Varying Persistence of Polychlorinated Biphenyls in Six California Soils under Laboratory Conditions

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Widespread reports of polychlorinated biphenyls (PCBs) as an apparently very stable environmental contaminant subject to biological magnification (RISEBROUGH et al. 1968; KOLMAN et al. 1969, and JENSEN et al. 1969) prompted a study of the relative behaviors of Aroclor® 1254 vs p,p'-DDT, both at ten ppm, in several distinct soil types.

Each fortified and control sample, moistened to 40% saturation, was inoculated and kept in an enameled tray loosely covered with a glass plate to retard water evaporation, substrate volatilization, and photodecomposition. Thus, the substrates would be subject to possible microbial degradation, chemical degradation, and adsorption to soil colloids, but not losses due to leaching or soil transport. Properties of the soils used were determined by HERMANSON and RIBLE (1967) (See Table I).

Experimental

Fortification. A hexane solution (one mg/ml) of either 30 mg of p,p'-DDT or Aroclor 1254 was added to 300 g of air-dried soil, which was then mixed and stirred until the solvent evaporated. This fortified subsample was then added to sufficient unfortified soil to yield a total weight equivalent to three kg of oven-dry soil. Since the soils had been stored for about four years in an air-dried condition, three g of 2-mm sieved inoculant soil collected from the local mountains was added to insure the presence of microorganisms. The combined sample was mixed for one hour in a Twin Shell Dry Blender, placed in a 10-1/8 in x 16-1/8 in x 2-3/8 in enameled tray, distilled water was added to adjust the moisture content to 40% of saturation, and the tray was covered loosely with a glass plate.

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Conditions. Trays were kept on shelves in a plant growth chamber at 30±1°C and about 70% relative humidity and continuously illuminated with "daylight" fluorescent tubes. Evaporative losses were replaced with distilled water three times a month to maintain a constant soil moisture level. Each sample was handmixed at this time, and tray positions in the chamber were interchanged.

Extraction. At each sampling interval, three subsamples of 20 g of oven-dry soil each were extracted without drying (SAHA et al. 1969). To each subsample in a 4-oz screw-cap bottle was added 40 ml of a 1:1 hexane-acetone mixture. The bottle, closed with aluminum foil and a teflon-lined cap, was shaken mechanically for one hour. The shaking was repeated twice, using 40 ml of fresh solvent and ten min each time. Subsample supernatants were combined and passed through 25 g of anhydrous Na_2SO_4. Soil, bottle, and Na_2SO_4 were rinsed with 40 ml more of hexane.

This total extract was reduced to about two ml using initially a Kuderna-Danish apparatus and finally a gentle stream of air. The extractives were transferred to a 160 mm x 90 mm ID column containing about 1.5 g of deactivated Florisil (15 g water/100 g) using three successive 5-ml portions of hexane to rinse the tube and elute the column. The volume of the eluate was adjusted to 10.0 ml, and the solution was analyzed by microcoulometric glc.

Each Laveen loamy sand extract was further cleaned up for analysis by electron capture by placing it on a 30 cm x 2.5 cm OD glass column packed with a ten cm height of 60-100 mesh Florisil and prewashed with 50 ml of hexane, and then eluting with 200 ml of nanograde hexane (REYNOLDS, 1969). The eluate was reduced to 50 ml and an aliquot analyzed.

Analysis. A Dohrmann Instruments Model S-200 furnace unit and Model C-200 microcoulometer with a T-300S titration cell were used for the microcoulometric determinations; operation was in Mode II at 200 ohms. Gas flow rates were 100 ml/min for nitrogen (carrier) and 100 ml/min for oxygen. The borosilicate column was 6 ft x 4 mm ID packed with a 1:1 mixture of 10% DC-200 and 15% QF-1, each coated on Gas-Chrom Q, 60-80 mesh. DDT quantitation was by peak area using internal standards, and Aroclor composition was estimated from peak heights.

