

# Factors Influencing Extraction of Aldrin and Dieldrin Residues from Different Soil Types

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Twenty-one solvent systems were evaluated for the extraction of aldrin and dieldrin on nonfortified sandy loam, muck, and clay soils under various experimental conditions. Extraction efficiencies ranged from 0.10 to 0.92 p.p.m. for aldrin and 0.09 to 0.87 p.p.m. for dieldrin, using an air-dried sandy loam with a blending procedure. Other factors evaluated were tumbling and Soxhlet extractions, moisture content of soils, contact time between soil and solvent, and amounts of coextractives.

Stepwise evaluation of these stages indicated the relative importance and interrelationship of the factors examined. No single factor was found of paramount importance and extrapolation of results from one soil type to another did not appear possible. Fortification techniques for establishing extraction efficiencies proved of dubious value; the range of efficiencies of five extraction systems was 91 to 97% for C<sup>14</sup> dieldrin-fortified soil, but only 36 to 67% for nonfortified, field-treated soil.

This study originated as part of a long-term project for finding either a universally applicable extraction technique for organochlorine insecticide residues in various agricultural soils or an efficient and practical solvent system for a particular soil-pesticide circumstance.

Methodology has been studied extensively for the determination of residues in various foods, but the situation is not as satisfactory for residues in soils. This may be attributed to many factors, not least of which is the complex nature of soil, an ever-changing system of almost infinite variability.

Fundamental studies on soil have been reviewed recently by Edwards (1966). The importance of the moisture content of soils in obtaining satisfactory extraction of organochlorine residues has been demonstrated (Harris, 1966). Because of the inherent complexity of soil and the difficulty of obtaining representative samples (Elgar, 1966), the reproducibility of organochlorine residue determinations is generally poorer for soil than for food.

Extraction is the first step in what is often a long multi-stage procedure. While much work has been done on cleanup of extracts and final determinative techniques, little has been done to evaluate extraction efficiencies and investigate the variables. The efficiency of extraction is of obvious importance, since residues not extracted are not estimated. The question as to whether fortification of extracts can be used as a reliable criterion of extraction efficiencies is controversial, and has been discussed at length by Gunther (1962).

Since soil is probably the largest reservoir of pesticide residues in our environment, it is essential to determine the residue content accurately to avoid making false recommendations for current pesticide use.

Of the many possible factors influencing the extraction of organochlorine residues, five have been studied and are reported here:

- Solvents, single systems and mixtures of two solvents.
- Contact time between solvent and soil.
- Processing, high speed blender, Soxhlet, and tumbler.
- Moisture, air-dried and wet.
- Soil types, sandy loam, clay, and muck.

Soils used in this work are representative of the basic soil types likely to be encountered throughout Canada. As was expected from the known field history of the samples used, aldrin (1,2,3,4,10,10-hexachloro-1,4,4a-,5,8,8a-hexahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene) and dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a-,5,6,7,8,8a-octahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene) concentrations were much higher than those of other pesticide residues, and for the sake of simplification in the initial experiments, only these two pesticides were considered. Since the analysis was carried out without cleanup, the amount of coextractives was measured to check interference in the gas chromatographic determination. Dieldrin-C<sup>14</sup> was used in fortification experiments to determine whether this technique could be used as a criterion for determining extraction efficiencies. All procedures for final analysis by gas-liquid chromatography (GLC) after extraction, such as filtration, partitioning and washing, and concentration were standardized, and both quantitative and consistent recovery of dieldrin-C<sup>14</sup> was confirmed (Chiba and Morley, 1968).

However, the results obtained apply only to the extraction of aldrin and dieldrin. This was largely dictated by the availability of suitable soils of known field history and the realization that to cover all of the possibilities would

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have been an immense task. The aim of the present work is to develop general principles on the basis of which only the most promising results will be taken and extended to other organochlorine residues in other soil types.

## MATERIALS AND METHODS

**Soils.** Throughout the study, air-dried soils were used as standards (air-dried at room temperature, 24° C.). For investigating the influence of moisture content, a known amount of water was added to the soil and tumbled in a jar for 1 hour. Figures for the partial analysis of the soils used are given in Table I.

**Solvents.** All solvents, except propylene carbonate, were distilled in glass (Burdick and Jackson Laboratories, Inc.) and checked before use for electron-capturing impurities. Propylene carbonate was obtained from Matheson Coleman & Bell.

