Singh S *et al.* (2021)
Notulae Scientia Biologicae
Volume 13, Issue 3, Article number 11028
DOI:10.15835/nsb13311028
Research Article

Persistence, dissipation behavior and health risk assessment of spiromesifen in brinjal (*Solanum melongena* L.) by LC-MS/MS

Susheel SINGH[1]*, Vanrajsinh SOLANKI[1], Rohan KANSARA[1], Nitisha PATEL[1], Kelvin GANDHI[1], Hemant PATEL[2]

[1]*Navsari Agricultural University, Food Quality Testing Laboratory, Navsari 396450, Gujarat, India; susheelsingh@nau.in (*corresponding author); vnrj26@gmail.com; rohankansara1988@gmail.com; nitishapatel210@gmail.com; kelvingandhi89@gmail.com*
[2]*Navsari Agricultural University, Polytechnic Diploma College, Navsari 396450, Gujarat, India; hmpatel@nau.in*

Abstract

Brinjal (*Solanum melongena*) is a versatile crop infected by several insects and pests. For the control of these pests, spiromesifen insecticide has been in use to reduce the damage and increase crop production worldwide. Therefore, a field trial was conducted to study dissipation and persistence behavior of spiromesifen 22.9% w/w SC in/on brinjal at the recommended dose (RD) 96 g a.i./ha and double to recommended dose 192 g a.i./ha (2RD). The quantitative analysis of spiromesifen was performed using ultra-high performance liquid chromatography- tandem mass spectrometry (UHPLC-MS/MS). Samples were processed by the Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method. The analytical method was validated using various parameters viz., linearity ($R^2 \geq 0.99$), sensitivity (LOD and LOQ), accuracy (recovery=70-120%) and precision (RSD≤20%). The spiroemsifen persisted up to 3 days at RD and 5 days at 2RD. The dissipation half-life (DT_{50}) of spriromesifen was 3.64 and 4.10 days at RD and 2RD in brinjal, respectively. However, residues of spiromesifen measured from soil at 0^{th} (2 hr) day and 10^{th} day were below the limit of quantification (BQL). The waiting period deciphered for spiromesifen applied in brinjal was 1 day at the recommended dose. Further, health risk assessment (health risk index<1 and percent health index<100) was performed on the basis of field trial which suggested that the application of spiromesifen in brinjal crop at recommended dose is safe for the end-users.

Keywords: brinjal; dissipation; health risk assessment; liquid chromatography; mass spectrometry; persistence; spiromesifen

Introduction

Brinjal (*Solanum melongena*) is a versatile crop adapted to various agro-climatic regions which can be grown throughout the year globally. It is also usually known as eggplant and extensively cultivated in Asian countries (India, Bangladesh, Pakistan, China) and also popular in Egypt, France, Italy and United States (Cork *et al.*, 2005 and FAOSTAT, 2019). In 2019, eggplant was the most commonly produced vegetable worldwide, contributing over 55.0 billion metric tons to global vegetable production (Anonymous, 2021). It is

Received: 14 Jul 2021. Received in revised form: 27 Jul 2021. Accepted: 09 Aug 2021. Published online: 18 Aug 2021.
From Volume 13, Issue 1, 2021, Notulae Scientia Biologicae journal uses article numbers in place of the traditional method of continuous pagination through the volume. The journal will continue to appear quarterly, as before, with four annual numbers.

an important crop of the human diet globally because its fruits are enriched with fiber, folic acid, manganese, magnesium, potassium, thaimin and vitamin B6 as well as low in fat and supply adequate calories (Muhammad *et al.*, 2019). Farmers have been cultivating it over the years due to higher profit, relatively fast-growing capacity, and low-risk involvement and easy technological adoption (Anonymous, 2019).

Several insects and pests attack the brinjal, including mites, eggplant shoot and fruit borers, leafhoppers, ants, stem borer and epilachna beetles, which cause major crop damage and low yields about 70-80% worldwide (Ara *et al.*, 2007, Borkakati *et al.*, 2019 and Gautam *et al.*, 2019). Hence, this study was conducted to find out the low-cost and effective plant-based pesticides to protect the brinjal field from pest attack.

Several insecticides *viz.*, acephate, chlorantraniliprole, flubendiamide, imidaclopride, triazophos, monocrotophos, afidopyropen, carbofuran, chlorpyrifos, cypermethrin, deltamethrin, *etc.* are being used to control the damage of insects and pests in brinjal in different zones throughout the world but harmful for mankind (CIBRC, 2020). Subsequently, numerous new molecules have been developed, which degrade easily in the environment and less harmful for mankind.

