Table II. Analysis of Variance of Strawberry
Yield Data in Table I

treatment	yield, tons/acre		
	1977–1978	1978–1979	both years
none	13.7	7.3	11.5
fertilizer	28.6	26.9	29.5
significant at	0.1%	0.1%	0.1%
urea	24.2		
other nitrogen	30.8		
significant at	0.1%		
21-0-0	29.3	25.3	28.0
16-20-0	32.2	28.6	31.0
significant at	5%	5%	1%
no N-Serve	27.3	25.5	28.3
N-Serve	29.8	28.3	30.6
significant at	5%	10%	5%

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Movement of Cypermethrin, Decamethrin, Permethrin, and Their Degradation Products in Soil

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The movement of the synthetic pyrethroid insecticides decamethrin, cis and trans isomers of cypermethrin, and cis and trans isomers of permethrin and their degradation products DCVA [cis,trans-3-(2,3-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate], PBAl (3-phenoxybenzyl alcohol), and PBAc (3-phenoxybenzoic acid) was examined in a Hagerstown silty clay, silty clay loam, and a Tifton loamy sand. Movement in both soil columns and soil thin-layer chromatographic (TLC) systems was compared. Decamethrin, cis- and trans-cypermethrin, and cis- and trans-permethrin were immobile in all soils. PBAl was only slightly mobile in each of the three soils examined. Both DCVA and PBAc were mobile in each of the three soils examined, and the separation of the cis and trans isomers of DCVA was observed in some soils. Both DCVA and PBAc were less mobile in acid soils than in an alkaline soil. Soil TLC provided an exceptionally comparable picture of soil movement of the compounds examined when compared with the unsaturated soil columns.

The new synthetic pyrethroid insecticides have great potential as agricultural insecticides, because of their high insecticidal activity, low mammalian toxicity, and adequate stability in air and light (Elliott et al., 1973). Although a considerable amount of information is available about their metabolism in plants and animals, only a limited amount has been published which describes their degradation and movement in soils.

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Kaufman et al. (1977) initially described the degradation of permethrin in soil. That investigation indicated that permethrin [(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] was rapidly degraded in soil and that soil microorganisms played a significant role in permethrin degradation. The principal mechanism of degradation of permethrin involves hydrolysis to 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (DCVA) and 3-phenoxybenzyl alcohol (PBAl). Further metabolism of both products was demonstrated by the measurement of the ^{14}C labels as $^{14}CO_2$. Similar results have been described by other investigators with cypermethrin [cyano-(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] (Roberts and Standen, 1977a), fen-

Table I. Chemical and Physical Characteristics of Soils

| | | cation-exchange capacity, mequiv/100 g | % | | | | |
soil type	pH		sand	silt	clay	organic matter	moisture at 0.33 bar
Hagerstown silty clay	5.5	12.5	7.0	50.0	43.0	4.31	29.1
Hagerstown silty clay loam	7.5	8.8	17.0	50.6	32.4	2.26	21.1
Tifton loamy sand	4.9	2.4	82.0	6.8	11.2	0.98	6.0

propathrin [cyano(3-phenoxyphenyl)methyl 2,2,3,3-tetramethylcyclopropanecarboxylate] (Roberts and Standen, 1977b), fenvalerate [cyano(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate] (Ohkawa et al., 1978), and permethrin (Kaneko et al., 1978).

Only limited information is available regarding the movement or leaching of the synthetic pyrethroid insecticides in soil. Kaneko et al. (1978) observed that while neither (+)-*trans*- nor (+)-*cis*-permethrin moved through a soil column with water, small amounts of degradation products such as 3-phenoxybenzoic acid (PBAc) and 3-(4-hydroxyphenoxy)benzyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate were eluted by water from soil columns which had been pretreated and aged before elution. Fenvalerate was immobile in light clay, sandy clay loam, and sandy loam soils but moved to a small extent in a sandy soil (Ohkawa et al., 1978). Small amounts of 2-(4-chlorophenyl)isovaleric acid, a degradation product of fenvalerate, were leached from aged light clay and sandy clay loam soils treated with fenvalerate. The purpose of this investigation was to examine the movement of several synthetic pyrethroid insecticides and their degradation products in soil columns and on soil thin-layer chromatographic plates and to compare the results obtained by both methods.

MATERIALS AND METHODS

Soils. The chemical and physical characteristics of the soils used in this investigation are listed in Table I. Soils of the Hagerstown series are Typic Hapludalfs, whereas the Tifton loamy sand is classified with the Plintic Paleudults. The soils were air-dried, mixed, and passed through a 4-mm screen before use in these investigations.

