The known unknowns:

Emerging chemical contaminants in the Puget Sound and beyond

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There are known knowns. These are things we know that we know.

There are known unknowns. That is to say, there are things that we know we don't know.

But there are also unknown unknowns. There are things we don't know we don't know.

Donald Rumsfeld

Outline

- A recently known known: brominated flame retardants in the environment

- Are ‘physical pollutants’ on the horizon?: microplastics in the ocean

Chemical Classes Studied: Common Features

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

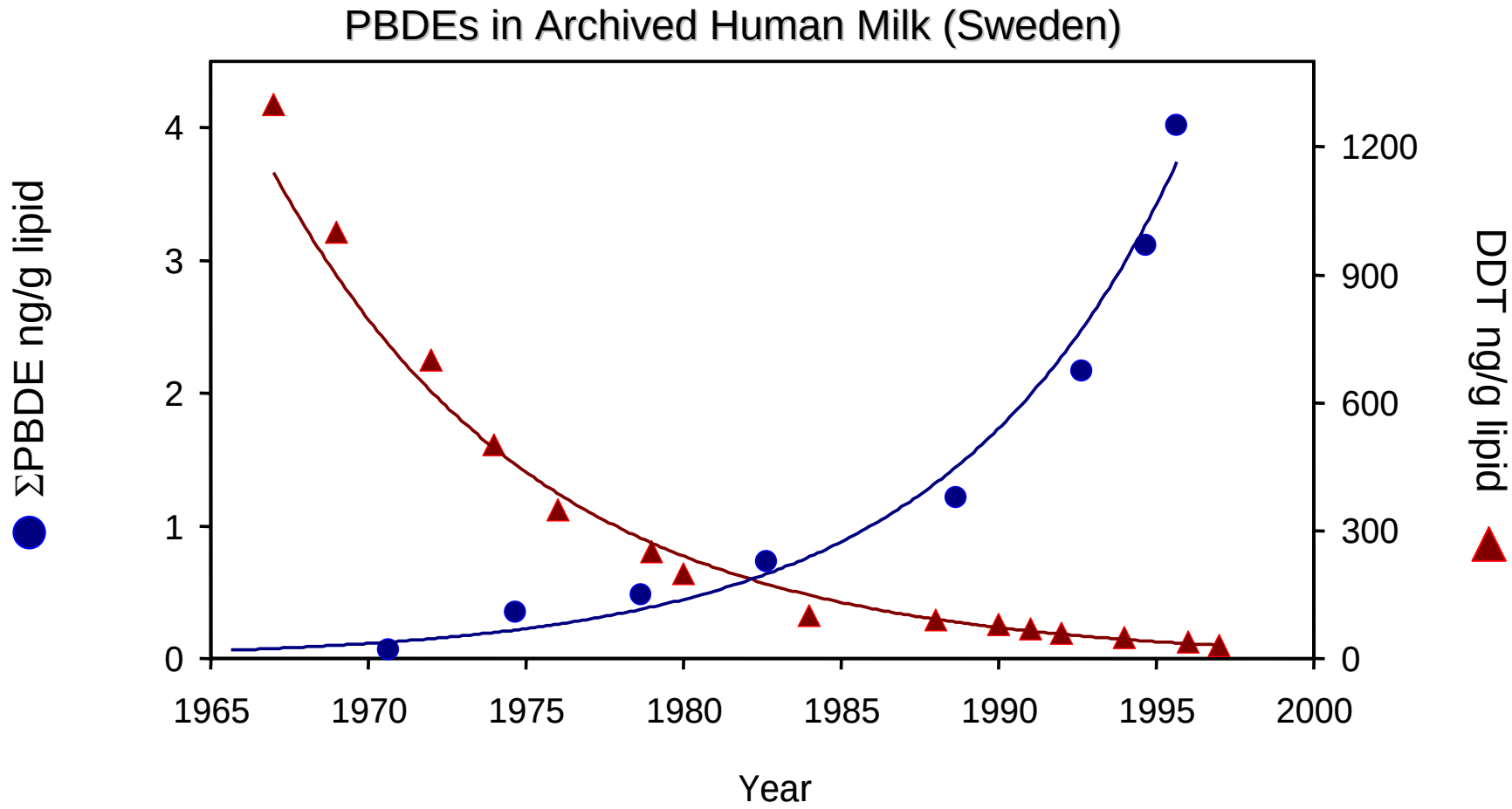
The issue at hand….

U.S. EPA Priority Pollutant List

International Screening Tools

Risk assessment limited by lack of information on ‘new’ materials

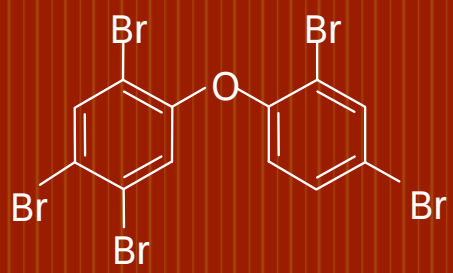
Part 1. Brominated Flame Retardants



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

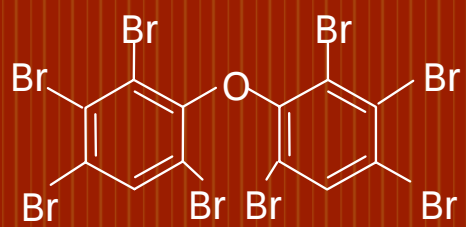
Meironyté et al., *Contaminants in Swedish Human Milk,* Organohalogen Cmpds. **38**, 1-4, 1998.

