PESTICIDES IN SOIL

"Apparent" Organochlorine Insecticide Contents of Soils Sampled in 1910[1]

B. E. Frazier, G. Chesters, and G. B. Lee

ABSTRACT

A total of 34 soil samples taken in Wisconsin between 1909 and 1911 were extracted for organochlorine insecticides and analyzed by gas chromatography on 3 columns—a mixed QF-1/IV-17 column; a mixed QF-1/DC-200 column; and a diethylene glycol succinate column. The samples had been stored continuously since collection in tightly sealed glass jars and presumably were free of insecticide contamination. Of the 34 samples 32 showed some "apparent" insecticide residues on at least one of the columns. Because peaks corresponding to particular organochlorine insecticides on chromatograms from one column did not recur on other columns, it was concluded that the peaks arose from co-extracted indigenous soil components. Peaks corresponding to heptachlor epoxide on the QF-1/OV-17 column and to aldrin on the QF-1/DC-200 column provided greatest interference in chromatographic determination.

Introduction

Multicolumn gas chromatography has been used successfully to determine qualitatively and quantitatively the content of organochlorine insecticides in soils; however, the method has not been tested extensively using soil samples known to be free of insecticides. The chromatogram of one uncontaminated soil revealed small interfering peaks, suggesting that concentrated soil extracts may show "apparent" insecticides where none exist (*1*). In another investigation, five uncontaminated soil samples gave gas chromatographic responses to γ-BHC, aldrin, and endrin (*2*). One response which was apparently caused by γ-BHC was in fact caused by sulfur. By use of multicolumn gas chromatography, aldrin-like compounds found in plant materials proved to be interfering compounds (*3*). Extraction and analytical procedures suitable for organochlorine insecticide determinations in soils must be able to disprove "apparent" residues when used on soils known to be free of insecticide residues.

In the routine analysis of soil samples for insecticides it is advantageous if methods can be designed to eliminate cleanup. Partitioning and Florisil cleanup steps are used commonly, but contamination from indigenous soil components may still be present (*2*), and a confirmatory analysis is necessary.

This investigation on insecticide-free samples was designed to determine the extent of interference with insecticide determination arising from indigenous soil components. Insecticide-free soils were obtained from a collection of 34 soil samples collected between 1909 and 1911 and stored in tightly stoppered glass jars since that time.

Methods and Materials

The soils (Table 1) consisted of samples with a wide range of textural class; their organic matter content ranged from 1.0% to 7.9%. An unpublished report on the soil samples indicates that organic matter was determined by a chromic acid wet oxidation method, but details of the procedure are not available. The textural class was obtained by observation. Although the description of the methodology is inadequate, it is believed that these data are as reliable as data which might be obtained presently on 60-year-old samples.

The organochlorine insecticides—γ-BHC, heptachlor and its epoxide, aldrin, dieldrin, endrin, *p,p'*-DDD, *p,p'*-DDT, and *p,p'*-methoxychlor—used as standards were those described earlier (*4*).

[1] From the Department of Soil Science, University of Wisconsin, Madison, Wis. 53706.

TABLE 1.—*Properties of soil samples used*

SAMPLE NO.	SOIL SERIES	TEXTURE	PERCENT ORGANIC MATTER
1	Ontonagon	clay	3.4
2	Miami	silt loam	2.2
3	Fayette	silt loam	1.4
4	Miami	silt loam	2.4
5	Dubuque	silt loam	1.8
6	Plainfield	sand	1.1
7	Tama	silt loam	4.1
8	Tama	silt loam	7.9
9	Morley	silt loam	2.7
10	Plano	silt loam	5.2
11	Oshkosh	silt loam	2.6
12	Plano	silt loam	5.7
13	Ontonagon	clay	3.0
14	Oshkosh	clay loam	1.7
15	Miami	silt loam	2.3
16	Goodman	silt loam	3.3
17	Fox	silt loam	3.7
18	Fox	silt loam	1.5
19	Warsaw	silt loam	5.3
20	Casco	sandy loam	2.3
21	Plainfield	sand	1.8
22	Plano	silt loam	6.2
23	Oshkosh	silt loam	2.1
24	Warsaw	sandy loam	2.9
25	Huntsville	silt loam	7.6
26	Miami	silt loam	1.5
27	Plainfield	sand	1.3
28	Tama	silt loam	4.3
29	Oshkosh	clay loam	3.9
30	Fayette	silt loam	4.4
31	Plainfield	sand	1.7
32	Hixton	fine sandy loam	1.5
33	Lomira	silt loam	2.3
34	Hochheim	gravelly loam	2.1

