Persistence of Fenvalerate in Alfalfa: Effect of Growth Dilution and Heat Units on Residue Half-Life

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Fenvalerate [cyano(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate] was applied to alfalfa at 0.14–0.15 kg/ha in three experiments, and the residues, crop growth, and weather were monitored for 28 days. Initial residues of 22.2–32.5 ppm declined exponentially with a half-life of 9–11 days. When fenvalerate was applied early in the season, the advantage of growth dilution of the residues was negated by cooler temperatures slowing the rate of decline of the chemical itself. The half-life of the chemical per se, with the effect of growth dilution removed, was 11–19 days, depending on the weather after application. Cumulative heat units were used to correlate residue decline to both time and temperature, and the concept of residue half-life in degree-days was introduced. The result was a half-life of 153–189 degree-days above 5 °C for fenvalerate residues in alfalfa.

Fenvalerate [cyano(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate] is one of the synthetic pyrethroid insecticides being evaluated at this laboratory for the control of weevils (*Hypera postica* Gyll.) and *Lygus* spp. in alfalfa (Charnetski and Schaber, 1980a,b). One concern is that fenvalerate residues are potentially toxic to bees. The National Research Council Canada (1981) rates fenvalerate as highly toxic to honeybees (*Apis mellifera* L.), LD_{50} = 0.408 μg/bee, and as hazardous to the alfalfa leafcutter bee [*Megachile rotundata* (F.)] any time application is made during flowering. The leafcutter bee is the primary pollinator of alfalfa grown for seed, and the need to spray insecticides to control high populations of insect pests often occurs close to the start of alfalfa flowering (June 20–30). After flowering, there is little growth of the alfalfa to dilute the insecticide residues, and the amount of insecticide to which the bees are exposed will depend on the persistence of the chemical residue. Thus, information on residue persistence is required to help establish a safety interval between insecticide application and placement of leafcutter bees in the field.

There have been few published reports on the persistence of fenvalerate in field crop situations. Harris et al. (1978) applied fenvalerate at 0.14 kg/ha to celery grown in outdoor microplots. Residue levels were 3.3, 1.7, 0.45, and 0.36 ppm after 0, 7, 14, and 21 days, respectively. Westcott and Lee (1978) reported a first-order decline with a half-life of 5 days for fenvalerate residues on wheat foliage. This rate of residue decline included a large growth dilution effect of the crop. Greenberg (1981) described a method for determining fenvalerate in grapes, peppers, and apples and presented residue data from field-treated samples. Although half-lives were not calculated, initial residues declined by half within 14 days. However, when fenvalerate was sprayed on grapes and peppers at higher rates, there was no residue decline within 14 days.

The half-life concept, derived from first-order kinetics (Gunther and Blinn, 1955; Gunther, 1969; Hamaker, 1972), is commonly used to describe pesticide disappearance. Often a mathematical model is fit to an observed set of residue data for the purpose of predicting rates of residue decline in other cropping situations. The first-order exponential model, the power rate model, the hyperbolic rate model, and the log residue–log time model have been described previously (Hamaker, 1972; Goring et al., 1975; Nigg et al., 1977a; Stamper et al., 1979). One method to improve the accuracy of residue predictions is to adjust for weather variables. Nigg et al. (1977a) have reviewed several successful weather models of pesticide disappearance. In the study of ethion decay in Florida citrus, Nigg et al. (1977b) assumed the effect of different weather variables to be linear and additive within an overall first-order model. The resultant multiple linear regression using time and weather accounted for 94% of the observed residue variation, compared to only 57% of the variation explained without the weather variables. The same type of multiple linear regression time–weather model has been used effectively for other pesticides on citrus (Nigg et al., 1978, 1979b; Nigg and Allen, 1979). In one study (Nigg et al., 1979a), the decline of parathion residues on Florida oranges was so related to weather variables that the time variable was not required in the overall model.

Walker (1974, 1976a–c, 1978), Smith and Walker (1977), Walker and Smith (1979), and Walker and Barnes (1981) have developed a successful weather model for predicting herbicide degradation rates in soils. Their approach was to first determine the relationships between residue degradation, soil moisture, and soil temperature in controlled experiments. Next, these relationships were applied to field residues where the fluctuations in soil moisture and soil temperatures were estimated empirically from standard meteorological records. Finally, the predicted changes in residue levels for a series of short time intervals were integrated over the entire period of interest.

