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University of Birmingham

CLASSICAL *versus* EMERGING FLAME RETARDANTS

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FLAME RETARDANT Research: from 2001 up to now …

FLAME RETARDANT Research: Collaboration with …

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Tim Grotenhuis	Wageningen University (The Netherlands)
Walter Vetter	Universität Hohenheim (Germany)
Mehran Alaee	Environment Canada (Canada)
Kim Fernie	Environment Canada (Canada)
Eric Reiner	University of Toronto (Canada)
Diana Aga	University of Buffalo (USA)
Jochen Mueller	National Research Centre for Environ. Toxicol. (Australia)
Ricardo Barra	University of Concepción (Chile)
Joao Torres	Federal University of Rio de Janeiro (Brazil)
William Ocampo	Pontificia Universidad Javeriana (Colombia)

CLASSICAL *versus* EMERGING FLAME RETARDANTS

1. Introduction to Flame Retardants
2. PBDEs: Penta-, Octa- and Deca-BDE
3. HBCD: Isomers and Enantiomers
4. Halogenated Norbornenes
5. Conclusions

1 Introduction to Flame Retardants

FLAME RETARDANTS: Materials added or applied to a material to increase the fire resistance of that product

- Inorganic (50%)
- **Brominated (25%)**
- Organophosphorous (20%)
- Nitrogen-based (5%)

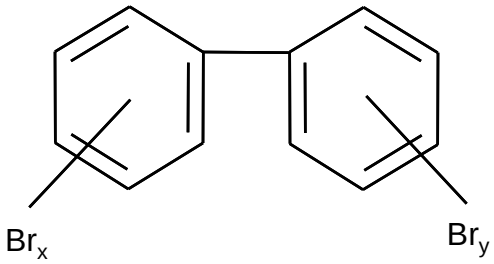
BFR Applications:

- Electronic circuitry
- Plastics
- Paper
- Wood
- Textiles
- Building materials

1 Chemical Structures of major BFRs

Polybrominated biphenyls (PBBs)

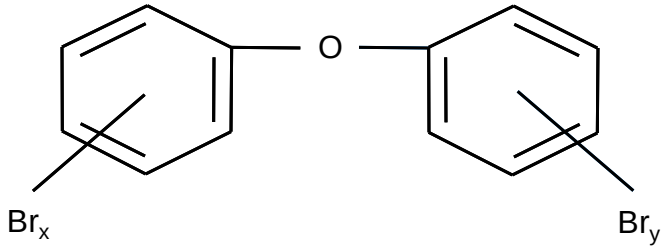
209 congeners



x + y = 1-10

Polybrominated diphenylethers (PBDEs)

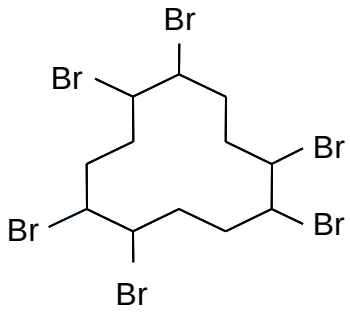
209 congeners



x + y = 1-10

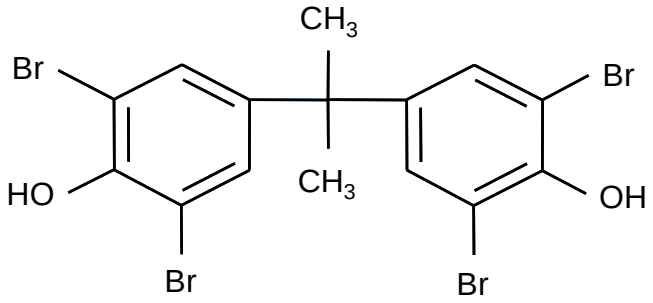
Hexabromocyclododecane (HBCD)

3 isomers



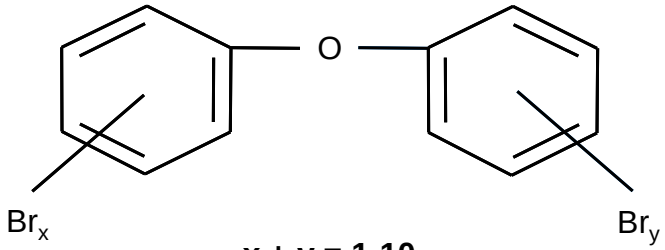
α-HBCD **β-HBCD** **γ-HBCD**

Tetrabromobisphenol A (TBBPA)



2 Technical mixtures of PBDEs

PBDEs
209 congeners



x + y = 1-10

PentaBDE Mixture

<0,2 % tri-BDEs (17,28)

24-37% tetra-BDEs (**47**)

50-60% penta-BDEs (**99**,**100**)

4-8% hexa-BDEs (153,154)

OctaBDE Mixture

10-12% hexa-BDEs

44% hepta-BDEs (**183**)

31-35% octa-BDEs

10-11% nona-BDEs

DecaBDE Mixture

97% deca-BDE (**209**)

2 Properties of PBDEs

- high chemical stability
- high lipophilicity

PERSISTENCY

BIOACCUMULATIVE POTENCY

TOXICITY

2 Environmental issues of PBDEs: Chronology

1970 Introduction of **BFRs** in consumer products

1973 Poisoning accident in the USA – **PBBs**

1979 **PBDEs** first detected in environment (soil and sludge) (USA)

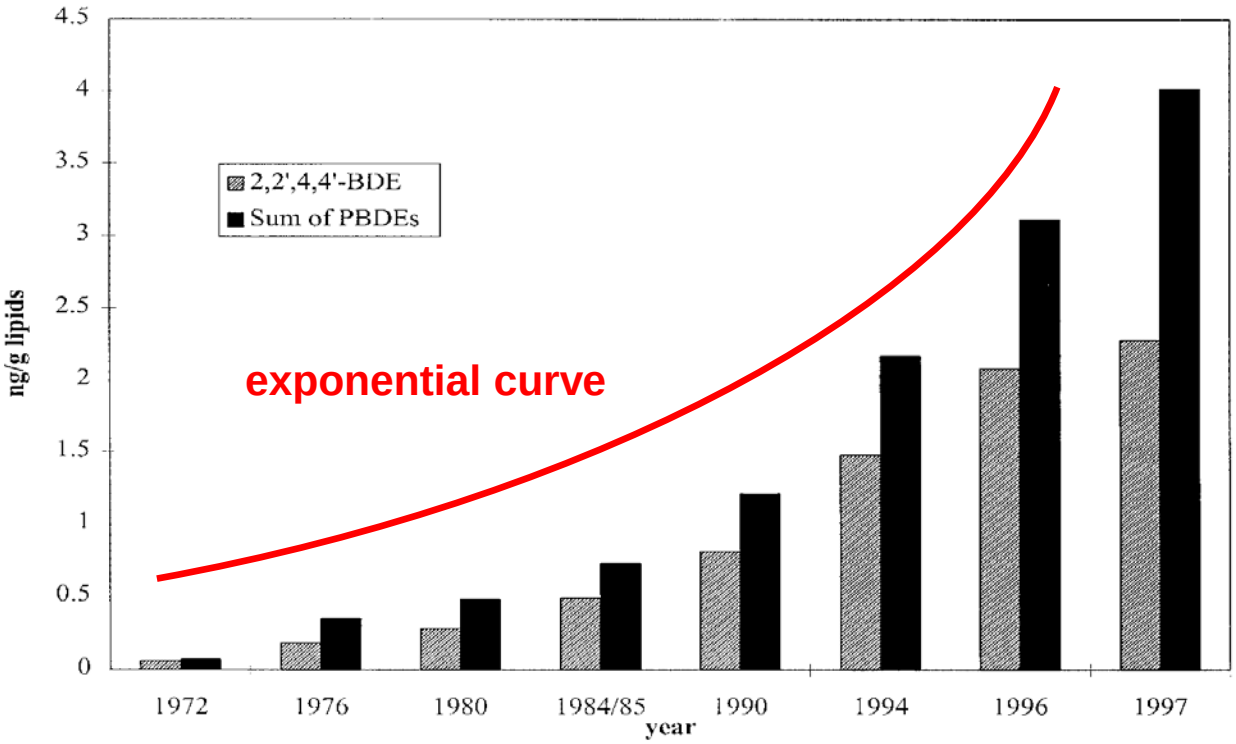
1981 **PBDEs** first discovered in fish river downstream from textile industries (Sweden)

1987 First indication of **PBDE** presence in remote areas - ubiquitous environmental contaminants

1999 Significant increase of **PBDEs** in human breast milk (10 times every 5 years)

2 Environmental issues of PBDEs: Chronology

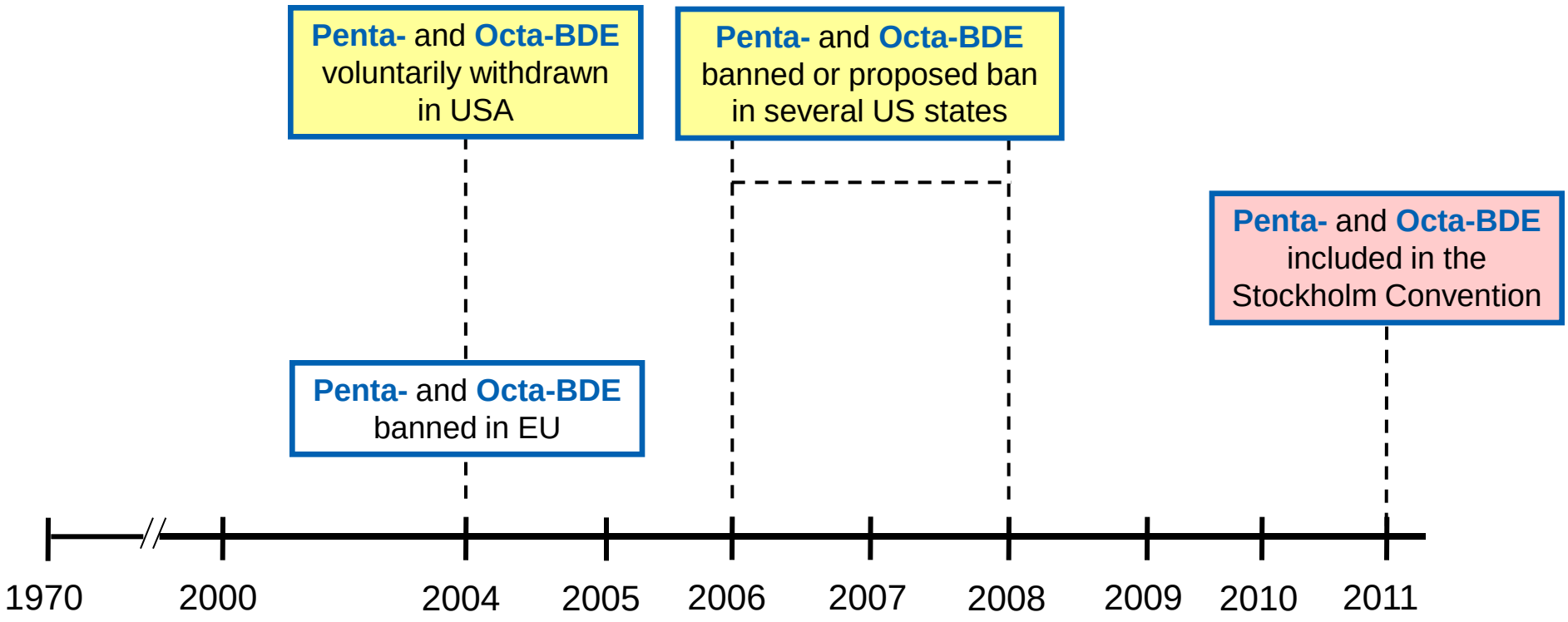
Concentrations of BDE-47 and ΣPBDEs in
Swedish human milk collected in different periods



1999 Significant increase of **PBDEs** in human breast milk (10 times every 5 years)

D. Meironyté, K. Norén, A. Bergman. J. of Toxicol. and Environ. Health, Part A, **1999**, 58, 329-341

2 Regulatory history of PBDEs



Stricter legal restrictions in Europe than in USA

2 BFR Production

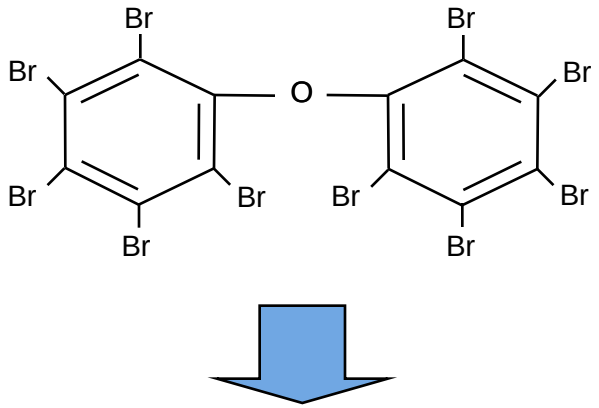
Usage of selected BFRs in different areas of the world in 2001 (in tonnes)

	America	Europe	Asia	Rest of the world	Total	% of total world usage
TBBPA	18000	11600	89400	600	119700	59
HBCD	2800	9500	3900	500	16700	8
Deca-BDE	24500	7600	23000	1050	56100	27
Octa-BDE	1500	610	1500	180	3790	2
Penta-BDE	7100	150	150	100	7500	4
Total	53900	29460	117950	2430	203790	

Penta-BDE and **Octa-BDE** mixtures have been banned in Europe. Then, their consumption has dropped in Europe, and a shift in production towards other BFRs like **Deca-BDE** and **HBCD** took place.

2 Deca-BDE: Environmental questions *(… 2004)*

Decabrominated diphenyl ether (BDE-209)



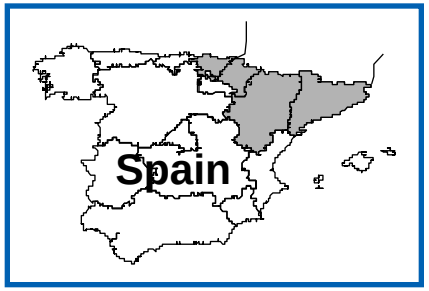
Experiments with caged fish (Rainbow trout and Juvenile carp) following dietary exposure showed a **slow but measurable uptake** of BDE-209 and the presence of lower brominated PBDEs (i.e. hexa-BDE-154)

- It may debrominate in the environment to form less-brominated BDE congeners, which are more bioavailable?
- It is bioavailable? Due to their large molecular size, their uptake rates decreased? Or, a rapid biotransformation increases their degradation rates?

