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Persistence and Dissipation of Flubendiamide Residues in Cabbage (*Brassica oleracea* L.) and Soil

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Abstract A field experiment was conducted during *rabi* 2015-16 to study the persistence of flubendiamide residues in cabbage (*Brassica oleracea* L.) and soil, following four application of flubendiamide 480 SC at 0.25 ml L^{-1} (single dose) and 0.5 ml L^{-1} (double dose) g a. i ha^{-1}. Analysis of cabbage samples in UPLC revealed that the flubendiamide residue persisted up to three days in both single and double dose after the last spray. The initial deposits of flubendiamide residues in cabbage heads on 0 day (2 h after last spray) were 0.42 mg kg^{-1} in single dosage and 0.55 mg kg^{-1} in double dosage of the chemical and reached below detectable limit by 5th day, showing 100% dissipation of flubendiamide at both the dosages. Soil samples collected after 15 days of last spray, did not show the presence of flubendiamide residue. Based on complete dissipation of the insecticide the wating period for harvest of crop was found to be five day after the last spray.

Keywords Cabbage, Flubendiamide, Dissipation, UPLC.

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Introduction

Vegetables are important crops in horticulture sector in India, occupying an area of 9.30 million ha with a total production of 162.8 million tonnes and an average productivity of 17.3 tonnes ha^{-1} [1]. Plant protection chemicals (more commonly known as pesticides) are widely used in agriculture to increase the yield, improve the quality of crops and extend the storage life of produce. They are directly applied to the crops to protect from pest attacks, thereby enhance the yield. Although many pesticides are known to dissipate within few days of application, some may still be present as residues as residues especially in the fruits and vegetbles after their harvest. However improper usage has been accompanied by hazards to man and the environment. Residues of most pesticides are the deposits of pesticide active ingredient, its metabolites or breakdown products present in all the compartments of agroecosystems. The most real risk of human is through consumption of residues in food as vegetables and fruits. Some of these pesticides in particular are persistent and very resistant to mecrobial degradation.

Cabbage (*Brassica oleracea* L.) is one of the most popular cruciferous vegetables grown throughout India and other countries. It is a cool season crop and thrives best in a cool and moist climate. India comes next to china in cabbages production occupying an area 4, 00, 000ha with production 9039.2 million tonnes with an average productivity of 22.6 tonnes ha^{-1} [1]. Many insect pest species attack the crop due to which use of pesticide is unavoidable in cabbage cultivation. Among the vegetable crops in India, cabbage is the maximum pesticide consuming crop. Moreover, plant is grown for its fleshy leaves, which may be served boiled, raw or fermented and there by more chance of pesticide intake by human beings. Among the different kinds of pesticides, insecticide consumption is more especially in vegetables. The applied insecticide may leave residues adhering to the surface of the crop or translocation into the tissues of the crop, sometimes the concentration may reach above the prescribed maximum residue limit (MRL) which may pose health hazard to the consumers. Flubendiamide belongs to the phthalic acid diamide chemical class and provides superior plant protection against abroad range of economically important lepidopterous pests species including diamondback moth, cabbage white butterfly, cluster caterpillar, *Helicoverpa* sp, *Heliothis* sp, *Spodoptera* sp., *Plutella* sp., *Trichoplusia* sp. and *Hyrotis* sp. The present study was carried out to investigate the persistence and dissipation of flubendiamide residues in cabbage and soil.

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Materials and Methods

A field experiment was conducted during *rabi,* 2015-16 at Main Agricultural Research Station, University of Agricultural Sciences, Dharwad. The experiment was conducted in a randomized block design using three replicates for each treatment, following four applications of flubendiamide (Fame) 480 SC at 0.25 ml L^{-1} (single dose) and 0.5 ml L^{-1} (double dose) at an interval of 15 days on cabbage heads using knapsack sprayer. The first spray was made at three week after transplanting and water was sprayed in the control plot. Cabbage heads were collected at 0 (2 h) , 1, 2, 3, 5, 7, 10 and 15 days after the last spray. Soil samples were analysed on 15^{th} day from the last spray.

Sample preparation for insecticide residue analysis by QuEChERS (Quick Easy Cheap Effective Rugged and Safe) method

Reference standards

Certified pesticide reference standards namely, Flubendiamide (98.3%), Obtained from Riedel-de-Haen (Seelze, Germany) were used for the analysis. HPLC grade solvents (acetonitrile and formic acid) were obtained from Merck India Ltd (Mumbai, India). Deionised water for use of a mobile phase was produced using Milli Q ultra-pure water system from Millipore (Milford, MA, USA). Dispersive solid phase extraction (d-SPE) material, viz., Primary Secondary Amine (PSA, 40 µm, Bondesil) was obtained from Agilent Technologies (Bangalore , India).