The purpose of this study was to measure the persistence of fenvalerate residues in alfalfa under different southern Alberta conditions. The secondary objective was to formulate a weather model that would accurately predict fenvalerate residues in treated alfalfa.

EXPERIMENTAL SECTION

Chemicals. Fenvalerate analytical standard (98.5% purity) and formulated product, 30% emulsifiable concentrate (EC), were supplied by Shell Canada Ltd., Toronto, Ontario, Canada. Aluminum oxide 504-C acidic from CAMAG (Switzerland) and SilicAR CC-4 from MallincKrodt, Inc., were held at 130 °C before use. Solvents were glass-distilled reagent grade.

Field Studies. Three field experiments were conducted at two locations over 2 years. In the first year (experiment A), the alfalfa was sprayed at the normal application time (near the start of flowering) and the persistence of fenvalerate monitored. In the second year, the persistence of fenvalerate in an early sprayed experiment where there

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was alfalfa growth dilution (experiment B) was compared to a later sprayed experiment with no alfalfa growth dilution (experiment C).

Experiment A was conducted in 1978 at Brooks, Alberta, Canada, on 3-year-old seed alfalfa (cv. Thor) with 76-cm row spacing. Plots were 7.62 × 4.88 m laid out in a randomized block design with four replicates. The fenvalerate EC product was applied June 27 at 0.15 kg/ha with a tractor-mounted plot sprayer. The total water volume was 112.3 L/ha applied at 275-kPa pressure through Tee Jet 65015 nozzles. At intervals of 0, 1, 3, 7, 14, and 28 days, 60 representative stems were sampled from 30 sites within each plot by cutting the stems at ground level. The alfalfa samples, as received from the field, were stored at −40 °C. Before analysis, samples were briefly thawed and were chopped by using a Hobart Model 84181-D food cutter. After the samples were thoroughly mixed, the total sample weight was determined and subsamples were taken, 20.0 g for residue analysis and 10.0 g (in duplicate) for alfalfa moisture determination (24-h oven drying at 110 °C).

Experiments B and C were conducted in 1979 at Lethbridge, Alberta, Canada, as separate experiments within one randomized block design, and unless otherwise noted, the same methods were used as in experiment A. The alfalfa (cv. Beaver) had been seeded as a forage crop at 17.8-cm row spacing in 1976. The plots, 12.2 × 4.89 m, were sprayed at 0.14 kg/ha on May 31 (experiment B) and on June 25 (experiment C) and were sampled at intervals of 0, 1, 4, 7, 14, and 28 days and of 0, 1, 4, 8, 14, and 28 days, respectively. Samplings consisted of 40 representative stems collected from 20 sites within each plot. Alfalfa samples were weighed, chopped, subsampled as before, and then stored at −40 °C before analysis.

Temperatures, hours of sunshine, total incoming radiation, wind, water evaporation, and rainfall were recorded at weather stations equipped by and reporting to the Atmospheric Environment Service of Environment Canada. These stations were located within 5 miles of the experimental sites.

Residue Analysis Method. *Extraction.* After a brief thawing, the 20.0-g chopped alfalfa samples were extracted by using a Waring Blendor at medium speed according to the following regime: 150 mL of 1:1 v/v acetone–hexane for 2 min, 150 mL of 1:2 v/v acetone–hexane for 2 min, and 150 mL of hexane for 2 min. Between solvent changes, the liquid extract was decanted and suction-filtered through a Büchner funnel containing a No. 1 Whatman 7.0-cm filter paper. After the third extraction, the alfalfa residue was transferred to the Büchner funnel, and the blender and residuum were washed with a final 50-mL rinse of 1:1 v/v acetone–hexane. Combined extracts were liquid–liquid partitioned with 350 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 (35 °C) to near dryness, and adjusted to a 25-mL volume in hexane. Extracts were then held at 0–4 °C before cleanup.

