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

(SALVELINUS ALPINUS)

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Chiral Compounds
$\alpha$-Hexachlorocyclohexane ($\alpha$-HCH)

$\textit{o,p}'$-DDT

$\textit{cis}$-chlordane

$\textit{^{13}C}_4$-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 \((n=4)\)

50 liter flow-through aquaria
aerated water at +10°C
14 h light:10 h dark cycle

Muscle and liver samples
Extraction and Clean Up

Mixing with Na$_2$SO$_4$

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 $\rightarrow$ 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

Decreasing $K_{ow}$

PCB-174  PCB-95

Peanut oil  Fish
Assimilation of PCBs

$C_{\text{max}}$ vs. $1/K_{\text{ow}} \times 10^7$

Steric effect coefficients (SECs)
Shaw and Connell, ES&T 18:18-23, 1984

Increasing steric hindrance
Assimilation of PCBs

![Diagram showing the assimilation of PCBs from oil to fish.]

- **C\text{\(_{max}\)}**: ng/g muscle tissue
- **SEC/K\text{\(_{ow}\)} * 10\(^7\)**

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**Graph**

- **X-axis**: CB-95, CB-132, CB-149, CB-136, CB-174
- **Y-axis**: ng/g muscle tissue
- **Legend**:
  - Purple bar: \(C_{max}\)
  - Pink line: \(SEC/K_{ow} * 10^7\)
Average $C_{max}$ vs SEC/$K_{ow}$

$r^2 = 0.86$

$p = 0.023$
Half-lives 8-10 days for all compounds

Primarily other clearance than biotransformation

HEPX was formed

Elimination

Liver samples
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

Excess of (+) → α-HCH

1-week 2-weeks

STDs

Muscle

Liver

5-weeks

Enantioselective biotransformation
Chiral results

**cis-Chlordane**

Assimilation seems to be non-enantioselective.
Chiral results

Formation resulted in a racemic mixture
Chiral results

$o,p'$-DDT

STDs

1-week

2-weeks

5-weeks

EF

0.53

0.52

0.51

0.50

0.49

0.48

0.47

Muscle

Liver

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 $\alpha$-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.
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