

Chiral Pesticides in Soils of the Fraser Valley, British Columbia

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Chiral organochlorine pesticides were examined in soils collected in 1989 from six farms in the Fraser Valley, British Columbia. Concentrations of pesticide residues were 1–2 orders of magnitude higher in muck soils (27–56% organic matter) than in silt loams (3–7% organic matter). Enantiomeric composition of α -hexachlorocyclohexane residues in muck soils indicated preferential breakdown of the (–) enantiomer, whereas α -hexachlorocyclohexane in the silt loams was racemic. Five of the soils contained racemic *o,p'*-DDT, but the (+) enantiomer was selectively lost in one silt loam soil. No enantioselective breakdown of *cis*- or *trans*-chlordane was found in any of the soils, but nonracemic traces of oxychlordane were found in one silt loam and three muck soils. Enantiomeric composition of heptachlor and heptachlor *exo*-epoxide in muck soils indicated loss of (–)-heptachlor and production of (+)-heptachlor *exo*-epoxide, suggesting that the metabolism of these two compounds in soil may be more complex than a simple conversion of heptachlor to heptachlor *exo*-epoxide.

Keywords: Organochlorine pesticides; chiral pesticides; soils; Fraser Valley; British Columbia

INTRODUCTION

Organochlorine (OC) pesticides were used heavily on farmlands in the United States and Canada during the 1960s and early 1970s. Because OC pesticides and their metabolites are highly persistent, residues remain in many soils, especially those of high organic content. Volatilization from reservoirs of accumulation, including soils, may be a significant source of these "old" pesticides to the atmosphere for decades after their usage has been stopped. Cycles of volatilization, aerial transport, and deposition lead to a migration of OC pesticides to colder temperate and polar regions (Wania and Mackay, 1996).

Several OC pesticides are chiral and are manufactured as racemic mixtures of enantiomers. Chiral compounds include α -hexachlorocyclohexane (α -HCH), *cis*- and *trans*-chlordane (TC, CC), heptachlor (HEPT), and *o,p'*-DDT. The metabolites oxychlordane (OXY), heptachlor epoxide (HEPX), and *o,p'*-DDD are also chiral. Pesticides are lost from soils by physical processes (volatilization, leaching, erosion), chemical breakdown, and microbial attack. The latter is the only known mechanism that can result in enantioselective degradation. Many authors have found enantioselective metabolism of chiral OC pesticides in biota (Buser and Müller, 1992, 1993, 1995a; Buser et al., 1992; Kallenborn et al., 1994; Möller and Hühnerfuss, 1993; Mössner et al., 1992, 1994; Müller et al., 1992; Pfaffenberger et al., 1994; Tanabe et al., 1996), α -HCH in freshwater and seawater (Falconer et al., 1995a,b; Faller et al., 1991; Hühnerfuss et al., 1992; Jantunen and Bidleman, 1996; Pfaffenberger et al., 1992; Ridal et al., 1997), and herbicides in soils (Müller and Buser, 1995; Garrison et al., 1996). Here we report the enantiomeric composition of chiral OC pesticides and their metabolites in agricultural soils from the Fraser Valley, British Columbia.

EXPERIMENTAL PROCEDURES

Materials. Reagents and standards were obtained from the following sources: chromatographic quality solvents (BDH Omnisolv), pesticide standards (Accustandard, Inc., New Haven, CT), neutral alumina (EM Science), silicic acid, 200 mesh (Mallinckrodt), enantiomerically pure pesticide standards (Axact Corp., Commack, NY), and α -HCH-*d*₆ (Cambridge Isotope Laboratories, Andover, MA).

Sample Collection. The Fraser Valley is an intensively farmed region of British Columbia where OC pesticides were applied prior to the mid-1970s. Surveys of soils from the valley found that OC pesticide levels declined between 1971 and 1989, although as of 1989 substantial residues were still present, especially in soils rich in organic matter (Szeto and Price, 1991). In this investigation, soils were analyzed from six farms in the Fraser Valley which had a history of vegetable growing for a least 25 years. The samples were those collected and frozen at –20 °C in 1989 by Szeto and Price (1991), who reported details of sampling methods, soil characteristics, and ranges of OC residues. Three silt loam (3–7% organic matter) and three muck (27–56% organic matter) soils were selected for examination of pesticide enantiomers.