Cleanup. A tandem microcolumn system was used in which sample extracts were first chromatographed on alumina and then on silica gel. Both adsorbents were deactivated to 6% moisture and were equilibrated overnight in a stoppered flask prior to use. The microcolumns consisted of disposable Pasteur pipets (14.6 × 0.75 cm i.d.) packed with 5 cm of adsorbent. A 0.5-mL aliquot of sample extract (0.4-g alfalfa equivalent) was applied to the alumina microcolumn. The extract was washed-in with 2 mL of hexane and then with 12 mL of 1:19 v/v ether–hexane, and both eluates were discarded. Fenvalerate was eluted with 10 mL of 1:9 v/v ether–hexane, and the eluate was collected in a 15-mL centrifuge tube. This eluate was evaporated to near dryness under a stream of dry nitrogen, 5 mL of hexane was added, and the eluate was reevaporated to less than 0.5 mL so that no ether remained. This concentrated eluate was quantitatively applied to the silica gel microcolumn and was washed-in with 2 mL of hexane rinsings and then with 5 mL of 1:19 v/v ether–hexane, and both eluates discarded. Fenvalerate was eluted with 10 mL of 1:9 v/v ether–hexane. The collected eluate was concentrated as before and was adjusted with hexane to an appropriate final volume (1–10 mL) for GC analysis.

Fortification. Method recoveries for fenvalerate were determined by analysis of alfalfa fortified at 40, 4.0, and 0.4 ppm. Freshly chopped alfalfa samples, 20.0 g each (fresh weight basis) contained in 500-mL Erlenmeyer flasks, were individually treated by evenly pipetting onto the tissue surface 4 mL of an appropriate solution of fenvalerate in hexane. The alfalfa was mixed with a spatula and the flask was capped with foil. After 1 h of equilibration at room temperature, the fortified alfalfa was remixed and stored at 5 °C for 3 days in the dark. The 5 °C temperature slowed any deterioration of the alfalfa tissue, while the 3 days were considered necessary for fenvalerate penetration and equilibration with the cooled tissue. Fortified samples were then frozen at −40 °C to simulate storage of field-treated samples.

Gas Chromatography. A Hewlett-Packard Model 5733A gas chromatograph equipped with a ^{63}Ni detector was used. Analyses were automated by the use of a Varian Model 8020 autosampler and a 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 an injector temperature of 250 °C, a column temperature of 230 °C, and a detector temperature of 350 °C, with 95% argon–5% methane carrier gas at a flow of 60 mL/min. Partial separation of the two fenvalerate peaks was achieved with retention times of 10.5 min for the *RS,SR* isomer pair and 11.7 min for the *RR,SS* isomer pair. This order of elution had been previously confirmed (Hill, 1981). Typical response for 800 pg of total fenvalerate injected was full-scale (1-mV) recorder deflection for each isomeric peak at attenuation 32. A linear response was observed from the minimum quantifiable limit of 40 to 4000 pg total fenvalerate injected. Sample injection volumes were 4 μL, and unknowns were quantified by comparison to appropriate alternating standards.

Calculations and Data Analysis. The levels of fenvalerate residue found in the alfalfa field experiments are reported without correction for analytical method losses and are expressed as ppm on a sample dry weight basis. This basis removes fluctuations due to moisture and is preferable for describing residue persistence in mathematical terms. Residue persistence curves were plotted as ppm of fenvalerate vs. days after spraying and by using a log transformation and linear regression (LR) were fit to the first-order exponential model $C = C_0e^{-\lambda t}$, where C is the concentration of fenvalerate at any time, C_0 is the concentration of fenvalerate at time zero, λ is the residue decline constant, and t is the time in days. The LR analysis (Seber, 1977) was designed to first plot the data from each of the four experimental replicates separately, to test for differences between the slopes (λ^{1-4}) and then the intercepts (C_0^{1-4}) of the regression lines, and, where

no significant differences existed, to combine the data and calculate one overall slope λ and intercept C_0 for the experiment. Thus the LR procedure determined if either the initial residue levels (C_0^{1-4}) or the residue decline rates (λ^{1-4}) were different between the replicates of an experiment. Where there were no differences between the residue decline rates of the replicates, the overall slope for the experiment was used to calculate the residue half-life (in days) from $t_{1/2} = 0.693/\lambda$. Where the residue decline rates, λ^{1-4}, were different, it is statistically more correct to calculate four separate residue half-lives for the experiment. The LR correlation coefficient was used as an indication of the "goodness of fit" of the exponential model to the residue data.