A Packard Model 7620 gas-liquid chromatograph was used for analysis of organochlorine insecticides. Gas chromatographic conditions were: carrier gas, N_2 with flow rate of 125 ml/minute; ^{3}H-foil electron-capture detector at 210 C, 50 volts; column temperature, 190 C; inlet temperature, 235 C; outlet temperature, 225 C.

The three types of columns were: (1) 2 parts 10% QF-1, 1 part 3% OV-17 on 60/80 mesh Gas Chrom Q (2 meters x 4 mm I.D.); (2) 1 part 17% QF-1, 1 part 11% DC-200 on 60/80 mesh Gas Chrom Q (2 meters x 4 mm I.D.); and (3) 10% diethcylene glycol succinate (DGS) on 60/80 mesh Gas Chrom Q (1 meter x 4 mm I.D.). The instrument incorporates the use of glass columns and on-column injection to avoid sample degradation resulting from contact of the sample with metal surfaces.

Air-dried soil from the surface 20 cm was extracted in quantities of 100 g or 50 g (when a limited amount was available) with 200 ml of a 41:59 Skelly B:acetone azeotropic mixture using a Soxhlet technique in all glass apparatus (5). Concentration of the extract to 25 ml was achieved by forced air evaporation at 40 C. For samples 1-9 inclusive a fivefold dilution of the 25 ml concentrated extract was required for quantitative gas chromatography. The concentrated extracts were not subjected to any method of cleanup.

Results and Discussion

Using three column gas chromatography most of the soil extracts gave peaks corresponding to organochlorine insecticides. On the QF-1/OV-17 column, 32 of 34 samples apparently showed measurable quantities of "heptachlor epoxide," and 24 samples contained "heptachlor"; peaks comparable to γ-BHC, aldrin, and dieldrin were found in a few samples (Table 2). On the QF-1/DC-200 column 20 of 34 samples apparently contained measurable quantities of "aldrin" with slight interference from "γ-BHC" and "dieldrin." A low degree of confusion between organochlorine insecticides and indigenous soil components was found on the DGS column; small amounts of "γ-BHC" and "heptachlor epoxide" would have been reported if this column had been used exclusively. No indigenous soil components which would interfere with determination of endrin, p,p'-DDD, p,p'-DDT, or p,p'-methoxychlor were found on any of the columns. Major interferences (>100 ppb) were found for "heptachlor epoxide" in soil samples 1-8 inclusive on the QF-1/OV-17 column and for "aldrin" in samples 1, 2, 5, and 6 on the QF-1/DC-200 column.

Chromatograms of the Skelly B:acetone extract of sample 9 on each of the three columns are shown in Fig. 1, 2, and 3. This sample was chosen because it was qualitatively similar to the other soil samples while showing a moderate amount of interference with in-

TABLE 2.—*"Apparent" organochlorine insecticide contents of air-dried soils sampled in 1910*

