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Degradation and Movement of Fluvalinate in Soil

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[*trifluoromethyl*-^{14}C]Fluvalinate is rapidly degraded on sandy loam, clay loam, and clay soils under aerobic conditions with initial half-lives of 6–8 days. The primary degradation products of fluvalinate are the anilino acid (**2**) and haloaniline (**3**), the latter primarily evolved as a volatile product. Under anaerobic conditions, the degradation was slower ($t_{1/2}$ on clay soil = 15 days) but with similar products formed. The flood water above the anaerobic soils contained, in addition to the above metabolites, a diacid (**4**) and 4-amino-3-chlorobenzoic acid (**5**). A small amount of $^{14}CO_2$ was produced from all soils. Fluvalinate does not leach through soil and rapidly adsorbs to soil from water with little desorption. The anilino acid metabolite (**2**) is of low to intermediate mobility as determined by soil thin-layer chromatography plates. Lettuce, radish, and wheat plants do not accumulate appreciable ^{14}C-labeled residues when growing in soil treated with [*trifluoromethyl*-^{14}C]fluvalinate.

Fluvalinate [α-cyano-3-phenoxybenzyl 2-[2-chloro-4-(trifluoromethyl)anilino]-3-methylbutanoate, active ingredient of Mavrik 2E insecticide] is an experimental insecticide with pyrethroid-like activity currently being developed by Zoecon Corp. for use against insect pests on various crops. Due to the likely exposure of soil to the chemical, it is necessary to determine the metabolic fate of fluvalinate in soils under various conditions. The present study deals with the degradation of fluvalinate on three soil types under aerobic and anaerobic conditions as well as the mobility of fluvalinate and a major metabolite in three soils [for the preceding report in this series, see Staiger et al. (1982)].

EXPERIMENTAL SECTION

Radioassay and Chromatography. Radioactivity was quantified by liquid scintillation counting (LSC) alone or in conjunction with sample combustion to $^{14}CO_2$ (Quistad et al., 1982). A Polytron homogenizer (Brinkman) was used to facilitate extraction of fluvalinate and degradation products from soil. The quantification of radiolabeled metabolites in extracts was achieved by using gradient-elution, reversed-phase liquid chromatography (LC) by coinjection of a known amount of radiolabeled extract together with authentic metabolite standards and collection of timed fractions for subsequent assay by LSC. The conditions for reversed-phase LC analysis of fluvalinate and metabolites have been described (Quistad et al., 1982). The following mixtures of methanol–0.1% acetic acid were used for elution: SS 1 (gradient 60–70% methanol over 15 min, 70–90% over 10 min, isocratic at 90% for 10 min); SS 2 (gradient 70–90% methanol over 20 min, isocratic at 90% for 10 min); SS 3 (isocratic at 50% methanol for 6 min, gradient 50–80% over 4 min, isocratic at 80% for 10 min); SS 4 (isocratic at 70% methanol). Purification of metabolites utilized thin-layer chromatography (TLC) on silica gel GF (Analtech, Newark, DE) with radioactive zones located with a radiochromatogram scanner (Packard Instruments, Downers Grove, IL).

Synthetic Standards. The preparation of [*trifluoromethyl*-^{14}C]fluvalinate (**1**) has been reported previously (Quistad et al., 1982) and was a mixture of *αR*,2*R*, *αS*,2*S*, *αR*,2*S*, and *αS*,2*R* stereoisomers. The radiochemical purity of combined isomers was 99.7% as judged by reversed-phase LC (SS 1) with a specific activity of 48.3 mCi/mmol determined by mass spectrometry.

Authentic samples of fluvalinate (**1**), the anilino acid (**2**), and the haloaniline (**3**) were synthesized by the Zoecon Chemical Research Department. Authentic standards of 4′-hydroxyfluvalinate, diacid **4**, desphenylfluvalinate (removal of the distal phenoxy ring), and an amide analogue of fluvalinate (resulting from addition of water to the cyano moiety) were available for chromatographic comparison.

