Comparison of Several Methods for Extracting Dieldrin-C^{14} From Soil[1]

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A number of solvents and combination of solvents have been used in the past to extract residues of organochlorine pesticides from soil (1-5). The extraction efficiencies of these solvents have been expressed usually as percentage recovery of a specific pesticide from a fortified ("spiked") sample. It has been pointed out, however, that such fortification studies do not give an accurate measure of the abilities of solvents to extract field-applied

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pesticides (6,7). Recently two attempts have been made to compare the efficiencies of several solvents in extracting organochlorine pesticide residues from soil. In the study of Collier, Cook, and Tardiff (8), soxhlet extraction with hexane:acetone (9:1) mixture was arbitrarily given 100% recovery efficiency and the efficiencies of several solvents were compared with this arbitrary standard. Chiba and Morley (9) also used this type of arbitrary standard to compare efficiencies of a number of solvent systems in extracting residues of field-applied pesticides. Neither of these studies prove that the "most efficient" solvent systems selected really extract 100% of the actual residue present in a weathered soil sample. The use of radioactive labeled compound is perhaps the only way to determine in absolute terms the extraction efficiency of a given process (6,7). This has been demonstrated by Mumma et al. (10) from their studies on the extraction of dieldrin-C^{14} from plants. Similar investigations with soil have not yet been reported in the literature.

This paper reports on the preliminary results on the efficiencies of several solvents to extract dieldrin-C^{14} from soil several months after treatment, and on the effect of water upon extractability.

Methods

Treatment of Soil with dieldrin-C^{14}

The dieldrin-C^{14} was provided by the Shell Development Co. and purified by thin layer chromatography. Radioautography was used to detect the radioactive dieldrin and labeled impurities.

The soil used in this investigation was a silt loam with 6% organic matter. One hundred grams of air dry soil was added to 600 mμc of dieldrin-C^{14} (specific activity 19.5 mc/mg) in 100 ml pentane and mixed thoroughly. The pentane was removed at room temperature; the soil air-dried and stored in a ground glass stoppered bottle at room temperature for four months. This treated soil is referred to as "dry soil" in the following pages.

Another 100 g of the same air dry soil was treated with 650 mμc of dieldrin -C^{14} in pentane, the solvent removed and the soil air dried. To simulate field moisture conditions, 20 ml of water was added to the soil and mixed as thoroughly as possible. The moist soil was then stored in a ground glass stoppered bottle at room temperature for four months. At the end of this period a portion of this soil was air dried and used for extraction studies. This soil is referred to as "wet soil" in the following pages.

Both the dry soil and wet soil samples used in this study were extracted in air dry condition because many soil extraction procedures are routinely carried out on air dry soil. Also, there was the difficulty of obtaining a small representative sample from moist soil because of problems encountered in mixing moist soil thoroughly.

Extraction Procedure

An accurately weighed amount (about 2 g) of the dieldrin-C^{14} treated soil was shaken for 1 hour with 10 ml of the appropriate solvent or solvent mixture 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 and filtered. The combined filtrate was evaporated to dryness in a rotary evaporator at 40-45°C. The residue was quantitatively transferred into counting vials with acetone and examined directly for total amount of radioactivity present in the sample. The different solvent systems used for this study were: 9:1 hexane-acetone (1), 1:1 hexane-acetone (2), 2:1 hexane-isopropanol (3), 1:1 hexane-isopropanol (5), acetonitrile (4), and 1:1 chloroform-methanol (10).

In the study of the effect of water on the

extractability of dieldrin from soil hexane-isopropanol (1:1) was chosen as the solvent. An accurately weighed amount of "dry soil" was mixed thoroughly with appropriate amount of water (Table 2) and allowed to stand at room temperature for 24 hours. At the end of this period the samples were extracted with hexane-isopropanol (1:1) in the same way described above.

The total amount of radioactivity present in the extracts was counted in Toluene solution with a Nuclear Chicago Mark 1 liquid scintillation counter. Counting efficiencies of the extracts were between 78 and 85%. The total amount of radioactivity present in each soil was determined by oxidation of the organic matter in the air dry soil to CO_2 by van Slyke method and determining $C^{14}O_2$.