A novel insecticide/acaricide, spiromesifen [3-(2,4,6-trimethylphenyl)-4-(3,3-dim-ethylbutyl-carbonyloxy)-5-spirocyclo-phenyl-3-dihydro-furanol-2] is characterized as a molecule of new chemical class of spirocyclic phenyl substituted tetronic acids. It is non-systemic in nature and inhibits lipid biosynthesis in mites (Nesrine Kissoum *et al.*, 2016). Owing to the unique chemical structure (Figure 1a), spiromesifen is an advantageous tool in resistance management in multiple cropping systems including vegetables and fruits. Spiromesifen was categorized as low acute toxic substance-exposed through different routes such as oral, dermal, inhalation, and leads to detrimental effects namely loss of body weight, effect on adrenal, thyroid, liver and spleen (EPA, 2013).

Though the spiromesifen is registered for control of red spider mite in brinjal and invariably is used by the farmers across the country but its persistence and dissipation behaviour are not available especially in the sub-tropical agro-climatic conditions in India. This study designed to develop and validate an analytical methodology for the quantification and confirmation of spiromesifen residues in brinjal using an analytical instrument LC-MS/MS. Therefore, the dissipation behaviour, persistence and health risk assessment of spiromesifen 22.9% SC in/on brinjal was reviewed under supervised field conditions.

Materials and Methods

Chemicals and reagents

The commercial insecticide formulation of Spiromesifen (22.9% w/w SC) was purchased from a local pesticide shop, Navsari, Gujarat, India. Certified reference material of spiromesifen having purity ≥99.9% was procured from Sigma-Aldrich Pvt. Ltd. (Bangalore, India). MS-grade acetone, acetonitrile, 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). The stock solution (1000 mg/L) was prepared with acetonitrile and stored at -20 °C. Further, this stock solution was diluted to prepare the intermediate and then formulated for working standards using methanol: water (80:20).

Apparatus

Samples were processed with the help of different apparatus including homogenizer (SRK Instruments, Gujarat, India), centrifuge (Eppendorf, Germany) and Turbovap (Caliper life science, PerkinElmer USA). The spiromesifen was analysed on Liquid Chromatography Mass Spectrometry (LCMS-QqQ), TSQ Quantum Access Max® equipped with UHPLC having Dinonex Ultimate 3000 RS Pump (Thermo Fisher, USA).

Field experiment

The Brinjal crop, var. GNRB-1(*surati ravayya*) was grown at Horticulture Polytechnic College farm, Navsari Agricultural University (NAU), Navsari, Gujarat, India (21° 18' N, 72° 84' E and 10 m above Mean Sea Level) by adopting Good Agricultural Practices (GAP). The spiromesifen (22.9% w/w SC) was tested as two foliar sprays at 15 days interval, the first spray was applied at the 50 percent flowering stage. Applied treatments of RD 96 g a.i./ha and 2RD 192 g a.i./ha were evaluated in reference to control (water spray only) as per Central Insecticide Board and Registration Committee (CIBRC). Data were recorded in year 2018 and 2019.

Sample collection and preparation

From each treatment across the three replications, approximately 1 kg brinjal fruits were picked at 0 day (2hr after application), 1, 3, 5, 7 and 10 days after the last spray of insecticide. The collected samples were packed air-tight and transported 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 day and 10 days (Malhat *et al.*, 2012; Ramasubramanian, 2012b). Before analysis, soil samples were air-dried homogenized thoroughly and strained through 2 mm mesh sieve to remove hard stones and used for the pesticide residues analysis.

Sample extraction and cleanup

The samples were evaluated at the Pesticide Residue Wing, Food Quality Testing Laboratory, NAU, Navsari, Gujarat, India. Each sample was analysed as per the modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method for fruits and vegetables (AOAC, 2007 and Sharma, 2013) and for soil (Asensio-Ramos *et al.*, 2010; Sharma, 2013).

(a) Fruit: The brinjal fruit samples were cut and homogenized by a heavy-duty variable homogenizer and a representative sample (15±0.1 g) was taken in 50 mL capacity polypropylene centrifuge tubes. In the 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 centrifuged 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. For further analysis, 2 mL aliquot was transferred to 15 mL capacity test tubes and dried with nitrogen (N_2) gas using TurboVap. Lastly, residues were reconstituted to 2 mL with methanol: water (80:20; v/v) for LC-MS/MS analysis. The samples were filtered through syringe filters (0.22 µm, pore size) before injected for quantification on the LC-MS/MS.