**Extraction Techniques.** METHOD A. OMNI-MIX BLENDER (HIGH SPEED). Air-dried soil (100 grams) and the extraction solvent (200 ml.) were blended for 5 minutes with external cold water cooling. The mixture was filtered with suction using Whatman No. 1 filter paper with a 1-cm. pad of SuperCel. The container was rinsed with 2 × 25 ml. of the solvent, the soil, filter paper, and pad were returned to the blender, and the extraction procedure was repeated. The filtrates were combined and transferred to a separatory funnel for partitioning. This was the standard procedure, listed in the tables as B 5 × 2.

This procedure was modified by adding anhydrous Na<sub>2</sub>SO<sub>4</sub> or by using moist soil in experiments where comparisons with the standard method were being made. When the extraction was done just once, 4 × 50 ml. of the solvent were used for rinsing instead of 2 × 25 ml. (B 5 × 1).

To check the influence of the contact time between solvent and soil, soil (100 grams) was kept in contact with solvent in a container for 19 hours (overnight) prior to carrying out the standard procedure (19 B 5 × 2).

**TUMBLING.** Anhydrous Na<sub>2</sub>SO<sub>4</sub> (50 grams) was added to soil (100 grams) and the mixture tumbled for an additional 2 hours, then treated as in Method A. This method is listed in the tables as Tumbler and has been used previously (Elgar, 1966).

**SOXHLET.** A soil-solvent ratio of 1 to 5 was used, and the steam bath was adjusted so that it took 5 minutes to complete one extraction cycle with methanol (b.p. 65° C.). In the case of mixed solvents soil extraction was actually

made by the azeotropes, but the normal 1-to-1 ratio of solvents was added to the flask initially so that working up procedures could be kept consistent.

**Partitioning and Washing.** After filtration, the solvent was partitioned by adding water and *n*-hexane when only a polar solvent was used for extraction. When only a non-polar solvent was used, the extract was simply washed with water. The ratio of polar solvent and water was maintained at 1 to 6. The initially separated aqueous layer was re-extracted with the nonpolar solvent (100 ml.), and the solvent was combined with the original nonpolar layer. Three washings of the combined layers were carried out, using the same amount of water as for the original separation.

After washing, nonpolar solvents were dried by percolation through a short column of anhydrous Na<sub>2</sub>SO<sub>4</sub>, and analyzed by GLC without cleanup. In extractions with methylene chloride, final transference to *n*-hexane was effected, since methylene chloride is electron-capturing and not suitable for GLC injection.

**Coextractives.** Coextractives were measured by evaporation of the solvent extract (20 ml., equivalent to 20 grams of soil) to constant weight in a beaker left on a bench overnight at room temperature.

**Analytical Methods.** All samples were analyzed by GLC, using an Aerograph Hi-Fi Model 600 with an electron-capture detector. Experimental parameters were:

Column temperature, 173° C. N<sub>2</sub> flow rate (20 ml. per minute). 15 p.s.i.

Injector temperature, 164° C. Column, DC-11 + QF-1 (3 to 2). 4% on Chromosorb W. Regular (60- to 80-mesh), Al, 2 feet × 1/8 inch.

Detector temperature, 173° C.

Injection volume (on column), 2 μl.

An Aerograph Model 204 with an electron-capture detector was used to obtain supplemental results. Experimental parameters were:

Column temperature, 190° C. N<sub>2</sub> flow rate, 36 ml. per minute.

Injector temperature, 220° C. Column, 10% QF-1 on Chromosorb W (60-to 80-mesh). Al, 5 feet × 1/8 inch.

Detector temperature, 210° C.

Injection volume (on column), 4 μl.

Scintillation counting of radioactive samples was carried out using a liquid scintillation spectrophotometer

Table I. Partial Analysis of Soils Used in Experiments

Soil No. and Type	Organic Matter (% C × 1.724)	Field Moisture Capacity, <sup>a</sup> ML./100 G. Soil	Air-Dried Moisture Content, %	Particle Size Analysis <sup>b</sup>			
				Sand	50-20 μ silt	20-2 μ silt	Clay <2μ
1 Grenville sandy loam	3.8	16	3.1	66.6	5.6	8.8	18.9
2 <sup>c</sup> .....	...	..	1.8	...	...	...	...
3 North Gower clay loam	4.9	25	3.2	29.8	28.6	6.8	34.7
4 North Gower Intergrade to Matilda clay loam	18.1	35	11.5	28.2	29.4	11.2	31.3

<sup>a</sup> Pressure-plate method, 1/3 atmo. percentage, (U. S. Department of Agriculture, 1954).