Extraction and Cleanup. Approximately 15 g of soil (either air-dried or damp weight) was mixed with granular anhydrous sodium sulfate and Soxhlet extracted with 250 mL of dichloromethane overnight in precleaned cellulose thimbles. Extracts were reduced into 20 mL of hexane by rotary evaporation and then further reduced into 1 mL of iso-octane by blowing down with a gentle stream of nitrogen. Extracts were cleaned up and fractionated on a column of silicic acid overlaid with neutral alumina and capped with sodium sulfate, as described by Keller and Bidleman (1984). The sample was applied in 1–2 mL of hexane and eluted with petroleum ether followed by dichloromethane. Fraction 1 (20 mL of petroleum ether) contained polychlorinated biphenyls, HEPT, *p,p'*-DDE, and a portion of the *o,p'*-DDT. Fraction 2 (60 mL petroleum ether) contained the remainder of the *o,p'*-DDT, *p,p'*-DDT, and *trans*-nonachlor (TN) and a portion of the TC, CC, and OXY. Fraction 3 (25 mL of dichloromethane) contained the remainder of the TC, CC, and OXY, as well as HEPX, HCHs, and endosulfans. The fractions were reduced into 1–2 mL of iso-octane by nitrogen blowdown, given further cleanup by shaking with 0.5 mL of 18 M sulfuric acid (omitted for HEPX), and adjusted to a suitable volume for analysis.

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Analysis. Quantitative analysis of soils was carried out by capillary gas chromatography with electron capture detection (GC-ECD) using a 60-m DB-5 column (0.25 mm i.d., 0.25 μ m film thickness, J&W Scientific) installed in a Hewlett-Packard 5890 GC and operated at a hydrogen carrier gas flow of 50 cm/s. Samples (2 μ L) were injected splitless (split opened after 1.0 min) at 90 °C. After a 1-min hold, the oven was programmed at 15 °C/min to 160 °C, 3 °C/min to 240 °C, and 20 °C/min to 270 °C and held for 10 min. Other conditions were injector 250 °C, detector 300 °C. Samples were quantified against four calibration standards with mirex as an internal standard using HP Chemstation software.

The enantiomeric composition of chiral pesticide residues was determined by capillary GC with detection by electron impact or negative ion mass spectrometry (EIMS, NIMS) using a Hewlett-Packard 5890 GC-5970B MS Engine. EIMS was used for *o,p'*-DDT; all other pesticides were run by NIMS. The instrument was operated in the selected ion monitoring mode using the following ions: *o,p'*-DDT (235, 237), α -HCH (255, 257), chlordanes (410, 412), nonachlors (444, 446), HEPT (300, 302), HEPX (386, 388), OXY (420, 422), and endosulfans (404). Two chiral columns were employed for enantiomeric separations: (1) Betadex-120 (20% permethylated β -cyclodextrin in SPB-25, 30 m, 0.25 mm i.d., 0.25 μ m film thickness, Supelco Corp.); (2) BSCD (20% *tert*-butyldimethylsilylated β -cyclodextrin in OV-1701, 30 m, 0.25 mm i.d., 0.25 μ m film thickness, BGB Analytik AG, Switzerland, column designation BGB-172). Samples (2 μ L) were injected splitless (split opened after 1.5 min) at 90 °C. After a 1-min hold the following oven programs were used for the two columns: Betadex, 15 °C/min to 140 °C, 1 °C/min to 190 °C, hold 10 min, 20 °C/min to 230 °C, hold 10 min; BSCD, 15 °C/min to 140 °C, 2 °C/min to 210 °C, hold 5 min, 20 °C/min to 240 °C, hold 10 min. Other conditions were as follows: helium carrier gas 40 cm s⁻¹, injector 250 °C, transfer line 250 °C, ion source 150 °C (NIMS) or 200 °C (EIMS), quadrupole 100 °C, methane reagent gas pressure (NIMS) 1.0 Torr.

