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Concentrations and Enantiomeric Ratios of Organochlorine Pesticides in Soils from the U.S. Corn Belt

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Past research has shown that selective enzymatic degradation of enantiomers by microorganisms does occur. This work was done to determine concentrations and enantiomeric ratios of several chiral organochlorine pesticides in soils from the Corn Belt region. Quantitative analysis was done by gas chromatography with electron capture detection using a DB-5 column. Concentrations were determined for 11 compounds (*o,p′*-DDT, *p,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE, *cis*-chlordane, *trans*-chlordane, heptachlor, heptachlor epoxide, dieldrin, α-hexachlorocyclohexane, and *trans*-nonachlor) in 38 agricultural soils and two garden soils. Residues were log-normally distributed, and geometric mean values (ng/g dry wt) were $\sum$DDT = 9.6, $\sum$chlordane = 1.4, dieldrin = 1.0, and HEPX = 0.58. HEPT and α-HCH were found infrequently. Concentrations in two garden soils were similar to those for agricultural soils. Enantioselective analysis was done by gas chromatography−mass spectrometry with chiral-phase capillary columns. Evidence of enantioselective degradation of OCs was found in 30 soils. *o,p′*-DDT and OXY showed differing enantiomeric patterns in different soils, while (+)TC, (−)CC, and (−)HEPX were in excess in all soils with nonracemic compositions. The two garden soils showed similar patterns of degradation. No correlations were found between ER and pesticide concentration or ER and % TOC for any of the compounds.

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 (*1*).

Several OC pesticides are chiral and are manufactured as racemic mixtures of enantiomers. Chiral pesticides include α-hexachlorocyclohexane (α-HCH), *cis*- and *trans*-chlordane (TC, CC), heptachlor (HEPT), and *o,p′*-DDT. The pesticide metabolites oxychlordane (OXY), heptachlor *exo*-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. Since the early 1990s, many papers have appeared that document the occurrence of nonracemic pesticide residues in the environment (*2*−*12*). Very little work has been published, however, on chiral OCs in soils. Falconer et al. (*11*) found nonracemic OC pesticides and their metabolites in agricultural soils from the Fraser Valley, British Columbia, and Finizio et al. (*13*) showed that the enantiomeric signature of residues in the soil of one farm was expressed upon volatilization into the air above the field. This work was done to determine the concentrations and enantiomeric composition of several chiral OC pesticides in soils from the north central Corn Belt region of the United States, with the idea that such information may be useful for identifying sources of old pesticides. Since freshly applied pesticides that volatilize into the atmosphere are subject to only nonbiological degradation processes, they should have racemic compositions. Pesticide residues volatilizing from soils that have been subjected to microbial degradation, however, may be nonracemic. Enantioselective breakdown in soils may result in pesticide residues that give an old source signature that could be used to track releases to the atmosphere.

Experimental Section

Sample Collection. Soil samples were taken during winter 1995 and spring/fall 1996 from four states in the Corn Belt of the United States: Ohio, Pennsylvania, Indiana, and Illinois. Samples were collected from 38 agricultural sites and two small home gardens (Figure 1) using a soil probe (when available) or clean garden tools. Of the 38 agricultural sites, 17 were government or university experimental farms while the remaining 21 were private farms. In each field, eight cores were collected at a depth of approximately 15 cm and pooled for analysis. Samples were placed in precleaned aluminum foil, sealed in plastic bags, and stored at 4 °C until extraction.

Extraction and Cleanup. Soil samples were thawed and mixed, and extraneous materials were removed (leaves, twigs, rocks, etc.). Approximately 15 g of the wet soil was mixed with anhydrous granular sodium sulfate and Soxhlet extracted with dichloromethane overnight in precleaned cellulose thimbles. Extracts were reduced and transferred into 1−2 mL isooctane by rotary evaporation and blown down with a gentle stream of nitrogen. Samples were cleaned up using 2 g of alumina (6% added water) capped with sodium sulfate and eluted with 20 mL of 5% dichloromethane/petroleum ether. The cleaned extracts were reduced, and the solvent was exchanged into isooctane by nitrogen blowdown, given further cleanup by shaking with 0.5 mL of 18 M sulfuric acid (omitted for HEPX and dieldrin), and adjusted to a volume of 2 mL for analysis. Mirex was added as an internal standard (soils were screened for Mirex and levels found to be below detection). A portion (10−20%) of each sample was removed before acid cleanup and analyzed for dieldrin and HEPX. Percent water was determined by drying the soil at ≈50 °C and determining the weight difference. Residues are thus reported on a dry weight basis.

Analysis. Quantitative analysis of samples was carried out with a Hewlett-Packard 5890 gas chromatograph equipped with an electron capture detector using a DB-5 column (60 m, 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific). Samples were injected splitless (split opened after

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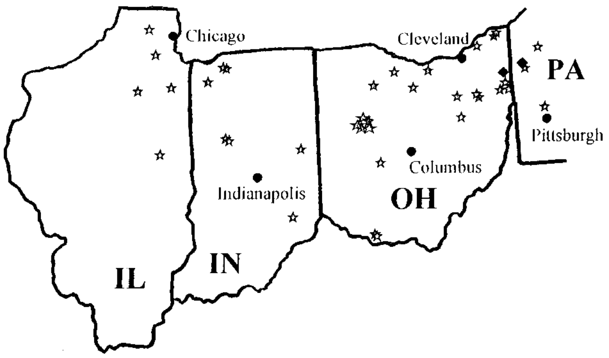

FIGURE 1. Locations of the 40 soil samples taken from the Corn Belt of the United States. Stars indicate the 38 agricultural soils; diamonds indicate the two garden soils.

