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Research article

Persistence, dissipation behavior and dietary risk assessment of a combi-product of chlorantraniliprole and λ-cyhalothrin in/on pigeonpea (*Cajanus cajan* L.)

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ABSTRACT

Pigeonpea (*Cajanus cajan* L.) is an annually cultivated food and forage crop, attacked by a large number of pests mainly pod borer (*Helicoverpa armigera*). For the control of this insect pest, a combination of broad-spectrum insecticides *viz.,* chlorantraniliprole and λ-cyhalothrin have been in use to reduce the pod damage and increase crop production worldwide. Therefore, a field trial was conducted to study dissipation and persistence behavior of insecticides combination (Chlorantraniliprole 9.26 % + λ-cyhalothrin 4.63 % ZC) in/on pigeonpea at the recommended dose (RD) 30 g a.i./ha and double recommended dose 60 g a.i./ha (2RD). The quantitative analysis was performed using ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) for chlorantraniliprole and Gas chromatography with electron captured detector (GC-ECD) for λ-cyhalothrin. The Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method was validated for its accuracy, precision and sensitivity. The chlorantraniliprole persisted upto 30 days and λ-cyhalothrin persisted upto 10 days at RD and 20 days at 2RD. The half-lives (DT_{50}) of chlorantraniliprole and λ-cyhalothrin were from 4.95 to 5.78 days and 2.48–4.33 days at recommended and double recommended dose in pigeonpea, respectively. However, residues of both insecticides measured from soil at 30th day and harvest time were below the limit of quantification (LOQ). The waiting period deciphered for chlorantraniliprole and λ-cyhalothrin applied as combi-product was 9 days at recommended dose. Dietary risk assessment (Risk quotient<1) was performed on the basis of field trial suggested the application of chlorantraniliprole and λ-cyhalothrin as combi-product at recommended dose is safe for the consumers.

1. Introduction

Pigeonpea (*Cajanus cajan* L.) is a rainfed food crop which is cultivated globally in the tropical and sub-tropical regions. India is one of the major growers of this leguminous crop among Asia, Africa, Latin America and the Caribbean region. Its mature pods are substantially consumed as green vegetables and are an opulent source of essential amino acids, vitamins, fibres and minerals, in diet across the developing world (Saxena et al., 2010; Sarkar et al., 2018). It is preferable pulse crop amongst the farmers of India, Myanmar, Nepal and Africa (Kenya, Malawi, Tanzania and Euganda) due to its greater adaptability and hardy nature as well as its significance in income generation and export potential (Simtowe et al., 2010; Sarkar et al., 2018). A wide spectrum of pests and diseases causing a drastic decline in yield make the crop less profitable (Oppewal and Cruz, 2017). Being located in humid to sub-humid climatic conditions, South Gujarat locations offer a favourable condition for infestation of several insect pests. Among the various pod borer complex, gram pod borer, blue butterfly, tur plume moth and tur pod fly cause heavy damage to pods resulting in an extensive loss in the pod yield (Sharma et al., 2010; Patra et al., 2016; Nair et al., 2017; Kerketta et al., 2018). Hence, it has become essential for farmers to apply insecticides to pigeonpea to impede losses.

Insecticides *viz.*, Ethion, Flubendiamide, Indoxacarb, λ-cyhalothrin, Chlorantraniliprole *etc.* are extensively used to oppress the pod borer infestation problem in pigeonpea in different zones of India (Central Insecticide Board and Registration Committee, 2020). Nowadays, farmers across the globe preferred amalgam of pesticides over its single counterparts due to a broad spectrum of pest control with

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cost-effectiveness and resistance management in pests. Recently, the mixture of chlorantraniliprole 9.26 % + λ-cyhalothrin 4.63 % ZC has been registered in India (CIBRC, 2020) to cater the protection from pod borer problem in pigeonpea. The pace of consumption of above combination product is picked in the past few years among the farmers of India to beat losses of pigeonpea. The residues of insecticides (chlorantraniliprole and λ-cyhalothrin) may persist in food commodities which may be toxic to human health through dietary intake (Kelageri et al., 2017; Solanki et al., 2019; Paramasivam, 2020; Sharma et al., 2021).

Though the combi-product is invariably used by the farmers in pigeonpea across the country but its persistence and dissipation behaviour in pigeonpea and its potential risk involved is not available for the sub-tropical agro-climatic conditions in India. Therefore, the study comprised of the dissipation behaviour, persistence and risk assessment of combi-product of chlorantraniliprole 9.26 % + λ-cyhalothrin 4.63 % ZC in/on pigeonpea in Gujarat was performed to discover the safe use of the combi-product and the estimation of potential risk to the final consumer.

