CHLORINATED FLAME RETARDANTS (DECHLORANES): ANALYSIS, OCCURRENCE AND BEHAVIOUR

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Norman Workshop: "New" brominated flame retardants as emerging contaminants in the environment
23–24 November, 2011. Stockholm, Sweden

CHLORINATED FLAME RETARDANTS (DECHLORANES): ANALYSIS, OCCURRENCE AND BEHAVIOUR

OUTLINE

- ⇨ Introduction
- ⇨ Analytical methods
- ⇨ Occurrence and Behaviour
- ⇨ Conclusions and Future research needs

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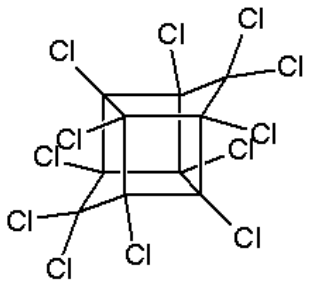
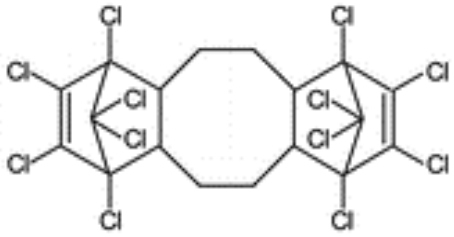
DECHLORANE PLUS

- DP was developed as a flame retardant to replace Mirex which was banned in the 1970s.
- DP is classified as a high production volume chemical in USA. DP worldwide annual production volume is estimated at about 5000 t.
- Manufacturers of DP include Oxychem (Buffalo, USA) and Anpon Electrochemical Co., Ltd (Jiangsu, China).
- DP applications: electrical hard plastic connectors, wire coatings and furniture.
- DP is a potential replacement for the now restricted Deca-BDE.

DECHLORANES AND RELATED COMPOUND

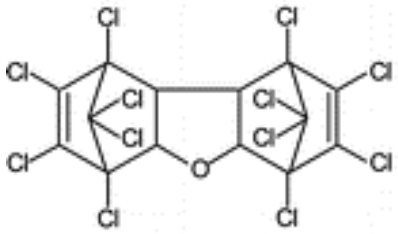


Mirex

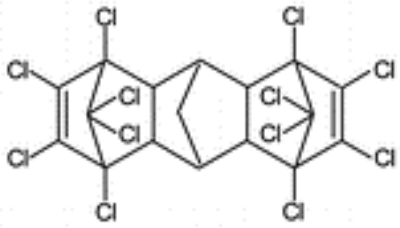


Dechlorane Plus (DP)

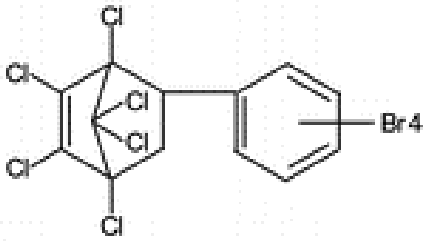
DP-like substances



Dechlorane 602



Dechlorane 603



Dechlorane 604

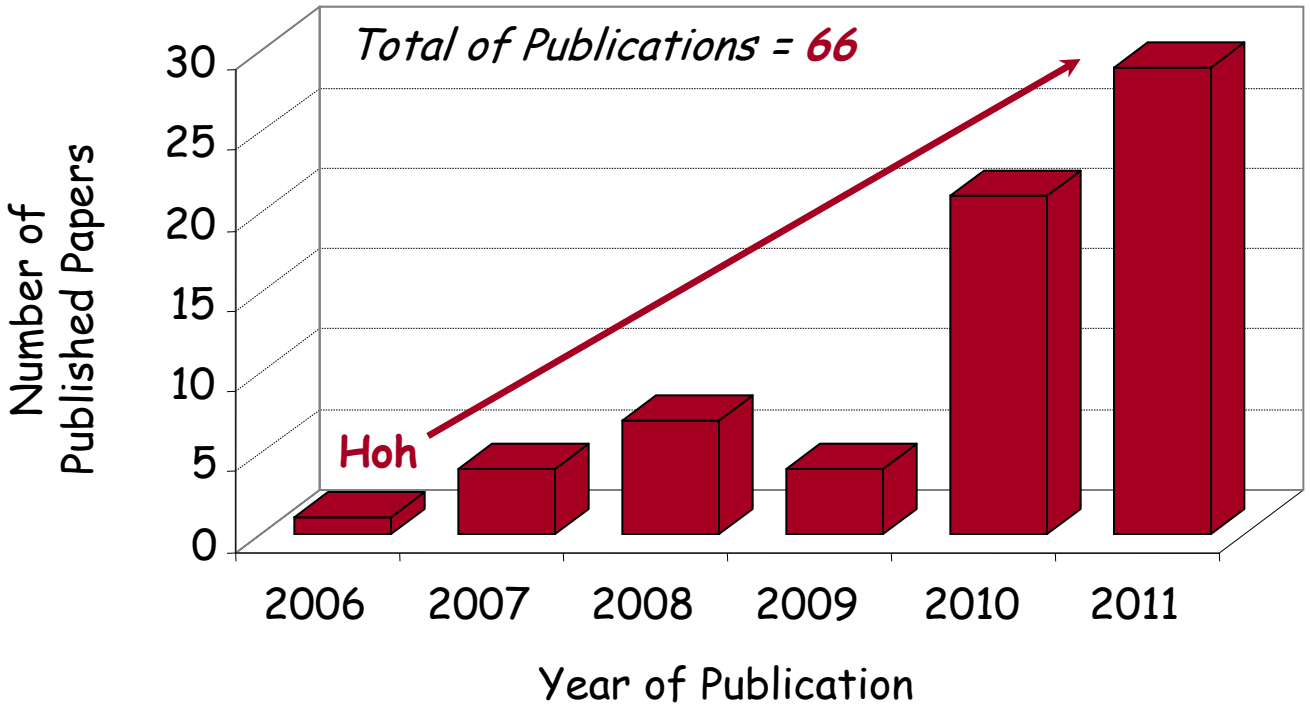
Physical properties of Dechlorane Plus

Chemical formula	$C_{18}H_{12}Cl_{12}$
Molecular mass	653.7
Melting point	350°C with decomposition
Vapor pressure (at 200°C)	0.006 mm of Hg
Water solubility	44 ng/L – 249 µg/L
Log K_{OW}	9.3

High chemical stability
High lipophilicity

PERSISTENT
BIOACCUMULATIVE

- 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.



DECHLORANE PLUS

- 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 …)

DECHLORANE PLUS – CONCENTRATION LEVELS

	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
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 (Blood)	43 ng/g lw (China)	

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

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

DECHLORANE PLUS – ANALYTICAL DETERMINATIONS

Sample Preparation

Cleanup Procedures

Instrumental Analysis

Similar to the ones used for the measurements of PBDEs and PCBs

GC-NCI-MS
GC-EI-HRMS

No information about the ANALYTICAL PARAMETERS of methodologies applied

Recovery?
Sensitivity?
Selectivity?
Reproducibility?

