Fate of Deltamethrin after Nine Years of Incubation in an Organic Soil under Laboratory Conditions†

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An organic soil treated with [^{14}C]deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl *cis*-(1*R*,3*R*)-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] was incubated in the laboratory. After 9 years, the soil was extracted by supercritical fluid (SF) extraction and the extracted material was fractionated by acid hydrolysis. The acid-soluble and acid-insoluble fractions were characterized, and the results were correlated with ^{14}C residues. Characterization by ^{13}C NMR and pyrolysis–field ionization mass spectrometry indicated that the materials soluble in the acids were rich in carbohydrates, nitrogen compounds, and carboxyl groups with lower concentrations of aliphatics (fatty acids, alkyl esters, and alkanes) and mono- and dilignins. The acid-insoluble fractions consisted primarily of aliphatics with long alkyl chains, aromatics, and some phenolic compounds. It is suggested that the alkyl–arylic or alkyl–phenolic structures in the soil organic matter play an active role in the adsorption of pesticides. Curie-point pyrolysis–gas chromatography/mass spectrometry of the SF fraction insoluble in 0.5 M HCl, rich in radioactivity, failed to show the presence of even traces of deltamethrin or its degradation products in the organic soil fraction. The only markers for the presence of deltamethrin in the more soluble fractions were the isolation of 1-bromododecane with the Br originating from deltamethrin and of phenoxybenzaldehyde.

INTRODUCTION

Deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl *cis*-(1*R*,3*R*)-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] is one of the most potent of synthetic pyrethroids. This insecticide is active against numerous species of insects when applied on field crops. During foliar applications a large portion of the insecticide may come in contact with the soil, where it could then be adsorbed readily by soil organic matter (OM) or subjected to various types of biotic and abiotic degradations. It is likely that certain components of the OM may retain the insecticide and/or its metabolites more firmly than others, thereby affecting the persistence and fate of the insecticide in the soil. Soil OM is a chemically complex material consisting of aliphatic, aromatic, and phenolic components. In a previous publication from this laboratory (Zhang et al., 1984) we reported on the persistence, degradation, and bound residue formation of deltamethrin in an organic soil under laboratory conditions. The present study, a continuation of this investigation, describes attempts to identify the insecticide or its degradation products in major organic matter fractions.

Our approach to this problem consisted of extracting the organic soil continuously incubated with [^{14}C]deltamethrin for 9 years by supercritical fluid (SF) extraction using a mixture of methanol and dilute NaOH. The resulting extract was then further fractionated by hydrolyzing separate portions with 0.5 and 6.0 M HCl. The acid-soluble and -insoluble fractions were separated and characterized by solid-state ^{13}C NMR and by pyrolysis–field ionization mass spectrometry (Py–FIMS), and the results were correlated with radioactivity. The fraction richest in radioactivity was also analyzed in considerable detail by Curie-point pyrolysis–gas chromatography/mass spectrometry (Cp Py–GC/MS).

Table I. Distribution of ^{14}C in the Organic Soil and Fractions Derived from It

material	radioactivity, dpm/g	% of radioactivity in the initial soil
organic soil	11911	100[a]
SF extract	7507	63
SF extract soluble in 0.5 M HCl	2155	29[b]
SF extract insoluble in 0.5 M HCl	3817	51[b]
SF extract soluble in 6.0 M HCl	2995	39[b]
SF extract insoluble in 6.0 M HCl	2263	30[b]

[a] Represents 32.2% of the initially applied ^{14}C. [b] Percent of radioactivity in SF extract.

MATERIALS AND METHODS

Chemicals. Deltamethrin (^{14}C-methyl-labeled and unlabeled) was a gift from Roussel-Uclaf-Procida through its subsidiary Hoechst of Canada Ltd. and had the radiochemical purity and specific activity of 98% and 56 mCi/mmol, respectively. An aliquot of the radiolabeled deltamethrin was mixed with cold deltamethrin and dissolved in acetone to give a concentration of 484 μg/mL (4.64×10^5 dpm). Stock solution of cold deltamethrin was prepared in hexane.

Soil. The soil, obtained from the Ste. Clothide Experimental Farm of the Agriculture Canada Research Station at St. Jean, PQ, was a humic mesisol. It had a pH of 5.6–5.8, contained 40.6% carbon, 2.6% nitrogen, and 16.8% mineral matter, and had a bulk density of 0.35 and a field capacity of 300%.

Incubation Experiment. Soil (30 g on oven-dry weight basis) was placed in an Erlenmeyer flask to which 500 μL of hexane solution containing labeled (0.5 μCi) and unlabeled deltamethrin was added to give an insecticide concentration of 10 mg/kg. The

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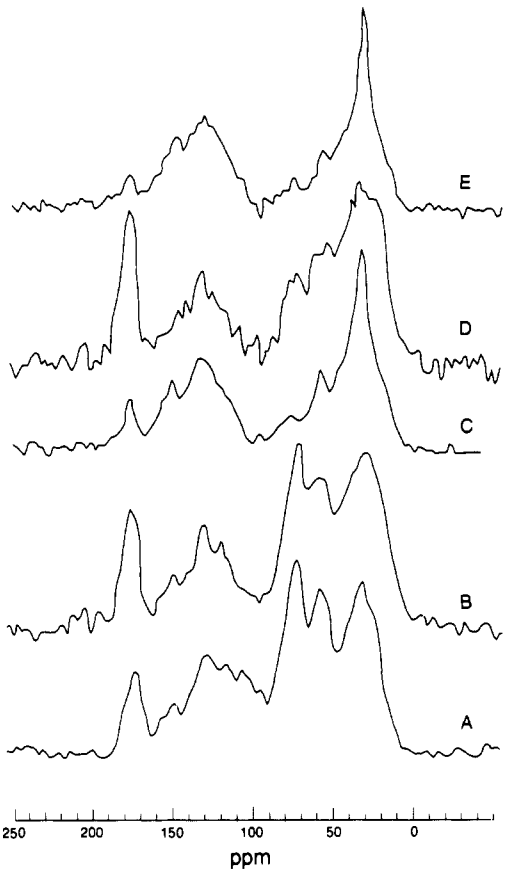

Figure 1. ^{13}CP/MAS NMR spectra of (A) SF extract, (B) SF extract soluble in 0.5 M HCl, (C) SF extract insoluble in 0.5 M HCl, (D) SF extract soluble in 6.0 M HCl, and (E) SF extract insoluble in 6.0 M HCl.

solvent was allowed to evaporate and the soil thoroughly mixed. The moisture content of the soil was maintained at 70% of field capacity during the course of the experiment. The soil was incubated at 21 ± 1 °C in the dark for about 9 years. At the end of the incubation period the soil was processed as described below.

