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Pesticide Residue Levels in Green Beans Cultivated in Souss Masa Valley (Morocco) After Multiple Applications of Bifenthrin and λ-Cyhalothrin

M. Bouri · R. Salghi · Lh. Bazzi · A. Zarrouk · A. Rios · M. Zougagh

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Abstract Dissipation of bifenthrin and λ-cyhalothrin pyrethroid insecticides, under environmental conditions, was evaluated on green beans grown in experimental greenhouses (Souss Massa valley, Morocco). Pesticide residues were determined by gas chromatography with micro electron-capture detector (GC-μECD) after dichloromethane extraction and cleanup on florisil phase cartridges. In the case of field experiments, a random block scheme was employed. Each block contained 25 plants in a single row and tests were carried out in triplicates applying pesticides at the recommended doses by the manufacturers. Fruit samples were periodically taken until the end of the preharvest interval (p.i.). The results obtained showed that the p.i of bifenthrin in green bean were 4 days in the winter and 3.5 days in the spring, whereas that for λ-cyhalothrin 8 days was found in the winter and 7.5 days in the spring. Consequently, it is possible to consider the European Union maximum residue limit (EU MRL) values compatible with the proper agricultural practices used for growing green bean in the plastic greenhouse of Souss Massa valley in South Morocco. Bifenthrin had a degradation of first-order kinetics, whereas that of levels for λ-cyhalothrin residue can not be interpreted by the use of a first order model.

Keywords Bifenthrin · λ-Cyhalothrin · Dissipation · Residues · Green beans · Greenhouses

M. Bouri · R. Salghi
Equipe de Genie de l'Environnement et de Biotechnologie, Ecole Nationale des Sciences Appliquees, B.P 1136, Agadir, Morocco

M. Bouri · A. Rios
Department of Analytical Chemistry and Food Technology, University of Castilla–La Mancha, Ciudad Real, Spain

Lh. Bazzi
Etablissement Autonome de Contrôle et de Coordination des Exportations, Laboratoire Régional d'Agadir, Agadir, Morocco

A. Zarrouk
LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, BP 4808, Oujda, Morocco

A. Rios · M. Zougagh
Regional Institute for Applied Science Research, IRICA, E-13004 Ciudad Real, Spain

M. Zougagh (✉)
Scientific and Technological Park of Albacete, E-02006 Albacete, Spain
e-mail: mohammed.zougagh@uclm.es

Green beans crops are considered high value cash crops for farmers In Morocco, as well as an import outsource of hard currency. Souss Massa valley is the major region for green beans production in Morocco, exporting about 85% to the European Union (EU). Green beans are highly susceptible to pest attacks. To prevent the decrease in harvest yield, a large number of pesticides are used to control insect pests that attack green beans plants. Pyrethroids such as bifenthrin and λ-cyhalothrin are among these pesticides. Considering that they are harmless for mammals under normal circumstances and toxic metabolites are absent, their maximum residue limits (MRLs) are, in general, higher than those of organophosphorous, organochlorine or carbamate pesticides (Off. J. Eur. Commun. L211/6, European Community 1993). Notwithstanding their relatively low toxicity, the residue analysis of pyrethroids in crops, foods and environmental matrices is of importance in agricultural and environmental sciences. The dissipation of these pyrethroid pesticides after their application

depends on various factors, including plant species, chemical formulation, application method, climatic conditions, physical environmental phenomena (mainly volatilization) and chemical degradation (in which sunlight plays a prominent role) (Fernández-Alba et al. 1994). Therefore, dissipation studies for a given crop, under particular conditions in each growing area, are needed to assess the suitability of the established preharvest intervals (p.i.) and to ensure that residue levels are below the MRLs (Off. J. Eur. Commun. L211/6, European Community 1993).

