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Chiral Pesticides as Tracers of Air-Surface Exchange

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Abstract

The enantiomers of chiral pesticides are selectively broken down in soil and water to yield residues and metabolites which are non-racemic. The distinctive enantiomer signatures of residues are preserved upon volatilization, providing site-specific tracers for air-soil and air-water exchange. Applications of enantiomeric tracers include distinguishing the atmospheric transport of freshly applied pesticides from those which are "recycled" from lakes, oceans and soil, and investigating biotic vs. abiotic degradation pathways. Examples are given for using pesticide enantiomers to follow volatilization from the Great Lakes and arctic waters, and as indicators of pesticide emissions from agricultural soils.

Introduction

Several organochlorine (OC) pesticides 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 from fresh pesticides on the basis of their enantiomeric ratios (ER = (+)/(-) enantiomers). 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. Here we show applications of pesticide enantiomers for following air-water gas exchange in the Great Lakes and the Arctic, volatilization of pesticide residues from soils and differentiation of sources to the atmosphere.

Experimental Methods

Air was drawn through a glass fiber filter followed by a polyurethane foam trap. Water samples were passed through glass fiber filters and resin columns (C₈-bonded silica or XAD-2). Several soil cores (upper 5 cm) were collected and pooled to obtain a representative sample for each field. Samples were extracted with organic solvents and cleaned up prior to GC analysis on an alumina-silica column. Pesticides were quantitatively determined by capillary GC with electron

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capture detection or negative ion mass spectrometry (NIMS). Locations and descriptions of collection and quantification methods are given in other publications¹⁻⁵.

Two chiral columns were used for enantiomeric analysis. Betadex-120 (20% permethylated β -cyclodextrin in SPB-25, 30 m x 0.25 mm i.d., 0.25 μ m film thickness, Supelco) and BGB-172 (20% tertbutyldimethylsilylated β -cyclodextrin in OV-1701, 30 m x 0.25 mm i.d., 0.25 μ m film thickness, BGB Analytik AG, Switzerland). In some cases tandem columns were employed to resolve specific interferences. The tandem columns 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 μ m film thickness, J&W Scientific). Temperature programs, injection conditions and ions monitored for detection by NIMS are given elsewhere^{1,2,4,6}.

Results and Discussion

Gas Exchange of α -Hexachlorocyclohexane (α -HCH)

The gas exchange of HCHs undergoes seasonal cycles in the Great Lakes due to changes in water temperature, air concentrations and stratification of the water column⁵⁻⁷. In arctic and subarctic waters the net exchange direction of α -HCH has reversed in response to declining atmospheric concentrations, from deposition in the 1980s to volatilization in the 1990s¹. The α -HCH in the technical product is racemic, whereas α -HCH in oceans and large lakes is non-racemic due to selective breakdown of one enantiomer. Thus volatilization of α -HCH can be distinguished from atmospheric transport of new pesticide by differences in the ER signatures.

In the Great Lakes (+) α -HCH is depleted in surface water relative to the (-) enantiomer, leading to ERs <1.00. In summer the ERs in the air layer 10 m above the lakes are also <1.00 when fugacity gradients show net volatilization of α -HCH (Figure 1). A distinct cyclic trend is seen for Lake Ontario in which the ER signatures vary from near-racemic in the winter, spring and fall deposition seasons to below 1.00 in summer^{6,8} (Figure 2). Depletion of (+) α -HCH is also seen in the surface water of the Arctic Ocean (ERs < 1.00), whereas (-) α -HCH is selectively lost in the Bering and Chukchi seas (ERs >1.00). The ERs of α -HCH in the air layer sampled 40 m above the open water regions of these seas track those in surface water, demonstrating the "two-way street" nature of gas exchange¹.

Volatilization of Chiral Pesticides from Soil

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. Several OCs are also still applied in other regions of North America, notably Mexico, Central America and some Caribbean countries. Selective breakdown of chiral pesticides in soil leads to non-racemic ER signatures which are preserved upon volatilization⁹. Examples are shown for soil and overlying air at farms in British Columbia (Figure 3) and Ohio (Figure 4). Once in the atmosphere, ER values are not altered by removal processes such as photolysis, OH radical attack and atmospheric deposition. Thus ER values are conservative in the atmosphere and provide unique

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opportunities to differentiate soil emissions of chiral pesticides from other releases such as new usage and volatilization from racemic sources.

Heptachlor-exo-epoxide (HEPX) is a persistent, bioaccumulative product of heptachlor which is formed by oxidation in the atmosphere and through enzymatic processes. Photolysis of heptachlor yields racemic photoheptachlor and HEPX, whereas incubation of heptachlor with rat liver microsomes produces HEPX which is enriched in the (+) enantiomer^{10,11}. Air samples from the Great Lakes, Alabama and South Carolina show consistent enrichment of (+)HEPX, as do soils. Non-racemic HEPX is also found in air and soil samples from a British Columbia farm⁹ (Figure 3). Thus the source of HEPX in ambient air is most likely volatilization of HEPX produced by microbial activity in soils rather than heptachlor photolysis.

