The Fate of Chiral Organochlorine Compounds and Selected Metabolites in Intraperitoneally Exposed Arctic Char

(*SALVELINUS ALPINUS*)

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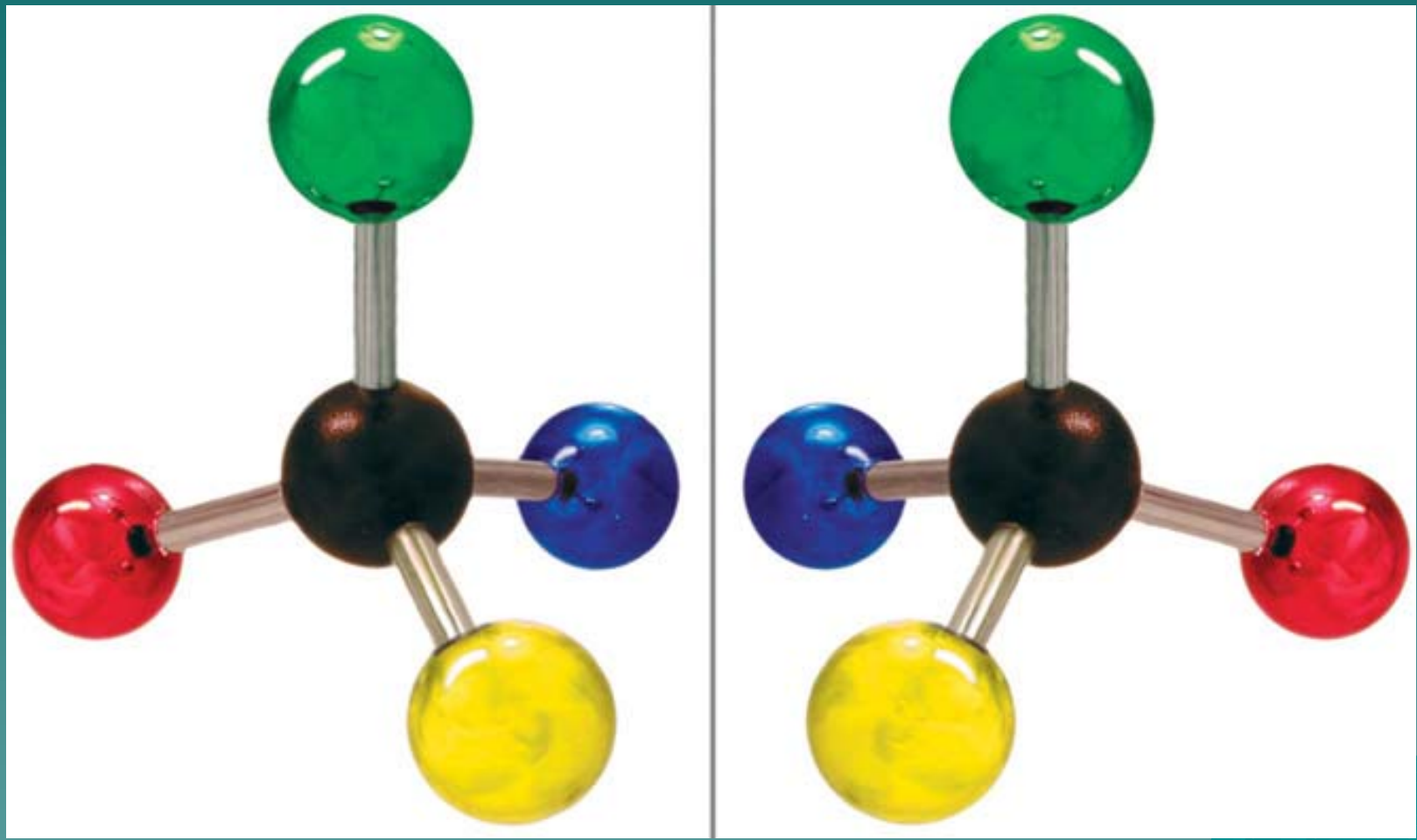
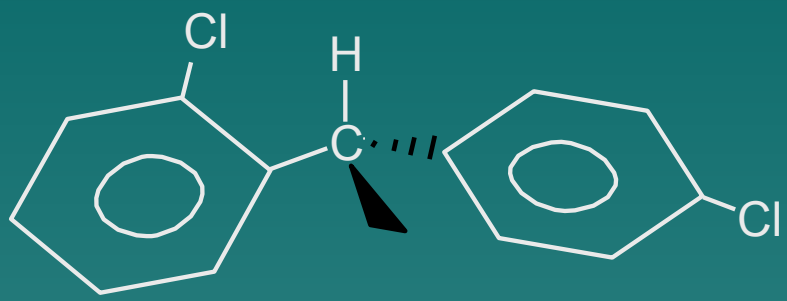
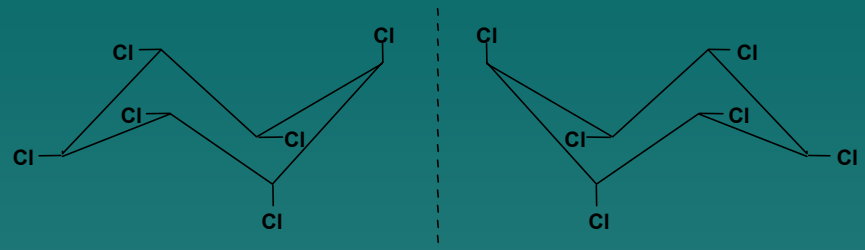
Chiral Compounds

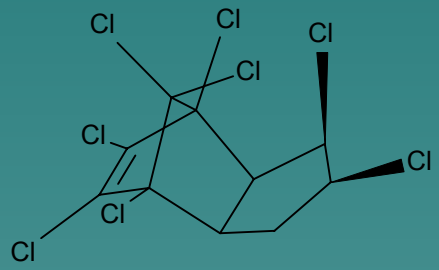




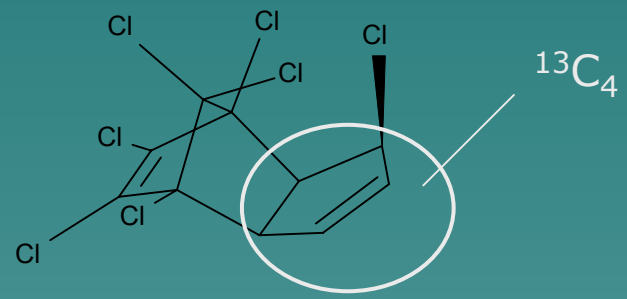
o,p'-DDT



α-Hexachlorocyclohexane (α-HCH)

