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Residue analysis of premix formulation of fipronil and imidacloprid and its metabolites in hot pepper (*Capsicum annum*)

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ABSTRACT

A field experiment was conducted during 2018–19 and 2019–20 at Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana to assess the dissipation pattern of a ready mix formulation i.e. fipronil and imidacloprid along with their metabolites in fruits of hot pepper (*Capsicum annum* L.). The Hot pepper variety Kranti was used for the study. Quantitative analysis was done on gas liquid chromatography (GLC) and high pressure liquid chromatography (HPLC) for fipronil and imidacloprid with their metabolites, respectively. At the suggested dose, fipronil residues were lower than 0.01 mg/kg in the studied years. However, in double doses, the total residues of fipronil were detected on the 5th (0.071 mg/kg) and 3rd (0.043 mg/kg) day for the 1st and 2nd year following drench application. Imidacloprid was detected only in the subsequent year's trial in double doses. Residual leftovers of imidacloprid metabolite (6-CNA) were lower than 0.01 mg/kg (LOQ). No residual leftovers were present in fully ripened red chilli and harvest time samples of soil.

Keywords: Combination product, Drench application, Green pepper, LOQ, Metabolites

Application of synthetic chemicals (pesticides, fertilizers, etc.) has protected the nutritional integrity of food thus facilitating the produce storage for year-round supplies (Kurubetta *et al*. 2018). However, non-judicious application of chemicals (pesticides) may result in contamination with their residues in agricultural produce, soil, water, and atmosphere. To reduce the pesticide residues in vegetables, pesticides should be applied in a mixture or combination whose efficacy needs to be assessed before their application.

Hot pepper (*Capsicum annum* L.) is damaged by different insects with thrips, mites, and pod borer being the serious threats for which different pesticides are applied (Jyot *et al*. 2013). Due to the resistance developed because of their continuous use, the application of mixed formulation is recommended for controlling insect-pests effectively with almost no resistance. A combination product named Lesenta 80 WG containing two insecticides (Fipronil 40% + Imidacloprid 40%) has been introduced by M/s Bayer Crop Science Limited having different modes of action to control sucking and piercing insect-pests and approved by CIBRC for its use within India (CIBRC 2021).

Fipronil of the Phenyl Pyrazole family, blocks the chloride channels of GABA-gated and glutamate-gated, resulting in hyper-excitation of nerves and muscles of insects. Fipronil, after being metabolized, produces sulfide-MB45950 by reduction (Ramesh and Balsubramanian 1999), sulfone-MB46136 *via* oxidation (Ngim and Crosby 2001, Anastassiades *et al*. 2003) and desulfinyl-MB46513 through photolysis (Hainzi and Casida 1996). As per USEPA 1996 report metabolite desulfinyl is more constant and lethal than the fipronil.

Imidacloprid, a neonicotinoid, acts on the CNS of insects and blocks nicotinergic neuronal pathway. It prevents acetylcholine from transmission between nerves, resulting in paralysis and death of insects. Imidacloprid gets converted into 6-chloronicotinic acid (6-CNA) by photo degradation. However, different researchers in various vegetables (Varghese *et al*. 2015, Mukherjee *et al*. 2021) but to our best knowledge have reported the dissipation behaviour of fipronil and imidacloprid, no/little study is available in the literature on the behaviour of combination product of them applied through drench application. A trial was thus carried out consecutively for two years (2018–19 and 2019–20) on hot pepper, to evaluate the persistence of Lesenta 80 WG, along with their toxic metabolites after drench application.

MATERIALS AND METHODS

Field experiment: A field experiment was conducted during 2018–19 and 2019–20 at Chaudhary Charan Singh