Cabbage sample preparation

Extraction was carried out according to a newer version of the QuEChERS (Quick, Easy,Cheap, Effective, Rugged and Safe) method to analyse the pesticide residues in cabbage samples [2]. The method involved crushing of 2 kg cabbage samples in a blender under ambient conditions. 200 g of the crushed sample was further homogenized at 5,00 0 rpm for 2-3 minutes using a homogenizer and 10 g of this homogenized sample was drawn in 50 ml polypropylene centrifuge tubes which was extracted with 10 ml acetonitrile (1% acetic acid) in presence of 6 g anhydrous magnesium sulfate and 1.5 g sodium acetate. The mixture was then centrifuged at 6000 rpm for 5 minutes. The supernatant (1 ml) was taken in a 2 ml Eppendorf tube and cleaned by Dispersive solid phase extraction (d-SPE) with 150 mg

$MgSO_4$ and 50 mg Primary Secondary Amine (PSA). The Eppendorf tube was centrifuged at 3,000 rpm for 5 minutes and the supernatant (1 ml) was transferred to vial. This supernatant was made up to one milliliter and filtered through 0.2 μm polyvinylidene difluoride (PVDF) membrane filters and then analyzed by Ultra Performance Liquid Chromatographic system (UPLC). Control cabbage samples, which did not receive any treatment with the test pesticides, were used as blanks.

Soil sample preparation

A representative homogenized soil sample (20 g each) was taken in a conical flask (250 ml) and shaken for half an hour using a mechanical shaker with 100 ml acetonitrile and the extract was filtered through filter paper (Whatman No. 42.) mounted on a buchner funnel. The pooled filtrate was concentrated to about 50 ml using a rotary evaporator with a water bath at 40°C and transferred to separatory funnel. The sample was partitioned thrice with 100 ml hexane (saturated with acetonitrile) and the upper hexane layer was discarded each time. The lower acetonitrile layer was partitioned against dichloromethane (3 × 100 m) by addition of 4 per cent saturated NaCl solution. The combined acetonitrile layer was collected and concentrated to dryness on a rotary evaporator (40°C). The residue was dissolved in acetonitrile for estimation by UPLC.

Estimation of residue content

Residues of insecticides were quantified by comparison of peak area of unknown or spiked samples run under identical conditions with that of standards. The retention time of flubendiamide was found to be 2.303.

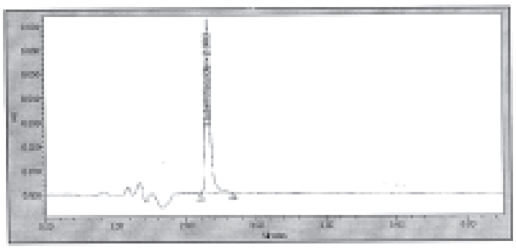

Fig. 1a. UPLC chromatogram of standard flubendiamide

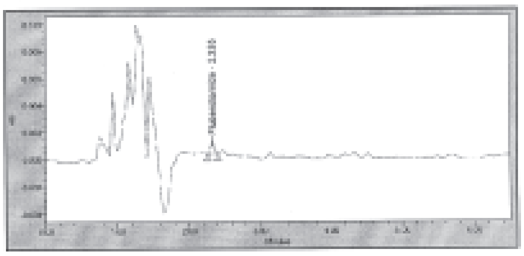

Fig. 1b. Chromatogram of flubendiamide (0.50 ml l^{-1}) treated cabbage sample on zero day (2 hrs after last spray)

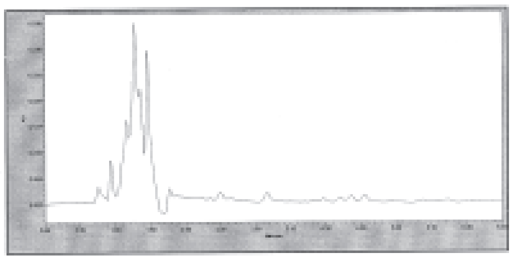

Fig. 1c. Chromatogram of flubendiamide (0.50 ml l^{-1}) treated cabbage sample on fifth day after last spray

Fig. 1a. UPLC chromatogram of standard flubendiamide. **Fig. 1b.** Chromatogram of flubendiamide (0.50 ml l^{-1}) treated cabbage sample on zero day (2 h after last spray). **Fig. 1c**. Chromatogram of flubendiamide (0.50 ml l^{-1}) treated cabbage sample on fifth day after last spray.