The half-life calculated by using the ppm of residue data [$t_{1/2}$(ppm)] is a measure of the rate of residue decline due to both the loss of the chemicals (mostly by degradation) and the dilution of the chemical by alfalfa growth. For determination of the rate of loss of the chemical alone, each ppm of residue was multiplied by the appropriate total sample dry weight to yield micrograms of fenvalerate per plot sample. This absolute amount of residue is independent of the amount of alfalfa growth that occurred between spraying and sampling. The micrograms of fenvalerate was then plotted vs. days after spraying, and by use of LR to fit the resulting curve to the same exponential function as before, a half-life (in days) for the loss of the chemical alone [$t_{1/2}(\mu g)$] was calculated. The micrograms of fenvalerate data were more variable than the original ppm of residue data due to the sampling error incorporated into the total sample dry weights. However, this direct method of correcting residues for growth dilution was considered better than the alternative method of adjusting the ppm of residues by relative growth factors (Hill et al., 1981).

After correction for growth dilution, residue decline was adjusted for weather. A procedure similar to that of Nigg et al. (1977b, 1978, 1979a,b) and Nigg and Allen 1979) was used to test different weather models. Using multiple linear regression (MLR), the micrograms of fenvalerate data and the weather data from the three field experiments were combined within an overall first-order model. The MLR analysis adjusted for differences between experiments, and for differences between replicates within each experiment, before correlating micrograms of fenvalerate to all possible combinations of time and weather variables. A simple but effective weather model was chosen in which fenvalerate residue decline was correlated to cumulative heat units only. Heat units are a function of both time and temperature and were calculated as degree-days according to the modified sine wave method of Allen (1976). This method uses daily maximum and minimum temperatures and assumes the temperature cycle is a sine wave in which the first and second minima are not necessarily the same. The number of degree-days above a given threshold temperature can also be determined. For expression of fenvalerate residue decline as a function of heat units, the micrograms of residue was plotted vs. degree-days above 5 °C. The resulting decline curve was fit to the first-order exponential model as before, and the half-life for the loss of the chemical [$t_{1/2}(\mu g)$] in terms of degree-days base 5 °C (deg-day$_5$) was calculated.

RESULTS AND DISCUSSION

The gas chromatographic separation of fenvalerate into *RS,SR* and *RR,SS* enantionmeric pairs (Hill, 1981) and the relative insecticidal activity of the four stereoisomers (Elliott and Janes, 1979; Nakayama et al., 1979) have been discussed previously. The OV-210 column gave enough separation of the two fenvalerate peaks (Figure 1) that the analytical method recovery and residue decline for each enantiomeric pair could be determined. However, since the results were essentially identical for both enantiomeric pairs, all data are presented as total fenvalerate.

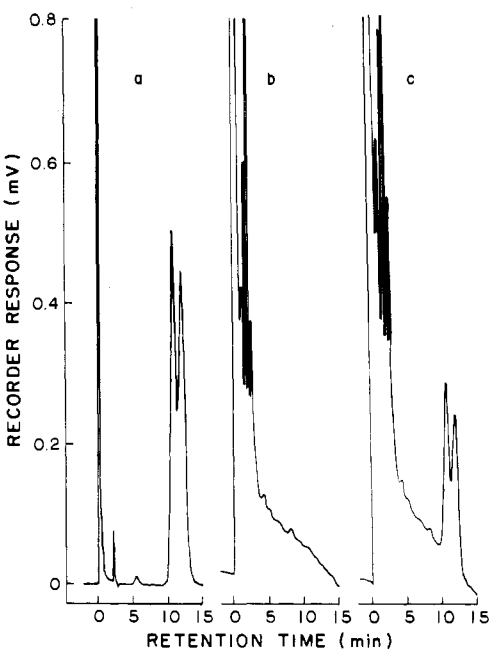

Figure 1. Typical chromatograms for the determination of fenvalerate in alfalfa: (a) 200 pg of fenvalerate in hexane, attenuation 16; (b) extract of untreated alfalfa, 1-mL final volume, attenuation 32; (c) extract of 0.4 ppm of fortified alfalfa, 1-mL final volume, attenuation 32.