(b) Soil: A representative soil samples (10 ± 0.1 g) were taken in 50 mL capacity polypropylene centrifuge tubes and 20 mL of acetonitrile was added into the sample. After adding 4 g $MgSO_4$ and 1.0 g NaCl, the tubes were vortexed for 1 min and centrifuged for 2 min at 2205× g. 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. Later, an aliquot of 4 ml was shifted to the test tube and subjected to dryness in turbovap. Finally, spiromesifen residues were reconstituted to 2.0 mL with methanol: water (80:20; v/v) filtered through syringe filters (0.22 µm, pore size).

Instrumental determination

LC-MS/MS analysis

The quantitative analysis of spiromesifen was performed on Thermo Scientific made TSQ Quantum Access MAX triple stage quadrupole mass spectrometer (MS) with a heated electrospray ionization (HESI) source. For analysis of the spiromesifen, an ultra-high performance liquid chromatograph (UHPLC) system (Model: Dionex Ultimate 3000 RS) facilitated with a quaternary pump system, an auto-sampler and column compartment were used. 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 solvent A: Water + 5 mM ammonium formate + 0.1% (v/v) formic acid and solvent B: Methanol + 5mM ammonium formate + 0.1% formic acid with gradient profile (t (min), %A): (0, 98), (0.5, 98), (2, 60), (20, 95), (22, 95), (25, 95).

The TSQ MS parameters of spiromesifen were optimized in positive ionization mode with capillary voltage 2950V, vaporizer temperature was 350 °C, sheath gas (N_2) 13 arbitrary unit, aux gas (N_2) 7 arbitrary unit, ion transfer capillary temperature 325 °C and tube lens 0.70V. The masses were monitored and optimized using standard parameters: Precursor ion 393.0 m/z and Product ions 294.9 m/z (Collision energy: 14eV) and 312.9 m/z (Collision energy: 5eV) (Figure 1b). The data were processed using the LCQUAN™ 2.9 QF1 software (Thermo Scientific).

Analytical method validation

The method was established and performance was validated as per SANTE guidelines (SANTE, 2017) by studying the parameters **(a)** Linearity: The linearity of spiromesifen in solvent was obtained using five calibration standards ranging from 0.001-0.1 mg/L (0.001, 0.005, 0.010, 0.025, 0.050 and 0.100 mg/L); **(b)** LOD and LOQ: Five repetitive responses on specific instruments for spiromesifen at different concentrations, (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 formula, LOD (mg/kg) = (mean of standard deviation/Slope) × 3 and LOQ (mg/kg) = (mean of standard deviation/Slope) × 10 (Patil *et al.*, 2018); **(c)** Accuracy and precision: The accuracy and precision were evaluated through a recovery study for spiromesifen. Three concentration levels of fortification for spiromesifen (0.010, 0.025 and 0.05 mg/kg) in brinjal fruit and soil were used with seven replications (n=7). The consistent result of the recovery study represents the precision which can be denoted by the relative standard deviation (RSD %).

Health risk index (HRI)

The residues obtained from brinjal fruits subjected to spray of spiromesifen at RD (96 g a.i./ha) and 2RD (192 g a.i./ha) were collected on 0 (2hrs) days were used to work out the different Health risk indices (HRI). The estimated daily intake (EDI) of spiromesifen residue was calculated by multiplying the product of insecticide concentration (mg/kg) with the average food consumption rate (g/day) divided by the mean body weight (kg) of different groups of Indian consumers (Anonymous, 2011). Health risk index (HRI) was calculated using the equation: Health risk Index (HRI) = EDI/ADI (European Food Safety Authority, 2007), where EDI is estimated daily intake and ADI is acceptable daily intake. ADI value of spiromesifen is 0.03 mg/kg bw/day (FAO, 2016). Health risk index more than 1 is considered as unsafe for human health and Health Index (HI) <100% represents an acceptable risk to human health (Hlihor *et al.*, 2019).

Statistical analysis

The dissipation of spiromesifen in brinjal 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 calculate the residual half-life (DT_{50}) and pre-harvest interval (PHI) e.g. waiting period.

Results and Discussion

Method validation

Initially, the insecticide extraction and detection method were verified based on data include linearity, LOD, LOQ, accuracy and precision (SANTE, 2017). After injecting working standard solution of spiromesifen (0.005 mg/kg) into the UHPLC, retention time (RT) was obtained 19.23 min. In chromatogram, no other peaks were observed indicating the absence of any interfering matrix compounds (Figure 1d). The maximum residue limits (MRLs) for pesticide in food was considered to ensure that the method was suitable for the determination of pesticide residue contents. The MRL of spiromesifen in brinjal is 0.5 mg/kg (European Food Safety Authority, 2019).