2. Materials and methods

2.1. Chemicals and reagents

The commercial formulation insecticide product Ampligo® (Chlorantraniliprole 9.3% +λ-cyhalothrin 4.6% ZC) was purchased from local pesticide shop, Navsari, Gujarat, India. Certified reference materials of chlorantraniliprole and λ-cyhalothrin having purity ≥99.9% were procured from Sigma-Aldrich Pvt. Ltd. (Bangalore, India). MS-grade acetone, acetonitrile, n-hexane, magnesium sulphate, sodium chloride, sodium sulphate, methanol and water were purchased from Merck (Darmstadt, Germany). LC/MS grade ammonium formate and formic acid (99.5+%, Optima™) were purchased from Fisher Chemical (Fair lawn, NJ, USA). Primary secondary amines (PSA) were procured from Supelco Sigma Aldrich (Germany). Stock solutions (each at 1000 mg/kg) of chlorantraniliprole in methanol and λ-cyhalothrin prepared in hexane:acetone (1:1, v/v) was prepared and stored at -20 °C. The stock solutions were diluted to formulate the intermediate and then working standards were prepared for further analysis.

2.2. Apparatus

Samples were processed using a heavy-duty variable speed homogenizer (SRK Instruments, Gujarat), centrifuge (Eppendorf, Germany) and Turbovap (Caliper life science, PerkinElmer USA). The chlorantraniliprole was analysed on LCMS-QqQ, TSQ Quantum Access Max® equipped with UHPLC having Dinonex Ultimate 3000 RS Pump (Thermo Fisher, USA). A gas chromatograph (Trace GC Ultra®) with Electron Capture Detector (ECD) and TRIPLUS auto-sampler AI 1310 (Thermo Fisher, USA) was used for λ-cyhalothrin analysis.

2.3. Field experiment

The field experiment on pigeonpea, var. *Vaishali* was conducted following Good Agricultural Practices (GAP). The experimental field was located at Mega Seed, Pulses and Castor Research Unit Farm, Navsari Agricultural University (NAU), Navsari, Gujarat, India with GPS position of 20^0 57′ N and 72^0 54′ E at an altitude of about 10 m above Mean Sea Level (MSL). The pre-mix formulation of Chlorantraniliprole 9.3% + λ-cyhalothrin 4.6% were tested as two foliar sprays at 15 days interval, the first spray being applied at 50 percent flowering stage. In accordance with Central Insecticide Board and Registration Committee (CIBRC), the treatments of recommended dose (RD) 30 g a.i./ha and double to the recommended dose (2RD) 60 g a.i./ha. were evaluated against the control (spray of water).

2.3.1. Sample collection and preparation

From each treatments across the three replications, approximately 1 kg pigeonpea pods were harvested at 0 day (2hr after application), 1, 3, 5, 7, 10, 20, 30 and 45 days after the last spray of insecticides. The collected samples were kept in air tight container and brought to the laboratory for pesticide residues analysis. Approximately, 1 kg of soil samples were collected from 5 sampling sites per treatment with standard soil sampling procedure at 0, 30 and at the time of harvest (Malhat et al., 2012; Ramasubramanian et al., 2012). Before analysis, soil samples were mixed thoroughly, air-dried, milled and strained through 2 mm mesh sieve to remove stones and taken for the pesticide residues analysis.

2.3.2. Sample extraction and cleanup

The samples were processed and analysed in the Department of Pesticide Residue, Food Quality Testing Laboratory, NAU, Navsari, Gujarat, India. Each sample were analysed as per the modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method for fruits and vegetables (Method AOAC, 2007; Sharma, 2013) and for soil (Asensio-Ramos et al., 2010; Sharma, 2013). The pigeonpea pod samples were cut and homogenized by heavy-duty variable homogenizer and a representative sample (15 ± 0.1 g) was taken in 50 mL capacity polypropylene centrifuge tubes. In sample, 1% acetic acid in acetonitrile (15 mL) was added and kept in a deep freeze for 10–20 min. The mixture of $MgSO_4$ (6.0 g) and sodium acetate (1.5 g) added and shaken for 1.0 min. The content was subjected to centrifugation for 2.0 min at 2205×g. The supernatant (6.0 mL) was transferred in 15 mL capacity polypropylene tubes containing anhydrous $MgSO_4$ (0.9 g) and PSA (0.3 g), vortexed for 1.0 min and then centrifuged again for 2.0 min at 1125×g. An aliquot (2.0 mL) transferred to 15 mL capacity test tubes and evaporated to dryness with nitrogen gas using TurboVap for further analysis. Residues were reconstituted to 2.0 mL with methanol:water (80:20; v/v) for LC-MS/MS analysis and with n-hexane:acetone (9:1; v/v) for GC-ECD analysis. The samples were filtered through syringe filters (0.22 μm, pore size) before injected for quantification on respective instrument.

A representative soil samples (10 ± 0.1g) were taken in 50 mL capacity polypropylene centrifuge tubes and 20 mL of acetonitrile was added into the sample. The content was shaken vigorously for 1 min, centrifuged at 2205× g for 2 min after adding 4 g $MgSO_4$ and 1.0 g NaCl. From this 10 mL aliquot was transferred to 15 mL centrifuge tube having 1.5 g $MgSO_4$ and 0.25 g PSA. The sample was centrifuged again at 1125×g for 2 min. Subsequently, an aliquot of 4 mL was transferred to the test tube and evaporated to dryness. Finally, chlorantraniliprole residues were reconstituted to 2.0 mL with methanol:water (80:20; v/v) and λ-cyhalothrin residues with n-hexane:acetone (9:1; v/v), filtered through syringe filters (0.22 μm, pore size).