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The Aroclor 1254 chromatograms shown in Figures 1B-1G each represents the extractives from 24 mg of soil. No correction for background, as determined from unfortified samples, was necessary for either substrate.

Data using an electron capture detector (tritium source) were obtained with a Varian model 1700 gas chromatograph fitted with a 5½ ft x 2 mm ID borosilicate column packed with a 1:1 mixture of 10% DC-200 and 15% QF-1. The carrier gas was helium, 30 ml/min; injection, column, and detector temperatures were 230°, 190°, and 205°C, respectively. A standard curve (nonlinear) was used for quantitation. No corrections for background, as determined by an unfortified sample, was required.

Results and Discussion

Figure 1A is the chromatogram obtained with a microcoulometric detector for 240 ng of Aroclor 1254. The major peaks, disregarding shoulders due to poor resolution, are numbered 1-7 for discussion purposes. Figures 1B-1G are microcoulometric chromatograms of extracts of soil moisture content of 40-45% saturation for 4-12 months. Each chromatogram represents the extractives obtained from 24 mg of soil. Thus, Fig. 1A represents a 100% recovery of Aroclor 1254 from 24 mg of soil fortified at ten ppm.

About 95% of the Aroclor 1254 added to Windy loam soil was recovered after one year had elapsed (Fig. 1B); the relative peak heights of the various compounds present remained unchanged demonstrating no preferential losses. Results for the Santa Lucia silt loam were identical with these. Both soils have high organic matter (Table I).

Figure 1C represents extractives from the Linne clay; after one year it still retained all the peaks but preferential losses of material were evident. While approximately 90% of the material comprising peak 7 was recovered, only about 40% was recovered from peak 1. Losses were most apparent for the first two major peaks. Results for Madera sandy loam were similar to those for Linne clay, although the soil characteristics were quite dissimilar (Table I). Figure 1D represents Mocho silt loam soil which differs from the clay and sandy loam in that, except for peaks 6 and 7, 25-50% losses of material were evident. The result was corrected for an 80% recovery of Aroclor 1254 from the initial sample.

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TABLE I

Chemical and physical data of some California soils*.

Soil type	Organic matter (%)	pH	Soil texture			Saturation percentage
			% sand	% silt	% clay	
Laveen loamy sand						
San Bernardino County	0.1	8.7	94	1	5	21
Windy loam						
Amador County	10.8	6.0	51	40	9	54
Madera sandy loam						
Coachella Valley	1.4	6.7	60	28	12	27
Santa Lucia silt loam						
Santa Barbara County	19.5	5.6	34	42	24	94
Mocho silt loam						
Santa Barbara County	1.9	7.9	18	58	24	45
Linne clay						
Santa Barbara County	3.3	7.5	37	25	38	48

*H. P. HERMANSON and J. M. RIBLE, unpublished data (1967)

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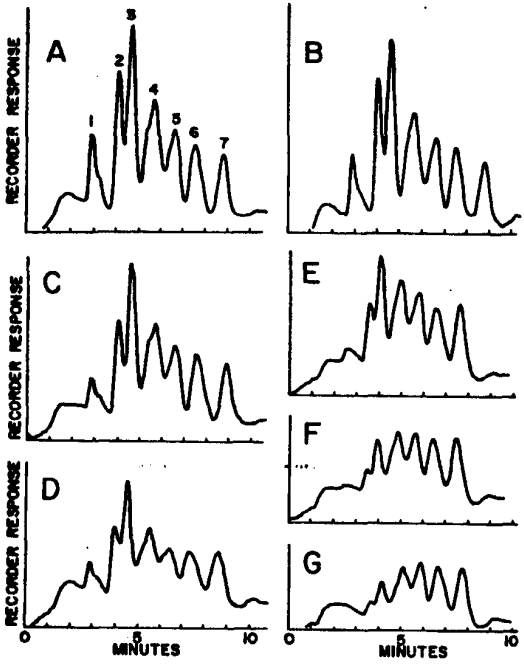