Table 1. Method validation parameters of spiromesifen in brinjal fruit and soil

Sr No.	Parameters	Particular	Spiromesifen		
			Fruit		Soil
1	Linearity (n=6)	Calibration concentration range	0.001-0.1 mg/L		
		Regression equation	y = 54545x + 11709		y = 91859x + 1331.1
		R^2 {R^2≥0.99}	0.999		0.995
2	Sensitivity (n=6)	LOD (mg/kg)	0.002		0.003
		LOQ (mg/kg) [LOQ<MRL]	0.009		0.009
3	Accuracy (n=7)	% Recovery [70-120%]	F level (mg/kg)	% (±SD)	% (±SD)
			0.010	103.95 ±9.79	75.86±13.99
			0.025	95.66±13.98	86.51±11.61
			0.050	92.35±14.91	97.15±11.83
4	Precision (n=7)	% RSD [≤ 20%]	F level (mg/kg)	%	%
			0.010	9.42	18.44
			0.025	14.62	9.26
			0.050	16.15	12.18

R^2: correlation coefficient; LOQ: Limit of quantification; LOD: Limit of detection; F level: Fortification level; ±SD: Standard deviation; RSD: Relative standard deviation; MRL: maximum residue limit (0.5 mg/kg for spiromesifen in brinjal); Values given in parenthesis [ ] and { } are the standard acceptance criteria as per SANTE, 2017

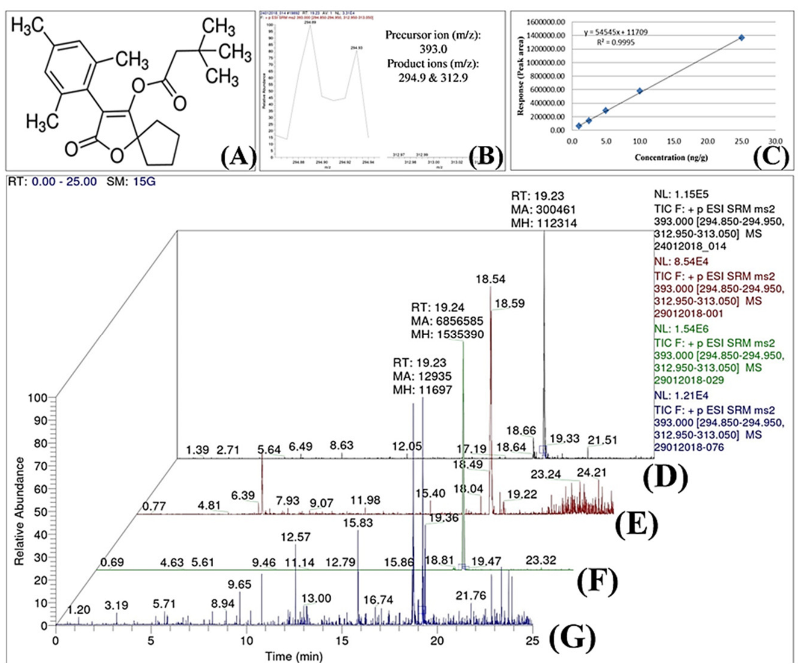

Figure 1. Optimization of chromatographic separation on UHPLC-MS/MS SRM of spiromesifen
(A) Chemical structure (B) Optimized precursor and product (m/z) ions (C) Specificity with linear response. UHPLC-MS/MS SRM three dimensional chromatograms of spiromesifen (D) at standard 0.005 mg/kg (E) in control (F) on 0 (2hr) day and (G) on 3rd day after spiromesifen application in brinjal fruit sample at recommended dose; RT: Retention Time; MH: Peak Height; MA: Peak Area

The linearity studies of spiromesifen at different levels (0.001, 0.005, 0.010, 0.025, 0.050 and 0.100 mg/L) in methanol: water (80:20; v/v) on LC-MS/MS as well as in blank brinjal fruit and soil extracts (i.e., in matrix-matched solutions) showed a linear response (Table 1 and Figure 1c). The correlation coefficient (R^2) value of spiromesifen was 0.999 and 0.995 for brinjal fruit and soil (Table 1). The obtained values were in accordance with the acceptable limit of $R^2 \geq 0.99$ and deviation of back calculated concentration from true concentration was ≤ 20%.