H.M. Stapleton et al. Env. Sci. Technol. **2006**, 40, 4653 - 4658

2 Deca-BDE: CASE STUDY I

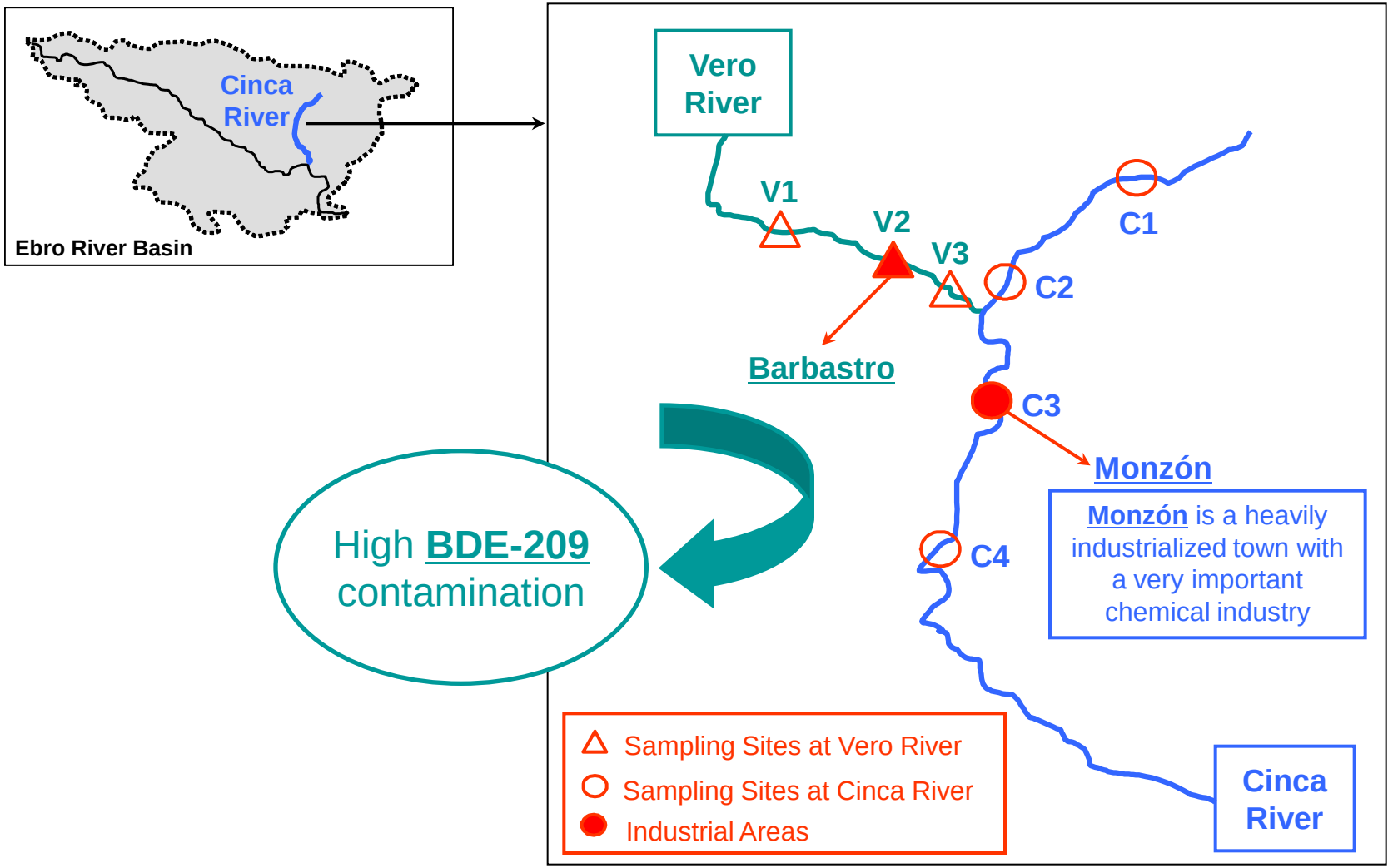
Integrated modelling of the river-sediment-soil-groundwater system; advanced tools for the management of catchment areas and river basins in the context of global change.



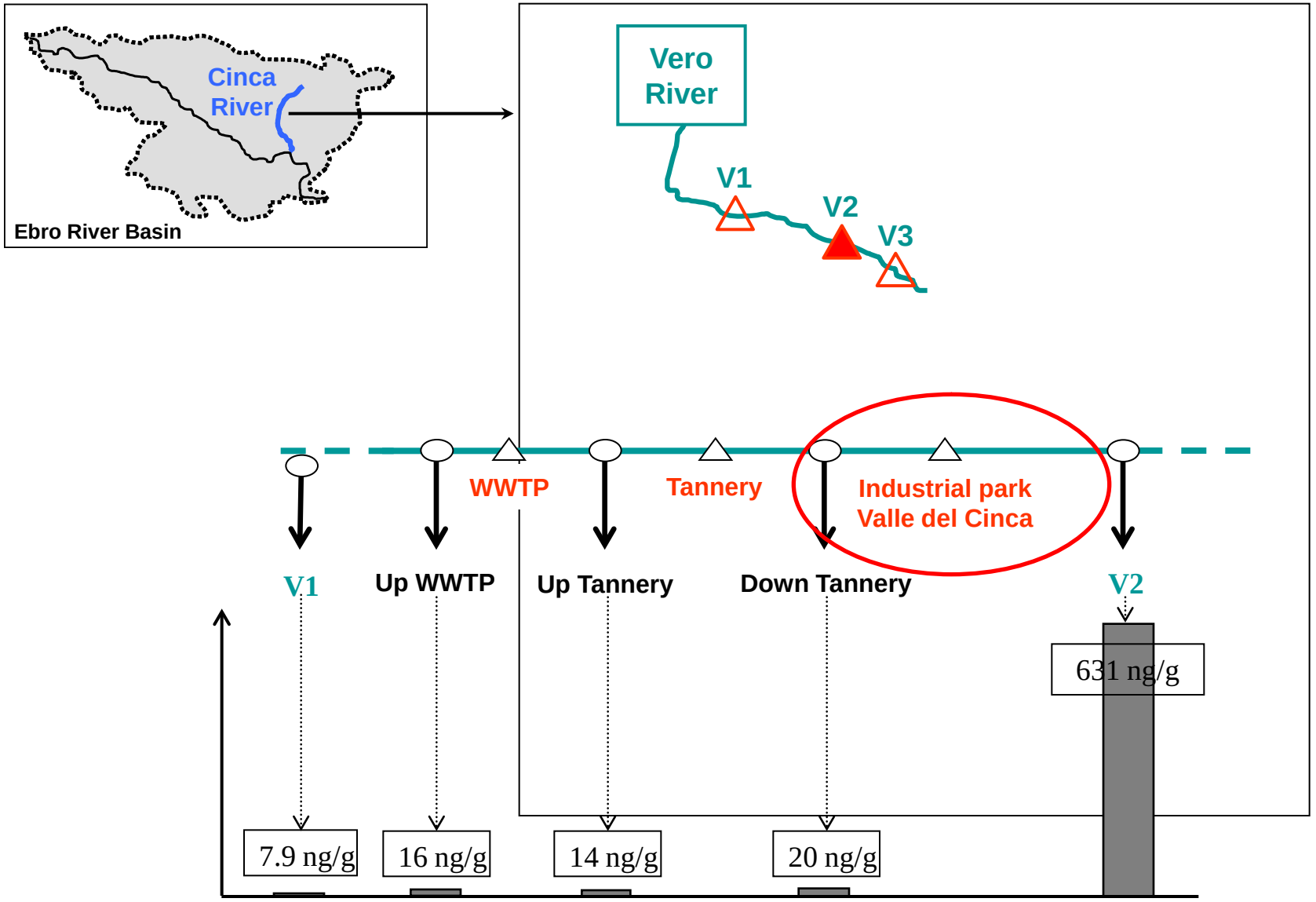
EBRO River Basin – RISK ZONES

E. Eljarrat, A. Labandeira, G. Marsh, D. Raldua, D. Barceló. Chemosphere, **2007**, 69, 1278-1286

2 CASE STUDY I – Sampling Sites



2 CASE STUDY I – Identification of Sources of Contamination



2 CASE STUDY I – Collected Samples

Identification of Sources of Contamination
Analysis of Industrial effluents

Three Industries:
- Textile Industry
  (Production of polyester fibers treated with flame retardants)
- Production of epoxy resins
- Polyamide polimerization

	BDE-209 (ng/L)
Polyester fibers production	5
Epoxy resins production	45
Polyamide polymerization	**2600**

2 CASE STUDY I – Collected Samples

	V1	V2	V3
2004	1 Sediment	1 Sediment	1 Sediment
	6 Barbel	-	8 Barbel
	-	-	2 Carp
2005	1 Sediment	1 Sediment	1 Sediment
	8 Barbel	-	5 Barbel

Sediment concentrations (expressed in ng/g dw)

	2004			2005		
	V1	V2	V3	V1	V2	V3
BDE-209	7.46	5395	1911	26.9	12459	7454
Total PBDEs	11.1	5531	1930	29.5	14395	7767

2 CASE STUDY I – Deca-BDE in Biota

Biota concentrations (expressed in ng/g lw)

Sampling: 2004
BDE-209 was detected in **9 out of 10** biota samples collected downstream an industrial park, at concentration levels ranging from **20 to 267 ng/g lipid weight**, whereas it was not detected in samples collected upstream

Sampling: 2005
BDE-209 was detected in **5 out of 5** biota samples collected downstream an industrial park, at concentration levels ranging from **69 to 773 ng/g lipid weight**, whereas it was not detected in samples collected upstream

Mean Value
67 ng/g lipid weight

Median Value
32 ng/g lipid weight

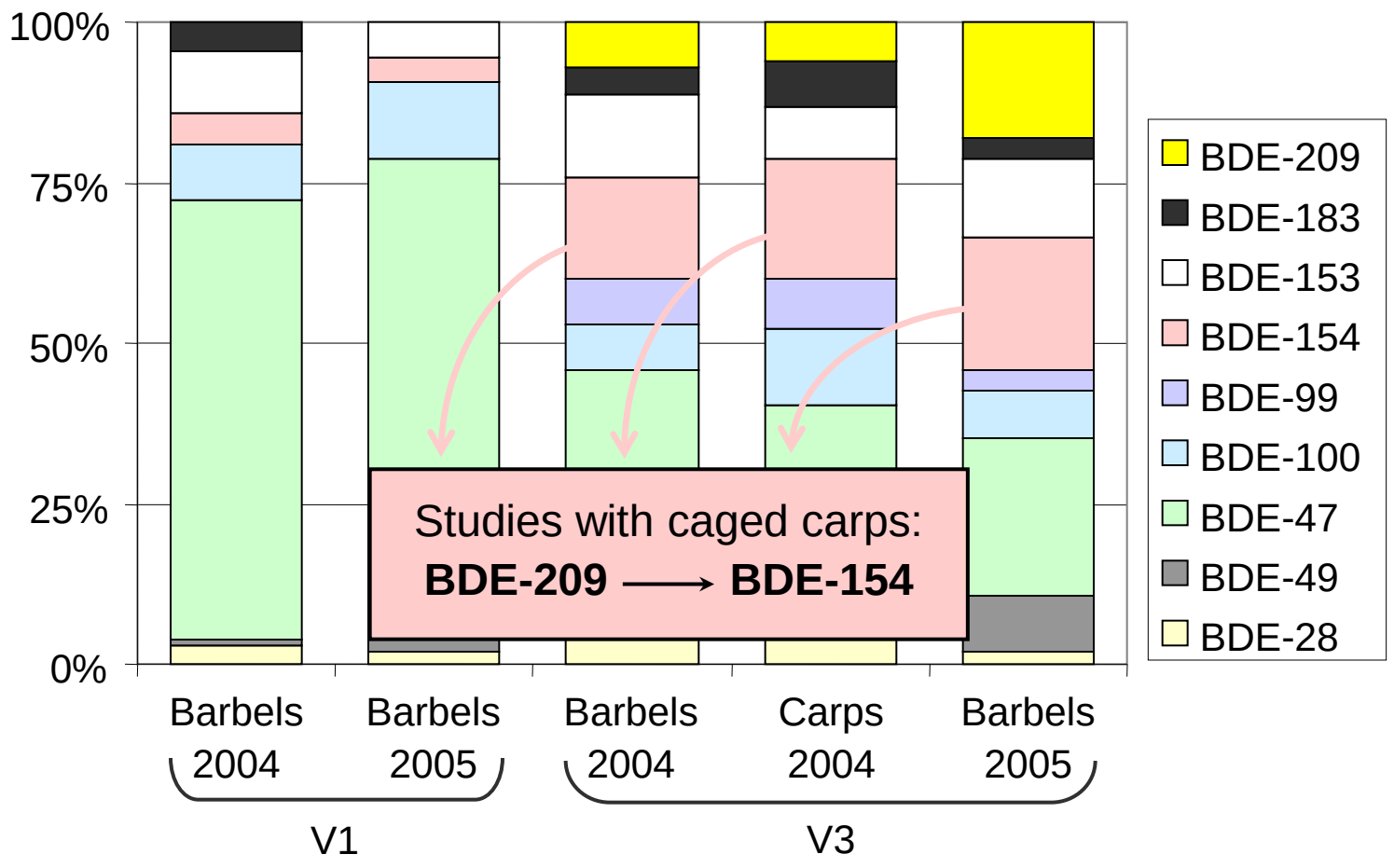
Increase of contamination with time

Mean Value
195 ng/g lipid weight

Median Value
86 ng/g lipid weight

2 CASE STUDY I – Deca-BDE in Biota

Percentage contribution of PBDE congeners to the ΣPBDEs



2 CASE STUDY I – Deca-BDE in Biota

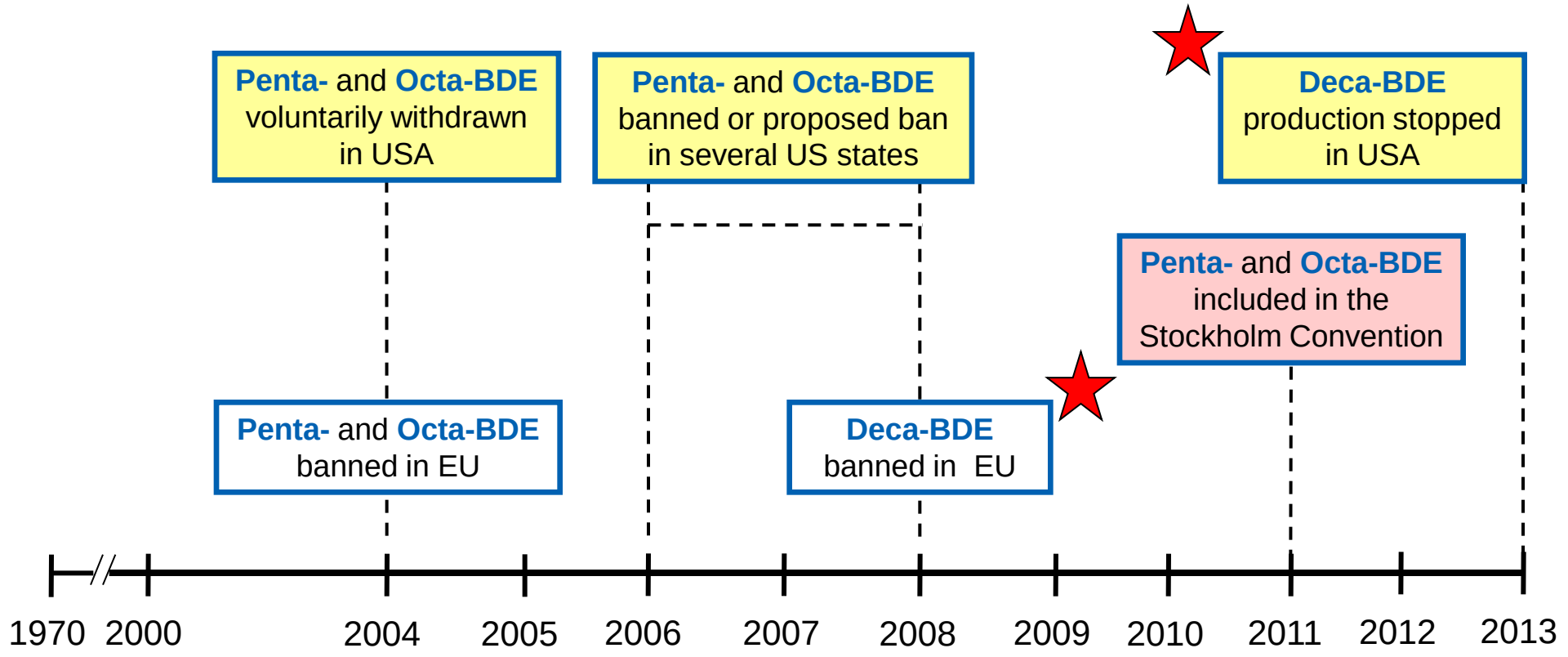
Fish to Sediment ratios

Ratios between concentrations of PBDEs in barbels (ng/g lw) and concentrations in sediments (ng/g organic carbon)