The synthesis of 4-amino-3-chlorobenzoic acid (**5**) was performed as follows: haloaniline **3** (100 mg) was heated to 90 °C in a capped, conical vial with 1 M methanolic KOH (1 mL) for 24 h. Isolation of the product was by TLC (three plates 20 × 20 cm silica gel GF, 1 mm thick, R_f = 0.27, hexane–ethyl acetate–acetic acid, 110:110:1, 2% yield), and following methylation (CH_2N_2) the structural assignment of **5** was verified by mass spectrometry: *m*/*z* (rel intensity) 187 (M^+, 13), 185 (M^+, 45), 156 (33), 154 (100), 128 (5), 126 (14), 90 (26).

Soil. Keeton sandy loam soil from Alameda Co., California, was supplied by Sam Keeton Loam and Gravel, San Jose, CA. Clay soil from Cameron Co., Texas, and clay loam soil from Yuma Co., Arizona, were supplied by field

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Table I. Characteristics of Soils[a]

sampling site	soil texture	% sand	% silt	% clay	% organic matter	cation-exchange capacity, mequiv/100 g	pH	bulk density	% mositure at 1/3 bar
California	sandy loam	68	22	10	0.2	7.1	8.1	1.44	5.6
Texas	clay	8	28	64	1.8	47.0	8.6	1.20	43
Arizona	clay loam	22	50	28	1.1	19.9	8.3	1.36	23

[a] All analyses performed by United States Testing Co., Inc., Memphis, TN 38118.

personnel. The results of soil analyses are shown in Table I. Additional soil was amended to produce the silt loam soil used in the leaching study only.

Treatment and Maintenance of Soil. The soil was dosed with an acetone solution of [*trifluoromethyl*-^{14}C]-fluvalinate (1, ~0.5 mL, ~120 μg) to give a treatment rate of 1.1 μg/cm^2 (0.11 kg/ha). Soil samples (100 g) were incubated in biometer flasks (Stanford Glassblowing Laboratories, Palo Alto, CA) and maintained daily with 16-h, fluorescent light (28 °C) followed by 8 h of dark (18 °C). The design of this incubation system was described by Laskowski et al. (1978). Samples maintained under aerobic conditions were provided with an oxygen supply, whereas those maintained under anaerobic conditions were kept under nitrogen atmosphere for 16 h prior to treatment and then flooded to a depth of 2–3 cm with tap water. Polyurethane plugs (Gaymar Industries) were positioned in the side arm separating the soil from 0.2 N NaOH (50–100 mL).

Analysis of Volatile Metabolites. At weekly intervals, aliquots from the NaOH trap were quantified by LSC. Radioactivity trapped in the NaOH was verified as $^{14}CO_2$ by two procedures. An aliquot of the NaOH solution was acidified and then purged with CO_2 (dry ice). A separate aliquot of certain samples (50 mL) was treated with a solution of barium chloride (30 mL, 0.4 M $BaCl_2$, and 0.5 M NH_4Cl) to precipitate $BaCO_3$. The aqueous phase after filtration was quantified by LSC.

At weekly intervals, the foam plugs were replaced and extracted with methanol, and aliquots of the extract were quantified by LSC. For each soil type the identity of products in the plugs was investigated by LC (SS 1) after combining the extracts for the entire collection period. In order to verify the structure of 2-chloro-4-(trifluoromethyl)aniline (**3**) in the plug extract, one of the plugs at 3 weeks posttreatment (sandy loam soil) was extracted with ether and an aliquot was derivatized by addition of heptafluorobutyric anhydride. After this was stirred for 1 h, aqueous $KHCO_3$ was added prior to extraction with ether. An aliquot of the ether was analyzed by LC (SS 4) by coinjection of the authentic heptafluorobutyramide derivative of the haloaniline.

Analysis of Soil Metabolites. Soil samples maintained aerobically were removed from the flask and extracted with methanol (or some samples with acetonitrile). The flood water was removed from the anaerobic samples with a pipet, and aliquots were quantified by LSC. The soils were then extracted as above. Unextractable ^{14}C-labeled residues in the dried soils were determined by combustion.

The levels of fluvalinate and metabolites in the extracts and flood water were investigated by LC (SS 1). The k' values of authentic standards were as follows: for fluvalinate (1), 19.1, for anilino acid **2**, 10.0, for the methyl ester of **2**, 13.9, for haloaniline **3**, 5.1, for diacid **4**, 3.2, and for 4-amino-3-chlorobenzoic acid (**5**), 1.4.