The LOD value of spiromesifen in brinjal fruit worked out was 0.002 mg/kg, while the LOQ value obtained was 0.009 mg/kg (Table 1). The observed LOQ value of spiromesifen was lower than maximum residue limit (MRL) values fixed for brinjal. It indicates that the instrument was sensitive enough to abide the internationally acceptable standard. The LOD value of spiromesifen in soil recorded was 0.003 mg/kg. The corresponding LOQ value worked out for spiromesifen was 0.009 mg/kg (Table 1).

The recovery of spiromesifen was ranged from 92.35 to 103.95% in brinjal fruit and 75.86 to 97.15% in soil, while the RSDs were ranged from 9.42 to 18.44% in brinjal fruit and soil (Table 1). All recoveries (70-120%) and RSDs (≤20%) results were obtained within the acceptable measures of SANTE guidelines.

Residue analysis

The persistence and dissipation pattern of spiromesifen in brinjal under sub-tropical agro-climatic conditions is depicted in Table 2. The spiromesifen residues in control samples (water spray only) were not detected (Fig. 1e), however, in treated samples on 0 day (2hr) was 0.091 and 0.192 mg/kg at RD and 2RD, respectively. The initial residues of spiromesifen steadily and progressively dissipated which were 0.024 and 0.079 mg/kg on 3rd day, respectively at both doses. It shows 31.86-87.50% loss of spiromesifen residue (Table 2; Fig. 1f and g). Thereafter, the residue of the spiromesifen was not detected at 5 days and 7 days at RD. While on the 5th day, spiromesifen residue was 0.024 mg/kg, and on the 7th day, it was below quantitation level (BQL) at 2RD (Table 2).

Table 2. Residues and dissipation pattern of spiromesifen in brinjal fruit and soil

Days after Application (days)	Average residues of spiromesifen (mg/kg) in fruit		
	Control	96 g a.i./ha (RD)[a]	192 g a.i./ha (2 RD)[b]
0 (2hr)	ND	0.091 (0.00)	0.192 (0.00)
1	ND	0.062 (31.86)	0.115 (40.10)
3	ND	0.024 (73.62)	0.079 (58.85)
5	ND	BQL	0.024 (87.50)
7	ND	BQL	BQL
10	ND	BQL	BQL
Dissipation equation	-	y = -0.1902x + 1.9723	y = -0.1689x + 2.2877
Correlation coefficient (R^2)	-	0.998	0.953
DT_{50} (days)	-	3.64	4.10
Waiting Period (days)	-	1.0	1.0
Average residues (mg/kg) in Soil			
0 (2hr)	ND	BQL	BQL
10	ND	BQL	BQL

a: Recommended dose; b: Double to the recommended dose; Values given in parenthesis () represents percent degradation of pesticide residues over residues obtained on 0 day (2 hrs after application); ND: Not detected; BQL: Below quantitation level (<LOQ); LOQ: Limit of quantitation; DT_{50}: Half-life values; Spiromesifen residue data are mentioned as mean of year 2018 and 2019

The dissipation regression equations for spiromesifen were y=-0.1902x + 1.9723 and y=-0.1689x + 2.2877 at RD and 2RD, respectively as mentioned in Table 2. The dissipation half-life (DT_{50}) worked out for spiromesifen were 3.64 and 4.10 days at RD and 2RD, respectively (Table 2). As per classifications based on agro-climatic conditions, Navsari is located in South Gujarat comes under heavy rainfall zone-I (Agro-ecological situation-III). This zone's climate is typically sub-tropical, with a humid and warm monsoon with heavy rains, somewhat cold winter and rather hot summer.

The contemporary finding on DT_{50} of spiromesifen is differing from the results reported with DT_{50} for brinjal 1.40-2.18 days (Vinothkumar *et al.*, 2018) and other fruits and vegetables like, green chilli 2.18-2.40 days (Sharma *et al.*, 2007), okra 1.65-1.68 days (Raj et al., 2012), tomato 0.93-1.38 days (Sharma *et al.*, 2014) and cucumber 2.12-2.19 days (Banerjee and Agyani, 2019). This variation could be the effect of the major environmental factors and processes *viz.,* relative humidity, temperature, wind, volatilization and photo-degradation at field conditions (Sharma *et al.*, 2014; Mate *et al.*, 2015; Vinothkumar *et al.*, 2018; Banerjee and Agyani, 2019; Solanki *et a*l., 2019) which are not reliable in different geographical zones.

