

Behavior of Chlorinated Insecticides in a Broad Spectrum of Soil Types

M. C. BOWMAN
Entomology Research Division, U. S.
Department of Agriculture, Tifton,
Ga.
M. S. SCHECHTER
Entomology Research Division, U. S.
Department of Agriculture, Belts-
ville, Md.
R. L. CARTER
Georgia Coastal Plain Experiment
Station, Tifton, Ga.

Electron-capture gas chromatography was employed in studying the behavior of 11 chlorinated insecticides in eight types of soil under controlled laboratory conditions to provide a better basis for understanding and predicting the fate of such pesticides in the field. Factors studied were volatilization, degradation, elution with a nonpolar solvent (hexane), and leaching of the toxicants by water. The effects of organic matter content, surface area, soil activation, and moisture (and its volatilization) were evaluated. Some of the data on the adsorption qualities of soils were obtained by utilizing the soil samples as adsorbents in chromatographic columns.

CHLORINATED organic insecticides in soils have been investigated for more than a decade; however, in most instances the early studies dealt with one insecticide, or not more than two or three, in a single type of soil and emphasis was placed only upon determination of residue levels or persistence. Methods such as total chlorine or bioassay not only failed in absolute measurement of a specific insecticide but offered little information concerning chemical degradation of the toxicant.

Later, as specific colorimetric and paper chromatographic methods became available, researchers began to study degradation of insecticides in soils and to evaluate some of the factors responsible for the behavior of a variety of insecticides in different types of soil. Barlow and Hadaway (2, 3) reported on the sorption of insecticides by soils and Lichtenstein (9) studied their movement under leaching and nonleaching conditions. Determinations of residues of parent insecticides and their degradation products in soils were reported by Gannon and Bigger (5), Lichtenstein and Polivka (10), and Lichtenstein and Schulz (11-14), and Harris and Lichtenstein (7) also investigated several factors that influenced the persistence of insecticides or their degradation in soils. Recently, Harris (6) reported the influence of soil type and moisture on the toxicity of insecticides in soils to insects. None of these studies, however, described the behavior of a large number of insecticides in a wide variety of soil types.

The increasing use of many chlorinated hydrocarbons has resulted in extensive deposition of these toxicants either directly or indirectly in the soil; hence, chemical and physicochemical information to aid in understanding and predicting their behavior has become even more imperative.

Electron-capture gas chromatography now provides a means of studying chlorinated hydrocarbon insecticides and their degradation products with speed, sensitivity, and precision not believed possible a few years ago. Our study, for which we employed that technique, was designed to measure several chlorinated hydrocarbon insecticides in a wide variety of soil types of agricultural importance according to the following characteristics: volatilization; degradation; elution by percolation with a highly nonpolar solvent (hexane) to obtain information on relative strengths with which toxicants are bound to the soils; elution with water to provide a basis for approximating insecticide movement and losses resulting from leaching; effects of moisture and soil activation on volatilization and degradation of insecticides; and effects of different levels of organic matter content on volatilization, degradation, sorption, and leaching. Determinations were made under carefully controlled conditions to permit direct comparisons of insecticide behavior. These data should afford a more precise estimation of the fate of the toxicants. When our data are correlated with persistence data already reported in the literature, an even more valid interpretation of their behavior may be obtained than is now available.

Experimental

Soils were sampled by layers in depth from several locations within a 50-mile radius of Tifton, Ga. The samples were air-dried at room temperature, sieved through an 18-mesh screen, thoroughly mixed by tumbling, and analyzed for texture as described by Bouyoucos (4). Sizes of the sand particles were determined in each sample by sieve analyses and loss of ignition by AOAC method 1.4 (7). The following samples, representing textures ranging

from medium to heavy or having high, medium, or low losses on ignition were then selected for this study: Lakeland sand (deep phase), Rutledge sand I, and Rutledge sand II with losses on ignition of 0.65, 6.49, and 25.85%, respectively, and Lynchburg loamy sand; Magnolia sandy clay loam; Greenville sandy clay; and Susquehanna sandy clay. These soils were further analyzed for organic matter by the modified method of Walkley-Black (8) and for pH.

Since the level of activation of soil greatly influences its sorption of insecticides, we equilibrated all soils used in this study with daily stirring at $45^{\circ} \pm 1^{\circ}$ C. for 2 weeks prior to use. This condition was arbitrarily chosen as the highest temperature to which soils in Georgia are likely to be subjected under field conditions. The samples, each about 3 liters, were then removed from the oven and sealed in airtight containers. To minimize deactivation resulting from atmospheric moisture, the containers were kept sealed except during actual removal of portions of the contents.

