Levels and Trends of Brominated Flame Retardants in the Environment: PBDEs and Beyond…



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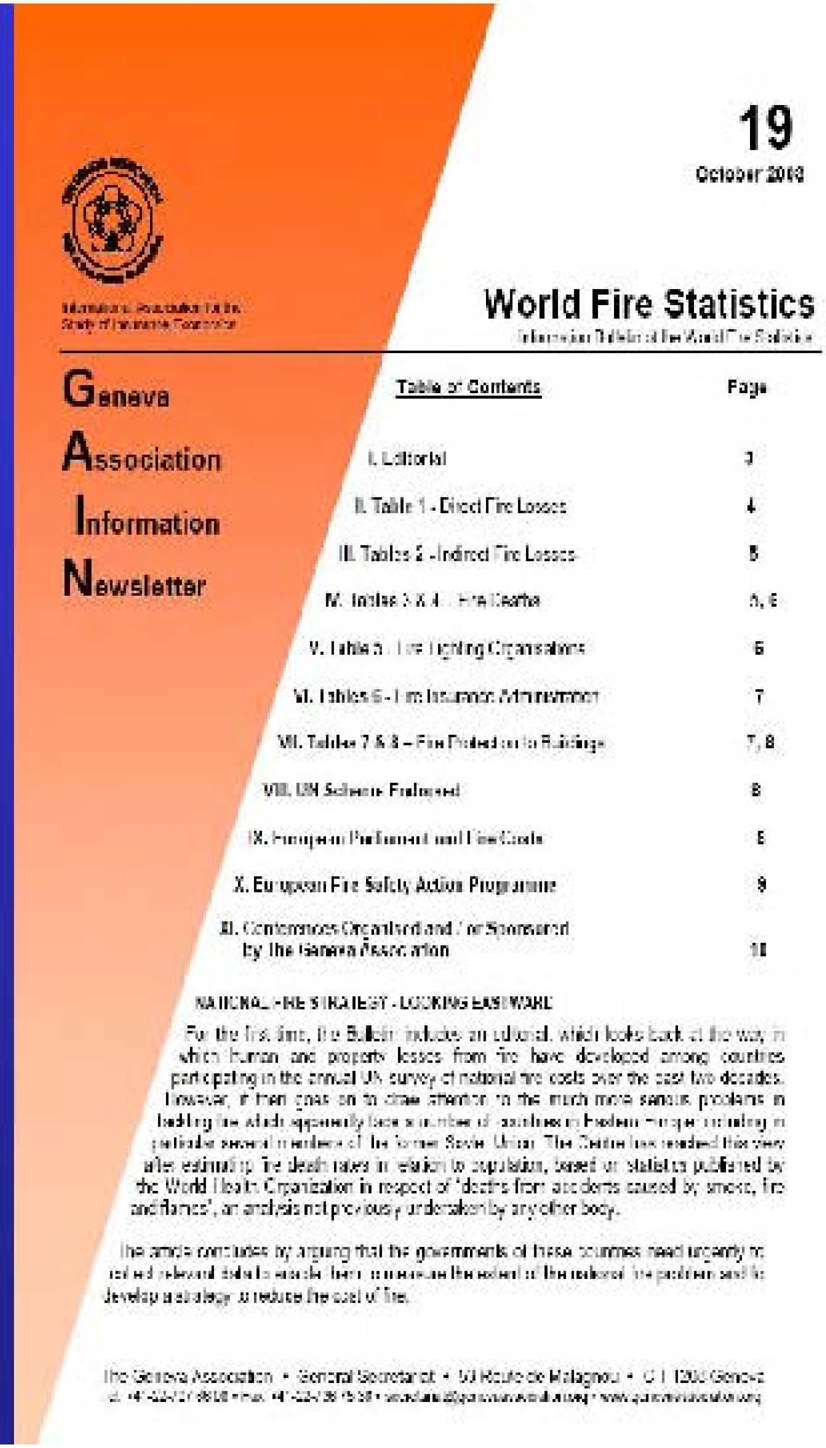
Environment Canada Environnement Canada

Fire Hazard:

- In Canada on average between 1986-1995, 67 000 fires were reported each year, which resulted 3700 injuries, 465 deaths.
- In the same time damage to properties was over $1.6 billion (0.17% GDP).
- In US, every year over 3,000,000 fire have been reported, which results in 29,000 injuries and 4,500 deaths.
- Direct losses over $8 billion corresponding to 0.11% of GDP.
- In UK on average 645 deaths/year are attributed to fire. Direct damage caused by fire is £1.2 billion/year corresponding to 0.14% of GDP.
- Losses to fire range between 0.10% (Japan) and 0.26% (Norway) GDP.
- Similar amount of funds are beings used in fire protection


19
October 2003

Geneva Association Information Newsletter

World Fire Statistics

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NATIONAL FIRE STRATEGY - LOOKING EASTWARD

For the first time, the Bulletin includes an editorial, which looks back at the way in which human and property losses from fire have developed among countries participating in the annual UN survey of national fire costs over the past two decades. However, it then goes on to draw attention to the much more serious problems in tackling fire which apparently face a number of countries in Eastern Europe including in particular several members of the former Soviet Union. The Centre has reached this view after estimating fire death rates in relation to population, based on statistics published by the World Health Organization in respect of 'deaths from accidents caused by smoke, fire and flames', an analysis not previously undertaken by any other body.

The article concludes by arguing that the governments of these countries need urgently to collect relevant data to enable them to measure the extent of the national fire problem and to develop a strategy to reduce the cost of fire.

The Geneva Association • General Secretariat • 53 Route de Malagnou • CH-1208 Geneva

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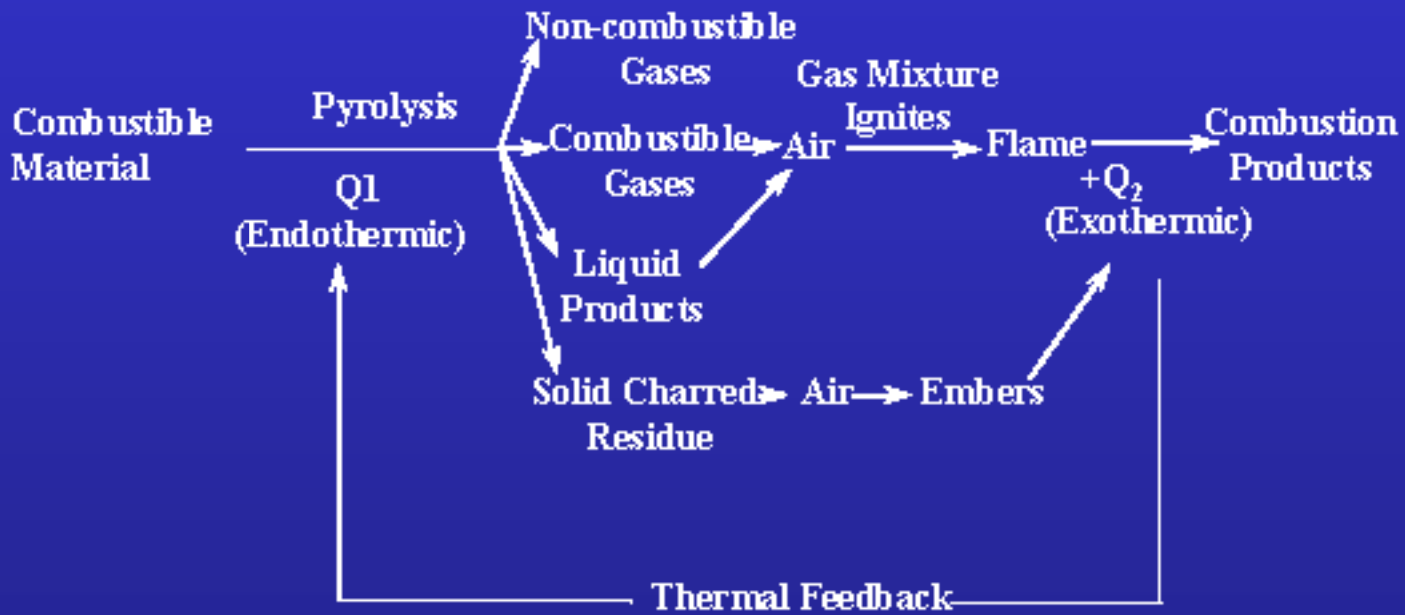
Flame Retardants:

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

The four steps of the combustion process



Troitzch, 1990

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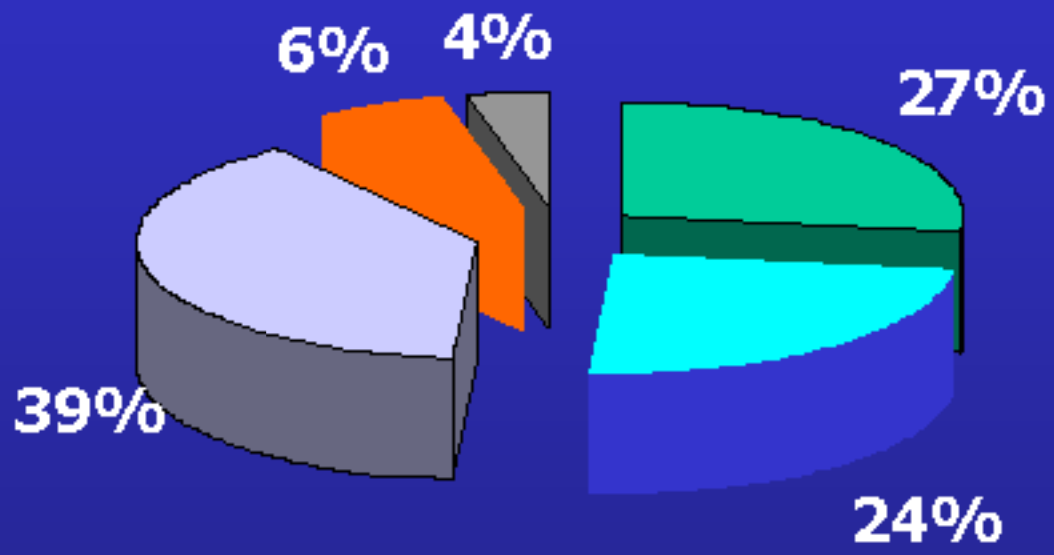
Historical Perspectives:

- Egyptians (about 450 BC) used alum to reduce the flammability of wood.
- Romans (about 200 BC) used a mixture of alum and vinegar for the same purpose.
- Mixture of clay and gypsum used to reduce flammability of theatre curtain. (1638)
- Alum was used to reduce the flammability of balloons.(1783)

Flame Retardant Worldwide Market in 1998



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Sources of BFRs

- Polymer Processing
- Formulating/applying to textiles
- Volatilization and leaching during use
- Particulate losses over use and disposal
- Application of Bio-solids to Agricultural Land

Types of BFRs

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
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)

BROMINATED POLYMERS

Brominated polystyrene
1,3-Butadiene homopolymer brominated
Poly(2,6-dibromo-phenylene oxide)
Poly-tribromostyrene
Dibromostyrene grafted PP
Polydibromostyrene
(Poly) pentabromobenzyl acrylate

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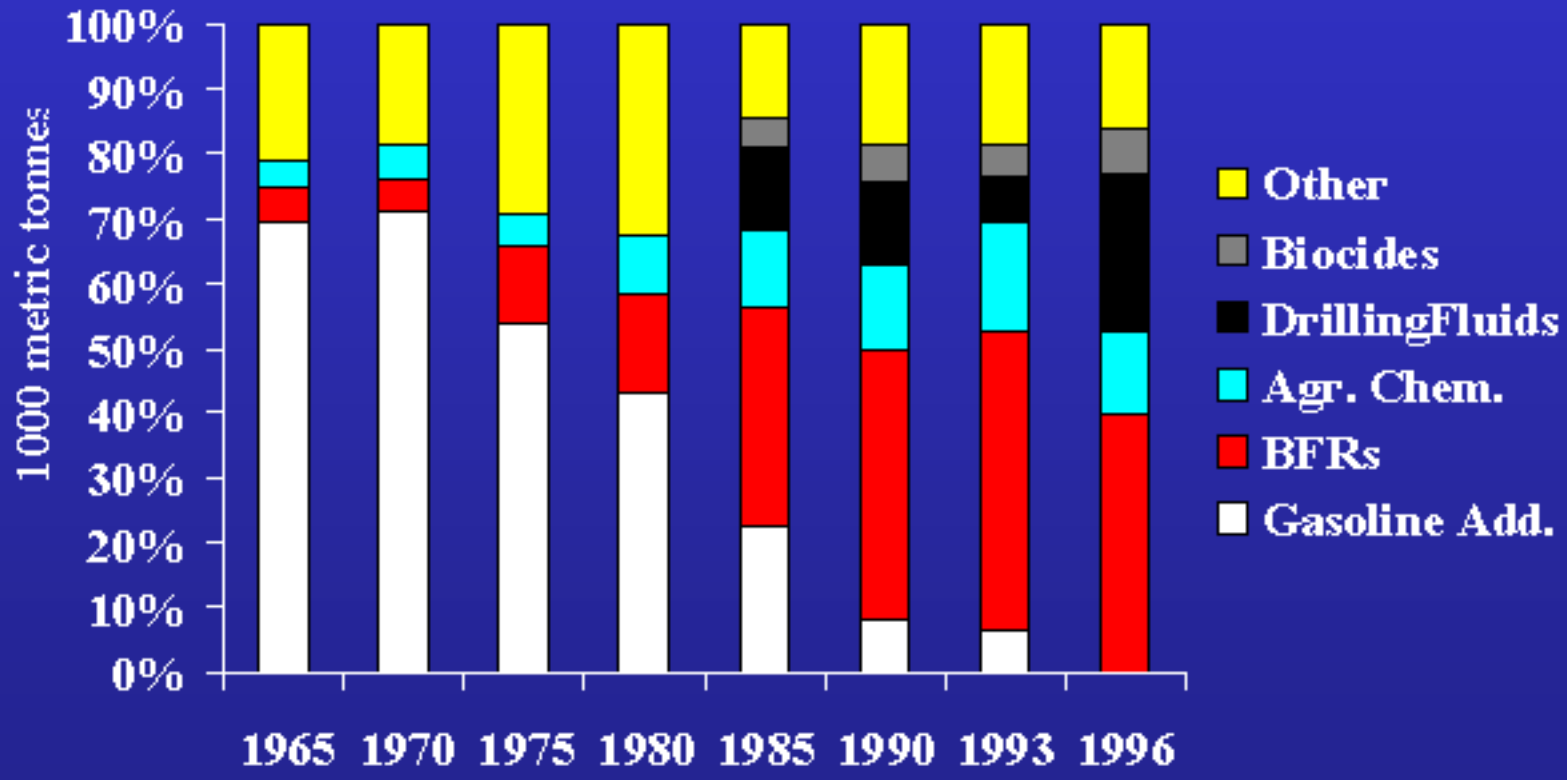
Amount of Bromine Used Globally for Production of Various Classes of Chemicals Between 1965 and 1996



From Grinbaum and Freberg, in Kirk-Othmer Encyclopedia of Chemical Technology 2002

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Major Brominated Flame Retardants Volume Estimates
Total Market Demand By Region in 2001

[MT]	Americas	Europe	Asia	Rest of World	Total
TBBPA	18,000	11,600	89,400	600	119,700
HBCD	2,800	9,500	3,900	500	16,700
Deca-BDE (DBDPO)	24,500	7,600	23,000	1,050	56,100
Octa-BDE (OBDPO)	1,500	610	1,500	180	3,790
Penta-BDE (PBDPO)	7,100	150	150	100	7,500

Based on 2001 BFR market demand (BSEF 2003)

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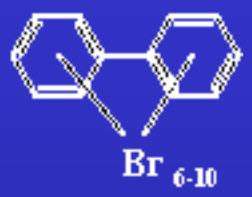
BFR Content of Polymer

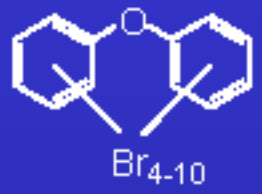
(from Arias 2001)

Polymer	BFR Content (%)	Type of BFR	Annual Production 1000 TPA
Polystyrene Foam	**0.8**-4	HBCD	600
High Impact Polystyrene	11-15	d-PBDE, Br PS	350
Epoxy Resin	19-33	TBBPA	300
Polyamides	13-16	d-PBDE, Br PS	200
Polyolefins	5-8	d-PBDE, DBS	200
Polyurethanes	10-18	p-PBDE, Br Polyols	150
Polyterephthalate	8-11	Br PS, der-TBBPA	150
Unsaturated Polyesters	13-**28**	TBBPA	150
Polycarbonate	4-6	Br PS, der-TBBPA	100
Styrene Copolymers	12-15	o-PBDE, Br PS	50

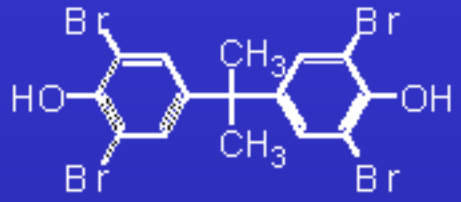
Overview:



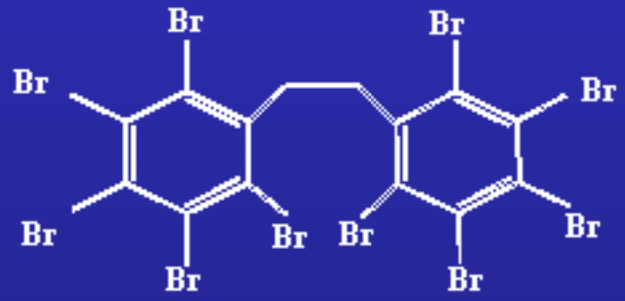
PBBs
11,885
US Production
(1970-1976)



PBDEs

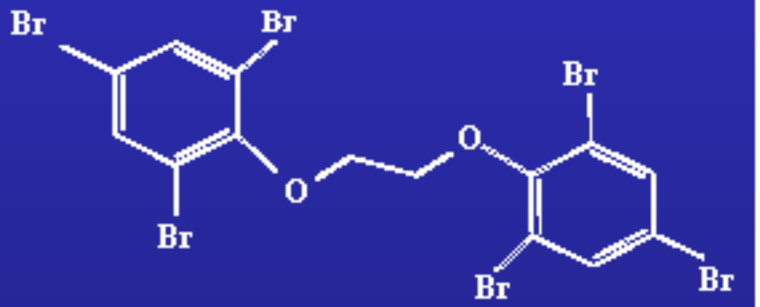


TBBPA



DBDPE

PBT/PBE
R=CH_3 or C_2H_5



TBE

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Overview:

α-HBCD

β-HBCD

γ-HBCD

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BACKGROUND:

- PBBs were introduced in early 1970's as flame retardants. Between 1970 and 1976, 11 885 m-tonnes of PBBs were produced in the US. Technical DeBB was in production in Europe till 2000.
- In 1981, Anderson and Blomkvist reported the presence of PBDEs in samples collected along Viskan River in Sweden.
- In 1987 Jansson and his colleagues first indicated that PBDEs are global contaminants by demonstrating their presence in fish eating birds and marine mammals in samples collected from Baltic Sea, North Sea and Arctic Ocean.
- In 1987 Watanabe and his colleagues detected PBDE congeners in marine fish, shellfish, and sediments from Japan; and in 1992 they reported the presence of PBDEs in air particulate from Japan and Taiwan.

BACKGROUND:

- In 1983, Stafford reported the presence of PBDEs in eggs and tissues of fish eating birds from the Great Lakes Region (6 states and Ontario)
- In 1991, Kuehl and his co-workers at EPA reported 180-220 ng/g of PBDEs in blubber from bottlenose dolphin on the south Atlantic US coast
- In 1995, Kuehl and Haebler reported up to 8000 ng/g PBDEs in bottlenose dolphin from the Gulf of Mexico.
- In 1983, Watanabe and his colleagues reported occurrence of TBBPA in mussel, river and marine sediments.
- In 1998, Sellström and her colleagues reported on occurrence of HBCD in fish and sediment from Viskan River
- In 1997 Research on PBDEs was started at NWRI
- In 1999 research was expanded to included PBBs, HBCD, and TBBPA
- Continue to add more BFRs to the list of analytes
- In 2004 we began investigation into brominated ploymers

Analytical Procedures

GC/ECD

GC/ECNI/MS

GC/HRMS

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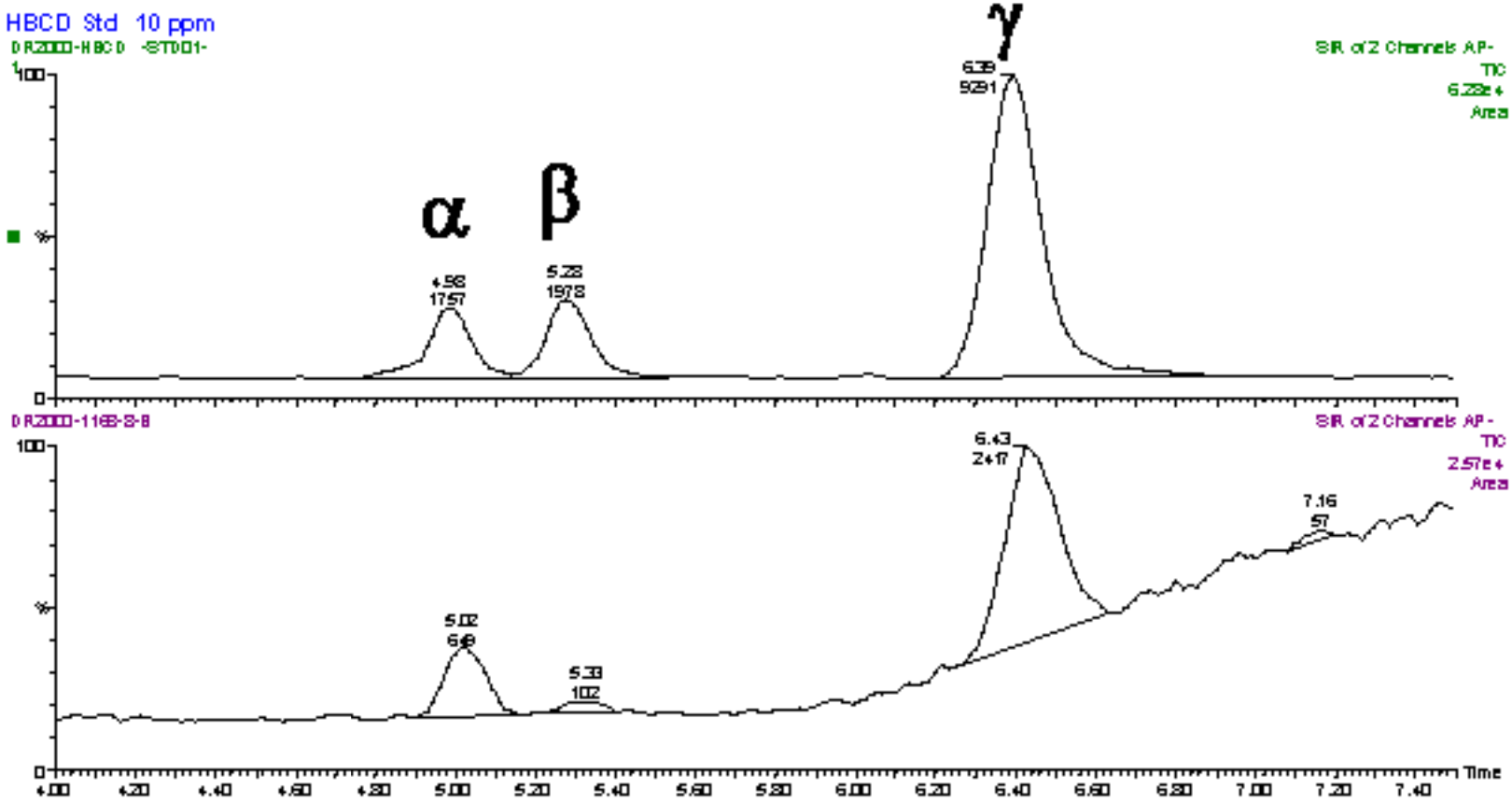
Analytical Procedures for Determination of BFRs in Environmental Matrices

- Each BFR has its own analytical requirements
  - TBBPA is a phenolic compound, BDE-209 and HBCD are thermally labile
  - Isomer specific analysis for HBCD can be accomplished using LC/MS methods
- PBDEs are amenable to GC analysis
  - 209 possible congeners (<120 congeners are commercially available)
  - co-elution between various congeners
- GC-ECD
  - the simplest and least selective detector used in determination of PBDEs
  - requires careful sample preparation
  - potential interference from PCBs and other organohalogen contaminants (BDE-47 & CB-180)
- CG-ECNI/MS (ISO method)
  - monitors bromine anion formed by dissociative capture
  - more selective than ECD, but susceptible to interferences from organobromine compounds such as Pentabromo Toluene with BDE-28, BB-153 with BDE-154, and BDE-153with TBBPA
- CG/HRMS
  - most selective technique (US-EPA Method 1614)
  - Susceptible to interferences from native and ^{13}C enriched PCBs

Negative APCI-LC-MS chromatograms showing a comparison of an HBCD technical mixture at 10 ppm and a suspended sediment sample from the Detroit River



From MacInnis et al. 2003

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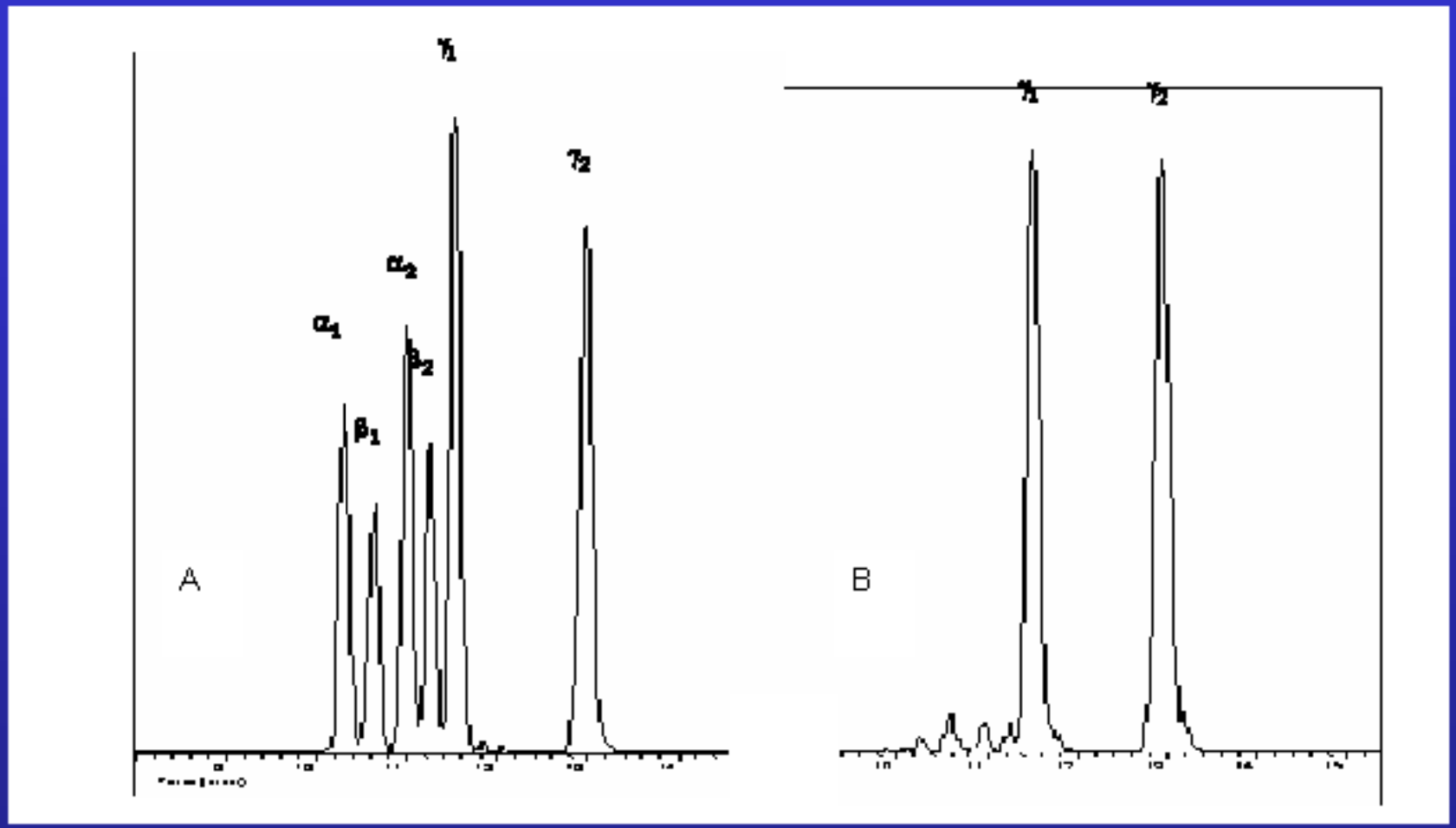
Chiral Separation of HBCD