Supercritical Fluid (SF) Extraction. The SF extractor employed was the same as that described by Schnitzer et al. (1986). The solvents and experimental conditions were as follows: solvent mixture, methanol (75)/0.01 M NaOH (25); temperature, 250 °C; pressure, 13.8 MPa; time, 2 h; sample weight, 2.0 g + 28.0 g of sand.

The extracted material was dried on a rotary evaporator at 45 °C to remove most of the solvents and then in a vacuum oven at 45 °C for 96 h and weighed. Yields of extracts resulting from 10 separate extractions averaged 0.43 ± 0.02 g.

Acid Hydrolysis. A portion (1 g) of SF extract was refluxed in a 200-mL round-bottom flask, equipped with a condenser, with 75 mL of 0.5 M HCl for 24 h. The insoluble residue was separated from the supernatant by filtration through a sintered glass funnel and washed with distilled water until most of the acid had been removed. The residue was then dried over P_2O_5 in a vacuum desiccator at room temperature. Its weight (average of 10 separate hydrolyses) was 0.37 ± 0.04 g.

The supernatant plus washings containing 0.5 M HCl and distilled water were then reduced repeatedly (×5) to close to dryness on a rotary evaporator to expel most of the hydrochloric acid. The remaining material was then dried in a vacuum oven at 50 °C. The weight of the supernatant averaged (10 separate determinations) 0.61 ± 0.06 g.

The hydrolysis procedures described above were repeated with 6.0 M HCl on another portion (1 g) of the SF extract. Average weights (on the basis of 10 separate determinations) were, of the residue, 0.32 ± 0.04 g, and, of the supernatant, 0.55 ± 0.06 g.

Pyrolysis–Field Ionization Mass Spectrometry (Py-FIMS). About 100 μg of solid sample was transferred to a quartz

Table II. Distribution of C in the SF Extract and in Fractions Derived from It As Determined by ^{13}C NMR

	% of total C				
		0.5 M HCl hydrolysis		6.0 M HCl hydrolysis	
chemical shift, ppm	SF extract	super-natant	residue	super-natant	residue
0–40	22.8	27.7	34.2	32.1	36.3
40–60	16.2	15.6	15.1	14.3	12.6
60–105	31.4	25.2	11.6	18.5	8.5
105–150	20.2	18.2	26.2	18.1	30.3
150–170	4.7	4.5	8.5	4.9	8.2
170–190	4.7	8.8	4.4	12.1	4.1
aliphatic C	70.4	68.5	60.9	64.9	57.4
aromatic C	24.9	22.7	34.7	23.0	38.5
aromaticity	26.1	24.9	36.3	26.2	40.1

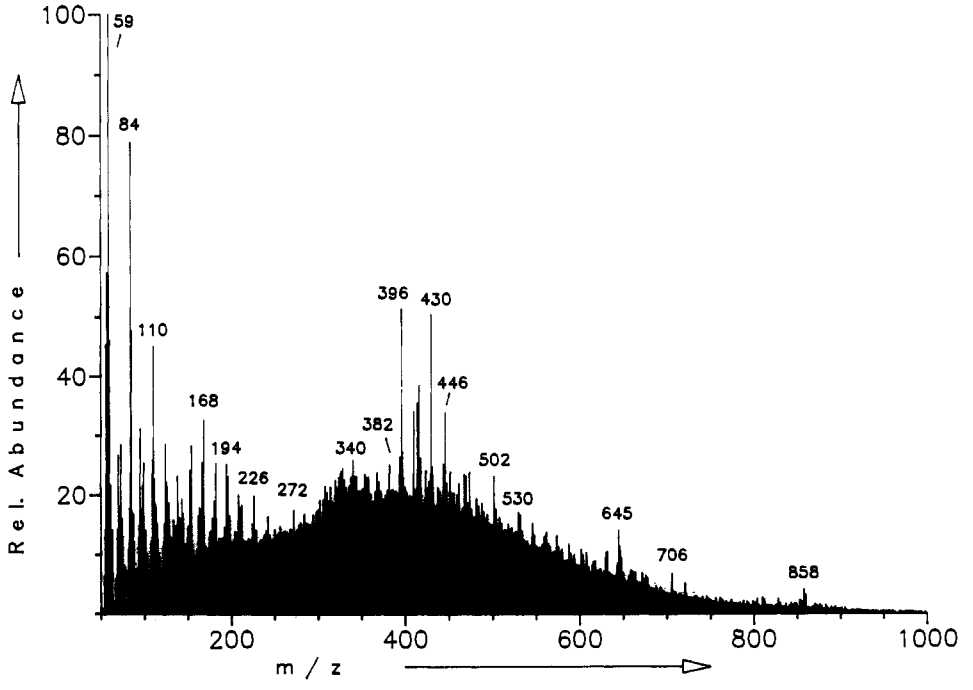

Figure 2. Py-FI mass spectrum of SF extract.