Soil Columns. The method of Harris (1964) was used for soil column leaching experiments. The columns were made from 2.5-cm (1-in.) segments of 7.6-cm (3-in.) (i.d.) machined aluminum tubing. Silicone stopcock grease was used to waterproof the joints between segments. The columns were supported by 9-cm Buchner funnels fitted with Whatman No. 2 filter paper. After the columns were uniformly packed with air-dried soil to a depth of 30.5 cm (12 in.), a second piece of filter paper was placed on the soil surface. A known volume of distilled water was then slowly added to each soil column. The excess water eluted through each column was collected and the volume recorded. The amount of water retained by each column was calculated as the volumetric water content (V_0). After the columns were wetted, they were allowed to equilibrate overnight.

Column leaching experiments were conducted with the Hagerstown silty clay and Tifton loamy sand. The mean volumetric water content (±variance) for columns of Hagerstown silty clay was 545.8 mL (±1.5%); for Tifton loamy sand, the content was 373.8 mL (±2%).

^{14}C chemical addition to each column was achieved by first adsorbing the chemical to a 50-g sample of the air-dried soil, thoroughly mixing the sample, and adding it to the top of a soil column after removal of the filter paper used in the initial watering of the column. A new filter paper disk was then added to the soil surface and the soil

column was slowly leached with one V_0 of distilled water. The leachate from each column was collected in uniform volumes and subsampled for liquid scintillation counting of its possible ^{14}C content.

After addition of one V_0 of water to each column, the columns were allowed to stand until all water movement through the column had stopped. The columns were then carefully segmented, and the contents of each segment transferred to a 500-mL flask and extracted with 100 mL of methanol by blending for 3 min. The extracts were vacuum-filtered and then brought to a uniform volume, and two 1-mL samples were removed for scintillation counting. The extracted soils were air-dried and weighed to determine the actual soil weight in each ring. The product concentration present in any individual segment was then calculated as a percentage of the total ^{14}C activity extracted from all segments of the column and its leachate.

After the extractable ^{14}C content of each segment extract was determined, the extracts were selectively pooled and concentrated in a rotary evaporator to remove the methanol. The residual extract (aqueous) was then acidified to pH 2 with concentrated HCl and partitioned with ether. The ether extracts were then concentrated to ~1 mL and submitted to thin-layer chromatographic analysis on silica gel F254 chromatoplates with appropriate standards. The solvent system used was benzene saturated with formic acid–diethyl ether (10:3 v/v). After development, the plates were exposed momentarily to ultraviolet light (UV, 254 nm) to locate UV absorbing spots and finally to no-screen medical X-ray film for 3–4 weeks. After autoradiography, and documentation, all radioactive spots were removed and analyzed for their ^{14}C content by liquid scintillation spectrometry.

Soil Thin-Layer Chromatography (TLC). The soil TLC technique of Helling and Turner (1968) was used to assess the relative mobility of several synthetic pyrethroids and their degradation products in three soils. The basic technique has been described in detail elsewhere (Helling, 1971a–c; Helling and Turner, 1968). Briefly, air-dried soil was sieved to ~250 μm, moistened with water until moderately fluid, and then applied to clean glass TLC plates with a commercial TLC spreader. The soil layer thickness was ~500 μm.

The ^{14}C-labeled compounds to be tested were spotted at 1.5 cm above the base of the plate. The base of each plate was then immersed in ~0.5 cm of water in a closed glass chamber and leached to a scribed line 11.5 cm from the base of the plate. In this manner the ^{14}C-labeled compound can be leached over a distance of 10 cm by ascending chromatography. The soil plates were air-dried after the usual 2–3-h development period. After being dried, the plates were autoradiographed for ~3 days. The resultant autoradiograph was considered indicative of pesticide movement, which was measured as the frontal R_f of the spot or streak. Center R_f values were also determined for comparisons of the two soil leaching methods.

Chemicals. ^{14}C-Labeled chemicals were used in all leaching studies. The chemical designations, names, and specific activities are listed in Table II. The radiopurity of all compounds was determined to be >98% by TLC

Table II. Designation, Chemical Name, ^{14}C-Label Position, and Specific Activities of Chemicals Used