RESULTS AND DISCUSSION

Quality Control. The enantiomeric ratio (ER) is defined as the area ratio of the (+)/(-) peaks eluting from the cyclodextrin column. All of the chiral pesticides in this study are manufactured as racemic mixtures of the two enantiomers. If no metabolism occurs, the ERs of the pesticide residues should be 1.00. Replicate injections of analytical standards yielded racemic ER values (Table 2) with a standard deviation of ± 0.02 for all compounds, demonstrating that chiral-phase GC-MS is capable of highly precise enantiomeric analysis.

Average ERs were calculated from replicate injections of two or more separately extracted portions of the soil. Standard deviations for the soil ERs in Table 2 ranged from 0.01–0.06, with an average value of 0.02. As a quality control protocol we set the following limits for acceptable ER values: (a) agreement of ER values at each of the two monitored ions within ± 0.05 ; (b) area ratios of the two monitored ions for samples and standards within $\pm 5\%$. To determine if soil matrix effects altered the enantiomer ratios, we spiked a control soil which contained very low residue levels with several racemic pesticide standards. The enantiomer ratios found for the extracted spiked compounds were also racemic.

For quantitative work, two silt loam and one muck soil were spiked with the recovery surrogate 2,2',4,5',6-pentachlorobiphenyl (PCB-103) prior to extraction. Recoveries were 74% and 102% from silt loams and 79% from muck soil. In a separate experiment, all six soils were spiked with α -HCH-*d*₆, which is chromatographically resolved from native α -HCH on a 60-m DB-5 column. Yields were $62 \pm 13\%$ for the silt loams and $109 \pm 3\%$ for the muck soils.

Table 1. Organochlorine Pesticide Residues in Fraser Soils (ng/g dry wt)

	silt loam			muck		
	farm 1	farm 2	farm 3	farm 1	farm 2	farm 3
α -HCH	0.26	0.80	2.3	85	10	259
γ -HCH	0.33	0.32	1.0	241	19	464
HEPT	0.16	0.11	1.0	109	241	75
HEPX	0.05	0.13	36	93	390	109
TC	0.07	0.16	115	340	979	288
CC	0.25	0.41	154	127	597	136
TN	0.32	0.54	119	88	367	98
<i>p,p'</i> -DDT	151	308	670	1960	2426	2808
<i>o,p'</i> -DDT	13	82	173	601	769	763
<i>p,p'</i> -DDE	67	60	333	336	380	378
<i>p,p'</i> -DDD	3.3	23	99	160	335	444

Concentrations of Pesticides in Soils. The levels of OC pesticides found in this work are given in Table 1. The highest concentrations were found in muck soils, while levels in the silt loams were 1–2 orders of magnitude lower. Szeto and Price (1991) reported the range of OC pesticide concentrations in Fraser soils and discussed the persistence of residues in various soil types. Compared to the values for individual soils, the levels of pesticides found in this work are somewhat higher, by an average of 33% for muck soils and 66% for silt loams. Reasons for these discrepancies are not known; however, the extraction methods used in the two studies were different: soxhlet extraction with dichloromethane (this work) and shaking with ethyl acetate (Szeto and Price, 1991). Side-by-side trials would be needed to compare the efficacy of each method. Subsequent work in our laboratory showed equivalent results for soil extractions done with dichloromethane or hexane–acetone azeotrope. In experiments with fortified soils, we obtained 62–109% recovery of spiked compounds whereas Szeto and Price reported recoveries of 74–111%. However the yields of spiked compounds are not necessarily the same as for residues which have been in the soil for a long time and are associated with the humic fraction. Freeman and Cheung (1981) found that dichloromethane was a more efficient solvent for extracting a phthalate ester from dried sediment than a more polar (methanol) or nonpolar (hexane) solvent. The explanation given was that the solubility parameter of dichloromethane more closely matched that of humic material, allowing the structure to swell and release the entrapped contaminant.

