Residues of Organochlorine Insecticides and Their Metabolites in Soils in the Atlantic Provinces of Canada

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The persistence and breakdown of chlorinated insecticides in soil samples collected in the Atlantic Provinces of Canada were studied. Soxhlet extraction of the soil samples was achieved using hexane–2-propanol, 3 to 1. The 2-propanol was removed and the hexane layer purified using a Florisil column. The nature of the insecticide residues and their metabolites was studied using electron-capture gas chromatography with two column types. Thin-layer chromatography and chemical conversion to structurally related compounds confirmed the presence of some insecticides. The soil samples were taken from agricultural lands in 1965 where organochlorine insecticides had been used. Forty-five per cent of all the soil samples investigated contained residues of DDT plus metabolites between 1 and 9 p.p.m. DDD and DDE were the chief metabolites of DDT. Thirty-two per cent of the total soil samples contained 0.75 p.p.m. of aldrin plus dieldrin. Heptachlor, heptachlor epoxide, and γ-chlordan were found in 9% of the soils analyzed in concentrations between 0.06 and 0.86 p.p.m. 1-Hydroxychlordene, a metabolite of heptachlor, was found in a small number of samples.

The persistence and breakdown of pesticides in soil under controlled conditions have been the subject of considerable study in recent years (*1*, *2*, *11*, *14*, *18*, *21*). Residues of organochlorine insecticides in farm soils have been investigated by several authors (*5*, *10*, *20*, *21*). The persistence and breakdown of insecticides in soils are related to a number of factors such as soil type and organic content, cultivation, rainfall, temperature, and soil microbial population (*6*). The conversion of aldrin and heptachlor to their epoxides (*8*) and DDT to DDE (*21*) in soil have been reported. Recently, Bowman, Schechter, and Carter (*2*) found that heptachlor was rapidly changed to 1-hydroxychlordene in dry soils with low organic content and that no conversion of heptachlor to its epoxide was detected in these soils. In another study, under field conditions, Bowman, Young, and Barthel detected a small amount of heptachlor epoxide and 1-hydroxychlordene in Norfolk fine sandy loam which had been exposed to heptachlor (*3*). Alexander (*1*) has indicated that many chemicals are resistant to degradation in the soil by microorganisms.

The objectives of this project were to establish quantitatively the extent to which residues of the organochlorine insecticides were occurring in Canadian Atlantic soils collected in Nova Scotia, New Brunswick, Newfoundland, and Prince Edward Island and the nature of the metabolites resulting from them.

Materials and Methods

Chemicals. The chemicals used were: DDDE, 1-chloro-2,2-bis(4-chlorophenyl)ethylene; γ-chlordan, 1,2,4,5,6,7,8,8 - octachloro - 3a,4,7,7a - tetrahydro - 4,7-methanoindan; and 1-hydroxychlordene, 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-ol.

Reagents. The following reagent grade solvents were distilled: acetone, *n*-hexane, dioxane, 2-propanol, and petroleum ether (30° to 60° C.).

Ethyl ether, U.S.P., was distilled, washed twice with water, and dried over anhydrous sodium sulfate, and a 2% v./v. anhydrous ethyl ether–alcohol solution was prepared therefrom.

Elution mixture 1, 120 ml. of ethyl ether was diluted to 1000 ml. with redistilled petroleum ether.

Elution mixture 2, 50 ml. of ethyl ether and 4 ml. of dioxane were diluted to 1000 ml. with petroleum ether.

Florisil commercially activated at 1200° F. was stored at 130° C. with three days' aging at room temperature in a stoppered bottle prior to use.

Silica gel-Camag DF-5.

Extraction mixture, consisted of *n*-hexane–2-propanol, 3 to 1.

Chromogenic agent, 1.7 grams of silver nitrate in 5 ml. of water and 10 ml. of 2-phenoxyethanol were diluted to 200 ml. with acetone (*19*).

Chlorine reagent, 0.3% chlorine in chloroform (*9*).