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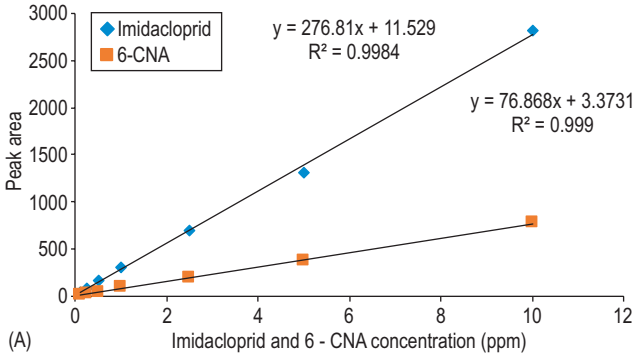
Haryana Agricultural University, Hisar, Haryana. Sowing of hot pepper cv. Kranti was done in the month of February in flat nursery beds to raise seedlings as per recommended in Package of Practices. Seedlings of hot pepper were transplanted in each plot of size 5 m × 5 m keeping proper line (45 cm) and plant (30 cm) spacing. From the time of sowing to till harvest climatic conditions was favourable having an average minimum temperature of 24.4°C. The average maximum temperature was recorded to be 40.8°C whereas the average relative humidity was recorded to be 57%. Roots of hot pepper plants were drenched using ready-mix formulation of fipronil 40% WG + imidacloprid 40% WG through irrigation system @500 and 1000 g/ha, respectively at fruiting stage.

Chemicals: All the standards having purity more than 98% and the formulation mixture (Lesenta 80 WG) were provided by the firm Bayer Crop Sci. Ltd., Bangalore (India). Standard stock solution (400 mg/kg) of fipronil, its metabolites, imidacloprid and 6-CNA were prepared individually in respective solvents. The standard stock solution was diluted further to obtain working standards of 1.0, 0.5, 0.25, 0.1, 0.05 and 0.01 and 10, 5, 2.5, 1, 0.5 and 0.1 µg/ml, respectively for verifying the purity and precision of standard reference material (SRM) using one-dimensional curve (Fig. 1A and 1B). No additional peak assures that SRM is pure and can be used for recouping the fruits of hot pepper and soil samples without spray.

Fruit samples (approximately 1 kg) were collected in carry bags at the time intervals of 0 (2 h afterwards of drenching), 1, 3, 5, 7, 10, 15, 20 and 30 days. Samples were brought to the laboratory for residue analysis and chemical analysis. Small bits of green chilli fruits were cut, macerated in to mixer to make the mush, 20 g of the fruit mush was used to extract the insecticide residues with acetone (100 ml) by shaking them for one and a half hours on an electric shaker. Filtrate was partitioned twice, first with dichloromethane and then with n-hexane. After partitioning samples were concentrated on a rotavapor until dry. The chemical leftover was reconstituted with n-hexane and acetonitrile. The final extract *per se* obtained was passed through filter of 0.2 µm PTFE and examined on gas liquid chromatography (GLC) and high pressure liquid chromatography (HPLC).



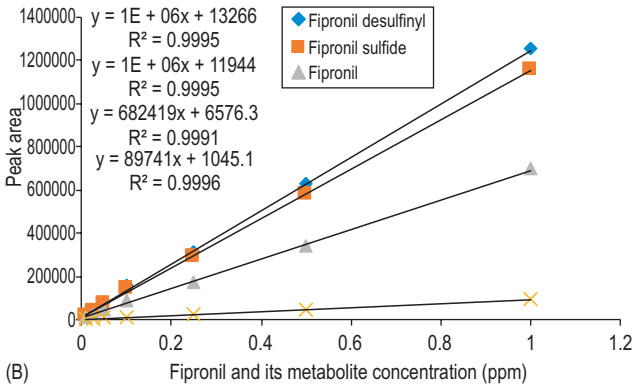


Fig. 1 Linearity curve of (A), Imidacloprid and 6-CAN; (B), Fipronil and its metabolite.

After 30 days of the treatment with the ready-mix formulation, soil samples were collected. The solid-phase extraction method of Kumari *et al*. (2008) was used. Soil sample (15 g) was meticulously blended along activated charcoal and florisil, 0.3 g each. The combined sample was placed in a glass column between two layers of stationary phase made of 10 g of anhydrous sodium sulfate each, and a mobile phase ratio 9:1 v/v consisting of 125 ml of n-hexane and acetone was employed for elution. The collected eluate was dried completely with the help of a rotavapour and remake with n-hexane and acetonitrile for the residue analysis.