Moisture analyses (loss at 105° C.) of the equilibrated samples provided information as to quantities of loosely bound water remaining after activation. We determined bulk densities first by vertically tapping a glass-stoppered graduated cylinder, containing 50 ml. of the equilibrated soil, against a rubber pad until no further change in the volume of the soil could be detected, and then dividing the weight of the soil (grams) in the cylinder by its compacted volume (milliliters).

Standard Insecticide Solutions. Solutions of the 11 insecticides evaluated were prepared in three groups: (1) lindane, heptachlor, endosulfan I, endosulfan II, and *p,p'*-DDT; (2) aldrin, heptachlor epoxide, and endrin; and (3) Telodrin (1,3,4,5,6,7,8-octachloro-1,3,3a,4,7,7a-hexahydro-4,7-methanoisobenzofuran), dieldrin, and TDE.

Those used for the elution studies (Tables II and III) contained 40 μ g. of each insecticide per milliliter of hexane, except *p,p'*-DDT and endrin which

were prepared at 80 and 200 $\mu\text{g.}$ per ml., respectively.

Solutions for use in the volatilization experiments (Tables IV, V, and VI) were prepared in either hexane or acetone to contain 75 $\mu\text{g.}$ in 4 ml. of solvent, except *p,p'*-DDT and endrin, which were prepared at 150 and 375 $\mu\text{g.}$, respectively.

In addition, separate solutions containing each of the insecticides were prepared in hexane or acetone at the above concentrations for use in tests to determine compatibility of the toxicants and their interaction as well as degradation products resulting from the parent compounds.

Elution of Insecticides from Soils by Percolation with Hexane or Water. Standard Shell-type chromatographic columns (2-cm. i.d.) were packed with 40 grams of each soil by applying vacuum (ca. 440 mm. of Hg) to the bottom and tapping the sides with a small rubber mallet for a few seconds. The vacuum was disconnected to permit application of 1 ml. of the insecticide solution to soil in the column, then reapplied for a few seconds to evaporate the hexane. During this operation the solvent penetrated no more than about 2 cm. into the soil. The solvent was evaporated to permit sorption of the insecticides in the soil; hexane (immiscible with water)

was not then present to interfere with the water elutions.

The treated soils in the columns were then eluted at atmospheric pressure by percolation with redistilled hexane or distilled water. Fractions representing 0 to 50, 50 to 100, 100 to 200, 200 to 300, 300 to 400, and 400 to 500 ml. of the hexane eluate were collected and either taken directly or concentrated by means of a jet of dry air for gas chromatographic analysis. In some instances the soils were also eluted with 100 ml. of a hexane solution containing 5% acetone (v./v.); this eluate was analyzed in the same manner.

Fractions representing 0 to 200, 200

Table I. Characteristics of Soils Selected for Experiments with Chlorinated Insecticides^a

Soil		Depth of Sample, Ft.	Mechanical Analysis, %			Organic Matter, %	Loss on Ignition, %	Bulk Density ^b , G./Ml.	Loss at 105° C. ^b , %	pH
Texture	Series		Clay	Silt	Sand					
Sand	Lakeland deep phase	2.5-3	4.4	2.6	93.0	0.42	0.65	1.66	0.05	5.1
	Rutledge I	0-1	2.0	4.0	94.0	6.56	6.49	1.37	1.98	5.5
	Rutledge II	0-1	6.0	5.0	89.0	19.43	25.85	0.83	16.72	5.5
Loamy sand	Lynchburg	3-4	13.4	4.6	82.0	0.17	2.42	1.56	0.38	5.7
Sandy loam	Magnolia	0-1	18.4	8.6	73.0	1.33	4.10	1.51	0.70	4.1
Sandy clay loam	Magnolia	2-4	31.4	6.6	62.0	0.72	5.30	1.45	1.00	4.2
Sandy clay	Greenville	1-2	37.4	4.6	58.0	0.57	7.02	1.34	1.74	4.7
	Susquehanna	2-3	34.6	9.4	56.0	0.77	8.16	1.46	3.02	4.9

^a Calculated on dry basis, unless otherwise indicated.

^b After air drying, sieving through 18-mesh screen, and equilibrating at 45° C. for 2 weeks.