Hydrobromic acid reagent, 20 ml. of acetic anhydride was mixed with 10 ml. of 48% HBr in a flask which was cooled in ice and allowed to stand for 30 minutes before use.

Apparatus. GAS CHROMATOGRAPHY. The analytical instrument employed was a Wilkens Aerograph Hi-Fi Model 600-C equipped with an electron-capture detector containing a 250-mc. tritium ionization source, operated at 90 volts' potential across the detector. The recorder employed was a 1-mv. Sargent Model SR. The analytical column employed consisted of a 4.5-foot by 0.25-inch borosilicate glass tube packed with a 10% stationary phase which consisted of 4% G.E. methyl silicone plus 6% D.C. QF-1 (FS-1265) fluorosilicone on 60- to 80-mesh, acid-washed Chromosorb W. Before use, the column was conditioned for three days at 225° C. under a nitrogen pressure of 10 p.s.i.a. The operating parameters were: column temperature, 190° C.; detector temperature, 190° C.; injector flash heater, 220° C.; carrier gas, prepurified nitrogen; flow rate, 200 ml. per minute; range, 10; attenuator, 4. The injector of the gas chromatograph was equipped with a borosilicate glass liner.

The Dow 11 column consisted of 60- to 80-mesh, acid-washed Chromosorb W coated with Dow 11, 5% by

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weight. Before use, the column was conditioned for 2 days at 230° C. under a nitrogen pressure of 10 p.s.i.a.

The Dow Corning 200/QF-1 column consisted of 10% Dow Corning 200 and 15% QF-1 by weight on DMCS treated, acid-washed, 80- to 100-mesh Chromosorb W. The column was conditioned for 3 days at 230° C. under a pressure of 10 p.s.i.a.

Thin-layer chromatography-Desaga applicator.

Ultraviolet light source, General Electric, G15T8, 15-watt germicidal lamp.

Chromatographic columns, 20 mm. o.d., 16-mm. i.d. × 300 mm.

Soil Sampling. The sampling procedure was that described by Harris, Sans, and Miles (*10*). An area of approximately 5 acres was selected in a field and five subareas were sampled within this site. The subareas, 4 feet square, were placed diagonal to the field perimeter. Twenty-five 6-inch cores were taken from each subarea and cores from all five subareas were pooled in order to obtain a representative sample from the field. The pooled sample (approximately 10 pounds of soil) was sealed and stored in a refrigerated room at 8° C.

The samples were collected during the fall of 1965 and analyzed during the winter and summer of 1966.

Soil Types. The Atlantic soils analyzed comprised mineral soils including gravelly loam and also a complete range in soil texture from sandy to clay loam.

Preparation of Soil Samples. The soil samples were air dried at room temperature (22° C.). Large clay lumps were broken, and the sample was sieved using a 2-mm. sieve (U.S. series No. 10, 9 mesh). With the exception of the Newfoundland samples, a 50-gram soil portion was weighed and placed in a sintered glass thimble of a Soxhlet extractor. The Newfoundland samples varied from 32 to 50 grams. The extraction was accomplished with 150 ml. of hexane–2-propanol, 3 to 1, so that the thimble emptied once every 15 minutes. The sample was extracted for 4 hours. Soxhlet extraction using acetonitrile as the solvent gave lower recoveries of insecticides.

Purification Technique. The Soxhlet extract was transferred to a 1000-ml. separatory funnel and 100 ml. of petroleum ether was added. The mixture was shaken briefly, after which 500 ml. of distilled water and 10 ml. of saturated sodium chloride solution were added. The aqueous layer was discarded. The hexane–petroleum ether layer was further extracted with two 500-ml. portions of water to remove 2-propanol and then was dried over anhydrous sodium sulfate, and flash evaporated to 5 or 10 ml. The concentrate was chromatographed on a 4-inch Florisil column. The Florisil column was prepared by a slurry technique to avoid occluding air with the column. The column was first eluted with 75 ml. of elution mixture 1 which was collected separately as eluate 1 followed by 250 ml. of elution mixture 2 which was collected as eluate 2.