Instrument used and method validation

Gas-liquid chromatography: Fipronil leftover and its degraded product were evaluated by using GLC **(**Model Shimadzu 2010 plus). Flow of mobile phase/carrier gas (N_2) was kept 60 ml/min and the temperatures for injector, column and detector were set at 280, 150 and 300°C. One microlitre aliquot of 1 ppm concentration was injected into injector port. Under these conditions, fipronil was obtained at a retention time (R_t) of 18.5 min, whereas its metabolites MB046513, MB045950 and MB046136, were obtained at 15.5, 18.2 and 20.1 min, respectively (Fig. 2A). The quantification limit (LOQ) and the detection limit (LOD) for fipronil and its degraded product was 0.01 mg/kg and 0.003 mg/kg, respectively. Laboratory temperature (<22ºC) and relative humidity (<60%) was maintained by using air-conditioner and under these conditions analysis was performed.

Reverse phase liquid chromatography: The chemical leftover of imidacloprid and 6-CNA were estimated by using reverse-phase HPLC (Model 1260 infinity by Agilent) equipped with photo diode array detector at 270 nm. Sample was injected in a C18 column (RP18) having particle size 5 µ pore size 80 µ, inner diameter of column 4.6 mm, length: 250 mm and carbon load 1%. Mixture of ACN and water in the ratio of 40:60 was used as a mobile phase, mode was kept as isocratic and 0.3 ml/min flow rate was maintained. Retention time (R_t) was 13.90 and 5.52 min for imidacloprid and 6-CNA, respectively (Fig. 2 B, C).

Linearity: A sequence of working solutions of different concentrations, i.e. 10–1000 ng/ml was prepared for fipronil and its metabolite, for imidacloprid and its metabolite concentration ranged from 50–5000 ng/ml. For obtaining