| designation	chemical name	^{14}C-label position	sp act., mCi/mmol
cis-cypermethrin	(±)-cyano-(3-phenoxyphenyl)methyl cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	carbonyl	54.8
trans-cypermethrin	(±)-cyano-(3-phenoxyphenyl)methyl trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	carbonyl	54.8
decamethrin	(S)-cyano-(3-phenoxyphenyl)methyl cis-(±)-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate	ethenyl or U-phenoxy	5.0 20.7
cis-permethrin	(3-phenoxyphenyl)methyl cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	carbonyl	50.0
trans-permethrin	(3-phenoxyphenyl)methyl trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	carbonyl	50.0
DCVA	cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid	carbonyl	54.8
PBAc	3-phenoxybenzoic acid	carbonyl	21.6
PBAl	3-phenoxybenzyl alcohol	U-phenoxy	19.8
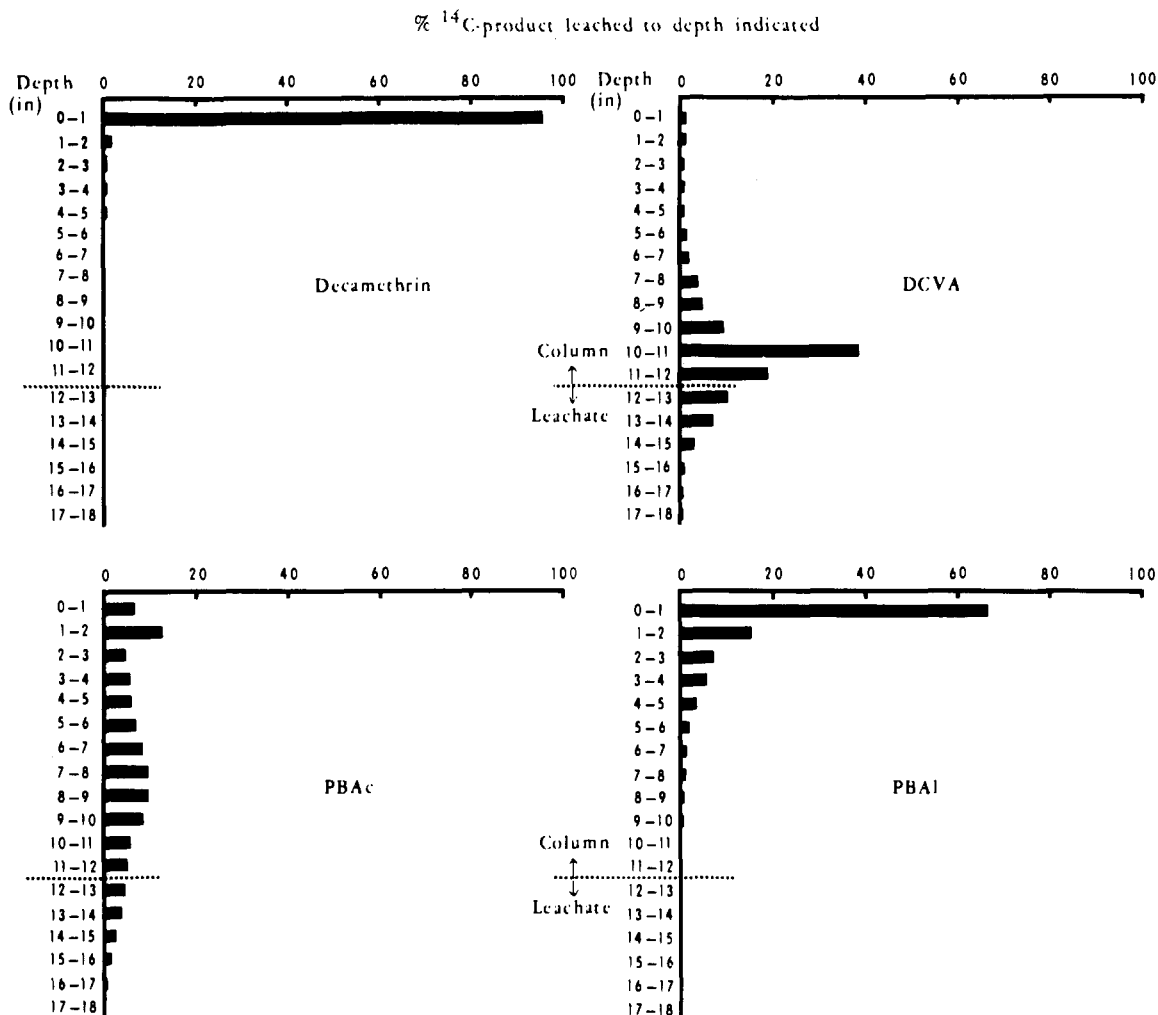
Figure 1. Mobility of decamethrin, DCVA, PBAc, and PBAl in soil columns of Hagerstown loamy clay.

analysis on silica gel F254 plates eluted with benzene saturated with formic acid–diethyl ether (10:3). The DCVA was applied as a 40% cis–60% trans mixture. All chemicals were applied as isotopic solutions in 25–50 µL of ethanol. Approximately 2-µg applications were used in all instances. For soil columns, this corresponds to a rate of ~4.4 g/ha. At least two replications were used for all treatments.

RESULTS AND DISCUSSION

Soil Columns. The degree of leaching of decamethrin, DCVA, PBAc, and PBAl through soil columns is illustrated in Figures 1 and 2. The results are presented as percent of the total radioactive carbon recovered from the leachate and by extraction from the soil segments. When decam-

ethrin is adsorbed to soils and added directly to moist soil columns and immediately leached, there is essentially no movement down through the soil column. Approximately 96–97% of the ^{14}C activity remained in the 0–2.5-cm (0–1-in.) layer of both the Hagerstown silty clay and Tifton loamy sand columns. Only 1.3% of the ^{14}C activity was present in the 2.5–5.1-cm (1–2-in.) layer of either soil, and less than 0.5% of the ^{14}C activity recovered was present in any other column segment. Essentially no ^{14}C radioactivity was detected in the leachate from soil columns treated with decamethrin.