The elution system was a modified version of that described by Onley (*16*). The two fractions were concentrated to a small volume and diluted to 5 ml. with hexane. These solutions were subjected to quantitative and qualitative evaluation using gas chromatography.

Gas Chromatography. The SE-30/QF-1 liquid phase on Chromosorb W was satisfactory for a number of organochlorine compounds (*12*). The Dow 11 column was chosen as an alternate for the identification of insecticides during the early phase of the work. At a later phase of this study, a 10% Dow Corning 200, 15% QF-1 column was more satisfactory than the Dow 11 column. The use of this column was recently described by Burke and Holswade (*4*). An aliquot of 5 to 10 μl. of the concentrated eluate was injected into the gas chromatograph. Reference chromatograms were prepared by injecting into the gas chromatograph a similar volume of a stock solution composed of the pure insecticides. For all quantitative studies, peak areas of known insecticide standards were compared with peak areas of unknown compounds. Standardization was carried out several times each day to check retention time and peak response for each insecticide. Care was taken to ensure that the response given by a particular insecticide was within the linear range.

Thin-Layer Chromatography. Thirty grams of silica gel was mixed with 70 ml. of water and stirred until a uniform slurry was obtained. A 0.2-mm. layer of the slurry was applied to a 20 × 20 cm. glass plate with the Desaga applicator. The coated plates were air dried and then further dried for one-half hour at 75° C. The plates were washed with absolute alcohol to remove materials which interfered at the development stage. The plates were activated at 130° C. for one-half hour and stored in a desiccator. An aliquot of eluate 1 or eluate 2 was then concentrated and spotted on the plate along with samples obtained from spiked blank soils. The chromatographic plate and developing tank were placed in a refrigerator at 4° C. and developed with hexane–ethyl acetate (9 to 1). The plate was removed from the tank, air-dried, sprayed with the chromogenic agent, and exposed to ultraviolet light for 5 minutes.

Chemical Confirmation. Eluate 1 which contained *p,p'*-DDT, and *o,p'*-DDT was refluxed for 30 minutes with a 5% solution of sodium hydroxide. These compounds were thereby converted to *p,p'*-DDE and *o,p'*-DDE, respectively. This solution was extracted with hexane, washed with water, and dried over anhydrous sodium sulfate.

With samples containing dieldrin, an aliquot of eluate 2 was taken and evaporated to dryness. One-half milliliter of HBr reagent was added to the residue, and the mixture was allowed to stand for 30 minutes at room temperature before use. Five milliliters of water, 3 ml. of hexane, and 1 ml. of saturated sodium sulfate solution were added to the residue, and the mixture was shaken. The hexane was separated, dried, and examined by gas-liquid chromatography.

With soil samples containing aldrin, an aliquot of eluate 1 was taken and evaporated to dryness. The residue was redissolved in 0.5 ml. of $CHCl_3$ and 0.1 ml. of chlorine reagent was added. After the solution stood for 5 minutes, the solvent was evaporated, and the residue was redissolved in 1 ml. of hexane and analyzed by gas chromatography.

Results and Discussion

Quantitative Recoveries. Quantitative recoveries of heptachlor, aldrin, heptachlor epoxide, *p,p'*-DDE, dieldrin, *o,p'*-DDT, DDD (rhothane), *p,p'*-DDT, γ-chlordan, and 1-hydroxychlordene were checked by adding these insecticides to air-dried soil samples at a concentration of 0.1 p.p.m. The insecticides were extracted from the soil samples and subjected to the column purification procedure. The recoveries of added insecticides and candidate metabolites ranged between 88 and 111%. The air-dried soil samples contained 3 to 5% moisture, and quantitative recovery calculations were based on the weight of these samples. No corrections were made for recoveries of insecticides found in agricultural soils based on the percentage recoveries of fortified samples at 0.1 p.p.m. Insecticide residue levels below 0.01 p.p.m. were reported as zero even when lower amounts of the insecticides were present.

