

Dissipation of Pyrethroid Residues in Peppers, Zucchini, and Green Beans Exposed to Field Treatments in Greenhouses: Evaluation by Decline Curves

MARIA MARTINEZ GALERA,^{*,†} MARIA D. GIL GARCIA,[†]
 JOSE A. RODRIGUEZ LALLENA,[‡] TRINIDAD LOPEZ LOPEZ,[§] AND
 JOSE L. MARTINEZ VIDAL[†]

Department of Hydrogeology and Analytical Chemistry, University of Almería, La Cañada de San Urbano, 04071 Almería, Spain, Department of Statistics and Applied Mathematics, University of Almería, La Cañada de San Urbano, 04071 Almería, Spain, and Laboratory of Pesticide Residue CUAM, El Ejido, 04700 Almería, Spain

Dissipation of seven pyrethroid insecticides under field conditions was evaluated on green beans, zucchini, and peppers grown in experimental greenhouses (Almería, Spain). Pyrethroid residues were determined by high performance liquid chromatography using continuous on-line post-elution photoirradiation with fluorescence detection after dichloromethane extraction and cleanup on florisil phase cartridges. Mathematically defined decline curves were established by determining optimal relationships between pyrethroid residues and time. Different models were used to find these curves. The 1st-order model achieved the best adjustment to the experimental data in 42.9% of cases. The RF (root function) 1st-order model was the best in 33.3% of times. Each of the 1.5th- and 2nd-order models provided the best adjustment in a 9.5% of the cases. Finally, the RF 1.5th-order model was the most appropriate in only 4.8% of cases. Half-life times for these three vegetables were estimated from the optimal models. The preharvest intervals for the residues in these three vegetables was obtained, taking into account the maximum residue levels established by the existing legislation. They were all lower than the ones specified by the makers of commercial formulations, which ensures a safe enough consumption.

KEYWORDS: Pyrethroids; decline curves; dissipation; residues; vegetables; greenhouses; HPLC-fluorescence

INTRODUCTION

The toxic effect of the synthetic pyrethroids is mainly induced by contact as opposed to ingestion. It depends on the ability of the compounds—in various formulations—to penetrate rapidly into the body of the insect and interact with the central and peripheral nervous system. Their action occurs on sodium channel within the lipophilic environment of the membranes and they act by modulating the opening and closing of the channels, leading to synaptic discharge, repetitive discharge, depolarization, and ultimately death. In contrast, following external or oral administration to mammals, pyrethroids are largely converted by hydrolysis or oxidation to metabolites, which are then eliminated in the feces or urine before sensitive sites in the host's body can be reached (*1*). Thus, the safety

ratio (expressed in terms of representative median lethal doses for insects/representative median lethal doses for mammals) is 500 for pyrethrins and 13 000 for deltamethrin, in relation to the values found for the organophosphate parathion and dimethoate (5 and 37, respectively). Insect susceptibility can be exploited by the use of pyrethroids at low doses, because in theory, these compounds pose a lower risk to mammals.

However, most of the synthetic pyrethroids show considerable field persistence due partly to their intrinsic molecular stability and partly to the type of formulation used for treatments (*2*). In addition, some pyrethroid insecticides such as esfenvalerate, fenvalerate, permethrin, and in general, synthetic pyrethroids (*3*) have been reported to have reproductive and endocrine-disrupting effect.

Despite the above-described risks, pyrethroid insecticides constitute the major alternatives to the acutely toxic organophosphates and carbamates (*4*). Therefore, it may be interesting to carry out studies on dissipation of these pesticides to determine safe preharvest intervals that do not exceed national or international maximum residue levels (MRLs). In manufac-

* To whom correspondence should be addressed. E-mail: mmartine@ual.es.

[†] Department of Hydrogeology and Analytical Chemistry, University of Almería.

[‡] Department of Statistics and Applied Mathematics, University of Almería.

[§] Laboratory of Pesticide Residue CUAM.

tured products, preharvest intervals for pyrethroids ranged between 3 and 15 days, according to the pesticide considered (5). However, it is well known that such intervals depend—among other factors—on the climatic conditions in which those pesticides are applied. Thus, an interesting target is to evaluate the dissipation of residues as a function of time under specific climatic conditions.

The aim of this work is to study the behavior of the more frequently used pyrethroid insecticides in the province of Almería—one of the main areas of intensive agricultural practice in Europe—under the particular climatic conditions developed in greenhouses. Specifically, we intend to evaluate whether the preharvest intervals suggested by manufacturers are safe enough. In this way, the methodology proposed by Timme et al. (6, 7) has been followed to determine the mathematical model that best fit the experimental data, as well as the corresponding preharvest intervals. The study has been carried out on green bean, pepper, and zucchini, which are the major vegetables marketed in that area.

EXPERIMENTAL PROCEDURES

Reagents and Apparatus. Analytical standards (pestanal quality) of fenprothrin (FENP), cyfluthrin (CYFL), deltamethrin (DELT), fenvalerate (FENV), acrinathrin (ACRI), tau-fluvalinate (FLUV), and bifenthrin (BIFE) were obtained from Dr. Ehrénstorfer (Augsburg, Germany).

