ENANTIOMER FRACTIONS OF CHLORDANE COMPONENTS IN SEDIMENT SAMPLES FROM U.S. GEOLOGICAL SURVEY SITES IN LAKES, RIVERS, AND RESERVOIRS

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Introduction

The environmental behavior of the enantiomers of cis- and trans-chlordane has been the topic of much research since the first chiral separations on cyclodextrin gas chromatography (GC) columns [1]. When chlordane is manufactured, it is always a racemic mixture (equal portion of two enantiomers)[2]. As the compounds move through the environment, physical processes, such as volatilization, photolysis, and OH radical reactions, are not likely to change the enantiomer signature [3]. However, biological processes, including uptake, depuration, and metabolism often are mediated by chiral molecules, such as enzymes that cause changes in the enantiomer signature [3].

Enantiomer behavior of chlordane has been reported in biota [4, 5], soil [6, 7], water [8], and air [9, 10]. Enantiomer signatures have been used to trace chlordane sources from soil in the Midwest [7], to air above the soil [11], and to air near the Great Lakes [12]. Additionally, evidence of biological degradation has been shown through enantiomer signatures [4, 5]. To date there have been no reports of chlordane enantiomer trends in sediment. Previous studies of toxaphene congeners [13] and PCB atropisomers [14] in sediment samples have shown interesting enantioselective behavior.

Because sediment cores are used as a historical record of contaminant deposition, it is important to ensure that the record is accurate and has not been changed by biological degradation. The goal of this research is to document the enantiomeric behavior of chlordane compounds in sediment samples. In addition to sediment cores, surficial and suspended sediment samples will help determine a likely source of contamination to sediment. Trends are analyzed with sediment type, location, deposition date, and concentration for various chlordane compounds.

Materials and Methods

Sediment samples in this study were collected as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) and NAWQA Reconstructed Trends programs. Several types of sediment samples were collected throughout the United States. Sixteen surficial sediments and eleven suspended sediment samples were collected from rivers, creeks, and lakes. Sediment cores were collected at five urban lake or reservoir sites and sectioned into 1 cm to 5 cm intervals

for a total of 60 slices. Details discussing collection, extraction, cleanup, and analysis for chlordane concentrations are published elsewhere [15, 16].

The sediment extracts were analyzed by using a Hewlett Packard 5890 series II gas chromatograph connected to a HP 5989A mass spectrometer. Enantiomer separations were performed with a chiral cyclodextrin GC column, γ-cyclodextrin 120 from Supelco. The temperature program used for analysis was a 1-min hold at 50 °C, ramped to 150 °C at 20 °C/min, ramped to 185 °C at 0.5 °C/min, ramped to 230 °C at 20 °C/min, and held for 2 minutes. Mass spectral conditions were the same as described previously for general instrumentation parameters and chlordane ion selection [9]. To detect chlordane compounds, the following ions were monitored: *m/z* 266, 300, 302, and 264 for heptachlor; *m/z* 318, 388, 390, and 392 for heptachlor epoxide; *m/z* 424, 422 and 352 for oxychlordane; and *m/z* 374, 376, 408, 410, and 412 for *cis*-and *trans*-chlordane.

Enantiomer fraction {EF; area(+)/[area(+) + area(-)]} was chosen as the enantiomer behavior measure. Quality-control criteria were applied in the calculation of the sample EF values. Because each ion was peak fit separately, there were three to five calculations of EF for each compound per chromatographic analysis. The difference between the EF for ions was required to be within 5% of the average EF for that sample analysis. To help ensure that there were no coeluting compounds that would interfere with the analysis, isotope ratios were examined for the two enantiomer peaks for each compound. The ratio of *m/z* 408:410 was used for the two chlordanes, and 388:390 was used for heptachlor epoxide. The difference of this ratio between enantiomer peaks was required to be within 10% of the average. If these criteria were not met, then the data were not considered reliable and were not used. Reliable ion EFs were combined for replicate chromatographic analyses before statistical analysis. Statistics were analyzed in Microsoft Excel using a *t*-test that assumed unequal variance with an α value of 0.05. Enantiomer fractions of samples were compared to the EFs calculated for racemic standards analyzed at the same time.

Results and Discussion

Table 1 lists the EF values for *cis*-chlordane (CC), *trans*-chlordane (TC), and heptachlor epoxide (HEPX) in surficial and suspended-sediment samples. Values listed in bold (Table 1) are statistically different from the racemic value of 0.50. The five measured heptachlor epoxide EF values in surficial sediment samples are significantly different from racemic, an expected result. When chlordane compounds are degraded to HEPX, the reaction occurs by two main routes: a) a photoreaction that will not change the enantiomer composition of parent or product and b) a biologically mediated mechanism that is known to change the enantiomer composition of the product [2]. The second route is by far the more prevalent one, and this is evident in the EF values for HEPX in sediment of 0.600 to 0.682. In general, the EF of CC is slightly greater than 0.50, while TC is slightly less than 0.50. Also, CC has more racemic EFs than does TC, caused by the slower degradation of CC compared to TC [17, 18].

