

Chiral chlordane components in environmental matrices

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Abstract

Chlordane, a persistent, bioaccumulative and toxic organochlorine pesticide, has been studied for many years. Since the advent of chiral analysis for environmental samples, over 2,400 measurements have been made of various chiral chlordane components. Chlordane enantiomer fractions most often have been reported for air and soil with studies suggesting volatilization from soil is an important source to ambient air, although urban termiticide usage also can influence chiral chlordane measurements. Sediment core studies suggest the small amount of enantioselective degradation of chlordane likely occurs prior to deposition. In general, enantioselective degradation of chlordanes in biota occurs more frequently resulting in more nonracemic values than in other environmental media. There is also more diversity in range and enantiomer preference in biota. Analysis in plants has shown the ability to enantioselectively uptake and transport chlordane compounds from soil to root, from air to leaf and within the plant itself. Observation and measurement of chlordane enantiomers can provide a better understanding of the fate, exposure, toxicity, and risk of chlordanes and other chiral compounds in the environment.

Introduction

History of chlordane use, regulations, and environmental distribution

Chlordane is a persistent, bioaccumulative and toxic organochlorine pesticide used in the United States for forty years (1). Due to its extensive usage, both agriculturally and residentially, and its long half-life in the environment, everyone in the US has been exposed to low levels of chlordane, typically from eating contaminated foods or contact with contaminated soil (2). The International Agency for Research on Cancer considers chlordane a possible human carcinogen (3) and chlordane was included in the Stockholm Convention as one of the original and infamous “Dirty Dozen” persistent organic pollutants (POPs) (4).

Technical chlordane consists of more than 140 compounds, including chlordanes, nonachlors and heptachlor (2). From its introduction in the 1940s to its eventual cancellation for all uses in the US in 1988, chlordane was used widely for both agricultural and residential pest control (1). Use for food crops was banned in 1978 and by 1983, all above-ground use ended. However, chlordane was used for subterranean termite control in the foundation of homes for another five years. Production was voluntarily stopped globally in 1997 by the major manufacturer, Velsicol Chemical Co. (5).

Of the multiple compounds found in the technical chlordane mixture, *cis*- and *trans*-chlordane and *trans*-nonachlor are the most abundant species representing ~28% of the mixture (6-8). The exact ratio of the *cis*-chlordane isomer (CC, also known as α -chlordane) to the *trans*-chlordane isomer (TC, also called γ -chlordane) in the technical mixture depends on the manufacturing process (9), but recent studies have reported this TC/CC ratio to be ~1.0–1.2 (7, 8).

Chlordane can undergo long-range transport due to its semivolatile nature and is considered a persistent organic pollutant (POP). Chlordane compounds and their degradation products have been

found throughout the globe from the US (10-12) to the Arctic (13-15), from Asia (16, 17) to Mexico (18) and in all media including air (16, 19, 20), soil (21, 22), water (23), food crops (24, 25) and biota (26-28). Chlordane can be taken up into edible plant tissues, both root and aerial, of a number of food crops (24, 25) and has been found to bioaccumulate to the highest trophic levels in food chains, such as the polar bear food chain (29), making human exposure by ingestion likely.

Oxychlordane (OXY) is a major metabolite of chlordane that has been found in various media and biota (3). Heptachlor (HEPT) is both a component of technical chlordane (~10% by weight) and a breakdown product of it (3). Technical heptachlor, a commercially sold pesticide in its own right, contained 20-22% *trans*-chlordane (30, 31) and thus may have increased the TC/CC ratio in the environment. Heptachlor epoxide (HEPX) is an oxidation product of both heptachlor and chlordane (3). It has been reported that some metabolites of chlordane, including oxychlordane, heptachlor, and heptachlor epoxide, are more toxic than the parent compounds (2).

Chirality of chlordane compounds

Many of the ~140 compounds that make up technical chlordane are chiral. Their chirality comes from having one or more chiral carbon atoms. For illustrative purposes, the carbon atoms of the methanoindene skeleton, common to all chlordane compounds, have been numbered on *cis*-chlordane in Figure 1. While there are chiral centers at both the bridgehead (carbons 3 and 9) and the shared ring carbon atoms (carbons 4 and 8), the strain on such a small ring and across the shared ring bond makes it impossible for both configurations (R or S) to exist at these chiral carbons. Instead, it is typically the carbons of the cyclopentane ring (carbons 5-7) that includes two unconstrained chiral centers (5 and 6) capable of creating stereoisomers. For example, chlordane has a total of six chiral centers, at carbons 3, 4, 5, 6, 8, and 9; however,

only the centers at carbons 5 and 6 can exist in all configurations, giving rise to a total of four stereoisomers [(+)- and (-)- *cis*- and *trans*-chlordane]. Nonachlor is achiral because of a mirror plane that runs through carbons 6, 10 and the double bond. Heptachlor, the two heptachlor epoxides, and oxychlordane have a chiral center at carbon 5, creating two stereoisomers for each. Other chiral chlordane compounds have been studied in environmental samples, including MC5 and U82, however, the bulk of research on chlordane stereoisomers has been done with *cis*- and *trans*-chlordane, *exo*- heptachlor epoxide, heptachlor and oxychlordane, and these works will be discussed here. Further references to heptachlor epoxide (HEPX) are for the *exo*-isomer (unless stated explicitly), as *endo*-HEPX is not naturally occurring.

	<i>cis</i> -	<i>trans</i> -
Chlordane		
Nonachlor		
Heptachlor		
Heptachlor	<i>exo</i> -Heptachlor epoxide	Oxychlordane

Figure 1. Chemical structures of chlordane compounds

Enantiomer separations

Many of the chiral compounds in technical chlordane and their degradates have been separated using enantioselective chromatography columns. ChirBase, a repository for stereoisomer separations, has entries for at least eleven chlordane compounds by both gas (GC) and liquid (LC) chromatography, as shown in Table 1 (32). Additional separations are found in the literature for *cis*- and *trans*-chlordane, *endo*- and *exo*-heptachlor epoxide, oxychlordane, heptachlor, Compound K, MC4, MC5, MC6, MC7, MC8, photochlordene, photo-heptachlor, photo-heptachlor epoxide, U81, and U82. While a few authors (33, 34) have published LC methods for small-scale preparative separations for chlordane compounds, all environmental measurements have been made using enantioselective gas chromatography with either electron capture detection or mass spectrometry. Reviews of such separations are available (35-37), whereas chromatographic conditions for individual experiments are usually published in the methods section of the research papers themselves.

Cyclodextrins (α -, β -, and γ -), and their many derivatives, are the most commonly used chiral stationary phases resulting from their stability, commercial availability, and history of successful separations of chlordane compounds. Due to the complexity of chlorinated contaminants in the environment, similar isotope patterns, and close retention times, caution and quality control measures are necessary to ensure that co-elutions do not occur. For example, endosulfan I coelutes with one of the *cis*-chlordane enantiomers on a Supelco γ -cyclodextrin column, however this co-elution does not occur on other stationary phases (38). It should be noted that single or enriched enantiomers of *cis*- and *trans*-chlordane, oxychlordane, heptachlor, and heptachlor epoxide A and B are commercially available and provide researchers with an easy way to determine the elution order of enantiomers for any chromatographic conditions (39).

