

Soil as a Source of Atmospheric Heptachlor Epoxide

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The chiral pesticide heptachlor can undergo photolysis to yield the racemic products heptachlor-*exo*-epoxide (HEPX) and photoheptachlor. Heptachlor is also metabolized to nonracemic HEPX in biological systems and soils. HEPX in ambient air samples from the southern United States and Lakes Ontario and Superior was nonracemic and enriched in the (+) enantiomer. Average enantiomer ratios (ER = areas of (+)/(-) HEPX) in these locations ranged from 1.51 to 2.02, and were similar to ER values of HEPX reported for agricultural soils. Airborne heptachlor was racemic, with ERs of 0.98–1.02. These results suggest that the main source of HEPX in ambient air is not photolysis of heptachlor, but rather metabolism of heptachlor in soils followed by volatilization of HEPX. The study exemplifies the use of chiral analysis for investigating the environmental fate of pesticides.

Introduction

Heptachlor is a chlorinated cyclodiene that was used for many years as an insecticide for agriculture, home lawns, and gardens and as a termiticide. The amount of heptachlor applied in the United States between 1971 and 1976 was estimated at 16 kt (1, 2), and additional quantities were released through the use of technical chlordane, which contains about 10% heptachlor (3). After 1983, the only permitted application of heptachlor was for subterranean termite control, and all U.S. registrations except for minor usage to control fire ant infestations in power transformers were canceled in 1988. Use of existing stocks of heptachlor-containing termiticide products by homeowners was also permitted (3).

Heptachlor is transformed in the environment by several pathways. Photolysis yields photoheptachlor and heptachlor epoxide (4, 5), both of which are persistent, bioaccumulative, and toxic (2). Epoxidation of heptachlor also occurs in soils,

mammals, and houseflies (3, 6), and hydrolysis to the less-persistent 1-hydroxychlordene takes place in water and soil (3, 7). Both the *endo*- and *exo*-epoxides of heptachlor are known, but the *exo* form (also known as isomer B and hereafter called HEPX) is more stable and is found almost exclusively in the environment (4, 6).

HEPX was frequently measured in air samples from southern Ontario (8, 9) and the Canadian Arctic (10–12). Surveys of the western Arctic Ocean (Canada Basin) found HEPX concentrations in surface water ranging from 5 to 20 pg/L, about five times more abundant than chlordane compounds (11, 13). HEPX accumulates in arctic plankton and benthic amphipods (14), and was reported in fish from the Slave River, NWT, Canada (15) and rivers feeding Lake Michigan (16). HEPX and photoheptachlor were identified in ringed seal blubber, polar bear fat and human plasma from northern Québec (2).

The origin of HEPX in air is unclear. Does it arise mainly from photolysis of heptachlor or by volatilization of the HEPX produced by metabolism of heptachlor in soils? Since HEPX is a chiral compound, examination of its two enantiomers provides some insight to this question. Photolysis of racemic heptachlor produces racemic HEPX, whereas metabolism of heptachlor in rats yields HEPX enriched in the (+) enantiomer (4, 5). Residues of HEPX in soil also contain an excess of the (+) enantiomer (17, 18). Volatilization of nonracemic HEPX should therefore impart a recognizable signature to HEPX residues in the atmosphere.

Experimental Section

Air samples were collected in Columbia, SC (August 1994–January 1995); at the Tennessee Valley Authority Environmental Research Institute in Muscle Shoals, AL (January–June 1996); at the Point Petre station of the International Atmospheric Deposition Network (IADN) on Lake Ontario (January–December 1992); and from shipboard on Lake Superior (August 1996) using previously described methods (8, 19). After sample cleanup and fractionation of the pesticides into groups, HEPX was determined by capillary gas chromatography with electron capture detection (GC–ECD) on 30 m DB-5 and DB-17 columns (Point Petre samples) or GC–negative ion mass spectrometry (GC–NIMS) on a 30-m DB-5MS column (Muscle Shoals and Lake Superior samples) according to described methods (13, 17, 18, 20). Heptachlor was not quantified by GC–ECD because of coelution with polychlorinated biphenyls from the cleanup columns but was determined in the Muscle Shoals samples by GC–NIMS.

The enantiomers of HEPX and heptachlor were determined by chiral-phase GC–NIMS using a BGB-172 column (20% *tert*-butylsilylated β -cyclodextrin in methylphenylcyanopropylpolysiloxane, 30 m \times 0.25 mm i.d., 0.25 μ m film, BGB Analytik AG, Switzerland). On this column the (+) enantiomers of both cyclodienes eluted first, as determined by injecting single-enantiomer standards obtained from Axact Corp. (Commack, NY). GC–NIMS conditions were as previously described (13, 17, 18). Ions 386/388 were monitored for HEPX, and 300/302 were monitored for heptachlor. As a quality control measure, the ion ratios for samples were required to be within $\pm 5\%$ of standard values for an acceptable enantiomeric identification (17, 18). Enantiomer ratios, ER = (+)HEPX/(-)HEPX for racemic standards were as follows: HEPX = 1.00 ± 0.01 ($n = 6$) and heptachlor = 0.97 ± 0.04 ($n = 8$).

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TABLE 1. Concentrations of Heptachlor-*exo*-epoxide (HEPX) and Enantiomer Ratios (ER^a) of HEPX and Heptachlor in Ambient Air

location and date	HEPX, pg/m ³	ER	
		HEPX	heptachlor
Columbia, SC Aug 1994–Jan 1995	not determined	1.51 ± 0.09 (9)	0.99–1.02 (2)
Muscle Shoals, AL Jan–June 1996	20 ± 19 (8)	1.70 ± 0.18 (6)	0.98 ± 0.02 (4)
Point Petre, Lake Ontario Jan–Dec 1992	7.3 ± 3.9 (7)	1.86 ± 0.05 (8)	1.01 ± 0.05 (6)
Lake Superior Aug 1996	19 ± 12 (6)	2.02 ± 0.10 (6)	not determined

^a ER = areas of (+)/(-) enantiomers, mean ± SD, and (number of samples).

