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Persistence of Fipronil Residues in the Cabbage Field Soil under Semi-arid Region of Rajasthan

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Fipronil is a phenyl pyrazole insecticide, which is used as broad spectrum insecticide to control pest such as diamondback moth, thrips, stem borers, leaf folder, termites, borers, jassids, and bollworms. A study was undertaken at Rajasthan Agricultural Research Institute, Durgapura, Jaipur during Rabi, 2020 to find out the persistence of fipronil residues in the soil of cabbage field, when sprayed at its recommended dose (5% SC, 40 g. a. i. ha^{-1}) and double of the recommended dose (5% SC, 80 g. a. i. ha^{-1}). The samples were extracted with acetonitrile and cleaned up using a modified QuEChERS method and the residues were analyzed by Gas Chromatography. The residue level of fipronil in cabbage field soil collected at harvest time of cabbage crop were below the detectable level (BDL) at the recommended dose and double of the recommended dose, respectively.

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1. INTRODUCTION

"Among crucifers cabbage (*Brassica oleracea* L. *var. capitata*) is one of the most important crop. It belongs to the family Cruciferae and the crop is mainly cultivated as the Rabi season crop in India. Total area of Cabbage in Rajasthan is 1171 hectare with annual production of 11040 MT" [1]. "It is being cultivated both in hills and plains and the reason is its wide adaptation to climatic range" [2]. It is one of the most popular nutritive vegetables in India, consumed both as raw and cooked form. It is grown throughout the year in India. Cabbage is a very rich source of all nutrients like vitamins viz., A, B1, B2 and C, minerals and best supporting component for protein, carbohydrates and antioxidants and it is consumed as both cooked and raw as salad.

"Reasons of low production of cabbage in the country could be attributed to many factors. The most important biotic factor causing considerable losses is, damage caused by various insect pests. Among all insect pest attack on cabbage, diamond back moth (*Plutella xylostella* L.) is the most destructive pest causes 52.00 per cent yield loss in crucifers" [3]. "The insect pest incidence in cabbage is commonly more during February to September, although it is noticed throughout the year. Insect pests are important biotic constraints in vegetable production in India, causing considerable losses" [4]. To mitigate the losses caused by insect pest a number of pest control methods is used by farmers. Chemical pest control being the most preferred strategy in practice, used in vegetables. Vegetables are important recipients of chemical pesticides in India. In order to meet the rising demands of vegetables for the increasing population, and to counter the impact of these insect pests, different types of pesticides are used [5]. To control insect pests damage in cabbage, farmers depend mainly on the application of insecticides like fipronil 05.00% SC (DBM), fipronil 80.00% WG (DBM), acetamiprid 20% SP (Aphids), carbofuran 03.00% CG (Nematode), flubendiamide 20.00% WG (DBM), chlofenapyr 10.00% SC (DBM), chlorantraniliprole 18.5% SC (DBM), chlorfluazuron 05.40% EC (DBM, Tobacco leaf eating caterpillar), chlorpyrifos 20.00% EC (DBM), cyantraniliprole 10.26% OD (Cabbage Aphid, Mustard Aphid), (DBM) [5,6]. "In cabbage, fipronil is found best effective for the management of DBM on cabbage" [7].

Fipronil is a member of a relatively new class of pesticides, the phenyl-pyrazole insecticide, is recommended and widely used as broad spectrum for foliar application and has a labeled claim for use in a large number of crops and effective against a wide range of crops Cabbage, chilli, cotton, grape and sugarcane and rice [8,9], insect pests and control pest such as rice stem borer, leaf folder, cockroaches, mosquitoes, locusts, ticks, and fleas at their larval and adult stages [10,11]. "It can be effectively delivered to the target pests via soil, foliar, bait, or seed treatment and is widely used to control many species of soil and foliar insects on various crops such as rice, vegetables and fruits" [12-15]. Fipronil acts on Central Nervous System of target insect and block GABA receptors (Ratra and Casida, 2001). Dissipation of fipronil in different crop soils have been reported in many crops, cabbage [4], cotton [16].

