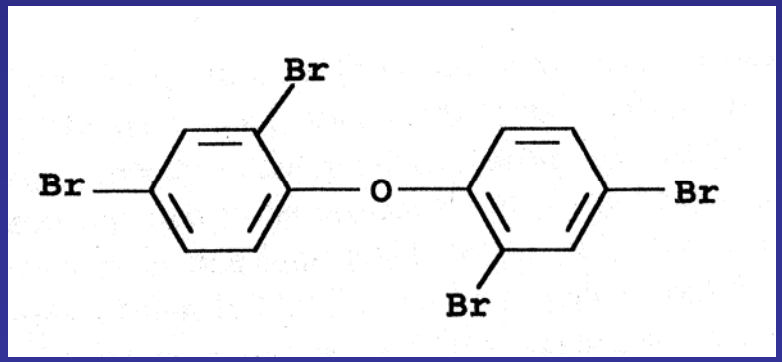
Types of Brominated Flame Retardants:

ADDITIVE BFRs

Decaabromobiphenyl
Decabromodiphenyl ethane
Decabromodiphenyl ether
Octabromodiphenyl ether
Pentabromodiphenyl ether
Tetrabromobisphenol A Derivatives
bis-(2,3-dibromopropyl ether)
bis-(2-hydroxyethyl ether)
bis-(allyl ether)
dimethyl ether
Hexabromocyclododecane
Bis(tribromophenoxy)-ethane
Pentabromotoluene
Bromo-chlorinated paraffins
Di-(2-ethylhexyl)tetrabromophthalic ester
Ethylene-bis-(tetrabromophthal imide)
Tetradecabromodi phenoxybenzene
1,2-Dibromo-4(1,2 dibromomethyl) cyclohexane
Ethylene-bis(5,6-dibromo-norbornane-2,3-dicarbox imide
1,3,5-tris(2,3-dibromo-propoxy)-2,4,6-triazine

REACTIVE BFRs

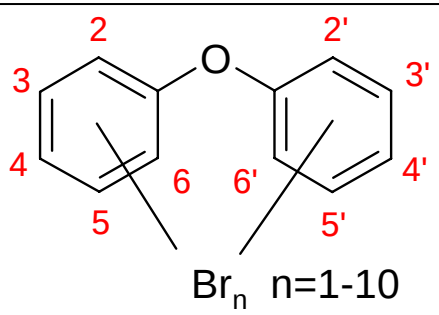
Tetrabromobis phenol A
Tetrabromobispenol S
2,4-Di-, 2,4,6-Tri- and pentabomophenol
Tribromoneopentyl alcohol
Vinylbromide
Tribromophenyl allyl ether
2,3-Dibromo-2-butene-1,4-diol
Tetrabromophthalic acid Na salt
Tetrabromophthalic anhydride
N,N´-Ethylene-bis-(tetrabromophthal imide)



Resins and Polymers	DecaBDE	OctaBDE	PentaBDE
Acrylonitrile-butadiene styrene		X	
Epoxy-resin	X		
Phenolic resins	X		X
Polyacrylonitrile	X		
Polyamide	X	X	
Polybutylene terephthalate	X	X	
Cross Linked Polyethylene	X		
Polyethylene terephthalate	X		
Polypropylene	X		
Polystyrene/HIPS	**X**	X	
Polyvinylchloride			X
Polyurethane			**X**
Unsaturated polyesters	X		X
Rubber	**X**		X
Paints/lacquers	X		X
Textiles	**X**		X

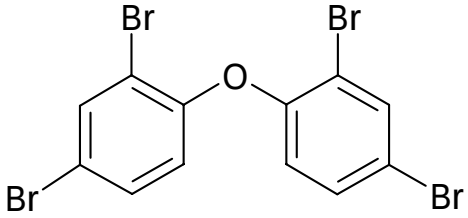
From: EBFRIP, 1990; Rahman et al., 2001

PBDE Nomenclature



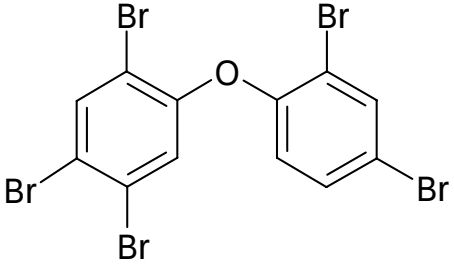
Polybrominated Diphenyl Ether (PBDE)

PentaBDE Congeners:



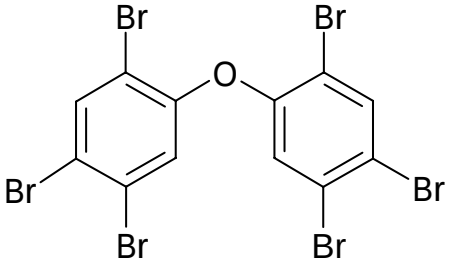
2,2',4,4'-tetrabromodiphenyl ether

BDE-47



2,2',4,4',5-pentabromodiphenyl ether

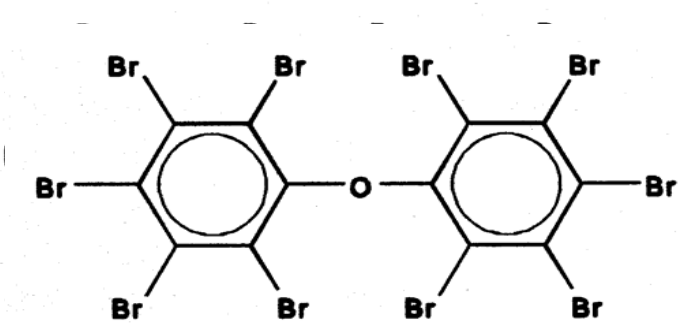
BDE-99



2.2',4,4',5,5'-hexabromodiphenyl ether

BDE-153

DecaBDE:

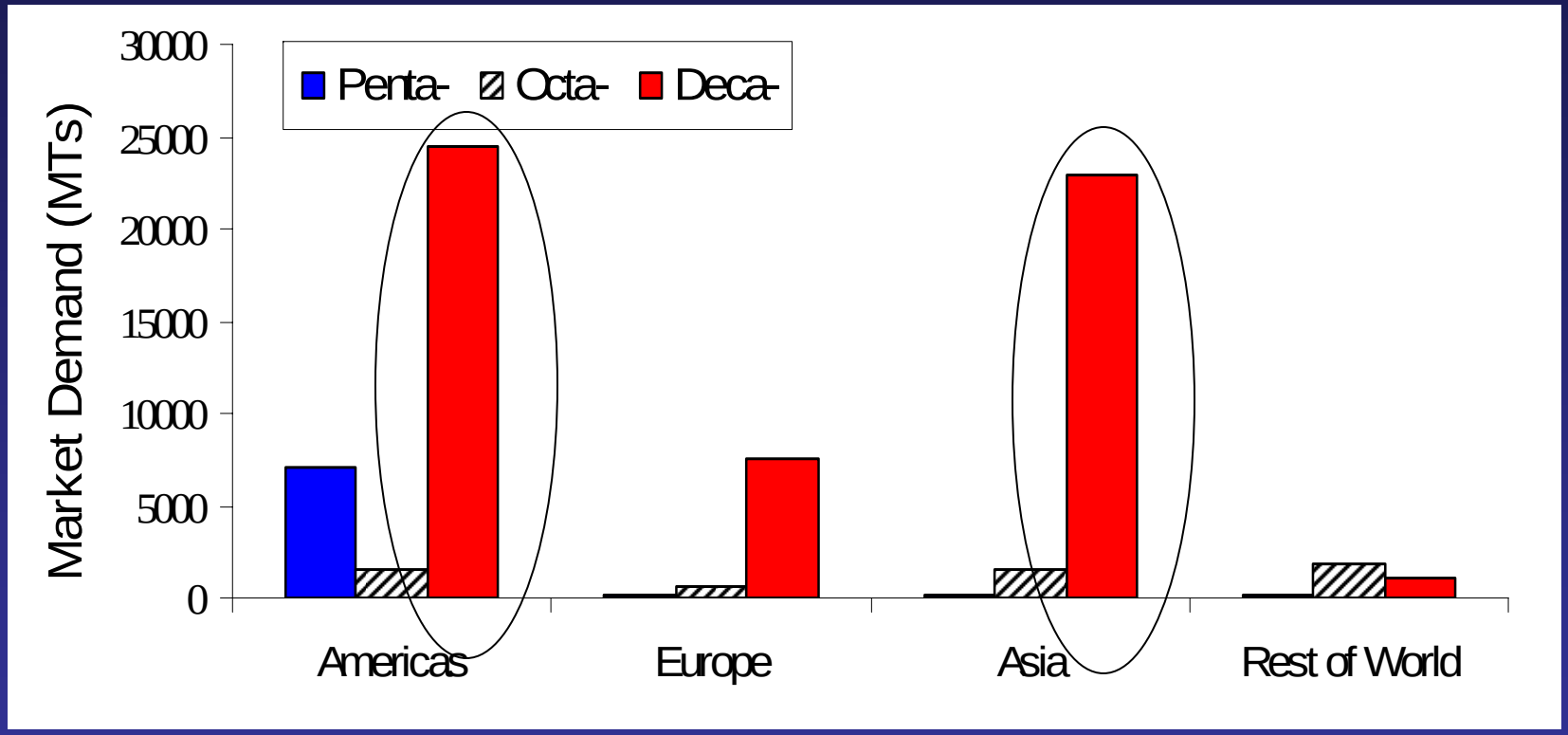


BDE 209

Congener (# Br)	Percent of Total
Penta-BDE Commercial Mixture	
BDE-47 (4)	27
BDE-85 (5)	1.6
BDE-99 (5)	43
BDE-100 (5)	9.8
BDE-153 (6)	8.5
BDE-154 (6)	9.3
hexa-BDE	1.1
Octa-BDE Commercial Mixture	
BDE-153 (6)	6.7
BDE-154 (6)	1.7
BDE-183 (7)	44
2 hepta-BDEs	2.5
3 octa-BDEs	34
BDE-207 (9)	12
Deca-BDE Commercial Mixture	
BDE-209 (10)	>97

Types of Products

Commercial Word Market Demand (2003) for PBDE Commercial Mixtures (Metric Tons)



Source: www.bsef.com

**Penta- and Octa-BDE commercial mixtures currently banned or phased out in U.S.

Potential Toxicity Observed in Laboratory Studies:

Evidence of developmental neurotoxicity (Viberg and Eriksson et al., 2002, 2003, 2005)

- PBDEs can pass the blood/brain barrier and accumulate
- neonatal exposure can induce persistent aberrations in spontaneous behavior, and also affect learning and memory functions in rodents
- one time oral exposure during neonatal period results in effects that worsen with age

"Critical window of development associated with "Brain Growth Spurt"

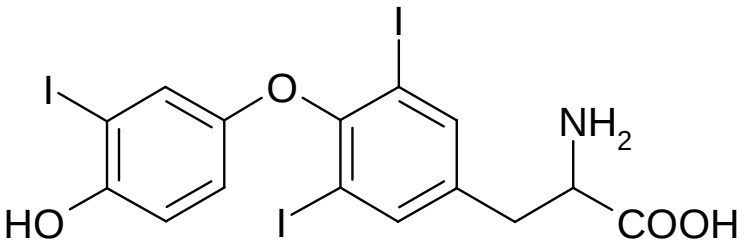
****European study finds PBDE levels in mothers milk positively associated with Cryptorchidism (Main et al., 2007)**

Observed thyroid toxicity:

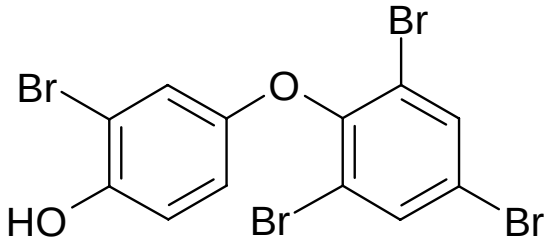
- *In vivo* exposure in fish, rodents and birds leads to reduced levels of circulating hormones (thyroxine and triiodothyronine, T4 and T3)
- induction of UDPGT enzyme activity (clearance of T4 and T3)
- CYP 2B enriched liver microsomes can metabolize BDEs to hydroxylated forms which are very potent competitors for transthyretin
- Activate PXR and steroid X receptors but not AhR

In general, the lower the degree of bromination, the more potentially toxic the compound…….however, debromination may lead to increased toxicity in environment

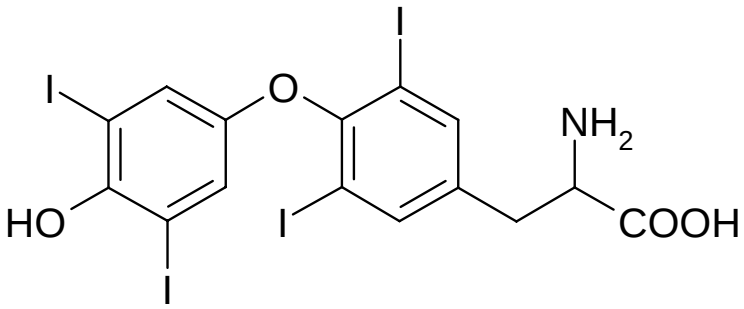
Hydroxylated PBDE Metabolites – Thyroid Hormone Mimics?



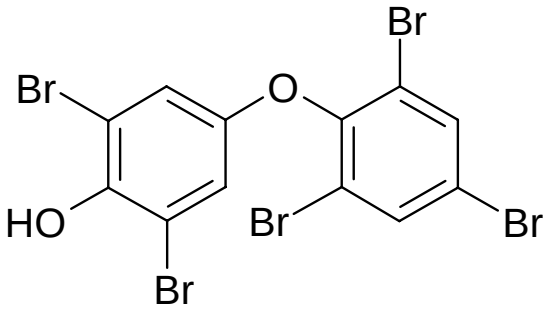
Triiodothyronine (T_3)



T_3-like HO-BDE



Thyroxine (T_4)