Results and Discussion

It is recognized that the conditions under which the soil samples were treated and stored in the present study are not the same as those to which field-applied residues are exposed, even when the soil was treated with water at field moisture level. Cost of C^{14}-labeled dieldrin and possible hazards from its use in the field excluded application of

labeled dieldrin in the field.

Except for Soxhlet extraction and extraction with acetonitrile the other procedures gave less recovery of dieldrin from the soil left for 4 months with 20% water ("wet soil") than from the soil left in dry condition (Table I). Mixtures of hexane-isopropanol or hexane-acetone gave poor recoveries from the wet soil (58-65%). This would indicate that some biodegradation of dieldrin occurred in the wet soil and not in the dry soil and that these degradation products are more difficult to extract from soil than dieldrin itself. This aspect of biodegradation of dieldrin in soil is now under investigation.

It is interesting to note that increasing the acetone concentration in acetone-hexane mixture from 10 to 50% reduces the efficiency of extracting dieldrin from "wet soil" by about 7% whereas about 4% more dieldrin was extracted from this soil by increasing the iso-propanol concentration in hexane-iso-propanol mixture. These changes in solvent concentration caused little change in the efficiency of extracting dieldrin from dry soil, however. Acetone-hexane mixtures seem to be a better solvent than hexane-iso-propanol mixtures, at least for "dry soil". Acetonitrile, however, extracted the same

TABLE I

Recoveries of dieldrin-C^{14} from Soil by Different Solvents

Solvent(s)	Extraction Method	% Recovery[a] of dieldrin-C^{14} (based on total radioactivity present in soil as determined by oxidation to $C^{14}O_2$ by Van Slyke Method)	
		Wet Soil[b]	Dry Soil[c]
Hexane-acetone (9:1)	1 hour shaking	64.6	85.4
Hexane-acetone (1:1)	"	58.0	85.4
Hexane-i-PrOH (2:1)	"	58.0	74.5
Hexane-i-PrOH (1:1)	"	62.0	74.0
Acetonitrile	"	79.2	79.1
Methanol-Chloroform (1:1)	Soxhlet 8 hours	99.9	100.0

[a]Average of duplicate analyses

[b]Air dry soil treated with dieldrin-C^{14} and left at room temperature for 4 months with 20% water but air dried before extraction.

[c]Air dry soil treated with dieldrin-C^{14} and left at room temperature for 4 months in air dry condition.

amount of dieldrin from either dry or wet soil and for the wet soil extraction efficiency was higher than the mixed solvents when the shaking procedure was employed. Exhaustive extraction in a Soxhlet with a polar solvent mixture like chloroform-methanol was required to extract all the activity present in the soil. This procedure has also been found to give 100% recovery of dieldrin-C^{14} from plants (10).

It has been suggested that addition of some water helps to desorb organochlorine pesticides from soil (8). This has been confirmed by the present study. Addition of water to dry soil increased the efficiency of extraction by 1:1 hexane-iso-propanol mixture (Table II) up to 20% water in the soil, when 97% of the activity was recovered. Increasing the water content beyond this level decreased the extraction efficiency. The Shell method (11) of extraction of organochlorine pesticide residues from soil uses more than 100% water (based on the weight of the soil) to make a slurry before extraction with hexane-iso-propanol (3:1). It is perhaps not surprising to see that this method gives poor recovery (12). The reason for this decrease in recovery efficiency with more than 20% water is not clear and requires further study.

TABLE II

Effect of Water on the Recovery of dieldrin-C^{14} from Air Dry Soil with Hexane-i-PrOH (1:1)[a]

% Water added (based on weight of air dry soil)	% Recovery[b] of dieldrin-C^{14} (based on total radioactivity present in the soil)
0.0	74.0
10.0	84.0
20.0	97.0
30.0	87.0
100.0	80.0

[a]Soil was treated with dieldrin-C^{14} and left at room temperature for 4 months in air dry condition.

[b]Average of duplicate analyses.

The effect of soil type on the extractability of dieldrin-C^{14} by these solvents are now being studied and the results will be reported later.

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