Chlordane was used in the U.S. as an agricultural insecticide until the mid-1970s, when it was restricted to termiticide applications. The pesticide was banned in 1988. The chlordane found in ambient air today may emanate from residues in agricultural soils and from volatilization of termiticides applied to house foundations. Soils from agricultural fields in Alabama contain low concentrations of non-racemic chlordane, whereas racemic chlordane is found in ambient air samples from northern Alabama and the city of Columbia, South Carolina. This suggests that airborne chlordane in these regions comes from sources other than volatilization from agricultural soils. By contrast, air samples from the Great Lakes show depletion of certain chlordane enantiomers, particularly (+)trans-chlordane (Figure 5). Thus "recycled" chlordane – possibly from local soils (Figure 4) or from the lake itself – is being contributed to Great Lakes air.

These examples demonstrate the possibilities of using enantiomers of chiral pesticides to follow degradation and exchange processes in the environment. To realize the full value of these tracers, more information is needed concerning the spatial variability of chiral pesticide residues, and the rates and mechanisms of enantioselective degradation in water and soils.

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Figures

1. Enantiomers of α -HCH in surface water and air of Lake Superior, Aug. 1996 (Betadex column).
2. Monthly variations in the water/air fugacity ratio and ER values of α -HCH in air over Lake Ontario⁶. Fugacity ratios <1.0 and >1.0 indicate net deposition and volatilization, respectively.
3. Enantiomers of α -HCH and HEPX in soil and overlying air at a British Columbia farm (BGB-172 column)⁹.
4. Enantiomers of trans-chlordane (TC), cis-chlordane (TC) and chlordane compound MC-5 in the soil and overlying air at an Ohio farm (Betadex column).
5. Chlordane enantiomers in air over Lake Superior, Aug. 1996. Note the slight depletion of (+)TC and (-)CC relative to the technical chlordane standard (tandem Betadex - DB-210 column used to resolve endosulfan I from (-)CC peak).

Figure 1

α -HCH Enantiomers in Lake Superior
Air and Water

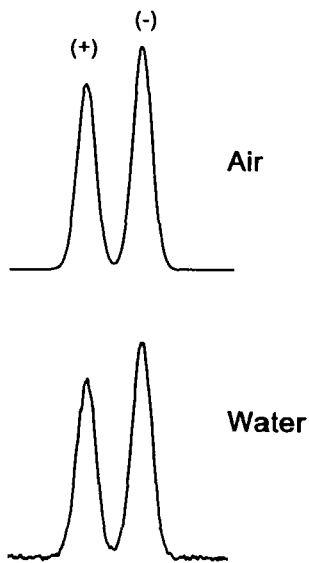


Figure 2

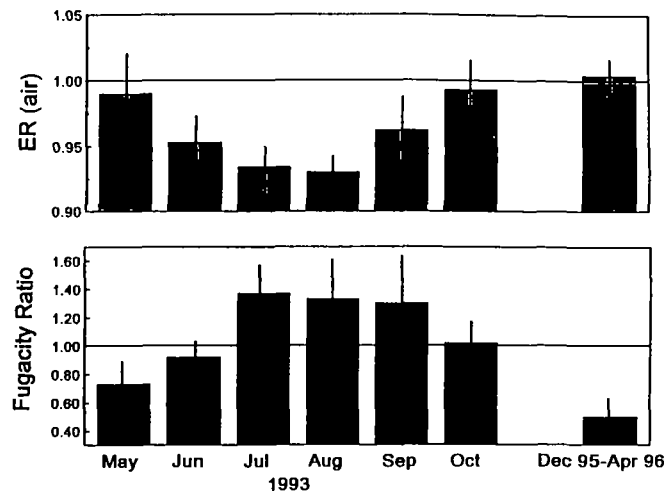


Figure 3

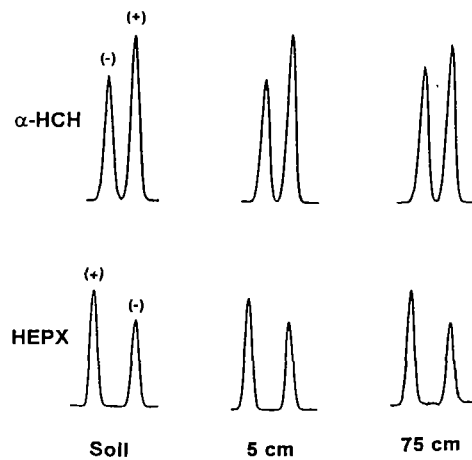


Figure 4

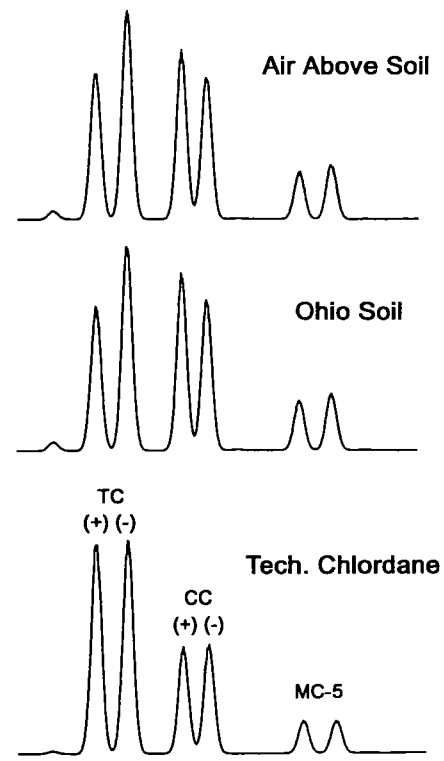


Figure 5