DECHLORANE PLUS – ANALYTICAL DETERMINATIONS

Development of analytical methods for the quantitative determination in different ENVIRONMENTAL, BIOTA and HUMAN matrices avoiding the use of HRMS

Report on the ANALYTICAL PARAMETERS of methodologies developed

Study of their applicability with REAL samples

SEDIMENT SAMPLES

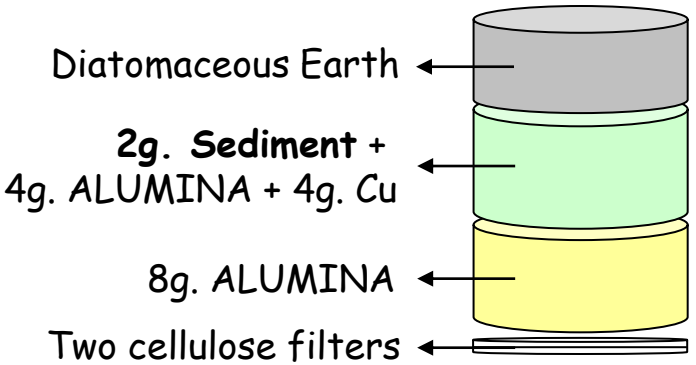
Lyophilization
Homogenization

Extraction + Purification (SPLE)

CH_2Cl_2:hexane (1:1)
Temperature: 100°C
Pressure: 1500 psi
Cycles: 2

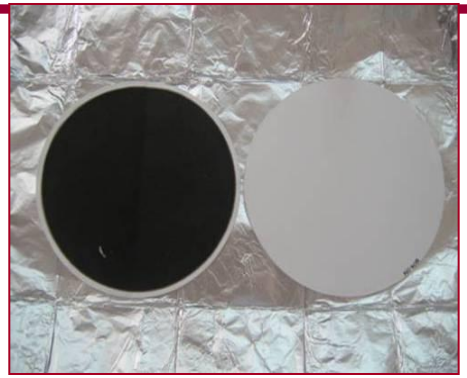
Instrumental Analysis

GC-NCI-MS



AIR SAMPLES

Quartz fiber filters
(Ø =15 cm)



Sampler:
MCV CAV/A high volume sampler 30 m^3/h during 24 hours

Extraction (PLE)
CH_2Cl_2:hexane (1:1)
Temperature: 100°C
Pressure: 1500 psi
Cycles: 2

Acid attack (H_2SO_4 conc.)

Purification: SPE
Alúmina-N (5 g)

Instrumental Analysis
GC-NCI-MS

BIOTA and HUMAN SAMPLES

Lyophilization
Homogenization

↓

Extraction (PLE)
CH_2Cl_2:hexane (1:1)
Temperature: 100°C
Pressure: 1500 psi
Cycles: 2

↓ → Determination of FAT CONTENT

Fat removal
Acid attack (H_2SO_4 conc.)

↓

Purification: SPE
Alúmina-N (5 g)

→

Instrumental Analysis
GC-NCI-MS

Human breast milk

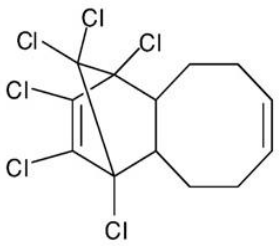
Instrumental Analysis by GC-NCI-MS

DB-5-ms capillary column
15 m, 0.25 mm i.d. x 0.10 μm film thickness

Temperature	Hold time
80°C	2 min
285°C	10 min

10°C/min

Total time: 32.5 min



1,5-DPMA

	t_R (min.)	m/z_1	m/z_2	Ratio
DPMA	13.6	35	237	1.2
Dec 602	18.0	614	35	3.9
Dec 603	20.9	638	35	1.6
Dec 604	21.3	79	81	1.0
syn-DP	22.8	654	35	1.7
anti-DP	23.4	654	35	1.1

Instrumental Analysis by GC-NCI-MS

Selection of chemical ionization moderating gas

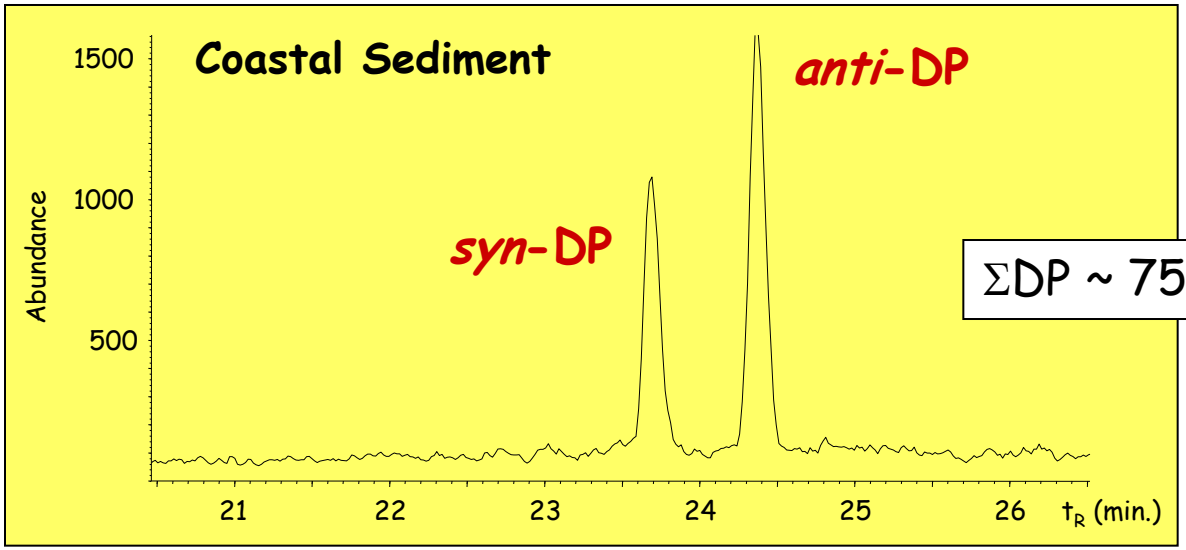
Ammonia *vs* Methane

	Instrumental LOD (injected fg)	
	Ammonia	Methane
Dec 602	926	96
Dec 603	30	5
Dec 604	187	17
syn-DP	61	12
anti-DP	23	9
DPMA	47	13
PBDEs	30 - 210	56 - 177