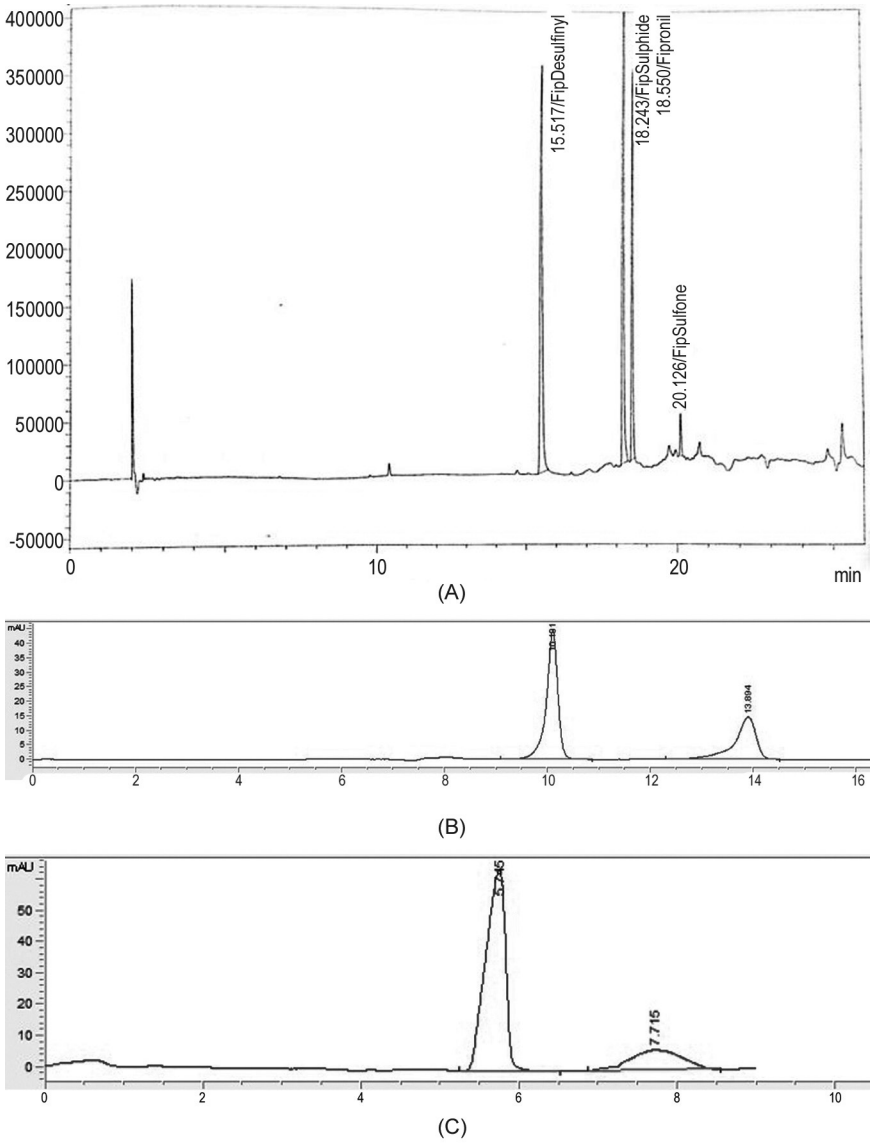


Fig. 2 Chromatogram of standards fipronil and its metabolites by GC (A); imidacloprid by HPLC (B); and 6-CNAby HPLC (C).

the good linearity each concentration was replicated five times. Calibration carried by the external standard method (Fig. 1 A, B).

Recouping experiment for hot pepper and soil: To ascertain the effectiveness of the extraction process, green/hot pepper and soil samples were treated with imidacloprid, 6-CNA, and fipronil at five distinct concentrations. The blanks samples were treated as per above said methodology to evaluate any interference from substrate in the sample.

LOD, LOQ and precision: The lower quantification limit (LOQ) was set at ten times the noise (S/N = 10, LOQ), whereas the lower detection limit (LOD) was set at a value equal to three times the noise (S/N = 3, LOD). Lower LOD and LOQ for fipronil, its metabolite, imidacloprid and 6-CNA were found to be 0.003 and 0.01 mg/kg. LOD is always kept lower then level of quantification because co-extractives are associated with matrix which intrudes with the elution of analyte.

Relative standard deviation ≤5% for analysis of replicates (n=5) on the same day known as repeatability and on separate days' term as reproducibility indicated the preciseness of the method.

RESULTS AND DISCUSSION

Recovery of insecticides: Overall recoveries obtained were more than 70% for all the insecticides (Table 1). As per Sante (2017), satisfactory results (within a specified range of ≤20%) were obtained at all the concentrations in hot pepper (Sante 2017). The linearity of MB06513, MB045950, fipronil and MB046136 was achieved with a R^2 value of 0.999, while for imidacloprid and 6-CNA, the value of R^2 was 0.998 and 0.999, respectively (Fig. 1).

Dissipation and Persistence

Fipronil with metabolites: In consecutive years, fipronil with metabolites, viz. MB06513, MB045950 and MB046136, were not detected @500 g/ha but @1000 g/ha residues were detected in both the years. During 2018–19, the residues of fipronil and MB046136 were found to be present on the 5th day of application (0.025 and 0.046 mg/kg), and dissipated lower than quantification limit on 15 and 20 days after application. The other two metabolites, viz. fipronil desulfinyl (MB06513) and fipronil sulfide (MB045950) were not detected even at higher dose. In the year 2019–20, the translocated residues of fipronil, MB045950 and MB046136) were present on the 3rd day of application (0.01, 0.01 and 0.023 mg/kg) at higher dose, whereas MB06513 was found to be present on the 7th day of application (0.02 mg/kg). On 10th day, all the residues reached below the level of 0.01 mg/kg except MB046136, where lower quantification limit reached on 15th day (Table 2). Aruna *et al*. (2015) studied the persistence behaviour of fipronil and its metabolites in citrus fruit of mandarin variety. Fipronil 80 WG @60 and 120 g a.i./ha was sprayed at the fruit formation initiation stage twice at an interval of 10 days. It was found that the total initial deposits (fipronil including metabolites) were 0.41 and 0.75 mg/kg at the suggested dose and double the suggested dose, respectively. The residues reached below the detection level of 0.005 mg/kg on the 15th and 20th day of the last application. Sunayana *et al*. (2014) also studied the persistence behaviour of fipronil and its metabolites in hot pepper. The total fipronil (fipronil and

