of these cases, the levels of 3-phenoxybenzoic acid in the soil were higher under anaerobic conditions with results indicating further degradation of the acid to $^{14}CO_2$ under aerobic conditions. Cyanide (as HCN) is readily converted to CO_2 and NH_3 by a wide variety of soil types (Strobel, 1967). With ^{14}CN-labeled fenvalerate, large amounts of $^{14}CO_2$ were evolved under aerobic and anaerobic conditions, with no detectable H^{14}CN found under the conditions tested (Ohkawa et al., 1978).

3-Phenoxybenzoic acid was found by Kaufman et al. (1981) to be of low mobility by soil thin-layer chromatography; however, they indicate that the mobility would be determined by the soil pH. Although this acid would be fairly mobile in agricultural soils having neutral to alkaline pH, Kaufman et al. (1981) observed that the relative lability in soil would tend to limit the amount available for leaching.

Conclusions. The above results indicate a minimal environmental impact of fluvalinate in agricultural soils. The immobility of fluvalinate as well as its rapid degradation are important features of an environmentally acceptable insecticide.

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Chlorpyrifos Applied to California Citrus: Residue Levels on Foliage and on and in Fruit

Yutaka Iwata,* Janet R. O'Neal, James H. Barkley, Travis M. Dinoff, and Margarete E. Düsch

Chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate], the active ingredient in Lorsban (trademark of Dow Chemical Co.) insecticide formulation, was field-applied to California orange and grapefruit trees. Applications, made in combination with oil, included two dilute and two low-volume spray rates. Residue data were obtained for assisting in setting worker reentry safety intervals and legal fruit tolerances. Dissipation curves over a 60-day postapplication period were obtained for chlorpyrifos and total 3,5,6-trichloro-2-pyridinol residues on and in citrus rind. No determinable residues (>0.03 ppm) were found in the edible portion of the citrus fruits. Dissipation data for chlorpyrifos and its oxygen analogue (oxon) on citrus foliage were determined. Both compounds dissipated rapidly, and the maximum oxon level found was 0.033 $\mu g/cm^2$ in a 3-day sample. Data indicated that low-volume applications did not give uniform spray coverage of grapefruit trees. It was speculated that the dense foliar structure of the tree prevented uniform coverage by low-volume equipment.

Chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate], the active ingredient in Lorsban insecticide formulation, shows good promise as a useful insecticide for California citriculture. Incorporated into a granular bait, it is effective against the Argentine ant, *Iridomyrmex humilis* (Mayr), and used as a spray, it gives good control of the California red scale, *Aonidiella aurantii* (Mask.). Petroleum oil sprays are often applied to California citrus trees to reduce populations of both mites and scale insects. When infestations of red scale are present, addition of insecticides such as malathion, carbaryl, and azinphosmethyl are recommended to enhance the effectiveness of the oil spray. Chlorpyrifos also promises to be an effective spray oil additive. Residue data are reported herein for chlorpyrifos applied to California citrus trees to assist regulatory agencies in setting fruit residue tolerances for consumer protection and for setting safe reentry waiting intervals for agricultural worker protection (Gunther et al., 1977).

Department of Entomology, University of California, Riverside, Riverside, California 92521.

EXPERIMENTAL SECTION

Treatment and Sampling. Mature trees of Navel orange, Reed grapefruit and Valencia orange were located on the University of California Citrus Research Center, Riverside, CA. The number of trees per acre was 121 for Navel orange (20 × 18 ft planting), 99 for grapefruit (21

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× 21 ft), and 115 for Valencia orange (18 × 21 ft). Three replicate field plots were used for each spray treatment rate tested. Applications were made on Aug 31, 1979, to Navel orange trees, Aug 14, 1981, to grapefruit trees, and Aug 17, 1981, to Valencia orange trees. Low-volume treatments were made with a Kinkelder machine equipped with an air tower, and dilute treatments were made with an oscillating boom spray rig. All treatments used Lorsban 4E, a 4 lb of active ingredient (AI)/gal emulsifiable concentrate (EC), commercial formulation.

Navel orange trees were treated with 5.0 and 10.0 lb of AI (2000 gal)$^{-1}$ acre^{-1} [5.6 and 11.2 kg (187 hL)$^{-1}$ ha^{-1}] and 10 lb AI (100 gal)$^{-1}$ acre^{-1} [11.2 kg (9.4 hL)$^{-1}$ ha^{-1}]. Grapefruit and Valencia orange trees were treated with a combination of Lorsban 4E and narrow-range, NR-440 type spray oil. Application rates were 5.0 and 10.0 lb of AI and 28 gal of oil (2000 gal)$^{-1}$ acre^{-1} [5.6 and 11.2 kg and 252 L (187 hL)$^{-1}$ ha^{-1}] and 5.0 and 10.0 lb of AI and 14 gal of oil (100 gal)$^{-1}$ acre^{-1} [5.6 and 11.2 kg and 131 L (9.4 hL)$^{-1}$ ha^{-1}].

Each of three Navel orange subplots consisted of eight trees. A 40 leaf disk sample was collected by excising five 2.54-cm-diameter disks from each tree such that each octant position around the tree was represented by five disks in the composite sample (Gunther et al., 1973).

Each of three Valencia orange subplots consisted of four trees from which samples were actually collected. A 32-fruit sample was collected by picking 1 fruit from each of the 8 octant positions from each of the 4 trees. A 40 leaf disk sample was collected by excising 10 disks from each of the 4 trees such that each octant position was represented by 5 disks in the composite sample.

Each of three grapefruit subplots consisted of eight trees from which samples were collected. A 20-fruit sample was collected from the 8-tree plot such that each quadrant was represented by 5 fruits. A 40 leaf disk sample was collected by excising 5 disks from each of the 8 trees such that each octant position was represented by 5 disks in the composite sample.

Processing. *Fruit: Chlorpyrifos.* Fruits were separated into rind and pulp (edible portion) as described by Gunther (1969). A 100-g aliquot of chopped rind or pulp was macerated with 300 mL of acetone for 5 min in a blender can. The extract was vacuum-filtered through a Büchner funnel A 50-mL aliquot of the extract was placed in a 125-mL separatory funnel with 50 mL of hexane, and the mixture was shaken gently for 30 s. The lower aqueous phase was discarded, and the upper phase was passed through a funnel containing Na_2SO_4 into a flask. The Na_2SO_4 and funnel were rinsed with 25 mL of hexane. The solvent was removed by using a rotary evaporator, and the residue was dissolved in acetone for analysis by gas chromatography (GC) for chlorpyrifos. Calculations assumed that the total acetone extract volume was 380 mL for the rind and 400 mL for pulp resulting from 300 mL of acetone plus 80 mL of water from rind and 100 mL of water from pulp for 100 g of substrate used.

