Plant Archives Vol. 25, Supplement 1, 2025 pp.838-845 e-ISSN:2581-6063 (online), ISSN:0972-5210

Plant Archives

Journal homepage: http://www.plantarchives.org
DOI Url : https://doi.org/10.51470/PLANTARCHIVES.2025.v25.supplement-1.112

PERSISTENCE OF TEBUCONAZOLE AND COMBINATION OF FIPRONIL AND IMIDACLOPRID IN CHILLI SOIL AFTER SPRAYING APPLICATION

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(Date of Receiving : 18-08-2024; Date of Acceptance : 12-10-2024)

ABSTRACT

The present investigation was conducted in the Department of Entomology, Dr. YS Parmar University of Horticulture and Forestry, Nauni, Solan (H.P). Persistence of tebuconazole and combination of fipronil + imidacloprid in chilli field soil was studied following the application at single dose 215 and 50 + 50 g a.i. ha^{-1} and double dose 430 and 100 + 100 g a.i. ha^{-1} after spray, respectively. Spray application on the crop leads to initial deposits of tebuconazole, ∑fipronil and ∑imidacloprid in soil as 0.104, 0.105 and 0.103 mg kg^{-1} at single dose and 0.204, 0.198 and 0.209 mg kg^{-1} at double dose, respectively. The samples were extracted with acetonitrile and cleaned up using a modified QuECheRS technique. The residues of tebuconazole, ∑fipronil and ∑imidacloprid were analysed on GC-ECD (Gas Chromatography- Electron Capture Detector, GC-MS (Gas Chromatography-Mass Sphectrometry) and HPLC (High Performance Liquid Chromatograph). The limit of quantification for tebuconazole, fipronil and imidacloprid was calculated to be 0.05, 0.001 and 0.05 mg kg^{-1}, respectively.
Keywords: Chromatography, Dissipation, Tebuconazole, Fipronil, Imidacloprid, Metabolites.

Introduction

Chilli (*Capsicum annuum* L.) serves as a significant vegetable and commercial spice crop cultivated across tropical and sub-tropical regions globally. Referred to as "red pepper," it holds a prominent position as a cash crop in India, primarily valued for its pungent fruits utilized in both immature and mature stages to enhance the spiciness of culinary preparations. Diverse cultivars are cultivated for various purposes such as vegetable spices, condiments, sauces, and pickles (Chaudhary, 2001). India stands out as a leading producer, exporter, and consumer of chilli worldwide, emphasizing its role as a crucial spice and vegetable crop within the country (Pathan *et al*., 2009). The crop is valued not only for its flavor but also for its nutritional content, including capsaicin, antioxidants, and vitamins A, C, and E, making it a key ingredient in daily meals, pickles, and chutneys (Kumar *et al*., 2000).

India ranks as the second largest global contributor to vegetable production, trailing only behind China with a 48% share, representing 14% of the total. In 2021-22, chilli was grown in an area of 400 thousand hectare in India with production of 4221 thousand metric tones (Anonymous, 2022). The low production of chilli is primarily due to insect pests and diseases. Key pests include chilli thrips (*Scirtothrips dorsalis*), yellow mite (*Polyphagotarsonemus latus*), and aphids (*Aphis gossypii*), while major diseases affecting the crop are powdery mildew (*Leveillula taurica*), fruit rot (*Colletotrichum capsici*), and bacterial wilt (*Pseudomonas solanacearum*). Farmers mainly use pesticides for control, with imidacloprid and fipronil proving effective against thrips, jassids, and aphids, and tebuconazole effective against powdery mildew and fruit rot (Tomlin, 1994). Tebuconazole, fipronil, and imidacloprid are systemic

pesticides that spread throughout all plant tissues, affecting any insects or fungal pathogens that come into contact with the plant. Tebuconazole, a triazole fungicide, inhibits fungal sterol biosynthesis by blocking demethylation. Fipronil, a phenyl pyrazole insecticide, targets pests by disrupting GABA-regulated chloride ion channels in neurons, causing uncontrolled central nervous system activity and death (Tingle *et al*., 2003). Fipronil degrades into various forms, including sulfide, sulfone, amide, and desulfinyl, with desulfinyl being notably more stable and toxic than the original compound (Hainzal and Casida, 1996; USEPA, 1998). Imidacloprid is a chloronicotinoid insecticide widely used to control a wide range of insect pests. Imidacloprid acts as a nicotinic acetylcholine receptor (nAchR) competitive modulator.