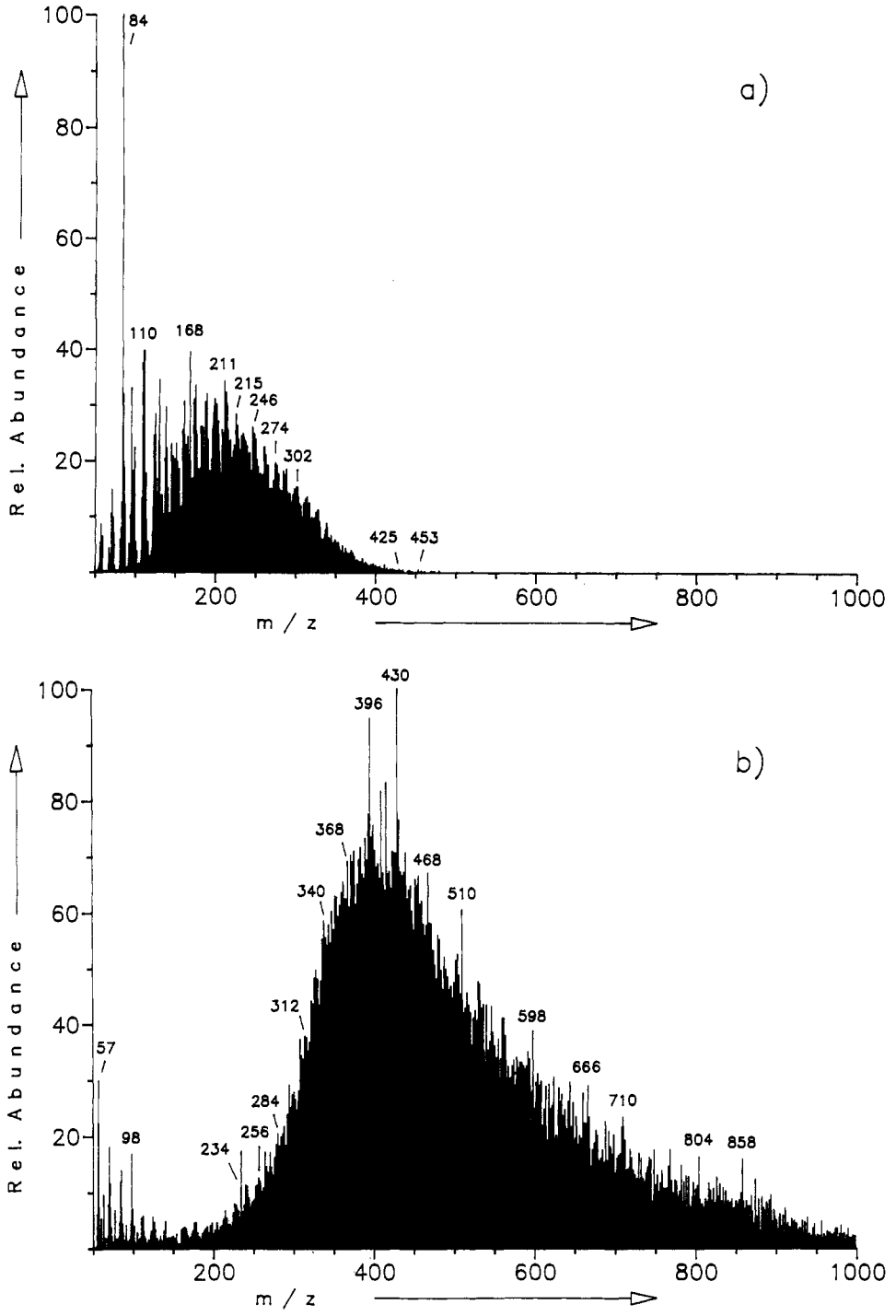

Figure 3. (a) Py–FI mass spectrum of the SF extract soluble in 0.5 M HCl. (b) Py–FI mass spectrum of the SF extract insoluble in 0.5 M HCl.

micro-oven and heated linearly in the direct inlet system of the mass spectrometer from 50 to 750 °C at a rate of 1 °C/s. A double-focusing Finnigan MAT mass spectrometer (Finnigan MAT, Bremen, Germany) was used. The ion source was kept at a pressure below 1 mPa and at a temperature of 250 °C. To avoid condensation of the volatilized products during the recording of the FI mass spectra, the emitter was flash-heated to 1500 °C between magnetic scans. Between 35 and 40 spectra were recorded in the mass range m/z 50–750. The FI signals of all spectra were integrated and plotted with the aid of a Finnigan SS200 data system to produce summed spectra.

Curie-Point Pyrolysis–Gas Chromatography/Mass Spectrometry (Cp Py–GC/MS). A Fischer Curie-point pyrolyzer (Type 0316) was used for this purpose. The sample dissolved in methanol was coated on the wire and allowed to dry. The final temperature was 500 °C and the total heating time 9.9 s. The pyrolyzer was connected to a 45-m DB5 column in a Varian 3700 gas chromatograph, programmed to rise from 40 to 280 °C at a rate of 3 °C/min. Mass spectra of the chromatographically separated compounds were run on a Finnigan MAT mass spectrometer in the electron impact (EI) mode.

The mass signals were identified with the aid of NBS, Wiley, and in-house mass spectral libraries and, if available, by comparisons of mass spectra of knowns with those of unknowns.

As described above, two types of pyrolysis were used: (a) heating at a linear heat from 50 to 750 °C and (b) flash pyrolysis, heating samples to 500 °C in less than 10 s. Also, two types of mass spectrometry were employed. With linear heating, we used FIMS and with flash pyrolysis, EIMS. The advantage of using FIMS over EIMS is that FIMS is a soft-ionization mass spectrometric method which tends to produce from complex pyrolysates mainly molecular ions and so significantly reduces mass spectrometric fragmentation. This facilitates the identification of the mass signals (Schulten, 1987).