Fruit: Total 3,5,6-Trichloro-2-pyridinol. The method used in conjunction with final quantification with a nitrogen detector was as follows. Ten grams of chopped rind, 40 mL of CH_3OH, and 5 mL of 10% NaOH solution were refluxed for 30 min. The cooled mixture was transferred to an Omni-Mixer can with the aid of 15 mL of CH_3OH and blended for 3 min. The macerate was filtered through a pad of Celite with the aid of two 15-mL CH_3OH rinses. The CH_3OH was removed with a rotary evaporator, and the residue was transferred to a separatory funnel with two 10-mL portions of water. After the addition of 8 g of NaCl and 40 mL of benzene, the mixture was shaken for 1 min; the benzene phase was discarded. Then, 0.7 mL of 85% H_3PO_4 was added, and the mixture was extracted twice with 40 mL of benzene each time. Each benzene extract was successively filtered through Na_2SO_4 into a collection flask; the Na_2SO_4 was then rinsed with 20 mL of benzene. The benzene was removed completely, and 5 mL of acetone and a 2-mL solution of CH_2N_2 in diethyl ether was added. After 15 mL of hexane was added, the diethyl ether and acetone were removed with a rotary evaporator. The derivative is somewhat volatile so the mixture cannot be taken to dryness. The residue was transferred to a column containing 5 g of Florisil topped with 10 g of Na_2SO_4 by using three 5-mL portions of hexane. The column was eluted with an additional 30 mL of hexane. The eluate was then analyzed after appropriate volume adjustment for 2-methoxy-3,5,6-trichloropyridine by GC with a nitrogen detector.

The method was altered slightly for citrus pulp. The amount of substrate, CH_3OH, and NaOH used were doubled. The blending step after the hydrolysis step was omitted. After addition of NaCl, two 80-mL portions of benzene were used. The amount of H_3PO_4 used was doubled. The Florisil column did not remove coextractives in the citrus pulp which interfered with quantification. Therefore, a column was packed with 10 g of activity-grade III, basic alumina. The derivatized residue and coextractives were transferred to the column with three 5-mL portions of hexane. An additional 10 mL of hexane was used to elute the column.

Although *N,O*-bis(trimethylsilyl)acetamide (BSA) could have been used to derivatize the trichloropyridinol, unlike BSA, excess CH_2N_2 could be easily eliminated without leaving behind any nitrogen-containing products in the extract solutions. This allowed the use of a nitrogen/phosphorus thermionic detector for quantification in addition to the electron-capture detector option which was also used. The formation of a stable derivative with CH_2N_2 also allowed for the advantageous use of a postderivatization sample cleanup step. Takei and Lee (1981) have reported the use of CH_2N_2 for the derivatization of trichloropyridinol in blood plasma samples. Diazomethane is potentially explosive, an insidious poison, and a strong irritant. Thus, to ensure its safe use, a researcher should be well informed about its preparation, properties, and handling techniques.

Dislodgeable Foliar Residues. The procedure of Iwata et al. (1977) was used. Briefly, the procedure entailed shaking the leaf disk sample 3 times, each time with 100 mL of water containing a surfactant, and then extracting the combined aqueous wash twice, each time with 50 mL of CH_2Cl_2 to recover residues for analysis. The CH_2Cl_2 was removed, and the residue was dissolved in acetone for analysis by GC for chlorpyrifos and its oxygen analogue (oxon).

Analytical Standards. Analytical standards of chlorpyrifos, its oxon [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphate], and 3,5,6-trichloro-2-pyridinol were provided by Dow Chemical U.S.A., Midland MI. 3,5,6-Trichloro-2-pyridinol was treated with a diethyl ether solution of CH_2N_2. The ether was removed, and the products were column chromatographed on Florisil. Hexane elution gave 2-methoxy-3,5,6-trichloropyridine with proton magnetic resonance (^{1}H NMR) singlets at δ 7.92 (H) and 4.02 (OCH_3) [in CCl_4; tetramethylsilane (Me_4Si) internal standard]; mp was 63–64 °C. Diethyl ether elution gave *N*-methyl-3,5,6-trichloro-2-pyridone with ^{1}H NMR singlets at δ 7.53 (H) and 3.73 (N–CH_3) (in CCl_4; Me_4Si internal standard)

and an infrared carbonyl absorption at 5.95 μm (in $CHCl_3$); mp was 137–138 °C. The ^1H NMR spectrum of the initial reaction mixture indicated an approximate 2:1 ratio of OCH_3 to $N-CH_3$ products.

Analysis. GC was employed, and residues of chlorpyrifos, its oxon, and 2-methoxy-3,5,6-trichloropyridine were quantified by using a Hewlett-Packard nitrogen/phosphorus thermionic detector. A ^3H electron-capture detector was used for the analysis of 2-methoxy-3,5,6-trichloropyridine in grapefruit samples. For analysis of chlorpyrifos and its oxon, a 1.2 m × 2 mm i.d. glass column packed with 5% OV-210 on 60–80-mesh Gas-Chrom Q (Alltech Associates) was used with a 30 mL/min nitrogen gas flow rate and a 210 °C column temperature. Retention times were 1.0 and 1.8 min for chlorpyrifos and its oxon, respectively. For the analysis of 2-methoxy-3,5,6-trichloropyridine, a 1.2 m × 2 mm i.d. glass column packed with 5% OV-101 on 80–100-mesh Ultra-Bond 20M (Ultra Scientific) was used with a 30 mL/min carrier gas flow rate and a 170 °C column temperature. Retention times were 0.95 and 2.75 min for 2-methoxy-3,5,6-trichloropyridine and *N*-methyl-3,5,6-trichloro-2-pyridone, respectively. Only the former peak was used for sample quantification.

Method Validation. All the following values are the mean of three replicate sample analyses; standard deviations are given. Although chlorpyrifos oxon residues in field samples of fruit were not sought, results of preliminary laboratory tests are presented herein as background information.

Chopped rind samples were each fortified in the blender jar prior to the addition of the acetone. For samples fortified with chlorpyrifos at 0.10, 1.0, and 10 μg/g (ppm), recoveries were 101 ± 6, 100 ± 3, and 101 ± 6%, respectively, and for samples fortified with chlorpyrifos oxon at 0.050, 0.10, and 1.0 ppm, recoveries were 107 ± 6, 95 ± 4, and 95 ± 9%, respectively.