The spiromesifen residues detected in soil were BQL at RD and 2RD on 0 day (2hr), respectively (Table 2). Meanwhile, spiromesifen was not directly applied to soil; its residues in soil were also BQL at the 10^{th} day. A less similar finding was also reported by Sharma et al. (2014), where spriomesifen residues were quantified up to 15 days in tomato soil when it was applied at RD (150 g a.i./ha) and 2RD (300 g a.i./ha) under different agro-climatic zones of India. Spiromesifen as an acaricide, is believed to be subjected to degradation from their moiety in the plant and different kinds of soils (Mate *et al.*, 2015). Different studies demonstrate that spiromesifen is rapidly degraded in soil and aqueous thoroughly metabolized to the final degradation product carbon dioxide. Major metabolites involved in the degradation are Sp-enol and 4-carboxy-Sp-enol (FAO, 2016). Consequently, spiromesifen unveils minute persistence behavior in different matrices and also it might be a potential reason for its faster degradation, when applied at RD and 2RD.

Health risk assessment

Generally, brinjal fruits are preferred by consumers and also used as a favorite home food in delicious cuisines of vegetarian and non-vegetarian people. Pesticides are a major part of different chemicals applied to the fruits. When pesticides exceed the maximum residue limit (MRL) on food crops, it could generate difficulty to the exporters and local consumers. Therefore, health risk estimations were studied based on pesticide residues detected in brinjal fruits. The health risk index (HRI) was calculated by dividing the EDI (mg kg^{-1}/day) by their corresponding values of acceptable daily intakes (ADI) for agricultural and veterinary chemicals (Anonymous, 2005). The average values of individual body weights involving different age groups in India are listed according to the official dietary guideline for Indians (Anonymous, 2011). Cumulative estimated health risk index values as well as Health Index (HI %) of spiromesifen residues recorded at RD and 2RD, are presented in Table 3.

Table 3. Health risk assessment of spiromesifen in brinjal for different groups of Indian consumers

Group	Particulars with age	Food consumption (g/day)	Body weight (kg)	Dietary risk assessment					
				96 g a.i./ha (RD)			192 g a.i./ha (2 RD)		
				EDI	HRI	%HI	EDI	HRI	%HI
Children	1-3 years	30	12.90	0.001	0.024	2.40	0.001	0.050	5.00
	4-6 years	30	18.00	0.001	0.017	1.70	0.001	0.036	3.60
	7-9 years	60	25.10	0.000	0.012	1.20	0.001	0.025	2.50
Boys	10-12 years	60	34.30	0.000	0.009	0.90	0.001	0.019	1.90
Girls	10-12 years	60	35.00	0.000	0.009	0.90	0.001	0.018	1.80
Boys	13-15 years	75	47.60	0.000	0.006	0.60	0.000	0.013	1.30
Girls	13-15 years	60	46.60	0.000	0.007	0.70	0.000	0.014	1.40
Boys	16-18 years	90	55.40	0.000	0.005	0.50	0.000	0.012	1.20
Girls	16-18 years	75	52.10	0.000	0.006	0.60	0.000	0.012	1.20
Men	Sedentary work	75	60.00	0.000	0.004	0.40	0.000	0.008	0.80
	Moderate work	90		0.000	0.005	0.50	0.000	0.010	1.00
	Heavy work	120		0.000	0.006	0.60	0.000	0.013	1.30
Women	Sedentary work	60	55.00	0.000	0.003	0.30	0.000	0.007	0.70
	Moderate work	75		0.000	0.004	0.40	0.000	0.009	0.90
	Heavy work	90		0.000	0.005	0.50	0.000	0.010	1.00

RD: Recommended dose; 2RD: Double to the Recommended dose; EDI: estimated daily intake; HRI: Health Risk Index; HI: Percent Health Index

Thus, it reflects that under the tropical agro-climatic conditions from 0 days after spray at both doses, the HRI values are lower than 1 and HI% are less than 100%. It indicates that the Spiromesifen 22.9% (w/w SC) will not cause any adverse effect after consumption of brinjal fruits. Therefore, the consumption of brinjal laced with product of Spriomesifen (22.9% w/w SC) at recommended dose with an observed waiting period of 1 day is safer as their HRI values are lower than 1.