Table II. Elution Characteristics of 11 Chlorinated Insecticides on Various Types of Soil as Determined by Percolation with Hexane

Soil	Fractions of Eluate ^a	Insecticide in Eluate Fractions, % of Insecticide Added										
		Aldrin	<i>p,p'</i> -DDT	Dieldrin	Endrin	Heptachlor	Heptachlor epoxide	Lindane	TDE	Telodrin	Endosulfan I	Endosulfan II
Lakeland sand deep phase	A	95	98	95	10	104	95	94	102	102	102	72
	B	T	T	T	4	1	T	0	0	T	T	34
	C	0	0	0	4	0	0	0	0	0	0	0
	Total	95	98	95	18 ^b	105	95	94	102	102	102	106
Rutledge sand I	A	95	90	93	98	105	104	107	92	94	95	99
	B	5	T	T	T	T	T	T	T	T	T	2
	C	T	0	0	0	T	0	T	0	0	0	0
	Total	100	90	93	98	105	104	107	92	94	95	101
II	A	100	97	92	104	105	102	100	92	90	93	86
	B	T	T	T	T	T	T	T	T	T	T	T
	C	0	0	0	0	T	0	T	0	0	0	0
	Total	100	97	92	104	105	102	100	92	90	93	86
Lynchburg loamy sand	A	94	49	39	0	82	85	89	84	102	11	0
	B	0	50	49	0	T	8	0	20	T	73	0
	C	0	0	T	0	0	0	0	0	0	6	0
	Total	94	99	88	0 ^b	82	93	89	104	102	90	0 ^b
Magnolia sandy loam	A	93	91	11	0	82	21	106	103	100	22	0
	B	0	0	87	0	T	81	T	T	T	59	0
	C	0	0	2	0	0	0	0	0	0	2	0
	Total	93	91	100	0 ^b	82	102	106	103	100	83	0 ^b
Magnolia sandy clay loam	A	101	91	T	5	96	49	106	102	65	0	0
	B	T	0	102	21	T	46	T	0	0	85	0
	C	0	0	T	T	0	0	0	0	0	12	0
	Total	101	91	102	26 ^b	96	95	106	102	65	97	0 ^b
Greenville	A	97	91	90	98	99	99	106	94	59	46	0
	B	T	0	3	0	T	T	0	0	T	59	0
	C	0	0	0	0	0	0	0	0	0	0	0
	Total	97	91	93	98	99	99	106	94	59	105	0 ^b
Susquehanna sandy clay	A	91	98	58	0	95	95	106	100	58	95	0
	B	T	0	44	0	T	4	T	0	T	T	0
	C	0	0	0	0	0	0	0	0	0	0	0
	Total	91	98	102	0 ^b	95	99	106	100	58	95	0 ^b

^a A = 0 to 100, B = 100-300, C = 300-500 ml.

^b Quantitatively recovered by eluting with 100 ml. of hexane-acetone solution (19:1, v./v.).

T. Trace (<0.5%).

Table III. Leaching Characteristics of Chlorinated Insecticides in Various Typas of Soil as Determined by Percolation with Distilled Water

Insecticide	Fractions of Eluate ^a	% of Added Insecticide Recovered from Eluate Fractions					
		Lakeland sand deep phase	Lynchburg loamy sand	Magnolia sandy loam	Magnolia loam	Green-ville sandy clay	Susque-hanna sandy clay
Aldrin	A	6	T	T	T	T	T
	B	10	T	0	0	0	0
	Total	16	T	T	T	T	T
Dieldrin	A	55	0	0	0	0	11
	B	10	39	1	4	11	44
	Total	65	39	1	4	11	55
Endosulfan I	A	61	46	T	T	0	0
	B	3	5	13	0	T	7
	Total	64	51	13	0	T	7
II	A	79	70	2	0	0	4
	B	3	8	28	5	7	20
	Total	82	78	30	5	7	24
Endrin I ^b	A	52	0	0	0	15	20
	B	20	0	0	0	36	75
	Total	72	0	0	0	51	95
II ^c	A	1	T	0	0	0	0
	B	0	1	0	0	0	0
	Total	1	1	0	0	0	0
III ^c	A	T	3	0	0	0	0
	B	0	2	0	0	0	0
	Total	T	5	0	0	0	0
IV ^c	A	6	53	0	T	T	T
	B	0	3	T	0	T	0
	Total	6	56	T	T	T	T
Heptachlor	A	8	T	0	0	0	0
	B	6	15	0	0	0	0
	Total	14	15	0	0	0	0
Hexachlor epoxide	A	72	0	0	0	39	24
	B	4	0	0	0	23	50
	Total	76	0	0	0	62	74
Lindane	A	63	62	86	64	45	68
	B	T	0	2	10	9	T
	Total	63	62	88	74	54	68

^a A = 0 to 800 and B = 800 to 1600 ml. of water.

^b Calculated on basis of response and quantity of endrin standard added.

^c Not added *per se*, degradation product of endrin.

T. Trace (<0.5%).

to 400, 400 to 800, and 800 to 1600 ml. of the aqueous eluate were extracted three times with 50-ml. portions of hexane which were combined, concentrated, and analyzed by gas chromatography. It was previously established that the insecticides could be quantitatively recovered from water in this manner. Dilutions of 1-ml. standards, identical to those added to the soil, were analyzed and used as the basis for calculating the percentage of each insecticide recovered in the various fractions.