Table 1. ChirBase entries for chlordane compounds.

Compound	GC entries	LC entries
1,5 Photo- <i>cis</i> -chlordane	3	
2,5 Photo- <i>cis</i> -chlordane	3	
Chlordene	3	1
<i>cis</i> -Chlordane	21	5
<i>endo</i> -HEPX	11	1
Heptachlor	17	3
Oxychlordane	16	1
Photo-heptachlor	3	
<i>trans</i> -Chlordane	21	5
<i>exo</i> -HEPX	16	2
U82	4	

Chiral chlordanes in the environment

While many of the chiral chlordane compounds have been measured in the environment, this review focuses on five: *cis*- and *trans*-chlordane, heptachlor, heptachlor epoxide, and oxychlordane. Over 2,400 enantiomer fraction [EF = (+)/(+) + (-)] or enantiomer ratio [ER = (+)/(-)] measurements for these five compounds have been made in environmental matrices. For this review, all data originally reported as enantiomer ratios were converted to enantiomer fractions to simplify comparison (EF = ER/1+ER). When ER was reported as E1/E2 because the elution order was unknown, other references were consulted to determine the elution order and make the correct conversion; this was impossible for only one reference, so that data was not included. The complete dataset is planned to be available at

<http://www.epa.gov/heasd/products/products.html> or by request from the corresponding author.

Figure 2 shows EF measurements by compound. The vast majority of measurements are for *cis*- and *trans*-chlordane. Heptachlor has very few measurements, likely due to low concentrations (possibly due to lower persistence) and difficulties in separating the heptachlor enantiomers. Figure 3 shows EF measurements by environmental or biological compartments. Air and soil were measured most often and water least. Each matrix will be discussed separately in this review.

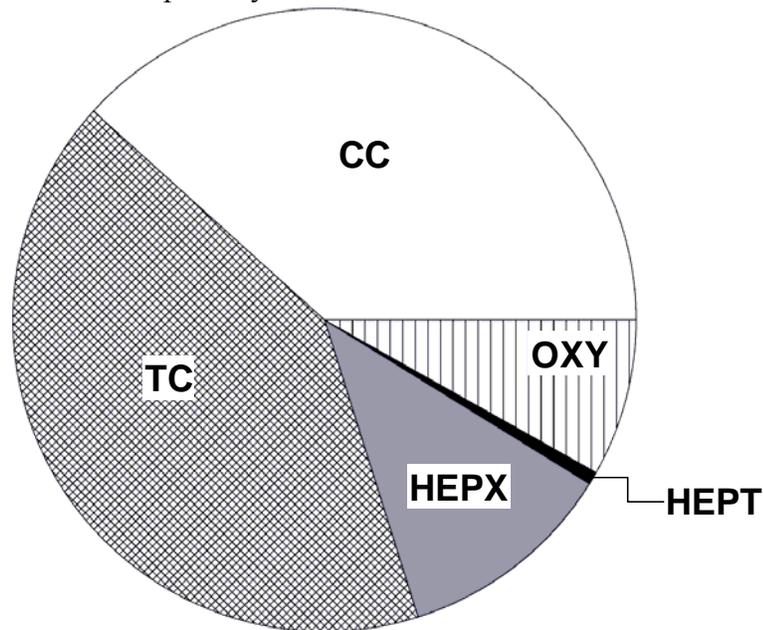


Figure 2. EF measurements by compound

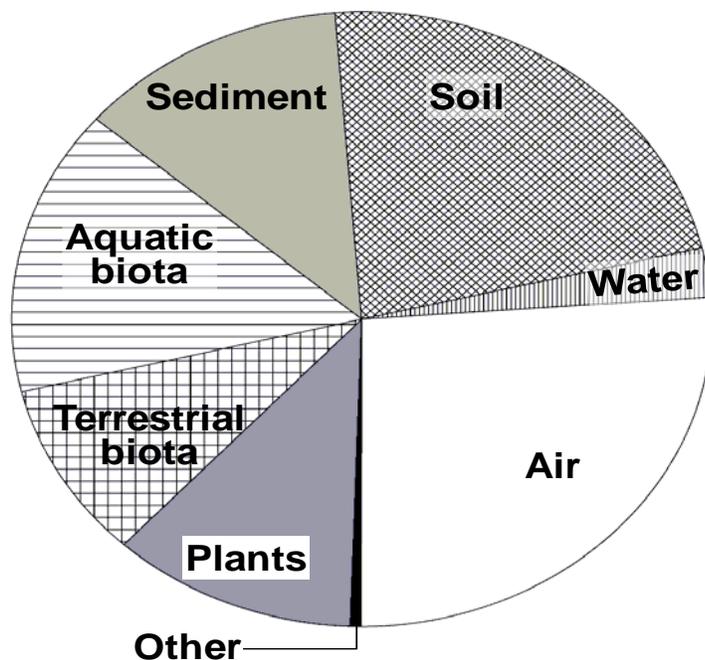


Figure 3. EF measurements by matrix

Air

Chiral chlordane compounds have been reported in ambient air (both rural and urban), indoor air, and air directly above soils. The most commonly reported are EFs for CC and TC in ambient air, although HEPX ambient air EFs are often reported with these. Both passive and active air samplers have been employed with the vast majority of samples taken from the northern hemisphere, primarily North America and Europe. EF values in published studies varied considerably although most samples, by far, showed CC to be either close to racemic or enriched in the (+)-enantiomer while TC tended to be either close to racemic or enriched in the (-)-enantiomer (Table 2). In general, TC tended to be more enantioselectively degraded than CC for most samples although variations, even within one study, can occur due to temporal trends

(13, 40), air-water/air-soil exchange (41, 42), spatial differences (40, 43) and wind direction (16).

HEPX was reported in ambient air samples about a quarter as often as CC and TC (Table 2). Reported values showed a consistent trend towards higher amounts of the (+)-HEPX enantiomer. It is not known whether this trend is due to selective degradation of the (-)-enantiomer of HEPX or selective formation of the (+)-enantiomer of HEPX from degradation of parent compounds; however, Bidleman et al. (44) suggested the most likely source of HEPX in ambient air is that produced by microbial activity in soils rather than HEPT photolysis. Unfortunately, HEPT is only seldom reported, usually due to low concentrations as it is readily degraded in the environment, and the majority of samples were found to be close to racemic. OXY EFs were only reported in one air study with a value of 0.519 found in a sample from Alabama (7).

Several studies have shown similar EF signatures [enrichment of (+)-CC and (-)-TC] in ambient air as found in soils from the same area (10, 45, 46); however, the influence of long range transport and urban termiticide use can affect the EFs in ambient air at any given location (16, 20, 45). For example, a study in Alabama (7) found ambient air EFs for CC and TC as well as MC5 (octachlordane) that were close to racemic. From this data and soil-air exchange models, the authors suggested evaporation from termiticide treated houses in the region might be responsible for the levels in ambient air instead of volatilization from soils. Genauldi et al. (16) used enantioselective analysis, quantitative analysis and air mass back trajectories to determine sources of chlordane in the Western US and South Korea. Their results suggested volatilization from urban soils and house foundations were likely the major source but that the Pacific Ocean may also be a source of racemic chlordane to these locations.