Conclusions

The goal of the current study was to assess the dissipation behaviour of spiromesifen in brinjal in order to suggest the use of formulation Spiromesifen (22.9 % w/w SC) to assure safe brinjal intake. At RD, spiromesifen residues in brinjal lasted up to three days. The DT_{50} of spiromesifen in brinjal was 3.64-4.10 days at RD and 2RD. The waiting period worked out for spiromesifen was 1 day at RD. When the formulation product Spiromesifen (22.9% w/w SC) is sprayed twice at 15-day intervals commencing from 50% flowering stage at 96 g a.i./ha (RD) to control insect pests under sub-tropical agro-climatic conditions in India, it is recommended to wait at least one day. In order to address the issue of food safety, the health risk assessment (HRI) was evaluated, which demonstrated that one-day waiting period is sufficient to eliminate the toxic effects of the spiromesifen on consumers, since HRI and HI were less than 1 and 100% from 0 day, respectively. As a result, it can be stated that spiromesifen spray at recommended dose poses no risk to the target consumers.

Authors' Contributions

Conceptualization of research (SS and VS); Designing of the experiments (SS); Contribution of experimental materials (HP); Execution of field/lab experiments and data collection (KG and NP); Analysis of data and interpretation (VS, RK and KG); Preparation of the manuscript (VS, RK and NP). All authors read and approved the final manuscript.

Acknowledgements

The authors are grateful to the In-charge Professor and Head of Polytechnic Horticulture, Navsari Agricultural University, Navsari, Gujarat, India for their support and assistance in conducting the field trial. This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Conflict of Interests

The authors declare that there are no conflicts of interest related to this article.

References

Anonymous (2005). Acceptable daily intakes for agricultural and veterinary chemicals. Australian Government, Office of chemical safety. Department of Health and Ageing pp 1-113.

Anonymous (2011). Dietary guidelines for Indian - a manual. National Institute of Nutrition, ICMR publication. pp 1-139.

Anonymous (2021). Retrieved 2021 June 14 from *https://www.statista.com/statistics/264065/global production-of-vegetables-by-type/*

Anonymous (2019). Retrieved 2021 June 14 from *https://www.agrifarming.in/brinjal-farming-profit-cost-yield income-eggplant*.

AOAC Method (2007). Official Methods of Analysis 2007.01, Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate. Retrieved 2021 march 14 from: *http://www.weber.hu/PDFs/QuEChERS/AOAC_2007_01.pdf*.

Ara, S, Nahar N, and Rahman M (2007). Incidence and damage estimation of brinjal shoot and fruit borer in five different brinjal varieties. Progressive Agriculture 18(2): 75-80. *http://doi.org/10.3329/PA.V18I2.18162*

Asensio-Ramos M, Hernandez-Borges J, Ravelo-Perez LM and Rodriguez-Delgado MA (2010). Evaluation of a modified QuEChERS method for the extraction of pesticides from agricultural, ornamental and forestal soils. Analytical and Bioanalytical Chemistry 396:2307-2319. *https://doi:.org/10.1007/s00216-009-3440-2*

Banerjee T, Agyani MK (2019). Risk assessment and persistence evaluation of Spiromesifen 240 SC on cucumber in India. International Journal of Postharvest Technology and Innovation 6(1):11-25. *https://doi.org/10.1504/IJPTI.2019.104175*

Borkakati RN, Venkatesh MR, Saikia DK (2019). Insect pests of Brinjal and their natural enemies. Journal of Entomology and Zoology Studies 7(1): 932-937.

Central Insecticide Board and Registration committee (2020) Approved Uses of Registered Insecticides Major uses of pesticides registered under the Insecticides Act, 1968. Retrieved 2020 March 16 from *http://ppqs.gov.in/sites/default/files/major_use_of_pesticides_insecticides.pdf*

Cork A, Alam SN, Talekar K, Talekar NS (2005). Development and commercialization of mass trapping for control of eggplant borer, Leucinodes orbonalis in South Asia. Indian Institute of Vegetable Research. *http://doi.org/10.1079/ber2005389*

EPA Environmental Protection Agency (2013). Retrieved 2021 June 30 from *https://www.federalregister.gov/documents/2013/01/16/2013-00728/spiromesifen-pesticide-tolerances*

European Food Safety Authority (EFSA) (2019). Retrieved 2021 June 19 from *https://efsa.onlinelibrary.wiley.com/doi/full/10.2903/j.efsa.2019.5579*

The Food and Agriculture Organization Corporate Statistical Database (FAOSTAT) (2019). Retrieved 2021 June 19 from *http://www.fao.org/faostat/en/#data/QI*

Food and Agriculture Organization (FAO) (2016). Retrieved 2021 June 19 from *http://www.fao.org/fileadmin/templates/agphome/documents/Pests_Pesticides/JMPR/Evaluation2016/SPIOMESIFEN.pdf*

