

Factors Affecting Extraction of Dieldrin-¹⁴C from Soil

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Dieldrin-¹⁴C was extracted from eight types of soils with various solvents under a variety of conditions. Recovery of dieldrin from soil was increased with reduced soil particle size, increased dielectric constant of the solvent, and the presence of water in the soil during extraction; soil type and method of extraction were also important. Depending on the soil type, common extraction solvents like acetonitrile, hexane-2-propanol, and hexane-acetone mixtures

extracted only 19 to 77% dieldrin from air-dried soil, while exhaustive extraction in Soxhlet with 1-to-1 chloroform-methanol gave 100% recovery. Addition of 20% water (80% for muck soil) to the air-dried soil immediately before extraction by 1-to-1 mixtures of hexane-2-propanol, hexane-acetone, and benzene-methanol gave 92 to 98% recovery for all types of soils.

A number of solvents and combination of solvents have been used to extract organochlorine pesticides from soil. Much work has been done on the cleanup of extracts and the final determinative techniques and very little attention has been given to the evaluation of extraction efficiencies. Recently a few attempts have been made to compare the efficiencies of several solvents in extracting organochlorine pesticides from soil. Collier *et al.* (1967) compared the extraction efficiencies of several solvents with that of Soxhlet extraction with hexane-acetone (9 to 1), which was given 100% extraction efficiency. Williams (1968) compared four methods of extracting organochlorine insecticides from soil and obtained highest recoveries when water was added to the soil prior to extraction with a mixture of hexane-acetone (41 to 59) in a Soxhlet apparatus. Chiba and Morley (1968) studied the efficiencies of 21 solvent systems in extracting aldrin and dieldrin from field-contaminated soils. While such studies are very useful for comparing the relative efficiencies of various extraction methods, they do not give the absolute recovery of the pesticide. Chiba and Morley (1967) obtained a maximum recovery of dieldrin from a sandy loam soil by extraction with dimethylformamide (DMF). Previous work in this laboratory indicated that DMF might not extract all the dieldrin present in soil (Saha *et al.*, 1969). This method extracted 78% of dieldrin-¹⁴C from a field-collected sandy loam soil, treated with dieldrin-¹⁴C in the same condition as received from the field.

The use of radioactive labeled compounds is perhaps the best way to determine the extraction efficiency of a given process (Gunther, 1962; Saha, 1968; Wheeler and Frear, 1966). The validity of the fortification of soil with radioactive dieldrin to determine recovery was questioned by Chiba and Morley (1968). They added dieldrin-¹⁴C to an air-dried sandy loam soil and recovered 91 to 96% of the added dieldrin-¹⁴C by five different solvent systems 2 days after fortification of the soil. The same solvents extracted only 36 to 67% of the dieldrin present in the same soil but resulting from aldrin application in the field. Work in this laboratory has also shown that air-dried soils treated with dieldrin-¹⁴C and stored in air-dried condition cannot be used for determining extraction efficiencies of field samples (Saha *et al.*, 1969), but true estimates of dieldrin recovery rates can be obtained if the air-dried, fortified soils are kept at near field moisture level for several months before redrying and extraction.

The object of the investigation reported was to study the factors influencing the extraction of dieldrin from soil and to find a method that would give close to 100% recovery. Soils treated with dieldrin-¹⁴C in the air-dry state but stored for 6 to 8 months with 20% water and subsequently air-dried were used to study recovery efficiencies of various solvents and methods.

EXPERIMENTAL

The dieldrin-¹⁴C (specific activity 72 mc. per mmole) was purchased from the Radiochemical Centre, Amersham, England. The material was analyzed by thin-layer and gas-liquid chromatography and was at least 99% pure.

Soil Treatment. Twelve soils of nine different classifications were used for these experiments. Partial analyses of the soils are given in Table I. Soil samples 1 to 8 were air-dried at room temperature and screened through a 20-mesh screen. Samples 9 to 12 were collected from farms in southwestern Saskatchewan and treated with dieldrin-¹⁴C in the condition in which they were received from the field.

Dry Soils. Two hundred grams of each soil (1 to 3 and 5 to 8) in the air-dried state were added to 4000 millimicrocuries of dieldrin-¹⁴C in 150 ml. of pentane and the solvent was removed in a flash evaporator. Each treated soil was mixed thoroughly by tumbling for 8 hours. One hundred grams of each treated soil were stored in the air-dried state in stoppered bottles for 6 to 8 months before they were used for extraction with solvents. These soils are referred to as dry soils (Table II).