<sup>b</sup> Method of Toogood and Peters (1953).

<sup>c</sup> Not analyzed, but from same field as soil 1 taken a year later after further treatment with aldrin. Natural moisture content 16.7%.

(Nuclear Chicago Model 703) at 0° C. Calculations were made by the channel-ratio method by using quenching curves. For counting, suitable aliquots were taken and scintillator solution (10 ml. of a toluene solution of 0.5% PPO and 0.05% POPOP) was added.

## RESULTS AND DISCUSSION

**Comparison of Extraction Efficiency of Solvents.** Table II shows the results obtained with nine single- and 12 mixed-solvent extraction systems using the standard blender method (Method A). All the mixtures except one (10% acetone-*n*-hexane) were in a 1-to-1 ratio (v./v.). Of nine single-solvent systems examined, dimethyl formamide (DMF) showed the best results, followed by dimethyl sulfoxide (DMSO) and acetone.

Benzene, methylene chloride, *n*-hexane, and propylene carbonate gave rather poor results, and methanol showed a very strong extraction preference for dieldrin. The use of propylene carbonate as an efficient extraction system has been advocated recently by Schnorbus and Phillips (1967).

Acetonitrile, a commonly used solvent for the extraction of organochlorine insecticide residues, showed intermediate values.

With regard to the amount of coextractives, the following marked tendency was found: Most polar solvents were very good (less coextractives), whereas nonpolar solvents were very poor. There was, however, no connection between the amount of pesticides found and the amount of coextractives. Of the mixed-solvent systems

examined, DMF-benzene and methanol-benzene were very efficient, and DMSO-benzene and methanol-methylene chloride were reasonably satisfactory. All other systems were much less efficient and not satisfactory (Table II). One mixture, 50% acetone-*n*-hexane, was rather poor with air-dried soil. Methanol mixed with other solvents, such as methylene chloride or benzene, looked very good, whereas its single use was rather poor. The reverse was true for acetone; alone it was very good, but in combination with benzene or *n*-hexane its extraction efficiency decreased, and the extraction of unfavorable coextractives increased (Table II).

**Contact Time between Solvent and Soil.** This factor was first investigated with 50% acetone-*n*-hexane, since a similar mixture (50% acetone-petroleum ether) was used for a soil survey in Ontario (Harris *et al.*, 1966). As seen in Table III, the time factor was very important when Method A was used: The results were only 0.51 p.p.m. for aldrin and 0.47 p.p.m. for dieldrin using the standard contact time, but all other modified methods showed nearly double the amount of each pesticide. From the practical point of view 19 hours' contact time with solvent followed by normal blending was one of the most promising methods, because the amount of pesticides extracted was very high, and coextractives were very low. One-hour blending showed satisfactory results, almost identical to those obtained from 5-hour blending. There appeared to be no advantage in extending the blending time for more than 1 hour.

Similar experiments were tried with DMF, which showed the best results among 21 solvent systems examined with the standard blending method. Unlike 50% acetone-*n*-hexane, the difference between varying contact times was very small. Thus, Method A using DMF as extraction solvent seems able to extract most residues of aldrin and dieldrin present in a sandy loam soil. Results with six other solvent systems using the 19-hour contact time followed by normal blending are also listed in Table III. Most of them showed much better results than those obtained with Method A. Of these solvents, methanol and 50% methanol-benzene were very satisfactory and almost as good as DMF.

**Soxhlet Extraction.** The Soxhlet method was very efficient with most solvent systems, although the amounts of coextractives were always highest in each comparison group of two or three extractions using the same extraction solvent (Table III). Rather poor results were obtained with this extraction method using the commonly used mixture of 50% 2-propanol-*n*-hexane. Of nine solvent systems examined, methanol, methanol-benzene, acetonitrile, and DMF were the most efficient. For aldrin 1.01 p.p.m. and for dieldrin 1.08 p.p.m. are presumed to be the total amount of each residue present in soil 1, since these were the maximum quantities extractable by exhaustive Soxhlet extraction—the usual yardstick by which extraction efficiencies are measured. From the practical point of view, however, there is very little advantage in using the Soxhlet procedure, since a stringent cleanup method is required because of the large amount of coextractives, resulting in a poor background with gas chromatography. An extreme example will be seen by reference to DMF, although this solvent, because of its