The diacid (**4**) was isolated from the flood water of the 2-week clay, anaerobic sample by extracting an acidified aliquot with ethyl acetate. The concentrated extract was methylated (CH_2N_2) prior to purification by TLC (hexane–ethyl acetate, 5:1). The dimethyl ester of **4** was eluted from the silica gel (R_f = 0.30) and shown to be coincident with an authentic standard upon LC (SS 1, k' = 9.2).

4-Amino-3-chlorobenzoic acid (**5**) was isolated from flood water of the 8-week clay, anaerobic sample by extraction as above and shown to be coincident with authentic standard on TLC (hexane–ethyl acetate–acetic acid, 120:120:1; R_f = 0.37) and LC (SS 3, k' = 2.3). An aliquot of **5** from TLC was methylated (CH_2N_2) and then shown by LC to be coincident with authentic methyl ester of **5** (SS 1, k' = 2.8).

In order to examine the possibilty of preferential metabolism of any of the four fluvalinate isomers, fluvalinate was isolated by TLC from the 8-week soil extracts of the clay (aerobic and anaerobic) and clay loam soils. After elution from the silica gel (R_f = 0.49 in hexane–ethyl acetate, 4:1), the fluvalinate isomers were separated by normal-phase LC [Haskel Model 28030 pump; Pirkle Type 1-A column, 5 μm, 0.46 × 25 cm (Regis Chemical Co.); Spectra Physics 8200 UV detector, 254 nm; elution at ca. 2.0 mL/min with pentane–ethyl acetate, 99:1; k' = 24.6, 26.7, 28.0, and 29.8 for $\alpha R,2R$, $\alpha S,2R$, $\alpha S,2S$, and $\alpha R,2S$ isomers, respectively]. For comparison, an aliquot of the [*trifluoromethyl*-^{14}C]fluvalinate used for the dose was analyzed under the same conditions.

Soil Leaching. Soil thin-layer chromatography plates were used according to Helling (1971a). Sandy loam, silt loam, and clay soils were air-dried and then sieved (300, 300, and 500 μm, respectively) to remove coarse particles. Soil plates were prepared by spreading a slurry of the soil in water on glass plates (5 cm × 20 cm) and then air-drying. [*trifluoromethyl*-^{14}C]Fluvalinate (1) and [*trifluoromethyl*-^{14}C]anilino acid **2** were applied at a rate of 1 μg/plate at about 2 cm from the bottom of the plate. Plates were developed with distilled water in a covered container and were removed when the solvent front reached 10 cm from the origin.

Adsorption vs. Desorption. Water treated with [*trifluoromethyl*-^{14}C]fluvalinate was shaken with soil to determine the level of adsorption to soil. Fluvalinate (0.11 μg) in 20 μL of acetone was added to 50 mL of distilled water, and an aliquot of the water quantified by LSC. Sandy loam soil (25 g air-dried) was added to the water and shaken for about 10 s. An aliquot (2 mL) of the mixture was added to a centrifuge tube containing 3 mL of distilled water and centrifuged for 10 min. An aliquot of the supernatant was quantified by LSC. The fluvalinate-treated water with soil was shaken continuously (Burrell wrist-shaken shaker) for an additional hour, with periodic analysis of aliquots. The mixture was filtered with glass-wool filter paper (Whatman) and an aliquot of the filtrate quantified by LSC.

The amount of desorption of fluvalinate from the soil was determined by adding untreated water (50 mL) to the above filtered soil. The mixture was shaken, and aliquots were quantified periodically as before (with and without filtration).

Table II. Anaerobic Soil Metabolism of [*trifluoromethyl*-^{14}C]Fluvalinate

clay soil	% applied dose				
	2 weeks	4 weeks	8 weeks	8 weeks[a]	12 weeks[a]
organic extract	64	55	38	21	9.6
fluvalinate (1)	53	27	10	2.0	0.7
anilino acid (2)	3.0	19	14	5.0	2.8
haloaniline (3)	4.9	6.1	10	13	5.4
volatile products collected in					
polyurethane plug (mostly 3)	4.7	10	22	47	50
NaOH trap (mostly $^{14}CO_2$)	0.1	0.4	1.0	2.8	2.8
flood water	18	23	16	5.6	6.5
fluvalinate (1)	0.4	0.2	0.1	<0.01	<0.01
anilino acid (2)	11	14	5.7	0.3	1.2
haloaniline (3)	2.0	3.0	3.9	3.1	1.3
diacid (4)	2.6	1.7	0.9	<0.2	0.5
4-amino-3-chlorobenzoic acid (5)	0.8	2.6	4.5	<0.2	0.4
unextractable residues	3.4	6.2	16	18	22
total recovery	90	94	93	94	91

[a] Maintained under aerobic conditions 4 weeks prior to flooding (establishing anaerobic conditions).