Enantiomeric Analysis and Composition of Pesticide Residues. Enantiomers of HEPT, HEPX, OXY, α -HCH, and *o,p'*-DDT were separated on the BSCD column. The first-eluting enantiomers for each of these compounds are reported to be (+) for HEPX and OXY, and (-) for α -HCH and *o,p'*-DDT (Müller and Buser, 1994; Buser and Müller, 1995a,b). These elution orders were confirmed for HEPX, OXY, and α -HCH enantiomers in this work with standards of the single-enantiomer pesticides, obtained from AXACT Co. (Conrack, NJ). Müller and Buser (1994) reported that the enantiomers of HEPT were unresolved on a BSCD/PS086 column. We obtained a slight separation on the BSCD/OV-1701 column (Figure 1), and by using a standard of pure (+)-HEPT (AXACT Co.) established this as the first-eluting enantiomer. The Betadex column was used for α -HCH, TC, and CC, and for each of these compounds the (+) enantiomer eluted first (Müller and Buser, 1994; Falconer et al., 1995a,b). ER values for the soils are given in Table 2 and example chromatograms are shown in Figures 1–4.

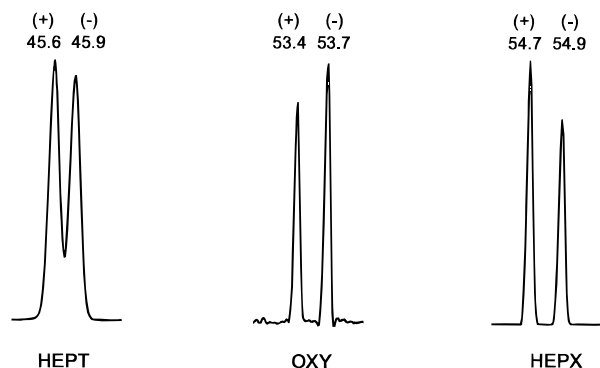


Figure 1. Enantiomer profiles of HEPT, OXY, and HEPX in muck soil 3. Numbers indicate the retention times on the BSCD column.

Table 2. Enantiomeric Ratios (ER)^{a,b} of Chiral Pesticides in Fraser Soils

	standard	silt loam			muck		
		farm 1	farm 2	farm 3	farm 1	farm 2	farm 3
α -HCH	1.00	1.02	0.97	1.01	1.32**	1.36**	1.21**
TC	1.00	0.98	0.99	1.00	0.98	0.97	0.98
CC	1.00	0.97	1.01	0.97	1.01	1.01	1.01
HEPT	1.01	NA ^c	NA	NA	1.11*	1.09*	1.05
HEPX	1.00	NA	NA	1.37**	1.37**	1.26**	1.20**
OXY	0.98	NA	NA	0.68**	0.58**	0.85**	0.75**
<i>o,p'</i> -DDT	1.01	0.83**	1.03	0.99	1.03	1.05*	1.02

^a ER = area ratio of (+)/(-) enantiomers. ^b * = significantly different from racemic at $\alpha < 0.05$. ** = significantly different from racemic at $\alpha < 0.01$. ^c NA = not analyzed (residues too low for good enantiomer peaks).