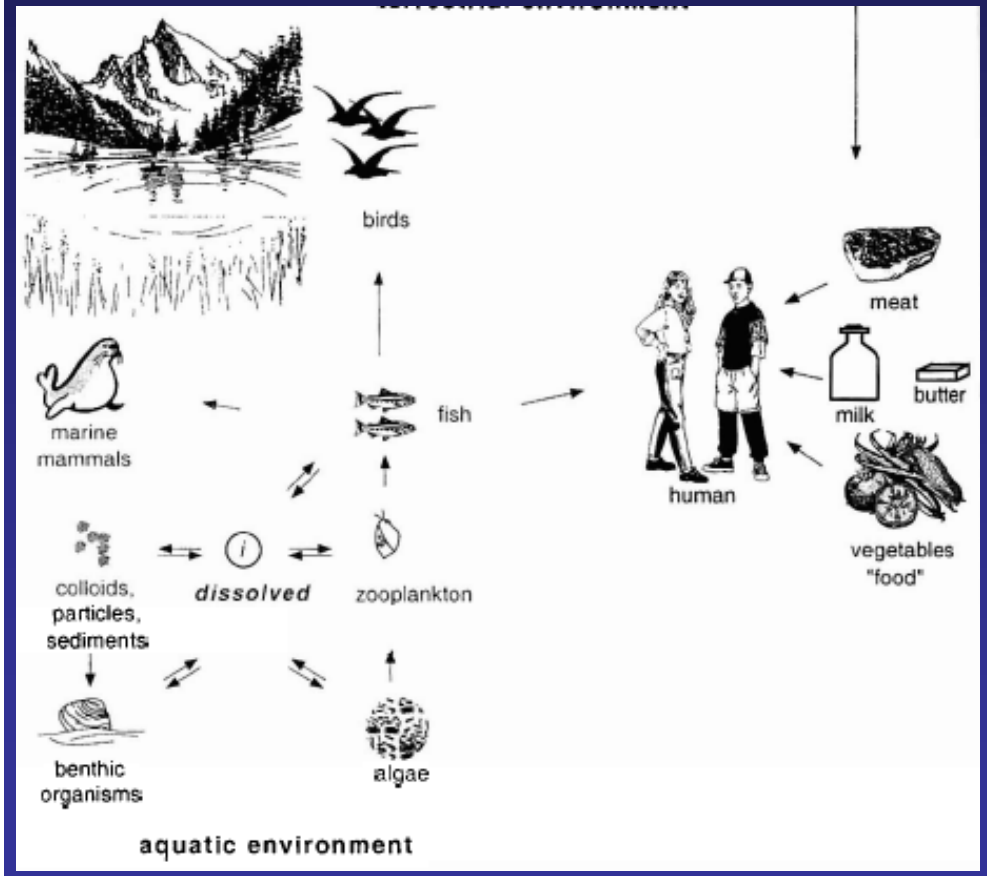


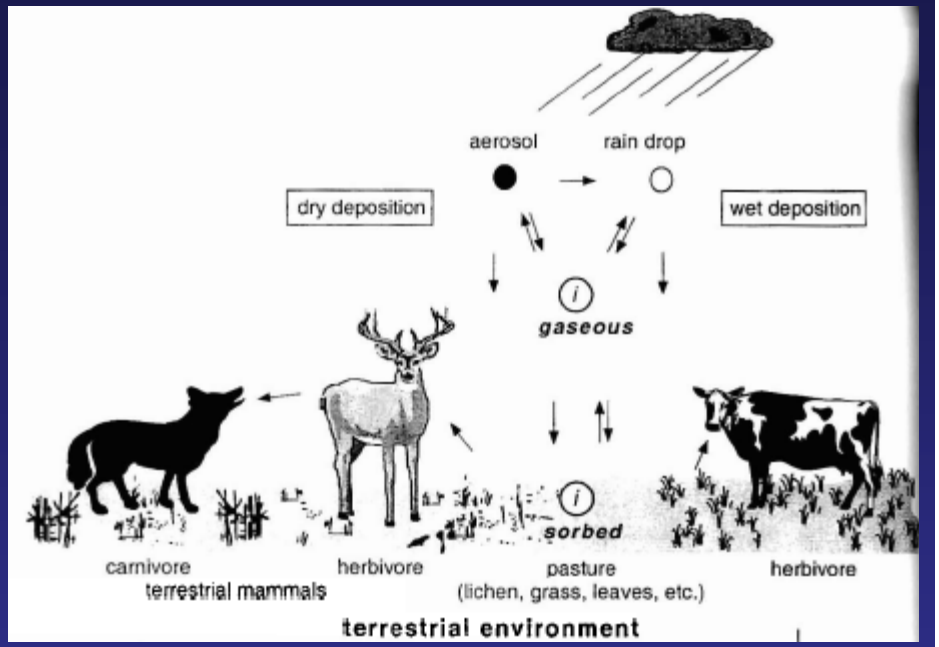
T_4-like HO-BDE

- *In vitro* assays have shown that thyroid-hormone-like HO-BDEs can competitively bind to thyroid transport proteins.

Wildlife Exposure to PBDEs:

Environmental Levels of BDE 209: Terrestrial vs Aquatic Contamination

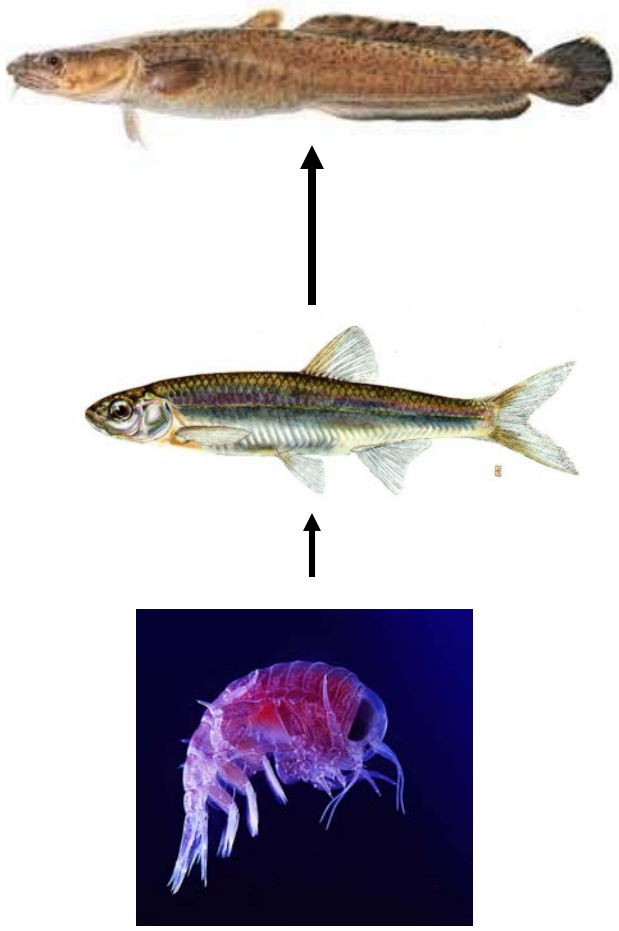




Historically, there has been a stronger focus on POPs in aquatic systems….

However, the terrestrial environment may be receiveing higher exposure to DecaBDE.

DecaBDE does accumulate in Aquatic Organisms and recent evidence Suggests Biomagnification



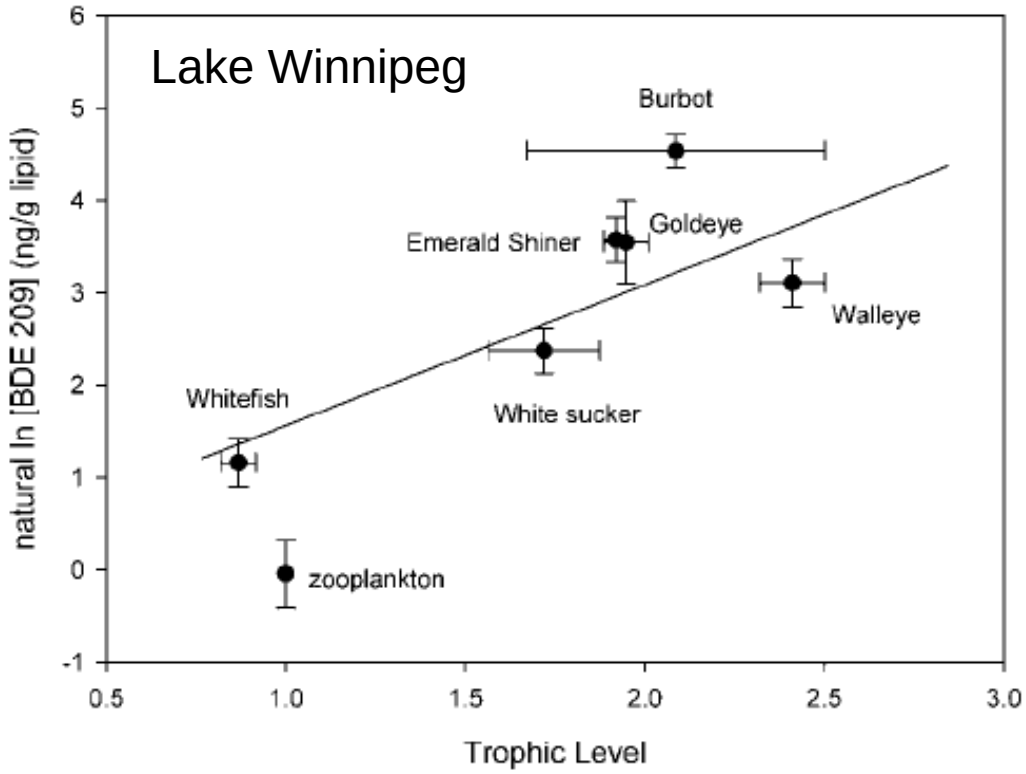


Fig. 5. Relationship between concentration (ng/g, lipid and control corrected; mean ± standard error) of decabromodiphenylether (BDE) 209 and trophic level (TL) for the Lake Winnipeg (Canada) food web. Regression analysis: ln [BDE 209] = 2.2804(TL) − 1.2225 (r^2 = 0.7359, p = 0.01).

(Law et al., 2006)

Environmental Levels of BDE 209 in Wildlife

Grizzly Bears Along British Columbia (Christensen et al., 2005):

ΣPentaBDEs: 0.2 to 5 ppb lipid

DecaBDEs: 0.1 to 42 ppb lipid

** Terrestrial feeding bears have higher BDE 209 concentrations in their tissues (as much as 90% of the burden was BDE 209)

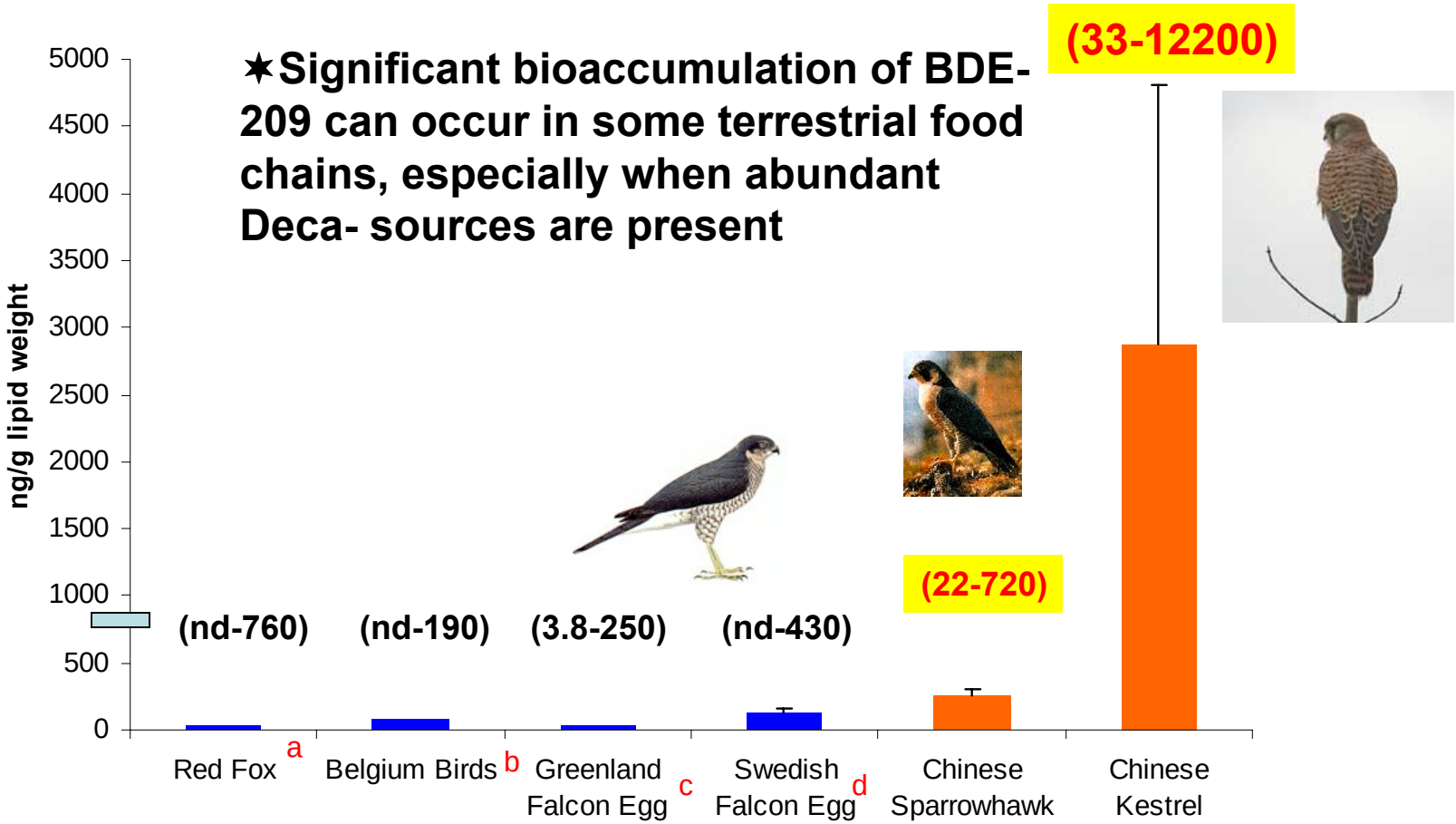
Red Foxes (Voorspoels et al., 2006):
(sampled ~30 individuals)

ΣPentaBDEs: 2 to 3 ppb lipid

DecaBDEs: <DL to 760 ppb lipid

**BDE 209 was the dominant congener (~80%) in almost half the foxes tested

Environmental Levels of BDE 209 in Birds



a. Voorspoels et al., ES&T, 2006, 40, 2937

b. Voorspoels et al., Environ. Pollut. 2006, 114, 218

c. Vorkamp et al., ES&T, 2005, 39, 8199

d. Lindberg et al., ES&T, 2004, 39, 93

(Data from Chen et al., 2007)

Human Exposure to PBDEs:

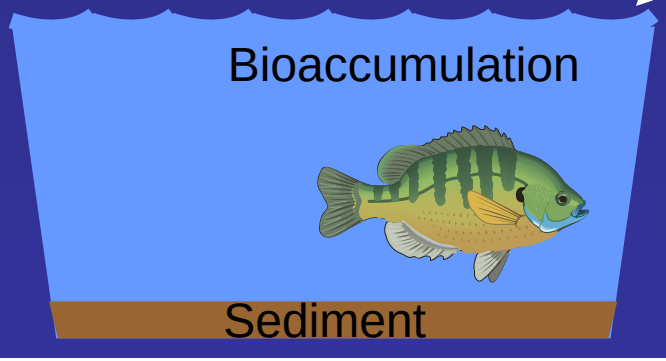
What are the Issues?

Exposure to Persistent Organic Pollutants:

Industrial pollution

Diet

Pesticide applications



What about Indoor Exposure to New POPs?

Work Environment

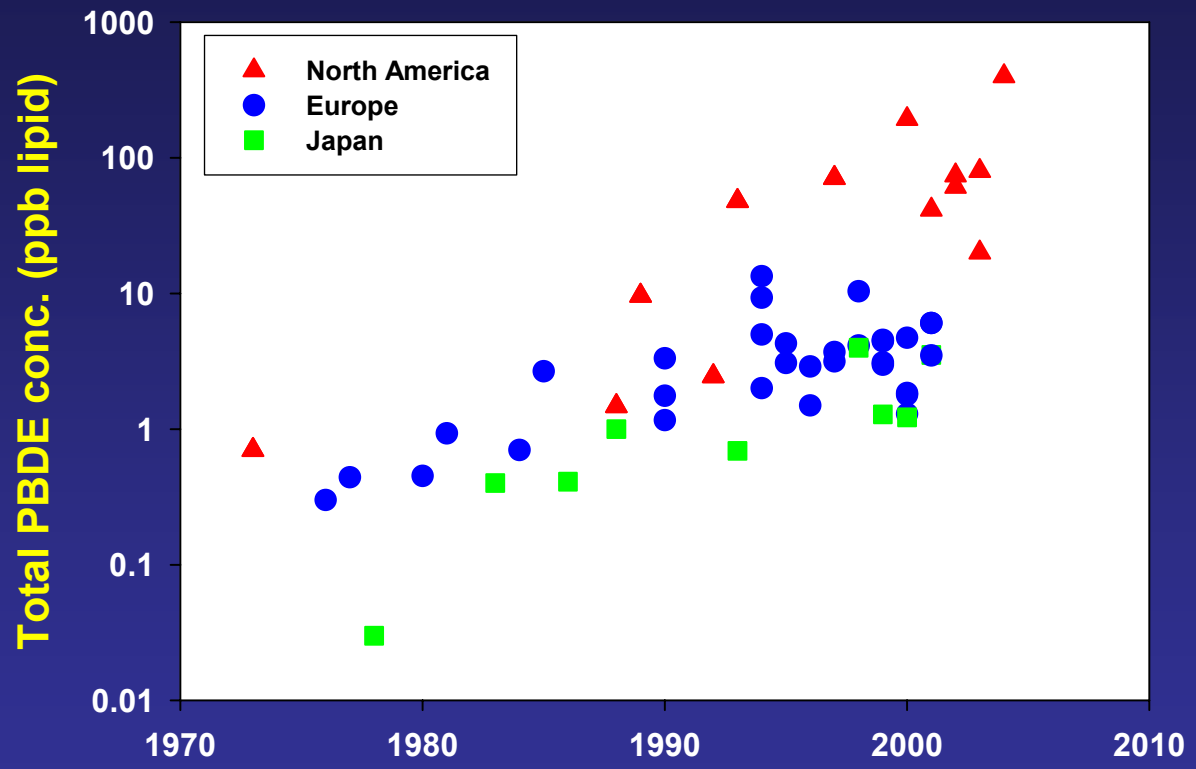
Homes

House Dust

Vehicles

PBDEs in Human Samples From Around the World (primarily pentaBDE)

Data from Hites et al., 2004



Total PBDE concentrations in human blood, milk and tissue (in ng/g lipid) shown as a function of sampling year.