Pesticides have become one of the indispensable components in intensive agriculture with the aim of maximizing yields at all stages of crop cultivation. Widespread spread of pesticides for their toxic residues are found in different environments/materials (Kumari *et al*., 2002). Pesticide residues find their way into the human body through food, water and the environment. Once a crop is treated with pesticides, only 1% of the pesticides hit the target, and the remaining 99% ends up in the environment. In soil, pesticides affect soil fertility by killing microorganisms. These toxic xenobiotic molecules can affect the physical, chemical and biological properties of the soil and affect the microbial population in the soil (Beevi *et al*., 2014) which ultimately affects soil fertility. Pesticide persistence in soil is influenced by loss mechanisms such as microbial degradation, chemical hydrolysis, photolysis, volatility, leaching, and surface runoff (Wasim *et al*., 2008). Soil conditions like moisture, temperature, pH, and organic matter impact degradation by affecting microbial growth and activity. The duration of an insecticide's biological activity in soil is crucial to its toxicity. The present investigation was conducted with the aim to generate the tebuconazole, fipronil and imidacloprid dissipation data and their persistence in chilli field soil.

Material and Methods

Location and crop raising

The study was conducted in the Department of Entomology at Dr. Y. S. Parmar University of Horticulture and Forestry in Nauni, Solan, Himachal Pradesh. The experimental site is located at an elevation of about 1,200 meters above sea level (30°51'33" N latitude, 77°10'6" E longitude) and receives annual rainfall between 1100-1300 mm, mostly during the monsoon season (June-August). Seedlings of *Capsicum annuum* variety Dhaulakuan Chilli-8 were procured from the Krishi Vigyan Kendra of UHF Nauni at Kandaghat, Solan. Plots measuring 3×2 meters were prepared, and seedlings were transplanted at a spacing of 60cm ×45cm between rows and plants, respectively, following the university's recommended practices.

Treatments

Pesticides mentioned in Table 1 were evaluated for their persistence in chilli field soil.

The experiment was laid out in a randomized block design (RBD) having three replications for each treatment.

Table 1 : Pesticides application methods, doses and dates of application on the chilli crop

Pesticides	Method of application	Single dose (g a.i. ha^{-1})	Double dose (g a.i. ha^{-1})	Stage of crop for application	Source company
Fipronil 40% + Imidacloprid 40%	Foliar Spray	50 + 50	100 + 100	50% fruiting	Bayer CropScience Ltd.
Tebuconazole	Foliar Spray	215	430	50% fruiting	Bayer CropScience Ltd.

Pesticides were applied on chilli crop at fruit development stage and repeated after 10 days. Control plots (no pesticide treatment) were treated with water only. The pesticides were sprayed using a knapsack sprayer fitted with a solid cone nozzle. Spray application was done on a clear day, when there was a minimum wind and all the necessary precautions were taken to avoid drifting of pesticides to adjoining plots. Also, application of lower concentration of pesticide prior to their respective higher concentration was considered. The sprayer and measuring cylinder were washed thoroughly after each application to avoid the carryover of pesticide from one treatment to another.

Chemical and reagents

Preparation of Standard Solutions

The stock solution of tebuconazole and fipronil (400 mg/kg) were prepared in acetone: hexane (0.5:9.5, v/v) and further working standard solutions of 40, 10, and 1 mg/kg were prepared in n-hexane through serial dilution method. Similarly, stock solutions of imidacloprid (400 mg/kg) was prepared in HPLC grade acetone: acetonitrile (0.5:9.5, v/v) acetonitrile: water (30:70). Reagent blank was run along with the actual samples to ensure non-interference by solvents and reagents.