DCVA is a degradation product of both cypermethrin and permethrin in soil (Kaneko et al., 1978; Kaufman et al., 1977; Roberts and Standen, 1977a). PBAc is a degradation product of cypermethrin, decamethrin, per-
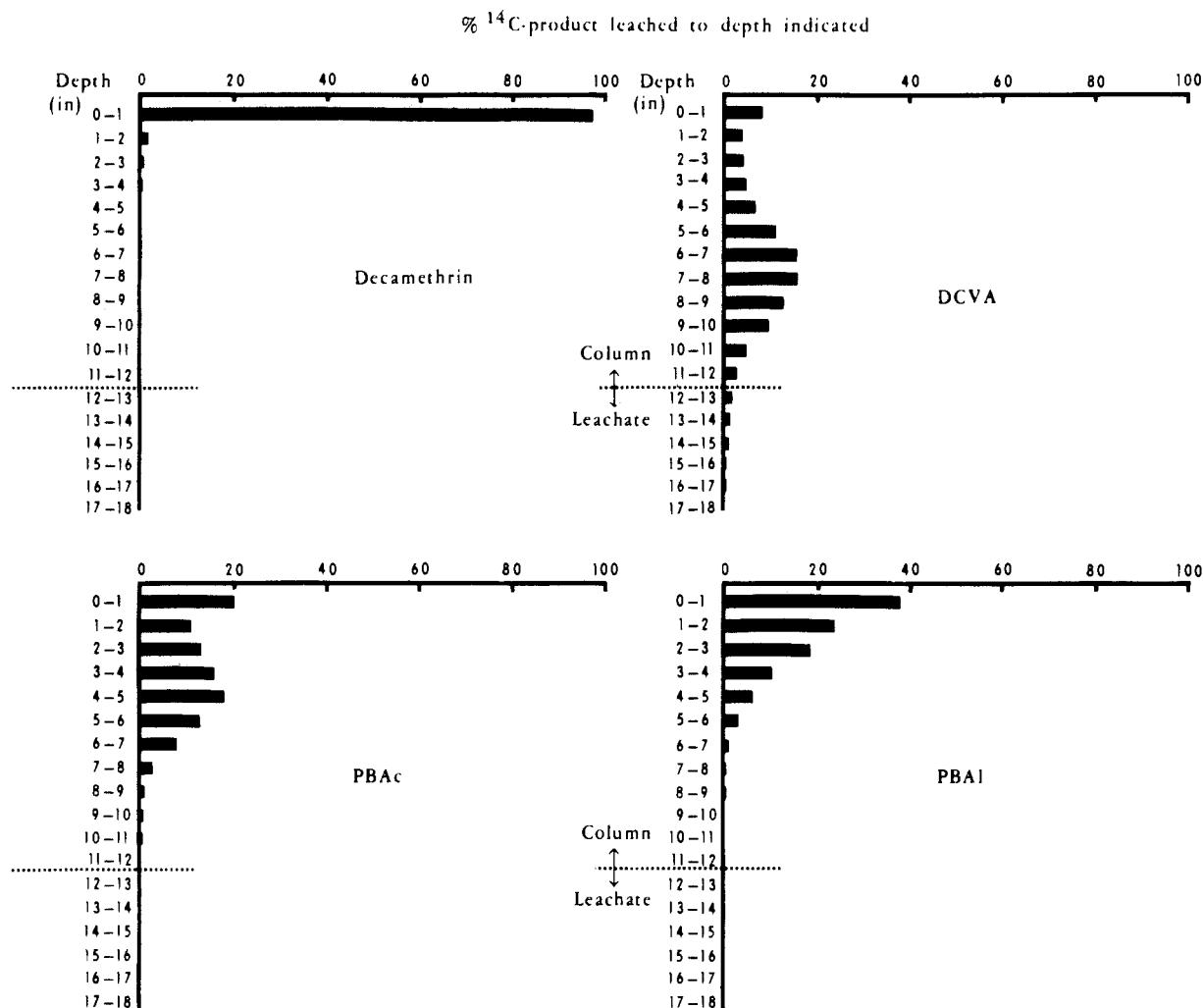
242   J. Agric. Food Chem., Vol. 29, No. 2, 1981

Kaufman et al.

% ^{14}C-product leached to depth indicated

Figure 2. Mobility of decamethrin, DCVA, PBAc, and PBAl in soil columns of Tifton loamy sand.