Table II. Comparison of Extraction Efficiencies of Solvents

Ex-trac-tion No.	Solvents	Soil 1 (sandy loam), air-dried		
		Co-ex-trac-tives, Mg./G.	Aldrin, P.P.M.	Dieldrin, P.P.M.
1	Methylene chloride	0.079	0.10	0.30
2	Methanol	0.032	0.10	0.55
3	Propylene carbonate	0.016	0.17	0.09
4	<i>n</i> -Hexane	0.110	0.21	0.19
5	Benzene	0.069	0.33	0.29
6	Acetonitrile	0.025	0.50	0.45
7	Dimethylsulfoxide (DMSO)	0.011	0.74	0.80
8	Acetone	0.032	0.81	0.73
9	Dimethylformamide (DMF)	0.022	0.92	0.87
10	50% acetone-CH <sub>2</sub> Cl <sub>2</sub>	0.140	0.30	0.38
11	50% 2-propanol- <i>n</i> -hexane	0.076	0.33	0.32
12	10% acetone- <i>n</i> -hexane	0.071	0.45	0.39
13	50% acetone- <i>n</i> -hexane	0.085	0.51 <sup>a</sup>	0.47 <sup>a</sup>
14	50% acetonitrile-acetone	0.061	0.57	0.51
15	50% acetone-benzene	0.130	0.60	0.44
16	50% acetonitrile- <i>n</i> -hexane	0.040	0.60	0.53
17	50% acetonitrile-benzene	0.086	0.61	0.55
18	50% DMSO-benzene	0.190	0.79	0.72
19	50% CH <sub>3</sub> OH-CH <sub>2</sub> Cl <sub>2</sub>	0.180	0.82	0.72
20	50% CH <sub>3</sub> OH-benzene	0.240	0.85	0.85
21	50% DMF-benzene	0.170	0.89	0.87

Extraction method, Omni-Mix high speed blender, two 5-minute extractions with 200 ml. of solvent per 100 grams of soil (B 5 × 2).

<sup>a</sup> Standard deviation: Aldrin ± 0.03; dieldrin ± 0.02 (eight determinations).

**Table III. Comparison of Extraction Efficiencies**

By changing contact time between solvent and soil using blending system and by Soxhlet extractor, soil 1 (sandy loam), air-dried

Extraction No.	Solvent	Method	Coextractives, Mg./G.	Aldrin, P.P.M.	Dieldrin, P.P.M.
13	50% acetone- <i>n</i> -hexane	B 5 × 2	0.085	0.51	0.47
22	50% acetone- <i>n</i> -hexane	19 B 5 × 2	0.097	0.83	0.87
23	50% acetone- <i>n</i> -hexane	B 1 hr. × 1	0.150	0.88	0.93
24	50% acetone- <i>n</i> -hexane	Soxhlet, 12 hr.	0.340	0.90	0.87
25	50% acetone- <i>n</i> -hexane	B 5 hr. × 1	0.190	0.92	0.89
9	Dimethylformamide	B 5 × 2	0.022	0.92	0.87
26	Dimethylformamide	B 2 hr. × 1	0.038	0.88	0.95
27	Dimethylformamide	19 B 5 × 2	0.048	0.88	1.02
28	Dimethylformamide	Soxhlet, 20 hr. <sup>a</sup>	0.470	0.99	1.08
29	Methanol	19 B 5 × 2	0.043	0.90	1.04
30	Methanol	Soxhlet, 12 hr.	0.180	1.01	1.06
31	50% CH <sub>3</sub> OH-benzene	19 B 5 × 2	0.320	0.97	0.95
32	50% CH <sub>3</sub> OH-benzene	Soxhlet, 12 hr.	0.490	0.92	1.07
33	Acetonitrile	19 B 5 × 2	0.033	0.72	0.66
34	Acetonitrile	Soxhlet, 12 hr.	0.200	1.00	1.05
35	Acetone	19 B 5 × 2	0.045	0.86	0.93
36	Acetone	Soxhlet, 12 hr.	0.062	0.89	0.90
37	Benzene	19 B 5 × 2	0.077	0.49	0.41
38	Benzene	Soxhlet, 12 hr.	0.570	0.81	0.86
39	50% 2-propanol- <i>n</i> -hexane	Soxhlet, 12 hr.	0.230	0.62	0.77
40	50% acetone-benzene	19 B 5 × 2	0.150	0.71	0.66
41	Methylene chloride	Soxhlet, 12 hr.	0.220	0.18	0.48

<sup>a</sup> Temperature of oil bath adjusted so that 5 minutes required to finish one extraction cycle.

high boiling point, is not suitable for routine use with the Soxhlet method. The amount of coextractives using a Soxhlet was approximately 10 times greater than that obtained from 19-hour contact time followed by normal blending. In most cases, the increase of contact time gave little improvement with aldrin, but a marked increase with dieldrin. This difference may be attributed to the difference in the polarities of these two compounds.