From Janák et al. 2004
A) Standard, B) Commercial Product

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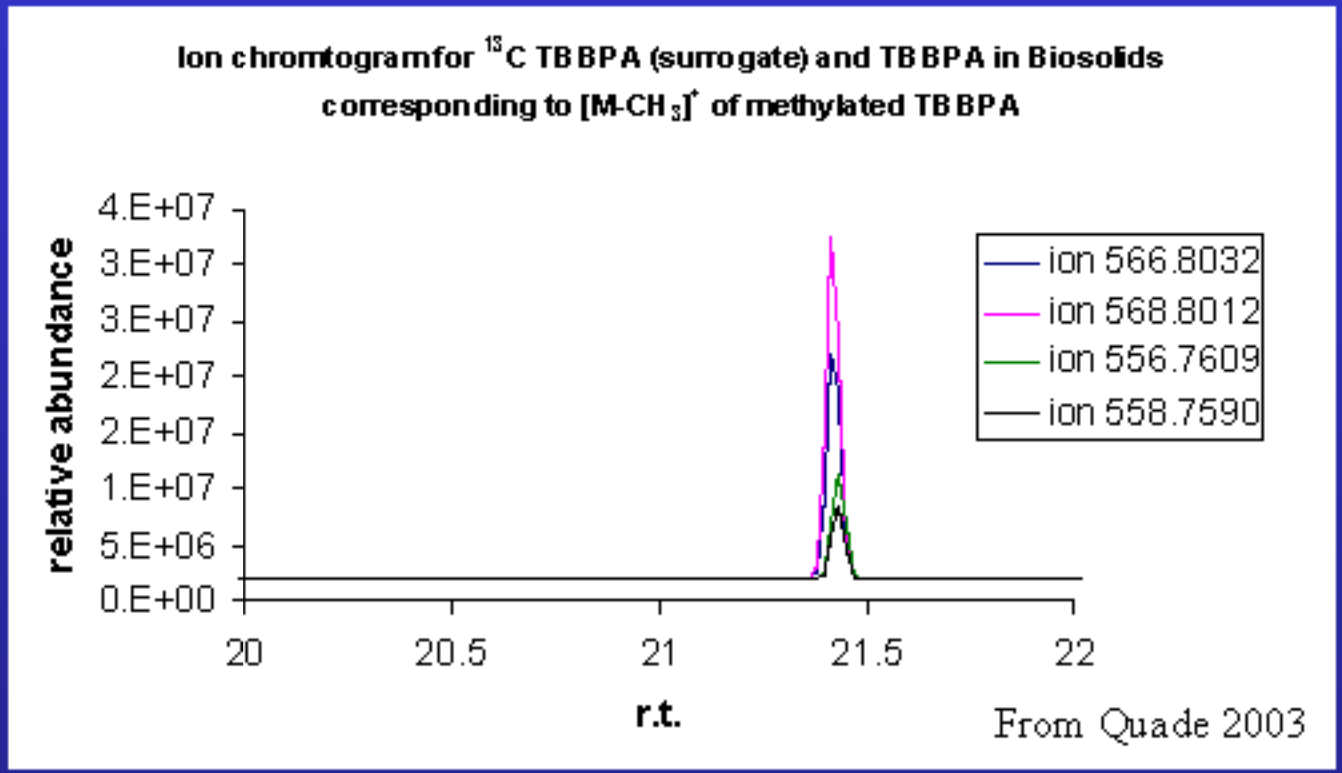
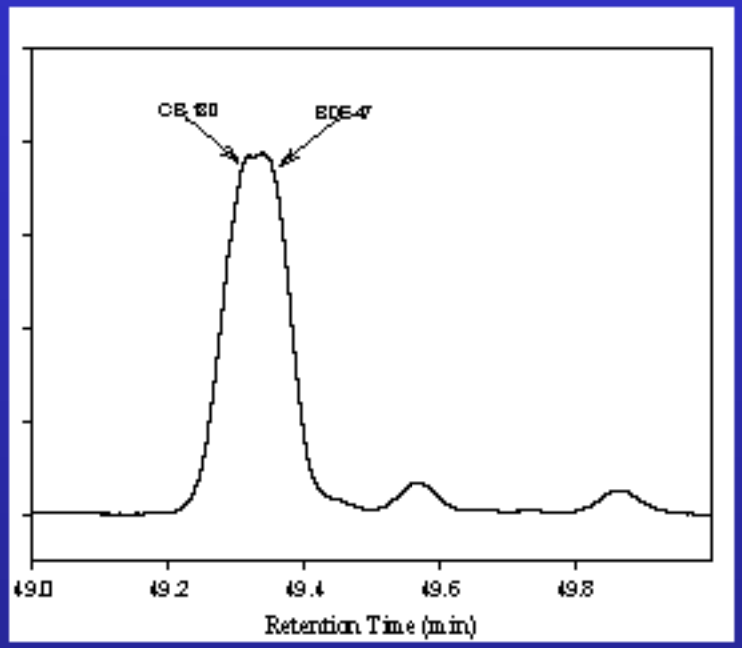
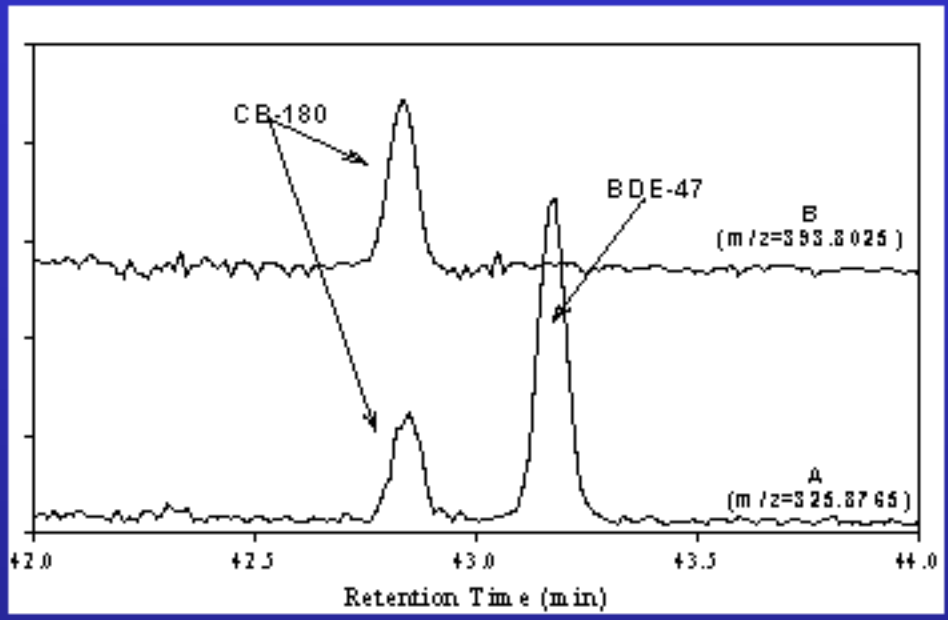
TBBPA in Biosolids



Potential Interference of CB-180 on determination of BDE-47

Co-elution between BDE47 and CB 180 on 30m 5% Phenyl Column





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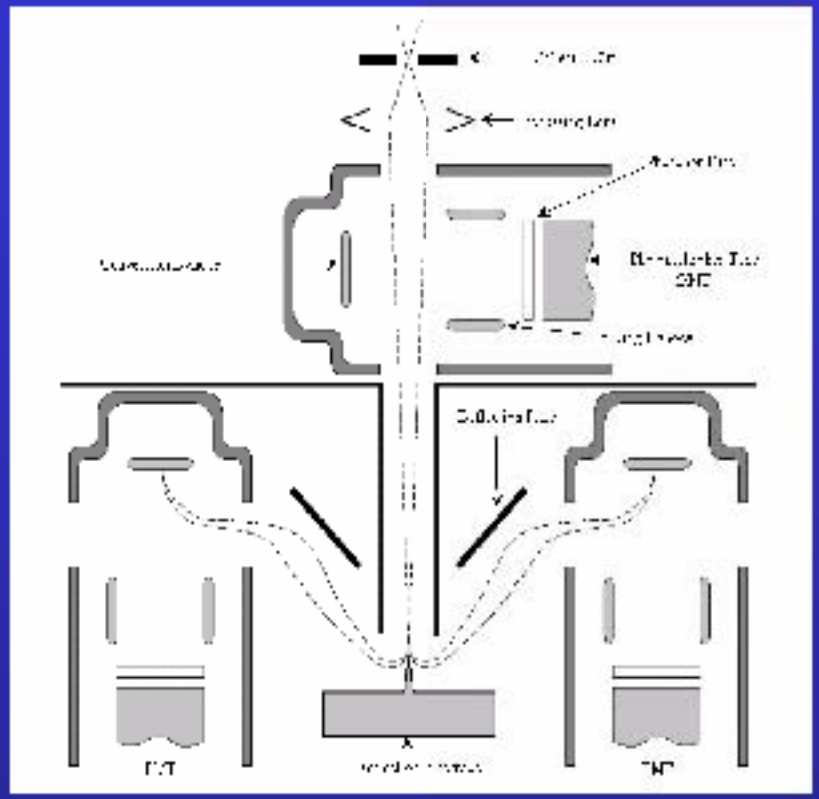
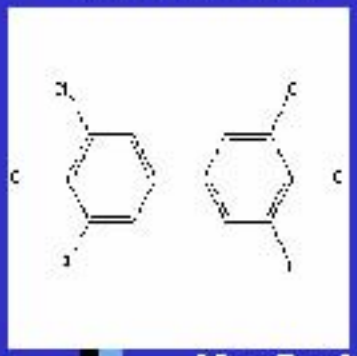
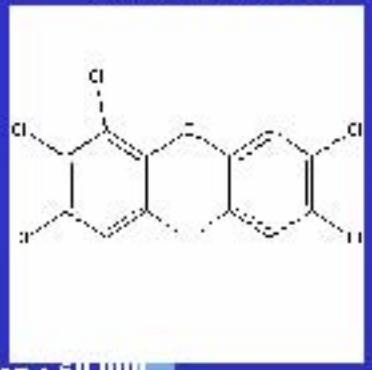


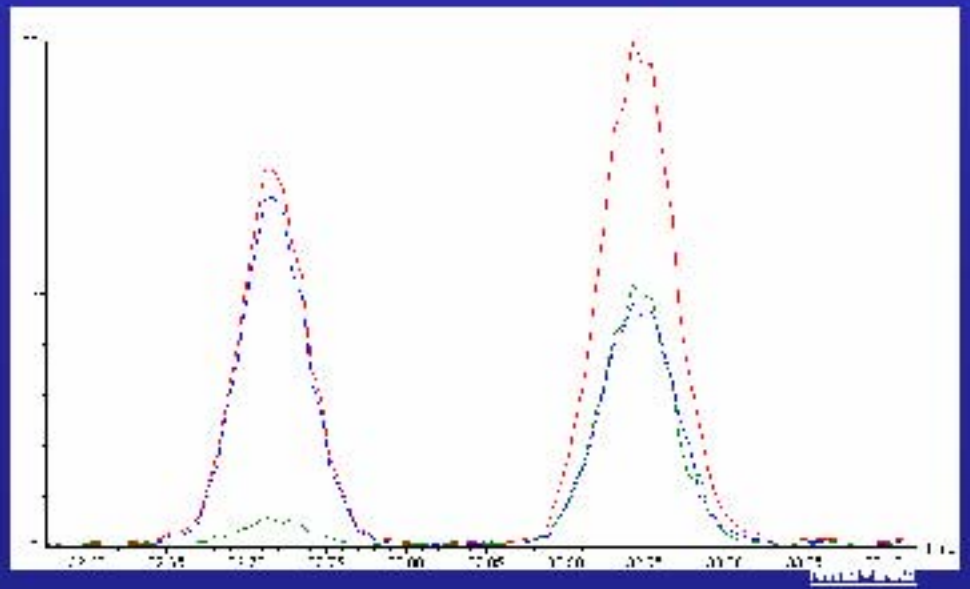
PCB169
Mass 357.8444 Da



1,2,3,7,8-PeCDD
Mass 357.8517 Da



Mass Resolution >50 000



From Worrall et al. 2005

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OH-PBDEs
Analytical Challenges

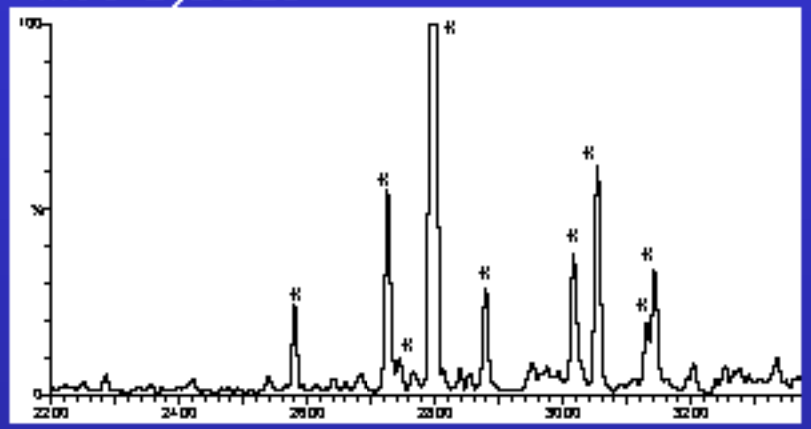
837 possible congeners
limited number of congeners available
18 congeners were identified in our studies

Representative GC-HRMS Chromatograms of OH-PBDEs

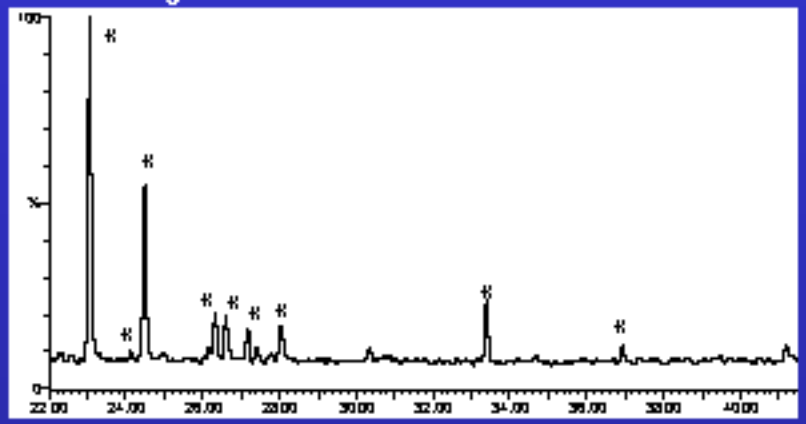
Water sample (Hamilton Harbor, Lake Ontario)

Quantification of un-identified OH-PBDEs is necessary.

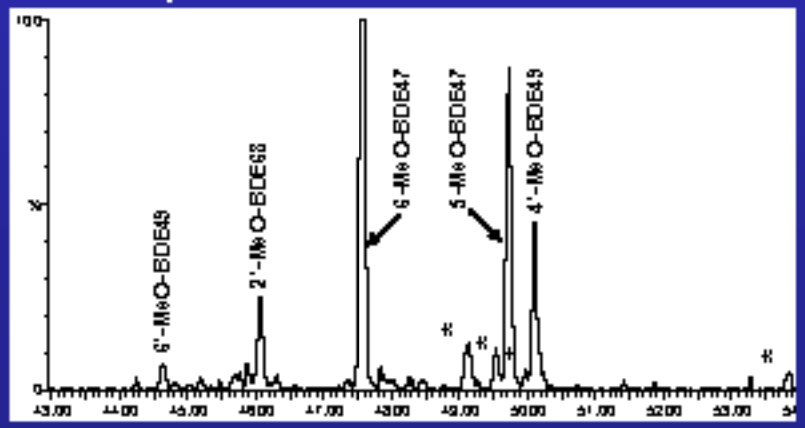
MeO-D_2BDEs



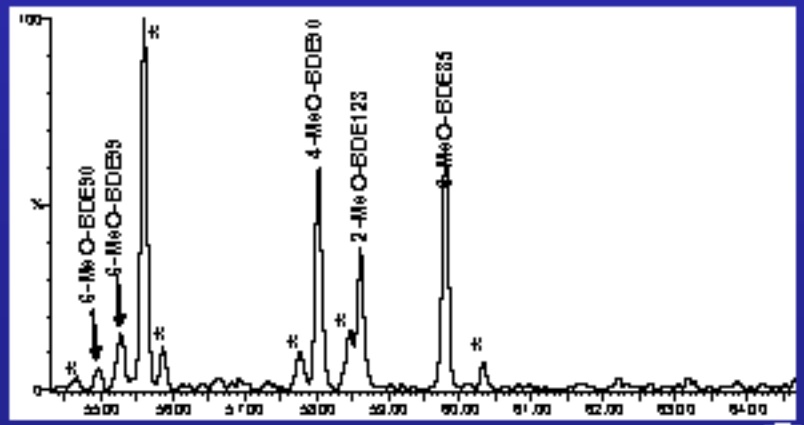
MeO-T_3BDEs



MeO-T_4BDEs



MeO-P_5BDEs



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*: un-identified OH-PBDE

From Ueno et al. 2005

Environmental Levels

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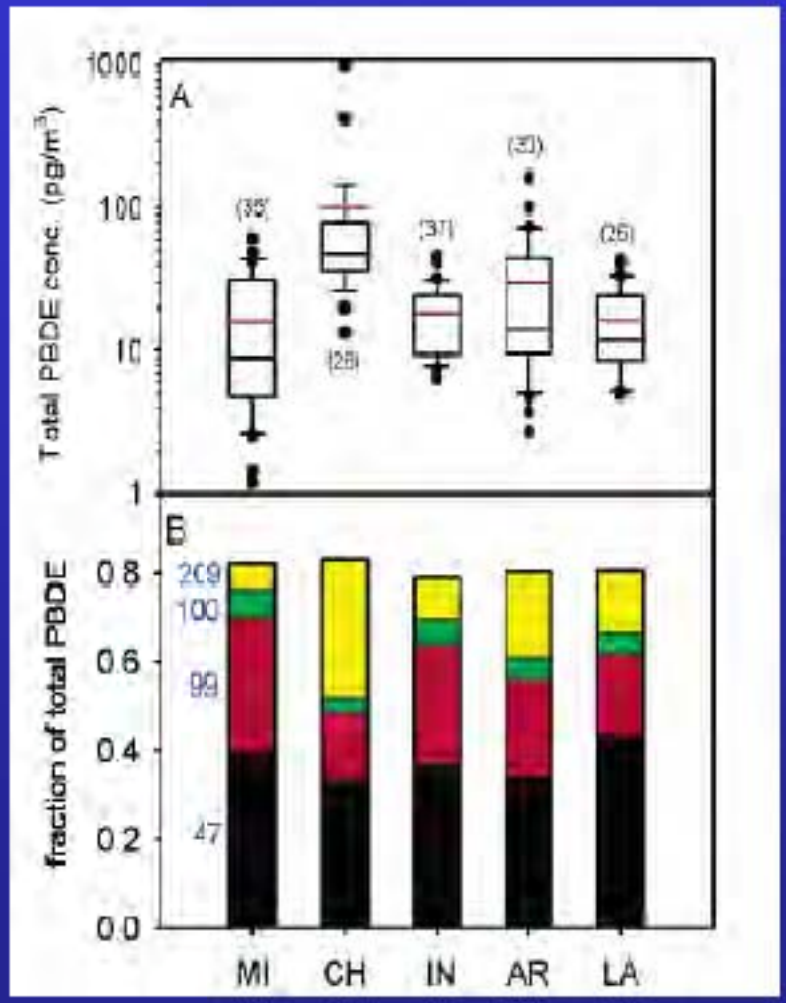
PBDEs in Air Samples from USA



MI: Lake Michigan
CH: Chicago
IN: Indiana (IU)
AR: Arkansas
LA: Louisiana
From Hoh and Hites 2005

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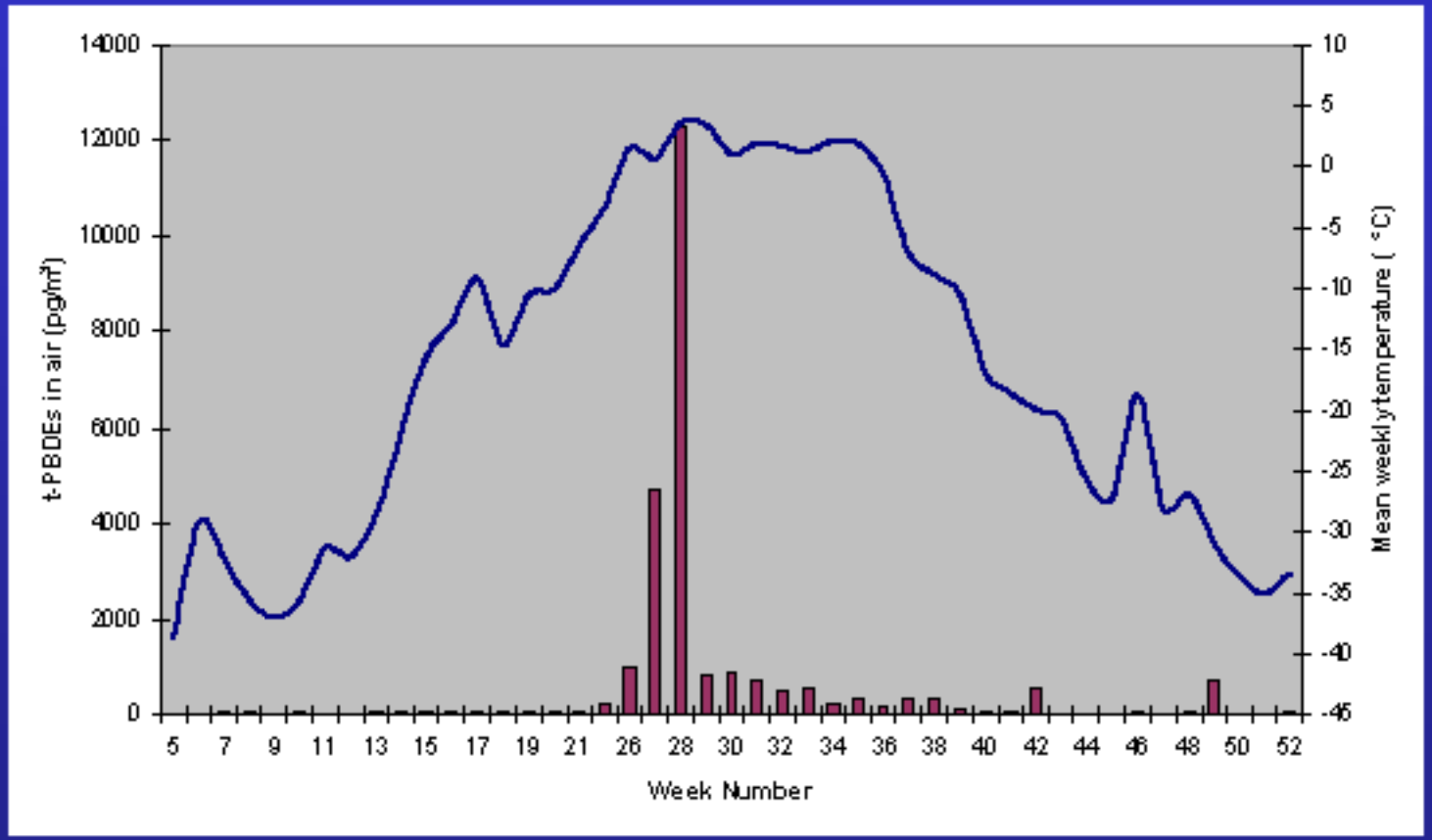
PBDE in Archived Air Samples from Alert in 1995



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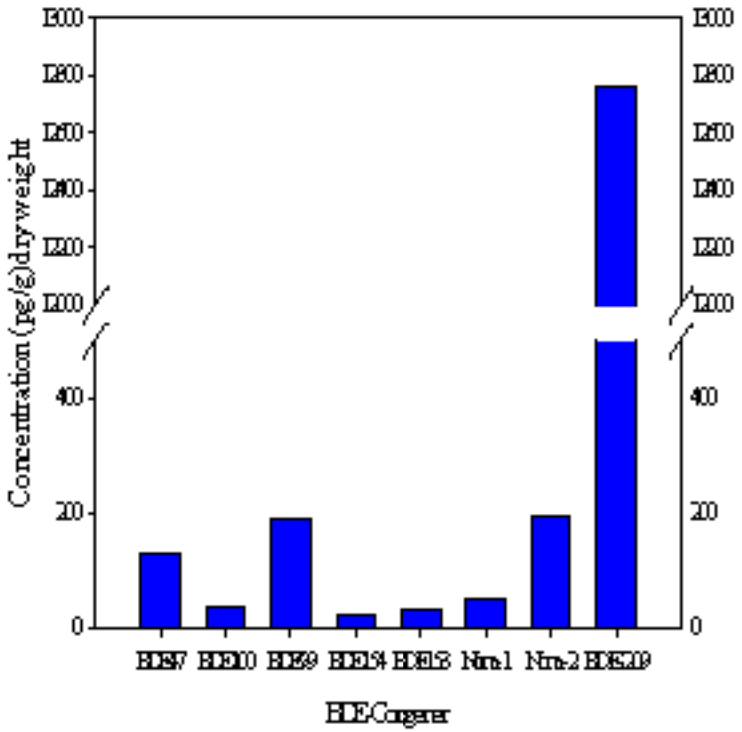
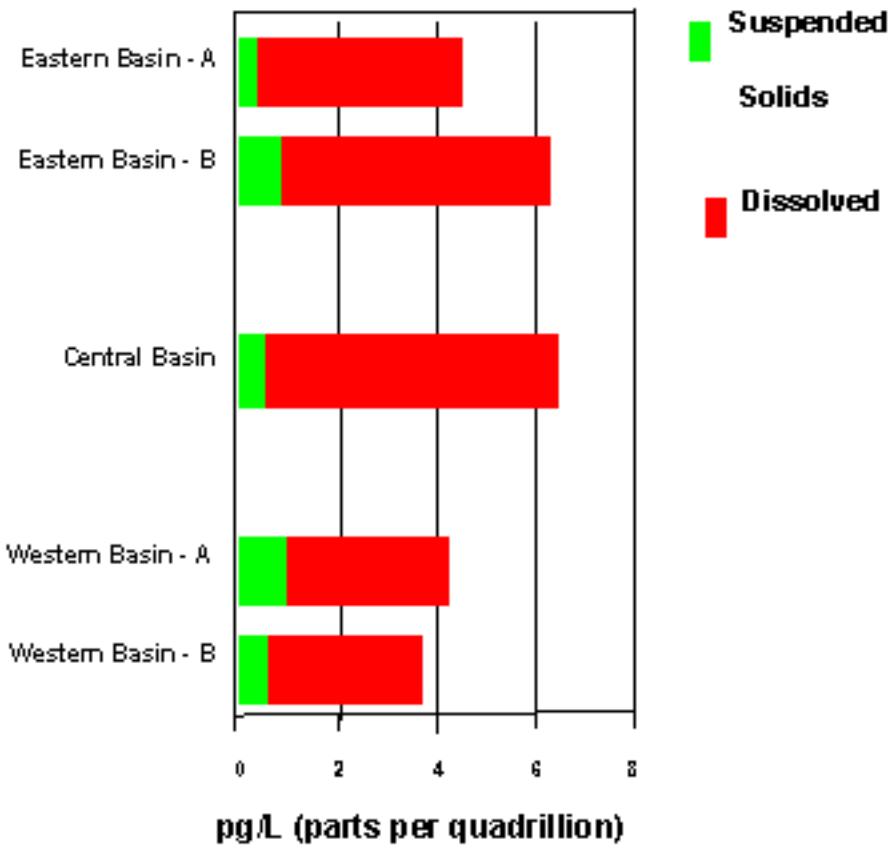
PBDEs in Lake Ontario Water and Sediment