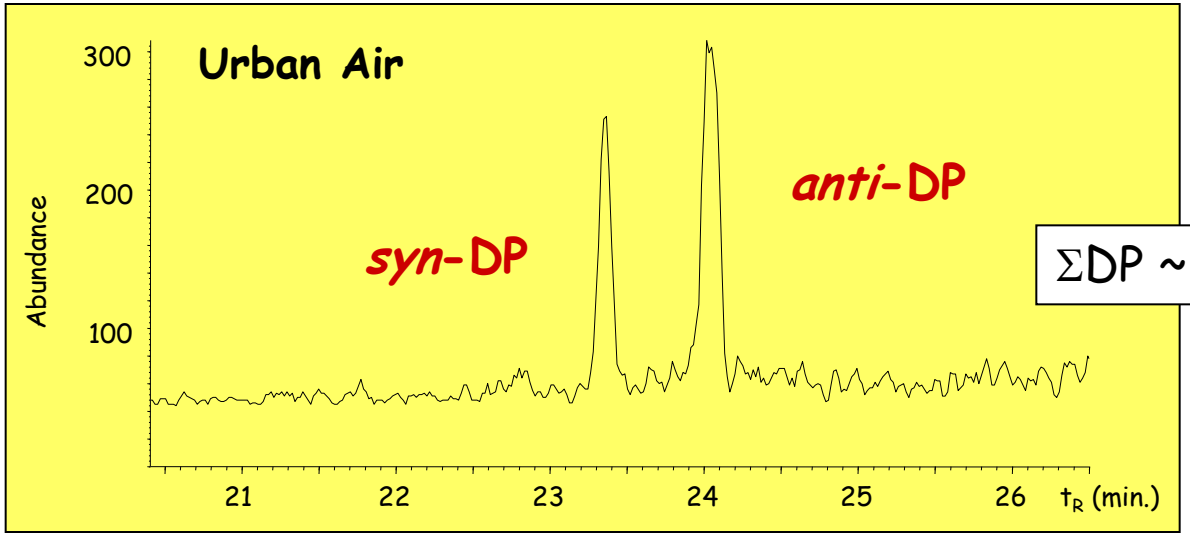
2.6 - 11 times

0.5 – 1.2 times

ENVIRONMENTAL SAMPLES - DP



ΣDP ~ 750 pg/g dw



ΣDP ~ 10 pg/m^3

Instrumental Analysis by GC-NCI-MS-MS

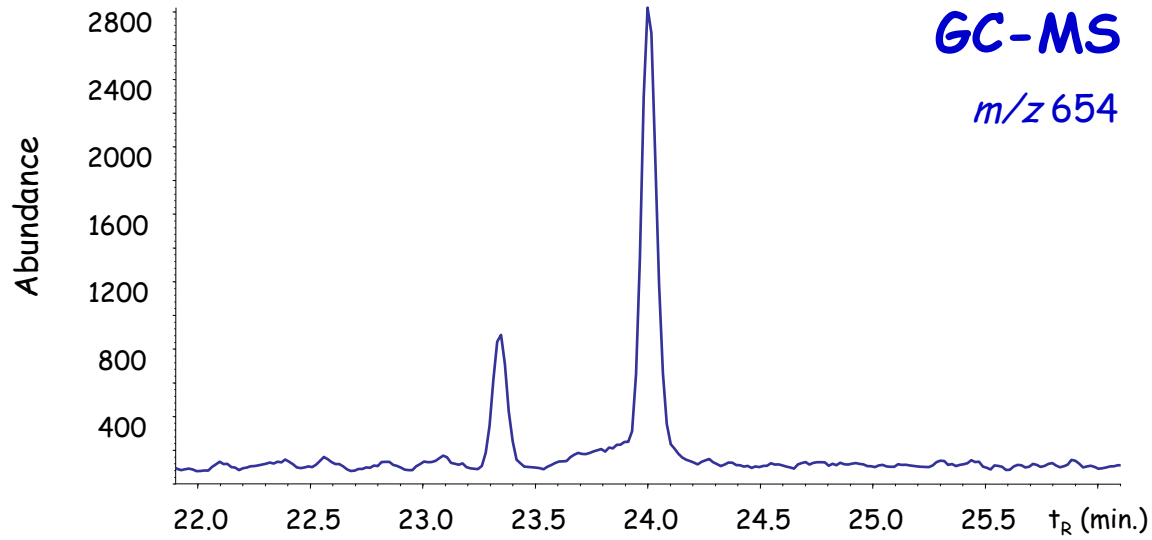
7890A GC coupled to
7000A triple quadrupole
(Agilent Technologies)

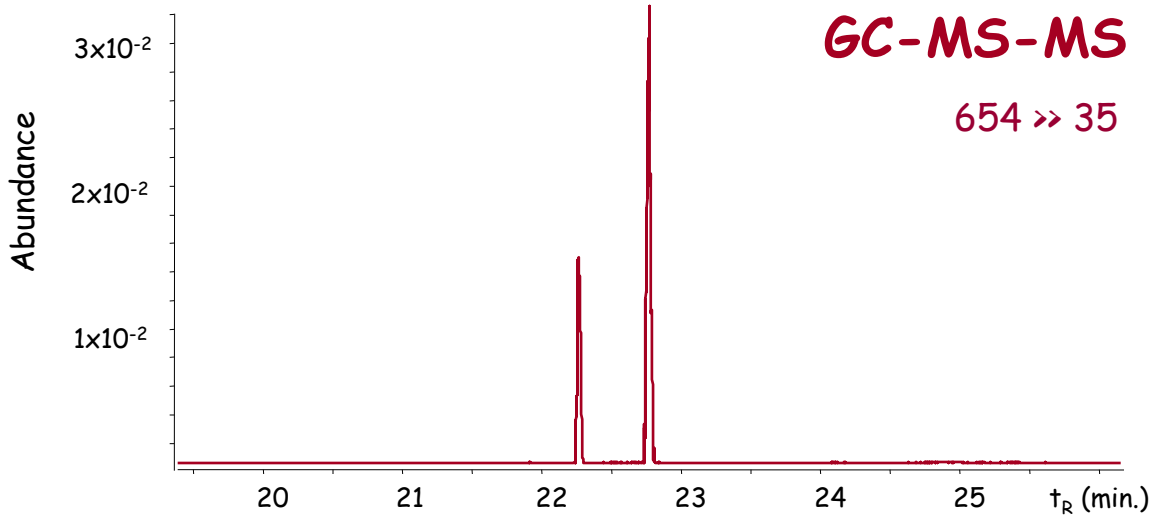
	Transition 1	*Transition* 2	Ratio
syn-DP	654>35	654>37	3.2
anti-DP	654>35	654>37	3.3