Moist Soils. The remaining 100 grams of each soil treated with dieldrin-¹⁴C were mixed thoroughly with 20 ml. of water and stored in stoppered bottles for 6 to 8 months. These soils are referred to as moist soils (Table II).

Field Soils. An aqueous suspension of dieldrin-¹⁴C was prepared by shaking 4000 millimicrocuries of dieldrin-¹⁴C in 1 ml. of acetone with 10 ml. of water containing 1% Triton X-100 (Rohm and Haas). About 230 grams of each soil (9 to 12) as received from field were spread in a 1-inch layer on an aluminum foil. The aqueous suspension of dieldrin-¹⁴C was then sprayed onto the soil with a 125-ml. reagent sprayer bottle, mixed thoroughly, and stored in a stoppered bottle for 6 to 8 months. Soils treated in this way are referred to as field soils (Table VI).

Greenhouse Soil. One thousand grams of air-dried soil (No. 4) were added to 50 μ c. of dieldrin-¹⁴C in 400 ml. of pentane and the solvent was removed in a flash evaporator. This treated soil was then packed into crocks and used for one year for growing wheat plants and carrots in the greenhouse.

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Table I. Partial Analysis of Soils Used in Experiments

Soil No.	Soil Type	Surface Area, Sq. M./G.	Organic Matter, %C × 1.724	% Oven-Dried Weight after Removal of Organic Matter		
				Sand, 0.05	Silt, 0.05-0.002	Clay, <0.002
1	Heavy clay	367.0	1.3	7.0	25.0	68.0
2	Silty clay loam	322.5	2.0	3.6	41.2	55.2
3	Silty clay	241.4	1.6	0.9	58.9	40.2
4	Clay loam-loam (greenhouse)		5.1	27.7	44.9	27.4
5	Loam	103.1	7.1	34.8	41.0	24.2
6	Sandy loam	98.5	3.6	64.9	23.6	11.5
7	Loamy sand	34.6	3.8	87.3	6.3	6.4
8	Muck		57.5	25.2	32.1	42.6
9	Heavy clay		2.6	5.9	26.9	67.1
10	Silty clay		3.3	6.0	43.7	50.3
11	Clay loam		3.0	24.1	43.6	32.4
12	Sandy loam		2.9	62.1	19.3	18.6

Table II.^a Effect of Soil Type on the Extraction of Dieldrin-¹⁴C by Various Solvents

^b% Recovery of Dieldrin-¹⁴C (Based on Total Radioactivity in Soil Determined by Van Slyke Method)

Solvent	Soil 1 (Heavy Clay)		Soil 2 (Silty Clay Loam)		Soil 3 (Silty Clay)		Soil 4 (Clay Loam- Loam- Greenhouse)	Soil 5 (Loam)		Soil 6 (Sandy Loam)		Soil 7 (Loamy Sand)		Soil 8 (Muck)	
	Dry	Moist	Dry	Moist	Dry	Moist	Moist	Dry	Moist	Dry	Moist	Dry	Moist	Dry	Moist
	Hexane	32.4	18.3	45.0	15.4	50.6	17.0	17.8	61.4	14.0	68.0	12.3	72.0	9.0	76.3
Hexane-acetone (9:1)	97.9	68.2	99.8	58.9	99.4	45.4	40.8	93.5	42.7	83.9	35.7	85.6	36.2	95.8	26.2
Hexane-acetone (1:1)	86.5	76.9	100.0	62.7	100.0	57.9	49.1	95.8	48.7	84.4	42.2	84.6	38.3	97.5	31.7
Hexane-2-propanol (1:1)	92.6	52.2	91.4	51.4	78.6	49.7	37.3	90.0	41.5	80.8	32.1	80.8	21.7	86.6	21.7
Hexane-2-propanol (2:1)	99.4	64.2	96.3	56.2	97.8	50.8	37.2	79.1	38.4	68.7	22.1	64.8	18.9	81.5	19.0
Acetonitrile	91.0	67.7	93.2	66.0	90.6	57.4	46.7	92.5	41.5	91.4	43.4	94.3	36.1	97.5	23.8
20% water + hexane	69.0	77.5	76.5	73.6	82.6	78.3	62.1	75.0	65.1	61.4	64.9	51.0	65.8	70.0	24.5
20% water + hexane-2-propanol (1:1)	97.1	90.6	96.3	97.3	97.2	90.8	94.0	96.6	90.2	88.9	94.0	91.5	91.0	97.0	64.6 (99.0) ^c
Hexane-acetone (1:1), Soxhlet	100.0	90.0	98.6	83.6	100.0	82.4	61.7	96.8	62.0	95.8	57.9	99.5	54.4	98.3	46.3
Chloroform-methanol (1:1), Soxhlet	100.0	99.5	100.0	100.0	99.9	99.7	100.0	99.3	99.7	100.0	100.0	100.0	99.8	100.0	100.0

^a For definition of dry and moist soil see experimental.