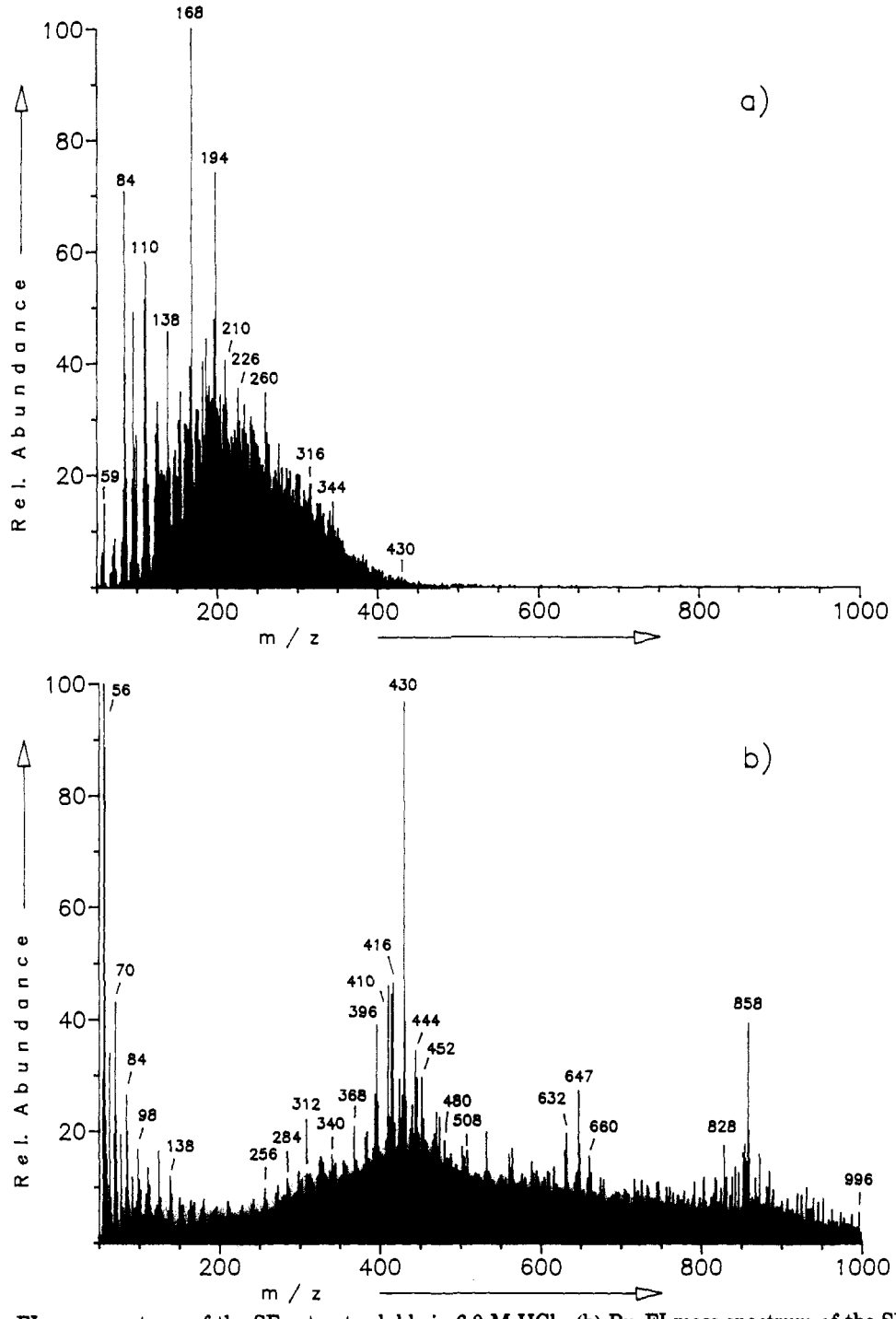

Figure 4. (a) Py–FI mass spectrum of the SF extract soluble in 6.0 M HCl. (b) Py–FI mass spectrum of the SF extract insoluble in 6.0 M HCl.

^{13}C NMR Spectra. ^{13}C CP/MAS (cross-polarization magic angle spinning) NMR spectra were recorded at a frequency of 45.28 MHz on 300 mg of thoroughly dried powders on a Bruker CXP-180 NMR spectrometer equipped with a Doty Scientific probe. Single-shot cross-polarization contacts of 2 ms were used with field amplitudes of 75 kHz. Up to 120 000 free induction decays were co-added with a delay time of 1 s. These were zero-filled to 4K before Fourier transformation. Magic angle spinning rates were ≈4 kHz. No line broadening was applied. Under the experimental conditions employed, there was no evidence of spinning side bands. The ^{13}C NMR spectra were interpreted as described by Schnitzer (1991).

Briefly, the integrated areas of ^{13}C NMR spectra were divided into the following regions: 0–40 ppm (C in straight-chain, branched, and cyclic alkanes and alkanoic acids); 41–60 ppm (C in branched aliphatics, amino acids, and OCH_3 groups); 61–105 ppm (C in carbohydrates and in aliphatics containing C bonded to OH, ether oxygens, and in five- or six-numbered rings bonded to O); 106–150 ppm (aromatic C); 151–170 ppm (phenolic C); and 171–190 ppm (C in CO_2H groups). Aromaticities were computed by expressing aromatic plus phenolic C (106–170 ppm) as a percentage of aliphatic plus aromatic plus phenolic C (0–170 ppm).

Determination of Radioactivity. Dried materials were assayed by combustion in a Packard sample oxidizer, Model 306. Liquid (extracts) were assayed in a Packard Model 3320 scintillation spectrometer.

RESULTS AND DISCUSSION

SF Extraction and Acid Hydrolysis. Following an incubation period of 9 years, the soil contained 32.2% of the initially applied ^{14}C. SF extraction with methanol/0.01 M NaOH removed 63% of this radioactivity, which

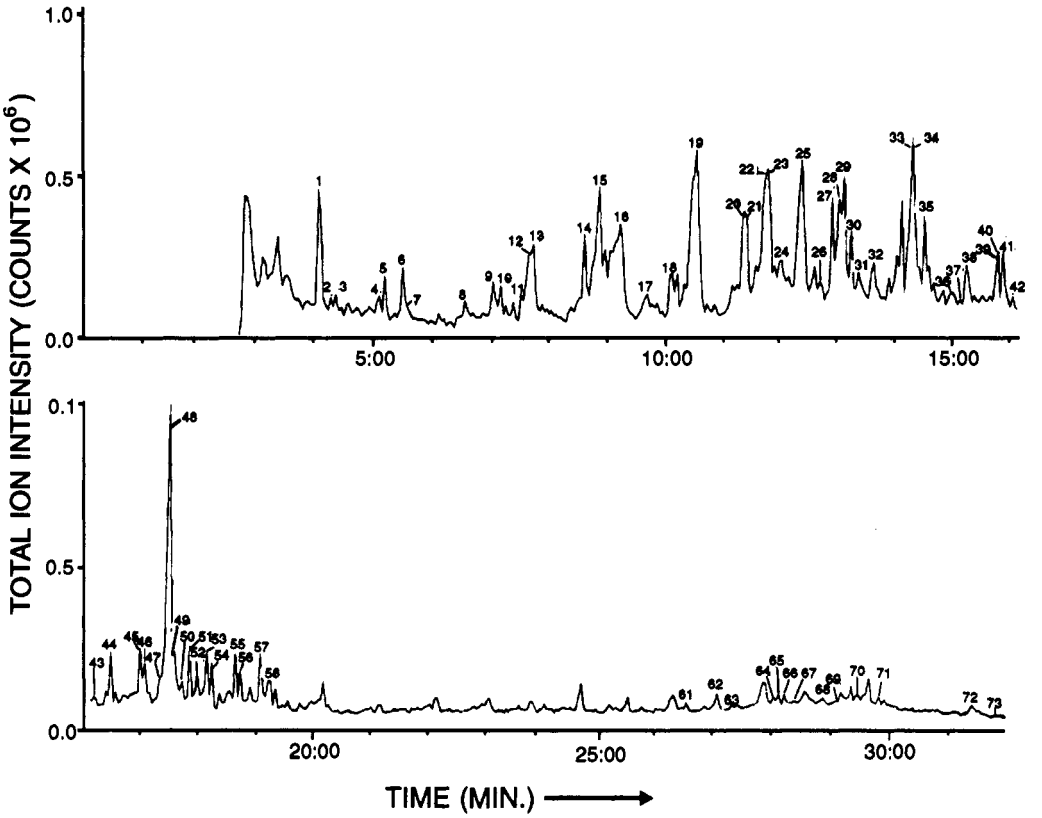

Figure 5. Cp Py–GC/MS chromatogram of SF fraction insoluble in 0.5 M HCl.

represents about 20% of the total radioactive residues in soil (Table I). However, only 21.5% of the total weight of organic soil was removed by this extraction. This indicates that the extract was enriched in ^{14}C residues which originated from the insecticide and/or metabolites. The SF extract was then partitioned by acid hydrolysis into two fractions: (a) material soluble in the acid and (b) material that was insoluble under these conditions. Two acid concentrations were used: 0.5 and 6.0 M HCl. In a previous investigation Schnitzer and Preston (1983) showed that hydrolysis with 6.0 M HCl removed proteinaceous materials and carbohydrates from humic materials and so "purified" the humic materials. As shown in Table I, more of the radioactivity in the SF extract was in the residue than in the supernatant after 0.5 M HCl hydrolysis, whereas the reverse was observed after 6.0 M HCl hydrolysis. Apparently, the stronger acid brought more of the residual ^{14}C into solution. Judging from the weights of the fractions, hydrolysis with 6.0 M HCl caused greater weight losses than hydrolysis with the more dilute acid mainly because of decarboxylation of CO_2H groups by the stronger acid (Schnitzer and Preston, 1983).