1.0 min) at an initial temperature of 90 °C. After a 1-min hold, the oven was ramped at 10 °C min^{-1} to 160 °C, 2 °C min^{-1} to 240 °C, 20 °C min^{-1} to 270 °C, and held for 10 min. Injector and detector temperatures were 250 and 300 °C, respectively. The carrier gas was hydrogen at 60 cm s^{-1}. Samples were quantified versus 4–5 standards that spanned a 80–100-fold concentration range. Chromatographic data was collected and processed using HP Chemstation software.

Determination of enantiomeric composition was done with a Hewlett-Packard 5890 GC-5989B MS Engine mass spectrometer (GC–MS) operated in the negative ion mode (NIMS). Separations were carried out using either a Betadex-120 column (20% permethylated β-cyclodextrin in SPB-35, 30 m, 0.25 mm i.d., 0.25 μm film thickness; Supelco Corp.) or a BSCD column (20% *tert*-butyldimethylsilylated β-cyclodextrin in OV-1701, 30 m, 0.25 mm i.d., 0.25 μm film thickness; BGB Analytik AG, Lettenstrasse 97, CH8134 Adliswil, Switzerland, column designation BGB-172). Samples (2 μL) were injected splitless (split opened after 1.0 min) at an oven temperature of 90 °C. After a 1-min hold, the following oven programs were used for the two columns: Betadex, 15 °C min^{-1} to 140 °C, 1 °C min^{-1} to 190 °C, hold 10 min, 20 °C min^{-1} to 230 °C, hold 10 min; BSCD, 15 °C min^{-1} to 140 °C, 2 °C min^{-1} to 210 °C, hold 10 min, 20 °C min^{-1} to 240 °C, hold 15 min. Carrier gas was helium at 50 cm s^{-1}; injector and transfer line temperatures were 250 °C. The ion source and quadrupole temperatures were 150 and 100 °C, respectively. Methane pressure was 1.0 Torr. The instrument was operated in the selected ion monitoring mode using the following ions: *o,p′*-DDT (*m*/*z* 246, 248), α-HCH (*m*/*z* 255, 257), chlordanes (*m*/*z* 410, 412), nonachlors (*m*/*z* 444, 446), HEPT (*m*/*z* 300, 302), HEPX (*m*/*z* 386, 388), OXY (*m*/*z* 420, 422), and endosulfans (*m*/*z* 404). Pesticide standard solutions were obtained from Supelco, Inc. (Bellefonte, PA). Single-enantiomer standards of chiral pesticides used to determine elution orders on chiral columns were purchased from AXACT Standards (203 Commack Rd., Suite 78, Commack, NY).

Enantiomers of 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 (*4, 5, 14*). The Betadex column was used for α-HCH, TC, and CC; for each of these compounds the (+) enantiomer eluted first (*14, 15*). These elution orders were confirmed for HEPX, OXY, TC, CC, and α-HCH enantiomers in this work with standards of the single-enantiomer pesticides. Endosulfan I was not quantified in this work but was monitored by GC–MS due to its interfering with the (−)CC enantiomer on the Betadex column. If large amounts of endosulfan I were present, a three-fraction silicic acid procedure was used for cleanup (*11*). Small amounts were corrected for by using the 410/404 or 412/404 ion ratios.

Quality Control. Because of the wide range of pesticide residues in the soils, a decision was made to quantitatively determine residues that were above a certain limit. This "limit of quantification" (LOQ) was defined for this study by multiplying the final extract volume (2.0 mL) by the concentration of the lowest calibration standard and dividing by the dry weight of an average soil sample. These LOQ values ranged from 0.04 to 0.06 ng/g for HCHs, chlordanes,

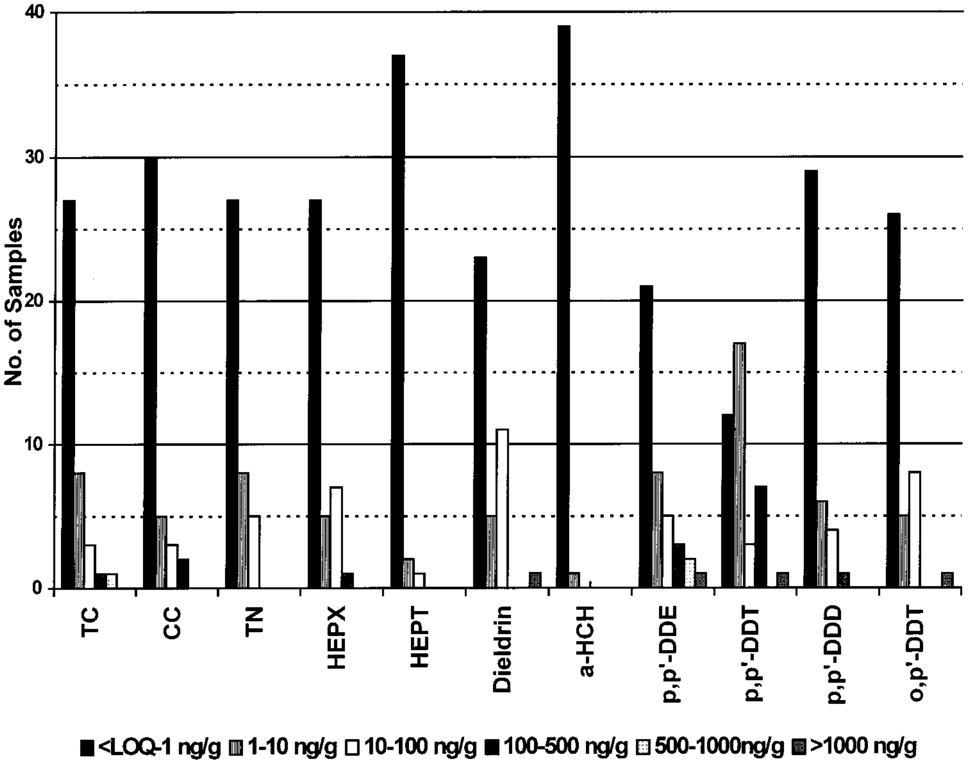

FIGURE 2. Frequency distribution for the 11 OC compounds determined (out of 40 soil samples).