To better determine the importance of soil volatilization on EFs in ambient air, several studies measured the EFs of chlordane

compounds in air directly above soils known to be contaminated with chlordane (10, 25, 47-49). Leone et al. (10) suggested that although the enantiomeric signatures in the air above the soil generally followed the same patterns as in the soil, both in direction of degradation and relative magnitude, dilution with bulk air caused the air above the soil to be less degraded enantioselectively than the soil. As shown in Figure 4, all studies observed that as the height of the sample collected increases, EFs for both CC and TC became closer to bulk ambient air (i.e., more racemic). Later studies by Eitzer et al. (47) and Meijer et al. (49) showed that, although air very close to the soil is likely near equilibrium with the soil, the fraction of chlordane contributed to air above the soil decreases quickly with height.

A few studies have looked at the EFs of chlordane compounds in indoor air in personal residences. In all studies, only CC and TC have been reported and values were considered racemic for both when compared to racemic standards (Table 2). In Leone et al. (50), it was suggested that a lack of enantioselective degradation of chiral pesticides in indoor environments was likely due to protection from sunlight, moisture, and microbial activity in the homes. High levels of parent relative to metabolite concentrations in the samples further suggest little degradation since application. Differences between the more racemic residues indoors versus non-racemic residues often found in ambient air and other media have been used to differentiate sources of chiral chlordanes (16, 44, 51).

Due to their relatively high Henry's law constants, chlordane compounds are readily transported across the globe by ambient air. A number of studies have looked at the change of atmospheric chlordane EFs seasonally, spatially, and temporally. Two studies (40, 45) used passive air samplers to look at spatial and seasonal trends in the Great Lakes and throughout North America. Both found strong urban – rural differences and an importance of local sources compared to more distant sources. Bidleman et al. (13) measured chlordane compounds in Arctic air samples collected

from 1984-1998 and found declining concentrations, likely due to bans in most developed countries in the late 80s, as well as a greater proportion of “recycled” chlordanes from soil emissions (instead of fresher, newer sources). With the withdrawal of chlordane from the world market in 1997, levels are expected to continue to decline and an increase in the importance of recycled sources is likely (13). In a separate study, Bidleman et al. (19) analyzed archived atmospheric deposition samples, soils, and lake sediment cores from Sweden, Iceland, and the Canadian Arctic representing ~50 years of chlordane accumulation. They found a shift in CC and TC EFs from racemic in historical atmospheric deposition and sediment samples to nonracemic in more recent samples while soil samples were nonracemic throughout, again suggesting a greater influence of soil emissions in current times. More research is needed to further elucidate influences of re-emissions of chlordanes from soils to air.

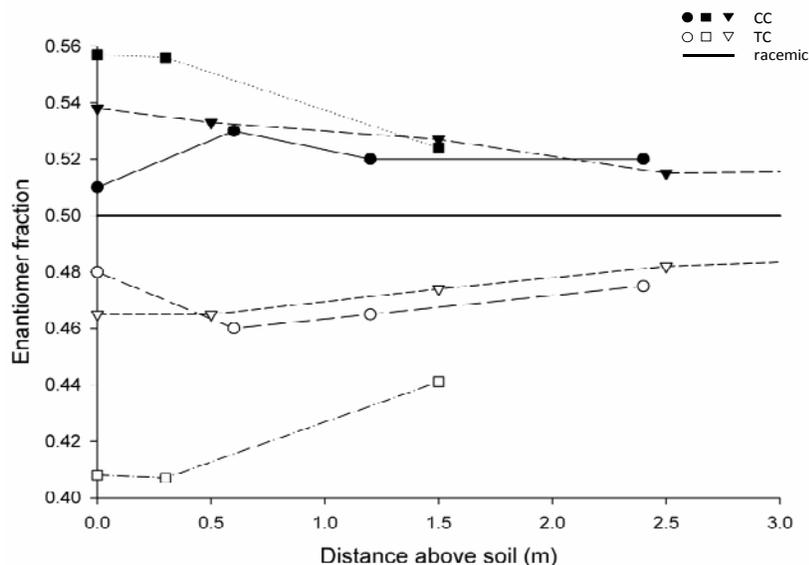


Figure 4. EFs of *cis*- and *trans*-chlordane measured in air above soil (●, ○25, ▼, ▽ 47, ■, □ 49)

Table 2. Chlordane EF measurements in environmental matrices

Sample type	CC	TC	HEPT	HEPX	OXY	Refs
Air						
<i>Ambient EF range</i>	0.413–0.619	0.372–0.554	0.493–0.521	0.528–0.805	0.591	(6, 7, 12, 13, 16, 19-25, 38, 40, 44, 45, 47, 51-54)
N ^a	204	219	8	58	1	
% NR (+) ^b	31%	0%	12%	100%		
%NR (-) ^b	4%	67%	0%	0%		
<i>Indoor EF range</i>	0.490–0.505	0.490–0.505	^c			(7, 50, 51, 55)
N	25	25				
% NR (+)	0%	0%				
%NR (-)	0%	0%				
Water						
<i>Water EF range</i>	0.468–0.519	0.452–0.515		0.500–0.980	0.500	(12, 23, 56, 57)
N	23	9		17	1	
% NR (+)	5%	0%		94%		
%NR (-)	20%	87%		0%		
Soil						
<i>Agricultural EF range</i>	0.409–0.740	0.237–0.885	0.507–0.526	0.530–0.879	0.367–0.650	(13, 16-19, 22, 24, 25, 39, 41, 43, 46-49, 51, 52, 58-66)
N	98	113	4	16	8	
% NR (+)	81%	2%		100%	29%	
%NR (-)	1%	84%		0%	71%	
<i>Background EF range</i>	0.08–0.846	0.341–0.616				(16-19, 21, 43, 47, 54, 60, 67)
N	103	114				
% NR (+)	51%	8%				
%NR (-)	34%	75%				

Sample type	CC	TC	HEPT	HEPX	OXY	Refs
Sediment						
<i>Suspended EF range</i>	0.503–0.527	0.463–0.530				(11)
N	11	11				
% NR (+)	37%	33%				
%NR (-)	0%	44%				
<i>Surficial EF range</i>	0.475–0.528	0.466–0.503		0.603–0.682		(11, 67, 68)
N	32	32		5		
% NR (+)	53%	0%		100%		
%NR (-)	7%	60%		0%		
<i>Cored EF range</i>	0.488–0.517	0.465–0.518				(11, 68, 69)
N	95	106				
% NR (+)	25%	3%				
%NR (-)	0%	21%				

a) N = number of measurements included in EF range.

b) % NR (+)= percent of measurements >0.51, thus showing predominance of the (+)- enantiomer.

% NR (–)= percent of measurements <0.49, thus showing predominance of the (–)- enantiomer.

0% signifies no measurements were in the selected range. The sum of %NR (+) and %NR (-) may be less than 100% as samples between 0.49-0.51 are considered racemic and not included in these two values.

c) Blank cells indicate no measurements reported.