^{13}C NMR Spectra of Extract and Fractions. The ^{13}C NMR spectrum of the SF extract (Figure 1A) exhibited distinct peaks in the aliphatic (0–105 ppm), aromatic (106–149 ppm), phenolic (150–169 ppm), and carboxyl (170–189 ppm) regions. The prominent signal at 32 ppm was due most likely to $(CH_2)_n$ in long alkyl chains, although other alkyl carbons might also have contributed to this chemical shift (Lindeman and Adams, 1971). The peak near 55 ppm appeared to be due to $-OCH_3$. Amino acids might also have contributed in this region; for example, α-carbons of arginine, glutamic acid, and lysine produce ^{13}C NMR signals in this area. The strong peak at 74 ppm was characteristic of C_2–C_5 ring carbons and the signals at 98 and 105 ppm of anomeric carbons in carbohydrates. Signals at 118 and 130 ppm may be assigned to aromatic carbons and those at 150 and 158 ppm to phenolic carbons. The broad peak near 180 ppm was due to C of carboxyl groups; carboxylic acids as well as amides and esters usually give signals at this chemical shift (Schnitzer and Preston, 1983).

The ^{13}C NMR spectrum (Figure 1B) of the SF extract which was soluble in 0.5 M HCl was very similar to that of the SF extract. The major signals were at 32 and 38 ppm (aliphatic C), 58 ppm (OCH_3), 60, 74, and 92 ppm (carbohydrates), 118, 130, and 138 ppm (aromatic C), 150 and 158 ppm (phenolic C), and 178 ppm (C in CO_2H groups). Especially noteworthy were the strong signals assigned to carbohydrates and CO_2H groups in this fraction.

The ^{13}C NMR spectrum of the SF extract which was insoluble in hot 0.5 M HCl is shown in Figure 1C. This spectrum was simpler than spectra A and B. The strongest signal was at 32 ppm [$(CH_2)_n$ in alkyl chains], followed by a broad aromatic resonance with a maximum at 132 ppm and signals of lower intensities at 58 ppm (OCH_3), 150 and 158 ppm (phenolic C), and 178 ppm (C in CO_2H groups). Peaks arising from carbohydrates and proteinaceous materials in the 60–105 ppm region were weak, indicating the removal of most of these substances by the acid.

The ^{13}C NMR spectrum of the SF extract that was soluble in hot 6 M HCl is shown in Figure 1D. This spectrum resembled the spectra shown in Figure 1A,B to a large extent, except that it exhibited a greater number of signals. The spectrum was dominated by peaks in the aliphatic (0–105 ppm) and CO_2H (170–189 ppm) regions but to a lesser extent by aromatic and phenolic resonances (106–169 ppm). Signals at 22, 28, and 32 ppm arose from aliphatic carbons in alkyl chains. The signal at 40 ppm may have included contributions from both alkyl carbons and amino acids (Schnitzer and Preston, 1983). In the 50–105 ppm region aliphatic carbons substituted by oxygen and nitrogen are usually observed. The peak near 58 ppm