Distilled water used in this experiment was previously extracted with hexane to remove materials that gave interfering peaks with electron-capture gas chromatography. About 3 grams of c.p. sodium chloride were added to each fraction of the aqueous eluate to prevent the formation of emulsions during extraction.

Volatilization and Effects of Moisture on Volatilization of Insecticides from Soils. In the experiments with dry soils only (Table IV), three sets of quadruplicate samples (15 grams) of each of the eight soils were weighed in 30-ml. low-form beakers for treatment with hexane solutions of each group of insecticides. Four milliliters of each

of the standard insecticide solutions were added to the sample in each beaker and to empty beakers. This volume was the approximate quantity of hexane required to wet the samples completely. The beakers were then placed in a gravity convection-type oven at 45° ± 1° C. After aging for 1, 2, 4, and 8 days, samples representing the three groups of insecticides in each type of soil were removed, transferred to glass-stoppered bottles containing 40 ml. of a hexane-acetone solution (4 to 1, v./v.), and mechanically tumbled for 1 hour. The supernatant solvent was either taken directly or diluted for gas chromatographic analyses. The beakers containing insecticides in the absence of soil were also removed at the various intervals; their contents were dissolved in the same volume of solvent and analyzed.

In tests evaluating the effects of soil activation and moisture on volatilization and degradation of insecticides (Table V), three sets of triplicate samples of four soils were prepared for treatment with the three groups of insecticides as described above. Acetone solutions (4 ml.) of these toxicants and sufficient distilled water were used to provide treatments of each soil type with acetone

solutions only, or with acetone solutions applied before or after saturation of the soil with distilled water. The treated samples were then aged at 45° ± 1° C. for 4 days and analyzed in the manner described above. The soils initially treated with water were saturated daily during the aging process and the quantities added to each were recorded. In preliminary experiments, essentially 100% recoveries were obtained from all types of both wet and dry soils treated with the 11 insecticides and immediately analyzed by the method described above.

Gas Chromatography. A Jarrell-Ash, Model 700, universal chromatograph equipped with a disk-chart integrator, and an electron-capture detector containing 100 mc. of tritium was used in this study. The U-shaped column was constructed of 3 feet of No. 316 stainless steel tubing (1/4-inch o.d.) and packed with 6.27 grams of Dow Corning purified high-vacuum silicone grease (5% w./w.) on acid-washed Chromosorb W (80 to 100 mesh). The column was operated isothermally at 180° C. with a nitrogen flow of 200 ml. per minute (outlet) at a pressure of 26 p.s.i. (inlet) and the detector and injection port were each at 200° C. The detector was operated at 16 volts.

Retention times (R_t) and responses, established by injecting hexane solutions (5 μ l.) containing 1-nanogram quantities of the 11 insecticides and some of their known degradation products, are shown superimposed in Figure 1. The R_t values in minutes were: lindane, 1.70; heptachlor, 3.20; aldrin, 4.15; 1-hydroxychlorodene, 4.20; Telodrin, 4.60; heptachlor epoxide, 5.35; endosulfan I, 6.85; dieldrin, 8.20; *p,p'*-DDE, 8.50; endrin, 9.30; endosulfan II, 9.40; TDE, 11.30; and *p,p'*-DDT, 15.05.

Five-microliter portions of the extracts or eluates from the treated soil were injected for analyses of the insecticides and their degradation products. Identification was based upon the R_t values, and the quantities of each material were calculated by relating the peak areas to those of standards analyzed on the same day. Amounts of insecticides injected were kept within the linear operating range of the detector. No response was obtained from untreated check samples carried through the analytical procedures and, since recoveries were shown to be essentially complete, the analytical results were not corrected.

Results and Discussion

Some of the characteristics of the soils used in this study are presented in Table I. Samples were selected from various depths, as indicated, to provide the wide range of soil textures and organic matter content. The upper layers generally represent the sandier textures and in soils with poor drainage—e.g., Rutledge—contained higher levels of organic matter. The samples from lower layers represented the heavier textures containing more clay. In all soils but the Lakeland deep phase and Rutledge I, over 70% of the sand fraction was larger than 250

Table IV. Persistence and Behavior of 11 Chlorinated Insecticides in Various Types of Soils at 45° C.