TABLE 1. Concentrations of DDT Components in Soil (ng/g)

sample	p,p'-DDE (ng/g)	p,p'-DDT (ng/g)	p,p'-DDD (ng/g)	o,p'-DDT (ng/g)	$\sum$DDTs (ng/g)	DDT/DDE ratio
Pennsylvania						
PA1	ND[a]	1.27	ND	ND	1.27	
PA2	1.07	ND	ND	ND	1.07	
PA3	ND	ND	ND	ND	ND	
PA4	ND	1.15	ND	ND	1.15	
Ohio						
OH1	236	138	3.20	15.4	392	0.6
OH2	ND	ND	ND	ND	ND	
OH3	ND	ND	ND	ND	ND	
OH4	1600	7640	461	2150	11800	4.8
OH5	ND	0.62	ND	ND	0.62	
OH6	7.64	8.03	ND	2.46	18.1	1.1
OH7	0.71	1.10	ND	1.02	2.84	1.6
OH8	1.23	2.10	ND	ND	3.33	1.7
OH9	ND	0.59	ND	0.52	1.11	
OH10	11.39	5.59	ND	0.58	17.6	0.5
OH11	ND	ND	ND	ND	ND	
OH12	1.88	2.67	ND	0.72	5.27	1.4
OH13	77.0	90.0	23.0	15.0	205	1.2
OH14	502	239	2.40	31.0	774	0.5
OH15	570	408	16.0	78.0	1070	0.7
OH16	319	171	2.90	37.0	530	0.5
OH17	5.00	9.20	14.0	1.40	30.0	1.8
OH18	ND	1.30	0.79	ND	3.00	
OH19	0.51	0.76	0.53	ND	2.20	1.5
OH20	0.79	5.20	0.89	0.94	7.80	6.6
OH21	132	161	9.30	43.0	345	1.2
OH22	84.0	126	8.60	49.0	268	1.5
OH23	ND	ND	0.76	ND	1.60	
OH24	1.90	3.50	ND	ND	6.10	1.8
Indiana						
IN1	ND	1.28	0.88	ND	2.16	
IN2	ND	1.54	ND	0.92	2.46	
IN3	ND	1.01	1.95	ND	2.96	
IN4	ND	ND	ND	ND	ND	
IN5	ND	ND	ND	ND	ND	
IN6	48.2	106	14.8	45.3	214	2.2
IN7	ND	2.08	ND	0.67	2.75	
Illinois						
IL1	ND	1.05	ND	ND	1.05	
IL2	2.39	4.85	ND	0.67	7.91	2.0
IL3	9.61	11.60	ND	1.83	23.0	1.2
IL4	ND	0.51	ND	0.81	1.32	
IL5	23.4	14.0	ND	2.05	39.5	0.6
Geometric Mean						
	3.75	4.67	1.20	1.79	9.63	

[a] ND, not determined; below detection.

TABLE 2. Concentrations of Pesticides in Soil (ng/g)

sample	TC (ng/g)	CC (ng/g)	TN (ng/g)	HEPX + OXY (ng/g)	HEPT (ng/g)	dieldrin (ng/g)	α-HCH (ng/g)	TC/CC ratios
Pennsylvania								
PA1	0.05	0.13	0.25	ND	ND	ND	0.06	0.40
PA2	10.1	20.5	22.8	1.27	0.33	3.47	0.53	0.50
PA3	ND[a]	ND	ND	ND	ND	ND	0.42	
PA4	0.61	0.23	0.15	0.07	ND	ND	0.15	2.67
Ohio								
OH1	ND	ND	ND	ND	0.38	ND	0.31	
OH2	6.08	6.36	5.39	1.59	ND	ND	0.07	0.96
OH3	ND	ND	ND	ND	ND	ND	ND	
OH4	564	188	94.9	121	56.2	4250	ND	3.00
OH5	4.36	1.94	2.15	15.2	0.35	70.9	0.14	2.25
OH6	ND	0.07	0.07	ND	0.13	0.66	0.05	
OH7	1.50	0.32	0.16	0.95	0.39	0.47	0.32	4.75
OH8	0.07	0.22	0.14	0.29	ND	ND	ND	0.33
OH9	0.74	0.15	0.07	0.37	0.15	ND	ND	5.00
OH10	ND	0.44	ND	ND	0.15	ND	0.44	
OH11	ND	ND	ND	ND	ND	ND	0.06	
OH12	0.58	1.23	1.23	0.94	ND	23.6	0.07	0.47
OH13	13.0	23.0	33.0	11.0	ND	20.0	ND	0.57
OH14	ND	ND	ND	ND	ND	ND	ND	
OH15	ND	ND	ND	ND	ND	ND	ND	
OH16	ND	ND	ND	ND	ND	ND	ND	
OH17	7.10	17.0	21.0	3.10	ND	4.30	ND	0.42
OH18	0.25	0.39	0.58	0.63	ND	0.20	ND	0.64
OH19	ND	ND	0.22	ND	ND	ND	ND	
OH20	0.44	0.68	0.63	0.16	ND	35.0	ND	0.65
OH21	0.16	0.13	0.15	0.26	ND	0.41	ND	1.23
OH22	0.33	0.31	0.61	0.46	ND	2.50	ND	1.06
OH23	0.90	0.35	0.78	2.60	ND	0.22	ND	2.57
OH24	ND	ND	ND	ND	ND	0.12	ND	
Indiana								
IN1	0.05	0.14	0.14	ND	ND	28.4	0.20	0.40
IN2	3.08	0.92	0.69	6.84	1.00	1.15	0.15	3.33
IN3	0.81	0.13	0.40	0.13	ND	ND	0.07	6.00
IN4	0.41	ND	2.43	0.61	0.41	14.0	0.27	
IN5	1.37	0.82	2.47	11.3	0.27	51.2	0.27	1.67
IN6	165	199	98.1	29.7	2.39	ND	1.23	0.83
IN7	14.0	5.17	4.83	39.8	1.21	68.9	0.07	2.70
Illinois								
IL1	0.14	0.14	0.28	0.98	ND	13.17	ND	1.00
IL2	0.06	0.07	0.22	0.45	0.15	11.5	ND	0.80
IL3	4.43	1.91	1.91	12.4	0.38	12.3	0.08	2.32
IL4	0.07	0.15	0.07	0.29	ND	ND	0.15	0.50
IL5	1.63	0.92	2.90	10.1	0.43	1.98	0.14	1.77
Geometric Mean								
	0.49	0.43	0.51	0.58	0.11	1.05	0.09	