Issue 1: PBDEs were doubling about every 5 years; recent leveling observed
Issue 2: U.S. and Canadian populations have the highest accumulation of PBDEs

What Levels of DecaBDE Have Been Measured in People?

Measured in ppb lipid (<DL -less than detection limits)

Tissue	Population	ΣPenta	ΣDeca	Reference
Breast Milk	U.S. adults (n=47)	6- 420 Mean 62	<DL to 8	2003 Schecter et al
Serum NHANES	U.S. Adults (n=2062)	<DL to 3680 Median = 34	NM	2008 Sjodin et al.
Adipose	U.S. Adults (n=52)	17 to 10,000 Mean 400	NM	2005 Johnson-Restrepo et al.,
Serum	Swedish Workers	<DL to 15	1 to 140	1999 Sjodin et al.
Serum	Swedish Workers	NM	3 to 230	2005 Thuresson et al
Serum	U.S. Foam Workers And Carpet Installers	1 to 7000 Mean 212	<DL	2008 Stapleton et al. (In Press)
Blood	Japanese Adults	0.3 to 6.6	1.3 to 31	2004 Takasuga et al.

What are the Levels of PBDEs in Children?
A Case Study from Berkeley, California

Data from Fisher et al., 2006

Blood Levels Measured in ppb lipid

	Date Measured	ΣPenta	ΣDeca	ΣPBDEs
Father Age 35	Sept. 04 Dec. 04	64 71	23 3	87 74
Mother Age 36	Sept. 04 Dec. 04	106 142	14 4	120 146
Daughter Age 5	Sept. 04 Dec. 04	247 244	143 11	390 255
Son Age: 18 mo	Sept. 04 Dec. 04	418 482	233 23	651 505

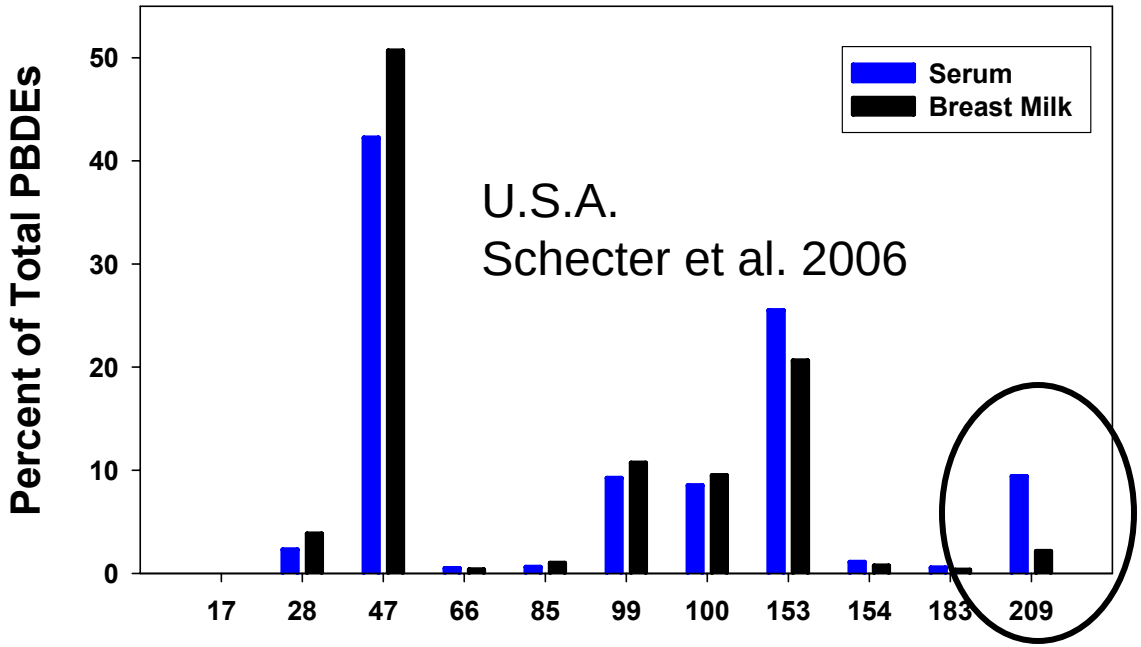
<DL -less than detection limits

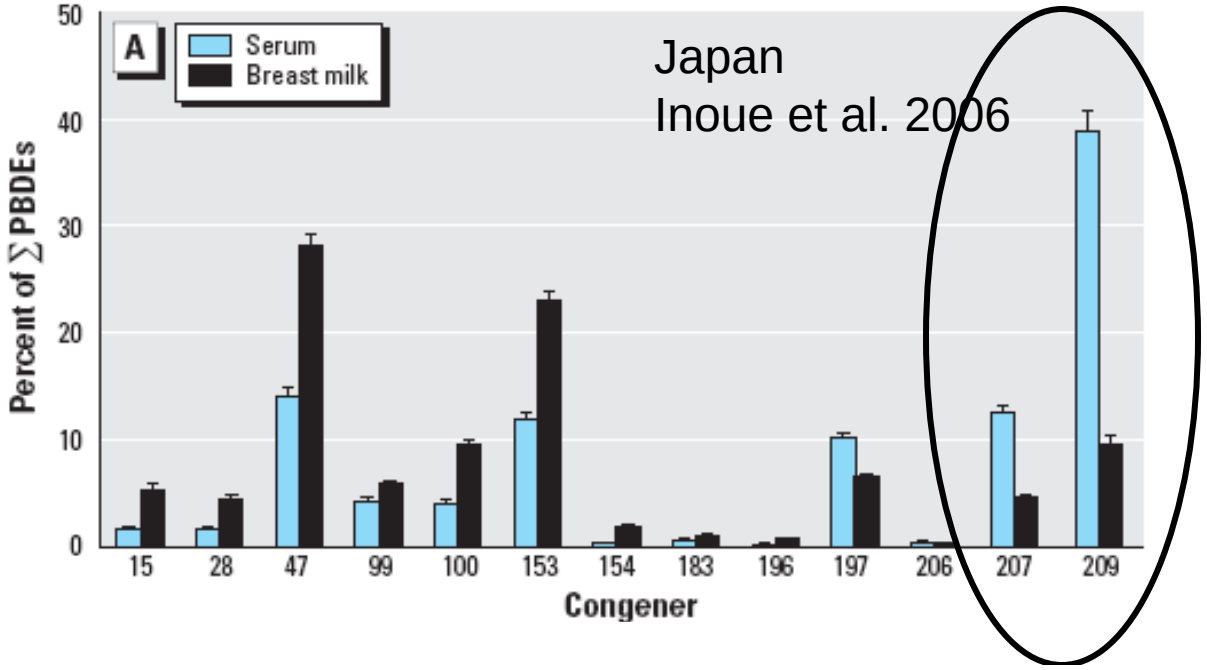
Exposure Modeling Suggest Children are Receiving 10X greater exposure to PBDEs (Jones-Otazo et al., 2005)

**BDE 209 not typically
The most abundant congener
In U.S. population…

**However, Japan and China
Use Primarily DecaBDE in
Products and no PentaBDE.
Tissues in the Japanese and
Chinese populations have a
Strong contribution from
BDE 209…….

**Suggests U.S. may see shift
If DecaBDE not banned from
Use.

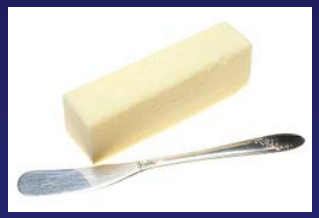




BDE 209 Measured in U.S. Food Items:

(Huwe et al., 2002 and Schecter et al., 2006)

Dairy Products



Butter	66 ppt
Cream Cheese	482 ppt
Milk	<DL to 6 ppt
Cheese	<DL to 18 ppt
Eggs	10 ppt

Fish

Wild Salmon	<DL
Farmed Salmon	20 to 681 ppt
Canned Tuna	5 to 9 ppt
Fresh Tuna	23 ppt
Shrimp	<DL
Tilapia	<DL

Meats

Bacon	<DL to 28 ppt
Ground Meats	<DL to 485 ppt
Pork Sausage	<DL to 50 ppt
Chicken Breast	48 ppt
Whole Chicken	300 to 3400 ppt

PBDEs Measured in Food Items: (Gomara et al., 2006)

Food Purchased in Spanish Supermarkets

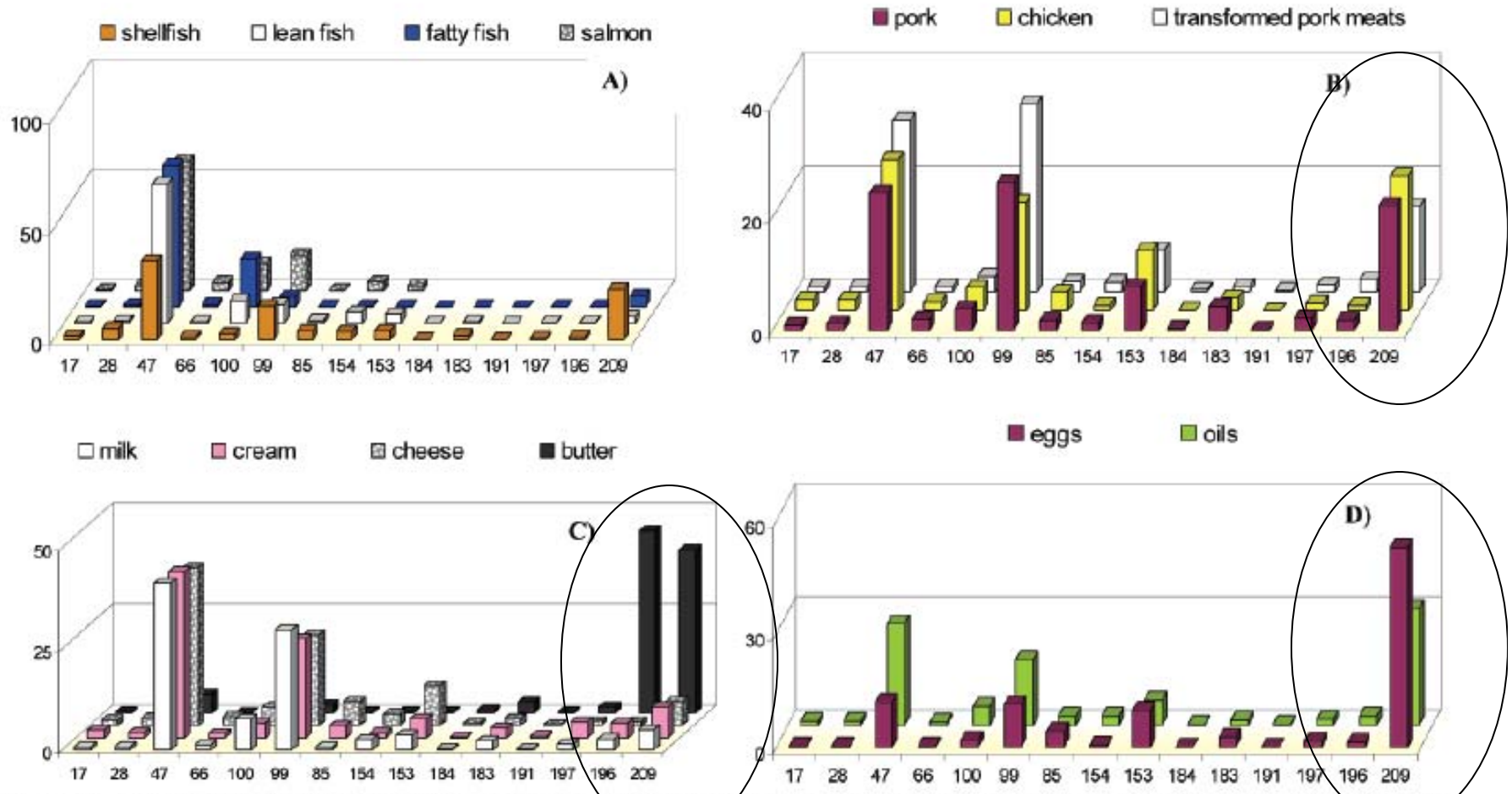


FIGURE 1. Percentages of contribution of the 15 congeners of BDE to the total BDEs in (a) fish and shellfish, (b) meats, (c) dairy products, and (d) oils and butters.

Are Children Receiving Greater Exposure to DecaBDE from House Dust?

Children Place Their Hands, Bottles, Toys,(etc.) in Mouth

Inadvertent ingestion of PBDEs associated with Dust

Measurement of PBDEs in Dust (ng/g dry weight, ppb)

Type of Dust	Study Location	Range ∑PBDEs	Range BDE 209	Reference
House	USA	700 - 69,000	143 – 66,000	Schecter et al., 2005
House	USA (n=17)	780 - 31,000	160 - 8750	Stapleton et al., 2005
House	USA (n=60)	200 -569,000	**60 - 544,000**	Allen et al., 2008*
House	Canada (n=68)	170 -170,000	74 – 10,000	Wilford et al., 2005
House	Germany	25 - 25,000	20 – 19,100	Knoth et al., 2003
House	Kuwait	1 - 390	0.8 - 340	Gevao et al., 2006
Car	USA		9500	Gearhart et al., 2006

*** Allen et al., 2008 – In Review**

What are the Toxic Thresholds and Margins of Safety for BDE 209?