2.4. Instrumental determination

2.4.1. LC-MS/MS analysis

The quantitative analysis of chlorantraniliprole, was performed on Thermo Scientific made TSQ Quantum Access MAX triple stage quadrupole mass spectrometer (MS) with a heated electrospray ionization (HESI) source. A Dionex made ultra-high performance liquid chromatograph (UHPLC) system (Model: Dionex Ultimate 3000 RS) equipped with an auto-sampler, a quaternary pump system and column compartment was used for analysis of the chlorantraniliprole. The separation was achieved on Hypersil Gold C18 column (150 × 4.6 mm, 5 μm particle size) with a flow rate of 0.3 mL/min at 30 °C. An elution gradient was used with solvents A (Water with 5mM ammonium formate, 0.1% formic acid) and B (Methanol with 5mM ammonium formate, 0.1% formic acid) with gradient profile (*t* (min), %A): (0, 98), (0.5, 98), (2, 60), (4.5, 98), (5, 98).

The TSQ MS parameters of chlorantraniliprole were optimized in positive ionization mode with capillary voltage 4500 V, vaporizer temperature was 350 °C, sheath gas (N_2) 48 arbitrary unit, aux gas (N_2) 18 arbitrary unit, ion transfer capillary temperature 325 °C and tube lens

145V. The masses were monitored and optimized using standard parameters: Precursor ion 484.0 m/z and Product ions 285.89 m/z (Collision energy: 17eV) and 452.93 m/z (Collision energy: 20eV) as depicted in Figure 1. Chromatogram of a chlorantraniliprole standard with retention time (RT) 1.42 min is presented in Figure 1. The data were processed using the LCQUAN™ 2.9 QF1 software (Thermo Scientific).

2.4.2. GC-ECD analysis

A gas chromatograph (TRACE GC ULTRA®) equipped with electron capture detector (ECD) and TRIPLUS auto-sampler (AI 1310) was used for quantitative analysis of λ-cyhalothrin from pigeonpea and soil samples. The chromatographic separation was executed on a capillary column (AB-5, 30 m × 0.25 mm i.d. x 0.25 μm FT, Thermofisher, USA). The 1.0 μL sample was injected under splitless mode into GC. Ultra-pure helium (99.999 %) gas was used as carrier gas at a flow rate of 1.0 mL/min. The oven temperature was initially maintained at 160 °C for 1 min and programmed with the ramp of 15 °C/min to manage the final temperature of 300 °C which was sustained for 3 min. Injector and detector temperatures were maintained at 230 and 300 °C, respectively. The reference current of ECD was 1.0 nA. Under these parameters, the retention time (RT) of λ-cyhalothrin was 37.33 min which showed in the λ-cyhalothrin chromatogram (Figure 2). The data were processed using the Xcalibur software (Thermo Scientific).