The rate of extraction with the Soxhlet method is another problem. As recently shown by Teasley and Cox (1966), it was rather difficult to obtain good reproducibility, perhaps because of difficulty in keeping a constant solvent recycling time. Three examples of different rates of extraction are given in Table IV. In spite of the slow rate for one cycle with acetonitrile, it was the best of the three solvents compared. This may be due in part to the extrac-

**Table IV. Rate of Extraction with Soxhlet System<sup>a</sup>**

Soil 1, air-dried

Extractions, Hours	Solvent					
	50% acetone- <i>n</i> -hexane		CH <sub>3</sub> CN		50% 2-propanol- <i>n</i> -hexane	
	Extraction No.					
	42		43		44	
Pesticide, P.P.M.						
	Aldrin	Dieldrin	Aldrin	Dieldrin	Aldrin	Dieldrin
1	0.32	0.31	0.41	0.50	0.36	0.38
2	0.43	0.39	0.60	0.81	...	...
3	0.48	0.45	0.71	0.92	0.51	0.57
4	0.54	0.49	0.77	0.97	...	...
5	0.59	0.54	...	...	...	...
6	0.61	0.56	0.85	1.02	0.75	0.87
7	0.63	0.59	...	...	...	...
12	0.85	0.80	...	...	...	...
14	(0.90) <sup>b</sup>	(0.87)	(1.00)	(1.05)	(0.62)	(0.77)
18	...	...	0.93	1.07	...	...
	...	...	...	...	0.84	1.01
Boiling point, ° C.	49		82		64	
One cycle, min.	1.3		18		10	
Coextractives, mg./g.						
Before partitioning	0.34		1.83		0.28	
After partitioning	0.34		0.20		0.23	

<sup>a</sup> Determination made without partitioning step.

<sup>b</sup> Continuous 12-hour extraction (separate run).

Table V. Influence of Moisture Content  
Soil type, sandy loam. Extraction solvent, 50% acetone-*n*-hexane

Extraction No.	Moisture Content, %	50 G. of Na <sub>2</sub> SO <sub>4</sub>	Method	Coextractives, Mg./G.	Aldrin, P.P.M.	Dieldrin, P.P.M.
Soil 1						
13	3.1 <sup>a</sup>	—	B 5 × 2	0.085	0.51	0.47
45	3.1	+	B 5 × 2	0.260	0.41	0.41
46	3.1	—	Tumbler	0.044	0.42	0.37
47	3.1	+	Tumbler	0.066	0.50	0.39
48	25 <sup>b</sup>	—	B 5 × 2	0.130	0.95	1.08
49	25	+	B 5 × 2	0.120	0.40	0.45
50	50	—	B 5 × 2	0.190	0.82	1.00
51	50	+	B 5 × 2	0.120	0.81	0.95
52	50	—	Tumbler	0.120	0.84	1.08
53	50	+	Tumbler	0.100	0.72	0.71
54	75	—	B 5 × 2	0.140	0.95	1.04
55	75	+	B 5 × 2	0.180	1.00	1.08
56	100	—	B 5 × 2	0.120	0.85	1.08
57	100	+	B 5 × 2	0.140	0.95	0.96
Soil 2						
58	1.8 <sup>a</sup>	—	B 5 × 2	0.088	2.35	0.90
59	1.8	+	B 5 × 2	0.110	1.20	0.40
60	1.8	—	Tumbler	0.072	1.25	0.45
61	1.8	+	Tumbler	0.110	1.55	0.50
62	16.7 <sup>c</sup>	—	B 5 × 2	0.310	2.42	1.24
63	16.7	+	B 5 × 2	0.910	2.59	1.18
64	16.7	—	Tumbler	1.830	2.59	1.30
65	16.7	+	Tumbler	1.050 <sup>d</sup>	2.59	1.18

<sup>a</sup> Air-dried.