Gas and Column Chromatography. Figure 1 shows a gas-liquid chromatogram of the standard insecticide mixture obtained by using the SE-30/QF-1 column. Two other columns, employing as liquid phases Dow 11 and Dow Corning 200/QF-1 on Chromosorb W, were found useful in separating and identifying insecticides and metabolites.

Eluate 1 which was first eluted from the Florisil column contained heptachlor, aldrin, γ-chlordan, *p,p'*-DDE, *o,p'*-DDE, *o,p'*-DDT, DDD, and *p,p'*-DDT. Eluate 2 contained heptachlor epoxide, 1-hydroxychlordene, and dieldrin. On the SE-30/QF-1 column, heptachlor epoxide and γ-chlordan had approximately the same retention time. Since, however, heptachlor epoxide was found in eluate 2 and γ-chlordan in eluate 1, no difficulty was encountered in estimating them. Similarly the pairs, dieldrin and *p,p'*-DDE, γ-chlordan and heptachlor epoxide could not be separated by the Dow 11 column alone, but could be distinguished because heptachlor epoxide and dieldrin appeared in eluate 2, while *p,p'*-DDE and γ-chlordan appeared in eluate 1.

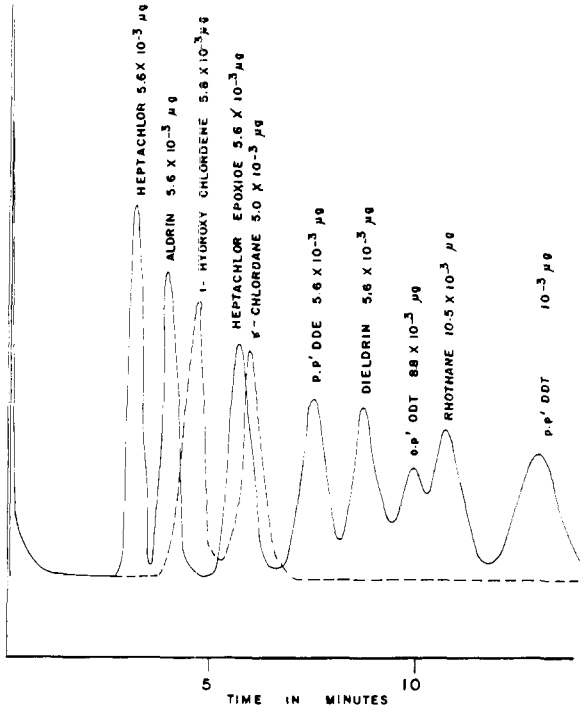

Figure 1. Separation of insecticides by means of a SE-30/QF-1 column

Insecticide Residues in Agricultural Soils. Table I gives the levels of insecticides and metabolites found in soils along with the available history of insecticides used and crop rotation followed on the land from which the samples were obtained. The soil samples were taken from agricultural lands where insecticides had been used and where residues might be expected.

Forty-five per cent of all the soils investigated contained residues of DDT plus metabolites between 1 and 9 p.p.m. A single Nova Scotia orchid sample contained 20 p.p.m. and a single Newfoundland sample contained 17 p.p.m. Two to seven known applications of DDT had been used on these agricultural lands with a wide range of crops being grown.

The chief metabolites of DDT in the soils included DDE and DDD. The latter appeared chiefly in New Brunswick and Nova Scotia soil samples. DDE appeared in almost all soils containing DDT. The highest levels of DDE and DDD in the soils were 2.91 and 1.81 p.p.m., respectively. DDD has been reported to be a metabolite of DDT in lake water (*13*). Harris, Sans, and Miles (*10*) have also reported the presence of DDD in soils which had been exposed to DDT.

Thirty-two per cent of the soil samples analyzed contained 0.75 p.p.m. of aldrin plus dieldrin. The highest concentrations of aldrin and dieldrin were 2.5 and 4.04 p.p.m., respectively. These are slightly higher than those reported by Harris, Sans, and Miles for Ontario soils. The aldrin and dieldrin residues were found in soils where the common crops grown were rutabagas, potatoes, and vegetables.