Fig. 1--Microcoulometric GLC chromatograms. (A) represents 240 ng of Aroclor 1254. Chromatograms B through G each represents the injection of the extractives from 24 mg of soil fortified at ten ppm and stored for 4-12 months at 30°C and a soil moisture of 40-45% of saturation. (B) Windy loam after 12 months. Note essential superimposability with A. (C) Linne clay after 12 months. Note relative decreased peak heights in earlier eluting peaks. (D) Mocho silt loam after 12 months. Overall recovery from this soil is about 20% less than from the others. Laveen loamy sand after (E) four, (F) eight, and (G) 12 months.

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The greatest change in Aroclor 1254 composition in the soil was with Laveen loamy sand (Figs. 1E-1G). After one year the characteristic Aroclor 1254 elution pattern was no longer readily recognizable. Although about 75% of peak 7 remained, almost all of the material comprising the first three peaks was gone, and losses of material from the next three peaks were evident. The Laveen loamy sand samples were reanalyzed using an EC detector. Better resolution of the peaks was obtained as smaller quantities of material were injected, and the stability of the EC detector greatly facilitated quantitation. The results are given in Table II.

TABLE II

Relative per cent recovery of Aroclor 1254 from fortified Laveen loamy sand.

Months	Peak 1	Peak 2	Peak 3	Peak 5	Peak 7
0	100	100	100	100	100
2	48	75	81	102	96
4	17	48	60	89	89
8	0	20	32	84	86
12	0	13	23	66	82

BAGLEY et al. (1970), BIROS et al. (1970), and STALLING and HUCKINS (1971) showed with glc-mass spectra data that Aroclor 1254 consisted predominantly of tetra-, penta-, and hexachlorobiphenyl isomers, and that the less chlorinated isomers eluted faster from the glc column. Thus, the material remaining in our Laveen loamy sand after one year consisted of mainly penta- and hexachlorobiphenyl isomers.

DDT, added separately to the same soils in parallel for comparison purposes, gave the results shown in Table III. Combined DDT and DDE remaining after one year accounted for over 70% of the DDT applied in each soil. With the possible exception of Aroclor 1254 added to loamy sand, the PCB and DDT-DDE residues were equally persistent in soil under our conditions.

NIMMO et al. (1971) demonstrated experimentally that Aroclor 1254 can enter the estuarine food chain from contaminated sediments either through organisms ingesting the sediment or absorbing the chemical

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TABLE III

Recovery of residues from soils fortified at 10 ppm with DDT*.

Soil type	Soil moisture (% of saturation)	Months after fortification: 0	1	4	8	8	12	12
		PPM						
		DDT	DDT	DDT	DDT	DDE	DDT	DDE
Santa Lucia silt loam	42	9.6	9.6	8.6	9.2	-	8.3	-
Windy loam	48	9.4	9.1	8.9	9.0	-	8.3	-
Madera sandy loam	41	10.6	9.2	7.8	7.8	1.2	6.7	1.2
Laveen loamy sand	39	10.0	9.3	8.0	7.9	Trace	7.3	Trace
Mocho silt loam	40	8.1	7.5	6.3	5.4	2.4	5.1	2.7
Linne clay	44	9.7	9.7	8.4	7.3	1.9	5.8	2.1

*ppm oven-dry weight

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from the water; the ratio of individual Aroclor isomers maintained integrity in the sediment and tissues of test animals. Laveen loamy sand clearly showed the composition of the persisting PCB residues in this soil was altered with time. If volatilization is mainly responsible for the observed loss of lesser chlorinated PCBs, these materials may, through aerial fallout, become unidentified contaminants far from the source of origin. The composition of the residues remaining in the soil and those obtained elsewhere through aerial fallout will be quite different; biological magnification of these residues clearly will not yield a recognizable glc pattern. Thus, suspected environmental pesticide residues should be subjected to careful evaluation as they could be PCBs of altered composition.

Acknowledgment

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