α -Hexachlorocyclohexane. The pattern of α -HCH breakdown was different in the two soil types (Figure 2). In muck soils the (-)- α -HCH enantiomer was preferentially degraded (ERs = 1.20–1.35), but residues in silt loam soils were close to racemic (ERs = 0.97–1.03) (Table 2). Müller et al. (1992) examined α -HCH in soil near a former HCH factory and found a slight depletion of the (-) enantiomer. A study in which sewage sludge was incubated with α -HCH showed more rapid degradation of the (+) enantiomer, whereas no enantioselectivity was observed in sterilized sludge (Buser and Müller, 1995b). Degradation of α -HCH enantiomers has been reported in other environmental media, often with reversals in selectivity. Preferential breakdown of (+)- α -HCH was found in seawater and a freshwater lake in the Arctic (Falconer et al., 1995a,b) and in Lake Ontario (Ridal et al., 1996). Different regions of the North Sea showed opposite patterns of degradation, with a preference for (+)- α -HCH loss in some sections and (-)- α -HCH in others (Faller et al., 1991). This reversal was also seen on arctic transects, where depletion of (-)- α -HCH was found in the Bering–Chukchi seas and (+)- α -HCH in the Canada Basin of the Arctic Ocean and the Greenland Sea (Jantunen and Bidleman, 1996). Enrichment of (+)- α -HCH has been found in sheep and eider duck livers (Möller et al., 1993; Pfaffenberger et al., 1992), tissues of neonatal northern fur seals (Mössner et al., 1992), and blubber of other cetaceans and several seal species (Hummert et al., 1995; Müller et al., 1992; Tanabe et al., 1996). Other studies found an excess of the (-) enantiomer in roe deer liver (Pfaffenberger et al., 1994), sheep brain (Möller et al., 1993), flounder liver and blue mussels (Pfaffenberger et al., 1992), and the blubber of hooded seals (Hummert et al., 1995). Such reversals in enantioselectivity may indicate differences in enzymatic breakdown processes or, in biological tissues, preferential

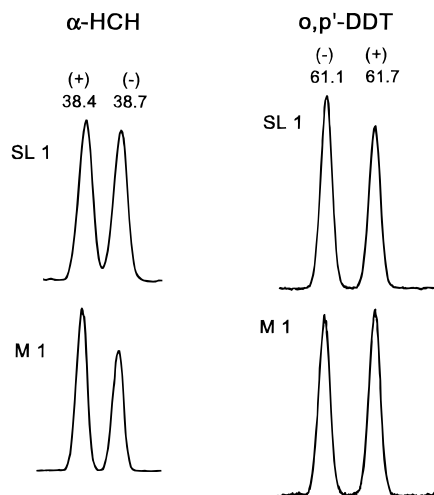


Figure 2. Examples of α -HCH (left, Betadex column) and *o,p'*-DDT (right, BSCD column) profiles in Fraser soils. SL = silt loam soils, M = muck soils.

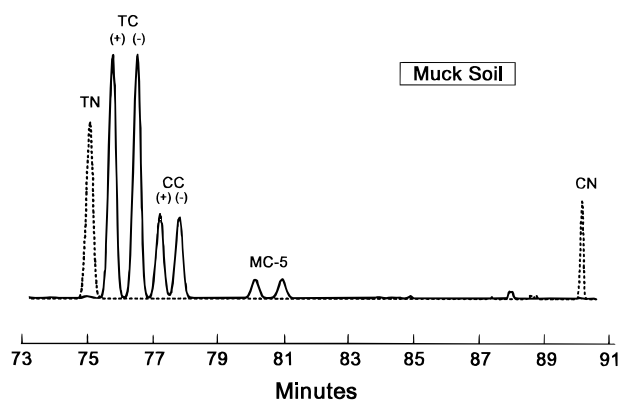


Figure 3. Components of technical chlordane in a muck soil, showing the elution order of the chiral *trans*- and *cis*-chlordane (TC, CC) and compound MC-5 (Miyazaki et al., 1985) and achiral *trans*- and *cis*-nonachlor (TN, CN) on the Betadex column.

accumulation of one enantiomer by selective permeation through membranes (Hühnerfuss et al., 1993; Möller et al., 1993; Mössner et al., 1994).

***o,p'*-DDT.** Depletion of (+)-*o,p'*-DDT was found in one silt loam (ER = 0.83, Figure 2). Residues in the other five soils were nearly racemic. The soil showing the selective degradation had the lowest concentration of *o,p'*-DDT, but was otherwise similar in characteristics to the other two silt loams. DDT reportedly binds to steroid hormone receptors and mimics the action of natural estrogens (Kupfer, 1975). McBlain et al. (1976) found that the two enantiomers of *o,p'*-DDT differed in estrogenic activity, the (-) enantiomer being far more active. Residues of *o,p'*-DDT in cod liver oil (Oehme et al., 1994) and human adipose tissue (Buser and Müller, 1995a) showed a lower abundance of the estrogenically more potent (-) enantiomer.