<sup>b</sup> Water added up to 25, 50, 75, and 100% of water-holding capacity.

<sup>c</sup> Natural field moisture content.

<sup>d</sup> Extract showed orange color, probably due to rubber gasket on Mason jar.

tion power of the solvent itself, but probably more to the higher solvent temperature when it comes in contact with the soil sample.

**Moisture Content.** COMPARISON OF BLENDING AND TUMBLING TECHNIQUES. Table V shows the significance of moisture content using the 50% acetone-*n*-hexane system with both blending and tumbling methods. To reduce the soil moisture content to a reasonably constant level, the effect of adding anhydrous Na<sub>2</sub>SO<sub>4</sub> to the soil prior to extraction was investigated (modification of Method A). The results showed that this modification was in general nonbeneficial. Without Na<sub>2</sub>SO<sub>4</sub>, very good results were obtained from all samples except that which was air-dried. With Na<sub>2</sub>SO<sub>4</sub>, a big difference was found between 50 and 25% moisture content, and the latter showed almost identical results with the air-dried sample. There was no significant difference in the amount of coextractives, except for the low value obtained from the air-dried sample. On the other hand, the difference between blending and tumbling was very small. Moist soil with no prior addition of Na<sub>2</sub>SO<sub>4</sub> was best, and the combination of dry soil and Na<sub>2</sub>SO<sub>4</sub> was the poorest, since it gave the least pesticide recovery and more coextractives than those without Na<sub>2</sub>SO<sub>4</sub>.

A similar experiment was tried using the same type of soil, obtained direct from the field (soil 2) with a moisture content of 16.7% (Table V). Tendencies between the contrasting factors were not so great as those found with soil 1.

Since DMF was excellent with the standard blending

method using air-dried sandy loam (Table II), the efficiency of this solvent was compared to that of others with clay loam (soil 3). An extensive comparison was also made with different methods and conditions (Table VI). These results were very different from those obtained with sandy loam. With air-dried soil and the standard blending method, mixed solvents (50% methanol-methylene chloride and 50% acetone-*n*-hexane) gave the best results. Dimethylformamide showed a strong extraction preference for dieldrin, but was rather poor for aldrin. Using soil to which water was added, up to 50% of its water-holding capacity, resulted in decreased recovery with DMF as an extraction solvent. Addition of anhydrous Na<sub>2</sub>SO<sub>4</sub> prior to extraction gave an even poorer result. Results with the tumbling method were slightly lower than those with the blending method.

One significant point observed was the large variation in the amount of coextractives. Thus, the blender method for methanol-methylene chloride extraction of the air-dried soil gave 26 times more coextractives than the lowest amount obtained by the DMF extraction.

**Validity of Fortification as a Measure of Extraction Efficiency.** Since the field-treated sandy loam soil (No. 1) already contained dieldrin, dieldrin-C<sup>14</sup> was used in fortification experiments. Recoveries of dieldrin-C<sup>14</sup> using five different extraction systems are given in Table VII. Four successive extractions were necessary to obtain 100% recoveries. It is difficult to make absolute comparisons of these results with those obtained in previous experiments with the nonfortified soil, since the amount of

**Table VI. Effect of Changing Possible Influencing Factors on Extraction Efficiency**  
Soil 3 (clay loam)<sup>a</sup>

Extraction No.	Method	Na <sub>2</sub> SO <sub>4</sub> , 50 Grams	Moisture Condition	Solvent	Coextractives, Mg./G.	Aldrin, P.P.M.	Dieldrin, P.P.M.
66	B 5 × 2	+	Wet <sup>b</sup>	Benzene	0.21	0.33	0.48
67	Tumbler	+	Wet	Benzene	0.21	0.32	0.49
68	Tumbler	+	Wet	DMF	0.13	0.27	0.42
69	B 5 × 2	+	Wet	DMF	0.12	0.34	0.51
70	B 5 × 2	-	Wet	DMF	0.19	0.41	0.59
71	B 5 × 2	-	Dry <sup>c</sup>	DMF	0.03	0.45	0.84
72	B 5 × 2	-	Dry	50% CH <sub>3</sub> OH-benzene	0.56	0.52	0.72
73	B 5 × 2	-	Dry	50% acetone- <i>n</i> -hexane	0.38	0.58	0.80
74	B 5 × 2	-	Dry	50% CH <sub>3</sub> OH-CH <sub>2</sub> Cl <sub>2</sub>	0.88	0.60	0.85

<sup>a</sup> Organic matter 4.9%.