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



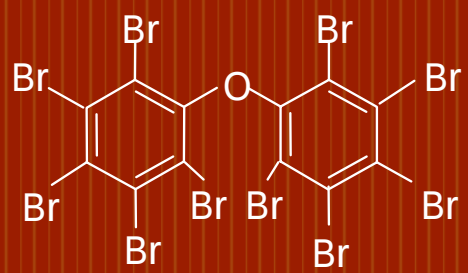
2,2',4,4',5-pentabromodiphenyl ether

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

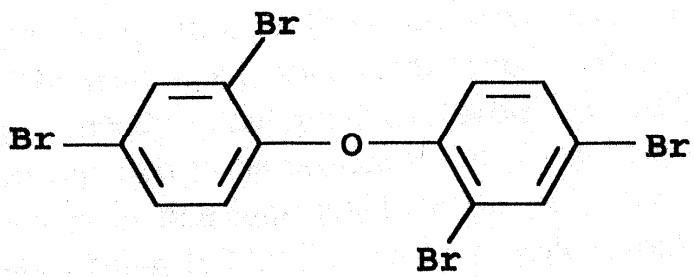
Types of Brominated Flame Retardants

ADDITIVE BFRs

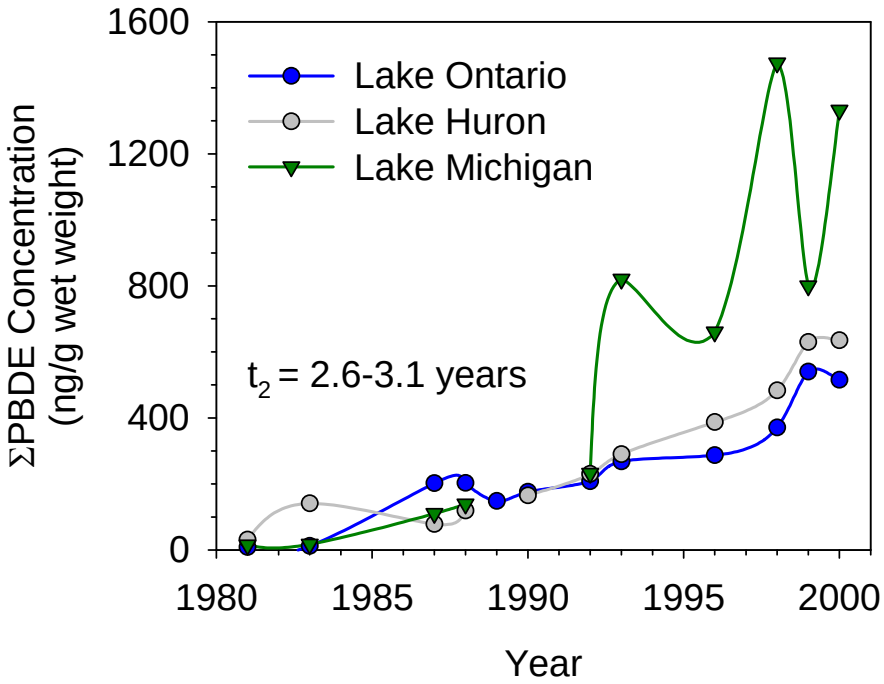
Decaabromobiphenyl
Decabromodiphenyl ethane
Decabromodiphenyl ether
Octabromodiphenyl ether
Pentabromodiphenyl ether
Tetrabromobisphenol A Derivatives
bis-(2,3-dibromopropyl ether)
bis-(2-hydroxyethyl ether)
bis-(allyl ether)
dimethyl ether
Hexabromocyclododecane
Bis(tribromophenoxy)-ethane
Pentabromotoluene
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)

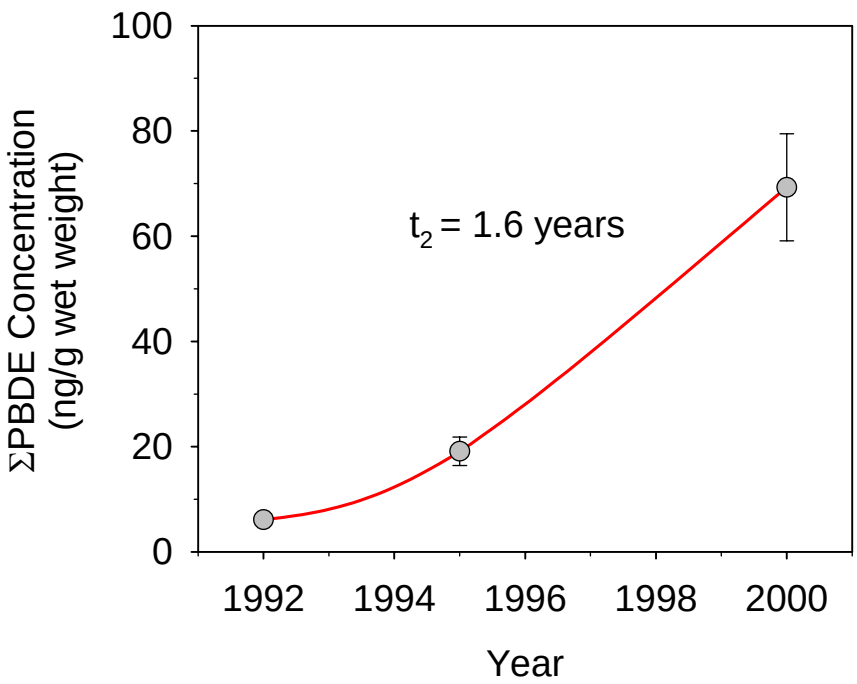


Great Lakes Herring Gull Eggs, Norstrom et al., 2002.



Σ PBDE will surpass Σ PCB in 2012-2017.