Solvents (pesticide residue grade) and anhydrous sodium sulfate were obtained from Scharlau (Barcelona, Spain). Distilled water provided by a Milli-Q water filtration/purification system from Millipore (Bedford, MA) was used.

All standards and samples were filtered through Millipore membrane Teflon filters (0.45 μm particle size) before injection into the chromatographic column. SPE cartridges 1000 mg florisil (Waters, Milford, MA) were used to clean up vegetable samples.

The high-performance liquid chromatograph was a Waters (Milford, MA), composed of a Model 600 E multisolute delivery system, a Rheodyne 7725i Manual injector valve with a 400- μl sample loop, a Temperature Control System, a Model 474 scanning fluorescence detector and a $\mu\text{Bondapak C18}$, 3.9 \times 300 mm (10 μm particle size) column (Waters, Milford, MA).

The photochemical reaction was carried out in a postcolumn photochemical reactor (Softron GmbH, Gynkotek HPLC, Germering, Germany) fitted with a knitted open tube reactor coil (5 m \times 1.6 mm (od), 0.3 mm (id)) and a low-pressure 4 W mercury lamp.

Field Experiment. Decline experiments were conducted in greenhouses of the Center of Investigation and Horticultural Development (CDIH) of La Mojonera (Almería, Spain), and the treatments with the pesticides were carried out under controlled conditions. The average of the daily maximum/minimum temperatures outside and inside the greenhouses throughout the study were 18.5/9.5 and 22.9/8.8 $^{\circ}\text{C}$, respectively, whereas the maximum/minimum absolute temperatures outside and inside the greenhouses were 20.9/5.5 and 25.6/6.7 $^{\circ}\text{C}$, respectively. Average relative humidities outside and inside the greenhouses were 62 and 72.5%, respectively, and average solar irradiations outside and inside the greenhouses were 4 and 2.4 $\text{kWh}/\text{m}^2 \cdot \text{day}$, respectively.

Green beans, peppers, and zucchinis were grown in flat-roof greenhouses with a size of 500 m^2 from each one, incorporating 1600, 880, and 1200 plants, respectively. Plants, receiving routine horticultural treatment, were sprayed on January 28, 2001 at the recommended doses (FENP and FENV, 1.5 mL/L; CYFL and ACRI, 0.8 mL/L; DELT, 0.5 mL/L; FLUV, 0.7 mL/L; and BIFE 0.4 mL/L) and at a rate of 1250 L/h.

The technical formulations were Meothrin 10 EC (FENP 10% EC, KenoGard, Barcelona, Spain), Baytroid (CYFL 5% SL, Bayer, Barcelona, Spain), Decis EC (DELT 2.5% EC, AgroEvo, Valencia, Spain), Somicidin 15 (FENV 15% EC, C. Q. Massó, Barcelona, Spain), Rufast (ACRI 15% EC, Rhône Poulenc, Madrid, Spain), Mavrik 10 (FLUV

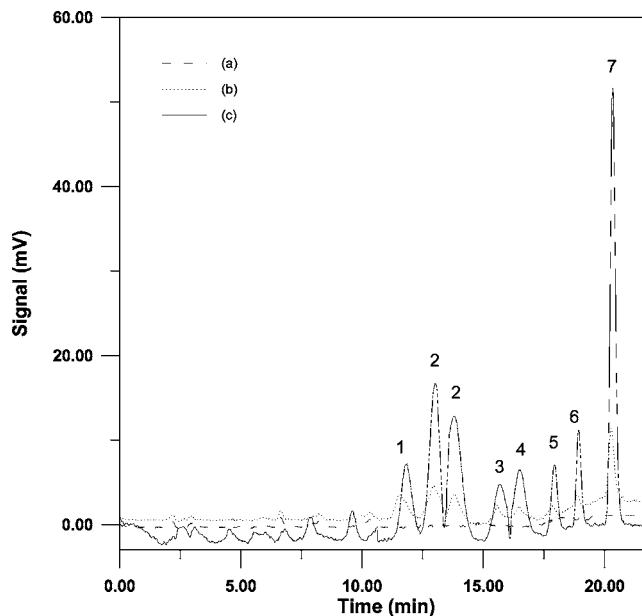


Figure 1. Chromatograms corresponding to: (a) a blank pepper extract; (b) a blank pepper extract spiked with (1) FENP (0.03 $\mu\text{g}/\text{mL}$), (2) CYFL (0.01 $\mu\text{g}/\text{mL}$), (3) DELT (0.01 $\mu\text{g}/\text{mL}$), (4) FENV (0.02 $\mu\text{g}/\text{mL}$), (5) ACRI (0.03 $\mu\text{g}/\text{mL}$), (6) FLUV (0.02 $\mu\text{g}/\text{mL}$) and (7) BIFE (0.008 $\mu\text{g}/\text{mL}$); and (c) a standard of 0.4 $\mu\text{g}/\text{mL}$ of all pyrethroids, using the optimized chromatographic conditions.

10% EC, Sipcam, Valencia, Spain), and Talstar 10 LE (BIFE 10% EC, FMC Foret, Valencia, Spain).

The applications were carried out using a high-volume pressurized handgun sprayer, operating at 3 L/min. During the experiment, climatic conditions were monitored and registered.

