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SOIL METHODS

Methods for Extracting Insecticides from Soil

JOHN I. TEASLEY and WILLIAM S. COX[1]

Southeast Water Laboratory, Department of the Interior, Athens, Ga.

Three separate extraction procedures for DDT- and endrin-contaminated soils were compared for reproducibility, as well as sample size and equipment needed. Two of the methods were developed by the authors; the third came from the Shell Development Manual of Method. The Immerex extractor is recommended because of its reproducibility, rugged equipment, and capability of handling large samples.

THE MILLIONS of pounds of insecticides used since the advent of DDT have mostly been used in agriculture. Because of their low water solubility and low vapor pressure, the majority of the chlorinated insecticides tend to persist in the soil—although sometimes as a metabolite or oxidation product, as in the case of DDE or dieldrin. These materials have been detected in surface waters (*4*).

Since the land is the major reservoir of these chemicals once they are applied, the determination of persistent insecticides in soils is of considerable interest from the standpoint of environmental health, as well as agriculture and wildlife conservation. Only comparatively recently, however, has general interest been shown in the amounts and types of pesticidal chemicals which tend to accumulate in the soil.

The big problem in soil residue studies is the collection of a truly representative sample of soil following such practices as tillage, crop rotation, and nonuniform application of chemicals. Major variations in soil type or soil series within a field would have obvious effects upon the analytical results of an insecticide study of the field.

The taking of representative soil samples has been discussed in detail by Lykken (*3*).

[1] Present address, Linden Laboratory, Atlanta, Ga.

From the analytical standpoint, the efficient extraction of the insecticides from the soil samples is a major problem. Soil samples, as submitted for analysis, may vary widely in moisture content; thus, it is usual to report results on an air-dried basis. Since many of the chlorinated organic insecticides are volatilized at temperatures as low as 50° C., the attempted removal of all moisture risks the loss of some of the insecticide content.

General methods for extracting insecticides from soil are not plentiful in the literature. The method of the Agricultural Division, Shell Development Co. (*5*) was used in this study. It has been compared to two other methods used by the authors during the past 3 years.

Methods

Reagents. All organic solvents are distilled, using all-glass distilling apparatus. The first 10% cut is discarded and the next 80% collected for use.

Petroleum ether, 30°–60° b.p. range.

Florisil, 60- to 100-mesh preactivated at 1200° F. Heat in 135° C. oven for 5 hours. Store in glass-stoppered bottles at 135° C. prior to use.

Apparatus. Gas chromatographic, Dohrmann Microcoulometric, Model C100 with a T-200S titration cell, and Micro Tek 2500R column oven.

Gas chromatographic column, 4-foot × 1/4-inch o.d., packed with 5% DC-200 (12,500 centistokes) on 80- to 90-mesh Anakrom ABS. Column temperature 180° C., gas flow N_2 at 100 cc. per minute.

Preparation of Sample. Air-dry the sample in a 9 × 9 × 2 inch, 2-quart borosilicate glass baking dish. When the soil is dry to the touch, reduce to a fine powder, using a grinding mill. Mix thoroughly and withdraw 100 grams for analysis.

EXTRACTION. Shell Development Co. Method. Weigh a representative sample (100 grams) into a 1000-ml. Erlenmeyer flask. Add enough distilled water to effect a slurry. Add 2 ml. of extraction solvent (*n*-hexane–isopropyl alcohol, 3+1) per gram of sample and shake vigorously for 20 minutes, using a wrist action shaker. Decant and collect the hexane phase into a separatory funnel. Repeat extraction of the mud-aqueous phase twice more, quantitatively decanting the hexane portions each time into the separatory funnel. Wash any remaining alcohol from the combined hexane extracts with water, dry over anhydrous sodium sulfate, and concentrate to 10 ml. or less.

Soxhlet Extractor Method. Weigh 100 grams of soil in an extraction thimble (Fisher, 123 × 43 mm.). Add 250 ml. of solvent (*n*-hexane–acetone, 9+1). Connect the extractor, and extract sample for 4 hours. Transfer the extracting solvent to a 500-ml. Kuderna-Danish evaporator with 3-ball Snyder column. Evaporate to 10 ml. or less.