The most common extraction procedures used for pyrethroids in liquid samples are those based on a liquid–liquid partitioning with acetonitrile–hexane (1:1) (Lentza-Rizos et al. 2001; Rosenblum et al. 2001). In solid samples different methods are employed: (1) pressurized fluid extraction (PFE) and supercritical fluid extraction (SFE) for rape seeds (Pihlstrom et al. 2002); (2) blending with ethyl acetate (Zrostlikova et al. 2002) and cryogenic extraction (Bordet et al. 2002) for animal fat; and (3) Soxhlet extraction for dietary composites (Rosenblum et al. 2001). The main clean-up procedures are based on gel permeation chromatography (GPC) (Pihlstrom et al. 2002; Zrostlikova et al. 2002; Barrek et al. 2003; Venant et al. 1990) and solid-phase extraction (SPE) with several phases, as alumina (Lentza-Rizos et al. 2001; Pihlstrom et al. 2002) graphitized carbon black (Ramesh and Balasubramanian 1998), florisil (Zehringer and Herrmann 2001), diatomaceous earth (Zehringer 2001) and mixtures florisil/C18 (Barrek et al. 2003) and diatomaceous earth/C18 (Di Muccio et al. 1999). Acetonitrile has been frequently employed as elution solvent in SPE procedures. On the other hand, pyrethroids determination is usually carried out by gas chromatography (GC) with electron capture detector (ECD) (Pang et al. 1994), because it is rapid, inexpensive, and convenient, despite the problems associated with instability of pyrethroids under GC conditions. GC systems with capillary columns coupled to mass spectrometers are also used for pyrethroid residues confirmation (Fernández-Alba et al. 1994) or as a detection system per se in the quantitative GC residue analysis (Brouwer et al. 1994).

At present, the literature on dissipation of bifenthrin and λ-cyhalothrin residues in foods after multiple applications is very sparse, but many papers monitoring pyrethroids in fatty materials, vegetable and fruits and developing analytical methods for determination of these pesticides have been published (Lentza-Rizos et al. 2001). Therefore, it may be interesting to carry out studies on dissipation of pyrethroids to determine safe preharvest intervals that do not exceed MRLs. In manufactured products, preharvest intervals for pyrethroids ranged between 3 and 15 days, according to the pesticide considered (De Liñan 2002). 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 objective is to evaluate the dissipation of residues as a function of time under specific climatic conditions.

The objective of this work was to evaluate the degradation behaviour and residue levels of bifenthrin and λ-cyhalothrin in green beans, the more frequently used pyrethroid insecticides in the Souss Massa valley-one the main areas of intensive agricultural practice in Morocco-under the particular climatic conditions developed in greenhouses.

Materials and Methods

Acetone, dichloromethane, *n*-hexane, diethyl ether and anhydrous sodium sulphate (pesticide residue grade) were obtained from Panreac (Barcelona, Spain). Florisil adsorbent (16–30 mesh) was obtained from Sigma–Aldrich (St. Louis, MO, USA). Certified standards of λ-cyhalothrin (99.6% purity) and bifenthrin (99.0% purity) Bifenthrin were supplied by Dr. Ehrenstorfer (Augsburg, Germany). Individual stock standard solutions of λ-Cyhalothrin and Bifenthrin were prepared in acetone. Standard solutions for gas chromatographic (GC) analysis were prepared by appropriate dilution of the stock standard solutions with *n*-hexane.

A Hewlett-Packard gas chromatograph 6890 model (Palo Alto, CA, USA) equipped with a split/splitless injection port, autosampler, a micro electron-capture detector (μECD) and an HP-5 fused-silica capillary GC column (25 m length, 0.32 mm internal diameter and 0.52 μm film thickness) were used. The chromatographic conditions were as follows: detector temperature, 300°C; injector temperature, 250°C; temperature programming from 80°C to 250°C (15°C/min), carrier gas (helium) flow rate, 2.6 mL/min; makeup gas (nitrogen) flow rate, 60 mL/min; injection volume, 1 μL; and splitless time, 0.1 min. Data acquisition and equipment control were performed by using a HP (Palo Alto, CA, USA) Chem-Station software, which was run under Microsoft Windows NT on an HP compatible personal computer. Each output unit on the ECD was equal to 5 Hz. The normal background frequency ranged from 20 to 120 on the display (100–600 Hz). The reference current was $\geq$0.5 nA and the range was 0.5–5.0 nA. Under these conditions, the retention times of bifenthrin and λ-cyhalothrin were 16.1 and 13.2 min, respectively.