Evidence of Developmental Toxicity (Viberg et al., 2003):

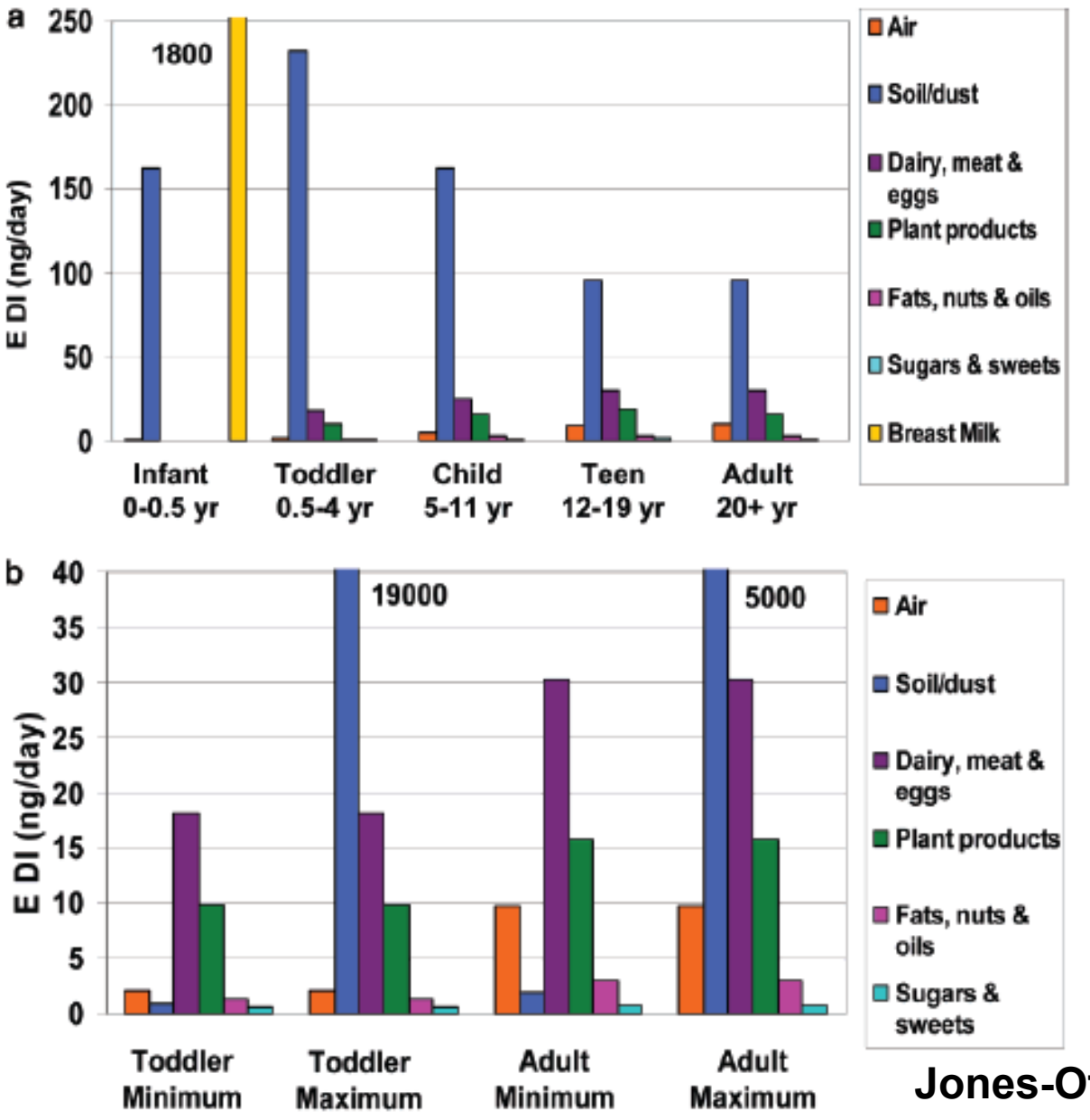
-BDE 209 can pass the blood/brain barrier and accumulate
-can result in altered behavior, memory and learning in mice
-one time oral exposure during neonatal period results in effects that worsen with age

"Critical window of development associated with "Brain Growth Spurt"

-effects observed at doses of 20 mg/kg body weight
-National Academy of Sciences Reference Dose = 4 mg/kg body weight
-EPA IRIS Reference Dose for BDE 209 (2007) = 0.01 mg/kg/body weight/day

*Concentrations of BDE 209 measured in dust as high as 0.5 mg/g dust
(assume ingest 100 mg/day in child = 0.05 mg/day)

PBDE Estimated Daily Intake Rates



Jones-Otazo et al., 2005

Collaborative Research Project: Exposure to PBDEs in Indoor Environments

**Collaborative research project between H.M. Stapleton and colleagues at Boston University School of Public Health

Objectives:

1. Compare indoor air and personal air levels of BDEs

2. Examine differences in BDE levels in dust collected from different rooms, over seasons and using different collection methods

3. Use XRF technology to determine sources of BDEs in the home environment

4. Quantify relative exposure via inhalation, dust ingestion and hand to mouth contact.

PBDEs in Indoor Air

- We are inhaling PBDEs in indoor air

  ~ 3.5 ng/day of decaBDE
  ~10 ng/day of pentaBDE
  (assumed inhalation rate of 20 m^3/day).

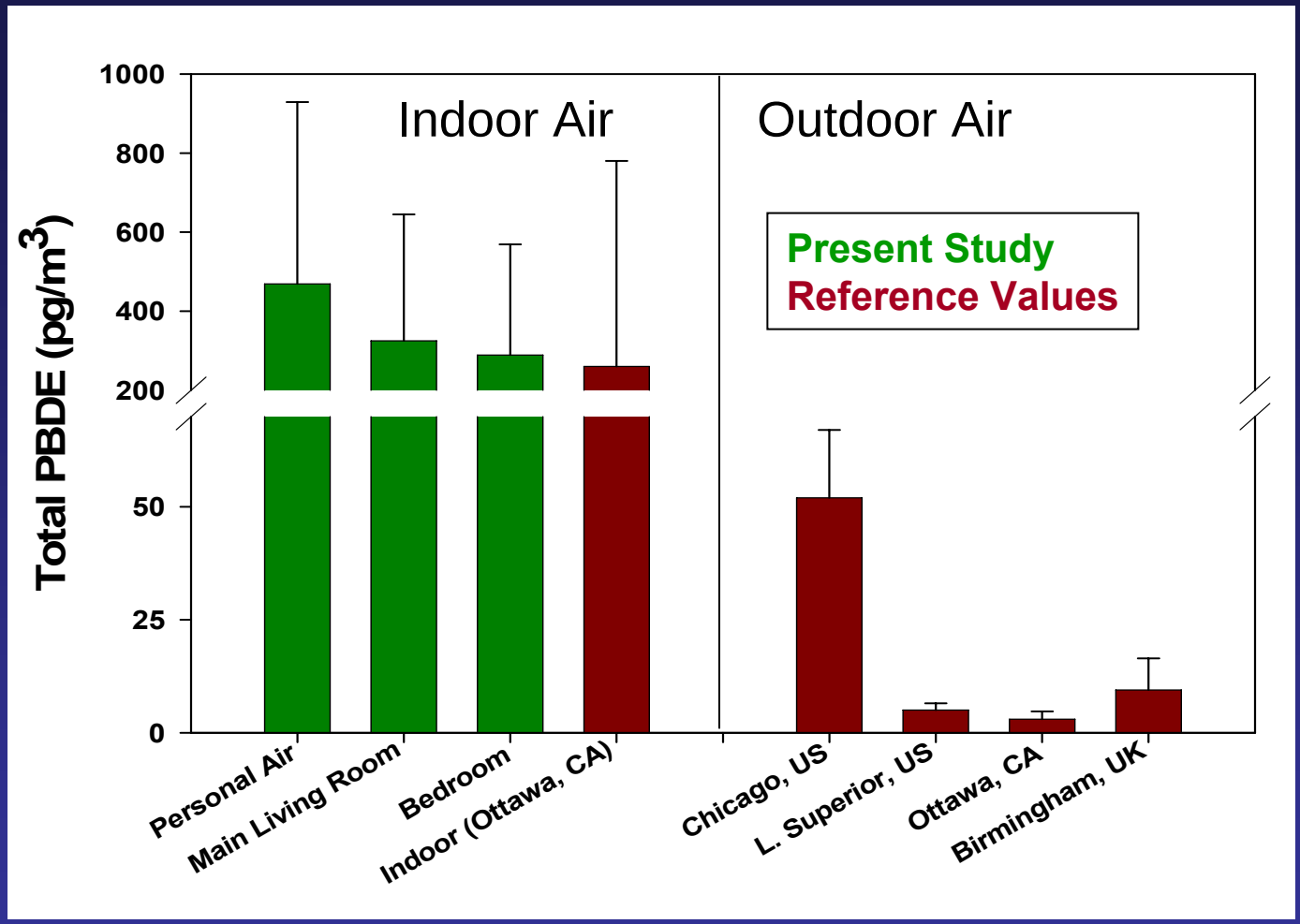
**Presence of personal "dust clouds" results in higher exposure than predicted by large volume air samplers

GM PBDE Concentrations in Air (pg/m^3)

Congener	Personal	Bedroom		Main living area	
BDE 17	7.6	8.1		7.0	
BDE 28/33	29.6	27.3		25.4	
BDE 47	226.8	157.9	**	145.1	**
BDE 49	9.1	6.0	**	7.2	
BDE 66	3.7	3.5		3.5	
BDE 85/155	3.8	2.7		2.5	
BDE 99	110.8	66.9	**	60.3	**
BDE 100	22.2	14.4	**	12.0	**
BDE 153	8.6	4.0	**	3.5	**
BDE 154	9.1	6.1	**	5.2	**
BDE 209	173.6	94.8	**	94.2	**
∑BDE	765.7	460.4		452.8	
∑BDE (no 209)	469.1	324.7		288.6	

(Data from Allen et al., 2007)
20 participants from Boston, MA

[Published in ES&T]



References:

Standberg et al., 2001
Wilford et al., 2004
Harrad et al., 2006

Findings:

- Differences in collection method
- Higher levels in living room
- No significant seasonal differences

Concentration units: ppb (ng/g)

BFR	Congener	Living Room GM (GSD)	Bedroom GM (GSD)	Vacuum Bag GM (GSD)
Penta-product				
	BDE 17	1.4 (12.8)	0.6 (8.7)	0.4 (11.2)
	BDE 28/33	16.3 (2.8)	10.5 (2.6)	6.4 (2.6)
	BDE 47	1,864.5 (2.9)	837.0 (3.3)	337.6 (4.2)
	BDE 49	29.6 (4.8)	23.6 (2.6)	12.4 (2.9)
	BDE 66	17.2 (4.9)	15.3 (2.9)	6.9 (3.9)
	BDE 75	9.3 (3.1)	5.3 (2.8)	3.6 (3.1)
	BDE 85/155	124.0 (3.1)	51.8 (4.1)	19.2 (4.7)
	BDE 99	2,460.0 (3.0)	1,170.0 (4.0)	536.4 (3.6)
	BDE 100	436.3 (3.0)	204.0 (3.9)	76.9 (4.1)
	BDE 138	20.9 (5.8)	12.1 (5.4)	5.2 (4.3)
	BDE 153	234.4 (2.9)	124.2 (4.5)	47.0 (4.2)
	BDE 154	182.8 (2.9)	94.4 (4.3)	35.0 (4.8)
	∑ Penta-product BDEs	**5,461.9 (2.9)**	**2,612.8 (3.8)**	**1,182.6 (3.5)**
Octa-product				
	BDE 183	27.9 (3.2)	32.9 (6.0)	15.1 (3.7)
	BDE 196	3.6 (9.0)	2.6 (11.8)	3.9 (6.1)
	BDE 197	2.7 (11.5)	3.3 (17.1)	5.6 (4.8)
	BDE 203	3.6 (6.4)	3.6 (10.0)	4.9 (4.7)
	∑ Octa-product BDEs	**49.8 (3.5)**	**55.1 (5.8)**	**35.2 (3.4)**
Deca-product				
	BDE 206	76.3 (4.3)	48.1 (3.8)	40.5 (5.5)
	BDE 207	45.9 (5.0)	25.3 (7.8)	26.6 (6.4)
	BDE 208	35.6 (5.7)	17.5 (7.1)	29.4 (7.1)
	BDE 209	4,502.1 (4.4)	1,702.8 (6.0)	1,811.2 (5.6)
	∑ Deca-product BDEs	**4,702.0 (4.4)**	**1,865.6 (5.6)**	**1,938.9 (5.6)**
BTBPE				
	BTBPE	16.1 (6.3)	8.2 (12.3)	11.3 (3.9)

(Currently in Review for Publication)

Characterizing PBDE Sources in the Home

XRF – X-Ray Fluorescence:

- Technology used to monitor lead in homes
- Analysis specific to each element

XRF Application to Identifying PBDE Sources:

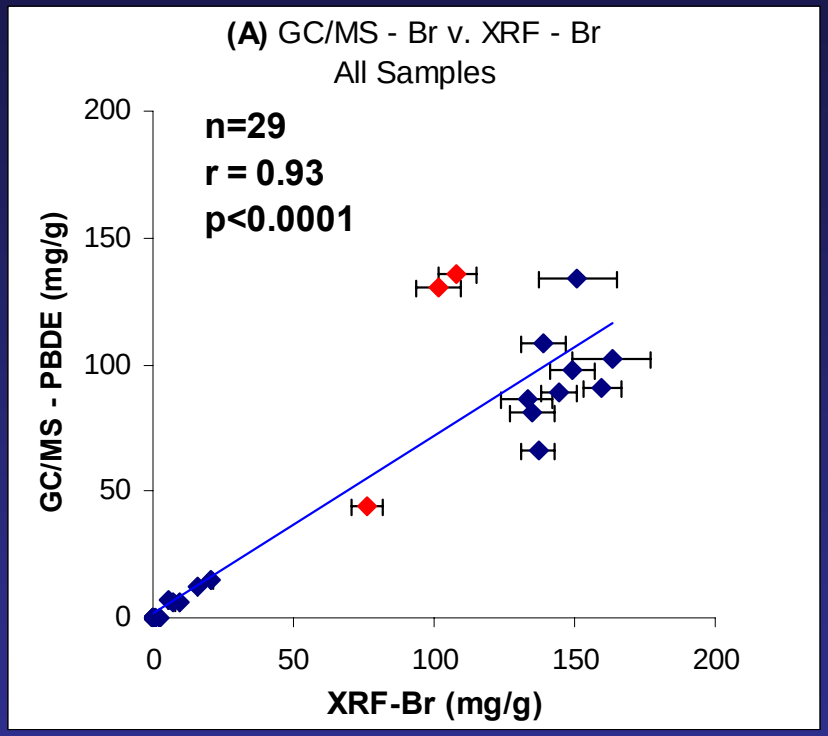
1) Validate XRF method

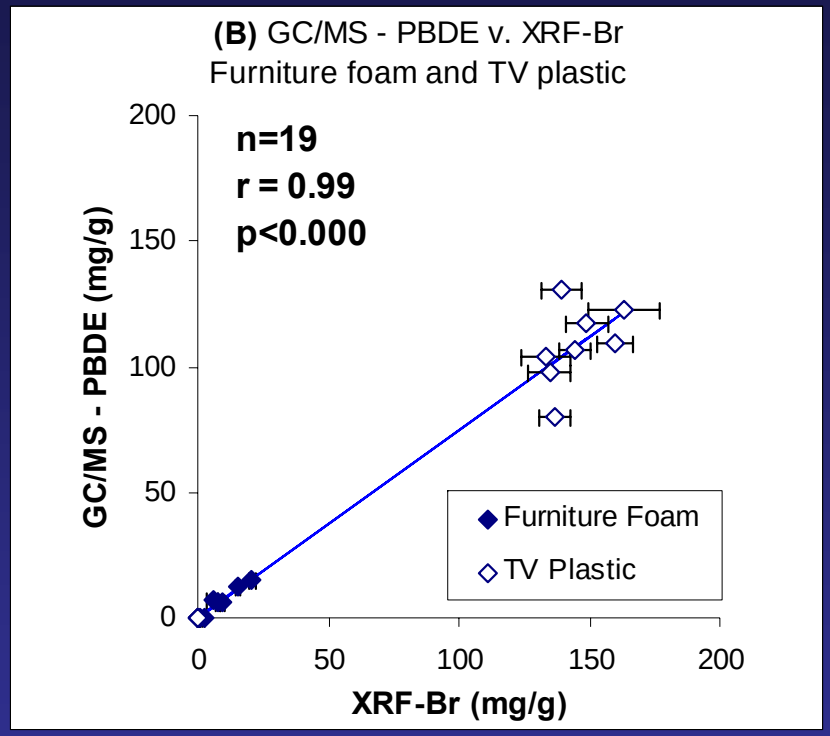
2) Use to determine [Br] in products found within the home (e.g. TVs, electronics, furniture, carpets, mattresses, etc.)