Sampling and Storage. Matured fruit samples of uniform size were drawn at 0 (1 h and 12 h post-spray), 1, 2, 3, 4, 5, 6, and 8 days after the application for the progressive dissipation of insecticides. Field sampling was carried out following general recommendations for the design, preparation, and realization of residue trials from the Commission of the European Communities (8). Fruits were picked from plants at random, not taking fruits from a 0.5 m wide strip around the edge of the plot or the ends of the rows. Green bean samples were taken from the entire plot at different heights of the plants, picking a large number of plants, so as to obtain a sample of sufficient weight, and about 12 fruits were taken from the entire crop for pepper and zucchini. The gross field samples of fruits, 2.5 kg each, were immediately transported to the laboratory in polyethylene bags and processed according to the Community methods of sampling for the official control of pesticide residues (9). Each fruit was cut in four pieces and two opposite quarters of each one were selected as a representative sample and were thoroughly mixed and divided into three subsamples. The samples were analyzed the same day of the collection to avoid problems of stability of the pyrethroids in the vegetable matrixes during the storage stage (10).

Analytical Procedure for Determining Pyrethroid Insecticides in Vegetables. All vegetables were analyzed by HPLC with photo-derivatization postcolumn and fluorimetric detection (11) after extraction with dichloromethane and cleanup with florisil cartridges. The analytical procedure is briefly described next.

Each sample (50 g) was extracted by blending in a high-speed Polytron for 2 min. with 105 mL of dichloromethane. Then, 80 g of sodium sulfate was added and the mixture was homogenized for 1 min. The extract was filtered through a 12-cm Büchner funnel and washed with 2 successive 25-mL portions of dichloromethane, with the rinsates being added to the extraction fraction. The filtered liquid was collected and evaporated to dryness in a rotating vacuum evaporator with a water bath at 40 ± 1 $^{\circ}\text{C}$ and subsequently reconstituted in 5 mL of hexane. A 1-mL sample of each extract was cleaned up by passing through a florisil (1 g) column, preconditioned with 2 mL of acetone followed

Table 1. Residue Levels (mg/kg) of Pyrethroids in Green Beans^a

time (days)	residue (mg/kg) ^a						
	FENP	CYFL	DELT	FENV	ACRI	FLUV	BIFE
0.04	1.3156 (7.2)	0.2557 (6.2)	0.1106 (6.8)	0.4759 (5.4)	0.2630 (7.4)	0.2519 (8.3)	0.1985 (7.8)
0.50	0.6152 (6.5)	0.1133 (9.7)	0.0672 (7.0)	0.2526 (6.5)	0.1728 (6.5)	0.1618 (6.2)	0.1237 (6.2)
1.00	0.4046 (7.1)	0.0545 (4.4)	0.0332 (5.0)	0.1519 (5.9)	0.0827 (5.3)	0.0941 (5.2)	0.0641 (6.0)
2.00	0.2190 (5.9)	0.0281 (5.2)	0.0238 (4.8)	0.0780 (5.0)	0.0463 (9.7)	0.0461 (4.9)	0.0364 (5.1)
3.00	0.2006 (5.6)	0.0149 (8.6)	0.0127 (5.2)	0.0459 (4.3)	0.0206 (5.7)	0.0180 (11.0)	0.0153 (5.1)
4.00	0.0672 (6.6)	0.0107 (7.3)	< LOQ	0.0240 (6.5)	0.0121 (7.2)	0.0103 (6.9)	0.0086 (6.0)
6.00	0.0078 (5.6)	< LOQ	< LOQ	0.0055 (5.8)	0.0037 (8.2)	0.0027 (4.7)	0.0026 (6.9)
8.00	0.0025 (4.2)	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.0003 (4.2)

^a LOQ = quantitation limit. Relative standard deviations in parentheses ($n = 3$).

Table 2. Residue Levels (mg/kg) of Pyrethroids in Peppers

time (days)	residue (mg/kg) ^a						
	FENP	CYFL	DELT	FENV	ACRI	FLUV	BIFE
0.04	0.2626 (6.3)	0.0427 (5.2)	0.0168 (8.3)	0.0866 (5.9)	0.0654 (6.0)	0.0345 (5.4)	0.0219 (6.0)
0.50	0.1946 (5.8)	0.0235 (7.2)	0.0093 (5.5)	0.0440 (5.8)	0.0454 (6.7)	0.0181 (4.8)	0.0107 (8.9)
1.00	0.1192 (6.7)	0.0186 (6.7)	0.0076 (8.1)	0.0275 (6.9)	0.0250 (6.4)	0.0111 (6.6)	0.0078 (4.3)
2.00	0.0952 (6.9)	0.0137 (4.1)	0.0051 (10.3)	0.0170 (6.6)	0.0181 (5.4)	0.0080 (5.9)	0.0044 (8.3)
3.00	0.0644 (5.7)	0.0078 (5.8)	< LOQ	0.0149 (4.6)	0.0160 (5.3)	0.0058 (8.9)	0.0023 (8.2)
4.00	0.0459 (5.4)	0.0055 (4.8)	< LOQ	0.0112 (13.6)	0.0124 (9.3)	< LOQ	0.0011 (6.9)
6.00	0.0091 (6.8)	< LOQ	< LOQ	0.0047 (12.0)	0.0075 (10.5)	< LOQ	0.0005 (9.6)
8.00	0.0007 (5.0)	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.0001 (7.6)

^a LOQ = quantitation limit. Relative standard deviations in parentheses ($n = 3$).