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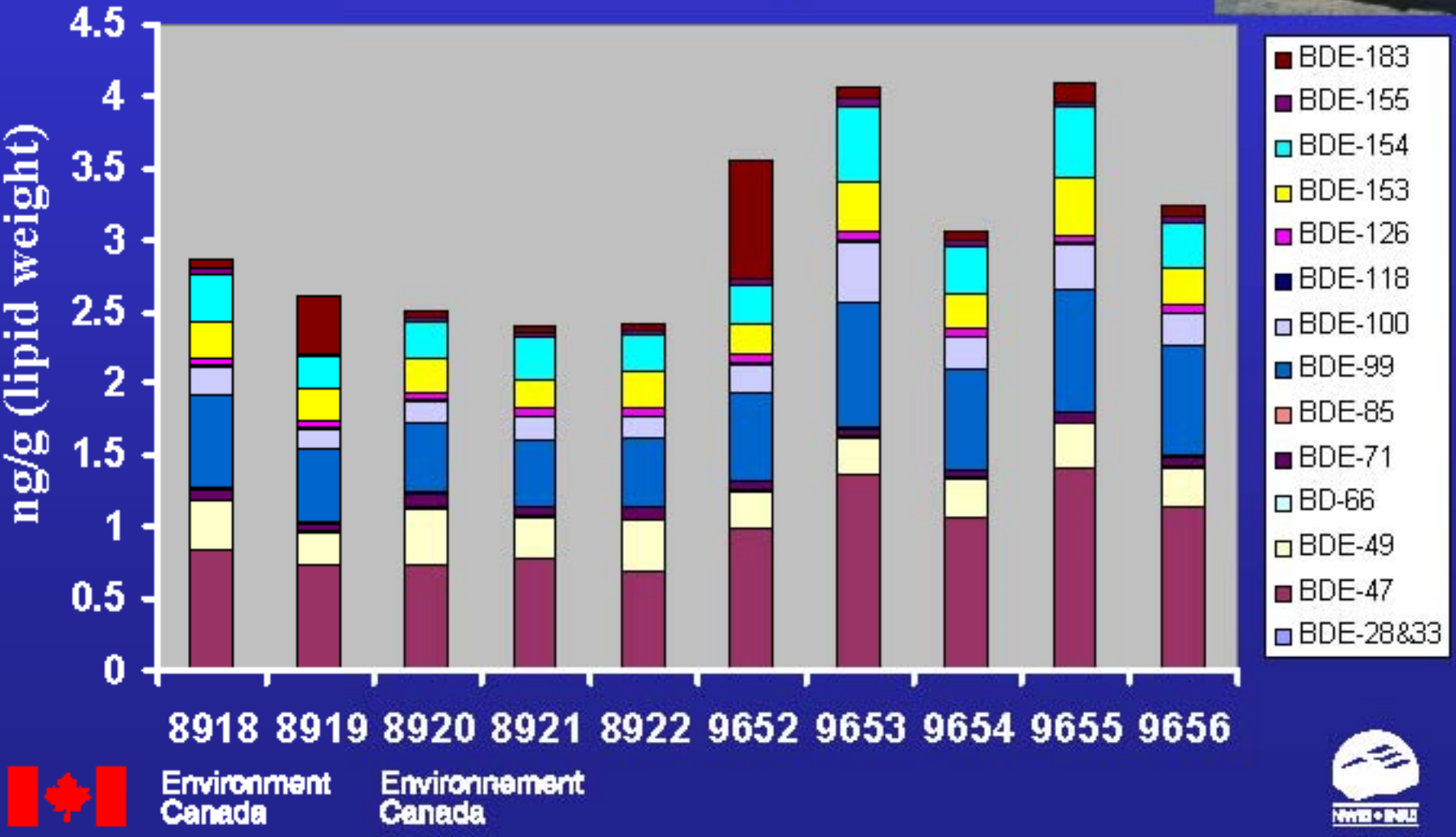
Water results from Luckey *et al.* 2001

Tri-Hepta BDE in Fulmer Eggs from Cape Vera & Prince Leopold Island



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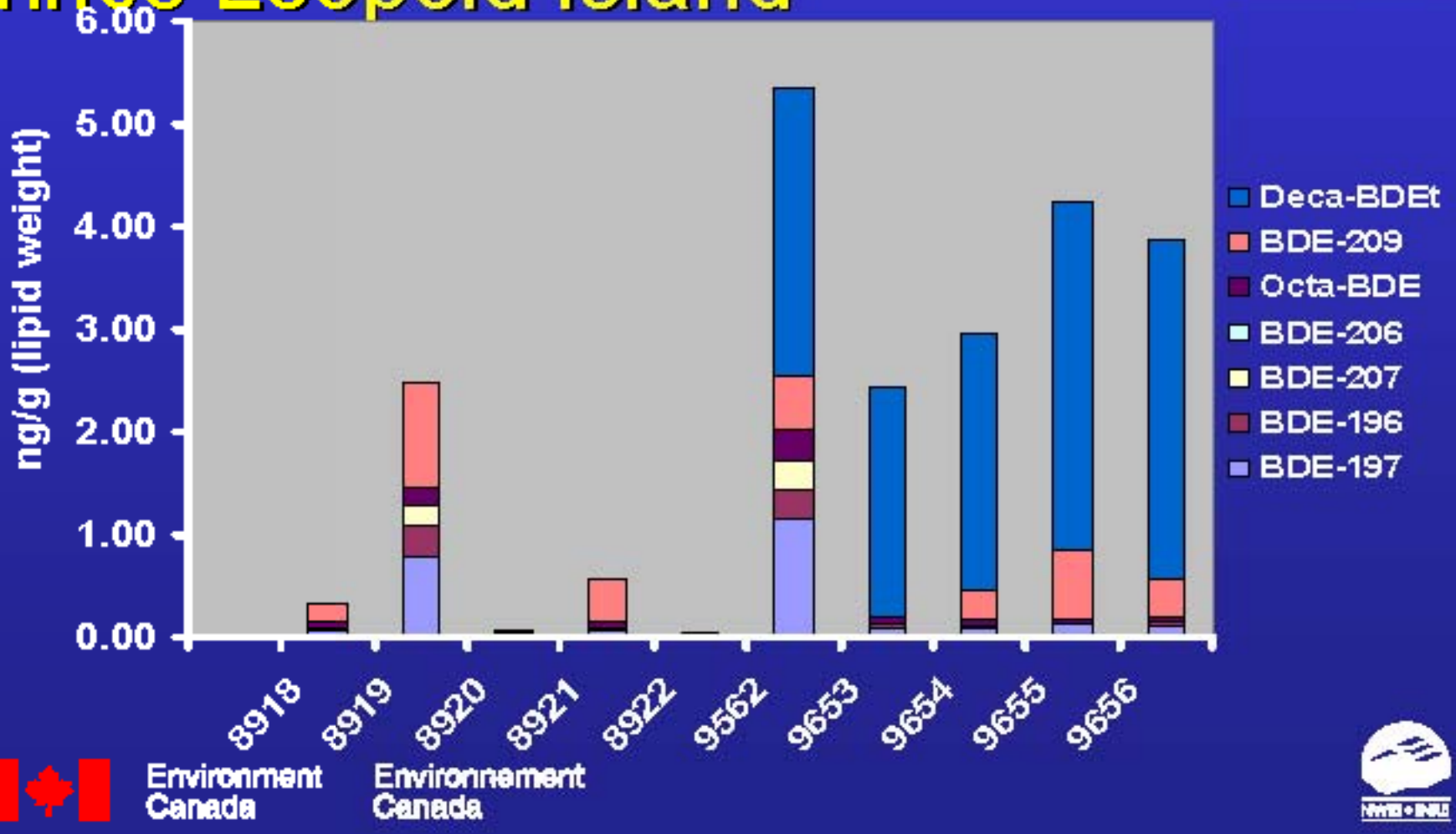
Octa-Deca BDE &Deca-BDEt in Fulmer Eggs from Cape Vera & Prince Leopold Island



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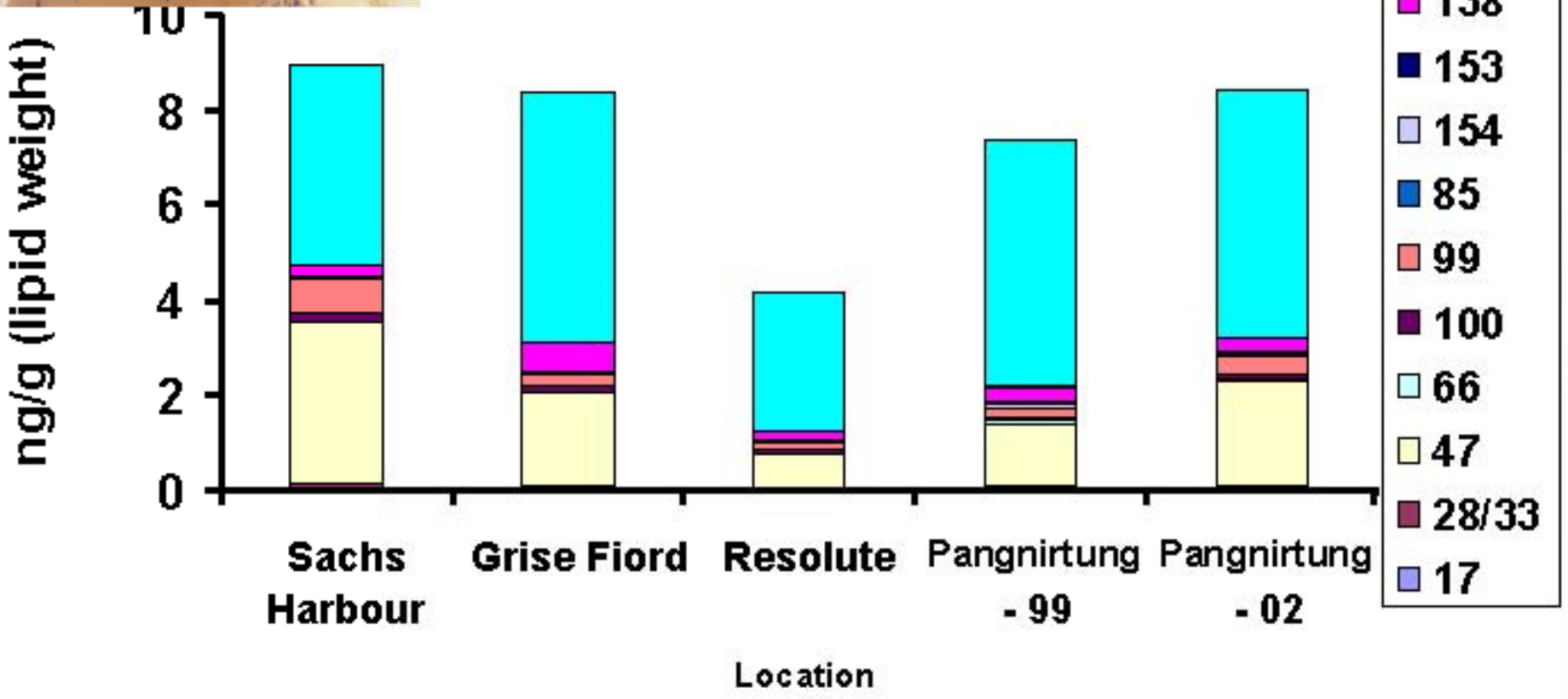
Brominated Flame Retardants in Ringed Seals



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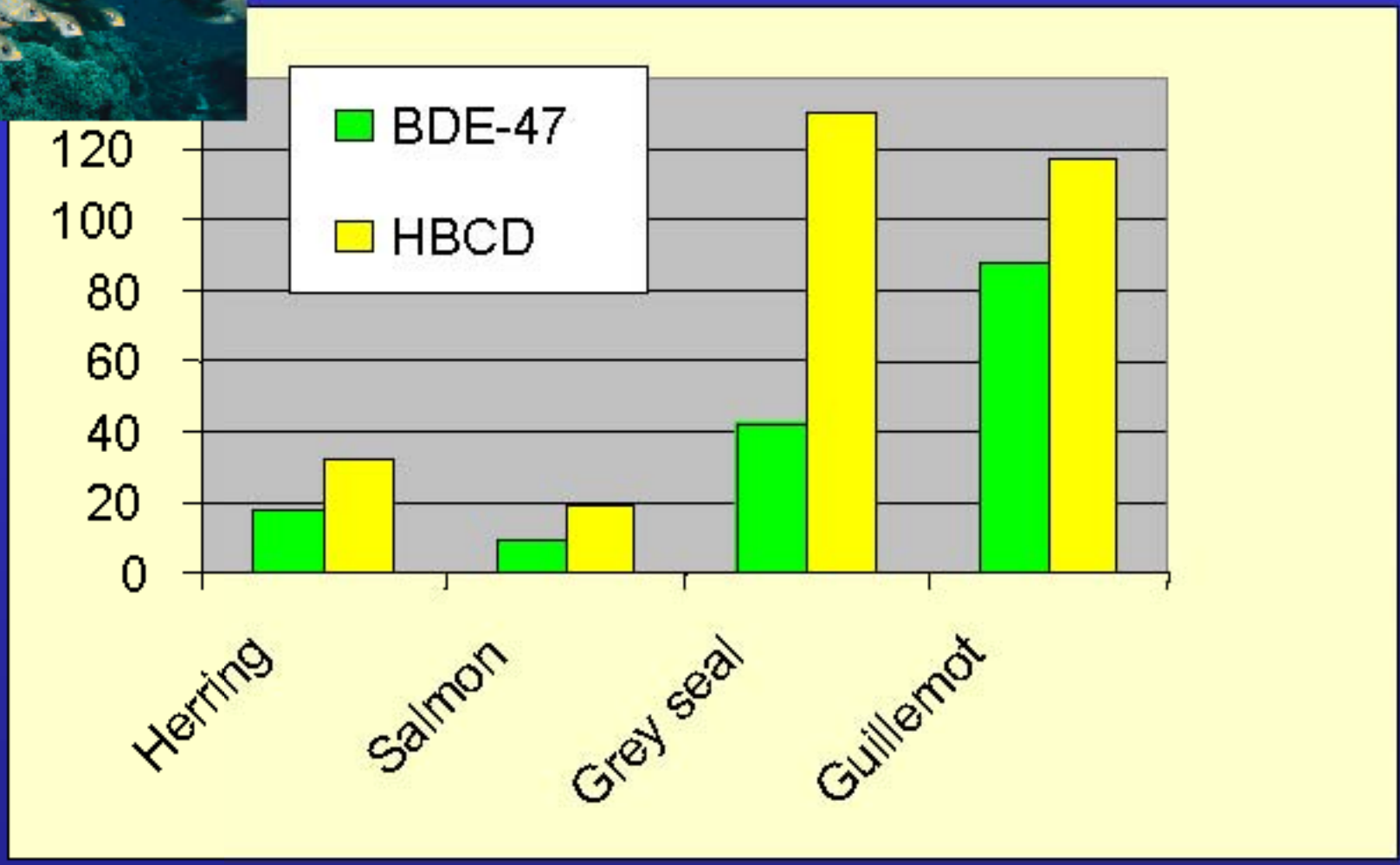
Species from the Baltic Sea



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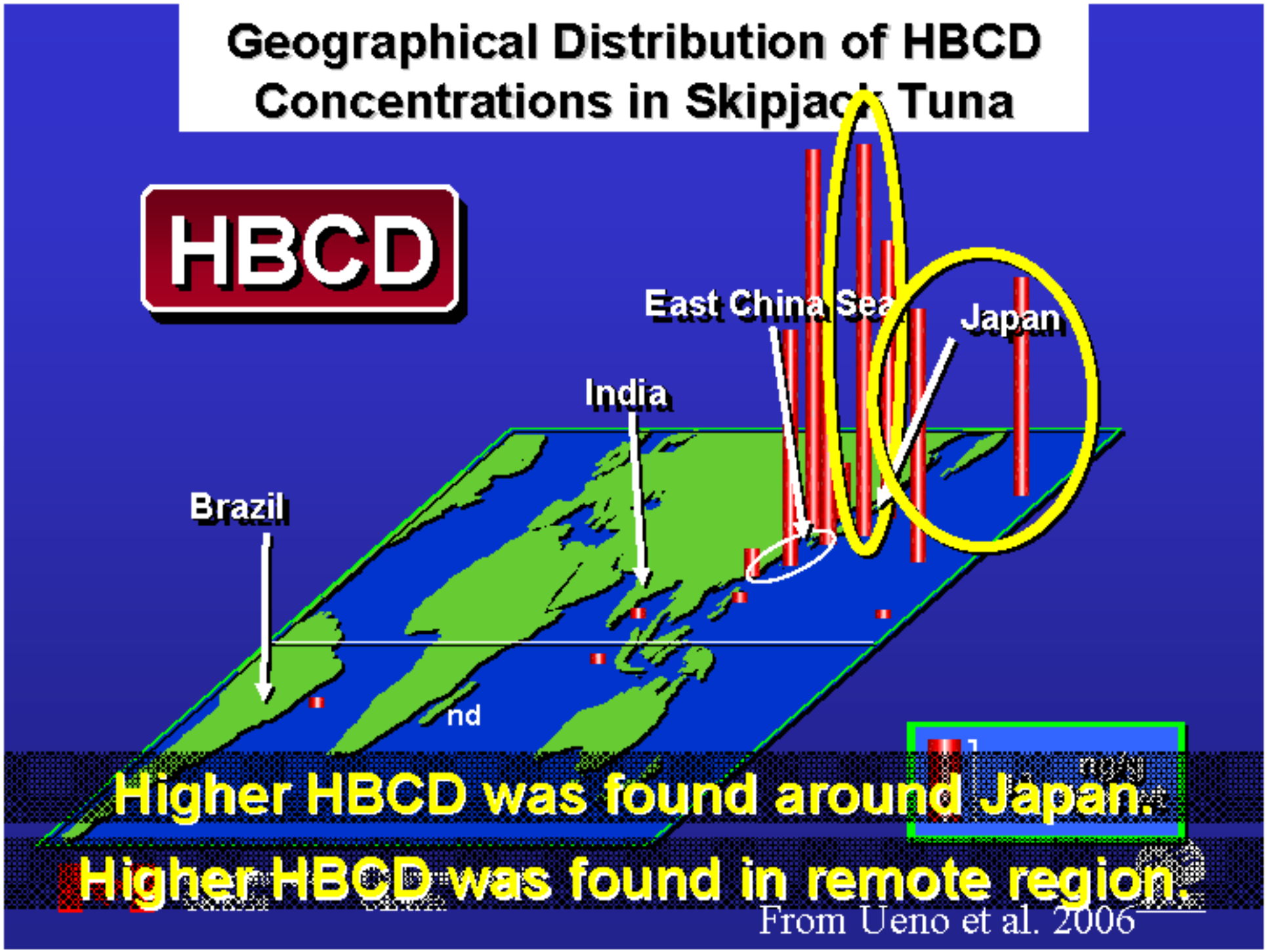
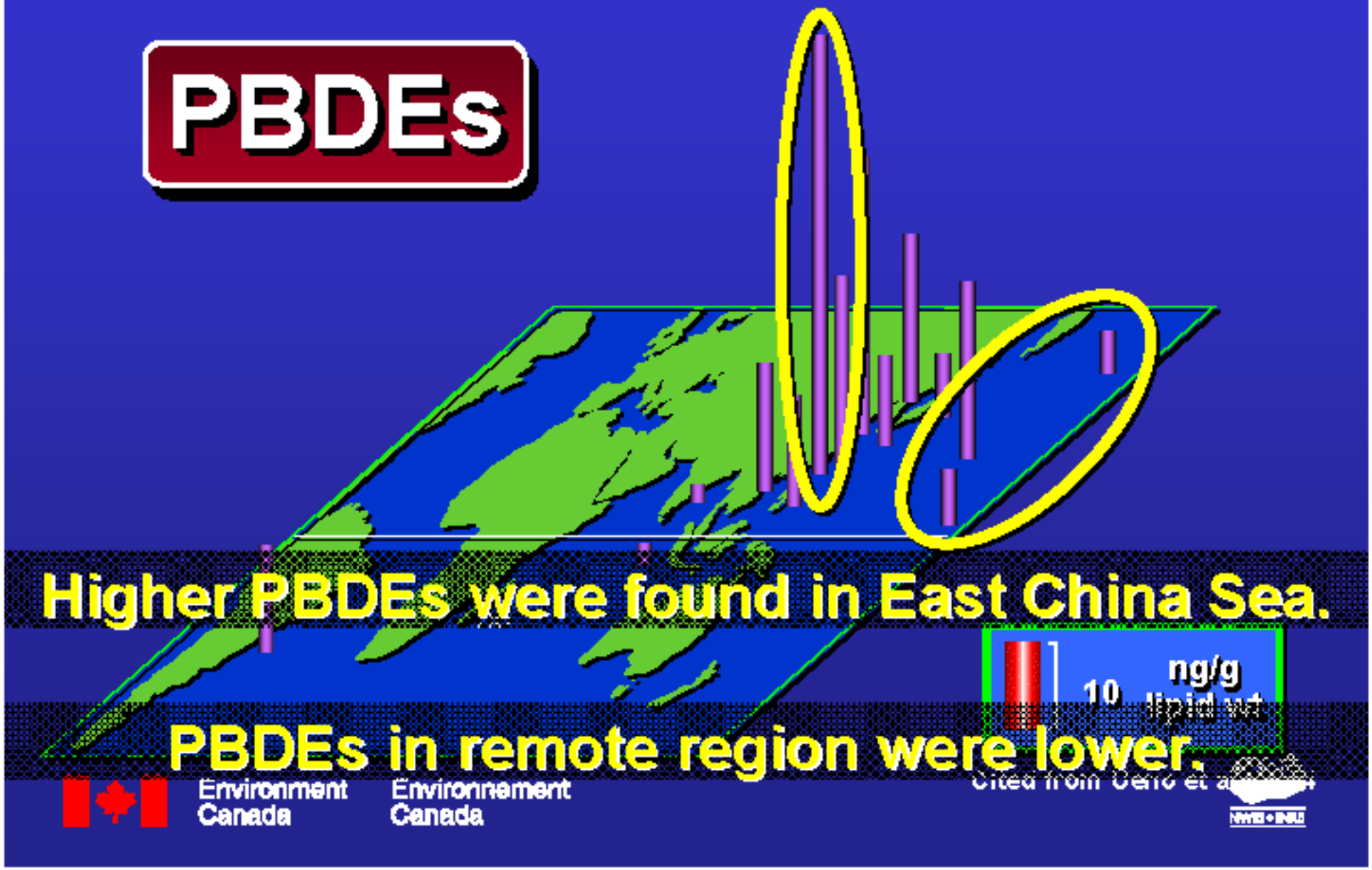
Athanasiadou, Thesis 2003

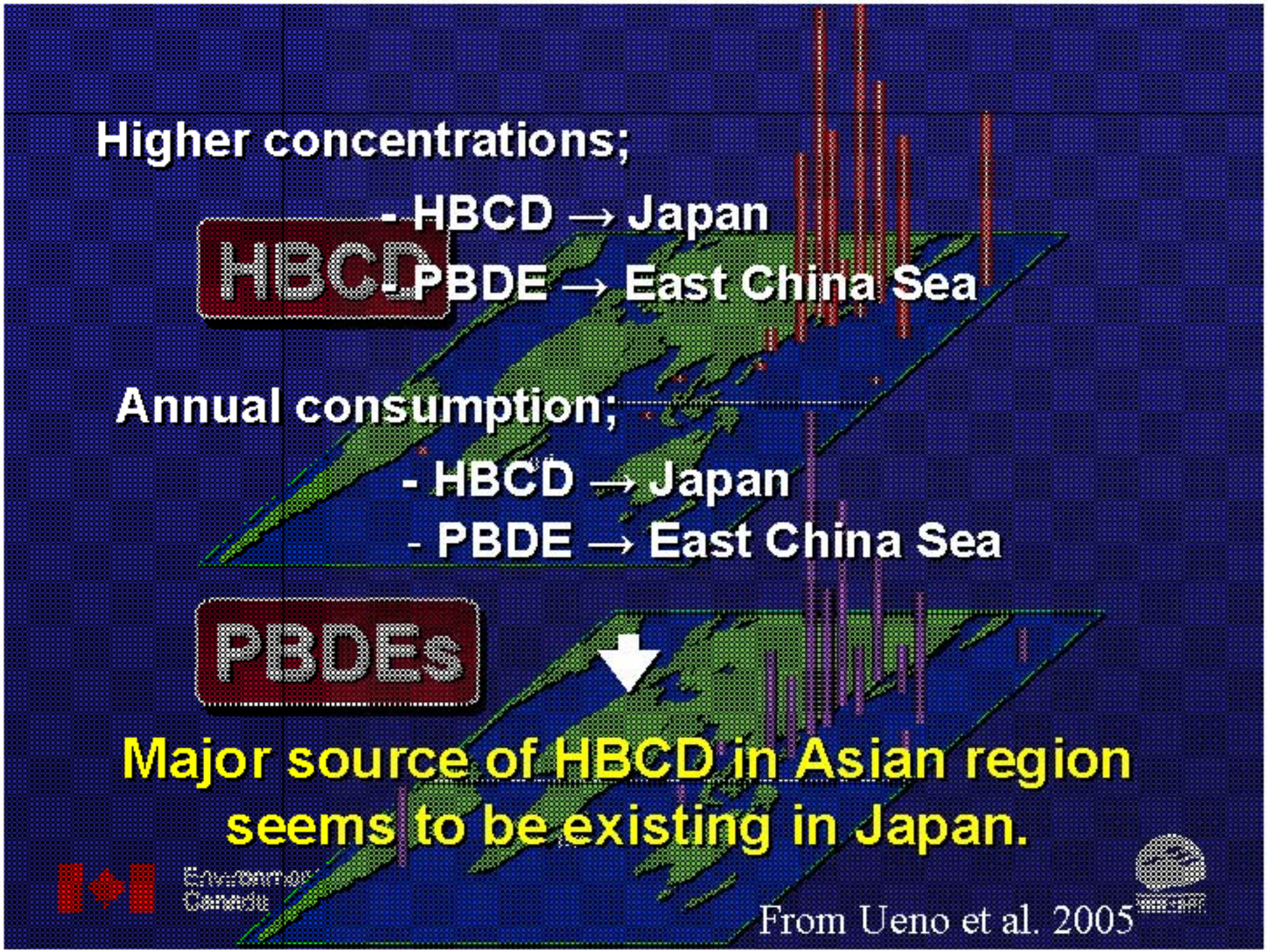
Geographical Distribution of HBCD Concentrations in Skipjack Tuna