3) Determine if dust PBDE levels correlate to [Br] measured by XRF

(Currently in Review for Publication)

XRF Validation Pilot Study:





Results: XRF measured bromine was highly correlated with GC/MS measurd bromine

Red points indicate TBBPA measured bromine by GC/MS

Figure 2.

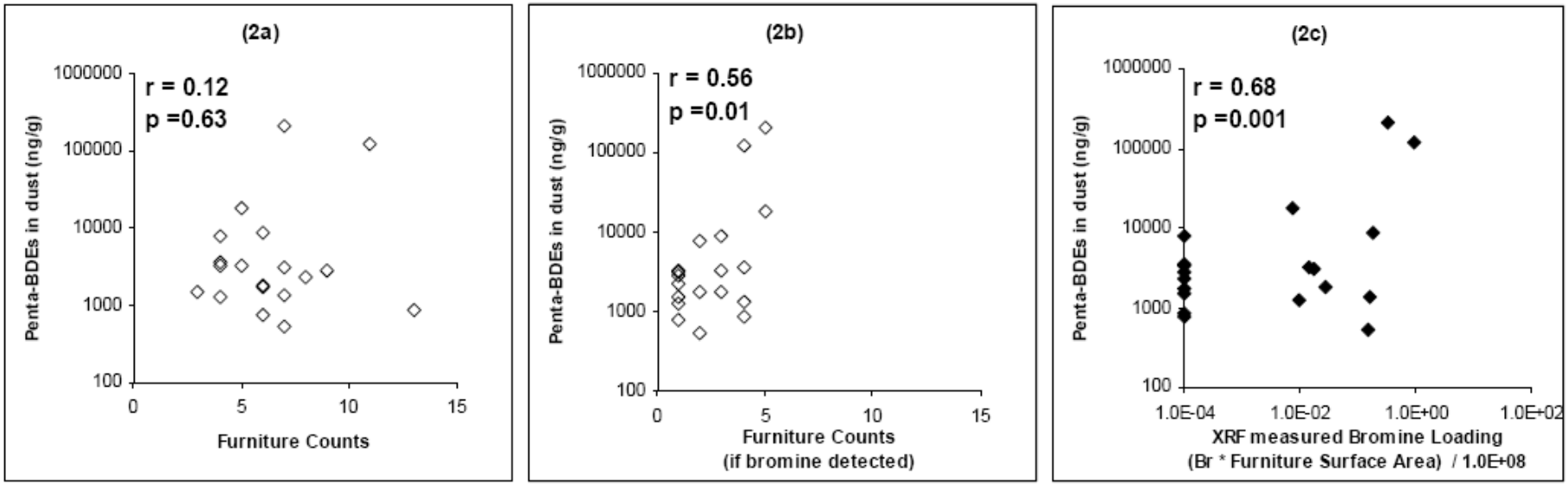
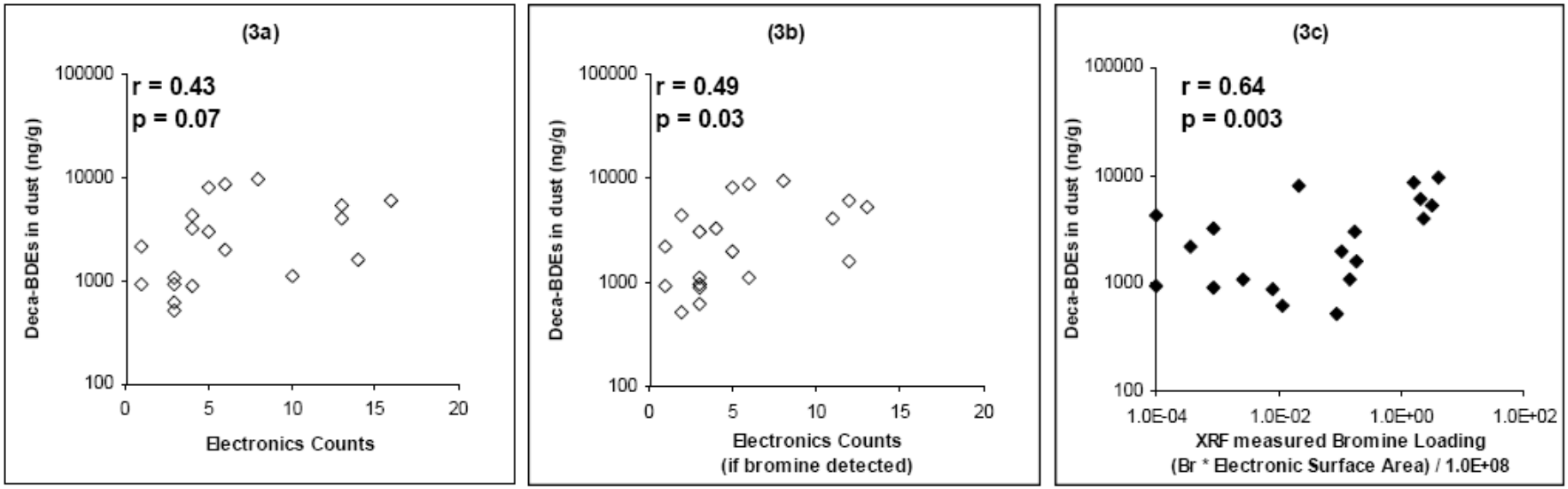

(2a)
r = 0.12
p =0.63
Penta-BDEs in dust (ng/g)
1000000
100000
10000
1000
100
0
5
10
15
Furniture Counts
(2b)
r = 0.56
p =0.01
Penta-BDEs in dust (ng/g)
1000000
100000
10000
1000
100
0
5
10
15
Furniture Counts
(if bromine detected)
(2c)
r = 0.68
p =0.001
Penta-BDEs in dust (ng/g)
1000000
100000
10000
1000
100
1.0E-04
1.0E-02
1.0E+00
1.0E+02
XRF measured Bromine Loading
(Br * Furniture Surface Area) / 1.0E+08

Figure 3.


(3a)
r = 0.43
p = 0.07
Deca-BDEs in dust (ng/g)
100000
10000
1000
100
0
5
10
15
20
Electronics Counts
(3b)
r = 0.49
p = 0.03
Deca-BDEs in dust (ng/g)
100000
10000
1000
100
0
5
10
15
20
Electronics Counts
(if bromine detected)
(3c)
r = 0.64
p = 0.003
Deca-BDEs in dust (ng/g)
100000
10000
1000
100
1.0E-04
1.0E-02
1.0E+00
1.0E+02
XRF measured Bromine Loading
(Br * Electronic Surface Area) / 1.0E+08

Therefore……items in our home are likely contributing to PBDE levels in dust……..but how does that translate to exposure???

- Estimates of PBDE exposure from dust are poor and assume an ingestion rate of dust/day (e.g. 100 mg dust/day)
- However, PBDEs may be adsorbing directly to surface oils of skin from contact with PBDE laden products (i.e. remote controls, keyboards,)
- Better estimates are needed to quantify hand to mouth transfer of PBDEs

Objectives:

1. Determine if PBDEs were detectable on hand wipe samples
2. Examine distribution of PBDE mass present on hand surface area among 30 individuals
3. Estimate exposure to PBDEs via hand to mouth contact using hand wipe measurements.

Hand Wipe Sampling and Methods:

Wipe Sample From
Top of Hand

Wipe Sample From
Bottom of Hand

- 33 volunteers/participants
  - 6 children (8-11 yrs), two families of four
  - 3 individuals- repeated sampling & top/bottom comparison
- Sterile gauze pads soaked in 3 mL isopropyl alcohol
- Wipe entire surface area of hand from wrist to finger tips
- Extract with 50 mL dichloromethane (3X by sonication)
- Clean-up extract using 6% deactivated alumina resin
- Analyze by gas chromatography/electron capture negative ionization mass spectrometry (GC/ECNI-MS) for suite of 35 PBDE congeners

Results:

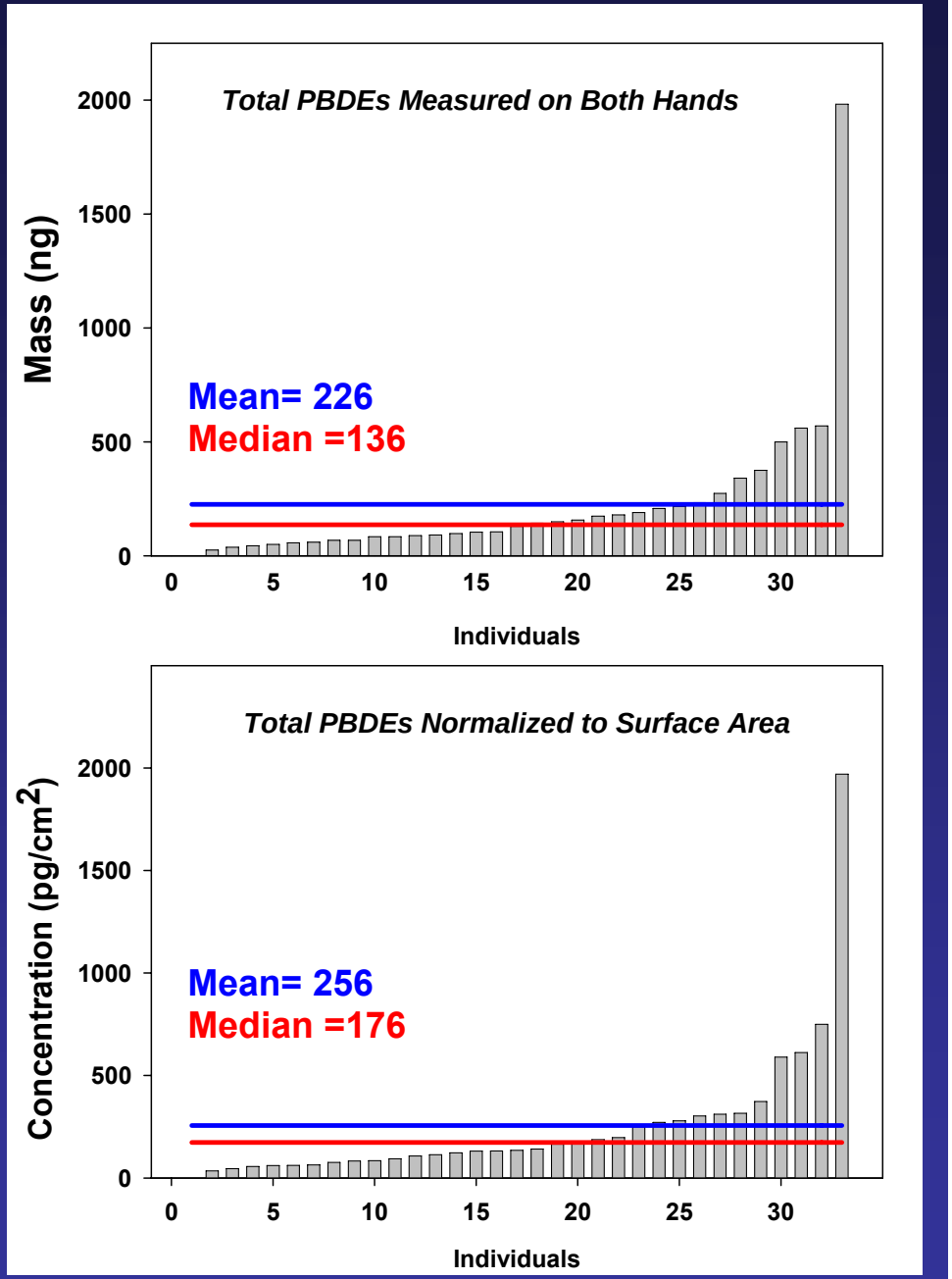
Range: 3 to 1980 ng total PBDE
Among all individuals

Children Only (n=6):
Range: 59 to 560 ng total PBDE
Median: 138 ng

BDEs 47, 99 and 100 Contribute
average of 67% of total BDEs

BDE 209 Levels:

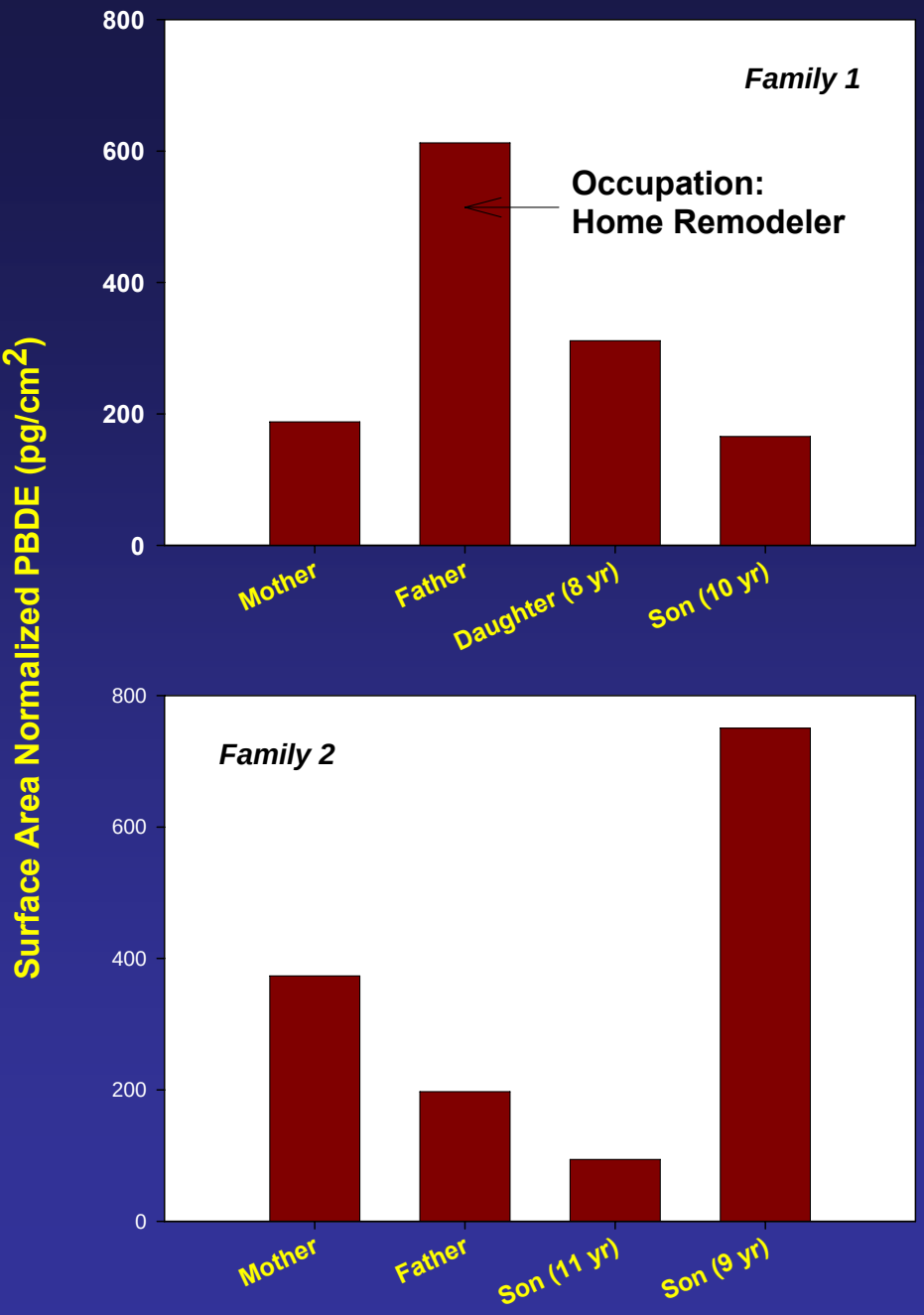
Min: <DL
Max: 270 ng
Median: 25.9 ng
Mean: 42.2 ng



