

**The Environmental Behavior of the
Flame Retardant Decachlorobiphenyl Ether:
Understanding the Risks of a New Class of Pollutant**



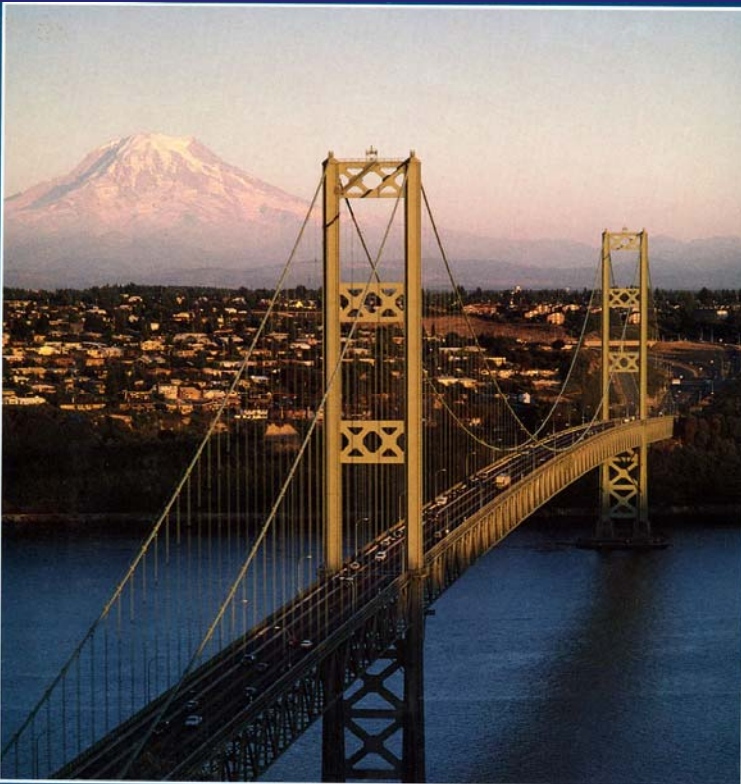
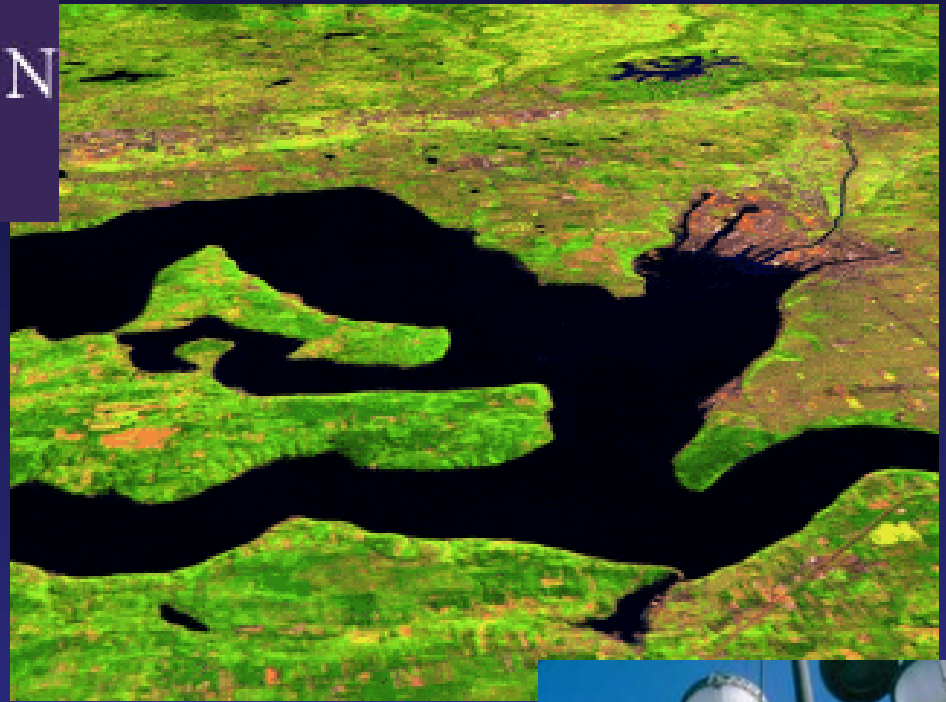
Joel E. Baker

**Port of Tacoma Chair in Environmental Science
Science Director, Center for Urban Waters**

University of Washington Tacoma

UNIVERSITY OF WASHINGTON TACOMA

Total Enrollment	2292
Freshmen (8.2%)	187
Other Undergraduate	1669
Graduate (19%)	436





Collaboration between:

1. City of Tacoma
2. UW Tacoma
3. Puget Sound Partnership

Focusing on:

1. Puget Sound restoration
2. Mitigating impacts in the urbanized environment

The Center for Urban Waters



For today's talk, thanks to:

Dr. Heather Stapleton

Duke University

Dr. Susan Klosterhaus

San Francisco Estuary Institute

Erin Dreis

Maryland Sea Grant REU

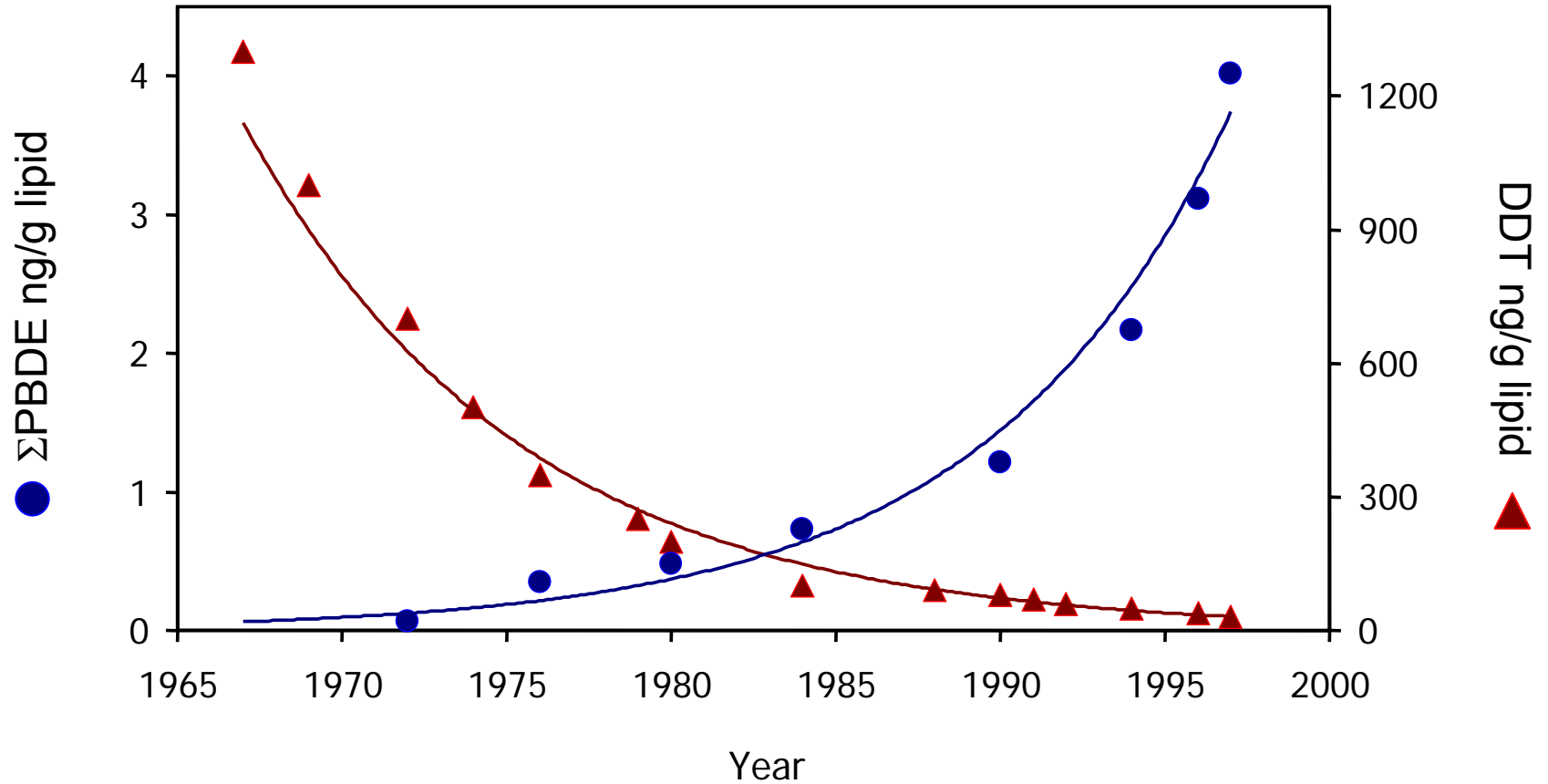
Dr. Robert Letcher

University of Windsor

Chemical Classes Studied: Common Features

- Dominated by anthropogenic sources
- Sufficiently persistent and mobile to be transported regionally to globally
- Bioaccumulative
- Human toxicants

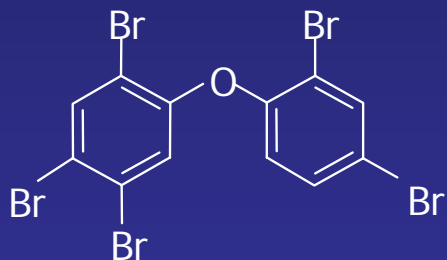
PBDEs in Archived Human Milk (Sweden)



Also decreasing: polychlorinated biphenyls (PCB), polychlorinated naphthalenes (PCN), and dioxins.

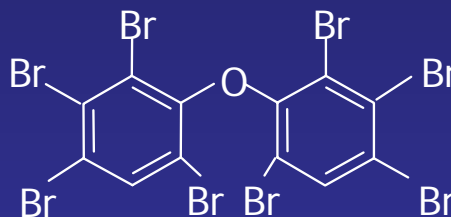
PBDE Commercial Mixtures

PBDE Mixture	Primary Congeners	Primary Application
'Penta-BDE'	BDEs 47, 99, 100, 153, 154	Polyurethane Foam
'Octa-BDE'	BDEs 153, 183, 196, 197, 203, 206, 207, 209	Thermoplastics
'Deca-BDE'	BDE 209	Thermoplastics



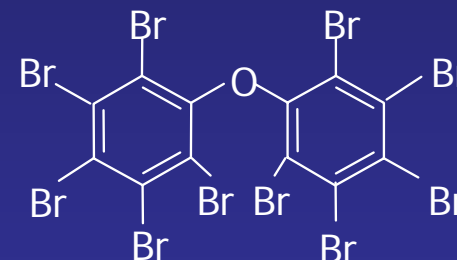
2,2',4,4',5-pentabromodiphenyl ether

BDE 99



2,2',3,3',4,4',6,6'-octabromodiphenyl ether

BDE 197



decabromodiphenyl ether

BDE 209

- Each mixture named for its primary constituent congeners
- Each congener named according to # of Br and position on the ring

Why do we 'need' flame retardant chemicals?

Consumer product-specific standards

- Performance-based
- Underwriters Laboratories (UL) Vertical Flame Test



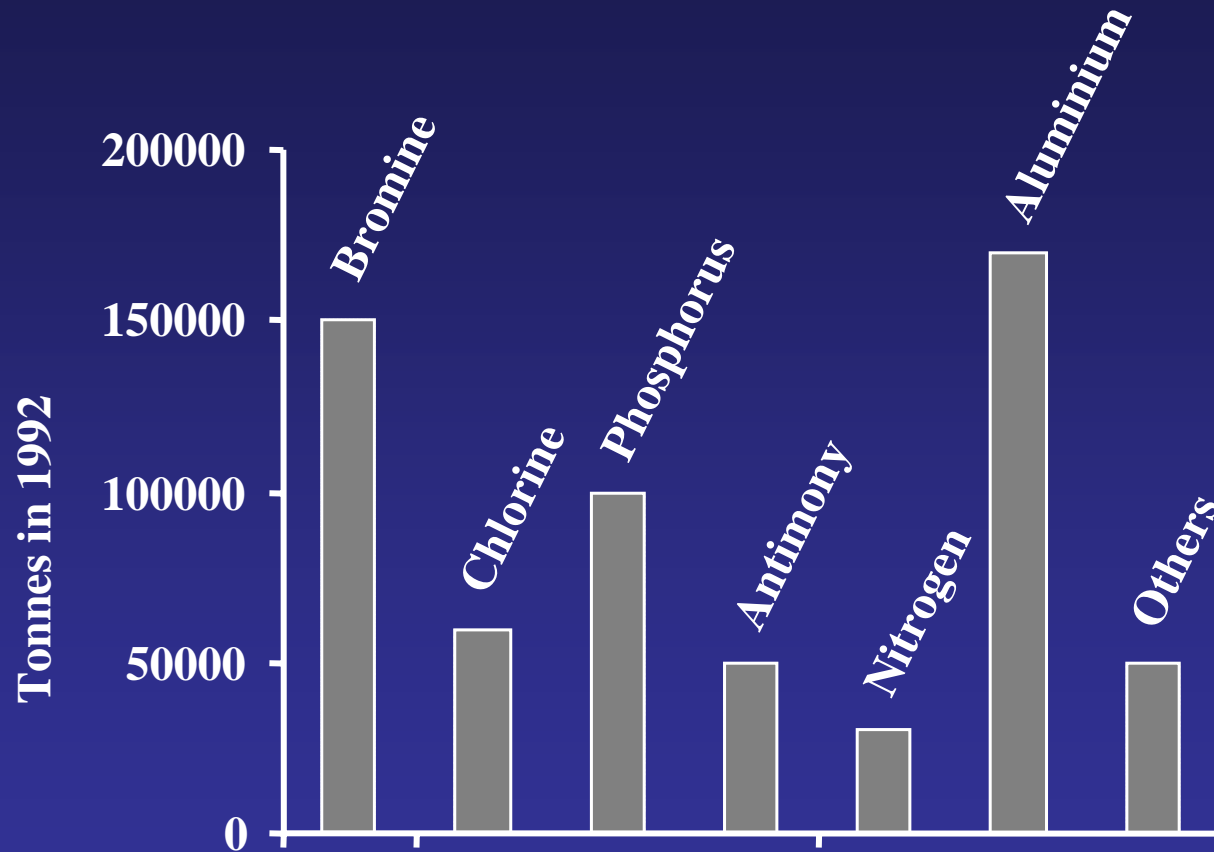
CA Furniture Flammability Standard (TB 117, 1975)

- Requires all polyurethane foam used as filling in seating furniture to pass stringent fire safety testing
- CA is first and only state to have this type of standard
- Penta-BDE primary chemical used



Halogenated FR chemicals are most effective

Types and Usage of Flame Retardant:



Types of Brominated Flame Retardants

ADDITIVE BFRs

Decabromobiphenyl

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

Tetrabromobisphenol S

2,4-Di-, 2,4,6-Tri- and pentabromophenol

Tribromoneopentyl alcohol

Vinylbromide

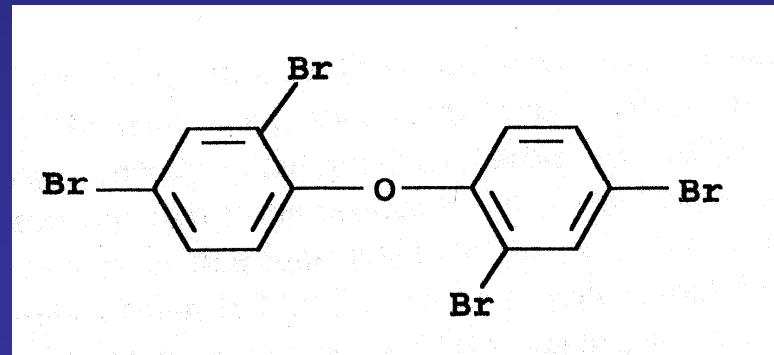
Tribromophenyl allyl ether

2,3-Dibromo-2-butene-1,4-diol

Tetrabromophthalic acid Na salt

Tetrabromophthalic anhydride

N,N'-Ethylene-bis-(tetrabromophthal imide)