	V1		V3	
	2004	2005	2004	2005
Tetra-BDE-47	3.83	1.82	4.91	0.67
Hepta-BDE-183	0.05	-	0.09	0.13
Deca-BDE-209	-	-	**0.0013**	**0.0011**

Fish to sediment ratios very much lower for BDE-209.
Potential indication of recent release of BDE-209 from the industrial park, that contaminated the sediment but not yet take up by fish

2 Regulatory history of PBDEs

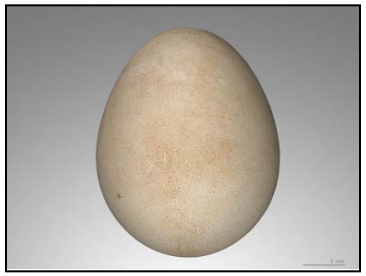


Stricter legal restrictions in Europe than in USA

2 Temporal trends of PBDEs

Bird eggs from Spain

White stork
Ciconia Ciconia



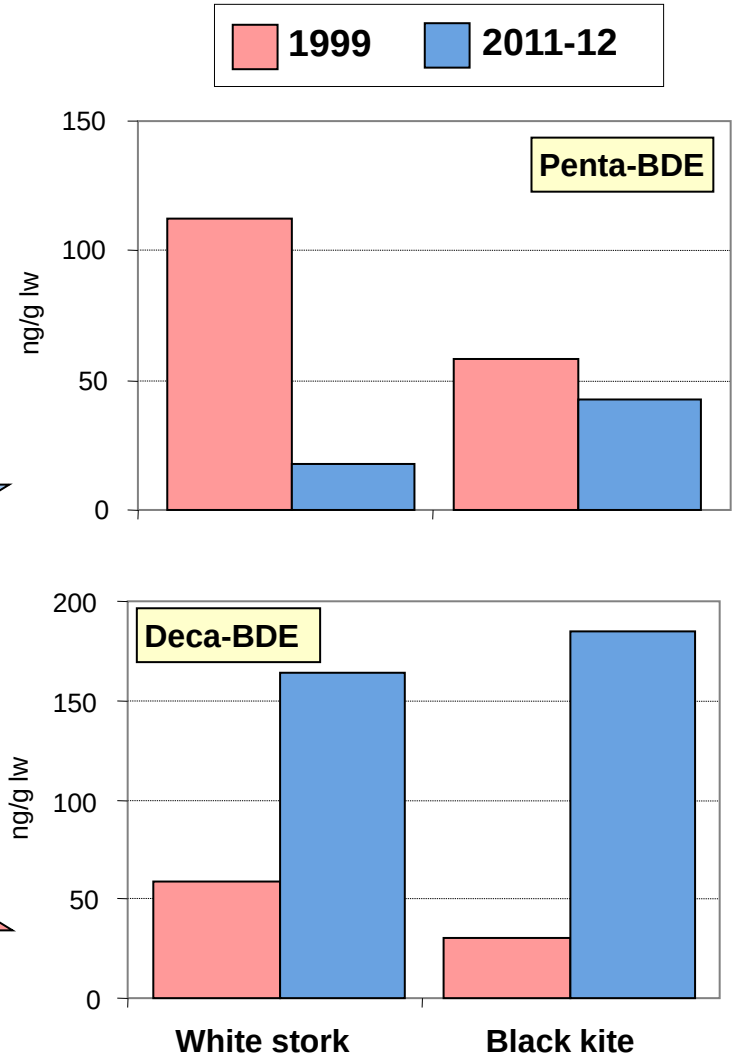
1999 **10 samples**
2011-12 **7 samples**

Black kite
Milvus Migrans

1999 **10 samples**
2011-12 **8 samples**

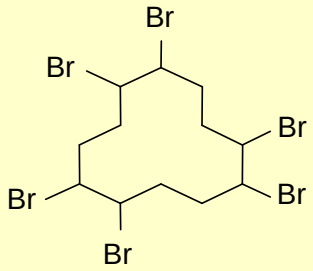
Penta mixture banned in 2004

Deca mixture banned in 2008



3 Hexabromocyclododecane: HBCD Environmental questions *(… 2004)*

Hexabromocyclododecane (HBCD)
3 isomers



α- HBCD **β- HBCD** **γ- HBCD**

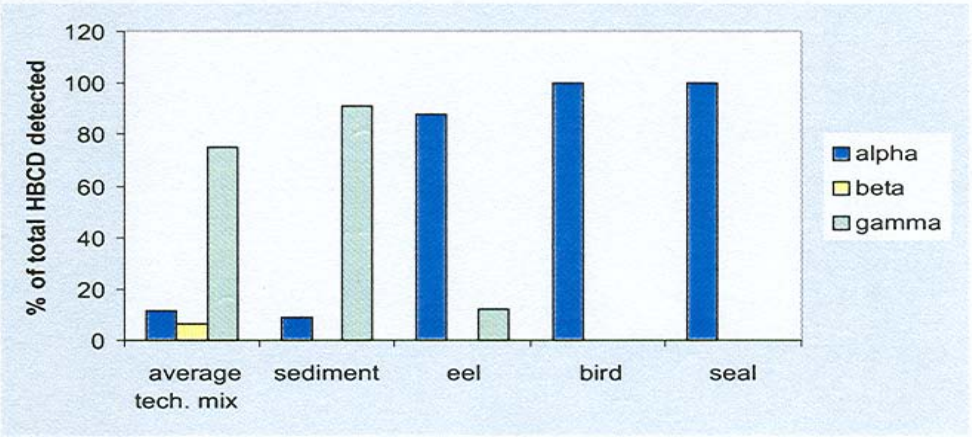


Fig. 2. HBCD diastereomeric distribution in an average technical HBCD mixture compared to different aquatic environmental compartments.

Technical Mixture

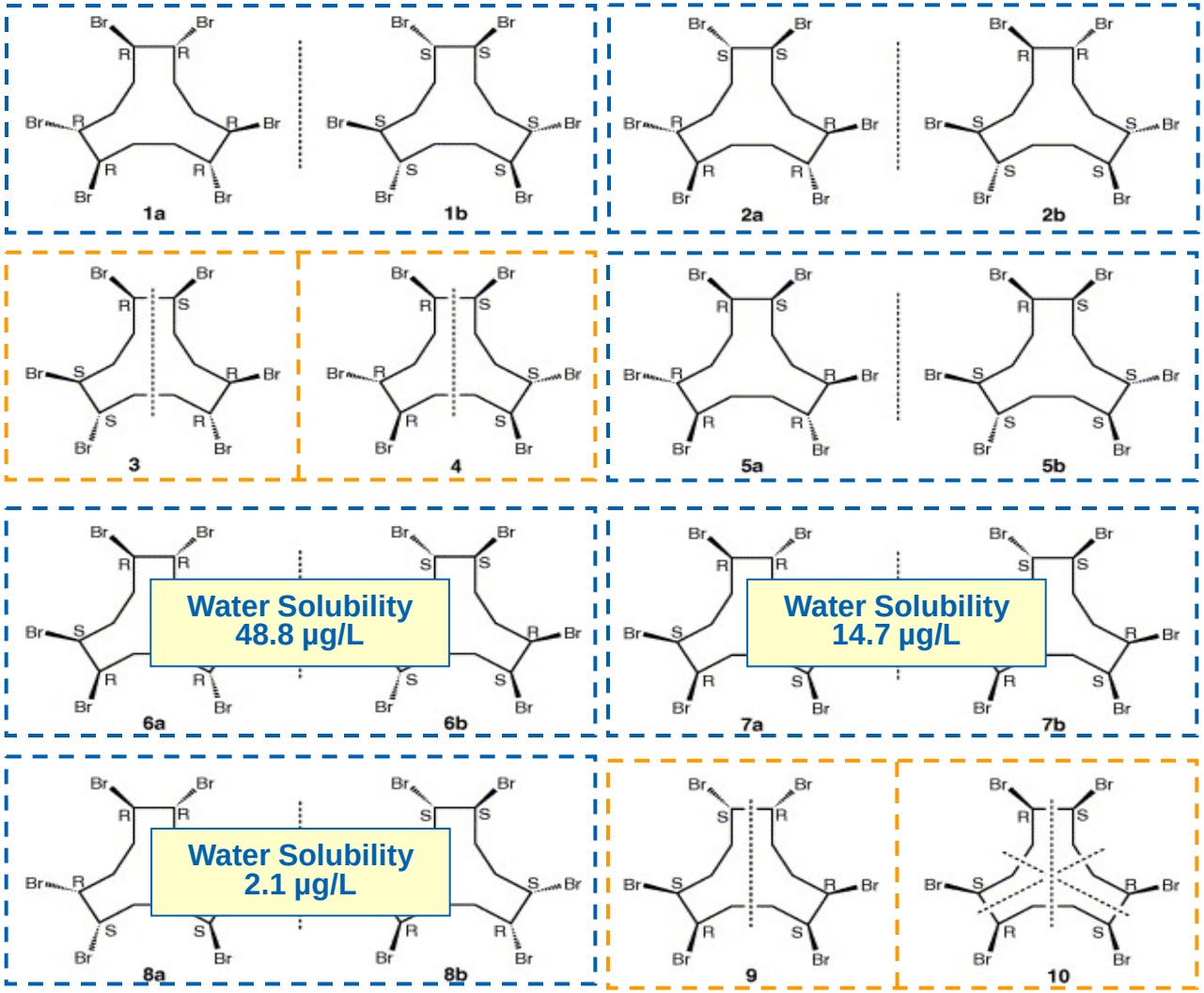
α- HBCD 10-13%

β- HBCD 1-12%

γ- HBCD 75-89%

Alpha is more bioavailable than gamma? Or, their bioaccumulation factor is greater? Or, biotransformation occur from gamma to alpha?

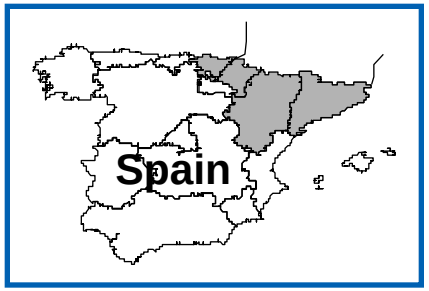
3 Hexabromocyclododecane: HBCD



16 possible stereoisomers: six pairs of enantiomers and four meso forms

3 HBCD: CASE STUDY I

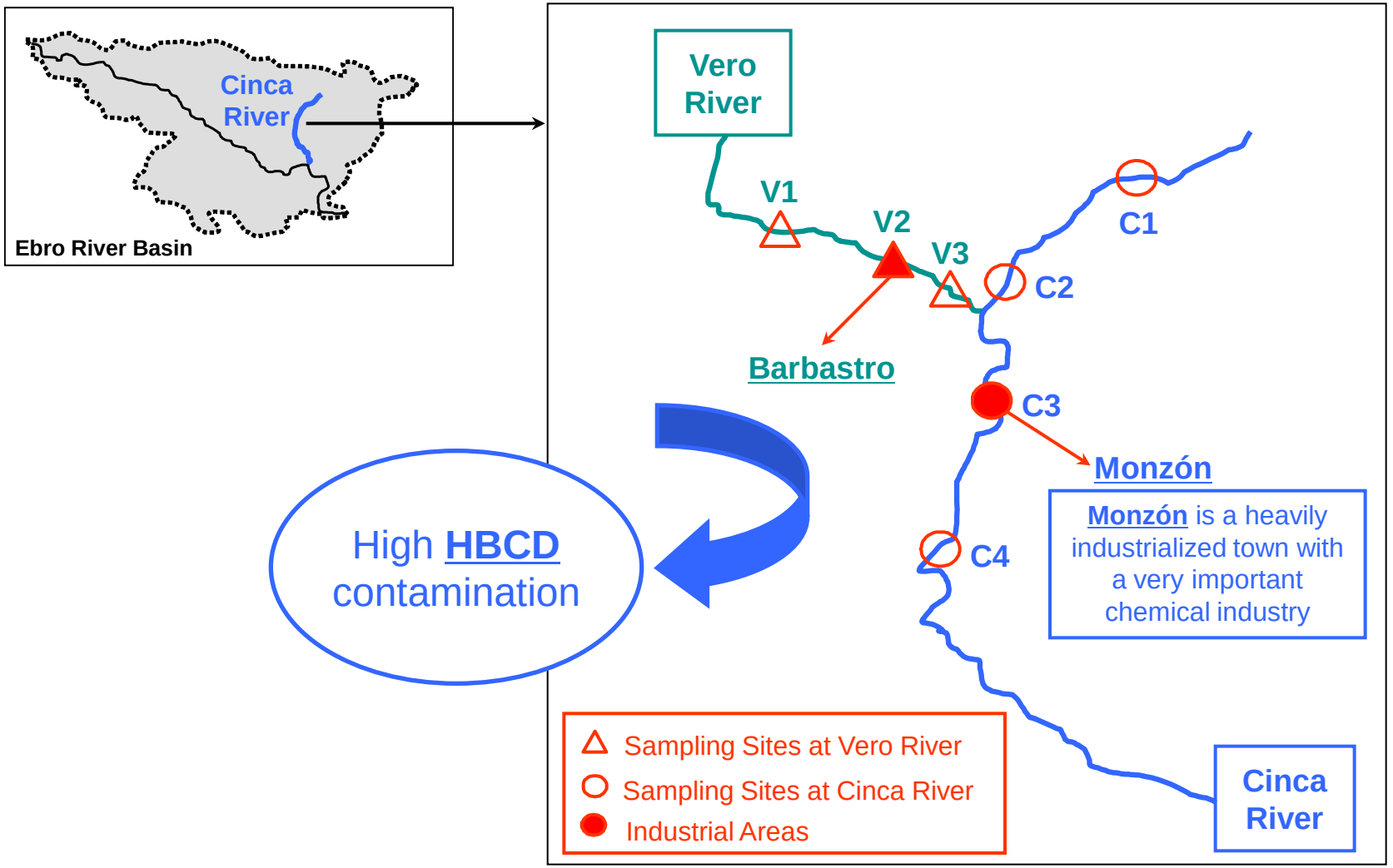
Integrated modelling of the river-sediment-soil-groundwater system; advanced tools for the management of catchment areas and river basins in the context of global change.