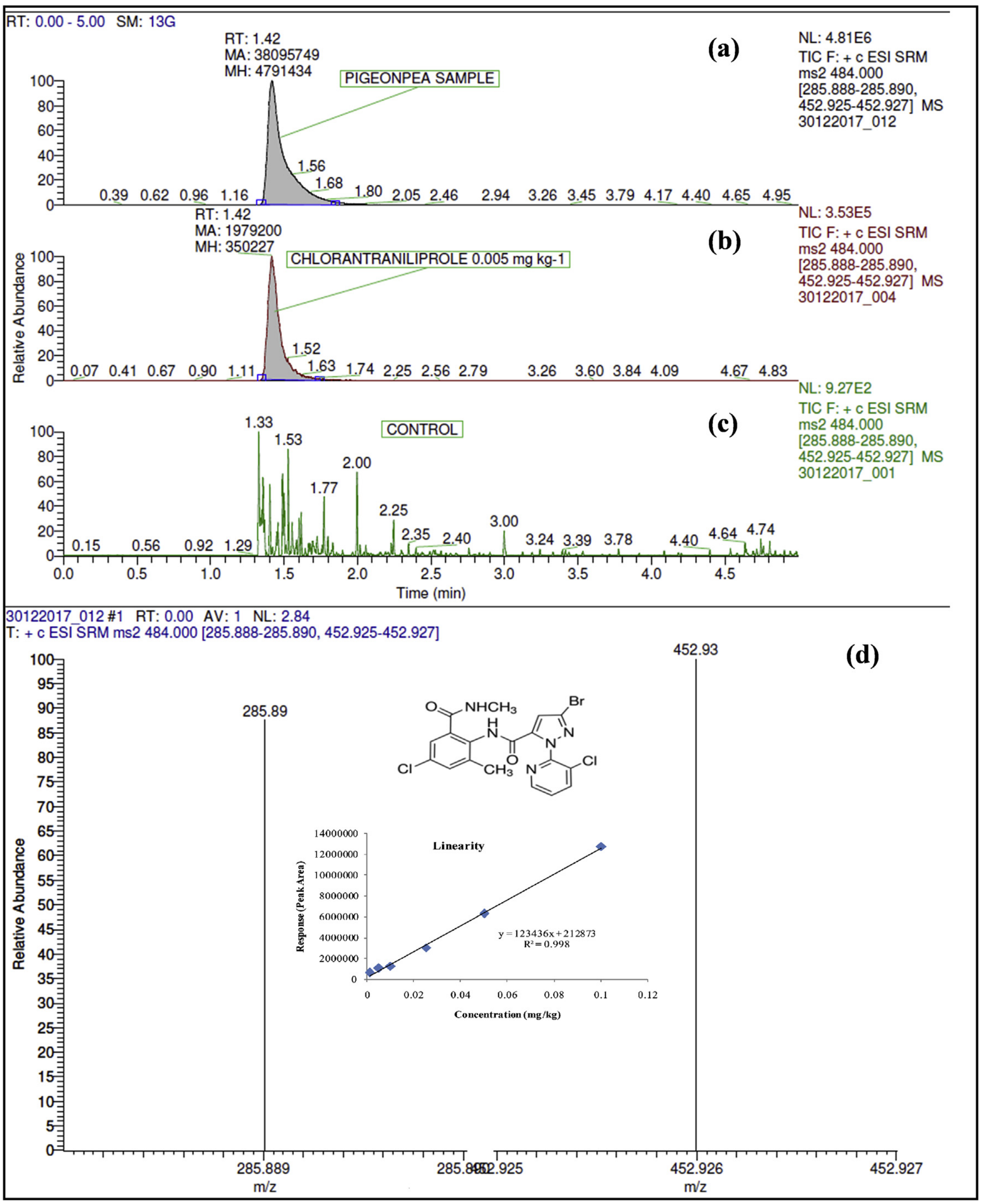

Figure 1. UHPLC-MS/MS SRM chromatograms of chlorantraniliprole (a) in pigeonpea sample (b) at standard 0.005 mg/kg (c) in control and (d) optimized ions (m/z) of chlorantraniliprole with linearity.

2.5. Analytical method validation

The performance of the method was developed and validated as per SANTE guidelines (SANTE, 2017) by studying different parameters that include the following aspects.

2.5.1. Linearity studies

The linearity of chlorantraniliprole and λ-cyhalothrin in their respective solvents were obtained using six calibration standards ranging from 0.001-0.1 mg/kg and 0.025–1.0 mg/kg, respectively. The linear relationships among the ratios of the peak area and the corresponding concentrations were observed.

2.5.2. LOD and LOQ

Five repetitive response on specific instruments for both insecticides at different concentration, (particularly in linear dynamic range) were recorded to establish the limit of detection (LOD) and the limit of quantification (LOQ) of the analytical method using the following