Table III. Cp Py–GC/MS of SF Extract Insoluble in 0.5 M HCl

peak	mass signals, m/z	assigned compound
1	55, 56, 62, 65, 67, 79, 89, 90, 91	methylbenzene
2	55, 56, 69, 70, 83, 100, 110, 112	3-chlorooctane
3	57, 63, 71, 85, 95, 110, 114	1-nonen-3-ol
4	51, 67, 73, 77, 81, 91, 106, 109, 124	1-ethynylcarbamate cyclohexanol
5	51, 52, 63, 65, 77, 79, 81, 89, 91, 94, 105, 106	1,3-dimethylbenzene
6	55, 56, 69, 70, 78, 84, 104, 124, 126	1-methyl-2-propylcyclopentane
7	57, 70, 84, 85, 86, 96, 99, 124, 128	2,4,6-trimethyloctane
8	55, 57, 60, 63, 67, 77, 79, 87, 91, 105, 120	1-ethyl-2-methylbenzene
9	55, 56, 57, 69, 70, 81, 83, 93, 97, 122, 136, 140	1-decene
10	57, 71, 85, 99, 113, 123	2,5,9-trimethyldecane
11	57, 71, 85, 91, 97, 105, 112, 120	1-(methylethyl)benzene
12	55, 65, 75, 94	phenol
13	56, 59, 63, 68, 70, 83, 91, 94, 110, 115, 117, 118	1-ethenyl-4-methylbenzene
14	55, 56, 57, 69, 70, 83, 97, 107, 124, 132, 154	8-methyl-2-decene
15	53, 81, 95, 109, 124	3,4,5-trimethyl-2-cyclopenten-1-one
16	53, 55, 74, 77, 79, 87, 95, 107, 108	4-methylphenol
17	51, 63, 65, 77, 82, 91, 92, 115, 130, 148	7-phenyl-5-hepten-2-one
18	51, 53, 60, 65, 77, 79, 91, 92, 107, 122	4-ethylphenol
19	57, 71, 85, 123, 138	2-methyl-5-(1-methylethyl)cyclohexanol
20	53, 65, 77, 78, 91, 103, 105, 110, 120	2,3-dihydrobenzofuran
21	57, 71, 99, 113, 152, 225, 240	3-methylheptadecane
22	55, 56, 69, 83,97, 107, 110, 111, 136, 152, 182	1-pentyl-2-propylcyclopentane
23	57, 65, 77, 81, 91, 94, 122, 137, 152	4-ethyl-2-methoxyphenol
24	51, 65, 79, 93, 97, 107, 125, 135, 140	3-methoxy-1,2-benzenediol
25	63, 65, 77, 79, 89, 91, 107, 135, 150	1-(2-hydroxy-5-methylphenyl)ethanone
26	69, 70, 83, 97, 111, 133, 155, 159, 239, 256	3,9-diethyl-6-tridecanol
27	57, 71, 85, 103, 113, 127, 131, 149, 164, 183	1-bromododecane
28	55, 66, 78, 91, 106, 122, 137, 149, 166	(1,1-dimethylethyl)-4-methoxyphenol
29	57, 69, 70, 83, 93, 107, 112, 139, 154	1-methoxy-4-methylbicyclo[2.2.2]octane
30	57, 71, 85, 99, 113, 127, 141, 155, 198	tetradecane
31	57, 65, 71, 84, 91, 103, 139, 154	3,4-dimethoxyphenol
32, 33	55, 63, 77, 91, 103, 121, 131, 149, 164	2-methoxy-4-(1-propenyl)phenol
34	54, 65, 67, 79, 82, 85, 95, 107, 125, 153, 168	4-hydroxy-3-methoxybenzoic acid
35	55, 57, 69, 70, 83, 97, 111, 125, 139, 153, 168, 194, 210	1-hexadecene
36	52, 63, 65, 77, 92, 94, 108, 123, 148, 151, 166	1-(2-hydroxy-5-methoxyphenyl)ethanone
37	55, 71, 83, 84, 91, 101, 109, 115, 121, 128, 134, 155, 170	2,3,6-trimethylnaphthalene
38	55, 77, 79, 91, 93, 107, 123, 151, 167, 182	2-(methylthio)benzoic acid methyl ester
39	55, 57, 69, 70, 83, 84, 97, 111, 125, 137, 165, 180, 181, 196	3-eicosene
40	55, 57, 69, 70, 83, 97, 112, 123, 139, 151, 169, 177, 190	2-dodecene
41	57, 71, 85, 99, 115, 127, 133, 155, 170	3-methyldodecane
42	55, 65, 70, 76, 84, 91, 97, 104, 111, 121, 131, 145, 149, 176, 192, 222	1,2-benzenedicarboxylic acid diethyl ester
43	51, 65, 74, 81, 89, 95, 128, 141, 175, 185, 190, 194	4-hydroxybenzenebutanoic acid methyl ester
44	57, 71, 85, 96, 112, 113, 127, 169, 172, 182	2,7,10-trimethyldodecane
45	55, 57, 67, 69, 70, 82, 83, 84, 97, 111, 125, 139, 153, 167, 187, 193, 214	1-tetradecanol
46	57, 71, 85, 99, 113, 127, 141, 155, 169, 183, 196, 240	heptadecane
47	84, 77, 81, 91, 103, 105, 119, 133, 151, 163, 179, 194	2,6-dimethoxy-4-(2-propenyl)phenol
48	57, 69, 70, 83, 97, 111, 112, 126, 127, 140, 181, 182, 196	7-methylenetridecane
49	69, 71, 83, 98, 111, 126, 127, 140, 196	2-isohexyl-6-methyl-1-heptene
50	57, 68, 73, 81, 95, 97, 109, 123, 137, 151, 166	decahydro-1,5-dimethylnaphthalene
51	57, 67, 71, 82, 85, 106, 109, 110, 123, 138, 151, 179, 181, 208, 219, 228, 246, 264	octahydro-1-(2-octyldecyl)pentalene
52	55, 67, 69, 81, 82, 83, 109, 111, 123, 137, 165, 182, 208, 230, 232, 264	3-octodecyne
53	57, 69, 71, 83, 84, 97, 111, 125, 126, 185, 199, 228, 252	5-octadecene
54	57, 58, 71, 72, 99, 113	2,7-dimethyloctane
55	55, 57, 69, 70, 83, 97, 111, 125, 126, 140, 143, 176, 196, 214, 235, 241	5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)-1-octanol
56	57, 71, 83, 97, 109, 123, 151, 185, 211, 213	6,10,14-trimethyl-2-pentadecanone
57	57, 69, 82, 95, 109, 123, 137, 169, 175, 193, 221, 278	3-eicosyne
58	57, 71, 85, 99, 113, 127, 141, 169, 197, 225, 268	nonadecane
59	51, 60, 74, 85, 91, 114, 149, 163, 179, 185, 224, 227, 239, 241, 255, 270	8-propylbenz[a]anthracene
60	57, 69, 71, 83, 97, 111, 143, 170, 181, 194, 230, 252, 269, 280	5-eicosene
61	57, 74, 87, 98, 143, 151, 186, 213, 241, 298, 339, 340, 382	tetracosanoic acid methyl ester
62	57, 71, 85, 99, 113, 141, 169, 182, 211, 233, 286, 312, 338, 350, 394	octacosane
63	59, 69, 74, 81, 97, 113, 135, 143, 180, 203, 225, 243, 284, 341, 353, 396	9-octylheptadecanoic acid methyl ester
64	59, 71, 85, 107, 135, 191, 255, 260, 282, 317, 326, 368	20-de(acetyloxy)-11-deoxy-20-oxocochlioquinone A
65	61, 69, 74, 87, 97, 112, 145, 190, 221, 265, 268, 294, 350, 367, 379, 410	hexacosanoic acid methyl ester
66	68, 79, 95, 109, 133, 161, 189, 191, 231, 232, 272, 368, 369, 406	2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexene
67	60, 68, 82, 96, 98, 111, 129, 138, 144, 192, 217, 252, 257, 281, 310, 333, 380, 402	cholest-20(22)-ene-3,6-diol
68	59, 60, 84, 97, 129, 201, 215, 229, 243, 297, 332, 369, 393, 424	dodecanoic acid hexadecyl ester

Table III (Continued)

peak	mass signals, m/z	assigned compound
69	67, 79, 91, 120, 121, 126, 147, 150, 163, 190, 197, 228, 237, 267, 331, 341, 355, 375, 396, 416	3,4-dihydro-2,5,8-trimethyl-2-(4,8,12-trimethyl)-2*H*-1-benzopyran-6-ol
70	59, 73, 75, 96, 109, 112, 135, 145, 158, 191, 207, 221, 327, 355, 396	not identified
71	64, 74, 91, 108, 128, 136, 149, 164, 165, 166, 190, 205	9-methoxyphenanthrene
72	55, 57, 85, 107, 111, 122, 159, 213, 273, 281, 303, 368, 381, 396, 414	14-methyl-3β,5α-ergost-8-en-3-ol
73	56, 69, 73, 75, 95, 107, 119, 147, 165, 191, 208, 213, 267, 296, 340, 357, 436, 456	lanostane-3,7,11-trione

was most likely due to $-OCH_3$, although amino acids may also have contributed to it. Signals at 62, 72, 74, 89, 92, 96, and 105 ppm arise from carbohydrates, whereas the resonances at 118, 128, 132, and 142 ppm indicated the presence of aromatic C. It is likely that the small resonances between 150 and 169 ppm were due to phenolic C and that the strong peak at 178 ppm was due to C in CO_2H groups; amides and esters could also have contributed to this peak. This spectrum suggests, in line with expectations, that the 6.0 M HCl brought into solution proteinaceous materials and carbohydrates along with long-chain aliphatics and aromatics and that this fraction was relatively rich in CO_2H groups.

The ^{13}C NMR spectrum of the SF extract which was insoluble in 6.0 M HCl (Figure 1E) showed the most prominent signal at 32 ppm [$(CH_2)_n$], followed in intensity by resonances at 130 ppm (aromatic C) and at 150, 155, 162, and 168 ppm (phenolic C). Peaks indicating the presence of C in CO_2H groups (178 ppm) and in OCH_3 groups and amino acids (58 ppm) were relatively weak. The very weak resonances at 62, 75, 80, 86, and 92 ppm showed that most of the carbohydrates and proteins had been removed by the hot acid.