EBRO River Basin – RISK ZONES

E. Eljarrat, A.de la Cal, D.Raldúa, C.Duran, D.Barceló. Environ. Sci. Technol., **2004**, 38, 2603-2608
E.Eljarrat, A.de la Cal, D.Raldúa, C.Duran, D.Barceló. Environ. Pollut., **2005**, 133, 501-508
P. Guerra, A. de la Cal, G. Marsh, E. Eljarrat, D.Barceló. J. of Hydrol**., 2009**, 369, 360-367

3 CASE STUDY I – Sampling Sites



3 CASE STUDY I – Collected Samples

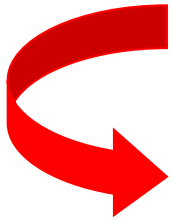
Identification of Sources of Contamination
Analysis of Industrial effluents

Two Industries:
- Production of EPS (Expandable polystyrene) treated with flame retardants and ABS (Acrylonitrile -butadiene-styrene)
- Production of PVC

	HBCD (ng/L)
EPS and ABS production	**4980**
PVC production	nd

3 CASE STUDY I – HBCD in Sediment and Biota

	2002				2004			
	C1	C2	C3	C4	C1	C2	C3	C4
Sediment	nd	nd	514 ng/g dw	90 ng/g dw	nd	nd	1613 ng/g dw	866 ng/g dw
Fish	nd	nd	0.2-1.6 µg/g ww	0.02-1.1 µg/g ww	nd	nd	-	52-104 µg/g lw



Increase of contamination with time

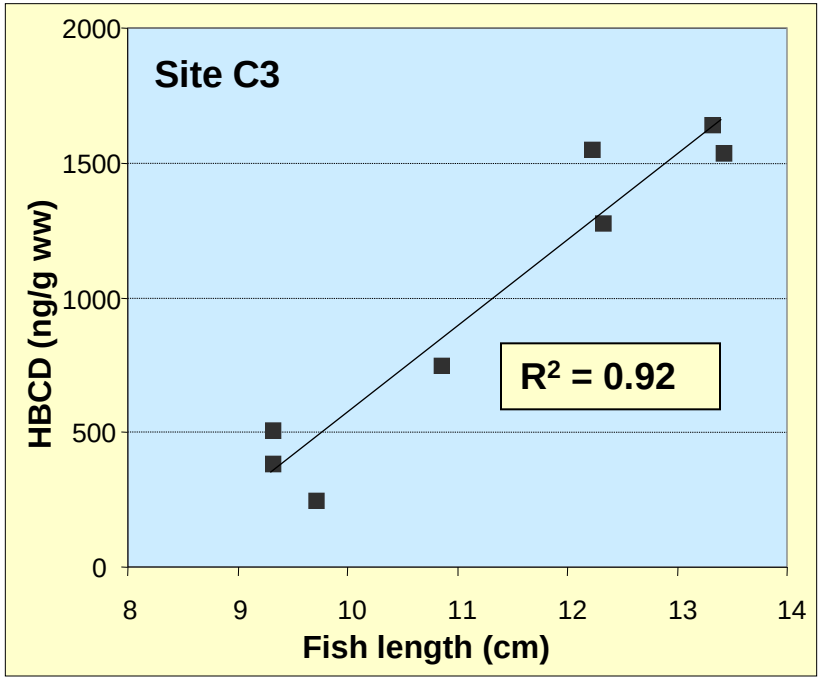
104 µg/g lw =

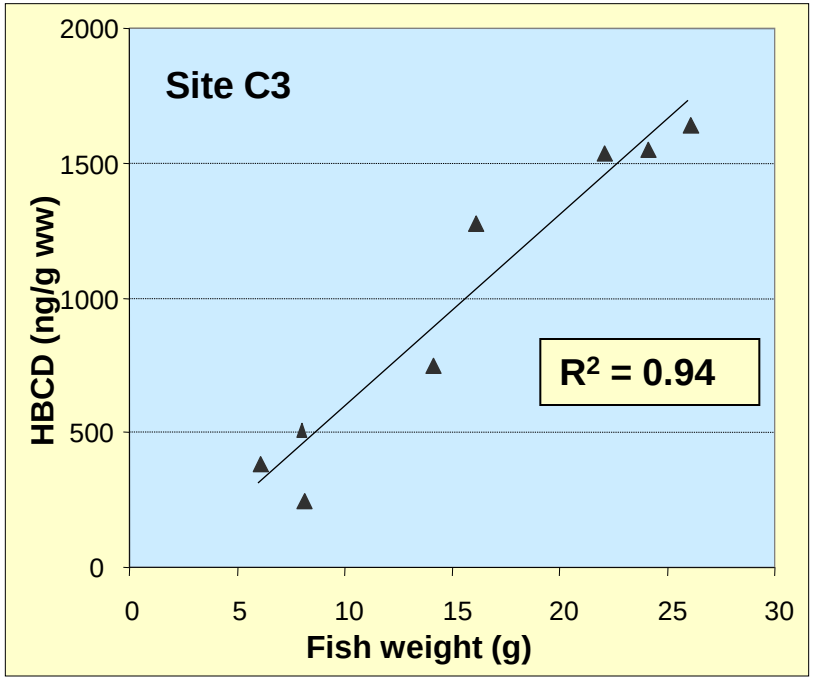
= 12 µg/g ww

3 CASE STUDY I – HBCD Bioaccumulation

Fish length and weight are directly related to fish age

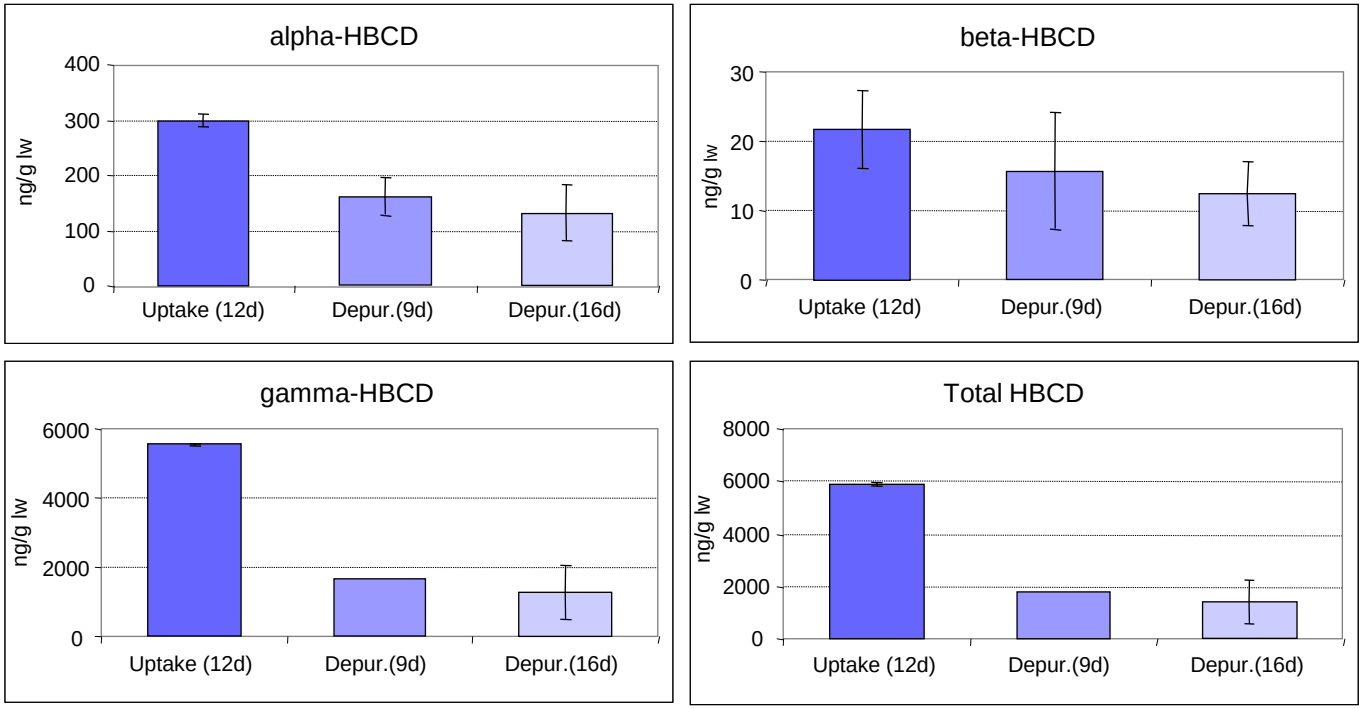
Length and Weight versus [HBCD]





3 CASE STUDY I – HBCD Depuration

Zebrafish (*Danio rerio*) were exposed to an industrial effluent (diluted 1:500) for 12 days. Then, depuration was studied after 9 and 16 days



Depuration rates for alpha and beta isomers (46 and 27% after 9 days, respectively) were lower than that of gamma isomer (70% after 9 days)

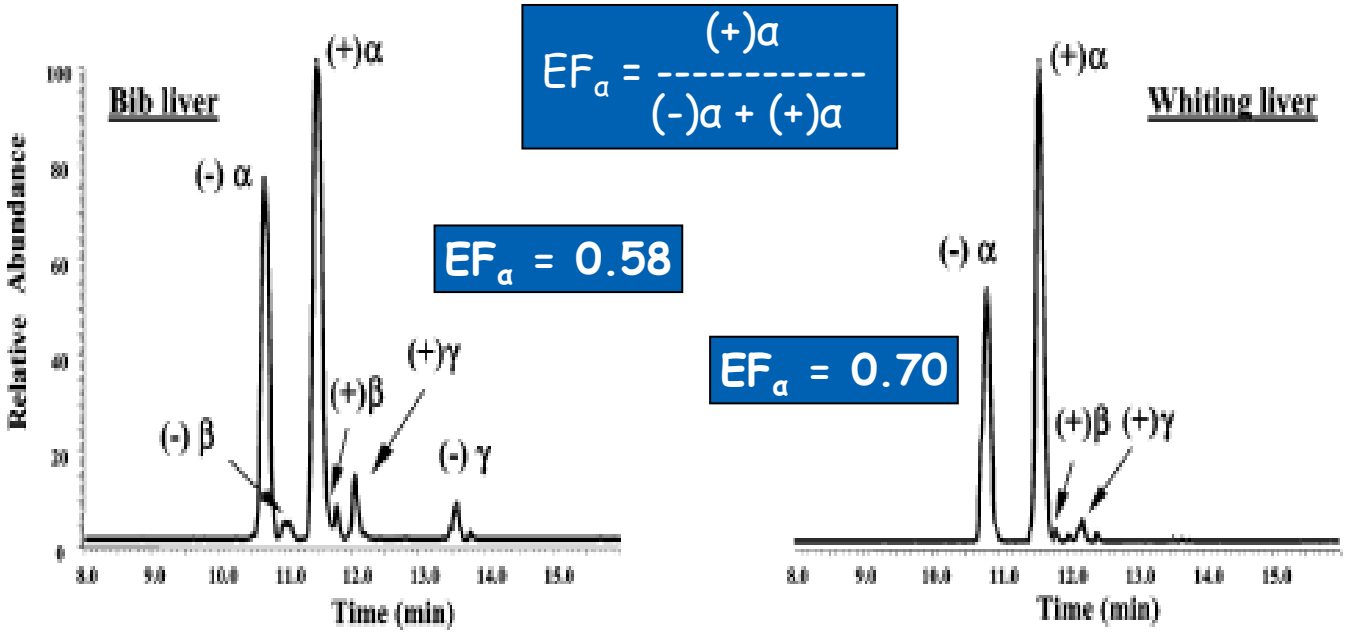
3 CASE STUDY II – HBCD in human milk

ENANTIOMERIC ACCUMULATION
Enantiomeric Fraction (EF)

$$EF = \frac{(+)\,A}{(-)\,A + (+)A}$$

where A+ and A- correspond to the peak areas of eluting enantiomers

HBCD in marine species



E. Eljarrat *et al*. Environ. Sci. Technol., **2009,** 43, 1940-1946

3 CASE STUDY II – HBCD in human milk

Samples from Spain

Concentration levels (ng/g lw)

33 samples analysed

HBCD detected in 31 samples

30 samples quantified

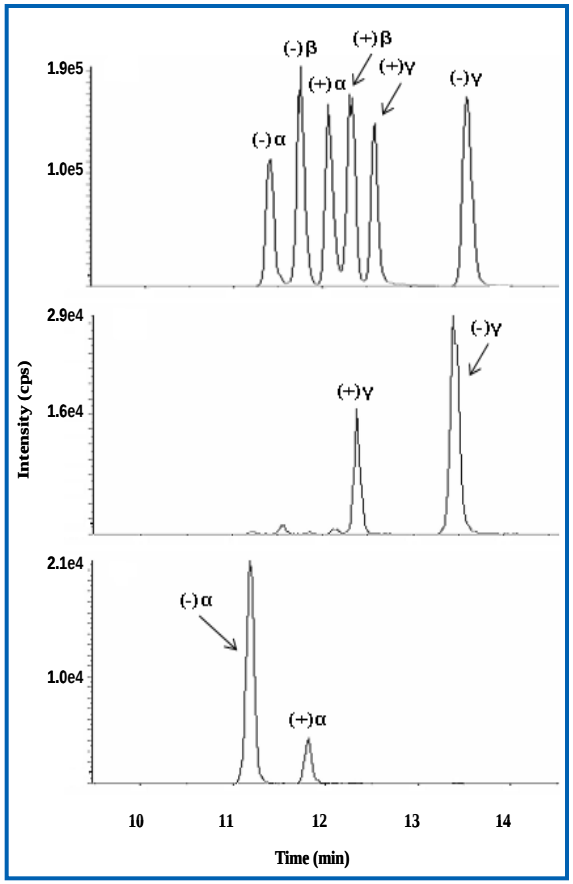
Sample Code	α-HBCD	β-HBCD	γ-HBCD	Total HBCDs
L-1	12	nd	176	188
L-2	1.59	nd	141	143
L-3	nq	nq	67	67
L-4	0.13	nq	69	69
L-5	0.3	nd	7.8	8.1
L-6	5.35	nd	22.6	28.0
L-7	nq	nq	27	27
L-8	2.2	nd	16	18
L-9	2.82	nd	13.7	16.5
L-10	nq	nd	7.9	7.9
L-11	2.21	nd	23.1	25.3
L-13	nq	nd	21.7	21.7
L-14	nd	nd	nd	nd
L-16	nd	nd	nd	nd
L-18	71.5	nq	nq	71.5
L-19	7.5	nd	29	37
L-20	18	nd	54	71
L-21	10	nd	25	35
L-22	19	nd	23	42
L-23	3.9	nd	9.5	13
L-24	1.1	nd	62	63
L-25	14	nd	9.1	23
L-26	1.8	nd	1.0	2.8
L-27	4.9	nd	61	65
L-28	14.7	nd	134	148
L-29	3.6	nd	nq	3.6
L-30	9.5	nd	18	28
L-31	2.1	nd	23	26
L-32	nq	nd	13	13
L-33	0.80	nd	5.4	6.2
L-34	nq	nd	nq	nq
L-35	2.8	nd	nq	2.8
L-36	122	nd	14.2	136