Soil sampling

Soil samples (1 kg) were taken from the spray site at intervals of 0, 1, 3, 5, 10, and 15 days. Soil samples were collected randomly from treatment and control plots at a depth of 0-5 cm at the time of sampling. Samples were placed on plastic sheets and dried in the laboratory at room temperature in the shade. The air-dried samples were broken by hand using a pestle and marble mortar, passed through a copper clay sieve with a serial number of 20 mm and thoroughly mixed to homogenize.

Soil extraction

Soil samples were analyzed by the QuEChERS method, which was modified for soil analysis (Asensio-Ramos *et al*., 2010). A representative 10 g of ground soil was taken in a 50 ml polypropylene centrifuge tube, in which 20 ml of acetonitrile was added and shaken for 1 min using a rotospin shaker. Then, 4g anhydrous magnesium sulfate and 1g sodium chloride was added and centrifuged at 3300 rpm for 3 minutes. After centrifugation, 10 ml of the supernatant was transferred to another 15 ml centrifugation tube containing 1.5 g of magnesium sulfate and 0.250 g of PSA, and shaken after 3 minutes. After shaking, the tube was sonicated for 3 minutes and then centrifuged at 4400 rpm for 10 minutes. A 4 ml supernatant aliquot from this tube was transferred to a turbo tube and evaporated to evaporation in a flow of air at 45° C. The dried residue was dissolved in 2 ml of n-hexane for dissolution (1µl) in GC -ECD/MS and the residue was dissolved (20µl) in HPLC in an acetonitrile:water solution (30:70).

Analysis

Tebuconazole residues were analysed using a Shimazdu GC-MS system (GCMS-QP 2010 plus) with a DB-5 capillary column (30m long, 0.25mm ID. and 0.25µm film thickness). The column operated in a multi ramp mode: an initial temperature of 80°C was held for 3 min., then raised to 180ºC @ 20°C min^{-1} (held for 2 min.), followed by an increase to 280°C @ 5°C min^{-1} with a 10 min. hold. The injection port, ion source, and interface temperatures were set to 250°C, 200°C, and 280°C, respectively with helium as the carrier gas at 1.02 ml min^{-1}. Residues were measured in Selected Ion Monitoring (SIM) mode using ions 125, 70, 250 and 83m/z, with a retention time of 25.193 min. for tebuconazole.

Estimation of fipronil and its metabolites residues

Fipronil and its metabolites were analysed using an Agilent 6890N GC equipped with DB-5 capillary column (30m length, 0.25mm ID. and 0.25µm film thickness) and an Electron Capture Detector (ECD). The column operated in a multi-ramp system: Initial oven temperature was set at 80º C for 3 min., raised to 180ºC @ 30ºC min^{-1} (held for 2 min.), then increased to 205°C @ 3º C min^{-1} for 0 min. and finally to 260°C @ 10º C min^{-1}, held for 15 min. The injection port and electron capture detector temperatures were set at 250°C and 300°C, respectively, with nitrogen gas flow at 1.00 ml min^{-1} as carrier gas. Retention times for fipronil, fipronil desulfinyl, fipronil sulfide and fipronil sulfone were 19.135, 15.947, 18.881 and 20.959 min., respectively.

Estimation of imidacloprid and its metabolite residues

Imidacloprid and 6-chloronicotinic acid residues were analyzed using a SHIMADZU LC-20AT Liquid Chromatograph with a DGU-20A5 degasser, SIL-20 AHT auto injector and SPD-M20A Photodiode Array Detector (PDA), paired with a Merck LiChrosorb® RP C18 (5µm) column (2.1 mm X 30 cm). The mobile phase, consisting of acetonitrile and water (30:70), was run in isocratic mode at a flow rate of 1 ml min^{-1}. Detection occurred at 270 nm, with retention times of 6.90 min. for imidacloprid and 3.9 min. for 6-chloronicotinic acid.

