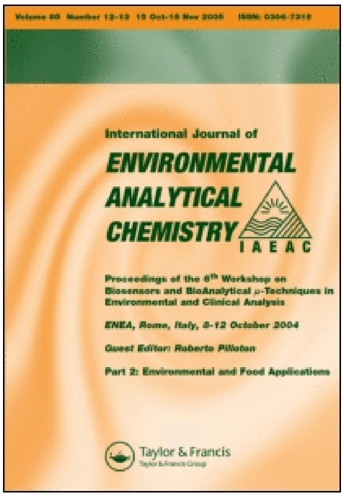

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Extraction of Residues of Dyfonate-ring-^{14}C from Soil[†]

(Key words: Dyfonate, Extraction, Soil, Residue)

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Residues of Dyfonate-ring-^{14}C were extracted from a clay loam soil with various solvents under a variety of conditions. Recovery of radioactivity from the soil was not related to the polarity (dipole moment) or the dielectric constant of the solvents. Commonly used solvents such as acetone, methanol, ethanol, and hexane/acetone (1:1) extracted only 28, 44, 27, and 25%, respectively, of the residues from the air-dried soil. The extraction efficiencies were increased to 46, 60, 54, and 49%, respectively, when 20% water was added to the soil prior to extraction with these solvents. The amount of water added to the soil and time of contact with water also affected the recovery of radioactivity from the soil. Any of the solvents or methods investigated failed to recover more than 60% of the radioactivity in the soil, indicating that residues of Dyfonate were strongly bound to the soil and were difficult to recover.

The organophosphorus insecticide Dyfonate (O-ethyl-S-phenyl-ethylphosphonodithioate) is effective as a soil insecticide to control wireworms in root crops[1–3] and several other soil-borne insects.[4] It has been shown that this

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insecticide persists in soil at least two years after application[5] and its residues are readily absorbed by root crops grown in treated soil.[5,6] It is thus necessary to develop methods for its determination in soils and plants.

Although numerous methods have been reported on the determination of residues of organophosphorus insecticides in crops, very few studies have been reported on their determination in soil. In the few instances where methods have been reported on the determination of organophosphorus insecticide residues in soil the extraction efficiencies have been determined by recovering known amounts of added insecticide to soil prior to extraction with solvent. However, experience with organochlorine insecticides has shown that such fortification techniques do not give an accurate measure of the abilities of solvents to extract field-applied insecticides.[7-9] The use of radioactive-labeled compound is perhaps the best way to determine the extraction efficiency of a given process.[8,10,11]

The object of the investigation reported here was to compare the efficiencies of several methods in recovering Dyfonate residues from soil and also to study some of the factors influencing the extraction of such residues.

EXPERIMENTAL

Ring-labeled Dyfonate-^{14}C (O-ethyl-S-phenyl-^{14}C(U)-ethylphosphonodithioate) was obtained from the Stauffer Chemical Co., Mountain View, California. The material was purified by preparative TLC on Silica Gel H using chloroform/hexane (2:3, v/v) as the solvent system and radioactive spots were detected by autoradiography. The purified material was reexamined by TLC and GLC using a flame photometric detector and was found to contain more than 99% Dyfonate. The purified material (94.6 μc) was mixed with 0.25 ml of a commercial formulation of Dyfonate containing 4 lb toxicant/gal (Dyfonate 4 E from the Stauffer Chemical Co.) and made up to 10.0 ml with acetone. The specific activity of the resulting mixture was measured by determining the Dyfonate and radioactivity content of an aliquot by gas chromatography and liquid scintillation counting, respectively. The specific activity of the resulting mixture was 0.72 μc/mg.

