Chiral Chlordane Components in Environmental Matrices

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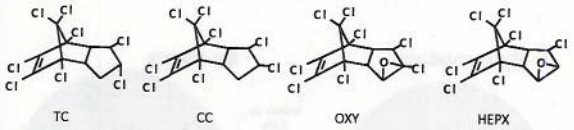
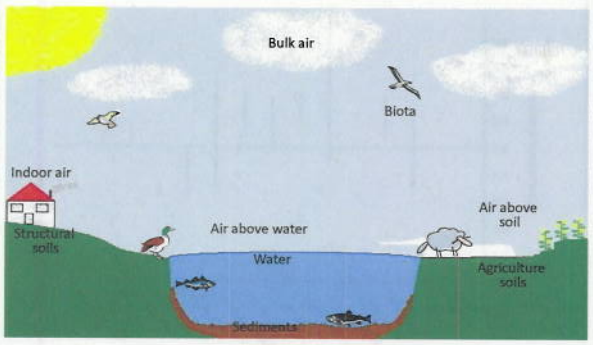
Chlordane



- Used in US 1940s - 1988 totaling >70,000 tons
- Agricultural and residential pest control
- >140 compounds in technical mixture
- TC, CC, TN most abundant
- TC, CC degrade to OXY; Heptachlor degrades to HEPX
- Many compounds in mixture are chiral

Chlordane in the environment

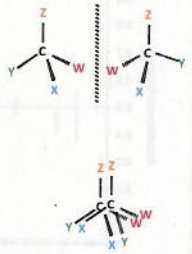


Chlordane Enantiomers

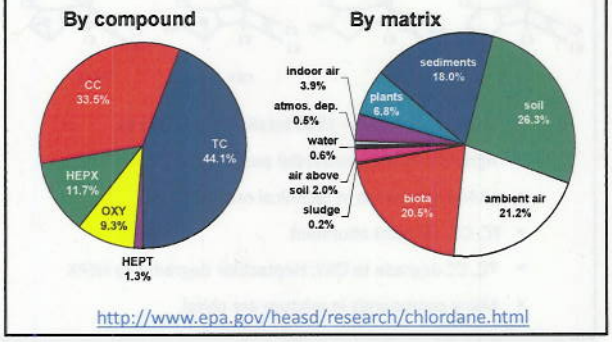
$$\text{Enantiomer Fraction} = EF = \frac{area\ (+)\ enantiomer}{area\ (-)\ enantiomer}$$

ChirBase entries for chlordane compounds

Compound	GC entries	LC entries
1,5-photo-cis-chlordane	3	
2,5-photo-cis-chlordane	3	
Chlordene	3	1
cis-Chlordane	21	5
endo-HEPX	11	1
Heptachlor	17	3
Oxychlordane	16	1
Photo-heptachlor	3	
trans-Chlordane	21	5
Exo-HEPX	16	2
U82	4	