Table 3. Residue Levels (mg/kg) of Pyrethroids in Zucchini

time (days)	residue (mg/kg) ^a						
	FENP	CYFL	DELT	FENV	ACRI	FLUV	BIFE
0.04	0.2778 (5.4)	0.0445 (8.9)	0.0193 (5.7)	0.1124 (4.3)	0.0633 (4.9)	0.0530 (4.2)	0.0332 (5.4)
0.50	0.1909 (4.6)	0.0315 (4.0)	0.0101 (11.7)	0.0552 (5.2)	0.0416 (5.0)	0.0262 (5.4)	0.0127 (8.4)
1.00	0.1333 (5.6)	0.0253 (5.4)	0.0045 (9.0)	0.0389 (5.0)	0.0328 (6.8)	0.0182 (6.9)	0.0084 (5.1)
2.00	0.0931 (6.4)	0.0172 (10.0)	0.0021 (6.1)	0.0247 (6.2)	0.0216 (5.3)	0.0110 (7.0)	0.0052 (8.0)
3.00	0.0542 (6.3)	0.0132 (7.6)	< LOQ	0.0117 (6.4)	< LOQ	0.0075 (10.8)	0.0028 (6.8)
4.00	0.0246 (4.0)	0.0051 (8.7)	< LOQ	0.0078 (5.5)	< LOQ	0.0050 (4.8)	0.0013 (5.0)
6.00	0.0086 (5.0)	< LOQ	< LOQ	0.0029 (6.2)	< LOQ	0.0024 (5.1)	0.0005 (6.3)
8.00	0.0034 (4.6)	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.0001 (7.2)

^a LOQ = quantitation limit. Relative standard deviations in parentheses ($n = 3$).

by 2 mL of hexane. The collection of the eluate started directly after applying the extract and was followed with 3 mL of hexane/acetone 90:10 (v/v). Cleaned up extracts were concentrated to nearly dryness in a rotating vacuum evaporator with a water bath at 40 ± 1 °C. The remaining solvent was allowed to evaporate under a slight N₂ stream, and the residue was redissolved in 1 mL AcN/Water 70:30 (v/v) and then filtered through a 0.45- μ m Teflon filter.

HPLC Procedure. Samples (400 μ L) of AcN/water 70:30 (v/v) solutions were analyzed by HPLC with fluorimetric detection. Samples were chromatographed by programmed gradient with AcN/water, as mobile phase, for 22 min at a flow rate ranging from 1.0 to 1.5 mL/min. The fluorimetric detection was performed at an excitation wavelength (λ_{ex}) of 283 nm and at an emission wavelength (λ_{em}) of 300 nm for all pesticides. The solvent program was as follows: Initially, 9 min isocratic with 30% water, 70% AcN with a flow rate of 1.5 mL/min, 3 min linear gradient to 20% water, and 80% AcN with a flow rate of 1.0 mL/min; then 5 min isocratic with 20% water and 80% AcN with 1.0 mL/min as flow rate; followed by an additional period of 1 min linear gradient to the initial conditions, and finally 3 min in the initial conditions. Sufficient time was allowed between subsequent analysis runs.

RESULTS AND DISCUSSION

Method Efficiency. The proposed method for determining pyrethroids in vegetables was previously evaluated (11). The

limits of quantitation (LOQs) ranged from 0.005 to 0.04 μ g/mL (corresponding to 0.5 and 4 μ g/Kg, respectively), and the upper limit of the linear range was 3 μ g/mL for all pesticides, whereas the lower limit was the LOQ for each pesticide. In all cases, the LOQs obtained in the experimental conditions were significantly lower than the MRLs established by the European Union and the Spanish legislation (12) for these pesticides. **Figure 1** shows chromatograms corresponding to (a) a blank pepper extract; (b) a blank pepper extract spiked with (1) FENP (0.03 μ g/mL), (2) CYFL (0.01 μ g/mL), (3) DELT (0.01 μ g/mL), (4) FENV (0.02 μ g/mL), (5) ACRI (0.03 μ g/mL), (6) FLUV (0.02 μ g/mL) and (7) BIFE (0.008 μ g/mL); and (c) a standard of 0.4 μ g/mL of all pyrethroids using the optimized chromatographic conditions. As can be seen, one well-resolved chromatographic peak was obtained for each pesticide, except CYFL, which yields two peaks corresponding to its cis and trans isomers, according to the solid standard used. On the other hand, interferences were not found at retention times of the analytes in the blank pepper extract and peaks at concentration levels near the LOQ levels were well defined. The same behavior was found in green beans and zucchinis.