^b Average of duplicate extractions. Total error in extraction and counting radioactivity, ±4%.

^c 80% water used.

At the end of the storage period all the moist, field, and greenhouse soils were air-dried at room temperature, screened through a 20-mesh screen, and mixed thoroughly by tumbling for 8 hours (Tables II to V).

Soils of Different Particle Size. A portion of the air-dried greenhouse soil treated with dieldrin-¹⁴C was screened through 40-, 60-, 80-, and 100-mesh screens and the fraction retained on each screen was used for extraction of dieldrin-¹⁴C by the methods described below. The total radioactivity present in each fraction was also determined by the method described below.

Solvents. The hexane, 2-propanol, acetone, methanol, acetonitrile, and chloroform were nanograde solvents (Burdick and Jackson Laboratories, Inc.). All other solvents and reagents were analytical reagent grade.

Extraction Methods. All soils were air-dried prior to extraction with solvents. Moisture content of the soils after air-drying was 1 to 3% for all soils except the muck soil, which had 6% water.

MECHANICAL SHAKER. An accurately weighed amount (2 grams) of soil was shaken for 1 hour with 10 ml. of the extracting solvent and allowed to stand for 10 minutes. The supernatant liquid was filtered and the residue re-extracted

twice, in the same way, with 10 ml. of solvent each time but with only 10 minutes' shaking. The combined filtrate was concentrated to about 15 ml. on a film evaporator, and transferred to a 25-ml. volumetric flask. One-millimeter aliquots of the extracts were counted in duplicate in a scintillation counter for total radioactivity present in the sample.

DMF and dimethylsulfoxide (DMSO) extracts were partitioned into petroleum ether and water. The petroleum ether layer was dried (Na₂SO₄), concentrated to about 15 ml., and transferred to 25-ml. volumetric flasks and 1-ml. aliquots were counted for total radioactivity in a scintillation counter.

SOXHLET. Two grams of soil were extracted in a micro-Soxhlet extractor with 15 ml. of the solvent mixture for 8 hours. The heating was adjusted to take about 3 minutes to complete one cycle. The extracts were transferred to 25-ml. volumetric flasks and 1-ml. aliquots were counted in a scintillation counter.

ULTRASONIC VIBRATION. Two grams of soil were added to 10 ml. of hexane-2-propanol (1 to 1) in an Erlenmeyer flask and placed in an ultrasonic cleaner for 1 hour. The supernatant liquid was filtered and the residue extracted twice with 10 ml. of solvent each time. Ultrasonic vibration was applied for only 10 minutes.

Table III. Effect of Soil Particle Size on Recovery of Dieldrin-¹⁴C from Clay Loam-Loam Soil (4) by 1-to-1 Hexane-2-Propanol (Mechanical shaker)

Mesh Size	% Recovery of Dieldrin- ¹⁴ C (Based on Total Radioactivity Present in Soil Fraction Determined by Van Slyke Method)
40-60	16.0
60-80	21.0
80-100	25.4
-100	55.7
Whole soil in ball mill	68.0
Whole soil	37.3

Table IV. Effect of Solvent Polarity^a and Solubility of Dieldrin in Solvent on the Extraction of Dieldrin-¹⁴C from Greenhouse Soil

(Clay loam-loam, 4)

Solvent	Dipole Moment $\mu \times 10^{18}$ E.S.U.	Dielectric Constant	Solubility ^b of Dieldrin in 100 ml. Solvent, G.	% Recovery ^c of Dieldrin- ¹⁴ C
Hexane	0.0	1.89	...	17.8
Dioxane	0.0	2.20	...	22.8
Carbon tetrachloride	0.0	2.24	48.0	20.6
Benzene	0.0	2.28	56.0	27.1
Chloroform	1.02	4.81	...	41.0
Ethyl acetate	1.78	6.02	...	51.6
Methylene chloride	1.54	9.08	...	55.7
2-Propanol	1.60	18.30	2.0	43.8
Acetone	2.88	20.70	26.0	67.3
Ethanol	1.70	24.30	4.0	73.7
Methanol	1.70	33.62	1.0	89.2
Dimethylformamide	...	37.00	...	86.0
Acetonitrile	3.84	37.50	...	46.7
Dimethyl sulfoxide	...	45.00	...	94.0

^a Dipole moments and dielectric constant values largely taken from "Handbook of Chemistry and Physics" (1962).

