

Using Enantiomeric Ratios to Determine Sources of Chlordane to Ambient Air

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Introduction

Organochlorine (OC) pesticides were used heavily on farmlands in the U.S. and Canada during the 1960's and '70's. Because OC pesticides and their metabolites are highly persistent, residues remain in many soils. Chlordane, an OC pesticide, has not been used in agriculture since 1983, but before that time 65% of chlordane applications were for crops, home lawns and gardens, turf and ornamentals (1). From 1983 until its ban in 1988, chlordane was used exclusively for structural termite control, resulting in greatly elevated levels in home air (1). Sources of chlordane to ambient air include volatilization from agricultural soils, emissions from house foundations and long range transport from countries still using chlordane.

Cis- and trans-chlordane (CC, TC), the main constituents of technical chlordane, are both chiral molecules which are manufactured as racemic mixtures. If degradation in the environment is dominated by non-enzymatic processes, the enantiomeric ratio (ER = (+)/(-) enantiomer) remains the same since the enantiomers have identical chemical and physical properties and abiotic processes are non-enantioselective. Chiral pesticides that are degraded by biological systems, however, often produce non-racemic residues. Past research has shown that selective enzymatic degradation of chlordane enantiomers by microorganisms does occur resulting in non-racemic signatures of chiral pesticides in soils from the midwestern U.S. (2). This work was done to determine if non-racemic enantiomeric signatures can be used to distinguish between releases of chlordane from agricultural soils vs. termiticide emissions.

Materials and Methods

Soil and air samples were collected in four states in the U.S. cornbelt region: Ohio, Pennsylvania, Indiana and Illinois, at different times from 1995-1997. At thirty eight farms, eight soil cores (~15 cm depth) were taken and pooled to obtain a representative sample for each field (2). Three types of air samples were collected: ambient, above-soil and indoor, using polyurethane foam (PUF) traps. A glass fiber filter was used ahead of the PUF (for ambient air and air-above-soil samples) to remove ambient air particles and soil dust. Only the gas phase (PUF) data is reported here. Ambient and above-soil samples were taken using a high volume air sampler following previously published methods (3). Seven ambient air samples were collected for 24-48 hours (flow rate=500 L/min) at non-agricultural, rural sites. Air-above-soil samples were collected ~10 cm above the soil for 4-8 hours (flow rate=500 L/min) at six fields which had previously been analyzed and found to contain high concentrations of chlordane in the soil. Indoor samples were taken using a low volume pump attached to a mass flowmeter (Sierra TrakII, Sierra Instruments, Inc., Monterey, CA) followed by a Teflon holder which contained the 5 cm diameter x 3.5 cm thick PUF. Twenty indoor air samples were collected over 4-8 hour periods (flow rate=30 L/min) in basements or lower levels of homes from the four cornbelt states. All air samples were extracted with organic solvents and cleaned prior to analysis using an alumina-silica column. Ambient and indoor air samples and soil samples were also collected around Muscle Shoals, Alabama and ambient and indoor air in Columbia, South Carolina (4).

Chlordanes were determined by achiral and chiral capillary gas chromatography with electron capture detection or negative ion mass spectrometry (NIMS). For quantitative work a 60 m x 0.25 mm i.d. DB-5 column (0.25 μ m film thickness, J&W Scientific) was used. Enantiomeric separations were carried out using a Betadex-120 column (20% permethylated β -cyclodextrin in SPB-35, 30 m, 0.25 mm i.d., 0.25 μ m film thickness; Supelco Corp.). Temperature programs, injection conditions and ions monitored for detection by NIMS are given elsewhere (2).