Experiments were conducted in a plastic greenhouse whose area is 400 m^2 situated in Massa (Agadir, Morocco). The planting density (variety Belma) was 10,589 plants/ha. In the case of field experiments, a random block scheme was employed. Each block contained 25 plants in a single row, and tests were carried out in triplicates. Tested blocks were partitioned and isolated from one another by leaving two untreated rows as guard rows. Bifenthrine and

Table 1 Details of pesticides and doses used

Active ingredient	Commercial formulation (CF)	CF dose (cc/hl)	Pre-harvest interval (days)	MRL UE(mg/kg) (community Directive 1993)	Technical data of sprayer		
					Work pressure (kgf/cm^2)	Suction capacity (L/min)	Spraying capacity (L/min)
Bifenthrin	BISECT 100 g/l	40	7	0.5	20	10	8
λ-Cyhalothrin	WARRIOR 10%	75	10	0.2	20	10	8

λ-cyhalothrine were sprayed at doses equivalent to 40 and 75 cc/hl, respectively using a hand operated Knapsack sprayer (Table 1).

Residue levels of pesticide were determined in green beans during 20 days in which up to two successive treatments with bifenthrin and λ-cyhalothrin. These pesticides were applied to plantations with intervals of 0,1, 2, 3, 4, 5, 6, 7 and 8 days for bifenthrin; 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 days for λ-cyhalothrin. Booth treatments were realized in winter and spring season and applied separately in two different zones.

Samples analysis of bifenthrin in winter were collected at 0, 1, 2, 3, 4, 5, 6, 7 and 8 days after treatment I (samples I + 0, I + 1, I + 2, I + 3, I + 4, I + 5, I + 6, I + 7 and I + 8) and at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10,11 and 12 days after treatment I′ with λ-Cyhalothrin (samples I′ + 0, I′ + 1 I′ + 2 I′ + 3 I′ + 4 I′ + 5 I′ + 6 I′ + 7; I′ + 8 I′ + 0 I′ + 9 I′ + 10 I′ + 11 and I′ + 12).

Samples analysis of bifenthrin in spring were collected at 0, 1, 2, 3, 4, 5, 6, 7 and 8 days after treatment II (samples II + 0, II + 1, II + 2, II + 3, II + 4, II + 5, II + 6, II + 7 and II + 8) and at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 days after treatment II′ with λ-cyhalothrin (samples II′ + 0, II′ + 1, II′ + 2 II′ + 3, II′ + 4, II′ + 5, II′ + 6, II′ + 7, II′ + 8, II′ + 0, II′ + 9, II′ + 10, II′ + 11 and II′ + 12).

In total, greenhouse samples consisted of 42 pieces of green beans taken at random from the whole plantation. Immediately after picking, the greenhouse samples were placed into polyethylene bags, stored at 4°C in a portable cooler and transported to the laboratory.

The method used to extract the pesticides from pepper samples was adapted from Charles and Raymond (Fernández-Alba et al. 1994). Each 50 g of sample was ground using a food processor and 150 mL of acetone was added. The mixture was homogenised for 2 min and then mixed for 2 h. The mixture was filtered through glass wool and the acetone residues were partitioned using saturated aqueous sodium chloride (30 mL), deionised water (300 mL) and dichloromethane (70 mL) in a separating funnel. The extraction was repeated with another 70 mL of dichloromethane and the combined extracts were dried over anhydrous sodium sulphate. The dichloromethane fraction was collected and evaporated on a rotatory evaporator at 40°C and the residues were dissolved in an acetone/hexane (1:9) mixture (10 mL). In the clean-up step, 1 mL of the extract was passed through a florisil column previously conditioned with 5 mL of acetone/diethyl ether (6:4) and 5 mL of diethyl ether. Pesticide residues were eluted with acetone/diethyl ether (6:4) (4 mL). All samples were separately extracted and analysed by gas chromatography six-times. Each sample was prepared and analysed in triplicate.