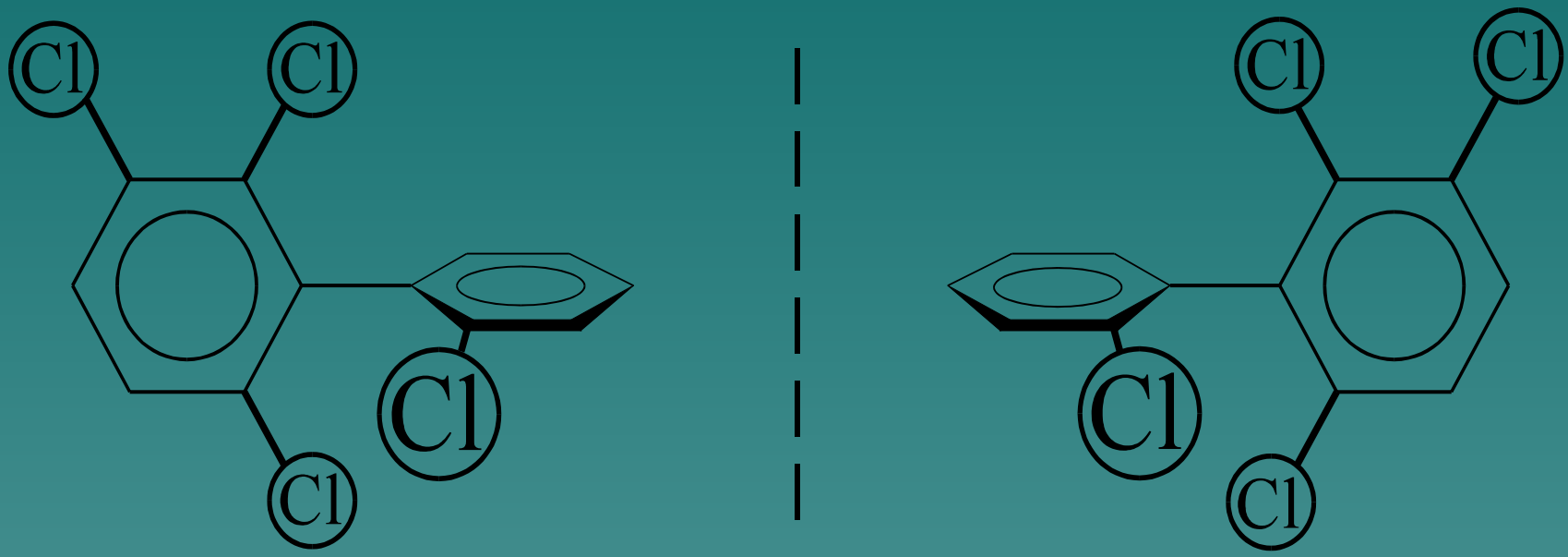


cis-chlordane

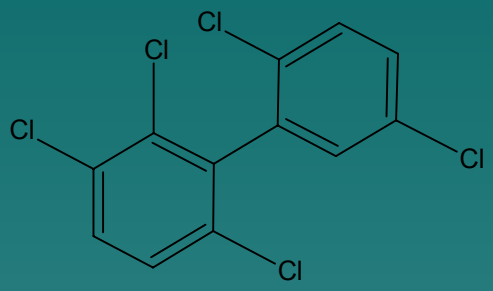


$^{13}C_4$- heptachlor

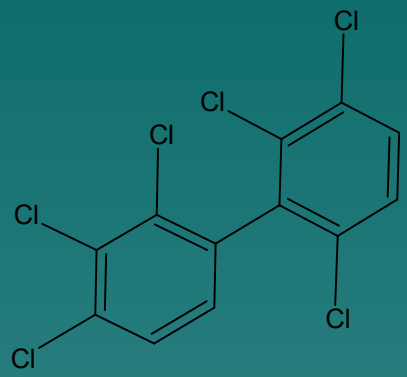
Atropisomeric PCBs



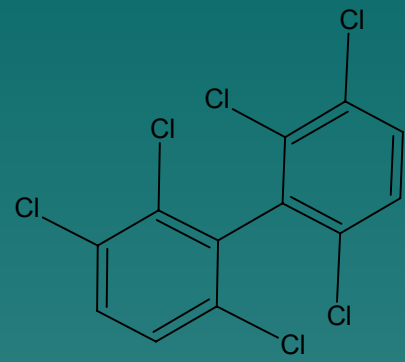
Mirror Plane



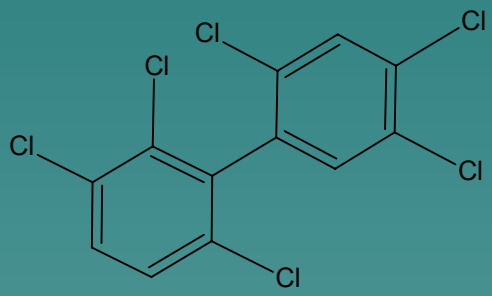
PCB-95



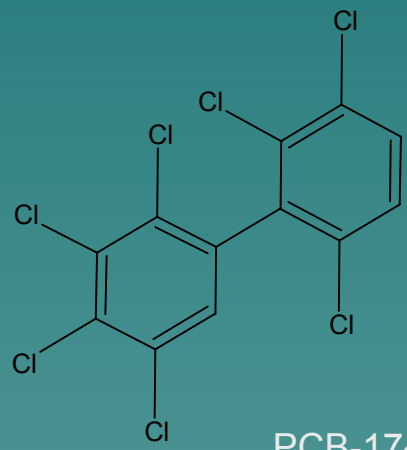
PCB-132



PCB-136



PCB-149



PCB-174

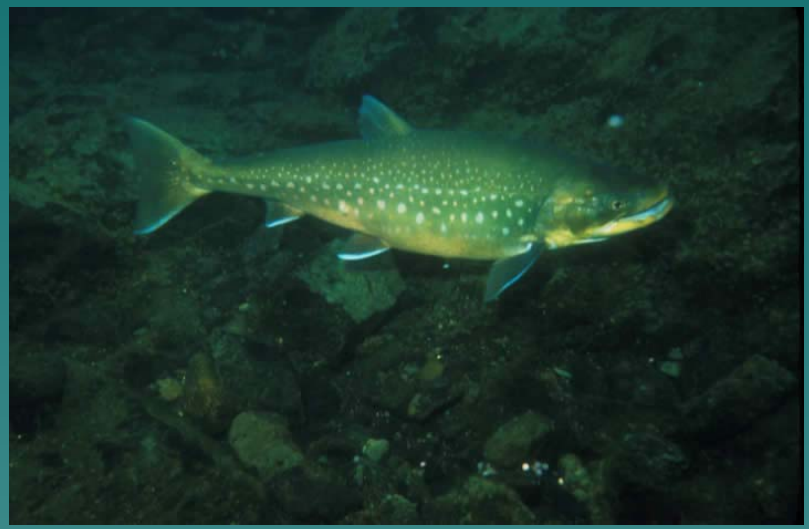
Arctic char

(*Salvelinus alpinus*)

Contaminants in peanut oil

~200 ng of each per g fish

Sampling



- Control cohort
- 1 week (*n*=3)
- 2 weeks (*n*=3)
- 5 weeks (*n*=4)