Table 1 Recovery of insecticides and their metabolites in hot pepper and soil

Spiking concentration (mg/kg)	Fipronil	Fipronil desufinyl (MB046513)	Fipronil sulphide (MB045950)	Fipronil sulphone (MB046136)	Imidacloprid	6-CNA
	Percent recovery ± SD					
	Hot pepper					
0.01	73.20±0.95	104.42±3.19	103.17±2.97	81.47±0.75	83.32±1.83	-
0.05	81.70±3.21	107.20±1.76	107.90±1.06	104.63±4.37	85.54±3.94	87.07±1.87
0.10	75.57±2.40	106.30±1.39	109.27±1.57	108.70±0.80	90.71±1.69	89.04±1.68
0.25	81.53±1.88	92.57±2.97	98.97±1.36	109.37±0.64	93.26±1.88	92.21±3.04
0.50	87.53±1.82	101.10±2.71	100.73±1.16	106.00±2.65	97.58±1.92	98.84±1.25
	Soil					
0.01	83.87±1.16	81.09±1.18	82.17±2.00	81.47±0.75	81.98±2.33	-
0.05	92.03±3.15	90.20±0.89	90.23±1.03	88.63±3.01	84.87±3.00	85.73±0.50
0.10	77.20±1.95	83.63±2.01	82.17±2.03	85.03±1.33	93.04±1.76	94.04±3.53
0.25	83.20±1.76	89.57±1.88	89.30±1.59	86.82±1.13	93.26±1.88	92.21±3.04
0.50	94.53±3.55	96.10±2.31	95.73±3.85	96.00±2.65	91.58±1.07	96.84±1.88

its metabolites) average initial deposits were found to be 0.409 and 0.808 mg/kg for suggested (50 g a.i./ha) and double the suggested dose (100 g a.i./ha), respectively. Desulfinyl was the main metabolite of fipronil followed by sulfone and sulfide. Matadha *et al*. (2019) applied the fungicide mixture fluopyram 17.7% + tebuconazole 17.7%, via soil application and studied its uptake by roots and its distribution in stem, leaves and fruits of tomato and sweet pepper plant tissues. The behaviour of compounds present in Luna was almost similar, and the distribution of the residues in the plant system was found to be greater in roots followed by leaves, stems and fruits. The limit of detection (LOD) and quantification (LOQ) of the method were determined as 1.5 µg/ kg and 0.005 mg/kg, respectively. A drench application of the formulation mixture in the soil was done by Sharma (2018) to study the persistence behaviour of fipronil and imidacloprid. Residues of fipronil along with its degrading products were discovered on 3rd day after drench application at both the rates of application (500 and 1000 g/ha). The residues initially increased, then decreased and finally reached below LOQ on 25th day after application at both doses.

Imidacloprid and 6-CNA: At a rate 500 g/ha no residues of imidacloprid and 6-CNA were discovered till harvesting in both the years. But during 2018–19, the initial residues of imidacloprid @1000 g/ha were found to be 0.076 mg/kg on the 5th day which got dissipated further. On the 15th day, the residues were found lower than quantification limit. In 2019–20 also, imidacloprid shows similar behaviour when applied @g/ha 1000 and detected on the 5th day (0.137 mg/kg) which dissipated with time, residues become lower than quantification limit at 15 days after treatment. Imidacloprid metabolite (6-CNA) residues were not detected at any dose (Table 2). Aruna *et al.* (2015) studied the persistence behaviour of fipronil and its metabolites in citrus fruit of mandarin variety. Fipronil 80 WG @60 and 120 g a.i./ha was sprayed at the fruit formation initiation stage twice at an interval of 10 days. It was found that the total initial deposits (fipronil including metabolites) were 0.41 and 0.75 mg/kg at the suggested dose and double the suggested dose, respectively. The residues reached below the detection level of 0.005 mg/kg on the 15th and 20th day of the last application. Sunayana *et al*. (2014) also studied the persistence behaviour of fipronil and its metabolites in hot pepper. The total fipronil (fipronil and its metabolites) average initial deposits were found to be 0.409 and 0.808 mg/kg for suggested (50 g a.i./ha) and double the suggested dose (100 g a.i./ha), respectively. Desulfinyl was the main metabolite of fipronil followed by sulfone and sulfide. Matadha *et al*. (2019) applied the fungicide studied fluopyram 17.7% + tebuconazole 17.7%, through soil drench and studied its uptake by roots and its distribution in stem, leaves and fruits of tomato and sweet pepper plant tissues. The behaviour of compounds present in Luna was similar, and the residues in the plant system was found to be greater in roots followed by leaves, stems and fruits. LOD and LOQ of the method were determined as 1.5 µg/kg and 0.005 mg/kg, respectively. A drench application of the formulation mixture in the soil was done by Sharma (2018) drenched the hot pepper field with the formulation mixture and found that the imidacloprid residues were found to be 0.280 mg/kg @500 g/ha and 0.443 mg/kg on the 3rd day after application and become less than quantification limit on 15th and 20th day at respective application rate. No residue of 6-CNA was found to be present under any of the applied doses. Dubey *et al*. (2006) applied imidacloprid in the apple tree basin @890 and 1780 g a.i./ha and it translocated to fruits on the 10th day of application. After 30 and 40 days of application, residues get diminished and not detected. Sur and Stork (2003) studied the uptake and translocation behaviour of imidacloprid in various plants and found that after uptake, imidacloprid translocated acropetally within the xylem and

