rine at the 5 position of the ring, the relative rate of ring opening appears to be much faster than with 2,4,5-T. Thus, if the analogous phenol and anisole metabolites are formed, they are rapidly degraded and do not appear at measurable levels in soil.

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Persistence and Distribution of Fenvalerate Residues in Soil under Field and Laboratory Conditions

Bernard D. Hill

An analytical method is described for determining fenvalerate [(*RS*)-α-cyano-3-phenoxybenzyl (*RS*)-2-(4-chlorophenyl)-3-methylbutyrate] residues in soil using hexane–acetone extraction, alumina microcolumn cleanup, and ^{63}Ni electron-capture gas chromatographic detection. Method recoveries ranged from 78.4 to 105% at the 0.005–1.0-ppm fortification levels. Methanol was an unsuitable solvent for residue analysis since fenvalerate exchanged the α proton with methanol, racemization occurred, and the amount of the *RS,SR* enantiomeric pair increased relative to that of the *RR,SS* pair. In a microplot field study, fenvalerate residues had an average half-life of 6 weeks in the 0–2.5-cm soil layer. Residues were not readily leached down to the 2.5–5.0-cm soil layer and lateral surface movement was minimal. Fenvalerate had an average half-life of 5.2 weeks in soil incubated in an environmental chamber. In both soil persistence studies, the *RS,SR* enantiomeric pair degraded slightly faster than the *RR,SS* pair.

Fenvalerate [(*RS*)-α-cyano-3-phenoxybenzyl (*RS*)-2-(4-chlorophenyl)-3-methylbutyrate] is one of the "second-generation" (Menn, 1980) synthetic pyrethroid insecticides being evaluated at this laboratory for possible control of cutworm species (McDonald, 1979) and alfalfa insect pests. Although fenvalerate has a relatively low mammalian toxicity (rat, acute oral LD_{50} 451 mg/kg), it is toxic to fish and potentially harmful residues could move from farmlands into water bodies.

Since much of an applied insecticide contacts the soil, this work was conducted to determine the persistence and possible movement of fenvalerate soil residues under southern Alberta conditions. An analytical method for fenvalerate soil residues, the instability of fenvalerate in methanol, a microplot field study, and an environmental chamber incubation study are described. It was of particular interest to determine whether results of an indoor incubation study would approximate the persistence of fenvalerate in field soils.

From an environmental chamber incubation study, Williams and Brown (1979) reported a half-life of 7 weeks

for fenvalerate in British Columbia soils. They showed that soil sterilization greatly reduced the rate of degradation of fenvalerate and permethrin and concluded that "microbial activity was the major factor in the loss of these insecticides".

EXPERIMENTAL SECTION

Soil. The Lethbridge clay loam contained 29.0% clay, 27.0% silt, and 44.0% sand with a cation-exchange capacity of 24.4 mequiv/100 g. It had an organic matter content of 2.1%, a moisture holding capacity of 19.8% at 30-kPa pressure, and a pH of 7.9 as a 1:1 soil–water slurry.

Chemicals. Fenvalerate analytical standard (98.5% purity) and formulated product, 30% emulsifiable concentrate (EC), were supplied by Shell Canada Ltd., Toronto, Ont. Standards of each fenvalerate enantiomeric pair were obtained from Shell Research Ltd., Sittingbourne, U.K. Aluminum oxide (Woelm acidic) was stored as received at 130 °C. Solvents were pesticide-grade or glass-distilled reagent grade.

Field Persistence Study. A microplot technique similar to that reported by Smith (1971, 1972) was used with a randomized block design and four replicates. On June 20, 1978, fenvalerate at 150 g/ha was applied to thirty-two 20 × 20 cm soil microplots situated behind a shelterbelt

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to minimize wind erosion. The EC product, 0.3 kg/L of active ingredient, was diluted with glass-distilled water, and 5.0 mL of this solution, containing 600 μg of the chemical, was pipetted dropwise onto the soil surface. After the droplets dried, the insecticide was evenly dispersed by mixing the surface with a spatula and then packing it lightly. Plots were maintained as weed-free fallow over the summer with the soil disturbed as little as possible. Weather records including temperature, rainfall, and soil moisture were kept.