Muscle and liver samples

50 liter flow-through aquaria

aerated water at +10°C

14 h light:10 h dark cycle

Extraction and Clean Up

Mixing with Na_2SO_4

Column extraction
acetone:hexane 2.5:1
hexane:diethylether 9:1

Fat removal

semi-permeable membrane devices (SPMD)

cyclopentane

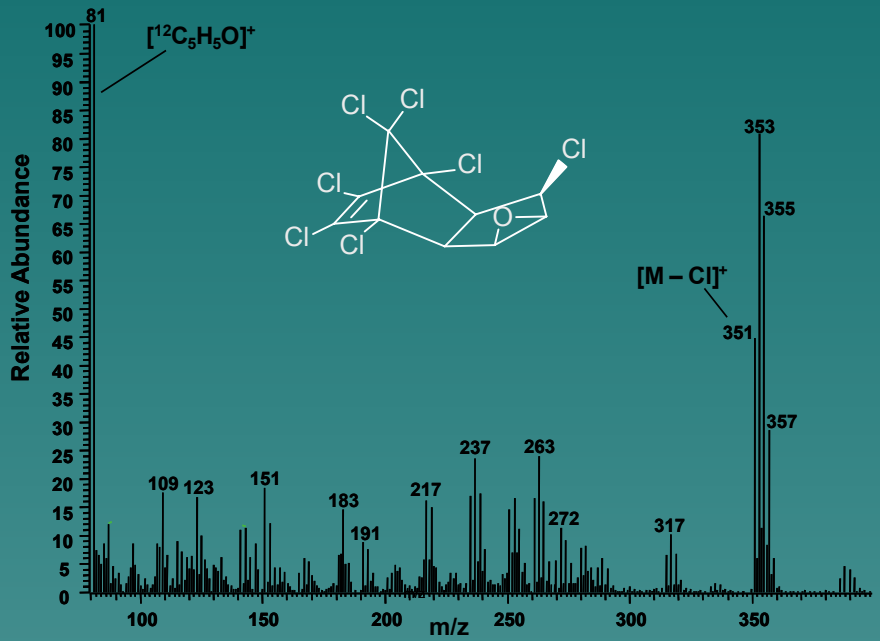
Florisil chromatography

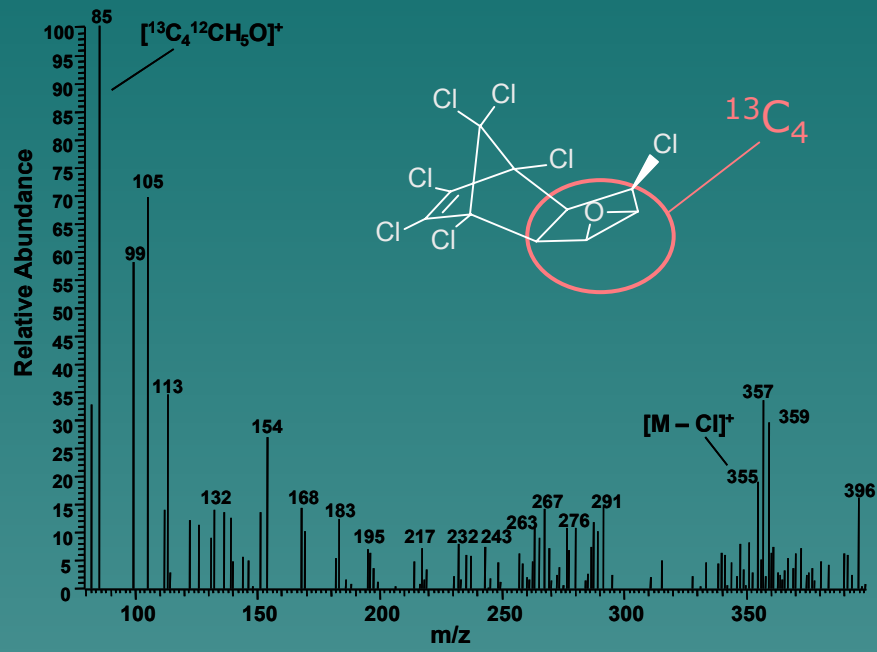
Instrumental analysis

- GC-MS
  EI+ and ECNI
  SIM and full-scan
- GC-ECD

- SP-5 (Supelco®)
  30 m, 0.32 mm, 0.25µm
- Chirasil Dex (Varian, Inc.)
  30 m, 0.25 mm, 0.25µm

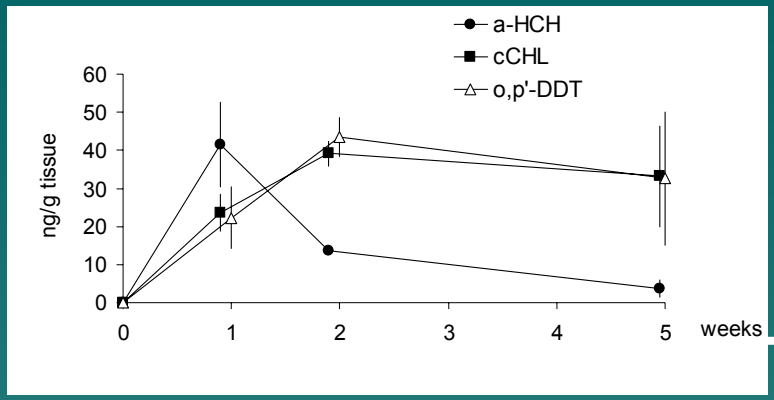
Metabolites



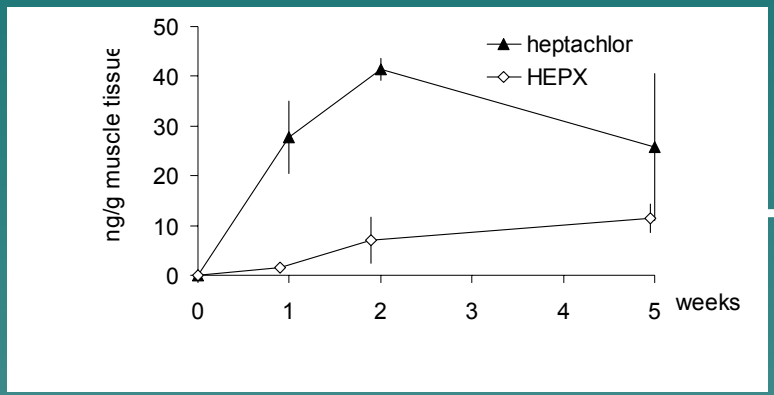


Heptachlor → Heptachlor-*exo*-epoxide (HEPX)