Table I. Recovery of Fenvalerate from Fortified Alfalfa

fortification level, ppm[a]	recovery,[b] %
40	94.4 ± 5.1
4.0	100 ± 6
0.4	91.6 ± 2.6

[a] Micrograms of fenvalerate per gram dry weight of alfalfa. These fortification levels corresponded to 10, 1.0, and 0.1 ppm of fenvalerate on a fresh weight basis. [b] Results are the mean percentage recovery from four replicates ± standard deviation.

The chromatograms for the determination of fenvalerate in alfalfa (Figure 1) show that the sensitivity for fenvalerate was good and the cleanup was adequate down to the lowest fortification level. Although there was broadening and tailing of the solvent peak at the 0.4-ppm level, there were no interferences at the retention time of fenvalerate. It should also be noted that all residues from the field experiments were well in excess of the 0.4-ppm method limit.

Recoveries of fenvalerate from the fortified alfalfa samples indicated that the residue analysis method was effective (Table I). At all fortification levels, mean recoveries were better than 90% with reasonable variation (standard deviation ≤ 6%) between replicate samples. The fortification studies were designed to simulate, as near as possible, the extractability of weathered residues from field samples. The fortification procedure did allow the fenvalerate to penetrate and equilibrate with the alfalfa tissue. A test was conducted in which a 4-ppm fortified sample was surface extracted by using the normal solvent regime but with 15-s solvent rinses and manual agitation instead of blending. A decrease in method recovery to 71.5% indicated that at least 28.5% of the fenvalerate had penetrated the alfalfa tissue during fortification. An attempt was made to shorten the extraction procedure by omitting

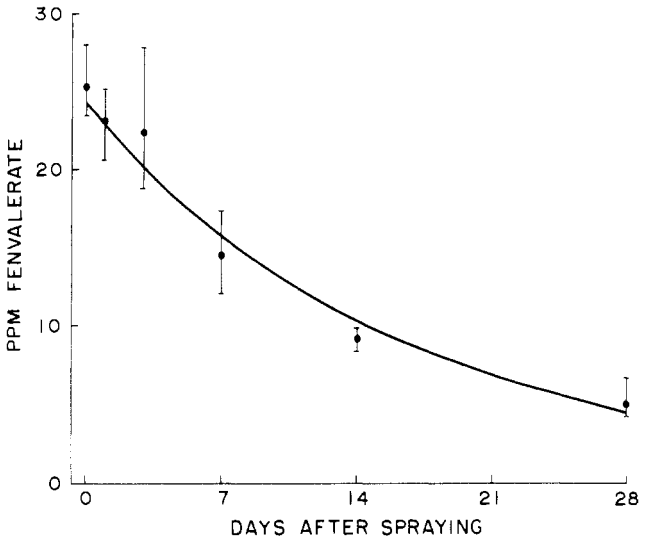

Figure 2. Experiment A. Disappearance of fenvalerate applied June 27 at 0.15 kg/ha. The mean and range of values from the four replicates are ppm of fenvalerate on a sample dry weight basis. Average moisture content of the alfalfa was 69.5%.

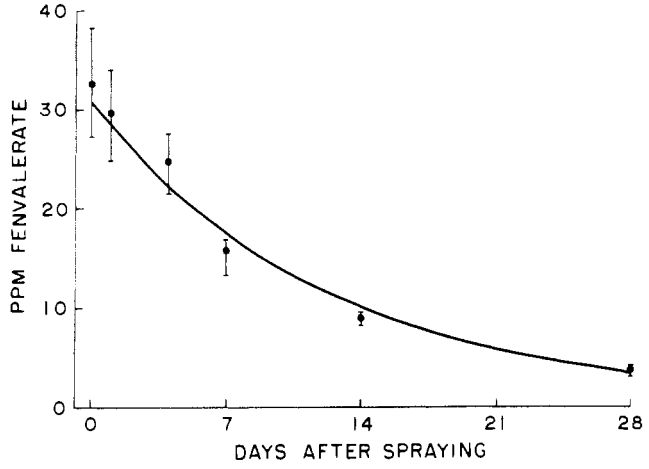

Figure 3. Experiment B. Disappearance of fenvalerate applied May 31 at 0.14 kg/ha. The mean and range of values from the four replicates are ppm of fenvalerate on a sample dry weight basis. Average moisture content of the alfalfa was 74.2%.

the 150-mL hexane-blending step. The decrease in fenvalerate recovery was minimal at the 4-ppm fortification level; however, this step was essential for good recoveries at the 0.4-ppm level.