[a] ND, not determined; below detection.

HEPT, and HEPX; 0.1 ng/g for dieldrin; and 0.5 ng/g for the DDT compounds. Blanks were processed by placing ≈15 g of sodium sulfate into a Soxhlet thimble and then extracting and analyzing using the same procedure as for samples. The concentrations of OCs in blank extracts at 1.0 mL volume were all lower than the LOQ; therefore, no blank corrections were made. Eight spike recovery experiments were done with soil where residues were close to or below the detection limit. Approximately 15 g of soil was spiked with the components of interest, extracted, and analyzed as for samples. After correcting for the native amounts in the soil, recoveries ranged from 78 to 127%; thus, no recovery corrections were made. One soil sample was extracted a second time immediately following the first extraction to determine completeness of extraction. Only one compound (dieldrin) was found in the second extraction at a value of 3.8% of the amount found in first extraction.

The enantiomeric ratio (ER) is defined as the area ratio of the (+)/(−) peak eluting from the cyclodextrin column. Replicate injections of analytical standards reflected racemic compositions with a standard deviation of ±0.03 or less for all compounds, demonstrating that chiral-phase GC−MS is capable of highly precise enantioselective analysis. Average ERs and standard deviations for the soils were calculated from replicate injections of two or more separately extracted portions of the soil. 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 ±5%. To determine if soil matrix effects altered the enantiomer ratios, we spiked a control soil that contained residues that were close to or below the detection limit with several racemic pesticide standards. Racemic compositions were found for the extracted spiked compounds.

Results and Discussion

OC Pesticide Concentrations in Soils. Concentration data for all soils is given in Tables 1 and 2. A frequency distribution for all compounds is shown in Figure 2. Information on soil

TABLE 3. Enantiomeric Ratios[a] (±SD) of Chiral Pesticides in Soils

sample	TC	CC	HEPX	OXY	*o,p′*-DDT
Pennsylvania					
PA1	0.63 ± 0.00	1.27 ± 0.00	NA[b]	NA	NA
PA2	0.60 ± 0.01	1.23 ± 0.04	ND[c]	1.73 ± 0.02	ND
Ohio					
OH1	NA	NA	ND	ND	0.83 ± 0.01
OH2	0.81 ± 0.01	1.04 ± 0.02	1.75 ± 0.00	0.96 ± 0.04	ND
OH4	0.90 ± 0.00	1.01 ± 0.01	1.17 ± 0.05	1.14 ± 0.03	0.98 ± 0.02
OH5	0.66 ± 0.00	1.31 ± 0.06	3.57 ± 0.00	0.98 ± 0.01	ND
OH8	0.75 ± 0.00	1.32 ± 0.01	NA	ND	0.82 ± 0.03
OH10	NA	NA	NA	NA	1.04 ± 0.01
OH12	0.70 ± 0.03	1.08 ± 0.01	2.20 ± 0.06	0.80 ± 0.03	1.19 ± 0.04
OH13	0.79 ± 0.01	1.10 ± 0.01	1.60 ± 0.01	0.89 ± 0.01	0.82 ± 0.01
OH14	ND	ND	ND	ND	0.79 ± 0.01
OH15	ND	ND	ND	ND	0.76 ± 0.01
OH16	ND	ND	ND	ND	0.86 ± 0.01
OH17	0.57 ± 0.02	1.27 ± 0.03	3.05	1.47 ± 0.03	0.99
OH18	0.48	1.30	2.42	1.41 ± 0.05	ND
OH20	0.60	1.56	7.27	1.65 ± 0.04	ND
OH21	0.76 ± 0.01	1.06 ± 0.01	ND	1.13	1.05
OH22	0.79	1.07	2.69	1.09 ± 0.02	1.19
OH23	0.65	1.29	2.80	0.98	ND
OH24	ND	ND	ND	ND	1.03
Indiana					
IN1	0.74 ± 0.00	1.20 ± 0.02	NA	NA	NA
IN2	0.93 ± 0.01	1.04 ± 0.01	1.78 ± 0.03	1.08 ± 0.03	1.07 ± 0.02
IN5	0.57 ± 0.01	1.28 ± 0.02	4.26 ± 0.07	0.80 ± 0.01	ND
IN6	0.85 ± 0.01	0.99 ± 0.02	ND	1.34 ± 0.02	ND
IN7	0.74 ± 0.00	NA	NA	NA	NA
Illinois					
IL1	0.55 ± 0.00	1.35 ± 0.01	NA	NA	NA
IL2	0.62 ± 0.01	1.20 ± 0.00	NA	NA	NA
IL3	0.74 ± 0.00	1.13 ± 0.01	2.36 ± 0.04	0.89 ± 0.02	1.14 ± 0.03
IL4	0.59 ± 0.01	1.25 ± 0.02	NA	NA	NA
IL5	0.66 ± 0.01	1.40 ± 0.02	3.36 ± 0.02	0.67 ± 0.03	1.08 ± 0.02

[a] Enantiomeric ratio is designated as (+) enantiomer/(−)enantiomer). [b] NA, not analyzed. [c] ND, not determined; below detection.

type, pH, and organic matter content was available for only a limited number of soils. For this reason, no attempts were made to correlate these properties to concentration data. Total organic carbon (% TOC) was determined for 23 soils. Twenty-one soils had values between 0.74 and 3.2 while the remaining two (IN2 and OH4) had values of 7.6 and 33.7% TOC, respectively. No correlation was found between ER and % TOC for any of the soils.