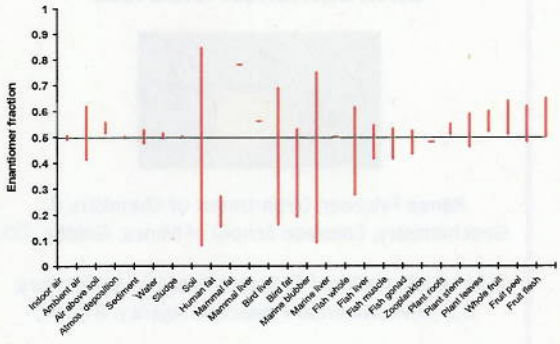


EF measurements reported by compound and matrix

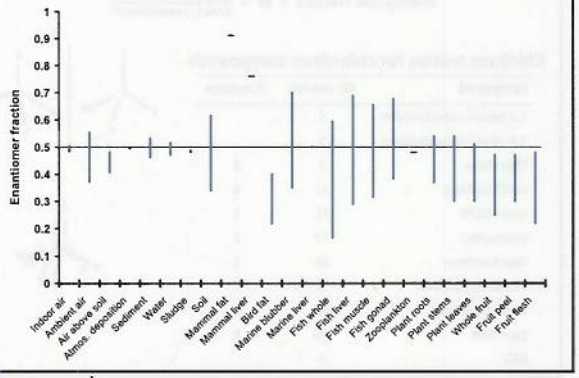


http://www.epa.gov/heasd/research/chlordane.html

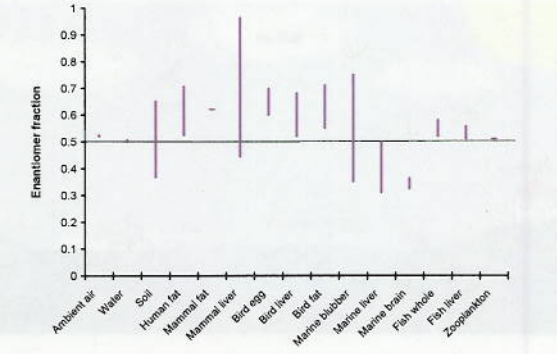
CC EFs in environmental matrices



TC EFs in environmental matrices



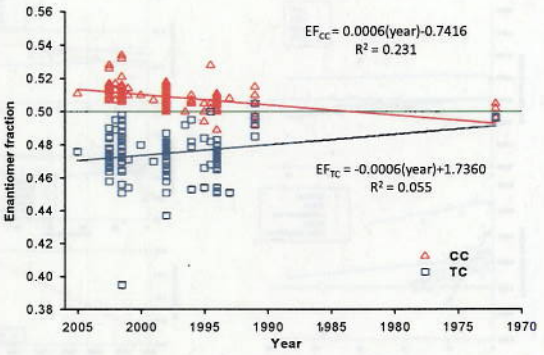
OXY EFs in environmental matrices



Chlordane EF measurements in Ambient and Indoor Air

Sample type	CC	TC	HEPT	HEPX
Ambient EF Range	0.413-0.619	0.372-0.554	0.493-0.521	0.528-0.805
N	204	219	8	58
%NR(+)	31%	0%	12%	100%
%NR(-)	4%	67%	0%	0%
Indoor EF Range	0.490-0.505	0.490-0.505		
N	25	25		
%NR(+)	0%	0%		
%NR(-)	0%	0%		

Chlordane EFs in ambient air over time



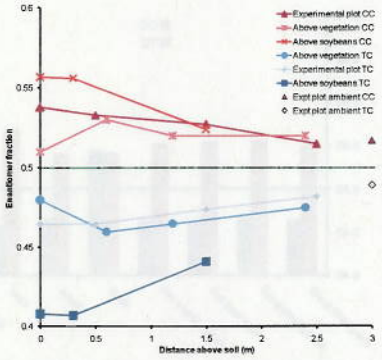
Chlordane EF measurements in Agricultural and Background Soils

Sample type	CC	TC	HEPX	OXY
Agricultural EF Range	0.409-0.740	0.237-0.885	0.530-0.879	0.367-0.650
N	98	113	16	8
%NR(+)	81%	2%	100%	29%
%NR(-)	1%	84%	0%	71%
Background EF Range	0.080-0.846	0.341-0.616		
N	103	114		
%NR(+)	51%	8%		
%NR(-)	34%	75%		