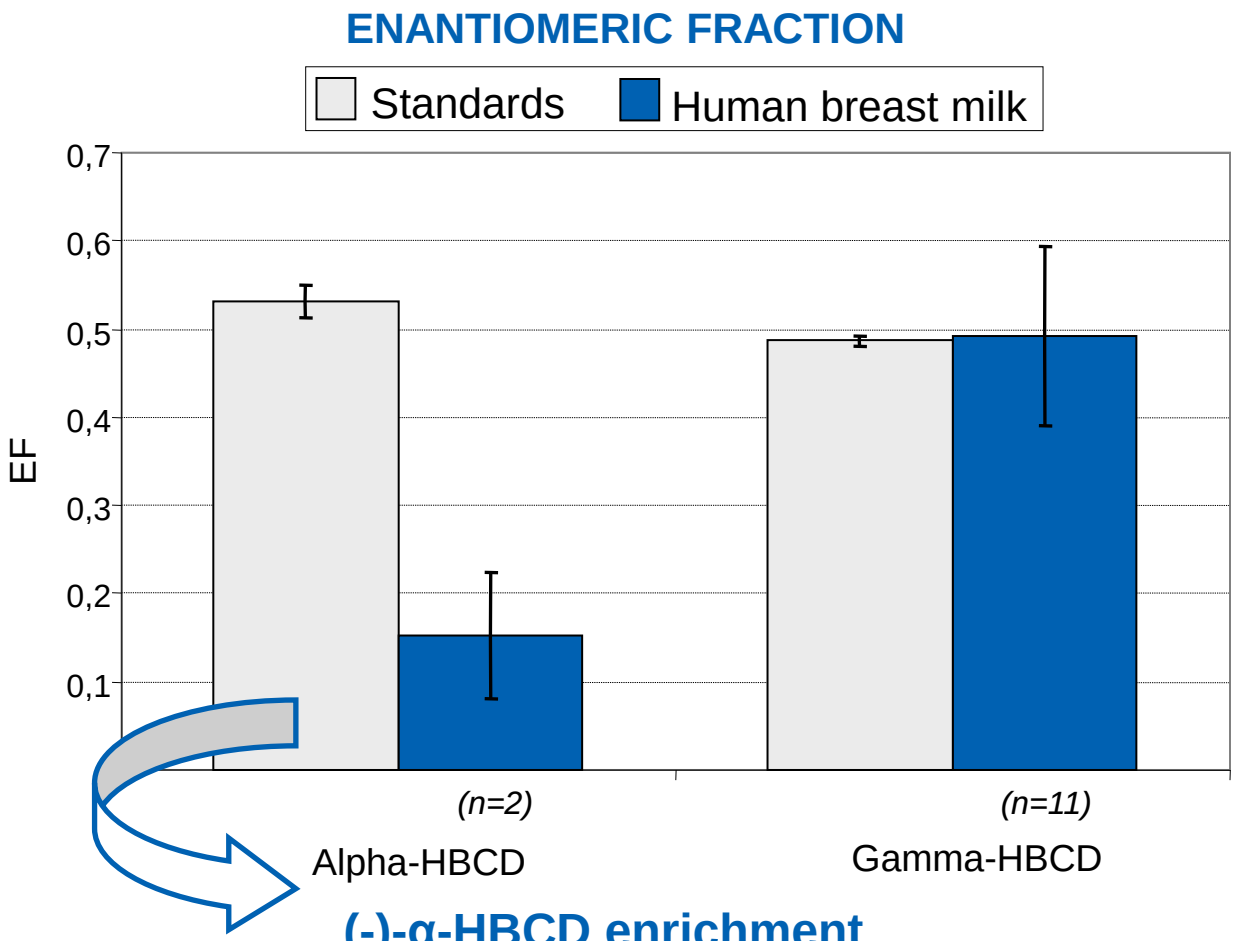
3 CASE STUDY II – HBCD in human milk

HBCD concentrations in human breast milk from different countries
Results expressed in ng/g of lipid weight

Country	Year	α-HBCD	β-HBCD	γ-HBCD	Total HBCD	Positive (n)
Sweden	2001	nr	nr	nr	ND-2.4	12 (33)
	2002-2003	nr	nr	nr	ND-1.5	24 (30)
Norway	2001	nr	nr	nr	0.25-2.0	nr (9)
	1993-2001	nr	nr	nr	0.4-20	49 (85)
Mexico	nr	nr	nr	nr	0.8-5.4	7(7)
Canada	2002-2003	3.8	nr	nr	0.4-19	nr (8)
USA	2002	0.5	nr	nr	0.2-0.9	nr (9)
Japan	1973-1988	ND	ND	ND	ND	nr
	1988-2006	0.43-1.9	ND	ND-2.6	0.43-4.0	11 (11)
Russia	2000-2002	nr	nr	nr	ND-1.67	11 (37)
France	2005	ND-5	ND	ND	ND-5	7 (23)
Spain	**2006-2007**	**ND-122**	**ND**	**ND-176**	**ND-188**	**30 (33)**

3 CASE STUDY II – HBCD in human milk



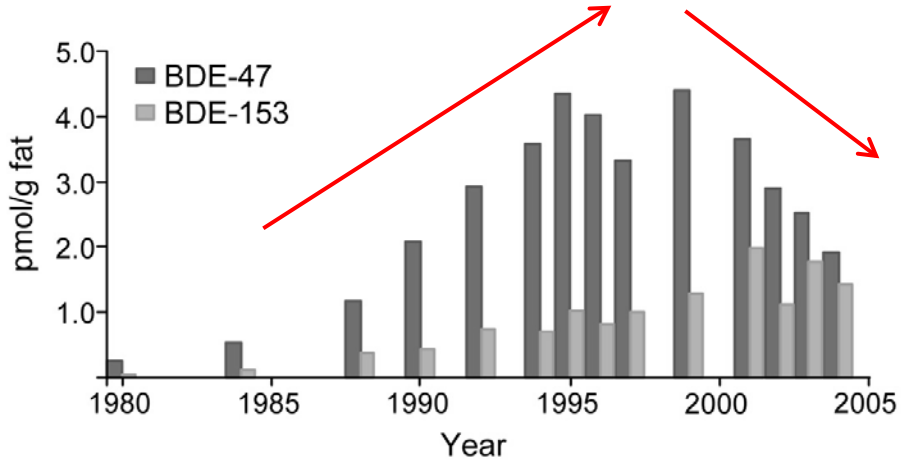


(-)-α-HBCD enrichment

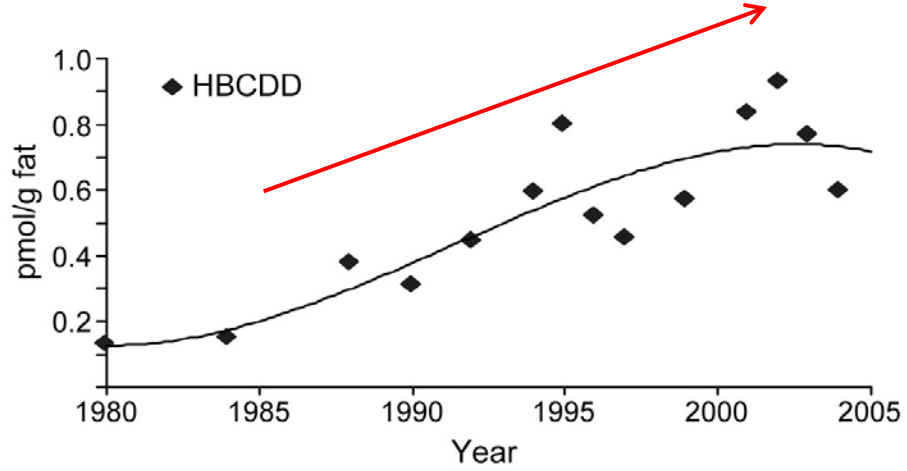
Selective enantiomeric enrichment in human body

3 Temporal trends: PBDEs *versus* HBCD

Temporal trend of BDE-47, BDE-153 and HBCD in milk samples from Sweden



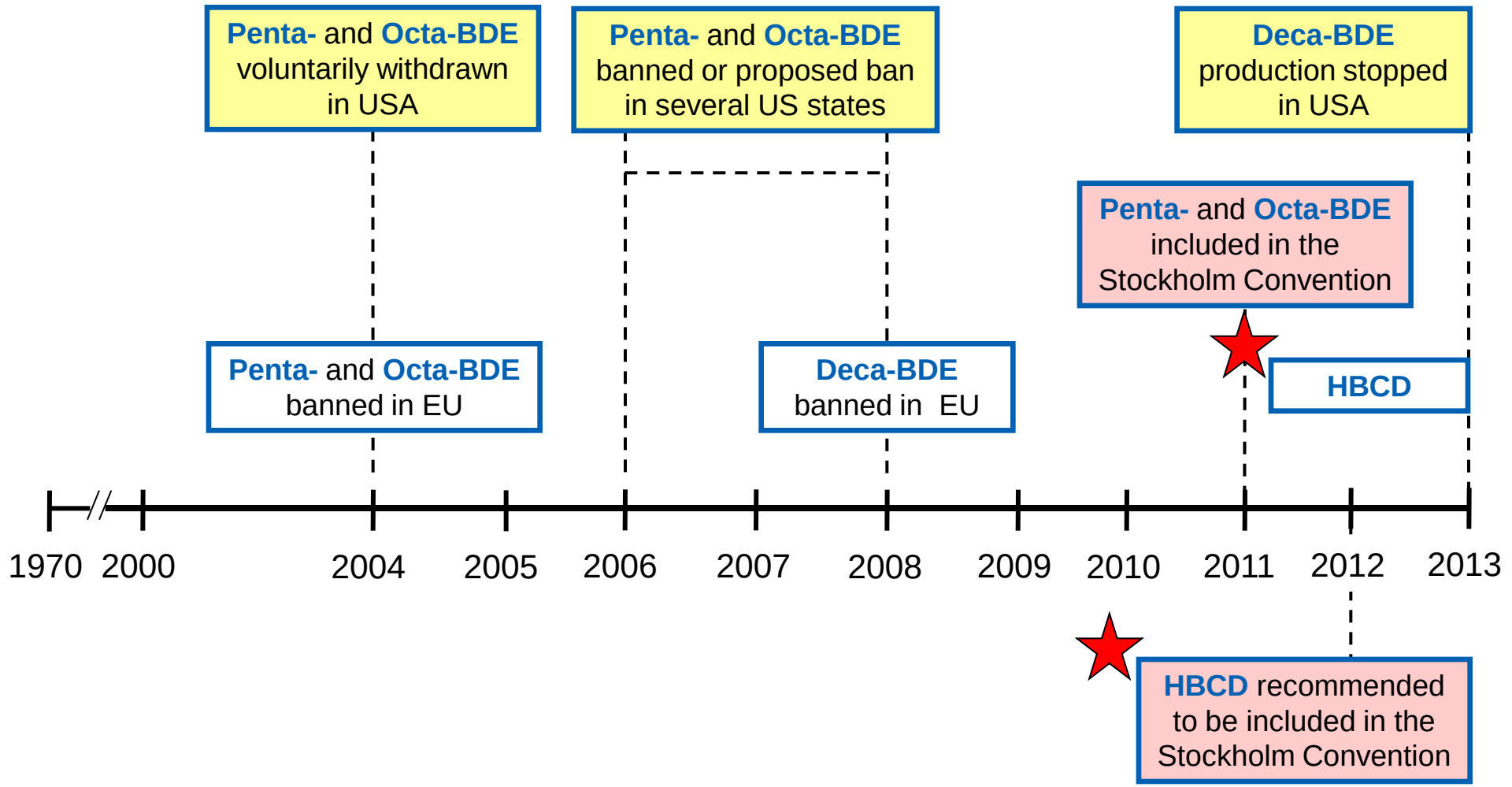
Penta- and **Octa-BDE** banned in EU (2004)



HBCD levels showed an increase, albeit not as pronounced as that yield before with PBDEs

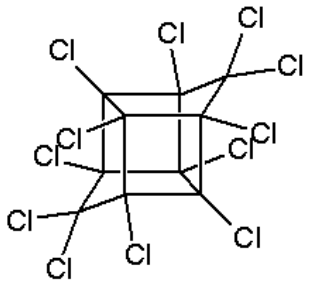
B. Fängström, I. Athanassiadis, T. Odsjö, K. Norén, A. Bergman. Mol. Nutr. Food Res. **2008**, 52, 187-193

3 Regulatory history of BFRs



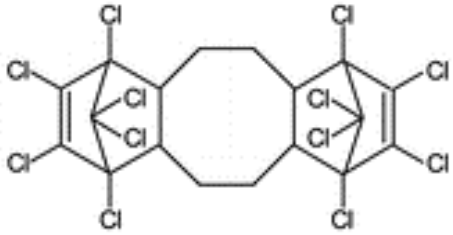
4 Halogenated Norbornenes (HNs)

Dechloranes



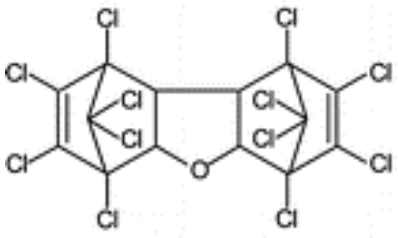
Mirex

Widely used as a pesticide and as FR to its ban in 1976.

