

CHANGES IN CHLORDANE SOURCES TO THE ATMOSPHERE ARE SUGGESTED BY CHIRAL SIGNATURES

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Introduction

Chlordane was used for half a century, from 1945 until its withdrawal from the world market in 1997. The insecticide was mainly used for agriculture, on home lawns and gardens and to treat house foundations for termite protection. Chlordane levels in air are highest in houses treated for termite control, intermediate in urban and rural environments, and lowest in the Arctic¹⁻⁴. Technical chlordane is a complex mixture which includes chlordanes, nonachlors and heptachlor. These, as well as the metabolites heptachlor exo-epoxide (HEPX) and oxychlordane (OXY), are widespread in arctic biota⁵. Because chlordane is persistent, bioaccumulative and toxic, it has been placed on two international lists of chemicals targeted for elimination: the UN-ECE Convention on Long-Range Transport of Atmospheric Pollutants (CLRTAP) and the UNEP Stockholm Convention on Persistent Organic Pollutants.

Trans- and cis-chlordane (TC, CC) undergo enantioselective degradation in soil to leave non-racemic residues⁶⁻¹⁰. In most cases, the (+) enantiomer of TC and the (-) enantiomer of CC are depleted, leading to enantiomer fractions, $EF = (+)/[(+) + (-)]$, that are <0.5 for TC and >0.5 for CC. Emissions of chlordane from soils showing enantioselective degradation carry these distinctive profiles into the atmosphere^{7,11,12}. Chlordanes in soil near house foundations and in the ambient air of homes are racemic^{1,8}. The EFs of TC and CC in ambient air samples in the Great Lakes region bordering Canada and the U.S. appear to be influenced by both soil and termiticide emissions^{7,12,13}.

Recently, we found that the EFs of chlordanes were non-racemic in air samples from arctic stations in Canada, Russia and Finland, and from a European Monitoring and Assessment Program (EMEP) station at Rörvik on the Swedish west coast¹⁴. HEPX was also non-racemic in these samples, showing an excess of the (+) enantiomer similar to soil residues. This led us to hypothesize that sources of chlordanes to the atmosphere have changed over time and are now influenced to a greater extent by re-emission from soils than current usage. Here we provide further evidence through the analysis of environmental samples representing different time periods of chlordane history: a) archived atmospheric deposition samples from the first large-scale study of PCB and DDT deposition in Sweden in 1971-73^{15,16}, b) air samples collected at Rörvik in 1998¹⁴, d) soils from southern Sweden, sampled in 2001, and d) a varved sediment core from the Canadian Arctic representing ~50 years of accumulation¹⁷.

Methods and Materials

Agricultural and background soils (upper 5-10 cm) were collected in southern Sweden at several locations that had been sampled previously for PCBs¹⁸. The soils were sieved, mixed with anhydrous sodium sulfate, Soxhlet extracted with dichloromethane and cleaned up as previously described¹⁹. Extracts of atmospheric deposition samples collected in southern Sweden, Iceland and Slovakia in 1971-73 were used without further cleanup^{15,16}. Extracts of sediment slices from a dated core collected from lake DV09 on Devon Island, NV, Canada (1999) were analyzed after shaking with 18M sulfuric acid for cleanup¹⁷. Sample extracts were concentrated to 20-50 μL for analysis by nitrogen blowdown. Chiral analysis was done using 20-30 m x 0.25 mm i.d., 0.25 μm

film thickness, capillary columns containing either BGB-172 (20% tert-butyldimethyl silylated β -cyclodextrin in OV-1701, BGB Analytik AG, Switzerland) or Betadex-120 (20% permethylated β -cyclodextrin in SPB-25, Supelco, U.S.A.) with detection by electron capture negative ion mass spectrometry (GC-ECNI-MS) and selected monitoring of the 410 and 412 ions. Operating conditions were similar to those previously described¹⁴.

Results and Discussion

Table 1 gives the average EFs for the Swedish soil and atmospheric deposition samples, and Figure 1 compares these to EFs from other locations. Chlordanes were below the quantitation limit of 0.02 ng/g dry weight in 7 of 8 soil samples. However, by concentrating the extracts to <50 μ L, the EFs could be determined. The two chiral columns used here give different elution orders for the chlordane enantiomers¹³. BDX: (+)TC, (-)TC, (+)CC, (-)CC; BGB: (+)TC, (+)CC, (-)CC, (-)TC. When analyses were done on both columns, the absolute difference in EFs averaged 0.006 for 7 atmospheric deposition samples and 0.040 for 4 soil samples.