	Instrumental LOD (injected fg)	
	GC-MS	*GC-MS-MS*
syn-DP	28	21
anti-DP	32	16

Instrumental Analysis by GC-NCI-MS-MS

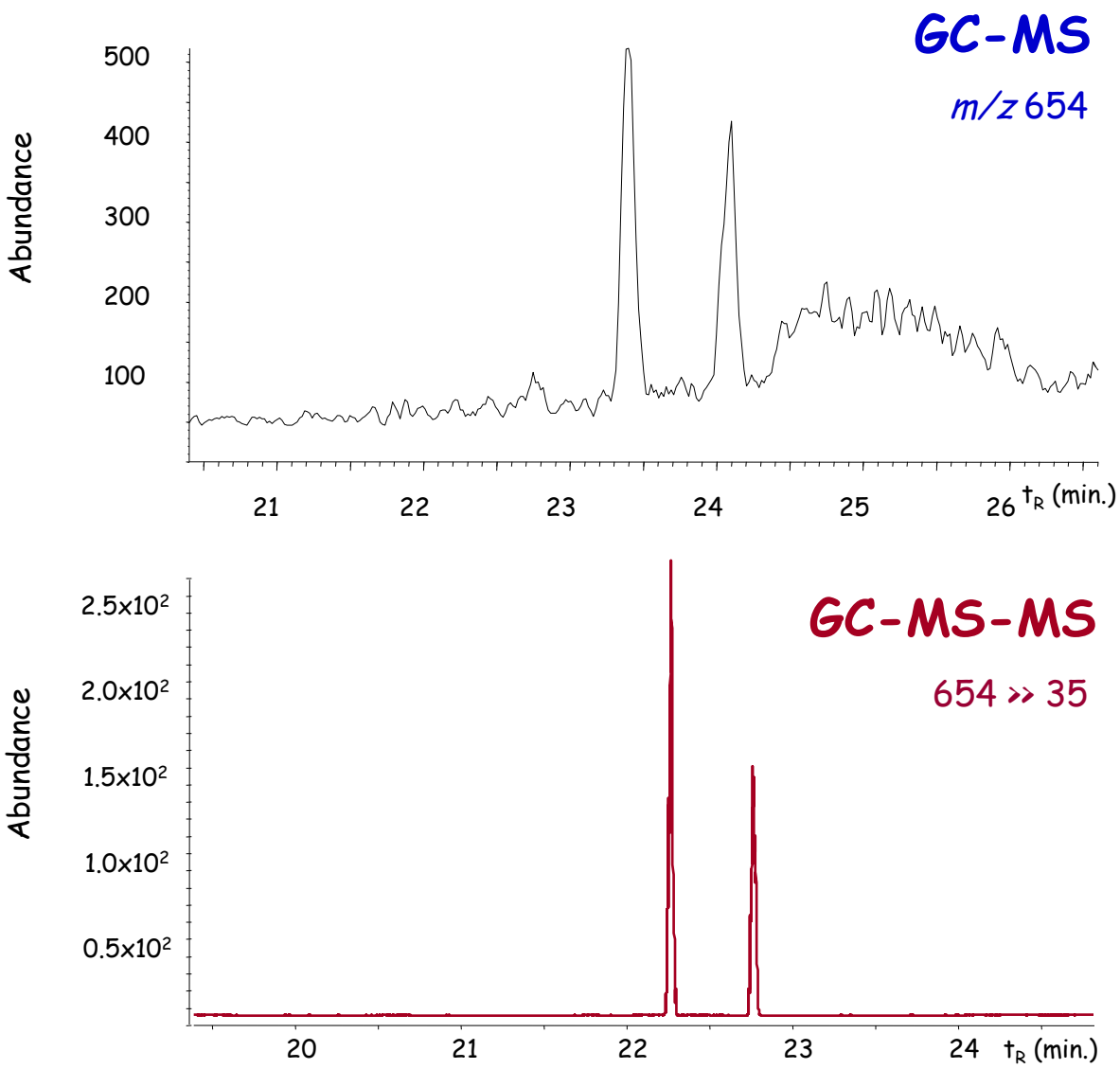
Sediment Sample





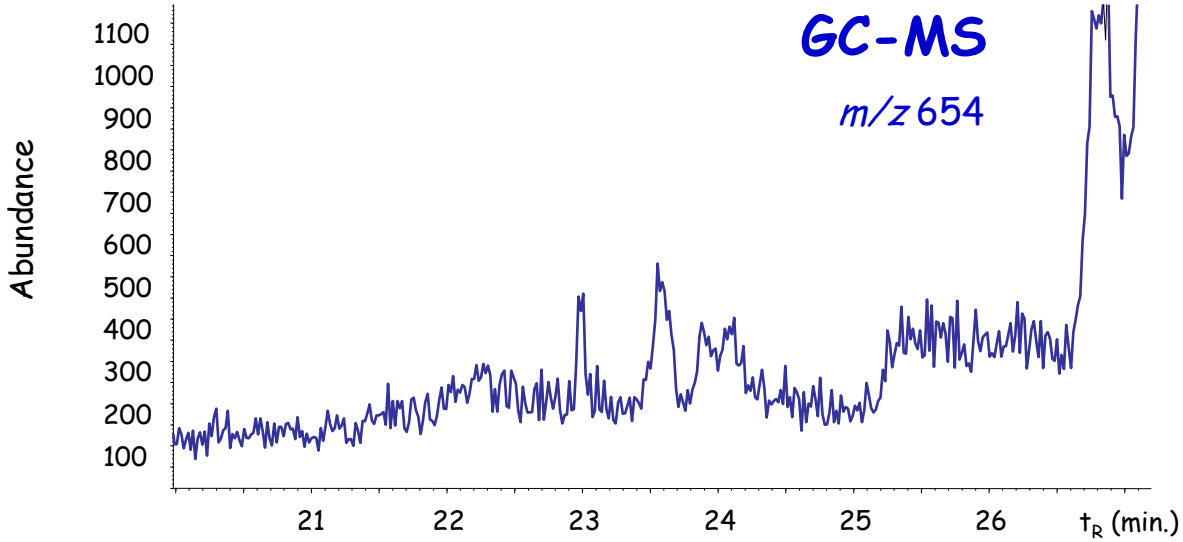
Instrumental Analysis by GC-NCI-MS-MS

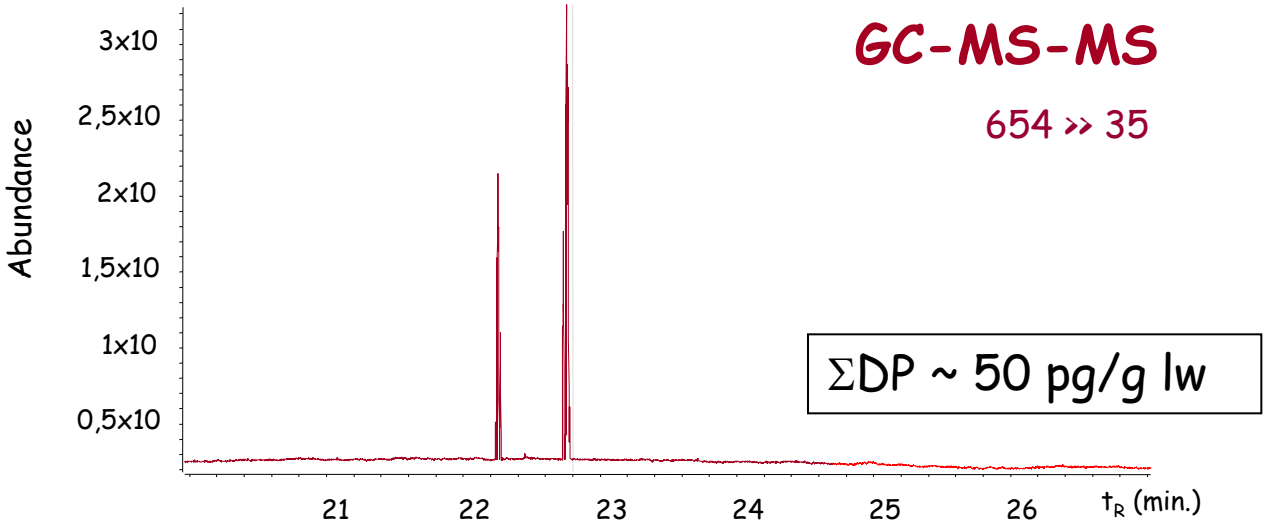
Fish Sample



Instrumental Analysis by GC-NCI-MS-MS

Human Milk Sample





ΣDP ~ 50 pg/g lw

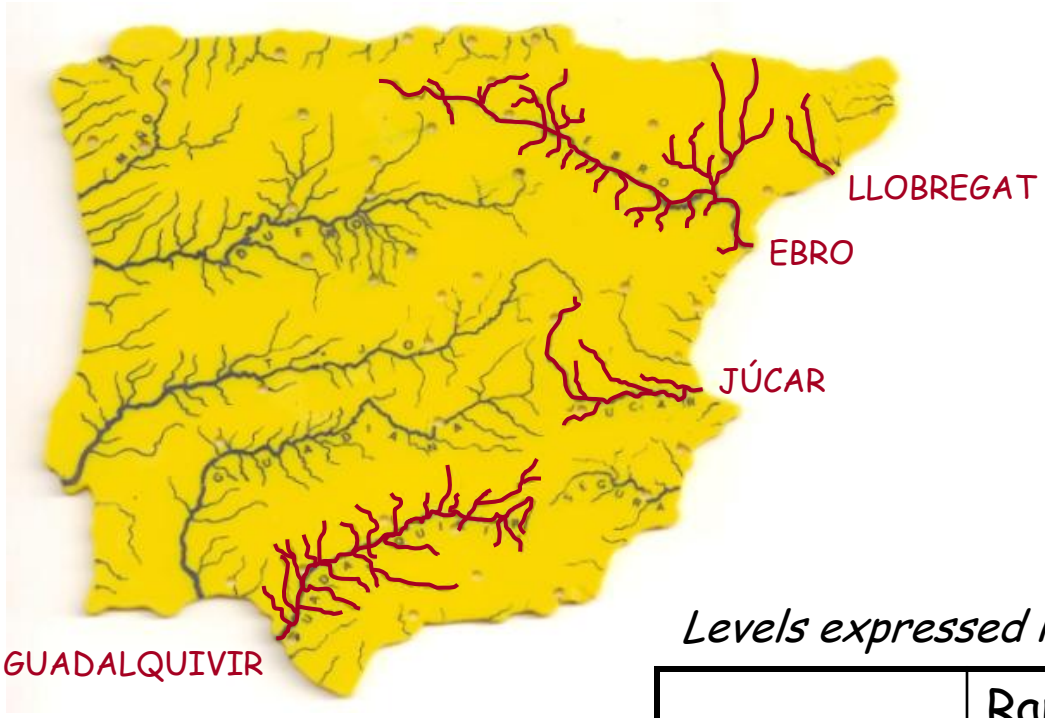
DECHLORANE PLUS – CONCENTRATION LEVELS

	Near production facilities	Other regions
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) 7000 ng/g dw (China)	Up to 8 ng/g dw
Soil	Up to 13400 ng/g dw (China)	Up to 5 ng/g
Sewage Sludge		2.5 – 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 (Blood) **Humans (Milk)**	43 ng/g lw (China) nd – 8.0 ng/g lw (Canada)	

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

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

SEDIMENTS FROM SPAIN – SCARCE Project



Levels expressed in ng/g dw

	Range	Mean
Ebro	0.07 – 1.61	0.51
Guadalquivir	0.06 – 0.10	0.08
Júcar	0.05 – 026	0.14
Llobregat	0.24 – 1.39	0.86

Isomeric ratio of DP: f_{anti} VALUES

$$f_{anti} = \frac{C_{anti}}{C_{anti} + C_{syn}}$$

Technical Product

f_{anti} = 0.65 - 0.75

	Range	Mean
Ebro	0.69 – 0.83	0.75
Guadalquivir	0.69 – 1.00	0.80
Júcar	0.63 – 1.00	0.75
Llobregat	0.69 – 0.77	0.74

Isomeric ratio of DP: f_{anti} VALUES

$$f_{anti} = \frac{C_{anti}}{C_{anti} + C_{syn}}$$

Technical Product

f_{anti} = 0.65 - 0.75

3 studies on aquatic biota (fish)

(Tomy et al., 2007; Kang et al., 2010; Wu et al., 2010)