Results for all the following tests were obtained with laboratory-treated fruits unless specified otherwise. Oranges were treated by individually immersing each whole fruit for about 10 s in a solution of 1.0 mL of Lorsban 4E and 50 mg of chlorpyrifos oxon in 800 mL of water. Fruits were allowed to stand for 1 day before processing.

To estimate the extraction efficiency of the acetone blending procedure, the plant matrix remaining after filtering the acetone rind macerate was Soxhlet-extracted with 1:9 $CH_3OH-CHCl_3$. The extraction was conducted for 2 h and then again for another 2 h with fresh solvent. Residues obtained for the second 2-h extraction were <0.01 ppm. When rind from water-washed fruits was used, the blending procedure yielded 5.6 ± 0.2 ppm of chlorpyrifos and 0.06 ± 0.01 ppm of oxon. Soxhlet extraction gave an additional 0.75 ± 0.05 ppm of chlorpyrifos and 0.03 ± 0.01 ppm of oxon. Thus, extraction efficiency for the blending procedure was about 90% for chlorpyrifos and 70% for the oxon. No corrections have been applied to the field sample data for fruits since the overall procedure was deemed satisfactory based upon the above results.

Laboratory-treated, unwashed fruits were stored at 8 °C. After 0, 2, and 7 days of storage, chlorpyrifos residues on and in the rind were 6.5 ± 0.4, 6.4 ± 0.3, and 7.4 ± 0.6 ppm. respectively, and oxon residues were 0.17 ± 0.03, 0.16 ± 0.02 and 0.19 ± 0.02 ppm, respectively. Thus, fruits can, if necessary, be stored for several days after sampling. Field samples collected for this study were processed, i.e., peeled, chopped, and frozen, within 2.5 days after sample collection.

Rind from laboratory-treated, washed fruits was chopped, and 100-g subsamples were stored for 0, 2, 3, and 5 weeks in a freezer. Residues were with increasing storage time 6.5 ± 0.4, 6.4 ± 0.1, 6.7 ± 0.6, and 6.4 ± 0.2 ppm, respectively, for chlorpyrifos and 0.17 ± 0.03, 0.22 ± 0.02, 0.22 ± 0.02, and 0.22 ± 0.02 ppm, respectively, for the oxon. Thus, residues were quite stable under frozen storage of substrate. Subsamples of 100 g of chopped orange rind prepared from three field samples collected 10 days postapplication were also kept under frozen storage to test storage stability of residues. The mean chlorpyrifos residue values after 1, 70, and 95 days were 0.83 ± 0.08, 0.76 ± 0.07, and 0.76 ± 0.05 ppm, respectively. No storage decomposition of residues was evident based on these values and their standard deviations. All field samples of chopped orange and grapefruit rind were stored frozen pending analysis. The elapsed times between sample collection and completion of analysis for chlorpyrifos on and in orange rind were 68, 71, 71, 62, 53, and 48 days for the 3-, 10-, 17-, 30-, 45-, and 59-day samples, respectively. The elapsed times between sample collection and completion of analysis for chlorpyrifos on and in grapefruit rind were 30, 29, 30, 24, 15, and 10 days for the 3-, 10-, 17-, 31-, 45-, and 59-day samples, respectively.

Acetone extracts prepared from orange rind were stored for 0, 2, 3, and 5 weeks at 8 °C. Residues were with increasing time 6.5 ± 0.4, 6.2 ± 0.3, 6.3 ± 0.3, and 6.3 ± 0.3 ppm, respectively, for chlorpyrifos and 0.17 ± 0.03, 0.23 ± 0.01, 0.25 ± 0.02, and 0.25 ± 0.02 ppm, respectively, for the oxon. Generally, all acetone extracts were analyzed within 1 week after preparation.

Aqueous leaf washes obtained from 40 leaf disks (2.5-cm diameter) were fortified with 400, 40, and 4 μg (equivalent to 1.0, 0.1, and 0.01 μg/cm^2 of leaf surface) of chlorpyrifos and its oxon, and recoveries were determined. Mean recovery values were 88 ± 3, 96 ± 5, and 91 ± 3%, respectively, for chlorpyrifos and 89 ± 8, 94 ± 1, and 89 ± 6%, respectively, for the oxon. No corrections have been made to the field sample data since recoveries were deemed satisfactory. All leaf disk samples were processed into CH_2Cl_2 extracts on the day of collection and were analyzed within 4 days after sample collection.

Samples of 10 g of chopped orange rind were fortified with either 5 μg (25 nmol) of 3,5,6-trichloro-2-pyridinol or 8.4 μg (24 nmol) of chlorpyrifos. The samples were analyzed for 2-methoxy-3,5,6-trichloropyridine, and mean recoveries were 87 ± 3% when trichloropyridinol was added and 85 ± 3% when chlorpyrifos was added. Except for one sample which contained 0.3 ppm, all field samples contained 0.4 ppm of trichloropyridinol or higher. Samples of 20 g of citrus pulp were fortified with either 1 μg of trichloropyridinol or chlorpyrifos. The samples were analyzed for 2-methoxy-3,5,6-trichloropyridine, and mean recoveries were 79 ± 2% when trichloropyridinol was added and 70 ± 3% when chlorpyrifos was added. All field sample residue values have been corrected for recovery based upon fortified samples run in parallel with the field samples analyzed.

RESULTS AND DISCUSSION

The temporary legal tolerance for combined residues of chlorpyrifos and metabolites in whole orange and lemon fruits is 2.5 ppm (*Fed. Regist.*, 1982). Reported here are residue data after application of chlorpyrifos as an oil spray to grapefruit and orange trees. Residue levels of both chlorpyrifos and total 3,5,6-trichloro-2-pyridinol were determined.