Heptachlor occurred in significant amounts in five samples and heptachlor epoxide in six samples. The highest levels of heptachlor and heptachlor epoxide were 0.95 and 0.44 p.p.m. With two exceptions, γ-chlordan, present as a contaminant in technical heptachlor, occurred in significant amounts in all soils which contained heptachlor and heptachlor epoxide. γ-Chlordan was found in seven soil samples which had been exposed to heptachlor at levels between 0.06 and 0.86 p.p.m. In several Prince Edward Island soil samples exposed to heptachlor, a compound was detected on the SE-30/QF-1 column which had the same retention time as 1-hydroxychlordene. The presence of a compound having the same retention time as 1-hydroxychlordene was later confirmed using a 10% DC-200/QF-1 column. Four Prince Edward Island soils which had been subjected to frequent applications of heptachlor contained 1-hydroxychlordene in concentrations between 0.01 and 0.33 p.p.m.

A 15 to 20% constituent of technical DDT (*7*), *o,p'*-DDT, was found consistently in DDT-treated soils. The highest concentration of *o,p'*-DDT found in any soil sample was 2.63 p.p.m.

Table I. Soil Samples, Insecticide Residue Analyses, 1965

Sample	Cropping and Insecticide History			Residues in Soil Samples, P.P.M.										
	Crops	Insecticide	Years of application	Total toxicant, lb./acre	Hept.	Hept. epox.	γ-Chlor.	Aldrin	Dieldrin	DDT *p,p'*	DDT *o,p'*	DDE	DDD	1-OH-C[a]
				Prince Edward Island										
1	Rutabagas	Aldrin	'63	12	0	0	0	0.73	0.75	0.44	0.11	0.05	0.62	0
	Potatoes	DDT	'61	3										
2	Rutabagas	Heptachlor	Alternated use for	?	0.09	0.01	0.17	0.61	0.30	0.27	0.07	0.09	0	0.03
	Potatoes	Aldrin, DDT	7 years											
3	Vegetables	Heptachlor	Alternated use for	?	0.95	0.44	0.86	0.09	0.36	3.49	0.63	0.23	0	0.33
		Aldrin, DDT	15 years											
4	Rutabagas	Heptachlor	'59	5	0.05	0.07	0.06	0	0	0.72	0.12	0.15	0	0
	Strawberries	DDT	'60, '61, '62	4										
5	Vegetables	Heptachlor	Alternated use for	?	0.26	0.08	0.27	0.02	0	0.86	0.21	0.15	0	0.01
		Aldrin, DDT	many years											
6	Potatoes	DDT	'51, '54, '57, '60, '63	10	0	0	0	0	0	1.17	0.16	0.12	0	0
7	Orchard (under trees)	DDT	'50–'63	20	0	0	0	0	0	0.06	0	0.03	0	0
8	Orchard (between trees)	DDT	'50–'63	20	0	0	0	0	0	0.08	0.01	0.03	0	0
9	Strawberries	DDT	'58–'64	6	0	0	0	0	0.02	0.71	0.15	0.12	0.10	0
10	Potatoes	DDT	'59–'64	7.5	0	0	0	0	0	0.01	0.04	0.03	0	0
11	Rutabagas	Aldrin	'64	5	0	0	0	0	0	0.02	0	0.01	0	0
12	Rutabagas	Heptachlor	'57–'60	10+	0.68	0.05	0.48	0.59	0.33	0	0	0	0	0.08
	Carrots	Aldrin	'60, '65	8+										
13	Carrots	Aldrin	'60, '61, '62, '63, '64		0	0	0	0.44	0.86	0.08	0.01	0	0	0
				Nova Scotia										
1	Orchard (between trees)	DDT	'57–'61	4.5	0	0	0	0	0	0.66	0.10	0.20	0	
2	Orchard (under trees)	DDT	'57–'61	4.5	0	0	0	0	0	1.37	0.22	0.42	0	
3	Carrots	Aldrin	'59, '61, '62, '65	30	0	0	0	2.13	4.04	0.15	0.05	0.02	0.03	
4	Vegetables	Aldrin	'65	6	0	0	0	0.49	0.17	0.01	0	0	0	
		DDT	'65	0.75										
5	Strawberries	DDT	'65	1	0	0	0	0.01	0	0.12	0.02	0.01	0	
6	Vegetables	Aldrin	'55–'65	12	0	0	0	0.39	0.38	0.43	0.10	0.05	0	
		DDT	'65	3										
7	Apple orchid	DDT	'55, '58, '59, '64	25	0	0	0	0.02	0.04	3.00	0.44	0.91	0.33	