Validation of method

The method's validity and efficiency depend on the agreement between the actual analyte concentration in the sample and the measured value. The procedure was validated according to SANTE guidelines (Anonymous, 2019) focusing of linearity of calibration curve, recovery precision and limit of quantification (LOQ). Linearity was assessed by analyzing five replicates at four to five concentration levels: 0.05-0.50 mg kg^{-1} for tebuconazole and imidacloprid (plus its metabolite), and 0.05-1.00 mg kg^{-1} for fipronil (plus its metabolites) (Fig. 1, 2, 3). The correlation coefficient (R^2) was then calculated.

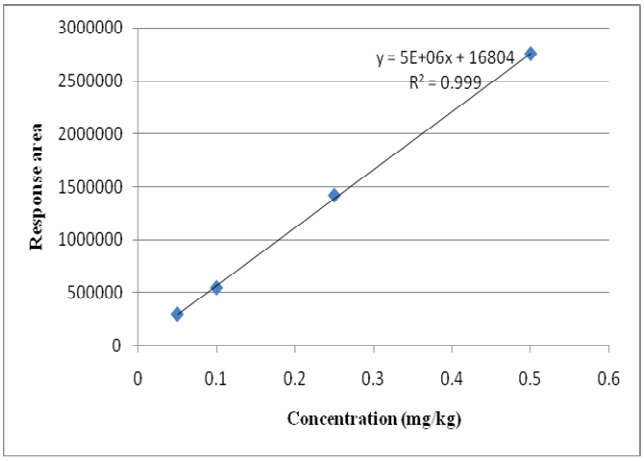

Fig. 1 : Linearity of tebuconazole

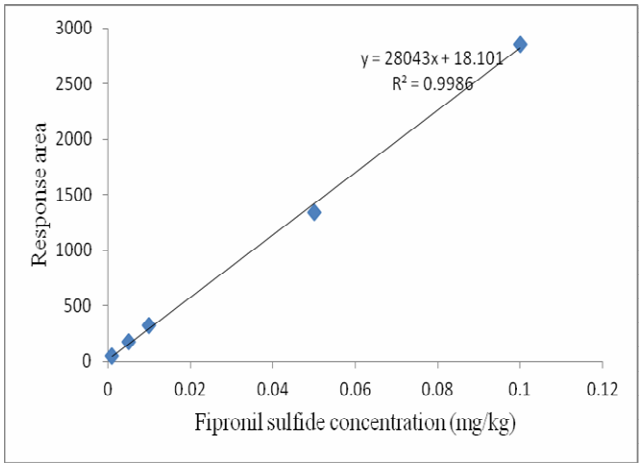

Fig. 2(c) : Linearity of Fipronil sulfide

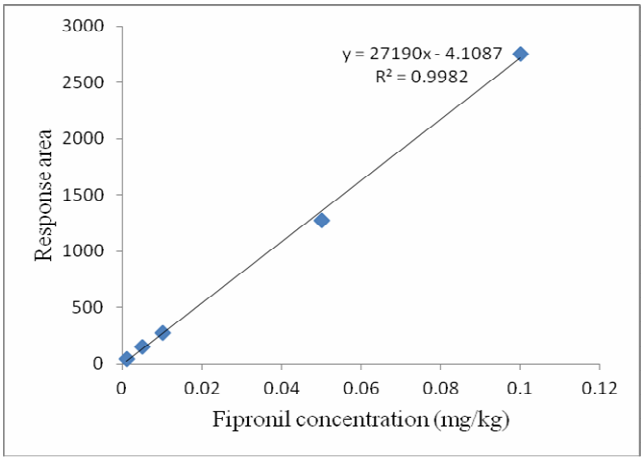

Fig. 2(a) : Linearity of Fipronil

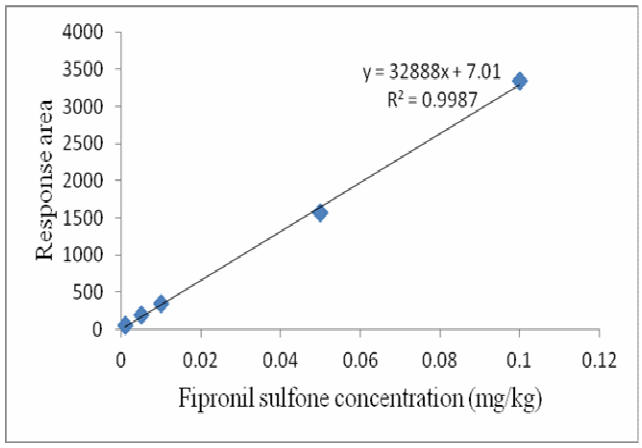

Fig. 2(d) : Linearity of Fipronil sulfone

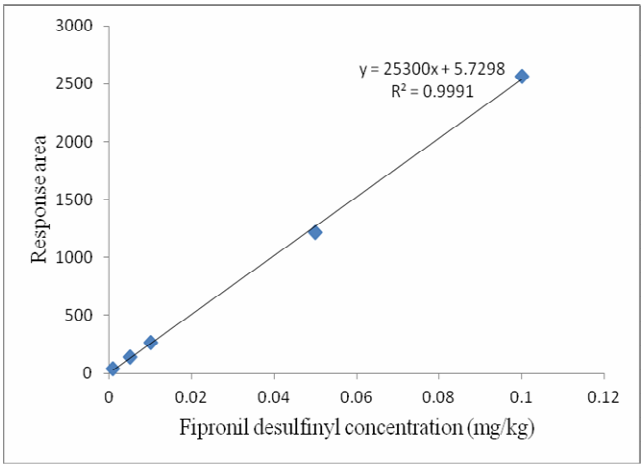

Fig. 2(b) : Linearity of Fipronil desulfinyl

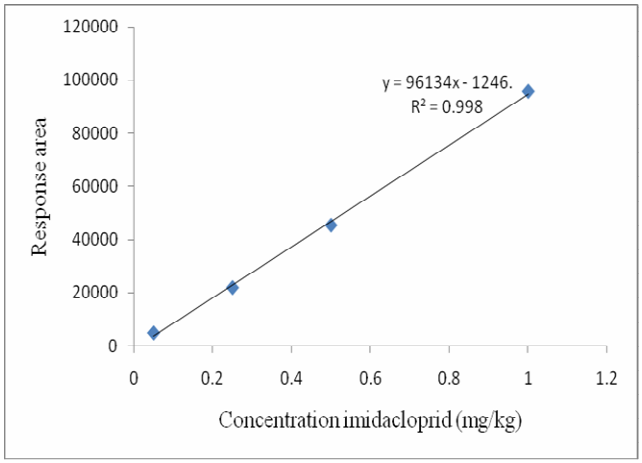

Fig. 3(a) : Linearity of imidacloprid

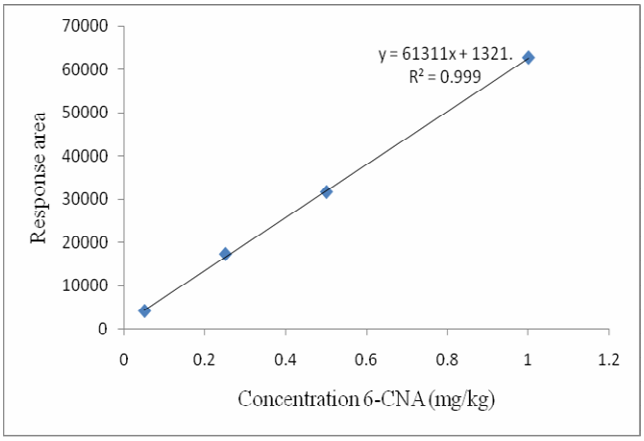

Fig. 3(b) : Linearity of 6-chloronicotinic acid

Result and Discussion