Insecticide	Days of Exposure	% of Added Insecticide Recovered from Soils after Periods of Exposure								
		Lakeland sand deep phase	Rutledge Sand		Lynchburg loamy sand	Magnolia sandy loam	Magnolia sandy clay loam	Greenville sandy clay	Susquehanna sandy clay	Glass surface 8 sq. cm.
			I	II						
Aldrin ^a	4	84 (T)	88	91	88 (T)	93 (T)	94	92	88 (T)	T
	8	76 (3)	77	88	73 (3)	90 (3)	92 (T)	88 (T)	87 (5)	0
<i>p,p'</i> -DDT	4	95	96	100	99	90	90	95	97	90
	8	92	99	100	87	89	88	86	99	73
Dieldrin	4	50	93	97	24	90	94	94	87	47
	8	46	84	95	22	82	84	83	76	T
Endosulfan I	4	24	79	100	52	9	0	0	50	46
	8	9	62	87	25	T	0	0	33	21
Endosulfan II	4	47	98	100	69	22	T	1	64	76
	8	35	100	97	54	12	0	0	56	55
Endosulfan III ^b	4	15	0	0	10	0	0	0	12	0
	8	6	0	0	13	0	0	0	11	0
Endrin ^c	4	0	0	47	0	0	0	0	0	62
	8	0	0	17	0	0	0	0	0	18
Endrin II ^d	4	48	2	5	25	48	57	49	21	0
	8	50	1	2	39	46	64	61	24	0
Endrin III ^e	4	0	33	5	17	0	2	0	14	0
	8	0	33	2	5	0	0	0	8	0
Endrin IV ^f	4	45	54	41	56	44	42	34	52	0
	8	46	55	30	55	45	36	35	51	0
Heptachlor	4	0	77	93	0	0	0	0	0	0
	8	0	62	79	0	0	0	0	0	0
Heptachlor epoxide	4	92	93	100	99	100	99	97	103	4
	8	93	95	93	98	97	100	97	100	0
1-Hydroxy-chlordene ^g	4	78	4	2	90	90	82	73	84	0
	8	74	12	6	85	86	70	71	85	0
Lindane	4	97	95	98	99	95	95	87	98	0
	8	93	92	96	94	93	87	83	96	0
TDE	4	95	100	100	89	98	99	100	100	70
	8	81	93	100	85	89	92	100	89	29
Telodrin	4	0	85	98	0	3	1	3	2	0
	8	0	77	93	0	0	0	0	0	0

^a Values in parenthesis denote percentage of aldrin converted to dieldrin.
^b Not added *per se*; degradation product of endosulfan I and II calculated as endosulfan II.
^c Calculated on basis of response and quantity of endrin standard added.
^d Not added *per se*; degradation product of endrin.
^e Not added *per se*; degradation product of heptachlor, calculated on basis of heptachlor added.
^f T. Trace (<0.5%).

microns. Differences between organic matter content and loss of ignition may be attributed to water being strongly sorbed by the clay or held by the organic matter. The clay portions of the soils consisted mostly of kaolinitic clay (non-swelling colloidal type) except Susquehanna, which contained a high proportion of the montmorillonite type which exhibits the characteristics of a

high-swelling colloidal clay when moistened.

After the R_t values of the 11 insecticides and some of their degradation products were established, the parent compounds were grouped as described, in a manner to permit determination of their known degradation products in the event that they were formed in the soils. For example, the group containing hep-

tachlor did not contain compounds with R_t values near those of 1-hydroxy-chlordene or heptachlor epoxide; the group containing *p,p'*-DDT permitted the determination of TDE and *p,p'*-DDE; and dieldrin was not added to the group containing aldrin.

Preliminary experiments with these insecticide groups and/or individual insecticides were then performed to

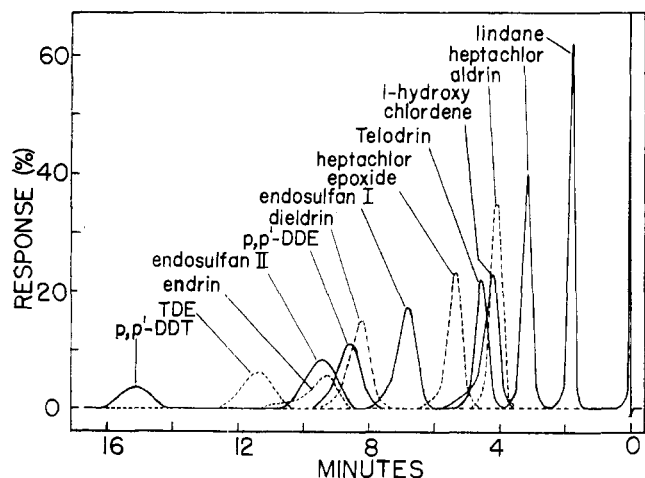


Figure 1. Gas chromatograms (superimposed) of 1-nanogram quantities of chlorinated insecticides and related compounds