The ^{13}C NMR data for all materials are summarized in Table II. These data were obtained by area integrations (Schnitzer, 1991). The information presented indicates that (1) the materials insoluble in the acids were richer in alkyl, aromatic, and phenolic C and had higher aromaticities than the initial SF extracts and the fractions soluble in the acids and (2) the fractions soluble in the acids were enriched in nitrogenous components and carbohydrates and also in CO_2H groups.

Py–FIMS of SF Extract and Fractions. The assignment of the major signals in the mass spectra (Figures 2–4) was based on the extensive research by Schulten and colleagues (Schulten and Simmleit, 1986; Hempfling et al., 1988; Schulten and Schnitzer, 1990; Schulten et al., 1991).

The Py–FI mass spectrum of the SF extract (Figure 2) showed the presence in this material of carbohydrates (mainly polysaccharides with pentose and hexose subunits) (*m/z* 60, 72, 84, 96, 98, 110, 112, 114, 126, 132, 144, and 162), phenols (*m/z* 94, 108, 110, 122, 124, 138, 140, and 154), monomeric lignins (*m/z* 124, 138, 140, 150, 152, 154, 164, 166, 168, 178, 180, 182, 194, 196, 208, 210, and 212), and phenoxybenzaldehyde (*m/z* 198). Present in lower concentrations were dimeric lignins (*m/z* 246, 260, 270, 272, 274, 284, 286, 296, 298, 300, 310, 312, 314, 316, 326, 340, 342, and 356). The presence of *n*-fatty acids, ranging from *n*-C_{16} to *n*-C_{34}, was indicated by signals at *m/z* 256, 270, 284, 298, 312, 326, 340, 354, 368, 382, 396, 410, 424, 438, 452, 466, 480, 494, and 508. Molecular ions at *m/z* 380, 394, 408, 422, 436, 450, 464, 478, 492, and 506 were probably *n*-C_{27}–C_{36} alkanes. The signals at *m/z* 416, 430, and 444 were most likely due to sterols. Uneven numbered signals at *m/z* 59 and 95 arose from acetamide and hydroxypyridine, respectively. This spectrum also showed the presence of small amounts of *n*-alkyl monoesters, ranging from C_{49} to C_{66}, at *m/z* 718, 732, 746, 760, 774, 788, 802, 816, 830, 844, 858, and 872.

The Py–FI mass spectrum of the SF extract soluble in hot 0.5 M HCl (Figure 3a) showed the presence as major components of carbohydrates (*m/z* 72, 84, 96, 98, 110, 112, 114, 126, 132, 144, and 162), phenols (*m/z* 94, 108, 110, 122, 124, 138, 140, and 154), monomeric lignins (*m/z* 124, 138, 140, 150, 152, 154, 164, 166, 168, 178, 180, 182, 194, 196, 208, 210, and 212), and phenoxybenzaldehyde (*m/z* 198). Minor components were dimeric lignins (*m/z* 246, 260, 270, 272, 274, 284, 286, 296, 298, 300, 310, 312, 314, 316, 326, 340, 342, and 356) and C_{28}–C_{30} *n*-alkanes (*m/z* 394, 408, and 422).

The Py–FI mass spectrum of the SF extract insoluble in 0.5 M HCl (Figure 3b) was dominated by C_{21}–C_{36} *n*-fatty acids (*m/z* 326, 340, 354, 368, 382, 396, 410, 424, 438, 452, 466, 480, 494, and 508), sterols (*m/z* 414, 416, 430, and 444), *n*-alkanes ranging from C_{28} (*m/z* 394) to C_{61} (*m/z* 856) and *n*-C_{40}–C_{60} alkyl monoesters (*m/z* 592, 620, 648, 662, 676, 704, 760, 788, 816, 830, 858, and 872). In addition, the spectrum showed small signals indicative of the presence of residual carbohydrates (*m/z* 84, 98, and 126) and of dimeric lignins.

The Py–FI mass spectrum of the SF extract soluble in hot 6 M HCl (Figure 4a) showed the dominance in this fraction of carbohydrates (*m/z* 72, 82, 84, 96, 98, 110, 112, 114, 126, 132, 144, and 162), phenols (*m/z* 94, 108, 110, 122, 124, 126, 138, 140, and 154), monomeric lignins (*m/z* 124, 138, 140, 150, 152, 154, 164, 166, 168, 178, 180, 182, 194, 196, 208, 210, and 212), and phenoxybenzaldehyde (*m/z* 198). In addition, smaller amounts of dimeric lignins and *n*-fatty acids, mostly in protonated forms (*m/z* 383, 396, 411, 425, and 453), were also detected. Signals at *m/z* 81 (methylpyrrole), 95 (dimethylpyrrole), 111, 125, 161, 175, 189, and 225 showed the presence of N compounds.

The Py–FI mass spectrum of the SF extract insoluble in hot 6.0 M HCl (Figure 4b) was dominated by C_{16}–C_{39} *n*-fatty acids (*m/z* 256, 270, 284, 298, 312, 326, 340, 354, 368, 382, 396, 410, 424, 438, 452, 466, 480, 494, 508, 522, 536, 550, 564, and 578), C_{40}–C_{50} *n*-alkyl monoesters (*m/z* 592, 606, 620, 634, 648, 662, 676, 690, 704, 718, and 732), and dilignins (*m/z* 246, 260, 270, 272, 274, 284, 286, 296, 298, 300, 310, 312, 314, 316, 326, 328, 330, 340, 342, and 356). Other components which were present in relatively high concentrations were *n*-C_{20}–C_{44} *n*-alkanes (*m/z* 282, 296, 310, 324, 338, 352, 366, 380, 394, 408, 422, 436, 450, 464, 478, 492, 506, 520, 534, 548, 562, 576, 590, 604, and 618) and sterols (*m/z* 414, 416, 430, 444, and 458). Small signals at *m/z* 84, 98, 110, 112, 114, 126, 132, 144, and 162 and at *m/z* 110, 122, 124, 126, 138, 140, and 154 showed the presence of small amounts of residual carbohydrates and phenols, respectively, which had resisted 6 M HCl hydrolysis.