Method Validation

The linearity of tebuconazole, fipronil (and its metabolites) and imidacloprid (along with its metabolite 6-chloronicotinic acid) was expressed through the coefficient of determination (R^2), with values exceeding 0.99, indicating good linearity in accordance with SANTE guidelines (Anonymous, 2019). The LOQ values were 0.05 mg kg^{-1} for tebuconazole and imidacloprid (and its metabolite 6-CNA), and 0.001 mg kg^{-1} for fipronil (and its metabolites). The tebuconazole recovery from chilli field soil at fortification levels between 0.05 and 0.50 mg kg^{-1} ranged from 92.80 to 96.40 per cent (Table 2). This is consistent with findings of Wang *et al*. (2015), who reported tebuconazole recoveries from ginseng-cropped soil between 80.2 to 97.5 per cent. Fipronil recovery from fortified chilli field soil at levels of 0.001-0.100 mg kg^{-1} ranged between 90.00- 116.80 per cent with an overall recovery ranged between 90.00-116.80 per cent. The average recovery of fipronil metabolites viz., fipronil desulfinyl, fipronil sulfide and fipronil sulfone ranged from 90.00 to 115.10, 90.00 to 102.00, and 90.00 to 100.60 per cent, respectively (Table 3). These findings align with Mandal (2012), who reported fipronil and metabolite recoveries between 85.10 to 95.70 per cent in sugarcane-cropped soil, and Saini *et al.