Food and Agriculture Organization (FAO) (2016). Spiromesifen ADI. Retrieved 2020 October 6 from *http://www.fao.org/fileadmin/templates/agphome/documents/Pests_Pesticides/JMPR/Evaluation2016/SPIROMESIFEN.pdf*

Gautam M, Kafle S, Regmi B, Thapa G, Paudel S (2019). Management of brinjal fruit and shoot borer (*Leucinodes orbonalis* Guenee) in Nepal. Acta Scientific Agriculture 3(9):188-195. *http://doi.org/10.31080/ASAG.2019.03.0632*

Hoskins WM (1961). Mathematical treatment of loss of pesticide residues. Plant Protection Bulletin 9:163-168. *http://doi.org/10.12691/env-2-3-2*

Kissoum N, Soltani N (2016). Spiromesifen, an insecticide inhibitor of lipid synthesis, affects the amounts of carbohydrates, glycogen and the activity of lactate dehydrogenase in Drosophila melanogaster. Journal of Entomology and Zoology Studies 4(1):452-456.

Hlihor RM, Pogacean MO, Rosca M, Cozma P, Gavrilescu M (2019). Modelling the behavior of pesticide residues in tomatoes and their associated long-term exposure risks. Journal of environmental management 233:523-259. *http://doi.org/10.1016/j.jenvman.2018.11.045*

Malhat F, Abdallah H, Hegazy I (2012). Dissipation of chlorantraniliprole in tomato fruits and soil. Bulletin of Environmental Contamination and Toxicology 88:349-351. *http://doi.org/10.1007/s00128-011-150465-y*

Mate CJ, Mukherjee I, Das SK (2015). Persistence of spiromesifen in soil: influence of moisture, light, pH and organic amendment. Environmental Monitoring and Assessment. 187(2):1-12. *http://doi.org/10.1007/s10661-014-4207-6*

Naeem MY, Ugur S (20190. Nutritional content and health benefits of eggplant. Turkish Journal of Agriculture-Food Science and Technology 29(7):31-36. *https://doi.org/10.24925/turjaf.v7isp3.31-36.3146*

Patil VM, Singh S, Patel KG, Patel ZP (2018). Effect of sun drying and grinding on the residues of six insecticides in chilli fruits. Pesticide Research Journal 30(2):140-6. *https://doi.org/10.5958/2249-524X.2018.00023.7*

Raj MF, Solanki PP, Singh S, Vaghela KM, Shah PG, Patel AR, Diwan KD (2012). Dissipation of spiromesifen in/on okra under middle Gujarat conditions. Pesticide Research Journal 24(1):25-27.

Ramasubramanian T, Paramasivam M, Salin KP, Jayanthi R (2012b). Dissipation kinetics of chlorantraniliprole in soils of sugarcane ecosystem. Bulletin of Environmental Contamination and Toxicology 89(6):1268-1271. *https://doi.org/10.1007/s00128-012-0855-9*

SANTE (2017) Guidance document on analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Retrieved 2020 October 5 from *https://www.eurl-pesticides.eu/docs/public/tmplt_article.asp?CntID=727*

Sharma KK, Mukherjee I, Singh B, Mandal K, Sahoo SK, Banerjee H, ... Patel AR (2014). Persistence and risk assessment of spiromesifen on tomato in India: a multilocational study. Environmental Monitoring and Assessment 186(12):8453-61. *https://doi.org/10.1007/s10661-014-4016-y*

Sharma KK, Rao CS, Dubey JK, Patyal SK, Parihar NS, Battu RS, Sharma V, Gupta P, Kumar A, Jaya M, Singh B (2007). Persistence and dissipation kinetics of spiromesifen in chili and cotton. Environmental Monitoring and Assessment. 132(1):25-31. *https://doi.org/10.1007/s10661-006-9499-8*

Sharma KK (2013). Pesticide residues analysis manual, IARI, New Delhi, pp 92-94.

Solanki VH, Singh S, Gandhi KD, Patel KG and Patel KN (2019). Persistence behaviour of pre-mix formulation of profenophos and cypermethrin in/on sapota fruit. International Journal of Current Microbiology and Applied Sciences 8(1):1250-1260. *https://doi.org/10.20546/ijcmas.2019.801.132*

Vinothkumar B, Shibani PV, Kaviya R, Kowshika J (2018). Dissipation pattern of spiromesifen in/on brinjal fruits. International Journal of Chemical Studies 6:2485-2488.