Sample No.	"Apparent" Insecticide Contents in PPB on Columns									
	QF-1/OV-17					QF-1/DC-200			DGS	
	Heptachlor Epoxide	Heptachlor	γ-BHC	Aldrin	Dieldrin	γ-BHC	Aldrin	Dieldrin	γ-BHC	Heptachlor Epoxide
1	823	3	3	0	0	0	141	0	0	0
2	807	3	2	0	0	0	294	0	4	0
3	742	1	0	0	0	0	13	0	0	0
4	696	5	2	0	0	0	63	0	9	0
5	564	20	9	5	0	0	164	0	9	0
6	378	5	6	0	0	0	100	0	3	0
7	188	1	1	0	0	0	60	0	0	0
8	156	0	2	0	0	0	26	0	0	0
9	51	2	0	0	0	0	43	0	2	0
10	49	3	2	0	0	0	8	0	0	2
11	43	5	2	1	0	0	0	0	0	0
12	40	5	2	0	0	0	0	0	0	3
13	33	8	0	2	0	0	12	0	2	2
14	28	6	0	0	0	0	8	0	3	0
15	25	8	2	2	0	0	0	0	3	0
16	20	0	0	0	0	0	41	0	0	0
17	19	4	0	0	0	0	4	0	0	0
18	14	3	0	0	0	0	4	0	2	0
19	9	1	1	0	0	0	20	0	0	0
20	8	2	0	0	0	0	0	0	0	0
21	7	8	0	9	0	0	0	40	4	6
22	7	2	0	0	0	0	0	0	0	0
23	7	1	0	0	0	0	6	0	0	4
24	4	0	2	0	0	6	5	0	0	0
25	4	1	0	0	0	0	0	0	0	0
26	4	4	0	0	3	0	0	0	2	1
27	3	2	0	0	0	0	0	0	0	0
28	3	0	0	0	0	0	0	0	0	0
29	2	0	0	0	0	0	0	0	0	0
30	2	0	0	0	0	0	0	0	0	0
31	2	0	0	0	0	0	3	0	0	0
32	1	0	2	0	0	0	3	0	0	0
33	0	0	0	0	0	0	0	0	3	0
34	0	0	0	0	0	0	0	0	2	0

secticide determination (Table 2). Extensive contamination by "heptachlor epoxide" and slight contamination by "γ-BHC" and "heptachlor" are indicated on the QF-1/OV-17 column (Fig. 1). "Aldrin" is the apparent contaminant found on the QF-1/DC-200 column (Fig. 2) while a small amount of "γ-BHC" was found on the DGS column (Fig. 3). Interfering peaks were classed as those which had a retention time (R_t) equal to R_t ±30 seconds of that of the standard insecticide. With a larger discrepancy in R_t-value, it is believed that the insecticide would be resolved satisfactorily from the indigenous soil contaminant.

From examination of Table 2, it can be seen that the "apparent" insecticide residues in the soil arise from indigenous compounds which display chromatographic characteristics similar to a particular organochlorine insecticide. However, the characteristic is unique to one of the columns and not displayed on either of the other two columns. The use of a combination of any two of the three columns described would reveal satisfactorily any chromatographic discrepancies arising from co-extraction of naturally occurring soil components. Six of the samples indicated small amounts of "heptachlor epoxide" on the DGS column which might be considered confirmatory for the "heptachlor epoxide" found on the QF-1/OV-17 column. However, no peaks corresponding to heptachlor epoxide were found on the QF-1/DC-200 column, and it is not believed that this discrepancy would lead to confusion if only two columns were used since the quantities of "heptachlor epoxide" on DGS are extremely small; the highest amount was 6 ppb for sample 21.

In Table 1 the samples are arranged in decreasing order of "apparent" insecticide contamination based on the "heptachlor epoxide" peak shown on the QF-1/OV-17 column. No relationship was found between "apparent" insecticidal contamination (Table 2) and the soil properties described in Table 1.

On each of the three columns a large peak was found which displayed an R_t-value greater than that for *p,p'*-methoxychlor on the QF-1/OV-17 and QF-1/DC-200 columns which are relatively nonpolar. However, on the relatively polar DGS column, the peak had a short R_t-value (comparable to that of dieldrin and endrin on the DGS column) which would interfere with insecticide determination (Fig. 3). This peak was found to result from the forced air evaporation of the soil extracts using Tygon tubing to blow air over the extracts. Small amounts of Tygon must have been dissolved by the Skelly B:acetone solvent during this procedure since Skelly B was capable of extracting the material from Tygon in less than 10 seconds (Fig. 3).