Water

Data on chlordane enantiomer signatures in natural waters are limited having been reported only in Arctic and North Atlantic marine systems (23, 56, 57) and three of the Great Lakes (12) (Table 2). Hoekstra et al. (57) analyzed seawater off the coast of northern Alaska and reported all samples to be approximately racemic for the only two chlordane components quantifiable (CC, HEPX). Two other studies, one in the North Atlantic/Arctic Ocean region (23) and another sampling a transect from the Chukchi to the Greenland Sea (56) found EFs of TC and CC to be slightly more variable, although averaging around 0.5 for both. Both studies also found HEPX displayed much stronger enantioselective signatures with values typically >0.6 . The authors suggested atmospheric transport of residues emitted from soils was the likely source of HEPX to Arctic surface water samples.

Jantunen et al. (12) measured EFs for CC, TC and HEPX in water from Lakes Superior, Erie, and Ontario. TC and HEPX were found to be nonracemic in all three lakes; however, CC EFs varied from nonracemic in Lake Ontario (0.480–0.485) to racemic (0.500–0.502) in the other two lakes. The authors suggested different atmospheric sources to the lakes could transport chlordanes with different EF signatures.

Soil

Results of enantioselective analyses of chlordanes in soils have been reported since the 1990s (46, 48, 59). Nonracemic residues of CC and TC, as well as HEPT, HEPX and OXY, are often found in soils due to enantioselective metabolism. Soils from different regions, with different land uses and histories can show varied selectivity and EFs can range from racemic (e.g., CC = 0.50 for an agricultural soil in British Columbia, Canada (59)) to very nonracemic (e.g., TC = 0.846 for a woodland soil in Switzerland (43)). Most soils showed enhancement of the (+)- enantiomer (EF >0.5) for CC, HEPT, and HEPX and the (–)- enantiomer (EF <0.5) for TC and OXY. For the parent compounds, EF values

greater than 0.5 and less than 0.5 indicate preferential metabolism of the (-)- and (+)- enantiomers, respectively. However, for the metabolites, HEPX and OXY, nonracemic EFs can occur either from preferential formation of one enantiomer from the parent compound and/or enantioselective degradation of one enantiomer of the metabolite.

In general, agricultural soils favored degradation of the (-)- CC and (+)- TC enantiomers (Table 2). However, various exceptions exist where racemic or even inverse EFs of CC and TC were found in agricultural soils. Reasons for differences in enantiomer signatures in the various studies were generally not attributable to total organic carbon, pH of soils, concentration of chlordanes or regional differences, although one study showed differences between soils from tilled agricultural fields and those from an ornamental nursery (60). Variability is likely due to differences in soil microbial communities, but further research is necessary.

A number of studies looked at background soils including grassland, forest, woodland, urban and rural but non-agricultural soils. The range of EFs for CC for background soils was greater than in agricultural soils and reversals in preference for the (+)- enantiomer were more common (Table 2). One study by Kurt-Karakus (43) looked at chiral pesticide signatures in background soils from around the globe. A significant positive correlation was found between deviation from racemic ($DFR = 0.50 - EF$) and the percent of soil organic matter (43). The authors suggested differences in degradation and reversals in patterns implied that the capability to degrade enantioselectively develops in a localized manner in background soils. They hypothesized that EFs could be used to examine the extent of “mixing” between soil microbial communities.

A few studies looked at more specific soil types. Soils near house foundations, where chlordane was used as a termiticide, were measured in Connecticut (60) and found to be racemic. The authors also found very little change in the compositional profile

from technical chlordane suggesting minimal degradation of chlordane in these soils since time of application. Two studies looked at amended soils — sludge-treated soils and commercial compost (62, 63). Both types of amended soils were found to follow the same enantioselective pattern for CC and TC as in agricultural soils. In sludge-treated soils, EFs for chlordanes were not statistically different from those measured in untreated soils from the same field. The authors determined the degradation preference of the soil microbial community for chlordanes was not affected by the addition of sludge to the soil (62). In the commercial compost, EFs along with compositional profiles for CC and TC were used to determine that the compost matrix was not the same as residential lawn/garden soils and, thus, not simply a soil diluted with compost (63).

A few studies measured EFs for HEPT, HEPX, and OXY (Table 2) and for all studies, HEPX was found to be very nonracemic (EFs $\gg 0.5$). Residues of OXY showed EFs both greater and less than racemic. It is unclear whether nonracemic HEPX and OXY arise from selective degradation of the metabolite, selective formation from the parent compound, or a combination of both.

Sediment

A few studies have characterized chlordane compounds in sediment and the majority only targeted *cis*- and *trans*-chlordane. When the metabolites HEPX and OXY were studied, they were only found occasionally or not at all (11, 27). These collective studies looked at suspended (11), surficial (11, 67, 68), and cored sediments (11, 68, 69), as well as a sediment reference material (27).

As in other environmental compartments, the EFs were usually >0.5 for CC and <0.5 for TC, although exceptions were reported in each case (Table 2). Surficial sediments showed the largest range but, overall, EFs in sediment did not deviate drastically from racemic with all samples within ± 0.04 of the racemic value. The

relatively small deviation from racemic, coupled with a lack of detectable metabolites likely indicates little enantioselective degradation occurred in sediments and/or their source materials. The EF for HEPX in surficial sediments ranged between 0.603–0.682 similar to values found in other matrices.

Measurements of chlordane EFs in cored sediments were the most prevalent and allow for temporal comparisons. *cis*-Chlordane EFs were generally closer to racemic in older/deeper core sections compared to EFs in newer core sections where the EF was usually >0.5. This pattern results in a negative slope for trend lines in an EF vs. depth plot (Figure 5). For CC, the trend (though not necessarily statistically significant) was found in eight of nine cores (shown in bold in Figure 5) at Long Island Sound at Hempstead Harbor, Little Neck Bay, and Manhasset Bay (68), Washington's Lake Ballinger, Texas' Como Lake, Georgia's Lakewood Park Lake, Massachusetts' Upper Mystic Reservoir, and California's West Street Basin (11). *trans*-Chlordane, showed the same trend of more racemic EFs in older/deeper core sections compared to newer core sections but the EF was usually <0.5. This results in an EF vs. time/depth trend line with a positive slope (Figure 6). This trend (though not necessarily statistically significant) was found for six of the ten cores (shown in bold in Figure 6) at Long Island Sound at Little Neck Bay and Throgs Neck (68), Washington's Lake Ballinger, Massachusetts' Upper Mystic Reservoir, California's West Street Basin (11), and Devon Island's Lake DV09 (69). Figure 5 and Figure 6 show that although the slope of the trend line for each location varies, they largely agree in the slope direction for a given compound, negative for CC and positive for TC, possibly indicating similar sources or processes.

The EF trends in sediment cores indicate older inputs of chlordane were from relatively fresh (i.e., racemic) sources, while more recent inputs indicate more weathered (i.e., nonracemic) sources. If enantioselective degradation was occurring within the sediments, the oldest/deepest core sections should have the greatest DFR due

to longer times for such reactions (11, 68). Due to the appearance of little or no enantioselective degradation, lack of metabolites, and larger DFRs in more recent sediments, it is more likely that most enantioselective degradation occurs before the sediment is deposited.