Decreasing f_{anti} with increasing trophic level

syn-DP is more bioaccumulative than anti-DP in aquatic biota

BIOTA SAMPLES – BROMACUA Project

FILTERING

Tagelus dombeii

FILTERING

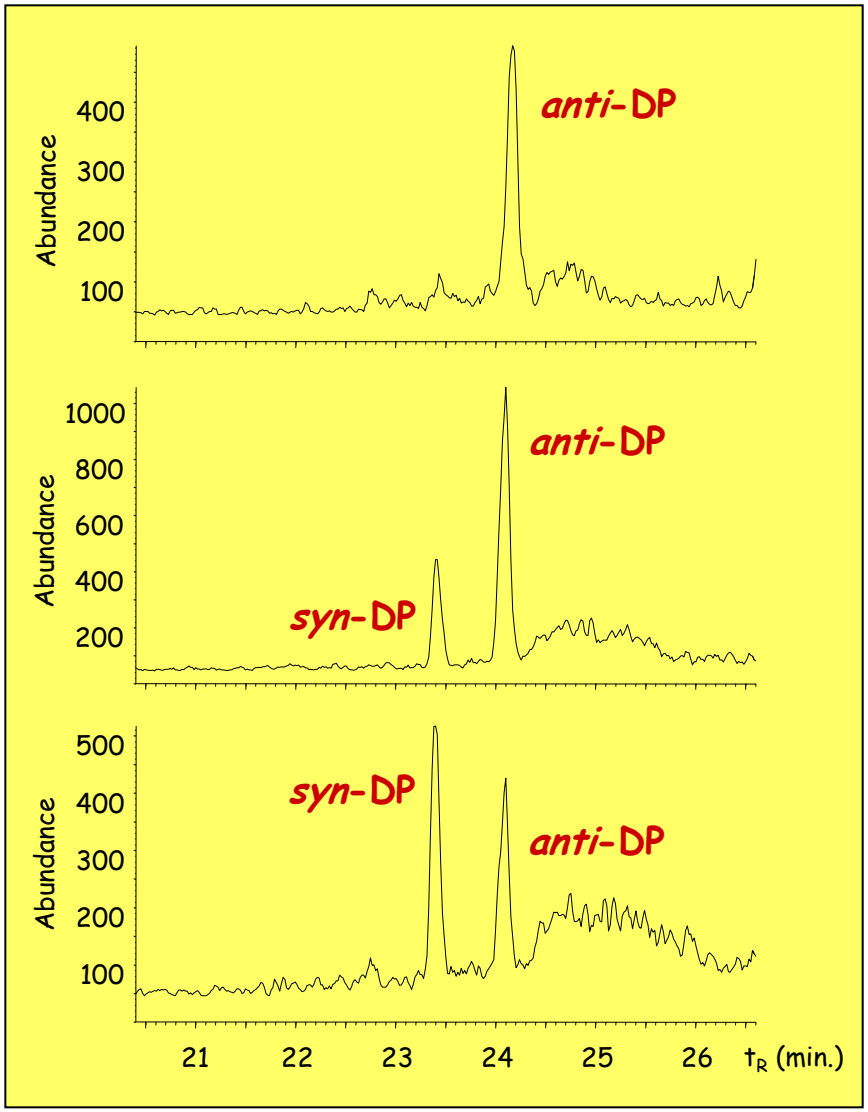
Fisurella sp

CARNIVORES

Pinguipes chilensis

High trophic level

Low f_{anti}

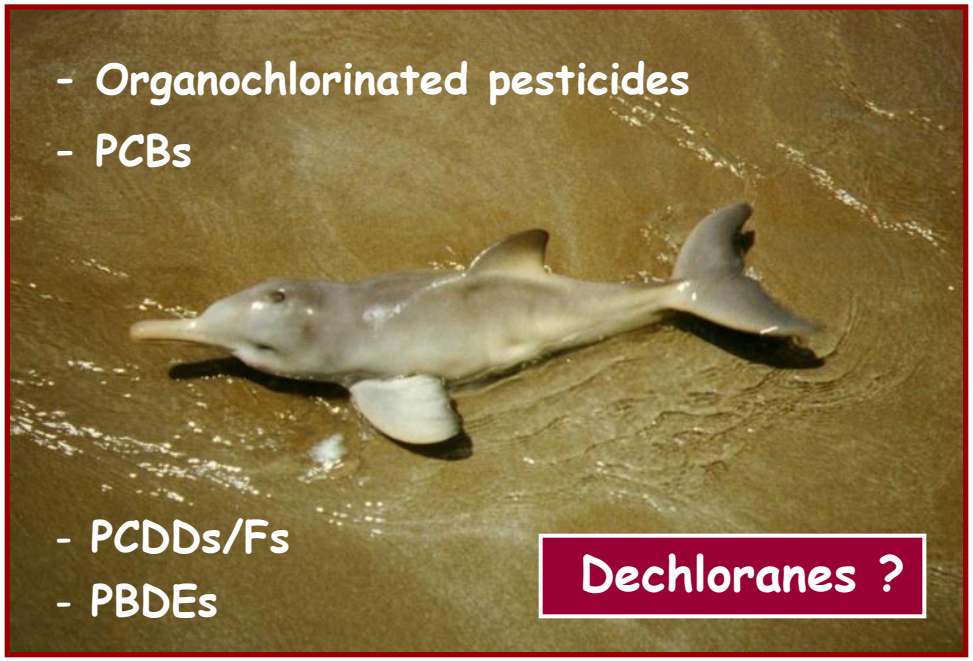


BIOTA SAMPLES – Dolphin samples

Franciscana (*Pontoporia blainvillei*)

Franciscana needs measures of conservation due to:

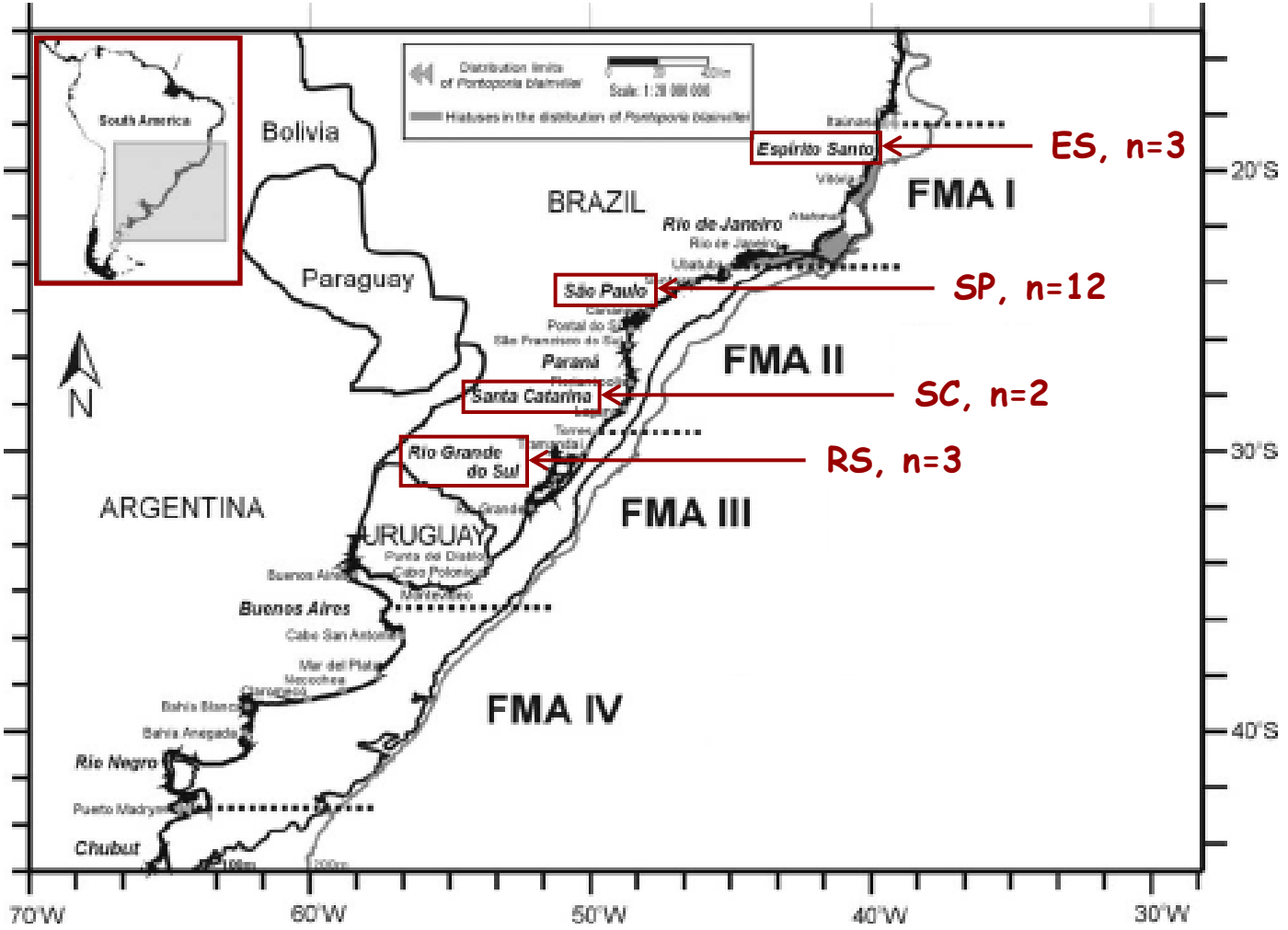
- its vulnerability to incidental capture
- Habitat degradation (anthropogenic contaminants)