^b Taken from Porter (1964).

^c Average of duplicate extractions and based on total radioactivity present in soil as determined by Van Slyke method.

HIGH SPEED BLENDER. Two grams of soil were blended with 15 ml. of solvent for 5 to 15 minutes. The mixture was filtered with suction using Whatman No. 1 filter paper and a 1-cm. pad of Super Cel. The container was rinsed twice with 5 ml. of solvent each time. The soil, filter paper, and pad were returned to the blender and the extraction procedure was repeated. The combined filtrate was concentrated to about 15 ml. and transferred to 25-ml. volumetric flasks. One-milliliter aliquots were counted in a scintillation counter for total radioactivity.

BALL MILL. The method was similar to that used for the determination of oil in oil seeds by the Swedish ball mill method (Troeng, 1955). Two grams of soil were placed in Swedish tubes, together with four large steel balls and 15 ml. of the solvent. The tubes were then stoppered and shaken horizontally (Eberback shaker unit, 240 strokes per minute) for 1 hour. The contents were filtered and the container was rinsed three times with 5 ml. of solvent each time. The combined extract was concentrated to about 15 ml. and transferred to 25-ml. volumetric flasks. One-milliliter aliquots were counted in a scintillation counter.

EXTRACTION OF SOILS IN PRESENCE OF WATER. To study the effect of water on the recovery of dieldrin-¹⁴C, 0.4 ml. of water was added to 2 grams of air-dried soil and mixed

Table V. Effect of Extraction Method on Recovery of Dieldrin-¹⁴C from Greenhouse Soil (4) with Hexane-2-Propanol (1:1)

Method No.	Description	% Recovery ^a of Dieldrin- ¹⁴ C	
		Air-dry soil	Air-dry soil + 20% water
1	Mechanical shaker, 1 hr.	37.3	94.0
2	Ultrasonic vibration, 1 hr.	49.8	97.0
3	Ball mill, 1 hr.	68.0	97.2
4	Blending, 5 min.	37.5	90.0
5	Blending, 15 min.	42.0	92.0
6	19-hr. contact with solvent, mechanical shaker, 1 hr.	43.0	93.0
7	19-hr. contact with solvent, blending, 5 min.	45.0	96.0

^a Average of duplicate extractions and based on total radioactivity determined by Van Slyke method.

Table VI. Recovery of Dieldrin-¹⁴C from Different Types of Field Soils (Mechanical Shaker Extraction) in Presence of 20% Water

Soil No.	Soil Type	Extraction Solvent		
		1:1 hexane-2-propanol ^b	1:1 hexane-acetone ^b	1:1 benzene-methanol
9	Heavy clay	95.7	94.2	95.1
10	Silty clay	93.2	98.0	95.9
11	Clay loam	91.7	93.1	94.1
12	Sandy loam	95.0	95.2	93.8

^a Based on total radioactivity present in soil as determined by Van Slyke method.

^b Taken from Saha *et al.*, 1969.

thoroughly and the wet soil was extracted with solvents as described previously. To study the effect of time of contact with water on the recovery of dieldrin-¹⁴C, 0.4 ml. of water was added to 2 grams of soil, mixed thoroughly, and allowed to stand at room temperature in stoppered flasks for up to 72 hours. The solvent mixture was added to the wet soils at the end of a specified contact time and extracted by methods described before. For routine extractions of soils in the presence of water about 5 to 10 minutes elapsed between the addition of water and extraction solvent (Tables II, V, and VI).

All extraction experiments were carried out in duplicate.

Determination of Total Radioactivity in Soil. The procedure for the determination of the total amount of radioactivity present in soil by Van Slyke wet combustion method has been described (Saha *et al.*, 1969).

Radioactivity was determined in a Beckman Model LS-100 scintillation counter using the channel ratio method. Aliquots of extracts were counted in either 0.4% PPO in toluene solution or dioxane containing 5% naphthalene and 0.6% PPO. The statistical error involved in counting radioactivity was 2 to 3% and counting efficiencies were 80 to 90%.