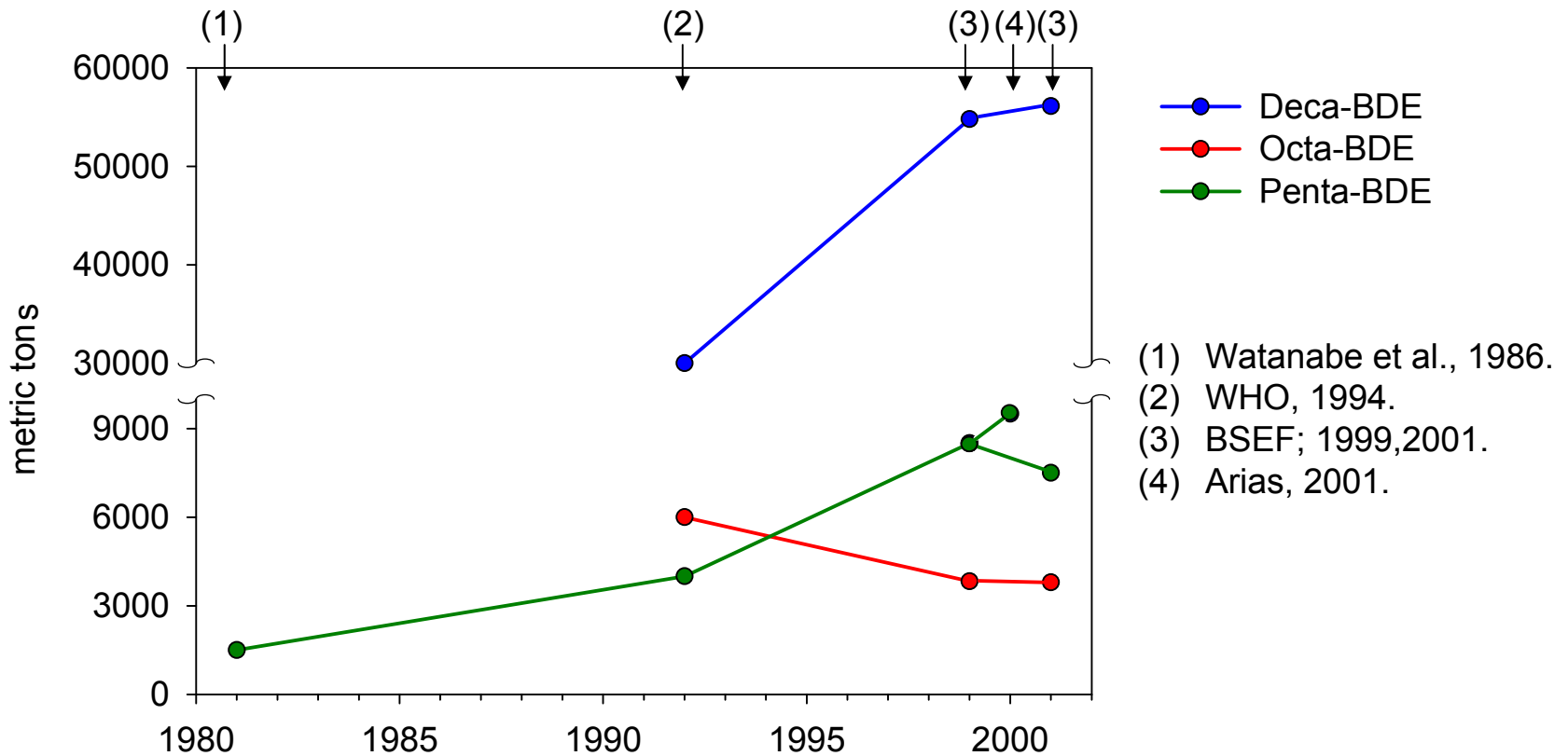
Total Market Demand By Region in 2001

(metric tons)

www.bsef.com

	Americas	Europe	Asia	Rest of World	Total
Deca-BDE	24,500	7,600	23,000	1,050	56,100
Octa-BDE	1,500	610	1,500	180	3,790
Penta-BDE	7,100	150	150	100	7,500

Historical Global Market Demand By Year



Congener (# Br)	Percent of Total
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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
nona-BDE	12

Deca-BDE Commercial Mixture

BDE-209 (10)	>98
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Congener (# Br)	Percent of Total	Flame Retards	US Demand (MT)
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Penta-BDE Commercial Mixture

BDE-47 (4)	27		
BDE-85 (5)	1.6		
BDE-99 (5)	43		
BDE-100 (5)	9.8	Flexible Polyurethane Foam (Furniture)	7,100
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	Acrylonitrile-butadiene- styrene (Business Equipment)	1,500
2 hepta-BDEs	2.5		
3 octa-BDEs	34		
nona-BDE	12		

Deca-BDE Commercial Mixture

BDE-209 (10)	>98	High Impact Polystyrene (Electronic Enclosures)	24,500
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Congener (# Br)	Percent of Total	MW	Log K _{OW}
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Braekevelt et al., 2003

Penta-BDE Commercial Mixture

BDE-47 (4)	27	485.8	6.81
BDE-85 (5)	1.6	564.7	
BDE-99 (5)	43	564.7	7.32
BDE-100 (5)	9.8	564.7	7.24
BDE-153 (6)	8.5	643.6	7.90
BDE-154 (6)	9.3	643.6	7.82
hexa-BDE	1.1	643.6	

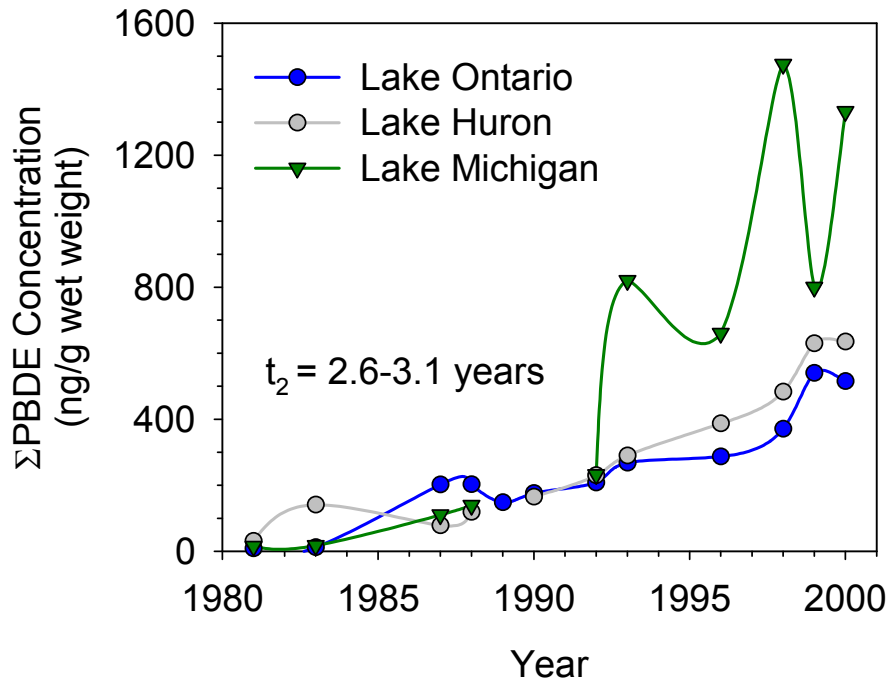
Octa-BDE Commercial Mixture

BDE-153 (6)	6.7	643.6	
BDE-154 (6)	1.7	643.6	
BDE-183 (7)	44	722.5	8.27
2 hepta-BDEs	2.5	722.5	
3 octa-BDEs	34	801.4	
nona-BDE	12	880.3	

Deca-BDE Commercial Mixture

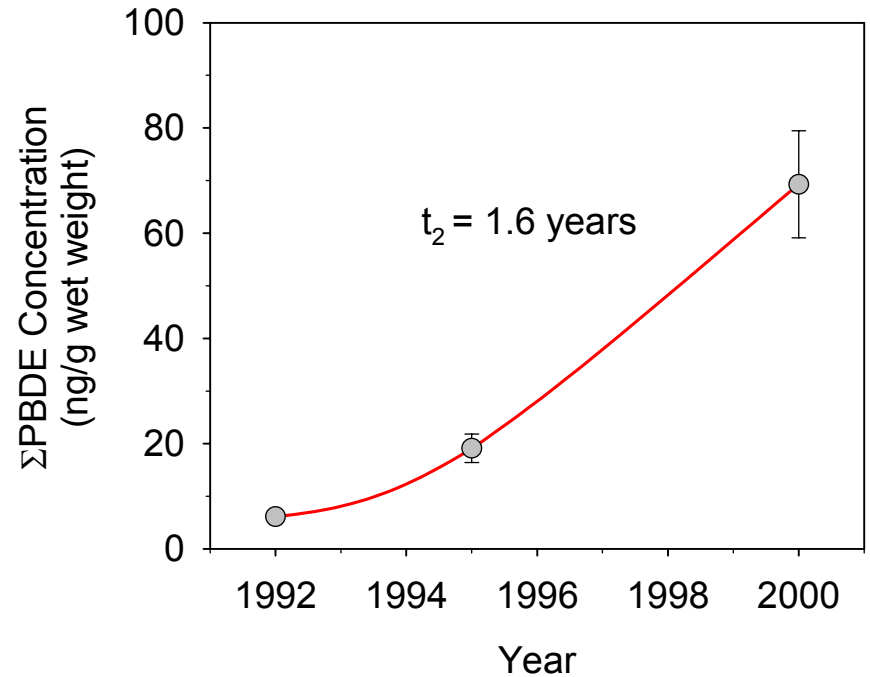
BDE-209 (10)	>98	959.2	10
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Great Lakes Herring Gull Eggs, Norstrom et al., 2002.



ΣPBDE will surpass ΣPCB in 2012-2017.

Columbia River Whitefish, Rayne et al., 2003



ΣPBDE will surpass ΣPCB by 2003.

Penta-BDE Commercial Mixture

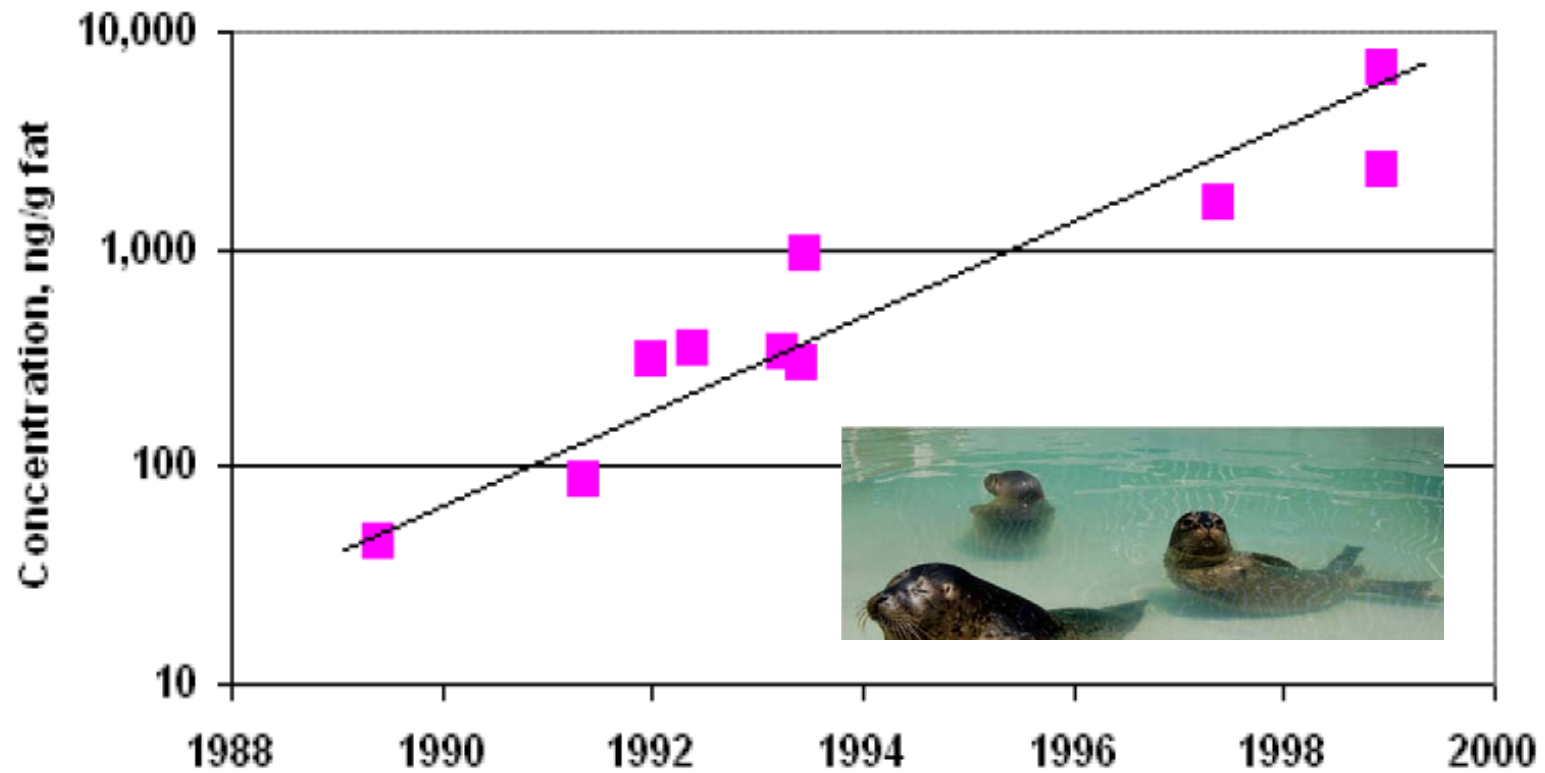
Octa-BDE Commercial Mixture

Deca-BDE Commercial Mixture

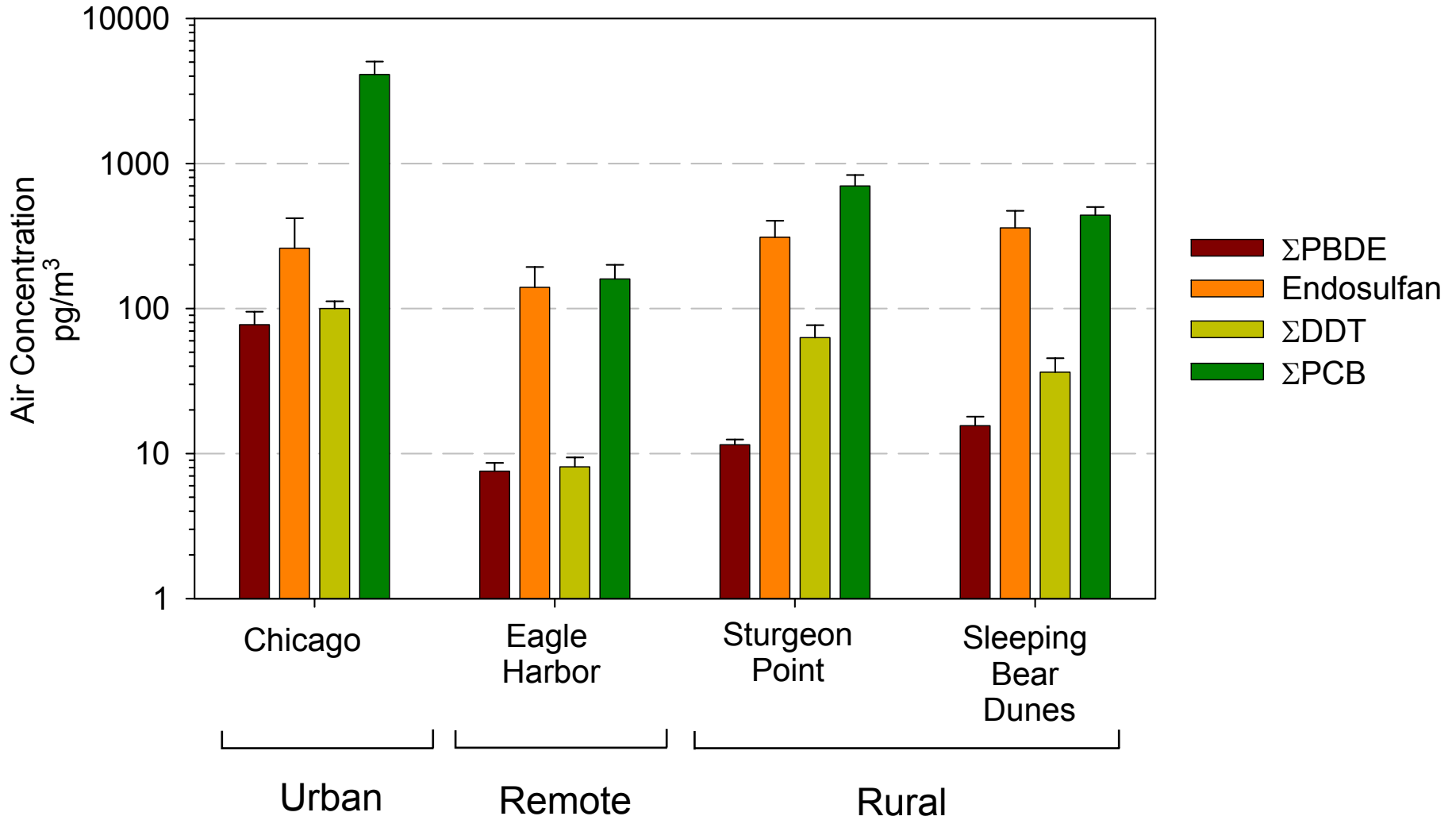
- Underwent a voluntary, industry and EPA sponsored, risk assessment in 2003.
- Penta- and Octa- being phased out in California, and production ending.