At intervals of 0, 0.5, 1, 2, 4, 8, and 16 weeks, the soil from the entire microplot was removed (whole-plot sampling) in two layers, 0–2.5 and 2.5–5.0 cm, and composite control samples of the 0–2.5-cm layer were taken from untreated areas within the experimental site. A spring sampling was taken 45 weeks after application to determine the winter carry-over of fenvalerate residues. At each of the six sampling dates after initial application of fenvalerate, duplicate microplots were treated and sampled immediately to determine the accuracy and precision of treatment and sampling techniques. Samples were taken in all four directions outside the treated microplots to check for lateral movement of fenvalerate residues after 3 and 4 weeks. These lateral samples consisted of eight 0–2.5-cm soil cores (2.3-cm i.d.) taken along a line 7.5 cm from and parallel to plot edges.

Soil samples, as received from the field, were stored at –40 °C. Before analysis, samples were thawed and air-dried overnight at room temperatures, rolled to break any lumps, and thoroughly mixed. Microplot samples ranged from 1.2 to 1.7 kg and subsamples were taken, 50.0 g for residue analysis and 20.0–30.0 g for soil moisture determination (oven drying at 110 °C).

Indoor Incubation Study. Soil was freshly collected from the microplot field area and air-dried, and any lumps were broken. After being screened through a 10-mesh sieve, the soil was placed in 12.7 cm diameter pots, misted with a fog nozzle, and kept in a moist condition for 4 days in an environmental chamber. Pots were then treated at a 70 g/ha rate with an aqueous solution of fenvalerate EC by using a simulated field sprayer (McDonald and Hall, 1965). This application theoretically gave a treatment of 88.7 μg of fenvalerate/pot. Treated pots were transferred back to the environmental chamber and maintained at a daily temperature regime of 20 °C for 16 h and 10 °C for 8 h. A light intensity of 18 klx was provided over the 16-h day by a combination of cool-white fluorescent and incandescent bulbs. This lighting arrangement was designed to have negligible ultraviolet effects yet facilitate soil surface drying as in field situations. Pots were weeded as necessary and the layout rerandomized weekly. The soil was misted to near saturation twice weekly with the result that soil moisture in the 0–2.5-cm layer fluctuated between 29 and 12%. Average relative humidity in the chamber was 75% during the day and 90% at night. The entire 0–2.5-cm soil layer (averaging 375 g) from duplicate pots was removed at intervals of 0, 0.43, 1, 2, 4, and 8 weeks. At 8 weeks, samples were also taken from the 2.5–5.0-cm soil layer and from untreated control pots. Soil samples were air-dried overnight and mixed, the moisture was determined, and duplicate 50.0-g subsamples were taken and stored at –40 °C until analysis. Results from the duplicate subsamples were averaged to give a value for each replicate pot.

Extraction. Just before extraction, the 50.0-g soil samples were wetted with 20 mL of glass-distilled water and allowed to equilibrate 1 h. The samples were extracted on a rotary platform shaker at 220 rpm according to the

following regime: 100 mL of acetone for 2 h, 75 mL of 1:1 v/v hexane–acetone for 2 h, and 75 mL of 1:1 v/v hexane–acetone for 15 min, followed by a final 5-min rinse using 100 mL of hexane. Between solvent changes, the soil was allowed to settle and the liquid extract decanted through prewashed glass wool into a 500-mL Erlenmeyer flask. Combined extracts were liquid–liquid partitioned with 550 mL of 2% NaCl solution in a 1-L separatory funnel and the hexane layer was separated. The remaining acetone–aqueous salt solution was reextracted with 100 mL of fresh hexane. The hexane extracts were combined, held overnight at room temperature, dried over 10 g of anhydrous Na_2SO_4, rotary evaporated ($\leq$40 °C) to near dryness, and adjusted to a 10-mL volume in hexane. Extracts were then held at 0–4 °C before cleanup.

Cleanup. A microcolumn system was used consisting of a disposable Pasteur pipet (14.6 × 0.5 cm i.d.) packed with 5 cm (1.3 g) of acid alumina (6% deactivated and equilibrated overnight). A 0.5-mL aliquot of sample extract (2.5-g soil equivalent) was applied to the microcolumn. The extract was washed-in with 1.5 mL of hexane and then with 4 mL of 1:19 v/v ether–hexane and both eluates were discarded. Fenvalerate was then eluted with 7 mL of 1:9 v/v ether–hexane, and the eluate collected in a 10-mL Kuderna Danish concentrating tube. The collected eluate was evaporated to near dryness under a stream of dry nitrogen and adjusted to an appropriate final volume (1–5 mL) for GC analysis using hexane.