Determination of Surface Area of Soils. Total surface area of soil particles was determined by the equilibrium ethylene glycol method of Bower and Goertzen (1959). About 1 gram of soil (in the condition used for extraction experiments) was dried over P₂O₅ in a vacuum desiccator for 5 to 7 hours until it reached constant weight. The dry soil was then wetted with 1 ml. of pure ethylene glycol and placed

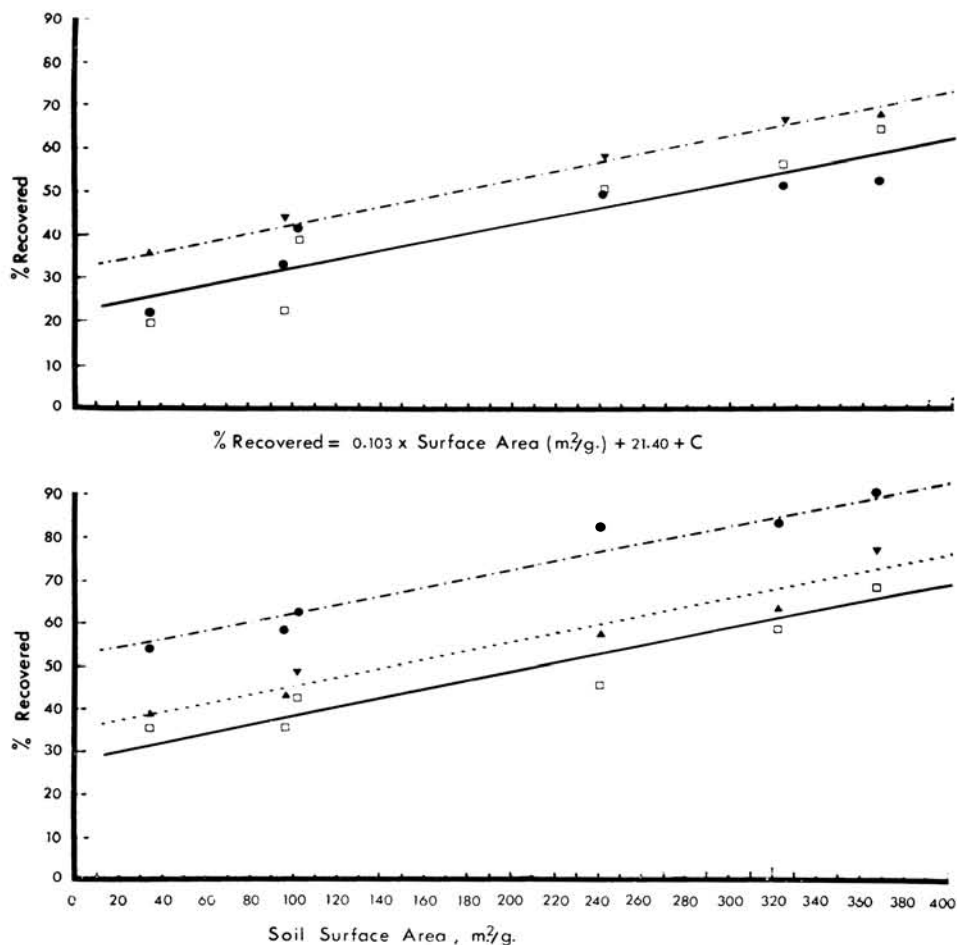


Figure 1. Effect of surface area on recovery of dieldrin-¹⁴C

	<i>Upper</i>	<i>Lower</i>
C	C	C
0.00 ● 1:1 hexane-2-propanol 0.34 □ 2:1 hexane-2-propanol 10.59 ▼ Acetonitrile	(Shaker) ——— (Shaker) - - -	30.32 ● 1:1 hexane-acetone (Soxhlet) - - - - 13.02 ▼ 1:1 hexane-acetone (Shaker) - - - - 6.40 □ 9:1 hexane-acetone (Shaker) ———

in a vacuum desiccator containing anhydrous calcium chloride at 0.02 mm. of Hg. While in the desiccator under reduced pressure the excess glycol distilled from the soil and was absorbed by calcium chloride. The vacuum was released after 16 hours and the sample weighed and kept under vacuum again. The process of distillation of excess glycol from the soil was continued and the weight of the soil was checked every 8 to 16 hours until there was no further loss in weight, indicating that only a monolayer of glycol remained in the soil. The surface area of the soil was then calculated from Equation 1.

$$A = W_g/W_s \times 0.00031 \quad (1)$$

where A = surface area (square meters per gram), W_g = weight (grams) of glycol retained by the sample, W_s = weight (grams) of sample on P₂O₅-dried basis, and 0.00031 = grams of glycol required to form a monolayer on 1 sq. meter of surface.