Recovery studies were checked at two concentration levels (5 and 50 μ g/Kg) using quantification calibration curves,

Table 4. Decline Curves, Their Corresponding Coefficients of Determination r^2 and the Test Quantity D (at a Level of Significance of 95%) for the Models that Best Describe the Dissipation Process of Pyrethroids in Green Beans

pesticide	decline curve	r^2	D
FENP	$aC = 10^{-0.3339t+0.0590}$	0.931	0.632
CYFL	$dC = 10^{-0.7872(t^{-1})-0.4339}$	0.995	0.664
DELT	$bC = 1/(1.9048t + 3.0492)^2$	0.972	0.653
FENV	$aC = 10^{-0.3076t-0.4258}$	0.919	0.626
ACRI	$aC = 10^{-0.3068t-0.6750}$	0.922	0.627
FLUV	$aC = 10^{-0.3304t-0.6566}$	0.967	0.650
BIFE	$aC = 10^{-0.3387t-0.7476}$	0.972	0.653

^a 1st-order model. ^b 1.5th-order model. ^d RF 1st-order model.

Table 5. Decline Curves, Their Corresponding Coefficients of Determination r^2 , and the Test Quantity D (at a Level of Significance of 95%) for the Models that Best Describe the Dissipation Process of Pyrethroids in Peppers

pesticide	decline curve	r^2	D
FENP	$aC = 10^{-0.2946t-0.4683}$	0.813	0.569
CYFL	$dC = 10^{-0.4799(t^{-1})-1.2632}$	0.985	0.659
DELT	$eC = 1/(5.1137 \cdot (t + 6.6657)^{-1})^2$	0.973	0.653
FENV	$dC = 10^{-0.5250 \cdot (t-0.9817)^{-1}}$	0.989	0.661
ACRI	$cC = 1/(18.6988t + 14.4224)$	0.982	0.658
FLUV	$dC = 10^{-0.5087 \cdot (t-1.3861)^{-1}}$	0.984	0.659
BIFE	$aC = 10^{-0.2784t-1.7815}$	0.903	0.617

^a 1st-order model. ^b 1.5th-order model. ^c 2nd-order. ^d RF 1st-order model. ^e RF 1.5th-order model.

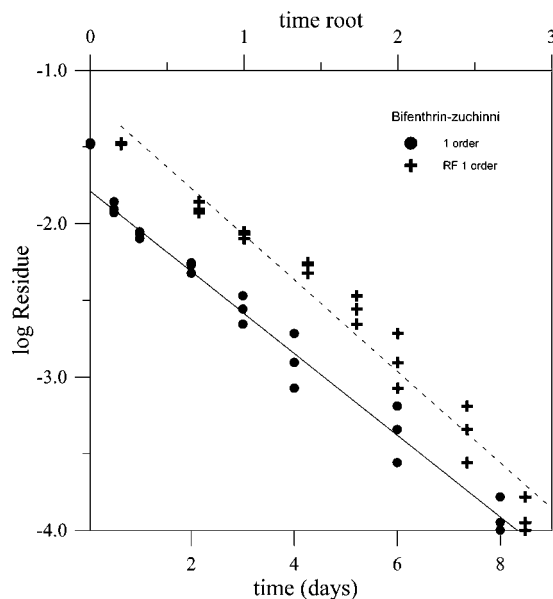
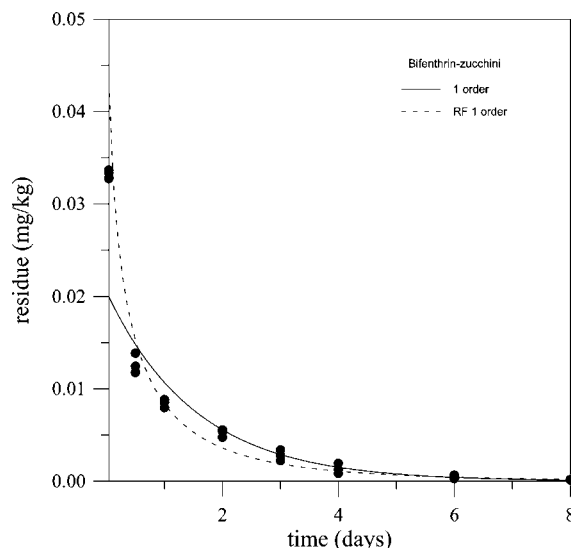
Table 6. Decline Curves, Their Corresponding Coefficients of Determination r^2 and the Test Quantity D (at a Level of Significance of 95%) for the Models that Best Describe the Dissipation Process of Pyrethroids in Zucchini

pesticide	decline curve	r^2	D
FENP	$aC = 10^{-0.2402t-0.5871}$	0.985	0.659
CYFL	$aC = 10^{-0.2116t-1.3615}$	0.957	0.645
DELT	$bC = 1/(7.6878t + 6.7239)^2$	0.976	0.655
FENV	$dC = 10^{-0.6938 \cdot (t-0.7455)^{-1}}$	0.956	0.645
ACRI	$cC = 1/(15.3908t + 15.5748)$	0.987	0.660
FLUV	$dC = 10^{-0.5821 \cdot (t-1.1537)^{-1}}$	0.996	0.665
BIFE	$dC = 10^{-0.8899 \cdot (t-1.1868)^{-1}}$	0.871	0.600

^a 1st-order model. ^b 1.5th-order model. ^c 2nd-order model. ^d RF 1st-order model.

prepared in matrix-matched standards of each vegetable to reduce the matrix effect in the analytical response. All recovery values (85–99% for pepper, 85–103% for zucchini, and 84–110% for green bean) were within accepted levels for residue determination ranges.