"In current decades, pesticide-fate studies have been a topic of significant interest around the world. The degradation process of pesticide in plants can be of physicochemical (volatilization, photolysis, hydrolysis, oxidation, etc.) or biochemical in nature" [17]. "Dissipation of pesticide is influenced by several factors, including plant growth (dilution), climatic factors like (rainfall, sunlight, temperature, etc.), application method of pesticide, uptake (of leaf, stem, and root), properties of pesticide, and possibly even plant species also" [18]. Numerous studies on the dissipation of pesticides, such as fipronil and others, in various vegetables grown elsewhere under various climatic circumstances and farming practises have been published. For instance, research has been performed in Spain [19], Canada [20], and India [21] often with different cultivars such as Chinese cabbage [22] mangoes [23] cowpeas [24] tomatoes [25] and pomegranates [26]. Above studies imply that the dissipation of different pesticides could be manipulated by using different cropping regimes. Insecticides applied on the crop ultimately get way into the soil. Pesticides in the soil rapidly act on the soil micro flora and fauna, beneficial microorganism, natural enemies, soil texture, resulting in deficient soil fertility and ultimately affect crop yield [27]. So persistence of these recommended insecticides in soil were studied out. So the present study was carried out to determine residue persistence of fipronil and its metabolites in cabbage field soil following treatment at the recommended dosage and double of the recommended dosage.

2. MATERIALS AND METHODS

2.1 Reagents and Instruments

Certified Reference Material (CRM) were procured from accu. Standard and all the solvents used were GC analytical grade. The chemicals acetone, acetonitrile, Na_2SO_4 (anhydrous Sodium Sulphate), primary secondary amine (PSA) and $MgSO_4$ (anhydrous Magnesium Sulphate) were used analytical regent grade and activated by heating at 30 0C for 12 hrs. and kept in desiccators. GC, Analytical balance, Mixer, Centrifuge and Turbovap-evaporator.

2.2 Experimental Design

The field experiment was conducted in (Rabi 2020-21) with four replications at Rajasthan Agricultural Research Institute, Durgapura, Jaipur, (Rajasthan) including untreated control.The experiment consist of three treatments viz. control, recommended dose of fipronil 5 SC (40 g. a. i. ha^{-1}) and double of the recommended dose fipronil 5 SC (80 g. a. i. ha^{-1}). All the essential good agronomic practices were also followed properly. There is no rainfall received during the whole experimental period. The first spray of insecticide was done at the fruit initiation stage using a hand operated knapsack sprayer and second spray after 10 days interval of first spray, and the control plots were sprayed with normal water at recommended dose (40 g. a. i. ha^{-1}) and double of recommended dose (80 g. a. i. ha^{-1}). Whereas one plot was left completely untreated and used for the sampling of soil as control in each treatment. It was ensured that the insecticide which is used for the investigation has not been used earlier in the experimental plot. About 1 kg of soil sample was collected randomly by quadrate method and from the control and treated plots of each treatments at the harvest time of cabbage crop. Analysis of fipronil and its metabolite residues in soil samples were estimated using a Gas Chromatography (GC) and confirmation on GC-MS column DB - 5 (30 m length, 0.25 mmID, 0.25 µm film thickness) and DB-1. The retention time of fipronil were observed to be 8.519 min and for metabolites MB 046513, MB 046136 and MB 045950 it is 6.594, 9.956, and 8.274 respectively. Soil samples were fortified with fipronil and its metabolites at different levels and analyzed.

2.2.1 Soil characteristic

Texture : loamy sand
pH : 8.1
EC : 0.19dSm-1
Organic carbon : 0.18% (Soil Laboratory, Rajasthan Agricultural Research Institute, Durgapura)

2.2.2 Sampling soil

“1 kg of soil samples Collected from the sprayed field of cabbage from each replication at the time of harvest for analysis. Soil samples were collected from the depth of 0-15 cm from each replication and treatment by quadrate method after removing surface left outs of crop and other material. After it samples were placed into separate plastic containers and allowed to shade dry at room temperature in the laboratory to remove lighten the moisture. The air dried samples were desegregated manually using a pestle and a marble mortar, passed through a No. 20 mm brass soil sieve and mixed thoroughly to achieve homogeneity of samples” [28].

2.2.3 Extraction QuEChERS

(Quick, Easy, Cheap, Effective, Rugged and Safe) a representative soil sample of 10 g were taken in a 50 ml centrifuge tube and added 20 ml acetonitrile. “For one minute test tube should be shaken vigorously, 4 g of magnesium sulphate and 1 g of sodium chloride (NaCl) were added. Citrate buffered medium (1g trisodium citrate dehydrate and 0.5 g of disodium hydrogen citrate sesquihydrate was added) to improve the recovery values. Centrifuge the sample at 3,300 rpm for 5 minutes and there is a layer of supernatant. 10 ml of the supernatant were taken into a 15 ml centrifuge tube and 1.5 g of magnesium sulphate and 250 mg PSA were for cleanup. The test tube was shaken for few seconds and then sonicated for 1 minute; and the tube was centrifuged for 10 minutes at 4,400 rpm. From the above centrifuge tube, 4 ml of aliquot were taken of and evaporated up to dryness using turbovap-evaporator at 40 ^{0}C and n-hexane washing was given two times to dissolve the residue. The dry residue was redissolved in 1 ml acetonitrile” [29]. In case, aqueous phase is noticed, little amount of anhydrous sodium sulphate were added and filtered through 0.22µ PTFE filters and samples was ready for analysis