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See Appendix for chemical names of compounds mentioned in this paper.

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FIGURE 1.—*Gas chromatograms of organochlorine insecticide standards and the Skelly B: acetone extract of soil sample 9 on a QF-1/OV-17 column*

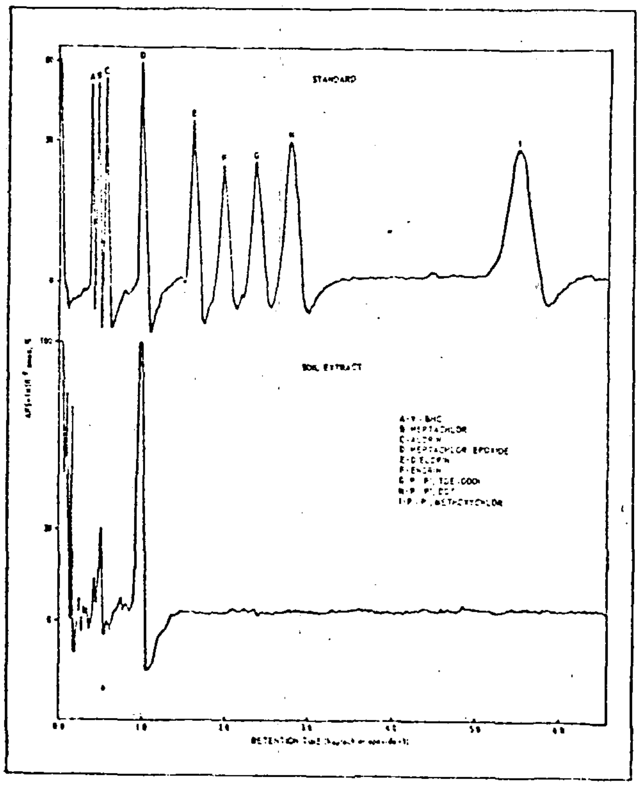

FIGURE 2.—*Gas chromatograms of organochlorine insecticide standards and the Skelly B: acetone extract of soil sample 9 on a QF-1/DC-200*

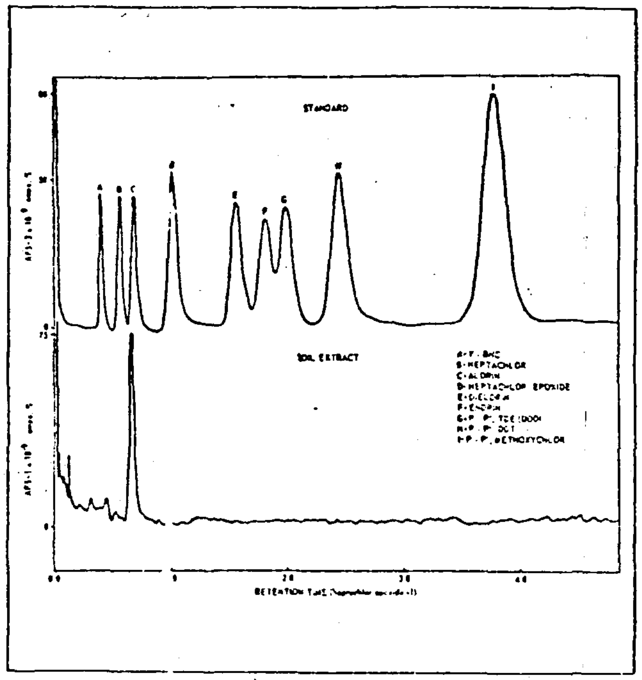

FIGURE 3.—*Gas chromatograms of organochlorine insecticide standards and the Skelly B: acetone extract of soil sample 9 and Tygon tubing on a DGS column*