One likely source of chlordanes to sediments is nearby soils. Wong et al. (67) collected seven soil samples within 100 m of sediment collection sites. They were unable to show a correlation between the CC and TC EFs of these two compartments; however, this may be due to the lakes receiving sediment inputs from several sources. Kurt-Karakus et al. (43) reported that some soils show a high spatial variability for EF, especially for different land and chlordane uses (e.g., agricultural, residential). In another study, surficial and suspended sediments collected at or near the same location as cores, though not necessarily at the same time, varied in their agreement with EFs in the top core slices (11). These variations indicate a need for additional research to understand interactions and influences of various sources of chlordanes to sediments.

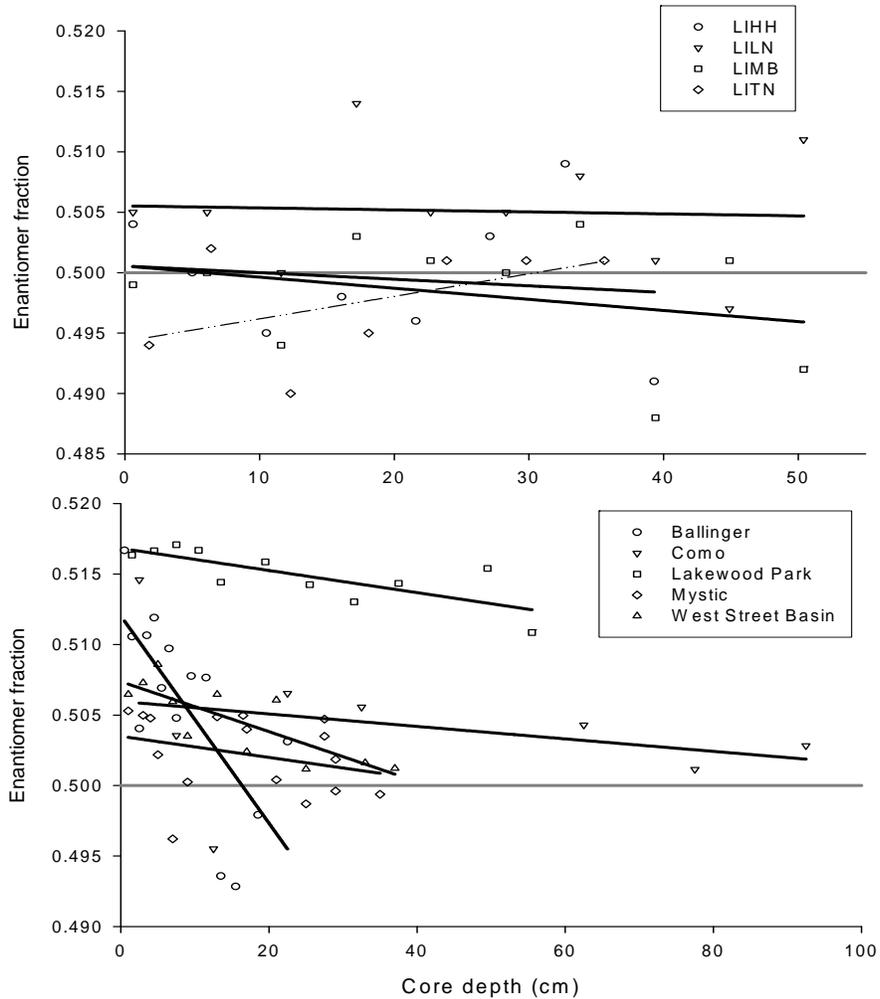


Figure 5. *cis*-Chlordane trends in sediment cores [LIHH = Hempstead Harbor, LILN = Little Neck Bay, LIMB = Manhasset Bay, LITN = Throgs Neck all in New York (68); Washington’s Lake Ballinger, Texas’ Como Lake, Georgia’s Lakewood Park Lake, Massachusetts’ Upper Mystic Reservoir, and California’s West Street Basin (11)]. Grey reference line at EF =0.50 indicates racemic.

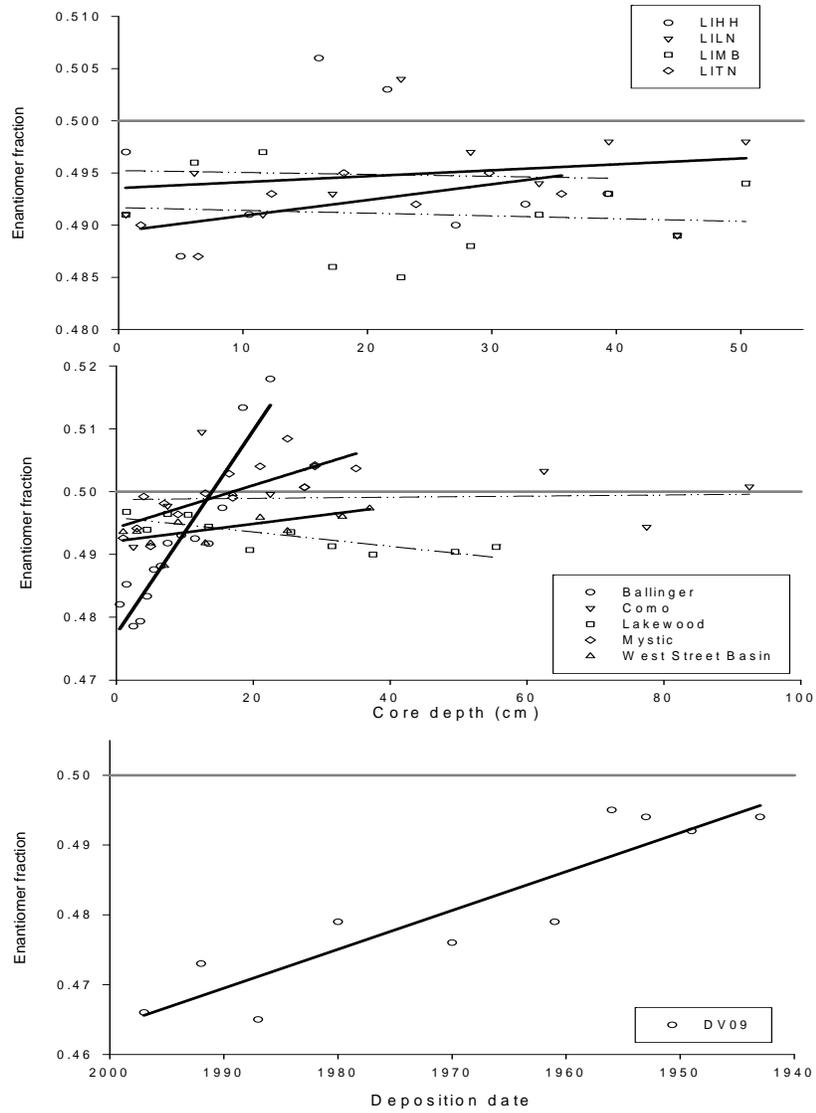


Figure 6. *trans*-Chlordane trends in sediment cores [Devon Island's Lake DV09 in the Canadian Archipelago (69), see Figure 5 for additional legend abbreviations]. Grey reference line at EF= 0.50 indicates racemic.