PBDEs IN SF BAY HARBOR SEALS

She et al. 2002

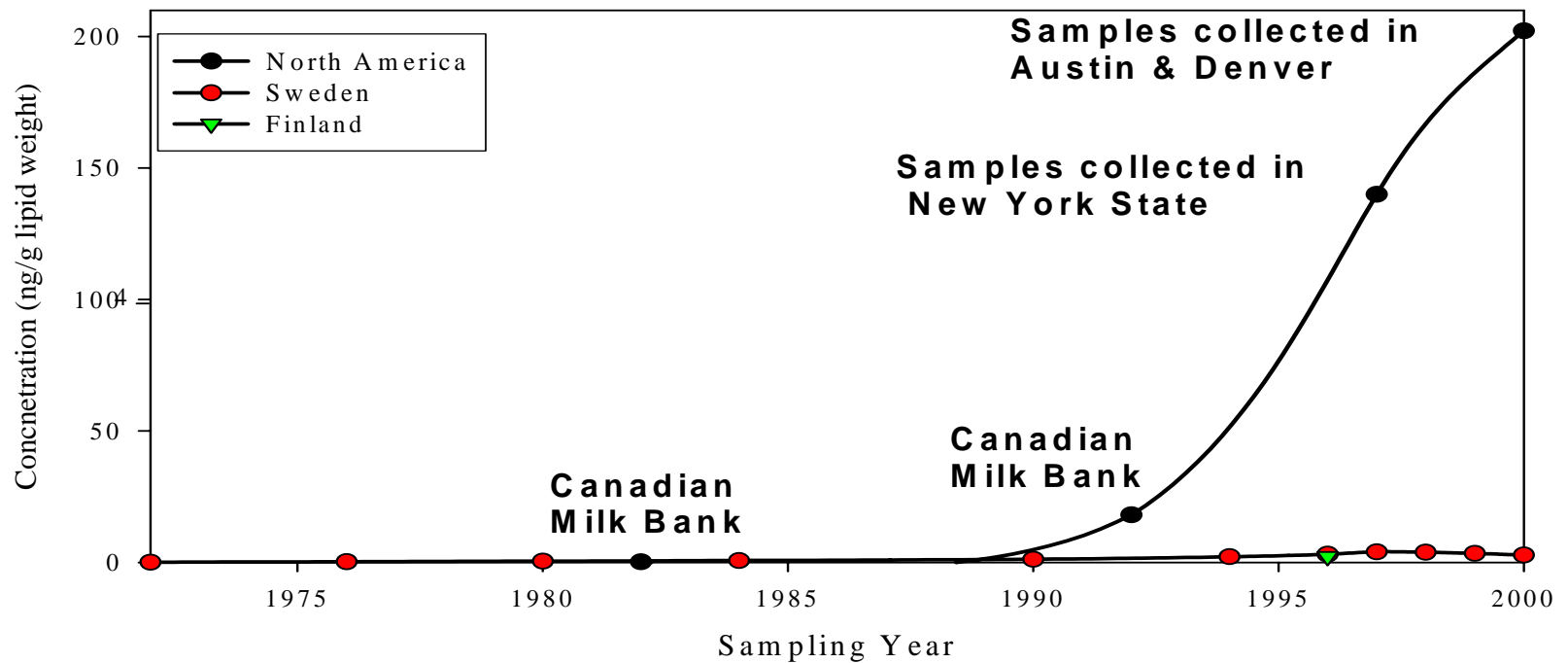


Organohalogenes in the Great Lakes Atmosphere



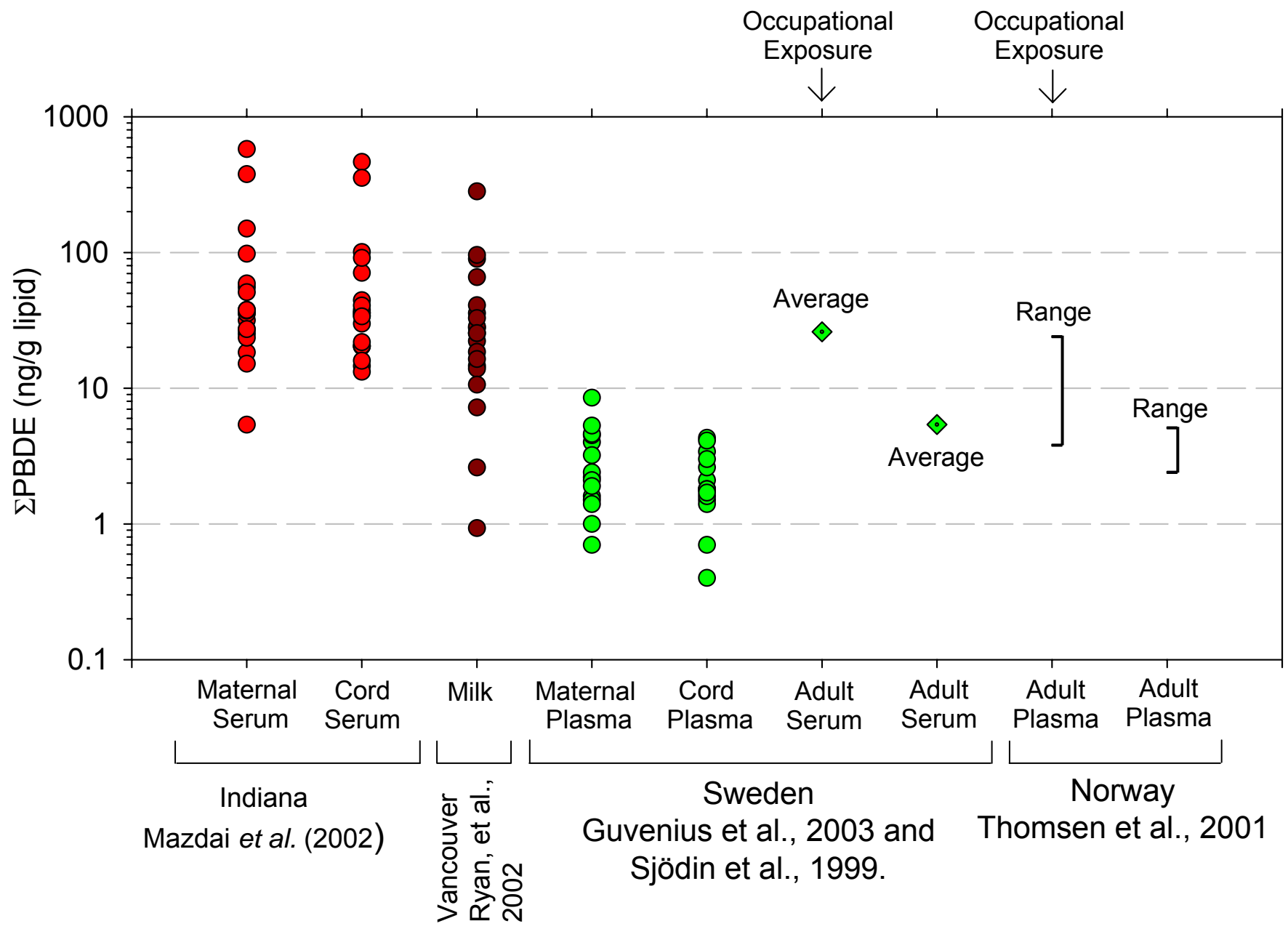
Global Human Exposure to BDEs is Increasing

Comparison Between Concentrations of PBDEs in Breast Milk from North America and Europe

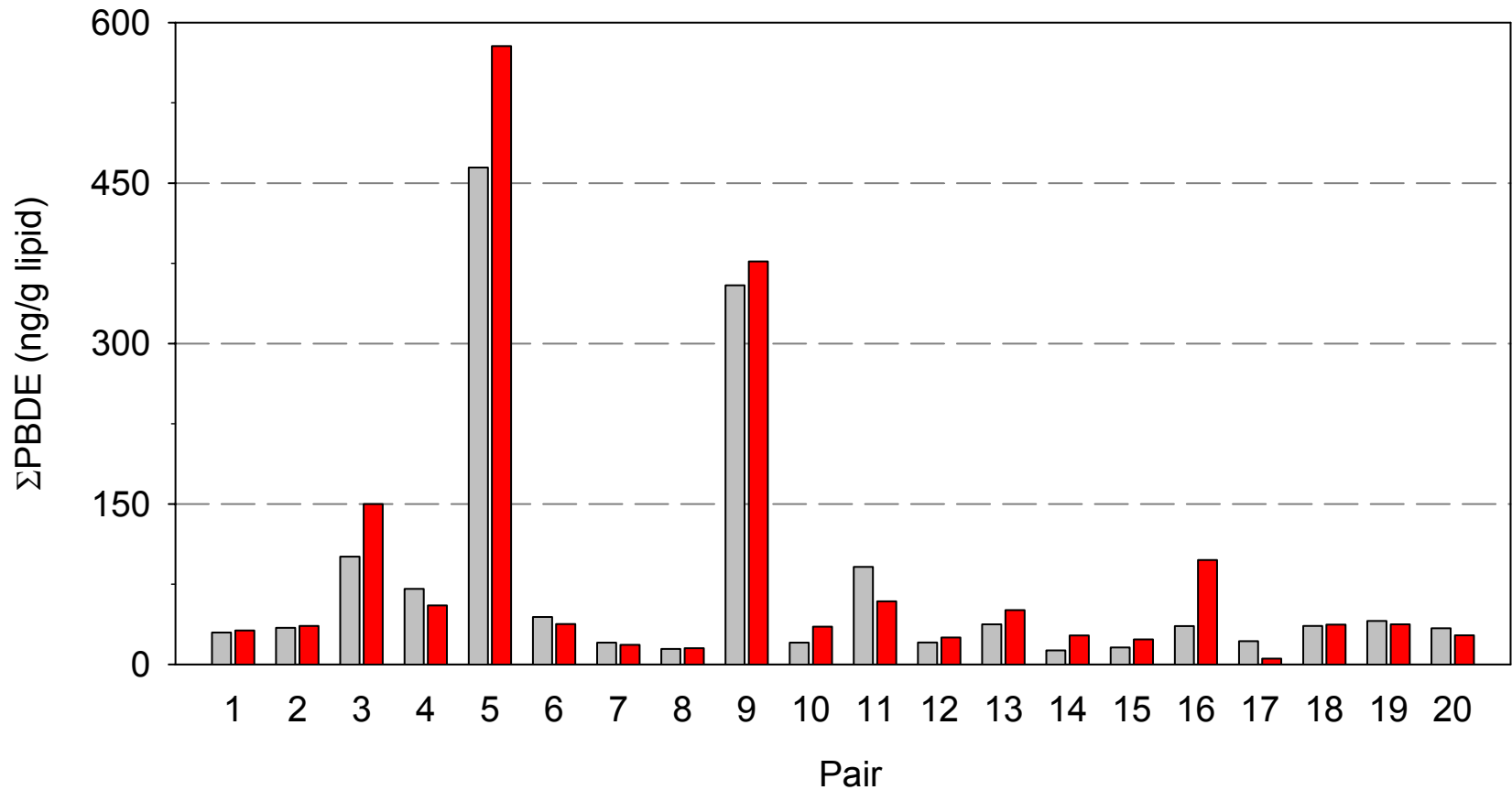


Canadian Milk Bank and New York State from Ryan and Patry 2000, Denver and Austin results from Papke et al 2001; Swedish data from Meironyte Guvernius and Noren 2001, Finnish data from Strandman et al. 2000

North American and European Levels



PBDE Concentration in Human Serum Samples

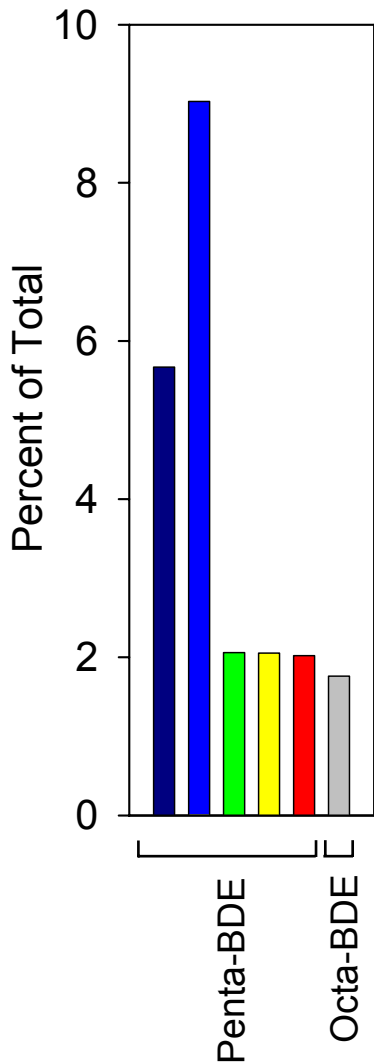


— Cord Serum
— Maternal Serum

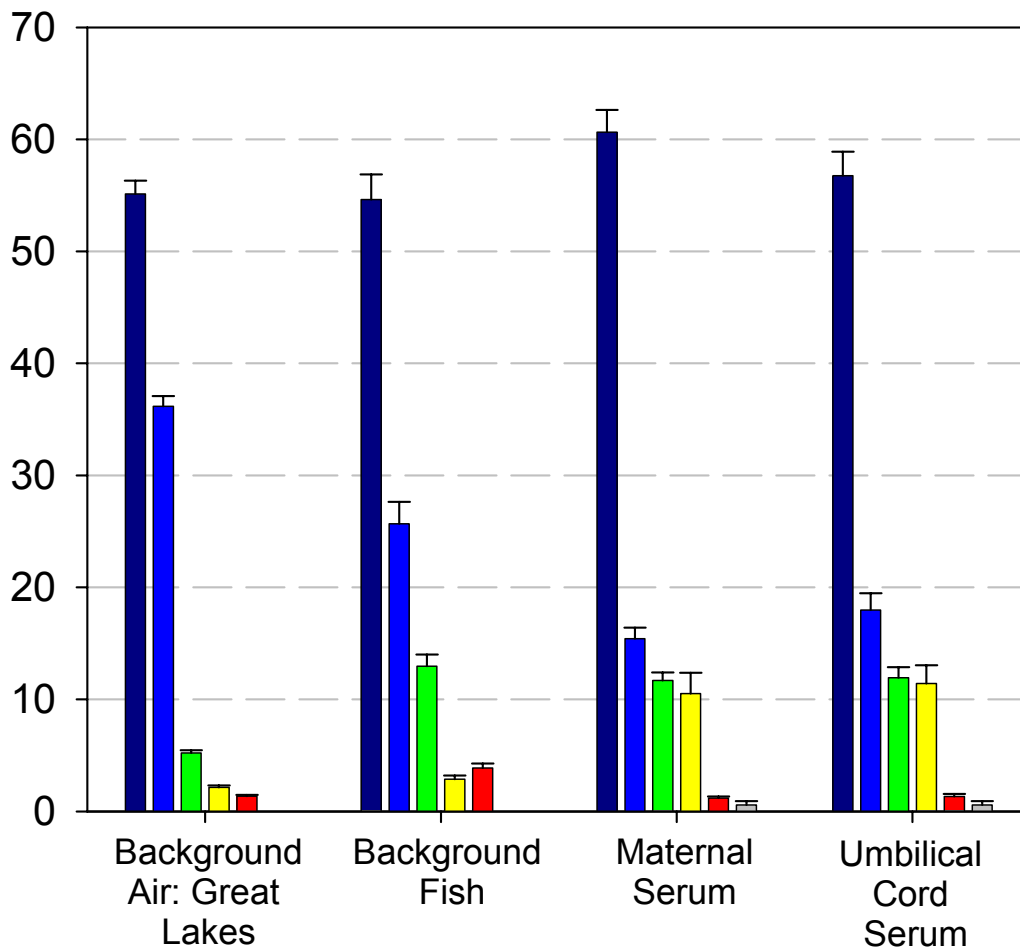
High levels could not be correlated to:

- Occupational exposure
- Age
- BMI

Commercial Mixtures Profile



Sample Profiles



- BDE-47 (4)
- BDE-99 (5)
- BDE-100 (5)
- BDE-153 (6)
- BDE-154 (6)
- BDE-183 (7)

Toxicology of PBDEs:

PentaBDE > OctaBDE > DecaBDE

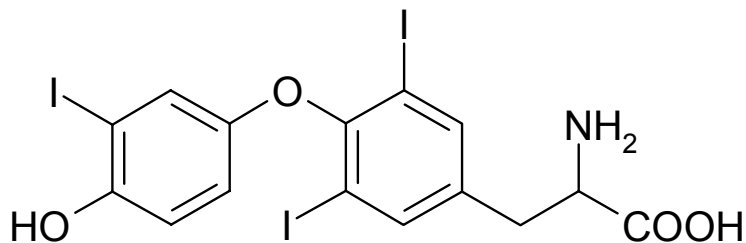
Based upon:

- neurobehavioral and developmental evidence**
- thyroid hormone effects (Meerts et al., 2000)**
- morphological effects (Balch et al., 2002)**
- carcinogenicity (Helleday et al., 1999)**

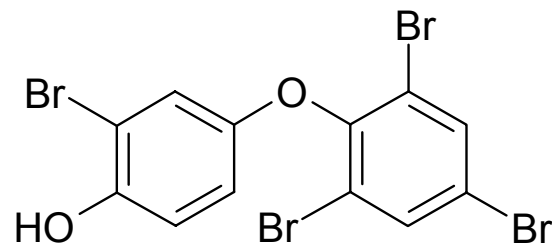
Metabolism: Detoxification or Activation?

- Formation of Hydroxylated (OH-) BDEs?**

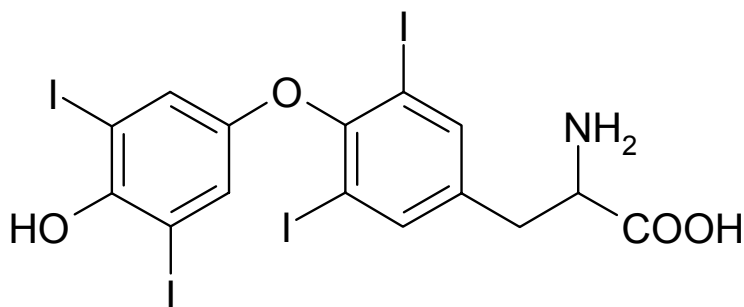
Hydroxylated PBDE Metabolites – Thyroid Hormone Mimics?



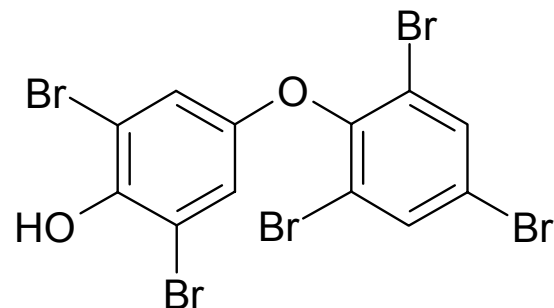
Triiodothyronine (T₃)



T₃-like HO-BDE



Thyroxine (T₄)



T₄-like HO-BDE

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

Sources of Flame Retardants to the Environment

BDE production facilities

- Few, thus unlikely responsible for widespread distribution



Facilities that manufacture products containing BDEs

- More widespread
- BDEs may be as high as 30% by weight in products



Facilities associated with use of products containing BDEs

Disposal or recycling of products (e.g. old furniture)



Mechanisms of entry:

volatilization

runoff

wastewater treatment plants (biosludge application)



PBDEs in Household Dust

PBDEs are heavily applied to furniture foam and carpets....so what kind of levels can we expect inside the house?



Dust Collected From

PBDE (ng/g dry wt.)

House	30,100
Townhouse	7,080
House	2,580
Basement 1-bedroom apartment	1,700
House	2,450
2-bedroom apartment	3,810
SRM 2585	5,120 ± 465

Implication: Domestic and occupational exposure likely important. Lead exposure as a model?

Food Web Accumulation and Transformation Of Brominated Flame Retardants

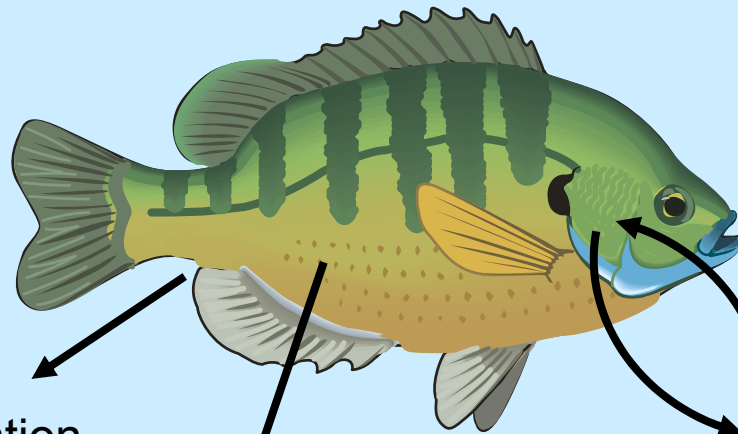
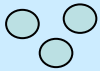
Atmospheric
Deposition



Sorbed Phase



Dissolved Phase

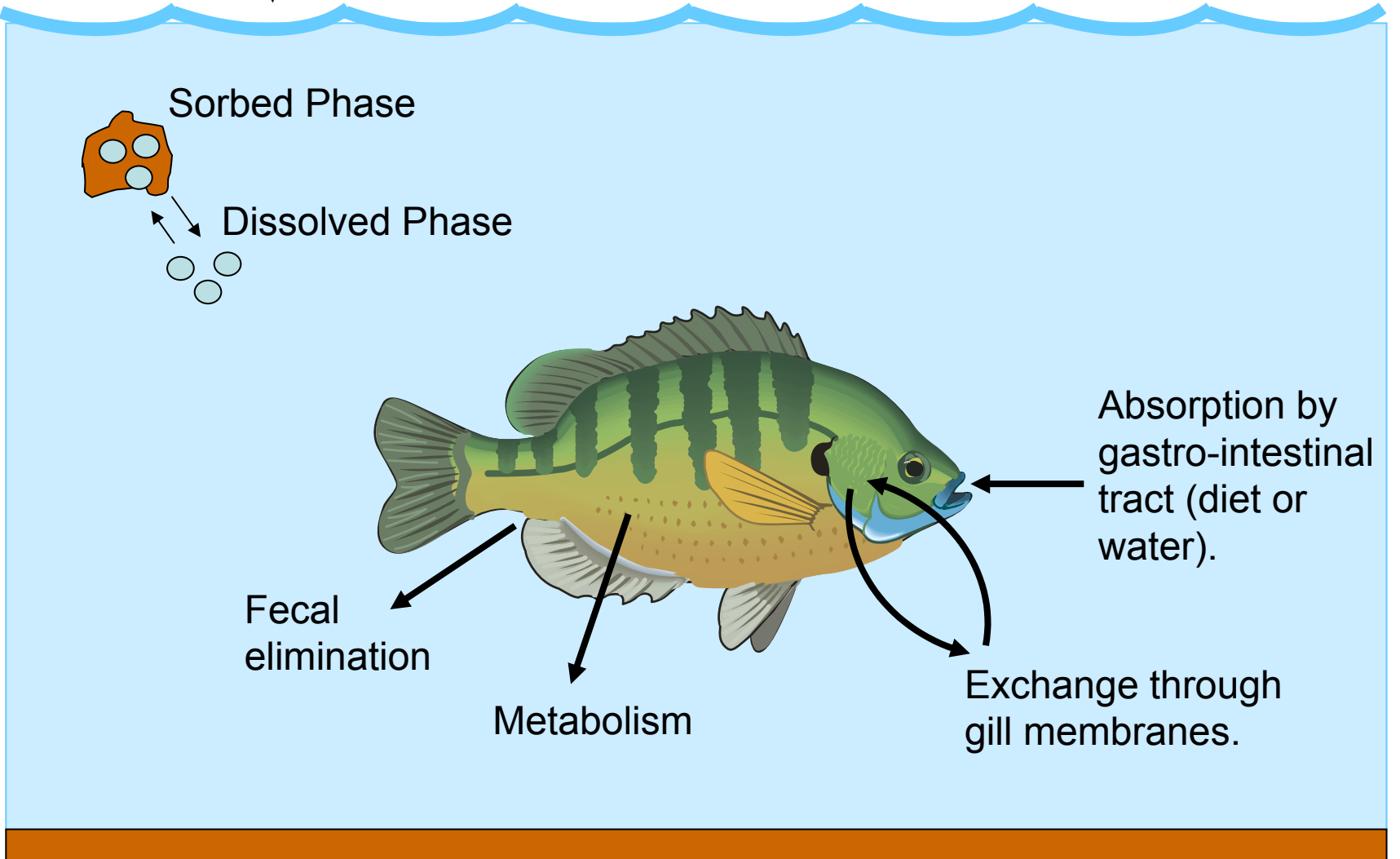


Absorption by
gastro-intestinal
tract (diet or
water).

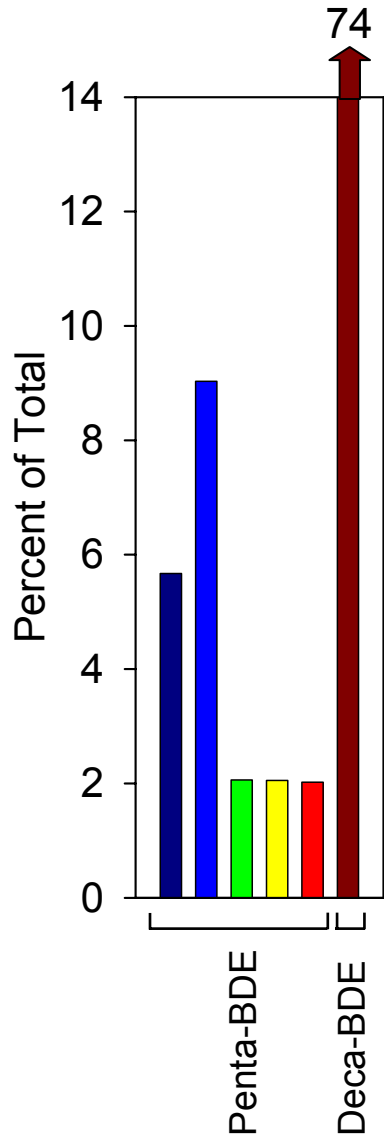
Fecal
elimination

Metabolism

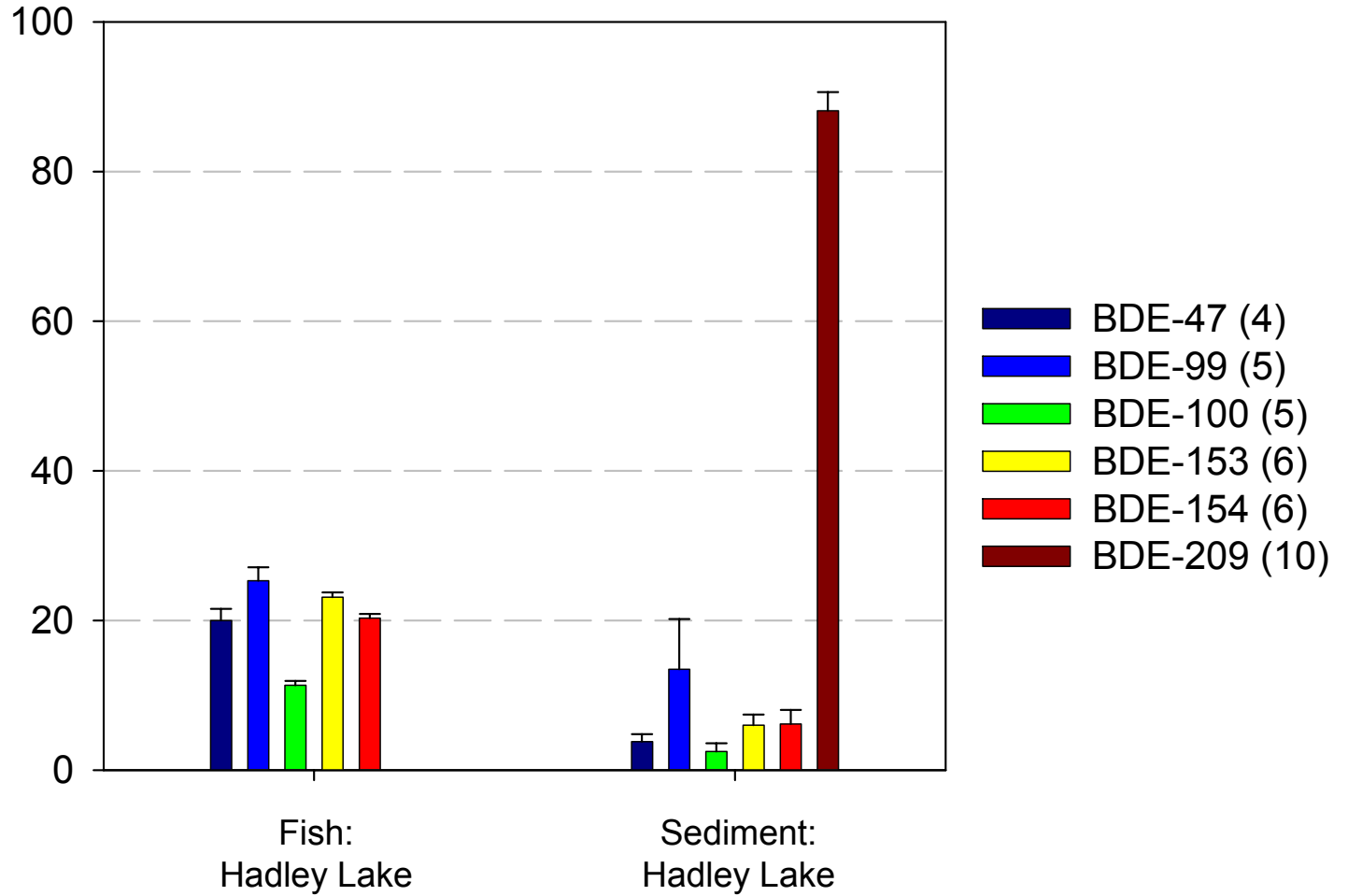
Exchange through
gill membranes.