Fortification. Method recoveries for fenvalerate were determined by analysis of soil fortified at 1.0, 0.1, 0.01, and 0.005 ppm. Soil samples, 50.0-g each (oven-dried basis) contained in 500-mL Erlenmeyer flasks, were individually treated by evenly pipetting onto the soil surface 20 mL of an appropriate solution of fenvalerate in 1:1 v/v acetone–water. After 1-h equilibration, samples were air-dried overnight, thoroughly mixed, and frozen at –40 °C. For simulation of field samples, fortified samples were thawed and air-dried overnight and then remixed before analysis.

Gas Chromatography. A Hewlett-Packard Model 5733A gas chromatograph equipped with a ^{63}Ni detector was used with a Honeywell Electronic 194 1-mV recorder. Part of the analyses was automated by installation of a Varian Model 8020 autosampler and 111C chromatography data system. The column, 0.97 m × 4 mm i.d. coiled glass, was packed with 6% OV-210 on 80–100-mesh Chromosorb W HP. The GC was operated at injector 250 °C, column 230 °C, and detector 350 °C, with 95% argon–5% methane carrier gas at a flow of 60 mL/min. Under these conditions, partial resolution of the two fenvalerate peaks was achieved. Retention times were 10.6 and 11.8 min with a typical response of 800 pg of fenvalerate producing a full-scale recorder deflection for each peak at attenuation 32. A linear response, measured either manually as peak height or integrated as peak area by the data system, was observed over the range 20–1000 pg for each peak. Previous reports (Chapman and Simmons, 1977; Westcott and Lee, 1978) have indicated that the two fenvalerate peaks have identical response factors with the ^{63}Ni detector. Sample injection volumes were 2–4 μL and unknowns were quantified by comparison to appropriate alternating standards. All residues were calculated on a soil dry weight basis and are reported without correction for analytical method losses.

RESULTS AND DISCUSSION

Fenvalerate has chiral centers in the alcohol and acid moieties, and the four possible stereoisomers are correspondingly designated *RS*, *SR*, *RR*, and *SS*. The isomers with the acid moiety in the *S* configuration, *RS* and *SS*,
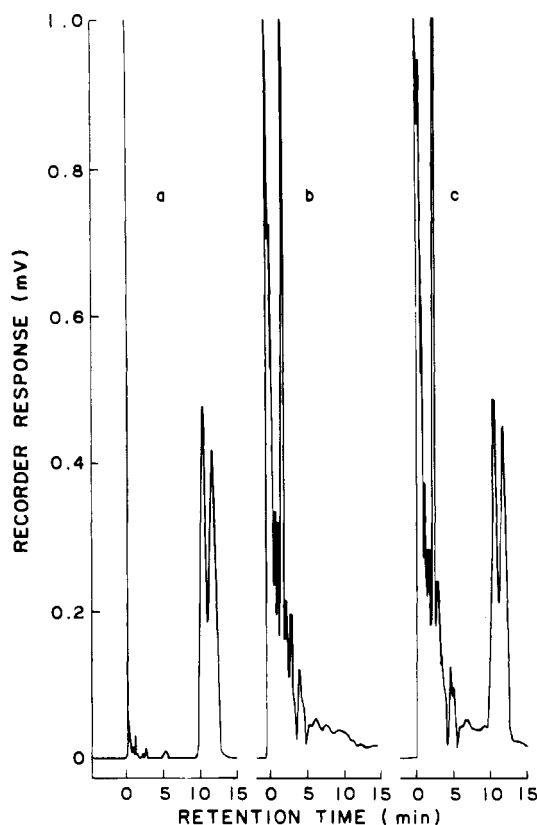
Fenvalerate Residues in Soil

J. Agric. Food Chem., Vol. 29, No. 1, 1981 **109**

Figure 1. Typical chromatograms (attenuation 32) for the analysis of fenvalerate in Lethbridge soil: (a) 400 pg of fenvalerate in hexane; (b) soil extract, 1-mL final volume, of microplot untreated control sample; (c) soil extract, 1-mL final volume, of microplot 45-week sample containing 0.041 ppm of fenvalerate.

Table I. Recovery of Fenvalerate from Fortified Soil

total fenvalerate added, ppm	enantiomeric pair	recovery,[a] %
1.0	RS,SR	92.0 ± 3.7
	RR,SS	91.7 ± 3.7
0.1	RS,SR	88.4 ± 2.9
	RR,SS	86.9 ± 2.7
0.01	RS,SR	105 ± 3
	RR,SS	99.1 ± 3.3
0.005	RS,SR	91.7 ± 10.5
	RR,SS	78.4 ± 10.3

[a] Results are the mean percentage recovery from four to six replicates ± standard deviation.

are insecticidally active (Nakayama et al., 1979), and of these, the SS isomer is the most active form of fenvalerate (Elliott and Janes, 1979).