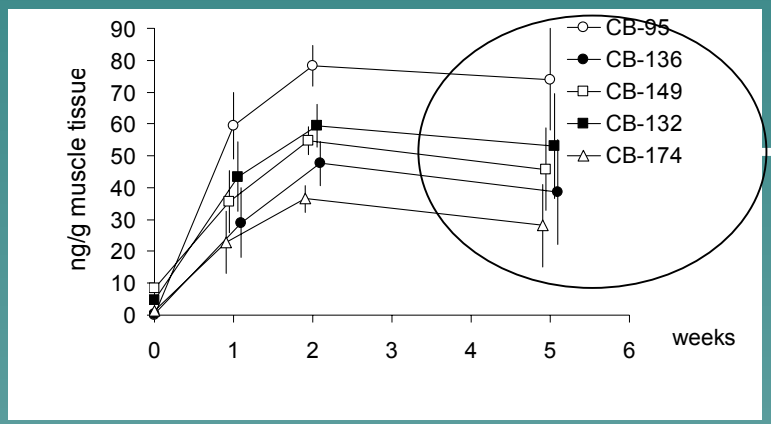
Muscle samples



α-HCH was eliminated

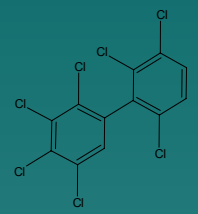


HEPX was formed

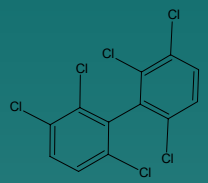


The PCBs were assimilated differently

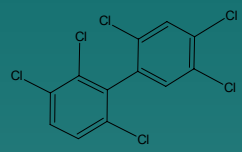
Increasing concentration



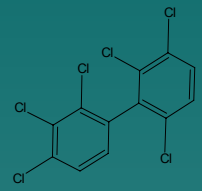
PCB-174



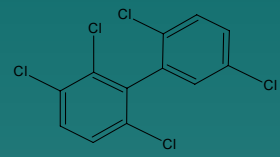
PCB-136



PCB-149



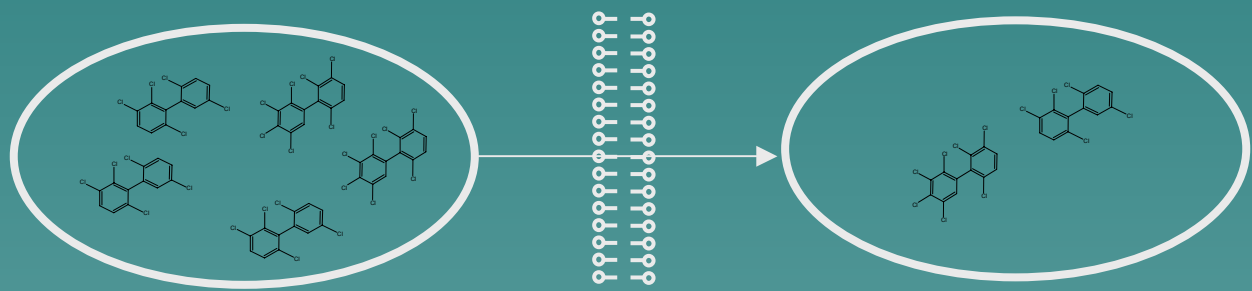
PCB-132



PCB-95

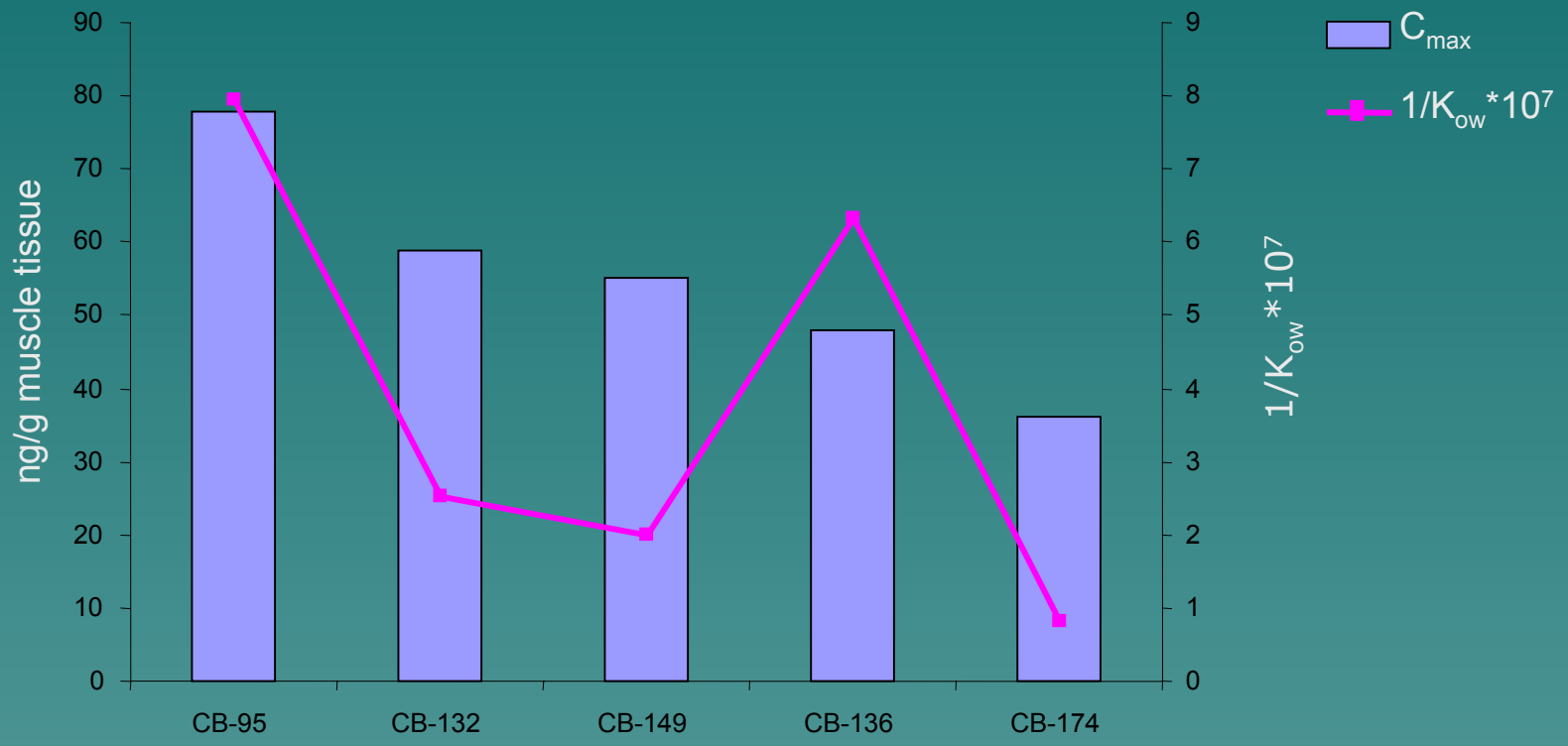
Decreasing K_{ow}

PCB-174 PCB-95



Peanut oil Fish

Assimilation of PCBs

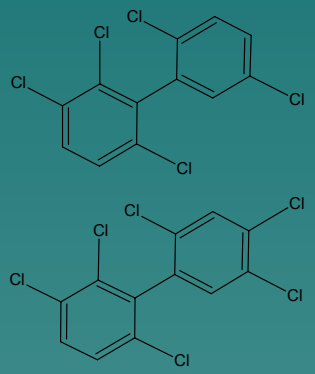


K_{ow} from Brodsky and Ballschmiter, *Fresenius' J Anal Chem,* 331:295-301, 1988

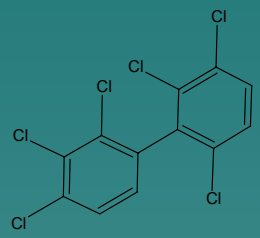
Steric effect coefficients (SECs)