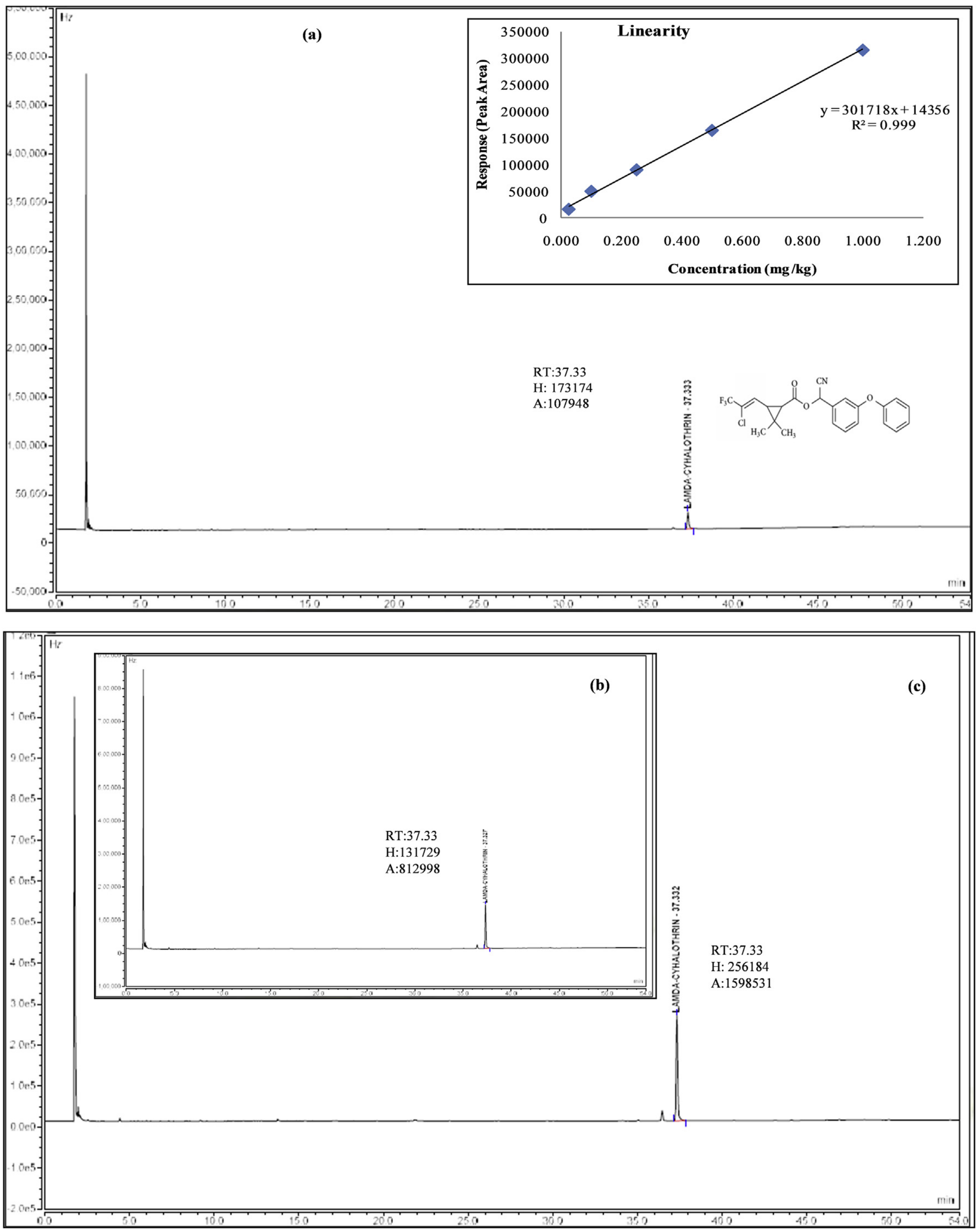

Figure 2. GC-chromatogram of λ-cyhalothrin (a) at standard 0.25 mg/kg with linearity (b) at recommended dose and(c) at double recommended dose in pigeon-pea sample.

Table 1. Method validation studies of chlorantraniliprole and λ-cyhalothrin in pigeonpea and soil.

Sr No.	Parameters	Particular	Chlorantraniliprole			λ-cyhalothrin			
			Pigeonpea		Soil	Pigeonpea		Soil	
1	Linearity (n = 5)	Calibration concentration range	0.001–0.1 mg/kg			0.025–1.0 mg/kg			
		Regression equation	y = 123436x + 212873		y = 41149x - 3543	y = 301718x + 14356		y = 57400x+ 62921	
		R^2 {$R^2 \geq 0.99$}	0.998		0.993	0.999		0.996	
2	Sensitivity (n = 5)	LOD (mg/kg)	0.001		0.001	0.013		0.030	
		LOQ (mg/kg)	0.004		0.003	0.040		0.090	
3	Accuracy (n = 7)	% Recovery [70–120%]	F level (mg/kg)	%	%	F level (mg/kg)	%	F level (mg/kg)	%
			0.005	87.58 ± 5.59	86.42 ± 11.58	0.05	74.85 ± 5.83	0.1	82.40 ± 7.31
			0.025	99.75 ± 8.93	88.10 ± 3.48	0.25	81.23 ± 5.90	0.5	85.21 ± 6.97
			0.050	100.35 ± 4.14	83.81 ± 6.09	0.5	77.47 ± 7.75	1.0	86.37 ± 7.86
4	Precision (n = 7)	% RSD [≤ 20%]	F level (mg/kg)	%	%	F level (mg/kg)	%	F level (mg/kg)	%
			0.005	6.39	13.40	0.05	7.79	0.1	8.87
			0.025	8.95	11.03	0.25	7.27	0.5	6.89
			0.050	4.12	7.27	0.5	10.01	1.0	9.10

R^2: correlation coefficient; LOQ: Limit Of Quantification; LOD: Limit of detection; F level: Fortification level; ±SD: Standard deviation; RSD: Relative standard deviation; Values given in parenthesis [ ] and { } are the standard acceptance criteria as per SANTE, 2017.

formula, LOD (mg/kg) = (mean of standard deviation/Slope) × 3 and LOQ (mg/kg) = (mean of standard deviation/Slope) × 10 (Patil et al., 2018).

2.5.3. Accuracy and precision

The accuracy and precision were evaluated through recovery study for both insecticides. Three concentration levels of fortification for chlorantraniliprole (0.005, 0.025 and 0.050 mg/kg) in pigeonpea and soil, while for λ-cyhalothrin (0.05, 0.25 and 0.50 mg/kg) in pigeonpea and soil (0.1, 0.5 and 1.0 mg/kg) were used with seven replications (n = 7). The consistency of the recovery study result reflects the precision, which can be represented by the relative standard deviation (RSD %).

2.6. Dietary risk assessment

The residues obtained from pigeonpea plants subjected to spray of combi-product (chlorantraniliprole and λ-cyhalothrin) at recommended dose (RD) 30 g a.i./ha and double recommended dose (DRD) 60 g a.i./ha collected on 0 days were used to work out the risk quotient (RQ). The estimated daily intake (EDI) of chlorantraniliprole and λ-cyhalothrin residue were calculated by multiplying the product of pesticide concentration (mg/kg) with the average food consumption rate (g/day) divided by the mean body weight of different group of Indian consumers (kg) (Anonymous, 2011). The long-term risk assessment of intakes compared to pesticide toxicological data was assessed by calculating the risk quotient (RQ), dividing the EDI by the relevant acceptable daily intake (ADI)

Table 2. Residues and dissipation pattern of chlorantraniliprole and λ-cyhalothrin in pigeonpea and soil.