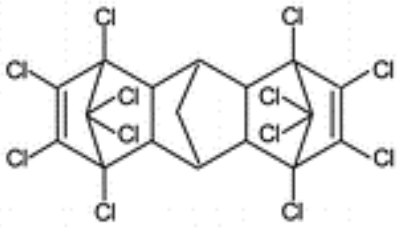


2 steroisomers:
syn- and ***anti-*DP**

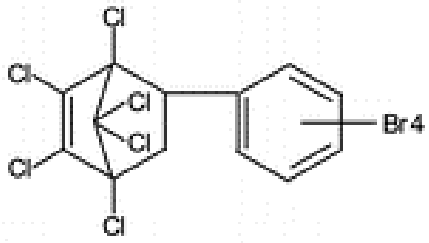
Dechlorane Plus (DP)



Dechlorane 602



Dechlorane 603



Dechlorane 604

4 Halogenated Norbornenes (HNs)

Physico-Chemical properties of Dechloranes

	Molecular Formula	Nominal mass (g/mol)	$LogK_{ow}$	Water solubility 25ºC, mg/l	LC_{50} µg/L
Dec 602	$C_{14}H_4Cl_{18}O$	614	8.05	$1.75e^{-5}$	n/a
Dec 603			11.2	$2.45e^{-8}$	n/a
Dec 604	$C_{13}H_4Br_4C$			$75e^{-8}$	n/a
DP	$C_{18}H_{12}Cl_{12}$	654	11.3	$1.68e^{-8}$	$>1e^5$

High chemical stability

High lipophilicity

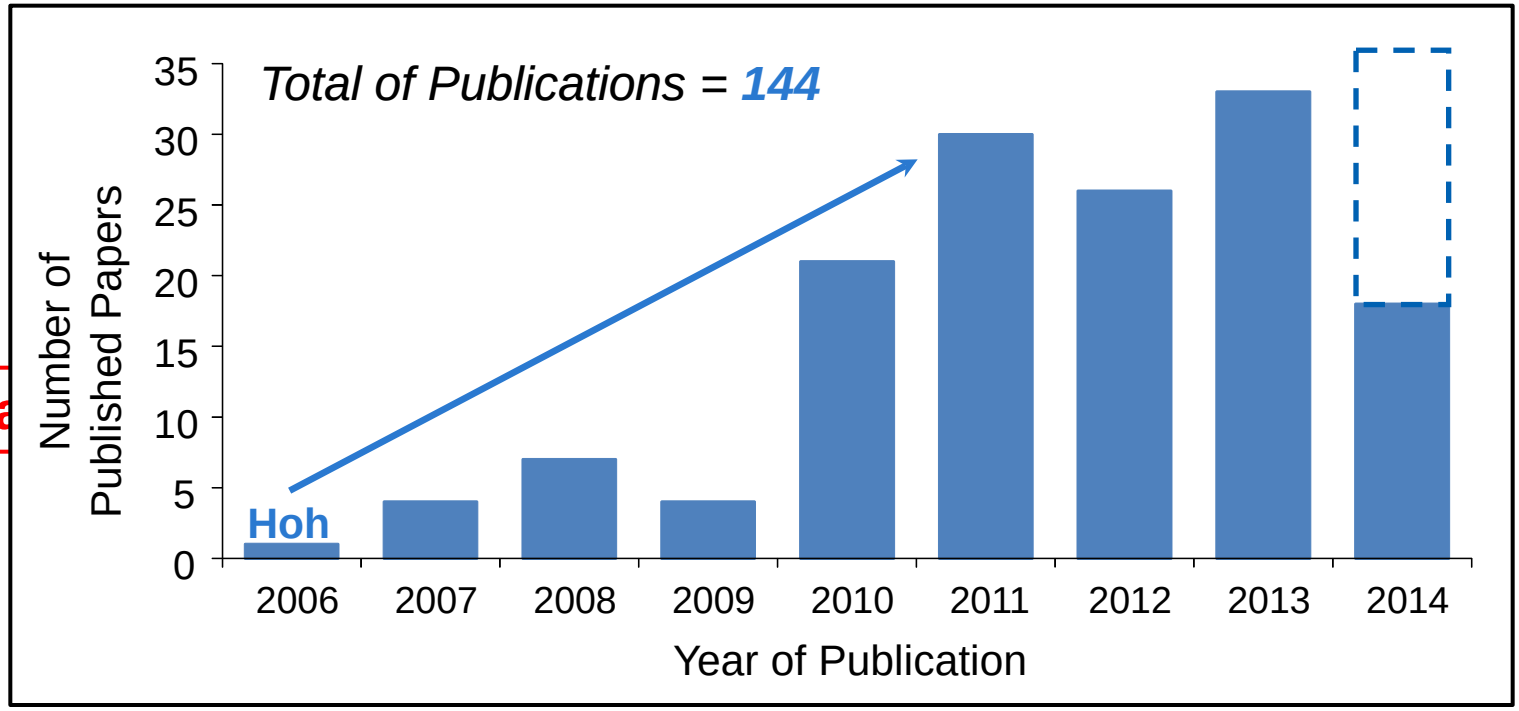
PERSISTENT

BIOACCUMULATIVE

4 Environmental issues of Dechloranes: Chronology

1976

30 yea



2006 First environmental report of **DP** (Hoh *et al*.)

2008 **Deca-BDE** banned in EU
DP is a potential replacement for **Deca-BDE**

2010 First environmental report of **Dechloranes 602, 603 and 604**

4 Halogenated Norbornenes (HNs)

Dechlorane plus (DP)

- **DP** is classified as a high production volume chemical in USA, but low production volume chemical in EU. Worldwide annual production volume is estimated at about 5000 t.
- **DP** applications: electrical hard plastic connectors, wire coatings and furniture.
- Manufacturers of **DP** include Oxychem (Buffalo, USA) and Anpon Electrochemical Co., Ltd (Jiangsu, China).

Dec 602, Dec 603, Dec 604

- **Dec 602** and **604** are listed in the *Canada's non domestic substance list* and in the *European Chemical Substances Information System*.
- **Dec 602** is usually used in nylon and **Dec 604** in electro-mechanical products.
- **Dec 603** is patented as FR but is also an impurity of the pesticides **Aldrin** and **Dieldrin**.
- **Dec 603** is usually used when the legal restrictions do not allow the use of **DP.**

4 Dechlorane Plus: State of the Art

- DP was first identified in the environment in 2006 (Hoh *et al*.). After that, some research has been performed on the occurrence and behavior of DP:
  - DP was detected in environment, biota and humans
  - Long-range atmospheric transportation of DP has been observed in remote areas
  - Behavior of the two isomers is not the same in the environment and in biota
- The main DP studies are focused near the two production facilities in China and USA. Very few studies in other regions of the world (Korea, Spain …)

4 Dechlorane Plus: Concentration Levels

Data on **Dec 602**, **603** and **604** concentration levels are even scarcer

	Near production facilities	Other regions of the world
Air	7300 – 26000 pg/m^3 (China)	Up to 15 pg/m^3
Indoor dust	2.3 – 5683 ng/g (Canada)	
Sediment	Up to 300 ng/g dw (Lake Ontario)	Up to 8 ng/g dw
	7000 ng/g dw (China)	
Soil	Up to 13400 ng/g dw (China)	Up to 5 ng/g
Sludge	45 – 194 ng/g dw	2 – 94 ng/g dw
Aquatic organisms	20 – 2000 ng/g lw (China)	Up to 11 ng/g lw
Terrestrial biota (Eggs)	38 – 65 ng/g lw (Great Lakes region)	Up to 2.5 ng/g lw
Humans	43 ng/g lw (**Blood**) (China)	Up to 8 ng/g lw (**Milk**)

Sverko *et al.,* Env. Sci. Technol **2011**, 45:5088-5098

Xian *et al.,* Env. Int. **2011**, 37:1273-1284

4 HNs: CASE STUDY III – HNs in Dolphins from Brazil

Franciscana (*Pontoporia blainvillei*)

Is the most impacted cetacean of the eastern coast of South America:

- included in the Brazilian government threatened species list (IBAMA, 2003)
- included in the Index II of the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES)
- included in the Red List of Threatened species (IUCN, 2008) as “Vulnerable”

Franciscana needs measures of conservation due to:

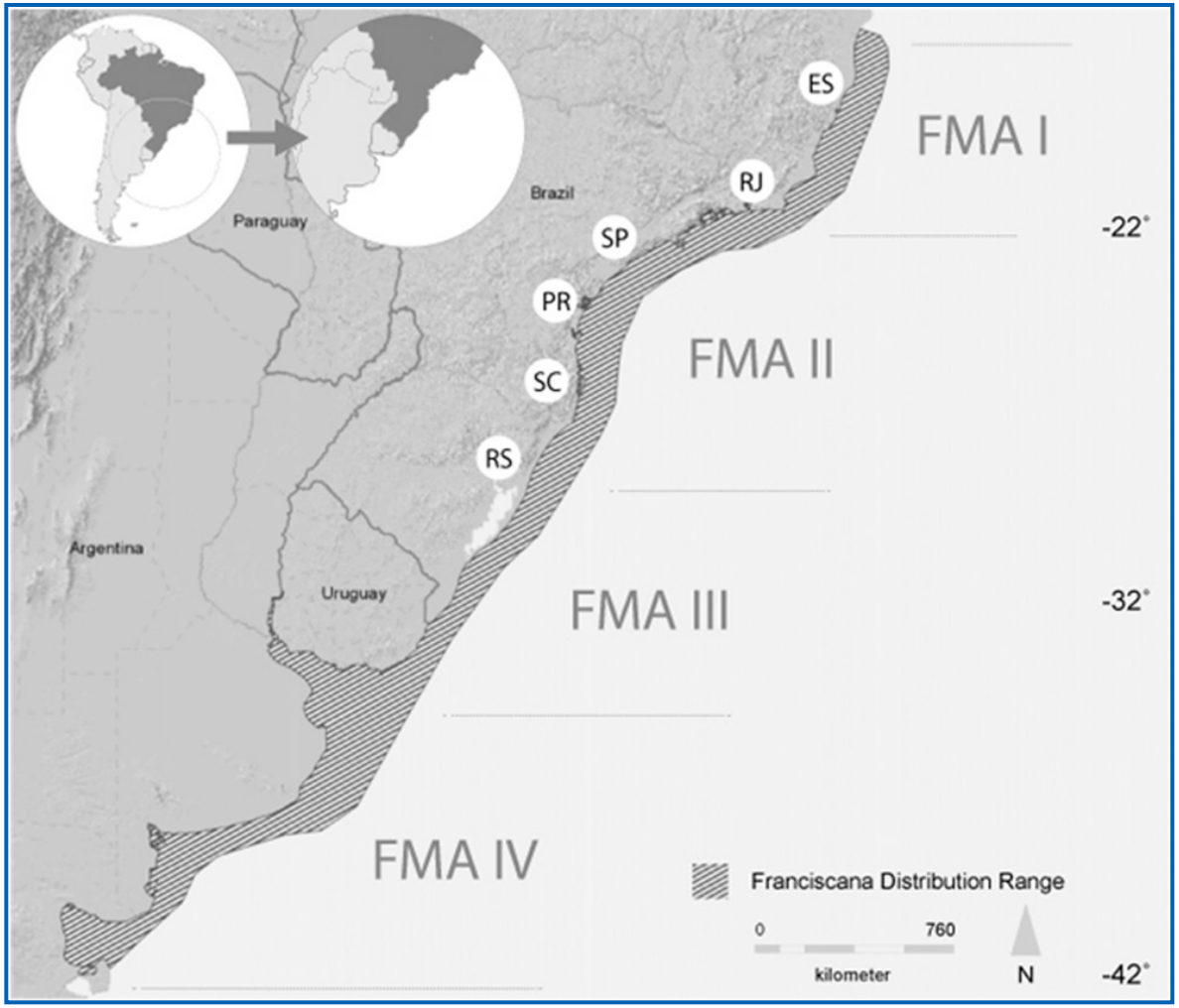
- its vulnerability to incidental capture
- habitat degradation (anthropogenic contaminants)

A. de la Torre *et al*. Environ. Sci. Technol., **2012,** 46, 12364-12372

4 HNs: CASE STUDY III – HNs in Dolphins from Brazil

Sampling location, distributted within the Franciscana Management Areas (FMA), at the States of:

ES - Espírito Santo
RJ - Rio de Janeiro
SP - São Paulo
PR – Paraná
SC - Santa Catarina
RS - Rio Grande do Sul



4 HNs: CASE STUDY III – HNs in Dolphins from Brazil

Franciscana

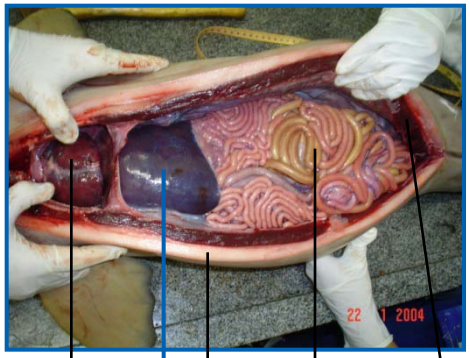
20 samples were either obtained from animals caught in drift nets or found stranded along the southeastern coast of Brazil between 1994 and 2008.

at the Lab.

length measurement

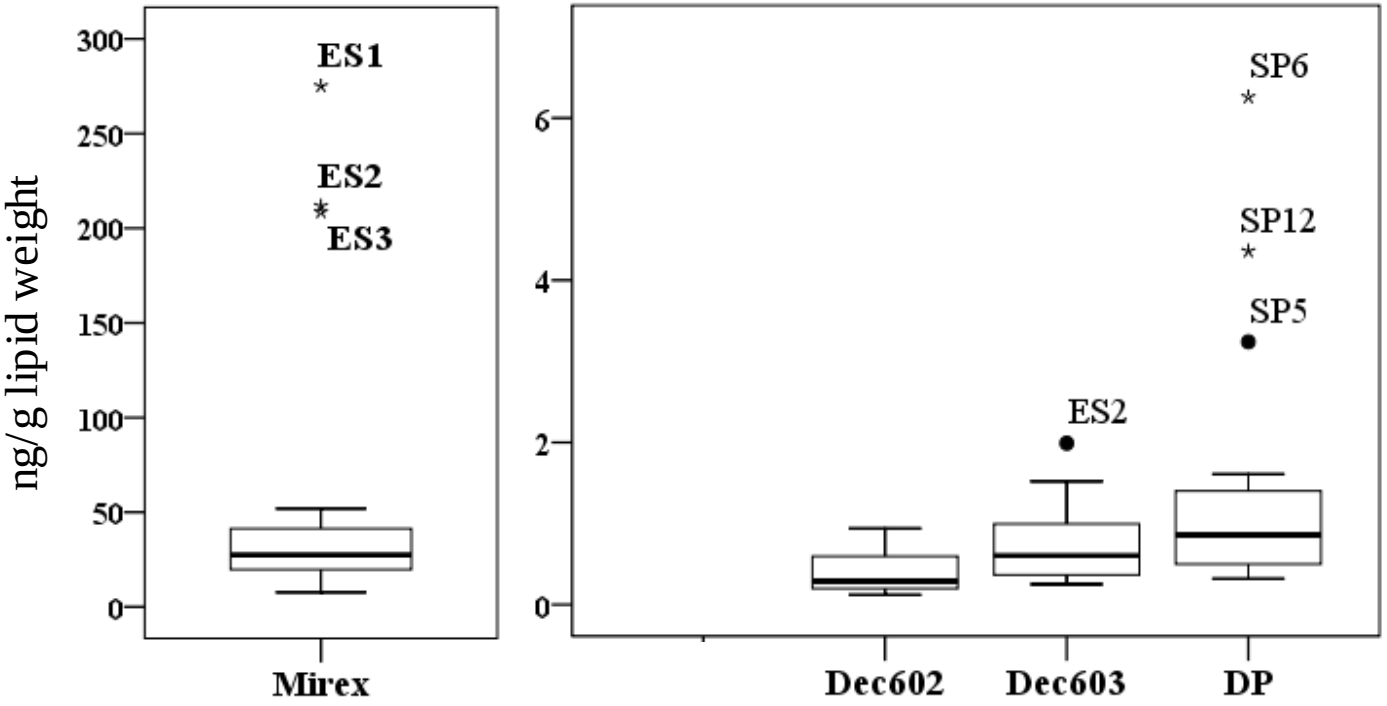
counting teeth

obtaining different organs and tissues



4 HNs: CASE STUDY III – HNs in Dolphins from Brazil

Mirex	20 out 20	[7.63 – 275 ng/g lw]	Mean = 64.7 ng/g lw
DP	16 out 20	[0.32 – 6.26 ng/g lw]	Mean = 1.53 ng/g lw
Dec 603	20 out 20	[0.25 – 1.99 ng/g lw]	Mean = 0.75 ng/g lw
Dec 602	19 out 20	[0.12 – 0.94 ng/g lw]	Mean = 0.38 ng/g lw