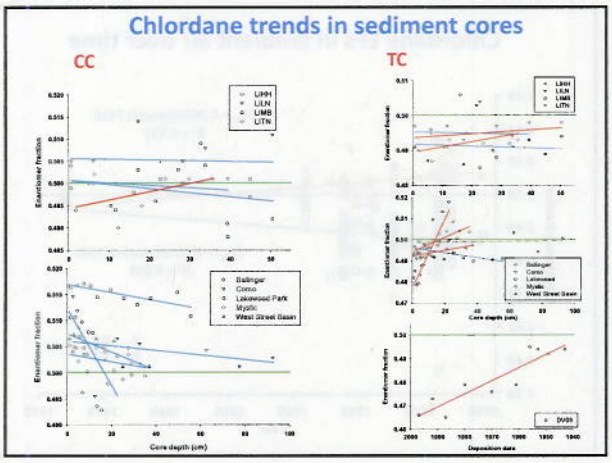
Chlordane EFs in air above soil

Indoor air
EF_{CC} = 0.49-0.505
EF_{TC} = 0.485-0.505

Air near Great Lakes
EF_{CC} = 0.413-0.619
EF_{TC} = 0.372-0.554



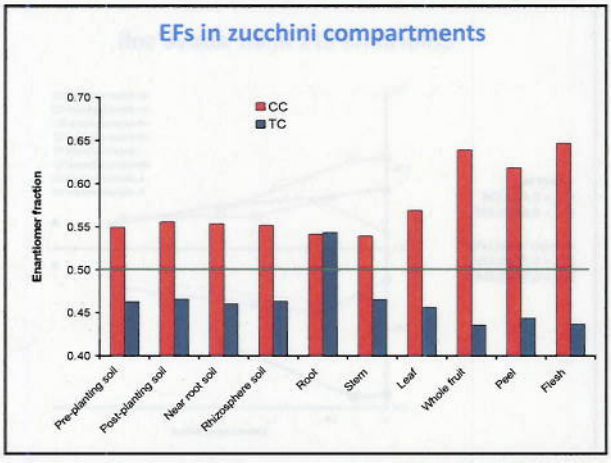
Chlordane trends in sediment cores



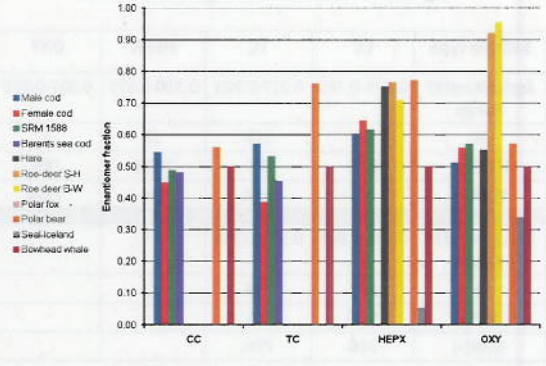
Chiral Chlordanes in Plants and Biota

Sample type	CC	TC	HEPX	OXY
All Plant				
%NR(+)	70%	14%	76%	
%NR(-)	20%	70%	24%	
All Biota				
%NR(+)	37%	31%	57%	65%
%NR(-)	52%	65%	39%	30%

EFs in zucchini compartments



EFs in liver in various species



Uses of Enantiomer Data

- Characterization of differences in toxicity, persistence, bioactivity
- Differentiation between degradation pathways
  - Physical weathering gives racemic signature (volatilization, chemical reactions, photolysis)
  - Biological processing gives a non-racemic signature (biodegradation, partitioning into organisms, depuration)
- Tracking sources and age of contamination
- Determining spatial, seasonal, temporal changes, long range transport
- Differences in metabolism mechanisms and rates between isomers
- More accurate risk assessments

Observations and Conclusions

- TC, ambient air, and soil most commonly measured
- TC, OXY and HEPX EFs usually <0.5, CC usually >0.5
- TC EFs in sediment and ambient air ↓over time, ↑nonracemic
- Air above soil shows similarity of EF in soil; ↑ ambient with height
- Indoor air racemic, ambient air nonracemic - different sources
- Soil likely source to both air and sediment
- EFs in biota/plants depend on species, organ, degradation

EFs - useful tool for determining sources and degradation pathways for POPs

Acknowledgements

Thanks to the authors and everyone who has collected samples and reported data for these projects!

(>2400 measurements of chiral chlordane components!!)

http://www.epa.gov/heasd/research/chlordane.html

Disclaimer: Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

A. Wayne Garrison

What "close to retirement" means to Wayne:

SINCE 1999...

- ~28 publications
- ~60 presentations