The theoretical limit of detection, defined as the concentration of analyte that gives a signal equivalent to the blank signal plus three times its standard deviation, was calculated for each individual pesticide. In this work, the limit of detection (LOD) was taken to be the amount of analyte that gave a signal that was clearly distinguishable from the background noise of the instrument (Miller and Miller 2001). The theoretical limit of quantification (LOQ) was defined as the concentration of analyte that gave a signal equivalent to the blank signal plus ten times its standard deviation (Miller and Miller 2001).

The analytical determinations were made in triplicate for each sampling on three field block samples. Mean values and standard deviations were calculated and analysed by JMP package program (SAS Ins., CARY, NC, USA) for analysis of variance. Statistical discrimination of the mean values was performed using the method of contrasts (Miller and Miller 2001).

Results and Discussion

The use of method consisting in combined GC-ECD with liquid–liquid extraction (LLE) and solid phase extraction (SPE) seemed to be an excellent way to determine the types and levels of pesticides in green beam samples in a highly selective and sensitive way. This method was previously validated before its use in our laboratory, according to the International Union of Pure and Applied Chemistry (IUPAC) criteria (Thompson et al. 2002).

The linear dynamic range, precision (as relative standard deviation) and sensitivity (as limit of detection) values for determination of bifenthrin and λ-cyhalothrin are reported in Table 2.

Table 2 Analytical parameters obtained with the proposed method

Analyte	Bifenthrin	λ-Cyhalothrin
Linear range μg mL^{-1}	0.025–0.200	0.010–0.100
$Y = (a \pm S_a)X + (b \pm S_b)$	(9,373.5 ± 166.4601) X − (0.875 ± 0.8750)	(20,041 ± 123.3099) X − (55.442 ± 7.5006)
R^2	0.9991	0.9999
$S_{x/y}$	22.6164	9.5515
LOD (μg mL^{-1})	0.002	0.001
LOQ (μg mL^{-1})	0.007	0.004
RSD (%) (n = 5)	4.7	5.3

a; slope a; b, Intercept; *R*, regression coefficient; $S_{x/y}$, standard deviation of residuals; LOD, limit of detection; LOQ, limit of quantification, RSD, relative standard deviation

Linear Range

Individual calibration graphs were run with mixtures of bifenthrin and λ-cyhalothrin at concentrations in the range 0.025–0.200 μg mL^{-1} for bifenthrin and 0.010–0.100 μg mL^{-1} for λ-cyhalothrin. Each solution was injected five times. The linear range, intercept and slope of the curve are given in Table 2 along with the regression coefficient for each pesticide.

Sensitivity

The LODs calculated in this way were 0.006 and 0.001 μg mL^{-1} for bifenthrin and λ-cyhalothrin, respectively. The limits of quantification (LOQ) were 0.019 and 0.004 μg mL^{-1} for bifenthrin and λ-cyhalothrin, respectively.

Precision

Untreated samples were fortified by the addition of an intermediate pesticide mixture solution. Samples were allowed to equilibrate for 2 h prior to extraction and were processed according to the procedure described above. The precision values for the method, expressed as relative standard deviation (RSD), were 4.7 and 5.3% (n = 5) for bifenthrin and λ-cyhalothrin, respectively.

Bifenthrin and λ-Cyhalothrin residue levels determined in all of the green bean samples analyzed during the study are indicated in Table 3. Typical chromatograms from the analysis of (a) the blank of green bean, (b) sample I + 5 and (c) sample II′ + 8 are shown in Fig. 1.

Table 3 show the data of the evolution of pesticide residues after a spraying experiment and the residues found on green bean at winter and spring season.

Residue levels in the green bean fruits ranged between 0.02 and 3.56 mg/kg for bifenthrin and 0.01 and 3.30 mg/kg for λ-cyhalothrin in the winter season and between 0.01 and 3.30 mg/kg for bifenthrin and 0.01 and 3.22 mg/kg for λ-cyhalothrin in the spring season.