Commercial Mixtures Profile



Fish and Sediment BDE Profiles

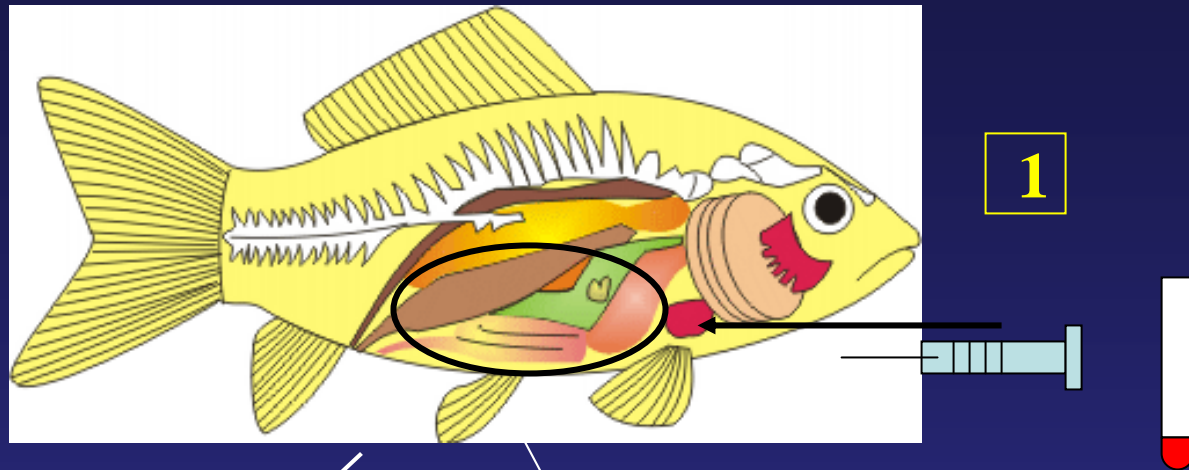


PBDE Accumulation and Metabolism in the Common Carp

1. Are PBDE congeners bioavailable to aquatic food webs?
2. What are the metabolic pathways?
3. What are the consequences of metabolites?
4. Is Deca-BDE absorbed?



Fish Sampling: (mass and length recorded)



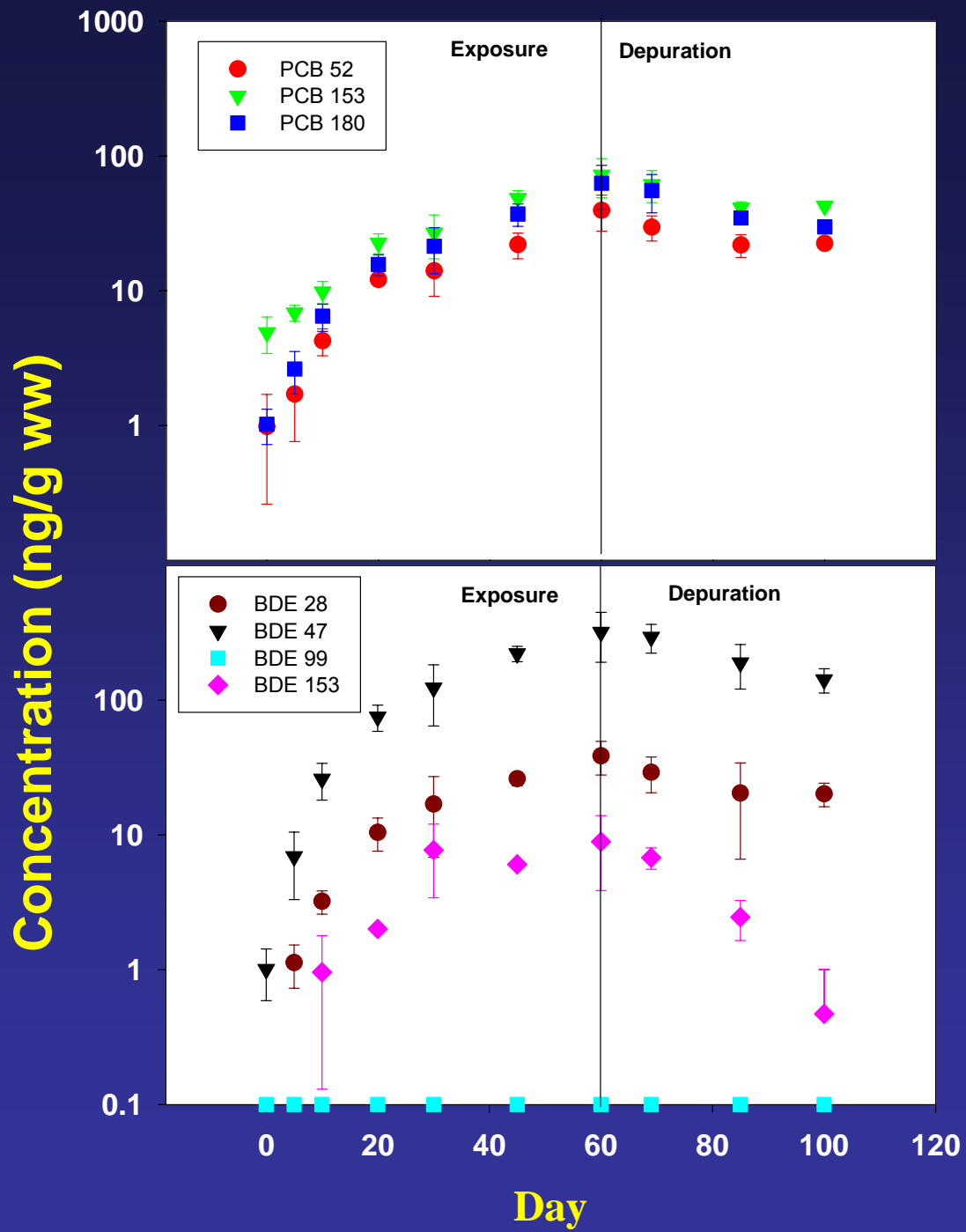
Hydroxylated metabolites

3

Remaining carcass homogenized
For extraction

2

Remove stomach cavity
↓
Isolate Liver, take mass
Composite among replicates
↙ ↘
Parent BDEs Metabolites



Assimilation Efficiency (%):

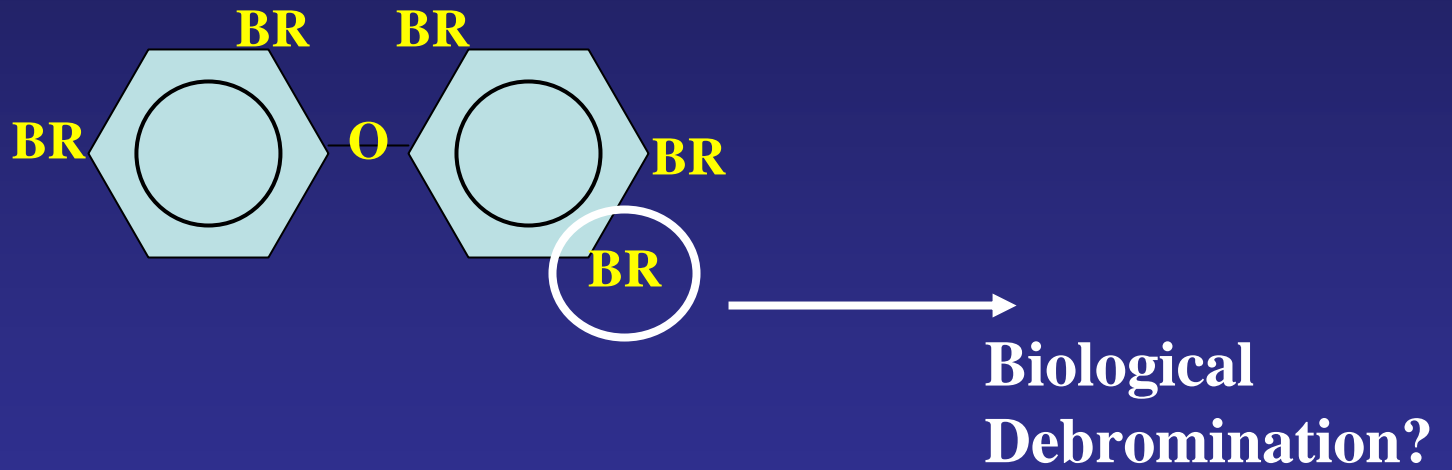
<u>Congener</u>	<u>Carp Tissues</u>	<u>Pike^a; Rainbow Trout^b</u>
PCB 52	38 ± 7	50 ± 20 ^a ; 38 ± 2 ^b
PCB 153	43 ± 4	70 ± 20 ^a ; 48 ± 3 ^b
PCB 180	40 ± 3	NA
BDE 28	20 ± 7	NA
BDE 47	93 ± 14	90 ± 20 ^a
BDE 153	4 ± 3	40 ± 10 ^a
BDE 99	0	60 ± 20 ^a

a - Burreau et al., 1997

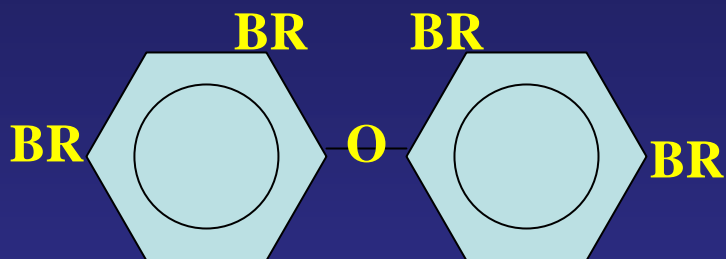
b - Fisk et al., 1998

Is debromination occurring in fish tissues?

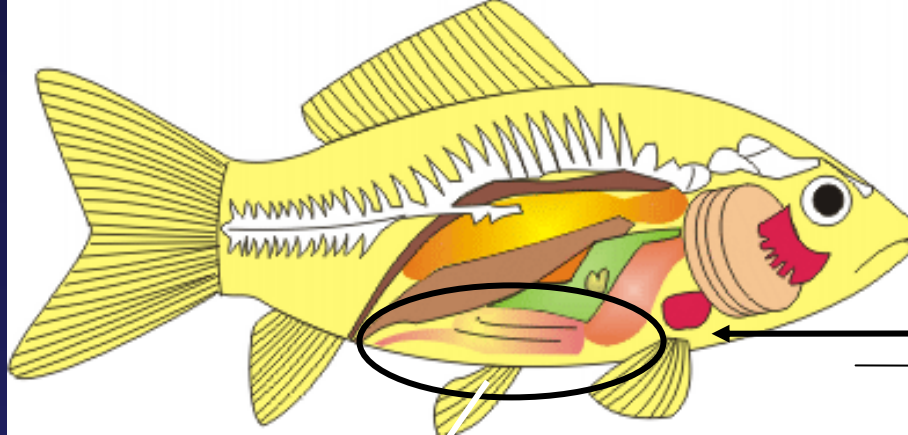
BDE 99:



BDE 99 becomes:



2,2',4,4'-tetrabromodiphenyl ether or BDE 47



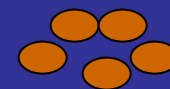
Intestine

**Debromination and Uptake
across intestinal wall**

Undigested food particles

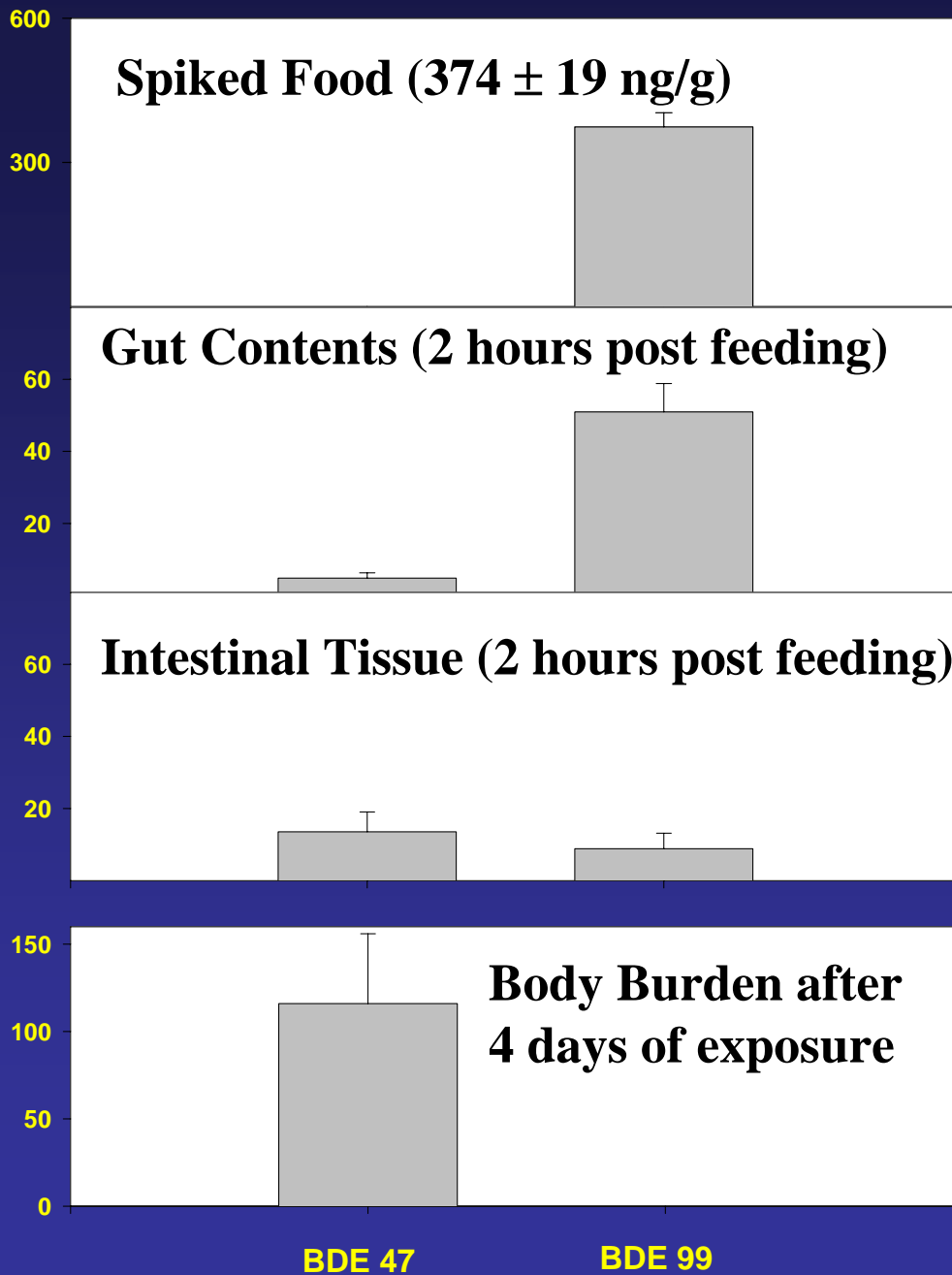
Feed fish and sacrifice after two hours:

**Separate intestine and
gut contents, and extract
for BDEs**

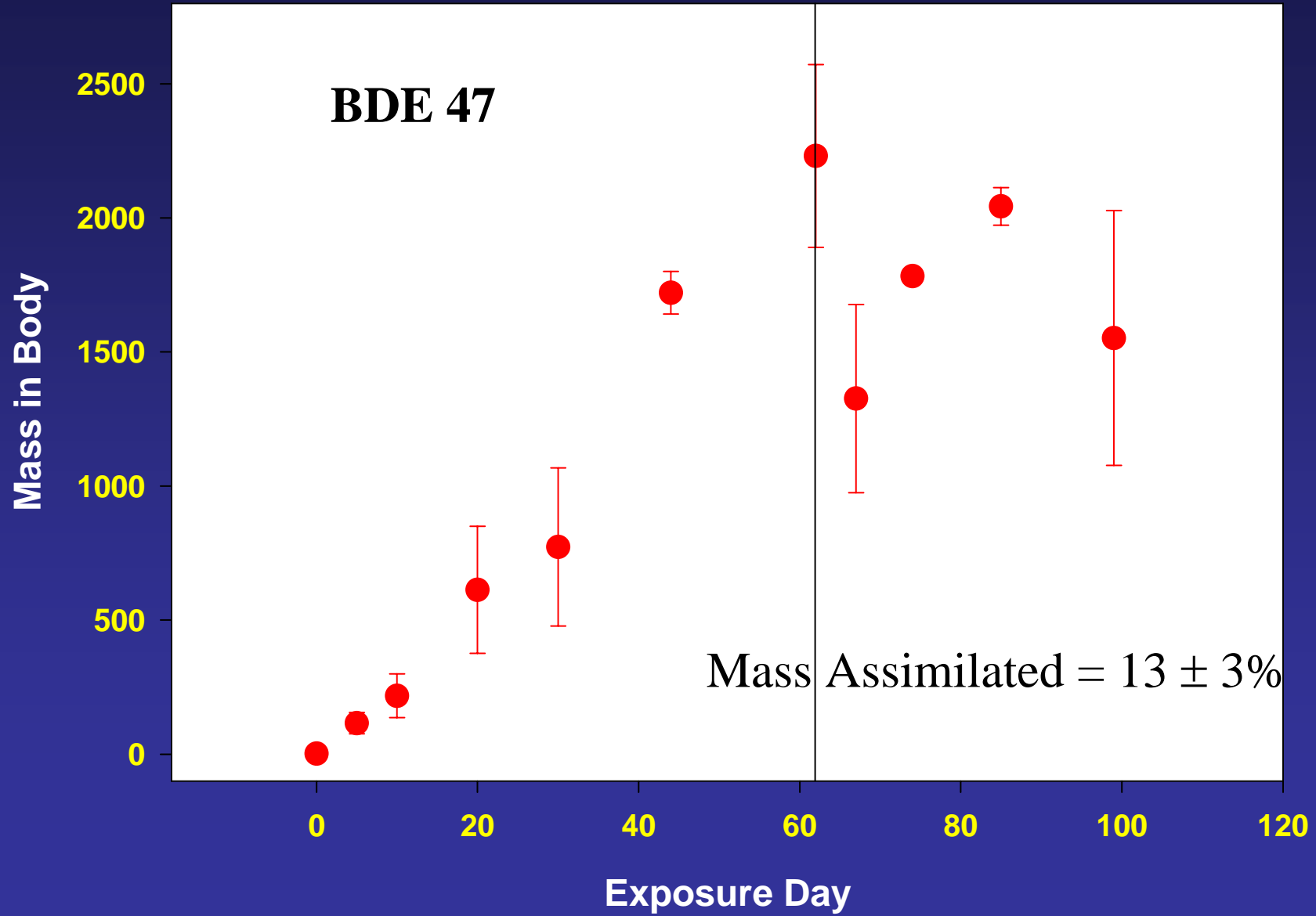


Dietary Exposure to BDE 99

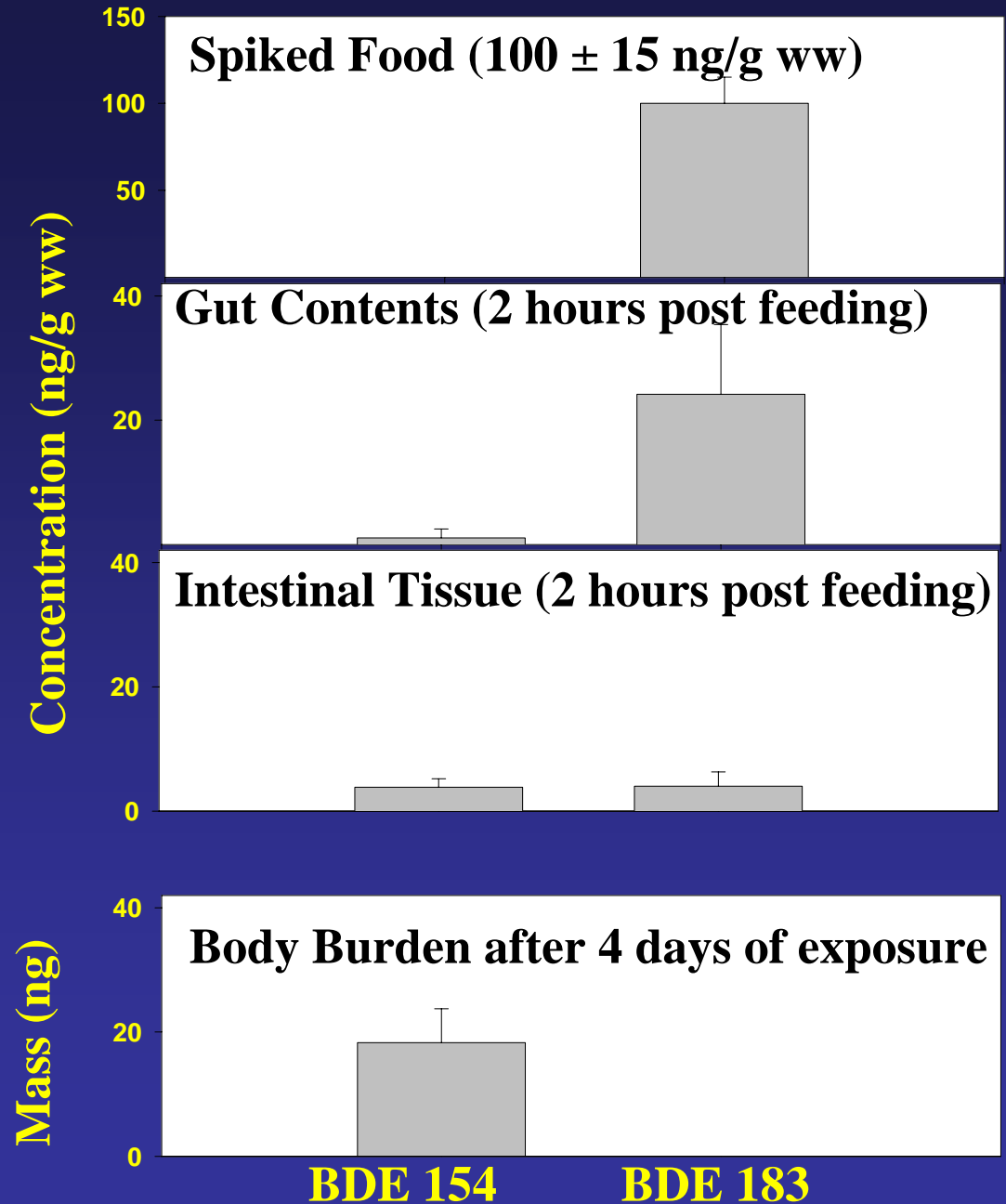
Concentration (ng/g ww)



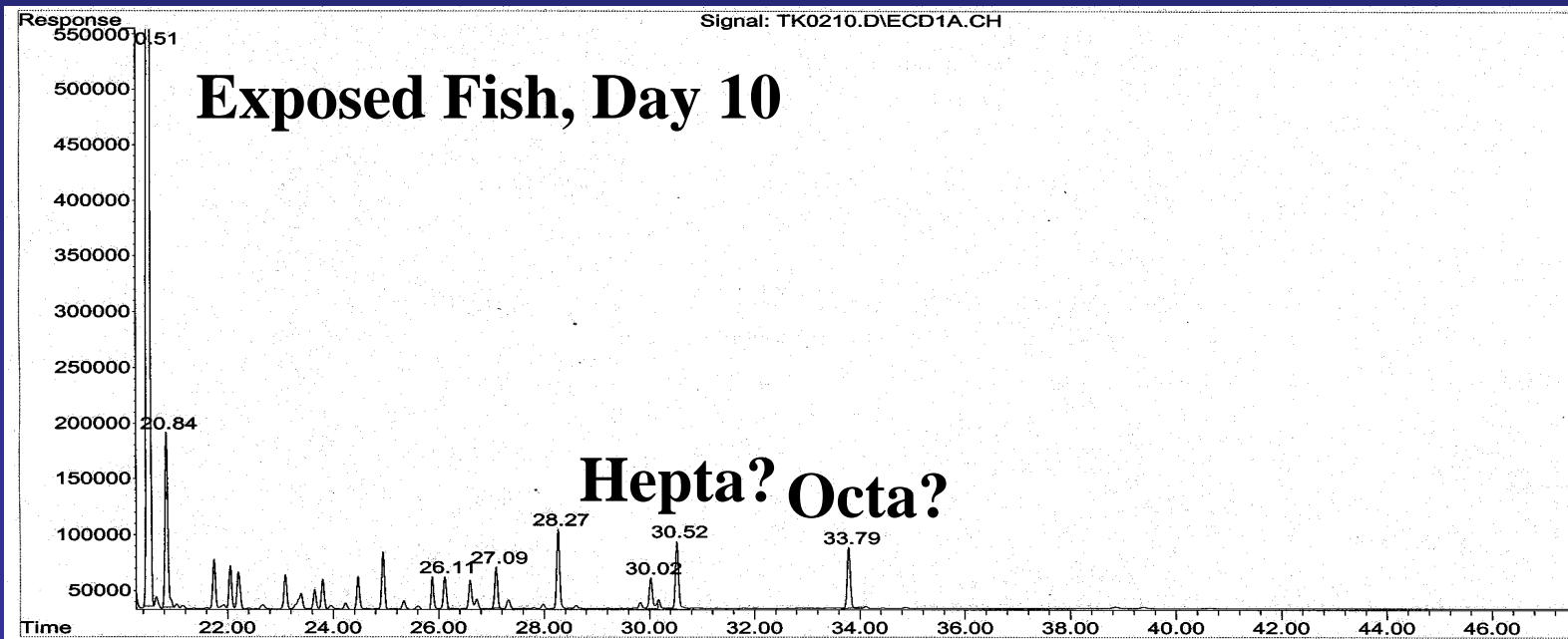
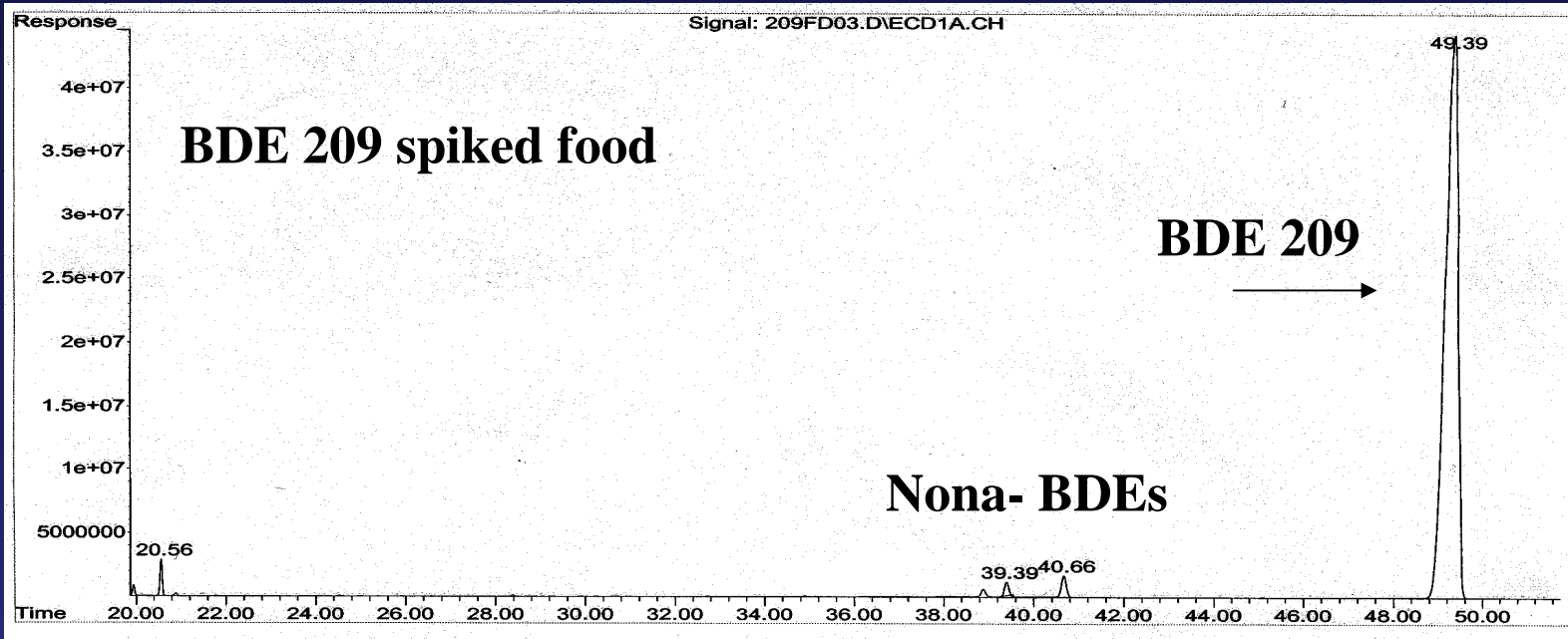
Body Burdens following Exposure to BDE 99