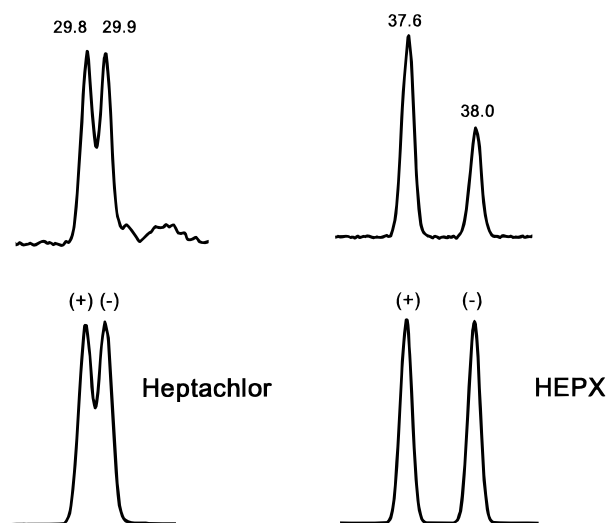


FIGURE 1. Chromatograms of (top) heptachlor and HEPX in an air sample from Point Petre; (bottom) racemic heptachlor and HEPX standards. Numbers indicate retention times (min) of the enantiomers.

Results and Discussion

Concentrations of HEPX in ambient air in Alabama and at the Great Lakes sampling locations are given in Table 1. HEPX concentrations in Alabama ranged from 4–9 pg/m³ in January–February to 29–51 pg/m³ in May–June, similar to the seasonality reported in southern Ontario (8, 9). This is consistent with temperature-driven volatilization from soil (21, 22). The enantiomeric composition of HEPX in air samples from all locations was distinctly nonracemic. ERs are given in Table 1, and sample chromatograms are shown in Figure 1. Average ERs ranged from 1.51 in Columbia to 2.02 over Lake Superior. The ERs were remarkably consistent in each location, exhibiting relative standard deviations of only 2.7–10.6% (Table 1) and showing no seasonal dependence (23).

Heptachlor was quantified only in Muscle Shoals air samples and, unlike HEPX, showed no seasonality, ranging from 27–45 pg/m³ in January–February to 31–49 pg/m³ in May–June. The enantiomers of heptachlor were only partially resolved on the BGB-172 column, although well enough to determine the ERs in air (Figure 1). The average ERs of heptachlor were 1.01 ± 0.05 (*n* = 6) at Point Petre and 0.98 ± 0.02 (*n* = 4) in Muscle Shoals and were not significantly different from the standard (*p* > 0.1). ERs of heptachlor in two air samples from Columbia were 0.99 and 1.02. These ERs are consistent with a study in which racemic heptachlor (ER = 1.03) was found in Norwegian air (4).

These results suggest that HEPX in ambient air does not arise mainly from heptachlor photolysis, although some racemic HEPX may come from this source. Release of HEPX

from soils is a more plausible explanation. ER values of HEPX averaged 1.30 ± 0.08 in soils of four British Columbia vegetable farms (18), 2.87 ± 1.52 (*n* = 14) in agricultural soils from the Corn Belt states of Ohio, Illinois, and Indiana (17), and 2.71–3.19 in an agricultural and cemetery soil from Alabama (24). The HEPX in air samples collected 5–140 cm above the soil at the British Columbia farm showed the same ER as HEPX in the soil itself, suggesting soil to air transfer (25). Thus HEPX is likely produced in soil by enantioselective epoxidation of heptachlor and subsequently volatilized. In the Great Lakes region, it is also possible that volatilization from water contributes some HEPX to the atmosphere. However nonracemic HEPX was also found in Columbia and Muscle Shoals, well away from large bodies of water.

How can the presence of racemic heptachlor in ambient air be explained? If (+) heptachlor in soil undergoes preferential epoxidation to (+) HEPX, the residual heptachlor should be nonracemic and have an ER < 1.0. However this was not observed in British Columbia soils, where the ER of heptachlor was 1.08 despite selective formation of (+) HEPX (ER = 1.30) (18). Heptachlor degradation in soil proceeds by at least two routes. Following its incorporation into the soil of an experimental field in Ohio, heptachlor was dissipated with a half-life of 0.91 yr (7). Two degradation products were identified, 1-hydroxychloridene and the more persistent metabolite HEPX. After 4.5 yr, heptachlor was not detectable and HEPX accounted for about 20% of the original heptachlor applied. Heptachlor is more volatile than HEPX and would be expected to dissipate more quickly by evaporation. Perhaps only a small proportion of the heptachlor in soil is converted to HEPX, and the rest is volatilized or degraded by processes that are not enantioselective or have a different preference for the heptachlor enantiomers. Another possibility is that racemic heptachlor is released from buildings that were protected against termites with heptachlor or technical chlordane. Although the enantiomeric composition of heptachlor in home air has not been determined, the *cis* and *trans* isomers of chlordane in the air of eight homes in Columbia and Muscle Shoals were racemic (24), suggesting that the heptachlor in this air would also be racemic. Atmospheric transport of recently applied heptachlor from outside the United States or Canada could also contribute racemic heptachlor to ambient air.

This study illustrates the application of enantiomeric signatures for distinguishing biotic and abiotic transformation pathways and elucidating sources to the atmosphere.

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