From the ^{13}C NMR and Py–FI mass spectrometric data it appeared that the two acid-soluble and the two acid-insoluble fractions resembled each other in chemical

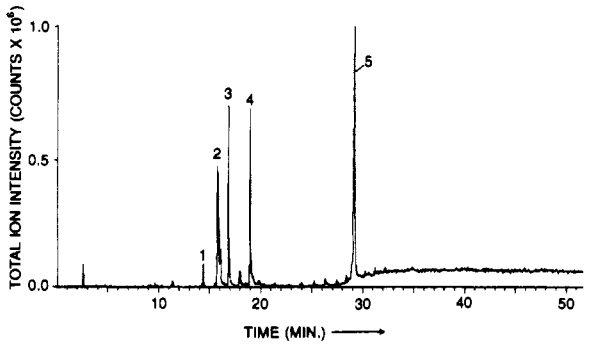

Figure 6. Cp Py–GC/MS of deltamethrin.

composition. The fractions soluble in the acids were rich in carbohydrates, nitrogen compounds, and carboxyl groups with lower concentrations of aliphatics (fatty acids, alkyl esters, and alkanes) and mono- and dilignins. On the other hand, the acid-insoluble fractions consisted primarily of aliphatics with long alkyl chains and aromatic and, to a smaller extent, phenolic compounds. It is possible that these major components had interacted to form alkyl–arylic or alkyl–phenolic structures as suggested recently by Schulten et al. (1991) and Schulten and Schnitzer (1993).

Relationship between ^{14}C Residues and Chemical Composition. From the data presented herein it appears that the 0.5 M HCl soluble fraction of the SF extract accounted for 61% of the weight of the SF extract but for only 29% of its radioactivity. By contrast, the 0.5 M HCl insoluble fraction of the same SF extract constituted only 37% of its weight but contained 51% of its radioactivity, so that the 0.5 M HCl insoluble fraction was enriched in radioactivity. As the ^{13}C NMR and Py–FI mass spectra of the latter fraction show, this material is made up essentially of alkyl–arylic or alkyl–phenolic structures, that is, of aromatic and phenolic rings substituted by long-chain alkyl chains. These are the structures that appear to be active in the adsorption of the pesticides. These structures are largely hydrophobic, which would facilitate the adsorption of the hydrophobic insecticide and/or metabolites. While the chemical compositions of both 0.5 and 6.0 M HCl soluble and insoluble fractions were very similar, there was a shift of ^{14}C residue content from the insoluble to the soluble fraction when the stronger acid was employed. This suggests that for the purpose of obtaining information on reactions of the pesticides with soil OM the use of the more dilute acid is preferable. It is possible, however, that even under these conditions some shift in radioactivity from the insoluble to the soluble fraction could have occurred.

Cp Py–GC/MS of SF Extract Insoluble in 0.5 M HCl. To obtain additional information on this fraction which was richest in radioactivity, we analyzed this material by Cp Py–GC/MS. The separation, illustrated in Figure 5, resulted in 73 subfractions. Major mass signals and tentative identifications of the latter are presented in Table III. An inspection of the data in Table III shows that the major organic components of this fraction were alkylbenzenes, alkylphenols, alkanes, alkenes, alcohols, fatty acids, and sterols. The data in this table are in general agreement with the chemical composition indicated for this fraction by Py–FIMS.

Cp Py–GC/MS of Deltamethrin. The purpose of this experiment was twofold: (a) to uncover what happens to deltamethrin when subjected to Cp Py–GC/MS and (b) to determine whether any deltamethrin degradation products could be identified among the compounds

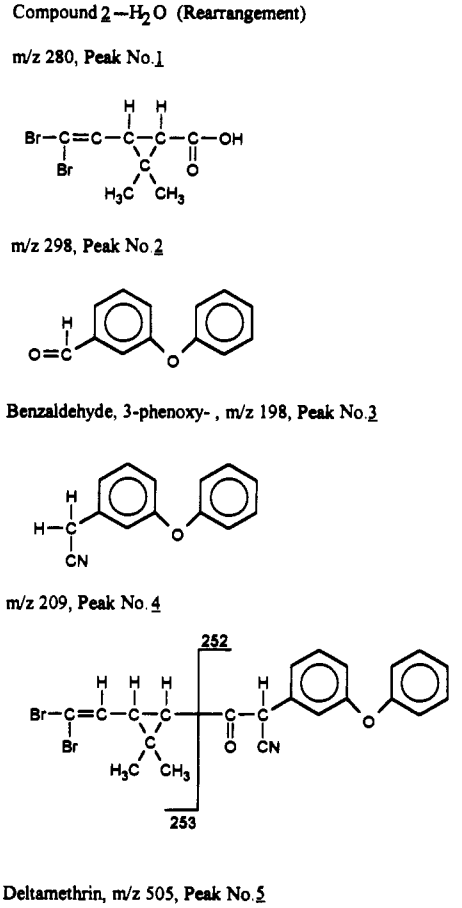

Figure 7. Fragmentation of deltamethrin resulting from Cp Py–GC/MS.

Table IV. Cp Py-GC/MS of Pure Deltamethrin

peak	mass signals, *m/z*	assigned compound
1	51, 65, 77, 91, 120, 171, 173, 199, 200, 201, 263, 265, 267, 280, 282	compound 2–H_2O
2	56, 83, 172, 174, 212, 215, 217, 219, 253, 255, 296, 298, 300	see Figure 7
3	51, 77, 115, 141, 169, 181, 197, 198, 199	see Figure 7
4	51, 77, 91, 141, 169, 180, 181, 182, 209, 210	see Figure 7
5	51, 65, 77, 91, 93, 172, 181, 208, 209, 251, 253, 255, 296, 298, 300, 503, 505, 507	see Figure 7

produced under the same experimental conditions from the SF extract insoluble in 0.5 M HCl. The gas chromatographic separation of deltamethrin is illustrated in Figure 6. The mass spectral data and tentative identifications of the five fractions are presented in Table IV and Figure 7. It is noteworthy that the most prominent peak in Figure 6 (peak 9) arises from nondegraded deltamethrin (Figure 7) and that the other peaks are fragments formed, most likely, during the pyrolysis. A comparison of the data in Table IV with those in Table III shows that none of the compounds listed in Table IV is listed in Table III. This indicates that although a measurable amount of radioactivity still persists in the 0.5 M HCl insoluble portion of the SF fraction, neither deltamethrin nor any of its degradation products can any longer be detected in this fraction. The only identified compound in Table III that bears witness to the earlier presence of deltamethrin is no. 27, 1-bromododecane [CH_3-

$(CH_2)_{10}CH_2Br]$, which suggests bromine addition to or substitution on long-chain aliphatics in the organic soil, with the bromine originating from deltamethrin.

Other Observations. Of considerable interest is the identification in the initial SF extract, and in the SF extracts soluble in 0.5 and 6.0 M HCl, respectively, of phenoxybenzaldehyde (m/z 198). This compound is also a significant degradation product of deltamethrin (peak 3 in Figure 6). Thus, the phenoxybenzyl structure constitutes a significant and most likely relatively stable portion of the deltamethrin structure (see Figure 7). Its detection in our more soluble fractions suggests that it could have originated from the applied deltamethrin and survived the 9-year incubation period. It is possible that phenoxybenzyl structures could have been formed from lignin or phenolic soil organic matter components. However, in our research on soil organic matter, in which we have used methods which are similar to those employed in this investigation, we have so far not found any detectable phenoxybenzyl structures.

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