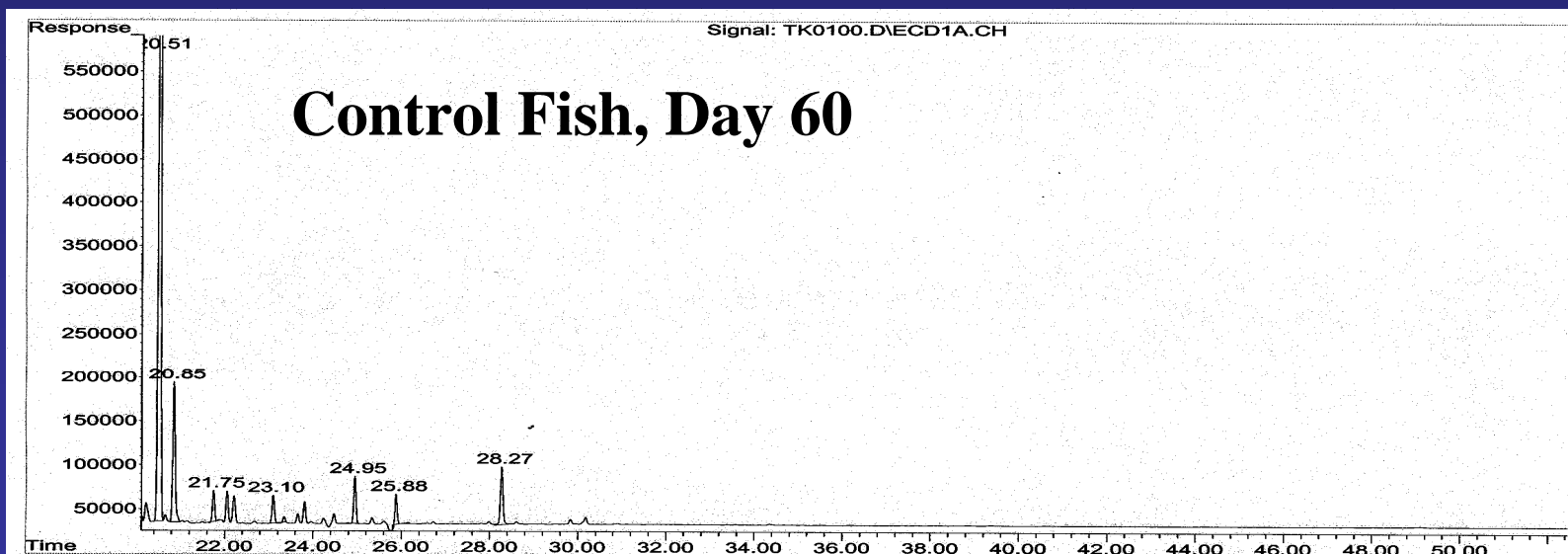
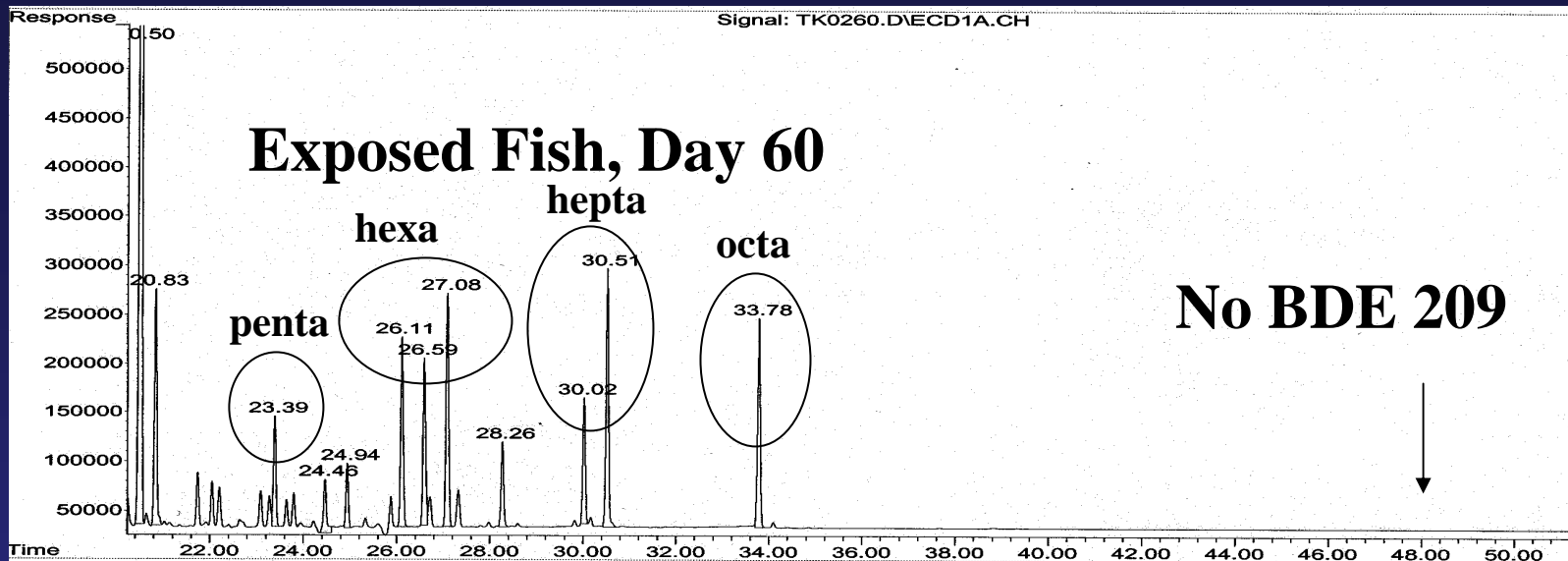


Dietary Exposure to BDE 183

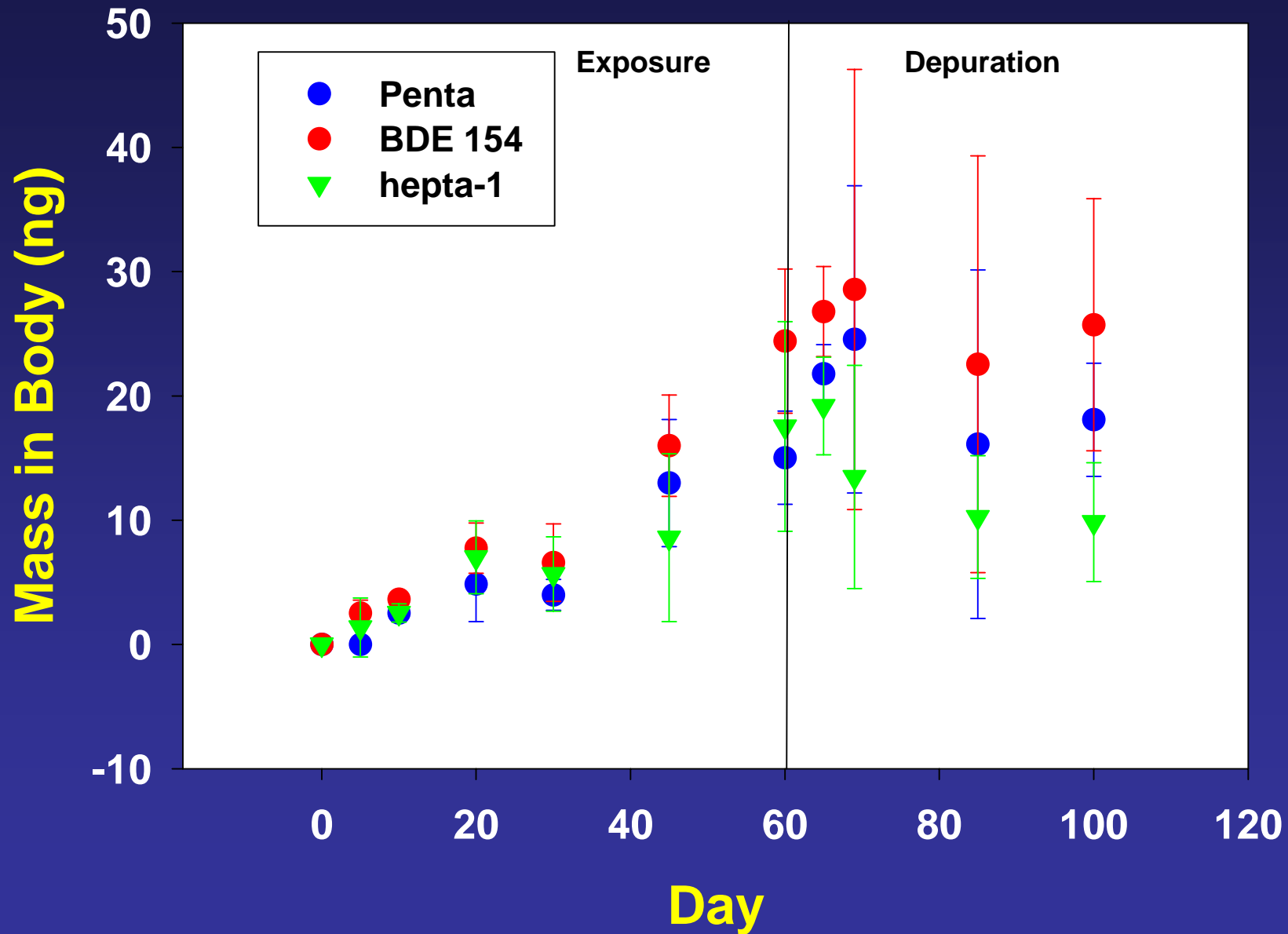


What about Exposure to BDE 209?





Exposure to BDE 209



Assimilation of BDE 209 in Carp:

$$\text{Minimal \% accumulated : } \frac{\sim 400\text{ng (penta-octa)}}{\sim 56000 \text{ ng}} = \boxed{0.7\%}$$

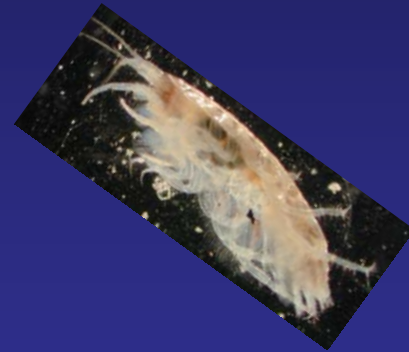
(on Day 60)

River Viskan sediment (Sellstrom et al., 1998)

BDE 209 ~ 16,000 ng/g dw

suggest **114 ng/g bioavailable**

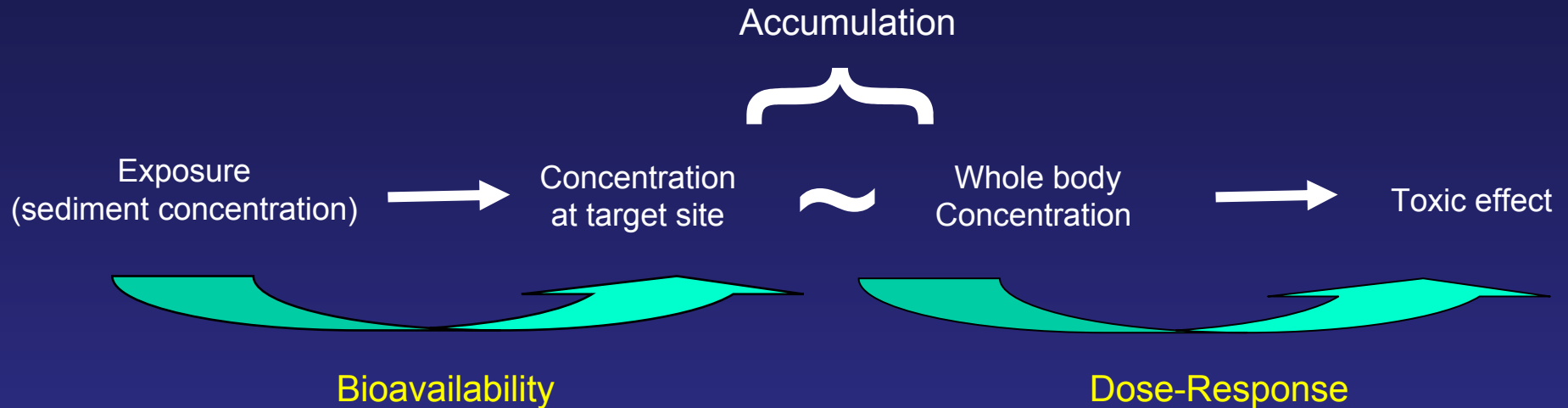
The bioavailability of brominated diphenyl ethers (BDEs) from urban estuarine sediments to deposit-feeding invertebrates



Susan Klosterhaus, with assistance from Erin Dreis

The importance of bioavailability from sediments

- Ecosystem managers are responsible for establishing sediment concentration guidelines that protect aquatic species

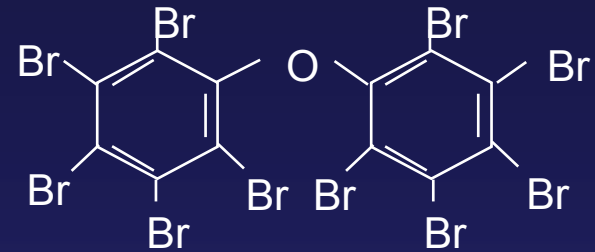


Several factors can potentially influence the bioavailability of a chemical from sediments

Bioavailability assessments are needed for managing BDEs in urban estuarine sediments:

- To determine potential for toxicity to organisms in direct contact with the sediments
- To determine extent of transfer from sediments to foodwebs

What do we know about Deca-BDE bioavailability to invertebrates?



- Earthworms accumulated BDE 209 from agricultural soils (Sellstrom et al. 2005).
- Minimally detected in oligochaete worms exposed to spiked sediment, but no accumulation from biosolids in a laboratory exposure (Ciparis and Hale 2005).
- Other studies report no detection, analytical difficulties, or don't measure at all.
- In other species, detection is sporadic and accumulation is generally low.

Deca-BDE was not detected in deposit feeders exposed to contaminated Chesapeake Bay sediment, despite sediment concentrations ranging from 50 – 4000 ng/g dry weight!

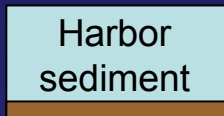
Is there a risk?

Laboratory exposure experiment with field-collected sediments



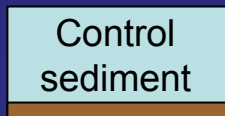
10 'clean' worms / tank

- Static renewal
- No feeding



Uptake phase: worms sampled days 2, 4, 8, 16, 28, 56

28 days



Elimination phase: worms sampled days 7, 14, 21 after transfer to clean sediment

Each sampling day:



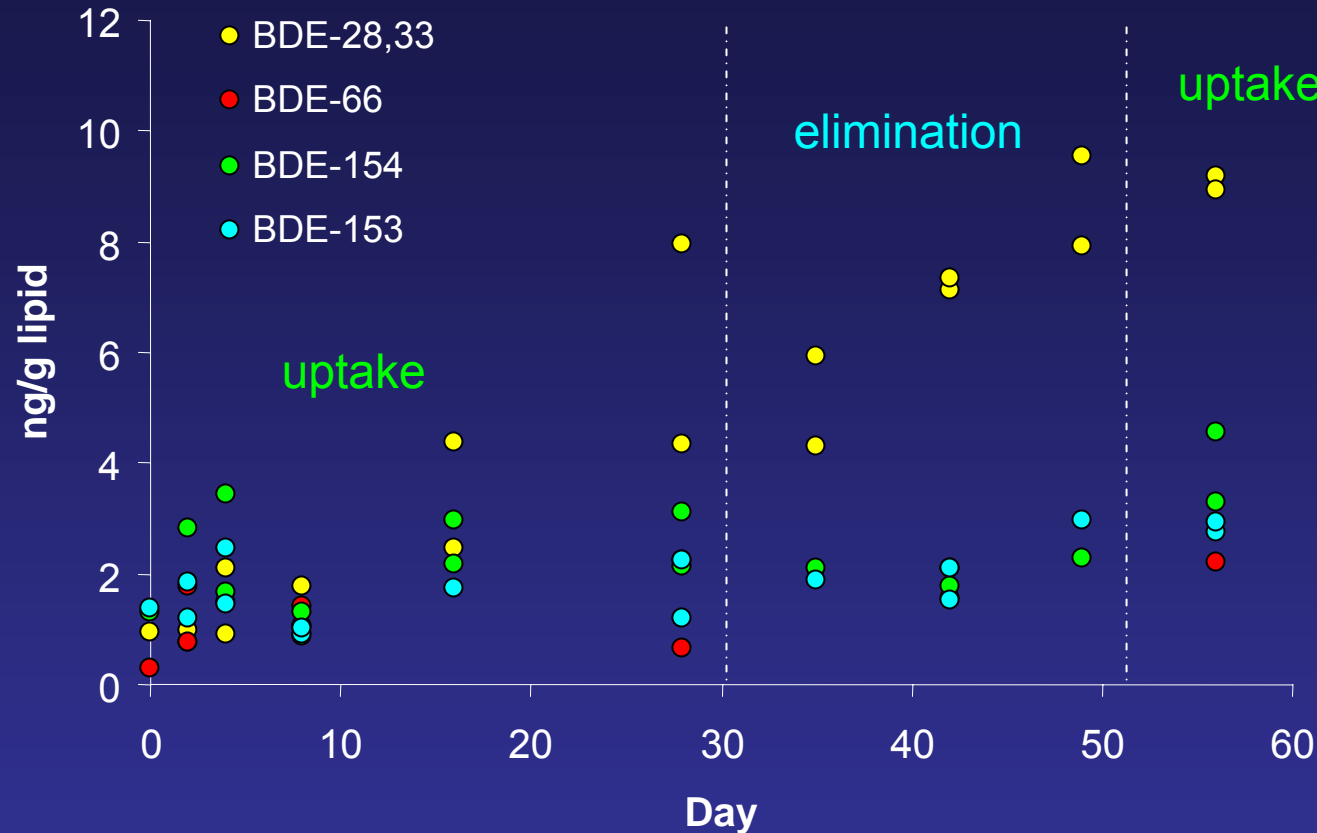
- composite worms from each tank (2 tanks/day)
- 24 hr gut purge