Table 3 Concentration of pesticide residues in green bean after chemical treatment

Winter season (1)		Spring season (2)	
Sample	Concentration (mg Kg^{-1}) ± RSD %	Sample	Concentration (mg Kg^{-1}) ± RSD %
First treatment bifenthrin			
I + 0	3.578 ± 2.8	II + 0	3.301 ± 1.6
I + 1	1.739 ± 3.2	II + 1	1.611 ± 1.6
I + 2	0.720 ± 4.5	II + 2	0.620 ± 3.5
I + 3	0.470 ± 2.5	II + 3	0.390 ± 4.6
I + 4	0.230 ± 2.6	II + 4	0.155 ± 5.5
I + 5	0.145 ± 3.5	II + 5	0.098 ± 4.6
I + 6	0.067 ± 5.3	II + 6	0.049 ± 3.6
I + 7	0.032 ± 2.6	II + 7	0.021 ± 4.5
I + 8	0.015 ± 3.5	II + 8	0.008 ± 4.2
Second treatment λ-Cyhalothrin			
I′ + 0	3.300 ± 1.5	II′ + 0	3.22 ± 4.3
I′ + 1	3.200 ± 2.6	II′ + 1	3.120 ± 4.8
I′ + 2	3.000 ± 3.5	II′ + 2	2.900 ± 5.9
I′ + 3	2.700 ± 3.4	II′ + 3	2.600 ± 3.8
I′ + 4	2.300 ± 2.5	II′ + 4	2.020 ± 3.9
I′ + 5	1.500 ± 5.1	II′ + 5	1.150 ± 3.6
I′ + 6	0.850 ± 4.3	II′ + 6	0.725 ± 2.4
I′ + 7	0.375 ± 3.9	II′ + 7	0.313 ± 1.3
I′ + 8	0.188 ± 4.1	II′ + 8	0.156 ± 1.6
I′ + 9	0.086 ± 3.8	II′ + 9	0.078 ± 3.4
I′ + 10	0.041 ± 3.6	II′ + 10	0.032 ± 4.7
I′ + 11	0.026 ± 5.3	II′ + 11	0.017 ± 4.9
I′ + 12	0.009 ± 3.9	II′ + 12	0.007 ± 5.0

Mean values ± RSD % of nine replicates, 3 field block samples × 3 analytical determinations

As shown in Fig. 1d the p.i. of bifenthrin in green bean were 4 days in the winter and 3.5 days in the spring, whereas that of λ-cyhalothrin was found 8 days in the winter and 7.5 days in the spring. We note that the two a.i. under study were different regarding dosage, p.i. and MRL.