Residue levels of chlorpyrifos and its oxygen analogue on foliage were also determined since these compounds are cholinesterase inhibitors and can pose a hazard to agricultural workers who come into extensive and prolonged

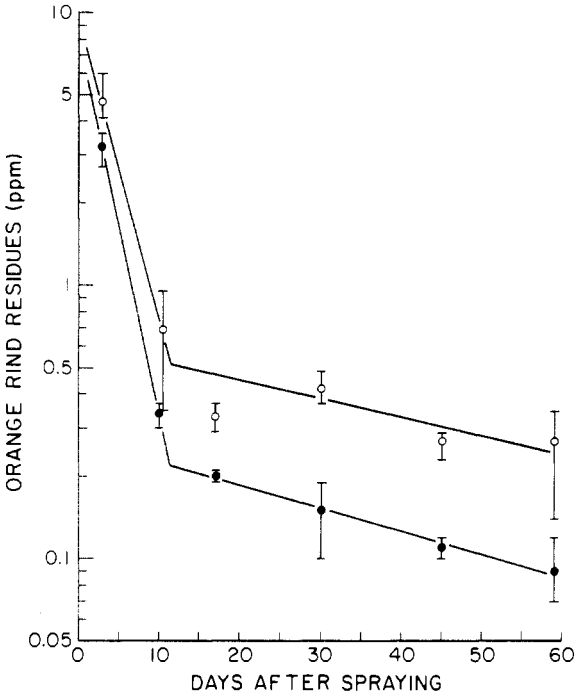

Figure 1. Chlorpyrifos residues on and in orange rind after an application of 5.0 lb of AI of Lorsban 4E/acre. Applications were made with 14 gal of NR-440 oil $(100\ gal)^{-1}\ acre^{-1}$ (○) and 28 gal of NR-440 oil $(2000\ gal)^{-1}\ acre^{-1}$ (●). Vertical lines indicate the range of values found for six samples; two subsamples prepared from each of the three replicate field plot samples were analyzed. Applications were made on Aug 17, 1981.

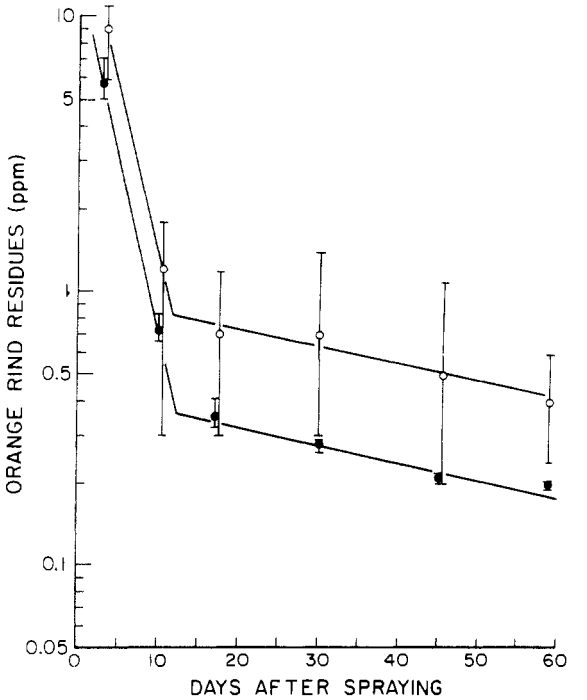

Figure 2. Chlorpyrifos residues on and in orange rind after an application of 10 lb of AI of Lorsban 4E/acre. Read caption to Figure 1 for additional details.

contact with treated foliage (Gunther et al., 1977).

Fruit Residues. Unwashed fruits were used to indicate the maximum amount of residues that would be present. Fruits were separated into rind and pulp (edible portion) samples, and the two substrates were analyzed separately. Chlorpyrifos residues on and in Valencia orange rind are shown in Figures 1 and 2. Residue dissipation is a complex process involving a number of factors (Gunther, 1969).

Table I. Mathematical Description of the Semilogarithmic Plots Shown in Figures 1-8

figure	treatment	-slope	intercept, ppm	correlation coefficient	half-life, days
1	low volume	0.27	11		2.6
		0.0154	0.61	0.789	45
1	boom	0.32	8.4		2.2
		0.0192	0.27	0.996	36
2	low volume	0.29	21		2.4
		0.0144	0.96	0.957	48
2	boom	0.30	14		2.3
		0.0139	0.43	0.970	50
3	low volume	0.232	13		3.0
		0.0128	1.15	0.931	54
3	boom	0.245	9.6		2.8
		0.0102	0.72	0.761	68
4	low volume	0.276	21		2.5
		0.0109	1.6	0.931	64
4	boom	0.232	13		3.0
		0.0108	1.2	0.790	64
5	boom	0.186	6.2	0.999	3.7
		0.0225	0.29	0.986	31
6	boom	0.177	8.9	0.999	3.9
		0.0204	0.44	0.997	34
7	boom	0.145	5.4	0.999	4.8
		0.0093	0.52	0.924	75
8	boom	0.103	5.8	0.991	6.7
		0.0140	0.96	0.707	50

Thus, the dissipation curves shown in Figures 1 and 2 and in subsequent figures are drawn only to indicate the trend exhibited by the limited residue data. Chlorpyrifos residues dissipated rapidly during the initial 2 week postapplication period and then dissipated thereafter at a considerably slower rate. Table I gives the mathematical descriptions of the lines which have been drawn in Figures 1–8. The mean half-life ($t_{1/2}$) values for the four applications were 2.4 ± 0.2 days for the initial rapid residue dissipation and 45 ± 6 days for the subsequent slower dissipation.

The data show that when chlorpyrifos is sprayed in combination with oil, the low-volume application leaves higher residues than the corresponding application with an oscillating boom. This has been generally noted previously with nonoil insecticide sprays, e.g., phenthoate (Iwata et al., 1981).

Figures 3 and 4 show the total chlorpyrifos residues on and in orange rind. Samples were analyzed for total 3,5,6-trichloro-2-pyridinol residues, and these residue values were converted to chlorpyrifos equivalents. Quantification of residues was based on the OCH_3 derivative. Results were corrected for losses as determined from untreated control samples fortified with trichloropyridinol at representative levels and carried through the entire procedure. Mean recoveries for added trichloropyridinol were 82 ± 8, 90 ± 5, 83 ± 7, and 88 ± 7% for the treatment series 5 and 10 lb of AI/2000 gal and 5 and 10 lb of AI/100 gal, respectively. The data indicate that a portion of the total residue curves are higher in value than the chlorpyrifos residue curves. Thus, part of the residues are present either as free or as conjugated trichloropyridinol. The mean $t_{1/2}$ values for the four applications were 2.8 ± 0.2 days for the initial rapid dissipation and 63 ± 6 days for the subsequent slower dissipation.