Table 2 Residues of fipronil and imidacloprid along with their metabolites in hot pepper and soil samples during 2018–19 and 2019–20

Days after Application	Fipronil		Fipronil desufinyl (MB046513)		Fipronil sulphide (MB045950)1		Fipronil sulphone (MB046136)		Total residues		Imidacloprid		6-CNA	
	Suggested dose (500 g a. i./ha)													
	2018–19	2019–20	2018–19	2019–20	2018–19	2019–20	2018–19	2019–20	2018–19	2019–20	2018–19	2019–20	2018–19	2019–20
0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
15	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
20	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
30 (red chilli at harvest)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
30 (soil at harvest)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Double the suggested dose (1000 g a. i./ha)													
0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
3	<LOQ	0.01	<LOQ	<LOQ	<LOQ	0.01	<LOQ	0.023	<LOQ	<LOQ	<LOQ	0.01	<LOQ	<LOQ
5	0.025	0.034	<LOQ	0.01	<LOQ	0.01	0.046	0.139	0.071	<LOQ	0.076	0.137	<LOQ	<LOQ
7	0.034	0.02	<LOQ	0.02	<LOQ	0.01	0.075	0.103	0.109	<LOQ	0.065	0.098	<LOQ	<LOQ
10	0.011	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.027	0.026	0.038	<LOQ	0.033	0.04	<LOQ	<LOQ
15	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.013	<LOQ	0.013	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
20	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
30 (red chilli at harvest)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
30 (soil at harvest)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Limit of quantification (LOQ) = 0.01 mg/kg; *values are average mean of three replicates.

degraded fast in the plant system.

Residues in red hot pepper and soil: The residues of the applied formulation at harvest were lower than quantification limit (<0.01 mg/kg) in ripe fruits of hot pepper as well as in soil samples (30 days after last application) in consecutive years (Table 2). Similar results were reported by Sharma (2018). The soil samples collected by Dubey *et al*. (2006) after 40 days of the application of imidacloprid in the apple tree basin at suggested and double the suggested dose were found to contain residues in the range of 0.14–3.61 mg/kg.

After drenching the hot pepper field with ready-mix formulation at prescribed and double of prescribed dose in consecutively years. of 2018–19 and 2019–20, it was found that the residues of fipronil were lower than quantification limit (0.01 mg/kg) at prescribed dose. Residues of fipronil appear on the 5th and the 3rd day after drenching at double dose of ready-mix formulation in 2018–19 and 2019–20, respectively. Imidacloprid was detected only in the 2nd year trial when applied at double of prescribed dose. Residue of 6-CNA was detected lower then quantification (0.01 mg/kg). No residues were detected in soil and fully ripened pepper collected at reap. So, it can be concluded that the premix formulation having the combined mixture of fipronil and imidacloprid can be used at the suggested dose in hot pepper had less persistence in the crop produce.

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