Dissipation of Pyrethroids in Green Beans, Peppers and Zucchini. The residue data obtained for these seven pyrethroids on green beans, peppers, and zucchinis are summarized in **Tables 1–3**. To evaluate the decline of pyrethroid residues in these vegetables, residue data should be subjected to statistical analysis. A linear regression can be obtained after an appropriate transformation of the residue and/or time values (6). Levels of residue can generally be interpreted by the use of a 1st-order model, which allows a linearization of data by plotting the logarithms of the residues ($\log C$ or $\ln C$) versus time. In fact, a number of studies have been carried out fitting decline curves at a 1st-order model for pyrethroids (13–15) and other pesticides (16–18). However, that interpretation is not always applicable, because the residues frequently diminish quicker at first and much more slowly at a later stage in comparison with the 1st-order model. In this way, Aguilera-del Real et al. (20, 21)

**Figure 2.** Representation of the regression lines in the linearized system for BIFE in zucchini corresponding to the 1st-order (●) and RF 1st-order (+) models.**Figure 3.** Representation of the decline curves for BIFE in zucchini corresponding to the 1st-order and RF 1st-order models.**Table 7.** Decline Times T/X and Their Standard Deviations $S_{T/X}$

model	T/X	$S_{T/X}^a$
1st-order	$(\log X/b)$	$S_b/b \cdot (T/X)$
1.5th-order	$ab(\sqrt{X}-1)$	$u \cdot (T/X)$
2nd-order	$ab(X-1)$	$u \cdot (T/X)$
RF 1st-order	$((\log X/b)^2)$	$2S_b/b \cdot (T/X)$
RF 1.5th-order	$(ab(\sqrt{X}-1))^2$	$2u \cdot (T/X)$
RF 2nd-order	$(ab(X-1))^2$	$2u \cdot (T/X)$

^a $S_b = \sqrt{\text{Var}(b)}$. $u = \text{Var}(a)/a^2 + \text{Var}(b)/b^2 - 2(\text{Cov}(a,b)/ab)$.

compared the results obtained by fitting the residue data to a 1st-order model and to the five other formal approaches proposed by Timme et al. (6), and they found that the 1st-order function was statistically legitimized in all cases. However, they also observed that half-life times for residues were shorter than those obtained from the 1st-order model when obtained using the model that best fits the experimental data.

Table 8. Estimated Value for $T/2$ (days) and Its Confidence Interval (CI), at a Confidence Level of 95%, for the Seven Pyrethroids in the Three Crops, Derived from Both the Optimal and the 1st-Order Models

pesticide	green bean				pepper				zucchini			
	optimal model		1st-order model		optimal model		1st-order model		optimal model		1st-order model	
	$T/2$	CI	$T/2$	CI	$T/2$	CI	$T/2$	CI	$T/2$	CI	$T/2$	CI
FENP	^a 0.90	0.84–0.96			^a 1.02	0.90–1.14			^a 1.25	1.22–1.29		
CYFL	^a 0.15	0.13–0.16	0.92	0.77–1.04	^a 0.39	0.33–0.45	1.45	1.29–1.61	^a 1.42	1.25–1.60		
DELT	^b 0.66	0.61–0.71	1.00	0.85–1.15	^a 0.29	0.25–0.33	1.23	0.92–1.54	^b 0.36	0.33–0.39	0.61	0.52–0.70
FENV	^a 0.98	0.93–1.03			^a 0.33	0.28–0.38	1.62	1.38–1.85	^a 0.19	0.16–0.22	1.19	1.09–1.29
ACRI	^a 0.98	0.92–1.05			^a 0.77	0.00–1.65	2.08	1.74–2.43	^c 1.01	0.96–1.06	1.32	1.13–1.51
FLUV	^a 0.91	0.87–0.95			^a 0.35	0.29–0.41	1.24	0.98–1.51	^a 0.27	0.24–0.29	1.45	1.28–1.61
BIFE	^a 0.89	0.85–0.93			^a 1.08	1.02–1.14			^a 0.11	0.09–0.14	1.06	0.98–1.14

^a 1st-order model. ^b 1.5th-order model. ^c 2nd-order model. ^d RF 1st-order model. ^e RF 1.5th-order model.

In our work, we also used these formal approaches in order to study the dissipation of the residues in vegetables prior to harvest and determine the statistical parameters which describe such behavior. The designation of these six models as 1st, 1.5th, etc. order, simply follows the conventional classification of rate equations for chemical reactions; it does not imply any reaction kinetic interpretation. Thus, for each vegetable and insecticide, residue and time values were transformed by using these six formal models, and the respective regression lines were computed, as well as their respective coefficients of determination R^2 , therefore obtaining the linearized system. These lines were subsequently converted to the original system (residue versus time), and thereby six decline curves were obtained. The modified coefficient of determination r^2 was later obtained in the original system and was used to select the optimal model (i.e., the curve that best fits the experimental data). As it is well known, $r^2 \leq 1$ and, the bigger this coefficient is, the better the decline curve fits the data. If r^2 becomes negative or zero for any model, then the fit is automatically rejected. If $r^2 > 0$, then the correlation is tested with the aid of the test quantity D (22); the correlation is confirmed when $D > 0$. **Tables 4–6** show the equations of the decline curves which best fit the data for each vegetable and pyrethroid, as well as the respective modified coefficients of determination r^2 with their corresponding test quantity D . Such coefficients r^2 are in general high, and $D > 0$ in all cases.