Days after Application (days)	Average Residues in Pigeonpea (mg/kg)				
	Chlorantraniliprole			λ-cyhalothrin	
	Control	30 g a.i./ha (RD)[a]	60 g a.i./ha (2 RD)[b]	30 g a.i./ha (RD)[a]	60 g a.i./ha (2 RD)[b]
0 (2hr)	ND	1.289 ± 0.067 (0.00)[#]	2.498 ± 0.064 (0.00)	0.604 ± 0.044 (0.00)	1.884 ± 0.071 (0.00)
1	ND	1.143 ± 0.042 (11.33)	2.167 ± 0.021 (13.25)	0.502 ± 0.068 (16.89)	1.574 ± 0.040 (16.44)
3	ND	0.997 ± 0.034 (22.65)	1.693 ± 0.063 (32.23)	0.181 ± 0.079 (69.98)	0.953 ± 0.059 (49.43)
5	ND	0.507 ± 0.059 (60.74)	1.271 ± 0.064 (49.12)	0.136 ± 0.074 (77.48)	0.753 ± 0.031 (60.03)
7	ND	0.489 ± 0.047 (62.06)	0.922 ± 0.054 (63.09)	0.059 ± 0.044 (90.23)	0.495 ± 0.052 (73.73)
10	ND	0.410 ± 0.055 (68.19)	0.355 ± 0.011 (85.79)	0.041 ± 0.029 (93.16)	0.207 ± 0.027 (89.01)
20	ND	0.097 ± 0.020 (92.47)	0.100 ± 0.008 (96.00)	BQL	0.084 ± 0.016 (95.56)
30	ND	0.026 ± 0.012 (97.98)	0.043 ± 0.002 (98.28)	BQL	BQL
45	ND	BQL	BQL	BQL	BQL
Dissipation equation	-	$y = 1.2707e^{-0.12x}$	$y = 2.3181e^{-0.14x}$	$y = 0.5526e^{-0.28x}$	$y = 1.6154e^{-0.16x}$
Correlation coefficient (R^2)	-	0.99	0.97	0.96	0.96
DT_{50} (days)	-	5.78	4.95	2.48	4.33
Waiting Period (days)	-	3.65	7.57	8.55	21.72
Average residues in Soil (mg/kg)					
0 (2hr)	ND	0.006 ± 0.001	0.030 ± 0.004	BQL	0.124 ± 0.002
30	ND	BQL	BQL	BQL	BQL
Harvest time	ND	BQL	BQL	BQL	BQL

a: Recommended dose; b:Double to the recommended dose; ±SD: Standard deviation; #Values given in parenthesis () represents percent degradation of pesticide residues over residues obtained on 0 day (2 h after application); ND: Not detected; BQL: Below quantitation level (<LOQ); LOQ:Limit Of Quantitation; DT_{50}: Half-life values.

Table 3. Dietary risk assessment of chlorantraniliprole and λ-cyhalothrin in pigeonpea for different groups of Indian consumers.

Group	Particulars with age	Food consumption (g/day)	Body weight (kg)	Dietary risk assessment					
				RD			2RD		
				C[a]	L[b]	(C + L)[c]	C[a]	L[b]	(C + L)[c]
				RQ[d]	RQ[d]	RQ[d]	RQ[d]	RQ[d]	RQ[d]
Children	1–3 years	30	12.90	0.00	0.07	0.07	0.00	0.22	0.22
	4–6 years	30	18.00	0.00	0.05	0.05	0.00	0.16	0.16
	7–9 years	60	25.10	0.00	0.07	0.07	0.00	0.23	0.23
Boys	10–12 years	60	34.30	0.00	0.05	0.05	0.01	0.16	0.17
Girls	10–12 years	60	35.00	0.00	0.05	0.05	0.00	0.16	0.16
Boys	13–15 years	75	47.60	0.00	0.05	0.05	0.00	0.15	0.15
Girls	13–15 years	60	46.60	0.00	0.04	0.04	0.00	0.12	0.12
Boys	16–18 years	90	55.40	0.00	0.05	0.05	0.01	0.15	0.16
Girls	16–18 years	75	52.10	0.00	0.04	0.04	0.00	0.14	0.14
Man	Sedentary work	75	60.00	0.00	0.04	0.04	0.00	0.12	0.12
	Moderate work	90		0.00	0.05	0.05	0.00	0.14	0.14
	Heavy work	120		0.00	0.06	0.06	0.00	0.19	0.19
Woman	Sedentary work	60	55.00	0.00	0.03	0.03	0.00	0.10	0.10
	Moderate work	75		0.00	0.04	0.04	0.00	0.13	0.13
	Heavy work	90		0.00	0.05	0.05	0.00	0.16	0.16