Metals

butyltins

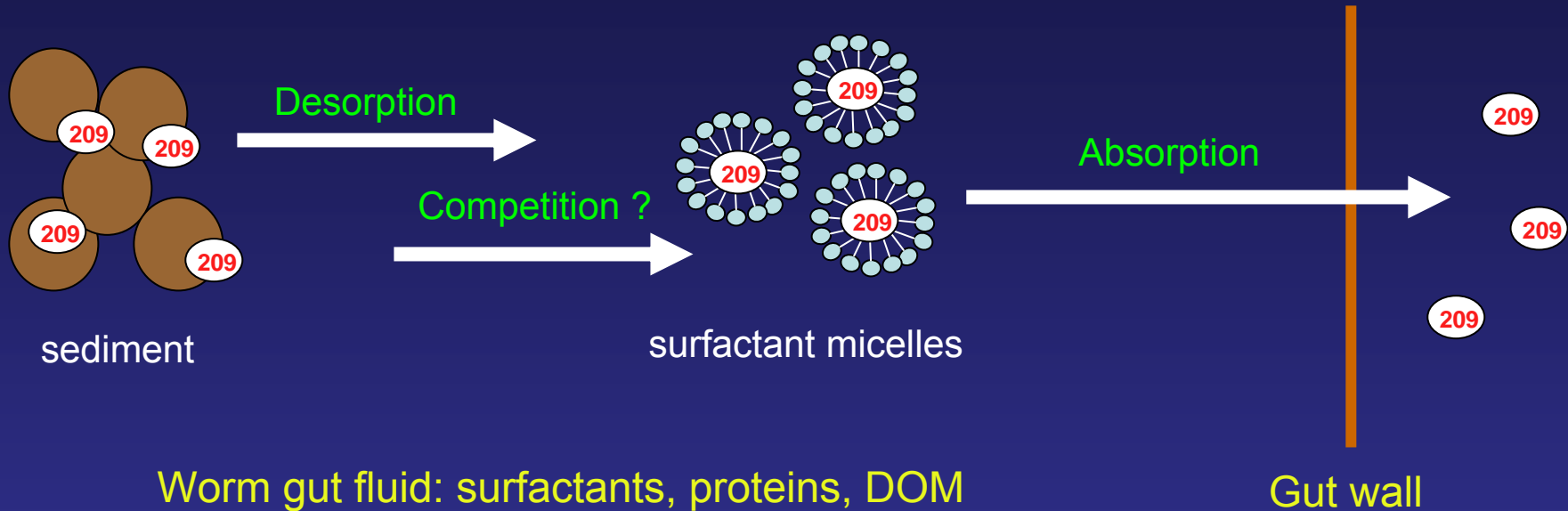
PCBs, PAHs, BDEs

BDEs: 28 day exposure to Baltimore Harbor sediment, 21 days of depuration



- Primary congeners in Penta-BDE mix (BDEs 47, 99, 100) were not detected in worms or amphipods, but were not detected in the sediments (< 1.5 ng/g dry)
- Biotransformation of BDE 28 from BDE 47?
- BDE 209 was not detected in worms or amphipods (< 3 ng/g wet weight)

What is limiting the bioavailability of BDE 209?

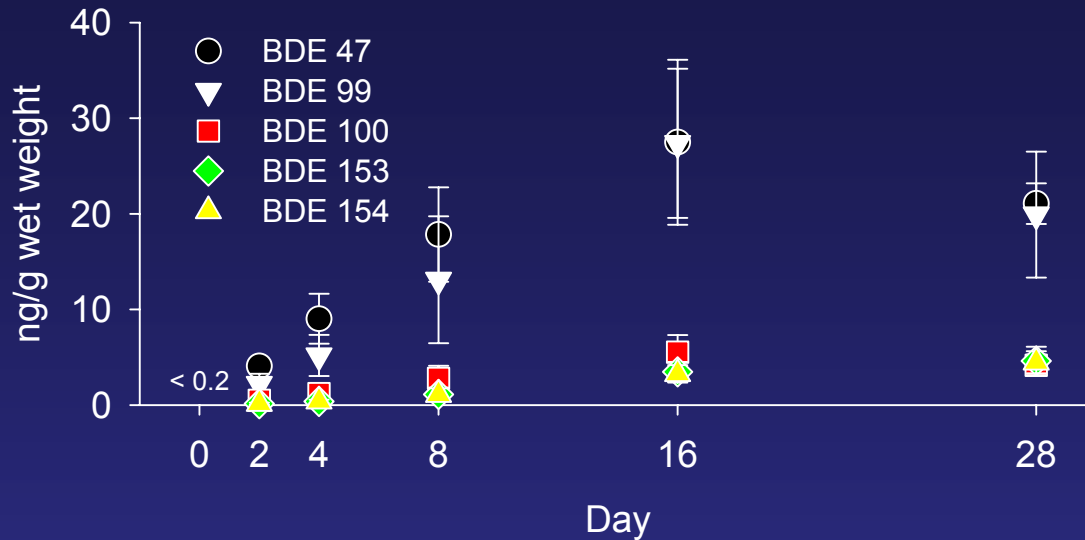


Possible limiting mechanisms:

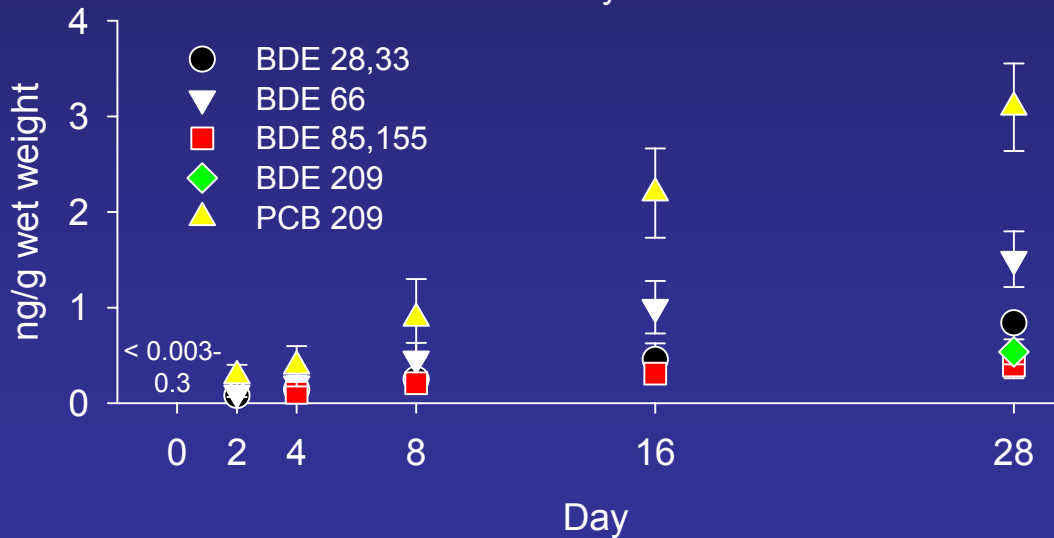
- (1) Desorption: solubilization from sediment into gut fluid
- (2) Competition for space in micelles (Voparil and Mayer 2000)
...if micelles become saturated, could limit capacity for HOCs, subsequent absorption.
- (3) Absorption: transfer in gut fluid and across the gut wall

Sediment-sorbed PAHs and chlorinated hydrocarbons are solubilized in gut fluid micelles prior to absorption (Weston and Mayer 1998; Voparil and Mayer 2000; Ahrens et al. 2001)

BDE accumulation over 28 days exposure to spiked sediment mixture



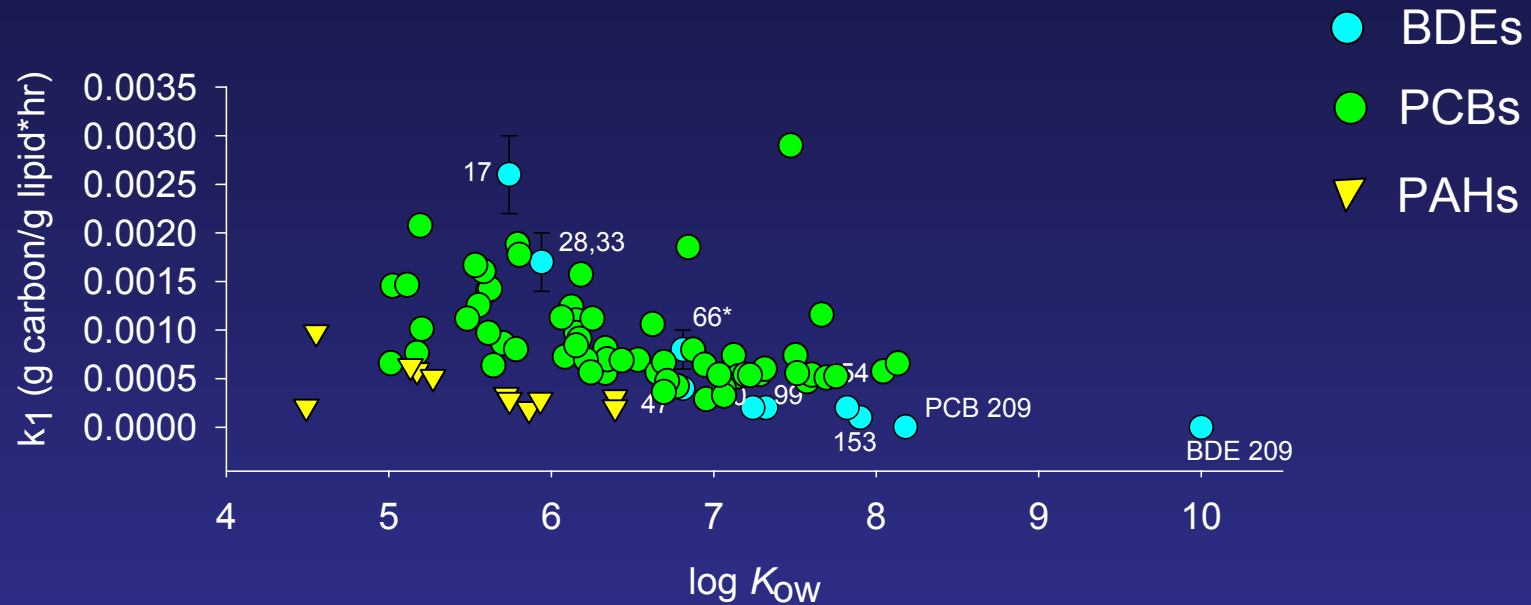
- Penta-BDEs accumulated to highest concentrations
- BDE 47 ≈ BDE 99 even though BDE 99 higher than BDE 47 in Penta-BDE mix



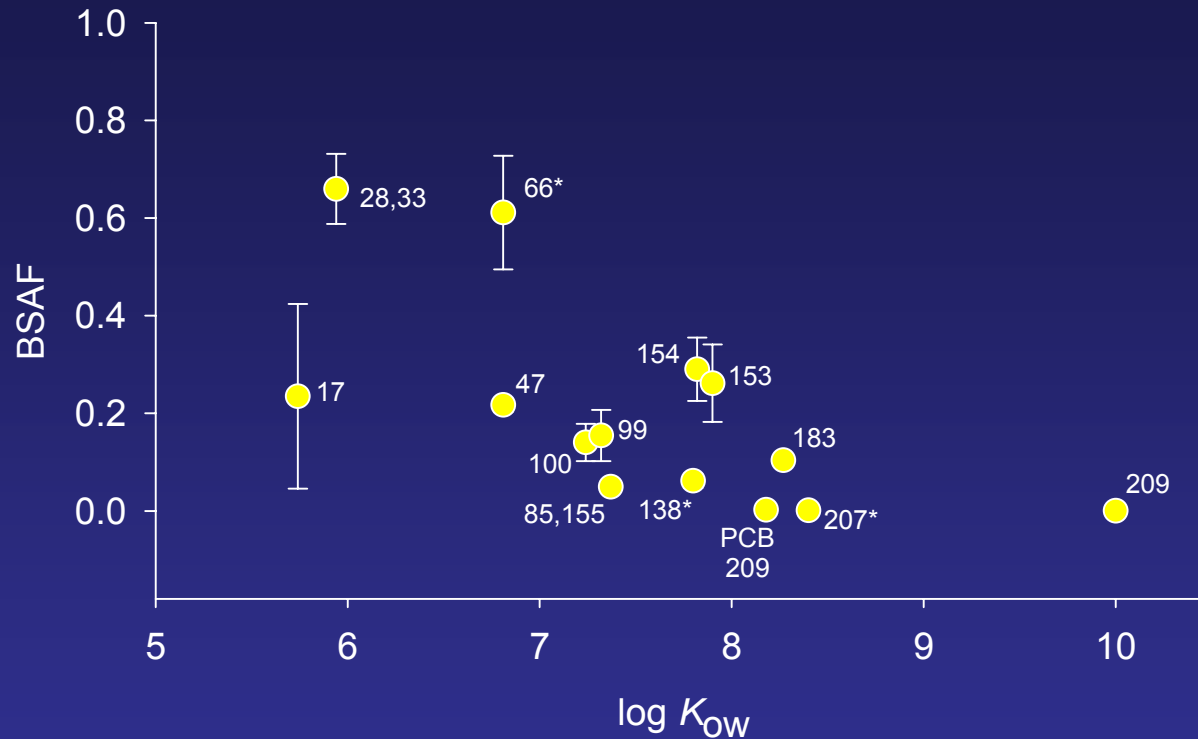
- Consistent with high bioavailability of BDE 47 in most biota
- BDE 209 accumulated, it can cross the gut wall

BDEs 17, 25, 75, 138, 183, 196, 207 (0.04-0.4 ng/g wet weight)

BDE uptake rate constants for *N. virens* exposed to spiked sediments



Bioavailability of BDEs to *Nereis virens* from spiked sediments



- Values are lower compared to field BSAFs, not at steady-state
- BSAF for BDE 209 was 3 orders of magnitude lower than BSAFs for the Penta-BDE congeners
- Even when bioavailability is at a maximum, availability of BDE 209 is very low

Bioavailability and Exposure to BDEs: Conclusions

- **Brominated flame retardants are ubiquitous in the environment, and levels are increasing.**
- **Human exposure likely results mainly from household and occupational dusts as well as dietary sources.**
- **Assimilation of BDE congeners in carp tissues depends upon their structure (range <1 – 58%).**
- **Debromination of BDEs is significant and forms numerous lower brominated congeners**
- **Less than 1% of BDE 209 is assimilated as lower brominated congeners. However, large production and use are charging up the environment with this source material.**
- **Although BDEs are being phased out, other halogenated (and other) flame retardants are entering the market.**

Regulatory Status of PBDEs

PBDE Mixture	Primary Application	Regulatory Status
Penta-BDE	Polyurethane Foam	- Restricted in CA (2006) - Produced ceased (2004)
Octa-BDE	Thermoplastics	- Restricted in CA (2006) - Production ceased (2004)
Deca-BDE	Thermoplastics	- No restrictions in CA - Banned in WA*, ME - Banned in European Union

*In a way. Deca banned in mattresses (where it was never used) and banned in televisions, computers and residential upholstered furniture by 2011, as long as a safer, reasonable and effective alternative has been identified...

Alternatives are inevitable...

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)

What is the potential for effects to humans and wildlife ?

	Production Volume (lbs)*	Bioaccumulation	Persistence	EcoToxicity	Mammalian Toxicity
Tetrabromobisphenol A (TBBPA)	100-500M	Low	Moderate	High	High
Hexabromocyclododecane (HBCD)	10-500K	High	High	High	High
Decabromodiphenylethane (DBDPE)	?	Low	High?	?	?
1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE)	1-10M	High?	Moderate?	?	?
Pentabromoethylbenzene (PBEB)	0	Moderate?	Moderate?	?	?
Dechlorane Plus (DP)	1-10M	Low	High	?	?
Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)	10-50M	?	Moderate?	Moderate	High
Triphenylphosphate (TPP)	10-50M	High?	Low?	High	?
Octyl tetrabromobenzoate (OTB)	?	?	?	High?	?

* EPA TSCA Inventory 2002

For Further Information:

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