In one individual, 94% of ΣBDE was from BDE 209

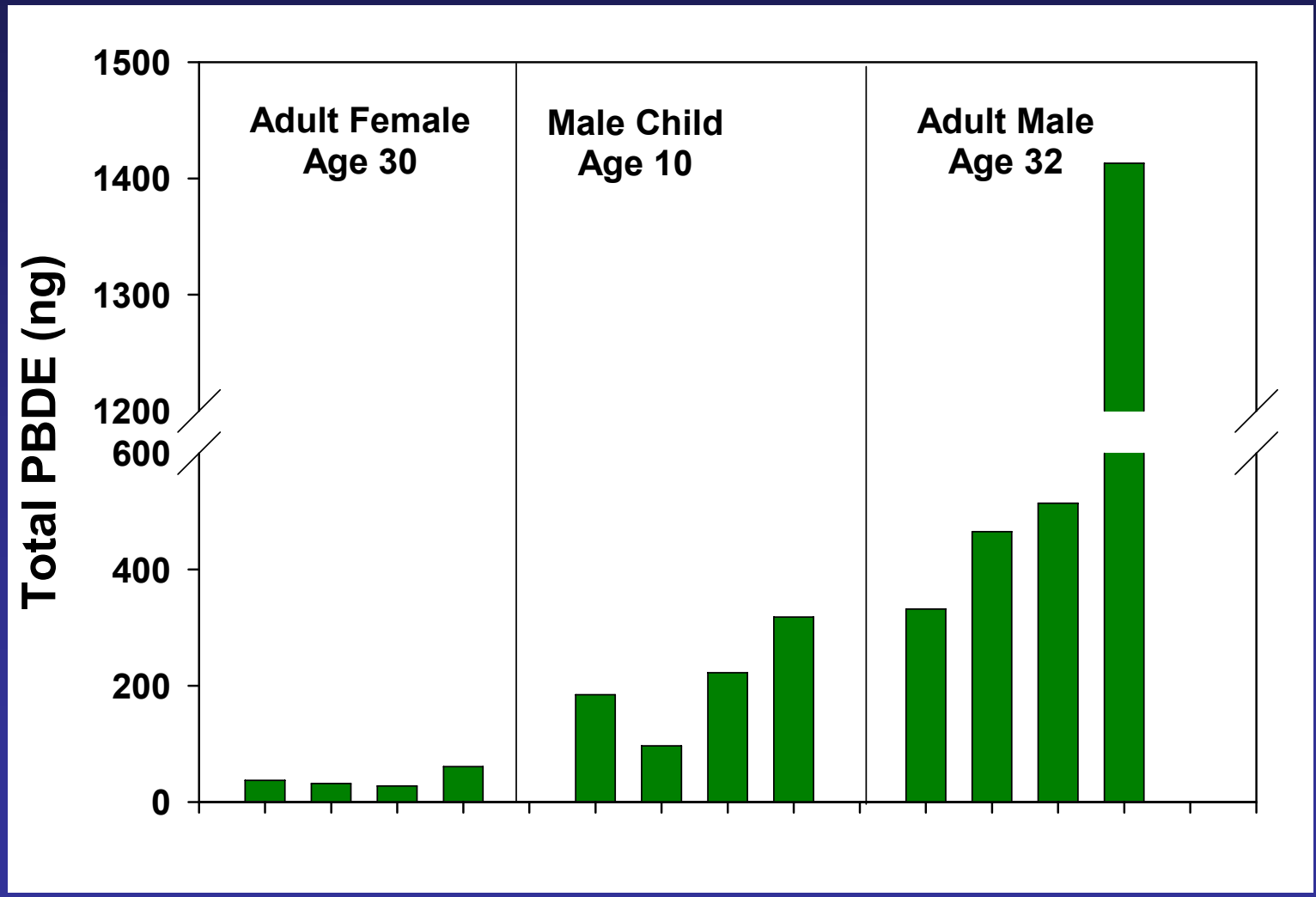
Concentrations Among Families:

- PBDE mass normalized to hand surface area
- Hand surface area calculated based on height, weight and gender
- Hand surface area is not a variable affecting differences in PBDE loadings

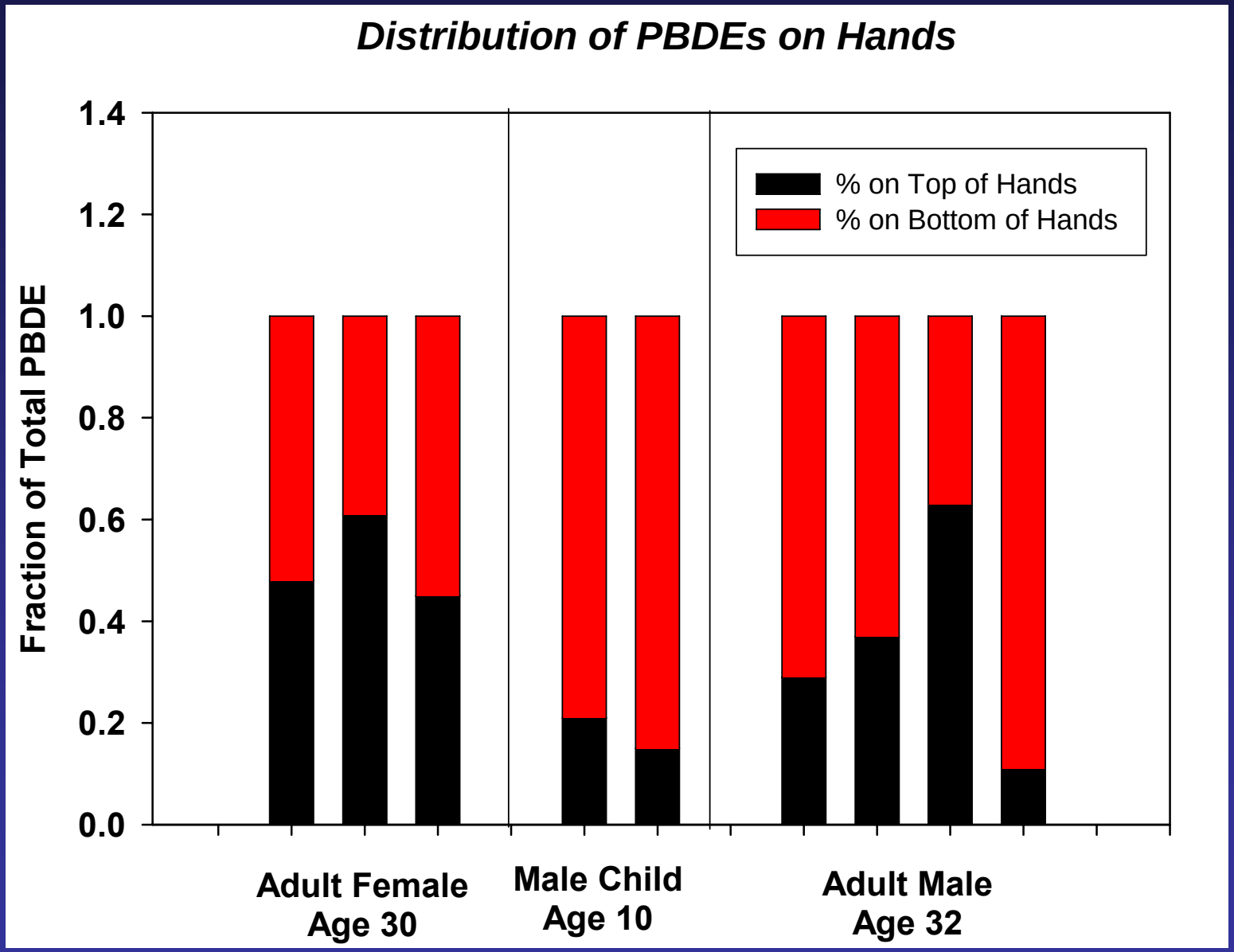


Repeated Wipe Collections from 3 individuals:

- Collected over two month period
- Some individuals consistent, others are not



PBDE Levels on Top and Bottom of Hands



Exposure Parameters for Hand to Mouth Contact

	Child (1-4)	Adult
Mouthing events per hour*	18	2
Fraction of hand surface area mouthed**	0.1	0.1
Hand to mouth transfer efficiency**	10 - 90%	
Hours of Contact per day	12	12
Median PBDE Level on Hand (ng)	130	
95th Percentile PBDE Level (ng)	564	

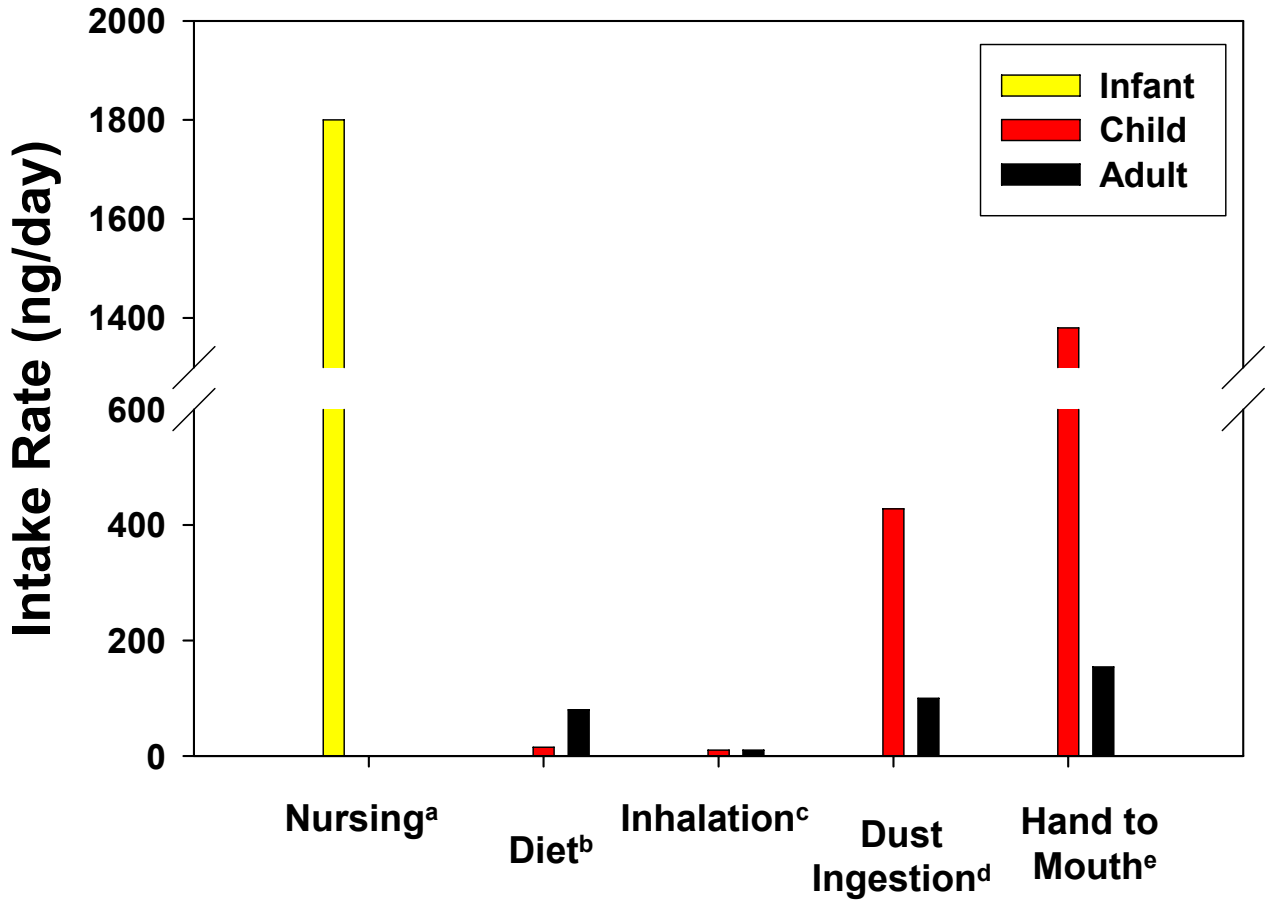
Exposure Rates via Hand to Mouth Contact (ng/day)

Assuming Transfer Efficiency of 50%:		
Median Exposure	1380	154
95th Percentile Exposure	6090	680
Assuming Median PBDE Levels on Hands:		
10% Transfer Efficiency	281	32
90% Transfer Efficiency	2530	280

* Factors taken from Tulve et al., 2002

**Factors Taken From SHED Model for CCA Treated Wood, Zartarian 2005

Estimates of Median PBDE Intake by Source In U.S. Population



a-assuming an infant weighs 5 kg and ingests 800 mL of breast milk/day (Schecter et al., 2005).
b-assuming adult weighs 65 kg and a child weighs 13 kg (Schecter et al., 2006).
c-assuming an inhalation rate of 20 m^3/day (Allen et al., 2007).
d-assuming that children ingest 100 mg of dust/day and an adult 20 mg dust/day (Stapleton et al., 2005).
e- Using model parameters estimates on previous slide and median BDE levels of 130 ng on hands.

Alternative Flame Retardant Chemicals

Potential Deca-BDE Replacements

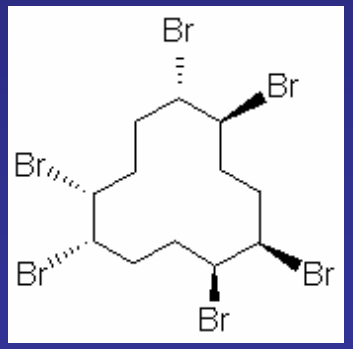
- Tetrabromobisphenol A (TBBPA)
- Hexabromocyclododecane (HBCD)
- Decabromodiphenylethane (DBDPE)
- 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE)
- Pentabromoethylbenzene (PBEB)
- Dechlorane Plus (DP)

Potential Penta-BDE Replacements

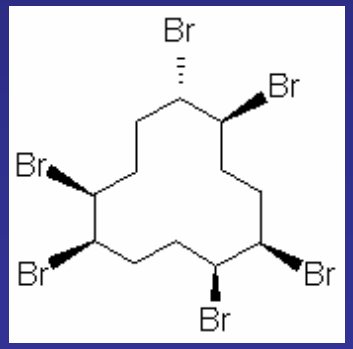
- Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)
- Triphenylphosphate (TPP)
- Octyl tetrabromobenzoate (OTB)

Hexabromocyclododecane (HBCD)

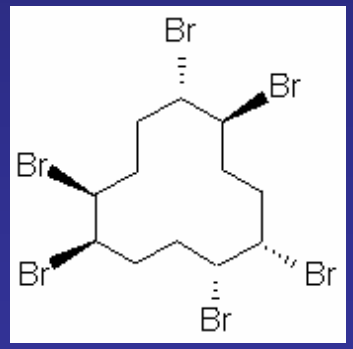
- High production volume chemical (#3 BFR)
- Additive flame retardant
- Used in polystyrene foams for thermal insulation in buildings (expanded and extruded Polysytrene, EPS and XPS), upholstery textiles, electrical equipment housings
- Detected in human serum ranging from <DL to 850 ng/g lipid (Thomsen et al 2007).