DDT. DDT was used extensively as an agricultural and vector control pesticide in the United States with peak production occurring in 1963 (*16*). Although it was banned in the United States in 1972, it is still used in many developing countries (*17, 18*). Levels for ΣDDT (*p,p′*-DDT + *p,p′*-DDD + *p,p′*-DDE + *o,p′*-DDT) in this study ranged from <LOQ to 11 846 ng/g with a geometric mean (GM) of 9.63 ng/g (Table 1), and at least one of the four DDT components was found in 33 out of the 38 agricultural soils sampled. *o,p*-DDD was below detection in all samples. The two garden soils had ΣDDT values of 30.0 ng/g (OH17) and 1.07 ng/g (PA2). Of the 33 soils above LOQ, nine had levels above 200 ng/g while the remaining samples were all below 40 ng/g. The ΣDDT concentration in the most contaminated soil (OH4 = 11 846 ng/g) was 10 times higher than the nearest sample and at least a factor of 1000 higher than most of the samples. OH4 is a muck soil (33.7% TOC) in which the major crops are celery, leeks, and radishes. It has been previously reported that OC pesticides persist much longer in soils with high organic matter content than soils with low organic matter content (*19, 20*). Forest soils in Maine that had been exposed to aerial application of DDT from 1958 to 1967 were sampled in 1993 for DDT levels (*21*). ΣDDT in these soils ranged from 270 to 1898 ng/g in sprayed areas and from 0 to 11 ng/g in unsprayed locations. By comparison to earlier studies in the same location, the authors suggested a 'half time' for disappearance of DDT residues of 20−30 yr (*21*). Szeto and Price (*20*) found ΣDDT levels in agricultural soils from British Columbia, Canada, ranging from 194 to 763 ng/g in silt loam soils and from 2984 to 7162 ng/g in muck soils. They reported a 70% reduction of DDT in the muck soils over a 19-year period along with the virtual disappearance in loamy sand soils (*20*). DDT breaks down to DDE and DDD in soil and, generally, with time the parent/metabolite ratio decreases (*21*); however, there is a large variability with soil type (*22*). Ratios of *p,p′*-DDT/*p,p′*-DDE in the present study were quite variable ranging from 0.5 to 6.6. Of the 21 soils that contained both components, six soils had ratios below 1.0, while the remaining 15 had ratios above 1.0.

Chlordane. Chlordane was used as an agricultural pesticide and termiticide until 1973, when its usage was limited to termite control (*23*). Before its cancellation in 1988, chlordane's primary agricultural use was for corn crops, and the heaviest usage area was the Corn Belt region of the north central United States (*24*).

Levels of chlordanes in samples above the LOQ ranged from 0.05 to 564 ng/g for TC and from 0.02 to 199 ng/g for CC (Table 2). TC was found in 27 of the agricultural soils while CC was found in 29 of the 38 soils. The majority of the soils were below 14 ng/g for TC and 23 ng/g for CC, except for two soils that had extremely high values for both compounds. One of the two outliers was the muck soil mentioned earlier (OH4, TC = 564 ng/g, CC = 188 ng/g). The other soil (IN6, TC = 165 ng/g, CC = 199 ng/g) was formerly the site of a house that had been treated with chlordane for termites. The house was torn down approximately 25 years

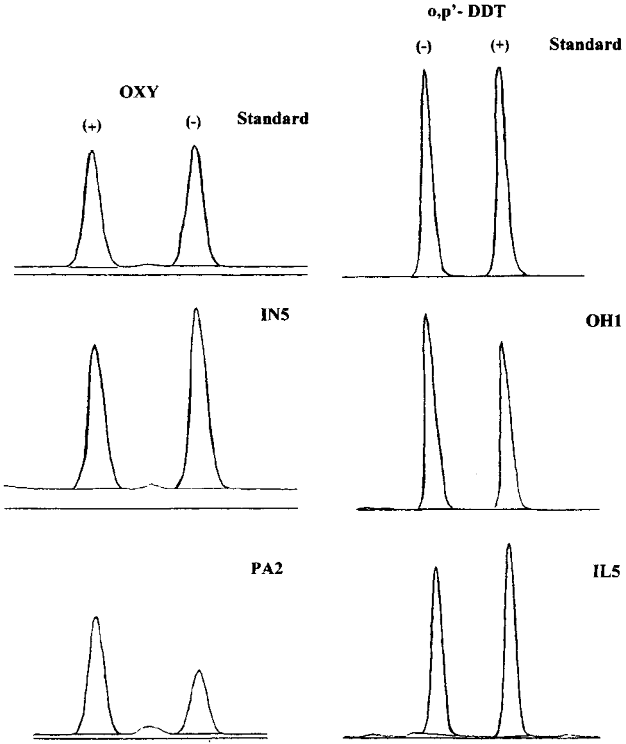

FIGURE 3. Enantiomer profiles of *o,p'*-DDT and OXY showing the different enantiomeric patterns in different soils.

ago, and the site has since been farmed for corn, soybean, and wheat. The OH17 and PA2 garden soils had concentrations of 7.10–10.2 ng/g for TC and 17.0–20.5 ng/g for CC, values that are higher than most of the agricultural soils, but not surprising as one of the major applications of chlordane before 1973 was for home and garden usage (*23*). Szeto and Price (*20*) reported the mean concentration for CC as 48 ng/g dry weight in silt loam and 174 ng/g in muck soils and for TC as 63 ng/g in silt loam and 508 ng/g in muck soils from British Columbia. The ratio of TC/CC in soils ranged from 0.33 to 6.0, while the ratio in technical chlordane is 1.8 (*25*).