Soil Treatment

The soil used in this study was collected from a farm in Saskatchewan. It was a clay loam soil with 5.1% organic matter and 27.7, 44.9, and 27.4% calculated on organic matter and moisture-free basis sand, silt, and clay, respectively. An aqueous suspension of Dyfonate was prepared by adding 9.9 ml of the acetone solution of Dyfonate-ring-^{14}C (93.7 μc, sp. act. 0.72 μc/mg) to 50 ml of water. About 6,900 g of the soil (about 6,000 g air-dry weight) as received from the field was spread in a 2-in. layer on aluminum foil. The aqueous suspension of Dyfonate-ring-^{14}C was then sprayed on to the soil with a 125-ml reagent sprayer bottle and mixed thoroughly. The treated soil was then packed in plastic pots and wheat was grown in it for about two months in the greenhouse. At the end of this period when the wheat plants were harvested, the soil was air-dried at room temperature, screened through a 14-mesh screen, and mixed thoroughly by tumbling for 8 hr. This air-dried soil was used for all extraction studies.

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

Extraction methods An accurately weighed amount (ca. 10 g) of the air-dried soil was shaken in a mechanical shaker for 1 hr with 50 ml of the extraction solvent or the solvent mixture and allowed to stand for 10 min. The supernatant liquid was filtered and the residue was re-extracted twice in the same way with 10 ml of solvent each time but shaken for 10 min only. The combined filtrate was made up to 100 ml in a volumetric flask. The radioactivity content of the extract was measured by counting aliquots in duplicate in a scintillation counter.

To study the effect of water on the recovery of Dyfonate-^{14}C residues, appropriate amounts of water were added to 10 g of air-dried soil and mixed thoroughly, and the wet soil was extracted with solvents as described above.

To study the effect of time of contact with water on the recovery of Dyfonate-^{14}C residues, 2.0 ml water was added to 10 g of soil, mixed thoroughly, and allowed to stand at room temperature in stoppered flasks. The solvent mixture was added to the wet soils at the end of a specified contact time and extracted by the mechanical shaker method described before.

Ten grams of soil were blended with 50 ml of a 1 : 1 hexane/acetone mixture for 5 min. The mixture was filtered under suction using Whatman No. 1 filter paper. The container and the residue were washed twice with 10 ml of the solvent mixture. The combined filtrate was made up to 100 ml in a volumetric flask and aliquots were counted in duplicate in a scintillation counter.

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 the soil by the Van Slyke wet combustion method has been described earlier.[8] The evolved $^{14}CO_2$ was trapped in a mixture of phenethylamine-ethanol-toluene (1:2:1) solution and counted in a scintillation counter.

Radioactivity was determined in a Packard Tri-Carb Model 3320 liquid scintillation spectrometer, operating at 4°C. Aliquots of soil extracts were counted in 10 ml of scintillation fluid containing 4 g PPO, 0.5 g dimethyl POPOP and 50 ml Triton-X-100 per liter of toluene. For counting extracts of moist soil, a few drops of methanol were added when needed to make the sample homogeneous. Samples were chilled for 8–12 hr before reproducible count rates were obtained. Unquenched counting efficiency was approx. 80% and quench corrections for all samples were made by the channels ratio method.

Determination of Dyfonate and its Oxygen Analog by Gas Liquid Chromatography

A Beckman GC-5 gas chromatograph fitted with a Flame Photometric detector was used. The chromatographic column was a 2.5-ft glass tube, 1/8 in. i.d., packed with 100 to 120 mesh acid-washed DMCS-treated Chromosorb W coated with 0.8% Carbowax-20M followed by re-coating with 8% SE-30. The operating conditions were: column, injector, and detector temperatures 135°, 170°, and 160°C, respectively. The carrier gas was helium; flow rate 80 ml/min. Flow rates for hydrogen, air, and oxygen were 150, 80, and 20 ml/min, respectively. Under these conditions retention times of Dyfonate and its oxygen analog were 9.0 and 7.0 min, respectively. The concentrations of Dyfonate and its oxygen analog in the soil extracts were determined by comparing the peak heights with those of the standards.