Rotational Crop Uptake. Sandy loam soil in clay pots was treated to a depth of ~5 mm with [*trifluoromethyl*-^{14}C]fluvalinate with an application rate of 0.1 kg/ha. After the soil was periodically watered for 31 days, lettuce, radish, and wheat seeds were planted. The plants were maintained in a greenhouse with occasional outdoor exposure to optimize growing conditions. When plants were estimated to be at half and full maturity, they were harvested and ^{14}C-labeled residues were quantified by combustion of aliquots to $^{14}CO_2$.

RESULTS AND DISCUSSION

The rapid degradation of fluvalinate on the three soil types is shown in Figure 1. The half-life of fluvalinate on sandy loam and clay loam was ca. 6 days, whereas on clay soil, it was ca. 8 days under the same aerobic conditions and 15 days when anaerobic. These short half-lives are in contrast to other pyrethroid-like compounds which have markedly longer half-lives in the dark, for example, permethrin [3 weeks (Williams and Brown, 1979)], fenvalerate [7 weeks (Williams and Brown, 1979)], and decamethrin [8 weeks (Chapman et al., 1981)].

The major metabolites extracted from the soil were the hydrolysis product (anilino acid **2**) and haloaniline **3**. The residues of **2** reached a maximum in the soil at 2–4 weeks (19–37% of the applied dose) and decreased thereafter. Haloaniline **3** in the soil represented 5–9% of the applied dose at 8 weeks.

Volatile products were major metabolites of fluvalinate. Polyurethane plugs effectively trapped haloaniline **3**, which represented 22–47% of the applied dose after 8 weeks. Thus, if the residue of **3** in the soil extracts is included, after 8 weeks 37–51% of the applied dose was recovered as haloaniline from aerobic soils and 36% of the applied dose from anaerobic soil. Radiolabel trapped in 0.2 N NaOH was primarily $^{14}CO_2$ as evidenced by quantitative loss of ^{14}C upon purging with CO_2 (after acidification) and ≥99% precipitation of ^{14}C as $Ba^{14}CO_3$. Hence, 3–9% of the applied dose was evolved as $^{14}CO_2$ after 8 weeks (Figure 1).

The degradation of fluvalinate under anaerobic conditions on clay soil was similar to that under aerobic conditions, although the rate of degradation was slower (Table II). Flooding a clay soil that had been treated with fluvalinate and incubated aerobically for 4 weeks did not appreciably alter the qualitative distribution of metabolites. Interestingly, the flood water was not an effective barrier to the volatilization of haloaniline **3** from soil since appreciable amounts of **3** were trapped in the polyurethane foam even when the soil was flooded. The flood water contributed 6–23% of the applied dose with the major product being the anilino acid (**2**). There were low levels of fluvalinate and haloaniline **3** in the water, as well as two products not found in the soil, the diacid (**4**) and 4-amino-3-chlorobenzoic acid (**5**). The presence of these products in the flood water (pH 6) is not surprising since the hydrolytic conversion of the CF_3 moiety to carboxyl has been shown when fluvalinate is maintained in aqueous buffer at pH 6 (Staiger et al., 1979).

Table III. Stereoisomers of Fluvalinate Isolated from Soil 8 Weeks Posttreatment As Determined by LC Analysis Using a Pirkle 1-A Column

soil type	% isomer			
	$\alpha R,2R$	$\alpha S,2R$	$\alpha S,2S$	$\alpha R,2S$
clay (aerobic)	28	26	23	23
clay loam	25	26	23	25
clay (anaerobic)	27	26	23	24
standard (fluvalinate before treatment)	23	24	25	28

Use of a Pirkle column gave effective separation of the four fluvalinate stereoisomers. Analysis of recovered fluvalinate maintained for 8 weeks on the clay (aerobic and anaerobic conditions) and the clay loam showed no substantial preferential degradation of any of the isomers (Table III).