Columbia River Whitefish, Rayne et al., 2003



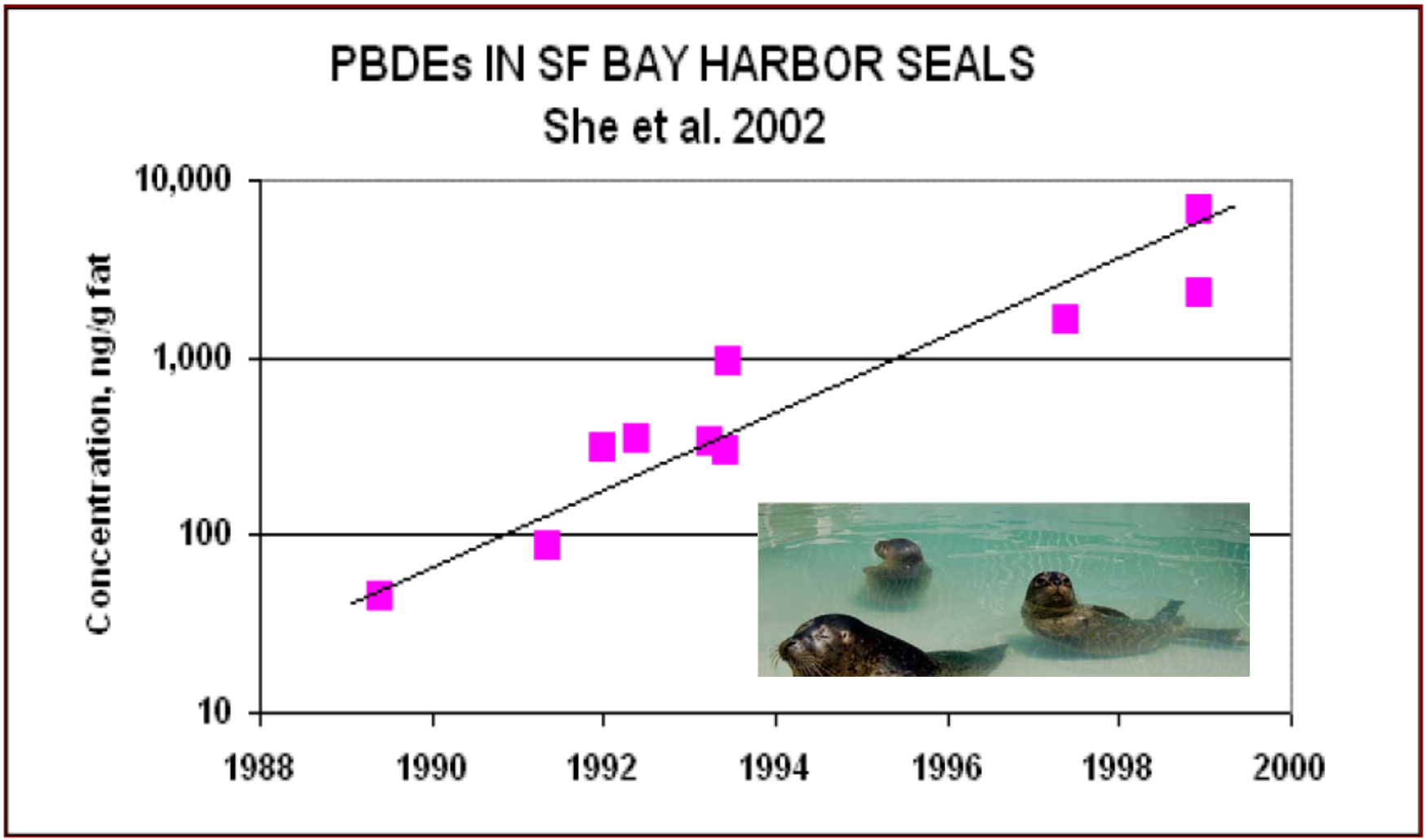
Σ PBDE will surpass Σ PCB by 2003.

Penta-BDE Commercial Mixture

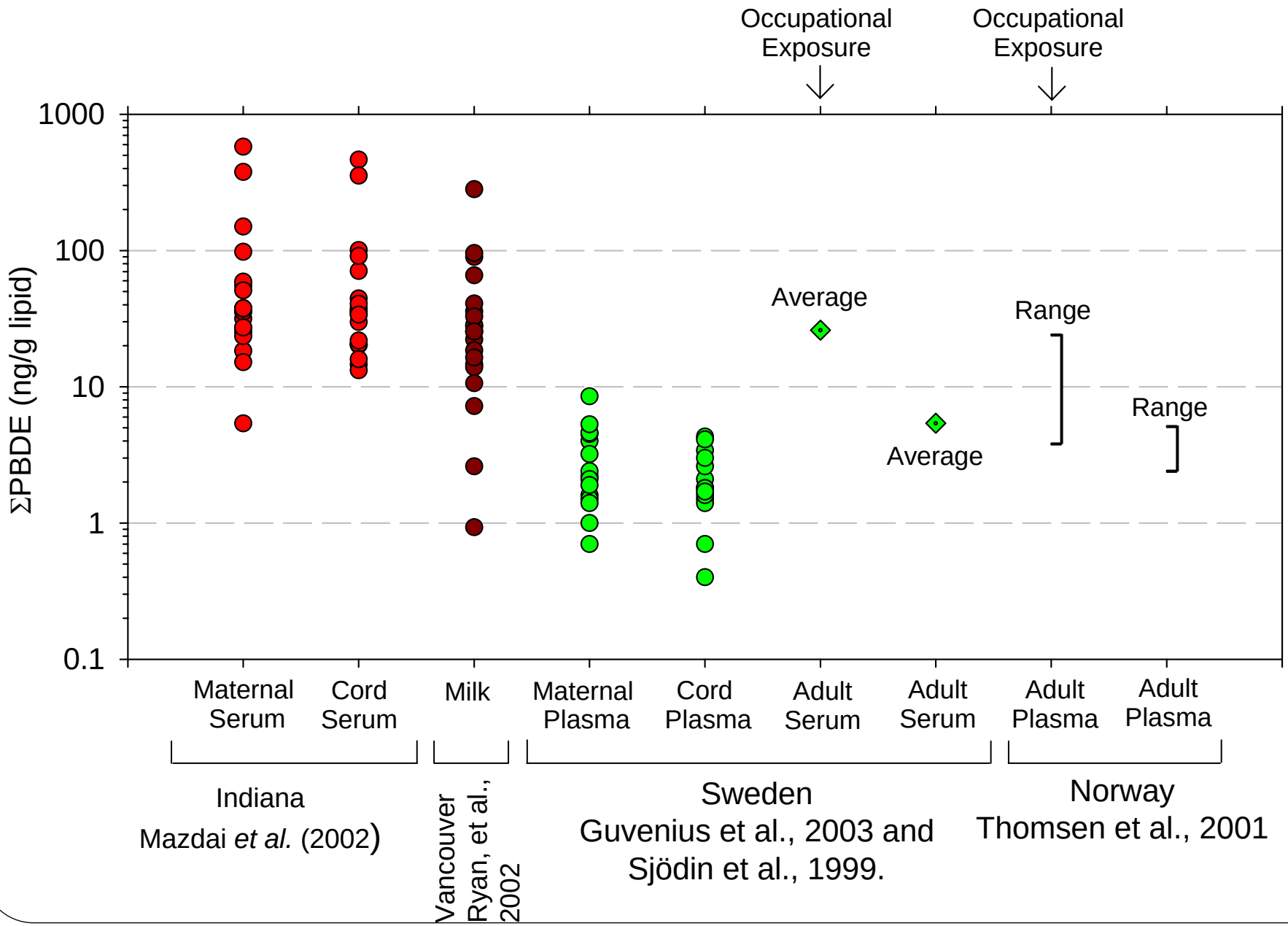
Octa-BDE Commercial Mixture

Deca-BDE Commercial Mixture

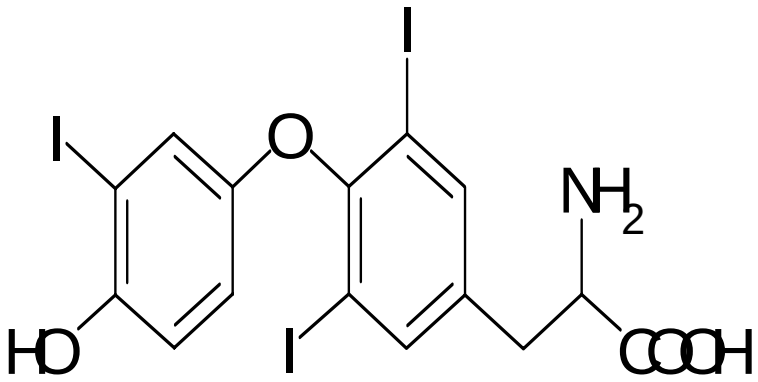
- Underwent a voluntary, industry and EPA sponsored, risk assessment in 2003.
- Penta- and Octa- being phased out in California, and production ending.