AREA OF STUDY - Southeastern coast of Brazil

Franciscana (*Pontoporia blainvillei*)

Endemic from the southwest Atlantic Ocean



CONCENTRATION LEVELS IN LIVER DOLPHIN SAMPLES

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

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

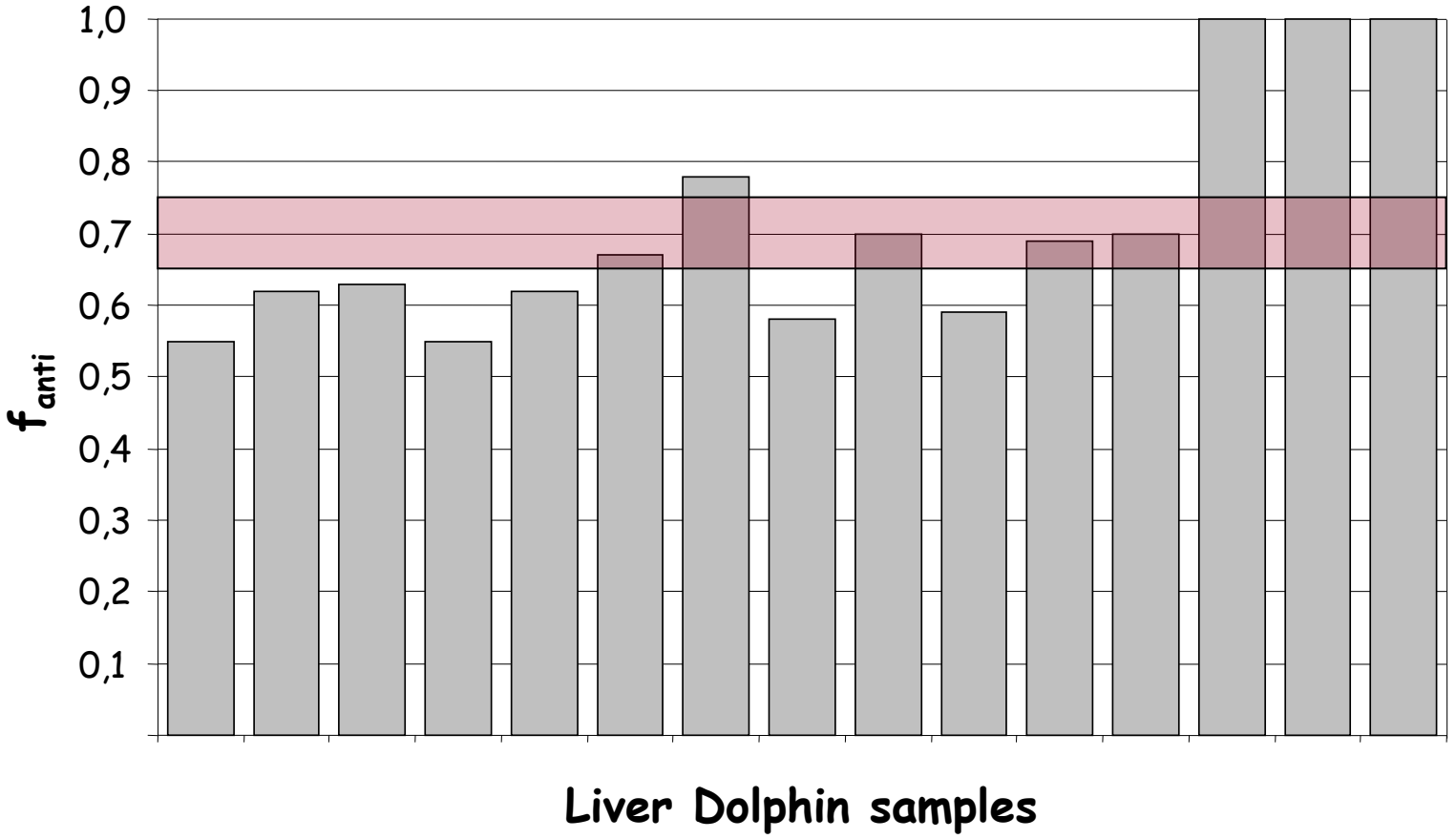
DDTs	11.4 - 14908
HCHs	38.8 - 1537
PCBs	4.28 - 27741
PCDDs/Fs + DL-PCBs	34 - 276
PBDEs	7.91 - 1797
Mirex	7.63 - 275
DP	0.32 – 6.26