Table III. TLC Analyses of Pooled Column Segment Extracts from Tifton Loamy Sand

column treatment	soil depth assayed, in.	% of ^{14}C on TLC plate identified as					
		decamethrin	DCVA cis	DCVA trans	PBAc	PBAl	other
decamethrin	0-1	92.4			1.5		6.1
DCVA	0-5		56.6	43.4			
	6-12		35.1	64.9			
PBAc	0-3				91.1		8.9
	4-8				92.2		7.8
PBAl	0-3				36.1	56.4	7.4
	4-6				81.0	19.1	

methrin, and PBAl in soil (Kaufman et al., 1977; Roberts and Standen, 1977a). Both DCVA and PBAc were mobile in both soils used in column leaching studies. Most of the DCVA remained in both soil columns, yet ca. 20% and <4% appeared in leachates from the silty clay (Figure 1) and loamy sand (Figure 2), respectively. By determining the V_0 of each soil column and the dry weight of soil in each column segment and by collecting the leachate in known volumes, it was possible to calculate how much further DCVA or PBAc would have penetrated the soil if longer columns had been used. By this calculation, we determined that 0.2% of the DCVA would have been detected at the 41-43-cm (16-17-in.) depth in both soil types. In the silty clay soil >92% of the [14C]DCVA was present in the zone equivalent to 18-38 cm with most (38.5%) occurring in the 25.4-27.9-cm (10-11-in.) layer. In the loamy sand soil, >95% of the DCVA was present in the 0-30.5-cm (1-12-in.) layer, with peak concentration

(30.7%) occurring at the 15.2-20.3-cm (6-8-in.) layer.

TLC analysis of pooled segment extracts from the Tifton loamy sand column (Table III) indicated that some separation of the cis and trans isomers of DCVA occurred during the column leaching process. A 40% cis-60% trans mixture of DCVA was used in this investigation. The final distribution of the cis-trans isomers indicated that the more polar trans isomer moved more readily than did the cis isomer. Similar, but more definitive results were obtained in soil TLC experiments with DCVA, which will be discussed later.

PBAc leached readily in both soils but was more mobile in the Hagerstown silty clay (Figure 1) than in the Tifton loamy sand (Figure 2). Kaneko et al. (1978) also observed that PBAc leached readily in aged soil columns originally treated with permethrin. TLC analysis of the pooled segment extracts (Table III) indicated that >90% of the ^{14}C activity present in these extracts was the parent PBAc.

Movement of Cypermethrin, Decamethrin, and Permethrin

J. Agric. Food Chem., Vol. 29, No. 2, 1981 **243**

Table IV. Pesticide Mobility Classification for Soil TLC Plates (Helling and Turner, 1968)

class	R_f range	description
1	0–0.09	immobile
2	0.10–0.34	low
3	0.35–0.64	intermediate
4	0.65–0.89	mobile
5	0.90–1.0	very mobile

Other products present in these extracts were tentatively identified as either the ortho- or para-hydroxylated derivatives of PBAc.

That both PBAc and DCVA should be relatively mobile in soil is not surprising. Both are organic acids and as such are quite polar. Helling and Turner (1968) and Helling (1971b,c) observed that the organic acids were the most mobile pesticides.

PBAl, a soil degradation product of permethrin (Kaneko et al., 1978; Kaufman et al., 1977), was only slightly more mobile than decamethrin in soil columns (Figures 1 and 2). Although <0.3% of the ^{14}C activity recovered was detected at the 20.3–22.9-cm (8–9-in.) level in both soils, the bulk (>96%) of the ^{14}C activity was present in the upper 13-cm zone in the silty clay soil and in the upper 15 cm of the loamy sand soil. TLC analysis of the pooled segment extracts revealed that considerable degradation of PBAl to PBAc occurred during the short duration of this experiment (Table III). More than 80% of the ^{14}C present in the 10–15-cm (4–6-in.) layers was actually PBAc and not PBAl. Thus, under field conditions PBAl would probably not move very far in soil.

Soil TLC. Soil TLC has been used successfully to characterize the mobility of a large number of pesticides in soil (Chapman et al., 1970; Helling, 1971b,c; Helling et al., 1971, 1974; Helling and Turner, 1968; Rhodes et al., 1970). It is a unique laboratory method in which soil is used as the absorbent phase in a TLC system. The relatively simple system yields quantitative data on pesticide mobility that appear to correlate well with trends noted in the literature (Helling and Turner, 1968). Due to its innate homogeneity, the adsorbent in soil TLC may best represent the milieu of a pesticide moving through soil aggregates rather than around them.

The relative mobilities of several synthetic pyrethroid insecticides and their degradation products were compared according to the pesticide mobility classification system developed by Helling and Turner (1968) for soil TLC plates (Table IV). On the basis of this system, decamethrin, cis- and trans-cypermethrin, and cis- and trans-permethrin were classified as low mobility to immobile compounds in the soils examined (Table V). On the basis of frontal R_f values measured, both cis-cypermethrin and trans-cypermethrin appear to be slightly more mobile than cis-permethrin, trans-permethrin, or decamethrin. These results demonstrated, however, that very little movement of any intact synthetic pyrethroid would occur through soil. Similar conclusions were reached by others in soil mobility investigations with fenvalerate (Ohkawa et al., 1978) and permethrin (Kaneko et al., 1978).