Similar trends are noted for sediment-core samples in the shift of EF from racemic. EFs for CC in sediment cores range from 0.493 to 0.517 (avg ± std err = 0.506 ± 0.001) while TC EFs range from 0.479 to 0.518 (0.496 ± 0.001). These values are similar to those found in suspended and surficial-sediment samples, but are not as different from racemic. The chlordane and heptachlor metabolites, oxychlordane and HEPX, are not present in detectable quantities in core samples. These facts indicate some biological degradation of chlordane, but because suspended sediments

also show this evidence, the degradation most likely is occurring in the soil where chlordane was initially applied. Our findings also suggest that the historical record of chlordane concentrations in sediment cores is not likely to be substantially altered by biological degradation in the core itself.

We compared our sediment chlordane EF values to EF values in other matrices. The sediment EFs agree very well (in both degree and direction of degradation) with those published for chlordane and heptachlor epoxide in air [9], agricultural soil [19], and soil near residential application [6]. In addition, the EF data show that there are some differences between the types of sediment. Surficial sediment shows the greatest deviation in EF from the racemic value, followed by suspended sediment, and then core slices. We hypothesize that these differences may be caused in part to the differences in chlordane bioavailability with the distinct types of sediment.

There are also differences in EF values between the sampling locations, which are probably caused by differences in agricultural and structural applications of chlordane, and unique microbe populations degrading chlordane compounds. There are no detectable differences in EF with changing chlordane concentration. We have discovered an interesting trend of EF values with core depth (deposition date). For TC, the EF values tend to increase slightly with core depth, but for CC, EF tends to decrease slightly with depth. Although this trend has been noted at several core locations, the differences in EF values are very small, and we do not believe the changes are caused by biodegradation in the buried sediment.

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Table 1. Chlordane enantiomer fractions (EFs) ± standard error measured in surficial and suspended sediment. Values in bold are statistically different from racemic.

Location	Type of sediment	cis-Chlordane	trans-Chlordane	Heptachlor epoxide
Racemic standard with OR samples		0.499 ± 0.001	0.500 ± 0.001	0.508 ± 0.002
Winchester, MA	Surficial	0.508 ± 0.001	0.496 ± 0.001	ND
Anaheim, CA	Surficial	**0.517 ± 0.002**	**0.476 ± 0.001**	ND
Atlanta, GA	Surficial	0.511 ± 0.002	**0.488 ± 0.001**	ND
Seattle, WA	Surficial	0.507 ± 0.003	**0.466 ± 0.001**	ND
Site 1 Portland, OR	Surficial	**0.508 ± 0.003**	**0.484 ± 0.001**	**0.663 ± 0.007**
Site 1 Portland, OR	Surficial	0.502 ± 0.003	**0.483 ± 0.001**	**0.670 ± 0.010**
Site 2 Portland, OR	Surficial	**0.514 ± 0.002**	**0.474 ± 0.001**	**0.682 ± 0.006**
Site 2 Portland, OR	Surficial	**0.514 ± 0.002**	**0.473 ± 0.001**	**0.680 ± 0.020**
Site 3 Portland, OR	Surficial	**0.512 ± 0.002**	**0.479 ± 0.002**	**0.600 ± 0.010**
Forestville, CT	Surficial	0.494 ± 0.006	**0.476 ± 0.002**	ND
North Haven , CT	Surficial	**0.530 ± 0.005**	**0.481 ± 0.005**	ND
Palmyra, PA	Surficial	0.492 ± 0.004	**0.476 ± 0.002**	ND
Hartsville, IN	Surficial	**0.598 ± 0.004**	**0.525 ± 0.001**	ND
Woodbridge, CA	Surficial	**0.606 ± 0.009**	**NA**	ND
Altamonte Springs, FL	Surficial	**0.618 ± 0.001**	**0.531 ± 0.004**	ND
Safe Harbor, PA	Surficial	**0.620 ± 0.009**	**NA**	ND
Winchester, MA	Suspended	**0.510 ± 0.001**	**0.467 ± 0.004**	ND
Winchester, MA	Suspended	0.503 ± 0.003	**0.485 ± 0.002**	ND
Winchester, MA	Suspended	0.507 ± 0.002	**0.463 ± 0.007**	ND
Winchester, MA	Suspended	0.508 ± 0.001	**0.479 ± 0.003**	ND
Winchester, MA	Suspended	0.508 ± 0.001	0.496 ± 0.003	ND
Ft. Worth, TX	Suspended	0.507 ± 0.003	**0.516 ± 0.004**	ND
Ft. Worth, TX	Suspended	**0.514± 0.003**	**0.517 ± 0.002**	ND
Ft. Worth, TX	Suspended	**0.523 ± 0.003**	**0.530 ± 0.010**	ND
Ft. Worth, TX	Suspended	**0.514± 0.005**	0.509 ± 0.005	ND
Ft. Worth, TX	Suspended	0.516± 0.030	0.500 ± 0.010	ND
Ft. Worth, TX	Suspended	**0.527 ± 0.004**	0.494 ± 0.004	ND

ND- not detected; NA- not analyzed