

Chlordane enantiomers as source markers in ambient air

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Abstract

Concentrations and enantiomer ratios (ERs) of chlordane were determined in samples from the southern U.S. to investigate sources of chlordane to the ambient air. Chlordane residues in soils from Alabama were low compared to the levels found in the Cornbelt region, but concentrations of chlordane in southern air were higher than most Great Lakes values. Soils in Alabama showed non-racemic chlordane ERs, whereas indoor air and ambient air had ERs close to racemic values. Thus, evaporation from soil may be a minor source of chlordane to ambient air in Alabama. The nearly racemic ER values in southern air, elevated chlordane levels in the City of Columbia and high indoor air concentrations indicate that chlordane in southern U.S. air also comes from racemic sources, such as termiticide treated houses or air transport from regions where chlordane is still in use. Non-racemic ER values in G.L. air suggest regional contributions such as volatilization from Cornbelt soils or from the lakes themselves. Heptachlor-*exo*-epoxide (HEPX) was non-racemic in all air and soil samples, indicating that the source of HEPX in air most likely is volatilization of HEPX produced by microbial activity in soils or water rather than heptachlor photolysis. This study demonstrates the possibilities of using enantiomers of chiral pesticides to follow degradation and exchange processes in the environment.

Introduction

Chlordane and heptachlor were used for agriculture, on lawns and gardens, and as a termiticide in the U.S. in the 1950's through 1980's. After the mid 1970s, the usage was restricted to termite control and all applications were canceled in 1988. Sources of chlordane and heptachlor in ambient air include volatilization from soils, emissions from houses treated for termite control, and long range transport from places where it still is in use, such as Mexico and other Latin American countries.

The main constituents of technical chlordane, *cis*-chlordane (CC), *trans*-chlordane (TC) and heptachlor are chiral and are produced as racemic mixtures. Selective breakdown of one enantiomer in water and soil leads to non-racemic residues which can be differentiated

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from fresh pesticides on the basis of their enantiomeric ratios (ER = (+)/(-) enantiomers). The metabolite heptachlor-*exo*-epoxide (HEPX) is a persistent chiral compound as well.

The ability to determine ER values with high precision ($\leq 2\%$ RSD) by GC-MS offers new opportunities to use chiral pesticides as tracers of vapor exchange with water and soil^{1,2,3,4}. In this study concentrations and enantiomer ratios (ERs) of chlordane were determined in samples from the southern U.S. to investigate sources of chlordane to the ambient air.

Samples and Experimental Methods

During 1994-1997 air and soil samples were collected in the southern U.S. In 1996 ambient air samples were taken from January to June outside a small town in Alabama ($n=8$) and from August 1994 to January 1995 in the city of Columbia, South Carolina ($n=9$). Indoor air of South Carolina homes was sampled in 1997 ($n=3$). Agricultural soil samples were collected 1996 across the state of Alabama ($n=32$). Several soil cores (upper 5cm) were collected and pooled to obtain a representative sample for each field. Air was drawn through a glass fiber filter followed by a polyurethane foam trap. Samples were extracted with organic solvents and cleaned up prior to analysis on an alumina-silica column.

Pesticides were analyzed by achiral and chiral capillary GC with electron capture detection or negative ion mass spectrometry (NIMS). For quantitative work a 30 m x 0.25 mm i.d. DB-5-MS column with a 0.25 μm film thickness was used (J&W Scientific). Two chiral columns were used for enantiomeric analysis. Betadex-120 (20% permethylated β -cyclodextrin in SPB-25, 30m x 0.25 mm i.d., 0.25 μm film thickness, Supelco) was used to resolve the enantiomers of TC and CC and BGB-172 (20% *tert*-butyldimethylsilylated β -cyclodextrin in OV-1701, 30 m x 0.25 mm i.d., 0.25 μm film thickness, BGB Analytik AG, Switzerland) for chiral analysis of HEPX. In some cases tandem columns was employed to resolve specific interferences. The tandem column consisted of a 30-m chiral column coupled to a 15-m DB-210 column (50% trifluoropropyl methylpolysiloxane, 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific). Temperature programs, injection conditions and ions monitored for detection by NIMS are given elsewhere^{1,2,4}.

Results

The chlordane residues in Alabama soils were low compared to levels found in the Cornbelt region, with geometric means showing a 10 fold difference (Alabama 0.17 ng/g and Cornbelt 1.9 ng/g).

In Figure 1 the concentrations of chlordanes (sum of TC, CC and *trans*-nonachlor) in air are illustrated. The mean concentration of in Columbia air, normalized to 20°C, was 335 pg/m^3 , which is significantly higher than summer values found at the Great Lakes (15-92 pg/m^3)⁵. Chlordane levels in Alabama air (mean=96 pg/m^3 , Feb.-June) were similar to summer values at Lake Erie⁵. Chlordane concentrations in the three homes were 1 100, 16 000 and 80 000 pg/m^3 . Similar high and variable chlordane values have been reported in U.S. houses⁶.

TRANSPORT AND FATE

The ERs are listed in Table 1. As can be seen chlordane ERs in Alabama soils were non-racemic, but the change in ER was smaller than in Ohio soils. Indoor air and ambient air samples were close to racemic. By contrast, air samples from the Great Lakes show a strong depletion of (+)-TC and a slight depletion of (-)-CC enantiomers. HEPX was non-racemic in all air and soil samples collected.