Chlordanes and Oxychlordane. Chromatograms of chlordane and nonachlor residues in Fraser soils are shown in Figures 3 and 4. Three pairs of enantiomers were separated on the Betadex column: TC, CC, and MC-5, the latter being tentatively identified from the published elution profiles of technical chlordane on a 20-m column containing 10% permethylated β -cyclodextrin in PS086 (PMCD; Buser et al., 1992). Also shown in Figure 3 are the achiral compounds TN and CN. It is interesting to note that TN precedes TC on the Betadex column, whereas TN falls between TC and CC

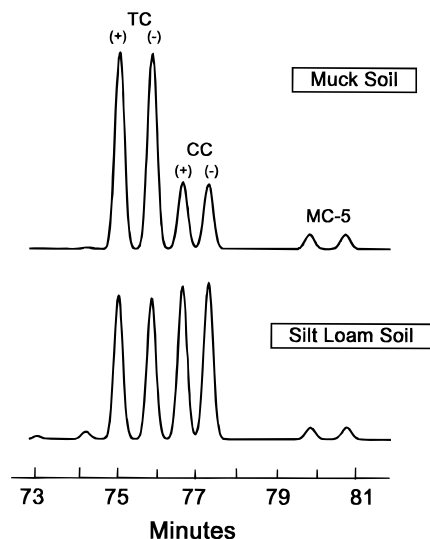


Figure 4. Profiles of chlordanes in a muck and silt loam soil, Betadex column.

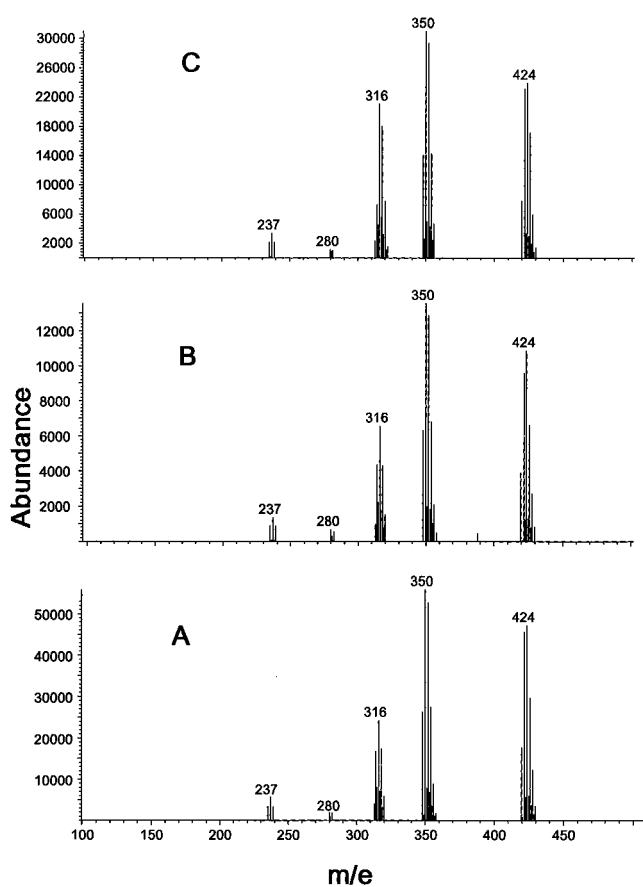


Figure 5. NIMS spectra of an OXY standard (A) and the (+)-OXY (B) and (-)-OXY (C) enantiomers in silt loam 3.

on the PMCD column of Buser et al. (1992). Because of this difference in elution behavior between the Betadex and PMCD columns, our assignment of MC-5 in the soils should be considered preliminary.

No enantioselective loss was found for either TC or CC (Figure 5). However, relative to the applied pesticide, muck soils were depleted in CC and silt loams in TC. The proportion of TC:CC is about 1.6 in technical chlordane (Miyazaki et al., 1985), 1.6–2.7 in muck soils, and 0.28–0.75 in silt loams (Table 1). The difference in proportion of TC:CC in soils from that of the technical product are likely due to nonenantioselective degradation or physicochemical processes.