Shaw and Connell, ES&T 18:18-23, 1984

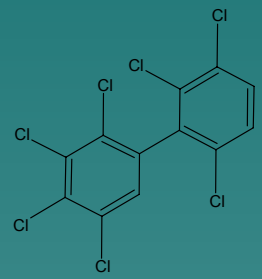
PCB-95
PCB-149
0.74



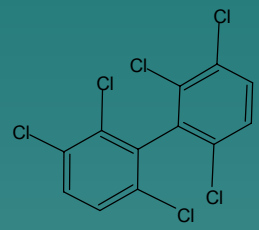
PCB-132
0.65



PCB-174
0.58

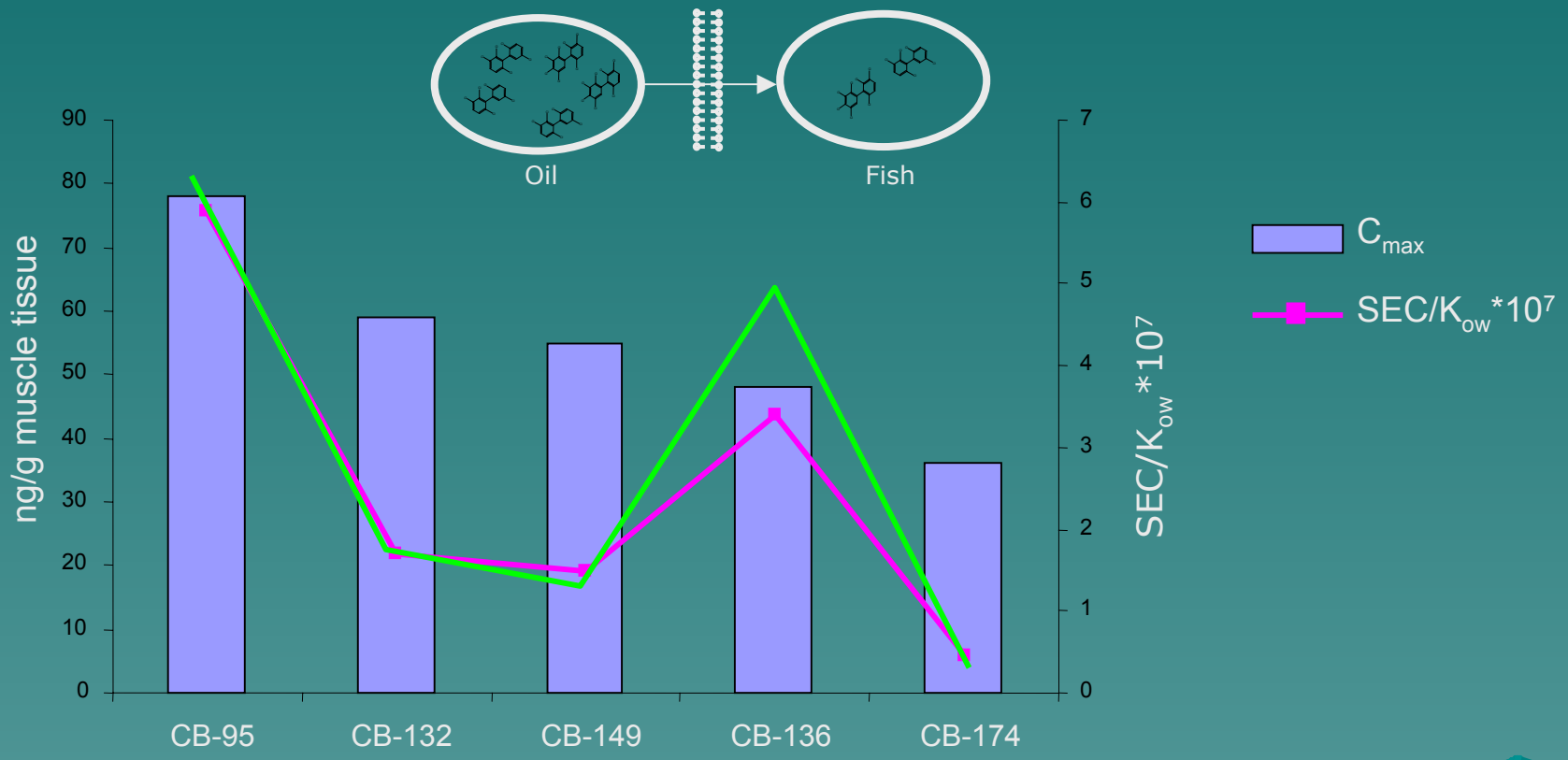


PCB-136
0.54

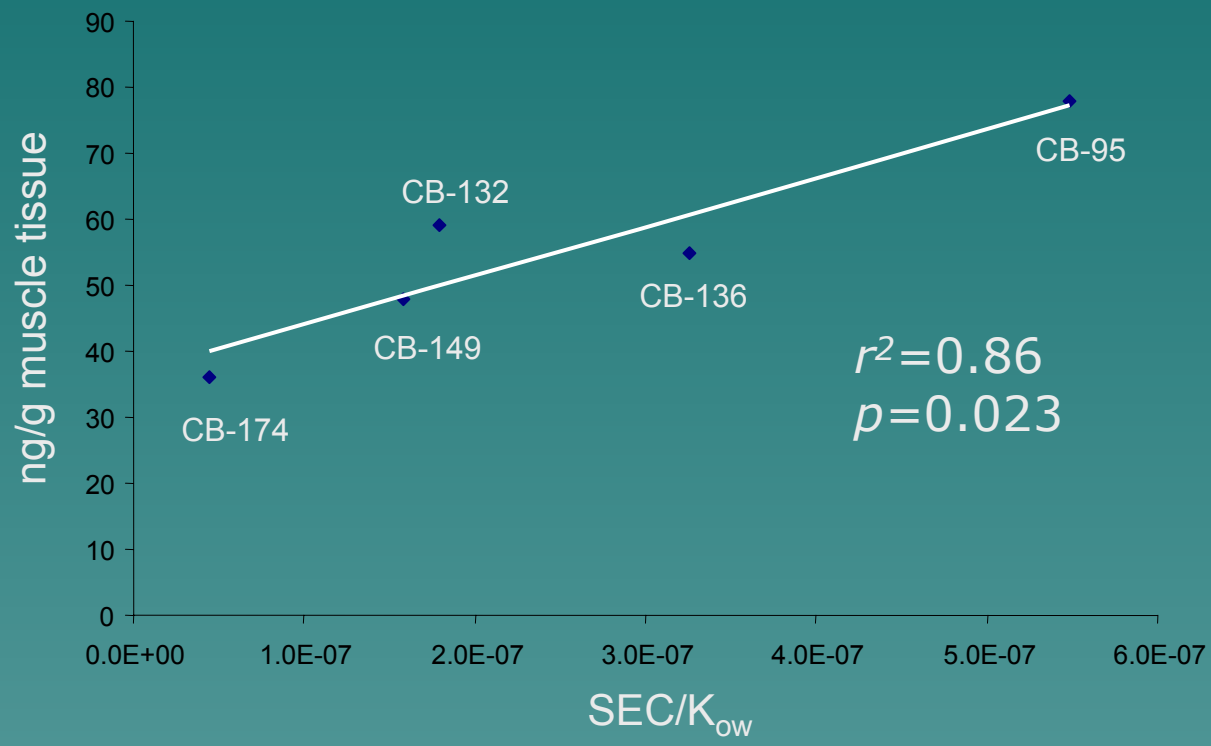


Increasing steric hindrance

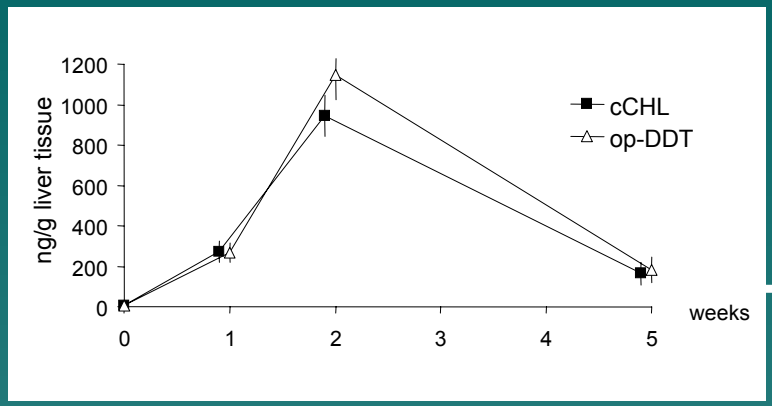
Assimilation of PCBs

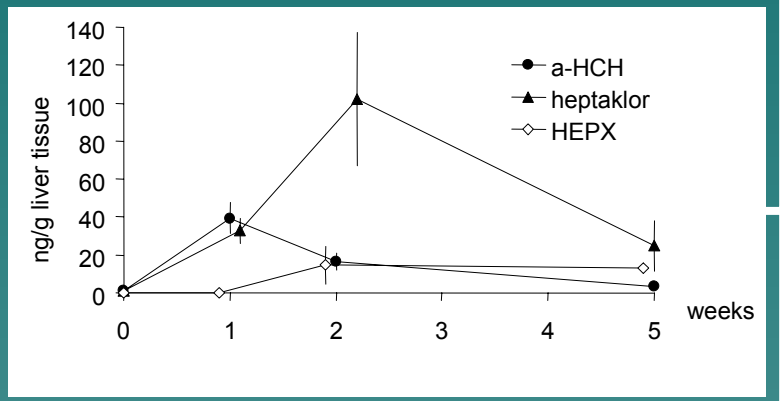


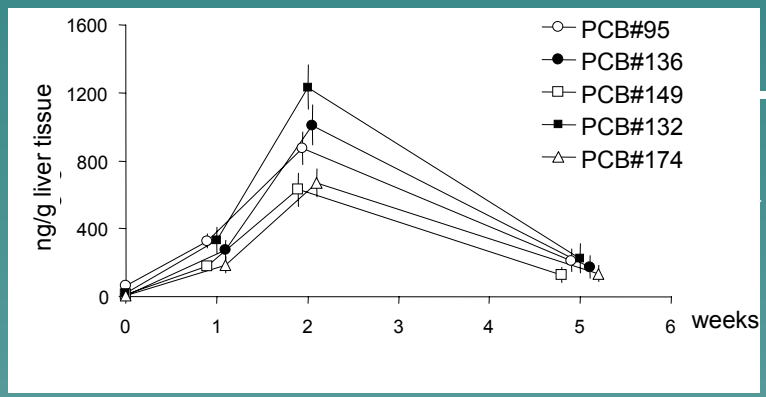