Results of the three field experiments showed that fenvalerate residues in the alfalfa declined in an exponential manner (Figures 2–4. The correlation coefficients for fit to the exponential model were 0.970, 0.985, and 0.990 for experiments A, B, and C, respectively. The variation between replicates on a given sample day (range of values indicated by the vertical bars in Figures 2–4) was reasonable (average standard deviation = 12.7%) for a field crop residue study. Sampling was a major source of variation because the alfalfa, a perennial crop, had a range of stem sizes and, to achieve a representative sample, all sizes were selected to comprise the 40- or 60-stem plot samples.

The 0-day levels of fenvalerate residues varied with the date of insecticide application (Figures 2–4). Experiments A and C, both sprayed in late June, had initial residues of 25.3 and 22.2 ppm, respectively. The 32.5-ppm initial residue of experiment B was significantly higher ($P = 0.05$) than that of the other experiments. Experiment B was sprayed in late May when the alfalfa was in an earler growth stage. Plants were small (20 cm high) with no

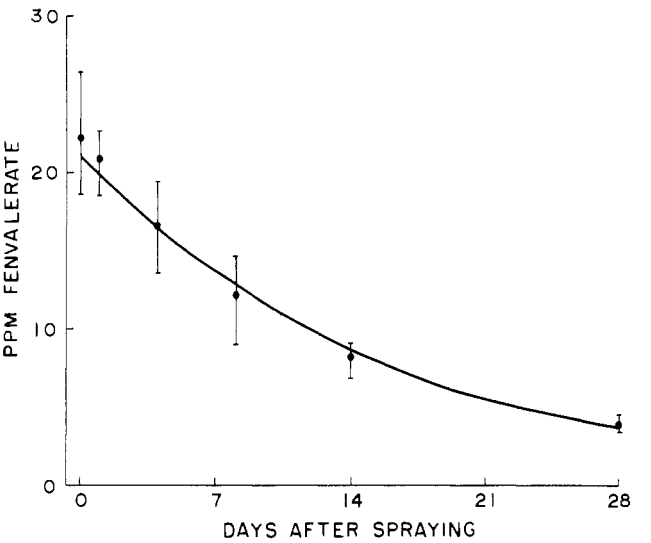

Figure 4. Experiment C. Disappearance of fenvalerate applied June 25 at 0.14 kg/ha. The mean and range of values from the four replicates are ppm of fenvalerate on a sample dry weight basis. Average moisture content of the alfalfa was 67.9%.

Table II. Rate of Decline of Fenvalerate Residues and Growth of the Alfalfa in Field Experiments

expt	$t_{1/2}$(ppm), days[a]	rel alfalfa growth[b]	$t_{1/2}(\mu g)$, days[c]	$t_{1/2}(\mu g)$, deg-days$_5$[d]
A	11	1.2	12	171
B	9	3.3	19	189
C	11	1.0	11	153

[a] Half-life due to the combined effect of residue decline and alfalfa growth dilution. Values not significantly different ($P = 0.05$). [b] Ratio of mean plot sample dry weight at 28 days to that at 0 day. [c] Half-life due to residue decline alone. The value of 19 is significantly different ($P = 0.01$) from the other values. [d] Half-life due to residue decline expressed in degree-days above 5 °C. Values not significantly different ($P = 0.05$).

branching or secondary stem development, and thus with less crop canopy there was more complete spray coverage than in the later sprayed experiments. At the end of the experiments, there were no significant differences in the levels of fenvalerate residues between experiments. The 28-day residue levels were 4.88, 3.66, and 3.97 ppm for experiments A, B, and C, respectively.

The $t_{1/2}$(ppm), which represent the actual, observed rates of residue decline, were very similar for all three experiments despite the differences in alfalfa growth dilution (Table II). However, the $t_{1/2}(\mu g)$ (days), which are the rates of residue decline with the effect of growth dilution removed, were significantly different ($P = 0.01$). The $t_{1/2}(\mu g)$ of 11 days is the overall half-life calculated for experiment C, although there were significant differences ($P = 0.05$) between the 16-, 10-, 9-, and 11-day half-lives of the individual replicates. Also, LR analysis of the micrograms of residue data showed that within experiments A and B there were differences ($P = 0.01$) between replicates in the initial amounts of fenvalerate deposited. Replicates with the largest alfalfa plants at the time of spraying had more micrograms of residue on the foliage, although residues were similar on a ppm basis. Interestingly, for experiments A and B, the rates of micrograms of residue decline between replicates were similar, despite the differences in micrograms of fenvalerate initially deposited.