Chlordane enantiomers in biota

Enantiomer fractions of chlordane compounds have been measured in a variety of biota, including plants, animals such as fish, birds, seals and even humans (summary in Table 3; examples from specific studies are offered in the appropriate subsections). Several studies targeted metabolic processes by dosing a particular species and measuring the EF over time (70-74). Overall, the EFs of chlordane compounds in biota are more frequently nonracemic than EFs measured in other environmental compartments. This is not surprising as the biotic environment is essentially chiral (amino acids, enzymes, proteins, etc.), whereas fate and transport in soil, sediment, air, and water can also be controlled by achiral physical-chemical processes. There are also more measurements of EFs for the degradates OXY and HEPX in biotic media as these compounds are found more frequently and in higher concentrations than in other environmental compartments. For both parent compounds and metabolites, the range of EFs is broader, likely because a broader collection of enantioselective reactions is possible.

Table 3. Chlordane EF measurements in aquatic and terrestrial biota

Sample type	CC	TC	HEPT	HEPX	OXY	Refs
Aquatic biota						
Microscopic EF range	0.48–0.62	0.45–0.51	0.52	^a	0.505–0.889	(15, 57, 72)
N ^b	8	12	1		6	
Fat/blubber EF range	0.072–0.78	0.16–0.91		0.099–0.68	0.351–0.75	(27, 29, 37, 57, 75-79)
N	23	24		24	24	
Liver/brain EF range	0.194–0.821	0.18–0.91		0.048–0.77	0.306–0.500	(29, 37, 39, 57)
N	9	12		13	12	
Fish						
Fish EF range	0.16–0.677	0.167–0.777		0.286–0.644	0.510–0.647	(27, 29, 37, 57, 71, 73-75, 79-84)
N	74	84		23	22	
Birds						
Liver EF range	0.16–0.69			0.51–0.77	0.52–0.68	(14, 85)
N	7			13	13	
Fat EF range	0.19–0.53	0.220.40		0.56–0.80	0.55–0.71	(14)
N	7	7		7	7	
Plasma EF range	0.267–0.350			0.680–0.693	0.626–0.634	(28)

Sample type	CC	TC	HEPT	HEPX	OXY	Refs
N	2			2	2	
Eggs EF range	0.255	0.01–0.581		0.615–0.730	0.219–0.697	(28, 39, 83, 86, 87)
N	1	7		4	20	
Terrestrial biota						
Terrestrial EF range	0.468–0.519	0.452–0.515		0.500–0.980	0.500	(26, 39, 70, 76, 88)
N	23	9		17	1	
All biota						
%NR(+) ^c	37%	31%		57%	65%	
%NR(-) ^c	52%	65%		39%	30%	

- a) Blank cells indicate no measurements reported.
- b) N = number of measurements included in EF range.
- c) % NR (+)= percent of measurements >0.51, thus showing predominance of the (+)- enantiomer.
 % NR (-)= percent of measurements <0.49, thus showing predominance of the (-)- enantiomer.
 0% signifies no measurements were in the selected range. The sum of %NR (+) and %NR (-) may be less than 100% as samples between 0.49-0.51 are considered racemic and not included in these two values.

Aquatic biota

Several studies have addressed biomagnification and aquatic food web relationships for chlordane enantiomers. Generally, the data show the higher the species on the food web, the higher the DFR for chlordane compounds, especially the parent compounds CC and TC.

Mysids (*Mysis relicta*) exposed to TC and *cis*- and *trans*-nonachlor via spiked sediment for 10 days showed an EF of *trans*-chlordane starting at a racemic value of 0.50 and quickly decreasing to 0.00 after 35 days (day 7, EF 0.16; day 10, EF 0.14; day 23, EF 0.02). The EF of OXY also started at racemic and then rose to 0.78–0.89 for all remaining time points. These data suggest that mysids are enantioselectively degrading (+)-TC and enantioselectively producing (+)-OXY (72).

A variety of seal species and tissues have been analyzed for chlordane enantiomers. Regardless of where the samples originated, the EFs of CC, TC, HEPX and OXY in liver and brain were <0.50 (enriched in the (–)- enantiomer), while the EFs for OXY in fat or blubber were generally > 0.50 (enriched in the (+)-enantiomer). One study reported average EFs in polar bear fat (f) and liver (l) as CC— 0.78 (f) and 0.56 (l), TC— 0.91 (f) and 0.76 (l), HEPX— 0.68 (f) and 0.77 (l), and OXY— 0.62 (f) and 0.57 (l) (29). Two whale species from the wild and a whale blubber reference material were analyzed and showed remarkably similar trends in EFs in all samples for CC (0.07–0.17), TC (0.64–0.89), HEPX (0.62–0.64), and OXY (0.59–0.75) (27, 57).

Enantioselective processes, whether enantioselective degradation within the individual or uptake of non-racemic residues through diet, are definitely occurring for chlordane compounds in aquatic biota contributing to nonracemic EFs found in various tissues.

Fish

Three studies measured chlordane EFs in fish oils, including one Standard Reference Material (SRM). The EFs in cod liver oils mostly showed CC <0.50, but TC, HEPX and OXY > 0.50 (27, 80, 84). In contrast, the EFs in fish oils were closer to racemic for CC and TC, with CC EFs reversed in the enriched enantiomer (84).

The enantiomer fraction of chlordane compounds in wild fish (herring, cod, char, salmon, trout) from various water bodies (Resolute Bay, Nunavut, Canada; River Dalälven, Sweden; Arctic Ocean; Baltic, Barents, and Ross Seas), have been reported (Table 3). As expected in biota, nonracemic EFs were most often measured for all compounds, although whole Arctic char had EFs near racemic (0.50–0.52) for CC, TC, HEPX, and OXY, and whole Arctic cod had EFs with a low DRF for CC and TC (0.47–0.53). However, slightly higher DFRs were found in Arctic cod for the metabolites HEPX and OXY (0.52–0.58) (29, 57). The enriched enantiomer in herring is reversed compared to cod and char for both CC and TC (37, 75, 79, 81). Two cohorts of Baltic salmon were studied, a control group and a group suffering from M74 syndrome, a disease which affects survival of fry. It has been suggested that negative health effects may cause metabolic changes, but no statistical differences in the concentration or EF of several chlordane compounds were found between the two groups, suggesting no relationship between the disease and chlordane body burden (79).

Gender and organ differences were noted for chlordane enantiomers in cod. The EF of CC in cod livers averaged 0.54 in males and 0.45 in females; for TC, EF averaged 0.57 in males and 0.39 in females. For both compounds, the difference was statistically significant, and the enriched enantiomer was reversed between genders (82). While the EF of CC ranged between 0.415–0.55 for cod muscle, gonad, and liver, the EF of TC ranged between 0.35–0.66 for muscle, 0.38–0.67 for gonad, and 0.29–0.69 for liver. The lowest and highest values for each tissue were

always from the same individual, an 11 year old female and a 9 year old male cod, respectively (81).