PBDEs IN SF BAY HARBOR SEALS
She et al. 2002
Concentration, ng/g fat
10,000
1,000
100
10
1988
1990
1992
1994
1996
1998
2000

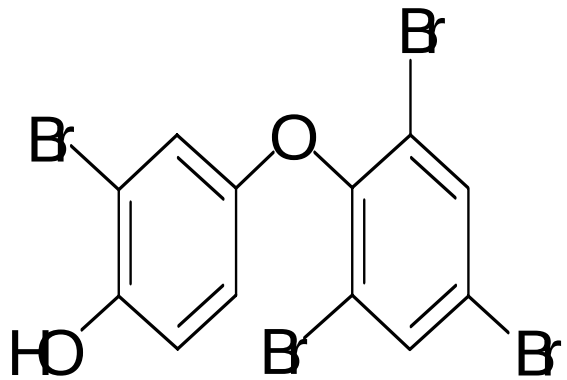
North American and European Levels



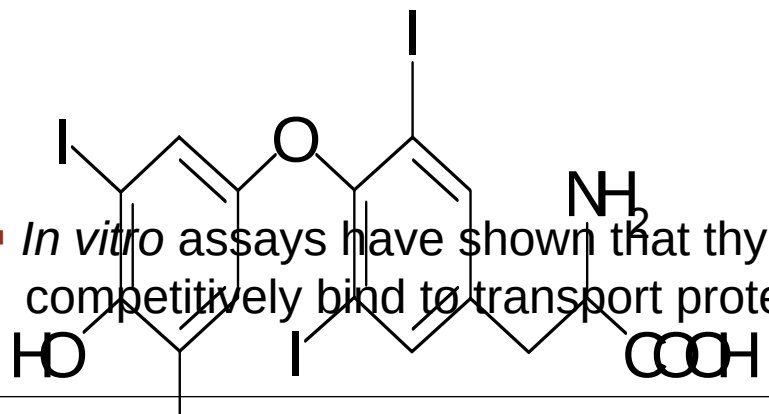
Hydroxylated PBDE Metabolites – Thyroid Hormone Mimics?

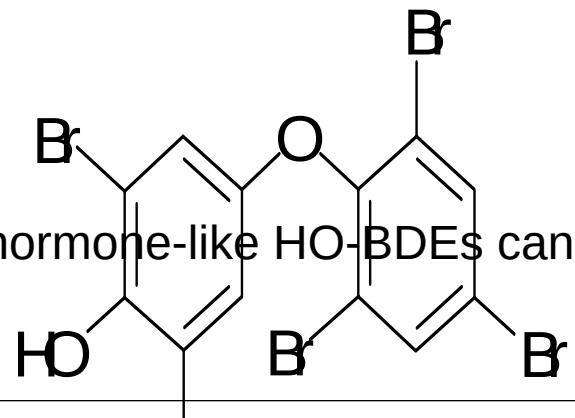


Triiodothyronine (T_3)



T_3-like HO-BDE





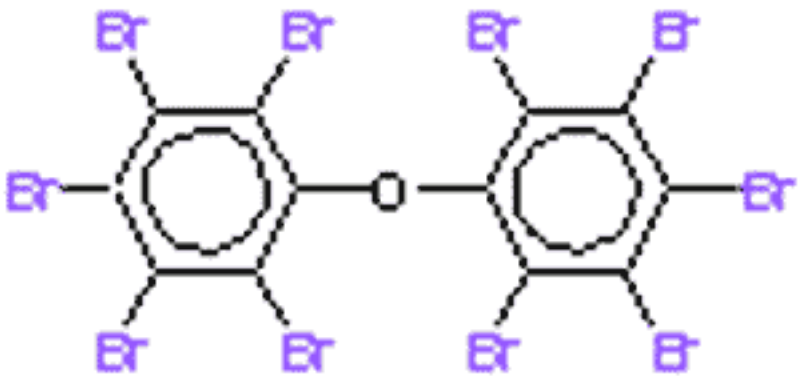
- *In vitro* assays have shown that thyroid-hormone-like HO-BDEs can competitively bind to transport proteins.