Chromatographically, the RS,SR enantiomeric pair eluted as the first fenvalerate peak, followed by the RR,SS enantiomeric pair as the second peak (Figure 1). This order was confirmed by authentic standards of the enantiomeric pairs obtained from Shell Research Ltd. The ratio of RS,SR to RR,SS in the fenvalerate analytical standard supplied by Shell Canada Ltd. was 0.984:1, based on integrated peak areas. The OV-210 column gave enough resolution that the degradation of each enantiomeric pair could be followed. This distinction is potentially important because the RR,SS enantiomeric pair is a much more powerful insecticide than the RS,SR pair (Elliott and Janes, 1979). Also, since enantiomer-dependent differences in the ratio of fenvalerate metabolism by mouse microsomal enzymes have been reported (Soderlund and Casida, 1977), one might also expect enantiomer-dependent differences in the degradation of fenvalerate soil residues.
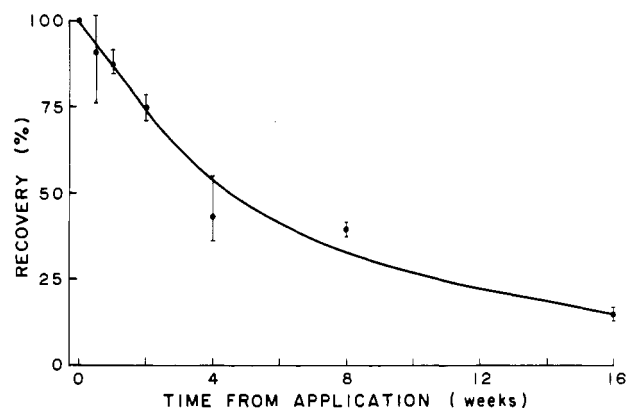

Figure 2. Disappearance of fenvalerate applied June 20 at 150 g/ha from the 0–2.5-cm microplot soil layer. Each value is a mean of four replicates and represents total fenvalerate (RS,SR + RR,SS) recovered. At the 0-week sampling, 100% recovery was 610 μg/plot or 0.419 ppm.

The analytical method used gave good recoveries as indicated by the analysis of fortified soil samples (Table I). Recoveries were lower for the more polar RR,SS enantiomeric pair, especially at the 0.005-ppm fortification level. The fortification procedure was designed to allow the fenvalerate to bind to the soil. The wetting action of the 1:1 v/v acetone–water spiking solution allowed the clay to expand and then, upon subsequent drying, contract as in field situations. The addition of water before extraction was essential to good recovery. Without this step, recoveries were 70–75%. Originally, a 1:1 v/v methanol–water spiking solution was used; however, a fenvalerate–solvent instability phenomenon was encountered. In the presence of methanol, the amount of the RS,SR enantiomeric pair increased relative to the RR,SS pair. A NMR exchange experiment showed that the α proton of fenvalerate slowly underwent proton–deuteron exchange with the solvent deuterated methanol. Both enantiomeric pairs exchanged α protons and racemization occurred. The RR,SS pair appeared to racemize faster than the RS,SR pair until an equilibrium was reached where the ratio of RS,SR to RR,SS had increased to 1.11:1. Similar proton exchange and racemization has been reported for decamethrin dissolved in methanol and used as "dark" controls during photolysis experiments (Ruzo et al., 1977). The exact mechanism of fenvalerate α proton exchange is unclear; however, because of this phenomenon, methanol and related solvents should be avoided in residue analysis for fenvalerate.

The microplot technique used to study the field persistence of fenvalerate proved workable and, due to the accuracy of pipet application and the reduction in errors with whole-plot samplings, gave less variation than is usual with large field plots. Fenvalerate applied to the 12 microplots over the summer and sampled immediately to determine microplot accuracy and precision gave returns of 97.0 ± 6.5% of the amount theoretically applied.