RESULTS AND DISCUSSION

Saha *et al.* (1969) showed that extraction efficiencies obtained from soils treated with dieldrin-¹⁴C in the air-dried state and stored in the same condition do not represent the true abilities of solvents to extract field-applied dieldrin. However, soils treated in the air-dried state and stored for 6 to 8 months with 20% water (near field moisture level) gave extraction efficiencies similar to those obtained from soils in

the state as received from field and treated with dieldrin-¹⁴C (Saha *et al.*, 1969). Thus the percentage recovery of dieldrin-¹⁴C from the moist soils (Table II) would closely reflect the abilities of solvents to extract field-applied dieldrin from field samples.

More dieldrin was extracted from the dry than from the moist soils (Table II) when no water was added to the soils prior to extraction with solvents. This again demonstrates that soils treated with dieldrin in the air-dried state and stored and extracted in the same condition cannot be used for recovery studies. Both dry and moist soils were extracted in the air-dry state. The lower recovery of dieldrin from the moist soils may be due to the fact that air drying before extraction binds the dieldrin strongly to the soil. Apparently no such strong binding of dieldrin with soil occurred when the soil was treated with dieldrin in the air-dried condition and stored in the same state. Addition of water to air-dried moist soil desorbed dieldrin, which could then be easily extracted by hexane-2-propanol (90 to 97% efficiency). The strong ability of water to desorb dieldrin was demonstrated by hexane extractions. Hexane can recover only 9 to 18% of the dieldrin present in moist soils when these are air-dried before extraction. When 20% water was present in the soils at the time of extraction, 65 to 78% of the dieldrin could be recovered by hexane extraction. Addition of 20% water was not enough to desorb all the dieldrin in the muck soil. The water content had to be increased to 80% before 99%

of the dieldrin could be recovered by extraction with 1 to 1 hexane-2-propanol.

Since dieldrin extraction efficiencies obtained with moist soils would closely reflect the true abilities of solvents to extract field-applied dieldrin (Saha *et al.*, 1969), the following discussion on the factors affecting the extraction of dieldrin from soil is based on the results obtained with moist soils. Since the greenhouse soil was used for one year for growing plants, it was used for most studies on factors affecting extraction.

Effect of Soil Type and Surface Area of Soils. Commonly used solvents such as hexane-acetone, hexane-2-propanol (in the absence of water), and acetonitrile (Decker *et al.*, 1965; Saha and McDonald, 1967; Stewart *et al.*, 1965) extracted 38 to 68% of the dieldrin present in soils with a clay content greater than 24% but only 19 to 49% from soils with less than 12% clay content. Exhaustive extraction in Soxhlet with 1 to 1 hexane-acetone did not extract all the dieldrin present in moist soils but gave higher recovery efficiencies with increasing clay content. It is possible that this reflects the increase in surface area which is a consequence of a higher clay content.

The effect of surface area of soil on the recovery of dieldrin-¹⁴C from the moist soils was estimated by regression analysis of the data presented in Table II. Recoveries with mixtures of hexane-acetone and hexane-2-propanol, acetonitrile, and 1 to 1 hexane-acetone in a Soxhlet apparatus were used for regression analysis. Linear relationship between surface area and percentage dieldrin recovered by these solvents gave a regression coefficient of 0.98 and the resulting equation:

$$\% \text{ recovered} = 0.103 \times A + 21.40 + C \quad (2)$$

where A is surface area of soil in square meters per gram and C is a constant, accounted for 96% of the variation within solvents. Variation between solvents is given by C , which has a different value for each solvent system. Thus the value of C determines the relative extraction efficiencies of the solvents. Soxhlet extraction with 1 to 1 hexane-acetone has the highest extraction efficiency (Figure 1, $C = 30.32$), followed by 1 to 1 hexane-acetone extraction ($C = 13.02$) in a mechanical shaker. The efficiencies of the other solvents are in the order: acetonitrile ($C = 10.59$) > 9:1 hexane-acetone ($C = 6.4$) > 2 to 1 hexane-2-propanol ($C = 0.34$) > 1:1 hexane-2-propanol ($C = 0.0$). Hexane-2-propanol (2 to 1) appeared to give higher recoveries than 1 to 1 hexane-2-propanol (Table II) from heavy clay, silty clay, and silty clay loam soils. But regression analysis of the data showed that these differences were not significant because of the $\pm 4\%$ error in extraction and counting radioactivity in extracts. These two solvent systems had very nearly the same extraction efficiencies. All solvents gave poor recovery of dieldrin from the muck soil and much less dieldrin than expected from the high surface area of this soil.