<sup>b</sup> Water added up to 50% of water-holding capacity.

<sup>c</sup> Air-dried, moisture content 3.2%.

dieldrin in the field-treated soil is unknown. However, the actual amount of dieldrin present in the soil is of no great significance, since the work is concerned only with the comparison of extraction efficiencies. If the assumption is made, however, that the maximum amount of dieldrin extracted (Table III) represents the total amount present, comparisons may be made. The value taken for dieldrin (1.08 p.p.m.) was arrived at as a result of more than 50 extractions under all sorts of conditions, including exhaustive Soxhlet extractions.

Table VII shows that recoveries obtained from the first two extractions using the B 5 × 1 method with five extraction systems were 96, 91, 97, 96, and 96%, respectively. With unfortified soil, however, using the standard B 5 × 2 method and taking 1.08 p.p.m. as representing 100% extraction, the respective figures were 67, 44, 36, 41, and 47% extraction of dieldrin. If 1.08 p.p.m. is in fact lower than the real residue amount, the respective percentage figures for the unfortified soil are even lower. Thus fortification procedures for evaluation of extraction efficiencies would appear to be of little use.

**Soil Types.** As anticipated, extraction efficiencies of solvents varied from one type of soil to another, and no single extraction system was universal for all types of soils. Results obtained with the blender method using seven

different solvent systems and three basic soil types are listed in Table VIII.

A mixture of 50% methanol-methylene chloride was probably the best all-round extractant, although this is not a suitable system for GLC with an electron-capture detector, since transference to *n*-hexane is required at the final stage.

Dimethylformamide was best with sandy loam; it was also good with muck and clay loams for dieldrin, but rather poor for aldrin.

The mixture of 50% methanol-benzene never showed the highest results among the solvents examined, but gave consistently high recoveries for both aldrin and dieldrin with all three types of soil samples. Therefore, this mixture may be one of the most promising solvents as a universal extractant. Two of the common solvents, acetonitrile and 50% 2-propanol-*n*-hexane, showed rather poor results in all cases. Acetonitrile was extremely poor with muck soil. However, the study with muck and clay soils should be extended to obtain more comprehensive results.

**Coextractives.** Since the main objective was to determine the efficiency of extraction, the number of steps in the procedure between extraction and determination was reduced to as few as possible, since in every step pesticides may be lost. Throughout the experiments, therefore, all gas chromatographic determinations were carried out without cleanup.

In the evaluation of extraction efficiencies, however, it is almost impossible to avoid considering cleanup, since an extraction method that is efficient for pesticides could also be efficient for extraction of unfavorable coextractives, and therefore requires a good cleanup procedure before determination by GLC.

This was true in the authors' experiment with Soxhlet extractions but not with some other methods, such as the overnight plus blending method, and the standard blending method with moist soil. The amount of coextractives was measured by weight to study the relationship between the amount of pesticide residues extracted and the amount of coextractives, and also to see how these coextractives affect the background and accordingly the final determination by gas chromatography.

Fortunately, the coextractives present did not affect the

**Table VII. Recoveries of Dieldrin-C<sup>14</sup> from Soil<sup>a</sup>**

Solvents	Soil 1 (sandy loam), air-dried				
	Method B 5 × 1				
	Extraction <sup>b</sup>				Total
1	2	3	4 <sup>c</sup>	Recoveries, %	
50% CH <sub>3</sub> OH-CH <sub>2</sub> Cl <sub>2</sub>	92.35	3.96	3.20	0.90	100.41
50% acetone- <i>n</i> -hexane	83.64	7.56	7.30	1.70	100.20
10% acetone- <i>n</i> -hexane	87.30	9.70	3.37	0.60	100.97
CH <sub>3</sub> CN	90.19	5.60	4.14	0.10	100.03
50% CH <sub>3</sub> CN-acetone	91.85	4.00	2.33	0.20	98.38

<sup>a</sup> 16 μg. of dieldrin-C<sup>14</sup> petroleum ether solution added to 100 grams of soil sample in flash evaporator, then petroleum ether evaporated very gently.

<sup>b</sup> Extractions made 2 days after dieldrin-C<sup>14</sup> fortification.

<sup>c</sup> Fourth extractions made after 5-day soaking of each soil sample in each solvent after third extraction.