TN concentrations for samples above the LOQ (29 of 38 samples) ranged from 0.07 to 98.1 ng/g. Again, the two soils that were outliers for TC and CC had much higher concentrations of TN than the majority of soils. The two garden soils had concentrations of TN higher than most of the agricultural soils (21.0 ng/g for OH17, 22.8 ng/g for PA2), similar to the trend for TC and CC. In British Columbia, Szeto and Price (*20*) found an average concentration of 59 ng/g in silt loam soils and 148 ng/g in muck soils.

Heptachlor and Heptachlor Epoxide. Before its cancellation in 1988, HEPT was used extensively on corn crops as well as for termite control (*26*). HEPT is rapidly converted into HEPX or other metabolites by most organisms (*27*). HEPT was found in only 16 of the samples with levels ranging from 0.13 to 2.39 ng/g for all of the soils except OH4, which contained 56.2 ng/g (Table 2). HEPT was <LOQ in the Ohio garden soil and 0.33 ng/g in the PA2 garden soil. In the British Columbia study, HEPT was found to be nondetectable in silt loam soils and ranged from 37 to 278 ng/g in muck soils (*20*).

Residues of HEPX and OXY were quantified as HEPX + OXY because the two compounds coeluted on the DB-5 column. Twenty-five samples were above LOQ for HEPX + OXY, ranging in concentration from 0.07 to 121 ng/g (Table 2). The OH4 soil again showed the highest value, with the other soil concentrations below 40 ng/g. Levels in the two garden soils fell between those of the agricultural soils with values of 1.27 ng/g for PA2 and 3.10 ng/g for OH17. In British Columbia soils, HEPX averaged 16 ng/g in silt loam soils and 174 ng/g in muck soils (*20*). One of the soils analyzed in this study (OH5) was an experimental farm used in the 1960s and 1970s for studies on volatilization of some OC pesticides from soils. For one study, the soil was treated with a single application of HEPT in May 1969 immediately before maize planting (*28*). The average values found in this soil 4 years after application were 50 ng/g HEPT and 200 ng/g HEPX (*28*). Our analysis of the same soils 23 years later showed a HEPT concentration of 0.35 ng/g and a HEPX + OXY concentration of 15.2 ng/g.

Dieldrin. Dieldrin was used extensively as a corn insecticide before its cancellation in 1970 and was further used as a termiticide until 1987 (*29*). Dieldrin is one of the most persistent of all pesticides and is the principal metabolite of aldrin, another widely used OC pesticide (*24*) that changes very quickly to dieldrin in the environment (*29*). Aldrin and dieldrin usage peaked in 1966 with the major area for aldrin usage being the Corn Belt region of the United States (*24*). In this study, levels of dieldrin in samples above the LOQ (21 out of 38) ranged from 0.12 to 4246 ng/g (Table 2). This

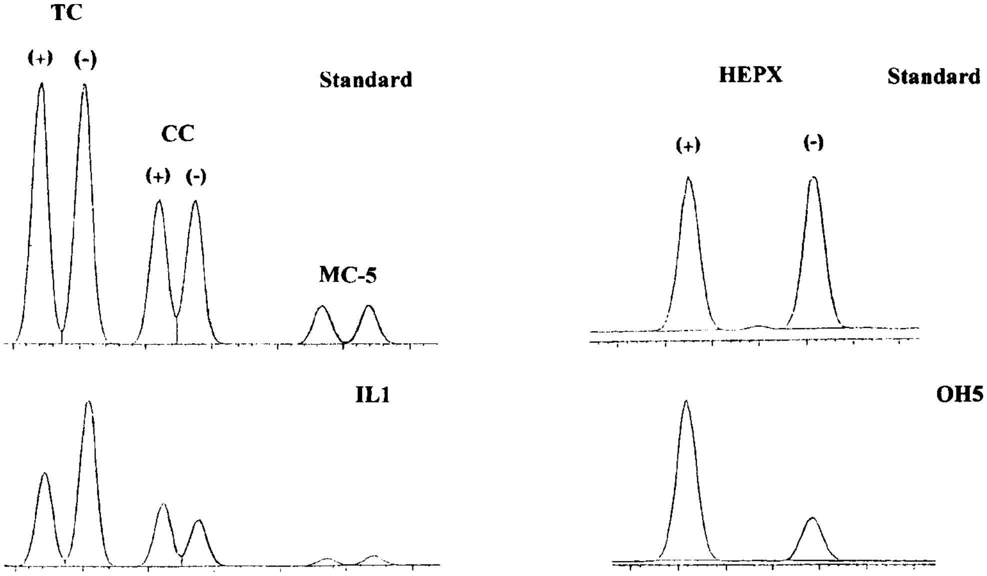

FIGURE 4. Profiles of chlordanes (left, Betadex column) and HEPX (right, BSCD column) in a soil and a standard.

range of concentrations was again dominated by the OH4 soil with all other soil concentrations below 71 ng/g. The two garden soils were similar in concentration with the OH17 soil at 4.30 ng/g and the PA2 soil at 3.47 ng/g. Szeto and Price (*20*) reported an average concentration of dieldrin in muck soils as 692 ng/g, but they were not able to detect this compound in silt loams. At the OH5 site, dieldrin was also studied after application in 1969 (*28*). The concentration of dieldrin found in the soil in 1973 was reported as 800 ng/g (*28*) while in the present study (23 years later) we found 70.9 ng/g. Loss of dieldrin at the OH5 site was followed for 7 years after the 1969 application (*28*). We constructed a first-order plot of mean soil residues (C_s, μg/g, Table 5 in ref *28*) vs time (t, years) and, after removing two outlying points at 0.34 and 1.31 years, obtained $\log C_s = -0.0574t + 0.525$ with $r^2 = 0.90$. Projecting this disappearance relationship to 1996, 31 years after application, gives an estimated $C_s = 0.056$ μg/g, which agrees excellently with 0.071 μg/g found in the present study.