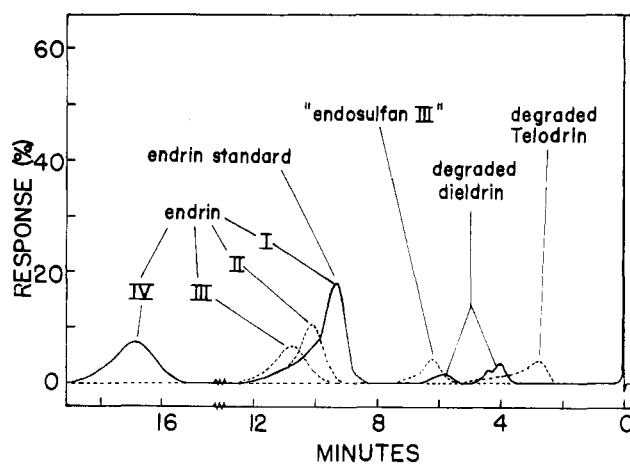


Figure 2. Gas chromatograms (superimposed) of endrin standard and degradation products of four chlorinated insecticides

Table V. Effects of Moisture on Persistence and Behavior of Chlorinated Insecticides in Four Types of Soil Exposed at 45° C. for 4 Days

Soil	Water Lost by Volatilization, Ml.	% of Added Insecticide Recovered														
		Aldrin	<i>p,p'</i> -DDT	Dieldrin	Endosulfan		Endrin ^a				Heptachlor	Heptachlor epoxide	1-Hydroxy-chlor-dene ^c	Lindane	Telodrin	TDE
					I	II ^b	I	II ^b	III ^b	IV ^b						
Lakeland sand	0 ^d	38 ^e	87	59	16	58 ^f	0	18	7	44	2	53	63	62	T	88
deep phase	12 ^g	18	51	43	28	56	15	8	4	31	5	36	3	16	12	62
Rutledge sand II	12 ^h	30	74	48	42	68	21	8	4	33	10	52	12	26	17	66
0 ^d	85	76	70	68	70	64	3	0	13	60	77	11	54	63	74	
14 ^g	76	86	75	75	83	72	1	0	11	57	85	7	54	64	81	
20 ^h	83	96	84	83	89	92	3	0	2	69	91	3	58	73	91	
Magnolia sandy loam	0 ^d	78 ^e	71	83	13	42	6	40	0	33	6	83	57	60	11	86
12 ^g	53	62	50	43	60	32	9	0	15	20	63	17	41	21	62	
12 ^h	67	66	69	50	69	30	30	0	16	28	74	21	49	33	76	
Greenville sandy clay	0 ^d	78 ^e	79	84	4	8	46	10	0	8	4	80	58	56	7	88
14 ^g	40	57	61	14	38	40	2	0	8	13	53	20	34	29	70	
14 ^h	61	66	67	20	50	67	2	0	8	27	73	16	44	29	77	

^a Calculated on basis of response and quantity of endrin standard added.

^b Not added *per se*; degradation product of endrin.

^c Not added *per se*; degradation product of heptachlor, calculated on basis of heptachlor added.

^d No water added.

^e Trace of dieldrin converted from aldrin.

^f About 12% of endosulfan III (calcd. as endosulfan II), also detected.

^g Soil saturated with water before addition of insecticide solution, soil then saturated daily.

^h Insecticide solution added before saturation of soil with water; soil then saturated daily.

determine the actual degradation products as well as their compatibility and interaction in each of the eight soils. Elution experiments with hexane and volatilization studies showed that the presence of microgram quantities of the various insecticides within the groups did not affect the behavior of the individual toxicants. Therefore, the toxicants were considered to be compatible with negligible interaction at these concentrations.

In the volatilization experiments, several insecticides degraded during exposure to various types of soil. Heptachlor, for example, was rapidly changed to 1-hydroxy-chlordene in dry soils with low organic matter content; however, conversion of heptachlor to its epoxide was not detected in any of these experiments. In dry sand, sandy loam, and sandy clay, both endosulfan I and II were converted to an unknown product "endosulfan III" (R_t 6.25 minutes). The possibility of this product's being the endosulfan ether, diol, or sulfate was eliminated, since their R_t values were shown to be 2.60, 5.85, and 13.15 minutes, respectively. Recoveries of endosulfan III were based upon the response and quantity of endosulfan II originally added to the sample. In dry soils with low organic matter content, dieldrin (R_t 8.20) yielded some gas chromatographic zones at shorter R_t values of 4.00, 4.40, and 5.85 minutes and Telodrin (R_t 4.60) at 2.70 minutes because of degradation, but these peaks were not calculated because of their small quantities. Slight conversion of aldrin to dieldrin was noted in several dry soils

after prolonged exposure. No degradation products of *p,p'*-DDT were detected.