α-HBCD
~ 6%

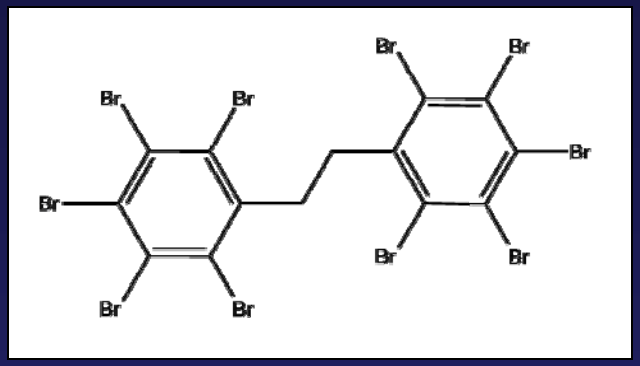


β-HBCD
~ 8%



γ-HBCD
~ 80%

Decabromodiphenylethane (DBDPE)



Application

- Applications similar to Deca-BDE

Occurrence and Bioaccumulation

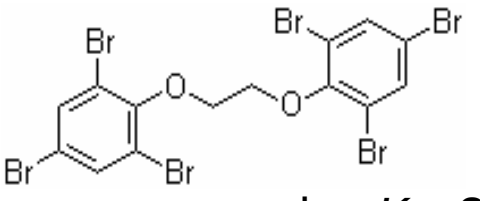
- Sewage sludge from Sweden and Canada (10-100 ng/g dry) (Kierkegaared et al. 2004; McCrindle et al. 2004)
- Great Lakes air (Hoh 2006)
- Tree bark in North America (Zhu and Hites 2006)
- Lake Winnipeg food web (Law et al. 2006)
- Not measured in CA or any urbanized estuary

Toxicity? We don't know; aquatic acute/chronic studies not available

1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE)

Application

- Additive flame retardant used in thermoplastics
- Replacement for Octa-BDE (Great Lakes Chemical)



log K_{ow} ?

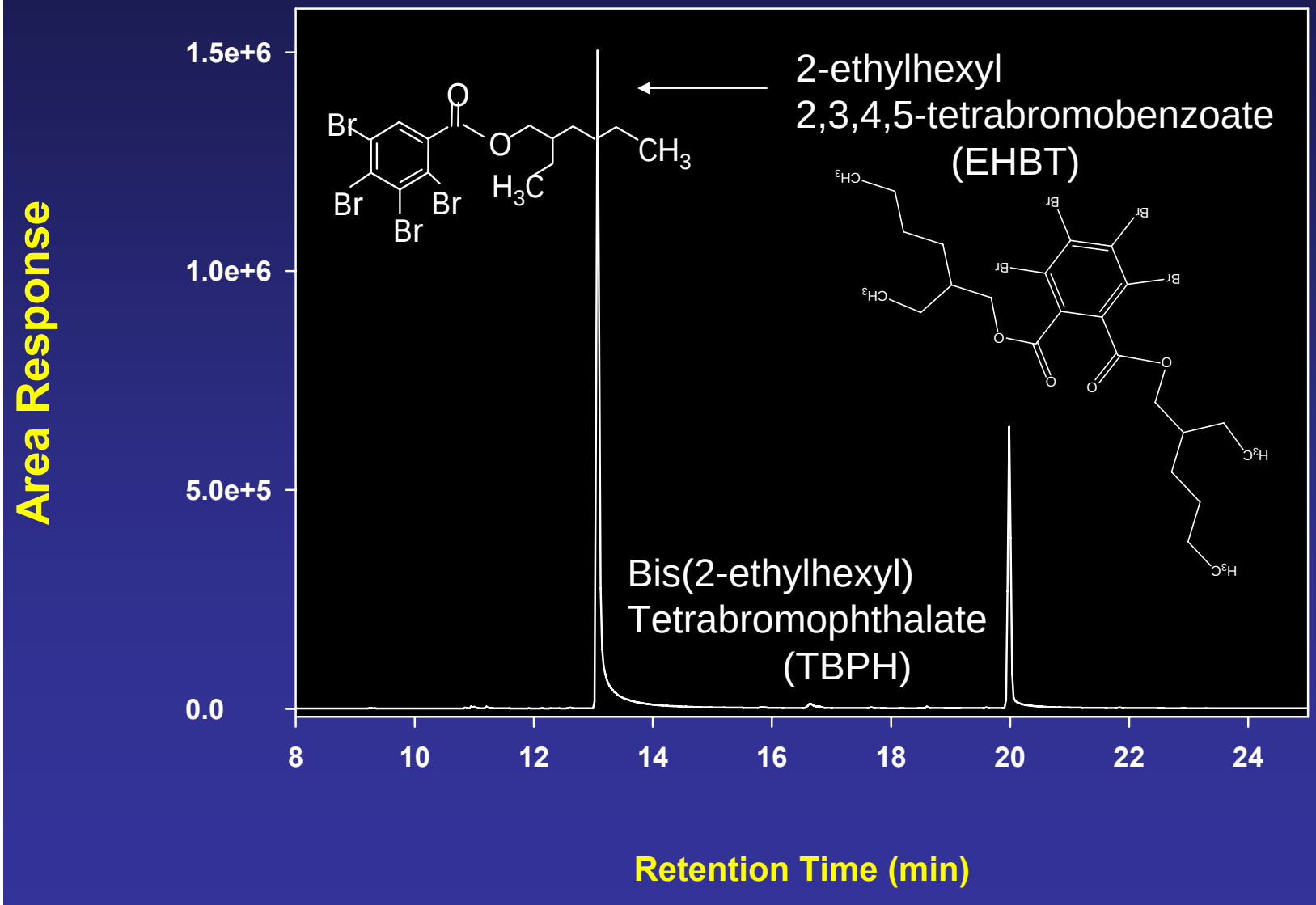
Occurrence and Bioaccumulation

- U.S. air, in concentrations similar to PBDEs (Hoh et al. 2005)
- Great Lakes sediment (Hoh et al. 2005)
- Tree bark in North America (Zhu and Hites 2006)
- Lake Winnipeg food web (Law et al. 2006)
- Herring gull eggs from the Great Lakes (Gauthier et al. 2007),
- Northern Fulmar eggs from the Faroe Islands (Karlsson et al. 2006)
- Between 1979 and 1998, concentrations increased in Ontario lake trout (Tomy et al. BFR 2007)

Toxicity

- Thyroid interference minimal (if any) in juvenile rainbow trout (Tomy et al. 2007)

Brominated compounds in Firemaster 550 [BZ 54]



Summary and Conclusions:

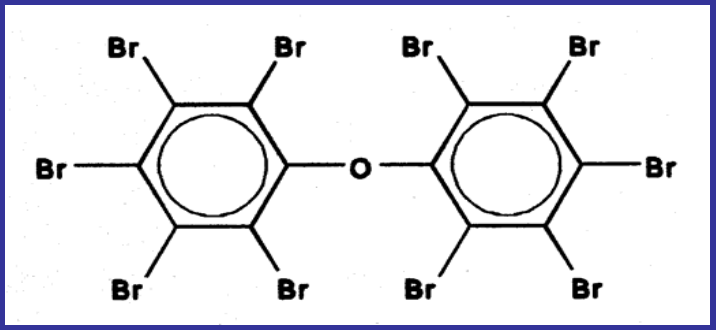
- PBDEs are found at greater concentrations in indoor environments relative to outdoor environments
- XRF analyses indicates foam is a likely source of PentaBDEs and TVs are likely a source of DecaBDE to indoor dust
- PBDEs are adsorbed to the surface of the skin and objects we come into contact with on a daily basis (e.g. remote controls, furniture, phones) may lead to increased adsorption of PBDEs to hands
- Hand to mouth contact is likely not an insignificant route of exposure and behavior that leads to increased hand to mouth contact (e.g. smoking, thumb sucking, finger foods) likely leads to increased exposure via inadvertent ingestion
- Alternate Brominated Flame Retardant chemicals are being detected in house dust, including BTBPE, DBDPE, HBCD and components of FM 550
- BDE 209 can be degrade to lower PBDE congeners via photolysis and metabolism

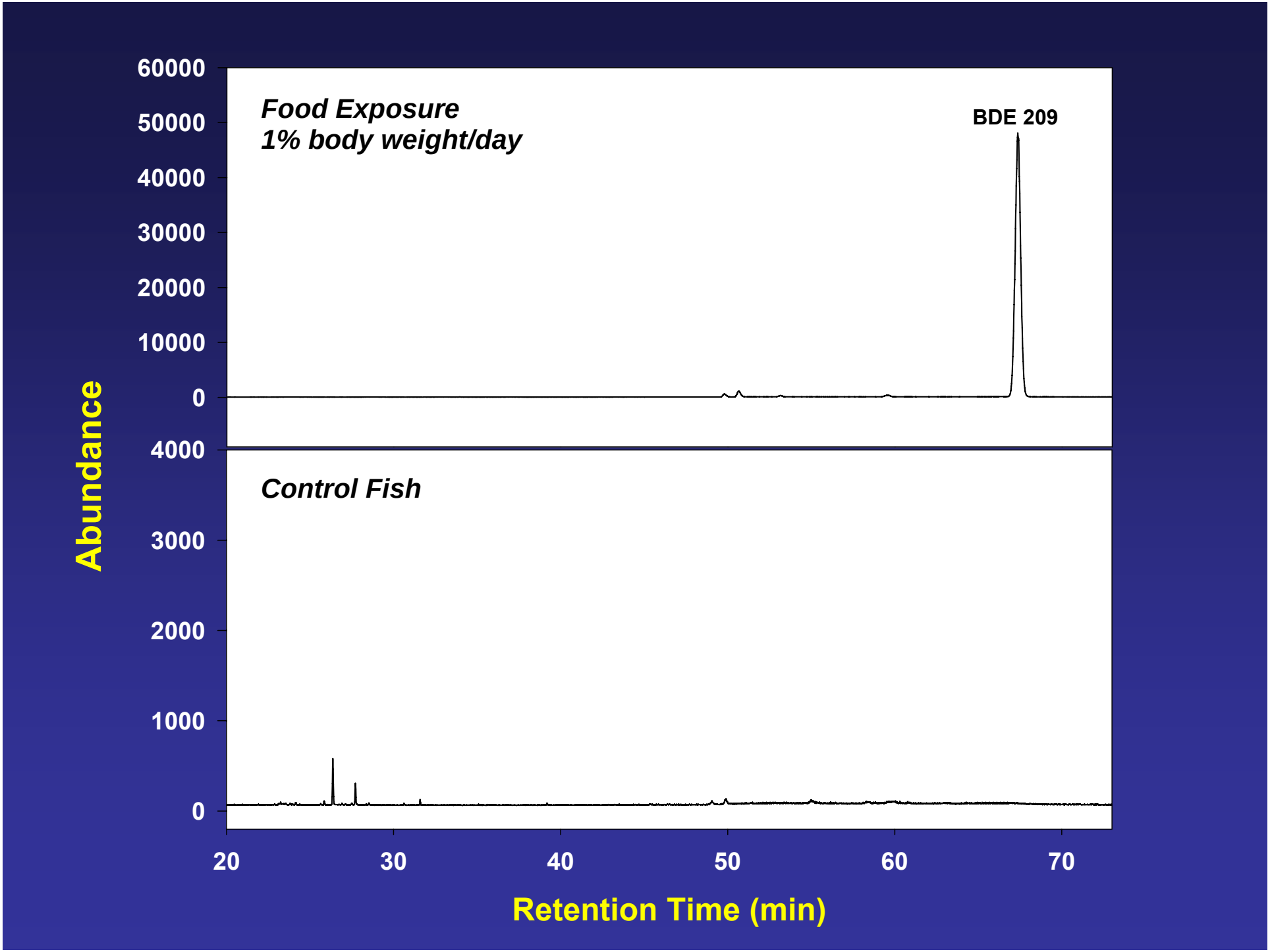
BDE 209 Exposure Studies With Both Carp and Rainbow Trout

Control 12 Fish	Exposure 1 12 Fish	Exposure 2 12 Fish	Exposure 3 12 Fish

USDA Center for Cool and Coldwater Aquaculture
Kearneysville, WV, USA
2005

- Dietary exposure to BDE 209 at ~1 ppm/day
- Examined uptake of BDE 209 in tissues and measured debrominated metabolites




Food Exposure
1% body weight/day
BDE 209
Control Fish
Abundance
60000
50000
40000
30000
20000
10000
0
4000
3000
2000
1000
0
20
30
40
50
60
70
Retention Time (min)

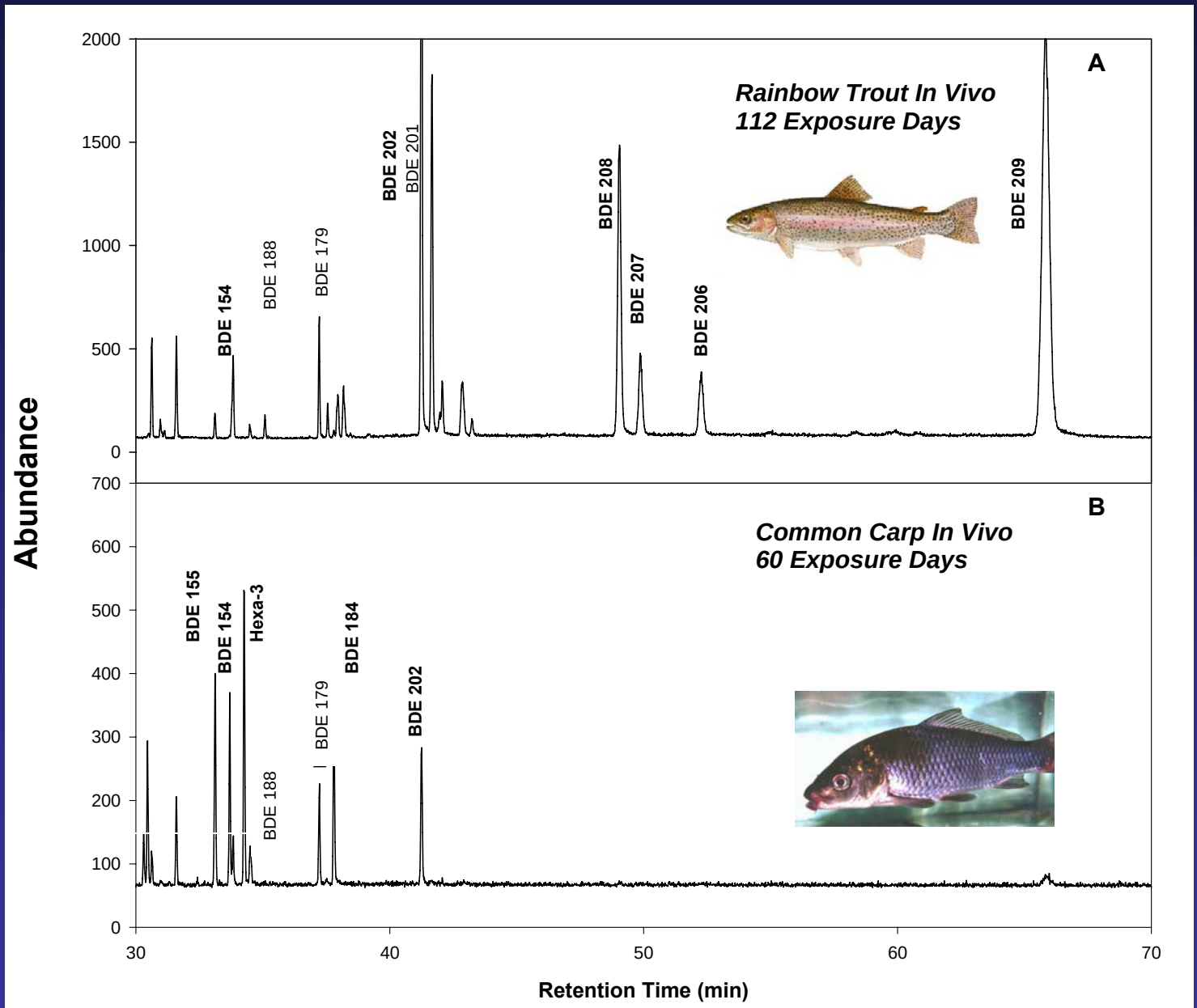
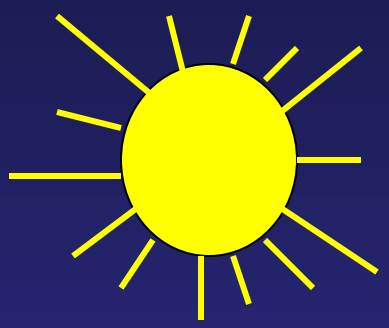
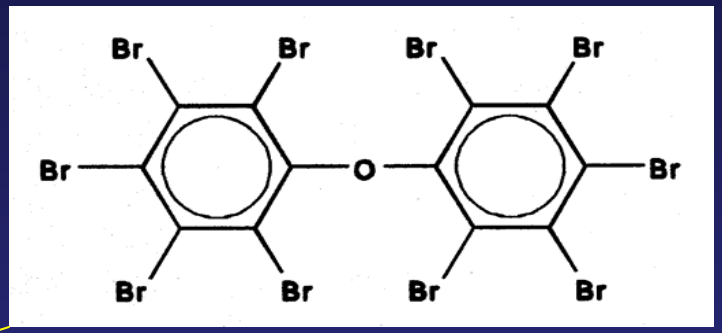


Figure 6. GC/ECNI-MS chromatograms comparing extracts from BDE 209 exposed rainbow trout (A) and BDE 209 exposed common carp (B).