α-Hexachlorocyclohexane. Technical HCH contains ~70% α-HCH and 10−15% γ-HCH (the insecticidally active isomer) (*30*). The mixture was used as a seed dressing as well as for controlling cockroaches and other pests. Technical HCH was banned in the United States in 1978, but the γ isomer (lindane) is still used (*31*). α-HCH was found in 21 samples but at very low levels (0.05−0.53 ng/g, Table 2). The PA garden soil (PA2) had the highest concentration while α-HCH in the OH4 soil (the high end outlier for almost all other compounds) was below detection. Most soils were below 0.05 ng/g for lindane. Szeto and Price (*20*) reported α-HCH as nondetectable in the British Columbia silt loam soils and an average of 56 ng/g in muck soils.

Enantiomeric Composition of Pesticide Residues. 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. ERs were determined for those samples from which good peak integrations could be obtained (as defined in the Quality Control section). ER values for the soils are given in Table 3, and example chromatograms are shown in Figures 3 and 4. Standard deviations for the soil ERs (Table 3) ranged from 0 to 0.07, with an average value of 0.02.

***o,p*′-DDT.** Enantioselective degradation of *o,p*′-DDT occurred in 11 of 17 soils. Selective degradation was observed for the (+) enantiomer in six soils with ERs ranging from 0.76 to 0.86, while five soils showed selective degradation of the (−) enantiomer (ER = 1.07−1.19). An example of the reversed enantioselectivity for *o,p*′-DDT in different soils is shown in Figure 3. Residues in the remaining six soils were close to racemic (ER = 0.96−1.05). Only one garden soil (PA2) had a concentration of *o,p*′-DDT high enough to determine an ER (ER = 0.99). In a previous study of soils from British Columbia, Canada, Falconer et al. (*11*) found depletion of (+)-*o,p*′-DDT (ER = 0.8) in one silt loam soil out of the six agricultural soils analyzed. Two other silt loam soils and three muck soils contained racemic *o,p*′-DDT. No apparent relationship between *o,p*′-DDT concentrations and enantiomeric ratios was found for soils.

Chlordane. The (+) enantiomer of TC was preferentially degraded in all soils with ERs ranging from 0.48 to 0.93. The (−) enantiomer of CC was degraded in most soils (ER = 1.06−1.56), except for four soils in which CC was close to racemic (ER = 0.97−1.02). Figure 4 is a chromatogram of the chlordane enantiomers in a standard and a typical soil. A third pair of chlordane enantiomers was separated on the Betadex column and was tentatively identified as MC-5 from the published elution profiles of technical chlordane on a 20-m column containing 10% permethylated β-cyclodextrin in PS086 (2). In the present study, the first-eluting enantiomer of this compound was depleted in many of the soils. Both garden soils showed preferential loss of (+)TC and (−)CC. Falconer et al. (*11*) found that both TC and CC were racemic in all six samples (both silt loam and muck soils) from British Columbia. No correlation to concentration was found in either study.

Heptachlor Epoxide. Levels of HEPT were too low for accurate enantioselective analysis in any of the soils in this study. HEPX was found in 16 of the soils and showed an enantiomeric excess of the (+) enantiomer in all (Table 3; Figure 4). It is unclear, however, whether nonracemic HEPX arises from selective degradation of HEPX, selective formation from HEPT, or a combination of both. Of the five chiral compounds, HEPX showed the largest differences with ERs ranging from 1.17 to 7.27. The OH4 soil, which had much higher concentrations of HEPX than the other soils, had the lowest ER (1.17); however, no other trends with concentration were discernible. The PA2 garden soil was below detection, but the Ohio garden soil (OH17) showed an excess of (+)-HEPX with an ER of 3.05. Falconer et al. (*11*) found HEPX in four British Columbia soils (three muck and one silt loam), all showing an excess of the (+) enantiomer.

Oxychlordane. OXY is the principal metabolite of CC, TC, and the nonachlors (*2*). The more abundant enantiomer [(+)OXY vs (−)OXY] changed in different soils (Figure 3). Out of 17 soils, 5 showed an excess of (−)OXY, 9 showed an excess of (+)OXY, and 3 were close to racemic (Table 3). As with HEPX, it is not known if enantiomeric differences of OXY are due to preferential degradation, selective formation or both. Both garden soils showed ERs greater than 1.0. Falconer et al. (*11*) found an excess of the (−) enantiomer of OXY in two British Columbia soils (one silt loam, one muck) where OXY was detectable. The ERs for OXY in soil may depend on the relative amounts of (+)- and (−)TC and CC that are metabolized since the (+) and (−) enantiomers of the chlordanes are expected to degrade to the corresponding OXY enantiomers (*32*). OXY was not determined quantitatively due to coelution with HEPX on the DB-5 column.

α-Hexachlorocyclohexane. α-HCH was too low for enantioselective analysis in all but one sample, a muck soil (OH4) that showed an ER of 0.98. Falconer et al. (*11*) found α-HCH in three silt loam soils from British Columbia to be close to racemic, while three muck soils showed degradation of the (−) enantiomer (ER = 1.21−1.36). Müller et al. (*33*) examined α-HCH in soil near a former HCH factory and found a slight depletion of the (−) enantiomer (ER = 1.099).