Phillips, Pollard, and Soloway (15) demonstrated that endrin thermally degrades during gas chromatography at 232° C., which might explain the shoulder and tailing effect obtained with a standard solution under our gas chromatographic conditions (Figures 1 and 2). In the volatilization experiments, with endrin in soil, the major peak at R_t 9.30 minutes usually diminished and zones of various magnitudes appeared at 10.15, 11.00, and 16.95 minutes. These zones are designated "endrins I, II, III, and IV" for the purpose of discussion. Endrin IV was calculated separately, since it was completely resolved. Since endrins I, II, and III were not resolved under the gas chromatographic conditions employed, the sum of these was calculated from their total area. The individual amounts of I, II, and III were then calculated by considering their contribution to the total area to be in proportion to the peak heights taken at their respective retention times.

The peak heights for endrin I, II, or III were corrected for the responses contributed by the other components; however, these values should be considered only as approximations because of the tailing of these compounds.

The calculations for recovery were based upon the response and quantity of endrin standard initially added to the soil samples. The peaks for endrin I, which may or may not be endrin *per se*, and those for endrin II, III, or IV may be due to the endrin breakdown or rearrangement products described by Phillips

et al. (15). Later, endrin aldehyde and the Δ keto compound were obtained from the Shell Chemical Co. for comparative purposes and their R_t values were found to correspond to those of endrins III and IV, respectively. Gas chromatographic zones for the degradation products of endrin, endosulfan, Telodrin, and dieldrin are shown superimposed in Figure 2.

The results obtained from percolating hexane through soils treated with the insecticides are presented in Table II. The height of the soil in the chromatographic columns ranged from 8 cm. for Lynchburg loamy sand to 17 cm. for Rutledge sand II, depending upon their bulk densities. Elution rates ranged from 0.2 to 7 ml. of hexane per minute for Susquehanna sandy clay and Lakeland sand, respectively. Endrin and endosulfan II were tightly sorbed to all soil types except Rutledge sands I and II, which demonstrated weak capacities for retaining any of the insecticides tested. The behavior of aldrin, heptachlor, lindane, TDE, and *p,p'*-DDT was about the same in all soil types, except on Lynchburg loamy sand where TDE and *p,p'*-DDT were more readily adsorbed. In general, the soils with higher clay and silt content gave longer retention times for the remaining insecticides. No degradation of the insecticides was detected during the elution tests with hexane.

Data from the leaching experiment with water are given in Table III. The elution rates ranged from 2 ml. of water per hour for Susquehanna sandy clay up to 200 ml. for Lakeland sand. The

fractions of eluate collected corresponded to 100 and 200 inches of water, which represent the average rainfall that would be obtained in Georgia during periods of 2 and 4 years, respectively. None of the insecticides were leached from Rutledge sand I or II (high organic matter content) except for a trace of lindane from Rutledge I contained in the last fraction. TDE and *p,p'*-DDT were not leached from any of the soils, except for 8 and 20% of TDE that was obtained in the fractions of 0 to 800 and 800 to 1600 ml. from Lakeland sand. Traces of Telodrin were detected in the last fraction from loamy sand, sandy loam, and sandy clay loam, and 47% was about evenly distributed between the fractions from Lakeland sand. The only degradation products detected in the aqueous eluate were those of endrin. Lynchburg loamy sand yielded 56% of endrin IV and 6% of a mixture consisting mostly of endrin III. Lindane was readily leached from all soils except Rutledge sands I and II. Although data were obtained on more fractions of eluates and for more periods than are shown in the tables, it was necessary to combine data in order to compress the tables into reasonable size. Complete results will be made available upon request to the senior author.

Persistence and degradation data for the insecticides in dry soils and on a glass surface at 45° C. are presented in Table IV. No insecticidal degradation was detected on glass and, as expected, losses were greater than from any of the soils. In all soils except Rutledge sands I and II, heptachlor was completely converted to 1-hydroxychloridene within 24 hours; small quantities of dieldrin converted from aldrin were also detected after prolonged exposure. Endrin I disappeared (or was converted to other compounds) from all soils except Rutledge sand II within 24 hours. Subsequently the relative proportions of endrin II tended to increase while endrin III decreased. Large quantities of endrin IV were obtained in all soils at every interval. Measurable amounts of endosulfan III were found only in the Lakeland sand, Lynchburg loamy sand, and Susquehanna sandy clay soils.