Average C_{max} vs SEC/K_{ow}



Liver samples







Elimination

HEPX was formed

Half-lives 8-10 days for all compounds

Primarily other clearance than biotransformation

Enantiomeric composition

Reference standards were racemic.

Did it change during the experiment?

Indication of that biotransformation occured.

Enantiomeric Fraction (EF)

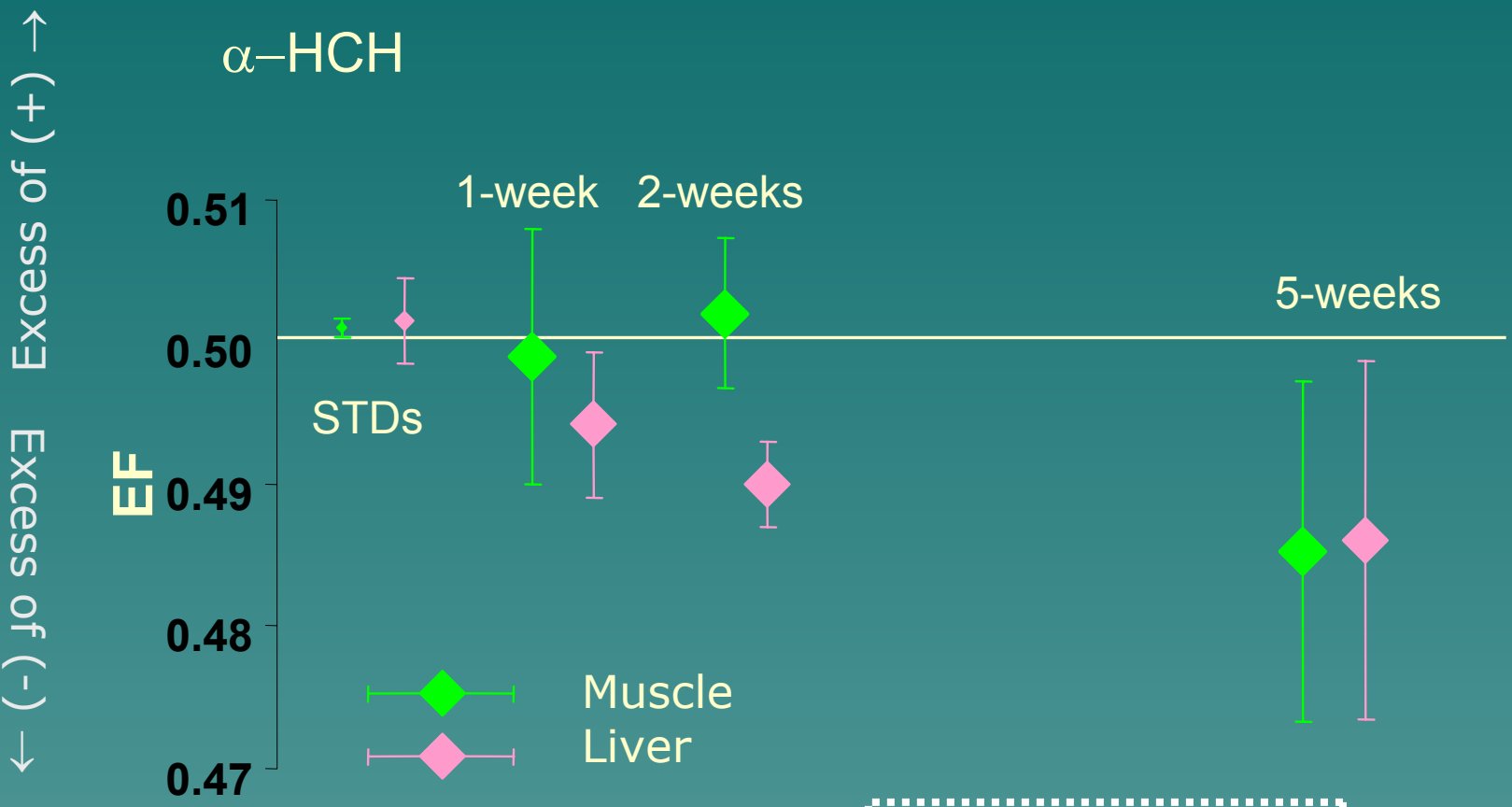
EF=Area of (+)/Area of (+) and (–)