The $t_{1/2}(\mu g)$ (days) values (Table II) indicate that although experiment B was sprayed early to take advantage

of increased growth dilution of residues, the rate of loss of the chemical residue per se was much slower than in experiment A or C. The trend of increased growth corresponding to a slower rate of loss of the chemical may also apply to experiment A compared to experiment C.

While it is possible that certain physiological functions related to growth could retard fenvalerate degradation, the differences in $t_{1/2}(\mu g)$ (days) between experiments were probably related to differences in the 0- to 28-day weather of each experiment. Average daily values for the weather variables were 12.6 deg-days$_5$, 10.6-h sunshine, 529-langleys total incoming radiation, 225-km wind, 8.4-mm water evaporation, and 0.7-mm rainfall. From MLR analysis, the best one-variable weather model used deg-days$_5$ (r = 0.977) and accounted for 95.5% of the variation observed in the residue data. The best two-variable model used total incoming radiation and water evaporation and accounted for 96.5% of the variation observed. The single-variable deg-days$_5$ model was chosen because it is simple, effective, and easy to interpret. That is, fenvalerate degradation was slower in experiment B due to the cooler temperatures (10.1 deg-days$_5$/day). The 5 °C threshold was applied because it is the threshold temperature for alfalfa growth (Schreiber et al., 1978; Gutierrez et al., 1979) and it is reasonable to assume there would be a chemical/physiological base temperature below which little chemical/metabolic degradation of fenvalerate would take place.

The MLR analysis was not totally definitive for selecting the deg-days$_5$ model over the other one-variable models. With the exception of rainfall (r = 0.903), all of the one variable weather models showed a good fit ($r \geq 0.966$) to the residue data. These high correlations were caused by the relatively constant summer weather of the Canadian prairies. That is, the weather variables (other than rainfall) accumulated in a regular and predictable manner and thus were highly correlated with time ($r \geq 0.980$) and with each other ($r \geq 0.947$). The MLR analysis also indicated that time (days) alone was a good model (r = 0.971) for the combined experiments. However, the best argument for adopting the deg-days$_5$ model over the time model is that the $t_{1/2}(\mu g)$ (deg-days$_5$) values were not significantly different (Table II). The half-life values of 153–189 deg-days$_5$ indicate that half of the fenvalerate in alfalfa would disappear after 15–19 days of mean temperature 15 °C or 10–13 days of mean temperature 20 °C or 8–9 days of mean temperature 25 °C. While the concept of degree-days has limitations (Edey, 1977), expressing residue half-life in degree-days does have merit for comparing temperature-dependent residue decline in different weather regimes. Also, the deg-days$_5$ model for residue decline should be readily adaptable to pest management systems many of which already use degree-days to predict insect phenology.

This study indicates that during the 0–28 days after application, honeybees and alfalfa leafcutter bees could be exposed to fenvalerate residues in alfalfa ranging from 33 to 3.7 ppm (dry weight basis). Since whole stems were sampled, the ppm data represent average residue levels throughout the crop. For improvement of residue predictions and reduction of the hazard to bees, the deg-days$_5$ model for estimating fenvalerate residues in different alfalfa crops is recommended.