Data for chlorpyrifos residues on and in grapefruit rind are shown in Figures 5 and 6. Unlike the corresponding data obtained for orange rind, the grapefruit data obtained for the low-volume applications were relatively erratic. Thus, lines to indicate the trend in residue levels with time were only drawn in Figures 5 and 6 for the data obtained

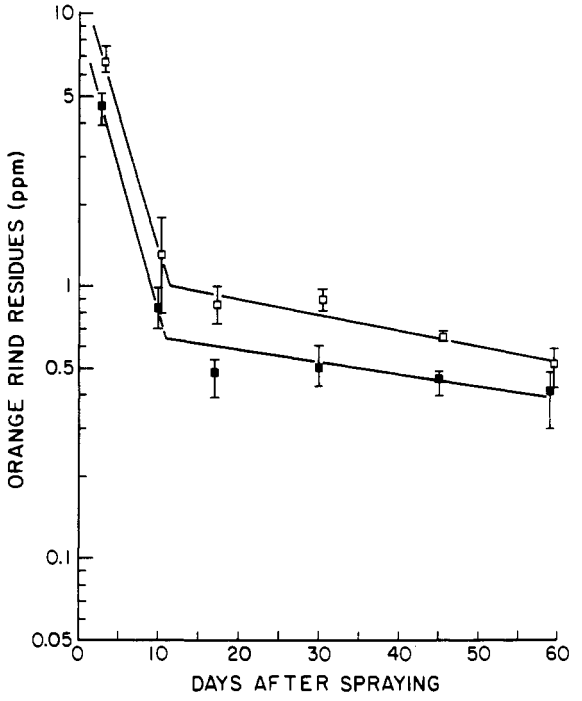

Figure 3. Total chlorpyrifos residues, as determined by analysis for total 3,5,6-trichloro-2-pyridinol, on and in orange rind after an application of 5.0 lb of AI of Lorsban 4E/acre. Applications were made with 14 gal of NR-440 oil (100 gal)$^{-1}$ acre^{-1} (□) and 28 gal of NR-440 oil (2000 gal)$^{-1}$ acre^{-1} (■). Vertical lines indicate the range of values found for the analysis of three samples; one sample prepared from each of three replicate field plot samples was analyzed. Applications were made on Aug 17, 1981.

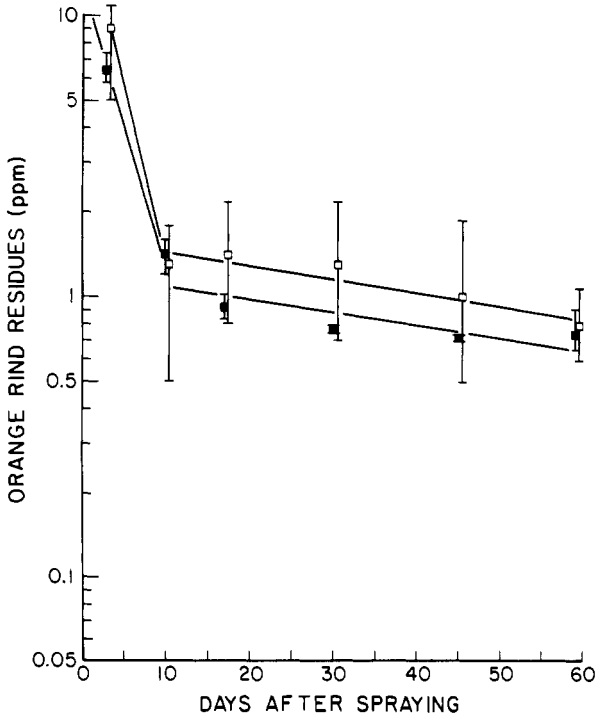

Figure 4. Total chlorpyrifos residues, as determined by analysis for total 3,5,6-trichloro-2-pyridinol, on and in orange rind after an application of 10.0 lb of AI of Lorsban 4E/acre. Read caption to Figure 3 for additional details.

for the application by the oscillating boom. It is believed that poor low-volume coverage was obtained because grapefruit trees have denser foliage than orange trees. The insecticide-bearing droplets were unable to effectively penetrate into the interior of the tree. Since grapefruits,

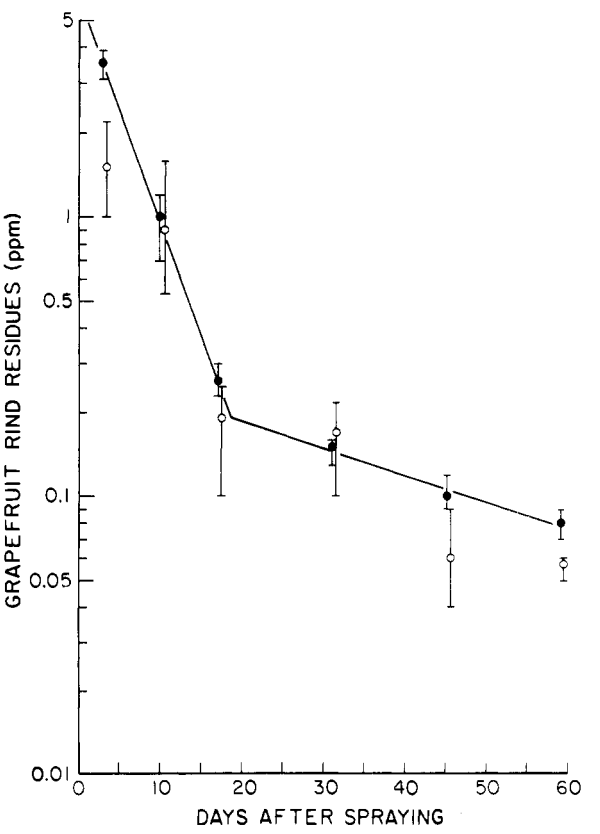

Figure 5. Chlorpyrifos residues on and in grapefruit rind after an application of 5.0 lb of AI of Lorsban 4E/acre. Applications were made with 14 gal of NR-440 oil (100 gal)$^{-1}$ acre^{-1} (○) and 28 gal of NR-440 oil (2000 gal)$^{-1}$ acre^{-1} (●). Dissipation curve lines are drawn only for the (●) data points. Vertical lines indicate the range of values found for six samples; two subsamples prepared from each on three replicate field plot samples were analyzed. Applications were made on Aug 14, 1981.

unlike oranges, are located within the tree as well as on the exterior of the tree canopy, interior fruits accepted less insecticide than the exterior fruits. Thus, if more interior fruits were collected during sampling than exterior fruits, the residue level found would be lower than anticipated. The range of values found for the field samples would also tend to be larger than anticipated. The data shown in Figures 5 and 6 indicate both these trends. Whereas the low-volume treatment left higher residues on oranges than the treatment with the oscillating boom, when the same amount of active ingredient was used in both cases, this was not the case for grapefruit. Again, this indicated that poor deposition was achieved by the low-volume application. Qualitatively, Figures 5 and 6 show that residues from both application methods follow the same dissipation trend. For the data for the oscillating boom, there was good agreement in the dissipation half-lives for the two dosage rates. For the 5 and 10 lb of AI/acre applications, the first portion of the curves was characterized by half-lives of 3.7 and 3.9 days, respectively, and the second portion by 31 and 34 days, respectively.