Three studies have investigated enantioselective degradation of chlordane compounds in fish over time. Juvenile rainbow trout were fed food containing HEPX for 32 days, followed by a 96 day depuration period. The EF of HEPX in trout carcasses did not change throughout the experiment, indicating that no enantioselective degradation of HEPX occurred (73). Another study with rainbow trout exposed the fish to racemic TC in food for 40 days with a 238 day depuration period. During the experiment, the EF of TC changed from nearly racemic (0.51) at day 13 to nonracemic (0.73) at day 278. The half-life of TC enantiomers was calculated as 231 days for the (+)- enantiomer and 107 days for the (-)- enantiomer (74). Another study exposed arctic char to racemic CC and heptachlor by a single intraperitoneal injection, and followed them and their metabolites in muscle and liver for five weeks. Average EFs of CC decreased slightly during the study (to 0.497–0.482 in muscle and 0.492–0.479 in liver). Enantioselective analysis of heptachlor was not attempted, but the EFs for HEPX in muscle from individual fish ranged between 0.447–0.541. The weekly averages were not statistically different than racemic, and HEPX was below detection in liver. Based on these results, the authors suggest that both CC and HEPT undergo at least some enantioselective degradation in arctic char (71).

Terrestrial biota

Liver in hare, deer, fox, and wolverine have been analyzed for chlordane enantiomers, along with exposure and degradation studies in rats. In liver, the EFs of CC, TC and HEPX were all >0.5 while OXY had a larger range (0.44–0.96) over the range of species (26, 39, 76, 88). Factors such as source and route of exposure, time since exposure, general health, and enzyme

induction may cause drastically different EF values between individuals.

Sprague-Dawley rats were exposed to either oxychlordane, *trans*-chlordane, or *trans*-nonachlor via daily oral gavage for 28 days and followed for 56 days after dosing concluded. Fat, liver and kidney were analyzed for the enantiomers of oxychlordane and *trans*-chlordane (70). The EF of the degradate OXY decreased in fat through the experiment regardless of the exposure chemical indicating more rapid depletion of (+)- OXY or enrichment of the (–)- enantiomer. The EF of OXY in fat was always higher in females than males, regardless of the exposure chemical or time. Similarly, the EF of TC decreased in all tissues over the time course of the experiment, frequently with no (+)- TC detected at later time points. The results for TC show enrichment of the opposite enantiomer than was found in fish studies (rat TC EF <0.5; fish TC EF >0.5). Females typically had higher TC EFs than males, but the difference was very small in fat. Bondy et al. (70) suggest gender differences may have been caused by differences in enzyme induction and/or metabolism.

Birds and eggs

Bird eggs, liver, fat, and plasma have been analyzed for chlordane enantiomers in a variety of species. The EFs of CC and HEPX in bird eggs were consistent (CC– 0.255 ± 0.009 and between 0.62–0.73 for HEPX) but ranged dramatically for TC (<0.01–0.581). In general, OXY EFs were between 0.60–0.70 in eggs (28, 39, 83, 87), except for one study that reported OXY EFs between 0.22–0.38 (86). The highest CC EF values in both fat and liver were from the Northern Fulmar (0.53-0.69), whereas all other species had EFs <0.50. For all other samples, there were no significant differences between liver and fat EFs or between species and all samples were shown to have the same enriched enantiomer as in eggs. Small differences in EFs were found between genders but they were not statistically significant. There were also minimal

differences between egg yolk and female plasma EFs, indicating that maternal transfer of contaminants in these birds is likely non-stereoselective.

Humans

While chlordane concentrations often have been quantified in humans, to date only one study has been published detailing chlordane enantiomers in humans. The study compared chlordane in adipose tissue of non-Hodgkin's lymphoma patients to a control group. The EFs of CC, HEPX and OXY were all non-racemic, whereas TC was not detected (89). Most chlordane compound EFs did not significantly differ between lymphoma patients and the control group, but there was a statistical difference for CC (EF= 0.15 control; 0.23 lymphoma patient) (89).

Plants

To date, only one research group, at the Connecticut Agricultural Station, has conducted enantioselective chlordane determinations in plants. Their New Haven campus has an experimental plot that was sprayed with technical chlordane in 1960 (60). This soil is well characterized and has been used extensively for research to understand the translocation of chlordane residues from soil to plant compartments.

In a series of studies, eight different food crops were exposed to chlordane contaminated soil. Roots, stems, leaves, fruit, peels, and xylem sap were analyzed for chlordane components. Table 4 shows the range of measured EFs in various crops and plant tissues. The EFs were similar in pumpkin, lettuce, spinach, pepper, and tomato for the equivalent compound and tissue (25). However, there are notable differences in the CC EFs for xylem sap of zucchini (0.53-0.60) and cucumber (0.46-0.48) (24, 66, 90), and both chlordanes EFs for aerial tissues of zucchini (0.50-0.55 CC; 0.45-0.46 TC) and cucumber (0.45-0.46 CC; 0.39-0.40 TC) and for

fruit of zucchini (0.53-0.65 CC; 0.40-0.49 TC) and cucumber (0.48-0.51 CC; 0.22-0.30 TC) (24, 66). Many of the EFs measured in plants were nonracemic, and EF differences between the plant compartments indicate transport processes in these plants may be enantioselective. The data suggests that the occurrence of enantioselective degradation of CC and TC in plant tissues themselves is unlikely as very little OXY was detected in zucchini plants (64), and an increase in DFR for CC and TC did not correspond to an increase in the concentration of OXY (61).

In one study, zucchini were exposed to chlordane by both soil and air routes, and chlordane was found to translocate to all plant tissues in both types of exposure. The air in the greenhouse contained racemic CC and TC (EF= 0.50) at high and low concentrations, but all tissues of zucchini, including leaves, which are the most likely tissue to uptake chlordane from air, contained nonracemic chlordane residues (64). For the soil route experiment, the EFs of chlordane in high, medium, and low concentration soils were nonracemic and similar in value, with CC = 0.53–0.55 and TC = 0.45–0.48 (64). This pattern was similar to that found in other soil studies where CC and TC are on opposite sides of the 0.50 racemic value. The EF pattern in roots, however, did not match that measured in soil, with CC EFs becoming more racemic (0.50–0.53) and TC changing enantioselectivity (0.51–0.54). This data suggests the soil-to-root transport mechanism was enantioselective (64). Additionally, transport within plants was found to also be enantioselective, as best depicted by the higher DFR EFs of CC in zucchini fruit (0.56–0.64) (64). The enantiomer and compound distributions into zucchini tissues were different for air and soil routes of exposure (64), which may be useful for source apportionment.

Table 4. Chlordane EF measurements in plants

Sample type	CC	TC	HEPX	Refs
Zucchini- Soil exposure				
Root EF range	0.50-0.55	0.42-0.56	a	(25, 61, 64, 66)
N ^b	13	13		
Stem EF range	0.47-0.58	0.36-0.53		(25, 61, 64)
N	11	11		
Leaf EF range	0.51-0.58	0.42-0.48		(25, 61, 64)
N	11	11		
Fruit EF range	0.53-0.65	0.40-0.49		(25, 61, 64)
N	17	17		
Xylem sap EF range	0.53-0.60	0.45-0.51	0.62-0.65	(24, 66, 90)
N	5	5	5	
Aerial tissue EF range	0.50-0.55	0.48-0.50	0.65-0.67	(24, 66)
N	3	3	3	
Zucchini- Air exposure				
Root EF range	0.46-0.49	0.50-0.55		(64)
N	4	4		
Stem EF range	0.46-0.47	0.47-0.52		(64)
N	4	4		
Leaf EF range	0.48-0.54	0.44-0.51		(64)
N	4	4		
Fruit EF range	0.53-0.62	0.40-0.49		(64)
N	4	4		
Other plants				
Root EF range	0.51-0.55	0.37-0.51	0.58	(25, 66)
N	9	9	2	
Stem EF range	0.46-0.59	0.30-0.54		(25)
N	4	4		
Leaf EF range	0.52-0.60	0.30-0.55		(25)