RESULTS AND DISCUSSION

The effect of the solvent polarity on the recovery of ^{14}C-labeled residues from the soil treated with Dyfonate-^{14}C was studied with 13 solvents (Table I) using the air-dried soil. Non-polar solvents extracted less residues than polar solvents as a group but, within the polar group, there was no correlation between dipole moment and extraction efficiency. Thus, acetone and acetonitrile, both having a higher dipole moment than that of methanol, extracted much less residues. Again ethanol and methanol, both having the same dipole moment, extracted 27 and 44% of the radioactivity present in the soil, respectively.

There was also no relation between the dielectric constants of the solvents and their abilities to recover residues of Dyfonate-^{14}C from the soil (Table I). Thus, dimethyl-formamide, acetonitrile, and dimethyl sulfoxide, all having higher dielectric constants than that of methanol, extracted much less

TABLE I

Effect of solvent polarity[a] on the extraction of residues of Dyfonate-ring-^{14}C from a clay loam soil

Solvent	Dipole moment $\times 10^8$ E.S.U.	Dielectric constant	Recovery[b] of ^{14}C-containing residues (%)
Hexane	0.0	1.89	9.1
Dioxane	0.0	2.20	13.5
Benzene	0.0	2.28	14.0
Chloroform	1.02	4.81	16.9
Ethyl acetate	1.78	6.02	17.0
Methylene chloride	1.54	9.08	18.9
2-Propanol	1.60	18.30	17.9
Acetone	2.88	20.70	27.8
Ethanol	1.70	24.30	26.8
Methanol	1.70	33.62	43.8
Dimethylformamide	—	37.00	32.8
Acetonitrile	3.84	37.50	28.8
Dimethyl sulfoxide	—	45.00	31.8

[a] Dipole moments and dielectric constant values largely taken from *Handbook of Chemistry and Physics.*[12]

[b] Average of duplicate extractions and based on total radioactivity present in soil as determined by the Van Slyke method.

residues. Maximum residues (44%) were extracted by methanol, and efficiencies of commonly used solvents such as acetone, ethyl acetate and acetonitrile were poor indeed.

A mixture of hexane and acetone (1:1) is commonly used for the extraction of insecticide residues from soil. This solvent mixture extracted only 25% of the radioactivity present in the air-dried soil (Table II). Whether the soil was extracted with the solvent mixture in a mechanical shaker or macerated in a blender the extraction efficiencies were similar. The extraction efficiencies were increased in both methods to about 33% when the soil was kept in contact with the solvent mixture for 18 hr.

Addition of water (20%, w/w) to the air-dried soil prior to extraction with solvent(s) increased the recovery of residues considerably (Table III). Only 9% of the radioactivity was recovered by hexane when the soil was extracted in the air-dried condition and addition of 20% water to the soil increased the extraction efficiency to about 29%. Similarly, extraction efficiencies of acetone, methanol, ethanol, and hexane/acetone (1:1) were increased by the addition of 20% water to the air-dried soil. Highest recovery of residues

TABLE II

Effect of extraction method on the recovery of residues of Dyfonate-ring-^{14}C from a clay loam soil with hexane/acetone (1:1)

Method No.	Description	Recovery[a] of ^{14}C-containing residues (%)
1	Mechanical shaker, 1 hr	25.2
2	Contact with solvent for 18 hr, mechanical shaker, 1 hr	32.9
3	Blending, 5 min	25.6
4	Contact with solvent for 18 hr, blending 5 min	32.8

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

TABLE III

Effect of addition of water (20%, w/w) to air-dried-soil on the recovery of ^{14}C-containing residues by various solvents

Solvent	Water added to soil (%)	Recovery[a] of ^{14}C-containing residues (%)
Hexane	0	9.1
	20	28.8
Acetone	0	27.8
	20	46.0
Methanol	0	43.8
	20	60.3
Ethanol	0	26.8
	20	53.6
Hexane/acetone (1:1)	0	25.2
	20	48.8

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

(60%) was obtained by methanol, followed by ethanol (54%), hexane/acetone (49%) and acetone (46%) when the soil was extracted with these solvents after the addition of 20% water.