Results and Discussion

Chlordane residues (sum of TC, CC and trans-nonachlor) in cornbelt soils were, on average, 10 times higher than levels found in soils from Alabama (geometric means-Cornbelt 1.4 ng/g, Alabama 0.17 ng/g). Average concentrations of chlordanes in ambient air in the cornbelt (0.041 ng/m³, n=4) were similar to annual means for chlordanes at Sturgeon Point on Lake Erie (0.034 ng/m³) (5). Ambient levels in two southern states were somewhat higher at 0.109 ng/m³ for rural Alabama and 0.295 ng/m³ in the city of Columbia, SC (6). Average indoor air concentrations in the cornbelt states (16.7 ng/m³, n=20) were similar to average levels in homes in Columbia (10.1 ng/m³, n=3) and rural Alabama (34.2 ng/m³, n=5). High indoor chlordane concentrations have been reported elsewhere (5). Figure 1 compares concentrations of chlordanes in the various samples.

Average ERs for samples are given in Table 1. Typical chromatograms have been previously published (4). Soils in the cornbelt region show an enantiomeric difference for both CC and TC: TC ERs less than 1.00 (showing degradation of the (+) enantiomer) and CC ERs greater than 1.00 (showing degradation of the (-) enantiomer). A comparison of ERs for cornbelt soils and air-above-soil samples was done for six fields. The enantiomeric signatures of pesticides in the air above the soil followed the same patterns as in the soil, both in direction of degradation and in relative magnitude. This preservation of ER profile upon volatilization has been previously described by Finizio et al., 1998 (7) for α -hexachlorocyclohexane, heptachlor and heptachlor epoxide. Chlordane ERs in Alabama soils were also non-racemic, but the difference smaller than in the cornbelt soils.

ERs for ambient air samples taken at the rural, non-agricultural locations in the cornbelt show the same general trend (although less pronounced) as was seen in soil and air-above-soil samples. Ambient air ERs in rural Alabama and in Columbia, SC were closer to racemic (4). In contrast, air samples over the Great Lakes show a depletion of (+)TC and a slight depletion of (-)CC enantiomers, similar to the ERs of the cornbelt soils. ERs of chlordanes in air from homes in the cornbelt states were all very close to racemic. Racemic chlordane was also found in indoor air for several homes in Columbia, SC and Alabama (4).

High concentrations of chlordanes (compared to average Great Lakes values) in indoor and ambient air from Columbia, South Carolina and intermediate levels near the town of Muscle Shoals, Alabama have been reported (6). Racemic cis- and trans-chlordane were found in air in both locations, while non-racemic chlordanes were reported in southern soils (4). These findings suggest termiticide treated houses, rather than soil emissions, are the main source of chlordane to southern U.S. air. Chlordane concentrations in home air from the Cornbelt region are much greater than average ambient air concentrations from the cornbelt region or the Great Lakes. However, ERs of chlordane in ambient air from the cornbelt and the Great Lakes lie between the ER values in air-above-soil (non-racemic) and home air (racemic). Lower concentrations coupled with non-racemic ER values imply a greater import of recycled agricultural sources. This data suggests that Great Lakes air may be a mixture of termiticide treated home air and emissions from regional soils.

References

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Acknowledgments

We would like to thank Elin Ulrich and Ron Hites, Indiana University, for assistance in collecting indoor air samples.

Table 1. Average Enantiomeric Ratios (\pm s.d.) for Air and Soil

<u>AIR</u>	<u>TC</u>	<u>CC</u>
Above-soil, Cornbelt (n=6)	0.74 (0.10)	1.11 (0.08)
Ambient, Cornbelt (n=3)	0.93 (0.03)	1.04 (0.04)
Indoor, Cornbelt (n=15)	0.99 (0.01)	0.98 (0.03)
Ambient, Alabama (n=20)	0.98 (0.03)	1.01 (0.04)
Ambient, South Carolina (n=7)	1.00 (0.01)	1.02 (0.01)
Indoor, AL & SC (n=8)	0.98 (0.01)	1.00 (0.01)
Lake Ontario (n=15)	0.92 (0.02)	1.03 (0.02)
<u>SOIL</u>		
Cornbelt region (n=38)	0.70 (0.12)	1.21 (0.14)
Alabama (n=9)	0.91 (0.05)	1.11 (0.10)