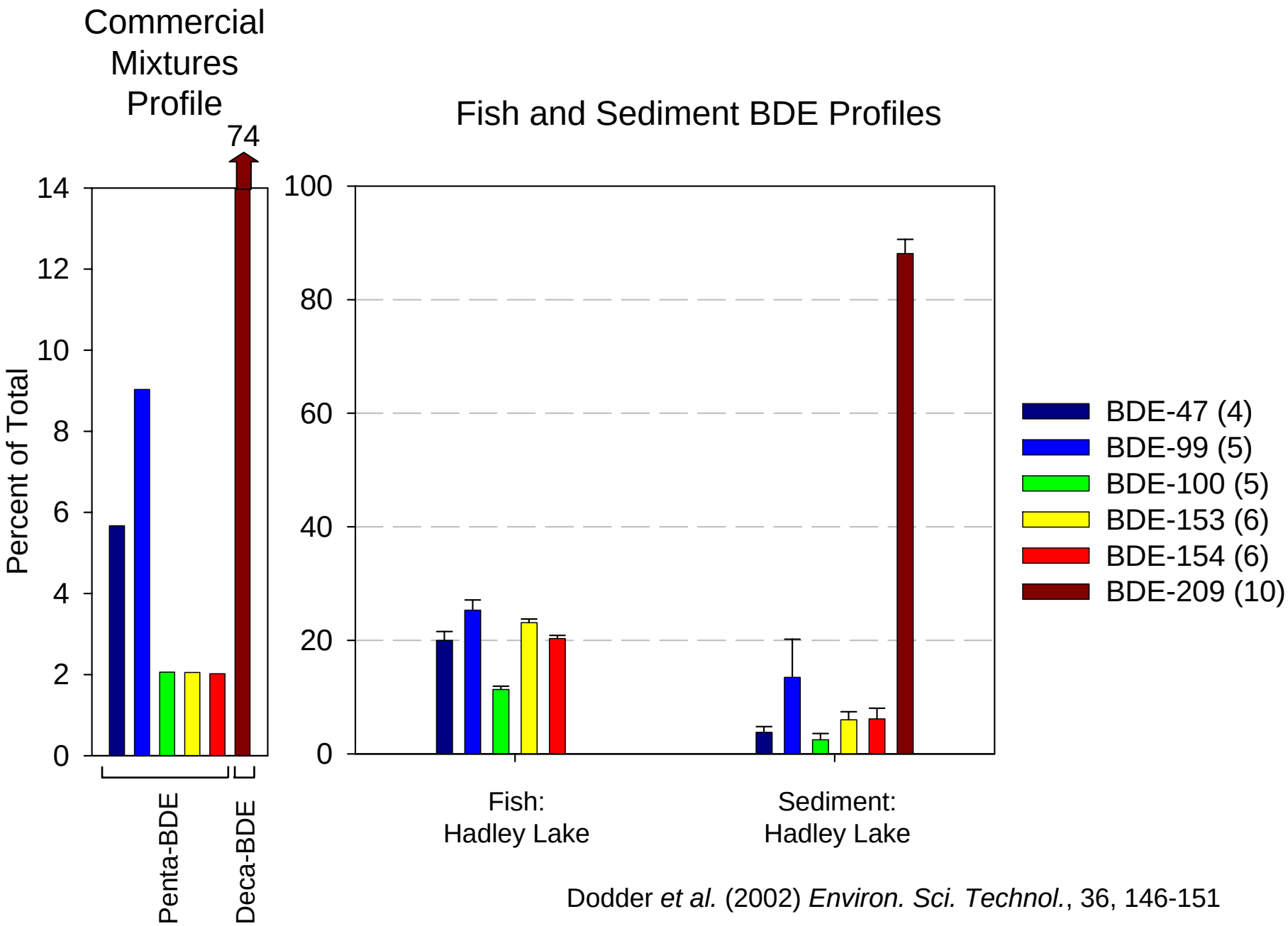
Change in Production

As a result of ‘Penta’ congeners being observed in the environment:

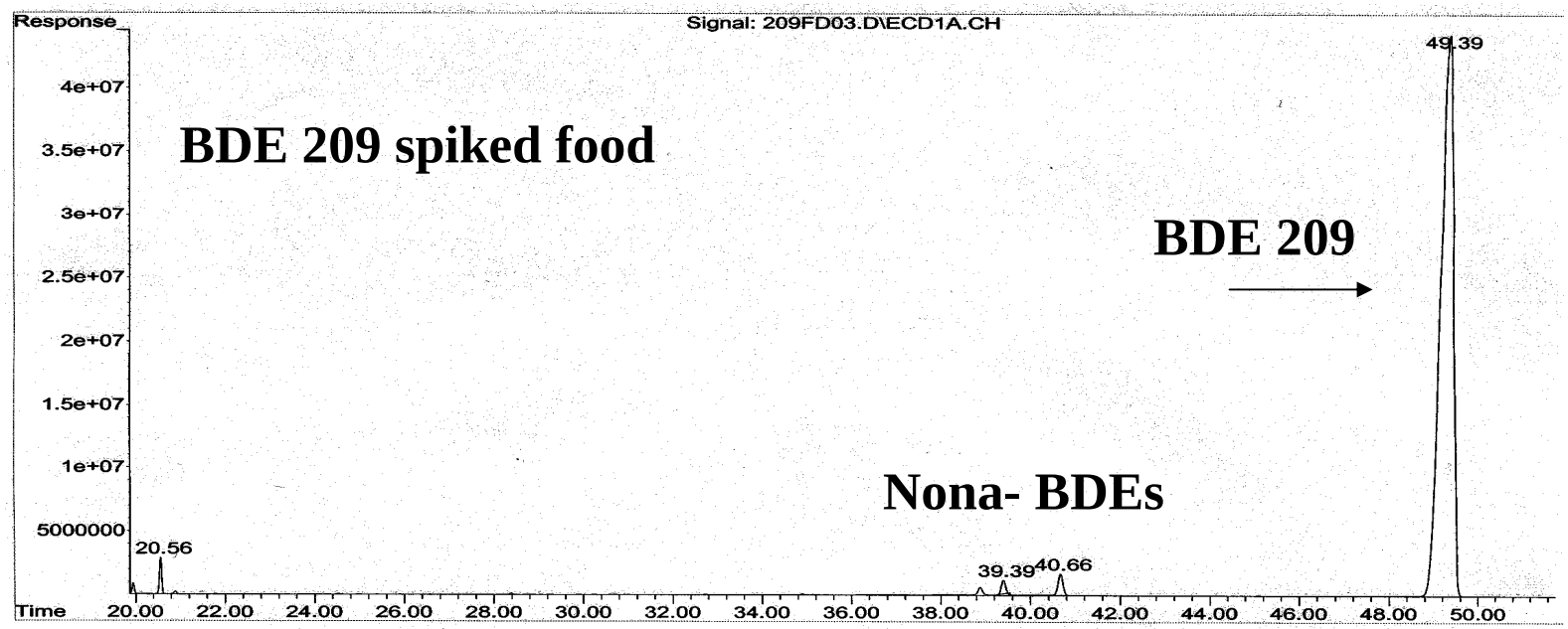
1.Penta mixture banned in Europe
2.Voluntary production phase out in U.S.