This linear relationship between extraction efficiency and surface area suggests that extraction efficiencies might be improved by a reduction in particle size, thus increasing the surface area. This was shown by the extraction of the greenhouse soil with 1 to 1 hexane-2-propanol (Table III). As the soil particle became smaller, more dieldrin could be extracted. Only 37% of the dieldrin could be recovered by extraction of the whole soil on a mechanical shaker, but the grinding effect of the ball mill process, in reducing particle size, increased this to 68%.

Effect of Solvent Polarity. The effect of solvent polarity on the extraction of dieldrin-¹⁴C was studied with 14 pure sol-

vents and the greenhouse soil (Table IV), using the mechanical shaker extraction method. Nonpolar solvents extracted less dieldrin than polar solvents as a group but, within the polar group, there was no correlation between dipole moment and extraction efficiency. Thus acetonitrile with dipole moment 3.84 extracted only 46.7% as compared to 89.2% for methanol ($\mu = 1.70$) or 73.7% for ethanol ($\mu = 1.70$), or 55.7% for methylene chloride ($\mu = 1.54$). Again methanol, ethanol, and 2-propanol having nearly the same dipole moments gave widely different recoveries of dieldrin. The wide variations in the extraction efficiencies of these solvents were not related to the solubility of dieldrin in these solvents. Dieldrin is 48 and 56 times more soluble in carbon tetrachloride and benzene, respectively, than methanol. But methanol extracted 89% dieldrin in the soil, compared to 20.6 and 27.1% by carbon tetrachloride and benzene, respectively. Extraction of dieldrin from soil appeared to be related to the ability of the solvent to desorb dieldrin from soil, polar solvents being more effective than nonpolar solvents.

Lederer and Lederer (1957) stated that in column chromatography the eluting power of a solvent is not related to its dipole moment. However, Jacques and Mathieu (1946) showed that the eluting power of solvents is related to their dielectric constant. A similar relationship (Figure 2) exists between dielectric constant and the efficiency of a solvent in extracting dieldrin from soil. Regression analysis of the data presented in Table IV (dielectric constant *vs.* per cent recovery) gave a regression coefficient of 0.99 and Equation 3

$$\% \text{ recovered} = 1.055 e^{0.2263\epsilon} \quad (3)$$

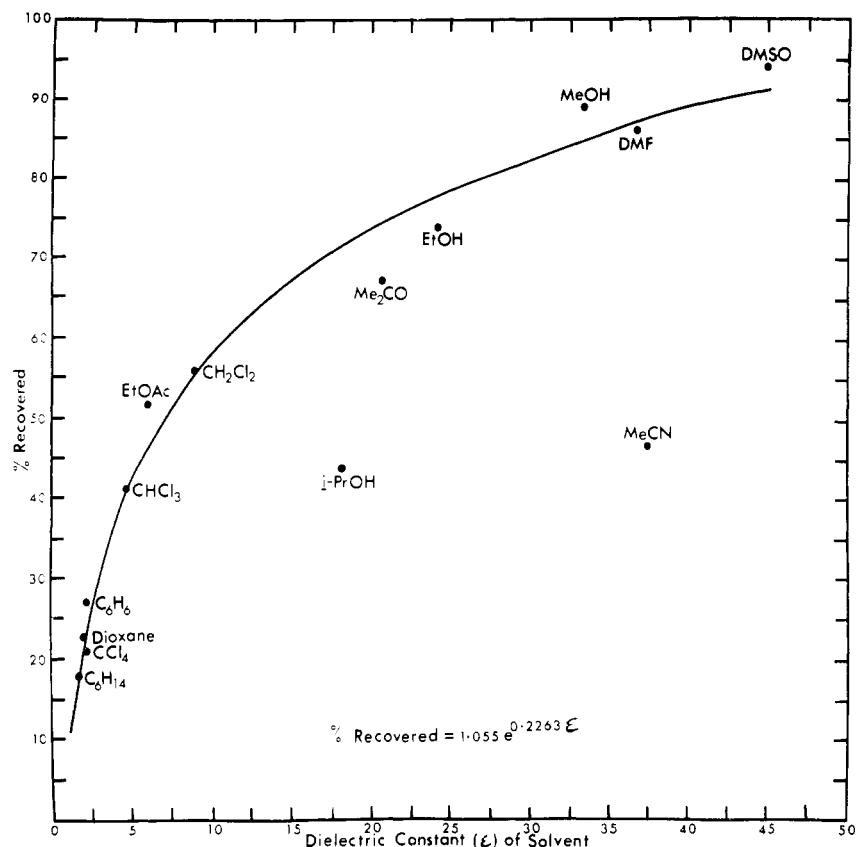
where ϵ is the dielectric constant of the solvent.