2.3 Standards

The reference standard of fipronil obtained from Pesticide Residues Laboratory, Division of Entomology, RARI, Durgapura, Jaipur, Rajasthan, was used for quantification.

(a.) Standard stock solution: The analytical grade fipronil with 99.2% purity was dissolved in 100 ml volumetric flask with acetonitrile to get 1000 mg kg^{-1} standard stock solution.

(b.) Intermediates stock solution: "The standard stock solution was brought at room temperature and 1 ml of standard stock solution was transfer to 100 ml volumetric flask, made up the volume and shaken well to obtain a homogenous intermediates stock solution of 10 mg kg^{-1}. This was utilized for further fortification of samples" [28].

(c.) Working standard: "From the ready intermediate stock solution, after brining to room temperature, working standard of 0.01 to 1 mg kg^{-1} were prepared by serial dilution techniques and labeled graduated test tubs. The working standards were used to find out retention time of these compounds and for quantitative determination of residues in samples" [28].

2.4 Linearity and Recovery Study

Linearity studies were performed for fipronil and its metabolites (MB 046513), (MB 045950), and (MB 046136) with the concentrations of 0.01, 0.05, 0.10, 0.25, 0.50, 0.75 and 1 ppm. The soil samples were fortified at 0.001, 0.005 and 0.01 mg kg^{-1} for fipronil by adding required quantity of 10 mg kg^{-1} intermediates stock solution to work out the recovery percent of analytical methodology.

2.5 Analysis of Fipronil Residues

The detection and quantification of fipronil residue in soil was performed by GC. Prior to analyze of the sample extract, different concentrations of standard solution pesticides were prepared and injected properly in the instrument. Insecticide compound were qualitatively identified by comparing the retention time of peaks and quantitatively estimated on the basis of area of chromatograms obtained in each test sample with that of the analytical standard. Sample results were expressed in mg kg^{-1}. From this value of actual amount of insecticide residue presented in the sample was determined by using the following formula.

2.5.1 Residue in analyzed soil samples

% Recovery = Sample peak area/Standard peak area × 100

Wt. of sample Analyzed (g) = Sample wt. (10 g) X Aliquot taken (4 mL)/Volume of extract (20 ml) = 2g

Residues (ig/g) = Peak area (Sample) x Conc.std (ppm) x µL std. injected x Final volume of the sample (1 mL)/Peak area (Std) x weight of the sample (2 g) x µL of sample injected.

2.6 Statistical Analysis

"Statistical analysis was performed on Microsoft Excel-2016 (Microsoft Corporation, USA). All analysis was performed in triplicate and the results were expressed as mean ± SD" [28].

3. RESULTS AND DISCUSSION

3.1 Degradation Process

After field application of fipronil on plants it undergo through biological and chemical process like oxidation, reduction, hydrolysis and photodegradation which leads to degradation of it and change the paraental molecule into different metabolites like sulfone, desulfinyl, and sulfide [30]. Desulfinyl and sulfone have been reported as major metabolites which have more mammalian toxicity than fipronil and high environmental persistence [30,31]. However degradation process is dependent on type of soil, agro climatic conditions and nature of plant species.

3.1.1 Recovery

Prior to sample analysis a recovery study was also performed to ensure the reliability of the results for fipronil and its metabolites desulfinyl (MB046513), sulfide (MB045950), and sulfone (MB046136) of cabbage field soil samples. The soil samples were spiked with fipronil at three fortification levels 0.001, 0.005 and 0.01 mg kg^{-1} and analyzed as per the methodology described above. The results of the recovery studies are presented in Table 1. The mean recovery of fipronil at the fortification level 0.001, 0.005 and 0.01 mg kg^{-1} was 88.0, 88.6 and 88.4. The mean recovery of fipronil metabolites desulfinyl (MB046513), sulfide (MB045950), and sulfone (MB046136) were (89.3, 92.7, 91.6) (88.0, 93.1, 89.0) and (87.8, 90.2, 87.6) percent respectively in soil. Reddy et al. [4] reported that percent recovery of fipronil in cabbage field soil samples were 85.13 and 86.75 at of 0.01 and 0.1 ppm level of fortification respectively. Hence the present investigation is in concurrence with the earlier workers. According to the guidelines of [32], any analytical method which records the mean recovery in the range of 70-120 percent is accurate and precise for analysis. Hence, the method applied in the present study for the extraction of fipronil, and its metabolites from cabbage field soil was accurate and precise. Recovery test was done at pesticide residue laboratory, Rajasthan Agricultural Research Institute, Durgapura, Jaipur.