Small amounts of OXY were identified in the three muck soils and in one silt loam which contained the highest chlordane residues (farm 3, Table 1). OXY was not quantified *per se*, but from relative NIMS responses we estimated that OXY in the soils ranged from about 1 to 3% of HEPX concentrations. OXY is considered to be a major metabolite of chlordanes and nonachlors in various organisms and cell cultures (Buser and Müller, 1992) and is widely found in human adipose tissue (Dearth and Hites, 1991). Beeman and Matsumura (1981) found that a microorganism isolated from soil was capable of transforming *cis*- and *trans*-chlordanes to OXY, HEPT, HEPX, and other metabolites. Full-scan NIMS spectra of the two OXY enantiomers in silt loam 3 are shown in Figure 5. All four soils showed an excess of (-)-OXY, with ERs ranging from 0.68 to 0.85 (Table 2), suggesting that some enantioselective metabolism of chlordanes/nonachlors must be occurring. However the concentrations of OXY in the soils were very low relative to the parent compounds, and enantioselective formation of OXY was apparently insufficient to perturb the racemic ERs of the residual TC and CC. The ERs of OXY in the soils were reversed from those in samples of fish, seal, penguin, and human adipose tissue (Buser and Müller, 1992; Müller and Buser, 1994) and roe-deer liver (Pfaffenberger et al., 1994), all of which contained an excess of the (+) enantiomer.

Heptachlor and Heptachlor Epoxide. Concentrations of HEPT were sufficiently high in the three muck soils to provide good enantiomer chromatograms, all of which showed a slight depletion of (-)-HEPT (ERs = 1.05–1.11, Table 2). Profiles of HEPX in the muck soils and silt loam 3, showed an excess of (+)-HEPX (ERs = 1.23–1.38, Table 2). By using standards of the two compounds we confirmed that the residues in soils were the *exo*, not the *endo*, isomer of HEPX. The former compound is considered to be the only isomer found to a significant extent in the environment (Donnelly et al., 1993).

The depletion of (-)-HEPT and enrichment of (+)-HEPX is puzzling, since metabolism of (-)-HEPT is expected to produce (-)-HEPX. This was demonstrated by Müller and Buser (1994) who reacted the single enantiomers of HEPT with CrO_3 and found that (-)-HEPT and (+)-HEPT are converted to their respective (-) and (+) epoxides. However these workers reported that incubating HEPT with rat liver homogenate yielded a HEPX metabolite with an ER = 3.94, while the ER of the remaining HEPT was 0.354. The authors noted that the reciprocal value for HEPT (2.84) was not equal to the ER of the HEPX product. In their system, (-)-HEPT apparently reacted faster but (+)-HEPX was more abundant, a discrepancy that could not be explained by the authors. It may be that metabolism of HEPT follows several pathways which have different enantioselectivities. For example, it has been shown that HEPT is also converted to 1-hydroxychlordene in soils (Freeman et al., 1975), but nothing is known about the chirality of this reaction. It is also unknown whether breakdown of HEPX itself is enantioselective.

The metabolism of HEPT and HEPX is obviously complex and varies substantially in different systems. Enrichment of (+)-HEPX (as was found in this study) was also seen in human adipose tissue (Müller and Buser, 1994), as well as the rat liver homogenate discussed above. However an excess of (-)-HEPX was found in herring oil, salmon muscle, and grey seal from

the Baltic Sea (Buser and Müller, 1992; Müller and Buser, 1994).

CONCLUSIONS

Several chiral OC pesticides show enantioselective breakdown and/or formation of chiral metabolites in Fraser Valley soils, with ER values significantly different from those of racemic standards. All of the OC pesticides measured in this work have been banned in the United States and Canada, but some are still used in Mexico and Central America. Volatilization of α -HCH in the Great Lakes (Ridal et al., 1997) and the Arctic Ocean (Jantunen and Bidleman, 1996) has been followed by measuring nonracemic α -HCH derived from the lake in the overlying air. In a similar way, the enantiomeric signatures of OC residues in soils may be useful for tracing their emissions to the atmosphere, since freshly applied pesticide is expected to be racemic.

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