PCBs > DDTs > PBDEs > HCHs > Mirex > DP

Isomeric ratio of DP: f_{anti} VALUES

Technical Product

f_{anti} = 0.65 - 0.75



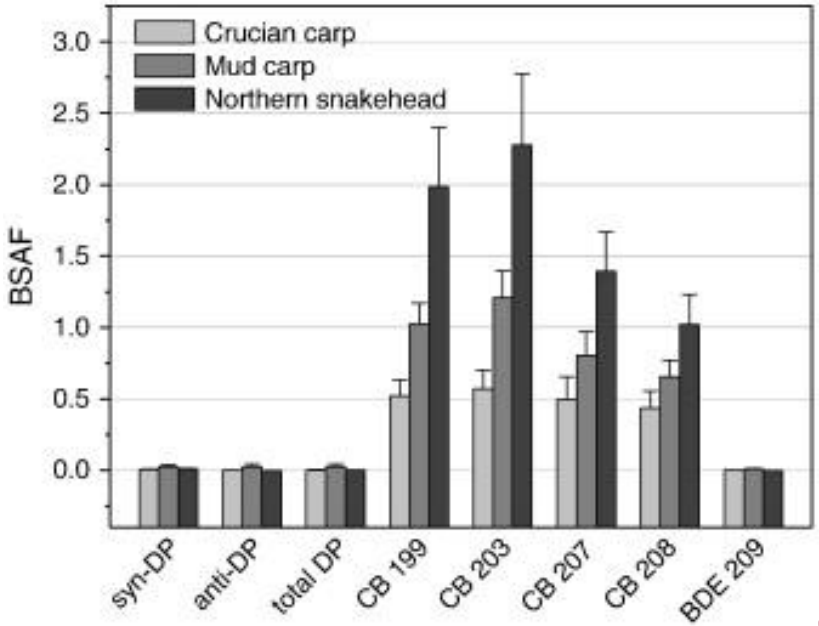
f_{anti} dolphin liver = 0.55 - 1

CONCLUSIONS AND FUTURE RESEARCH NEEDS

- DP was present in numerous environmental matrix (air, dust, soil and sediment), wildlife and humans, indicating the prevalence of this chemical in the environment. More data are needed about the concentration levels in other world regions away from production facilities.
- The detection of DP in sediment cores suggested the environmental persistence of this compound.
- The detection of DP in samples from Greenland to Antarctica implies that DP is subjected to long-range atmospheric transport.
- DP has been detected in wildlife with elevated concentration levels in higher trophic level organisms, indicating that DP is potentially bioaccumulative. More data are needed to better understand the bioaccumulation behaviors of DP.

CONCLUSIONS AND FUTURE RESEARCH NEEDS

Information on bioaccumulation parameters (BAFs, BSAFs, BMFs) for DP is limited, and the results are inconsistent among species and ecosystems.



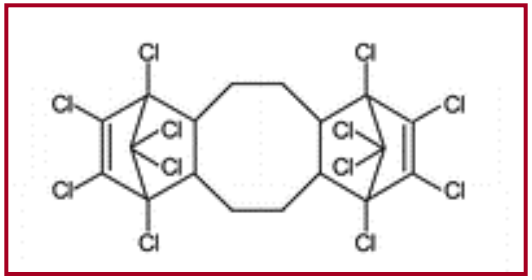
Biota-sediment accumulation factors (BSAFs) for DP isomers compared to those for extremely hydrophobic polychlorinated biphenyls (CBs 199, 203, 207, and 208) and decabromodiphenyl ether (BDE 209), in three bottom fish species (crucian carp, mud carp and northern snakehead) from an e-waste recycling site, South China. Error bars represent ± 1 standard error.

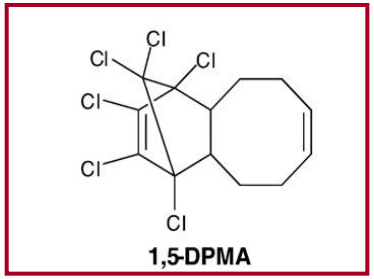
BSAFs for DP comparable to those for deca-BDE-209.

Zhang *et al.*, Env. Int. **2011**, 37:1357-1361

CONCLUSIONS AND FUTURE RESEARCH NEEDS

- Some DP related compounds, such as DPMA, have been investigated. Careful examination of technical DP mixtures revealed the presence of DPMA as impurities. Moreover, studies on lake trout suggested a greater bioaccumulation of DPMA due to its smaller molecular size. More studies are needed on the analytical procedure of DPMA (avoiding acid attack), and on the occurrence and behaviour of this compound.

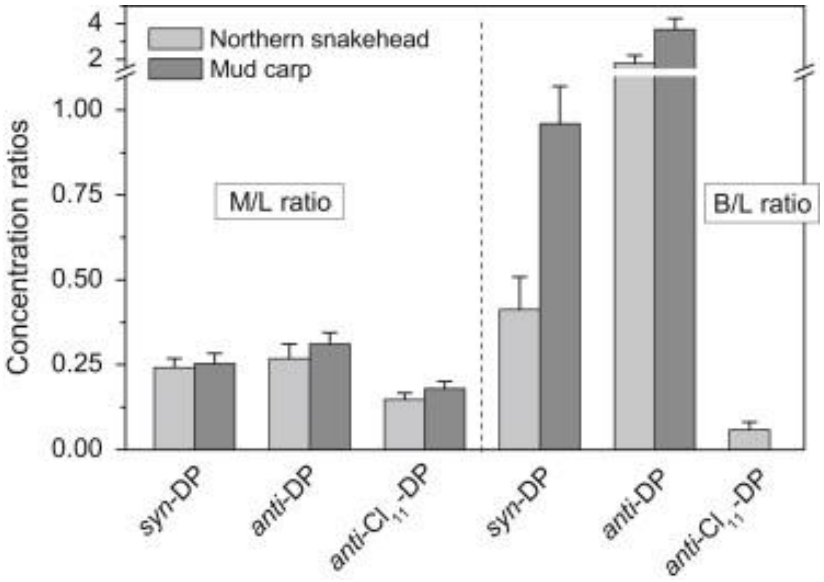




- Information on the different behavior of *syn*- and *anti*-DP have demonstrated a need to treat the isomers individually when assessing the impact of DP on the environment and on human exposure.

CONCLUSIONS AND FUTURE RESEARCH NEEDS

Information on tissue distribution of DP is limited.



Lipid-normalized muscle/liver concentration ratios (M/L ratio) and brain/liver concentration ratios (B/L ratio) for *syn*-, *anti*-, and *anti*-Cl11-DP isomers in northern snakehead and mud carp collected form an e-waste recycling site in South China. The B/L ratio for *anti*-Cl11-DP could not be calculated for mud carp due to the low levels of this isomer found in the brain.

High persistent retention in the brain compared to the liver was observed for anti-DP, suggesting that this isomer can across the blood-brain barrier of fish, and may cause adverse effects to the nervous system in the exposed biota. Further research is needed on the neurotoxicity of anti-DP.

Zhang *et al.*, Env. Pollution **2011**, 159:3647-3652

CONCLUSIONS AND FUTURE RESEARCH NEEDS

- Toxicity data for DP are rarely reported. Most of the toxicity data were provided by DP manufacturers. More acute and chronic toxicity data, including also those from academic communities, are needed for a better environmental and human risk assessment.

- Other Dechloranes, such as Dec602, Dec603 and Dec604, have been also recently studied. Their widespread occurrence, generally at lower concentration levels than DP, demonstrates the need for further research studies.

ACKNOWLEDGEMENTS

- Spanish Ministry of Science and Innovation through the CEMAGUA and SCARCE Projects
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