Optimal models in green beans were those of 1st-order for FENP, FENV, ACRI, FLUV and BIFE, the RF 1st-order model for CYFL and the RF 1.5th-order for DELT. In peppers, the optimal models were those of 1st-order for FENP and BIFE, the RF 1st-order for CYFL, FENV and FLUV, the RF 1.5th-order for DELT and the 2nd-order for ACRI. Finally in zucchini, the optimal models were those of 1st-order for FENP and CYFL, the RF 1st-order for FENV, FLUV, and BIFE, the 1.5th-order model for DELT and the 2nd-order for ACRI.

It is interesting to note that the optimal model in the original system (the model with the best r^2) does not always agree with the optimal model in the linearized system (the model whose coefficient of determination R^2 is the highest). For instance, the RF 1st-order and the 1st-order models were the two best models for BIFE in zucchini. In the linearized system (**Figure 2**), the coefficients of determination are $R^2 = 0.960$ and $R^2 = 0.971$, respectively. Thus, the 1st-order model fits the transformed data better than the RF 1st-order. However, in the original system (**Figure 3**), the modified coefficients of determination are $r^2 = 0.871$ and $r^2 = 0.782$, respectively. Therefore, the RF 1st-order model was considered optimal. The RF 1st-order model shows the fast diminution of residue for the earlier data better than the 1st-order, as can be observed in **Figure 3**.

Table 9. MRLs (mg/kg) for Pyrethroids in Green Bean, Pepper, and Zucchini Established by the European Union Legislation Or, Failing that, by the Spanish Government (Indicated by *)

pesticide	green bean	pepper	zucchini
FENP	0.02*	0.50*	0.10*
CYFL	0.05	0.30	0.02
DELT	0.20	0.20	0.10
FENV	0.02	0.02	0.02
ACRI	0.30*	0.20*	0.02*
FLUV	0.10*	0.50*	0.01*
BIFE	0.50	0.20	0.1

Decline Times (T/X). The T/X parameter denotes the time after which the residue concentration has decreased to a fraction $1/X$ of the initial concentration (6). In dissipation studies, the establishment of $T/2$ (half-life time) and $T/10$ (90% decrease) is particularly useful.

The relative rate of decline throughout the entire dissipation process remains constant only for the 1st-order model (7, 19); the half-life time is therefore independent of the initial concentration. However, this is not the case for the other models studied in this paper, because the rate of decline decreases progressively during the course of the dissipation process.

In the present work, the parameter $T/2$ has been estimated from the optimal model as well as from the 1st-order model (when this model is not optimal) by using the general formulas for the decline times T/X derived by Timme et al. (7). These formulas are shown in **Table 7** along with their corresponding standard deviations $S_{T/X}$, which lead to the achievement of confidence limits for the decline times, namely $T/X \pm t_{\alpha, n-2} \cdot S_{T/X}$, where $t_{\alpha, n-2}$ is the value from the table of the Student's t -distribution (two tails) with $n - 2$ degrees of freedom and p -value α . An explanation of the notation used in **Table 7** can be found in the Appendix.

The decline times $T/2$ and their confidence intervals—at confidence level 95%—are shown in **Table 8**. For the optimal models, the estimated values for $T/2$ can be observed as being lower than 0.98 days for green beans, 1.08 days for peppers and 1.42 days for zucchinis. It is worthwhile to point out that the estimated values for $T/2$ were lower than the ones obtained from the 1st-order model whenever this was not optimal, in agreement with results found by Aguilera-del Real et al. (20, 21).

Preharvest Intervals. The half-life parameter provides information about the persistence of pesticides in crops. However, in practice, it is far more interesting to determine the preharvest intervals (i.e., the time lapsed before residues reach a level lower than the MRLs established by competent organisms). The current MRL values for pyrethroids are showed in **Table 9** (12).

Table 10. Predicted Value τ (Days) and Its Prediction Interval PI (at Confidence Level 95%), Derived from Both the Optimal and the 1st-Order Models

pesticide	green bean				pepper				zucchini			
	optimal model		1st-order model		optimal model		1st-order model		optimal model		1st-order model	
	τ	PI	τ	PI	t	PI	τ	PI	τ	PI	τ	PI
FENP	^a 5.27	4.42 – 6.13			^a 0	-2.19 – 0.96			^a 1.72	1.32 – 2.12		
CYFL	^d 1.21	0.97 – 1.48	1.58	0.67 – 2.48	^a ND	ND	ND	ND	^a 1.59	0.84 – 2.35		
DELT	^b ND	ND	ND	ND	^a ND	ND	ND	ND	^b 0	-0.34 – 0.25	ND	ND
FENV	^a 4.14	3.67 – 4.62			^d 1.87	1.23 – 2.63	2.39	1.04 – 3.73	^d 1.89	1.27 – 2.62	2.41	1.64 – 3.18
ACRI	^a 0	-1.14 – 0.12			^c 0	-1.50 – 0.43	ND	ND	^c 2.24	2.06 – 2.43	2.07	1.65 – 2.49
FLUV	^a 1.04	0.62 – 1.45			^a ND	ND	ND	ND	^d 2.11	1.68 – 2.60	2.64	1.57 – 3.71
BIFE	^a ND	ND			^a ND	ND			^a ND	ND	ND	ND

^a 1st-order model. ^b 1.5th-order model. ^c 2nd-order model. ^d RF 1st-order model. ^e RF 1.5th-order model. ^f ND = not determined.