LITERATURE CITED

Allen, J. C. *Environ. Entomol.* **1976**, *5*, 388–396.
Charnetski, W. A.; Schaber, B. D. "Pesticide Research Report: Expert Committee on Pesticide Use in Agriculture"; Agriculture Canada: Ottawa, Canada, 1980a; p 160 (abstract only).
Charnetski, W. A.; Schaber, B. D. "Pesticide Research Report: Expert Committee on Pesticide Use in Agriculture"; Agriculture Canada: Ottawa, Canada, 1980b; p 161 (abstract only).
Edey, S. N. "Growing Degree-Days and Crop Production in Canada"; Agriculture Canada: Ottawa, Canada, 1977; Publication 1635, pp 1–62.
Elliott, M.; Janes, N. F. In "Advances in Pesticide Chemistry"; Geissbuhler, H., Ed.; Pergamon Press: Oxford, 1979; Part 2, pp 166–173.
Goring, C. A. I.; Laskowski, D. A.; Hamaker, J. W.; Meikle, R. W. In "Environmental Dynamics of Pesticides"; Haugue, R.; Freed, V. H., Eds.; Plenum Press: New York, 1975; pp 135–172.
Greenberg, R. S. *J. Agric. Food Chem.* **1981**, *29*, 856–860.
Gunther, F. A. *Residue Rev.* **1969**, *28*, 1–119.
Gunther, F. A.; Blinn, R. C. "Analysis of Insecticides and Acaricides"; Interscience: New York, 1955; pp 1–696.
Gutierrez, A. P.; Regev, U.; Shalit, H. *Environ. Entomol.* **1979**, *8*, 101–107.
Hamaker, J. W. In "Organic Chemicals in the Soil Environment"; Goring, C. A. I.; Hamaker, J. W., Eds.; Marcel Dekker: New York, 1972; Vol. 1, pp 253–340.
Harris, C. R.; Svec, H. J.; Chapman, R. A. *J. Econ. Entomol.* **1978**, *71*, 642–644.
Hill, B. D. *J. Agric. Food Chem.* **1981**, *29*, 107–110.
Hill, B. D.; Charnetski, W. A.; Schaalje, G. B. *Proc. Annu. West. Can. Pestic. Residue Workshop, 16th* **1981**, 1–6.
Nakayama, I.; Ohno, N.; Aketa, K.-I.; Suzuki, Y.; Kato, T.; Yoshioka, H. In "Advances in Pesticide Chemistry"; Geissbuhler, H., Ed.; Pergamon Press: Oxford, 1979; Part 2, pp 174–181.
National Research Council Canada "Pesticide-Pollinator Interactions"; Environmental Secretariat: Ottawa, Canada, 1981; Publication NRCC 18471, pp 1–190.
Nigg, H. N.; Allen, J. C. *Environ. Sci. Technol.* **1979**, *13*, 231–233.
Nigg, H. N.; Allen, J. C.; Brooks, R. F. *Proc. Int. Soc. Citric., 1977* **1977a**, *2*, 437–441.
Nigg, H. N.; Allen, J. C.; Brooks, R. F.; Edwards, G. J.; Thompson, N. P.; King, R. W.; Blagg, A. H. *Arch. Environ. Contam. Toxicol.* **1977b**, *6*, 257–267.
Nigg, H. N.; Allen, J. C.; King, R. W. *J. Agric. Food Chem.* **1979a**, *27*, 578–582.
Nigg, H. N.; Allen, J. C.; King, R. W.; Thompson, N. P.; Edwards, G. J.; Brooks, R. F. *Bull. Environ. Contam. Toxicol.* **1978**, *19*, 578–588.
Nigg, H. N.; Reinert, J. A.; Fitzpatrick, G. E. *Bull. Environ. Contam. Toxicol.* **1979b**, *21*, 697–702.
Schreiber, M. M.; Miles, G. E.; Holt, D. A.; Bula, R. J. *Agron. J.* **1978**, *70*, 105–109.
Seber, G. A. F. "Linear Regression Analysis"; Wiley: New York, 1977; pp 197–205.
Smith, A. E.; Walker, A. E. *Pestic. Sci.* **1977**, *8*, 449–456.
Stamper, J. H.; Nigg, H. N.; Allen, J. C. *Environ. Sci. Technol.* **1979**, *13*, 1402–1405.
Walker, A. *J. Environ. Qual.* **1974**, *3*, 396–401.
Walker, A. *Pestic. Sci.* **1976a**, *7*, 41–49.
Walker, A. *Pestic. Sci.* **1976b**, *7*, 50–58.
Walker, A. *Pestic. Sci.* **1976c**, *7*, 59–64.
Walker, A. *Weed Res.* **1978**, *18*, 305–313.
Walker, A.; Barnes, A. *Pestic. Sci.* **1981**, *12*, 123–132.
Walker, A.; Smith, A. E. *Pestic. Sci.* **1979**, *10*, 151–157.
Westcott, N. D.; Lee, Y. W. *Proc. Annu. West. Can. Pestic. Residue Workshop, 13th* **1978**, 164–169.

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