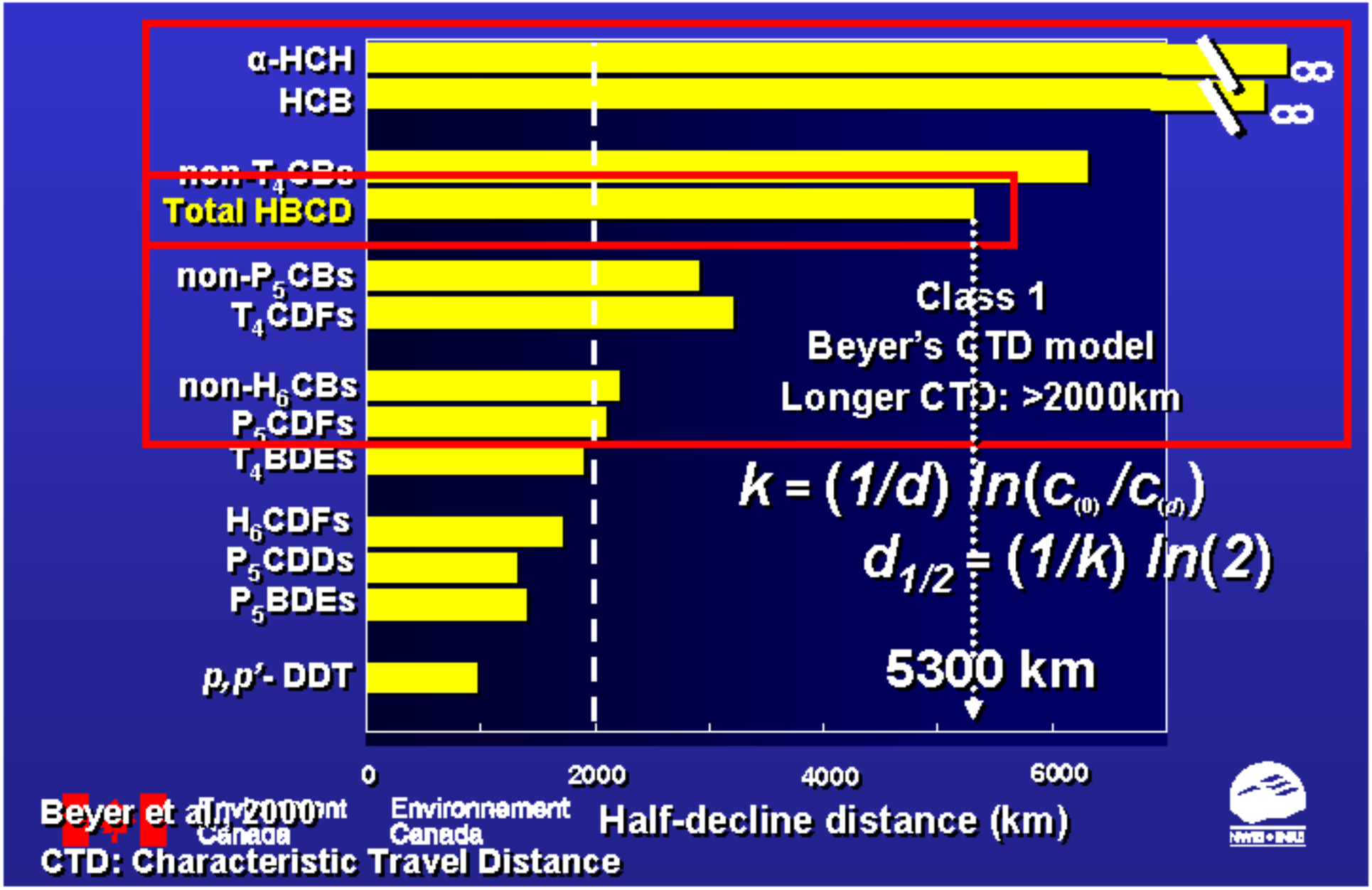
From Ueno et al. 2006

Geographical Distribution of PBDEs Concentrations in Skipjack Tuna




Higher concentrations;
- HBCD → Japan
- PBDE → East China Sea
HBCD
Annual consumption;
- HBCD → Japan
- PBDE → East China Sea
PBDEs
Major source of HBCD in Asian region seems to be existing in Japan.
Environment Canada
From Ueno et al. 2005

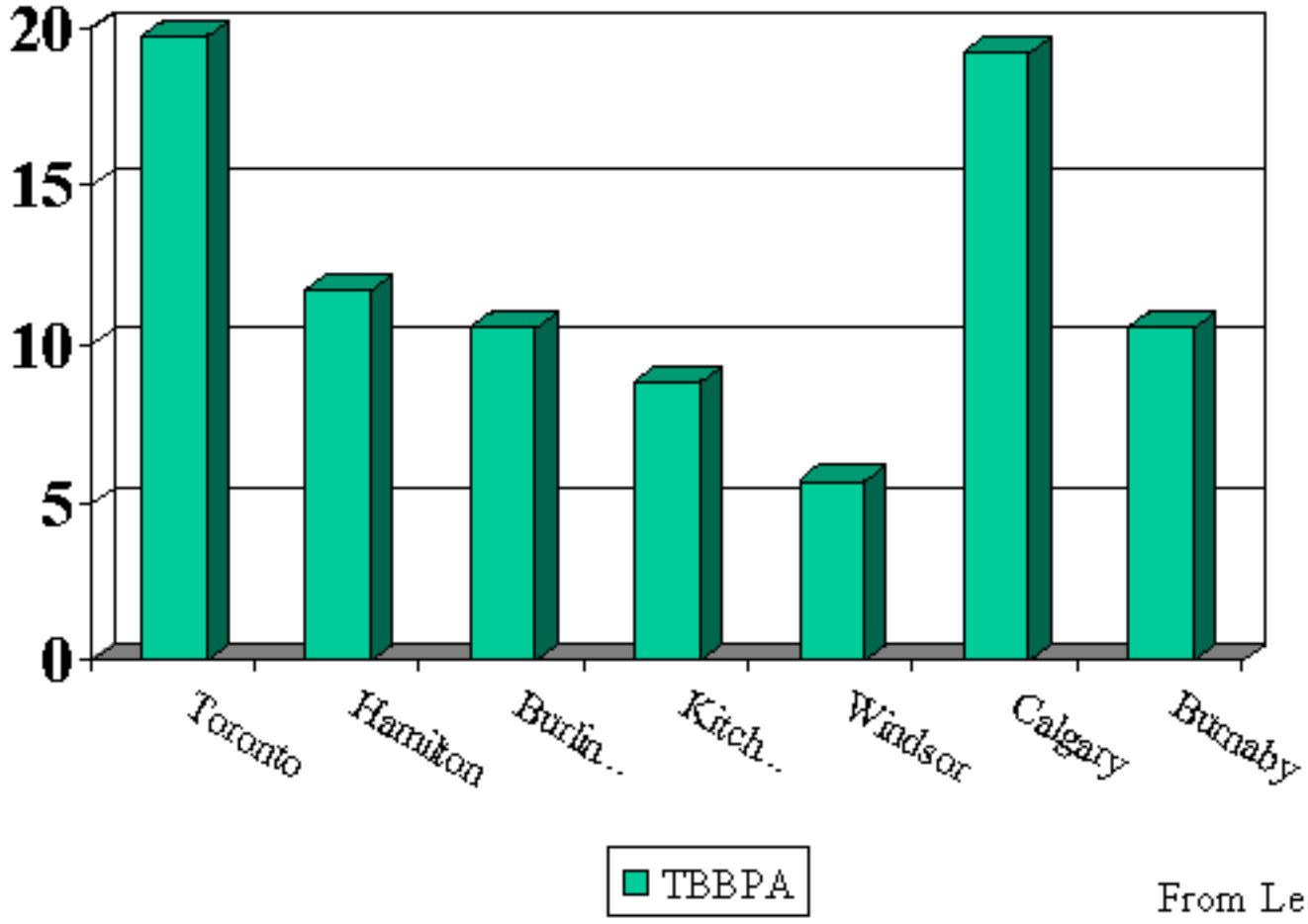
Empirical Half-Decline Distances ($d_{1/2}$) Calculated from HBCD and Other Organohalogen Concentrations in Skipjack Tuna



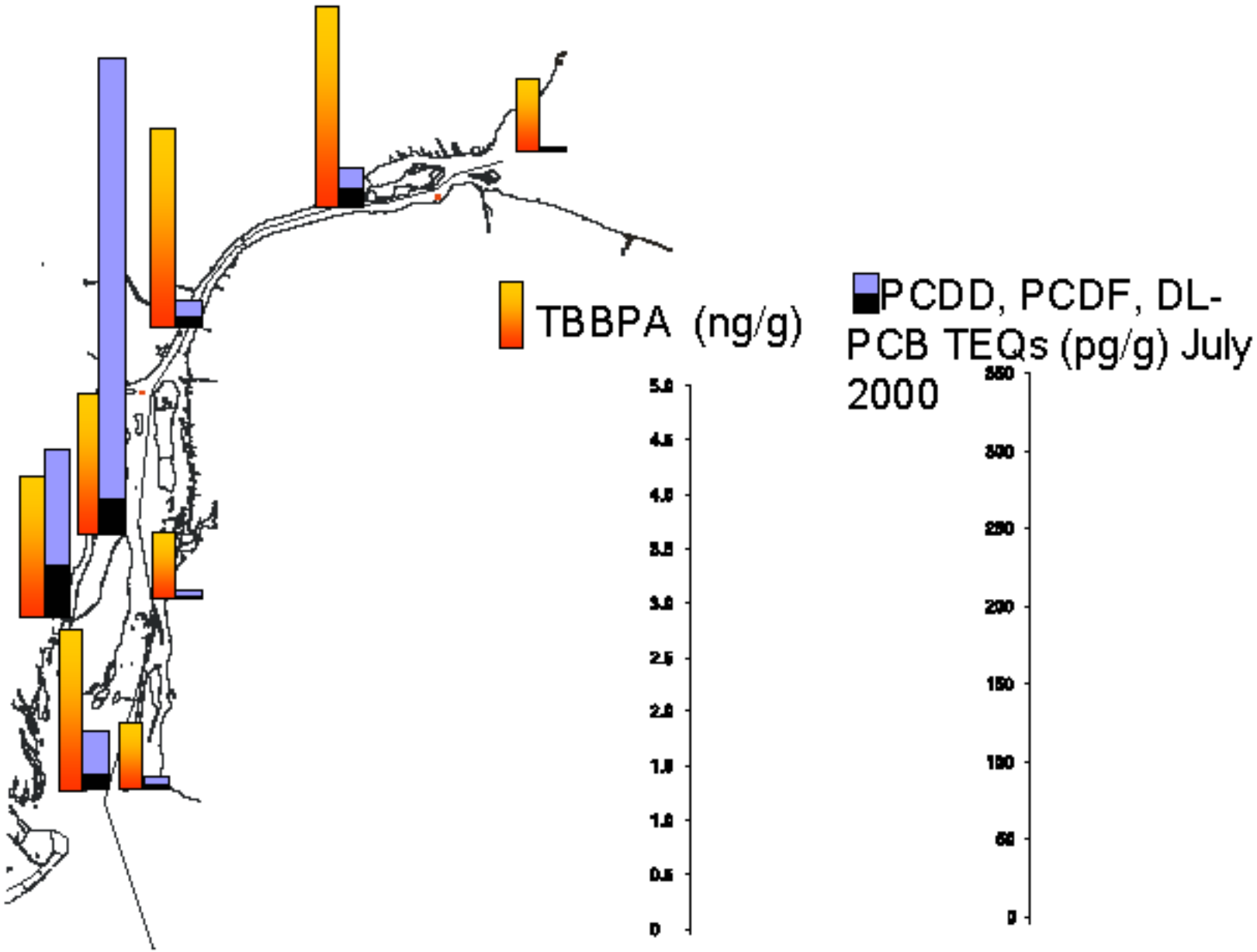
Beyer et al., 2000

CTD: Characteristic Travel Distance

Concentration of TBBPA (ng/g dry weight) in Sewage Sludge from STP across Canada



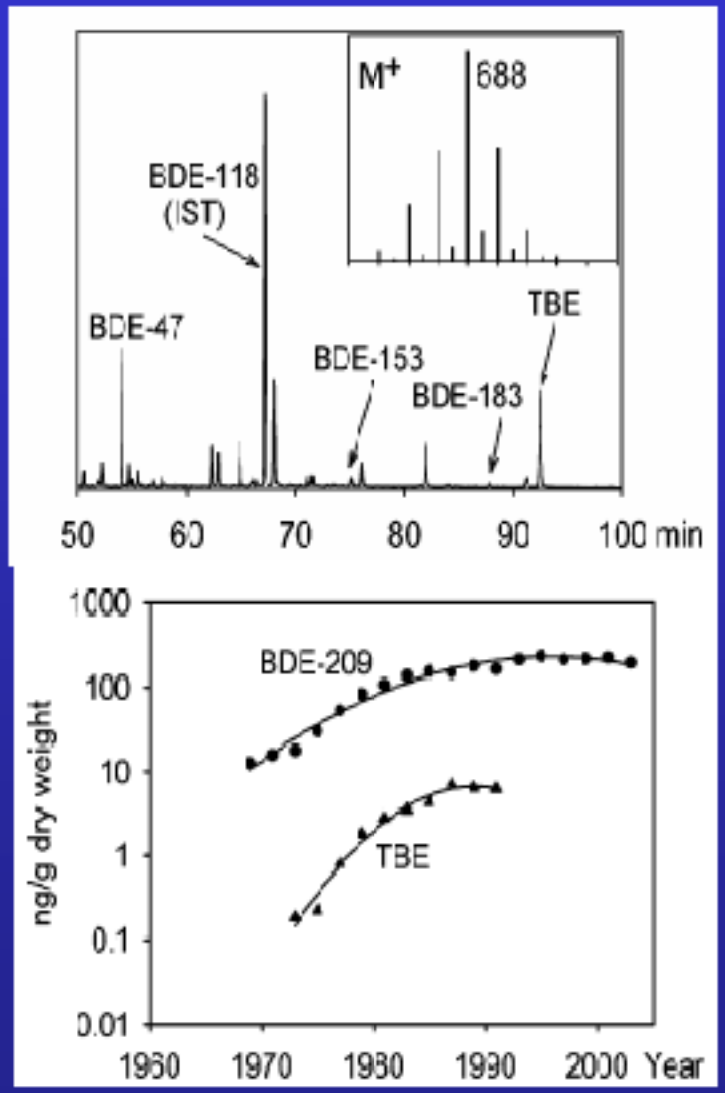
From Lee and Peart 2002



From Quade *et al.* 2003

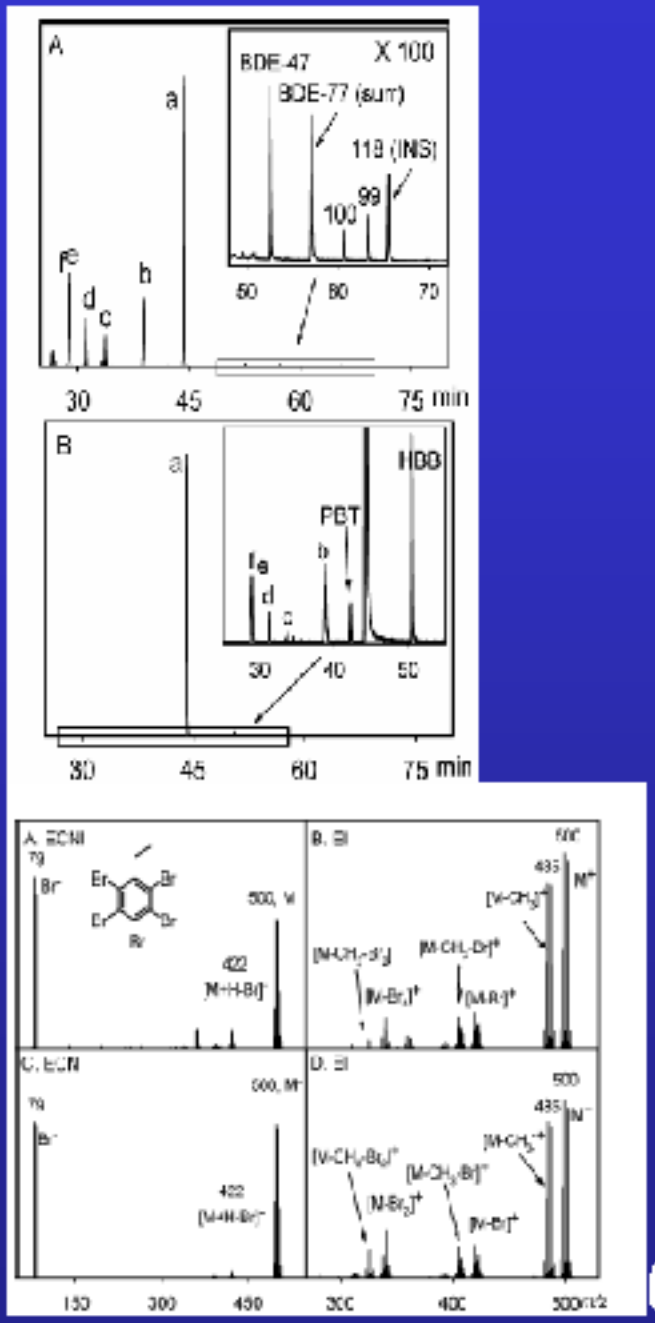
Other BFRs

TBE



Environment Canada Environnement Canada

PBT & PBE

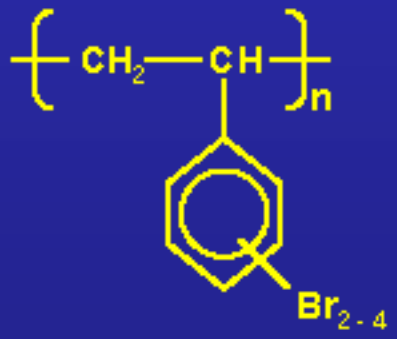


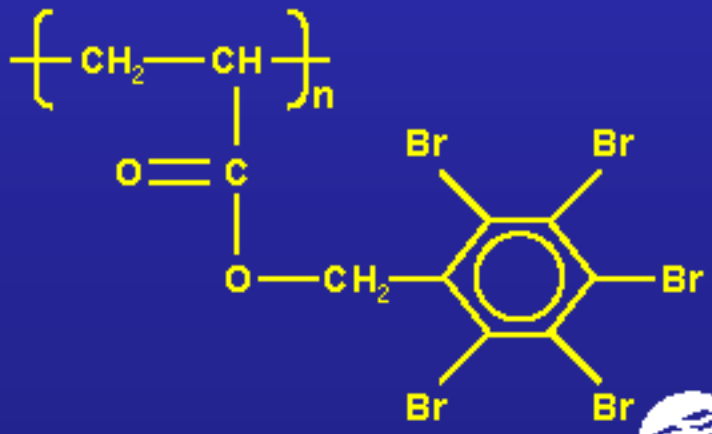
From Hoh et al. 2005

Potential Sources

polymeric BFR samples

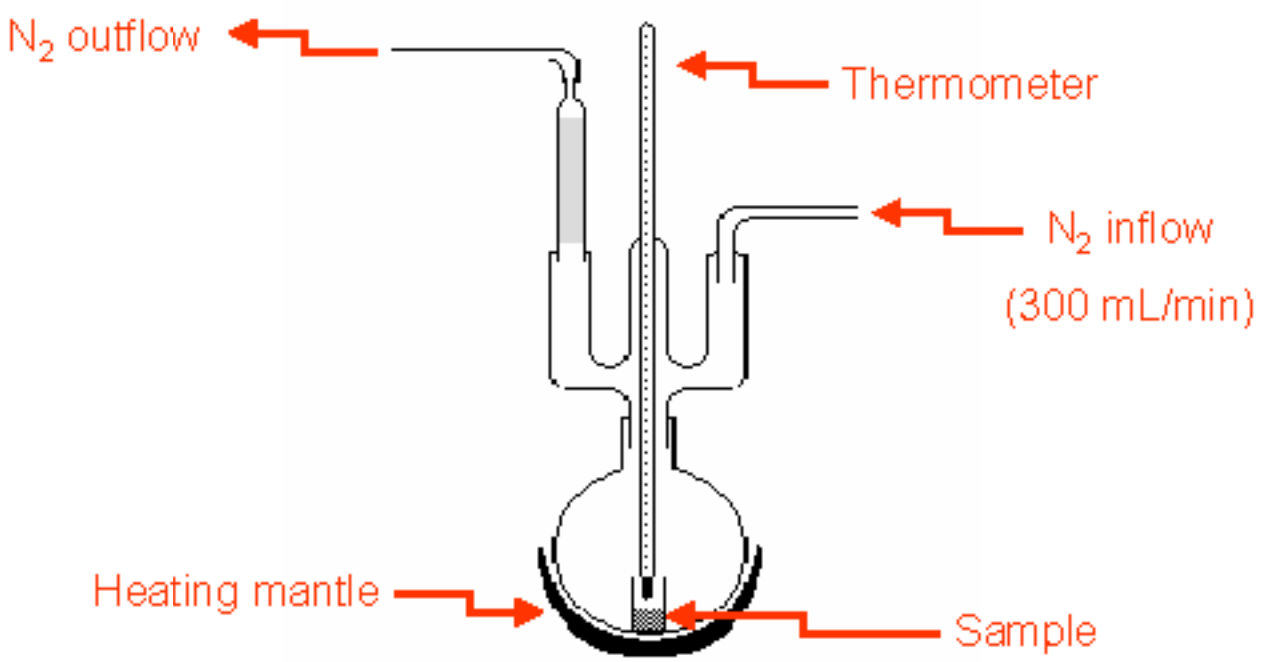
	PBS-64	PPB-BA (≈ FR-1025)
Supplier:	GLCC	Sigma-aldrich
MW:	≈ 30 000	≈ 80 000
Br:	≥ 64 %	≥ 69 %
Use:	Engineering thermo-plastics (PBT/PET)	Engineering thermo-plastics (PBT/PET)





Environment Canada Environnement Canada

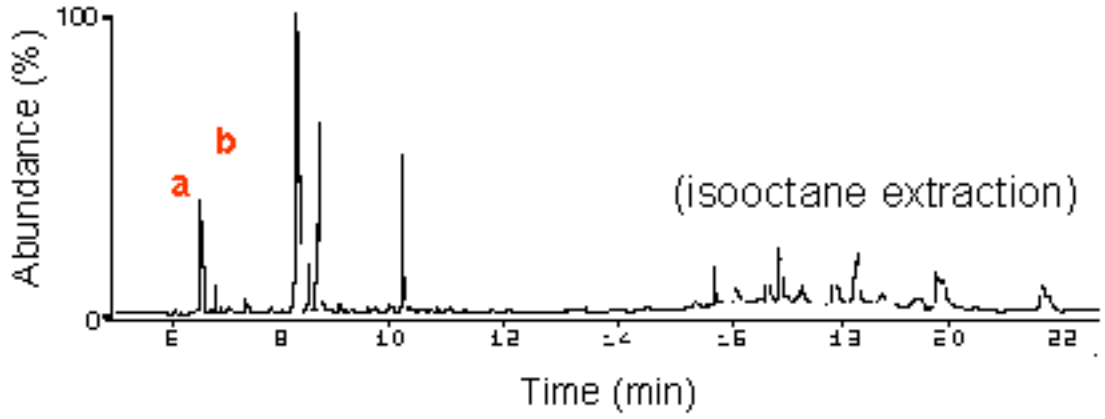
Experimental setup

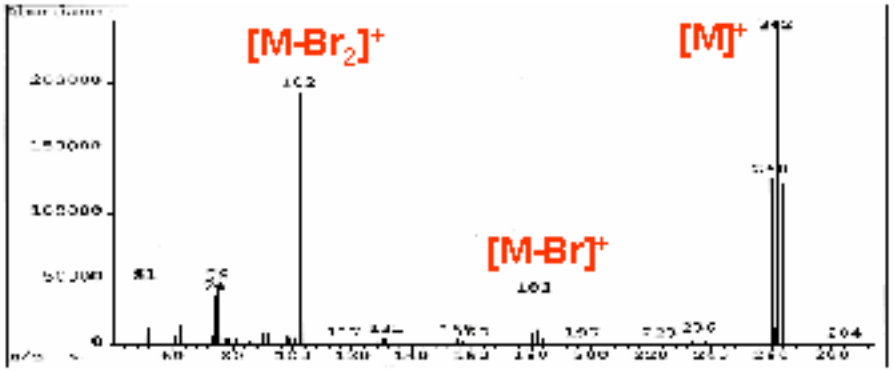


Environment Canada Environnement Canada

(based on Wolf et al., 2000)

Dibromostyrenes

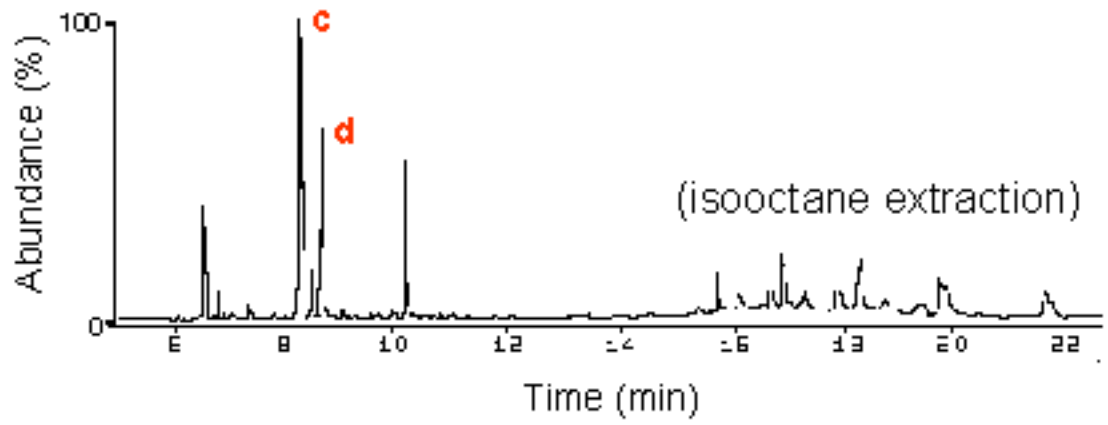


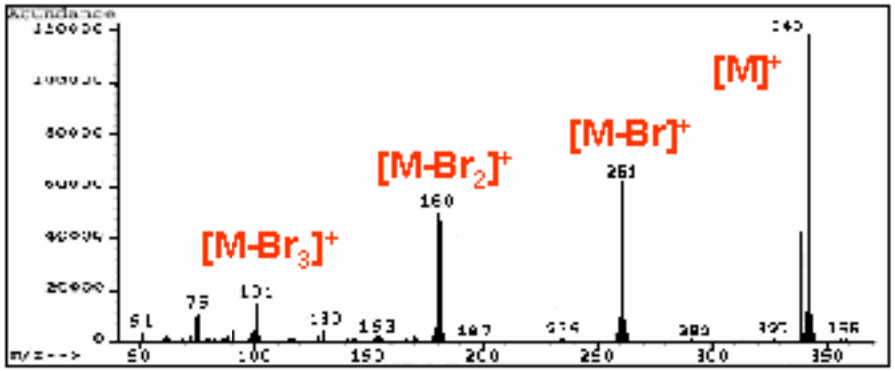


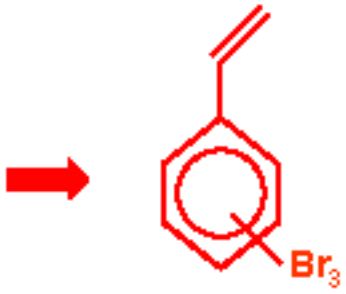
Environment Canada Environnement Canada

(from Gouteux et al. 2005)