In the soils examined, the pyrethroid degradation products DCVA, PBAl, and PBAc were all more mobile in the soils examined than any of the parent materials (Table V). Nonetheless, PBAl would still be classed as a compound of low mobility (class 2) in the silty clay loam and silty clay soils, whereas in the Tifton loamy sand soil it was intermediate (class 3) in mobility. The organic acids PBAc and DCVA varied in their mobility classification from intermediate (in the silty clay or loamy sand) to mobile (in the silty clay loam). This is not surprising in

Table V. Soil TLC of Synthetic Pyrethroid Insecticides and Their Degradation Products

compound	soil type	R_f values frontal	R_f values central
decamethrin	silty clay loam	0.04	0.02
	silty clay	0.05	0.03
	loamy sand	0.04	0.02
cis-cypermethrin	silty clay loam	0.13	0.06
	silty clay	0.08	0.04
	loamy sand	0.12	0.06
trans-cypermethrin	silty clay loam	0.13	0.07
	silty clay	0.10	0.05
	loamy sand	0.16	0.08
cis-permethrin	silty clay loam	0.10	0.05
	silty clay	0.04	0.02
	loamy sand	0.08	0.04
trans-permethrin	silty clay loam	0.08	0.04
	silty clay	0.05	0.02
	loamy sand	0.09	0.05
DCVA	silty clay loam	0.87	0.72
	silty clay	0.45[a]	0.31[a]
		0.61[b]	0.54[b]
	loamy sand	0.51	0.29
PBAc	silty clay loam	0.73	0.53
	silty clay	0.39	0.22
	loamy sand	0.36	0.18
PBAl	silty clay loam	0.26	0.13
	silty clay	0.21	0.10
	loamy sand	0.35	0.19

[a] Cis isomer of DCVA. [b] Trans isomer of DCVA.

view of the known effects of soil chemical physical characteristics on the movement of chemicals in soil. Helling (1971b,c) and Helling and Turner (1968) noted that with few exceptions all of the organic acid pesticides which they examined were class 4 (mobile) or class 5 (very mobile) compounds. Many researchers have suggested that adsorption is an important—perhaps dominant—factor influencing pesticide movement. Solution or soil pH affects adsorption of many pesticides (Bailey et al., 1968; Helling, 1971b; McGlamery and Slife, 1966; Weber, 1970); low pH suppresses ionization of organic acids, thus increasing adsorption and decreasing their mobility. This was demonstrated directly with the organic acid herbicides dicamba (3,6-dichloro-o-anisic acid) and fenac (2,3,6-trichlorophenylacetic acid) when their mobility increased as soil pH was adjusted upward (Helling, 1971b). Although we examined only three soils, each having a different pH level, our results suggest that DCVA and PBAc would be fairly mobile in agricultural soils having a neutral to alkaline pH.

Soil organic matter content is generally inversely correlated with pesticide mobility in soil. Here, however, both DCVA and PBAc were least mobile in the loamy sand, which had the lowest organic matter content (0.98%), and most mobile in the silty clay loam soil, which was intermediate (2.26%) in its organic matter content but high (7.5) in pH. Thus, soil pH seemed to be the primary factor affecting mobility of these two compounds in soil.