Acknowledgments

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Literature Cited

(1) Wania, F.; Mackay, D. *Environ. Sci. Technol.* **1996**, *30*, 390A−396A.
(2) Buser, H.-R.; Müller, M. D. *Anal. Chem.* **1992**, *64*, 3168−3175.
(3) Buser, H.-R.; Müller, M. D. *Environ. Sci. Technol.* **1993**, *27*, 1211−1220.
(4) Buser, H.-R.; Müller, M. D. *Anal. Chem.* **1995**, *67*, 2691−2698.
(5) Buser, H.-R.; Müller, M. D. *Environ. Sci. Technol.* **1995**, *29*, 664−672.
(6) Mössner, S.; Spraker, T.; Ballschmiter, K. *Chemosphere* **1992**, *24*, 1171−1180.
(7) Mössner, S.; Barudio, I.; Spraker, T.; Antonelis, G.; Early, G.; Gerachi, J. R.; Becker, P. R.; Ballschmiter, K. *Fres. J. Anal. Chem.* **1994**, *349*, 708−716.
(8) Tanabe, S.; Kumaran, P.; Iwata, H.; Tatsukawa, R.; Miyazaki, N. *Mar. Pollut. Bull.* **1996**, *32*, 27−31.
(9) Jantunen, L. M.; Bidleman, T. F. *J. Geophys. Res.* **1996**, *101*, 28837−28846.
(10) Garrison, W.; Schmitt, P.; Martens, D.; Kettrup, A. *Environ. Sci. Technol.* **1996**, *30*, 2449−2455.
(11) Falconer, R. L.; Bidleman, T. F.; Szeto, S. Y. *J. Agric. Food Chem.* **1997**, *45*, 1946−1951.

(12) Ridal, J. J.; Bidleman, T. F.; Kerman, B. R.; Fox, M. E.; Strachan, W. M. *Environ. Sci. Technol.* **1997**, *31*, 1940−1945.

(13) Finizio, A.; Bidleman, T. F.; Szeto, S. Y. *Chemosphere* **1998**, *36*, 345−355.

(14) Müller, M. D.; Buser, H.-R. *Anal. Chem.* **1994**, *66*, 2155−2162.

(15) Falconer, R. L.; Bidleman, T. F.; Gregor, D. J.; Semkin, R.; Teixeira, C. *Environ. Sci. Technol.* **1995**, *29*, 1297−1302.

(16) U.S. PHS. *Toxicological Profile for 4,4′-DDT, 4,4′-DDE, 4,4′-DDD*; U.S. Department of Health & Human Services, Public Health Service; U.S. Government Printing Office: Washington, DC, 1992; Draft for public comment.

(17) Ramesh, A.; Tanabe, S.; Murase, H.; Subramanian, A. N.; Tatsukawa, R. *Environ. Pollut.* **1991**, *74*, 293−307.

(18) Matthiessen, P. *Environ. Pollut. B* **1985**, *10*, 189−211.

(19) Edwards, C. A. *Persistent Pesticides in The Environment*; CRC Press: Cleveland, OH, 1973; pp 6−21.

(20) Szeto, S. Y.; Price, P. M. *J. Agric. Food Chem.* **1991**, *39*, 1679−1684.

(21) Dimond, H.; Owen, R. B. *Environ. Pollut.* **1996**, *92*, 227−230.

(22) Hitch, R. K.; Day, H. R. *Bull. Environ. Contam. Toxicol.* **1992**, *48*, 259−264.

(23) U.S. PHS. *Toxicological Profile for Chlordane*; U.S. Department of Health & Human Services, Public Health Service; U.S. Government Printing Office: Washington, DC, 1992; Draft for public comment.

(24) von Rumker, R.; Lawless, E. W.; Meiners, A. F.; Lawrence, K. A.; Kelso, G. L.; Horay, F. *Production, Distribution, Use & Environmental Impact Potential of Selected Pesticides*; U.S. EPA, Office of Pesticide Programs: Washington, DC, 1974; EPA 540/1-74-001.

(25) Sovocool, G. W.; Lewis, R. G.; Harless, R. L.; Wilson, N. K.; Zehr, R. D. *Anal. Chem.* **1977**, *49*, 734−740.

(26) U.S. PHS. *Toxicological Profile for Heptachlor, Heptachlor Epoxide*; U.S. Department of Health & Human Services, Public Health Service; U.S. Government Printing Office: Washington, DC, 1992; TP-92/11.

(27) Nomeir, A. A.; Hajjar, N. P. *Rev. Environ. Contam. Toxicol.* **1987**, *100*, 1−22.

(28) Freeman, H. P.; Taylor, A. W.; Edwards, W. M. *J. Agric. Food Chem.* **1975**, *23*, 1101−1105.

(29) U.S. PHS. *Toxicological Profile for Aldrin, Dieldrin*; U.S. Department of Health & Human Services, Public Health Service; U.S. Government Printing Office: Washington, DC, 1992; TP-92/01.

(30) Iwata, H.; Tanabe, S.; Sakai, N.; Tatsukawa, R. *Environ. Sci. Technol.* **1993**, *27*, 1080−1098.

(31) Voldner, E. C.; Smith, L. Production, usage and atmospheric emissions of 14 priority toxic chemicals. In *Proceedings of a Workshop on Great Lakes Atmospheric Deposition*, International Joint Commission, Ontario, Canada, Oct 29−31, 1986; 1990; Appendix 2.

(32) Müller, M. D.; Buser, H.-R. *Environ. Sci. Technol.* **1995**, *29*, 2031−2037.

(33) Müller, M. D.; Schlabach, M.; Oehme, M. *Environ. Sci. Technol.* **1992**, *26*, 566−569.

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