Sample type	CC	TC	HEPX	Refs
N	8	8		
Fruit EF range	0.48-0.56	0.22-0.47		(25)
N	6	6		
Xylem sap EF range	0.46-0.53	0.42-0.50	0.43-0.58	(24, 66, 90)
N	6	6	6	
Aerial tissue EF range	0.45-0.48	0.39-0.47	0.44-0.63	(24, 66)
N	4	4	3	
All plants				
%NR(+) ^c	70%	14%	76%	
%NR(-) ^c	20%	70%	24%	

- a) Blank cells indicate no measurements reported.
- b) N = number of measurements included in EF range.
- c) % NR (+)= percent of measurements >0.51, thus showing predominance of the (+)- enantiomer.
 % NR (-)= percent of measurements <0.49, thus showing predominance of the (-)- enantiomer.
 0% signifies no measurements were in the selected range.
 The sum of %NR (+) and %NR (-) may be less than 100% as samples between 0.49-0.51 are considered racemic and not included in these two values.

Uses of enantiomer data

As chlordane compounds are global contaminants that still are found routinely in all environmental media and many species, determining the transport and fate of these chemicals is very important for understanding exposure and effects. To get a better handle on their cycling through the environment and biosphere, more information on the biotic and abiotic degradation of chlordanes is necessary. In general, physical-chemical processes like photolysis, movement between environmental compartments, and non-biological chemical reactions will not change the enantiomer composition (33). Biologically mediated processes like

adsorption, distribution, metabolism and excretion in an organism very often involve chiral biological molecules and, thus, can change the enantiomer composition of environmental contaminants (91). Chlordane was produced as a racemic mixture (75), and no anomalous achiral reactions are known that change the enantiomer signature. Generally, racemic enantiomer signatures in the environment indicate it has undergone only achiral reactions whereas nonracemic signatures indicate biologically mediated processing. By examining differences in the enantiomeric signature of various samples, we can learn something of the path/s the chemicals have taken since their application and better determine their future transport and fate.

The first reported uses of chiral chlordane analyses were as tracers of air-surface exchange (42, 92). These first studies, along with more recent ones, used chiral chlordanes to help distinguish the atmospheric transport of freshly applied pesticides from those which are “recycled” from lakes and soil, to determine sources of pesticides, and to investigate biotic vs. abiotic degradation pathways (52, 53, 93). A few studies used enantioselective analysis to better understand air-water gas exchange and the amount of biotic processing of chlordanes in sediments (11, 12, 23); however, most work in environmental media has focused on using chiral chlordanes to track air-soil exchange.

The use of enantioselective analysis to follow air-soil exchange has shown the increasing importance of soil emissions of chlordanes to local and regional ambient air signatures, as discussed in an earlier section. Several authors have used differences in chlordane enantiomeric signatures to differentiate urban chlordane use (termiticides) from rural use (agricultural pesticide) (7, 45, 47, 67). Bidleman and Falconer derived a relationship to estimate the contribution of chiral compounds from two different sources (94). The authors suggested some advantages for using enantiomeric analysis rather than concentration data alone which include lower sample variability for repeat analyses and the fact that EFs are not affected by analytical recovery factors

or abiotic degradation processes during sample storage and recovery.

The use of chiral chlordane analysis to learn about spatial, seasonal and temporal changes in chlordane residues has been discussed already. Several authors have also used enantioselective analysis, along with traditional data (e.g., concentrations, parent-metabolite ratios), to study long range transport of chlordanes (13, 16, 45). From their studies of chiral pesticides in air from Alabama, Jantunen et al. (7) determined that atmospheric transport from the southern US is a continuing source of chlordane to the Great Lakes whereas Genauldi et al. (16) combined enantiomer data with other measurements to determine differences in air masses from Asia, the western US, and South Korea.

Other uses include determining differences in metabolism mechanisms and rates between the CC and TC isomers (17, 38), determining patterns in long-term weathering of chlordane in soil (60), differentiating surface waters from deeper ocean waters (23), and determining that the main source of HEPX in ambient air is metabolism of HEPT in soils, not HEPT photolysis (44). Incorvia-Mattina et al. (25) determined that many plants grown in contaminated soils alter both concentrations and EFs of chlordanes during uptake and translocation to aerial tissues. The authors suggested that, due to these processes, vegetative matter may contain higher insect toxicities than soil residues. Further work on enantioselective uptake by plants might also help elucidate mechanisms for phytoaccumulation.

Several studies with chlordane compounds have used enantiomer fractions to help determine degradation pathways. As mentioned earlier, the EFs of CC and TC in sediment cores are slightly nonracemic suggesting the enantioselective degradation of chlordane occurred before arriving in sediments (11) and that chlordane compounds in this matrix are stable. This evidence can be combined with concentration patterns or other data to make a

stronger case for preservation of historic use patterns within sediment cores.

Generally, enantiomer signatures in biota are more nonracemic than in environmental compartments. There are several processes that can contribute to nonracemic EFs in biota including enantioselective uptake from the environment (e.g., air, water), ingestion of nonracemic patterns from food/prey, or enantioselective degradation in the test subject itself. Plant studies have shown that uptake of chlordane from soil via roots and from air via leaves is enantioselective (64). A time course study showed that fish tissues have EFs that match the EF of their food at minimal time since exposure (74). In species where chlordane degradation is minimal, studies have concluded that accumulation from food is nonstereoselective, thus preserving the enantiomer signature of the lower trophic level (15, 57). Studies in fish, mysids, and rats with chlordane compounds indicate that some species do enantioselectively degrade chlordane compounds (70, 72, 74). A careful examination of a system can likely pinpoint the enzymes involved and determine enantiomer rate constants and half-lives for both parent and degrade compounds. Nonracemic EFs for degradation products like HEPX and OXY are more complicated to interpret because they may have been enantioselectively formed from a parent compound or enantioselectively degraded themselves.

Conclusions

The studies of chlordane discussed in this review highlight the usefulness of continued monitoring of pesticide enantiomers. Small differences in the environment, be it the exact plant tissue or the gradient of EF with height above soil, can lead to significant differences in enantiomer signature. These differences are important to understanding the mechanisms of pesticide fate and transport. Characterizing enantiomer patterns in biota, plants and environmental media could also point to possible differences in

exposure (e.g., plant and animal tissues consumed, respired air, soil ingested during hand-to-mouth activities, etc.). Differences in enantiomer exposure combined with differences in enantiomer toxicity may result in a differential risk for the two enantiomers.

Interpretation of chiral chlordane data is a complex endeavor due to uncertainties such as high variability in EFs over small spatial distances and the very limited knowledge of enantioselective degradation rates and mechanisms. Analytical challenges include a limited number of commercially available chiral columns able to separate chlordanes in complex environmental matrices and variability in stationary phase composition within chiral columns. Future work with chiral chlordane data depends on solving some of these problems. Even so, the use of chlordane EFs, in tandem with traditional measurements, can be a powerful tool for better understanding our environment.

Disclaimer

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