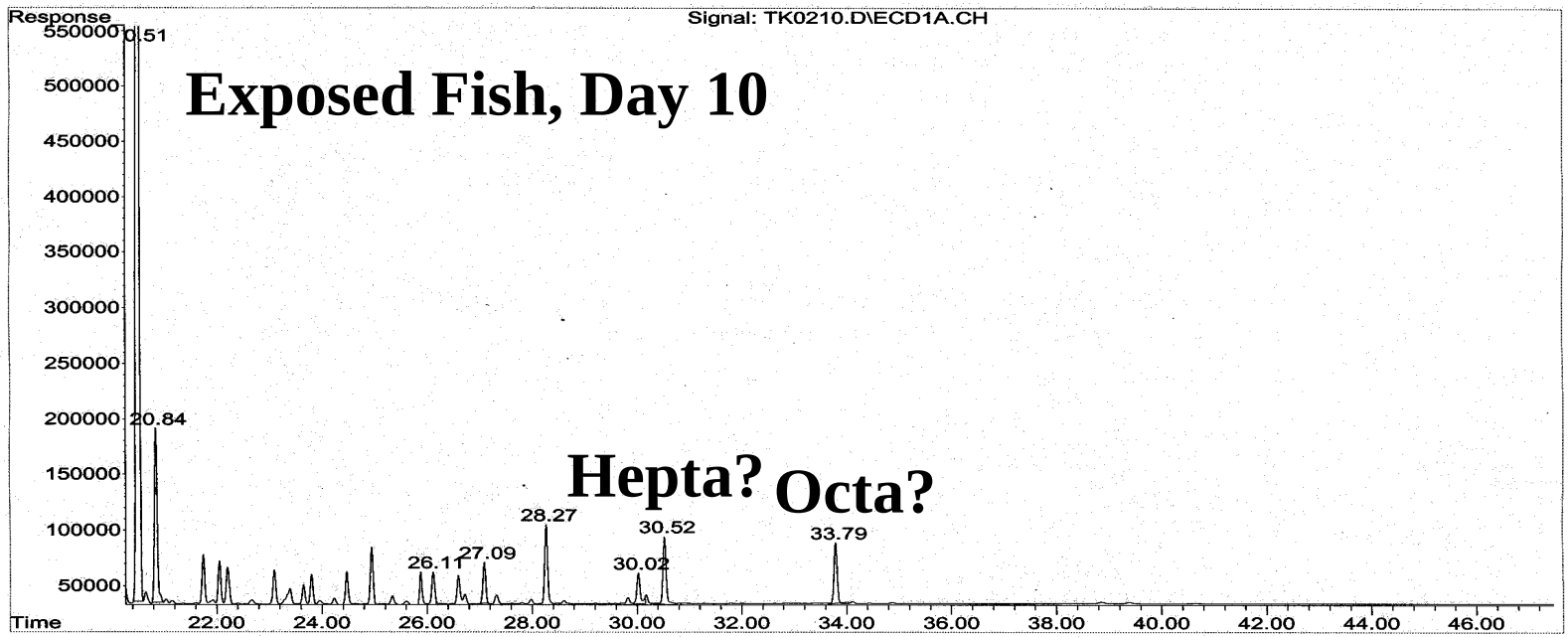
However, what are the alternatives?