Tribromostyrenes



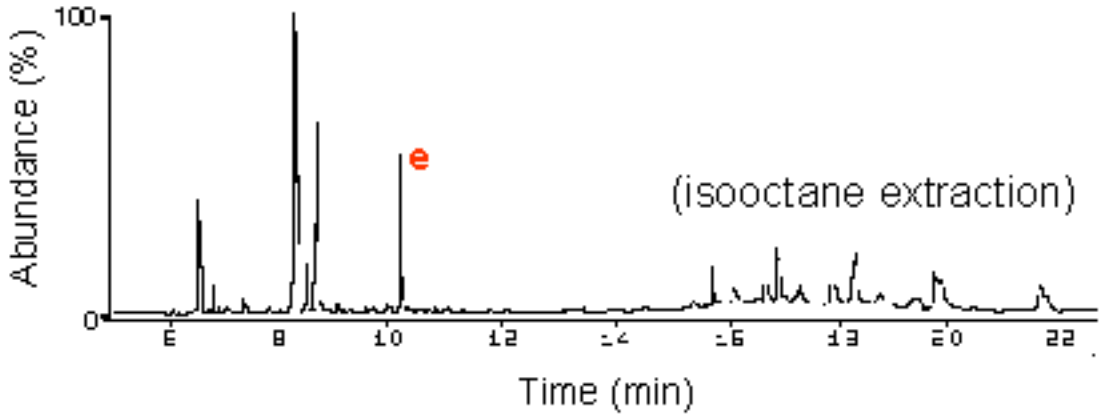


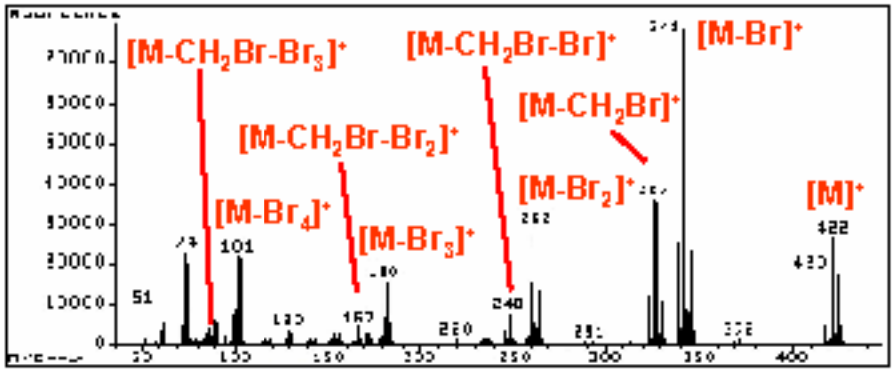


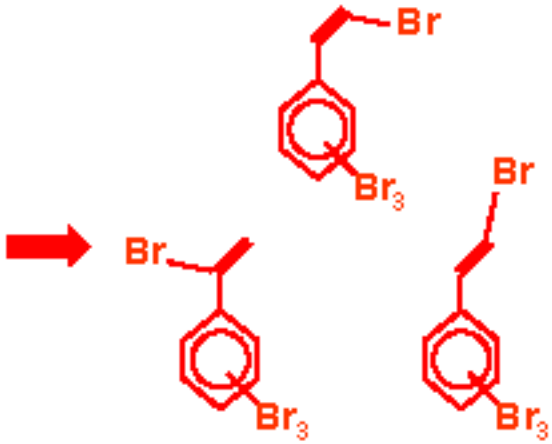
Environment Canada Environnement Canada

(from Gouteux et al. 2005)

(bromoethenyl) tribromobenzene



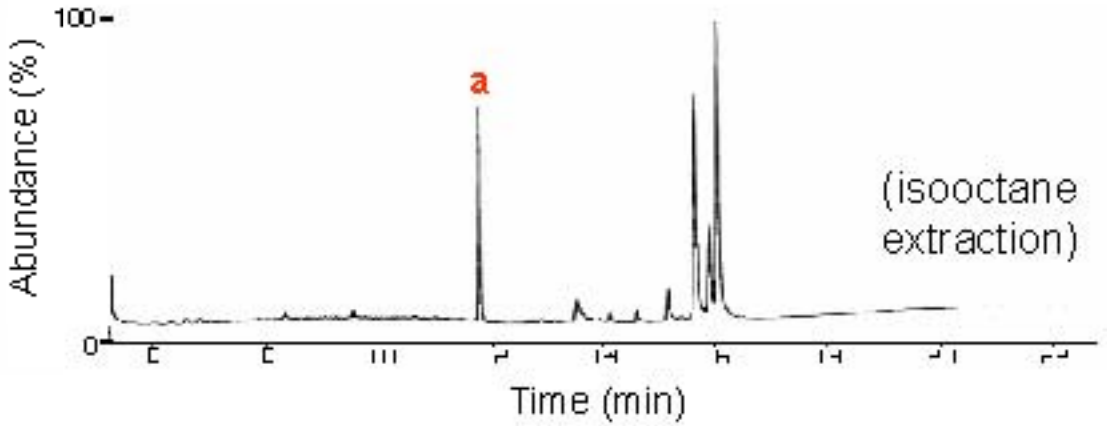


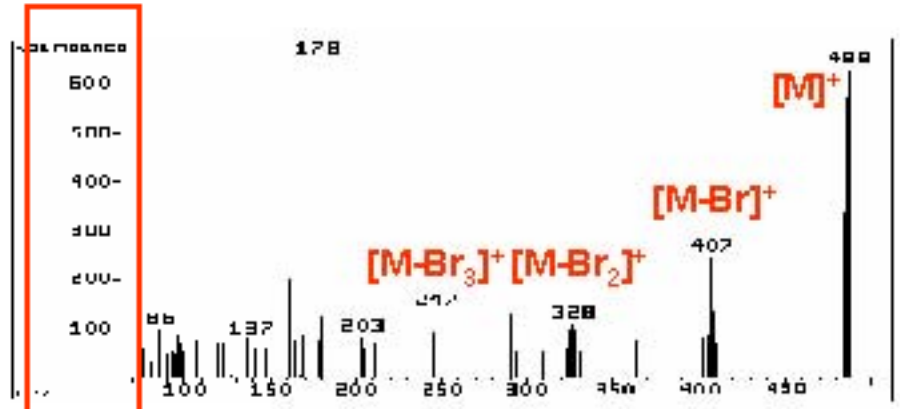


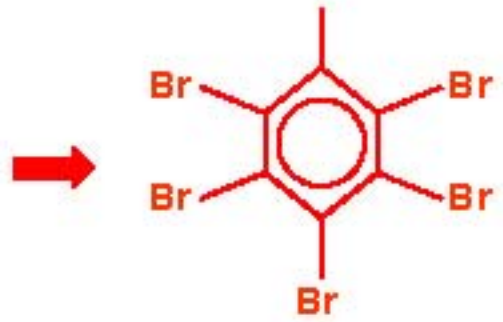
Environment Canada Environnement Canada

(from Gouteux et al. 2005)

2,3,4,5,6-pentabromotoluene (PBT)







Environment Canada Environnement Canada

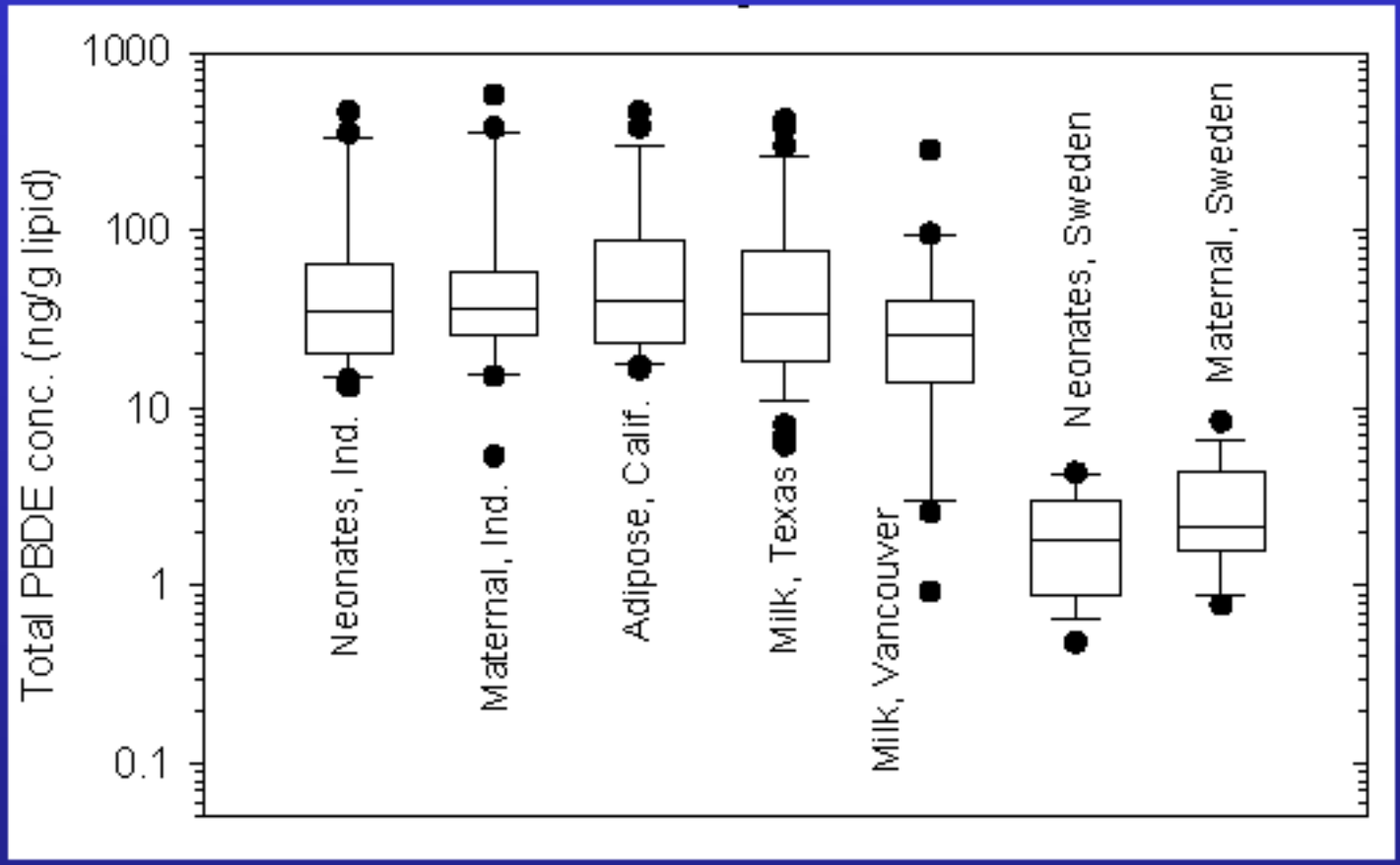
(from Gouteux et al. 2005)

(NIST library)

Human Tissue

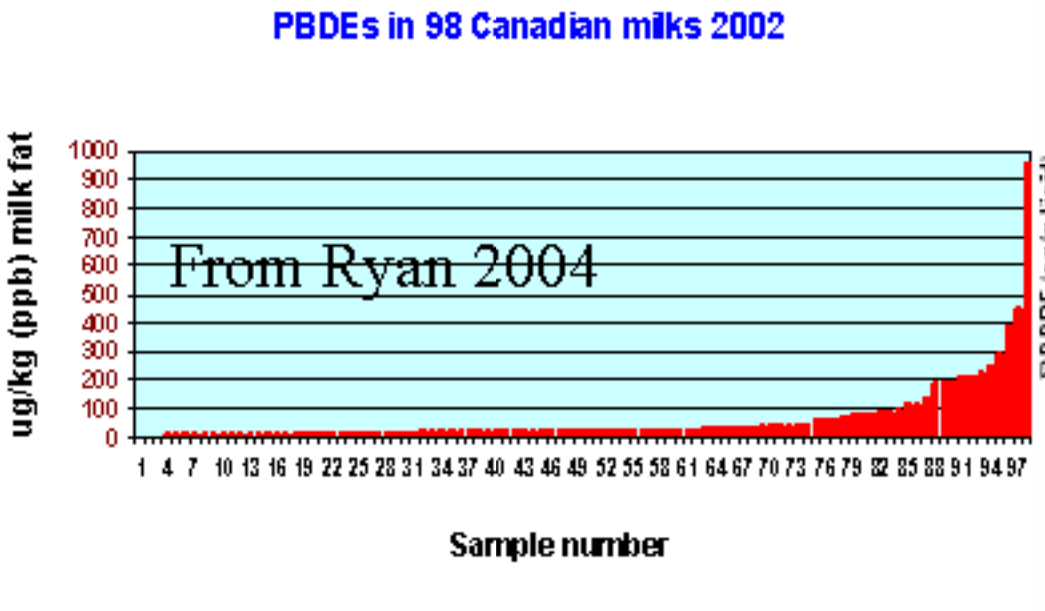
Environment Canada Environnement Canada

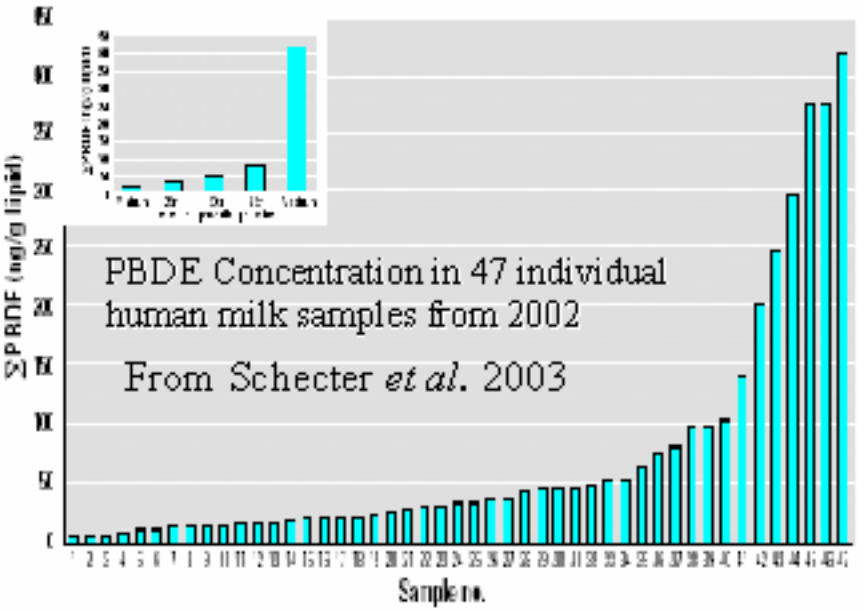
Distributions of the ΣPBDE concentrations in human blood, milk, and tissue from different locations.

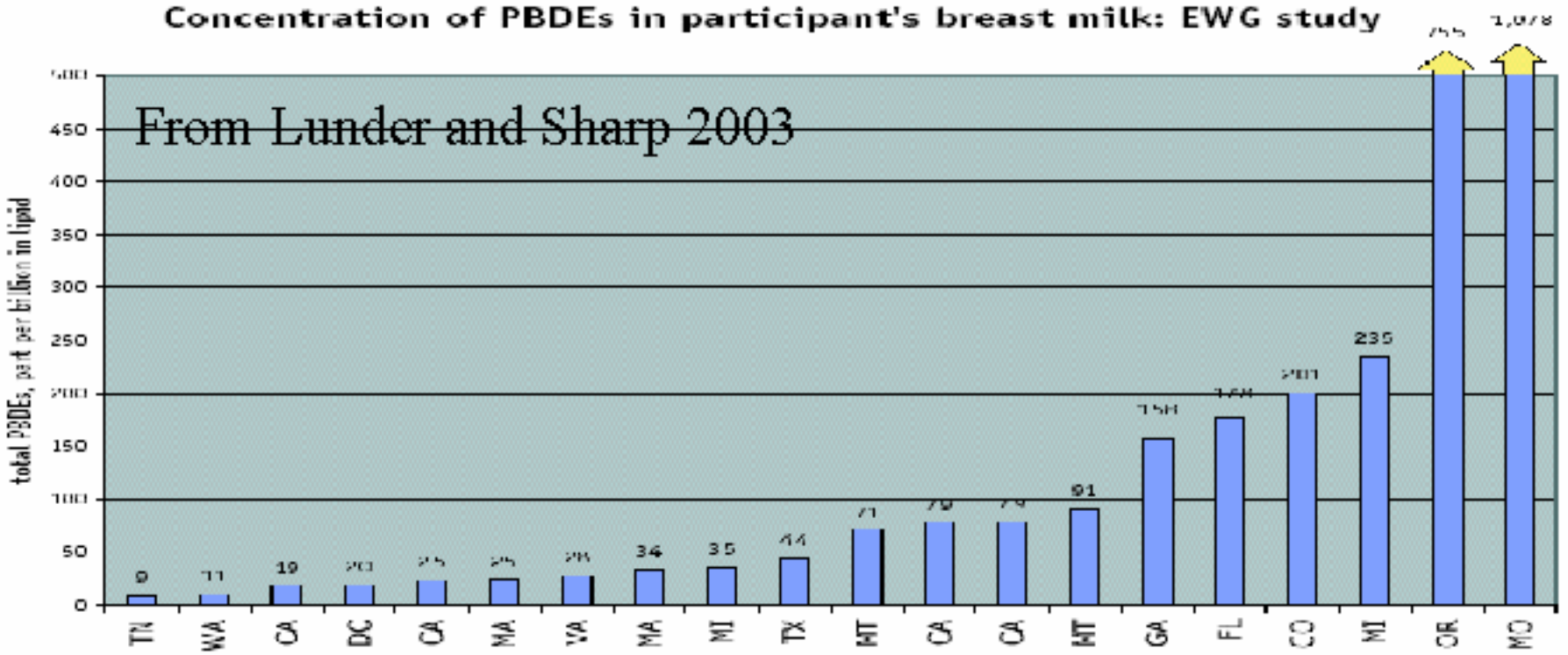


Environment Canada Environnement Canada

From Hites 2004


PBDEs in 98 Canadian milks 2002
ug/kg (ppb) milk fat
From Ryan 2004
Sample number

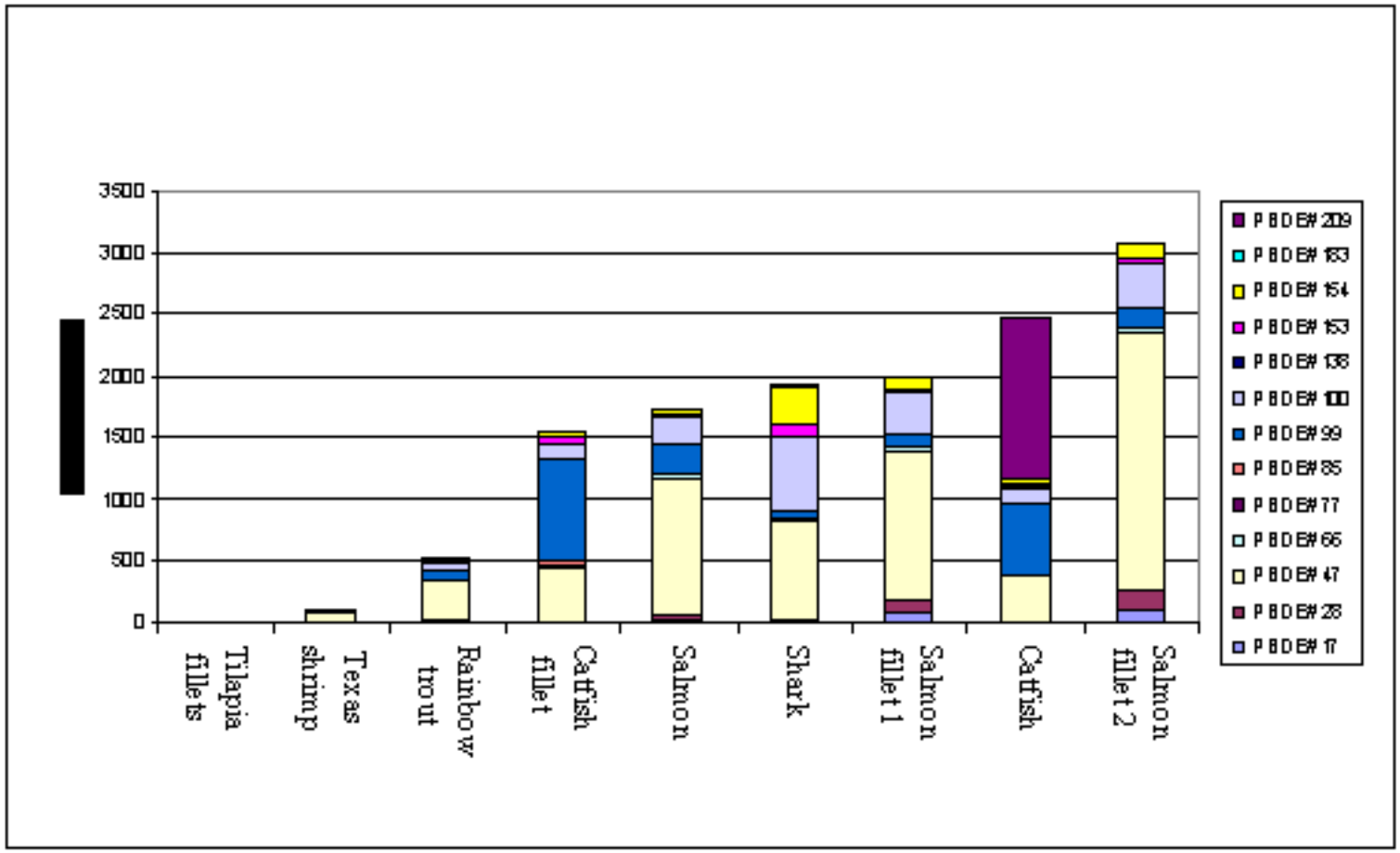

PBDE Concentration in 47 individual human milk samples from 2002
From Schecter *et al.* 2003
Sample no.


Concentration of PBDEs in participant's breast milk: EWG study
From Lunder and Sharp 2003
total PBDEs, part per billion in lipid
TN
WA
CA
DC
CA
MA
VA
MA
MI
TX
MT
CA
CA
MT
GA
FL
CO
MI
OR
MO

Exposure Routes

- Food
- OTHER?
  - Inhalation?
  - Ingestion of Dust?

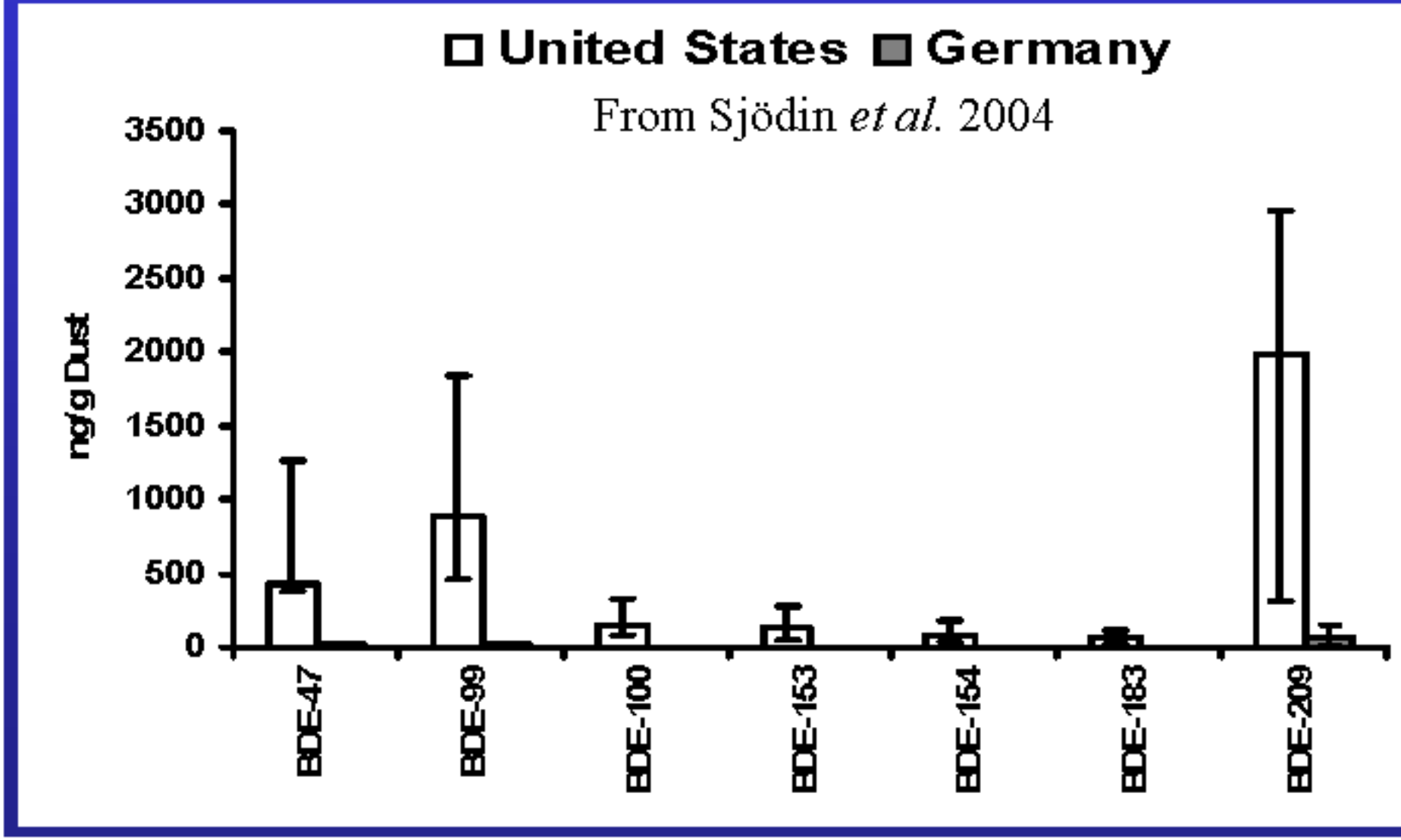
PBDE congener levels (median value = 1725 ppt) and profiles in USA fish products (**ppt** w.w.).