Table 1. Average ERs in air and soil

	TC	CC	HEPX
AIR			
Outside town in Alabama	0.98	1.03	1.70
City of Columbia, SC	1.00	1.02	1.50
Indoor air, SC	0.98	0.99	NA
Lake Superior	0.87	1.09	1.99
Lake Ontario	0.91	1.03	1.86
SOIL			
Alabama	0.92	1.13	2.71
Combelt region	0.71	1.19	2.69

NA: not analyzed

Discussion

Loss of pesticide residues from soil by evaporation is a significant source of atmospheric contamination. Years after their ban in Canada and the U.S., OC pesticides continue to volatilize from agricultural soils, and house foundations where they were used as termiticides.

The ER profiles in soil, resulting from selective breakdown of chiral pesticides, have been shown to be preserved upon volatilization². However, the enantiomer signature of chlordane residues in Alabama soil was reflected to only a slight extent in the air (Figure 2 and Table 1). Thus, evaporation from soil may be a minor source of chlordane to ambient air in Alabama. The ER values in southern air suggest that airborne chlordane also comes from racemic sources such as termiticide treated houses or long range transport from regions where chlordane is still in use. The very high concentrations in indoor air and the elevated levels in the city of Columbia air also imply that volatilization from termiticide treated houses is a significant source to the southern U.S. air. Non-racemic ER values in G.L. air suggest regional contributions, such as volatilization from Cornbelt soils or from the lakes themselves (Table 1 and Figure 3).

Enzymatic metabolism of heptachlor yields non-racemic HEPX, whereas photolysis produces racemic HEPX^{7,8}. The consistent (+)-enantiomer enrichment in air from all sampling sites suggests that the source of HEPX in air most likely is volatilization of HEPX produced by microbial activity in soils or water rather than heptachlor photolysis.

This study demonstrates the possibilities of using enantiomers of chiral pesticides to follow degradation and exchange processes in the environment.

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Figures

1. Concentration of chlordane in ambient air from southern U.S., the Great Lakes and indoor air from homes in South Carolina (pg/m^3).
2. Enantiomers of *trans*-chlordane (TC), *cis*-chlordane (CC) and octachlordane compound MC-5 in the soil and overlying air at an Alabama farm (β -DEX column).
3. Enantiomers of *trans*-chlordane (TC), *cis*-chlordane (CC) and chlordane compound MC-5 in the soil at an Ohio farm and over Lake Superior (β -DEX column).

Fig 1. Concentration of chlordane in air (pg/m^3)

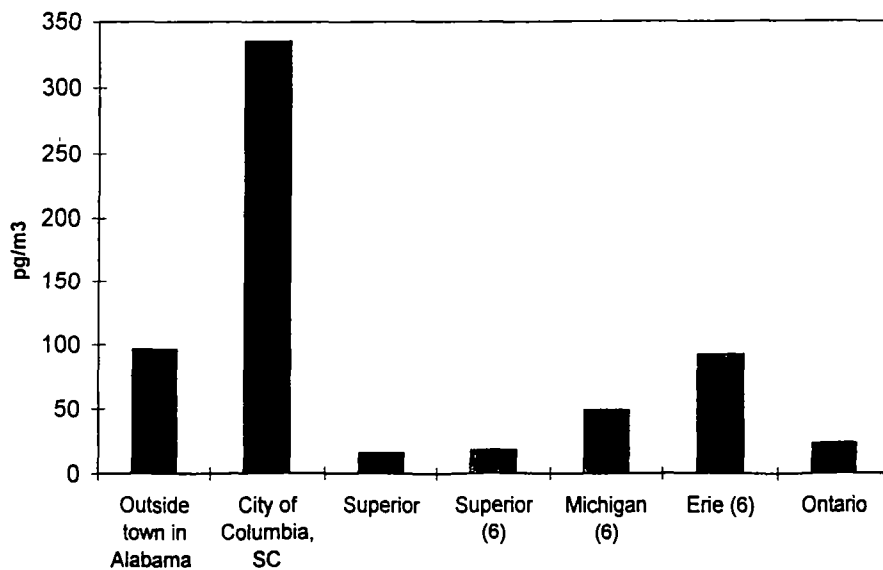


Fig. 2

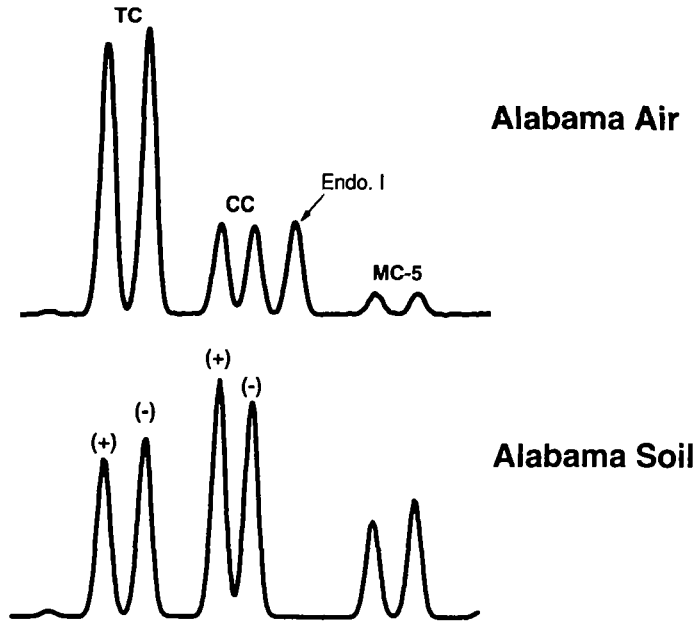


Fig. 3