* (2014) who observed recoveries between 85.60 to 93.10 per cent in spiked soil at similar fortification levels. Imidacloprid recovery rates from chilli field soil at 0.05 to1.00 mg kg^{-1} ranged from 93.20 to 101.20 per cent, while its metabolite, 6-chloronicotinic acid recovery ranged from 78.50 to 98.00 per cent (Table 2). These findings are closely aligned with Akoijam (2014), who reported similar recovery rates for imidacloprid and its metabolite in various soil types spiked at different fortification levels.

Table 2 : Recovery of tebuconazole, Imidacloprid and 6-chloronicotinic acid from fortified soil

Fortification level (mg kg^{-1})	Tebuconazole		Imidacloprid		6-chloronicotinic acid	
	Amount recovered ± SD (mg kg^{-1})	Recovery (%)	Amount recovered ± SD (mg kg^{-1})	Recovery (%)	Amount recovered ± SD (mg kg^{-1})	Recovery (%)
0.05	0.048 ± 0.005	96.00	0.050 ± 0.003	100.00	0.049 ± 0.002	98.00
0.10	0.094 ± 0.009	94.00	-	-	-	-
0.25	0.232 ± 0.029	92.80	0.253 ± 0.009	101.20	0.222 ± 0.010	80.60
0.50	0.482 ± 0.063	96.40	0.466 ± 0.039	93.20	0.403 ± 0.027	78.50
1.00	-	-	0.992 ± 0.005	99.20	0.785 ± 0.013	98.00