Environment Canada Environnement Canada

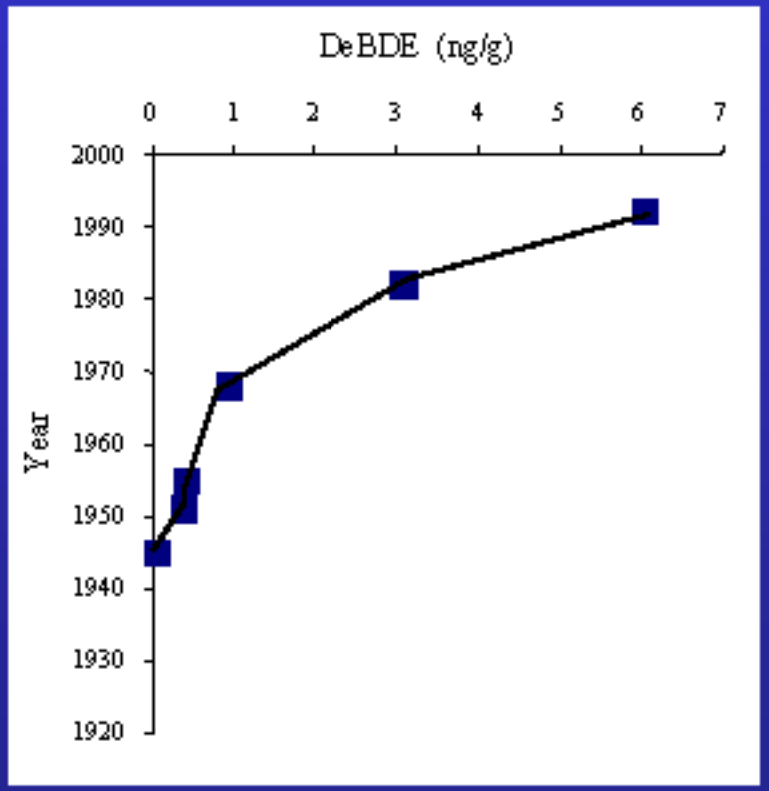
From Schecter *et al.* 2004

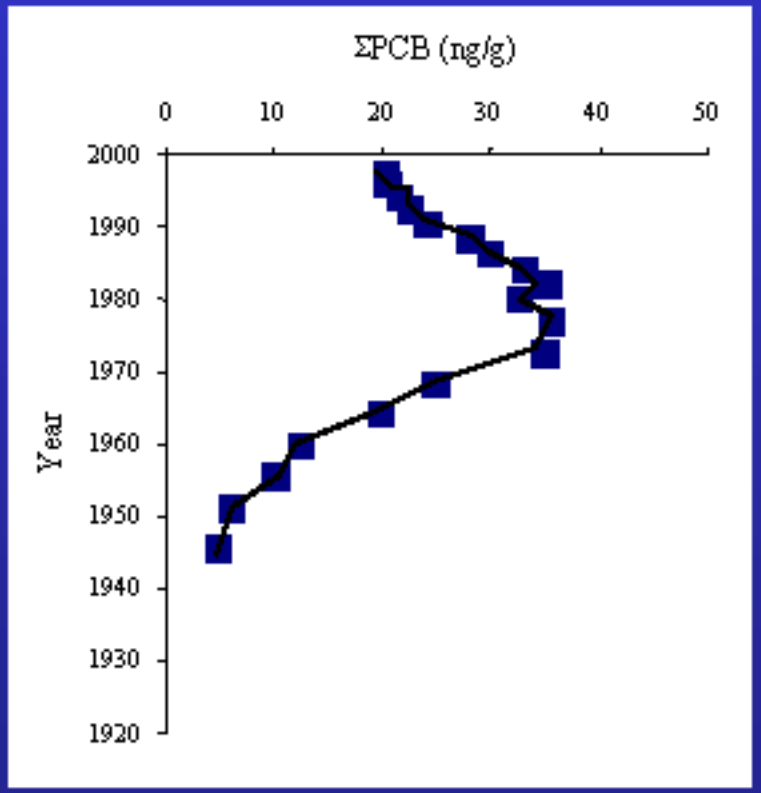
Concentration of PBDEs in household dust samples from Germany and the United States



Temporal Trends

Concentration of BDE-209 in a Sediment Core from St. Lawrence Estuary



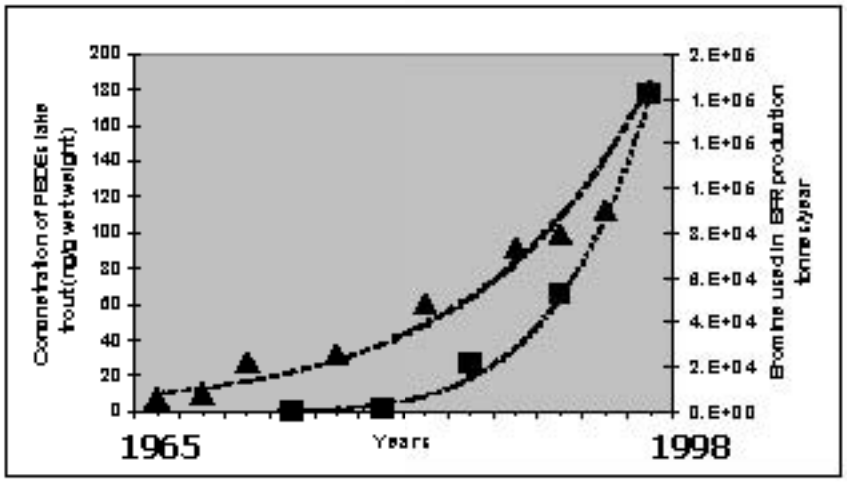


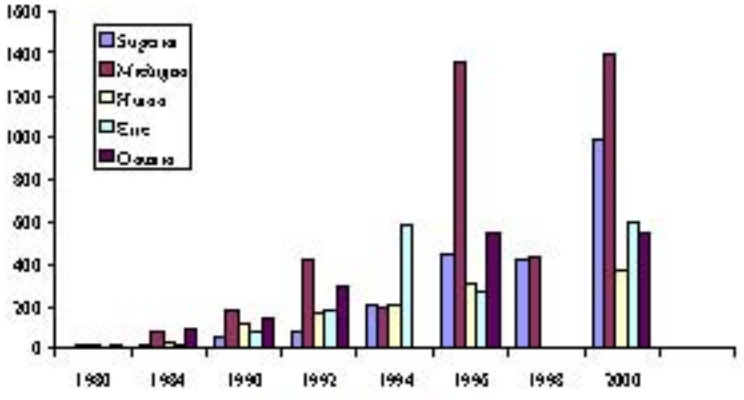
Environment Canada Environnement Canada

From Lebeuf *et al.* 2002

Temporal Trends of PBDEs in the Biota from the Great Lakes

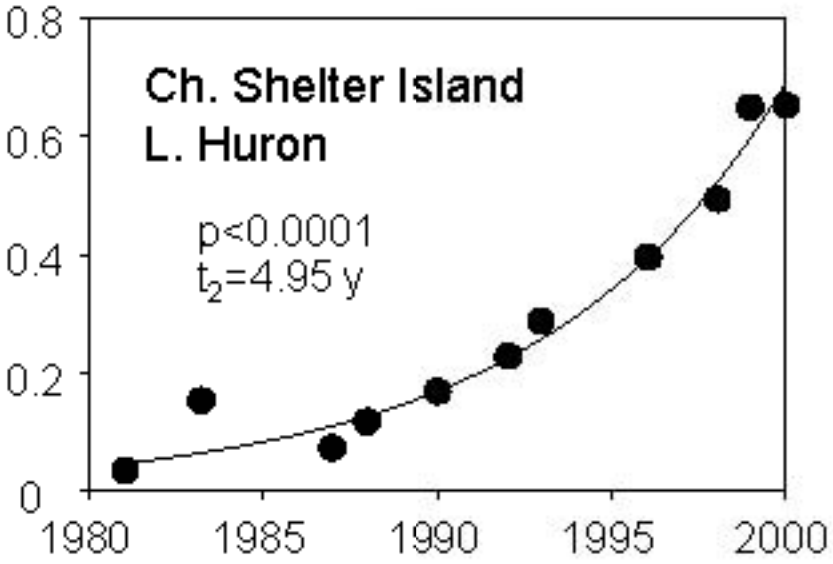
from Luross *et al.* 2000, Norstrom et al. *2002*, Zhu & Hites 2004, and Chernyak et al. 2002

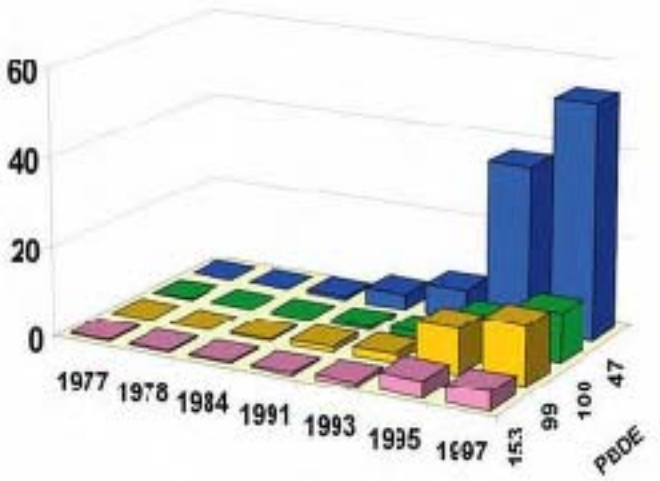




FBDE Trends

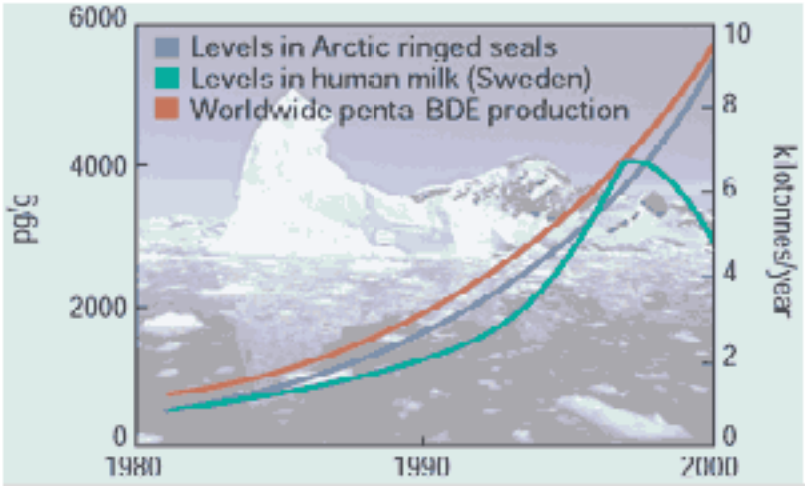
LAKE ST. CLAIR WALLEYE

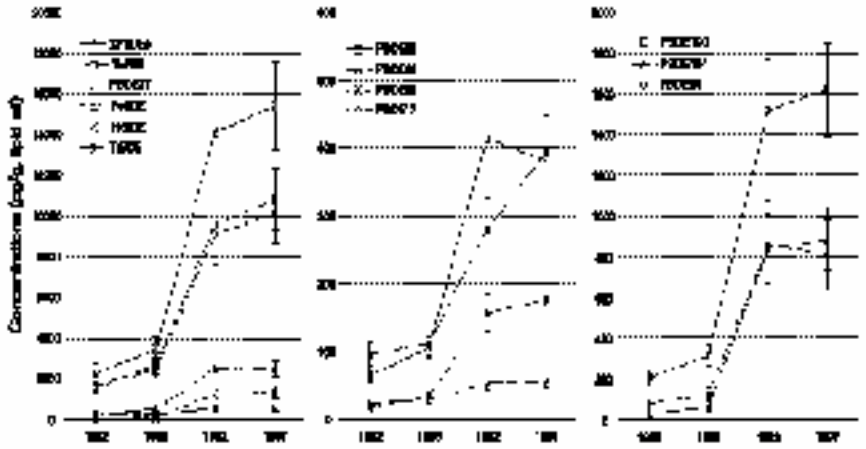


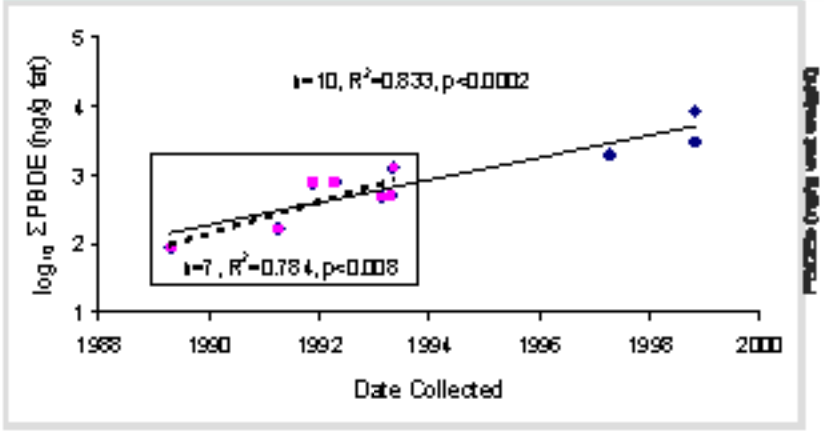


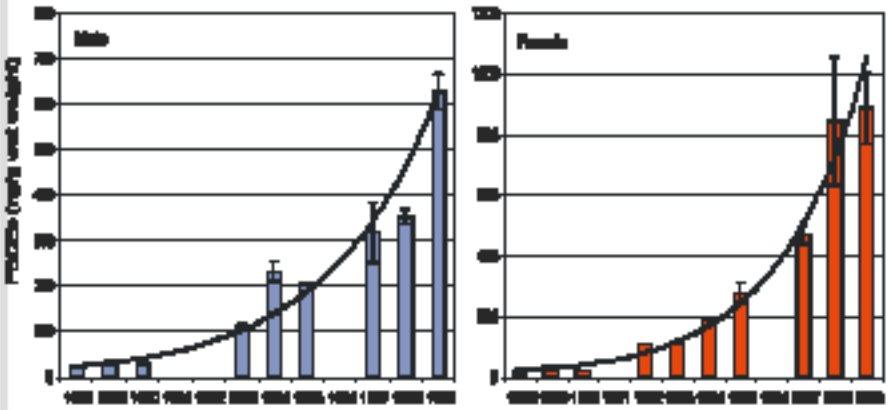
Temporal Trends of PBDEs in the Marine Mammals

from Ikonomou *et al.* 2002, Law *et al.* 2003, She et al. 2002, and Lebeuf *et al.* 2002





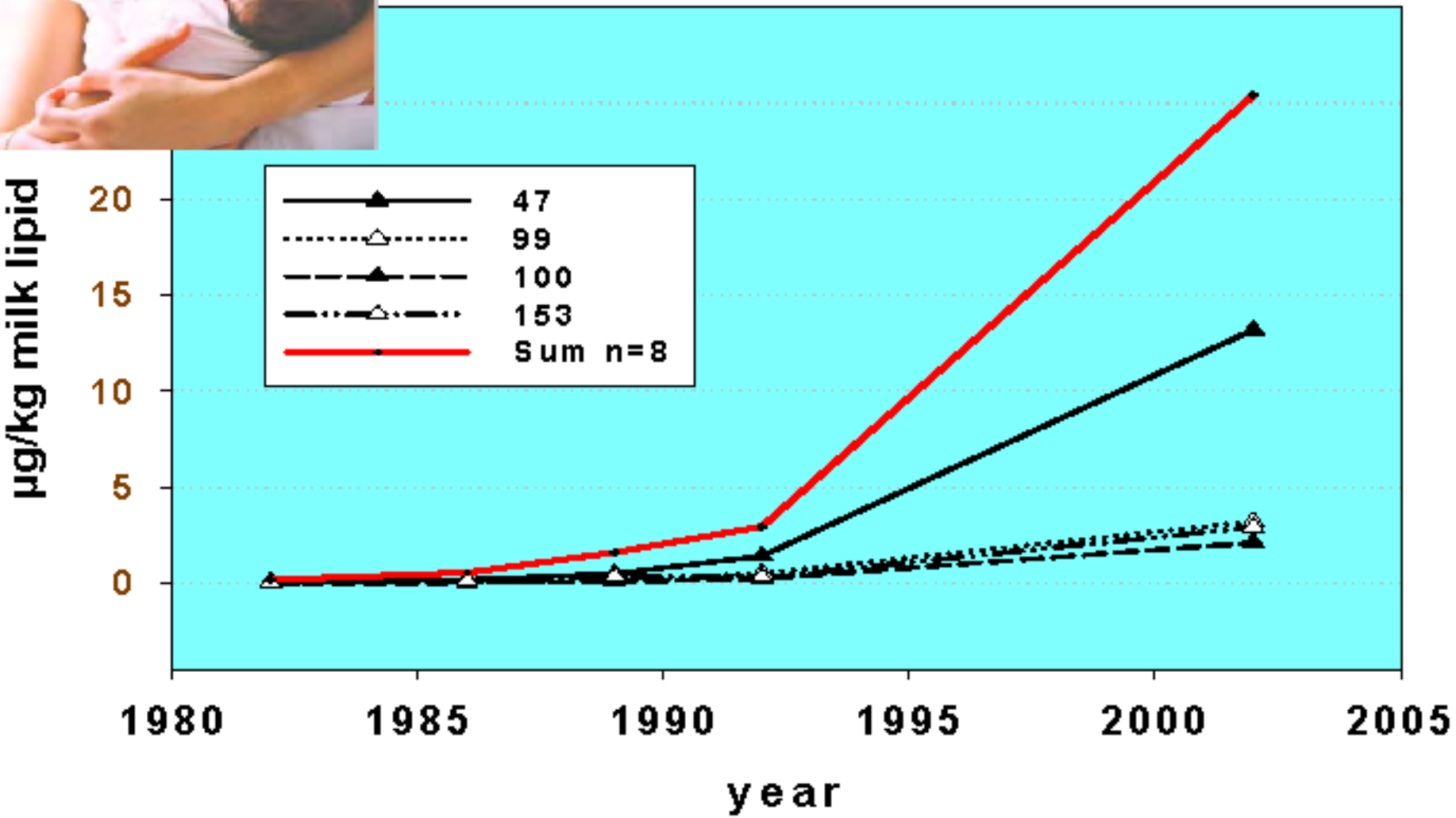




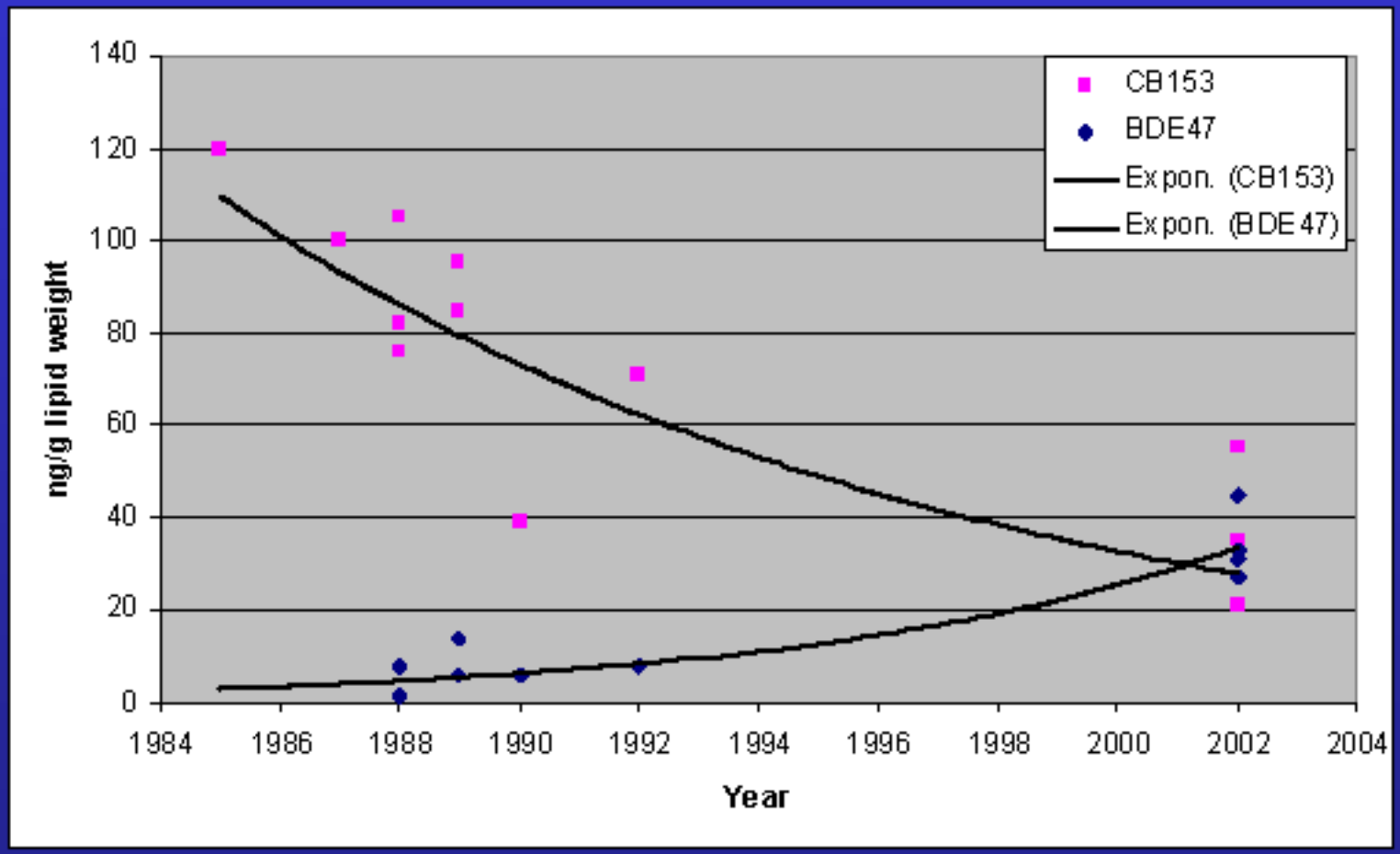
Environment Canada Environnement Canada

Trends of PBDEs in Canadian human milk

From Ryan *et al.* 2003



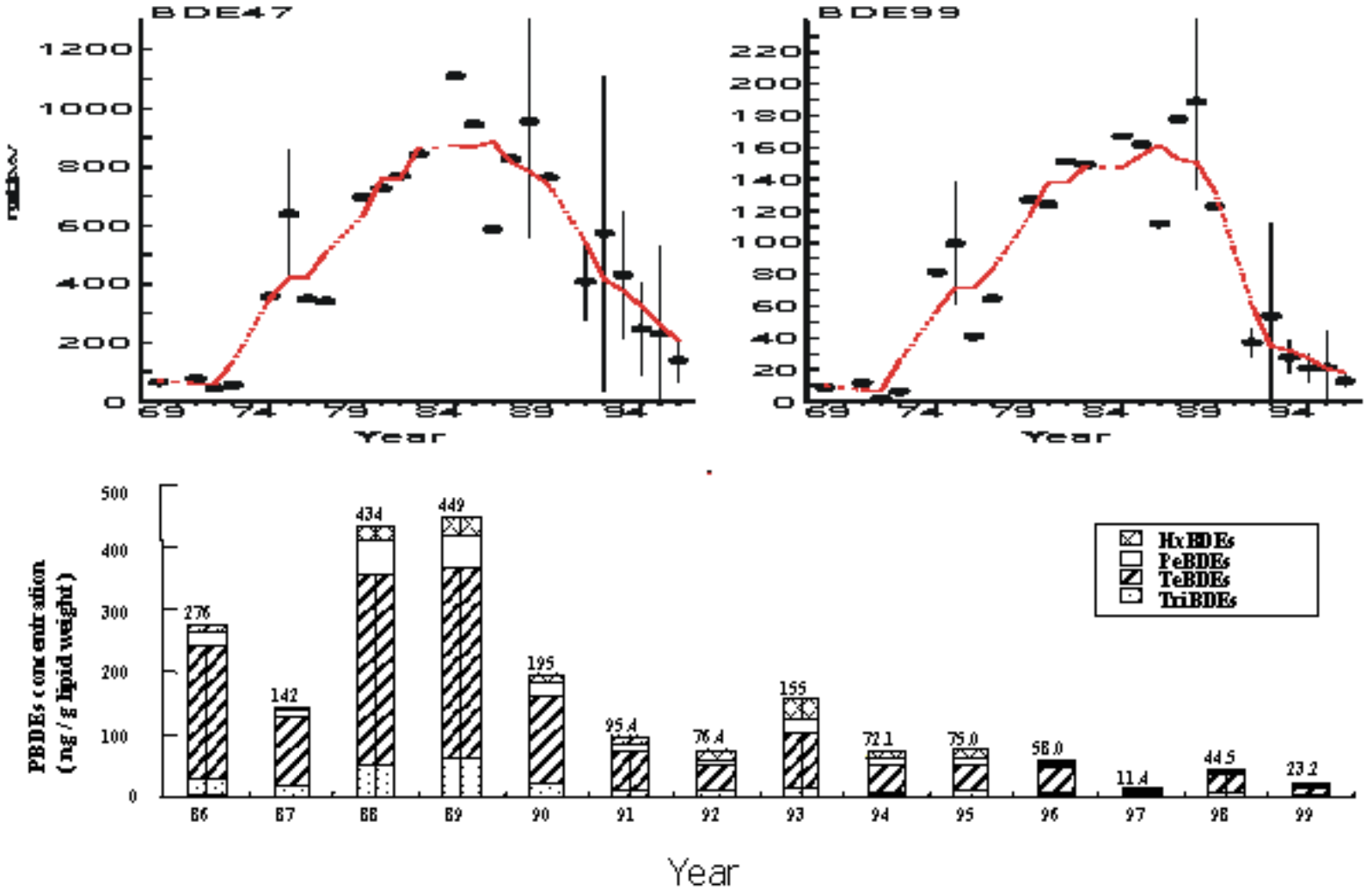
Temporal Trend of BDE-47 and CB-153 in Human Plasma Serum from US



From Sjödin *et al.* 2003

Environment Canada Environnement Canada

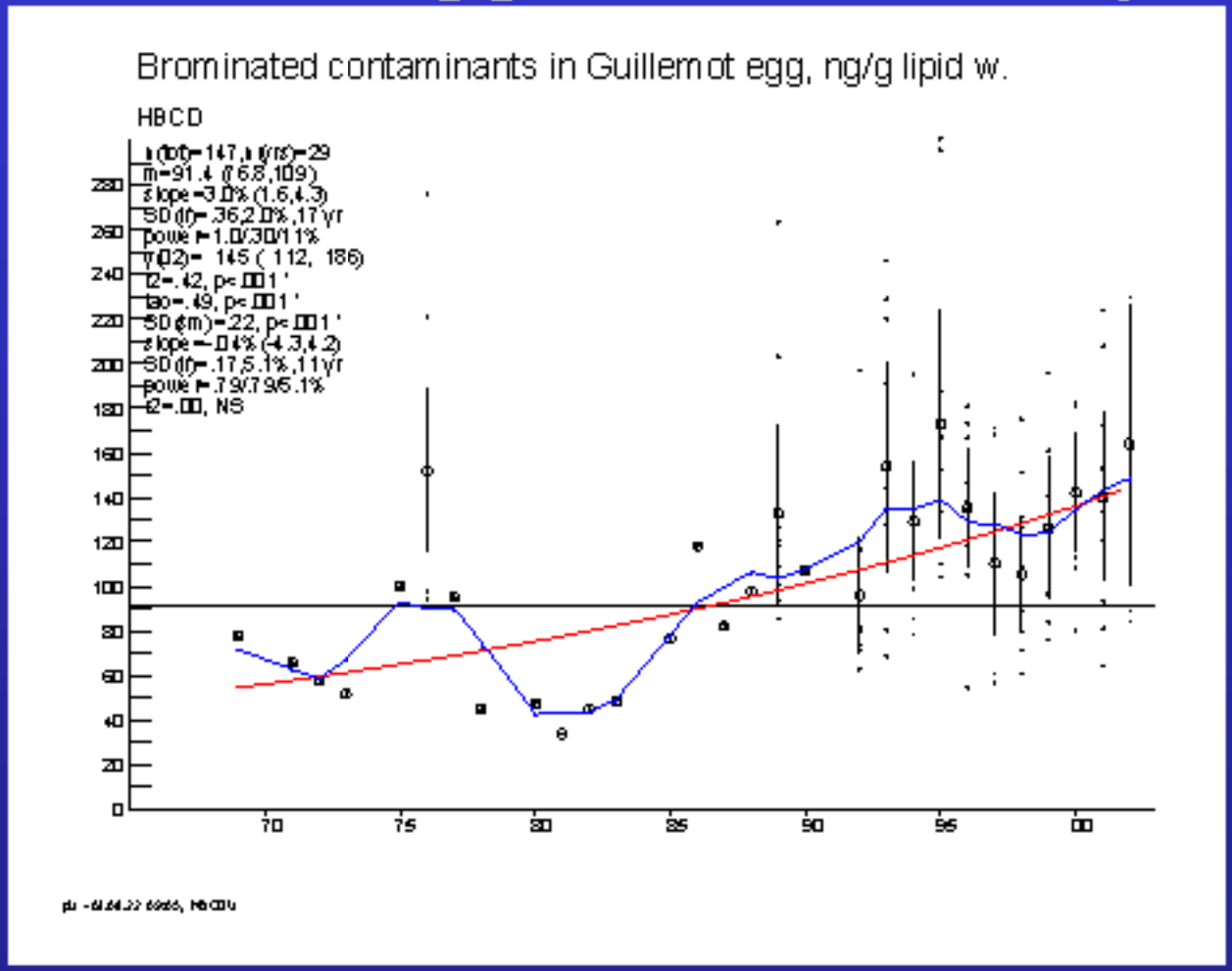
Temporal Trends of PBDEs in Europe and Japan