The effect of the addition of different amounts of water to the air-dried soil on the recovery of residues of Dyfonate-^{14}C is given in Table IV. There was a sharp increase in the extraction efficiency of hexane/acetone (1:1) when only 10% water was added to the air-dried soil. Although addition of more water to the soil recovered more residues, the increase in the extraction efficiency was less pronounced. Thus increasing the amount of water from 10 to 100% increased the extraction efficiency of this solvent mixture from about 44 to 56%.

TABLE IV

Effect of the amount of water added to air-dried-soil on the recovery of ^{14}C-containing residues by hexane/acetone (1:1)

Water added (w/w) (%)	Recovery[a] of ^{14}C-containing residues (%)
0	25.2
10	44.4
20	48.8
30	47.6
40	48.9
50	51.6
100	55.5

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

The time of contact with water prior to extraction of the soil with hexane/acetone (1:1) apparently affected the extraction efficiency (Table V). Increasing the time of contact with water from 0 to 10 min increased the extraction efficiency from 40 to 49%. Highest recovery of residues was obtained when the time interval between the addition of water to air-dried soil and extraction by the solvent mixture was 30 min. Further increase in the time of contact appeared to decrease the extraction efficiency without any apparent reason.

The efficiencies of the various solvents and methods were determined by comparing radioactivity in the extracts with that in the soil as obtained by the wet combustion of the soil by the Van Slyke method. Thus the radioactivity in the various soil extracts may be due to Dyfonate and/or its degradation products. McBain *et al.*[6] showed that Dyfonate is readily metabolized by potato plants. Schulz and Lichtenstein[5] detected only Dyfonate in the extracts of soil treated in the field with this insecticide, indicating that Dyfonate is either not degraded in the soil or the degradation products could not be extracted and detected by the methods used by these investigators.

TABLE V

Effect of time of contact with water (20%, w/w) on the recovery of ^{14}C-containing residues by 1:1 hexane/acetone (mechanical shaker extraction)

Time of contact	Recovery[a] of ^{14}C-containing residue (%)
Immediately	40.1
10 min	48.8
30 min	54.7
4 hr	51.8
16 hr	47.7
24 hr	47.5

[a] Average of duplicate analysis and based on total radioactivity determined by the Van Slyke method.

In the present study acetone, methanol, ethanol, and hexane/acetone (1:1) extracts of the soil in the presence of 20% water (Table III) were examined by gas chromatography, using a flame photometric detector. Only Dyfonate was detected in these extracts by using either the phosphorus or the sulfur filter in the flame photometric detector and about 80–87% of the radioactivity in these extracts was present as Dyfonate and no oxygen analog was detected. These extracts were also examined by TLC on Silica Gel H, developed in chloroform/ethyl acetate (1:1) and the radioactive spots were detected by autoradiography. McBain *et al.*[6] separated Dyfonate and seven of its degradation products by this method. However, the soil extracts showed one major radioactive spot representing Dyfonate and two other minor products of unknown identity. Thus these solvents extracted mainly Dyfonate and very little of the degradation products.

The highest amount of radioactivity recovered by any solvent or method used in this study was only 60%, obtained by extraction with methanol after the addition of 20% water to the soil (Table III). Attempts to recover more radioactivity by treatment of the soil with mild acid or alkali, before extraction with methanol, were unsuccessful, indicating that Dyfonate residues were strongly bound to the soil. These results are in contrast with those obtained in a previous study with dieldrin-^{14}C,[9] where 92 to 98% of the residues present in various mineral soils could easily be extracted with hexane/acetone (1:1) in the presence of 20% water. Further work is required to develop a method of extracting all the residues of Dyfonate from soil and to identify the degradation products.

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