Table VIII. Comparison of Extraction Efficiency Using Three Different Soil Types  
Extraction method B 5 × 2

Solvent	Soil 1				Soil 3				Soil 4			
	Ex-traction No.	Co-extractives, mg./g.	Aldrin, p.p.m.	Dieldrin, p.p.m.	Ex-traction No.	Co-extractives, mg./g.	Aldrin, p.p.m.	Dieldrin, p.p.m.	Ex-traction No.	Co-extractives, mg./g.	Aldrin, p.p.m.	Dieldrin, p.p.m.
DMF	9	0.022	0.92	0.87	71	0.034	0.45	0.84	78	0.08	0.44	0.75
50% acetone- <i>n</i> -hexane	13	0.085	0.51	0.47	73	0.380	0.58	0.80	79	2.02	0.51	0.58
50% CH <sub>3</sub> OH-benzene	20	0.240	0.84	0.84	72	0.560	0.52	0.72	80	3.66	0.52	0.75
50% CH <sub>3</sub> OH-CH <sub>2</sub> Cl <sub>2</sub>	19	0.180	0.72	0.82	74	0.880	0.60	0.85	81	3.95	0.61	0.79
CH <sub>3</sub> CN	6	0.025	0.56	0.49	75	0.053	0.31	0.52	82	0.42	0.33	0.25
50% 2-Propanol- <i>n</i> -hexane	11	0.076	0.33	0.32	76	0.100	0.30	0.46	83	1.32	0.43	0.62
Benzene	5	0.069	0.33	0.29	77	0.100	0.18	0.23	84	0.75	0.34	0.33

background at the concentration range of 0.1 to 1.0 p.p.m. for aldrin and dieldrin. The extracts from the muck soil showed some background interference, but it was still possible to determine the residue content without cleanup. Even with sandy loam, however, if the residue level is less than 0.1 p.p.m., some extracts, such as DMF with a Soxhlet extraction, may require cleanup.

No correlation was found between amount of coextractives and efficiency of pesticide extraction. Use of suitable extraction systems decreased the amount of coextractives and increased the amount of aldrin and dieldrin.

Possible interference by coextractives in the determination of aldrin and dieldrin by GLC using a d.c. electron-capture detector was considered, since Lovelock (1963) has shown that this interaction is possible. Use of two different columns for both qualitative and quantitative determinations suggested that interaction between coextractives and residues was absent.

#### CONCLUSIONS

On the basis of this work, some tentative conclusions were reached which, hopefully, will act as guidelines for further work. These conclusions were reached mainly on the basis of extraction of aldrin and dieldrin from a sandy loam soil (soil 1), and may not be applicable to heavier-textured soils.

The 50% acetone-*n*-hexane system was of particular interest and was examined in detail, since a similar mixture of 50% acetone-petroleum ether has been used for a survey of organochlorine insecticide residues in Canadian soils (Harris *et al.*, 1966). Experimental variables were shown to be of importance for this system. Extraction of aldrin ranged from 0.40 to 1.01 p.p.m. and dieldrin from 0.37 to 1.08 p.p.m., depending on the method of extraction. Maximum extraction of both aldrin and dieldrin could easily be obtained from soil to which water had been added prior to extraction.

However, the 50% acetone-*n*-hexane system is a relatively inefficient extractant (Table II) and use of more efficient extraction solvents may eliminate the need for prior deactivation of the soil with water. This was shown to be the case using DMF as extraction solvent and increasing the contact time between solvent and soil (Table III).

The question of contact time between soil and extracting system is of prime importance; the normal blending time

of 5 minutes is certainly too short a contact time. In a comparison of blending, tumbling, and Soxhlet techniques the contact time factor plays a large part, since times of 2 × 5 minutes, 2 hours, and 12 hours are being compared. Comparison at equal contact times (2 hours) would indicate blending to be the more efficient procedure.

Use of field-treated instead of fortified soils has shown poor extraction efficiencies with many of the commonly used extraction solvents. Experiments with dieldrin-C<sup>14</sup> have shown that fortification, at best, is a poor criterion of extraction efficiency.

Some evidence for preferential extraction of pesticides by solvents has been obtained. A preliminary examination of other soil types (Tables VI and VIII) using a similar experimental approach showed similar general tendencies and results.

In the authors' opinion, the most promising and practical extraction technique is overnight contact between soil and solvent, followed by blending. Work using this technique in combination with the more promising solvent systems is now under way.

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