Although both products are mobile in soil, their relative lability in soil would tend to limit the amount available for leaching. Nevertheless, Kaneko et al. (1978) observed small amounts of PBAc in the eluate of 20-cm soil columns of a sandy clay loam (pH 6.3) that had been treated with trans-permethrin and incubated for 21 days before being leached. 4-Hydroxypermethrin [3-(4-hydroxyphenoxy)-benzyl (±)-cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] was eluted from a 20-cm soil column of a light clay (pH 5.5) that had been treated with cis-permethrin and incubated 21 days before being leached. Ohkawa et al. (1978) noted that hardly any ^{14}C activity was eluted from soils incubated with [cyano-^{14}C]-(±)-fenval-
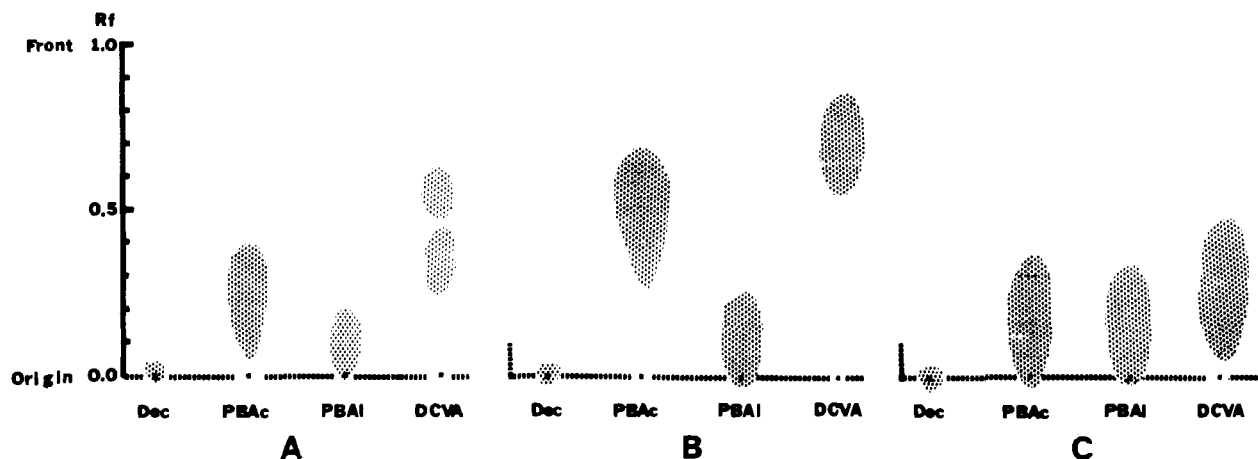
Figure 3. Mobility of decamethrin, DCVA, PBAc, and PBAl in soil TLC plates [(A) Hagerstown silty clay; (B) Hagerstown silty clay loam; (C) Tifton loamy sand].

Table VI. Comparative Mobility of Decamethrin, DCVA, PBAc, and PBAl in Soil Column and TLC Systems

compound	soil type[a]	frontal R_f column	frontal R_f TLC	central R_f column	central R_f TLC
decamethrin	Hagerstown sic	0.04	0.05	0.02	0.03
	Tifton ls	0.04	0.04	0.02	0.02
DCVA	Hagerstown sic	0.67	0.45[b] 0.61[c]	0.49	0.31[b] 0.53[c]
	Tifton ls	0.51	0.51	0.30	0.29
PBAc	Hagerstown sic	0.66	0.39	0.33	0.22
	Tifton ls	0.34	0.36	0.17	0.18
PBAl	Hagerstown sic	0.22	0.21	0.11	0.10
	Tifton ls	0.25	0.35	0.13	0.19

[a] Sic, silty clay; ls, loamy sand.   [b] Cis isomer of DCVA.
[c] Trans isomer of DCVA.

erate for 30 days before leaching, whereas 2-(4-chlorophenyl)isovaleric acid was obtained in effluents from soils similarly treated with [carbonyl-^{14}C]-(±)-fenvalerate.

It was particularly interesting to note that the cis and trans isomers of DCVA were distinctly separated during soil TLC in the silty clay soil (Table V and Figure 3). Only a single eluted spot was distinguishable from DCVA on soil TLC plates prepared from the loamy sand and silty clay loam. Trace amounts (<0.5%) of the cis- or trans-DCVA were detectable in soil TLC plates spotted with cis- or trans-permethrin, respectively. Under these conditions, distinctly different frontal and center R_f values could be determined for both isomers in the loamy sand also, but not in the silty clay loam. Frontal R_f values for the cis- and trans-DCVA isomers in the loamy sand were 0.40 and 0.52, respectively. The frontal R_f value for the cis,trans-DCVA mixture on loamy sand TLC plates was 0.51, as expected (Tables V and VI). Partial separation of the cis and trans isomers was also noted in the soil column studies with DCVA (Table III).

DCVA is a degradation product of both cypermethrin and permethrin. The corresponding degradation product of decamethrin is DBVA [3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylic acid]. Although we did not examine the mobility of DBVA in this investigation, we surmise that DBVA would be somewhat less mobile in soil than its chloro analogue, DCVA. Within a homologous series of chemicals such as the s-triazines or phenylureas, mobility generally is inversely related to molecular weight and/or chemical structure or both. Although generalizations regarding mobility as a function of molecular

structure were tenuous with the phenylureas, the addition of halogen substituents to the aromatic ring did reduce leaching (Helling, 1971b; Helling et al., 1971). Substituting chlorine substituents with bromine substituents further reduced mobility. For example, replacement of the 4-chlorine substituent of linuron [3-(3,4-dichlorophenyl)-1-methylurea] with a 4-bromine substituent to form chlorbromuron [3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea] reduced the mobility from R_f 0.17 (linuron) to R_f 0.14 (chlorbromuron). Thus, by analogy one could reasonably expect that DBVA would be less mobile in soil than DCVA.