A summary of the degradation of fluvalinate is shown in Figure 2. There is no evidence for the formation of 4′-hydroxyfluvalinate or conversion of the CN to $CONH_2$ (or COOH) as have been shown with fenvalerate (Ohkawa et al., 1978). The maximum amount of radiolabel coeluting with authentic standards of 4′-hydroxyfluvalinate or the amide analogue of fluvalinate was 0.8 and 0.7% of the applied dose, respectively. However, the conversion of CN to $CONH_2$ for the intact ester is a significant thermal reaction for **1** on soil. Desphenylation of the 3-phenoxy moiety was not found for fluvalinate, in contrast to soil metabolism of fenvalerate (Ohkawa et al., 1978).

Incorporation of radioactivity into the soil (i.e., bound residues) was a relatively minor route of degradation. After 8 weeks, only 10–20% of the applied dose was unextractable under aerobic conditions and 16% under anaerobic conditions. Bound residues for permethrin (Kaneko et al., 1978), cypermethrin (Roberts and Standen, 1977a), and phenothrin (Nambu et al., 1980) under laboratory conditions represented as much as 32, 30, and 50%, of the applied dose, respectively.

Although not investigated in the present study, it is anticipated that the metabolism of fluvalinate on sterilized

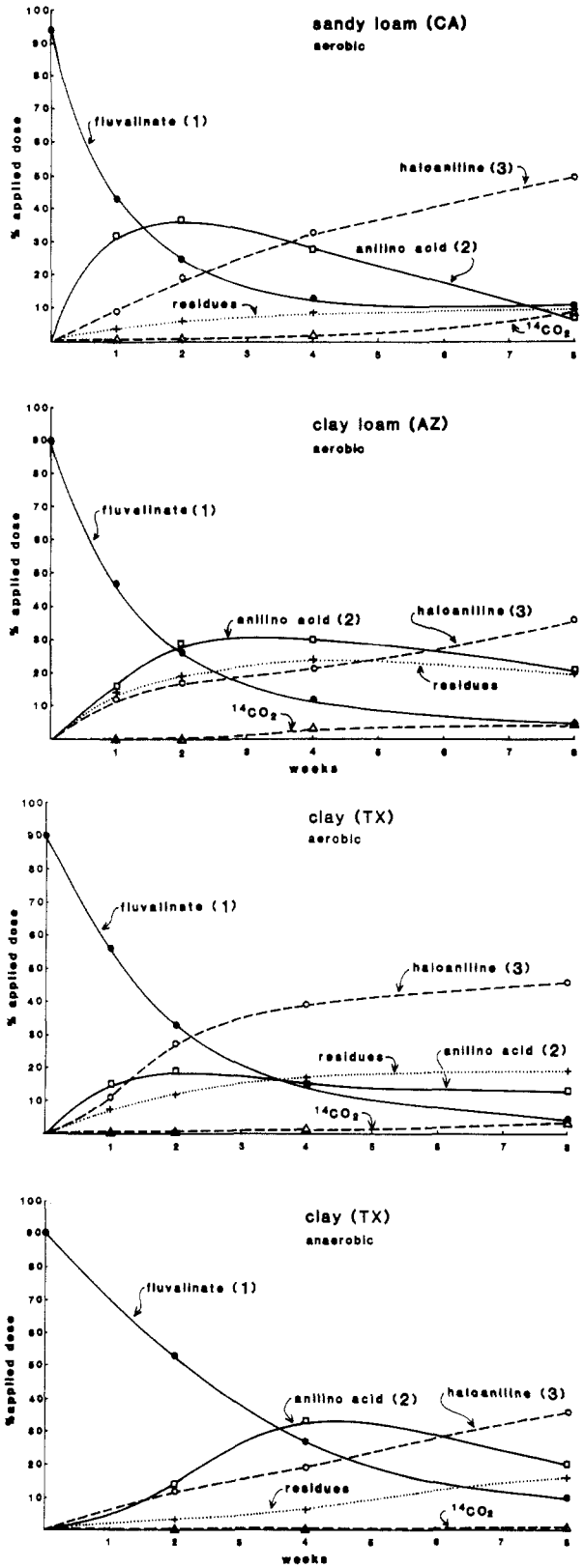

Figure 1. Degradation of fluvalinate on soil under aerobic and anaerobic conditions.

soil would be significantly slower than on microbially active soil. This was found to be the case with permethrin, cypermethrin, fenvalerate, and decamethrin (Chapman et al., 1981).