3.1.2 Residues

The residues of fipronil were confirmed by Gas Chromatography (GC). Residues of fipronil and metabolites in cabbage field soil at recommended dose and double of the recommended dose is presented in Table 2. Residues of fipronil and its metabolites in soil under cover of cabbage crop have been studied (obtained from three treatments i.e. control, recommended dose (40 g. a. i. ha^{-1}) and double of the recommended dose (80 g. a. i. ha^{-1}) are given in Table 2. The soil samples were collected at harvest time of cabbage crop. In cabbage field soil samples the residues of fipronil and its metabolites at harvest

Table 1. Percent recovery of fipronil and its metabolites in soil at different fortification levels

Level of fortification (mg kg^{-1})	Replications	Percent recovery in Soil			
		Fipronil	Metabolites		
			Desulfinyl (MB046513)	Sulfide (MB045950)	Sulfone (MB046136)
0.001	R_1	87.0	87.0	87.0	85.0
	R_2	85.0	89.0	89.0	91.0
	R_3	88.0	94.0	85.0	87.0
	R_4	92.0	87.0	91.0	88.0
Mean ± SD		88.0 ± 2.550	89.3±2.861	88.0±2.236	87.8±2.165
0.005	R_1	86.2	99.4	86.4	91.4
	R_2	91.4	90.2	98.1	86.1
	R_3	87.0	94.2	96.8	94.6
	R_4	89.8	86.8	91.2	88.6
Mean ± SD		88.6 ± 2.098	92.7±4.695	93.1±4.669	90.2±3.169
0.01	R_1	85.6	87.4	87.1	86.7
	R_2	86.2	89.7	89.5	88.5
	R_3	89.5	96.5	93.4	90.1
	R_4	92.3	92.7	85.9	85.2
Mean ± SD		88.4±2.697	91.6±3.408	89.0±2.865	87.6±1.846

Table 2. Residues (mg kg^{-1}) of fipronil and its metabolites (MB046513), (MB045950) and (MB046136) in soil under cabbage crop at recommended dose (40 g. a. i. ha^{-1}) and double of the recommended dose (80 g a. i. ha^{-1}).

Days	Replications	Fipronil (On both doses)	Fipronil metabolites (On both doses)		
Soil control			Desulfinyl (MB046513)	Sulfide (MB045950)	Sulfone (MB046136)
		Average* residues ± SD	Average* residues ± SD	Average* residues ± SD	Average* residues ± SD
	R_1	ND	ND	ND	ND
	R_2	ND	ND	ND	ND
	R_3	ND	ND	ND	ND
	R_4	ND	ND	ND	ND
Soil at harvest time	R_1	ND	ND	ND	ND
	R_2	ND	ND	ND	ND
	R_3	ND	ND	ND	ND
	R_4	ND	ND	ND	ND

ND = Not Detected *******Average of four replications* time of cabbage crop was not detected in the samples of recommended dose (40 g. a. i. ha^{-1}) and double of the recommended dose (80 g. a. i. ha^{-1}). There is no residue detected in control samples of soil. Present results are in agreement with Mohapatra et al. [33] who did not found the residues of fipronil in soil samples collected after 15 days of applications fipronil. Similarly, Mukherjee et al. [9] studied the paddy field soil samples and there is no residue detected after at harvest time. The results are also similar with Chopra et al. [34], Mandal and Singh [35], and Wu et al. [16], which reported no detectable residues of fipronil and its metabolites in soil at crop harvest time. Different crops have different persistence of fipronil and it depends on temperature, humadity, ph of soil and water, microorganism in soil, and plant species [36].

4. CONCLUSION

The fipronil sprayed twice in cabbage crop. First spray were done at the head initiation stage and second spray were done 10 days after first spray at the recommended dose 40 g. a. i. ha^{-1} and double of the recommended dose 80 g. a. i. ha^{-1}. At the harvest time of cabbage there is no residue is detected in both the doses. So fipronil and its metabolites is completely dissipated and soil is free from pesticide.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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