Figures 7 and 8 show the total chlorpyrifos residues on and in grapefruit rind. Samples were analyzed for total 3,5,6-trichloro-2-pyridinol residues, and these residue values were converted to chlorpyrifos equivalents. Quantification was based only on the OCH_3 derivative. Results have been corrected for losses by use of fortified samples. For the 5 and 10 lb of AI/acre oscillating boom applications, half-lives were 4.8 and 6.7 days, respectively, for the first portion of the curve and 75 and 50 days, respectively, for the second portion of the curves.

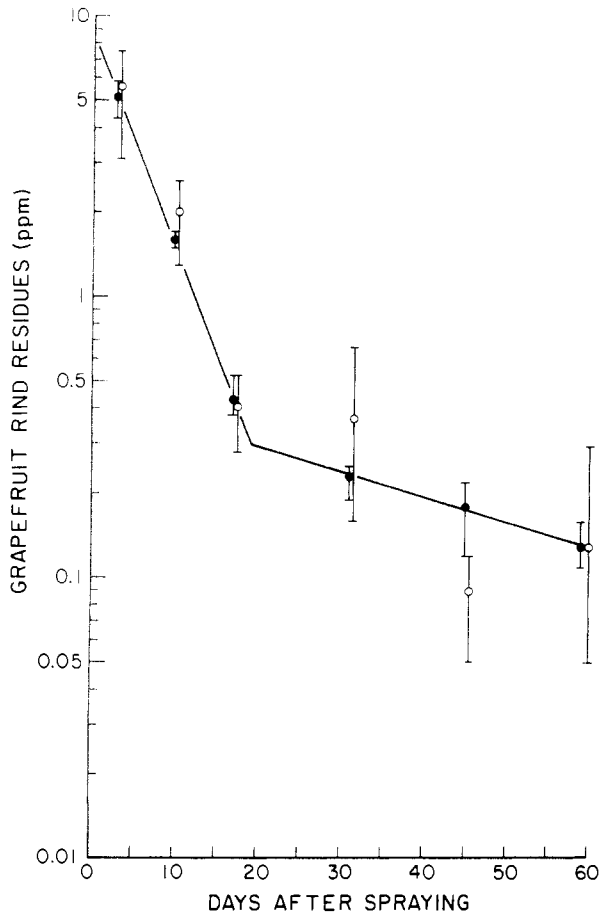

Figure 6. Chlorpyrifos residues on and in grapefruit rind after an application of 10 lb of AI of Lorsban 4E/acre. Read caption to Figure 5 for additional details.

The pulp (edible portion) of the orange and grapefruits was analyzed separately for chlorpyrifos. One field sample prepared from each of three replicate treatment plots was analyzed. Samples were collected 3, 10, 17, 31, 45, and 59 days postapplication. No residues of chlorpyrifos above the 0.03 ppm detectable level were present in either the Valencia orange or grapefruit samples. Recoveries from control samples fortified with 0.05 ppm of chlorpyrifos and analyzed with the samples were 90 ± 10% for oranges and 87 ± 9% for grapefruits. The lack of residues in the edible portion of the fruit is generally observed with spray treatments since the rind acts as a barrier to insecticide penetration.

Only the pulp samples collected from orange tree plots treated with 10 lb of AI of Lorsban 4E and 14 gal of NR-440 oil (100 gal)$^{-1}$ acre^{-1} were analyzed for total trichloropyridinol residues. Two field samples collected 3, 17, and 45 days postapplication were analyzed and contained less than 0.03 ppm of chlorpyrifos equivalents.

Since no chlorpyrifos residues were present in the pulp, residues on a whole-fruit basis would be one-fifth of the Valencia orange rind value and one-fourth of the grapefruit rind value since Valencia oranges are 18.7 ± 6.3% and grapefruits 23.0 ± 3.2% by weight (Gunther, 1969).

Dislodgeable Residues. On Aug 31, 1979, chlorpyrifos was applied as a water spray to Navel orange trees. The maximum air temperature on the day of application was 32.2 °C, and for 23 days postapplication the daily maximum air temperature was at or above 35.0 °C. Between 7 and 18 days postapplication, the temperature was at or above 37.8 °C. Chlorpyrifos residues dissipated rapidly under these climatic conditions. For the 5.0 lb of AI (2000 gal)$^{-1}$ acre^{-1} oscillating boom application, residues were 0.013 ± 0.002 and 0.005 ± 0.002 μg/cm^2 after 4 and 10 days,

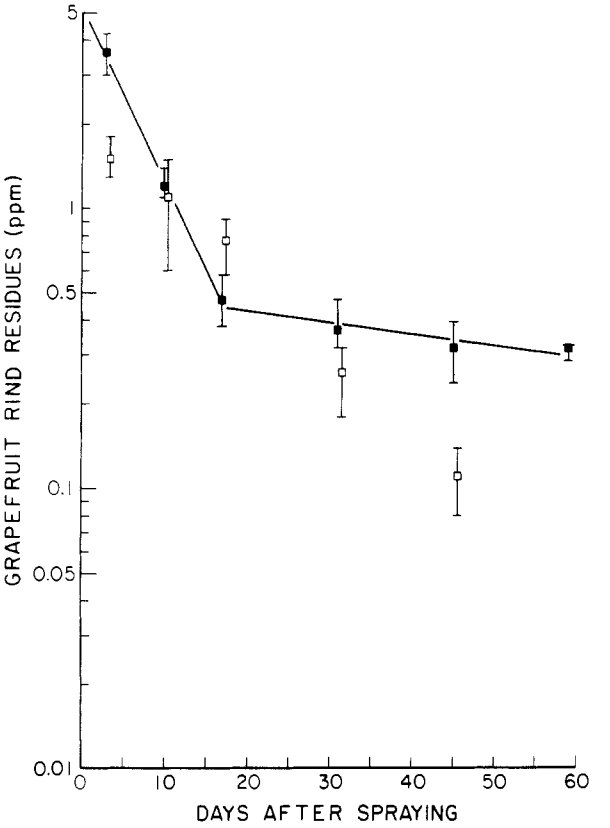

Figure 7. Total chlorpyrifos residues, as determined by sample analysis for total 3,5,6-trichloro-2-pyridinol, on and in grapefruit rind after an application of 5 lb of AI of Lorsban 4E/acre. Applications were made with 14 gal of NR-440 oil (100 gal)$^{-1}$ acre^{-1} (□) and 28 gal of NR-440 oil (2000 gal)$^{-1}$ acre^{-1} (■). Dissipation curve lines are drawn only for the (■) data points. Vertical lines indicate the range of values found for the analysis of three samples; one sample prepared from each of three replicate field plot samples was analyzed. Applications were made on Aug 14, 1981.