Movement of Fluvalinate. There was no movement of fluvalinate on thin-layer plates of silt loam, sandy loam, or clay soil when developed with water, and therefore, fluvalinate is classified as immobile [class 1, according to

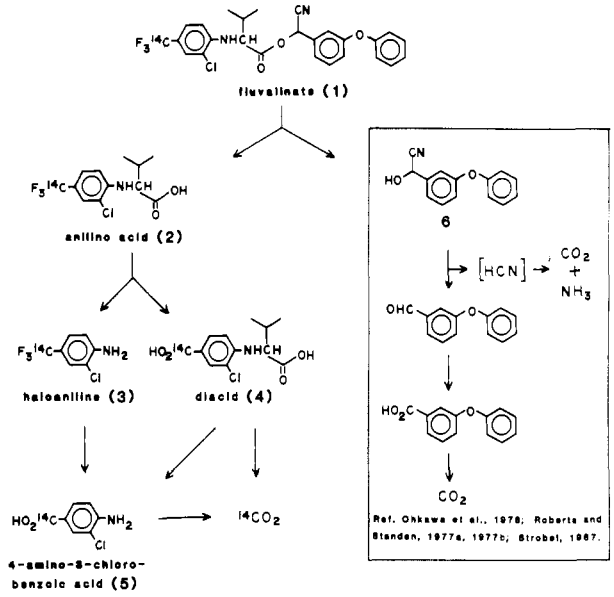

Figure 2. Degradation products from fluvalinate in soil.

Helling (1971b)]. Anilino acid **2**, a major metabolite of fluvalinate, was found to be of low to intermediate mobility (class 2–3), with the greatest mobility on sandy loam (R_f = 0.60) and the lowest on clay (R_f = 0.34). The immobility of fluvalinate agrees with results from other pyrethroids where little movement was found for permethrin, cypermethrin, and decamethrin (Kaufman et al., 1981), as well as fenvalerate (Ohkawa et al., 1978).

The affinity of fluvalinate for soil was further exemplified by its rapid adsorption to soil. When soil is added to water containing fluvalinate, there is rapid binding of the chemical to soil particles as evidenced by a 72% decrease of fluvalinate concentration in the water. After filtration through glass–wool paper, the filtrate contained only 1% of the initial levels of fluvalinate. The addition of water to fluvalinate-treated soil superficially appeared to solubilize some fluvalinate (44% increase in ppb in water); however, again on filtration, the levels of ^{14}C-labeled residues in the water dropped dramatically, which indicates fluvalinate adsorption to small soil particles.

Plants grown in soil that has been treated 30 days previously with ^{14}C-labeled fluvalinate (0.1 kg/ha) do not accumulate significant concentrations of radioactive residues (<0.1 ppm). The highest residues were found in radishes (root portion only) harvested at half-maturity (0.06 ppm equiv as fluvalinate). Mature radishes, lettuce, and wheat grown as rotational crops in similar fluvalinate-treated soil accumulated only 0.01–0.024 ppm equiv as fluvalinate. The short half-live of fluvalinate on sandy loam soil would minimize the exposure to any seeds planted 30 days after a fluvalinate treatment.

Fate of the Alcohol Moiety. Since fluvalinate is radiolabeled at the trifluoromethyl group of the acid portion of the ester, any products from the alcohol portion could not be monitored. However, four pyrethroids (i.e., cypermethrin, fenpropanate, fenvalerate, and deltamethrin) give the same alcohol as fluvalinate from hydrolytic cleavage and have been studied on soils.

Hydrolysis of ester linkage of fluvalinate would give the cyanohydrin (**6**), a transient product which decomposes readily to 3-phenoxybenzaldehyde and cyanide (Figure 2). The aldehyde in turn is readily oxidized to 3-phenoxybenzoic acid, which was found with benzyl-labeled cypermethrin (Roberts and Standen, 1977a) and benzyl-labeled fenpropanate (Roberts and Standen, 1977b). In both

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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Registry No. 1, 69409-94-5; 1 trifluoromethyl-^{14}C, 85236-40-4; 2, 76338-73-3; 3, 39885-50-2; 4, 85236-41-5; 5, 2486-71-7.

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

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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).

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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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