Table 11. Preharvest Intervals (Days) Specified by the Makers of the Commercial Formulates for Green Bean, Pepper, and Zucchini

pesticide	green bean	pepper	zucchini
FENP	7	7	
CYFL			
DELT	3	3	3
FENV			
ACRI			
FLUV	7		7
BIFE	3		3

In the present work, using the data contained in **Table 9**, we calculated the time τ required for residues to decrease to the corresponding MRL value, as well as the respective prediction intervals. With this aim, we proceeded as proposed by Walter et al. (7), taking into account that the RSD(%) was not dependent on concentration, as can be seen in **Tables 1–3**, and therefore, weighted regression was not used. Calculations were made for the optimal model and for the 1st-order, when this was not optimal, using the formulas summarized in the Appendix. Then, preharvest intervals were established as the right extreme of the prediction interval, in such a way that the upper tolerance limit of residues at this PHI is lower than the MRL for each pesticide and vegetable, with a confidence level of 97.5%. The results obtained are summarized in **Table 10**. Residue levels found 1 h after application were sometimes lower than the MRLs established by the European Union and the Spanish legislation (**Table 9**). That was the case for DELT, ACRI, and BIFE in green beans, all the pyrethroids except FENV in peppers, and DELT and BIFE in zucchinis. In these cases, the time τ and the respective prediction interval were also computed; if the right endpoint of this interval is lower than or equal to zero, then the preharvest time is zero, and “ND” was written in the corresponding position in **Table 10**.

For the crops in which the 1st-order and the optimal model were not the same, it can be observed that the preharvest times derived from the optimal model were generally lower than those obtained from the 1st-order model, as it also happened with the half-life times.

In all cases, preharvest intervals specified by the makers of the commercial formulates were higher than those obtained in the present study, as shown by comparing data in **Tables 10** and **11**, which means that the preharvest times suggested by the makers are safe enough.

APPENDIX

Notation Used In Table 7. Let t (= time) and C (= residue concentration) be the variables in the original system. Let X

and Y be the variables in the linearized system: (a) $X = \sqrt{t}$ for the three RF models and $X = t$ for the remaining other three; (b) $Y = \log C$ for both 1st and RF 1st-order models, $Y = 1/\sqrt{C}$ for both 1.5th and RF 1.5th-order models, and $Y = 1/C$ for both 2nd and RF 2nd-order models.

If a and b are the estimates of the intercept on the ordinate and the slope of the regression line in the linearized system, respectively, it is known that

$$\text{Var}(a) = \left(\frac{1}{n} + \frac{\bar{X}^2}{S_{xx}} \right) s^2, \quad \text{Var}(b) = \frac{s^2}{S_{xx}}, \quad \text{and} \quad \text{Cov}(a,b) = \frac{\bar{X}}{S_{xx}} s^2$$

Here, s^2 denotes the residual variance (i.e. $s^2 = 1/(n-2)(S_{yy} - S_{xy}^2/S_{xx})$, where $S_{xx} = \sum (X_i - \bar{X})^2$, $S_{yy} = \sum (Y_i - \bar{Y})^2$, and $S_{xy} = \sum (X_i - \bar{X}) \cdot (Y_i - \bar{Y})$).

Calculation Of τ . For the 1st, 1.5th, and 2nd-order models, the predicted time τ is computed as follows:

$$\tau = \bar{X} + \frac{b}{M}(Y_0 - \bar{Y})$$

where $Y_0 = \log C_0$, C_0 is the MRL for the corresponding vegetable and pesticide,

$$M = b^2 - \frac{t_{\alpha, n-2}^2 s^2}{S_{xx}}$$

and the endpoints of the respective prediction interval are given by

$$\tau \pm t_{\alpha, n-2} \frac{s^2}{M} \sqrt{\left(1 + \frac{1}{n}\right)M + \frac{(Y_0 - \bar{Y})^2}{S_{xx}}}$$

For the RF 1st, 1.5th, and 2nd-order models, the predicted time τ and the endpoints of the associated prediction interval are given by

$$\tau = \left(\bar{X} + \frac{b}{M}(Y_0 - \bar{Y}) \right)^2 \quad \text{and} \quad \left(\bar{X} + \frac{b}{M}(Y_0 - \bar{Y}) \right) \pm t_{\alpha, n-2} \cdot \frac{s^2}{M} \sqrt{\left(1 + \frac{1}{n}\right)M + \frac{(Y_0 - \bar{Y})^2}{S_{xx}}}$$

respectively.

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