Environment Canada Environnement Canada

From Sellström *et al.* 1999 and Ohta *et al.* 2001

Temporal trend of HBCD in Guillemot Egg, the Baltic Proper



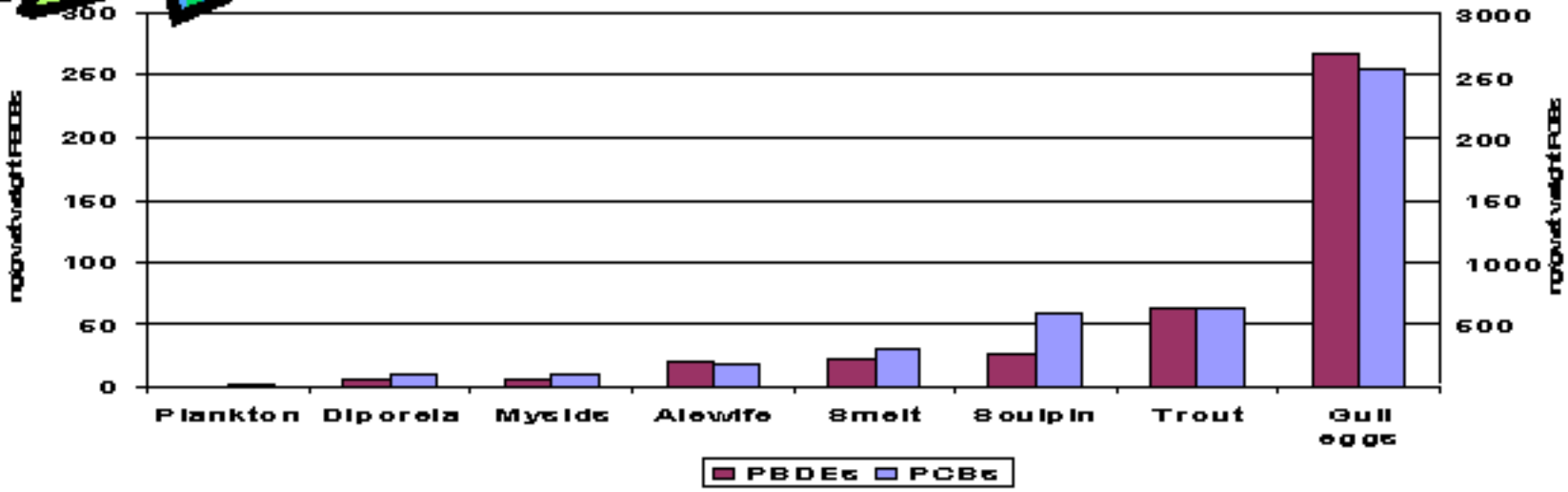
From Sellström *et al.*, 2003

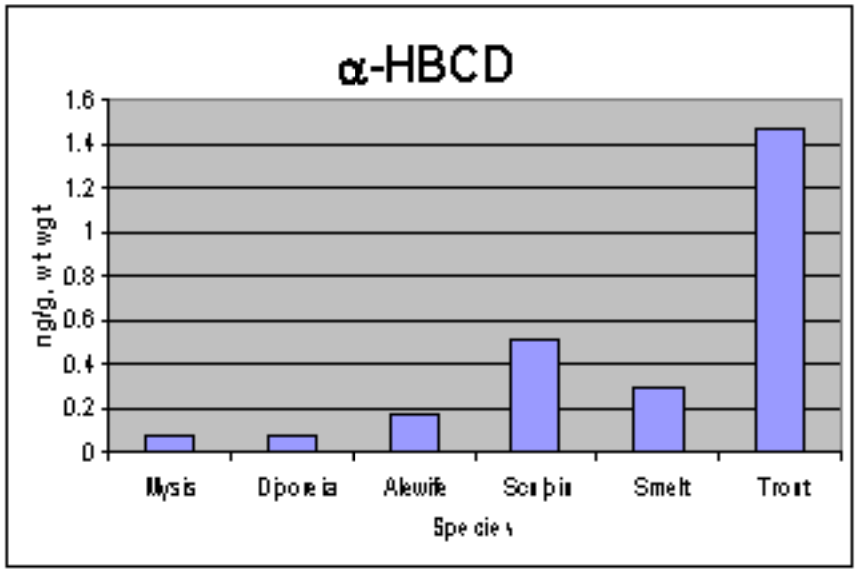
Environment Canada Environnement Canada

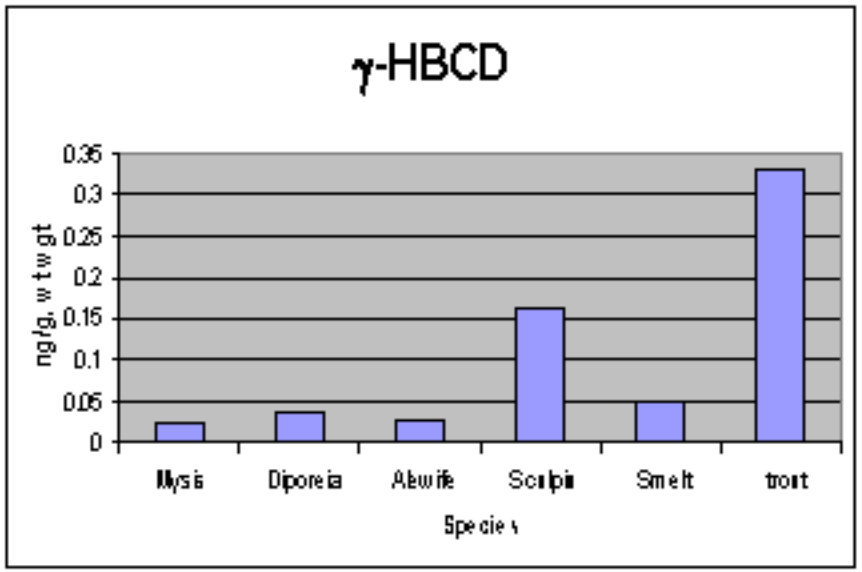
Biomagnifcation & Metabolism

Environment Canada Environnement Canada

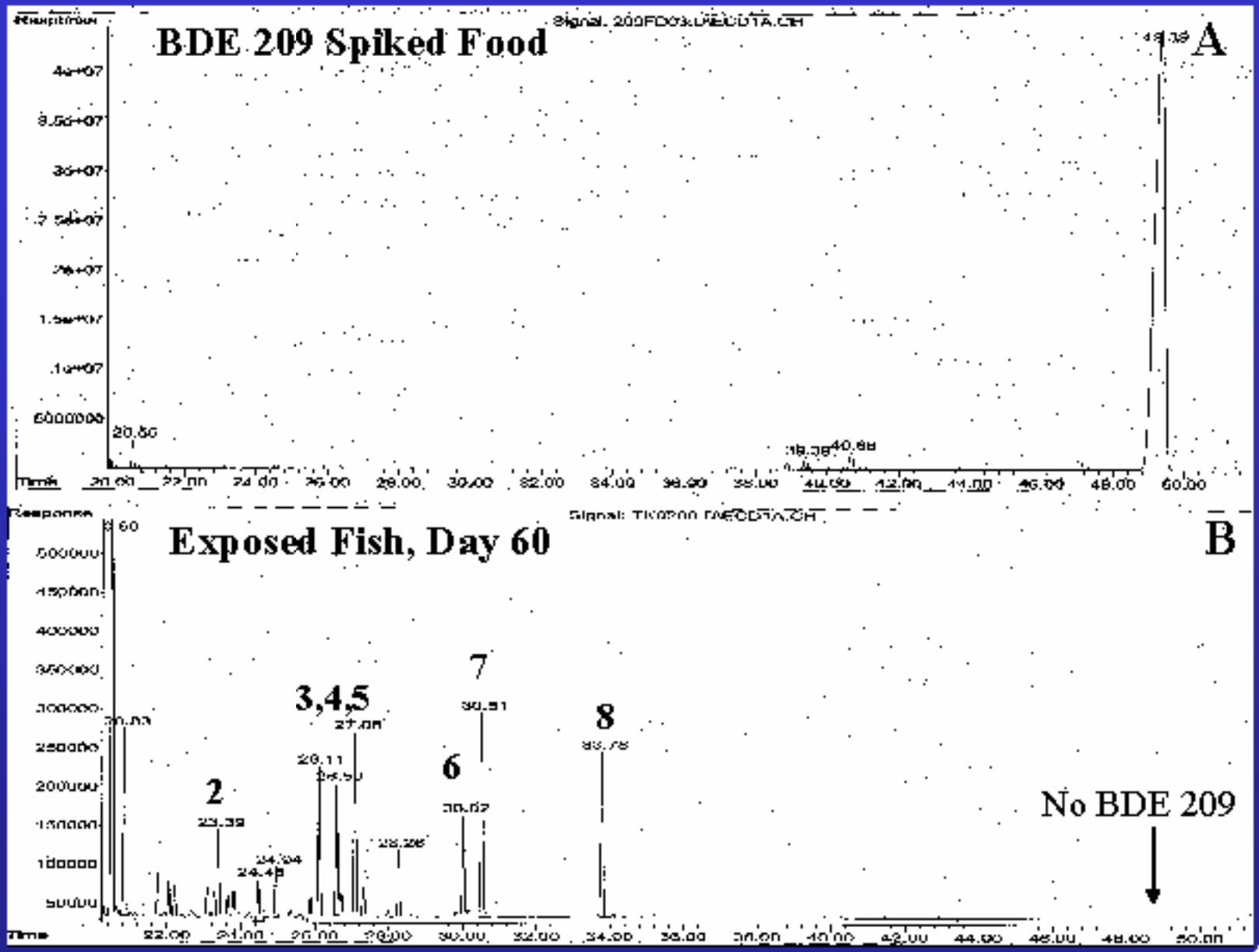
Biomagnification of HBCD, PBDEs and PCBs in Lake Ontario Food Web







PCB data from Metcalfe and Metcalfe 1995; PBDEs in gull eggs from Norstrom et al. 2002



Environment Canada Environnement Canada

From Stapleton 2003

Debromination of BDE-209 Under Aerobic and anaerobic conditions

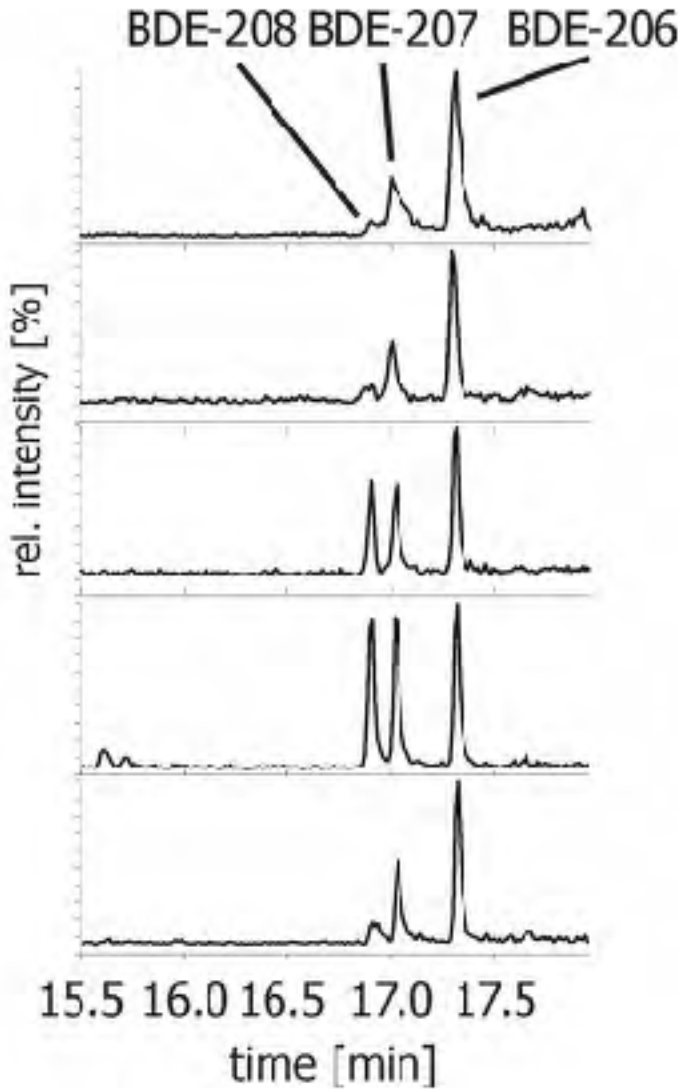
a) technical DecaBDE (used in this study)

b) anaerobic degradation 7 days

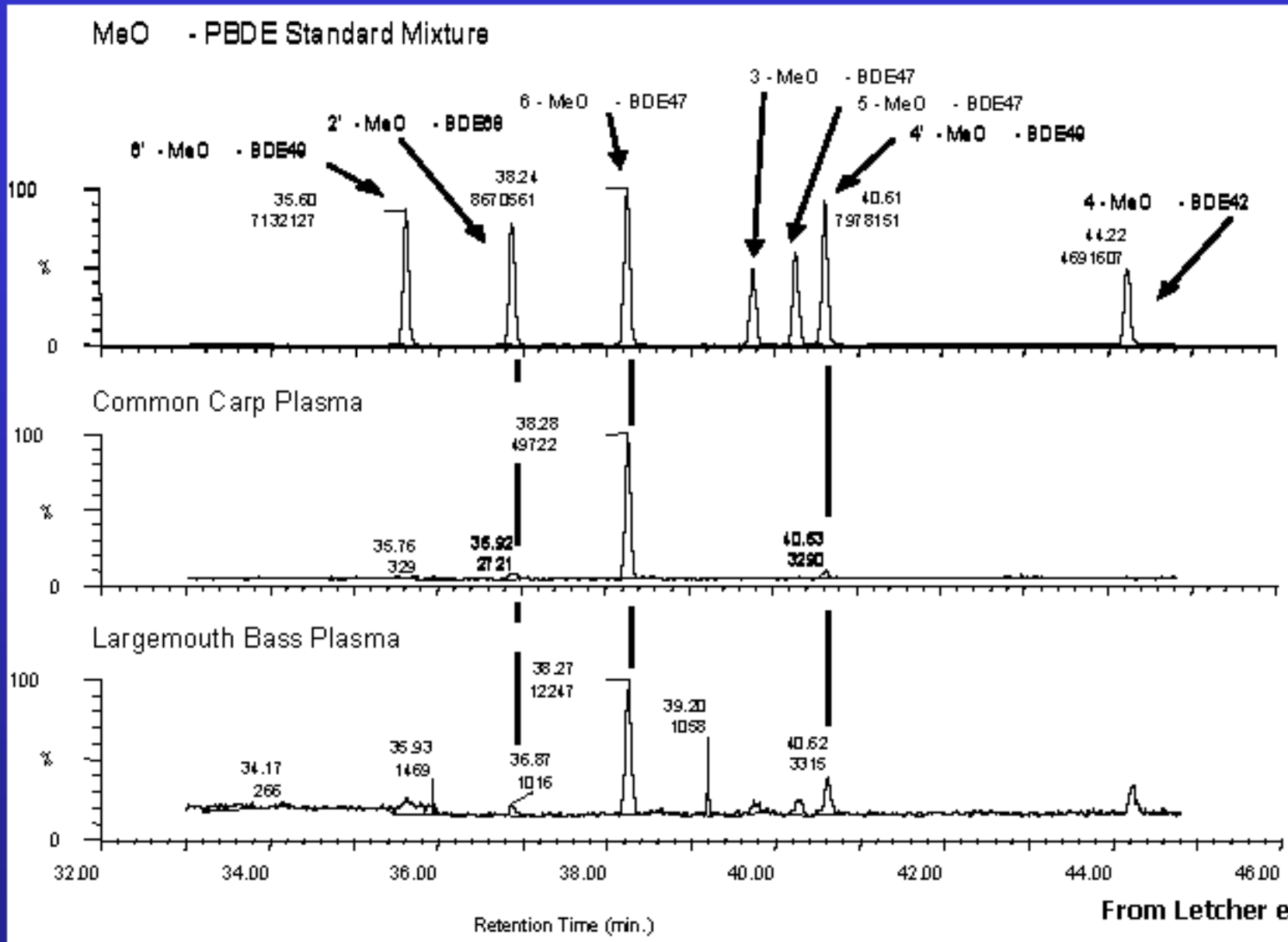
c) anaerobic degradation 63 days

d) anaerobic degradation 237 days

e) sterile control 237 days



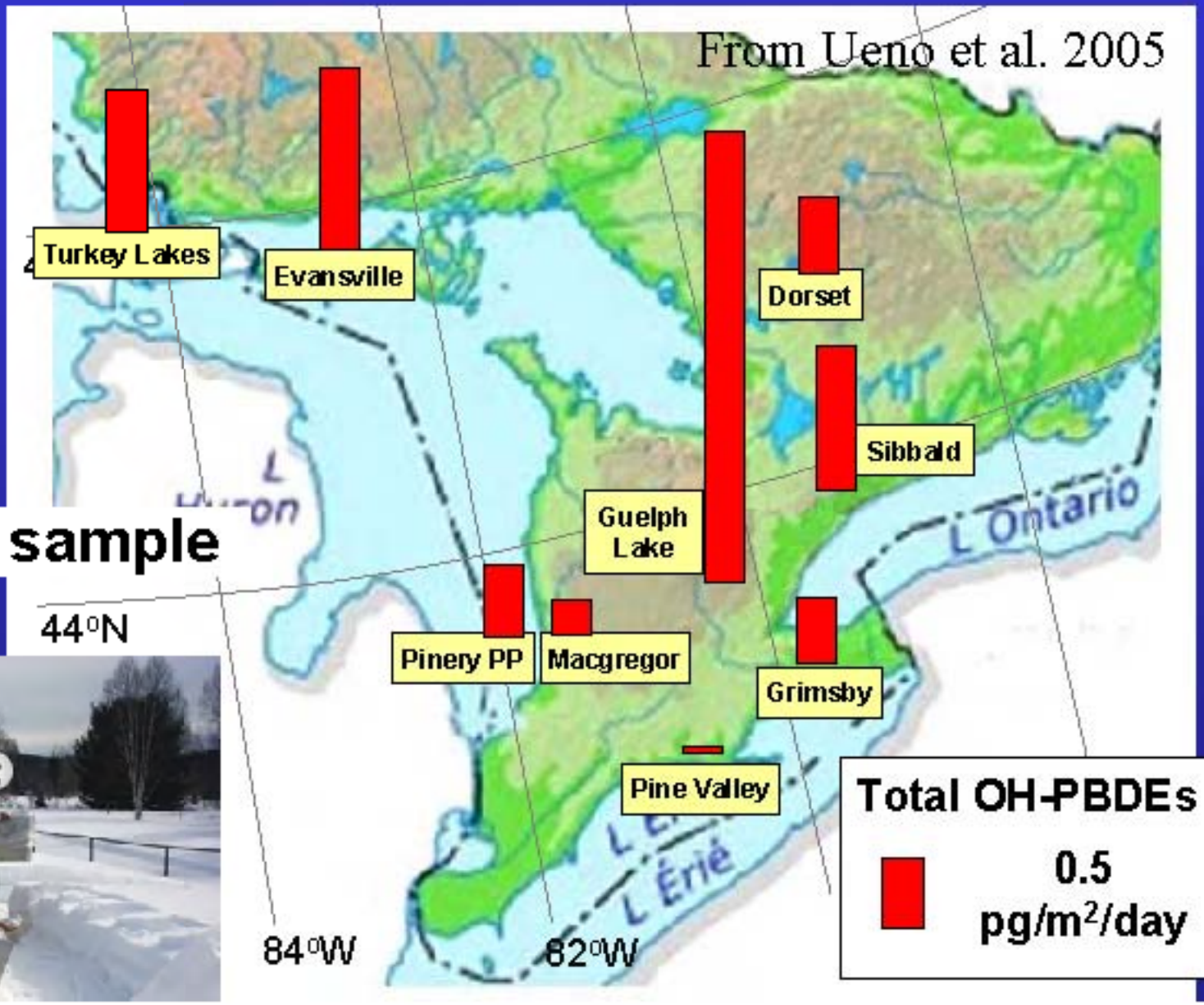
From Gerecke *et al.* 2004



From Letcher et al 2003

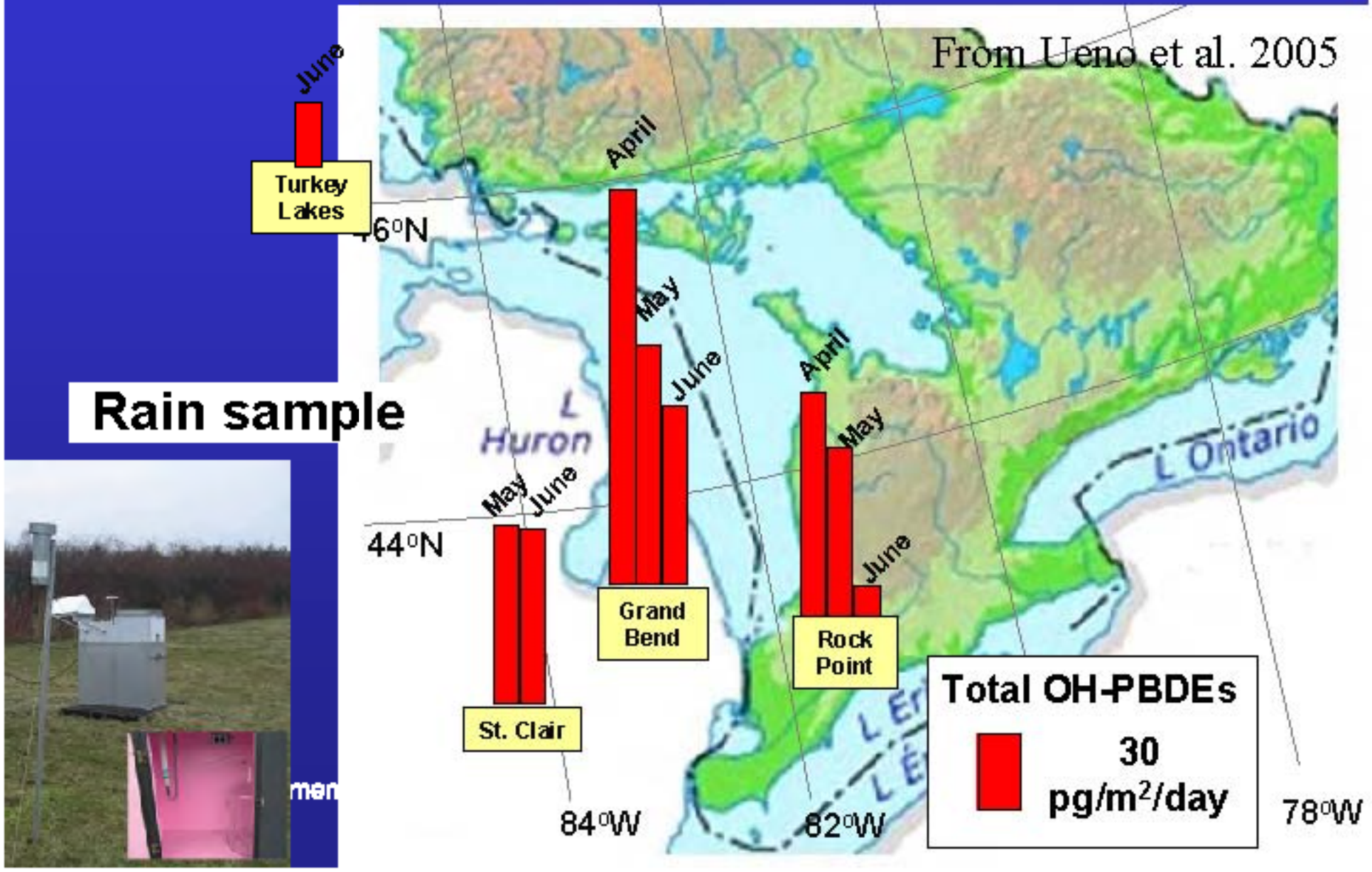
Environment Canada Environnement Canada

Geographical Distribution of OH-PBDE Fluxes in Snow Samples



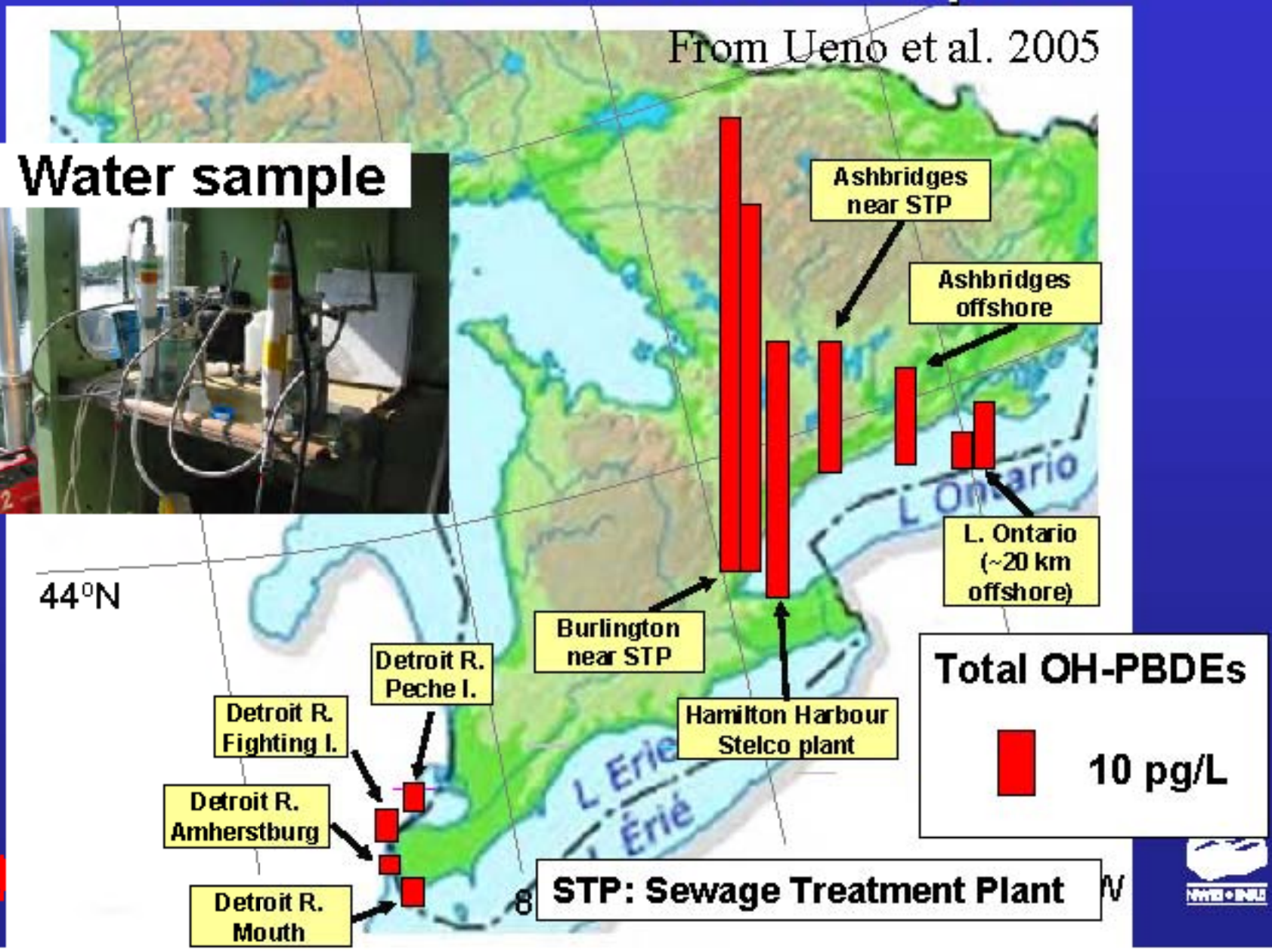
Snow sample

Geographical Distribution of OH-PBDE Fluxes in Rain Samples



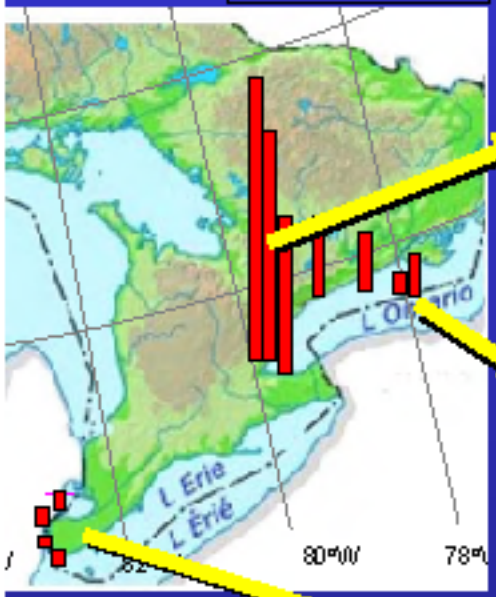
Rain sample

Geographical Distribution of OH-PBDE Concentrations in Water Samples



Homologue Profiles of OH-PBDEs in Water Samples

Water

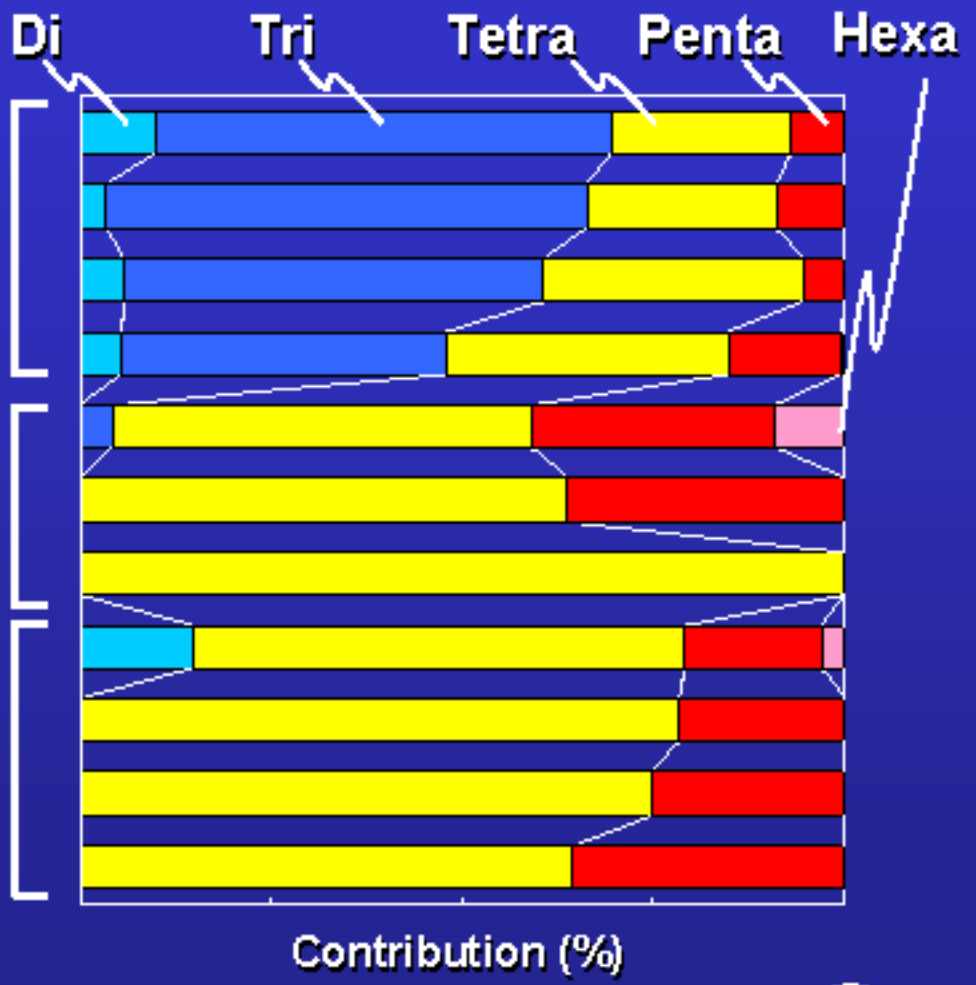


L. Ontario (near STP)

L. Ontario (open water)

Detroit R.