Immerex Extractor Method. Weigh

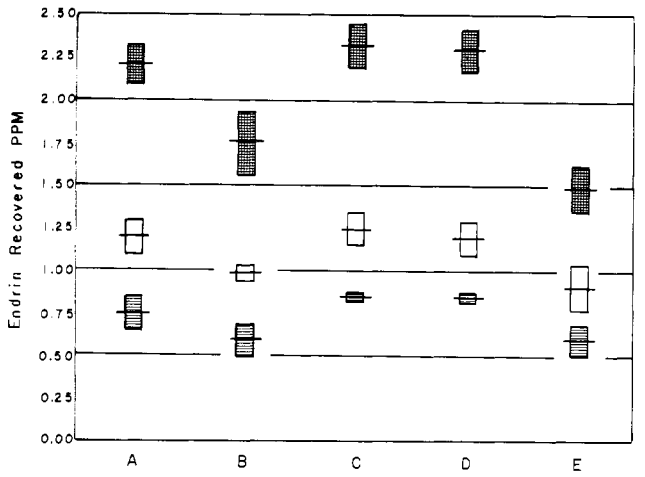

Figure 1. Recovery of endrin from cotton field soil samples

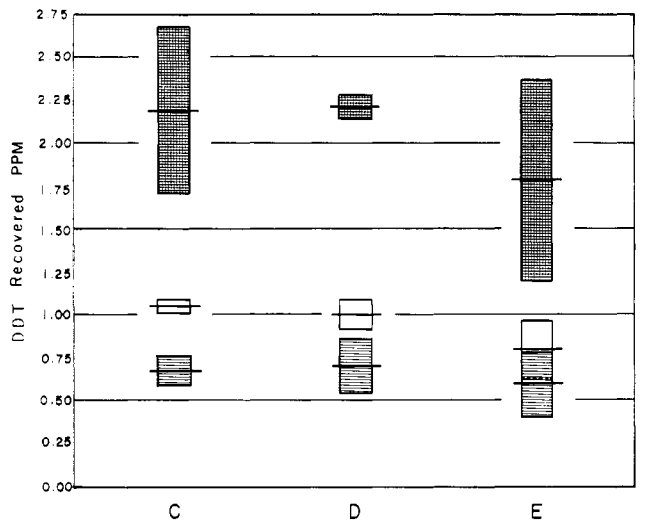

Figure 2. Recovery of DDT from cotton field soil samples

100 grams of soil on filter paper. Place in an extractor basket, and add 250 ml. of solvent (*n*-hexane–acetone, 9+1) to base unit. Assemble the extractor and extract sample for 16 hours. Transfer extracting solvent to a Kuderna-Danish evaporator. Evaporate to 10 ml. or less.

Column Chromatography (*2*). Transfer the concentrated extracts to a prepared Florisil column prewetted with petroleum ether, using a small amount of petroleum ether to complete transfer. Using 250 ml. each of mixed ethers (6+94 and 15+85), elute the column. Evaporate eluates just to dryness. Dissolve in 1.00 ml. of benzene.

Determination. Using microcoulometric gas chromatography, determine the insecticides present in each fraction (*1*).

Results and Discussion

The mean recovery of residue obtained by the various extraction procedures is shown in Figures 1 and 2. The 95% confidence interval on the mean was computed by (*6*):

$$\bar{X} \pm t_{0.05,\, n-1} \cdot S_{\bar{X}}$$

where

$\bar{X}$ = mean recovery indicated by three replicates.

t = Student's t.

$S_{\bar{X}}$ = standard error of the mean.

The magnitude of the confidence interval is indicative of the precision of the method.

The over-all precision of endrin recovery was comparable for all methods and concentrations (Figure 1). However, the 4-hour Immerex extraction and the Shell method gave consistently lower recoveries than those noted for other methods. In addition, both of these methods became increasingly less efficient with soil containing higher concentrations of endrin residue. The differences in mean recoveries among the Shell method *vs.* the 16-hour Immerex and 16-hour Soxhlet extractions were statistically significant for all samples. However, there were no statistically significant differences among the means of sample 1 for the 4-hour Immerex, the 4-hour Soxhlet, and the Shell methods.

The recovery experiments with DDT involved only the 16-hour Soxhlet, the 16-hour Immerex, and the Shell methods. Although the differences in mean DDT recovery were not statistically significant among methods within samples, the Shell method is lacking in precision, as judged by the overlap of the confidence limits for samples 1 and 2 and the spread of the confidence limit for sample 3 (Figure 2). Similarly, the 16-hour Soxhlet procedure is lacking in precision for concentrations greater than 2.0 p.p.m. The 16-hour Immerex method gave mean recoveries for DDT which were good with respect to both efficiency and precision.

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