[a] 1-Hydroxychlordene.

Table I. Continued

Sample	Crops	Insecticide	Years of application	Total toxicant, lb./acre	Residues in Soil Samples, P.P.M.									
					Hept.	Hept. Epox.	γ-Chlor.	Aldrin	Dieldrin	DDT *p,p'*	DDT *o,p'*	DDE	DDD	1-OH-C[a]
Nova Scotia														
8	Rutabagas	Aldrin	'65	5	0	0	0	1.03	0.18	0	0	0	0	
9	Vegetables	Aldrin	'59, '60, '63, '65	30	0.11	0	0.23	2.17	1.14	3.80	0.55	0.61	0	
		DDT	'60, '63, '64	10										
10	Carrots	Aldrin	'61, '63, '65	15	0	0	0	0.37	0.21	0.30	0.06	0.05	0.05	
11	Potatoes	Aldrin	'63, '64, '65	5	0	0	0	0.01	0	0.54	0.09	0.07	0	
		DDT	'63, '64, '65	6										
12	Potatoes	Aldrin	'61	4	0	0	0	0.28	0.30	0.75	0.14	0.12	0.20	
		DDT	'57, '65	3										
13	Vegetables	Aldrin	'60–'65	10	0	0	0	0.99	0.38	0	0	0	0	
14	Vegetables	Aldrin	'57, '60, '65	11	0	0	0	0.67	0.60	1.11	0.26	0.12	0.25	
		DDT	'64	3										
15	Orchard (between trees)	?	.....	?	0	0	0	0	0	1.29	1.43	0.49	1.09	
16	Orchard (under trees)	?	.....	?	0	0	0	0.09	0.52	1.42	0.70	1.47	0.52	
17	Orchard (under trees)	?	.....	?	0	0	0	0	0.11	13.82	1.54	2.91	1.81	
18	Orchard (between trees)	?	.....	?	0.02	0	0	0.15	0.16	0.46	0.23	0.28	0.07	
New Brunswick														
1	Orchard (under trees)	DDT	'62, '63	6	0	0	0	0	0.05	0.80	0.35	0.29	0.29	
2	Orchard (between trees)	DDT	'62, '63	6	0	0	0	0.01	0.08	0.70	0.19	0.19	0.26	
3	Orchard (under trees)	DDT	'57, '59	3–6	0	0	0	0	0	2.56	0.29	0.23	0.23	
4	Orchard (between trees)	DDT	'57, '59	3–6	0	0	0	0.01	0	0.48	0.07	0.08	0.05	
5	Corn	DDT	'57, '58, '59	3–6	0	0	0	0	0.04	0.28	0.07	0.06	0.17	
		DDD	'57	3										
6	Strawberries	DDT	'64	1	0	0	0	0	0	1.06	0.41	0.24	0.35	
7	Potatoes	DDT	'48–'65	45	0	0	0	0	0	2.08	0.52	0.29	0	