Table 3 : Recovery of Fipronil and its metabolites from fortified soil

Fortification level (mg kg^{-1})	Fipronil		Fipronil desulfinyl		Fipronil sulfide		Fipronil sulfone	
	Amount recovered ± SD (mg kg^{-1})	Recovery (%)	Amount recovered ± SD (mg kg^{-1})	Recovery (%)	Amount recovered ± SD (mg kg^{-1})	Recovery (%)	Amount recovered ±SD (mg kg^{-1})	Recovery (%)
0.001	0.0009 ± 0.0001	90.00	0.0009 ± 0.0001	90.00	0.0009 ± 0.0001	90.00	0.0009 ± 0.0001	90.00
0.005	0.0054 ± 0.0003	108.00	0.0055 ± 0.0002	110.00	0.0051 ± 0.0003	102.00	0.0049 ± 0.0003	98.00
0.010	0.0106 ± 0.0002	106.00	0.0113 ± 0.0006	113.00	0.0098 ± 0.0003	98.00	0.0095 ± 0.0002	95.00
0.050	0.0569 ± 0.0016	113.80	0.0569 ± 0.0012	113.80	0.0486 ± 0.0009	97.20	0.0486 ± 0.0009	97.20
0.100	0.1168 ± 0.0021	116.80	0.1151 ± 0.0032	115.10	0.0987 ± 0.0015	98.70	0.1006 ± 0.0012	100.60

Dissipation and Persistence of pesticide after spraying on crop

Tebuconazole

The average initial deposits of 0.104 mg kg^{-1} in chilli field soil decreased to 0.050 mg kg^{-1} on the 1st day and decreased below the level of determination on the 3rd day of tebuconazole application @ 215 g a.i. ha^{-1} (Table 4). At double dose (430 g a.i. ha^{-1}), 0.204 mg kg^{-1} initial deposits were observed which decreased to 0.102 and 0.063 mg kg^{-1} on 1st and 3rd day, respectively, and reached below the determination limit in subsequent sampling intervals (Table 4).

Table 4 : Dissipation pattern of tebuconazole residues in chilli field soil after spraying chilli crop @ 215 and 415 g a.i ha^{-1}

Interval (days)	Tebuconazole			
	215 g a.i. ha^{-1}		430 g a.i. ha^{-1}	
	Mean residues (mg kg^{-1}) ± SD	Dissipation (%)	Mean residues (mg kg^{-1}) ± SD	Dissipation (%)
0	1.760 ± 0.100	-	2.784 ± 0.362	-
1	0.800 ± 0.084	54.54	1.783 ± 0.111	35.95
3	0.450 ± 0.039	74.43	0.892 ± 0.063	67.95
5	0.212 ± 0.025	87.95	0.483 ± 0.037	82.65
7	0.063 ± 0.007	96.42	0.231 ± 0.018	91.70
10	BDL	-	0.071 ± 0.012	97.44
15	BDL	-	BDL	-
Control	ND	-	ND	-

BDL = Below Determination Limit; ND = Not Detected

Fipronil

Spray application of fipronil resulted in initial soil deposits of 0.105 and 0.198 mg kg^{-1}, which decreased to 0.003 and 0.009 mg kg^{-1} by the 3rd day, showing dissipation rates of 97.14 and 95.45 per cent for single and double doses, respectively. Among the metabolites of fipronil, fipronil desulfinyl residues were initially 0.008 and 0.015 mg kg^{-1}, and declined to 0.001 and 0.002 mg kg^{-1} after one and three days for single and double doses, respectively (Table 5). Among the metabolites, fipronil sulfide residues were undetectable on the day of application at a single dose, but were present at 0.001 mg kg^{-1} at double dose. Fipronil sulfone residues were 0.001 and 0.005 mg kg^{-1} at single and double dose on the day of application, and these residues fell below detectable levels after one day (Table 5). However, the residues of parent molecule fipronil were 0.096 and 0.177 mg kg^{-1} at single and double dose, respectively on the day of application. At the single dose, residues persisted up to three days, while at the double dose, residues decreased to 0.018 and 0.009 mg kg^{-1} after one and three days, respectively (Table 5). Our result aligned with the finding of Saini *et al*. (2014) who reported that fipronil application at 50 g a.i. ha^{-1} resulted in initial soil deposits of 0.122 mg kg^{-1}, which reduced to 0.002 mg kg^{-1} over 90 days. However, at double dose, initial deposits of 0.193 mg kg^{-1} diminished to 0.005 mg kg^{-1} over the same period.