RD: Recommended dose; 2RD: Double to the Recommended dose; a: Chlorantraniliprole; b: λ-cyhalothrin; c: Cumulative (Chlorantraniliprole +λ-cyhalothrin); d: Risk quotient.

expressed in mg/kg bodyweight (bw)/day. ADI values of chlorantraniliprole and λ-cyhalothrin are 1.58 mg/kg bw/day (European Food Safety Authority, 2012) and 0.02 mg/kg bw/day (World Health Organization, 2015). Numerically, the RQ value is more than 1 indicates the chemical poses risk to the consumers (Sanchez-Bayo et al., 2002; Patra et al., 2020; Botle et al., 2020).

2.7. Statistical analysis

The dissipation of chlorantraniliprole and λ-cyhalothrin in pigeonpea was calculated by using Single First Order dissipation model using the equation $C_t = C_0e^{-kt}$, Where C_t is insecticide concentration at time t, C_0 is initial concentration, k is the rate constant. The residues data were subjected to statistical analysis according to Hoskins (1961) to compute the residual half-life (DT_{50}) and pre-harvest interval (PHI) *i.e.* waiting period.

3. Results and discussion

3.1. Method validation

The linearity studies of chlorantraniliprole at different levels (0.001, 0.005, 0.010, 0.025,0.050 and 0.100 mg/kg) in 9:1 v/v methanol:water on LC-MS/MS and λ-cyhalothrin (0.025, 0.05, 0.10, 0.25, 0.50 and 1.0 mg/kg) in 1:1 v/v n-hexane:acetone on GC-ECD as well as in blank pigeonpea plant and soil extracts (i.e., in matrix-matched solutions) showed a linear response (Figures 1 and 2). The correlation coefficient R^2 ($n = 5$) values of chlorantraniliprole were 0.998 and 0.993 for pigeonpea and soil, while in case of λ-cyhalothrin values were 0.999 and 0.996 for pigeonpea and soil, respectively (Table 1). The obtained values were in accordance with the acceptable limit of $R^2 \geq 0.99$ as per SANTE guidelines (2017).

The LOD value of chlorantraniliprole and λ-cyhalothrin in pigeonpea worked out were 0.001 and 0.013 mg/kg, respectively while the LOQ values obtained for chlorantraniliprole was 0.004 mg/kg and for λ-cyhalothrin was 0.040 mg/kg (Table 1). The observed LOQ values of chlorantraniliprole and λ-cyhalothrin were lower than maximum residue limit (MRL) values fixed for pigeonpea *i.e.*, 0.8 and 0.05 mg/kg, respectively (CODEX ALIMENTARIUS International Food Standards, 2020). It indicates that the respective instruments were sensitive enough to abide the internationally acceptable standard. The LOD value of chlorantraniliprole and λ-cyhalothrin in soil recorded were 0.001 and 0.030 mg/kg, respectively. The corresponding LOQ values worked out for chlorantraniliprole and λ-cyhalothrin were 0.003 and 0.090 mg/kg, respectively (Table 1).

The recovery of chlorantraniliprole was ranged from 83.81 to 100.35% in pigeonpea and soil, while the RSD was ranged from 4.12 to 13.40%. In case of λ-cyhalothrin, recovery in pigeonpea and soil was ranged from 74.85 to 86.37% and RSD found in the range from 7.27 to 10.01% (Table 1). All the results of recoveries and RSDs were within the acceptable criteria of SANTE guidelines (SANTE, 2017) *i.e.* Recovery (70–120%) and RSD (≤20%).

3.2. Residue analysis

The persistence and dissipation pattern of chlorantraniliprole and λ-cyhalothrin in pigeonpea under South Gujarat agro-climatic conditions are depicted in Table 2. The chlorantraniliprole residues on 0 day (2hr) were 1.289 and 2.498 mg/kg at RD and 2RD dose, respectively. The initial residues of chlorantraniliprole steadily and progressively dissipated which were 0.507 and 1.27 mg/kg on 5[th] day, respectively for both doses. It shows 49–60% loss of chlorantraniliprole residue (Table 2). Thereafter, the residues of the above insecticide were detected up to 30 days at either rate of application. However, its residues were below quantitation level (BQL) at either dose from the samples collected at the time of harvest. In case of λ-cyhalothrin, the residues detected were 0.604 and 1.884 mg/kg at the RD and 2RD in pigeonpea on 0 days (2hr). The residues of λ-cyhalothrin observed on 1[st] day were 0.502 and 1.574 mg/kg at RD and 2RD dose, respectively. The chemo-dynamic study reveals that the residues of λ-cyhalothrin recorded on 10[th] and 20[th] day at RD and 2RD were 0.041 and 0.084 mg/kg respectively and these were in lieu of 93.16–95.56% of their initial concentration. Thereafter, the residues of λ-cyhalothrin were found below quantitation limit (Table 2).