Fenvalerate was found to persist mainly in the 0–2.5-cm soil layer. Residues from the June 20 insecticide application declined steadily until, 16 weeks later on Oct 10, 15.1% of total applied fenvalerate remained (Figure 2). Mean temperatures over the 16 weeks ranged between 22 and 8 °C, total rainfall was 354 mm occurring mostly at 2–4 and 8–12 weeks, and average soil moisture in the 0–2.5-cm layer fluctuated between 16.4 and 5.8%. For half-life determination, the residue data were fit to the first-order exponential decay equation $y = y_0 e^{-\lambda t}$, where half-life = 0.693/λ (Goring et al., 1975). The half-lives were 5.9 weeks for the RS,SR enantiomeric pair, 6.0 weeks for
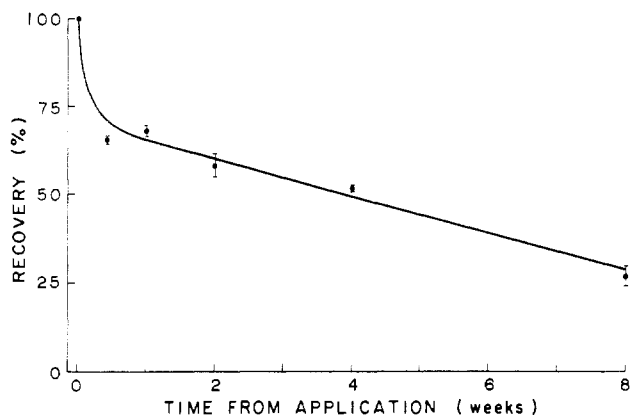
Figure 3. Disappearance of fenvalerate applied at 70 g/ha from the 0–2.5-cm potted soil layer. Each value is a mean of two replicates, each analyzed in duplicate, and represents total fenvalerate (RS,SR + RR,SS) recovered. At the 0-week sampling, 100% recovery was 81.5 µg/pot or 0.212 ppm.

the RR,SS pair, and the data for each enantiomeric pair had a correlation coefficient $r = -0.970$ for "goodness of fit" to the exponential decay model. Since the degradation was very similar for both enantiomeric pairs, only the data for total fenvalerate are presented (Figure 2).

The spring sampling taken 45 weeks after application showed that 11.3% total fenvalerate remained. Residues had declined little over the winter, which had been particularly cold and harsh. This observation coincides with results from freezer check samples that showed no significant degradation of fenvalerate soil residues in –40 °C storage over 23 weeks. The winter carry-over does not appear large enough to cause residue accumulation with new summer applications.

Less than 0.5% of applied fenvalerate was found in any of the 2.5–5.0-cm soil samples taken over the 45-week sample period. No fenvalerate was detected until 4 weeks after application, and at every sample date there were plots with no detectable residue in the lower soil layer. Even less fenvalerate, <0.1% of applied, was detected in any of the 3- and 4-week lateral samples despite a 0–4-week rainfall of 95.4 mm, including a 25.9-mm downpour 15 days after application. Also, residues were not detected in any of the 0–2.5-cm composite control samples collected between 0 and 45 weeks. These results indicate that fenvalerate was not readily leached downward and that lateral surface movement was very limited.

The degradation of fenvalerate in soil incubated in the environmental chamber was similar to microplot field results (Figure 3). The RS,SR enantiomeric pair had a half-life of 5.0 weeks and the RR,SS pair a half-life of 5.3

weeks with correlation coefficients of $r = -0.917$ and -0.909, respectively, for fit to the exponential decay model. There was a trace of fenvalerate, 1.2% of applied, in one of the 2.5–5.0-cm soil samples, none in the duplicate 2.5–5.0-cm sample, and none in untreated controls. The initial (0–2 weeks) disappearance of fenvalerate appeared to be faster in the indoor pot experiment than in the outdoor microplot experiment. If fenvalerate soil residues are degraded mainly by microbial activity as suggested by Williams and Brown (1979), initial microbial activity might have been higher indoors or the lower indoor application rate might have had an effect.

Results of this work indicate that fenvalerate residues, with an average half-life of 6.0 weeks in the field and 5.2 weeks when incubated indoors, are moderately persistent in Lethbridge soil. These results are comparable to the average half-life of 7.0 weeks for fenvalerate incubated in British Columbia soils (Williams and Brown, 1979). In both persistence studies reported here, the RS,SR enantiomeric pair degraded slightly faster than the insecticidally more active RR,SS pair. The data of Soderlund and Casida (1977) on mouse microsomal esterase plus oxidase activity showed the same enantiomer-dependent order of metabolism rates. While moderately persistent, it appears that fenvalerate residues remain bound to the soil and have very limited mobility.

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