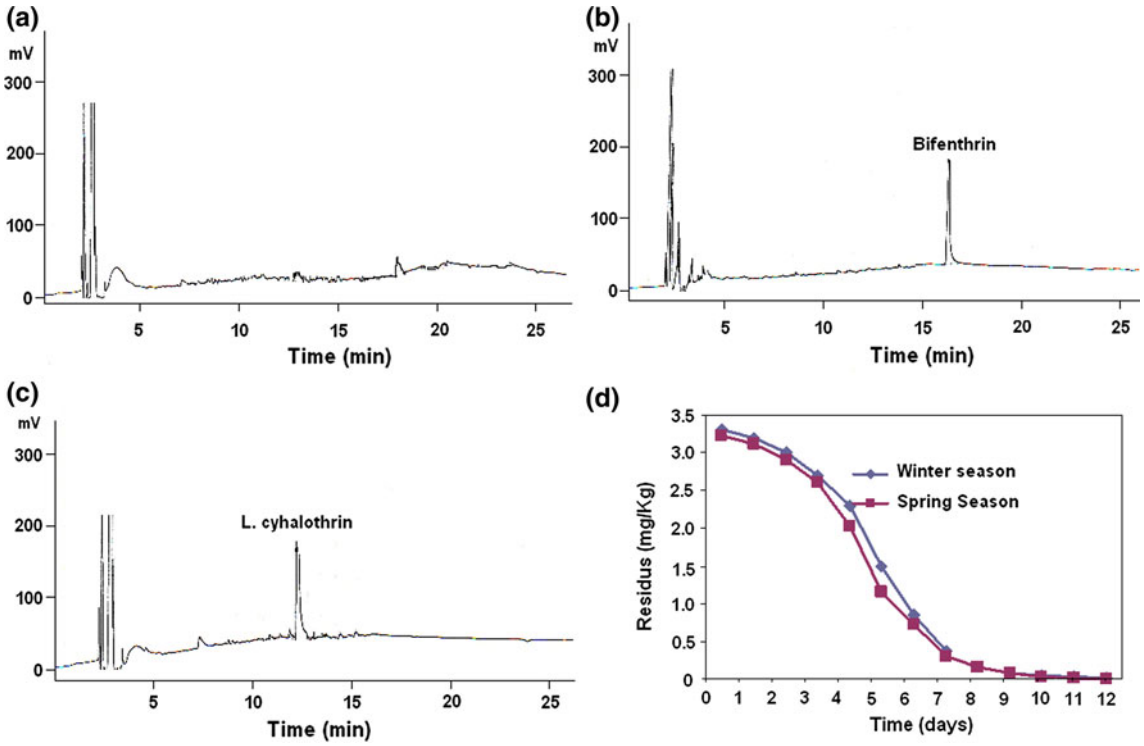

Fig. 1 **a** Chromatograms from the analysis of a blank green bean sample. **b** Chromatogram from the analysis of sample I + 5. **c** Chromatogram from the analysis of sample II′ + 8 and **d** dissipation curves for λ-Cyhalothrin in green bean samples

Table 4 Kinetic parameters for bifenthrin decline

Winter season				Spring season			
Time (days)	$\ln C_0/C_t$	K ($days^{-1}$)	$t_{1/2}$ (days)	Time (days)	$\ln C_0/C_t$	K ($days^{-1}$)	$t_{1/2}$ (days)
1	0.72	0.72	0.96	1	0.72	0.72	0.97
2	1.60	0.80	0.86	2	1.67	0.84	0.83
3	2.03	0.68	1.02	3	2.14	0.71	0.97
4	2.75	0.69	1.01	4	3.06	0.76	0.91
5	3.21	0.64	1.08	5	3.52	0.70	0.98
6	3.97	0.66	1.05	6	4.21	0.70	0.99
7	4.72	0.67	1.03	7	5.04	0.72	0.96
8	5.45	0.68	1.02	8	6.00	0.75	0.92
Mean	–	0.69	1.00	Mean		0.74	0.94
R^2	0.9969			R^2	0.9959		

In particular, the p.i. of bifenthrin and λ-cyhalothrin is 7 and 10 days, respectively. Consequently, it is possible to consider these MRL values compatible with the proper agricultural practices used for growing green bean in the plastic greenhouse of Souss Massa valley in South Morocco. Similar results were found by Garau et al. (2002) concerning azoxystrobin, pyrimethanil, cyprodinil and fludioxonil in tomatoes.

Plotting the residual concentrations against time for each data set (Table 4), first order kinetics were found for bifenthrin in the winter and spring season. The correlation coefficient (R^2) resulted > 0.99 in winter and spring season, proving the quality of fitting. The first-order kinetic parameters calculated show that the values of half life time ($t_{1/2}$) in two period, 1.00 and 0.94 days, respectively. Decay constant (K) being about 93% higher than in spring season. This result confirms that the degradation of bifenthrin was rapid in spring period.

The dissipation curves of λ-cyhalothrin in green bean at winter and spring season was shown in Fig. 1d. The curves

(Fig. 1d) showed a rapid decrease of residue levels during the two periods, but then only a slow reduction. Levels of λ-cyhalothrin residue not can be interpreted by the use of a 1st-order model. In fact, a number of studies have been carried out fitting decline curves at a 1st-order model for pyrethroids (Jaglan et al.1995) and other pesticides (Castillo-Sánchez et al. 2000). 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 first order model.

We have studied the pesticide residue levels in green beans cultivated in souss masa valley (Morocco) after multiple applications of bifenthrin and λ-cyhalothrin. The results obtained showed that the p.i. of bifenthrin in green bean were 4 days in the winter and 3.5 days in the spring. whereas that of λ-cyhalothrin was found 8 days in the winter and 7.5 days in the spring. Consequently, it is possible to consider these MRL values compatible with the proper agricultural practices used for growing green bean in the plastic greenhouse of Souss Massa valley in South Morocco. The bifenthrin had a degradation of first-order kinetics whereas that a levels of λ-cyhalothrin residue not can be interpreted by the use of a first order model.

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