Table I. Continued

Sample	Crops	Insecticide	Years of application	Total toxicant, lb./acre	Hept.	Hept. Epox.	γ-Chlor.	Aldrin	Dieldrin	DDT *p,p'*	DDT *o,p'*	DDE	DDD	1-OH-C
	Cropping and Insecticide History				Residues in Soil Samples, P.P.M.									
					New Brunswick									
8	Potatoes	Aldrin	'63	2	0	0	0	0.09	0.14	0.23	0.03	0.02	0	
		DDT	'63, '64	6										
9	Potatoes	DDT	'53, '56, '59, '62	12	0.15	0	0	0.06	0.01	4.24	1.20	1.74	1.21	
10	Broccoli	Aldrin	'62, '65	0.5	0	0	0	0.14	0.02	0.18	0.13	0.05	0	
		Endrin	'62, '65	0.5										
11	Potatoes	DDT	'49–'63	20–40	0	0	0	1.42	0.06	0.50	0.13	0.07	0.16	
12	Brussel sprouts	Aldrin	'65	3	0	0	0	0	0	0.75	0.31	0.19	0.25	
13	Rutabagas	Heptachlor	'57	1.25	0.01	0	0	0.07	0.11	0	0	0	0	
14	Rutabagas	Aldrin	'65	15	0.01	0.05	0.22	0.01	0	0	0	0	0	
15	Cabbage	Aldrin	'61	4	0	0	0	0.02	0	0.49	0.09	0.05	0.05	
	Corn	DDT	'64	1										
					Newfoundland									
1	Potatoes	Aldrin	'64	2.5	0	0	0	0.48	0.15	0.03	0	0.11	0	
		DDT	'64	2.5										
2	Root crop	Aldrin	'63	6	0	0	0	0.28	0.52	0.97	0.18	0.07	0	
3	Root crop	Aldrin	'61, '63, '65	7.5	0	0	0	1.39	0.68	13.84	2.63	0.65	0	
4	Cabbage	Aldrin	'60, '61, '65	24	0	0	0	2.50	0	5.41	0.97	0.28	0	
	Lettuce	DDT	'60, '61, '63, '64, '65	5										
5	Cabbage	Aldrin	'55, '58, '62, '64	10	0	0	0	0.40	0.36	0.84	0.18	0.05	0	
		DDT	'55, '58, '62, '64	5										
6	Root crop	Aldrin	3 of 4 years–'65	45	0	0	0	1.50	1.35	1.12	0.24	0.07	0	
		DDT	3 of 4 years–'65	15										
7	Turnips	Aldrin	'62, '63	5	0	0	0	0.29	1.45	0.41	0.09	0.02	0	
	Cabbage	DDT	'62, '63	3										
8	Root crop	Aldrin	'59, '60, '61, '62	20	0	0	0	0.13	0.08	1.40	0.26	0.03	0	
		DDT	'59–'65	7										
9	Cabbage	DDT	'63, '64, '65	6.75	0	0	0	0.03	0	1.56	0.34	0.03	0	
10	Root crop	Aldrin	'62, '63	7.5	0	0	0	0	0	0.34	0.08	0.03	0	
		DDT	'62, '63	3										

Chemical Conversion Results. Chromatograms were obtained from soil samples containing *p,p'*-DDT and *o,p'*-DDT before and after treatment with sodium hydroxide. These compounds were converted to *p,p'*-DDE and *o,p'*-DDE by sodium hydroxide, and the peaks obtained after treatment of soil samples containing them had the same retention time as pure authentic samples of *p,p'*-DDE and *o,p'*-DDE. Aldrin, dieldrin, heptachlor, and heptachlor epoxide do not react with sodium hydroxide.

Figure 2 shows the chromatogram of eluate 2 containing dieldrin, the same eluate after treatment with HBr, and a reference sample of pure dieldrin treated with the same reagent. Under the reaction conditions employed, dieldrin was converted to two compounds, which had longer retention times on the SE-30/QF-1 column than dieldrin. No attempts were made to identify these peaks. O'Donnell, Johnston, and Weiss (*15*) have shown that on treatment with hydrobromic acid–acetic anhydride at 120° C., dieldrin is converted to 6-acetoxy-7-bromo-6,7-dihydroaldrin. Hamence, Hall, and Caverly (*9*) report that only one compound was detected under the above reaction conditions when gas chromatography was employed as the analytical tool.