The dissipation regression equations were, for chlorantraniliprole $y = 1.2707e^{-0.129x}$ ($R^2 = 0.99$) and for λ-cyhalothrin $y = 0.5526\ e^{-0.283x}$ ($R^2 = 0.96$) at RD, while $y = 2.3181\ e^{-0.142x}$ ($R^2 = 0.97$) for chlorantraniliprole and $y = 1.6154\ e^{-0.16x}$ ($R^2 = 0.96$) for λ-cyhalothrin at 2RD, as mentioned in Table 2. The dissipation half-life (DT_{50}) worked out for chlorantraniliprole were 5.78 and 4.95 days at RD and 2RD, respectively. Similarly, λ-cyhalothrin, the DT_{50} was recorded 2.48 and 4.33 days at respective doses (Table 2). As per classifications based on agro-climatic conditions, Navsari located in South Gujarat comes under heavy rainfall zone-I (Agro-ecological situation-III). The climate of this zone is typically sub-tropical, characterized by humid and warm monsoon with heavy rains, quite cold winter and fairly hot summer. The present finding on DT_{50} of chlorantraniliprole is differing from the results reported with DT_{50} for cauliflower 1.25–1.36 days (Kar et al., 2012), tomato 3.30 days (Malhat et al., 2012) okra 1.60–1.70 days (Vijayasree et al., 2015), brinjal 1.58–1.80 days (Vijayasree et al., 2015), green chilli 1.58–1.80 days (Ahlawat et al., 2019), 1.26 days (Paramasivam, 2020). This variation might be the resultant of the prevailing environmental factors and processes *viz.,* temperature, relative humidity, volatilization and photo-degradation at field conditions (Dong et al., 2011; Kar et al., 2012; Zhang et al., 2012; Solanki et al., 2019; Paramasivam, 2020) which are not consistent in different geographical regions.

The chlorantraniliprole residues detected in soil were 0.006 mg/kg and 0.030 mg/kg, while in case of λ-cyhalothrin, these were BQL and 0.124 mg/kg at RD and 2RD dose on 0 day (2hr), respectively. However, the residues of above insecticides in soil were BQL on 30 days after application as well as at the time of harvest of pigeon pea (Table 2). More or less the similar findings were also reported by Ramasubramanian et al. (2016), where chlorantraniliprole residues were quantified up to 30 days in sugarcane soilwhen it was applied at recommended (75 g a.i./ha) and double the recommended (150 g a.i./ha) doses. It is observed that the pace of the dissipation of λ-cyhalothrin was rapid with respect to chlorantraniliprole in the soil as well as in plants. Lambda-cyhalothrin being a synthetic pyrethroid, is believed to be subjected to degradation through photolytic ester cleavage from their moiety in the plant as well as in environmental matrices such as soil. Thus, λ-cyhalothrin exhibits short persistence behavior in different matrices and also it might be a potential reason for its faster degradation concerning chlorantraniliprole, when applied as combi-product at RD and 2RD.

3.3. Dietary risk assessment

The cumulative dietary risk quotient (RQ) calculated based on the collective pesticide residues for both the insecticides present in the combi-product was less than 1 from 0 day (2hr) at RD and DRD (Table 3). It signifies that pigeonpea collected from the field was safe for consumption. It indicates that the combi-product will not cause any adverse effect to consumer after consumption of pigeonpea. Therefore, the consumption of pigeonpea laced with combi-product of chlorantraniliprole and λ-cyhalothrin at recommended dose with an observed waiting period of 9 days are safer as their RQ values are lower than 1 as recommended by Paramasivam (2020).

4. Conclusions

The current investigation was to appraise the dissipation behavior of chlorantraniliprole and λ-cyhalothrin in pigeonpea to propose the apt use of the combi-product Ampligo® (Chlorantraniliprole 9.26 %+λ-cyhalothrin 4.63 % ZC) to ensure safe consumption of pigeonpea. The residues of chlorantraniliprole and λ-cyhalothrin in pigeonpea were persisted upto 30 and 20 days at RD, respectively. The DT_{50} of chlorantraniliprole and λ-cyhalothrin in pigeonpea were 4.95–5.78 days and 2.48–4.33 days at RD and 2RD, respectively. The individual waiting period worked out for chlorantraniliprole and λ-cyhalothrin was 3.65 and 8.55 days at RD. Thus, it is suggested to observe minimum 9 days waiting period when the combi-product is applied twice at 15 days interval starting from 50 per cent flowering stage at the rate of 30 g a.i./ha to manage the pod borer under sub-tropical agro-climatic conditions of South Gujarat in India. Considering food safety concern, the dietary risk assessment was worked out which revealed that 9 days waiting period is quite sufficient to nullify the toxic effect of these insecticides to the consumers as RQ values were below 1 from 0 day. Therefore, it can be concluded that spray of combi-product of chlorantraniliprole and λ-cyhalothrin at recommended do not pose any health risk to consumers.

Declarations

Author contribution statement

Rohan V. Kansara; Vanrajsinh H. Solanki: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Susheel Singh: Conceived and designed the experiments; Analyzed and interpreted the data.

Digvijaysinh Chauhan: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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