4 HNs: CASE STUDY III – HNs in Dolphins from Brazil

Concentration levels expressed in ng/g lw,
with the exception of PCDDs/Fs + DL-PCBs, expressed in pg TEQ/g lw

DDTs	**11.4 - 14908**
HCHs	**38.8 - 1537**
PCBs	**4.28 - 27741**
PCDDs/Fs + DL-PCBs*	**34 - 276**
PBDEs	**7.91 - 1797**
Mirex	**7.63 - 275**
DP	**0.32 – 6.26**

PCBs > DDTs > PBDEs > HCHs > Mirex > DP

4 HNs: CASE STUDY IV – HNs in Dolphins from Spain

28 blubber samples collected during February 2012

- 8 samples of *Delphinus delphis*
- 20 samples of *Tursiops Truncatus*

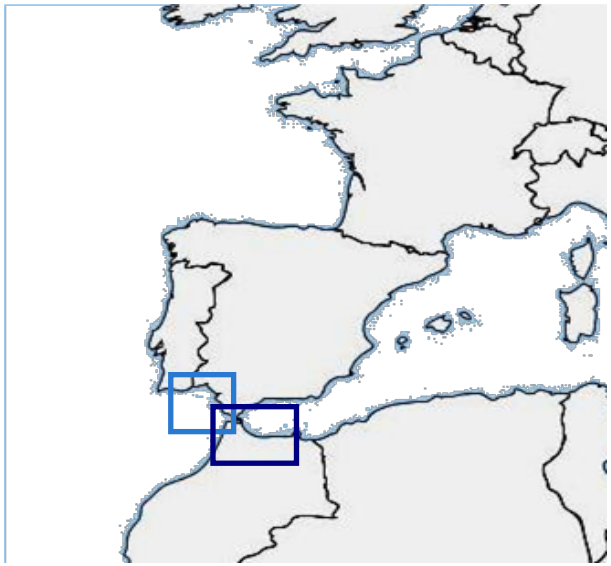
Biopsy Sampling

- Minimal damage
- Small sample amount
- Without individual information (age, sex …)

Gulf of Cádiz **Strait of Gibraltar**

Tursiop Truncatus

Delphinus Delphis



4 HNs: CASE STUDY IV – HNs in Dolphins from Spain

Concentration levels of HNs (ng/g lw)

	Mirex	Dec602	Dec603	*syn*-DP	*anti*-DP	Total DP
Dd (Gulf)	**nq-53.3**	**nd-2.83**	**nq-3.30**	**nd-14.2**	**nd-12.9**	**nd-27.1**
Tt (Gulf)	**nq-157**	**1.22-16.6**	**0.84-15.2**	**nd-11.4**	**nd-9.68**	**nd-21.1**
Tt (Strait)	**18.9-501**	**2.14-13.7**	**0.11-5.63**	**nd-5.44**	**nd-5.00**	**nd-5.00**
Frequency of detection (%)		**74**	**96**	**87**		

In general, HN levels in ***Delphinus Delphis*** are lower than those of ***Tursiop Truncatus***.

In general, levels in **Strait of Gibraltar** are lower than those of **Gulf of Cádiz**.

4 HNs: CASE STUDY IV – HNs in Dolphins from Spain

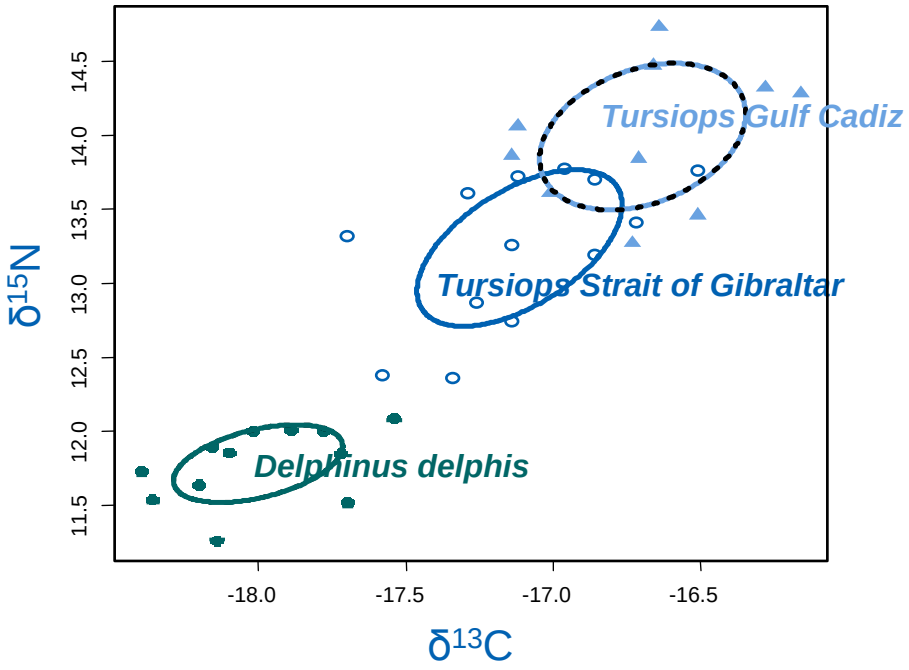
Analysis of Stable Isotopes of Nitrogen: to characterize the food chain.

The $\delta^{15}N$ is the ratio between $^{15}N/^{14}N$. This ratio increases with the trophic level, due to a preferential excretion of the lighter isotope, ^{14}N.

$^{13}C/^{12}C$: Related to diet

$^{15}N/^{14}N$: Related to the trophic position

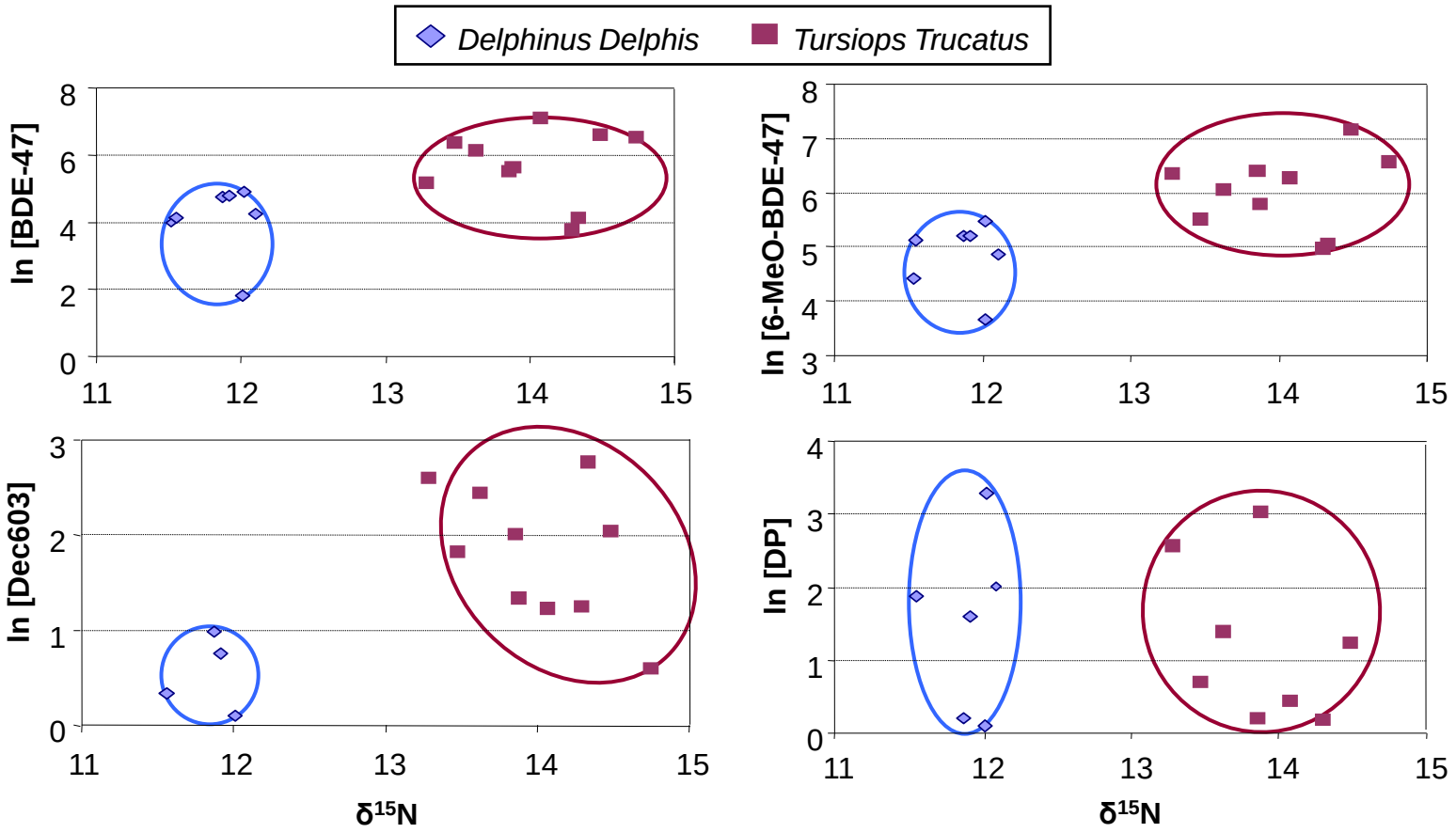
	$\delta^{13}C$	$\delta^{15}N$
Delphinus delhpis	**-17.54 to -18.40**	**11.52 to 12.09**
Tursiops truncatus	**-16.16 to -17.70**	**12.74 to 14.28**



Significant differences in the isotopic nitches of *Delphinus delphis* and *Tursiops truncatus* were found (Permutation test (*Turner 2010*), $p<0.01$)

4 HNs: CASE STUDY IV – HNs in Dolphins from Spain

Stable Nitrogen Relationship with Concentration Level



PBDEs (BDE-47) and MeO-PBDEs (6-MeO-47) showed biomagnification capacity (Consistent with literature)

Dec 603 showed biomagnification capacity, in contrast with DP

4 HNs: CASE STUDY V – HNs in Bird Eggs

Bird Eggs from Doñana National Park (Spain)

Doñana National Park has a unique biodiversity in Europe. Mainly emphasizes the marsh, of extraordinary importance as a transit, breeding and wintering **birds for thousands of European and African species**. Many of these species, especially those who are at higher levels within the food chain, are especially sensitive to the harmful effects of environmental pollution.

E. Barón, M. Máñez, A. Andreu, F. Sergio, F. Hiraldo, E. Eljarrat, D. Barceló. Environ. Int. **2014**, 68, 118-126

4 HNs: CASE STUDY V – HNs in Bird Eggs

Bird Eggs from Doñana National Park (Spain)

Order	Species	Scientific name	N
Falconiformes	Black kite	*Milvus migrans*	**22**
	Red kite	*Milvus milvus*	**2**
	Western marsh harrier	*Circus aeruginosus*	**1**
	Booted eagle	*Áquila pennata*	**6**
	Common kestrel	*Falco tinnunculus*	**13**
	Black-winged kite	*Elanus caeruleus*	**1**
Ciconiiformes	Glossy ibis	*Plegadis falcinellus*	**4**
	Purple heron	*Ardea purpurea*	**3**
	White stork	*Ciconia ciconia*	**34**
Strigiformes	Barn owl	*Tyto alba*	**1**
Charadriiformes	Slender-billed gull	*Chroicocephalus genei*	**3**
	Black-headed gull	*Chroicocephalus ridibundus*	**7**
	Gull-billed tern	*Gelochelidon nilotica*	**8**
Anseriformes	Gadwall	*Anas strepera*	**10**