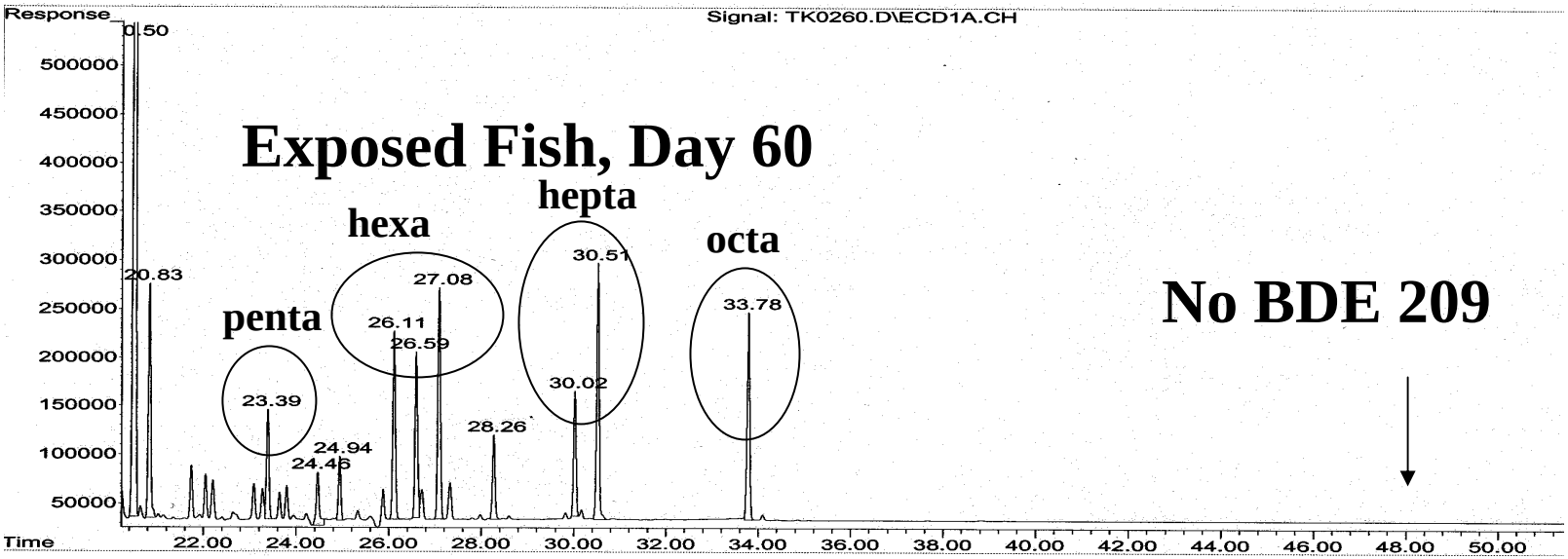


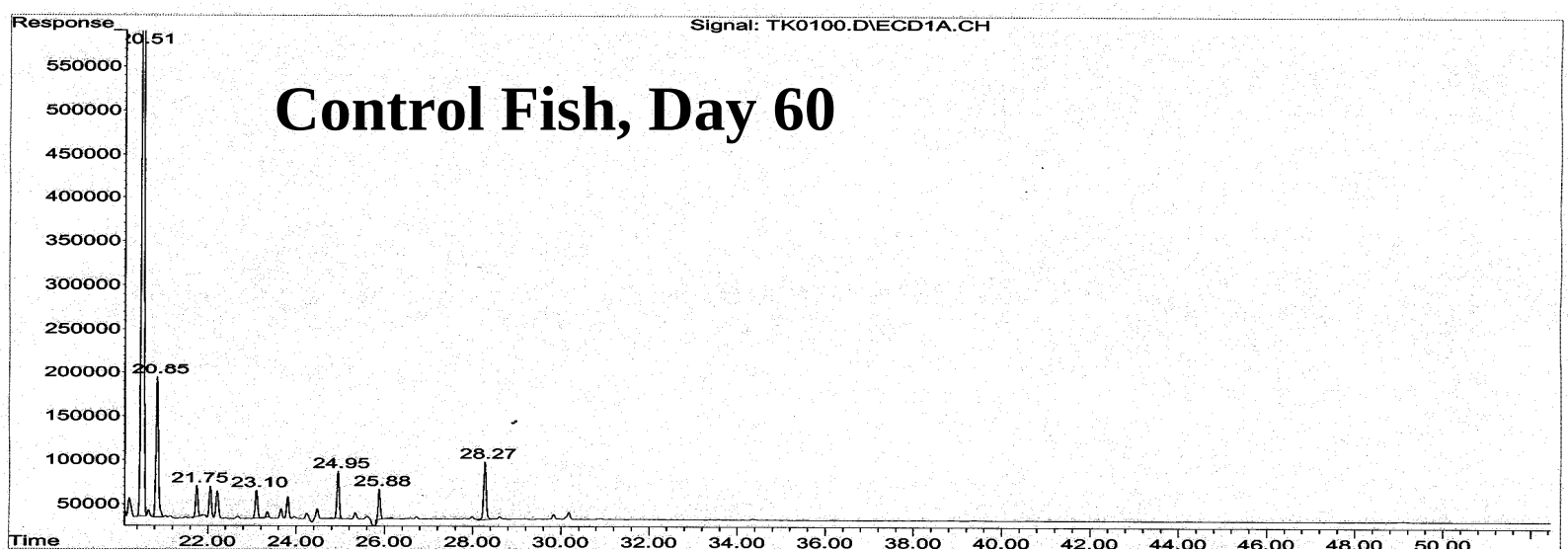


Dodder *et al.* (2002) *Environ. Sci. Technol.*, 36, 146-151


Response
Signal: 209FD03.D\ECD1A.CH
BDE 209 spiked food
BDE 209
Nona- BDEs
49.39
20.56
39.39
40.66
Time


Response
Signal: TK0210.D\ECD1A.CH
Exposed Fish, Day 10
Hepta?
Octa?
0.51
20.84
26.11
27.09
28.27
30.02
30.52
33.79
Time





Analogy to DDT?

‘Newer’ BFRs

Stapleton et al. (2008)

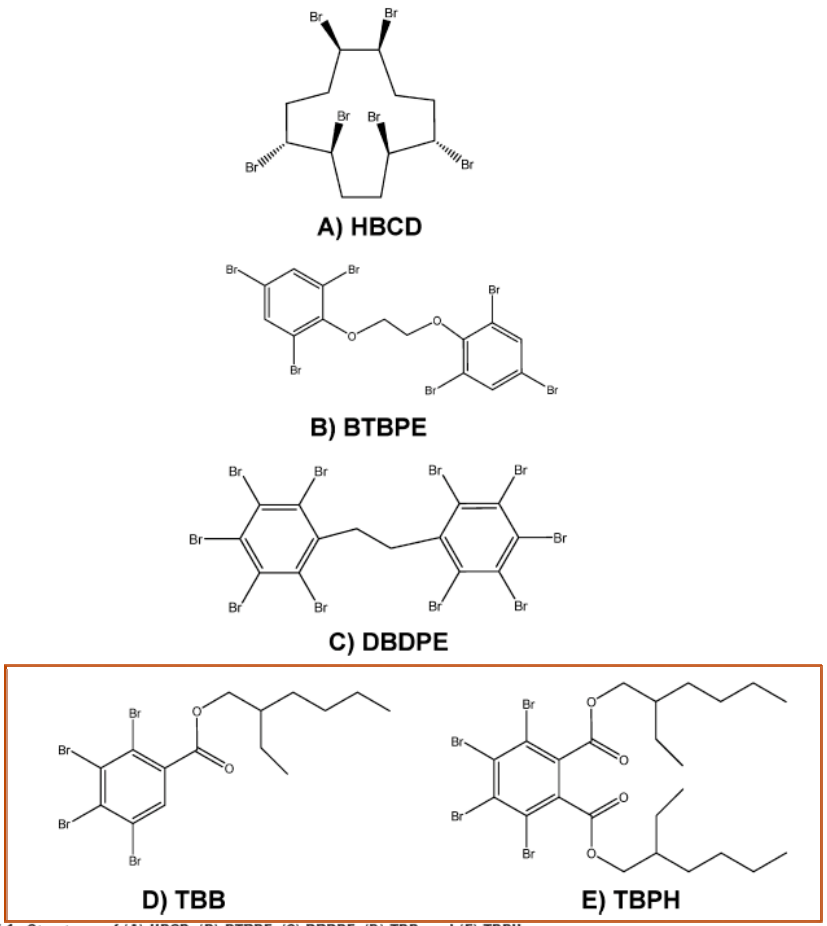


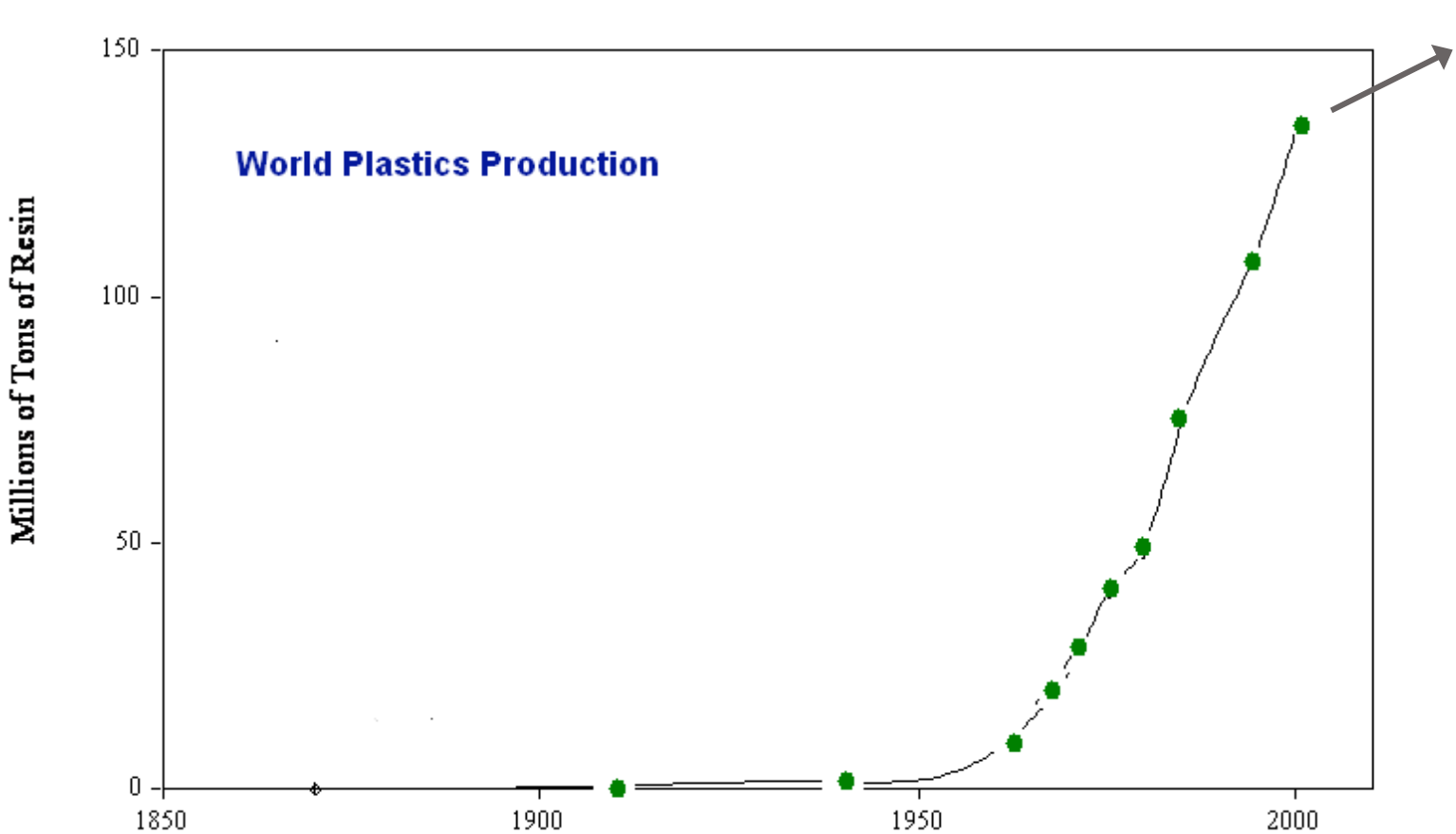
FIGURE 1. Structures of (A) HBCD, (B) BTBPE, (C) DBDPE, (D) TBB, and (E) TBPH.