Acetonitrile and 2-propanol were exceptions to this generalization and were excluded from the regression analysis. These solvents extracted less dieldrin from soil than expected from their dielectric constants. Since the mechanism of adsorption of dieldrin by soil components is not known, the anomalous behavior of these two solvents cannot be explained.

Effect of Extraction Method. The method of extraction influenced the recovery of dieldrin from a given soil by a given solvent (Table V). An increase in the contact time with solvent increased the recovery efficiency when the soil was extracted in the air-dry state (compare efficiencies of method 1 *vs.* 6 and 4 *vs.* 7). Chiba and Morley (1968) also obtained higher extraction efficiencies with increased contact time. Blending for 15 minutes extracted more dieldrin than blending for 5 minutes. Ultrasonic vibration increased the extraction efficiency considerably. Extraction in a ball mill gave the highest recovery of dieldrin; this is perhaps due to an increase in the surface area of the soil. These different methods had little effect on the recovery of dieldrin when 20% water was present in the soil at the time of extraction by the solvent. The ability of water to desorb dieldrin from soil was so great that the effects of difference in methods of extraction were of little consequence.

Effect of Time of Contact with Water. The time interval between the addition of water to air-dried soil and extraction by solvent had little effect on the recovery of dieldrin. Almost the same amount of dieldrin (93 to 95%) was extracted from the soil, when the time of contact with water was increased from 5 minutes to 72 hours. The ability of water to desorb dieldrin must be related to its high dielectric constant ($\epsilon = 80.0$), a property by which the interaction between electrical charges is reduced (Hine, 1962). This also explains

Figure 2. Effect of dielectric constant of solvent on recovery of dieldrin-¹⁴C from soil



why solvents with higher dielectric constant extracted more dieldrin. There appears to be some kind of electronic interaction between dieldrin and some component(s) of soil, solvents with high dielectric constants being required to break the soil-dieldrin complex. The actual mechanism involved in this dieldrin-soil interaction is not clear and work should be done to investigate this.

Suggested Method for Extraction of Dieldrin from Soil. Exhaustive extraction in Soxhlet with 1 to 1 chloroform-methanol mixture is an effective method for recovering dieldrin from all soils. This method, however, is not recommended for routine determination of dieldrin in soil, as co-extractives are appreciable in Soxhlet extracts (Chiba and Morley, 1968) and can interfere in the determination of dieldrin by electron-capture gas chromatography. Extraction of moist soils as received from the field would give greater than 90% recoveries, but this is not recommended because of the difficulty in mixing wet soils so as to obtain a representative sample. Therefore, field samples should be air-dried, ground, and mixed, a representative sample taken, and then 20% water added immediately before extraction with solvents. Twenty per cent water is suggested, because this amount gave more than 90% recovery for all common types of soils. Up to 80% water should be added to muck soils, but the addition of more than 20% water to ordinary soils should be avoided, since in one case 30% or more water reduced the recovery rate (Saha, 1968). Once the dieldrin is desorbed, it can be extracted by a mixture of a polar and a nonpolar solvent. Three such solvent systems were compared for the recovery of dieldrin-¹⁴C from four types of field soils by the mechanical shaker method (Table VI). There was no significant difference between 1 to 1 hexane-2-propanol (92 to 96% recovery), 1 to 1 hexane-acetone (93 to 98% recovery), and 1 to 1 benzene-methanol (94 to 96% recovery). In this laboratory agitation of soil-solvent mixture on a mechanical shaker is

preferred, as it is simple and a large number of samples can be extracted simultaneously.

The results obtained here apply only to the extraction of dieldrin from soil. Similar studies with other organochlorine pesticides are under way.

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