EF=0.50 means racemic

EF>0.5 means excess of (+)

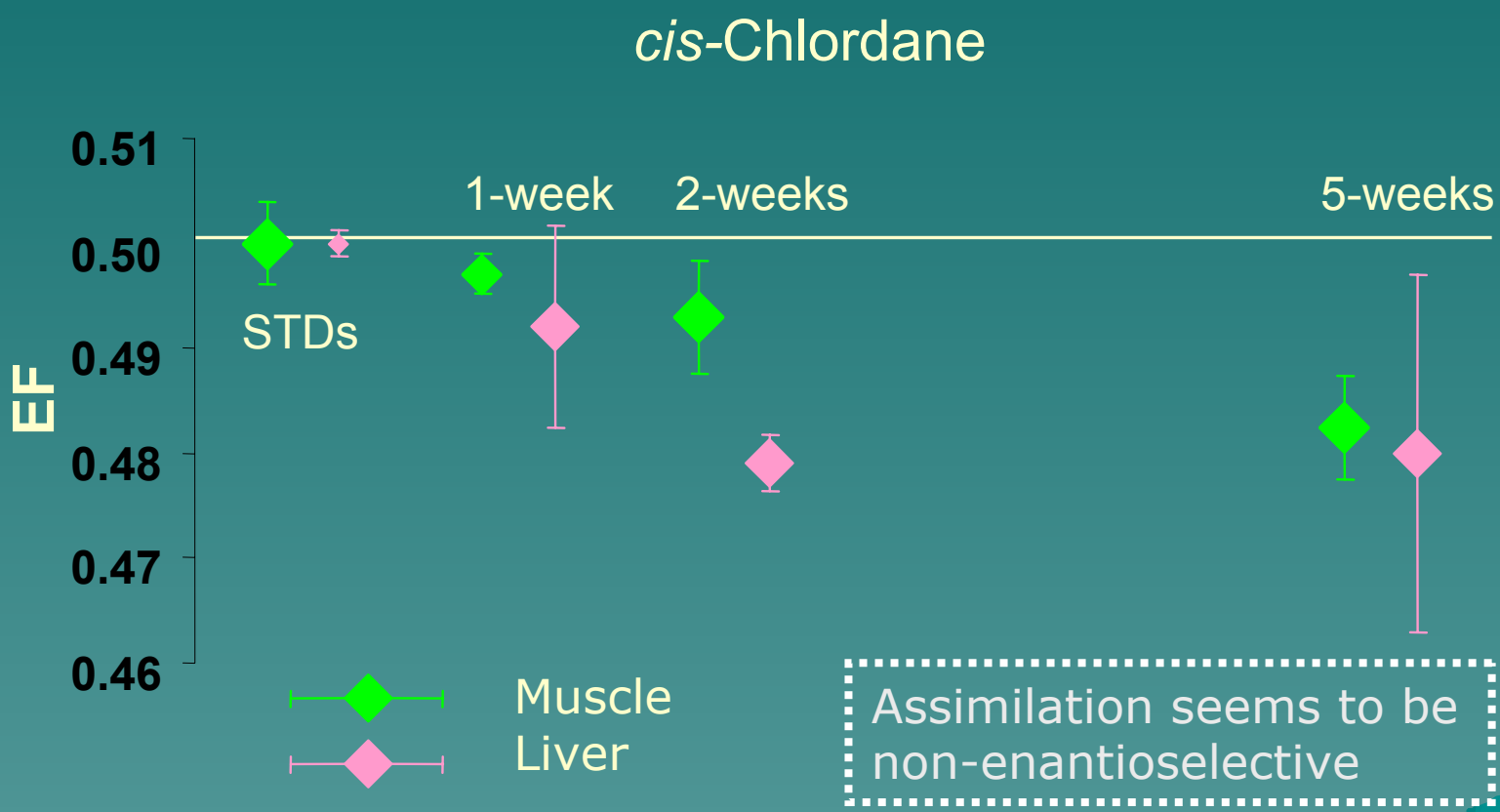
EF<0.5 means excess of (–)