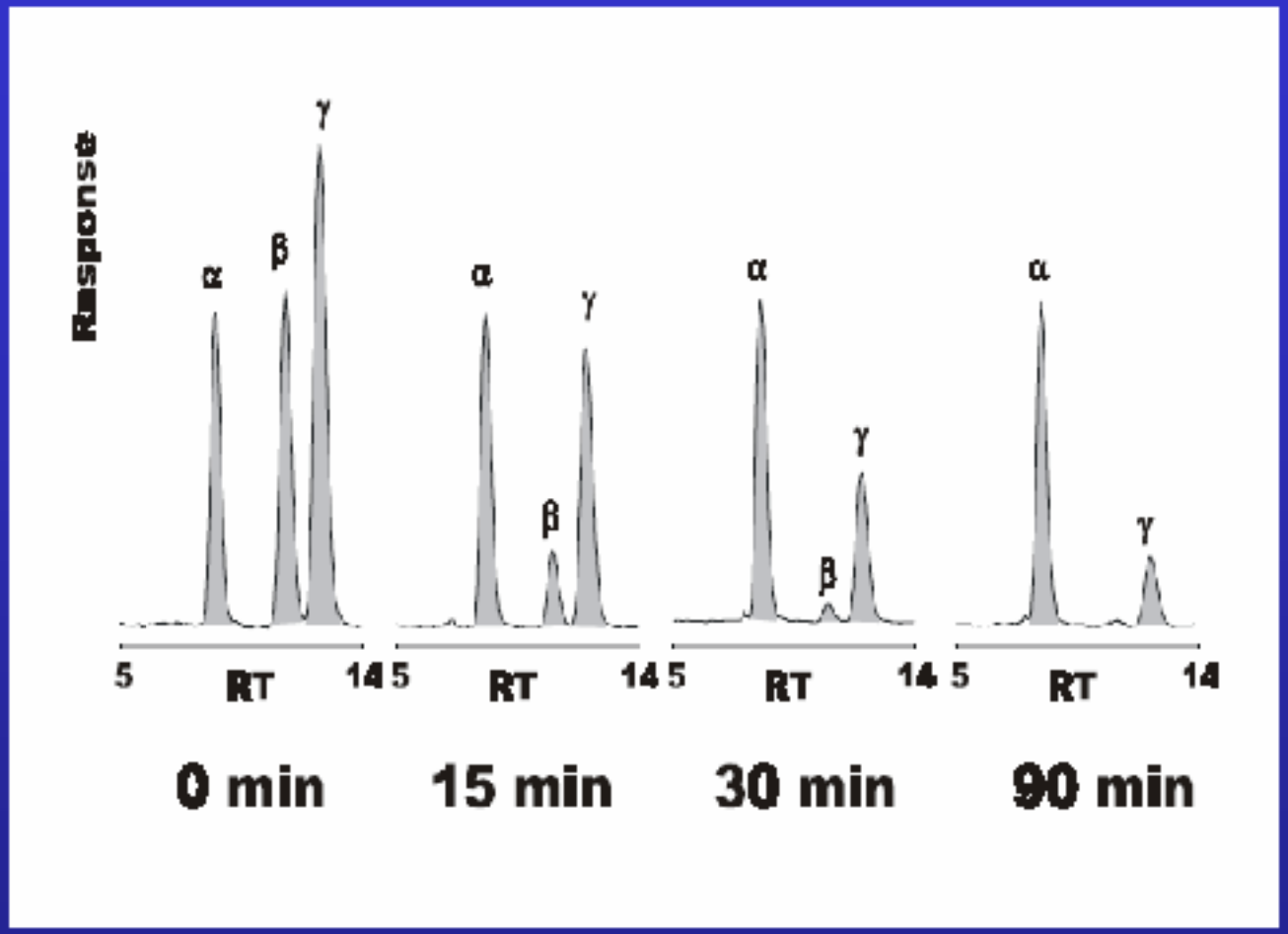
Higher percentage of lower Br congeners were found near STP.



Environment Canada Environnement Canada

From Ueno et al. 2005

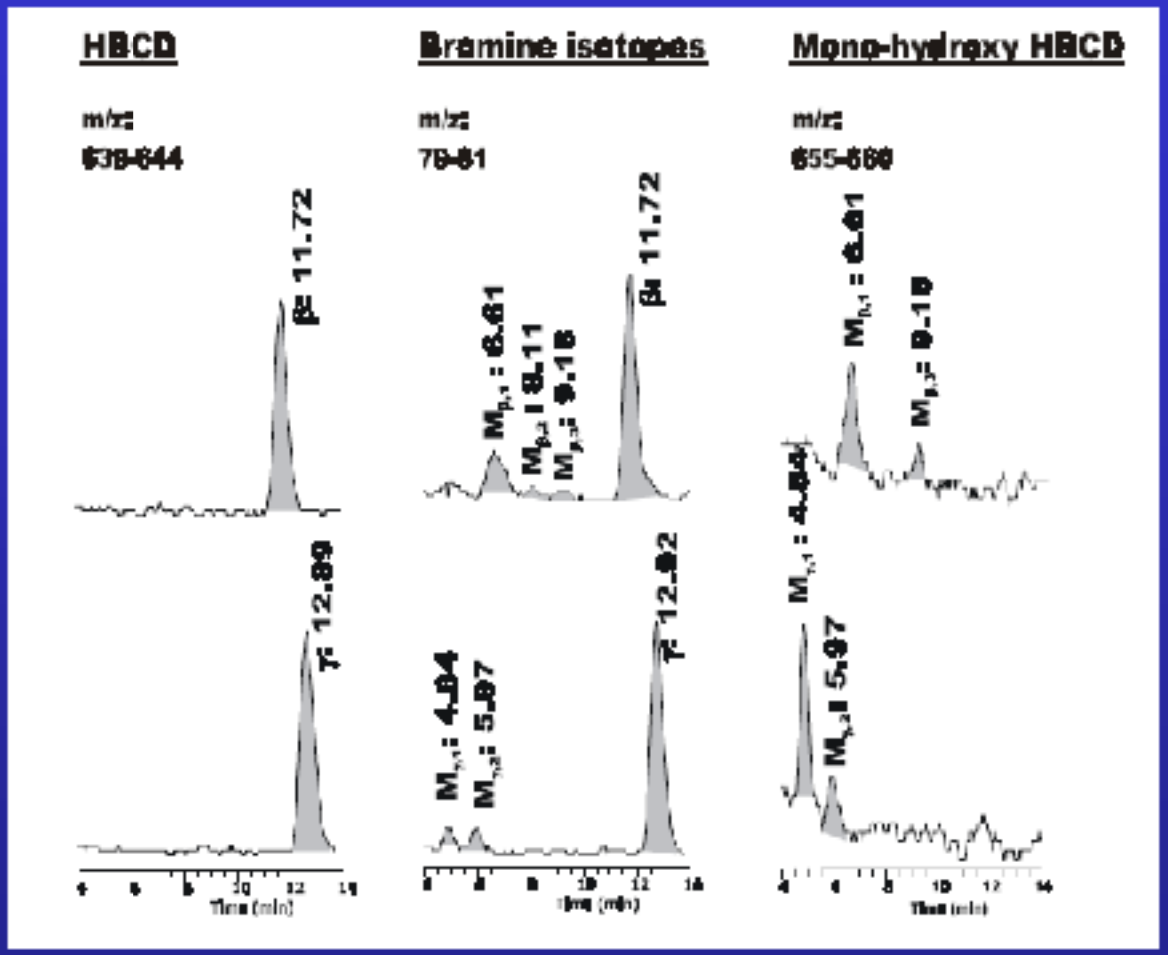
HBCD isomers in an in vitro assay using hepatic microsomes of pre-induced rats



From Boon et al. 2005

Environment Canada Environnement Canada

LC-MS chromatograms of the parent compounds and the different metabolites of β- and γ-HBCD



From Boon et al. 2005

Environment Canada Environnement Canada

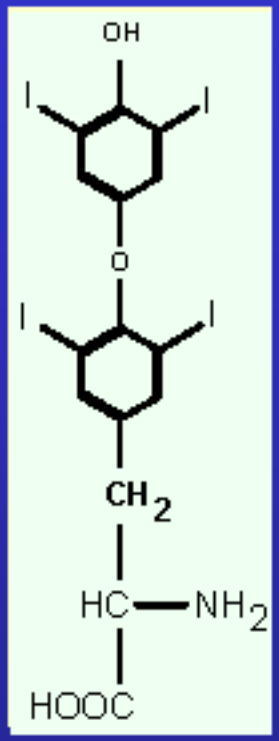
Overview of PBDE Toxicity:

- T4-TTR binding competition by PBDE metabolites[1]
- Estrogenic activity of hydroxylated PBDEs (ER-CALUX)[2]
- Neurotoxic effects of PBDE congeners[3]
- Commercial mixture DE-71 inhibits tail resorption at a dose of 60 µg/tadpole[4]
- PBDE congeners are weak AhR agonist, with REP around 10^{-4} or less, similar to reported PCN and PAH.[5]
- PBDE congeners which have the highest CYP 1A1 induction activity, 77, 119, 126, are not widely found congeners in the environment.[5]
- Carcinogenicity study NIH[6]

1- Meerts *et al.* 2000
2-Meerts *et al.* 2001
3-Eriksson *et al.* 1998, and 1999
4-Babich and Metcalfe 2001
5-Chen *et al* 2001
6-NTP Technical Report CAS No 1163-19-5

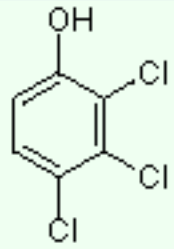
Relative potency BFRs in T_4-TTR binding competition

T_4



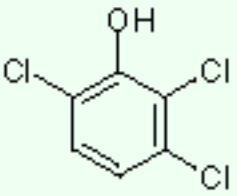
1

2,3,4-triCP



0.04

2,3,6-triCP

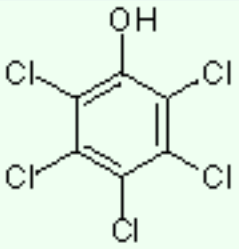


0.06

2,4,6-triBP

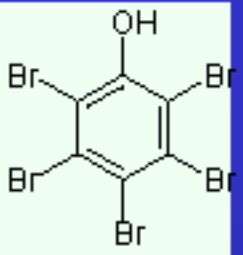
1.20

PCP



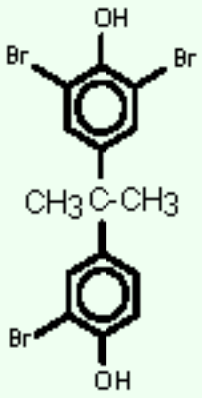
2.50

PBP



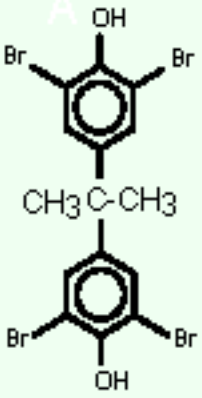
7.14

TriBBPA



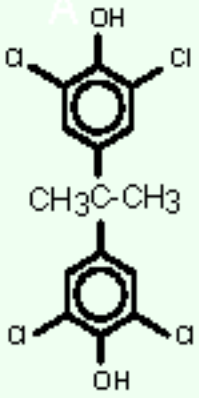
0.58

TBBP



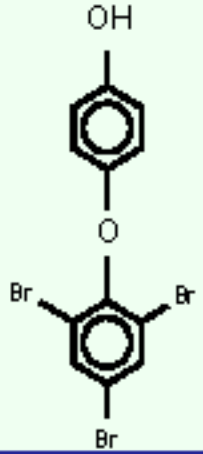
10.6

TCBP



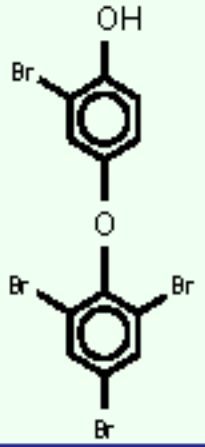
0.76

T2-like



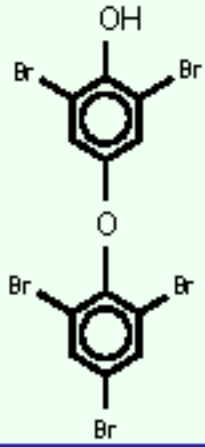
0.41

T3-like



1.22

T4-like

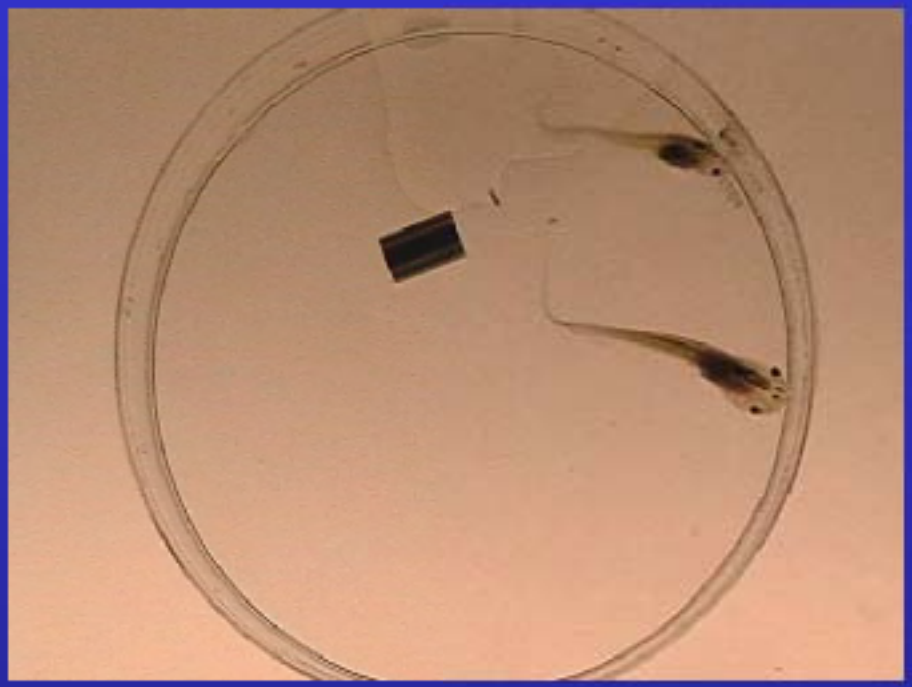


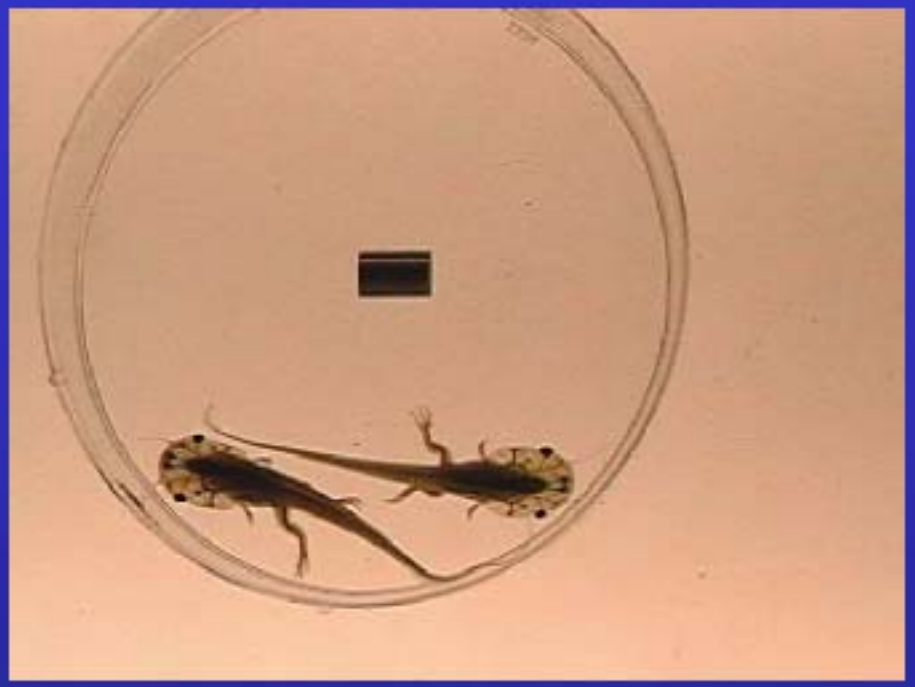
1.42

Meerts et al, 2000. *Toxicol. Sci.* 56:95-104

Environment Canada Environnement Canada

DE-71 Feeding Trials





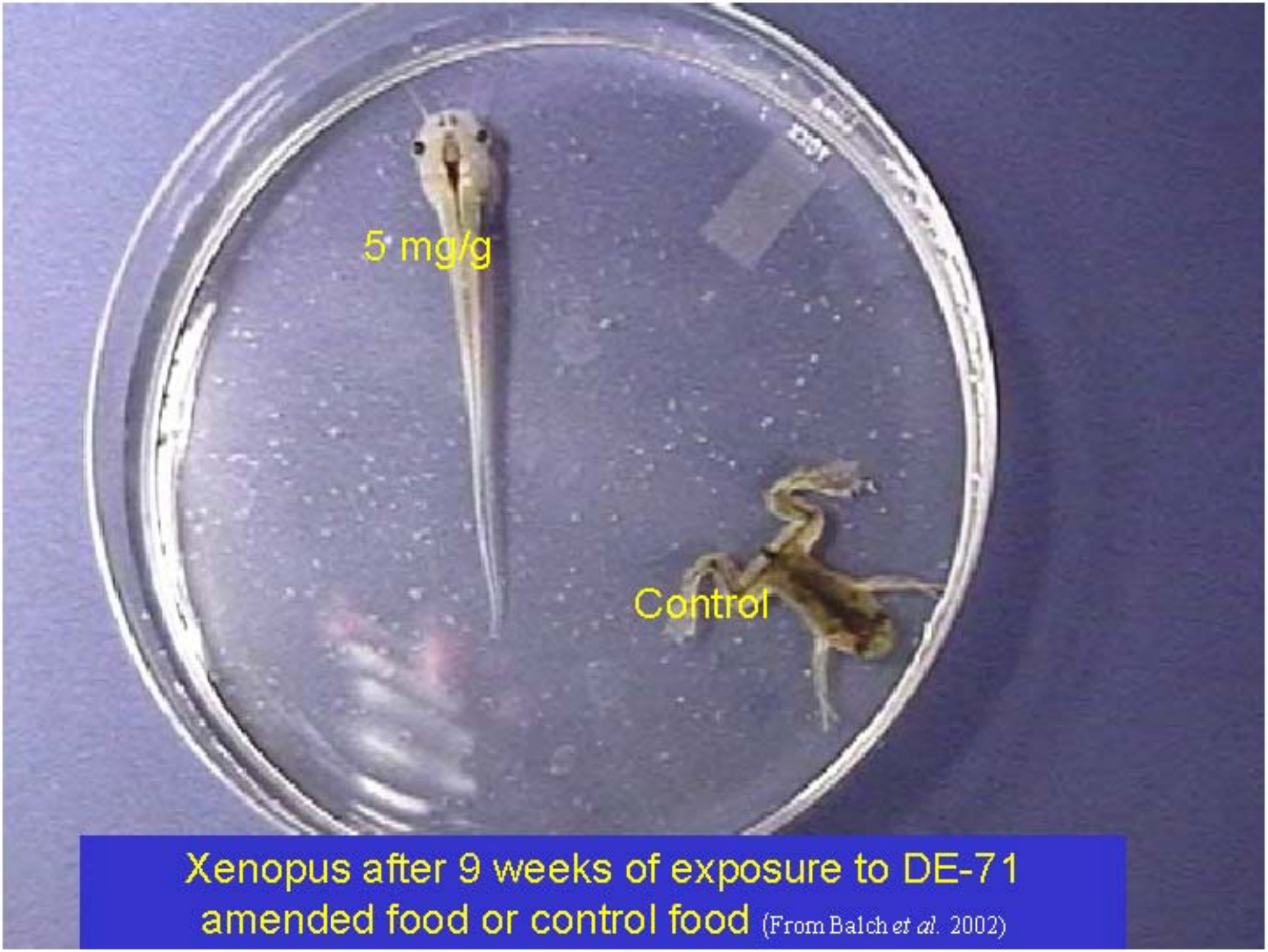
1 mg / g DE-71

Acetone Control

Developmental condition at 6 weeks of age

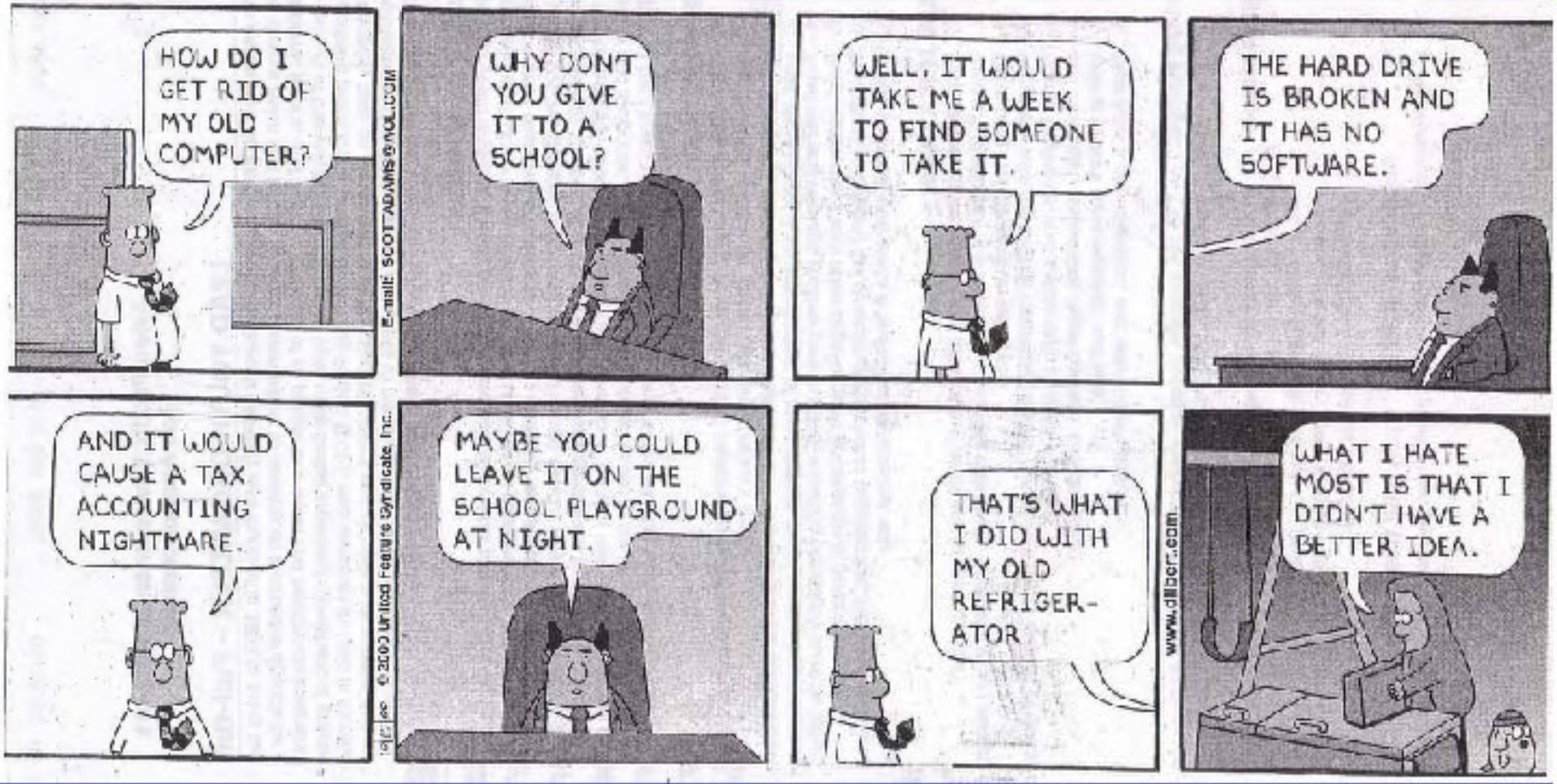
Environment Canada Environnement Canada

From Balch *et al.* 2002



Xenopus after 9 weeks of exposure to DE-71 amended food or control food (From Balch *et al.* 2002)


Future Trends...
•About 60 million new PC's enter market a year
•About 12 million PC and 10 million TV sets disposed of annually
•Estimated that 2 million tons of electronics equipment


HOW DO I GET RID OF MY OLD COMPUTER?
WHY DON'T YOU GIVE IT TO A SCHOOL?
WELL, IT WOULD TAKE ME A WEEK TO FIND SOMEONE TO TAKE IT.
THE HARD DRIVE IS BROKEN AND IT HAS NO SOFTWARE.
AND IT WOULD CAUSE A TAX ACCOUNTING NIGHTMARE.
MAYBE YOU COULD LEAVE IT ON THE SCHOOL PLAYGROUND AT NIGHT.
THAT'S WHAT I DID WITH MY OLD REFRIGER-ATOR
WHAT I HATE MOST IS THAT I DIDN'T HAVE A BETTER IDEA.
E-mail: SCOTTADAMS@AOL.COM
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