The EFs of chlordanes in Swedish soils were <0.5 for TC and >0.5 for CC (Table 1). This preferential loss of (+)TC and (-)CC was similar to the enantioselectivity reported for other soils in the U.S. and England^{6-9,19} (Figure 1). The EFs of the historical atmospheric deposition samples were essentially racemic, averaging 0.496 ± 0.002 for TC and 0.500 ± 0.003 for CC. This contrasts with the significantly ($p < 0.001$) non-racemic EFs in 1998 air samples from Rörvik: 0.463 ± 0.013 for TC and 0.511 ± 0.005 for CC¹⁴. EFs were also significantly non-racemic at three arctic stations for TC ($p < 0.001$) and at one station for CC ($p < 0.01$) (Figure 1)¹⁴. The non-racemic chlordanes in recent air samples, along with decreasing proportions of TC/(TC+CC) from 1984-98, suggests that the sources of chlordane to the Arctic have changed and are now more influenced by soil emissions¹⁴.

The record of chlordane deposition in sediments of arctic lake DV09 provides further evidence of changing sources. EFs of TC show a decrease from sediment layers deposited in the 1940s and 50s to recent times (Figure 2). The less racemic EFs in recent sediment layers were accompanied by lower proportions of TC/(TC+CC)¹⁷.

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Table 1. Enantiomer fractions (EFs) of trans-chlordane and cis-chlordane in soil and historical atmospheric deposition samples.

	trans-chlordane			cis-chlordane		
	mean or range	s.d.	n	mean or range	s.d.	n
<i>soil, 2001</i>						
agricultural	0.397	0.010	3	0.538-0.588		2
non-agricultural	0.427	0.017	5	0.532	0.048	5
<i>atmospheric deposition, 1971-73</i>						
Sweden	0.496	0.002	6	0.502	0.001	6
Iceland	0.497	0.004	3	0.496	0.001	3
Slovakia	0.495-0.499		2	0.500-0.501		2

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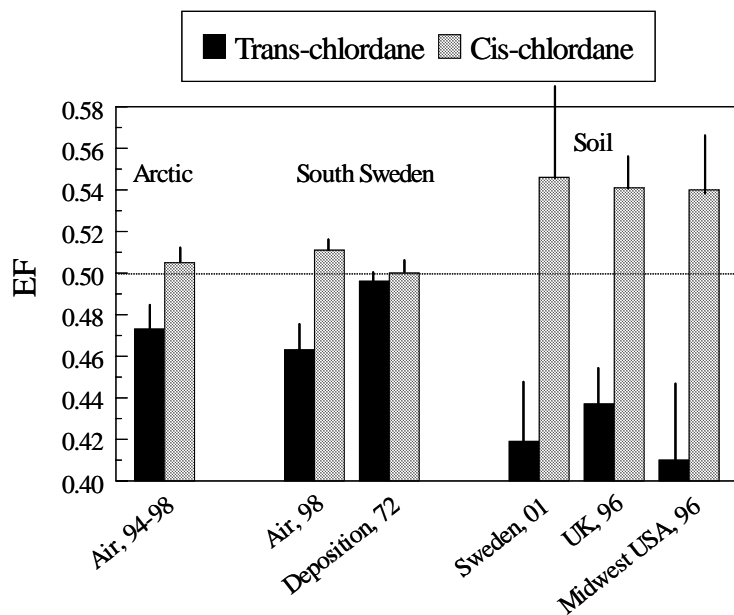


Figure 1. Enantiomer fractions (EFs) of trans- and cis-chlordane in 2001 soil and 1971-73 atmospheric deposition samples (this work), compared to EFs in air at Rörvik (1998)¹⁴, arctic air (1994-96)¹⁴, and soil from the midwest U.S. (1996)⁶ and the U.K. (1996)¹⁰.

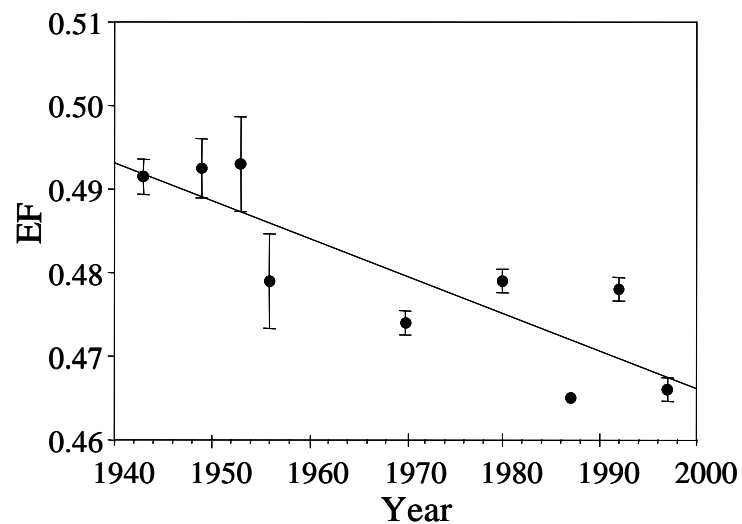


Figure 2. Trans-chlordane enantiomer fraction (EF) in a laminated sediment core collected in 1999 from Lake DV-09, Devon Island, Nunavut, Canada¹⁷. For $EF = m \cdot year + b$: $m = -0.000451$, $b = 1.37$, $r^2 = 0.72$.