2-ethylhexyl 2,3,4,5-tetrabromobenzoate

(2-ethylhexyl)tetrabromophthalate

Microplastics in Aquatic Ecosystems

Global Resin Production



T. Andrady, RTI

Potential sources of microplastics

1. Abrasion of ‘macro’ plastics, especially on beaches

2. Deliberate production and use

Do Zooplanktons Ingest Microparticles?

No good quantitative data on ingestion.

In this preliminary experiment the krill species *Euphasia pacifica* *was placed in water containing dispersed microparticles of polyethylene.*

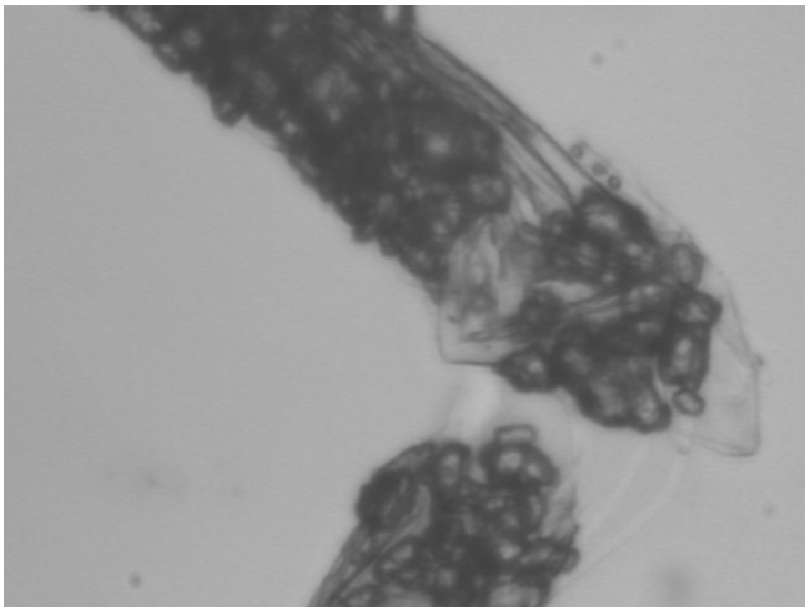
- The zooplankton ingested the plastic microparticles freely.

- When exposed to a mixture of the staple algae and microparticles both were ingested with little or no preference

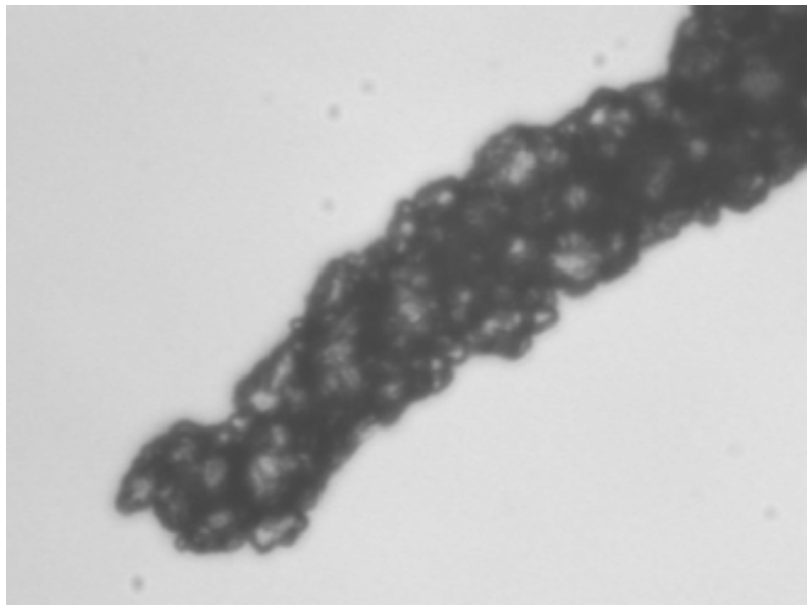
Field study with Professor Alice Aldredge

T. Andrady, RTI

Polyethylene Ingestion



Plastic Particles in gut



Plastic in Fecal Pellet

1. Average particle size = 20 microns
2. Fresh zooplankton sample tested in a container

T. Andrady, RTI

Microplastics Research Questions

1. What are the relative importance of sources?

2. At what level do microplastics interfere with aquatic communities?

3. Are microplastics an important geochemical phase?

4. Do microplastics ‘deliver’ pollutants to aquatic food webs?

5. Is leaching of microplastic components an important source of individual chemicals?

NOAA Marine Debris Program for Workshop Proceedings

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our sound, our community, our chance