115 unhatched egg samples from 14 bird species

Different feeding and migratory behavior

4 HNs: CASE STUDY V – HNs in Bird Eggs

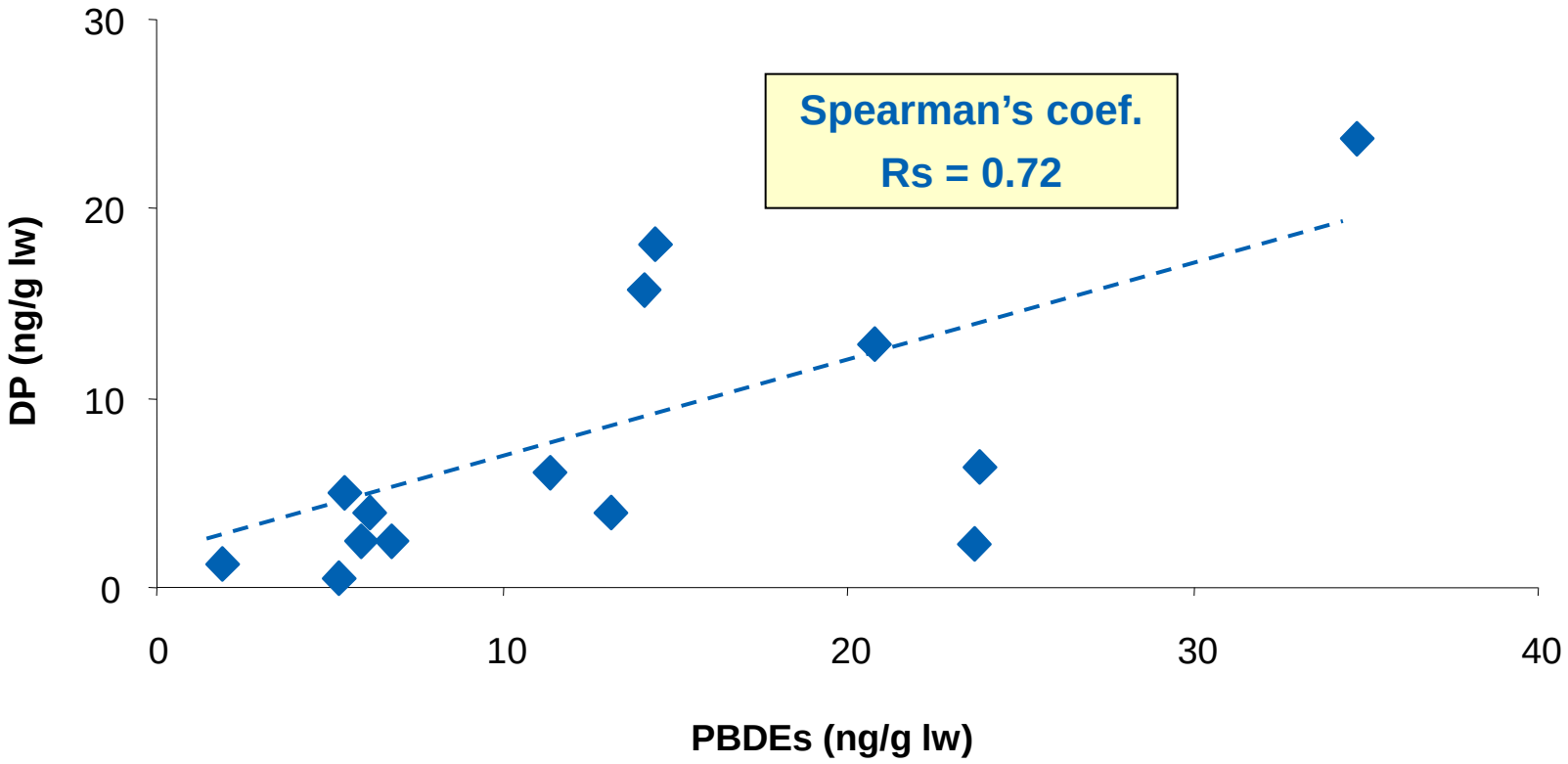
Concentration Levels (mean values) expressed in ng/g lw

Order	Specie	ΣPBDEs	ΣDechloranes
Falconiformes	Black kite	13.6	30.9
	Red kite	14.2	45.9
	Western marsh harrier	23.4	161
	Booted eagle	18.3	29.9
	Common kestrel	12.7	8.88
	Black-winged kite	1.72	22.6
Ciconiiformes	Glossy ibis	11.1	11.8
	Purple heron	23.6	14.9
	White stork	34.5	66.1
Strigiformes	Barn owl	5.20	7.25
Charadriiformes	Slender-billed gull	5.03	39.4
	Black-headed gull	5.98	63.4
	Gull-billed tern	6.62	23.6
Anseriformes	Gadwall	5.66	5.93

HN levels **similar or higher** than those of PBDEs

4 HNs: CASE STUDY V – HNs in Bird Eggs

PBDE and HN Correlation

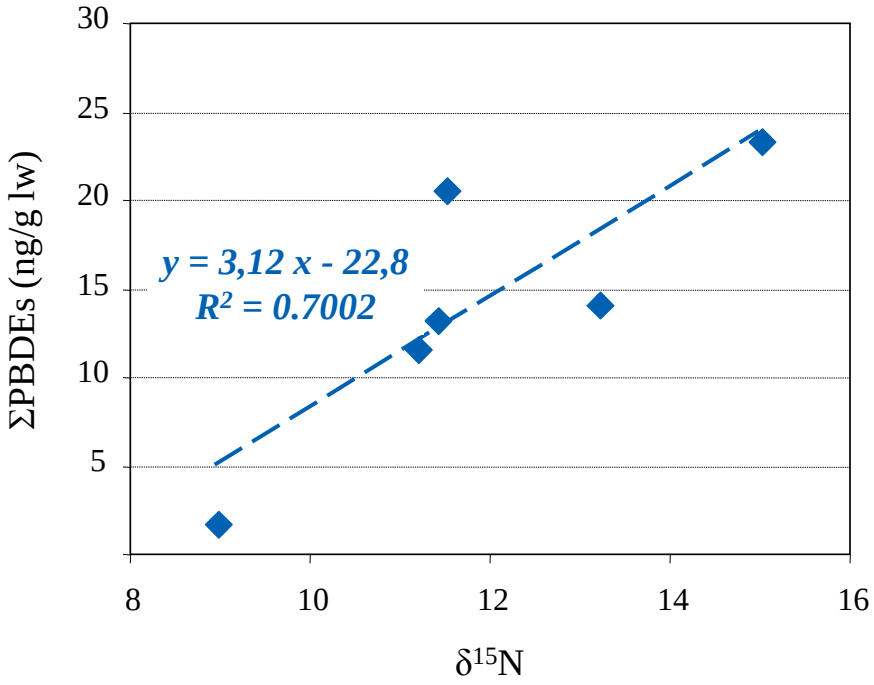


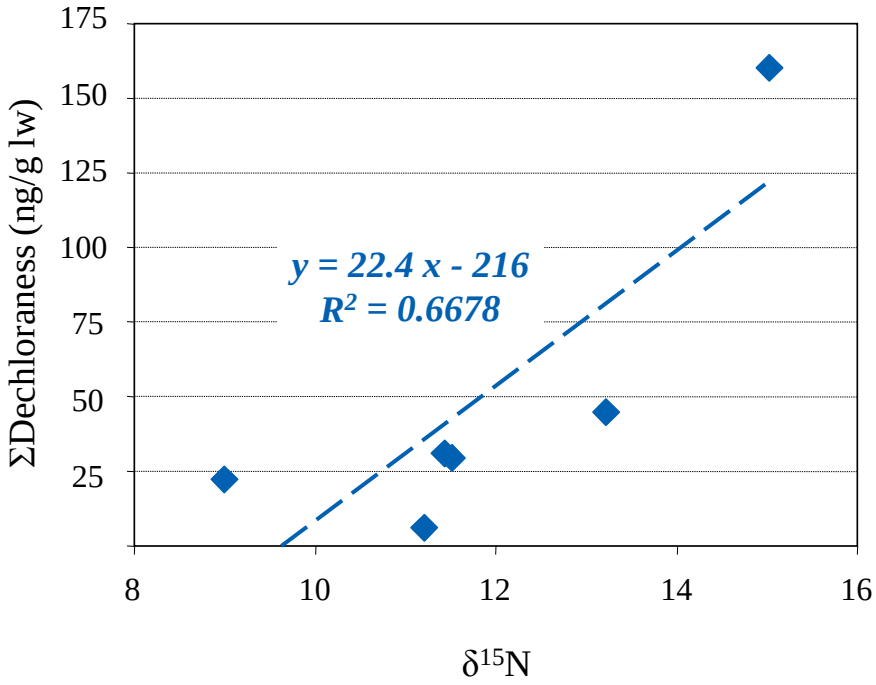
4 HNs: CASE STUDY V – HNs in Bird Eggs

Biomagnification Study
FALCONIFORMES

Western marsh harrier
Red kite
Booted eagle
Black kite
Common kestrel
Black-winged kite

TL



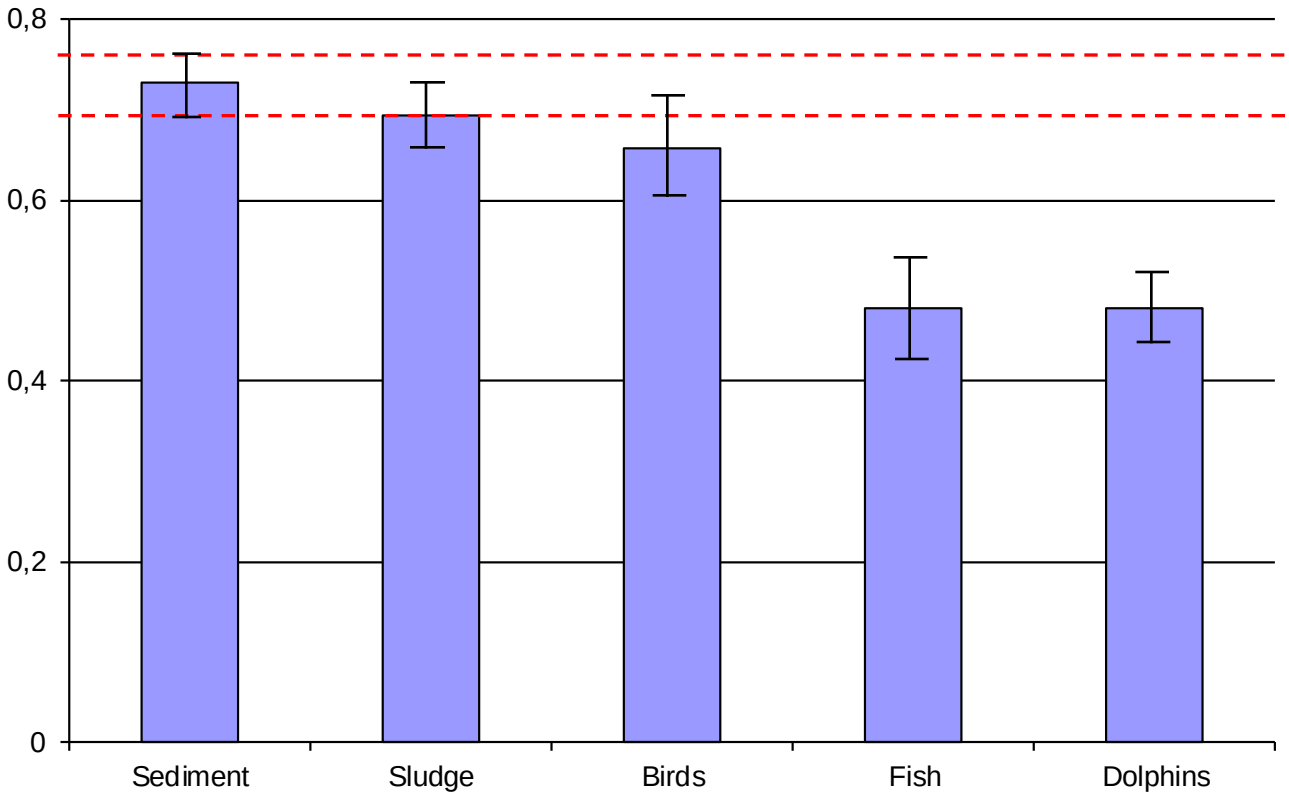


Like **PBDEs**, **HNs** BIOMAGNIFY

4 HNs: Dechlorane Plus: F_{anti}

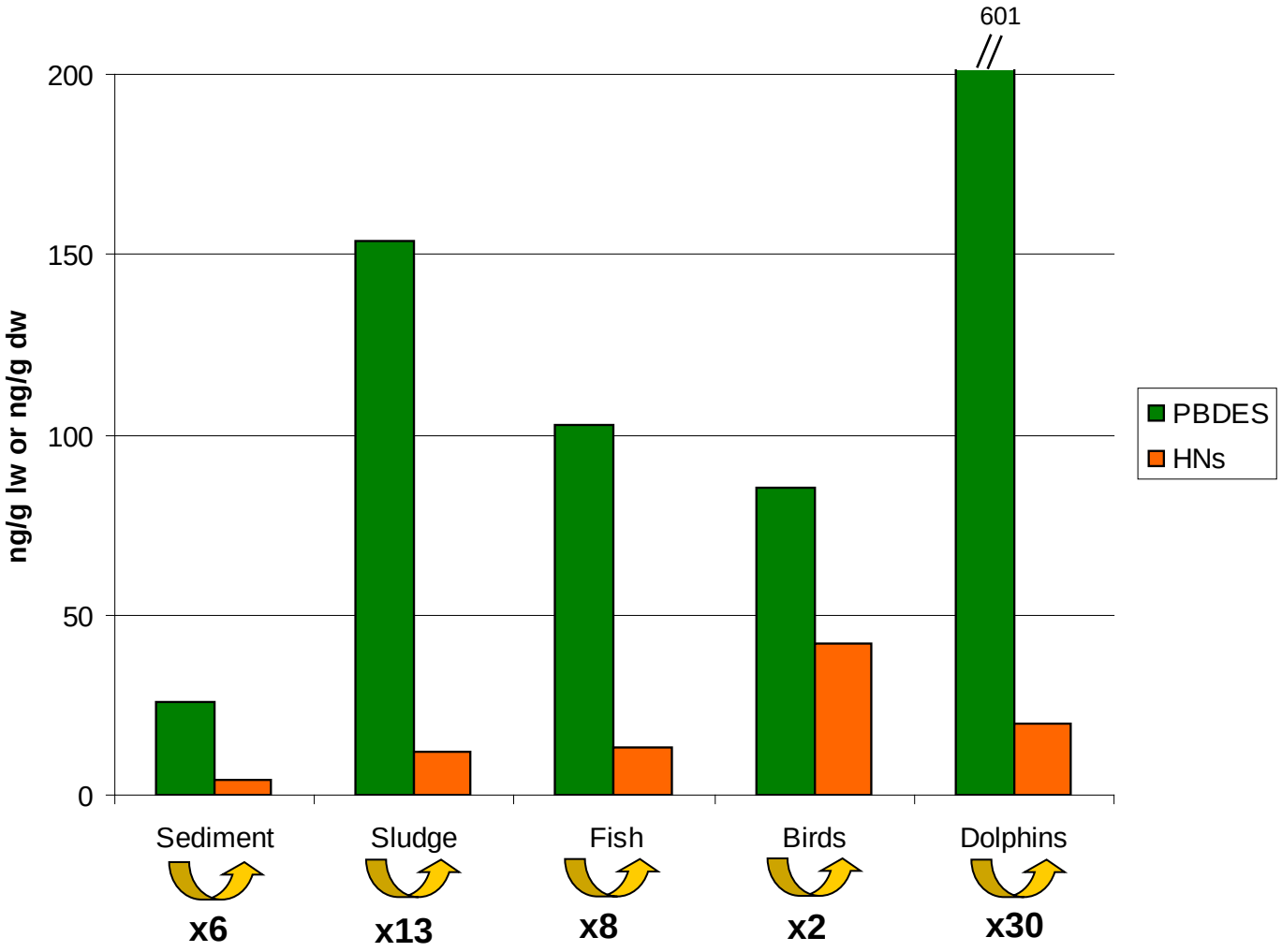
Dechlorane plus isomer ratio (Fanti)

$$F_{anti} = \frac{[anti\text{-DP}]}{[syn\text{-DP}]+[anti\text{-DP}]}$$



Commercial mixture
F_{anti} between 0.65-0.75

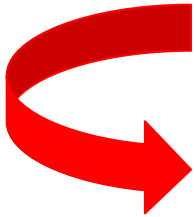
4 HNs: PBDE *versus* HN levels



PBDE levels still higher than HN levels in all matrices, but HNs present in all matrices!

5 CONCLUSIONS

What happens with HALOGENATED NORBORNENES?



It’s the same old story?

5 CONCLUSIONS