Data in Table V demonstrate the combined effects of soil activation and volatilization of water on persistence and degradation of insecticides in four types of soil. Generally, soils that were not deactivated with water lost less insecticide, while those deactivated with water prior to the addition of insecticides lost the most. Degradation was markedly diminished in wet soils. A comparison of the residues in dry soils in two separate tests (Tables IV, 4-day exposure, and V, 0 ml. of water lost) revealed that more insecticide was lost in the latter test,

Table VI. Effect of Volatilization of Water on Persistence of Chlorinated Insecticides in Lakeland Sand Exposed at 45° C. for 4 Days

Top Area of Sand Layer, Sq. Cm.	Water Lost by Volatilization, Ml.	% of Added Insecticide Recovered ^a					
		<i>p,p'</i> -DDT	Endosulfan I	Endosulfan II	Heptachlor	1-Hydroxychloridene ^b	Lindane
7.9	4 ^c	84	43	70	12	26	61
	22 ^{c,d}	76	42	67	18	0	12
17.1	4 ^c	86	45	72	18	28	64
	32 ^{c,d}	74	22	51	6	10	7
28.6	4 ^c	87	42	70	14	19	58
	39 ^{c,d}	64	13	46	4	6	6

^a Mean of duplicate analyses.

^b Not added *per se*; degradation product of heptachlor calculated on basis of quantity of heptachlor added.

^c Saturated with water before addition of acetone solution of insecticides.

^d Saturated with water twice daily during first 3 days of exposure.

where moisture effects were also studied. This loss was attributed to the dry soil being deactivated by highly humid conditions resulting from volatilization of water from the wet soils, which were also confined in the same oven. These data also suggested that the volatilization of water could have affected the persistence of all insecticides in samples with low organic matter content. However, Lichtenstein and Schulz (14) found that the persistence of DDT was not affected by the amounts or water evaporated from soils or glass surfaces, or by enlargement of surfaces onto which DDT had been deposited.

Apropos of this point, an additional experiment was designed to include six insecticides in Lakeland sand. Samples (15 grams) of sand were weighed into 30-, 100-, and 250-ml. beakers; surface areas of the bottoms of these containers were 7.9, 17.1, and 28.6 sq. cm., respectively. After the sand was evenly distributed over the bottoms of the beakers, each sample was saturated with distilled water (4 ml.) and then acetone solutions (4 ml.) containing the insecticides were added. The samples were aged in an oven at 45° C. for 4 days; some were saturated with water twice daily for the first 3 days and others were not.

Results are given in Table VI. Since all these samples were deactivated with water before the insecticide was added, differences in levels of residue may be attributed to differences in areas of tops of sand layers or in amounts of water volatilized. These data indicated that a fourfold increase in sand area had no appreciable effect on persistence; however, insecticidal loss varied directly with quantity of water volatilized. It appears that the insecticides, including DDT, did in fact "codistill" with the water under the conditions of this test.

The information obtained from the different experiments in this study clearly indicated that leaching, volatiliza-

tion, and degradation of many of the chlorinated insecticides were much less in soils having high organic matter content such as Rutledge sands I and II. The data in Table V indicated that codistillation might also have been diminished because of organic matter content.

Acknowledgment

The authors gratefully acknowledge the technical assistance of James L. Mullis, Entomology Research Division, Tifton, Ga.

Literature Cited

- (1) Assoc. Offic. Agr. Chemists, "Official Methods of Analysis," 1945.
- (2) Barlow, F., Hadaway, A. B., *Bull. Entomol. Res.* **46**, 547-59 (1955).
- (3) Barlow, F., Hadaway, A. B., *Nature* **178**, 1299-1300 (1956).
- (4) Bouyoucos, G. J., *Soil Sci.* **42**, 225-9 (1936).
- (5) Gannon, N., Bigger, J. H., *J. Econ. Entomol.* **51**, 1-2 (1958).
- (6) Harris, C. R., *Nature* **202**, 724 (1964).
- (7) Harris, C. R., Lichtenstein, E. P., *J. Econ. Entomol.* **54**, 1038-45 (1961).
- (8) Jackson, M. L., "Soil Chemical Analysis," Prentice-Hall, Englewood Cliffs, N. J., 1958.
- (9) Lichtenstein, E. P., *J. Econ. Entomol.* **51**, 380-3 (1958).
- (10) Lichtenstein, E. P., Polivka, J. B., *Ibid.*, **52**, 289-93 (1959).
- (11) Lichtenstein, E. P., Schulz, K. R., *Ibid.*, **52**, 118-24 (1959).
- (12) *Ibid.*, pp. 124-31.
- (13) *Ibid.*, **53**, 192-7 (1960).
- (14) *Ibid.*, **54**, 517-22 (1961).
- (15) Phillips, D. E., Pollard, G. E., Soloway, S. B., *J. AGR. FOOD CHEM.* **10**, 217-21 (1962).

Received for review January 25, 1965. Accepted May 14, 1965. Division of Agricultural and Food Chemistry, 148th Meeting, ACS, Chicago, Ill., September 1964. The use of trade or proprietary names does not necessarily imply the endorsement of these products by the U. S. Department of Agriculture.