Soil samples containing aldrin were treated with the chlorine reagent and gave two peaks on the SE-30/QF-1 column which had identical retention times as pure aldrin treated with the same reagent. Chlorine adds to the unchlorinated double bond of aldrin to form the *trans*-dichloride (*17*). Under the same reaction conditions, chlorine did not add to the double bond in *p,p'*-DDE.

Figure 3 shows the separation of several insecticides and related materials found in soil samples in eluates

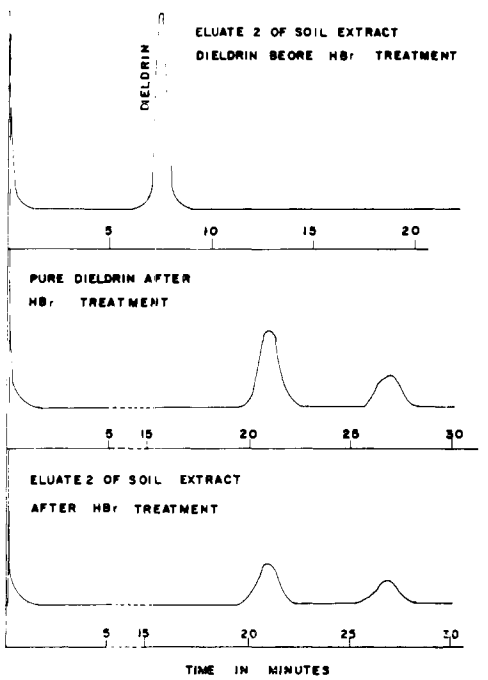

Figure 2. Treatment of dieldrin with HBr along with a soil sample containing dieldrin before and after treatment

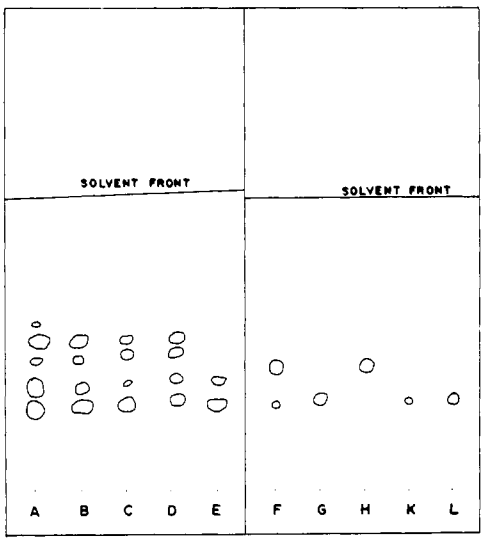

Figure 3. Thin-layer chromatography

A. Standard solution of insecticides (top to bottom) aldrin, *p,p'*-DDE, heptachlor, *o,p'*-DDT, *p,p'*-DDT.
B,C,D,E. Eluate 1 of soil samples containing several insecticides.
F. Standard mixture of dieldrin and heptachlor epoxide.
G,H,K,L. Eluate 2 of soil samples containing heptachlor epoxide and dieldrin

1 and 2 using thin-layer chromatography. The behavior of reference materials is presented also. Better separation and less diffusion of the spots occurred when the chromatographic tanks and solvent were kept at 4° C. The quantity of insecticide in the soil samples was estimated visually after development by comparing the spot size and intensity with known standards of the pure insecticides chromatographed on the same plate. The semiquantitative estimations of the amounts of insecticides present in the sample using thin-layer chromatography was in general agreement with the results obtained by gas-liquid chromatography. The solvent system hexane–ethyl acetate (9 to 1) did not move 1-hydroxychlordene on a thin-layer plate. However, a developing system consisting of hexane–ethyl acetate (7 to 3) separated 1-hydroxychlordene from dieldrin and heptachlor epoxide.

The results reported in this paper indicate that significant amounts of insecticides may be present in agricultural soils where organochlorine compounds have been frequently applied. This study was exploratory in nature and the data are not statistically representative of the Atlantic Provinces. Insecticides can be absorbed from soils by certain plants, and it is important to know the insecticide levels in selected soil samples in order to prevent contamination of crops by insecticides.

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