The relative mobilities of several compounds in both soil columns and by TLC systems (Table VI) were compared. Column R_f values were calculated by determining the maximum depth to which the eluted water would have penetrated if the column had been longer than 30 cm. This depth was used as the "solvent front" value for the purpose of calculation. Column frontal R_f values were calculated by using that maximum depth at which a minimum of 2% of the ^{14}C activity applied could be detected. Center R_f values were calculated by first determining the point of maximum ^{14}C activity (Figures 1 and 2) and then including all segments with ^{14}C activity above and below point, until a total of ~98% of the ^{14}C activity applied was accounted for. Soil TLC frontal and center R_f values were calculated as usual, based on detection of ^{14}C activity by X-ray film. In general, excellent agreement was obtained in a comparison of the relative mobilities of these chemicals in the two systems. If the R_f values obtained in both systems (Table VI) are compared by the system of Helling and Turner (1968) (Table IV), one will observe that there is excellent agreement in the results obtained by the two systems. The only notable exception is the relative mobility of PBAc in the silty clay soil. However, the distinctions here between mobility classes are somewhat arbitrary, and both systems indicate that PBAc will leach through soil to some extent.

SUMMARY AND CONCLUSIONS

The results of this investigation indicated that the synthetic pyrethroid insecticides decamethrin, permethrin, and cypermethrin are immobile in soil and cannot be readily leached through soil. PBAl, a direct hydrolysis product of permethrin degradation, and a metabolite of PBAc produced during degradation of decamethrin and cypermethrin, is of low mobility (class 2) in soil and would probably not be particularly mobile in the soil environment. PBAc is a degradation product of all three synthetic pyrethroids insecticides examined herein and is produced

during microbial metabolism of PBA1 in soil. As organic acids, both PBAc and DCVA could be expected to be somewhat mobile through soil. The extent of their mobility, however, is determined by the soil pH, as well as by the rate of their degradation in soil. Both compounds are degraded in soil (Kaneko et al., 1978; Roberts and Standen, 1977a,b), and neither can be considered persistent. Only trace amounts of PBAc were eluted from soils which had been incubated for several weeks prior to leaching (Kaneko et al., 1978). Based on the results obtained with the few compounds examined in this investigation, it seems that soil TLC and soil columns provide a comparable measure of the mobility of chemicals in soil. Due to its ease in handling, processing, reproducibility, ease of analysis, and limited space requirements, soil TLC should be the method of preference.

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Metabolism of N-Nitrosopendimethalin and N-Nitropendimethalin by a Streptomyces Isolated from Soil

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[^{14}C]-N-Nitrosopendimethalin (1) [N-(1-ethylpropyl)-N-nitroso-3,4-dimethyl-2,6-dinitrobenzenamine], a contaminant of the dinitroaniline herbicide pendimethalin, was metabolized to several products by a Streptomyces sp. isolated from soil. Identifications were made by chemical ionization and electron impact mass spectrometry, chromatographic and spectral comparisons, and synthesis. Reduction of a nitro group was characteristic of all metabolites; hydroxylation of ring methyl groups was also present in some metabolites. Metabolism of [^{14}C]-N-nitropendimethalin (2) [N-(1-ethylpropyl)-3,4-dimethyl-N-2,6-trinitrobenzenamine] yielded two hydroxymethyl metabolites.

Alkyl nitrosamines and nitrosated herbicides have been detected in certain herbicide formulations. These disclosures have prompted research on the environmental fate and possible human exposure to these nitrosamines. N-Nitrosopendimethalin (1; Figure 1) (Bontoyan et al., 1978, 1979) and N-nitropendimethalin (2) (Bontoyan, 1979) were detected as contaminants of the dinitroaniline herbicide pendimethalin (3) [N-(1-ethylpropyl)-3-4-dimethyl-2,6-dinitrobenzenamine]. Radiolabeled 1 was included in a study of aerobic soil degradation of herbicide-related nitrosamines (Oliver et al., 1979); in one experiment, 50% of the radioactivity was recovered as intact 1 after 4 months. Thin-layer chromatography of the soil extract revealed a few additional bands; however, the

amounts of material were too small for isolation and identification. Both 1 and 2 were found to degrade more rapidly than pendimethalin, 3, in flooded anaerobic soil (Smith et al., 1979). This paper describes the isolation and identification of metabolites from the degradation of 1 and 2 by an aerobic soil microorganism.

MATERIALS AND METHODS

Reagents. All solvents were glass distilled and used without further purification except for diethyl ether which was redistilled just prior to use. Pendimethalin-1-ethyl-^{14}C (0.043 μCi/mg) was supplied by American Cyanamid, Agricultural Division, Princeton, NJ. The labeled material was >99% pure by thin-layer chromatography (TLC) and autoradiography. We are also indebted to American Cyanamid for supplying samples of 3-[(1-ethylpropyl)-amino]-6-methyl-2,4-dinitrobenzenemethanol (17) and 4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitrobenzenemethanol (13). Syntheses of 1 (Oliver et al., 1979) and 2 and N^2-(1-ethylpropyl)-4,5-dimethyl-3-nitro-1,2-benzenediamine (5) (Smith et al., 1979) have been described.

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