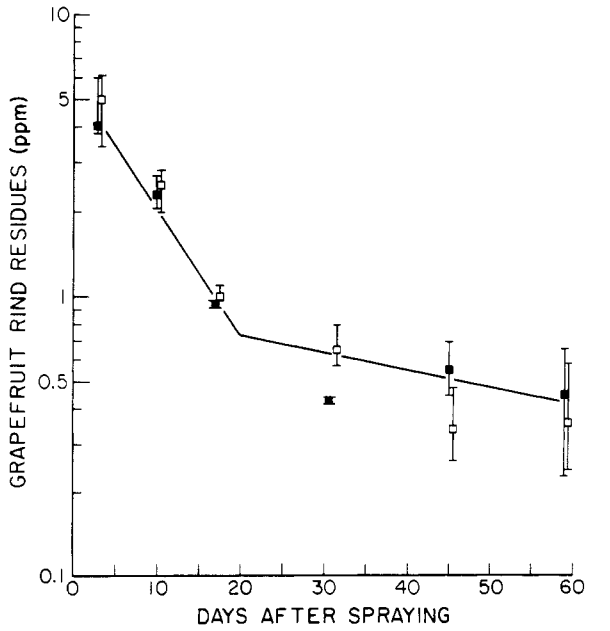

Figure 8. Total chlorpyrifos residues, as determined by sample analysis for total 3,5,6-trichloro-2-pyridinol, on and in grapefruit rind after an application of 10 lb of AI of Lorsban 4E/acre. Read caption to Figure 7 for additional details.

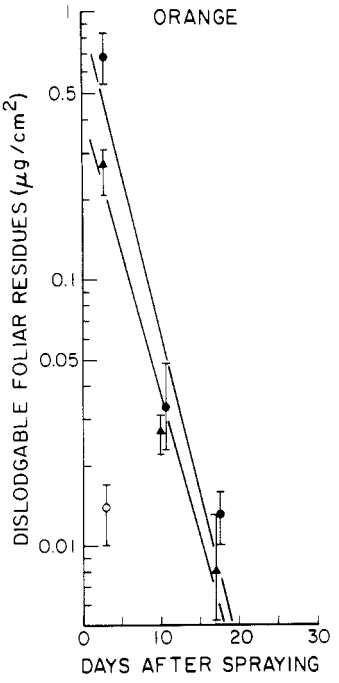

Figure 9. Dislodgeable foliar residues on orange trees after application of 10 lb of AI of Lorsban 4E (2000 gal)$^{-1}$ acre^{-1} (▲) and (100 gal)$^{-1}$ acre^{-1} (●). Applications were made in combination with oil. Closed symbols represent chlorpyrifos residues and open symbols the corresponding oxon residues. Vertical lines give the range of values found for three field samples.

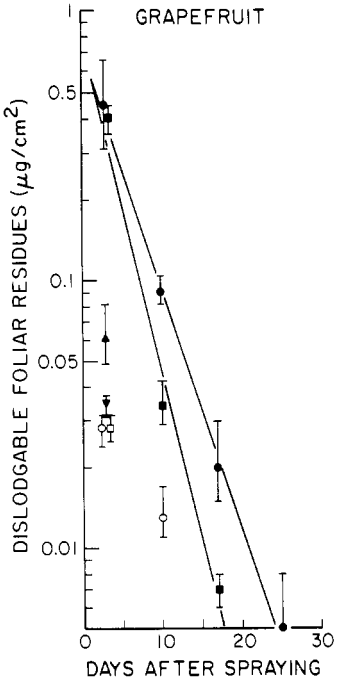

Figure 10. Dislodgeable foliar residues on grapefruit trees after low-volume applications of 5 (■) and 10 (●) lb of AI (100 gal)$^{-1}$ acre^{-1} and after oscillating boom applications of 5 (▼) and 10 (▲) lb of AI (2000 gal)$^{-1}$ acre^{-1}. Applications were made in combination with oil. Closed symbols represent chlorpyrifos residues and open symbols represent the corresponding oxon residues. Vertical lines give the range of values found for three field samples.

respectively. For the 10 lb of AI (2000 gal)$^{-1}$ acre^{-1} application, residues were 0.031 ± 0.003, 0.012 ± 0.002, and 0.006 ± 0.001 μg/cm^2 at 4, 10, and 17 days postapplication, respectively. For the 10 lb of AI (100 gal)$^{-1}$ acre^{-1} application with low-volume equipment, residues were 0.080 ± 0.013, 0.021 ± 0.002, 0.015 ± 0.003, and 0.008 ± 0.001 μg/cm^2 at 4, 10, 17, and 31 days, respectively. Two field samples were collected from each of three replicate plots for analysis. Due to the very rapid dissipation of residues, no meaningful dissipation curve line could be described. No oxon above the 0.01 μg/cm^2 level sought was present due to the very rapid disappearance of the parent insecticide and probably of any oxon formed.

In Aug 1981, chlorpyrifos was applied in combination with oil to grapefruit and orange trees. The maximum air temperature was, except for 1 day, at or above 33.3 °C for at least 16 days postapplication, and 9 of these days had temperatures between 37.2 and 43.3 °C. Total rainfall over the 62-day, sample-collection period was only 5.9 mm, and the maximum rainfall over a 24-h period was 3.3 mm. Residues dissipated rapidly. Data are shown in Figure 9.

For the 10 lb of AI (2000 gal)$^{-1}$ acre^{-1} and (100 gal)$^{-1}$ acre^{-1} applications, chlorpyrifos dissipated with half-lives of 2.8 and 2.4 days, respectively. A trace amount of oxon (0.014 ± 0.004 μg/cm^2) was found only in the 3-day sample. One field sample was collected for each of three replicate field plots on each sampling date for each application rate.