Table 5 : Persistence of fipronil and its metabolites residues in chilli field soil after spray application on the crop @50 and 100 g a.i ha^{-1}

Days	50 g a.i ha^{-1}					100 g a.i ha^{-1}				
	Fipronil desulfinyl	Fipronil sulfide	Fipronil	Fipronil sulfone	∑ Fipronil	Fipronil desulfinyl	Fipronil sulfide	Fipronil	Fipronil sulfone	∑ Fipronil
	Mean Residues (mg kg^{-1} ± SD)									
0	0.008± 0.001	BDL	0.096 ± 0.003	0.001 ± 0.001	0.105 ± 0.002	0.015 ± 0.002	0.001 ± 0.001	0.177 ± 0.004	0.005 ± 0.001	0.198 ± 0.004
1	0.001 ± 0.001	BDL	0.009 ± 0.001	BDL	0.010 ± 0.001	0.003 ± 0.001	BDL	0.015 ± 0.001	BDL	0.018 ± 0.001
3	BDL	BDL	0.003 ± 0.001	BDL	0.003 ± 0.001	0.002 ± 0.001	BDL	0.007 ± 0.001	BDL	0.009 ± 0.001
5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Control	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

BDL = Below Determination Limit; ND = Not Detected

Imidacloprid

Initial deposits of imidacloprid in chilli field soil were 0.103 and 0.209 mg kg^{-1}, which decreased to 0.055 and 0.051 mg kg^{-1}, showing 46.10 and 75.59 per cent dissipation after 1 and 3 days for single and double doses, respectively. Residues of imidacloprid were not detected in subsequent samples, and residues of 6-chloronicotinic acid levels were below detection limits (Table 6). The results are in close agreement with those of Sanyal *et al.* (2006), who reported 0.152 and 0.298 mg kg^{-1} imidacloprid residues in tea soil, persisting up to 5 and 7 days for standard and double doses, respectively. However, Sharma and Singh (2014) reported higher residues of imidacloprid and its metabolites at 4.29 and 7.81 mg kg^{-1}, respectively, in soil samples collected 7 days after application at 20 and 80 g a.i ha^{-1}, respectively.

Table 6 : Persistence of imidacloprid residues in chilli field soil after spraying chilli crop @ 50 and 100 g a.i. ha^{-1}

Days after last application	Imidacloprid			
	50 g a.i. ha^{-1}		100 g a.i. ha^{-1}	
	Mean residues (mg kg^{-1}) ± SD	Dissipation (%)	Mean residues (mg kg^{-1}) ± SD	Dissipation (%)
0	0.103 ± 0.002 (BDL)	-	0.209 ± 0.005 (BDL)	-
1	0.055 ± 0.005 (BDL)	46.60	0.091 ± 0.006 (BDL)	56.45
3	BDL (BDL)	-	0.051 ± 0.001 (BDL)	75.59
5	BDL (BDL)	-	BDL (BDL)	-
Control	ND		ND	

Values in parenthesis are residues of 6- chloronicotinic acid; BDL = Below Determination Limit; ND = Not Detected

Conclusion

The analytical method QuEChERS was validated for detection of tebuconazole, fipronil and imidacloprid in chilli for extraction followed by residue analysis using GC-MS for tebuconazole, GC-ECD for fipronil and HPLC equipped with PDA detector for imidacloprid. The limit of quantification for tebuconazole and imidacloprid was calculated to be 0.05 mg kg^{-1}, whereas for fipronil, it is 0.001 mg kg^{-1}. Residues of tebuconazole in chilli field soil persisted up to 7 and 10 days at single and double dose application. Residues of ∑fipronil persisted for 3 days after spraying at both the recommended and double the recommended dose, respectively. Imidacloprid residues persisted for 1 and 3 days at recommended and double the recommended dose, respectively in chilli field soil. Whereas, the residues of 6-chloronicotinic acid were undetectable from the start of sampling.

Acknowledgements

The authors are thankful to M/s Bayer CropScience, Maharashtra, India for providing the necessary analytical standards and formulated products during the study.

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