Stapleton et al., *Environ. Sci. Technol*. 40 (15): 4653-4658

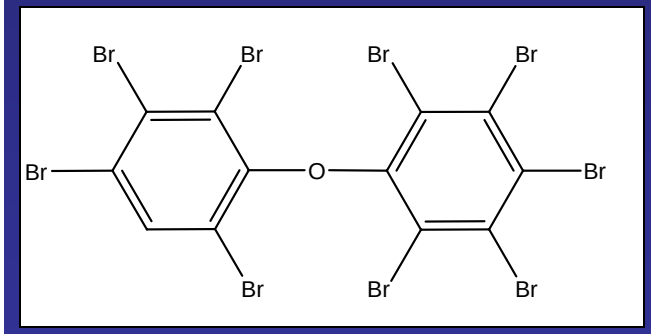
Exposure to Sunlight Leads to Degradation:
(primarily "debromination")



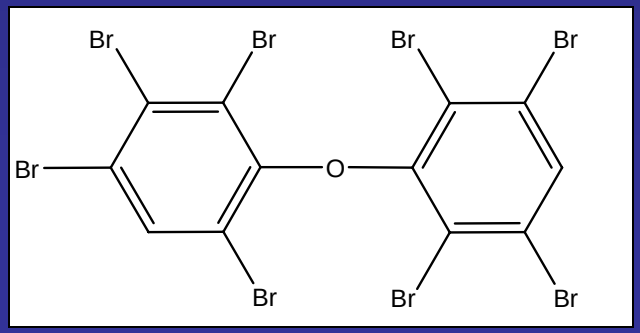


BDE 209

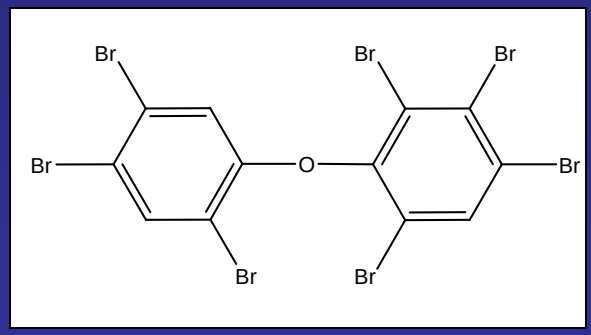
Congeners found in OctaBDE



BDE 207

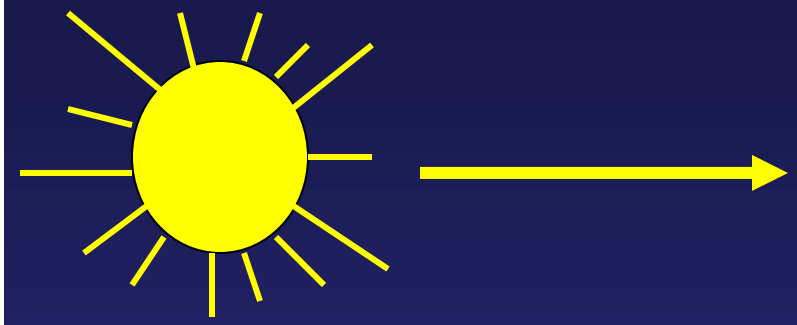


BDE 201



BDE 183

Does DecaBDE Degrade When Exposed to Sunlight?

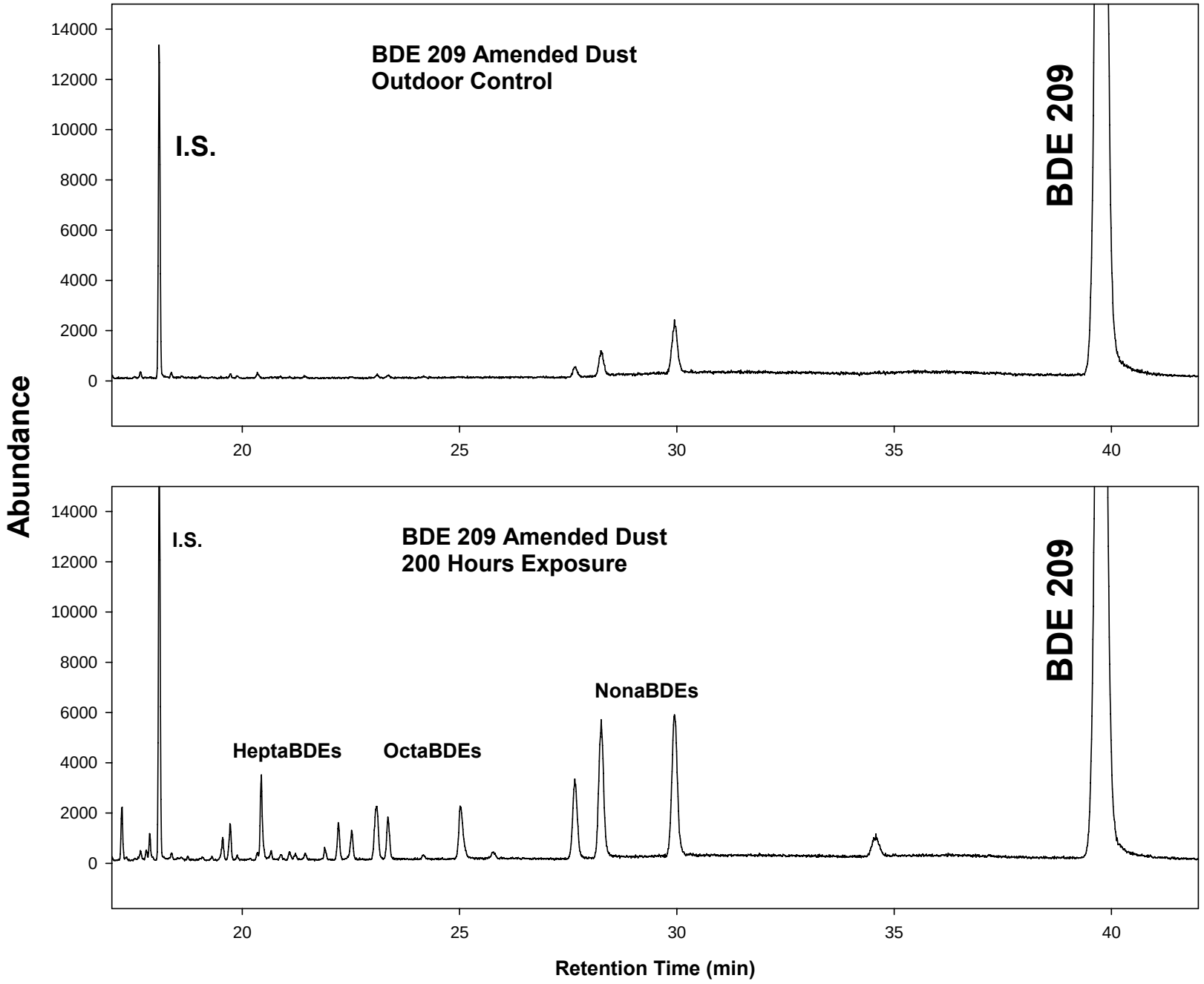


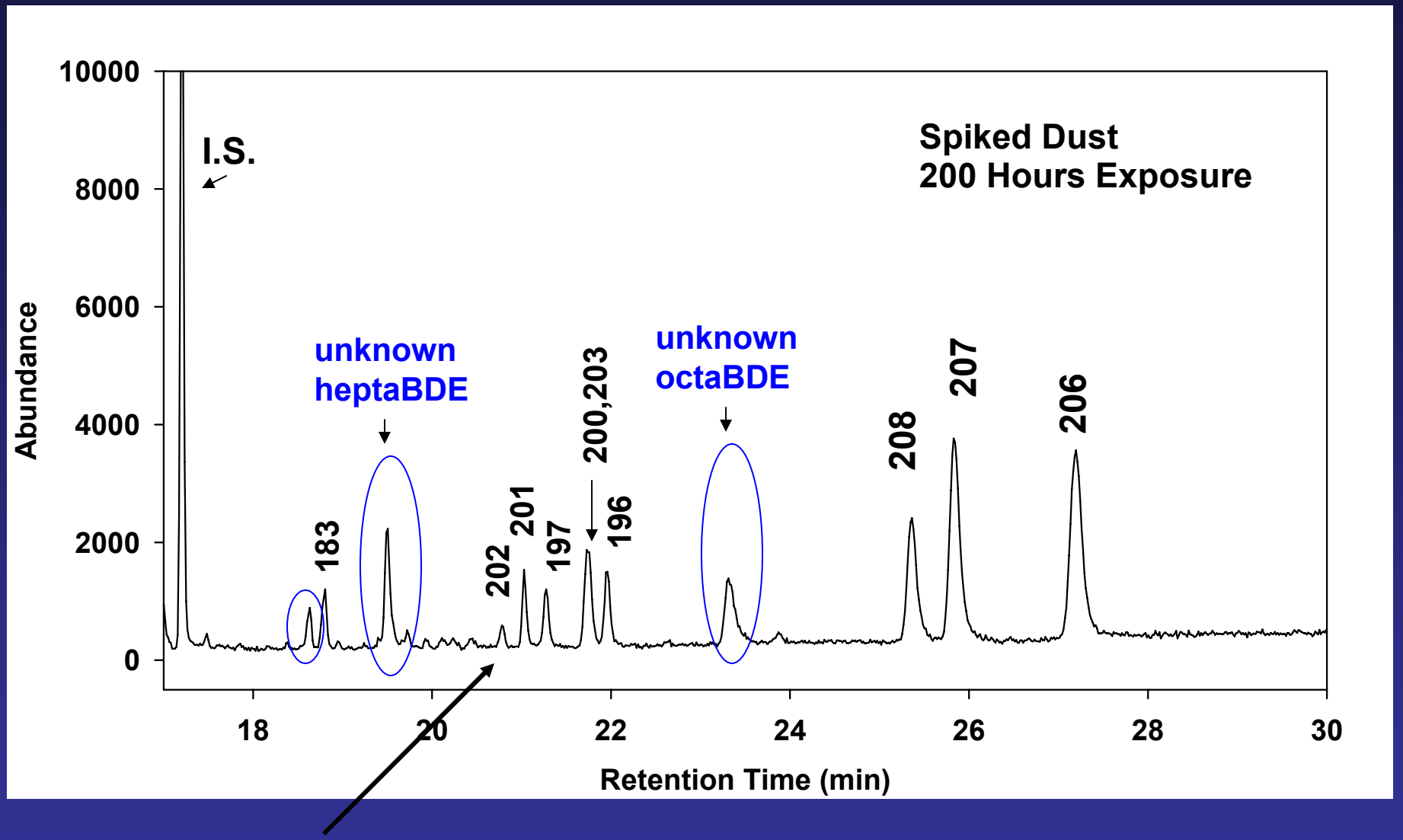
NIST, Gaithersburg, MD
USA, Sept.-Oct. 2005
(Stapleton and Dodder, 2008)

0.5 grams Dust in plastic cuvettes

***Tested the ability of natural sunlight to degrade/debrominate DecaBDE**

***Will DecaBDE degradation lead to formation of congeners found In OctaBDE and PentaBDE commecial mixtures (which are more Persistent and potentially more toxic)**


BDE 209 Amended Dust
Outdoor Control
I.S.
BDE 209
BDE 209 Amended Dust
200 Hours Exposure
I.S.
HeptaBDEs
OctaBDEs
NonaBDEs
BDE 209
Abundance
Retention Time (min)
14000
12000
10000
8000
6000
4000
2000
0
20
25
30
35
40



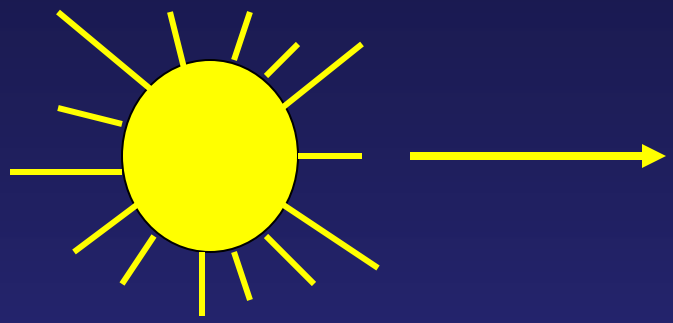
*Degradation products not found in any commercial mixtures: e.g. BDE 202
Indicators of DecaBDE debromination

*BDE 202 has been measured in house dust (Allen et al., 2006)

Half-Lives of DecaBDE Among Studies

Study	Matrix	Light Source	Half-Life (hours)
Söderström et al., 2004	Silica gel	UV Lamp	<0.25
	Sand	UV Lamp	12
	Sand	Sunlight	13
	Sediment	UV Lamp	40-60
	Sediment	Sunlight	30
	Soil	UV Lamp	150-200
Eriksson et al., 2004	MeOH/Water	UV Lamp	0.5
Ahn et al., 2005	Montmorillonite	UV Lamp	866
	Montmorillonite	Sunlight	5198
	Kaolinite	UV Lamp	1052
	Kaolinite	Sunlight	9780
	Sediment	UV Lamp	3616
	Sediment	Sunlight	23,760
Stapleton and Dodder, 2008	Dust	Sunlight	408

Is DecaDBE Debromination Environmentally Relevant?



Photolysis of DecaBDE requires wavelengths In the UV range…..some windows block UV Wavelengths…..reduces energy to degrade DecaBDE.

However……

- impossible to exclude all sunlight from homes, offices and automobiles (DecaBDE present in car dust)

-DecaBDE found in sewage sludge and biosolids (up to 5,000 ppb) which are land applied in many regions……..will receive sunlight exposure

-DecaBDE found in E&E Waste…landfills receive sunlight exposure leaching from landfills (Danon-Schaeffer et al., 2006) will expose DecaBDE to sunlight.

Acknowledgments:

Funding: -Duke University, Nicholas School of the Environment & Earth Sciences

- CIREEH, Boston University

All study participants

Reviewers/Comments:

- Dr. Linda Birnbaum, EPA
- Dr. Nicolle Tulve, EPA