Chiral results

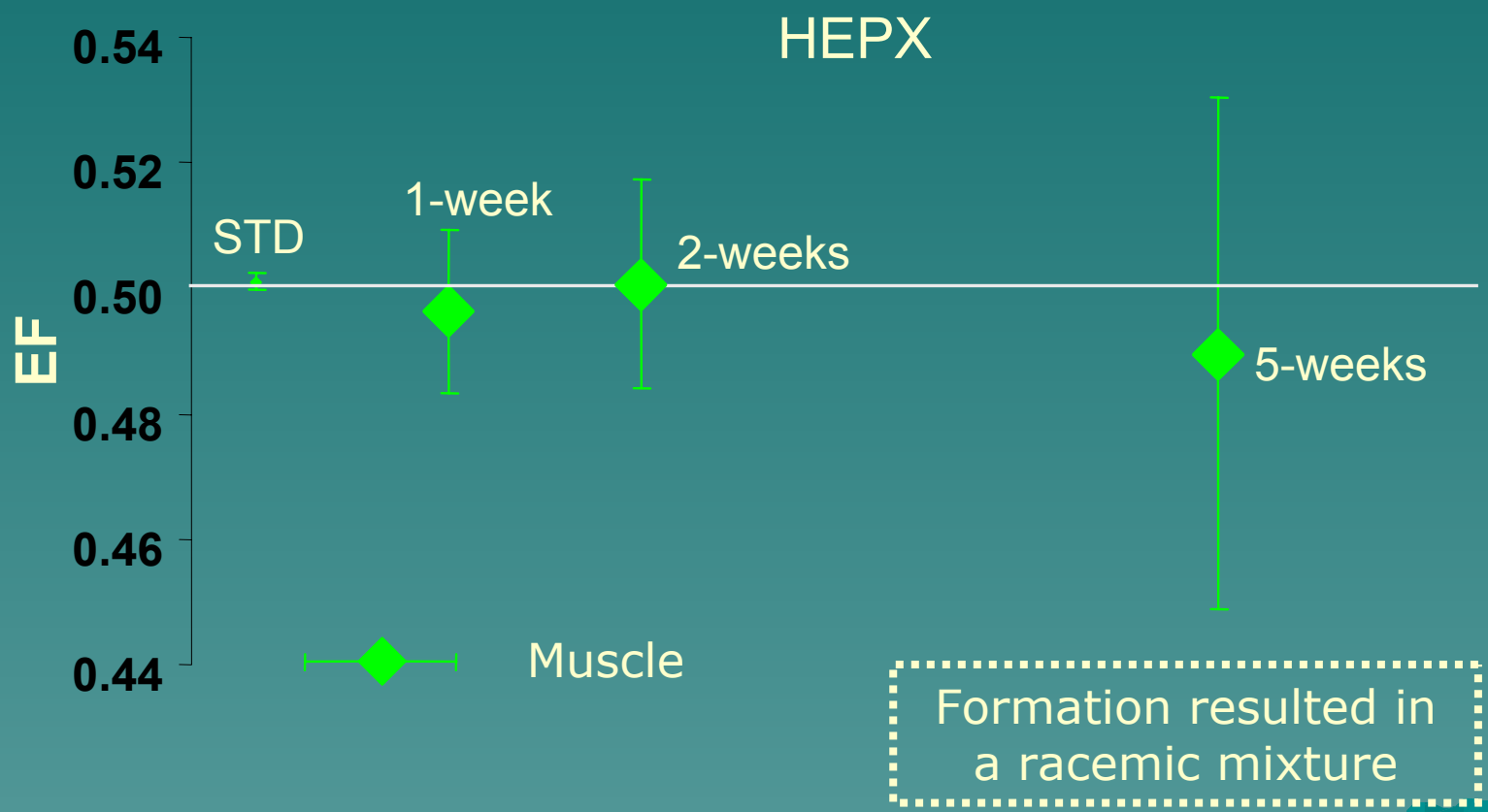


Enantioselective biotransformation

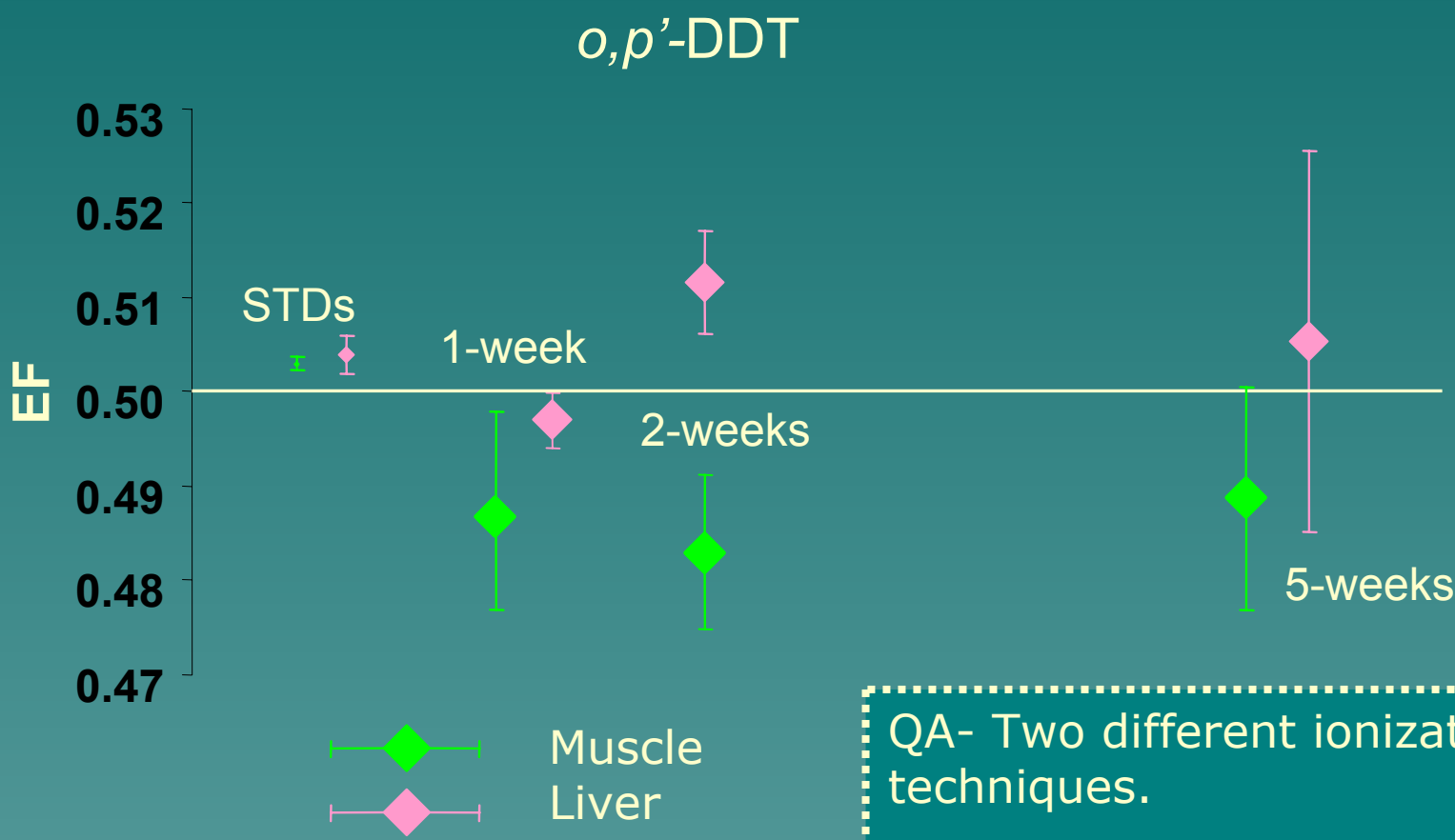
Chiral results



Chiral results



Chiral results



QA- Two different ionization techniques.

Different trends in liver and muscle.

Chiral results PCBs

- PCBs 95, 149 and 174, no apparent enantioselective biotransformation.
- PCB 132 increasing proportion of (+) in muscle.
- PCB 136 increasing proportion of (+) in muscle and liver.

Summary 1(2)

Assimilation

- The contaminants were assimilated.
- The assimilation appeared to be non-enantioselective.
- K_{ow} and steric effects seem to influence assimilation.

Elimination

- Slow elimination in muscle with exception of α-HCH.
- Fast and similar elimination in liver of all compounds – indicate primarily other clearance than biotransformation.

Summary 2(2)

Biotransformation?

- HEPX was formed - racemic mixtures.
- Chiral time trends for some compounds.

Species specific differences?

- Enantiomeric excess vary among species.
- Enantioselective biotransformation seems to be species specific.

Thanks to:

- My co-authors:

Patrik Andersson, Peter Haglund, Umeå University, Sweden

Håkan Berg, University of Texas, USA

Per-Erik Olsson, Örebro University, Sweden

- Terry Bidleman, Meteorological Service of Canada for some of the chiral analyses and for putting the GC-MS instrument at our disposal.

- Per Byström, Department of Ecology and Environmental Science, Umeå University, for calculations on feed and growth.

Thank you for the attention!