Results and Discussion

The UPLC chromatograms for flubendiamide residue are depicted in Fig. 1a to Fig. 1c. The chromatogram of sample analyzed on 0 day (2h after last spray) clearly indicated the presence of flubendiamide residue (RT of 2.335 min). But, however, the peak for the residue was absent on fiflth day, indicating complete dissipation of the chemical. The residue levels of flubendiamide in cabbage heads at different intervals of time after the last spray and at harvest are presented in Table 1. The initial deposits of flubendiamide residues in cabbage heads on 0 day (2 h after last spray) were 0.42 mg kg^{-1} in single dosage and 0.55 mg kg^{-1} in double dosage of the chemical. The residue levels were above the maximum residue limit (0.2 mg kg^{-1}).

The residues of flubendiamide in cabbage remained above MRL after one day of the last spray recording 0.28 and 0.46 mg kg^{-1} single and double dosage, respectively. The dissipation of chemical after one day of spray was to the extent of 33.3 and 29.0% in single dosage and double dosage, respectively. The residue contents were further reduced to 0.19 and 0.31 mg kg^{-1} on 2nd day in single and double dosage, respectively. On 2nd day, flubendiamide residue reached below the MRL in single dose, whereas in double dose the residue was still above the MRL. The insecticide was dissipated by 54.7 and 56.3% in single and double dosage, respectively by 2nd day. The insectcide residue on 3 rd day was 0.07 and 0.12 mg kg^{-1} and thus reached below MRL. The insecticide residue reached below detectable limit by 5th day at both the dosages. The flubendiamide residues in cabbage heads and soil at harvest were not detected.

Insecticide residues were not detected both in cabbage heads and soil of control where only water spray was taken.

Flubendiamide residues was initially higher and above the MRL up to one day after last spray (Fig. 1b). On 3rd day the residue reached below MRL and dissipated to 83.3 and 78.1% in single (0.25 ml L^{-1}) and double (0.50 ml L^{-1}) dose, respectively. By 5th day the residue reached below detectable limit and showed 100% dissipation in both the dosages (Fig. 1c). The higher temperature during the last spray of the chemical might have helped in faster photodegradation. In the study by sahoo et al. [3] and Das et al. [4] also reported dissipation of applied flubendiamide in 7 and 10 days for lower and higher dosages, respectively in chilli and okra. Kooner et al. [5] who found the average initial deposits of flubendiamide in tomato at 0.09 and 0.016 mg kg^{-1}, respectively, which is dissipated to below limit of quantification (LOQ) in 3 and 5 days at lower (48 g a. i.ha^{-1}) and higher (96 g a i ha^{-1}) dosages, respectively. Mahapatra et al. [6], flubendiamide residue persisted for 10 days in cabbage and dissipated with the half life of 3.9 and 4.45 days, respectively, when applied at 24 and 48 g a.i. ha^{-1} dosages.

The present findings are also in agreement with Chawla et al. [7] reported that flubediamide residue reached below detectable limit 0.05µg g^{-1} on 5th and 10th day in brinjal fruits at 90 (single dose) and 180 (double dose) g a.i.ha^{-1} respectively. According to Sharma and Parihar complete dissipation of flubediamide in tomato applied at 48 and 96 g a.i. ha^{-1} dosages took place in 5 and 7 days, respectively.

Table 1. Persistence and dissipation of flubendiamide in cabbage heads (mg kg^{-1}) at different time intervals after the last spray and at harvest. BDL : Below Detectable Limit, MRL : Maximum Residue Limit.

Days after spraying (DAS)	Single dose @ 0.25 ml L^{-1}		Double dose @ 0.50 ml L^{-1}	
	Residue level	Dissipation %	Residue level	Dissipation %
0 (2 h after harvest)	0.42	–	0.55	–
1	0.28	33.3	0.46	29.0
2	0.19	54.7	0.31	56.3
3	0.07	83.3	0.12	78.1
5	BDL	100	BDL	100
7	BDL	100	BDL	100
10	BDL	100	BDL	100
15 (at harvest)	BDL	100	BDL	100
Soil at harvest	BDL	100	BDL	100

MRL : 0.2 mg kg^{-1}

Conclusion

The flubendiamide residue persisted in cabbage up to three days, and it reached below MRL of 0.2 mg kg^{-1} in two days when applied @ 0.25 ml L^{-1}. The flubendiamide insecticide dissipated completely on 5th day of the last spray at both dosages. Thus the insecticide flubendiamide may be considered safe chemical and based on complete dissipation of the insecticide the wating period for harvest of crop was found to be five day after the last spray.

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