Dislodgeable residues on grapefruit leaves treated at 5.0 and 10 lb of AI/acre are shown in Figure 10. For the low-volume applications at the 5.0 and 10 lb of AI (100 gal)$^{-1}$ acre^{-1} rates, dissipation half-lives were 2.4 and 3.4 days, respectively. On day 3 the oxon residues were 0.028 ± 0.004 and 0.028 ± 0.005 μg/cm^2 for both the 5- and 10-lb rates, respectively. On day 10, oxon residues were <0.01 and 0.013 ± 0.003 μg/cm^2, respectively, for the 5- and 10-lb rates. For the oscillating boom applications at the 5 and 10 lb of AI (2000 gal)$^{-1}$ acre^{-1} rates, the only residues found above the 0.01 μg/cm^2 level sought were in the 3 day postapplication samples. Residues were 0.035 ± 0.003 μg/cm^2 for the 5-lb rate and 0.061 ± 0.018 μg/cm^2 for the 10-lb rate. One field sample was collected for each of three replicate field plots on each sampling date for each application rate.

As discussed previously with rind residues, the low-volume application gave higher residues than application with an oscillating boom in the case of oranges when equal amounts per acre were used. Whereas residues on grapefruit leaves were essentially identical, indicating poor low-volume coverage of grapefruit trees with low-volume equipment.

Dislodgeable residue levels are affected by levels of foliar dust, soil type within the grove, climatic factors such as air temperatures, and other factors (Gunther et al., 1977). The data presented above represent only a limited case. However, the data do indicate the chlorpyrifos and its oxon are not persistent compounds under the conditions that chlorpyrifos would be used in California.

Studies of insecticides in soil are important since soil contamination results during the spraying operation. The fate of chlorpyrifos in moist soil and on air-dry soil has been reported by Getzin (1981a,b). Since dislodgeable residues on foliage are sorbed to soil dust on the leaves, studies involving air-dry soil are useful. Getzin (1981b) concluded that clay-catalyzed hydrolysis and volatilization were the principal routes of chlorpyrifos dissipation from dry soil. Volatilization was not considered a major route, however, unless there was high relative humidity and soils contained a large amount of sorbed water. Half of the applied chlorpyrifos was lost in 8 days at 25 °C and in 3 days at 35 °C (Getzin, 1981b). These observations are consistent with the rapid initial losses observed for dislodgeable foliar residues. Neither ultraviolet light nor sunlight altered the stability of chlorpyrifos on dry soil, and 8-day exposure did not produce detectable oxon residues (Getzin, 1981b).

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Electron-Capture Gas Chromatographic Determination of Diflubenzuron and Permethrin in Soil and Water

Sammie Smith,* Guye H. Willis, and Leslie L. McDowell

An electron-capture gas chromatographic method is described for the determination of diflubenzuron in the presence of permethrin in soil and water. Diflubenzuron is derivatized to *N*-(4-chlorophenyl)-trifluoroacetamide by using trifluoroacetic anhydride with trimethylamine as a catalyst. Permethrin remains unchanged by the derivatization reaction. Mean recoveries for soil and water at two fortification levels were 87%, 92%, and 94% for diflubenzuron, *cis*-permethrin, and *trans*-permethrin, respectively.

The insect growth regulator diflubenzuron [Dimilin, *N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide] cannot be analyzed directly by electron-capture gas chromatography (ECGC) because the compound either decomposes or irreversibly adsorbs on GC columns commonly used for pesticide analyses (Corley et al., 1974). As a result, high-performance liquid chromatography (HPLC) methods were developed and successfully used to determine residues of diflubenzuron in water (Schaefer and Dupras, 1976), soil and plants (Schaefer and Dupras, 1977; Mansager et al., 1979), manure (Oehler and Holman, 1975), and fish (DiPrima et al., 1978; Schaefer et al., 1979). However, because GC offers the possibility of higher sensitivity, several derivitization procedures involving the formation of a thermally stable diflubenzuron derivative, easily detectable by ECGC, have been developed. DiPrima (1976) reported the determination of diflubenzuron in aquatic vegetation by hydrolyzing the extracted diflubenzuron to 4-chloroaniline and derivatizing with heptafluorobutyric anhydride to form *N*-(4-chlorophenyl)-heptafluorobutyramide, which is easily detectable by ECGC. A similar method (DiPrima, 1977) was reported for soil and sediment. Worobey and Webster (1977, 1978) reported the determination of diflubenzuron as its trifluoroacetyl derivative. Their method involved the direct derivatization of diflubenzuron with trifluoroacetic anhydride to form *N*-(4-chlorophenyl)trifluoroacetamide. Cleavage of diflubenzuron occurred during the reaction, eliminating the need for a separate hydrolysis step. DeMilo et al. (1978) were able to similarly derivatize diflubenzuron with trifluoroacetic anhydride but added pyridine as a catalyst to obtain quantitative conversion. However, we found none of the aforementioned ECGC procedures satisfactory for reasons to be mentioned later.

The synthetic pyrethroid insecticide permethrin [3-phenoxybenzyl(±)-*cis*,*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] can be analyzed directly and easily by ECGC, as was reported recently by Fujie and Fullmer (1978) for permethrin residues in plant, animal, and soil matrices and by Carroll et al. (1981) for permethrin residues on cotton plants and in soil and water. Permethrin, however, readily undergoes ester cleavage to 3-phenoxybenzyl alcohol and the dichlorovinyl acids, which is the basis of a derivatization procedure reported by George and McDonough (1975).

This paper presents the results of our efforts to develop a more satisfactory ECGC analytical procedure for diflubenzuron residues in water and soil, because of anticipated field studies involving both diflubenzuron and permethrin in agricultural runoff. In order to shorten analysis time, we also wanted to be able to determine permethrin directly on the same GC column used for derivatized diflubenzuron, since it was highly probable that both diflubenzuron and permethrin would be present together in the same runoff samples.

EXPERIMENTAL SECTION

Apparatus. A Micro Tek Model DSS-162 gas chromatograph, upgraded with a solid-state temperature programmer and dual-channel electrometer and equipped with a high-temperature ^{63}Ni electron capture detector and a Hewlett-Packard Model 3388A plotting integrator was employed for isothermal analyses. A glass column, 1.2 m long × 6 mm o.d. × 4 mm i.d. and packed with 3% SP2401 on 100–120-mesh Supelcoport, was used at 120 °C for

Soil and Water Pollution Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture and Louisiana Agricultural Experiment Station, Baton Rouge, Louisiana 70893, and Sedimentation Laboratory, Agricultural Research Service, U.S. Department of Agriculture and Mississippi Agricultural and Forestry Experiment Station, Oxford, Mississippi 38655.